Reduction and Immobilization of Radionuclides and Toxic Metal Ions Using Combined Zero Valent Iron and Anaerobic Bacteria

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Background

- The use of Fe(0)-based technologies to treat contaminated groundwater is increasing.
- Sulfate (SO_4^{2-}) is present at many waste sites.
- Sulfate reducing bacteria (SRB) can oxidize iron metal.
  - Examples: biocorrosion of steel tanks, piping, etc.
- SRB transform many hazardous compounds: toxic organic compounds, heavy metals, radionuclides.
- Combined abiotic/biotic systems have been shown to increase reduction rates for halogenated organics.

Hypothesis

- Combined abiotic-biological system can synergistically combine both processes to maximize metal ion reduction in an engineered permeable reactive barrier.
- Design of either *in-situ* or *ex-situ* metal ion reduction processes based on biotic, abiotic or a combined abiotic/biotic reduction scheme requires a more thorough understanding of the rates of the reaction and the parameters which impact the rates.

Project Objectives

- The overall goal of this project is to develop a combined abiotic/microbial, reactive, permeable, *in-situ* barrier with sufficient reductive potential to prevent downgradient migration of toxic metal ions.
  - The field-scale application of this technology would utilize anaerobic digester sludge, Fe(0) particles for supporting anaerobic biofilms, and suitable aquifer material for construction of the barrier.
- Successful completion of this goal requires testing of the two hypotheses listed above by evaluating the rates of <u>metal ion reduction</u> in abiotic and combined abiotic/biotic systems under a range of environmental conditions.

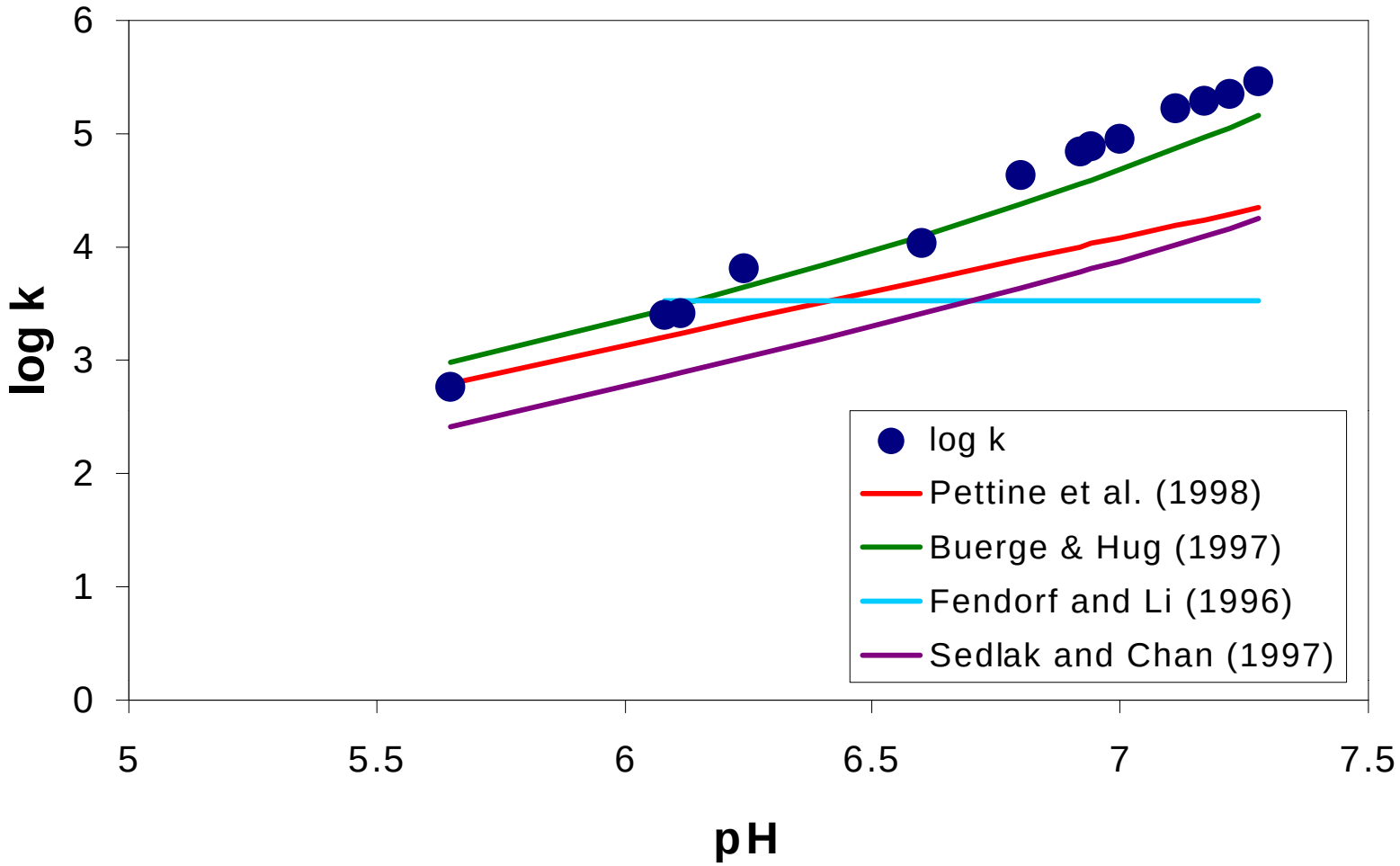
Abiotic Experiments

Kinetics of Fe(II) Reduction of Cr(VI)

