2007-05-08

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INVESTIGATION OF THE IRON OXIDATION KINETICS IN MANTUA RESERVOIR

by

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A thesis submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Master of Science

Department of Civil and Environmental Engineering

Brigham Young University

August 2007

BRIGHAM YOUNG UNIVERSITY

GRADUATE COMMITTEE APPROVAL

of a thesis submitted by

Scott H. Lathen

This thesis has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

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BRIGHAM YOUNG UNIVERSITY

As chair of the candidate's graduate committee, I have read the thesis of Scott H. Lathen in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university and department style requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

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ABSTRACT

INVESTIGATION OF THE IRON OXIDATION KINETICS IN MANTUA RESERVOIR

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Master of Science

Irrigation of the municipal cemetery in Brigham City, Utah resulted in stained headstones in 2001 and 2002. The water used in the irrigation came from Mantua reservoir, a medium sized impoundment situated near the mouth of Box Elder Canyon. In order for Brigham City to establish a city wide secondary pressurized irrigation system using water from Mantua reservoir, the cause and the source of staining problem must be determined. Previous research (Wallace 2006) determined that the source of the staining was the reduction of iron found in Mantua Reservoir sediments that occurred when seasonal variations in the reservoir caused anaerobic conditions. The reduced iron then dissolved in the water and was used in the irrigation system, causing re-oxidation of the iron. The oxidized iron then precipitated out on the headstones causing the staining. The

purpose of this investigation is to determine the iron oxidation kinetics after the re-aeration of the water which will help determine appropriate mitigation methods. A secondary purpose is to confirm the Mantua reservoir's capacity to become anaerobic, resulting in the conditions which cause staining.

Using laboratory investigations and computer modeling, I determined that on re-aeration, fifty percent of the dissolved iron in the water precipitates in five hours. Using first-order kinetics to model this process, I found the rate constant of the kinetic reaction to be 0.0029 min^{-1}. Fitting a geochemical computer model of the iron oxidation kinetics in Mantua reservoir, which uses a higher-order kinetics model to better model this process, to experimental kinetic data yielded a rate constant of $4\text{x}10^{13}$ /atm x min.

I also recreated the staining process in the laboratory using concrete. This was successful and provided visual evidence that the iron precipitates out of the water and stained the concrete within a couple of hours of application. Field data collected from Mantua reservoir showed that the dissolved oxygen concentration in the reservoir drops regularly below levels consistent with equilibrium to the atmosphere. While my field measurements did not record anaerobic conditions, based on the patterns shown, this study shows that it would be possible for anaerobic conditions to occur during warmer weather.

ACKNOWLEDGMENTS

First, I wish to thank Dr. Gus Williams for his advice and technical assistance throughout the entire duration of this study. I would also like to thank Rob Wallace for finding this project and conducting the initial research that provides the basis for this study.

The project was funded in its entirety by the Division of Public Works of Brigham City, Utah.

Finally, I would like to thank my wife for her support and her sacrifice to support and assist me in this project.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 Introduction

Brigham City, Utah installed a pressurized irrigation system to provide more effective water use and make irrigation more efficient. The system was restricted to just irrigating the city cemetery in the initial installation, though expansion to the rest of the City was planned. The system ran without serious problems until 2001, when workers found the headstones in the municipal cemetery were stained a dark reddish brown (Bigelow 2002). Ferric iron (Fe^{3+}) had precipitated from the irrigation water, caused the staining on the headstones, and is the source of the red color of the stain (Wallace 2006). The water used in the pressurized irrigation system comes from Mantua Reservoir.

After the first appearance of the staining, the city shock treated the pipeline with bactericides in order to eliminate a biofilm observed to be lining the pipes. At this time, it was thought that the biofilm was the main factor causing the staining. The city also introduced iron and manganese sequestering agents, as well as chlorinated the water in an effort to prevent a recurrence of the staining. The staining did not occur during the remainder of that watering season, however the staining did return during the 2002 irrigation season despite the continued water treatments initiated the previous year.

Due to the continued staining from the system, Brigham City refrained from using Mantua water in the irrigation system and has switched to culinary water (Bigelow 2002).

Figure 1-1 is a photograph taken from the Brigham City cemetery sexton's report on the staining.

Figure 1-1: Headstone staining (Wood 2002)

The staining has not occurred in a predictable pattern or at a constant frequency and it has been difficult to establish common links between the staining events, this caused significant difficulty in determining the source and cause of the staining so they can use the Mantua water in the pressurized irrigation system and expand the irrigation system beyond the cemetery.

In 2005, Brigham City initiated a feasibility study to explore the possibility of creating a city wide pressurized irrigation system. Mantua Reservoir was identified as one potential and preferred source for the irrigation water (Bigelow 2005). This proposed expansion is not feasible using water from Mantua Reservoir until the threat of iron staining is removed. The city wants to understand the source of the staining, the mechanisms and situations that cause staining, and develop potential measures that can be taken to eliminate or minimize the problem.

1.1 Mantua Reservoir Background

Mantua Reservoir, shown in Figure 1.2, is a medium-sized reservoir located at the top of Box Elder Canyon just east of Brigham City. Table 1-1 summarizes the significant attributes of Mantua Reservoir (Loveless *et al* 1997).

Table 1-1: Attributes of Mantua Reservoir

Elevation (ft):	5159
Surface Area	554
Watershed Area	5559
Capacity (acre-	10450
Mean Depth (ft):	14
Max Depth (ft):	20
Length (miles):	1.12
Width (miles):	1.02
Shoreline (miles):	2.1

Mantua Reservoir is a shallow reservoir that has a fairly large surface area. These two characteristics make the water unusually warm, exceeding the state guidelines of 20°C for a cold water fishery, promoting the growth of a myriad of aquatic life (Loveless *et al* 1997). Mantua also has a high loading of nutrients including phosphorus loadings that usually exceed regulations. The reservoir, shown in Figure 1-2, supports large blooms of blue-green algae and the production of macrophytes. The large quantity of aquatic organisms contributes to a low amount of dissolved oxygen (DO) in the system (Loveless *et al* 1997). The lake's beneficial use classification is 3A, a cold water fishery, 2B, for recreational use, and 4, protected for agricultural irrigation uses (Utah Department of Environmental Quality 2000).

Figure 1-2 : Mantua Reservoir

In the course of the Clean Lakes Study (Loveless *et al* 1997) it was observed that during the period from May to September, the DO concentration within one meter of the reservoir bottom was depressed below acceptable levels which were 3.0 mg/L. The DO conditions improved between July 18th and August 10th because of increased wind action, resulting in better mixing in the reservoir, mixing the aerated surface water with the lower waters. The low DO concentrations in the summer resulted from the hot stagnant conditions, decomposition of organic matter, and photosynthesis by aquatic vegetation (Loveless *et al* 1997).

The area surrounding the reservoir contributes to the characteristics in Mantua Reservoir that result in low DO. The Mantua Fish Hatchery is located at the head waters of Maple Creek, a major contributor to Mantua Reservoir. The hatchery is a major point source for total phosphorus loading to the reservoir which supports the high level of biological activity observed. Also of significance to this study is the composition of the sediments surrounding the reservoir and forming the bed of the reservoir. These sediments have a very high quantity of iron (III) minerals in the soil. Loveless *et a*l (1997) gives the iron concentration in the lake bed sediments as 16,600 and 13,300 (mg/kg) respectively in the North and South arms of the reservoir. Wallace (2006) found the concentration of ferric iron in the reservoir sediments to be 16,500 mg/kg dry weight in sediment samples taken near the outlet and dam.

Big Creek is the outlet for Mantua Reservoir and has an average flow of 21 cubic feet per second. Brigham City captures Big Creek at the reservoir outlet and pipes the water into the city for power and irrigation uses. The head difference between the reservoir and the city also allows the water to be used as a power generating source (Loveless *et al* 1997).

Previous research by Wallace (2006) determined that the iron found in the sediments of Mantua Reservoir is responsible for the staining of the Brigham City. The research concluded that when conditions cause the hypolimnion of the reservoir to become anaerobic, the ferric iron in the sediments is reduced to ferrous iron. Ferrous iron has a solubility constant sixteen orders of magnitude higher (Sawyer e*t al* 2003) than ferric iron and therefore readily dissolves into the reservoir water. This dissolution process is catalyzed by biological activity which greatly increases the rate at which the iron dissolves. The iron-rich water is then taken into the reservoir outlet and piped to Brigham City in a closed system that is not re-aerated. When the iron saturated water leaves the Brigham City irrigation system and is sprayed onto the cemetery lawn, the water is re-aerated causing the ferrous iron to oxidize to ferric iron. At this point, the water becomes over saturated with respect to iron which then precipitates onto the headstones of the cemetery causing the observed staining (Wallace 2006). The reason the observed staining occurred intermittently was because the exact conditions which would cause the reservoir to go anaerobic are not common. These conditions occur at night during low-water, high-temperature, and low-wind conditions. Under these conditions degradation of biological matter in the reservoir uses the available oxygen and under these conditions there is no mechanism for re-aeration of the hypolimnion waters at the bottom of the reservoir.

1.2 Objectives

The objective of my research is to determine the kinetics of the oxidation of ferrous iron to ferric iron and the subsequent precipitation of the ferric hydroxides, the source of the staining in Brigham City. Understanding the kinetics of this reaction will allow various treatment and mitigation alternatives to be evaluated. Previous research (Wallace 2006) determined that iron in the reservoir water does undergo reduction and oxidation based on the dissolved oxygen conditions in the water and is potentially catalyzed by microorganisms, speeding up the dissolution of the iron from the sediments to the water. The knowledge of the iron chemistry which occurs and causes this problem allows Brigham City to focus on remediation of the iron at the source. Modeling the kinetics of the oxidation reaction will allow Brigham City to choose the most effective treatment method and aid in design of a chosen treatment system.

In order to determine the reaction kinetics, I have used both experimental procedures and theoretical models. The experimental approach involved taking water and sediment samples from Mantua and allowing them to go anaerobic. The anaerobic conditions forced the reduction of ferric iron found in the sediments allowing the newly formed ferrous iron to dissolve in the water. I then re-aerated the water, causing the oxidation of the ferrous iron back to the ferric state, and recorded the amount of ferrous iron remaining after established time periods had elapsed. By repeating the experiment at various times, I generated a rate curve which describes the iron oxidation kinetics for the combination of Mantua Reservoir water and sediments.

In an effort to confirm the findings of Wallace (2006) who determined the staining mechanism, I recorded the reservoir DO levels over an extended period of time to determine if DO levels near the bottom of the reservoir were significantly depleted at night. Also using the water and sediment samples collected from the reservoir I have replicated the staining seen in the Brigham City cemetery.

I developed the theoretical geochemical model using PHREEQC, developed by Parkhurst and Appelo (1999), to model the oxidation kinetics. The parameters used to create and define this model were taken from the Clean Lakes Study (Loveless *et al* 1997) performed on Mantua Reservoir. After the development of a preliminary model based on these data, I used the experimental data obtained from the laboratory procedures using Mantua Reservoir water and sediments to refine the model to fit the measurements I had which characterize Mantua Reservoir. A model of the iron oxidation kinetics allows a number of different scenarios to be evaluated and recommendations can be made to determine the treatment options available to Brigham City.

2 Chemistry

2.1 Chemical Conditions of Mantua Reservoir

Previous studies conducted on Mantua Reservoir (Loveless *et al* 1997 and Wallace 2006) determined the general geochemistry that governs the reservoir. The Clean Lakes Study (Loveless *et al* 1997) described the nutrients, metals, and chemicals found in the reservoir, the inlets to the reservoir, and in the sediments forming the lake bed. Of particular interest to my research is the amount of iron that was found in the sediment and water of the reservoir and the DO conditions of Mantua. The study found that iron levels in the reservoir water averaged less than 20 μg/L over the course of the study. However, the iron levels in the lake bed sediments were quite high in both the north and south arms of the reservoir with measurements of 16,600 mg/Kg and 13,300 mg/Kg respectively (Loveless *et al* 1997).

The Clean Lakes Study (Loveless *et al* 1997) also recorded the DO in Mantua Reservoir. The DO levels found in this study were a source of extra concern during the summer months, May through September, because they were low. This is the same time of the year as when the cemetery staining occurred. During these months the DO was measured to be less than 3.0 mg/L within one meter of the reservoir bottom. The water above one meter from the bottom generally had measured DO levels within acceptable parameters. Exceptions occurred on several days, most notably July 18th, when low DO levels were measured farther from the reservoir bottom. On July 18th the DO was measured at only 1.0 mg/L two meters from the bottom. This indicates that under some conditions, the DO levels in the bottom of the reservoir could become anaerobic.

Research by Wallace (2006) concluded that low DO, especially completely anaerobic conditions, would cause the iron in the sediments to reduce to the ferrous state and dissolve in the reservoir water. Iron reduction is a geochemical process that is probably accomplished by the microorganisms in the water using iron (III) as the terminal electron acceptor instead of oxygen (Sawyer *et al* 2003). This biological process also speeds up the iron dissolution. Ferrous iron (Fe^{2+}) has a solubility product (ksp) that is fifteen orders of magnitude higher than ferric iron allowing the ferrous iron to dissolve into the reservoir water at significantly higher amounts that are possible under aerated conditions (Sawyer *et al.* 2003). Once the anaerobic reservoir water, with the dissolved ferrous iron, is re-oxygenated, such as through the action of being sprayed out of a sprinkler system, the iron (II) oxidizes to form the insoluble iron (III) which is over-saturated with respect to iron. The excess iron then precipitates as ferric hydroxide compounds causing the staining observed in the cemetery (Wallace 2006). In order to characterize and replicate these natural conditions Wallace (2006) collected water and sediment samples from Mantua. These samples were placed in BOD bottles, allowing the water to become anaerobic. The bottles were opened and DO was measured to confirm anaerobic conditions. At this point the water was stirred in order to accomplish aeration. At each stage, the original water, the anaerobic water in contact with the sediments, and the re-aerated water, the concentration of ferrous iron in solution was measured using the phenanthroline method and a spectrophotometer. Figure 2-1 is a bar chart showing the concentration of ferrous iron in the water under the various DO conditions measured in this study to characterize the processes observed using water and sediment collected at Mantua reservoir.

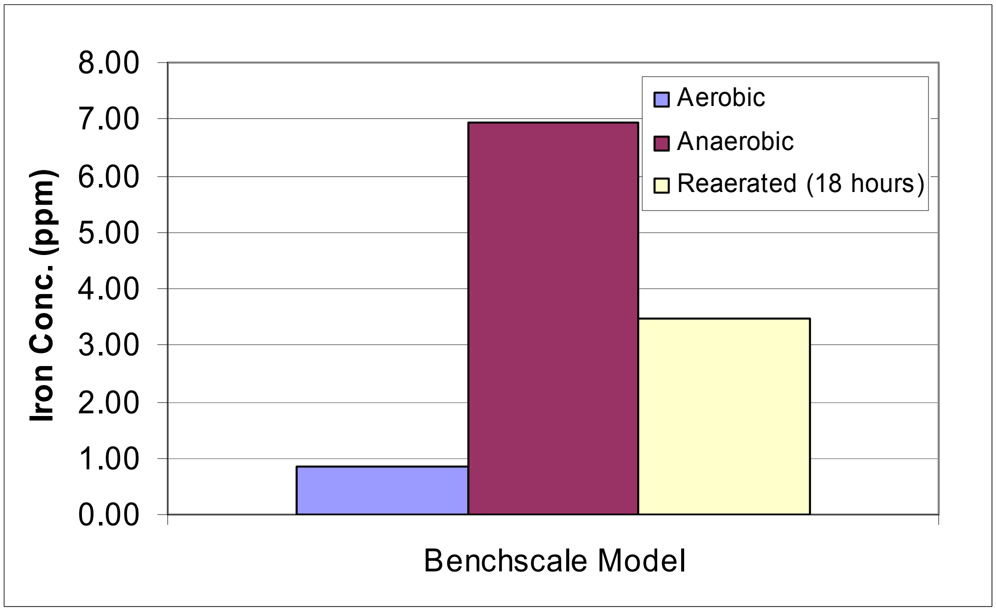

Figure 2-1: March 31st results (Wallace 2006)

The water under anaerobic conditions contains a significantly higher concentration of ferrous iron, this represents the conditions that could occur during warm, wind-free summer nights at Mantua. Upon re-oxygenation the ferrous iron concentration in solution drops from almost 7 ppm to about 3.5 ppm, the iron is precipitated from solution. This drop in iron concentrations from the anaerobic water conditions to the re-aerated water conditions is attributed to the oxidation of the ferrous iron creating insoluble ferric iron that precipitates out of the reservoir water and causes the problematic staining on the headstones (Wallace 2006).

2.2 Iron Oxidation Kinetics

The research of Wallace (2006) demonstrated that the mechanism for the headstone staining was the change in the aerobic condition of the water and the subsequent reduction and oxidation of the iron found in the lake bed sediments. In addition to knowing the staining mechanism, it is important to know the kinetics of the reaction in order to provide treatment recommendations.

Only minor changes in environmental conditions are necessary to initiate the oxidation or reduction of iron in natural systems (O'Neil 1985). The mixing of oxygen, at even small amounts, with the ferrous iron oxidizes the iron, forming the insoluble ferric iron (Fe^{3+}) which then will precipitate out of the water and cause staining (Sawyer et. al. 2003). Equation 2-1 is the reaction describing the oxidation of ferrous iron and the precipitation of ferric hydroxides:

$$4Fe^{2+} + O_2 + 10H_2O \leftrightarrow 4Fe(OH)_{3(s)} \downarrow + 8H^+ \qquad (2\text{-}1)$$

Iron oxidation kinetics has been vigorously studied resulting in established mathematical models used to predict the rate of iron oxidation in various systems. Singer and Stumm (1970) investigated iron oxidation kinetics, determining that the rate of oxidation follows a predictable model. Their research yielded the widely accepted equation (equation 2-2) describing the kinetics of ferrous iron oxidation.

$$\frac{-d\left[Fe^{2+}\right]}{dt} = k\left[Fe^{2+}\right]\left[OH^-\right]^2 Po_2 \qquad (2\text{-}2)$$

Po_2 is the partial pressure of the atmospheric oxygen exerted on the water surface and can be replaced with the DO concentration in the water (Stumm and Lee 1961). The rate constant, *k,* varies with the experimental method used to determine it. Equation 2-2 is first order with respect to the ferrous iron concentrations and second order with respect to the concentration of the hydroxyl ions. As a result, the greater the pH of the water, the faster the ferric iron forms and can precipitate (Houben 2004). Table 2-1 summarizes different values used for the rate constant.

Table 2-1: Rate Constants for Iron Oxidation[2]

Rate Constant[1] k ($1/mol^3$ x min)	Temperature (°C)	Reference
$0.8\text{-}1.7 \times 10^{16}$	10	Davison and Seed (1983)
1.4×10^{16}	25	Tamura et al. (1976)
0.7×10^{16}	10	Millero et al. (1987)
$1.7(\pm 0.4) \times 10^{16}$	10	Laxen and Sholkovitz (1981)
6.0×10^{16}	25	Stumm and Morgan (1996)

[1] rate constant for concentration of dissolved oxygen

[2] Modified from Houben (2004)

Equation 2-2 can be arraigned to be a function of pH instead of the hydroxyl ion concentrations (Houben 2004). This results in equation 2-3 which shows the oxidation rate as a function of both the DO concentration and the pH (or $[H^+]$):

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][H^+]^{-2}[O_{2(aq)}] \tag{2-3}$$

where *k* is the kinetic rate constant, $[Fe^{2+}]$ is the concentration of the ferrous iron dissolved in the water, $[H^+]$ is the concentration of the hydrogen ions, and $[O_{2(aq)}]$ is the concentration of DO in the aqueous solution. At pH values less than 3.5, the rate of iron oxidation is independent of the pH and that term is dropped from the equation. When this term is dropped, the rate constant increases to 1.0×10^{-7} (Singer and Stumm 1970).

Since the oxidation of ferrous iron is proportional to the concentration of ferrous iron in the reservoir, when other parameters are held constant, first-order kinetics can be used to determine the experimental rate constant (*k*). Equation 2-4 is the equation that describes these first-order kinetics (Sawyer *et al* 2003).

$$C = C_0 e^{-kt} \tag{2-4}$$

where C is the final concentration of the substance, C_0 is the initial concentration at $t = 0$, t is the time that the reaction proceeds, and k is the kinetic rate constant for the reaction. It should be noted that while all these equations use k as the rate constant, it is different for each equation used.

2.3 Factors Affecting Iron Oxidation Kinetics

A number of factors can influence the rate of ferrous iron oxidation (Liang 1993). Various environmental conditions, the presence of other ions, and the presence of iron oxidizing bacteria can all increase the rate of oxidation. Of the possible environmental factors, an increase in pH has the most dramatic effect on the kinetics of the system. A unit increase in the pH will result in a 100-fold increase in the oxidation rate of the ferrous iron (Morgan and Stumm 1996). Though less dramatic, a 15 degree Celsius change in the system, for a constant pH, will result in a 10-fold increase in the oxidation rate (Morgan and Stumm 1996). At high pH levels, greater than 7, the oxidation of the soluble ferrous iron in the system can happen in just minutes (Appelo and Parkhurst 2005). The increased oxidation rate resulting from a higher pH is a consequence of enhanced electron-transfer capacity (Houben 2004).

