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ABIOTIC DEGRADATION OF TRICHLOROETHYLENE BY IRON MINERALS

by

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A thesis submitted in partial fulfillment of the requirements
for graduation with Honors in the Environmental Sciences

Michelle Scherer
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ABSTRACT

Trichloroethylene (TCE) is a dense liquid chemical often used as an industrial degreaser. TCE poses public health risks as a probable carcinogen, with growing evidence of negative effects to developmental, reproductive, and hepatic health. Traditional cleanup of aquifers contaminated with TCE is expensive, difficult, and inconsistent because TCE sinks to the bottom of an aquifer, making access and precise location challenging. Exploring the potential for iron minerals within an aquifer, such as magnetite, to break down TCE at the site of contamination opens the door to natural attenuation of TCE, reducing costs and carbon emissions related to cleanup. Though magnetite alone is not effective in breaking down TCE, magnetite in the presence of aqueous sulfide may form iron (II) sulfide (mackinawite), a mineral with proven success in reductive dechlorination of TCE. For this study, reactors were made at pH 6 and 7 with magnetite, sulfide, and TCE. There was no reduction of TCE in any of these reactors. However, in each of these reactors, the concentration of aqueous sulfide dropped dramatically, and one reactor showed evidence of the formation of greigite (Fe_3S_4). Further research should explore the reaction between magnetite, sulfide, and TCE at higher pHs, and more work is needed in characterizing solid products of the reaction between magnetite and sulfide.

BACKGROUND

Chlorinated ethenes, such as trichloroethene (TCE), have historically found widespread use due to their effectiveness as organic solvents, gaining much of that use as dry-cleaning chemicals and industrial degreasers (ATSDR 2014). Through its widespread use, widespread contamination of soil and groundwater followed. TCE has proven to be extraordinarily difficult to clean up after contamination, largely due to its high density. TCE is a dense non-aqueous phase liquid (DNAPLs), which means it is denser than water and will sink to the bottom of an

aquifer (Russell et al. 1992). There, TCE will slowly dissolve, providing a consistent source of contamination away from easy access for cleanup. TCE, along with the closely related tetrachloroethylene (PCE), are the most common volatile organic compounds detected at levels that threaten health in groundwater (Zogorski et al. 2006). The chemicals can be found in trace levels in many wells across America; PCE is more common, being detected in 2% of domestic wells and 5.3% of public wells at the 0.2 µg/L threshold. In 1.5% of wells, both PCE and TCE have a concentration of at least .2 µg/L (Zogorski et al. 2006). This pervasiveness in the environment poses a huge threat to public health given the risks these chemicals pose. Most notably, TCE and PCE are classified as Class 2A carcinogens, meaning they are probable causes of cancer in humans, by the International Agency for Research on Cancer (ATSDR 2014). Other potential health effects of TCE include liver damage, cognitive deficits, vision problems, disruptions of developmental and reproductive health, and damage to the heart and kidneys (ATSDR 2014, Yeh and Kastenberg 1991). When water is sourced from an aquifer contaminated by TCE, exposure can occur by drinking the water or by inhaling its fumes, most commonly in the shower.

Inhalation of TCE is a significant concern because it is a highly volatile chemical. Though its volatility adds to the potential health risks, this property can be used in efforts to clean up TCE. Techniques like air stripping and in-well aeration bubble air through contaminated water, which gives TCE an opportunity to volatilize and leave the water. This method demands new construction at contaminated sites, though, which can result in a costly cleanup (Russell et al. 1992). It also has the drawback of not truly eliminating TCE, simply changing its state to a gas. Much effort has been put into the use of bioremediation for cleanup of sites contaminated

with TCE, and though it can convert TCE into other, benign chemicals, problems with cost, time, efficacy, and commitment remain (Russell et al. 1992, Shen and Wilson 2007, Peale et al. 2010).

Here, the benefits of research on the natural attenuation of TCE become apparent. With more knowledge about the processes that lead to natural degradation of these chemicals, cleanup can be better targeted. The process of biologically-mediated abiotic degradation (BMAD) remains relatively unexplored, and questions remain about how it applies to the attenuation chlorinated solvents like TCE. BMAD is a pathway of degradation where microbes do not directly work to eliminate pollutants, but natural products created by those microbes go on to cause a reaction that results in reducing the concentration of a contaminant. Particularly, the importance of aqueous Fe^{II} and S^{II} in the process of BMAD is ripe for exploration. Sites that have conditions conducive to natural degradation can be left to eliminate TCE over time. This results in a cost savings along with savings in energy and resources.

Fe^{II} and S^{II} are products of anoxic respiration of microorganisms that reduce Fe^{III} or sulfate (Dong et al. 2009). This research examined a pathway where aqueous Fe^{II} and S^{II} cause the degradation of TCE by altering the solid-state chemistry of iron-containing aquifer sediments, reducing Fe^{III} and resulting in a greater amount of available Fe^{II} in the aquifer sediments (Gorski and Scherer 2011). That greater available Fe^{II} , with its high reductive potential (W.J. Lee and Batchelor 2003), could result in a greater rate of reduction of chlorinated ethenes like PCE and TCE (Gorski et al. 2010, Liang et al. 2009) (Figure 1). Previous studies have also found that iron (II) sulfide is effective at degrading TCE (Butler and Hayes 1999, Jeong et al. 2007).