Experimental Design

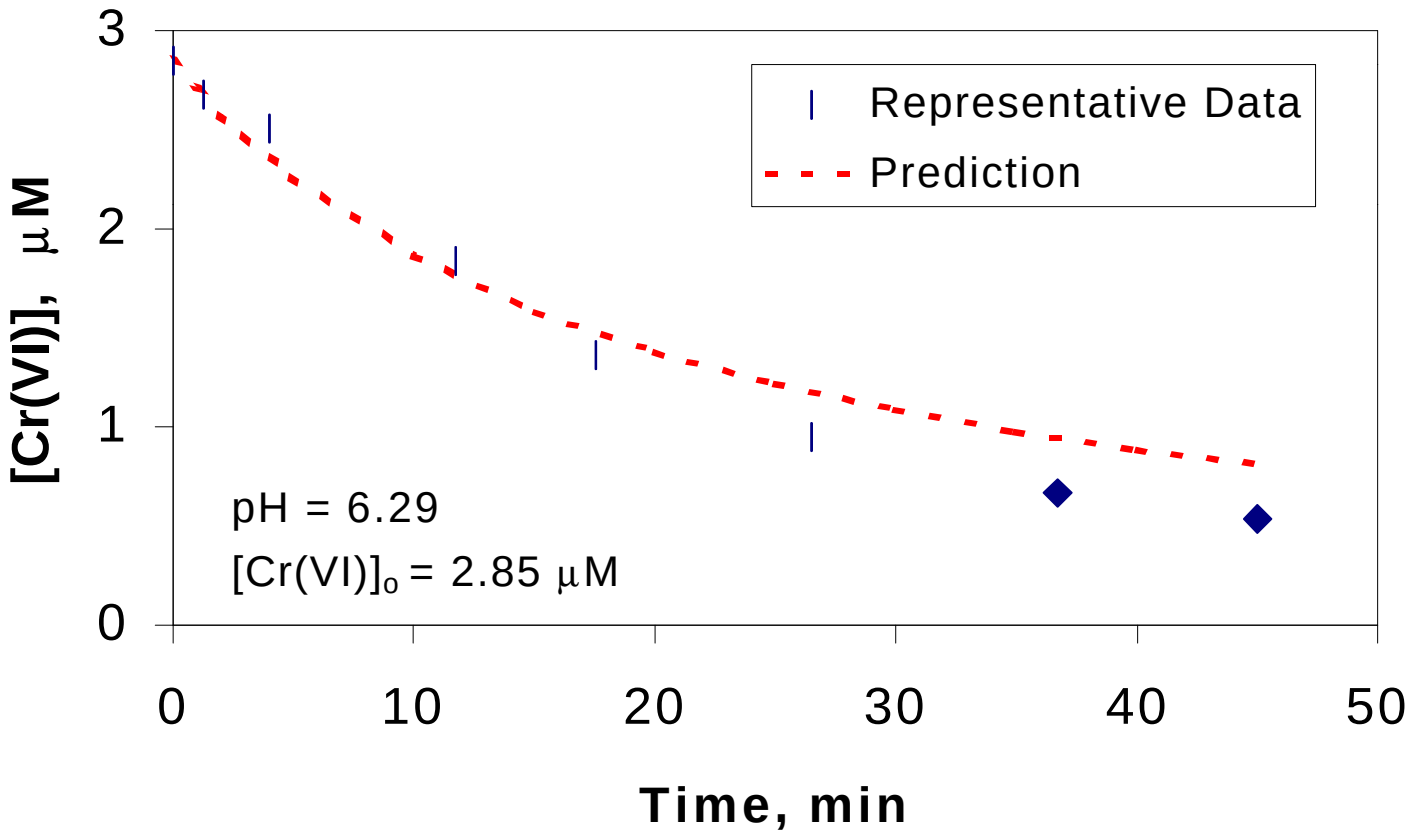
- Reactor: 1.5 L jacketed batch reaction flask.
- Special precautions: All experiments were conducted in a glove box under an argon atmosphere. Deoxygenated water, used for all solutions, was prepared by bubbling 99.999% argon through boiled Nanopure water. Tests showed that this could reduce dissolved oxygen levels to below 0.16 mM.
- Analytical Methods: Cr(VI) was measured using the diphenyl-carbazide method (APHA 1995. Fe(II) was measured using the Ferrozine method (Stookey 1970)
- Experimental Conditions:
  - T = 23°C
  - I = 0.01M NaCl
  - Mixing rate = 400 rpm
  - pH = 5.5 to 7.5 (HEPES buffer)
  - $[Fe(II)]_o$:$[Cr(VI)]_o$ = 3:1
  - $[Cr(VI)]_o$ = 1 to 3 μM

Comparison of Rate Constants



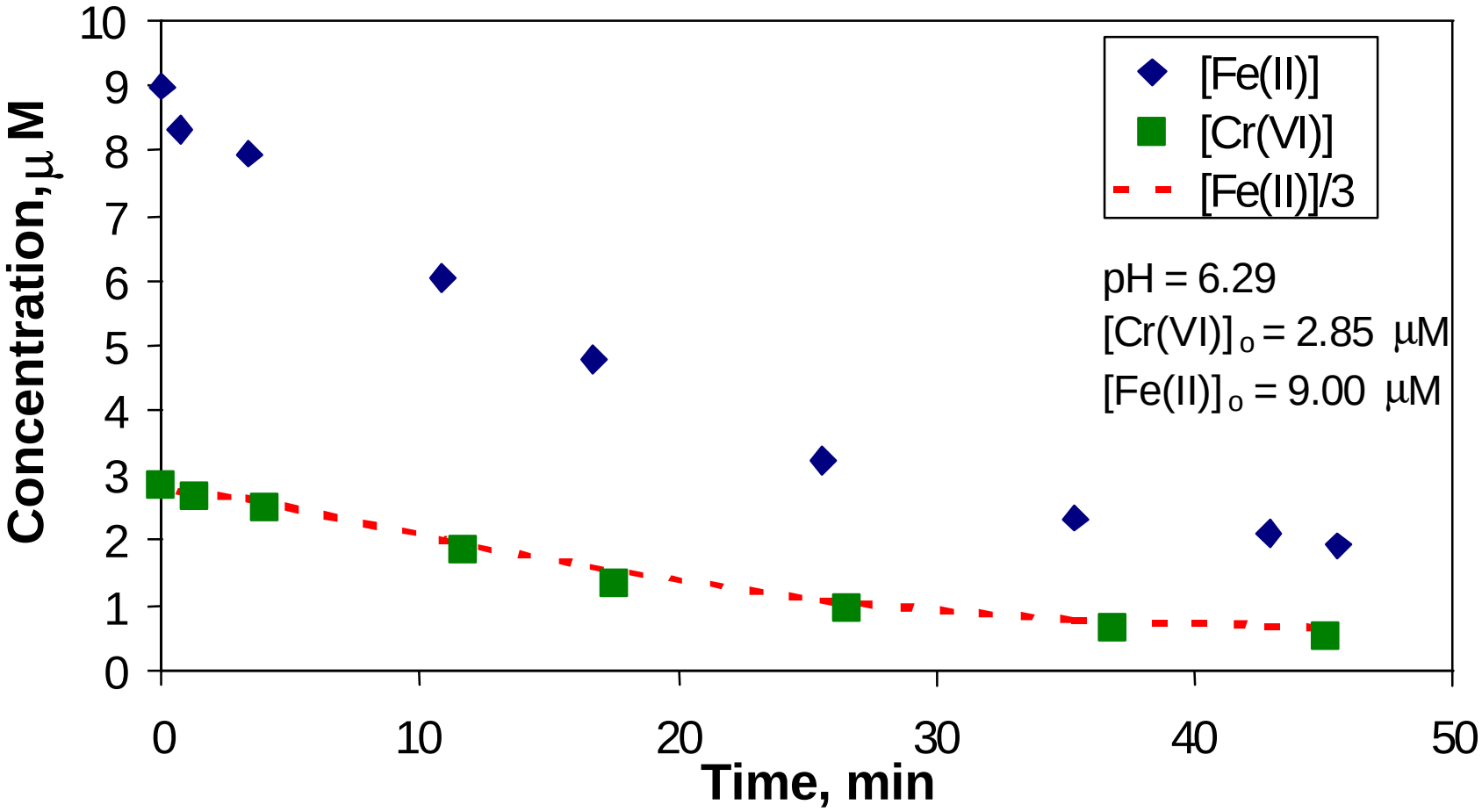
Comparison of our experimentally determined rate constants with those of other workers at similar conditions.