The presence of other metal ions can also have a catalytic effect on the oxidation of ferrous iron; particularly Cu^{2+} and Co^{2+} in trace amounts increase the reaction rate (Morgan and Stumm 1996). Other anions that form complexes with iron will also speed up the reaction (Morgan and Stumm 1996). Of particular note, when ferric iron is added to the water, it acts as a catalyst for the ferrous to ferric iron reaction (Tamura *et al* 1976). As a result, the more ferrous iron oxidized to the ferric state, the faster the reaction proceeds. Tamura *et al* (1976) proved that the catalytic effect of ferric iron happens as the ferrous iron in solution sorbs onto the suspended ferric iron particles. The ferrous iron is then oxidized on the surface of the ferric iron particles. Rising pH linearly increases the sorption of ferrous iron due to the higher amount of negative surface charge of the oxide. The increased rate of oxidation from the inclusion of ferric iron in the system leads to a new kinetic model based on equations 2-2 and 2-3 (Tamura *et al* 1976). Equation 2-5 is the revised kinetic model:

$$\frac{-d\left[Fe^{2+}\right]}{dt} = k_1\left[Fe^{2+}\right]\left[H^+\right]^{-2}\left[O_{2(aq)}\right] + k_2\left[Fe^{3+}\right]\left[Fe^{2+}\right]\left[H^+\right]^{-2}\left[O_{2(aq)}\right] \qquad (2\text{-}5)$$

where k_2 is the product of the equilibrium constant for the sorption of Fe^{2+} onto ferric oxide and the rate constant of the oxidation at the surface. The value of this constant is given as 1.71×10^{-5} mol/min (Tamura *et al* 1976). Equation 2-5 indicates that the pH has a more significant impact on the homogenous portion of the equation than on the heterogeneous part. Therefore the effect of ferric iron on the reaction rate is more important at lower pH levels. The catalytic effect of ferric iron is significant only when the concentrations of ferrous iron is greater than 3 mg/L otherwise there is insufficient catalytic surface to greatly impact the kinetics (Tamura *et al* 1976). This implies that once precipitation and staining start, it will proceed rapidly.

In addition to metal ions and physical environmental conditions, the presence of iron oxidizing bacteria will significantly increase the rate of the reaction (Okereke and Stevens 1991), just as iron-reducing bacteria can significantly increase the dissolution rate from the sediments (Wallace 2006). The presence of microbes can accelerate the reaction rate by a factor of 10^6 (Singer and Stumm 1970). *Thiobacillus ferrooxidans* are the bacteria most responsible for the oxidation of ferrous iron in low DO conditions. *T. ferrooxidans* are acidophilic chemolithotrophs that will increase the oxidation rate of Fe^{2+} when the pH values in the water fall below 3.5 (Okereke and Stevens 1991). The effect of the microbes on the kinetics of the reaction varies greatly depending on the environmental conditions present. Included in the variables which can affect the system is the actual concentration of the bacteria present in the system. An increase in the concentration of *T. ferrooxidans* results in an increase in the rate of the reaction. Equation 2-6 describes the oxidation rate of ferrous iron based on the bacterial concentration, the ferrous iron concentration, and the temperature of the system (Okereke and Stevens 1991):

$$\begin{aligned} Y &= 0.68(B) + 0.02(B)(T) + 1.8x10^{-4}(T^2) - 0.46(B^2) \\ &- 5x10^{-5}(F)(T) - 1.2x10^{-3}(F)(B) - 0.22 \end{aligned} \qquad (2\text{-}6)$$

where B is the bacterial cell concentration (mg/mL) and F is the ferrous iron concentration (millimolar) with T being the temperature in degrees Celsius (Okereke and Stevens 1991).

3 Methods and Experimental Procedures

3.1 Sampling Methods and Locations

In order to determine the kinetic reaction coefficient (*k)* for iron oxidation, water and sediment samples were collected from Mantua Reservoir and used in laboratory procedures to determine the ferrous iron content of the reservoir water at various oxidation states. The water entering the irrigation system is the water of highest concern for this study. The reservoir outlet that supplies the irrigation system is located on the west side of the reservoir. The samples collected for this study were taken from a floating pier, also located on the west side of the reservoir, approximately 100 feet from the reservoir outlet. Figure 3-1 is an aerial photo of Mantua Reservoir. The floating pier (not visible in the figure) is located at the south west corner of the reservoir. The outlet is approximately 100 ft to the north from the pier, along the western shore of the reservoir.

I used a soil auger to remove samples of the reservoir bottom sediments. These samples were taken from the sediments beneath the floating pier. After collecting the sediment samples in buckets, the remainder of each bucket was filled with water collected from the surface of the reservoir. Surface water has low dissolved ferrous iron due to the aerobic conditions present at the water and air interface (Campbell 1989). After collection, the sediment and water samples were transported back to the laboratory for analysis.

Figure 3-1: Aerial view of Mantua Reservoir

The samples used in the laboratory procedures were collected on two separate occasions. The first sample set was taken on September 8, 2006 in the early afternoon. The second sampling date was on October 6, 2006 also in the early afternoon. The procedures used for collecting the samples were the same for both days.

3.2 Qualitative Procedures

The first experiments performed were qualitative methods to confirm the findings of Wallace *et al* (2006) that the change in oxidation state of iron found in the lake bed sediments would cause the observed staining by first dissolving then precipitating iron from the sediments. In order to accomplish this objective, samples of water and sediment from Mantua Reservoir were subjected to the same conditions that we believe are responsible for the staining and the results were documented.

To perform these experiments, first the sediment and water from Mantua Reservoir was transferred to a BOD bottle. The bottle was a standard 300 mL BOD bottle with 1.25 inches of sediment on the bottom and the remainder filled with reservoir water. The BOD bottle was sealed and placed in a dark cabinet, to prevent photosynthesis from generating oxygen. Prior to the transfer of the water and sediment to the BOD bottles, a 16 oz bottle of Sprite was added to the water in the 5 gallon bucket, in order to renew the food source for the microbes. This was necessary to compensate for the delay between the time the water was collected from the reservoir and when it was used in the laboratory procedures. During this time, the bacteria used all the available food initially present in the reservoir water.

After allowing the BOD bottles to sit in the cabinet for three days, to completely deplete the DO, the water was sprayed onto a concrete core sample using a pump, simulating the action of a sprinkler in the Brigham City Cemetery irrigation system. I photographed the concrete core samples immediately before spraying with the Mantua water and several times over the next day to compare the amount of visible staining. These results are presented in Section 5.2.

3.3 DO Testing in Mantua Reservoir

Along with laboratory procedures to confirm the findings of Wallace (2006), we also deployed a sonde in Mantua Reservoir to record the fluctuation of DO levels in the reservoir. The purpose of the DO measurements was to prove that the oxygen state of the reservoir fluctuates and that the DO levels will reach sufficiently low levels to allow the reduction of ferric iron to soluble ferrous iron (Sawyer *et al* 2003). Wallace (2006) established conditions which could cause staining, but did not confirm that these conditions occur in Mantua Reservoir, which was the goal of these measurements. The data obtained from the sonde was correlated with weather station data in order to prove the hypothesis that temperature and wind conditions (which provides mixing of the reservoir water) contribute to the depletion of oxygen in the lower layers of the reservoir and that under the right conditions, water at the bottom of Mantua Reservoir could become anaerobic, dissolving high levels of iron from the sediments.

I used a YSI 600 OMS (optical monitoring sensor) sonde with an additional DO probe. The sonde is internally powered and capable of storing up to 150,000 bits of data. The DO probe is a YSI 6150 Optical Dissolved Oxygen Sensor. Optical sensors do not require changing a membrane frequently in order to achieve accurate results (YSI Incorporated 2006). Prior to deployment, the sonde and accompanying DO probe were calibrated according to the procedures in the operating manual (YSI Incorporated 2006). The sonde was deployed by swimming underneath the floating pier and using 8 feet of rope to attach it to a brace on the underside of the pier. This positioned the sonde about 2 to 3 feet above the sediment. The sonde was not positioned lower in case the reservoir levels changed during the measuring period, lowering the dock and potentially having the sonde contact the sediments.

The probe was set to record for a period of thirty days starting on September 8th, 2006. The sonde took readings every 15 minutes over this time period. The parameters measured were time, temperature, DO concentration, resistivity, total dissolved solids

(TDS), and salinity. Of these parameters, the DO concentration and temperature were the only data used in this study. The probe was retrieved on October 8th, 2006 using a DO probe recovery device that I constructed using a broom and an old metal hanger. The data was uploaded from the sonde to a computer and analyzed using the software included with the probe. The results of these measurements and discussions are included in Section 5.1.

3.4 Laboratory Procedures

In order to determine the iron oxidation kinetics of Mantua Reservoir I used the collected samples to determine the kinetics rate constant (k). The laboratory procedures involved forcing the water samples to go anaerobic while in contact with the sediments, re-aerating the samples, and simultaneously recording the concentration of ferrous iron remaining in the water during the re-aeration period. The following sub-sections detail the steps required to accomplish each phase of the laboratory procedures.

3.4.1 Anaerobic Conditions

After transporting the samples from Mantua Reservoir to the lab, they were kept stored in sealed buckets until there was sufficient time to conduct the experimental procedures. The samples collected on September 8th, 2006 (the day the probe was deployed) were run on October 21st, 2006. The delay between collecting the samples and running the experimental procedures necessitated the addition of a food source for the microbes in order for them to use the available oxygen in the water and aid in the oxidation and reduction processes. The food source added was a 16 oz. bottle of Sprite. The sample bucket, which included two inches of sediment, was then sealed and stored in a dark refrigeration room at normal room temperature of about 20 degrees Celsius. The bucket and water samples were then left overnight to allow time for the microbes to use all of the DO in the water as well as oxygen in the headspace of the bucket. In order to confirm the anaerobic state of the Mantua water samples, a YSI model DO probe was used to confirm the DO oxygen state of the water, which for these tests was zero.

3.4.2 Standards

To measure the concentration of ferrous iron in the Mantua water as it was re-aerated, a set of standards was prepared with known concentrations of iron. These standards were used to create a calibration curve to quantify experimental results.

To create the calibration curve I needed to determine the iron concentration range needed to fit the experimental data. For each trial, conducted with samples gathered on different days, new standards and calibration curves were created. Wallace *et al* (2006) found the maximum concentration of iron to be slightly less than 7 ppm for the samples collected on March 31st, 2006 with the minimum being essentially 0 ppm within the ranges of the method used. As a result, the four points I used for the calibration curve were nominally 1 ppm, 2 ppm, 5 ppm, and 8 ppm, which provided a smooth curve and bracketed the iron concentration range I required.

The standards were created by dissolving ferric chloride ($FeCl_3$) in de-ionized (DI) water in a 1000-mL volumetric flask. In order to achieve an iron concentration of 100 ppm, 0.495 grams of ferric chloride were dissolved in the DI water. This produced an iron concentration of 102.265 mg/L in the 1000 mL flask. This concentrated standard was then diluted to the desired concentrations necessary for the calibration curve by mixing 1, 2, 5, and 8 mL, respectively from the concentrated 100 ppm standard into a 100 mL volumetric flask and filling with DI water. The actual concentrations of the four points on the calibration curve are given in Table 3-1. The spreadsheet used to calculate the necessary iron concentrations for the points on the calibration curve and the calculations used is included in Appendix C.

Table 3-1: Standards

Desired Concentration (ppm)	Actual Dilution (ppm)
1	1.023
2	2.045
5	5.113
8	8.181

The calibration curve was created by measuring the known iron standards concentrations using the same procedures that the iron concentrations in the Mantua samples were measured. First, ten mL from each of the four standard concentrations were placed in test vials that fit the spectrophotometer. A packet of FerroVer Iron Reagent was then added to each vial. The reagent is a phenanthroline based powder that dissolves and creates a colorimetric change in the sample, the strength of which varies based on the concentration of the iron present. Each standard was measured in the spectrophotometer at a wavelength of 510 nanometers, the necessary wavelength to accurately determine the iron concentration (APHA 1995). The amount of light absorbed by each standard was recorded and a calibration curve was created based on the absorbance and the associated concentration of iron. Normally the calibration curve would be piecewise linear, using each measured data point. However, for these data, the curve approximated a straight line. To make calculations simpler, a linear trend line was fit to the calibration points creating a linear equation that determines iron concentration based on the absorbance of a sample. Figure 3-2 is the calibration curve created using the ferric chloride standards.

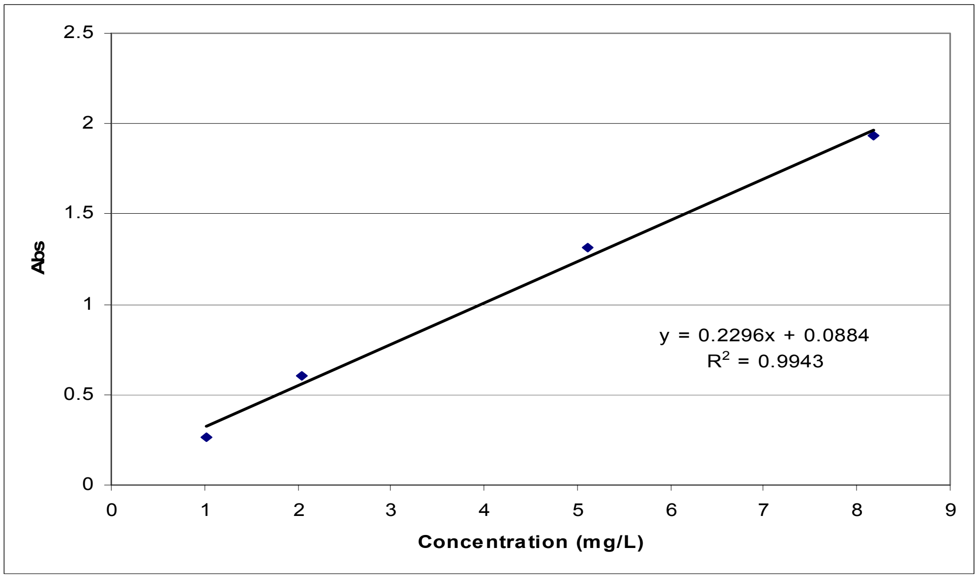

Figure 3-2: Iron standards calibration curve

3.4.3 Re-aeration and Iron Measurement

To measure the experimental results, the anaerobic state of the Mantua water sample was first confirmed, and then the procedure used to measuring the iron concentration in the standards was followed to measure the iron concentration in the Mantua water. First the water in the sample bucket was decanted from the sediment by pouring it into a smaller container. Immediately upon opening the bucket of anaerobic water, a sample was removed and the iron was measured. This sample was an attempt to measure the amount of dissolved iron before any aeration. A mixer was then placed in this bucket to provide adequate re-oxygenation to the entire water sample.

At specified times, a sample of the Mantua water was removed from the mixing bucket and filtered using a bottle top filter and a vacuum pump. The purpose of the filtration was to ensure that the ferric iron that had already precipitated was removed from the sample and measure only the remaining ferrous iron in the reservoir water. After the sample was filtered, two ten mL test vials were prepared with the FerroVer reagent. The absorbance or these two vials were then measured in the spectrophotometer at the required wavelength of 510 nanometers. The recorded absorbance for each sample was compared to the calibration curve in order to determine the concentration of ferrous iron in the water, which was averaged for the two samples taken. This process was repeated as quickly as possible, being constrained by the time required to filter each sample. The result was a kinetics curve relating time since re-aeration to the concentration of ferrous iron remaining in the water. From the kinetics curve, and using the first-order kinetics equation (equation 2-4), the rate constant for iron oxidation kinetics in Mantua Reservoir was determined. This is discussed more fully in Section 5.3.

4 Computer Modeling Procedures

4.1 PHREEQC

To better understand the iron oxidation kinetics of Mantua Reservoir I created a computer model. The model allowed me to evaluate the kinetics of iron oxidation for any conditions that may be present at the reservoir, based on the kinetic models present. The parameters that can be adjusted in the model related to iron precipitation kinetics include the water temperature, pH, and the loading rates of the various nutrients and inorganic constituents. The current conditions of the water at Mantua reservoir could be used to setup the model and using the experimentally determined *k*, the kinetics for iron oxidation can be predicted under various conditions.

The program used to develop the model of Mantua Reservoir was PHREEQC. PHREEQC was developed by Parkhurst and Appelo for United States Geological Survey (USGS). The program was created to conduct low temperature aqueous geochemical calculations (Parkhurst and Appelo 1999). In this case low temperatures are those expected in the surface environment, in many geochemical applications, the reactions take place at high temperatures deep underground. The primary use of PHREEQC is as a speciation program to calculate saturation indices and the distribution of aqueous species. Kinetic reactions can also be modeled using an embedded Basic editor. The kinetic rate expressions are written using Basic and then PHREEQC interprets the code and runs the kinetic calculations (Parkhurst and Appelo 1999).

4.2 Mantua Model Development

To develop a model of the iron oxidation kinetics taking place in Mantua Reservoir water, I used example 9 of the PHREEQC models provided with the program which was created to conduct kinetic calculations for the oxidation of ferrous iron to ferric iron. Example 9 is titled “Kinetic Oxidation of Dissolved Ferrous Iron with Oxygen” (Parkhurst and Appelo 1999) and is included in Appendix B. I used this example model as the basis for the iron oxidation kinetics model developed for Mantua Reservoir.

Example 9 is used in the documentation to demonstrate the ability of PHREEQC to conduct kinetic calculations for the oxidation of Fe^{2+} to Fe^{3+} in water (Parkhurst and Appelo 1999). The rate equation, Equation 4-1, used in the model was adapted from Singer and Stumm (1970):

$$\frac{dm_{Fe^{2+}}}{dt} = -\left(2.91x10^{-9} + 1.33x10^{12}\alpha^{2}_{OH^{-}}P_{O_2}\right)m_{Fe^{2+}} \tag{4-1}$$

where *t* equals the time in seconds, a^{2}_{OH} is the activity of the hydroxyl ion, m_{Fe2+} is the total molality of ferrous iron in solution, and P_{O2} is the partial pressure of the oxygen (Parkhurst and Appelo 1999). The kinetics rate equation is solved using a 4th- and 5th-order Runge-Kutta-Fehlberg algorithm that is embedded within PHREEQC. PHREEQC calculates equilibrium before starting a kinetic calculation and again when each kinetic reaction increment is added. The model calculates equilibrium for all solution-species, and for all exchange, equilibrium-phase, solid-solutions, surface assemblages and gas phases that are defined. A check is performed to ensure that the difference between the fourth- and fifth-order estimates of the integrated rate over a time interval does not vary by more than a user-defined tolerance. Failure to achieve results within the user defined tolerances will automatically restart the integration with a smaller time interval (Parkhurst and Appelo 1999).

The model I created of Mantua reservoir was based on the example provided with the program. Like the example, the purpose of the Mantua model is to simulate the oxidation of ferrous iron to ferric iron using oxygen in a natural water system, however the two models use separate geochemical environments. The PHREEQC model of Mantua Reservoir is presented in Appendix B. Several changes were required to adapt the example model to reflect the conditions present at Mantua reservoir. The first section of the Mantua model, SOLUTION_MASTER_SPECIES and SOLUTION_SPECIES, decouples the valence state of iron and defines the possible iron species found in the water (Parkhurst and Appelo 1999). This section of the code remained unchanged from the example in the Mantua model.

The next section of the model, starting with EQUILIBRIUM_PHASES 3, defines the conditions at Mantua Reservoir and defines the species that have the potential to precipitate out of the water, in this case ferric hydroxide. This section is followed by the SOLUTION1 section which defines the concentrations, in mmol/kilograms of water (kgw), of the applicable constituents and the physical characteristics of the water; this section was modified to match measured conditions at Mantua. Of particular importance is the concentration of ferrous iron in the water, also expressed in mmol/kgw. The EQUILIBRIUM PHASES 1 heading defines the partial pressure of atmospheric oxygen that serves to aerate the water and cause the oxidation of the ferrous iron. This value is the negative log of the partial pressure for oxygen in the atmosphere at 5000 feet of elevation for the Mantua model (Parkhurst and Appelo 1999).

The final section of the PHREEQC model code is the kinetics calculation. The RATES data block is used to define the kinetics rate equation (see equation 4-1) used in the model calculations. This is followed by the KINETICS data block which invokes the rate expression and defines the parameters, especially the time increments. The final section of the code defines the desired output form of the results. For the Mantua model, a graph is created showing the total concentrations of ferrous and ferric iron versus time was created (Parkhurst and Appelo 1999).

After developing a generic model for Mantua Reservoir which used the measured field environmental data, I refined the model by adjusting the rate constant to fit the observed kinetics data for the oxidation of ferrous iron that was measured in the laboratory. This required adjusting the rate constant in Equation 4-1 by an order of magnitude from the value used in the example model. This rate increase can be attributed to microorganisms catalyzing the reaction, a factor that is not considered in the rate constant provided in the example. Mantua has significant biological activity and the example problem did not consider biological activity.