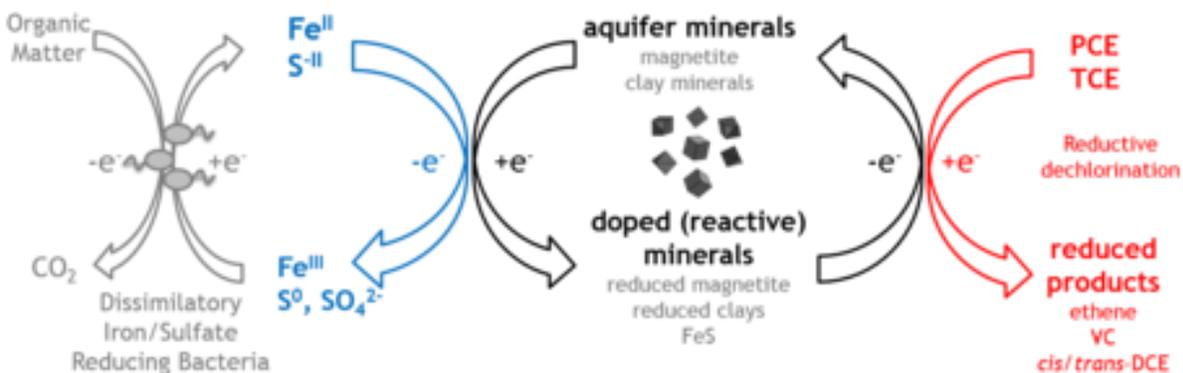


Figure 1: Conceptual framework for biologically mediated abiotic degradation of chlorinated solvents by iron minerals (Scherer et al. 2014)

HYPOTHESES / RESEARCH QUESTIONS

This research seeks to connect the degradation of TCE with iron minerals found in aquifers. At its core, this research sought to test three hypotheses:

- Iron minerals found in aquifers (i.e. magnetite) can provide a natural avenue for breakdown via reductive dechlorination of TCE.
- Iron (II) sulfide, an effective agent of dechlorination of TCE, can form from magnetite and aqueous sulfide.
- Once formed, the iron (II) sulfide from the reaction of magnetite and sulfide can degrade TCE.

METHODS

In order to carry out this experiment, methods were needed to measure iron (II) and total iron, sulfide, and TCE and products of its degradation. In addition, iron minerals needed to be synthesized and characterized.

Measurements of TCE and its products of degradation (acetylene, ethylene, and ethane) were made using gas chromatography (GC). TCE was measured from a liquid sample pulled from the reactor and extracted with hexanes using an electron capture detector (ECD). Its products were measured from a sample of the gaseous headspace in the reactor using a flame ionization detector (FID). Liquid TCE standards, along with a 2% acetylene, ethylene, and ethane gas standard, were created and sampled to generate a calibration curve prior to each sampling run for reactors Henry's law constants were used to calculate the total mass of TCE, acetylene, ethylene, and ethane both in solution and in the headspace.

Aqueous iron (II) and total aqueous iron can be measured spectrophotometrically using 1,10-phenanthroline (Harvey et al. 1955). 1 mL of a sample is taken; for measuring total iron, a reductant, hydroxylamine HCl, is added, while for iron (II) measurements, ammonium fluoride is added. In both situations, phenanthroline and an ammonium acetate buffer are added. After sitting for 20 to 30 minutes, the absorbance of the sample is measured at 510 nm. Standard solutions were created from ferrous ammonium sulfate; the concentration of aqueous iron in samples and standards is kept at under 200 μM to ensure an accurate reading. Higher concentrations can saturate the sample to the point of maximum measurable absorbance.

Aqueous sulfide was measured using the methylene blue method outlined by Reese et al. (2011). From this, I developed the standard operating procedure for measuring sulfide in the lab (attached, Appendix A). Because of its high purity, sodium sulfide was used to create the

standards in generating a calibration curve for the methylene blue method (Figure 2). The samples taken were downsized to 1.5 mL. To ensure an accurate reading, concentration of a sample was targeted at less than 50 μM , though reasonable accuracy could be expected up to 100 μM concentration for the same reason aqueous iron was kept below 200 μM . Absorbance is measured at 667 nm. In some reactors, sodium hydrosulfide was used in place of sodium sulfide because of its less basic pH in solution. However, sodium hydrosulfide is less consistently pure, so concentration of the sodium hydrosulfide stock was back-calculated using the calibration curve from the sodium sulfide standards.