Comparison of Data to Observed Rate Law



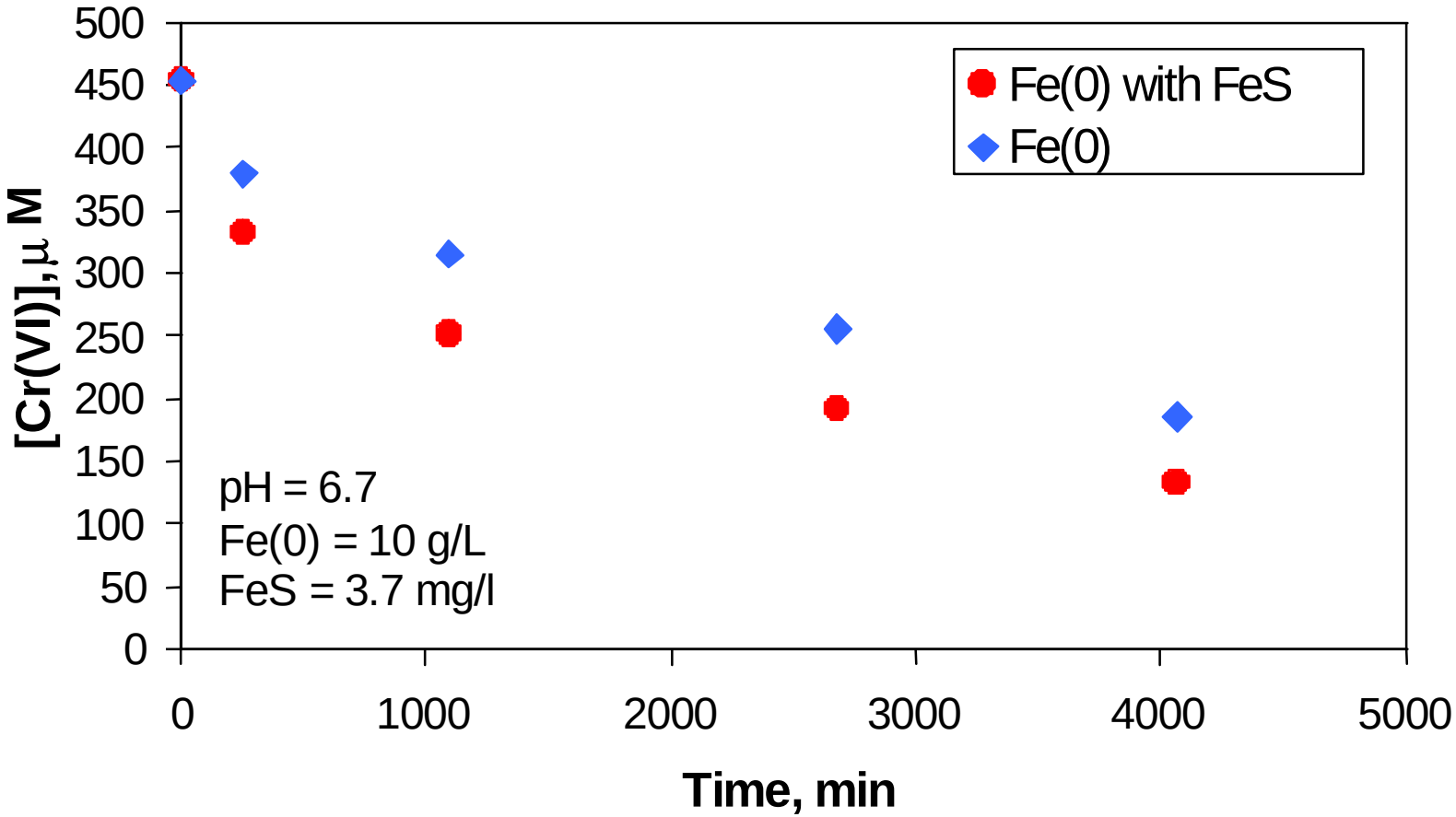
The 2nd order rate law $-d[Cr(VI)]/dt = k[Cr(VI)][Fe(II)]$ was used to fit experimental data collected over a range of pH from 5.5 to 7.5. An equation relating log k to pH was developed and used to predict the data shown.

Cr(VI) Reduction by Fe(II): Typical Results



This plot shows the loss of Cr(VI) and Fe(II) for an experiment run at T=23 C and I = 0.01M. The Fe(II) data reflects the 3:1 Fe(II) to Cr(VI) reaction stoichiometry.

Reduction of Cr(VI) in Fe(0) and Fe(0)/FeS Systems



The addition of low concentrations of FeS increased the initial rate of Cr(VI) reduction. This initial rapid reduction in Cr(VI) concentration is related to the amount of FeS added to the system. In experiments containing only Cr(VI) and FeS, we observed an initial ten percent decrease in Cr(VI) within ten minutes.

Conclusions

- The kinetics of Cr(VI) reduction were consistent with those obtained by Buerge and Hug (1997).
- However, literature data shows significant variations in observed rates and points to the need to investigate reduction rates under a range of experimental conditions.
- The proposed reaction stoichiometry between Cr(VI) and Fe(II) ($[Fe(II)]_o$:$[Cr(VI)]_o$ = 3:1) is followed in our experiments.
- Our experimental data were fit to a 2nd order rate law:

Abiotic Reduction

Short Term and Long Term Kinetics of Fe(0)
Reduction of Cr(VI)

Experimental Design

- Short-term experiments with Cr(VI) and Fe(0):
  - Reactor: 1.5 liter jacketed batch reactor (containing 750 ml of 4 mM HEPES buffered deoxygenated water).
  - Fe(0) and Cr(VI) : Fisher 40 mesh iron filings were placed in the flask and allowed to equilibrate for approximately 2 hours. Cr(VI) was then added, the pH was adjusted to 7, and the system was allowed to react for two hours while pH and Cr(VI) removal were monitored.
- Long-term experiments with Cr(VI), Fe(0) and soil
  - Reactor: 150 ml batch serum bottles
  - Fe(0) and Cr(VI): The reactor contents from the short term experiments were transferred to 150 mL serum bottles in order to carry out long-term batch bottle experiments under different conditions. The iron to solution ratio was maintained in the bottles.
  - Aquifer Material: 15 g of Ottawa sand, Savannah River soil, or Oak Ridge soil were added to selected bottles and placed on a lab shaker. Cr(VI) concentrations were monitored over several days.