5 Experimental and Modeling Results and Discussion

5.1 Field Results

Field measurement of the conditions at Mantua Reservoir was used to support my work and verify previous work. The deployment of the DO probe at Mantua Reservoir to measure DO values over time, served to confirm that the anaerobic conditions necessary to support the conclusions of Wallace (2006) could occur in the field. Data was collected by the sonde every fifteen minutes over a four week period starting the beginning of September, 2006 and ending the first week of October, 2006. A sample of the raw data obtained by the sonde is included in Appendix A. Figure 5-1 is a plot of the DO concentration and the water temperature of Mantua Reservoir over the period tested.

As expected, the DO concentration increases with lower water temperatures. Water has a greater capacity to dissolve and store oxygen at colder temperatures (Sawyer *et al* 2003). Of particular interest for the purposes of this study was the variation in the DO. Large variations, up to 6 ppm, occurred over relatively short periods as seen by the large repetitive changes between 50 to 150 hours and 500 to 600 hours. For example, on September 11th, 2006 (75 hours), starting at around 2:00 pm, the DO concentration in the reservoir steadily dropped from about 8.0 mg/L to 3.62 mg/L at 5:30 pm on the same day. The corresponding water temperature at the time only dropped one-tenth of a degree Celsius (from 19.28 degrees to 19.18). Using weather station data obtained from a site in

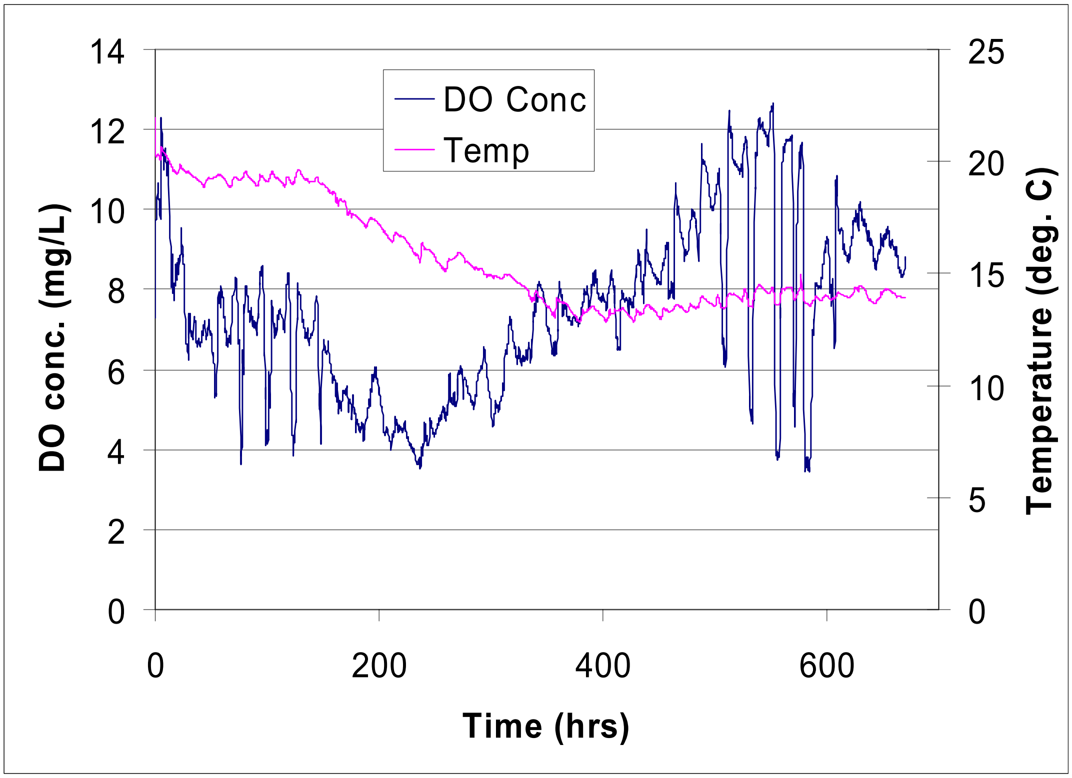

Figure 5-1: DO and temp measurements

nearby Brigham City, the maximum wind velocity during this period peaked at 5 miles per hour (mph) at 5:30 pm and the corresponding temperature at this time was 82 degrees Fahrenheit (Utah Department of Air Quality 2006). Although Mantua Reservoir and Brigham City are only about 5 miles apart (Mantua Reservoir TMDL 2000), the reservoir is located within the sheltered Box Elder Canyon so the wind and temperature profiles could vary significantly between the two locations. Also there is a difference of 782 feet in elevation between the weather station and the reservoir that could result in different wind velocities and air temperature at the two locations. The data collected from Mantua Reservoir includes ten instances in the one-month period, like the one described above, where a sharp drop in the DO concentration occurred over a matter of a few hours.

A number of factors could have significant effect on the data collected and the data might not reflect the exact conditions at the water-sediment interface. Wallace (2006) concluded the reduction of iron in the sediments under anaerobic conditions, and the subsequent dissolution of the ferrous iron into the reservoir water, occurred immediately above the sediments at the bottom of the lake. The DO probe was deployed about two feet off the lake bottom for fear of dropping reservoir water levels, sinking the sonde into the sediments. At a greater depth, the DO concentration most likely drops more during the calm periods than the values measured as there is less mixing and diffusion of the oxygen from the atmosphere (Loveless *et al* 1997).

Another important consideration is the time period when the sonde was deployed. The staining was observed in the middle of summer (Wood 2002), during hot temperatures, stagnant wind conditions, and low water levels in the reservoir. However, the probe collected data at the end of summer and the beginning of fall, when the atmospheric and water temperatures are beginning to drop and there was more wind. This is significant because, based on Henry's law (Sawyer *et al* 2003) as the water temperature drops the water has a greater capacity for dissolved oxygen and the biological processes that use the available oxygen in the reservoir begin to slow. Henry's law, given in equation 5-1, states that the amount of gas that will dissolve into a liquid, at constant temperature, is proportional to the partial pressure of the gas above the liquid (Sawyer *et al* 2003).

$$K_H = \frac{P_{gas}}{C_{equ}} \tag{5.1}$$

P_{gas} is the partial pressure of the gas above the water, C_{equ} is the equilibrium concentration of the gas dissolved into the liquid, and K_H is the Henry's law constant at a given temperature (Sawyer *et al* 2003). K_H for water at 20° Celsius is 0.73 atm-m^3/mol and the atmospheric partial pressure of oxygen at 5000 feet of elevation is 0.16 atm (Sawyer *et al* 2003). Using equation 5.1, the equilibrium DO concentration for Mantua Reservoir is 0.22 mol/m^3 or 7.19 mg/L. Assuming complete mixing with the atmospheric oxygen, Mantua Reservoir would have the above calculated DO concentration. K_H is sensitive to temperature however, and slight changes in temperatures significantly affect the solubility limits for oxygen.

Spikes in the recorded DO concentration above the theoretical saturation limit of the reservoir could indicate the possibility that an air bubble was resting on the optical sensor of the probe, inflating the recorded DO concentration or that photosynthesis of the aquatic life caused the DO levels to become supersaturated. The sharp drops in DO concentration indicate that there is a lack of mixing in the lower layers of the reservoir with the saturated upper layers and that biological processes are quickly using the available oxygen.

Though the field measurements did not record the hypolimnion in an anaerobic state, the dips indicate that there are regular periods of reduced mixing between the water layers of the reservoir and under the correct conditions could result in anaerobic water in the hypolimnion. Measurements in warmer weather, with warmer water which would reduce the DO capacity of the water, and increased biological activity that would more quickly use the available oxygen would make anaerobic conditions more likely. Deploying the sonde at a greater depth would measure conditions near the sediment-water interface where there is less mixing of the hypolimnion with the upper reservoir water levels and further increase the likelihood of anaerobic conditions occurring which are favorable for the reduction of ferric iron. Despite the limitations of the field measurements, the regular large drops in DO concentration provide evidence of the ability of Mantua Reservoir to become anaerobic in the lower water levels. This corresponds to the research conducted by Loveless *et al* (1997) which found that the DO levels dropped below acceptable levels in the summer months.

5.2 Qualitative Staining Results

I performed qualitative experiments to recreate the staining observed in the Brigham City cemetery and to determine the amount of time necessary for visual staining. This experiment consisted of spraying water saturated with iron onto concrete as described in Section 3.2.

The primary results from this experiment are qualitative observations of the staining evident over a measured period of time. Table 5-1 is the recorded observations at each respective time.

Table 5-1: Staining Observations

Time	Observations
11:02	Concrete sprayed
12:05	Concrete still drying, no visual
1:03	Iron precipitates visually
2:00	More precipitates on lid
3:00	Faint staining evident on
10:00	Noticeable staining on

Figures 5-2 and 5-3 are photographs of the concrete before spraying with water and after the staining occurred and are indicative of the results obtained from the staining experiment. The faint brownish hue, visible in Figure 5-3, is the result of the precipitation of the insoluble ferric iron from the water after being re-aerated by contact with the atmosphere and spraying on the concrete. Though not as visible on the concrete cores, a white surface (a bucket lid), placed under the core to catch the excess water spray, and clearly showed precipitated iron after this experiment. These ferric iron precipitates appeared and caused visible staining approximately two hours after the concrete core was sprayed with anaerobic Mantua Reservoir water. The iron precipitated out of the water before evaporation could take effect to eliminate the water.

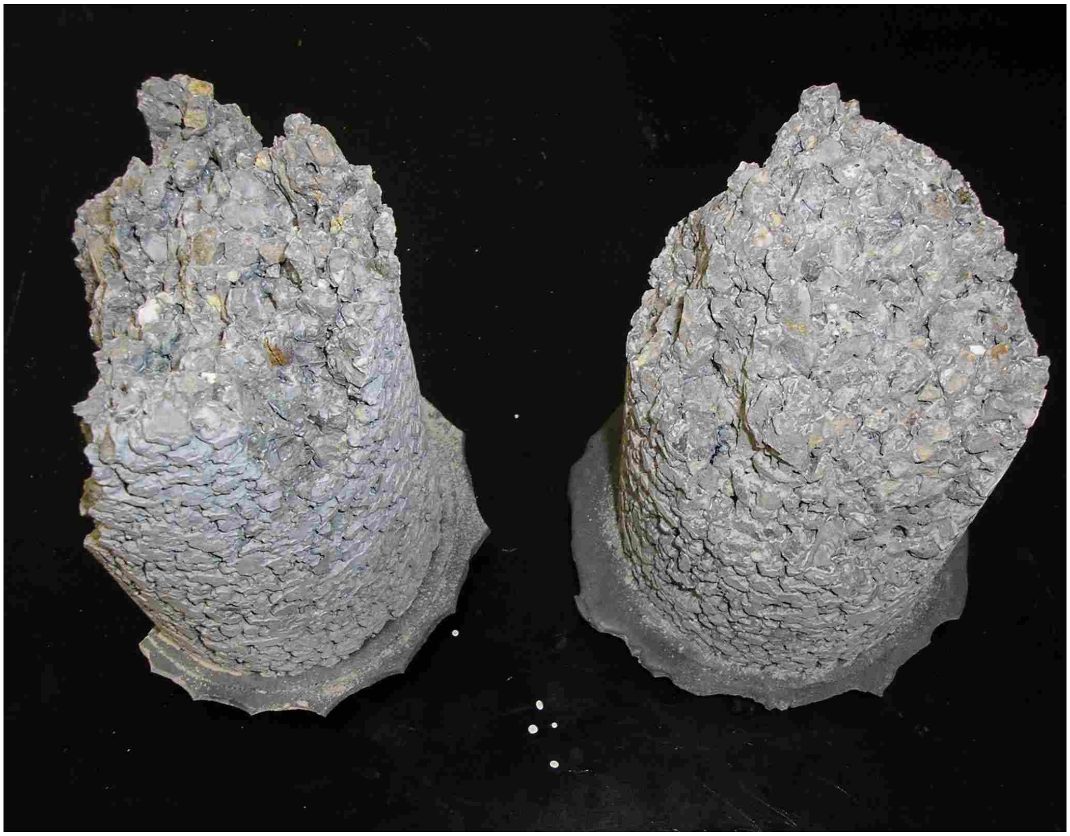

Figure 5-2: Concrete before spraying

Figure 5-3: Stained concrete

One difference between the observed field conditions and the qualitative lab experiment is the duration of the exposure. In Brigham City's cemetery, the headstones are exposed to the Mantua water through the irrigation system. A typical zone in an irrigation system is run for approximately 30 minutes. During that time the headstones will be sprayed every few seconds by one or more nearby sprinklers. In contrast, due to the very limited supply of anaerobic Mantua water, I was only able to spray the concrete core continuously for about two minutes. The effect of this difference is that the headstones have the potential for many times the iron exposure and therefore more evident staining. However, as shown by Wallace (2006) staining will only occur when the irrigation water is anaerobic and iron-rich, a condition which will only occur rarely, when the correct conditions happen at Mantua Reservoir.

The difference between the materials sprayed could also change the kinetics of the iron precipitation. The materials in concrete contain high carbonate quantities, giving concrete a basic pH (Mindness *et al* 2003). As seen in the equations that describe the iron oxidation kinetics (equations 2-2, 2-3, 2-5, and 4-1), the rate at which ferrous iron is oxidized to ferric iron is a function of the pH of the system. As the water becomes more basic through contact with the concrete the pH rises and the rate of oxidation is increased. Though the concrete has the potential to increase the oxidation rate of the ferrous iron, the water observed on the bucket lid exhibited precipitated iron quicker than the concrete despite having less contact time as it ran off the concrete. This experiment indicates that staining could occur very rapidly, on the order of a few hours, after spraying the headstones with water.

5.3 Quantitative Experimental Results

The purpose of the laboratory experiments was to determine the kinetics of iron oxidation in Mantua Reservoir and provide information that could be used to predict and understand the precipitation reactions. The primary objective was to determine the rate constant (*k*) that governs the oxidation rate in the reservoir water. This rate constant can then be used in models of the reservoir in order to predict the speed of the reaction and assist in the development of remediation options.

Table 5-2 presents the results of these experiments (described in Section 3.4). Table 5-2 contains the amount of iron in the water from Mantua Reservoir after various time increments. This table includes the date and time that all of the samples were removed from the bucket of water and also the times that they were actually run in the spectrophotometer. The delay was caused by excessive fouling of the bottle top filters from the suspended sediments. The amount of time between each sample is also included. Table 5-2 also includes the average absorbance measured for each sample and the associated concentration as determined using the calibration curve.

Table 5-2: Spectrophotometer Results

Date	Sample	Time Removed	Run Time	ΔT (min)	abs	[Fe] mg/L	Average [Fe] mg/L
Oct. 21	1-1	11:25	11:28	0	2.365	9.92	9.87
	1-2				2.344	9.82	
	2-3				NA	NA	8.69
	2-4	11:45	11:55	27	2.083	8.69	
	3-5	12:10	12:20	62	1.706	7.05	7.04
	3-6		12:23	65	1.705	7.04	
	4-7	12:37	12:55	97	1.369	5.58	5.53
	4-8		1:00	102	1.346	5.48	
	5-9	1:35	1:47	149	1.333	5.42	5.43
	5-10		1:50	152	1.339	5.45	
	6-11	3:43	3:55	277	1.662	6.85	6.79
	6-12		3:58	280	1.635	6.74	
	7-13	6:50	7:05	467	0.722	2.76	2.76
	7-14		7:10	472	0.721	2.76	
	8-15	9:10	9:20	542	0.628	2.35	2.33
	8-16		9:23	545	0.619	2.31	
Oct. 22	9-17	3:31	3:48	1650	0.106	0.08	0.07
	9-18		3:51	1653	0.104	0.07	

From these results it is evident that the oxidation and precipitation of ferrous iron in Mantua Reservoir water proceeds quickly. An initial concentration of almost 9.0 mg/L drops to almost nothing in a little over a day. After just two hours, the concentration dropped by about 3.0 mg/L (from 8.69 mg/L to 5.42 mg/L).

The first three samples were discarded because I added a couple drops of hydrochloric acid (HCl) to each vial in an effort to acid digest all of the iron. Acid digestion insures that all of the iron that was in solution after filtration remained in solution and did not precipitate (Sawyer *et al* 2003). However, use of the FerroVer reagent eliminates the need for acid digestion. This was realized when the second batch of water was removed and split into two samples (2-3 and 2-4). I added the HCl to sample 2-3 and only added the reagent to 2-4. The samples with the acid turned a milky white color and precipitates settled to the bottom of the vial; the reagent reacted with the HCl in a way which made the sample unusable. Sample 2-4 and all of the subsequent samples produced the expected colorimetric change. Figure 5-4 is a graph of the total time elapsed versus the iron concentration remaining in the water.

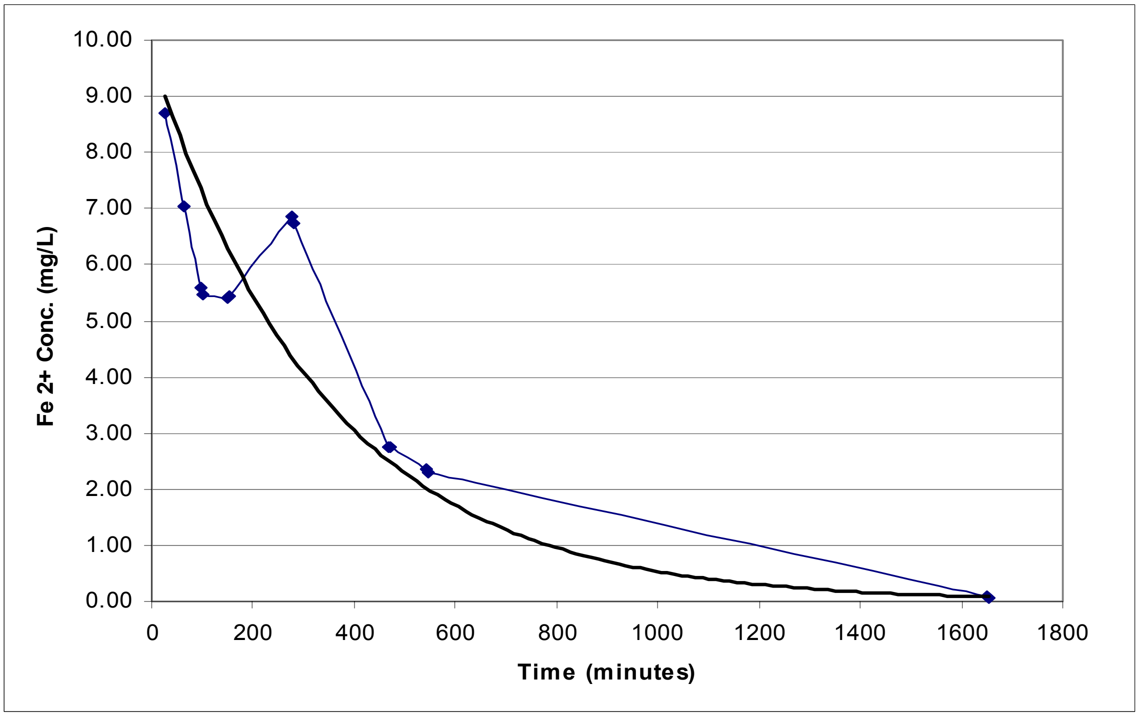

Figure 5-4: Iron oxidation over time

Figure 5-4 includes a trend line, its associated exponential equation, and an R-squared value. R-squared for this trend line is 0.9779. Removing the outlier point and using the average time elapsed and concentration yields Figure 5-5.