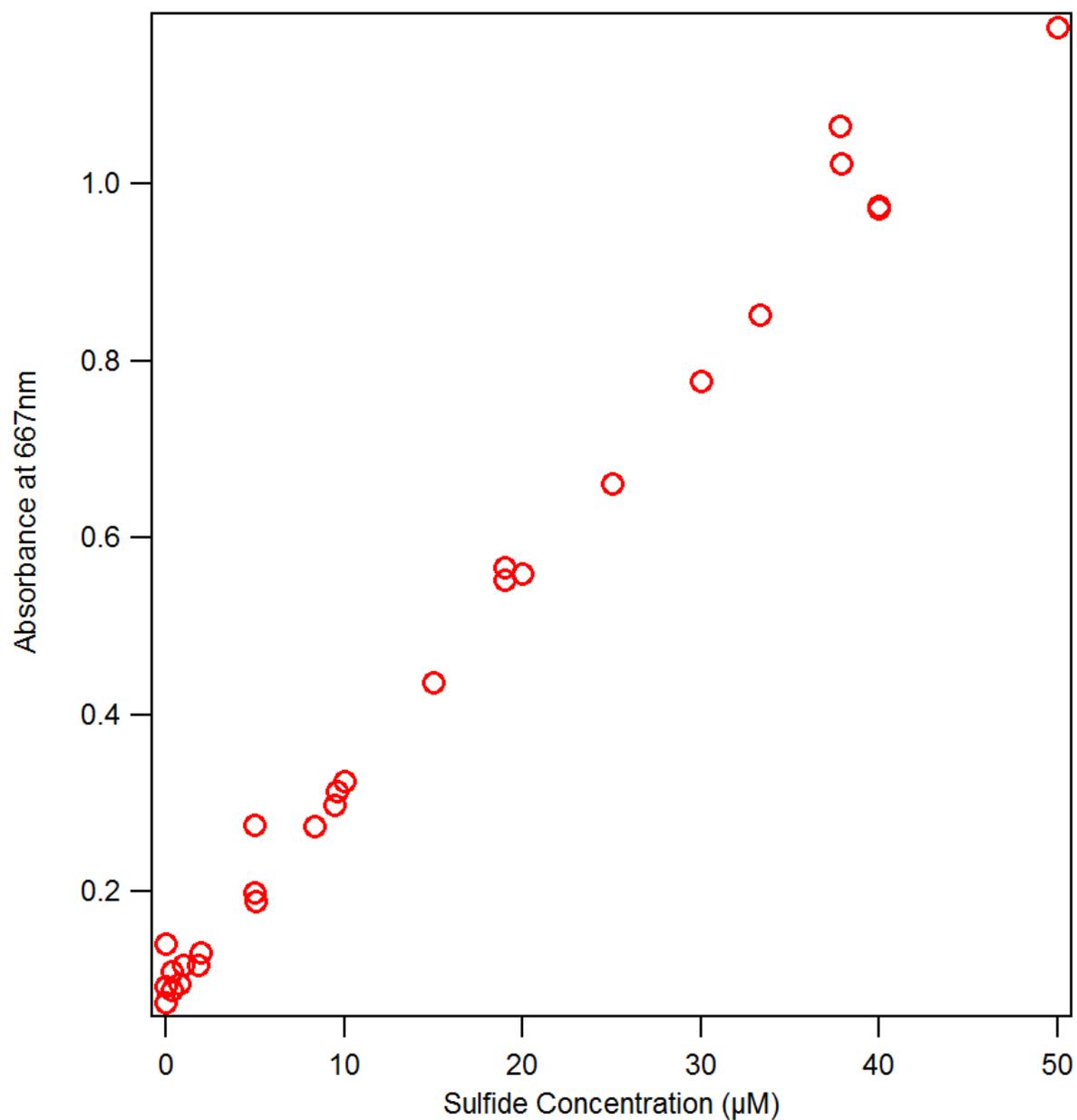


Figure 2: Measured absorbance of sulfide samples at different concentrations using the methylene blue method. Sulfide standards were prepared immediately before testing from sodium sulfide stock.

The magnetite used in these experiments was all synthesized in the lab. FeCl_2 and FeCl_3 salts were combined in degassed deionized water at a target stoichiometry of 0.50 (that is, twice as much iron (III) as iron (II)). pH was then raised to 11 with sodium hydroxide to precipitate the

magnetite. This mixture was then stirred overnight with a stir bar and stir plate. All work was performed in the glovebox to minimize alteration of the stoichiometry by oxygen. Lastly, the magnetite was filtered out and freeze dried. Several methods are available for confirming the stoichiometry of magnetite. The simplest method applies the phenanthroline method of determining aqueous iron concentration to magnetite dissolved in hydrochloric acid; one can find the stoichiometry by comparing the concentrations of aqueous iron (II) and total iron in the acid. Additionally, X-ray diffraction (XRD) and Mössbauer spectroscopy can be used to determine the stoichiometry of magnetite.

All reactors were prepared at 150 mL liquid volume. They were kept in glass vials with a total volume of 161 mL and sealed with thin viton septa. Reactors were stored upside down on a shaker.

RESULTS

First, controls were created to demonstrate the ability of the method to hold and measure TCE and its products. The TCE control and the TCE and sodium hydrosulfide control were created at pH 7.5 and buffered with MOPS. The concentration of TCE was targeted at 50 μM , and for the sodium hydrosulfide control, the sulfide concentration was targeted at 5 mM. The concentration of TCE over time in these controls is shown in Figure 3. In these controls, there was no significant loss of TCE or any measurable products of reaction, even nine months after their creation.