Media Characteristics

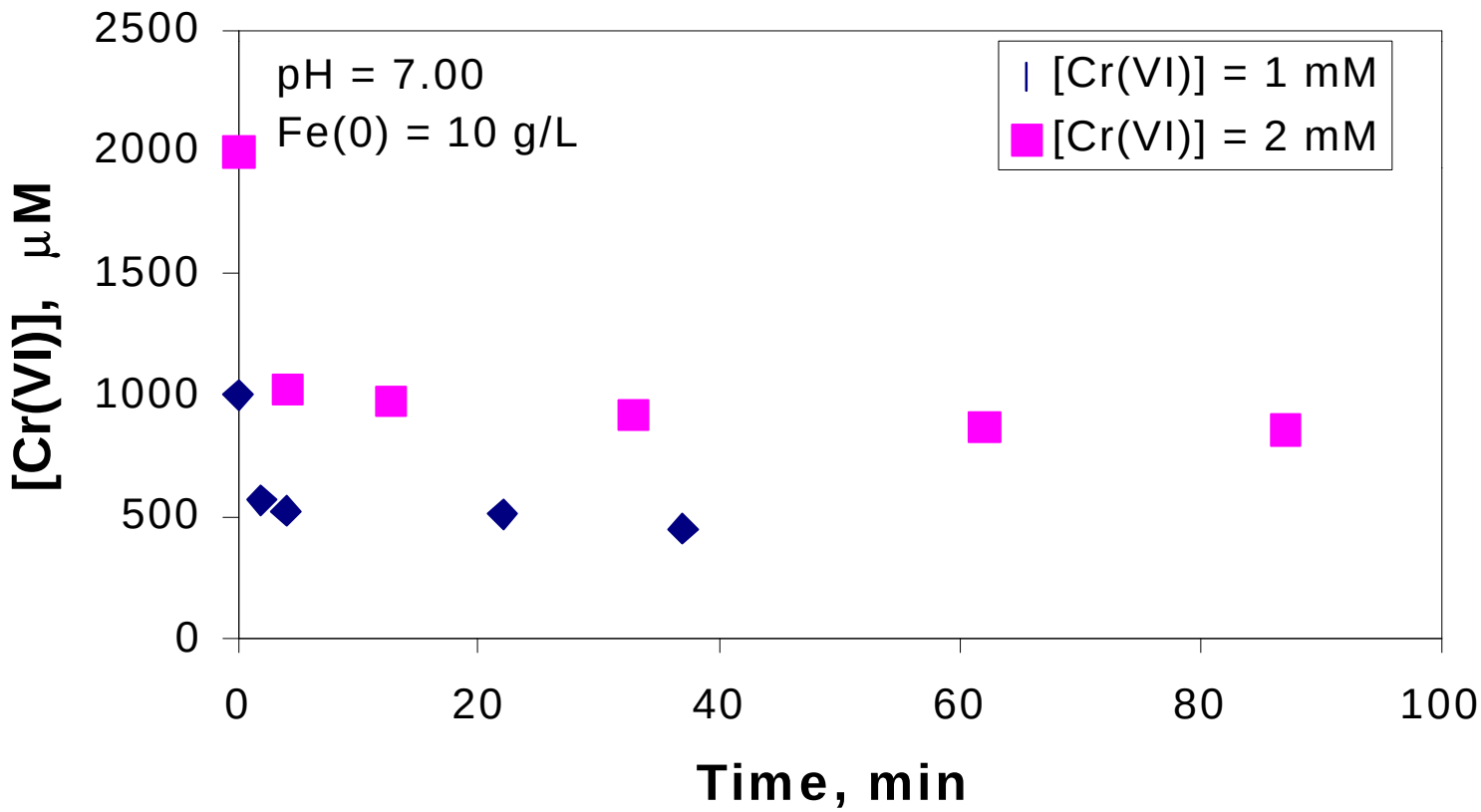
- Soil Characteristics

Soil type	Sand%	Silt%	Clay%
Oak Ridge*	31	50	19
Savanna River*	89	2	9
Ottowa Sand	100	0	0

*Provided by P.M. Jardine (ORNL)

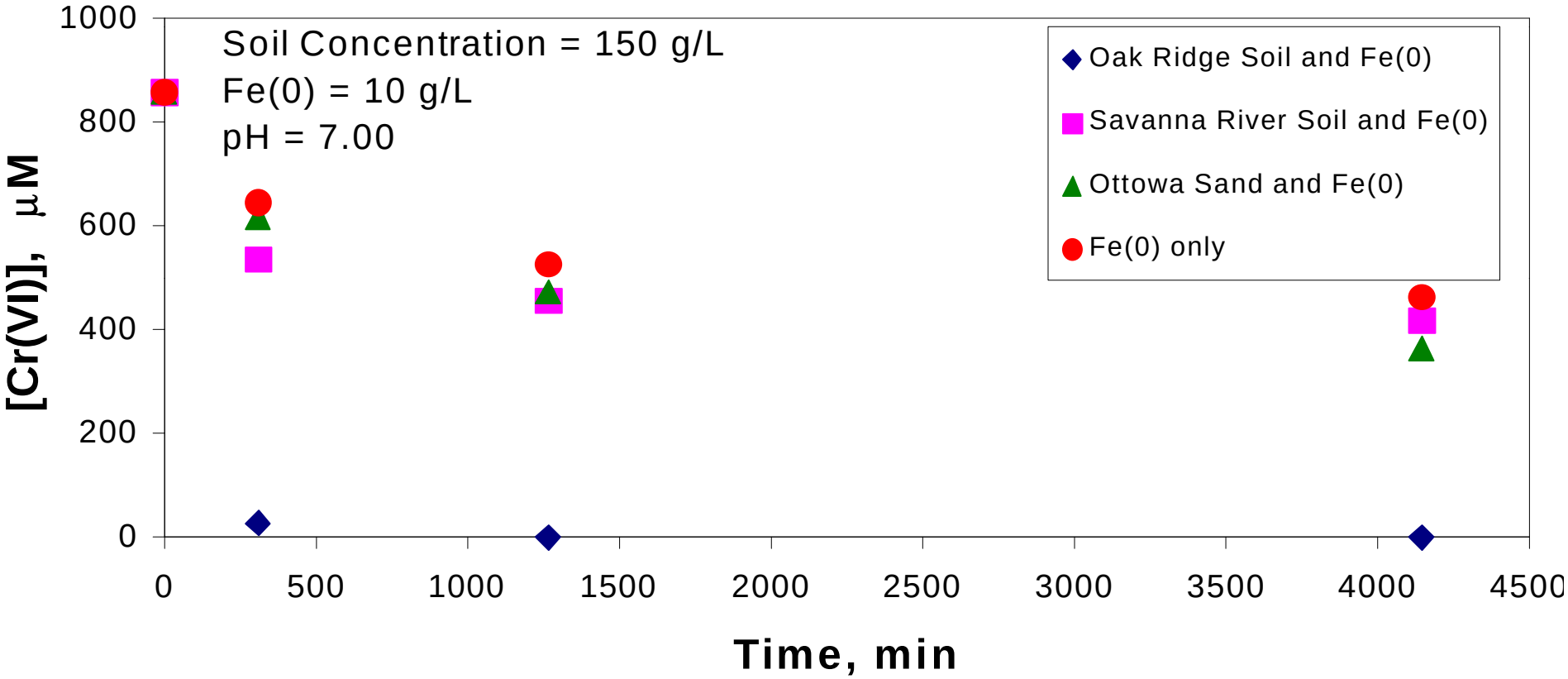
- Iron Characteristics
  - Degreased Iron Filings (Fisher Scientific)
  - <40 mesh
  - Surface Area ≈1.6 m^2/g