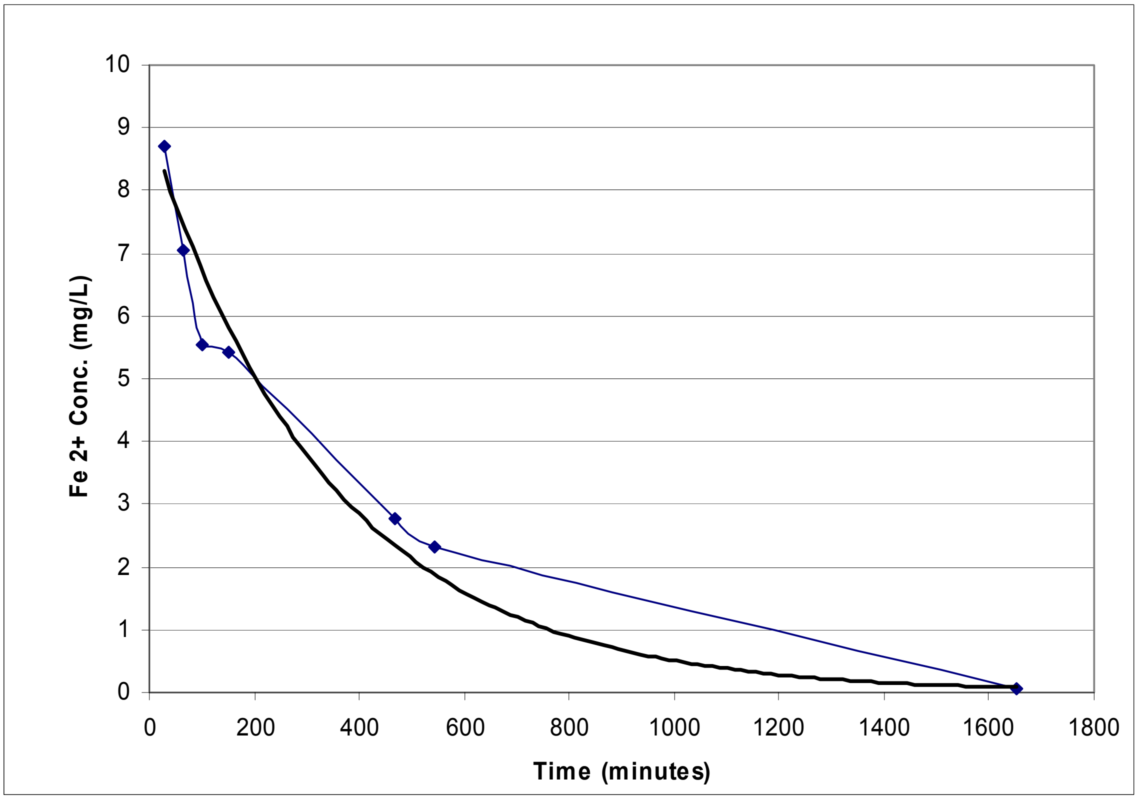

Figure 5-5: Revised iron oxidation over time

By removing the outlier point the R-squared value moves closer to one, with a value of 0.9918, indicating that the trend line is a better fit to the data. Equation 5-2 is the equation for the revised trend line:

$$y = 8.9877e^{-0.0029x} \tag{5-2}$$

where x is the time in minutes and y is the iron concentration in mg/L remaining in the water. This equation is the form of equation 2-4 describing first-order kinetics with x corresponding to t and y to C. This gives a rate constant k for Mantua Reservoir water of 0.0029 min^{-1}, based on my experimental results

5.4 PHREEQC Model Results

Mantua Reservoir was first modeled using the default rate constant provided with the iron oxidation kinetics example (see equation 4-1 and Section 4.2). The model-produced result is a plot of the change in concentration of both ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) versus time. Figure 5-6 is the plot produced using the default rate constant.

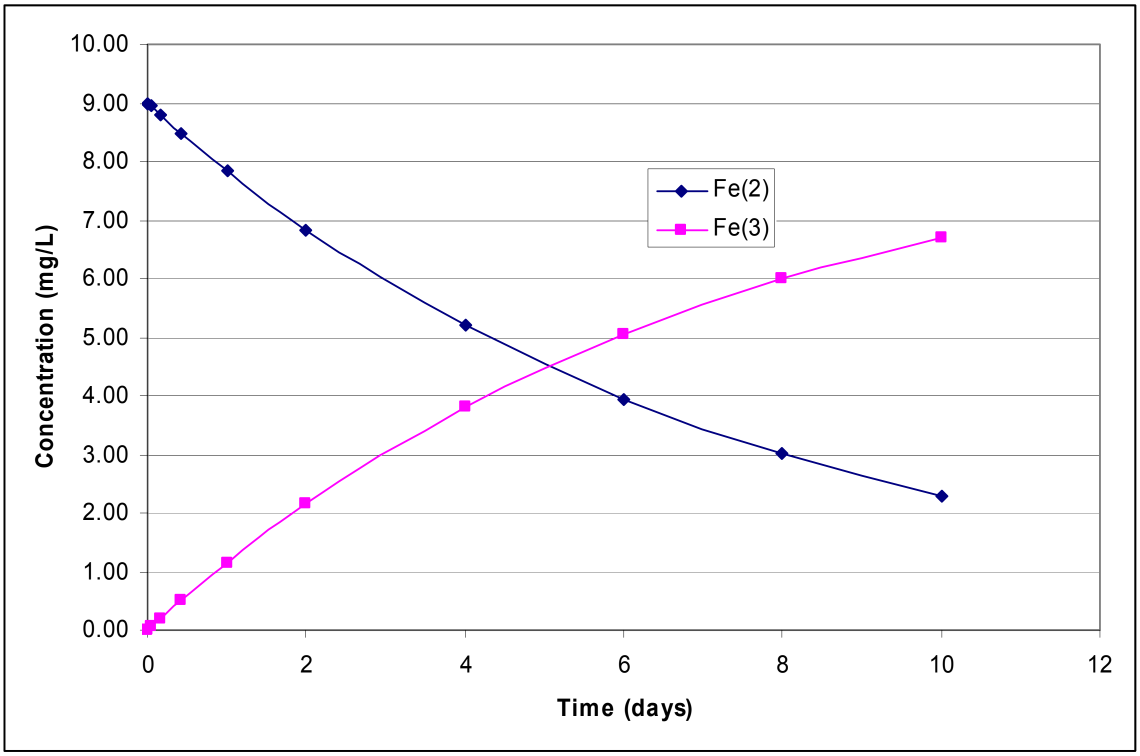

Figure 5-6: Change in iron concentration using default *k*

As the ferric iron concentration rises, due to the solubility product being extremely low (K_{sp}= 2.79x10^{-39}), the aqueous solution becomes supersaturated with respect to iron (III) (Sawyer *et al* 2003). The insoluble ferric iron will then begin to precipitate out of the solution. Using the default rate constant, after five days the ferrous iron concentration in the water has dropped by fifty percent. However, this model does not cause the oxidation to occur at close to the same rate as seen experimentally, with the experimental and observed reaction rates being much faster. Again, this discrepancy is probably the result of a biological component to the iron oxidation as was discussed in Section 2.3.

In order to more accurately predict the iron oxidation kinetics in Mantua Reservoir water, the model was modified to use the measured kinetic data from my laboratory experiments. Through a trial and error process of adjusting the rate constant, I created a model that closely matched the experimental data. Figure 5-7 is a plot of the concentration of ferrous iron over time based on the revised model and on the experimental data.

The rate constant found was 4x10^{13} /atm x min, thirty times bigger than the default value. This value is different than the one shown in Figure 5-5 because a different kinetics equation was used in the PHREEQC model rather than the first-order model presented above. Using the fitted theoretical rate constant from calibrating the PHREEQC model to the laboratory results, the complete oxidation of ferrous iron in Mantua Reservoir water was modeled.

Figure 5-8 presents the same parameters as Figure 5-6, but the data were calculated by applying the calibrated rate constant from the Mantua water experimental

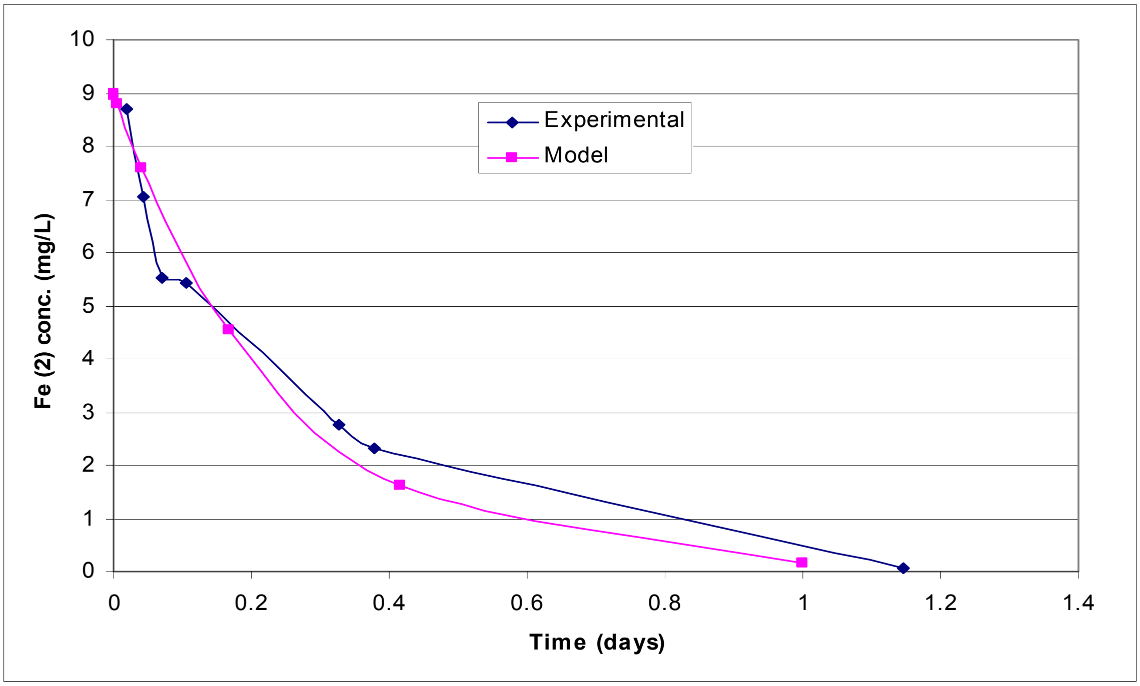

Figure 5-7: Model vs experimental iron concentrations

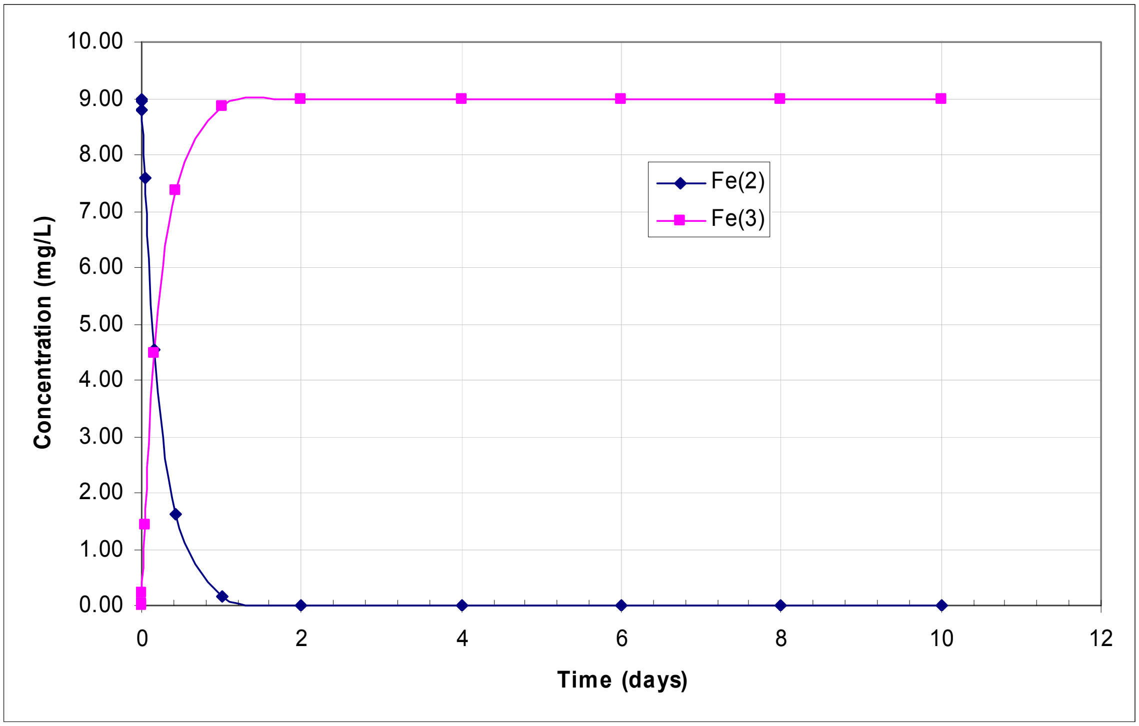

Figure 5-8: Model of Mantua iron oxidation kinetics

results. Figure 5-8 shows that after one day there is virtually no ferrous iron (0.15 mg/L) remaining in the reservoir water and after only four hours half of the ferrous iron dissolved in the water has been oxidized to ferric iron. This matches both observations and laboratory experiments. This also matches the staining events in the Brigham City cemetery, where staining occurred overnight and no stain build-up was noticed.

I propose that the explanation for the difference in the rate constants between the PHREEQC example model and the Mantua water model is the catalytic effects of microorganisms. As Okereke and Stevens (1991) proved with their research, the presence of iron oxidizing bacteria greatly increases the rate of iron oxidation. The presence of microbes can accelerate the reaction rate by a factor of 10^6 (Singer and Stumm 1970). *Thiobacillus ferrooxidans* are the most common microbes that oxidize ferric iron. Based on the research of Okereke and Stevens (1991), the right microbes could easily accelerate the kinetics of iron oxidation by an order of magnitude which would account for the differences found.

6 Conclusions

The purpose of this research was to confirm the capacity of Mantua Reservoir to achieve anaerobic conditions, causing the reduction and eventual oxidation of iron, and to determine the ferrous iron oxidation kinetics and thus how quickly staining could occur. Knowing the rate of the oxidation reaction will assist in the determination of practical remediation efforts by determining the residence time of the water after treatment before it could be used in the irrigation system.

The efforts to confirm the potential for Mantua Reservoir revealed that even in early fall, the DO concentration in the hypolimnion fluctuates severely. Though the study was conducted when the water temperature was already decreasing, causing an increase in the potential equilibrium DO concentration, the fact that the DO levels oscillated gave evidence that anaerobic conditions are likely in the lower water layers of Mantua Reservoir during the warmer summer conditions. The field data collected confirmed the results obtained by Loveless *et al* (1997) as part of the Clean Lakes Study. Their field work found DO levels as low as 3.0 mg/L within a meter of the bottom. Anaerobic conditions are required for the reduction of ferric iron, which is found in abundance in Mantua sediments. Reduced iron, in the ferrous state, is much more soluble than ferric iron and dissolves into the water only to be oxidized upon re-aeration through the irrigation system (Sawyer *et al* 2003).

The iron oxidation kinetics for Mantua Reservoir were determined using three different methods. The first method was a qualitative observation of the staining caused by iron precipitation on a cement core. Though the conditions of the experimentally derived staining differed from the field conditions, iron precipitation was evident after only two hours of observation. This showed that if the anaerobic conditions existed in Mantua Reservoir resulting in high amounts of dissolved iron, the use of the pressurized irrigation system would cause staining to appear on the headstones within a matter of hours.

The experimental results of the iron oxidation for Mantua yielded results that showed the iron was quickly oxidized and precipitated from the Mantua water. The ferrous iron was almost completely gone after 26 hours and had been reduced by over a third in just a couple of hours. Fitting a simple first order kinetics equation to the experimental data yielded a rate constant of 0.0029 min^{-1}, giving a half life of 239 minutes or approximately 4 hours. As with the qualitative results, the kinetics experiment has proved that the iron will precipitate out of the water and cause staining in Brigham City.

The creation of a geochemical computer model, using PHREEQC, also confirmed the speed of the iron oxidation kinetics. Using an example provided with the software as a foundation, and modifying the example to match the measured physical and chemical properties of Mantua Reservoir, resulted in a model in which the computed ferrous iron concentration dropped by fifty percent over the course of five days. This was not a good fit to the experimental data and therefore the model was calibrated to the experimental results from the actual Mantua water. The rate constant in the calibrated model was

$4x10^{13}$ /atm x min. With the rate constant calibrated to experimental results and a computer model of the oxidation kinetics, the oxidation of iron was predicted for any changing conditions of the reservoir. Model calculations showed that the majority of the iron would precipitate in a few hours.

6.1 Application

Knowing the iron oxidation kinetics of Mantua Reservoir water makes remediation recommendations possible. The purpose of this section is not to exhaustively study all of the technology available for the removal of dissolved iron in water but rather to provide an overview of possibilities for Brigham City to employ at Mantua Reservoir or in their irrigation system. (For a comprehensive study on iron treatments refer to *Iron and Manganese Treatment for Small Systems*, a thesis prepared by Harry Campbell for Brigham Young University, 1989).

There are two general approaches that could be applied. The first and recommended approach is to change conditions at Mantua Reservoir so that the hypolimnion does not become anaerobic. In addition to addressing the staining problem, this approach has the potential to address several other problems noted at Mantua including water quality and aesthetics. The second approach is to treat iron rich water after it leaves Mantua Reservoir before being used for irrigation.

The simplest and preferred solution to the staining problem would be to prevent iron from dissolving from the sediment under anaerobic conditions. Prevention would involve precluding the reservoir from becoming anaerobic in the hypolimnion by aeration or circulation. There are numerous commercial systems designed to aerate lagoons and reservoirs that could potentially be used at Mantua. During the course of my lab experiments, there were numerous failed attempts to conduct the experimental phase of the kinetics investigation. Invariably the failure was a consequence of excessive DO in the water preventing iron from dissolving from the sediments, as little as 2.0 mg/L, in the water sample. (The one successful attempt had a DO concentration of 1.0 mg/L after opening the bucket and mixing to a small degree by using a field DO probe which might have caused some of the DO in solution). In any cases where the water contained measurable amounts of DO, after testing with the spectrophotometer, these failed tests only included trace amounts of iron because the iron was never dissolved from the sediments.

From these failures, I learned that very little oxygen is necessary to prevent the dissolution of iron from the sediments. As a result, remediation methods that increase the dissolved oxygen in the hypolimnion would successfully prevent ferric iron from being reduced and then dissolved as ferrous iron into the water column. Diffusers laid on the bed of the reservoir, near the outlet, would prevent the system from going anaerobic and also oxidize any iron already dissolved in the water causing it to precipitate and settle out before reaching the irrigation system. Another preventative measure would be to put a floating mixer anchored in the area of the outlet (this area is already restricted to recreational activities). This would have the effect of mixing the DO saturated surface waters with lower layers that have the greatest potential for becoming anaerobic. Like the diffusers this would prevent the microorganisms from using the ferric iron found in the reservoir sediments as an electron acceptor and would oxidize any ferrous iron dissolved in the water. Both types of systems, and others such as sprayers and mixers, are commercially available.

The second general category is treating the water before irrigation. The basic idea of iron removal most commonly employed is the oxidation of the ferrous iron and subsequent clarification of the water, either using filtration or precipitation (Campbell 1989). This is exactly the process that is occurring in the system comprising Mantua Reservoir and the Brigham City secondary irrigation system. The major difference is the location of the removal of the iron hydroxide precipitates. In an engineered process they will be either removed in a settling basin or using a filtration system (Campbell 1989). In Brigham City's system the iron precipitates settle out on the headstones of the cemetery.

A solution would be to cause the iron to settle out, after oxidation, in a controlled location. This could be as simple as cascading the water over rocks, or other obstacles, far enough up the system to allow the iron (III) a chance to settle out. Immediately below the dam, before entering the penstock would allow treatment while retaining the pressure head required for power generation. The cascading water would be re-aerated and cause the oxidation of the ferrous iron. The reaction rate is fast enough, as determined by this study, to cause the iron to oxidize and settle out before entering the penstock and reaching the sprinklers of the city irrigation system. To prevent the iron precipitates from causing problems in the pipe distribution network a small settling pond, with a hydraulic detention time of a couple of hours, could be placed after the cascade to give the majority of the iron hydroxides a place to settle out.