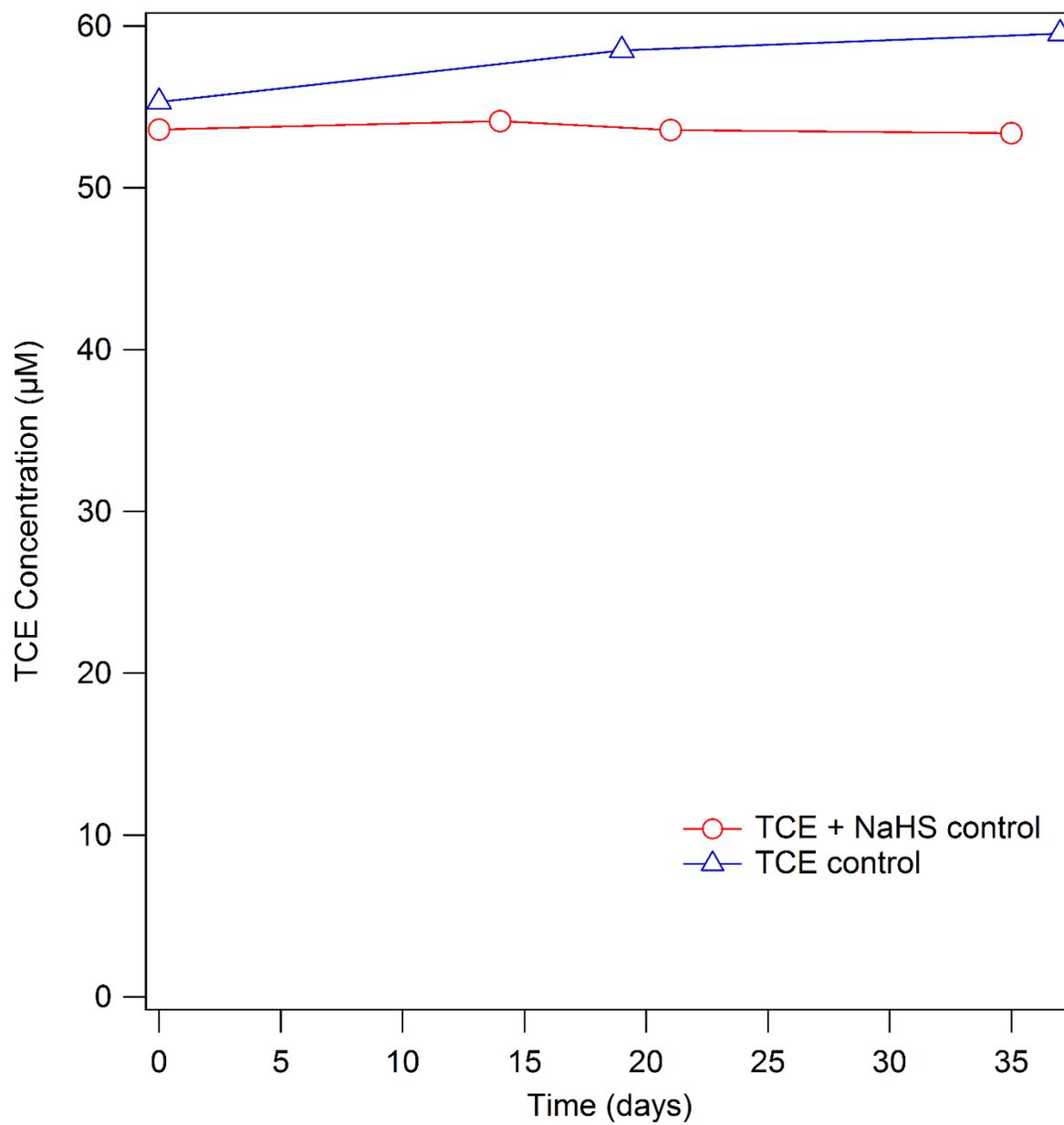


Figure 3: Concentration of TCE over time in control reactors. Reactor conditions are 150mL aqueous volume, with 50µM TCE in 10mM MOPS and 10mM NaCl; the NaHS control has 5 mM NaHS.

Iron (II) sulfide was used as a positive control to show the degradation of TCE and the measurement of products. Previous studies (Butler and Hayes 1999, Jeong et al. 2007) have shown the effectiveness of iron (II) sulfide in reductive dechlorination of TCE. Here, the iron (II) sulfide was freshly precipitated by combining iron (II) stock from iron (II) chloride and sulfide stock from sodium sulfide. Mass loading was 2 g/L of iron (II) sulfide, assuming that all iron (II) reacted with all the sulfide. Figure 4 shows the reaction of TCE in this reactor over time, resulting in acetylene as the main product with some ethylene measured in the last sample.

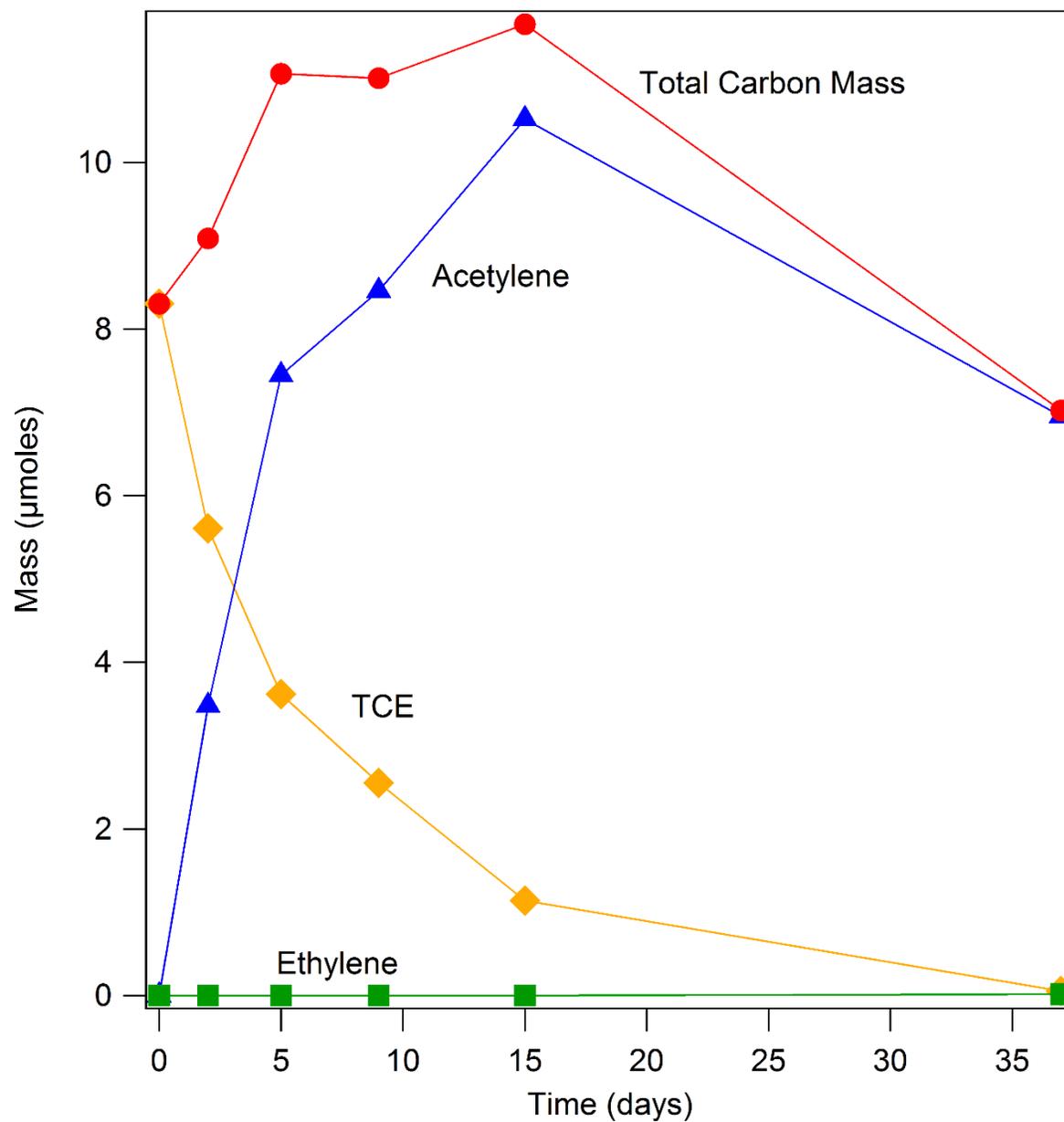


Figure 4: Mass of TCE, acetylene, and ethylene over time in iron sulfide reactor. Target conditions: 150 mL reactor, 2 g/L freshly precipitated iron sulfide, 50 μM TCE, buffered by MOPS.