Short Term Reduction of Cr(VI) by Fe(0)



These results show the initial rapid reduction of Cr(VI) followed by a slower reduction rate at T=23 C and I = 0.01M. Most of the rapid reduction is attributed to Fe(II) present in the system prior to Cr(VI) addition.

Long Term Reduction of Cr(VI) by Fe(0) & Soil



A comparison of Cr(VI) reduction by Fe(0) alone and in the presence of various aquifer materials shows no significant differences between the Fe(0) systems and the Ottawa Sand/Fe(0) and Savannah River/Fe(0) soil systems. However, a significant increase in Cr(VI) reduction occurred in the Oak Ridge soil/Fe(0) system.

Conclusions

- Oak Ridge Soil greatly enhanced the reduction of Cr(VI) by Fe(0). This is consistent with increased rates of reduction observed in the presence of aluminosilicate bearing materials.
- The rate of Cr(VI) reduction by Fe(0) was not as significantly affected by the presence of sandy aquifer materials such as Savanna River Soil or Ottowa sand.
- The rate of Cr(VI) reduction by Fe(0) is much slower than reduction by Fe(II) or FeS.

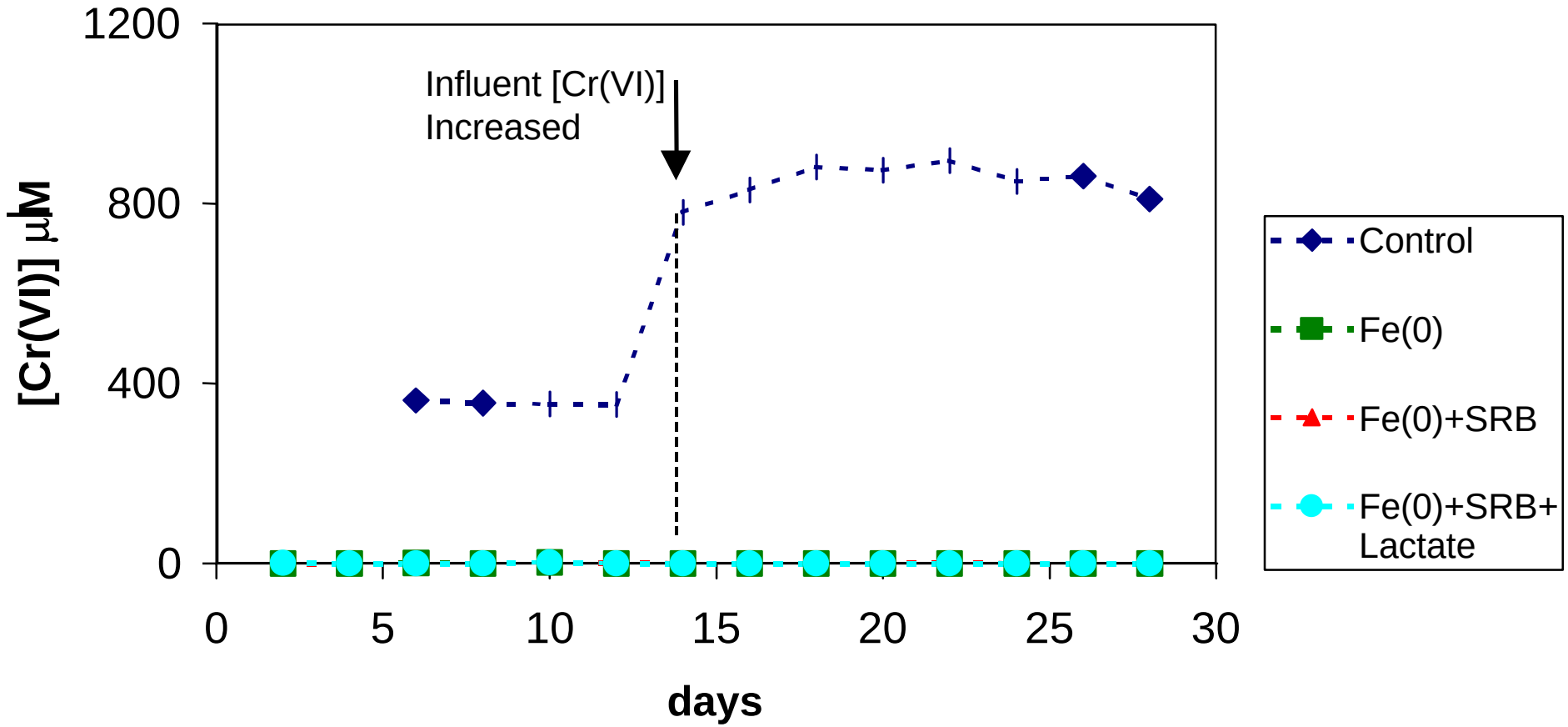
Column Experiments

Abiotic vs. Combined Abiotic/Biotic
Reduction of Cr(VI)