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Appendix A. Field Data

Table A-1: Field Data Collected from Mantua Reservoir (24 hour period, 9/11/2006)

DateTime M/D/Y	Temp C	ODO Conc (mg/L)	Resistivity KOhm.cm	TDS g/L	Salinity ppt	SpCond mS/cm	ODO% %
9/11/2006 0:00	19.39	7.97	5.83	0.125	0.09	0.192	86.7
9/11/2006 0:15	19.38	8.07	5.84	0.125	0.09	0.192	87.7
9/11/2006 0:30	19.38	7.93	5.84	0.125	0.09	0.192	86.2
9/11/2006 0:45	19.37	7.86	5.84	0.125	0.09	0.192	85.4
9/11/2006 1:00	19.37	7.81	5.84	0.125	0.09	0.192	84.9
9/11/2006 1:15	19.37	7.93	5.84	0.125	0.09	0.192	86.1
9/11/2006 1:30	19.33	7.85	5.84	0.125	0.09	0.192	85.2
9/11/2006 1:45	19.31	7.8	5.85	0.125	0.09	0.192	84.6
9/11/2006 2:00	19.29	7.75	5.85	0.125	0.09	0.192	84
9/11/2006 2:15	19.25	7.52	5.85	0.125	0.09	0.192	81.5
9/11/2006 2:30	19.24	7.41	5.85	0.125	0.09	0.192	80.3
9/11/2006 2:45	19.22	7.3	5.85	0.125	0.09	0.192	79.1
9/11/2006 3:00	19.21	7.33	5.85	0.125	0.09	0.192	79.4
9/11/2006 3:15	19.19	7.13	5.86	0.125	0.09	0.192	77.2
9/11/2006 3:30	19.14	6.98	5.86	0.125	0.09	0.192	75.5
9/11/2006 3:45	19.14	6.92	5.86	0.125	0.09	0.192	74.9
9/11/2006 4:00	19.14	7.03	5.86	0.125	0.09	0.192	76.1
9/11/2006 4:15	19.11	6.91	5.86	0.125	0.09	0.192	74.7
9/11/2006 4:30	19.12	6.96	5.86	0.125	0.09	0.192	75.2
9/11/2006 4:45	19.07	6.81	5.86	0.125	0.09	0.192	73.5
9/11/2006 5:00	19.02	6.66	5.87	0.125	0.09	0.192	71.8
9/11/2006 5:15	19.01	6.6	5.86	0.125	0.09	0.193	71.2
9/11/2006 5:30	19.02	6.68	5.86	0.125	0.09	0.193	72.1
9/11/2006 5:45	19	6.77	5.87	0.125	0.09	0.193	73
9/11/2006 6:00	18.97	6.72	5.88	0.125	0.09	0.192	72.5
9/11/2006 6:15	18.92	6.57	5.88	0.125	0.09	0.192	70.7
9/11/2006 6:30	18.91	6.64	5.89	0.125	0.09	0.192	71.4
9/11/2006 6:45	18.93	6.7	5.88	0.125	0.09	0.192	72.1
9/11/2006 7:00	18.93	6.77	5.88	0.125	0.09	0.192	72.9
9/11/2006 7:15	18.88	6.68	5.89	0.125	0.09	0.192	71.9
9/11/2006 7:30	18.9	6.71	5.89	0.125	0.09	0.192	72.2
9/11/2006 7:45	18.86	6.75	5.9	0.125	0.09	0.192	72.6
9/11/2006 8:00	18.91	6.84	5.89	0.125	0.09	0.192	73.6
9/11/2006 8:15	18.94	6.75	5.89	0.125	0.09	0.192	72.7
9/11/2006 8:30	18.85	6.71	5.9	0.125	0.09	0.192	72.2
9/11/2006 8:45	18.84	6.64	5.9	0.125	0.09	0.192	71.4
9/11/2006 9:00	18.86	6.95	5.9	0.125	0.09	0.192	74.7
9/11/2006 9:15	18.91	7.05	5.9	0.125	0.09	0.192	75.9
9/11/2006 9:30	18.88	7.18	5.9	0.125	0.09	0.192	77.3
9/11/2006 9:45	18.94	7.31	5.89	0.125	0.09	0.192	78.7
9/11/2006 10:00	19	7.45	5.89	0.125	0.09	0.192	80.3
9/11/2006 10:15	19.09	7.7	5.87	0.125	0.09	0.192	83.2
9/11/2006 10:30	19.16	7.82	5.87	0.125	0.09	0.192	84.6
9/11/2006 10:45	19.25	7.88	5.85	0.125	0.09	0.192	85.4
9/11/2006 11:00	19.31	7.87	5.84	0.125	0.09	0.192	85.4
9/11/2006 11:15	19.3	7.88	5.85	0.125	0.09	0.192	85.5
9/11/2006 11:30	19.27	7.87	5.86	0.125	0.09	0.192	85.3
9/11/2006 11:45	19.27	7.87	5.86	0.125	0.09	0.192	85.3
9/11/2006 12:00	19.27	7.89	5.86	0.125	0.09	0.192	85.6
9/11/2006 12:15	19.27	8	5.86	0.125	0.09	0.192	86.8
9/11/2006 12:30	19.3	8.14	5.86	0.124	0.09	0.192	88.3

9/11/2006 12:45	19.3	8.25	5.86	0.125	0.09	0.192	89.6
9/11/2006 13:00	19.28	8.28	5.86	0.125	0.09	0.192	89.8
9/11/2006 13:15	19.27	8.29	5.85	0.125	0.09	0.192	89.9
9/11/2006 13:30	19.27	8.28	5.86	0.124	0.09	0.192	89.8
9/11/2006 13:45	19.27	8.24	5.86	0.125	0.09	0.192	89.3
9/11/2006 14:00	19.28	8.18	5.86	0.124	0.09	0.191	88.7
9/11/2006 14:15	19.25	7.98	5.86	0.125	0.09	0.192	86.5
9/11/2006 14:30	19.24	7.77	5.86	0.125	0.09	0.192	84.3
9/11/2006 14:45	19.23	7.65	5.86	0.125	0.09	0.192	82.9
9/11/2006 15:00	19.22	7.5	5.86	0.125	0.09	0.192	81.2
9/11/2006 15:15	19.21	7.23	5.86	0.125	0.09	0.192	78.3
9/11/2006 15:30	19.2	7.12	5.86	0.125	0.09	0.192	77.1
9/11/2006 15:45	19.2	6.65	5.84	0.125	0.09	0.192	72
9/11/2006 16:00	19.19	6.74	5.83	0.125	0.09	0.193	72.9
9/11/2006 16:15	19.2	5.83	5.82	0.126	0.09	0.193	63.1
9/11/2006 16:30	19.19	5.62	5.8	0.126	0.09	0.194	60.8
9/11/2006 16:45	19.19	5.49	5.8	0.126	0.09	0.194	59.4
9/11/2006 17:00	19.18	5.03	5.77	0.127	0.09	0.195	54.5
9/11/2006 17:15	19.18	4.33	5.72	0.128	0.09	0.197	46.9
9/11/2006 17:30	19.18	3.62	5.68	0.129	0.09	0.198	39.2
9/11/2006 17:45	19.19	3.97	5.66	0.129	0.09	0.199	42.9
9/11/2006 18:00	19.19	3.84	5.66	0.129	0.09	0.199	41.6
9/11/2006 18:15	19.2	3.91	5.66	0.129	0.09	0.199	42.4
9/11/2006 18:30	19.21	3.97	5.66	0.129	0.09	0.199	43
9/11/2006 18:45	19.23	4.05	5.69	0.128	0.09	0.197	43.9
9/11/2006 19:00	19.24	4.5	5.8	0.126	0.09	0.194	48.8
9/11/2006 19:15	19.27	6.51	5.8	0.126	0.09	0.194	70.6
9/11/2006 19:30	19.28	6.47	5.79	0.126	0.09	0.194	70.2
9/11/2006 19:45	19.28	6.16	5.76	0.127	0.09	0.195	66.8
9/11/2006 20:00	19.3	6.05	5.75	0.127	0.09	0.195	65.6
9/11/2006 20:15	19.29	5.89	5.75	0.127	0.09	0.195	63.9
9/11/2006 20:30	19.34	6.89	5.78	0.126	0.09	0.194	74.8
9/11/2006 20:45	19.39	7.61	5.8	0.126	0.09	0.193	82.7
9/11/2006 21:00	19.47	7.41	5.78	0.126	0.09	0.193	80.7
9/11/2006 21:15	19.51	7.72	5.79	0.125	0.09	0.193	84.1
9/11/2006 21:30	19.53	7.84	5.79	0.125	0.09	0.193	85.4
9/11/2006 21:45	19.55	7.93	5.79	0.125	0.09	0.193	86.4
9/11/2006 22:00	19.56	8.06	5.79	0.125	0.09	0.193	87.9
9/11/2006 22:15	19.55	8.1	5.79	0.125	0.09	0.193	88.3
9/11/2006 22:30	19.54	8.09	5.8	0.125	0.09	0.193	88.2
9/11/2006 22:45	19.54	8.08	5.8	0.125	0.09	0.193	88.1
9/11/2006 23:00	19.52	7.98	5.8	0.125	0.09	0.193	86.9
9/11/2006 23:15	19.48	7.91	5.8	0.125	0.09	0.193	86.2
9/11/2006 23:30	19.44	7.86	5.81	0.125	0.09	0.193	85.5
9/11/2006 23:45	19.39	7.78	5.81	0.125	0.09	0.193	84.6

Appendix B. PHREEQC Files

B-1: Partial input file for Example 9 (Parkhurst and Appelo 1999)

```
TITLE Example 9.--Kinetically controlled oxidation of ferrous iron.
# Decoupled valence states of iron.
SOLUTION_MASTER_SPECIES
Fe_di             Fe_di+2    0.0     Fe_di              55.847
Fe_tri            Fe_tri+3   0.0     Fe_tri             55.847
SOLUTION_SPECIES
Fe_di+2 = Fe_di+2
        log_k   0.0
Fe_tri+3 = Fe_tri+3
        log_k   0.0
#
# Fe+2 species
#
Fe_di+2 + H2O = Fe_diOH+ + H+
        log_k   -9.5
        delta_h 13.20   kcal
#
#... and also other Fe+2 species
#
#
# Fe+3 species
#
Fe_tri+3 + H2O = Fe_triOH+2 + H+
        log_k   -2.19
        delta_h 10.4    kcal
#
#... and also other Fe+3 species
#
PHASES
Goethite
        Fe_triOOH + 3 H+ = Fe_tri+3 + 2 H2O
        log_k   -1.0
END
SOLUTION 1
        pH  7.0
        pe 10.0  O2(g) -0.67
        Fe_di  0.1
        Na  10.
        Cl  10.  charge
EQUILIBRIUM_PHASES 1
        O2(g)           -0.67
RATES
Fe_di_ox
-start
10  Fe_di = TOT("Fe_di")
20  if (Fe_di <= 0) then goto 200
30  p_o2 = 10^(SI("O2(g)"))
40  moles = (2.91e-9 + 1.33e12 * (ACT("OH-"))^2 * p_o2) * Fe_di * TIME
200 SAVE moles
-end
KINETICS 1
Fe_di_ox
```

```
        -formula  Fe_di  -1.0  Fe_tri  1.0
        -steps 100 400 3100 10800 21600 5.04e4 8.64e4 1.728e5 1.728e5 1.728e5
1.728e5
INCREMENTAL_REACTIONS true
SELECTED_OUTPUT
        -file ex9.sel
        -reset false
USER_PUNCH
-headings Days  Fe(2)  Fe(3)  pH  si_goethite
10 PUNCH SIM_TIME/3600/24 TOT("Fe_di")*1e6, TOT("Fe_tri")*1e6, -LA("H+"),
SI("Goethite")
       END
```