Work conducted in this lab has demonstrated the effective lack of reaction in magnetite and TCE reactors, regardless of stoichiometry (Culpepper et al. 2017). The last set of hypotheses for this study – that magnetite will react with sulfide to produce iron (II) sulfide, which could then degrade TCE – was tested in two steps. The first step was to find evidence that aqueous sulfide would react with magnetite. For this, 1 mM sulfide was combined with 5 g/L magnetite and compared to sulfide at the same concentration with no magnetite. Within four days, the sulfide in the magnetite reactor had all but disappeared, while there had been no significant decrease in sulfide concentration in the absence of magnetite (Figure 5).

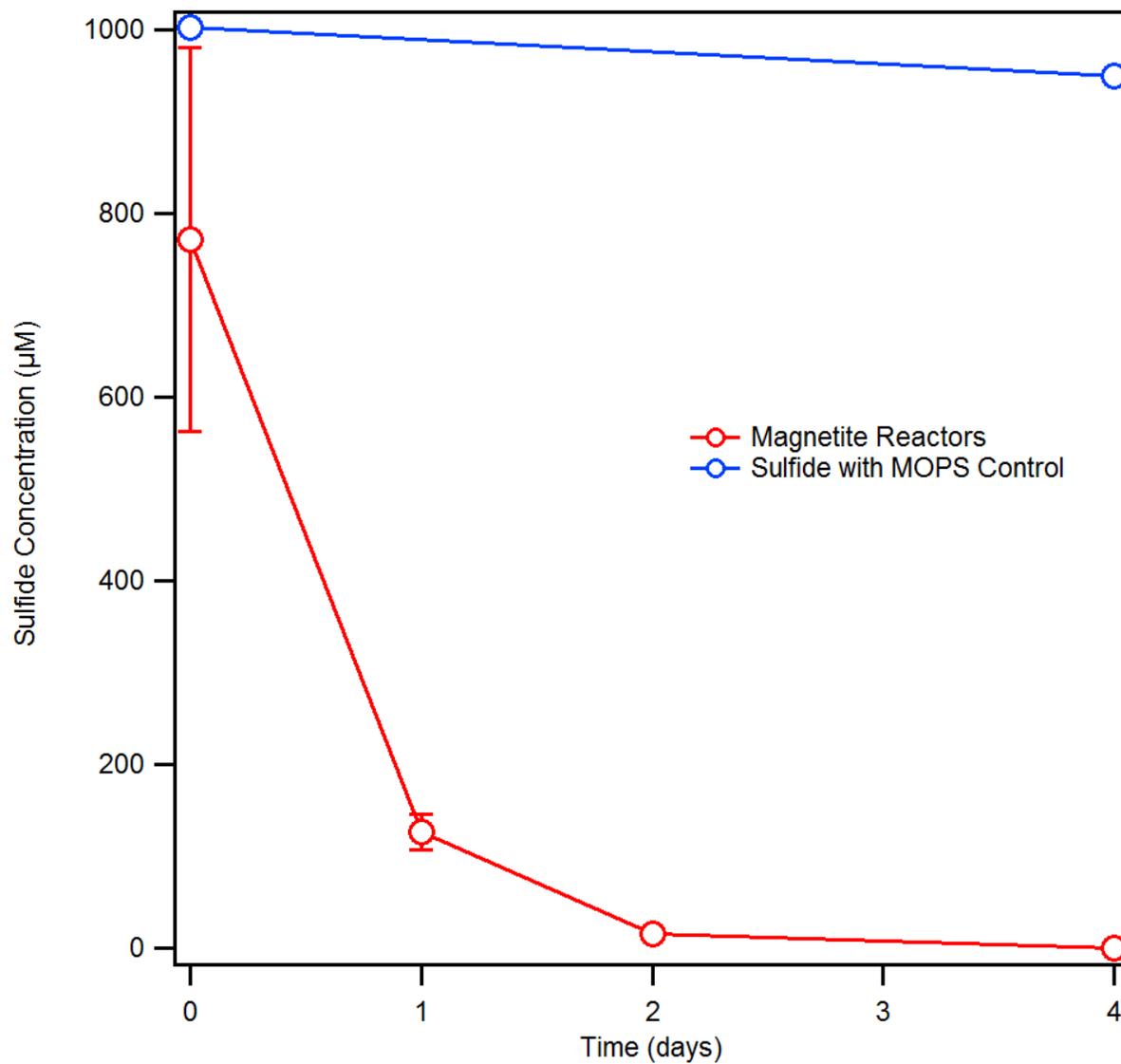


Figure 5: Concentration of sulfide over time with and without magnetite. Initial concentration is 1mM sodium sulfide in 10mM MOPS and 10mM NaCl at pH 7.5, with 5g/L magnetite mass loading in the magnetite/sulfide reactors.

Lastly, reactors were created combining magnetite, sodium hydrosulfide, and TCE to measure any potential degradation of TCE over time. Five reactors were made: one each at pH 6 and 7 with 5 mM sodium hydrosulfide, 5 g/L magnetite, and 50 μ M TCE. Additionally, two more reactors were made following these conditions, but 1 mM iron (II) was added to these reactors. Finally, one reactor was made at pH 6 with 5 g/L magnetite and left to sit for 10 days before 5 mM sodium hydrosulfide and 50 μ M TCE were added. Over the time period measured for these reactors, there was no significant decrease in concentration of TCE, and no products of reaction were detected (Figure 6).