Experimental Design

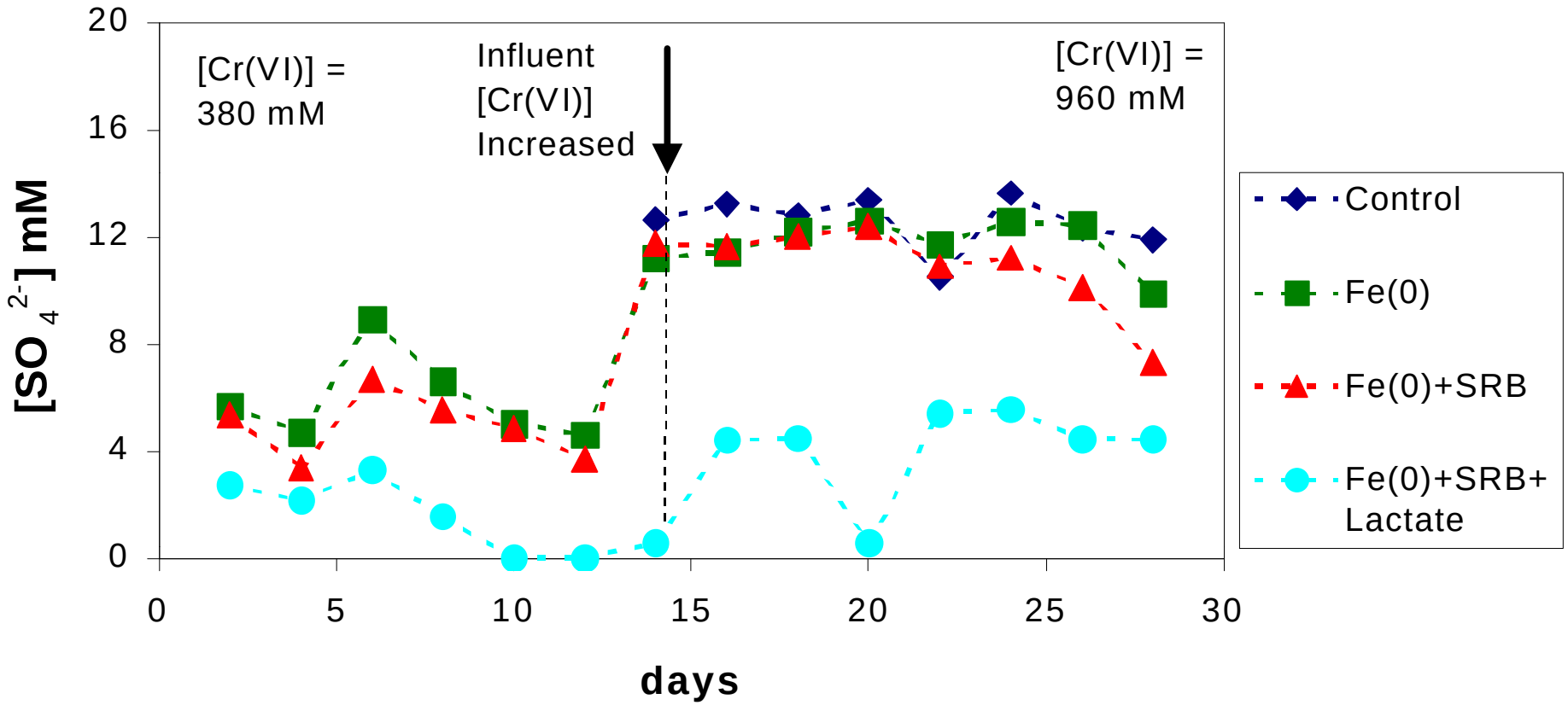
- Reactors: Continuous Flow Column Reactors (2.25 cm ID x 9.2 cm)
- Cell source: Lactate-enriched, sulfate reducing bacteria (SRB) stock culture.
- Fe(0) source: 5 g super fine steel wool (Rhodes).
- Influent: Buffered basal medium (pH=7) with sulfate and Cr(VI); one column was added with lactate.
- Volumetric flow rate: 10 ml/d.
- Effluent analysis: Cr(VI), sulfate, lactate, ORP and pH.
- Special Conditions: Columns were maintained under reducing conditions.

Cr(VI) Breakthrough Curves



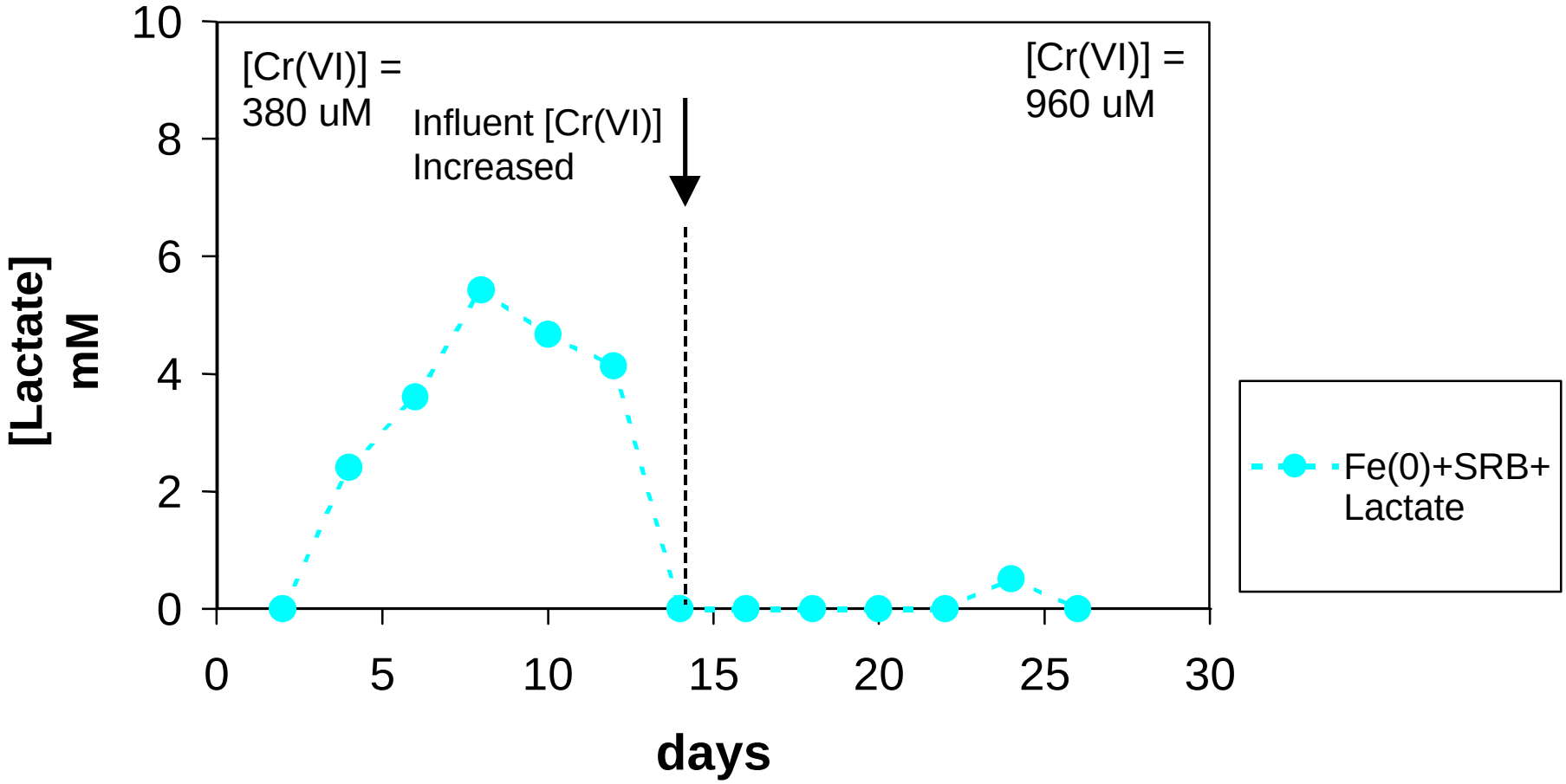
Cr(VI) concentrations in the column reactor effluents. The Cr(VI) concentration was increased from 380 to 960 uM after 14 days.