B-2: Mantua PHREEQC model complete input and output file

```
Input file: F:\Thesis\Kinetics17.pqi
Output file: F:\Thesis\Kinetics17.pqo
Database file: E:\Program Files\USGS\Phreeqc Interactive 2.12.5\phreeqc.dat

------------------
Reading data base.
------------------

             SOLUTION_MASTER_SPECIES
             SOLUTION_SPECIES
             PHASES
             EXCHANGE_MASTER_SPECIES
             EXCHANGE_SPECIES
             SURFACE_MASTER_SPECIES
             SURFACE_SPECIES
             RATES
             END
------------------------------------
Reading input data for simulation 1.
------------------------------------

             DATABASE E:\Program Files\USGS\Phreeqc Interactive
2.12.5\phreeqc.dat
             TITLE Example 9.--Kinetically controlled oxidation of ferrous
                              iron. Decoupled valence states of iron.
             SOLUTION_MASTER_SPECIES
             Fe_di                Fe_di+2    0.0     Fe_di
55.847
             Fe_tri               Fe_tri+3   0.0     Fe_tri
55.847
             SOLUTION_SPECIES
             Fe_di+2 = Fe_di+2
                     log_k   0.0
             Fe_tri+3 = Fe_tri+3
                     log_k   0.0
             Fe_di+2 + H2O = Fe_diOH+ + H+
                     log_k   -9.5
                     delta_h 13.20   kcal
             Fe_di+2 + Cl- = Fe_diCl+
                     log_k   0.14
             Fe_di+2 + CO3-2 = Fe_diCO3
                     log_k   4.38
             Fe_di+2 + HCO3- = Fe_diHCO3+
                     log_k   2.0
             Fe_di+2 + SO4-2 = Fe_diSO4
                     log_k   2.25
                     delta_h 3.230   kcal
             Fe_di+2 + HSO4- = Fe_diHSO4+
                     log_k   1.08
             Fe_di+2 + 2HS- = Fe_di(HS)2
                     log_k   8.95
             Fe_di+2 + 3HS- = Fe_di(HS)3-
                     log_k   10.987
             Fe_di+2 + HPO4-2 = Fe_diHPO4
                     log_k   3.6
             Fe_di+2 + H2PO4- = Fe_diH2PO4+
                     log_k   2.7
             Fe_di+2 + F- = Fe_diF+
                     log_k   1.0
             Fe_tri+3 + H2O = Fe_triOH+2 + H+
                     log_k   -2.19
                     delta_h 10.4    kcal
             Fe_tri+3 + 2 H2O = Fe_tri(OH)2+ + 2 H+
                     log_k   -5.67
                     delta_h 17.1    kcal
             Fe_tri+3 + 3 H2O = Fe_tri(OH)3 + 3 H+
                     log_k   -12.56
                     delta_h 24.8    kcal
             Fe_tri+3 + 4 H2O = Fe_tri(OH)4- + 4 H+
                     log_k   -21.6
                     delta_h 31.9    kcal
             2 Fe_tri+3 + 2 H2O = Fe_tri2(OH)2+4 + 2 H+
                     log_k   -2.95
                     delta_h 13.5    kcal
             3 Fe_tri+3 + 4 H2O = Fe_tri3(OH)4+5 + 4 H+
                     log_k   -6.3
                     delta_h 14.3    kcal
             Fe_tri+3 + Cl- = Fe_triCl+2
                     log_k   1.48
                     delta_h 5.6     kcal
             Fe_tri+3 + 2 Cl- = Fe_triCl2+
                     log_k   2.13
             Fe_tri+3 + 3 Cl- = Fe_triCl3
                     log_k   1.13
             Fe_tri+3 + SO4-2 = Fe_triSO4+
                     log_k   4.04
                     delta_h 3.91    kcal
             Fe_tri+3 + HSO4- = Fe_triHSO4+2
                     log_k   2.48
             Fe_tri+3 + 2 SO4-2 = Fe_tri(SO4)2-
                     log_k   5.38
                     delta_h 4.60    kcal
             Fe_tri+3 + HPO4-2 = Fe_triHPO4+
                     log_k   5.43
                     delta_h 5.76    kcal
             Fe_tri+3 + H2PO4- = Fe_triH2PO4+2
                     log_k   5.43
             Fe_tri+3 + F- = Fe_triF+2
                     log_k   6.2
                     delta_h 2.7     kcal
             Fe_tri+3 + 2 F- = Fe_triF2+
                     log_k   10.8
                     delta_h 4.8     kcal
             Fe_tri+3 + 3 F- = Fe_triF3
                     log_k   14.0
                     delta_h 5.4     kcal
             EQUILIBRIUM_PHASES 3
                 Fe(OH)3(a) 0 10
             END
-----
TITLE
-----
```

```
 Example 9.--Kinetically controlled oxidation of ferrous
                iron. Decoupled valence states of iron.

-----------------
End of simulation.
-----------------

------------------------------------
Reading input data for simulation 2.
------------------------------------

             SOLUTION 1
                    pH  4.535
                    pe -0.924  O2(g) -0.785
                    Fe_di  0.161
                    Na  0.4183
                    Cl  0.3216  charge
                           K   0.0527
                           Mg  0.9719
                           Mn  0.0003951
                           Ca  147.6
                           Alkalinity 29.67
                           C   138.9
                           S   15.79
             EQUILIBRIUM_PHASES 1
                    O2(g)           -0.785
             RATES
             Fe_di_ox
             start
             10  Fe_di = TOT("Fe_di")
             20  if (Fe_di <= 0) then goto 200
             30  p_o2 = 10^(SI("O2(g)"))
             40  moles = (2.91e-9 + 4e13 * (ACT("OH-"))^2 * p_o2) * Fe_di *
TIME
             200 SAVE moles
             end
             KINETICS 1
             Fe_di_ox
                    formula  Fe_di  -1.0  Fe_tri  1.0
                    steps 100 400 3100 10800 21600 5.04e4 8.64e4 1.728e5
1.728e5 1.728e5 1.728e5
             INCREMENTAL_REACTIONS true
             SELECTED_OUTPUT
                    file kin17.sel
                    reset false
             USER_PUNCH
             headings Days  Fe(2)  Fe(3)  pH  si_Fe(OH)3(a)
             10 PUNCH SIM_TIME/3600/24 TOT("Fe_di")*1e6, TOT("Fe_tri")*1e6,
-LA("H+"), SI("Fe(OH)3(a)")
             END
-----------------------------------------
Beginning of initial solution calculations.
-----------------------------------------

Initial solution 1.


pH will be adjusted to obtain desired alkalinity.

-----------------------------Solution composition------------------------------
---

             Elements            Molality       Moles

             Alkalinity        2.967e-002  2.967e-002
             C                 1.389e-001  1.389e-001
             Ca                1.476e-001  1.476e-001
             Cl                2.367e-001  2.367e-001  Charge balance
             Fe_di             1.610e-004  1.610e-004
             K                 5.270e-005  5.270e-005
             Mg                9.719e-004  9.719e-004
             Mn                3.951e-007  3.951e-007
             Na                4.183e-004  4.183e-004
             S                 1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.434      Adjust alkalinity
                                       pe  =  15.168      Equilibrium with
O2(g)
                        Activity of water  =   0.991
                           Ionic strength  =  4.068e-001
                       Mass of water (kg)  =  1.000e+000
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -3.112e-015
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                               Iterations  =  19
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587722e+001

----------------------------Distribution of species----------------------------
---

                                                    Log       Log
Log
             Species             Molality    Activity  Molality  Activity
Gamma

             H+                4.766e-006  3.678e-006    -5.322    -5.434
-0.113
             OH-               4.154e-009  2.698e-009    -8.382    -8.569
-0.187
             H2O               5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)           0.000e+000
             CH4               0.000e+000  0.000e+000  -141.384  -141.344
0.041
C(4)            1.389e-001
```

```
            CO2             1.092e-001  1.200e-001    -0.962    -0.921
0.041
            HCO3-           2.043e-002  1.438e-002    -1.690    -1.842
-0.152
            CaHCO3+         9.116e-003  6.417e-003    -2.040    -2.193
-0.152
            MgHCO3+         5.781e-005  4.225e-005    -4.238    -4.374
-0.136
            Fe_diHCO3+      5.274e-005  3.854e-005    -4.278    -4.414
-0.136
            CaCO3           9.811e-006  1.077e-005    -5.008    -4.968
0.041
            NaHCO3          2.172e-006  2.386e-006    -5.663    -5.622
0.041
            CO3-2           7.466e-007  1.834e-007    -6.127    -6.737
-0.610
            Fe_diCO3        1.074e-007  1.179e-007    -6.969    -6.928
0.041
            MnHCO3+         1.037e-007  7.582e-008    -6.984    -7.120
-0.136
            MgCO3           4.001e-008  4.394e-008    -7.398    -7.357
0.041
            NaCO3-          1.378e-009  1.007e-009    -8.861    -8.997
-0.136
            MnCO3           7.846e-010  8.617e-010    -9.105    -9.065
0.041
Ca            1.476e-001
            Ca+2            1.293e-001  3.498e-002    -0.889    -1.456
-0.568
            CaSO4           9.212e-003  1.012e-002    -2.036    -1.995
0.041
            CaHCO3+         9.116e-003  6.417e-003    -2.040    -2.193
-0.152
            CaCO3           9.811e-006  1.077e-005    -5.008    -4.968
0.041
            CaHSO4+         2.982e-007  2.180e-007    -6.525    -6.662
-0.136
            CaOH+           2.141e-009  1.565e-009    -8.669    -8.806
-0.136
Cl            2.367e-001
            Cl-             2.367e-001  1.559e-001    -0.626    -0.807
-0.181
            Fe_diCl+        7.893e-006  5.768e-006    -5.103    -5.239
-0.136
            MnCl+           5.141e-008  3.757e-008    -7.289    -7.425
-0.136
            MnCl2           2.328e-009  2.557e-009    -8.633    -8.592
0.041
            MnCl3-          1.502e-010  1.098e-010    -9.823    -9.960
-0.136
Fe_di         1.610e-004
            Fe_di+2         9.396e-005  2.681e-005    -4.027    -4.572
-0.545
            Fe_diHCO3+      5.274e-005  3.854e-005    -4.278    -4.414
-0.136
            Fe_diCl+        7.893e-006  5.768e-006    -5.103    -5.239
-0.136
            Fe_diSO4        6.292e-006  6.909e-006    -5.201    -5.161
0.041
            Fe_diCO3        1.074e-007  1.179e-007    -6.969    -6.928
0.041
            Fe_diOH+        3.126e-009  2.284e-009    -8.505    -8.641
-0.136
            Fe_diHSO4+      2.285e-010  1.670e-010    -9.641    -9.777
-0.136
            Fe_di(HS)2      0.000e+000  0.000e+000  -274.519  -274.479
0.041
            Fe_di(HS)3-     0.000e+000  0.000e+000  -411.734  -411.870
-0.136
H(0)          0.000e+000
            H2              0.000e+000  0.000e+000   -44.396   -44.355
0.041
K             5.270e-005
            K+              5.222e-005  3.439e-005    -4.282    -4.464
-0.181
            KSO4-           4.793e-007  3.503e-007    -6.319    -6.456
-0.136
            KOH             2.927e-014  3.214e-014   -13.534   -13.493
0.041
Mg            9.719e-004
            Mg+2            8.364e-004  2.511e-004    -3.078    -3.600
-0.523
            MgSO4           7.770e-005  8.532e-005    -4.110    -4.069
0.041
            MgHCO3+         5.781e-005  4.225e-005    -4.238    -4.374
-0.136
            MgCO3           4.001e-008  4.394e-008    -7.398    -7.357
0.041
            MgOH+           3.362e-010  2.457e-010    -9.473    -9.610
-0.136
Mn(2)         3.951e-007
            Mn+2            2.228e-007  5.916e-008    -6.652    -7.228
-0.576
            MnHCO3+         1.037e-007  7.582e-008    -6.984    -7.120
-0.136
            MnCl+           5.141e-008  3.757e-008    -7.289    -7.425
-0.136
            MnSO4           1.389e-008  1.525e-008    -7.857    -7.817
0.041
            MnCl2           2.328e-009  2.557e-009    -8.633    -8.592
0.041
            MnCO3           7.846e-010  8.617e-010    -9.105    -9.065
0.041
            MnCl3-          1.502e-010  1.098e-010    -9.823    -9.960
-0.136
            MnOH+           5.608e-013  4.098e-013   -12.251   -12.387
-0.136
Mn(3)         4.528e-017
            Mn+3            4.528e-017  2.693e-018   -16.344   -17.570
-1.226
Na            4.183e-004
            Na+             4.132e-004  2.950e-004    -3.384    -3.530
-0.146
            NaSO4-          2.933e-006  2.143e-006    -5.533    -5.669
-0.136
            NaHCO3          2.172e-006  2.386e-006    -5.663    -5.622
0.041
            NaCO3-          1.378e-009  1.007e-009    -8.861    -8.997
-0.136
```

```
            NaOH            4.784e-013  5.253e-013   -12.320   -12.280
0.041
O(0)          3.828e-004
            O2              1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)         0.000e+000
            H2S             0.000e+000  0.000e+000  -137.962  -137.921
0.041
            HS-             0.000e+000  0.000e+000  -139.241  -139.429
-0.187
            S-2             0.000e+000  0.000e+000  -146.277  -146.912
-0.635
            Fe_di(HS)2      0.000e+000  0.000e+000  -274.519  -274.479
0.041
            Fe_di(HS)3-     0.000e+000  0.000e+000  -411.734  -411.870
-0.136
S(6)          1.579e-002
            CaSO4           9.212e-003  1.012e-002    -2.036    -1.995
0.041
            SO4-2           6.490e-003  1.449e-003    -2.188    -2.839
-0.651
            MgSO4           7.770e-005  8.532e-005    -4.110    -4.069
0.041
            Fe_diSO4        6.292e-006  6.909e-006    -5.201    -5.161
0.041
            NaSO4-          2.933e-006  2.143e-006    -5.533    -5.669
-0.136
            HSO4-           7.091e-007  5.183e-007    -6.149    -6.285
-0.136
            KSO4-           4.793e-007  3.503e-007    -6.319    -6.456
-0.136
            CaHSO4+         2.982e-007  2.180e-007    -6.525    -6.662
-0.136
            MnSO4           1.389e-008  1.525e-008    -7.857    -7.817
0.041
            Fe_diHSO4+      2.285e-010  1.670e-010    -9.641    -9.777
-0.136

------------------------------Saturation indices------------------------------
---

            Phase               SI log IAP  log KT

            Anhydrite         0.07   -4.29   -4.36  CaSO4
            Aragonite         0.14   -8.19   -8.34  CaCO3
            Calcite           0.29   -8.19   -8.48  CaCO3
            CH4(g)         -138.48 -141.34   -2.86  CH4
            CO2(g)            0.55   -0.92   -1.47  CO2
            Dolomite         -1.44  -18.53  -17.09  CaMg(CO3)2
            Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
            H2(g)           -41.21  -44.36   -3.15  H2
            H2O(g)           -1.51   -0.00    1.51  H2O
            H2S(g)         -136.92 -137.92   -1.00  H2S
            Halite           -5.92   -4.34    1.58  NaCl
            Hausmannite      -8.92   52.11   61.03  Mn3O4
            Manganite        -1.10   24.24   25.34  MnOOH
            O2(g)            -0.78   -3.68   -2.89  O2
            Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
            Pyrolusite        3.46   44.84   41.38  MnO2
            Rhodochrosite    -2.83  -13.96  -11.13  MnCO3
            Sulfur         -101.60  -96.72    4.88  S


-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.   Kinetics defined in simulation 2.

            Time step: 100 seconds  (Incremented time: 100 seconds)

            Rate name       Delta Moles Total Moles   Reactant
Coefficient

            Fe_di_ox        -7.679e-007  1.000e+000   Fe_di
-1
                                                      Fe_tri
1

-------------------------------Phase assemblage-------------------------------
---

                                                         Moles in assemblage
            Phase               SI log IAP  log KT    Initial       Final
Delta

            O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001-
1.920e-007

-----------------------------Solution composition-----------------------------
---

            Elements           Molality       Moles

            C                 1.389e-001  1.389e-001
            Ca                1.476e-001  1.476e-001
            Cl                2.367e-001  2.367e-001
            Fe_di             1.602e-004  1.602e-004
            Fe_tri            7.679e-007  7.679e-007
            K                 5.270e-005  5.270e-005
            Mg                9.719e-004  9.719e-004
            Mn                3.951e-007  3.951e-007
            Na                4.183e-004  4.183e-004
            S                 1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.434      Charge balance
                                       pe  =  15.168      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.068e-001
                       Mass of water (kg)  =  1.000e+000
```

```
              Total alkalinity (eq/kg)  =  2.967e-002
                    Total CO2 (mol/kg)  =  1.389e-001
                   Temperature (deg C)  =  25.000
               Electrical balance (eq)  = -1.008e-014
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                            Iterations  =  41
                               Total H  = 1.110421e+002
                               Total O  = 5.587722e+001

----------------------------Distribution of species----------------------------
---

                                                     Log       Log
Log
           Species          Molality    Activity  Molality  Activity
Gamma

           H+               4.767e-006 3.678e-006   -5.322    -5.434
-0.113
           OH-              4.154e-009 2.698e-009   -8.382    -8.569
-0.187
           H2O              5.551e+001 9.911e-001    1.744    -0.004
0.000
C(-4)        0.000e+000
           CH4              0.000e+000 0.000e+000 -141.384  -141.344
0.041
C(4)         1.389e-001
           CO2              1.092e-001 1.200e-001   -0.962    -0.921
0.041
           HCO3-            2.043e-002 1.438e-002   -1.690    -1.842
-0.152
           CaHCO3+          9.116e-003 6.417e-003   -2.040    -2.193
-0.152
           MgHCO3+          5.781e-005 4.225e-005   -4.238    -4.374
-0.136
           Fe_diHCO3+       5.249e-005 3.836e-005   -4.280    -4.416
-0.136
           CaCO3            9.811e-006 1.077e-005   -5.008    -4.968
0.041
           NaHCO3           2.172e-006 2.386e-006   -5.663    -5.622
0.041
           CO3-2            7.466e-007 1.833e-007   -6.127    -6.737
-0.610
           Fe_diCO3         1.068e-007 1.173e-007   -6.971    -6.931
0.041
           MnHCO3+          1.037e-007 7.582e-008   -6.984    -7.120
-0.136
           MgCO3            4.001e-008 4.393e-008   -7.398    -7.357
0.041
           NaCO3-           1.378e-009 1.007e-009   -8.861    -8.997
-0.136
           MnCO3            7.846e-010 8.617e-010   -9.105    -9.065
0.041
Ca           1.476e-001
           Ca+2             1.293e-001 3.498e-002   -0.889    -1.456
-0.568
           CaSO4            9.212e-003 1.012e-002   -2.036    -1.995
0.041
           CaHCO3+          9.116e-003 6.417e-003   -2.040    -2.193
-0.152
           CaCO3            9.811e-006 1.077e-005   -5.008    -4.968
0.041
           CaHSO4+          2.982e-007 2.180e-007   -6.525    -6.662
-0.136
           CaOH+            2.141e-009 1.564e-009   -8.669    -8.806
-0.136
Cl           2.367e-001
           Cl-              2.367e-001 1.559e-001   -0.626    -0.807
-0.181
           Fe_diCl+         7.855e-006 5.741e-006   -5.105    -5.241
-0.136
           MnCl+            5.141e-008 3.757e-008   -7.289    -7.425
-0.136
           MnCl2            2.328e-009 2.557e-009   -8.633    -8.592
0.041
           MnCl3-           1.502e-010 1.098e-010   -9.823    -9.960
-0.136
           Fe_triCl+2       5.669e-011 1.617e-011  -10.246   -10.791
-0.545
           Fe_triCl2+       1.541e-011 1.126e-011  -10.812   -10.948
-0.136
           Fe_triCl3        1.599e-013 1.756e-013  -12.796   -12.756
0.041
Fe_di        1.602e-004
           Fe_di+2          9.352e-005 2.668e-005   -4.029    -4.574
-0.545
           Fe_diHCO3+       5.249e-005 3.836e-005   -4.280    -4.416
-0.136
           Fe_diCl+         7.855e-006 5.741e-006   -5.105    -5.241
-0.136
           Fe_diSO4         6.262e-006 6.876e-006   -5.203    -5.163
0.041
           Fe_diCO3         1.068e-007 1.173e-007   -6.971    -6.931
0.041
           Fe_diOH+         3.111e-009 2.274e-009   -8.507    -8.643
-0.136
           Fe_diHSO4+       2.275e-010 1.662e-010   -9.643    -9.779
-0.136
           Fe_di(HS)2       0.000e+000 0.000e+000 -274.522  -274.481
0.041
           Fe_di(HS)3-      0.000e+000 0.000e+000 -411.736  -411.872
-0.136
Fe_tri       7.679e-007
           Fe_tri(OH)2+     7.299e-007 5.334e-007   -6.137    -6.273
-0.136
           Fe_triOH+2       2.095e-008 5.978e-009   -7.679    -8.223
-0.545
           Fe_tri(OH)3      1.686e-008 1.852e-008   -7.773    -7.732
0.041
           Fe_triSO4+       7.471e-011 5.460e-011  -10.127   -10.263
-0.136
           Fe_tri+3         5.776e-011 3.436e-012  -10.238   -11.464
-1.226
           Fe_triCl+2       5.669e-011 1.617e-011  -10.246   -10.791
-0.545
           Fe_triCl2+       1.541e-011 1.126e-011  -10.812   -10.948
-0.136
           Fe_tri(OH)4-     6.228e-012 4.551e-012  -11.206   -11.342
-0.136
```

```
           Fe_tri(SO4)2-    2.369e-012 1.731e-012  -11.625   -11.762
-0.136
           Fe_triCl3        1.599e-013 1.756e-013  -12.796   -12.756
0.041
           Fe_tri2(OH)2+4   1.452e-013 9.618e-016  -12.838   -15.017
-2.179
           Fe_triHSO4+2     1.885e-015 5.377e-016  -14.725   -15.269
-0.545
           Fe_tri3(OH)4+5   2.721e-016 1.072e-019  -15.565   -18.970
-3.405
H(0)         0.000e+000
           H2               0.000e+000 0.000e+000  -44.396   -44.355
0.041
K            5.270e-005
           K+               5.222e-005 3.439e-005   -4.282    -4.464
-0.181
           KSO4-            4.793e-007 3.503e-007   -6.319    -6.456
-0.136
           KOH              2.927e-014 3.214e-014  -13.534   -13.493
0.041
Mg           9.719e-004
           Mg+2             8.364e-004 2.511e-004   -3.078    -3.600
-0.523
           MgSO4            7.770e-005 8.532e-005   -4.110    -4.069
0.041
           MgHCO3+          5.781e-005 4.225e-005   -4.238    -4.374
-0.136
           MgCO3            4.001e-008 4.393e-008   -7.398    -7.357
0.041
           MgOH+            3.362e-010 2.457e-010   -9.473    -9.610
-0.136
Mn(2)        3.951e-007
           Mn+2             2.228e-007 5.916e-008   -6.652    -7.228
-0.576
           MnHCO3+          1.037e-007 7.582e-008   -6.984    -7.120
-0.136
           MnCl+            5.141e-008 3.757e-008   -7.289    -7.425
-0.136
           MnSO4            1.389e-008 1.525e-008   -7.857    -7.817
0.041
           MnCl2            2.328e-009 2.557e-009   -8.633    -8.592
0.041
           MnCO3            7.846e-010 8.617e-010   -9.105    -9.065
0.041
           MnCl3-           1.502e-010 1.098e-010   -9.823    -9.960
-0.136
           MnOH+            5.608e-013 4.098e-013  -12.251   -12.387
-0.136
Mn(3)        4.528e-017
           Mn+3             4.528e-017 2.693e-018  -16.344   -17.570
-1.226
Na           4.183e-004
           Na+              4.132e-004 2.950e-004   -3.384    -3.530
-0.146
           NaSO4-           2.933e-006 2.143e-006   -5.533    -5.669
-0.136
           NaHCO3           2.172e-006 2.386e-006   -5.663    -5.622
0.041
           NaCO3-           1.378e-009 1.007e-009   -8.861    -8.997
-0.136
           NaOH             4.784e-013 5.253e-013  -12.320   -12.280
0.041
O(0)         3.828e-004
           O2               1.914e-004 2.102e-004   -3.718    -3.677
0.041
S(-2)        0.000e+000
           H2S              0.000e+000 0.000e+000 -137.962  -137.921
0.041
           HS-              0.000e+000 0.000e+000 -139.241  -139.428
-0.187
           S-2              0.000e+000 0.000e+000 -146.277  -146.912
-0.635
           Fe_di(HS)2       0.000e+000 0.000e+000 -274.522  -274.481
0.041
           Fe_di(HS)3-      0.000e+000 0.000e+000 -411.736  -411.872
-0.136
S(6)         1.579e-002
           CaSO4            9.212e-003 1.012e-002   -2.036    -1.995
0.041
           SO4-2            6.490e-003 1.449e-003   -2.188    -2.839
-0.651
           MgSO4            7.770e-005 8.532e-005   -4.110    -4.069
0.041
           Fe_diSO4         6.262e-006 6.876e-006   -5.203    -5.163
0.041
           NaSO4-           2.933e-006 2.143e-006   -5.533    -5.669
-0.136
           HSO4-            7.092e-007 5.183e-007   -6.149    -6.285
-0.136
           KSO4-            4.793e-007 3.503e-007   -6.319    -6.456
-0.136
           CaHSO4+          2.982e-007 2.180e-007   -6.525    -6.662
-0.136
           MnSO4            1.389e-008 1.525e-008   -7.857    -7.817
0.041
           Fe_diHSO4+       2.275e-010 1.662e-010   -9.643    -9.779
-0.136