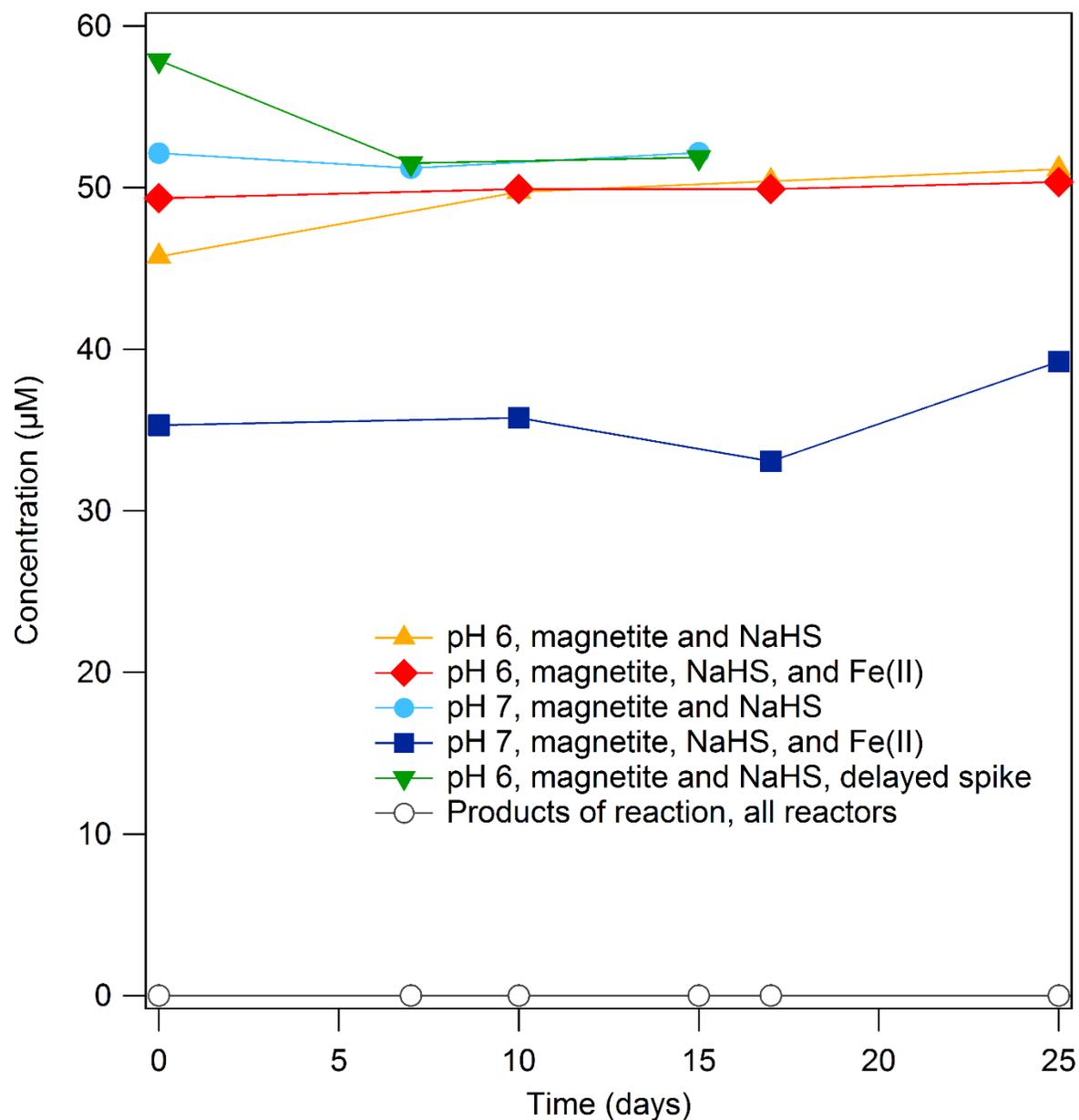


Figure 6: Concentration of TCE over time in magnetite and sulfide reactors. Target conditions: 150 mL reactor, 5 g/L magnetite, 5 mM sulfide, 50 μM TCE, pH 6 buffered by MES, pH 7 buffered by MOPS. Reactors with Fe(II) had 1 mM iron (II) added.

Sulfide concentration in reactors with magnetite, sulfide, and no additional iron (II) was measured, with the pH 7 reactor and the pH 6 with delayed spike of sulfide being measured 36 days after the initial sulfide spike, and the pH 6 reactor being measured 46 days after the initial sulfide spike. All these reactors had measured sulfide of less than 6.5 μM , or approximately

0.1% of the initial sulfide concentration of 5 mM. Solids in these three reactors were tested using XRD. Results are shown in Figures 7-9. The solids from all reactors indicated the presence of magnetite. Only the reactor at pH 6 with the delayed sulfide spike showed signs of another mineral, with peaks matching those of greigite in the reading.