Sulfate Breakthrough Curves

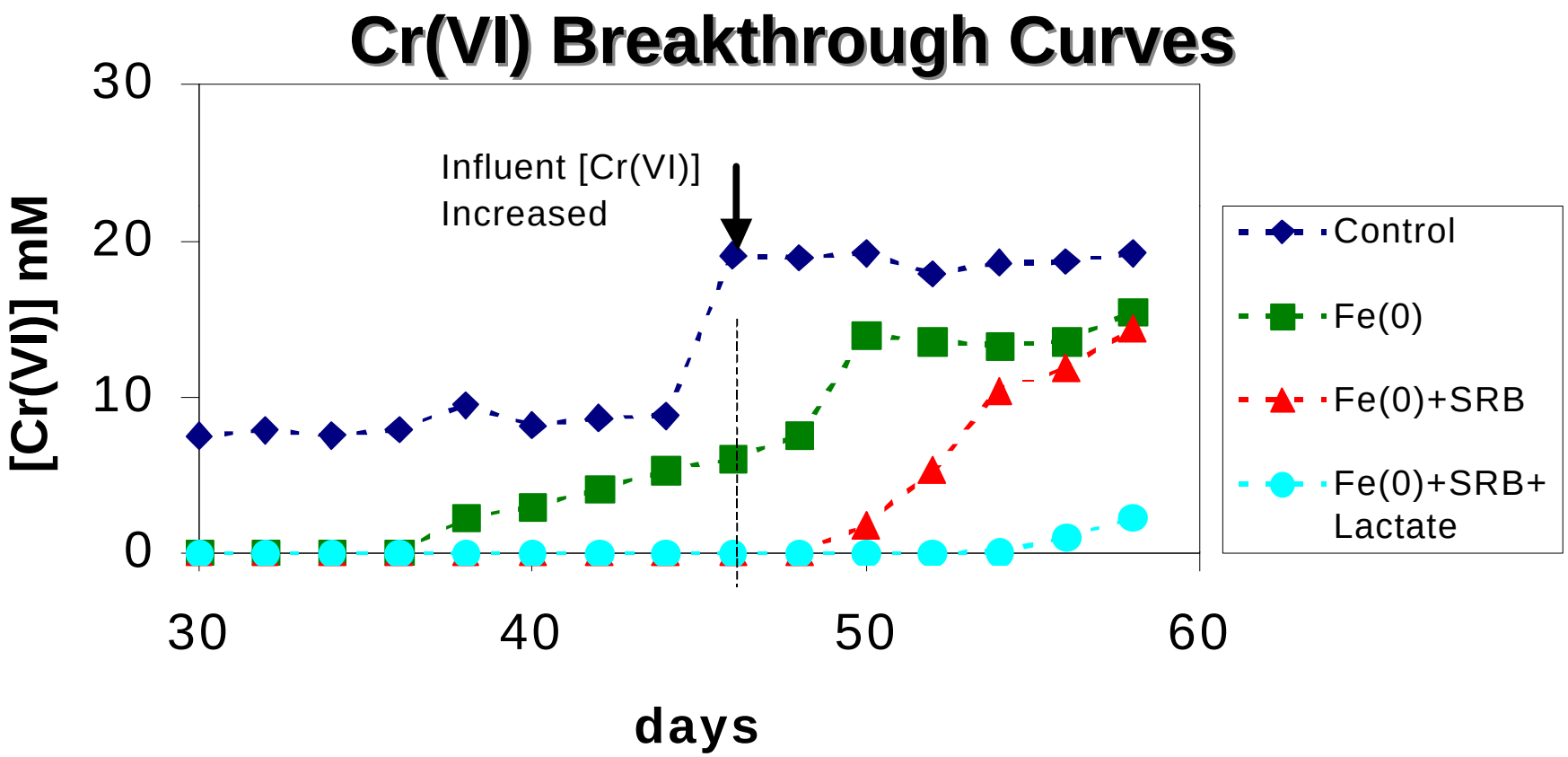


Sulfate concentrations in the column reactor effluents. The influent sulfate concentration was initially 10.41 mM and was increased to 12.5 mM after 14 days. Lower sulfate reduction was observed in the Fe(0) + SRB column because hydrogen was the only electron donor present.