           Fe_triSO4+       7.471e-011 5.460e-011  -10.127   -10.263
-0.136
           Fe_tri(SO4)2-    2.369e-012 1.731e-012  -11.625   -11.762
-0.136
           Fe_triHSO4+2     1.885e-015 5.377e-016  -14.725   -15.269
-0.545

------------------------------Saturation indices------------------------------
---

           Phase              SI log IAP  log KT

           Anhydrite        0.07   -4.29   -4.36  CaSO4
           Aragonite        0.14   -8.19   -8.34  CaCO3
           Calcite          0.29   -8.19   -8.48  CaCO3
           CH4(g)        -138.48 -141.34   -2.86  CH4
           CO2(g)           0.55   -0.92   -1.47  CO2
           Dolomite        -1.44  -18.53  -17.09  CaMg(CO3)2
           Gypsum           0.28   -4.30   -4.58  CaSO4:2H2O
           H2(g)          -41.21  -44.36   -3.15  H2
           H2O(g)          -1.51   -0.00    1.51  H2O
           H2S(g)        -136.92 -137.92   -1.00  H2S
```

```
          Halite          -5.92   -4.34    1.58  NaCl
          Hausmannite     -8.92   52.11   61.03  Mn3O4
          Manganite       -1.10   24.24   25.34  MnOOH
          O2(g)           -0.78   -3.68   -2.89  O2
          Pyrochroite    -11.57    3.63   15.20  Mn(OH)2
          Pyrolusite       3.46   44.84   41.38  MnO2
          Rhodochrosite   -2.83  -13.96  -11.13  MnCO3
          Sulfur        -101.60  -96.72    4.88  S

Reaction step 2.

Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.  Kinetics defined in simulation 2.

          Time step: 400 seconds  (Incremented time: 500 seconds)

          Rate name       Delta Moles Total Moles   Reactant
Coefficient

          Fe_di_ox        -3.032e-006  1.000e+000   Fe_di
-1
                                                    Fe_tri
1

------------------------------Phase assemblage-----------------------------
---

                                                     Moles in assemblage
          Phase              SI log IAP  log KT    Initial      Final
Delta

          O2(g)           -0.79   -3.68   -2.89 1.000e+001 1.000e+001-
7.581e-007

----------------------------Solution composition---------------------------
---

          Elements           Molality       Moles

          C                1.389e-001  1.389e-001
          Ca               1.476e-001  1.476e-001
          Cl               2.367e-001  2.367e-001
          Fe_di            1.572e-004  1.572e-004
          Fe_tri           3.800e-006  3.800e-006
          K                5.270e-005  5.270e-005
          Mg               9.719e-004  9.719e-004
          Mn               3.951e-007  3.951e-007
          Na               4.183e-004  4.183e-004
          S                1.579e-002  1.579e-002

---------------------------Description of solution-------------------------
---

                                       pH  =   5.434     Charge balance
                                       pe  =  15.168     Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.068e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.967e-002
                    Total CO2 (mol/kg)     =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.518e-014
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  47
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587723e+001

---------------------------Distribution of species-------------------------
---

                                                            Log      Log
Log
          Species             Molality    Activity  Molality  Activity
Gamma

          H+                4.767e-006  3.678e-006    -5.322    -5.434
-0.113
          OH-               4.154e-009  2.698e-009    -8.382    -8.569
-0.187
          H2O               5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)         0.000e+000
          CH4               0.000e+000  0.000e+000  -141.384  -141.344
0.041
C(4)          1.389e-001
          CO2               1.092e-001  1.200e-001    -0.962    -0.921
0.041
          HCO3-             2.042e-002  1.438e-002    -1.690    -1.842
-0.152
          CaHCO3+           9.115e-003  6.417e-003    -2.040    -2.193
-0.152
          MgHCO3+           5.780e-005  4.225e-005    -4.238    -4.374
-0.136
          Fe_diHCO3+        5.149e-005  3.763e-005    -4.288    -4.424
-0.136
          CaCO3             9.809e-006  1.077e-005    -5.008    -4.968
0.041
          NaHCO3            2.172e-006  2.385e-006    -5.663    -5.622
0.041
          CO3-2             7.464e-007  1.833e-007    -6.127    -6.737
-0.610
          Fe_diCO3          1.048e-007  1.151e-007    -6.980    -6.939
0.041
          MnHCO3+           1.037e-007  7.581e-008    -6.984    -7.120
-0.136
          MgCO3             4.000e-008  4.393e-008    -7.398    -7.357
0.041
          NaCO3-            1.378e-009  1.007e-009    -8.861    -8.997
-0.136
          MnCO3             7.845e-010  8.615e-010    -9.105    -9.065
0.041
Ca            1.476e-001
          Ca+2              1.293e-001  3.498e-002    -0.889    -1.456
-0.568
          CaSO4             9.212e-003  1.012e-002    -2.036    -1.995
0.041
          CaHCO3+           9.115e-003  6.417e-003    -2.040    -2.193
-0.152
          CaCO3             9.809e-006  1.077e-005    -5.008    -4.968
0.041
          CaHSO4+           2.983e-007  2.180e-007    -6.525    -6.662
-0.136
          CaOH+             2.140e-009  1.564e-009    -8.669    -8.806
-0.136
Cl            2.367e-001
          Cl-               2.367e-001  1.559e-001    -0.626    -0.807
-0.181
          Fe_diCl+          7.707e-006  5.632e-006    -5.113    -5.249
-0.136
          MnCl+             5.141e-008  3.757e-008    -7.289    -7.425
-0.136
          MnCl2             2.328e-009  2.557e-009    -8.633    -8.592
0.041
          Fe_triCl+2        2.806e-010  8.005e-011    -9.552   -10.097
-0.545
          MnCl3-            1.502e-010  1.098e-010    -9.823    -9.959
-0.136
          Fe_triCl2+        7.627e-011  5.574e-011   -10.118   -10.254
-0.136
          Fe_triCl3         7.912e-013  8.689e-013   -12.102   -12.061
0.041
Fe_di         1.572e-004
          Fe_di+2           9.175e-005  2.617e-005    -4.037    -4.582
-0.545
          Fe_diHCO3+        5.149e-005  3.763e-005    -4.288    -4.424
-0.136
          Fe_diCl+          7.707e-006  5.632e-006    -5.113    -5.249
-0.136
          Fe_diSO4          6.143e-006  6.746e-006    -5.212    -5.171
0.041
          Fe_diCO3          1.048e-007  1.151e-007    -6.980    -6.939
0.041
          Fe_diOH+          3.052e-009  2.230e-009    -8.515    -8.652
-0.136
          Fe_diHSO4+        2.232e-010  1.631e-010    -9.651    -9.788
-0.136
          Fe_di(HS)2        0.000e+000  0.000e+000  -274.530  -274.489
0.041
          Fe_di(HS)3-       0.000e+000  0.000e+000  -411.744  -411.880
-0.136
Fe_tri        3.800e-006
          Fe_tri(OH)2+      3.612e-006  2.640e-006    -5.442    -5.578
-0.136
          Fe_triOH+2        1.037e-007  2.958e-008    -6.984    -7.529
-0.545
          Fe_tri(OH)3       8.344e-008  9.163e-008    -7.079    -7.038
0.041
          Fe_triSO4+        3.698e-010  2.702e-010    -9.432    -9.568
-0.136
          Fe_tri+3          2.859e-010  1.700e-011    -9.544   -10.769
-1.226
          Fe_triCl+2        2.806e-010  8.005e-011    -9.552   -10.097
-0.545
          Fe_triCl2+        7.627e-011  5.574e-011   -10.118   -10.254
-0.136
          Fe_tri(OH)4-      3.081e-011  2.252e-011   -10.511   -10.647
-0.136
          Fe_tri(SO4)2-     1.173e-011  8.569e-012   -10.931   -11.067
-0.136
          Fe_tri2(OH)2+4    3.556e-012  2.355e-014   -11.449   -13.628
-2.179
          Fe_triCl3         7.912e-013  8.689e-013   -12.102   -12.061
0.041
          Fe_tri3(OH)4+5    3.297e-014  1.299e-017   -13.482   -16.886
-3.405
          Fe_triHSO4+2      9.330e-015  2.662e-015   -14.030   -14.575
-0.545
H(0)          0.000e+000
          H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K             5.270e-005
          K+                5.222e-005  3.439e-005    -4.282    -4.464
-0.181
          KSO4-             4.793e-007  3.503e-007    -6.319    -6.456
-0.136
          KOH               2.926e-014  3.214e-014   -13.534   -13.493
0.041
Mg            9.719e-004
          Mg+2              8.364e-004  2.511e-004    -3.078    -3.600
-0.523
          MgSO4             7.770e-005  8.533e-005    -4.110    -4.069
0.041
          MgHCO3+           5.780e-005  4.225e-005    -4.238    -4.374
-0.136
          MgCO3             4.000e-008  4.393e-008    -7.398    -7.357
0.041
          MgOH+             3.362e-010  2.457e-010    -9.473    -9.610
-0.136
Mn(2)         3.951e-007
          Mn+2              2.228e-007  5.917e-008    -6.652    -7.228
-0.576
          MnHCO3+           1.037e-007  7.581e-008    -6.984    -7.120
-0.136
          MnCl+             5.141e-008  3.757e-008    -7.289    -7.425
-0.136
          MnSO4             1.389e-008  1.525e-008    -7.857    -7.817
0.041
          MnCl2             2.328e-009  2.557e-009    -8.633    -8.592
0.041
          MnCO3             7.845e-010  8.615e-010    -9.105    -9.065
0.041
          MnCl3-            1.502e-010  1.098e-010    -9.823    -9.959
-0.136
          MnOH+             5.607e-013  4.098e-013   -12.251   -12.387
-0.136
Mn(3)         4.528e-017
          Mn+3              4.528e-017  2.693e-018   -16.344   -17.570
-1.226
Na            4.183e-004
          Na+               4.132e-004  2.950e-004    -3.384    -3.530
-0.146
          NaSO4-            2.933e-006  2.143e-006    -5.533    -5.669
-0.136
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            NaHCO3          2.172e-006  2.385e-006    -5.663    -5.622
0.041
            NaCO3-          1.378e-009  1.007e-009    -8.861    -8.997
-0.136
            NaOH            4.783e-013  5.253e-013   -12.320   -12.280
0.041
O(0)          3.828e-004
            O2              1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)         0.000e+000
            H2S             0.000e+000  0.000e+000  -137.962  -137.921
0.041
            HS-             0.000e+000  0.000e+000  -139.241  -139.428
-0.187
            S-2             0.000e+000  0.000e+000  -146.277  -146.912
-0.635
            Fe_di(HS)2      0.000e+000  0.000e+000  -274.530  -274.489
0.041
            Fe_di(HS)3-     0.000e+000  0.000e+000  -411.744  -411.880
-0.136
S(6)          1.579e-002
            CaSO4           9.212e-003  1.012e-002    -2.036    -1.995
0.041
            SO4-2           6.490e-003  1.449e-003    -2.188    -2.839
-0.651
            MgSO4           7.770e-005  8.533e-005    -4.110    -4.069
0.041
            Fe_diSO4        6.143e-006  6.746e-006    -5.212    -5.171
0.041
            NaSO4-          2.933e-006  2.143e-006    -5.533    -5.669
-0.136
            HSO4-           7.092e-007  5.183e-007    -6.149    -6.285
-0.136
            KSO4-           4.793e-007  3.503e-007    -6.319    -6.456
-0.136
            CaHSO4+         2.983e-007  2.180e-007    -6.525    -6.662
-0.136
            MnSO4           1.389e-008  1.525e-008    -7.857    -7.817
0.041
            Fe_triSO4+      3.698e-010  2.702e-010    -9.432    -9.568
-0.136
            Fe_diHSO4+      2.232e-010  1.631e-010    -9.651    -9.788
-0.136
            Fe_tri(SO4)2-   1.173e-011  8.569e-012   -10.931   -11.067
-0.136
            Fe_triHSO4+2    9.330e-015  2.662e-015   -14.030   -14.575
-0.545

----------------------------Saturation indices----------------------------
---

            Phase               SI log IAP  log KT

            Anhydrite         0.07   -4.29   -4.36  CaSO4
            Aragonite         0.14   -8.19   -8.34  CaCO3
            Calcite           0.29   -8.19   -8.48  CaCO3
            CH4(g)         -138.48 -141.34   -2.86  CH4
            CO2(g)            0.55   -0.92   -1.47  CO2
            Dolomite         -1.44  -18.53  -17.09  CaMg(CO3)2
            Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
            H2(g)           -41.21  -44.36   -3.15  H2
            H2O(g)           -1.51   -0.00    1.51  H2O
            H2S(g)         -136.92 -137.92   -1.00  H2S
            Halite           -5.92   -4.34    1.58  NaCl
            Hausmannite      -8.92   52.11   61.03  Mn3O4
            Manganite        -1.10   24.24   25.34  MnOOH
            O2(g)            -0.79   -3.68   -2.89  O2
            Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
            Pyrolusite        3.46   44.84   41.38  MnO2
            Rhodochrosite    -2.83  -13.96  -11.13  MnCO3
            Sulfur         -101.60  -96.72    4.88  S

Reaction step 3.

Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.           Kinetics defined in simulation 2.

Kinetics 1.  Kinetics defined in simulation 2.

             Time step: 3100 seconds  (Incremented time: 3600 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox       -2.162e-005  1.000e+000   Fe_di
-1
                                                      Fe_tri
1

----------------------------Phase assemblage----------------------------
---

                                                   Moles in assemblage
             Phase               SI log IAP  log KT    Initial      Final
Delta

             O2(g)            -0.79   -3.68   -2.89 1.000e+001 1.000e+001-
5.405e-006

---------------------------Solution composition---------------------------
---

             Elements           Molality       Moles

             C                1.389e-001  1.389e-001
             Ca               1.476e-001  1.476e-001
             Cl               2.367e-001  2.367e-001
             Fe_di            1.356e-004  1.356e-004
             Fe_tri           2.542e-005  2.542e-005
             K                5.270e-005  5.270e-005
             Mg               9.719e-004  9.719e-004
             Mn               3.951e-007  3.951e-007
             Na               4.183e-004  4.183e-004
             S                1.579e-002  1.579e-002

--------------------------Description of solution--------------------------
---
```

```
                                       pH  =   5.434      Charge balance
                                       pe  =  15.169      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.068e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.970e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.519e-014
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  44
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587724e+001

---------------------------Distribution of species---------------------------
---

                                                     Log       Log
Log
             Species          Molality    Activity  Molality  Activity
Gamma

             H+              4.770e-006  3.681e-006    -5.321    -5.434
-0.113
             OH-             4.151e-009  2.696e-009    -8.382    -8.569
-0.187
             H2O             5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)          0.000e+000
             CH4             0.000e+000  0.000e+000  -141.384  -141.344
0.041
C(4)           1.389e-001
             CO2             1.093e-001  1.200e-001    -0.962    -0.921
0.041
             HCO3-           2.041e-002  1.437e-002    -1.690    -1.843
-0.152
             CaHCO3+         9.111e-003  6.414e-003    -2.040    -2.193
-0.152
             MgHCO3+         5.778e-005  4.223e-005    -4.238    -4.374
-0.136
             Fe_diHCO3+      4.440e-005  3.245e-005    -4.353    -4.489
-0.136
             CaCO3           9.798e-006  1.076e-005    -5.009    -4.968
0.041
             NaHCO3          2.171e-006  2.384e-006    -5.663    -5.623
0.041
             CO3-2           7.456e-007  1.831e-007    -6.128    -6.737
-0.610
             MnHCO3+         1.037e-007  7.579e-008    -6.984    -7.120
-0.136
             Fe_diCO3        9.031e-008  9.917e-008    -7.044    -7.004
0.041
             MgCO3           3.995e-008  4.388e-008    -7.398    -7.358
0.041
             NaCO3-          1.376e-009  1.006e-009    -8.861    -8.997
-0.136
             MnCO3           7.837e-010  8.606e-010    -9.106    -9.065
0.041
Ca             1.476e-001
             Ca+2            1.293e-001  3.498e-002    -0.889    -1.456
-0.568
             CaSO4           9.213e-003  1.012e-002    -2.036    -1.995
0.041
             CaHCO3+         9.111e-003  6.414e-003    -2.040    -2.193
-0.152
             CaCO3           9.798e-006  1.076e-005    -5.009    -4.968
0.041
             CaHSO4+         2.985e-007  2.182e-007    -6.525    -6.661
-0.136
             CaOH+           2.139e-009  1.563e-009    -8.670    -8.806
-0.136
Cl             2.367e-001
             Cl-             2.367e-001  1.559e-001    -0.626    -0.807
-0.181
             Fe_diCl+        6.648e-006  4.859e-006    -5.177    -5.313
-0.136
             MnCl+           5.142e-008  3.758e-008    -7.289    -7.425
-0.136
             MnCl2           2.329e-009  2.557e-009    -8.633    -8.592
0.041
             Fe_triCl+2      1.879e-009  5.362e-010    -8.726    -9.271
-0.545
             Fe_triCl2+      5.109e-010  3.733e-010    -9.292    -9.428
-0.136
             MnCl3-          1.502e-010  1.098e-010    -9.823    -9.959
-0.136
             Fe_triCl3       5.300e-012  5.820e-012   -11.276   -11.235
0.041
Fe_di          1.356e-004
             Fe_di+2         7.915e-005  2.258e-005    -4.102    -4.646
-0.545
             Fe_diHCO3+      4.440e-005  3.245e-005    -4.353    -4.489
-0.136
             Fe_diCl+        6.648e-006  4.859e-006    -5.177    -5.313
-0.136
             Fe_diSO4        5.300e-006  5.820e-006    -5.276    -5.235
0.041
             Fe_diCO3        9.031e-008  9.917e-008    -7.044    -7.004
0.041
             Fe_diOH+        2.631e-009  1.923e-009    -8.580    -8.716
-0.136
             Fe_diHSO4+      1.927e-010  1.408e-010    -9.715    -9.851
-0.136
             Fe_di(HS)2      0.000e+000  0.000e+000  -274.593  -274.553
0.041
             Fe_di(HS)3-     0.000e+000  0.000e+000  -411.808  -411.944
-0.136
Fe_tri         2.542e-005
             Fe_tri(OH)2+    2.416e-005  1.766e-005    -4.617    -4.753
-0.136
             Fe_triOH+2      6.941e-007  1.980e-007    -6.159    -6.703
-0.545
             Fe_tri(OH)3     5.577e-007  6.125e-007    -6.254    -6.213
0.041
             Fe_triSO4+      2.477e-009  1.810e-009    -8.606    -8.742
-0.136
             Fe_tri+3        1.915e-009  1.139e-010    -8.718    -9.944
-1.226
```

```
             Fe_triCl+2        1.879e-009  5.362e-010    -8.726    -9.271
-0.545
             Fe_triCl2+        5.109e-010  3.733e-010    -9.292    -9.428
-0.136
             Fe_tri(OH)4-      2.058e-010  1.504e-010    -9.687    -9.823
-0.136
             Fe_tri2(OH)2+4    1.593e-010  1.055e-012    -9.798   -11.977
-2.179
             Fe_tri(SO4)2-     7.854e-011  5.740e-011   -10.105   -10.241
-0.136
             Fe_tri3(OH)4+5    9.880e-012  3.893e-015   -11.005   -14.410
-3.405
             Fe_triCl3         5.300e-012  5.820e-012   -11.276   -11.235
0.041
             Fe_triHSO4+2      6.254e-014  1.784e-014   -13.204   -13.749
-0.545
H(0)           0.000e+000
             H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K              5.270e-005
             K+                5.222e-005  3.440e-005    -4.282    -4.464
-0.181
             KSO4-             4.793e-007  3.503e-007    -6.319    -6.456
-0.136
             KOH               2.924e-014  3.211e-014   -13.534   -13.493
0.041
Mg             9.719e-004
             Mg+2              8.364e-004  2.511e-004    -3.078    -3.600
-0.523
             MgSO4             7.770e-005  8.533e-005    -4.110    -4.069
0.041
             MgHCO3+           5.778e-005  4.223e-005    -4.238    -4.374
-0.136
             MgCO3             3.995e-008  4.388e-008    -7.398    -7.358
0.041
             MgOH+             3.359e-010  2.455e-010    -9.474    -9.610
-0.136
Mn(2)          3.951e-007
             Mn+2              2.228e-007  5.917e-008    -6.652    -7.228
-0.576
             MnHCO3+           1.037e-007  7.579e-008    -6.984    -7.120
-0.136
             MnCl+             5.142e-008  3.758e-008    -7.289    -7.425
-0.136
             MnSO4             1.389e-008  1.525e-008    -7.857    -7.817
0.041
             MnCl2             2.329e-009  2.557e-009    -8.633    -8.592
0.041
             MnCO3             7.837e-010  8.606e-010    -9.106    -9.065
0.041
             MnCl3-            1.502e-010  1.098e-010    -9.823    -9.959
-0.136
             MnOH+             5.604e-013  4.096e-013   -12.251   -12.388
-0.136
Mn(3)          4.532e-017
             Mn+3              4.532e-017  2.696e-018   -16.344   -17.569
-1.226
Na             4.183e-004
             Na+               4.132e-004  2.950e-004    -3.384    -3.530
-0.146
             NaSO4-            2.933e-006  2.143e-006    -5.533    -5.669
-0.136
             NaHCO3            2.171e-006  2.384e-006    -5.663    -5.623
0.041
             NaCO3-            1.376e-009  1.006e-009    -8.861    -8.997
-0.136
             NaOH              4.780e-013  5.249e-013   -12.321   -12.280
0.041
O(0)           3.828e-004
             O2                1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)          0.000e+000
             H2S               0.000e+000  0.000e+000  -137.961  -137.921
0.041
             HS-               0.000e+000  0.000e+000  -139.241  -139.428
-0.187
             S-2               0.000e+000  0.000e+000  -146.277  -146.912
-0.635
             Fe_di(HS)2        0.000e+000  0.000e+000  -274.593  -274.553
0.041
             Fe_di(HS)3-       0.000e+000  0.000e+000  -411.808  -411.944
-0.136
S(6)           1.579e-002
             CaSO4             9.213e-003  1.012e-002    -2.036    -1.995
0.041
             SO4-2             6.490e-003  1.449e-003    -2.188    -2.839
-0.651
             MgSO4             7.770e-005  8.533e-005    -4.110    -4.069
0.041
             Fe_diSO4          5.300e-006  5.820e-006    -5.276    -5.235
0.041
             NaSO4-            2.933e-006  2.143e-006    -5.533    -5.669
-0.136
             HSO4-             7.097e-007  5.187e-007    -6.149    -6.285
-0.136
             KSO4-             4.793e-007  3.503e-007    -6.319    -6.456
-0.136
             CaHSO4+           2.985e-007  2.182e-007    -6.525    -6.661
-0.136
             MnSO4             1.389e-008  1.525e-008    -7.857    -7.817
0.041
             Fe_triSO4+        2.477e-009  1.810e-009    -8.606    -8.742
-0.136
             Fe_diHSO4+        1.927e-010  1.408e-010    -9.715    -9.851
-0.136
             Fe_tri(SO4)2-     7.854e-011  5.740e-011   -10.105   -10.241
-0.136
             Fe_triHSO4+2      6.254e-014  1.784e-014   -13.204   -13.749
-0.545

------------------------------Saturation indices------------------------------
---

             Phase               SI log IAP  log KT

             Anhydrite         0.07   -4.29   -4.36  CaSO4
             Aragonite         0.14   -8.19   -8.34  CaCO3
             Calcite           0.29   -8.19   -8.48  CaCO3
             CH4(g)         -138.48 -141.34   -2.86  CH4
             CO2(g)            0.55   -0.92   -1.47  CO2
             Dolomite         -1.44  -18.53  -17.09  CaMg(CO3)2
             Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)           -41.21  -44.36   -3.15  H2
             H2O(g)           -1.51   -0.00    1.51  H2O
             H2S(g)         -136.92 -137.92   -1.00  H2S
             Halite           -5.92   -4.34    1.58  NaCl
             Hausmannite      -8.92   52.11   61.03  Mn3O4
             Manganite        -1.10   24.24   25.34  MnOOH
             O2(g)            -0.79   -3.68   -2.89  O2
             Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite        3.46   44.84   41.38  MnO2
             Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
             Sulfur         -101.60  -96.72    4.88  S

Reaction step 4.

Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.   Kinetics defined in simulation 2.

             Time step: 10800 seconds  (Incremented time: 14400 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox        -5.450e-005  9.999e-001   Fe_di
-1
                                                       Fe_tri
1

-----------------------------Phase assemblage-----------------------------
---

                                                    Moles in assemblage
             Phase               SI log IAP  log KT    Initial      Final
Delta

             O2(g)            -0.79   -3.68   -2.89 1.000e+001 1.000e+001-
1.363e-005

----------------------------Solution composition----------------------------
---

             Elements           Molality       Moles

             C                 1.389e-001  1.389e-001