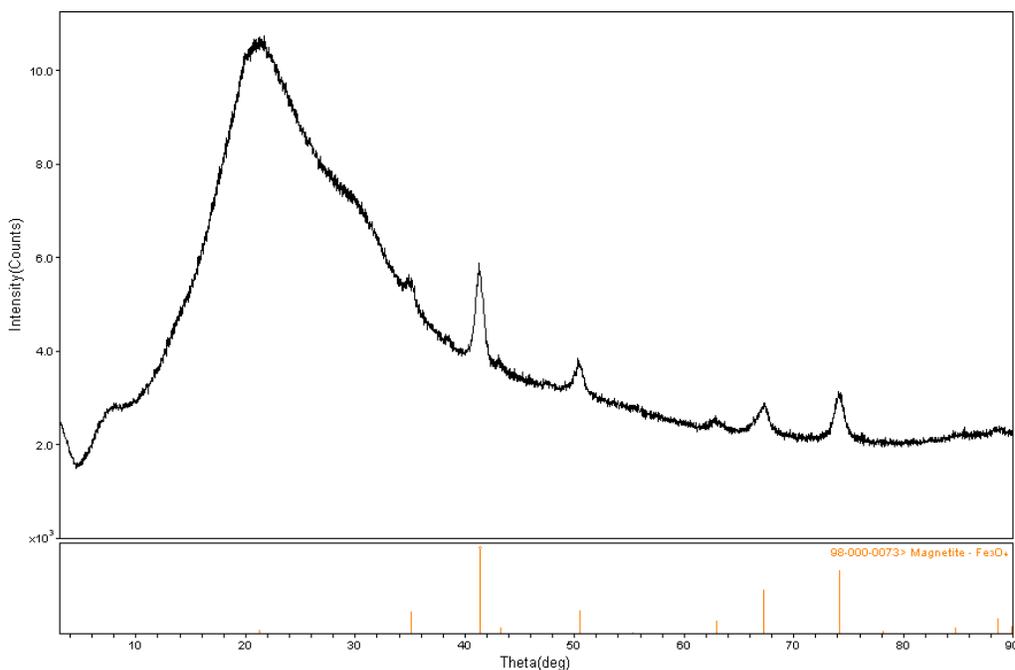


Figure 7: XRD results of solids from reactor with initial conditions of 5 mM sodium hydrosulfide, 50 μM TCE, and 5 g/L magnetite at pH 6. Peaks match that of magnetite, shown below the XRD results.

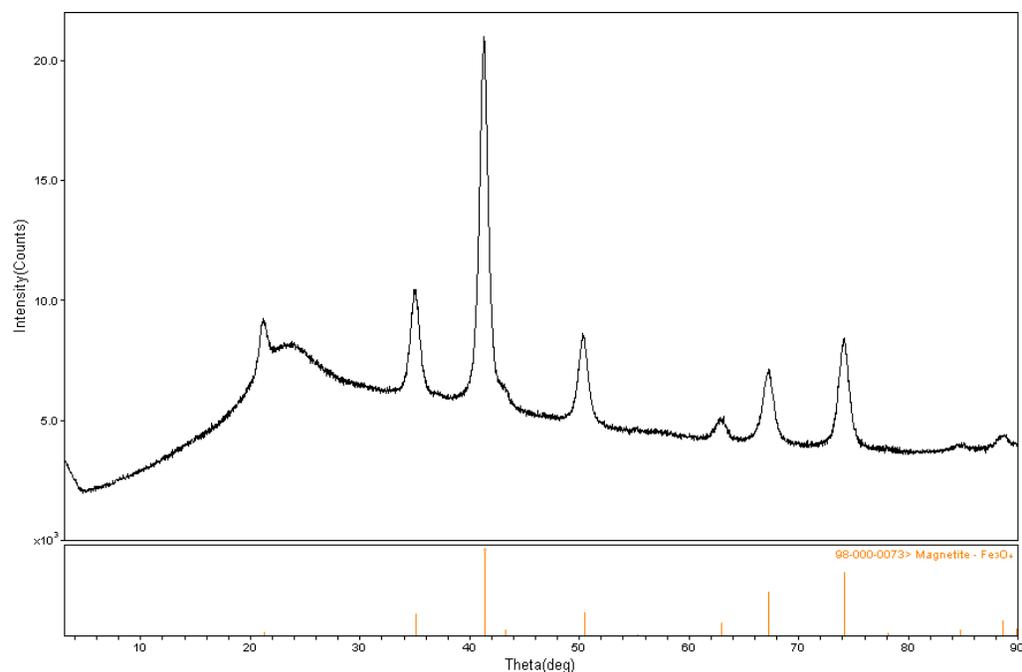


Figure 8: XRD results of solids from reactor with initial conditions of 5 mM sodium hydrosulfide, 50 μM TCE, and 5 g/L magnetite at pH 7. Peaks match that of magnetite, shown below the XRD results.