Lactate Breakthrough Curve

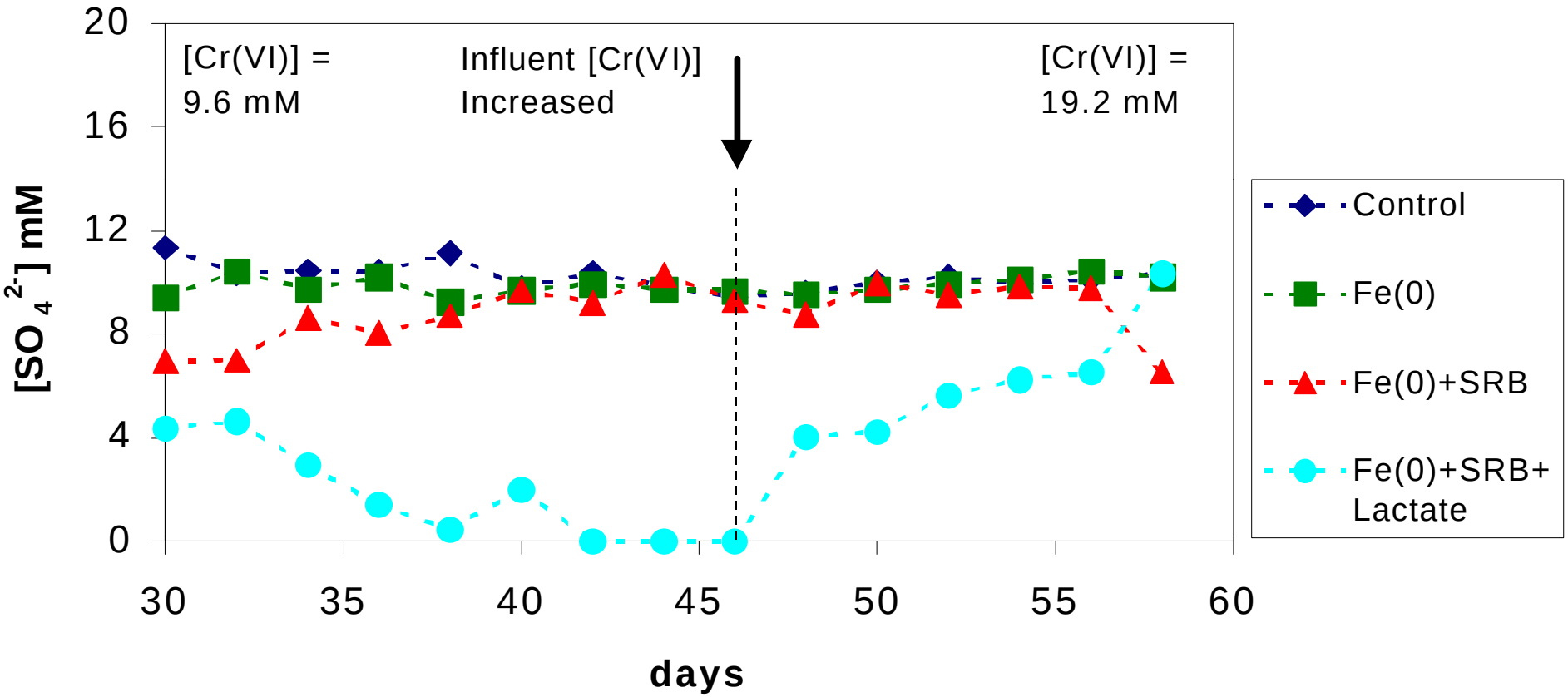


Lactate concentrations in the column reactor effluents. The influent lactate concentration was 20.8 mM. Lactate served as an electron donor for the SRB to reduce sulfate to sulfide.



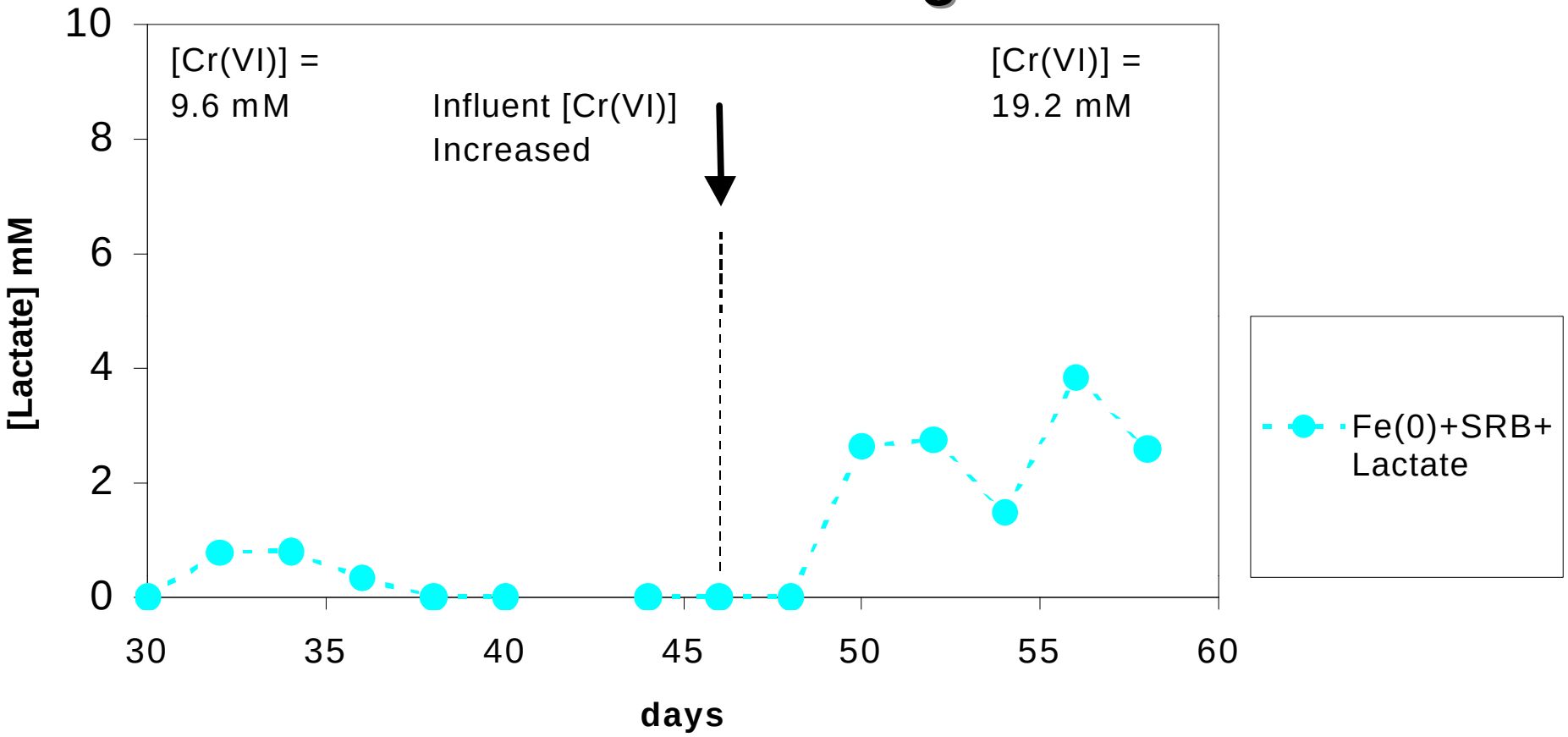
The Cr(VI) concentration was increased from 9.6 to 19.2 mM after 46 days. At an influent concentration of 9.6 mM, Cr(VI) breakthrough occurred in the abiotic column (Fe(0)) after six days at that concentration. At the highest influent concentration of 19.2 mM, Cr(VI) breakthrough occurred in the abiotic/biotic columns (Fe(0)+SRB; Fe(0)+SRB+lactate) after 4 and 10 days at that concentration, respectively.

Sulfate Breakthrough Curves



The influent sulfate concentration was 10.41 mM. An increase in sulfate concentration in the Fe(0)+SRB+lactate column preceded Cr(VI) breakthrough.

Lactate Breakthrough Curve



The influent lactate concentration was 20.8 mM. Lactate served as electron donor for the SRB to reduce sulfate to sulfide. An increase in lactate concentration in the Fe(0)+SRB+lactate column preceded Cr(VI) breakthrough.

Conclusions

- At low Cr(VI) concentrations, both the abiotic and combined abiotic/biotic systems effectively reduced Cr(VI).
- The combined abiotic/biotic systems (Fe(0) and SRB) exhibited better performance for Cr(VI) reduction compared to the abiotic system (Fe(0) only) at high Cr(VI) concentrations.
- The addition of lactate to the abiotic/biotic systems improved the performance of the abiotic/biotic system at higher initial Cr(VI) concentration up to 19.2 mM. This result is consistent with the observation that many SRB prefer lactate to hydrogen as an electron donor.

References

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IMPLICATIONS FOR IN-SITU BIOREMEDIATION

- Biocorrosion-promoted chromium reduction may be a significant process in permeable, metal-containing, reactive barriers.