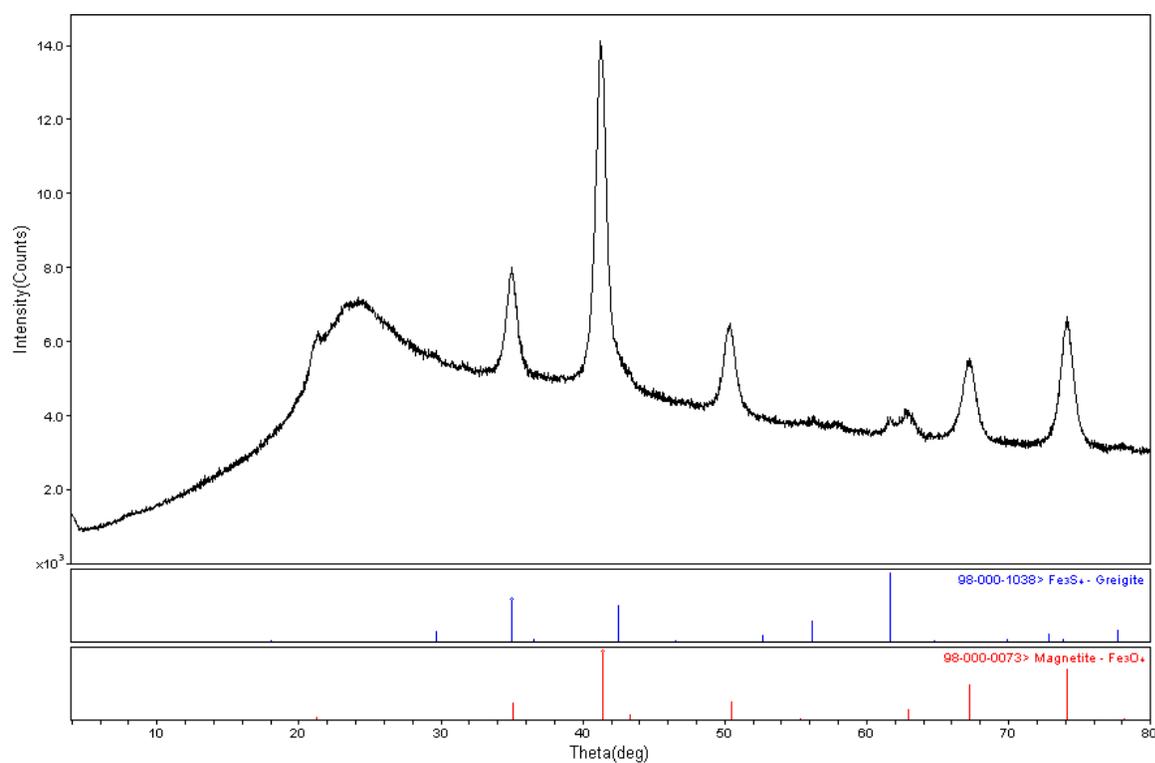


Figure 9: XRD results of solids from reactor with initial conditions of 5 g/L magnetite at pH 6, with 5 mM sodium hydrosulfide and 50 μM TCE added 10 days after initial creation. Peaks match that of magnetite and greigite, shown below the XRD results.

DISCUSSION

The initial goal of this research was to test the efficacy of magnetite in degrading TCE. Research by Johnathan Culpepper found that magnetite alone is not practical for reductive dechlorination of TCE (Culpepper et al. 2017). This led to exploration of the connection between magnetite and iron (II) sulfide, which previous studies along with research in this lab (Figure 4) have shown to be effective at breaking down TCE. As such, the focus shifted to finding whether aqueous sulfide could transform magnetite to iron (II) sulfide, and whether the iron (II) sulfide formed in this reaction could degrade TCE. Experiments here showed that concentration of aqueous sulfide decreases rapidly in the presence of magnetite (Figure 5), indicating that a reaction is taking place. XRD results of the solids from the reactors with 5 mM sodium hydrosulfide, 5 g/L magnetite, and 50 μ M TCE at pHs 6 and 7 only showed magnetite, though a decrease in sulfide concentration was present in each of these reactors. The XRD result for solids from the reactor at pH 6 with magnetite and a delayed spike in 5 mM sodium hydrosulfide indicated the presence of greigite (Fe_3S_4) in addition to magnetite, though neither iron (II) sulfide or pyrite were detected. This points to the formation of iron sulfides other than iron (II) sulfide.

At the pHs measured for these reactors (6 and 7), no reaction between the TCE and solids in the reactors was measured. However, though more aqueous iron (II) from magnetite is likely to be available at low pHs (Sidhu et al. 1981), previous research has found that iron (II) sulfide reacts with TCE faster at more basic pHs (Butler and Hayes 2001). This suggests two important steps in further research: magnetite and sulfide reactors at pH 6 and 7 may need more time before there is a measurable reaction if the reaction is slow. Alternatively, magnetite, sulfide, and TCE reactors could be made at higher pHs (like pH 8); there may be less aqueous iron (II) available, but the literature suggests any iron (II) sulfide that formed would react more quickly

compared to reactors at lower pHs. The detection of greigite in one reactor could also point to iron (II) sulfide not forming, which could also explain the lack of reaction; other studies have found greigite to be less reactive with TCE than iron (II) sulfide (He et al. 2010). Still, iron (II) sulfide may be forming in quantities too small to detect with XRD; adding more sulfide to a reactor could give greater clarity to the iron sulfide products from reaction between sulfide and magnetite.

Environmental Significance

Current methods for remediating areas contaminated by chlorinated solvents like TCE are costly, lengthy, energy-intensive, and often ineffective. Research into biologically-mediated abiotic degradation of TCE opens the possibility of natural attenuation of TCE. By finding situations where TCE will react away with aquifer minerals, carbon emissions from drilling wells for traditional methods of remediation will drop, and complete reaction of TCE through BMAD reduces public health concerns, like cancer risk, for those who source their water from a contaminated aquifer. However, since in this research, no iron (II) sulfide was detected, and one reactor showed the formation of greigite, the conditions in this research may not be the most effective in breaking down TCE.

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Appendix A:**Methylene Blue method for measuring sulfide concentration**

Reagent: Add 1.6g N,N-dimethyl-p-phenylenediamine sulfate and 2.4g ferric chloride (FeCl_3) to 100 mL of 6M HCl (50% concentrated HCl, 50% DI water) in a volumetric flask. Add a stir bar and let it mix. Cover in foil and refrigerate for storage.

Standards: Degas 1L DI water. Put a rubber cap on the container, insert 22 gauge syringe, and attach tubing to the syringe. Then, add a second 22 gauge syringe to act as a vent, making sure the second syringe is out of the water. Connect the syringe with the tubing to a nitrogen tank and bubble nitrogen through the water for 1 to 1.5 hours. To get the stock, add 1.8g of sodium sulfide to 150mL degassed DI water to get a 50mM stock solution.

Procedures:

1.5 mL of sample

Add 120 μL diamine reagent

Maximum color development will occur after 20-30 minutes.

Allow diamine reagent to equilibrate to room temperature before running tests.

Absorbance is measured at 667 nm.

Avoid concentrations of sulfate as high as 100 μM to ensure an accurate reading.

Absorbance can drop as the sample is left in the cuvette and exposed to air, so measure the absorbance immediately after transferring from the microcentrifuge tubes. Also, given sulfide's reactivity with oxygen, take care to minimize potential contact with the air by minimizing headroom in the microcentrifuge tubes and keeping them closed as much as possible.