             Ca                1.476e-001  1.476e-001
             Cl                2.367e-001  2.367e-001
             Fe_di             8.109e-005  8.109e-005
             Fe_tri            7.991e-005  7.991e-005
             K                 5.270e-005  5.270e-005
             Mg                9.719e-004  9.719e-004
             Mn                3.951e-007  3.951e-007
             Na                4.183e-004  4.183e-004
             S                 1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.433      Charge balance
                                       pe  =  15.169      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.067e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.975e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.542e-014
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  34
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587726e+001

----------------------------Distribution of species----------------------------
---

                                                    Log       Log
Log
             Species           Molality    Activity  Molality  Activity
Gamma

             H+                4.778e-006  3.687e-006    -5.321    -5.433
-0.113
             OH-               4.143e-009  2.691e-009    -8.383    -8.570
-0.187
             H2O               5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)          0.000e+000
             CH4               0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)           1.389e-001
             CO2               1.093e-001  1.200e-001    -0.961    -0.921
0.041
             HCO3-             2.039e-002  1.435e-002    -1.691    -1.843
-0.152
             CaHCO3+           9.101e-003  6.407e-003    -2.041    -2.193
-0.152
             MgHCO3+           5.771e-005  4.218e-005    -4.239    -4.375
-0.136
             Fe_diHCO3+        2.653e-005  1.939e-005    -4.576    -4.712
-0.136
             CaCO3             9.770e-006  1.073e-005    -5.010    -4.969
0.041
             NaHCO3            2.168e-006  2.381e-006    -5.664    -5.623
0.041
             CO3-2             7.433e-007  1.826e-007    -6.129    -6.739
-0.610
             MnHCO3+           1.036e-007  7.572e-008    -6.985    -7.121
-0.136
             Fe_diCO3          5.387e-008  5.916e-008    -7.269    -7.228
0.041
             MgCO3             3.984e-008  4.375e-008    -7.400    -7.359
0.041
             NaCO3-            1.372e-009  1.003e-009    -8.863    -8.999
-0.136
```

```
             MnCO3            7.816e-010  8.584e-010   -9.107   -9.066
0.041
Ca             1.476e-001
             Ca+2             1.293e-001  3.499e-002   -0.888   -1.456
-0.568
             CaSO4            9.215e-003  1.012e-002   -2.036   -1.995
0.041
             CaHCO3+          9.101e-003  6.407e-003   -2.041   -2.193
-0.152
             CaCO3            9.770e-006  1.073e-005   -5.010   -4.969
0.041
             CaHSO4+          2.991e-007  2.186e-007   -6.524   -6.660
-0.136
             CaOH+            2.136e-009  1.561e-009   -8.670   -8.807
-0.136
Cl             2.367e-001
             Cl-              2.367e-001  1.559e-001   -0.626   -0.807
-0.181
             Fe_diCl+         3.978e-006  2.907e-006   -5.400   -5.537
-0.136
             MnCl+            5.144e-008  3.759e-008   -7.289   -7.425
-0.136
             Fe_triCl+2       5.929e-009  1.692e-009   -8.227   -8.772
-0.545
             MnCl2            2.329e-009  2.558e-009   -8.633   -8.592
0.041
             Fe_triCl2+       1.612e-009  1.178e-009   -8.793   -8.929
-0.136
             MnCl3-           1.503e-010  1.098e-010   -9.823   -9.959
-0.136
             Fe_triCl3        1.672e-011  1.836e-011  -10.777  -10.736
0.041
Fe_di          8.109e-005
             Fe_di+2          4.735e-005  1.351e-005   -4.325   -4.869
-0.545
             Fe_diHCO3+       2.653e-005  1.939e-005   -4.576   -4.712
-0.136
             Fe_diCl+         3.978e-006  2.907e-006   -5.400   -5.537
-0.136
             Fe_diSO4         3.171e-006  3.482e-006   -5.499   -5.458
0.041
             Fe_diCO3         5.387e-008  5.916e-008   -7.269   -7.228
0.041
             Fe_diOH+         1.571e-009  1.148e-009   -8.804   -8.940
-0.136
             Fe_diHSO4+       1.155e-010  8.440e-011   -9.937  -10.074
-0.136
             Fe_di(HS)2       0.000e+000  0.000e+000 -274.815 -274.774
0.041
             Fe_di(HS)3-      0.000e+000  0.000e+000 -412.028 -412.164
-0.136
Fe_tri         7.991e-005
             Fe_tri(OH)2+     7.595e-005  5.551e-005   -4.119   -4.256
-0.136
             Fe_triOH+2       2.186e-006  6.236e-007   -5.660   -6.205
-0.545
             Fe_tri(OH)3      1.750e-006  1.922e-006   -5.757   -5.716
0.041
             Fe_triSO4+       7.814e-009  5.711e-009   -8.107   -8.243
-0.136
             Fe_tri+3         6.041e-009  3.593e-010   -8.219   -9.445
-1.226
             Fe_triCl+2       5.929e-009  1.692e-009   -8.227   -8.772
-0.545
             Fe_triCl2+       1.612e-009  1.178e-009   -8.793   -8.929
-0.136
             Fe_tri2(OH)2+4   1.580e-009  1.047e-011   -8.801  -10.980
-2.179
             Fe_tri(OH)4-     6.448e-010  4.713e-010   -9.191   -9.327
-0.136
             Fe_tri3(OH)4+5   3.081e-010  1.214e-013   -9.511  -12.916
-3.405
             Fe_tri(SO4)2-    2.478e-010  1.811e-010   -9.606   -9.742
-0.136
             Fe_triCl3        1.672e-011  1.836e-011  -10.777  -10.736
0.041
             Fe_triHSO4+2     1.976e-013  5.639e-014  -12.704  -13.249
-0.545
H(0)           0.000e+000
             H2               0.000e+000  0.000e+000  -44.396  -44.355
0.041
K              5.270e-005
             K+               5.222e-005  3.440e-005   -4.282   -4.463
-0.181
             KSO4-            4.794e-007  3.503e-007   -6.319   -6.456
-0.136
             KOH              2.919e-014  3.206e-014  -13.535  -13.494
0.041
Mg             9.719e-004
             Mg+2             8.364e-004  2.511e-004   -3.078   -3.600
-0.523
             MgSO4            7.772e-005  8.535e-005   -4.109   -4.069
0.041
             MgHCO3+          5.771e-005  4.218e-005   -4.239   -4.375
-0.136
             MgCO3            3.984e-008  4.375e-008   -7.400   -7.359
0.041
             MgOH+            3.354e-010  2.451e-010   -9.474   -9.611
-0.136
Mn(2)          3.951e-007
             Mn+2             2.229e-007  5.919e-008   -6.652   -7.228
-0.576
             MnHCO3+          1.036e-007  7.572e-008   -6.985   -7.121
-0.136
             MnCl+            5.144e-008  3.759e-008   -7.289   -7.425
-0.136
             MnSO4            1.390e-008  1.526e-008   -7.857   -7.816
0.041
             MnCl2            2.329e-009  2.558e-009   -8.633   -8.592
0.041
             MnCO3            7.816e-010  8.584e-010   -9.107   -9.066
0.041
             MnCl3-           1.503e-010  1.098e-010   -9.823   -9.959
-0.136
             MnOH+            5.596e-013  4.090e-013  -12.252  -12.388
-0.136
Mn(3)          4.541e-017
             Mn+3             4.541e-017  2.701e-018  -16.343  -17.568
-1.226
```

```
Na             4.183e-004
             Na+              4.132e-004  2.951e-004   -3.384   -3.530
-0.146
             NaSO4-           2.933e-006  2.144e-006   -5.533   -5.669
-0.136
             NaHCO3           2.168e-006  2.381e-006   -5.664   -5.623
0.041
             NaCO3-           1.372e-009  1.003e-009   -8.863   -8.999
-0.136
             NaOH             4.772e-013  5.240e-013  -12.321  -12.281
0.041
O(0)           3.828e-004
             O2               1.914e-004  2.102e-004   -3.718   -3.677
0.041
S(-2)          0.000e+000
             H2S              0.000e+000  0.000e+000 -137.960 -137.919
0.041
             HS-              0.000e+000  0.000e+000 -139.240 -139.427
-0.187
             S-2              0.000e+000  0.000e+000 -146.277 -146.912
-0.635
             Fe_di(HS)2       0.000e+000  0.000e+000 -274.815 -274.774
0.041
             Fe_di(HS)3-      0.000e+000  0.000e+000 -412.028 -412.164
-0.136
S(6)           1.579e-002
             CaSO4            9.215e-003  1.012e-002   -2.036   -1.995
0.041
             SO4-2            6.490e-003  1.450e-003   -2.188   -2.839
-0.651
             MgSO4            7.772e-005  8.535e-005   -4.109   -4.069
0.041
             Fe_diSO4         3.171e-006  3.482e-006   -5.499   -5.458
0.041
             NaSO4-           2.933e-006  2.144e-006   -5.533   -5.669
-0.136
             HSO4-            7.110e-007  5.196e-007   -6.148   -6.284
-0.136
             KSO4-            4.794e-007  3.503e-007   -6.319   -6.456
-0.136
             CaHSO4+          2.991e-007  2.186e-007   -6.524   -6.660
-0.136
             MnSO4            1.390e-008  1.526e-008   -7.857   -7.816
0.041
             Fe_triSO4+       7.814e-009  5.711e-009   -8.107   -8.243
-0.136
             Fe_tri(SO4)2-    2.478e-010  1.811e-010   -9.606   -9.742
-0.136
             Fe_diHSO4+       1.155e-010  8.440e-011   -9.937  -10.074
-0.136
             Fe_triHSO4+2     1.976e-013  5.639e-014  -12.704  -13.249
-0.545

------------------------------Saturation indices-------------------------------
---

             Phase               SI log IAP  log KT

             Anhydrite         0.07   -4.29   -4.36  CaSO4
             Aragonite         0.14   -8.19   -8.34  CaCO3
             Calcite           0.29   -8.19   -8.48  CaCO3
             CH4(g)         -138.48 -141.34   -2.86  CH4
             CO2(g)            0.55   -0.92   -1.47  CO2
             Dolomite         -1.44  -18.53  -17.09  CaMg(CO3)2
             Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)           -41.21  -44.36   -3.15  H2
             H2O(g)           -1.51   -0.00    1.51  H2O
             H2S(g)         -136.92 -137.92   -1.00  H2S
             Halite           -5.92   -4.34    1.58  NaCl
             Hausmannite      -8.92   52.11   61.03  Mn3O4
             Manganite        -1.11   24.23   25.34  MnOOH
             O2(g)            -0.79   -3.68   -2.89  O2
             Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite        3.46   44.84   41.38  MnO2
             Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
             Sulfur         -101.60  -96.71    4.88  S

Reaction step 5.

Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.  Kinetics defined in simulation 2.

             Time step: 21600 seconds  (Incremented time: 36000 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox       -5.198e-005  9.999e-001   Fe_di
-1
                                                      Fe_tri
1

-------------------------------Phase assemblage--------------------------------
---

                                                   Moles in assemblage
             Phase             SI log IAP  log KT    Initial      Final
Delta

             O2(g)           -0.78   -3.68   -2.89 1.000e+001 1.000e+001-
1.300e-005

-----------------------------Solution composition------------------------------
---

             Elements           Molality       Moles

             C               1.389e-001  1.389e-001
             Ca              1.476e-001  1.476e-001
             Cl              2.367e-001  2.367e-001
             Fe_di           2.911e-005  2.911e-005
             Fe_tri          1.319e-004  1.319e-004
             K               5.270e-005  5.270e-005
             Mg              9.719e-004  9.719e-004
             Mn              3.951e-007  3.951e-007
             Na              4.183e-004  4.183e-004
```

```
              S                1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.433      Charge balance
                                       pe  =  15.170      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.067e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.980e-002
                    Total CO2 (mol/kg)     =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.537e-014
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  85
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587729e+001

----------------------------Distribution of species----------------------------
---

                                                    Log       Log
Log
              Species          Molality    Activity  Molality  Activity
Gamma

              H+               4.786e-006  3.693e-006    -5.320    -5.433
-0.113
              OH-              4.137e-009  2.687e-009    -8.383    -8.571
-0.187
              H2O              5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)           0.000e+000
              CH4              0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)            1.389e-001
              CO2              1.094e-001  1.201e-001    -0.961    -0.920
0.041
              HCO3-            2.036e-002  1.434e-002    -1.691    -1.844
-0.152
              CaHCO3+          9.090e-003  6.399e-003    -2.041    -2.194
-0.152
              MgHCO3+          5.765e-005  4.213e-005    -4.239    -4.375
-0.136
              CaCO3            9.743e-006  1.070e-005    -5.011    -4.971
0.041
              Fe_diHCO3+       9.515e-006  6.954e-006    -5.022    -5.158
-0.136
              NaHCO3           2.166e-006  2.379e-006    -5.664    -5.624
0.041
              CO3-2            7.412e-007  1.820e-007    -6.130    -6.740
-0.610
              MnHCO3+          1.035e-007  7.565e-008    -6.985    -7.121
-0.136
              MgCO3            3.973e-008  4.363e-008    -7.401    -7.360
0.041
              Fe_diCO3         1.929e-008  2.118e-008    -7.715    -7.674
0.041
              NaCO3-           1.369e-009  1.000e-009    -8.864    -9.000
-0.136
              MnCO3            7.797e-010  8.562e-010    -9.108    -9.067
0.041
Ca              1.476e-001
              Ca+2             1.293e-001  3.499e-002    -0.888    -1.456
-0.568
              CaSO4            9.216e-003  1.012e-002    -2.035    -1.995
0.041
              CaHCO3+          9.090e-003  6.399e-003    -2.041    -2.194
-0.152
              CaCO3            9.743e-006  1.070e-005    -5.011    -4.971
0.041
              CaHSO4+          2.996e-007  2.190e-007    -6.523    -6.660
-0.136
              CaOH+            2.132e-009  1.558e-009    -8.671    -8.807
-0.136
Cl              2.367e-001
              Cl-              2.367e-001  1.559e-001    -0.626    -0.807
-0.181
              Fe_diCl+         1.428e-006  1.044e-006    -5.845    -5.981
-0.136
              MnCl+            5.146e-008  3.761e-008    -7.289    -7.425
-0.136
              Fe_triCl+2       9.818e-009  2.801e-009    -8.008    -8.553
-0.545
              Fe_triCl2+       2.669e-009  1.950e-009    -8.574    -8.710
-0.136
              MnCl2            2.330e-009  2.559e-009    -8.633    -8.592
0.041
              MnCl3-           1.504e-010  1.099e-010    -9.823    -9.959
-0.136
              Fe_triCl3        2.769e-011  3.041e-011   -10.558   -10.517
0.041
Fe_di           2.911e-005
              Fe_di+2          1.700e-005  4.851e-006    -4.769    -5.314
-0.545
              Fe_diHCO3+       9.515e-006  6.954e-006    -5.022    -5.158
-0.136
              Fe_diCl+         1.428e-006  1.044e-006    -5.845    -5.981
-0.136
              Fe_diSO4         1.139e-006  1.251e-006    -5.944    -5.903
0.041
              Fe_diCO3         1.929e-008  2.118e-008    -7.715    -7.674
0.041
              Fe_diOH+         5.633e-010  4.117e-010    -9.249    -9.385
-0.136
              Fe_diHSO4+       4.154e-011  3.036e-011   -10.382   -10.518
-0.136
              Fe_di(HS)2       0.000e+000  0.000e+000  -275.258  -275.217
0.041
              Fe_di(HS)3-      0.000e+000  0.000e+000  -412.471  -412.607
-0.136
Fe_tri          1.319e-004
              Fe_tri(OH)2+     1.253e-004  9.161e-005    -3.902    -4.038
-0.136
              Fe_triOH+2       3.614e-006  1.031e-006    -5.442    -5.987
-0.545
              Fe_tri(OH)3      2.884e-006  3.167e-006    -5.540    -5.499
0.041
              Fe_triSO4+       1.294e-008  9.457e-009    -7.888    -8.024
-0.136
              Fe_tri+3         1.000e-008  5.949e-010    -8.000    -9.226
-1.226
              Fe_triCl+2       9.818e-009  2.801e-009    -8.008    -8.553
-0.545
              Fe_tri2(OH)2+4   4.318e-009  2.860e-011    -8.365   -10.544
-2.179
              Fe_triCl2+       2.669e-009  1.950e-009    -8.574    -8.710
-0.136
              Fe_tri3(OH)4+5   1.390e-009  5.474e-013    -8.857   -12.262
-3.405
              Fe_tri(OH)4-     1.061e-009  7.752e-010    -8.974    -9.111
-0.136
              Fe_tri(SO4)2-    4.104e-010  3.000e-010    -9.387    -9.523
-0.136
              Fe_triCl3        2.769e-011  3.041e-011   -10.558   -10.517
0.041
              Fe_triHSO4+2     3.278e-013  9.353e-014   -12.484   -13.029
-0.545
H(0)            0.000e+000
              H2               0.000e+000  0.000e+000   -44.396   -44.355
0.041
K               5.270e-005
              K+               5.222e-005  3.440e-005    -4.282    -4.463
-0.181
              KSO4-            4.794e-007  3.504e-007    -6.319    -6.455
-0.136
              KOH              2.915e-014  3.201e-014   -13.535   -13.495
0.041
Mg              9.719e-004
              Mg+2             8.365e-004  2.512e-004    -3.078    -3.600
-0.522
              MgSO4            7.773e-005  8.536e-005    -4.109    -4.069
0.041
              MgHCO3+          5.765e-005  4.213e-005    -4.239    -4.375
-0.136
              MgCO3            3.973e-008  4.363e-008    -7.401    -7.360
0.041
              MgOH+            3.349e-010  2.447e-010    -9.475    -9.611
-0.136
Mn(2)           3.951e-007
              Mn+2             2.230e-007  5.921e-008    -6.652    -7.228
-0.576
              MnHCO3+          1.035e-007  7.565e-008    -6.985    -7.121
-0.136
              MnCl+            5.146e-008  3.761e-008    -7.289    -7.425
-0.136
              MnSO4            1.390e-008  1.527e-008    -7.857    -7.816
0.041
              MnCl2            2.330e-009  2.559e-009    -8.633    -8.592
0.041
              MnCO3            7.797e-010  8.562e-010    -9.108    -9.067
0.041
              MnCl3-           1.504e-010  1.099e-010    -9.823    -9.959
-0.136
              MnOH+            5.589e-013  4.085e-013   -12.253   -12.389
-0.136
Mn(3)           4.550e-017
              Mn+3             4.550e-017  2.707e-018   -16.342   -17.568
-1.226
Na              4.183e-004
              Na+              4.132e-004  2.951e-004    -3.384    -3.530
-0.146
              NaSO4-           2.933e-006  2.144e-006    -5.533    -5.669
-0.136
              NaHCO3           2.166e-006  2.379e-006    -5.664    -5.624
0.041
              NaCO3-           1.369e-009  1.000e-009    -8.864    -9.000
-0.136
              NaOH             4.764e-013  5.232e-013   -12.322   -12.281
0.041
O(0)            3.828e-004
              O2               1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)           0.000e+000
              H2S              0.000e+000  0.000e+000  -137.958  -137.918
0.041
              HS-              0.000e+000  0.000e+000  -139.239  -139.427
-0.187
              S-2              0.000e+000  0.000e+000  -146.277  -146.912
-0.635
              Fe_di(HS)2       0.000e+000  0.000e+000  -275.258  -275.217
0.041
              Fe_di(HS)3-      0.000e+000  0.000e+000  -412.471  -412.607
-0.136
S(6)            1.579e-002
              CaSO4            9.216e-003  1.012e-002    -2.035    -1.995
0.041
              SO4-2            6.490e-003  1.450e-003    -2.188    -2.839
-0.651
              MgSO4            7.773e-005  8.536e-005    -4.109    -4.069
0.041
              NaSO4-           2.933e-006  2.144e-006    -5.533    -5.669
-0.136
              Fe_diSO4         1.139e-006  1.251e-006    -5.944    -5.903
0.041
              HSO4-            7.123e-007  5.206e-007    -6.147    -6.284
-0.136
              KSO4-            4.794e-007  3.504e-007    -6.319    -6.455
-0.136
              CaHSO4+          2.996e-007  2.190e-007    -6.523    -6.660
-0.136
              MnSO4            1.390e-008  1.527e-008    -7.857    -7.816
0.041
              Fe_triSO4+       1.294e-008  9.457e-009    -7.888    -8.024
-0.136
              Fe_tri(SO4)2-    4.104e-010  3.000e-010    -9.387    -9.523
-0.136
              Fe_diHSO4+       4.154e-011  3.036e-011   -10.382   -10.518
-0.136
              Fe_triHSO4+2     3.278e-013  9.353e-014   -12.484   -13.029
-0.545

------------------------------Saturation indices------------------------------
---
```

```
             Phase               SI log IAP  log KT

             Anhydrite         0.07   -4.29   -4.36  CaSO4
             Aragonite         0.14   -8.20   -8.34  CaCO3
             Calcite           0.28   -8.20   -8.48  CaCO3
             CH4(g)         -138.48 -141.34   -2.86  CH4
             CO2(g)            0.55   -0.92   -1.47  CO2
             Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
             Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)           -41.21  -44.36   -3.15  H2
             H2O(g)           -1.51   -0.00    1.51  H2O
             H2S(g)         -136.92 -137.92   -1.00  H2S
             Halite           -5.92   -4.34    1.58  NaCl
             Hausmannite      -8.93   52.10   61.03  Mn3O4
             Manganite        -1.11   24.23   25.34  MnOOH
             O2(g)            -0.78   -3.68   -2.89  O2
             Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite        3.46   44.84   41.38  MnO2
             Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
             Sulfur         -101.59  -96.71    4.88  S

Reaction step 6.

WARNING: Element Fe_di has negative moles in solution, -4.123295e-006.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.  Kinetics defined in simulation 2.

             Time step: 50400 seconds  (Incremented time: 86400 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox       -2.642e-005  9.998e-001   Fe_di
-1
                                                      Fe_tri
1

-----------------------------Phase assemblage-----------------------------
---

                                                    Moles in assemblage
             Phase               SI log IAP  log KT    Initial      Final
Delta

             O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001-
6.607e-006

---------------------------Solution composition---------------------------
---

             Elements           Molality       Moles

             C                 1.389e-001  1.389e-001
             Ca                1.476e-001  1.476e-001
             Cl                2.367e-001  2.367e-001
             Fe_di             2.681e-006  2.681e-006
             Fe_tri            1.583e-004  1.583e-004
             K                 5.270e-005  5.270e-005
             Mg                9.719e-004  9.719e-004
             Mn                3.951e-007  3.951e-007
             Na                4.183e-004  4.183e-004
             S                 1.579e-002  1.579e-002

--------------------------Description of solution--------------------------
---

                                       pH  =   5.432      Charge balance
                                       pe  =  15.170      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.066e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.983e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  1.721e-013
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  85
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587730e+001

--------------------------Distribution of species--------------------------
---

                                                        Log       Log
Log
             Species            Molality    Activity  Molality  Activity

Gamma

             H+                4.790e-006  3.696e-006    -5.320    -5.432
-0.113
             OH-               4.133e-009  2.684e-009    -8.384    -8.571
-0.187
             H2O               5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)          0.000e+000
             CH4               0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)           1.389e-001
             CO2               1.094e-001  1.201e-001    -0.961    -0.920
0.041
             HCO3-             2.035e-002  1.433e-002    -1.691    -1.844
-0.152
             CaHCO3+           9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             MgHCO3+           5.761e-005  4.211e-005    -4.239    -4.376
-0.136
             CaCO3             9.730e-006  1.068e-005    -5.012    -4.971
0.041
             NaHCO3            2.165e-006  2.377e-006    -5.665    -5.624
0.041
             Fe_diHCO3+        8.762e-007  6.403e-007    -6.057    -6.194
-0.136
             CO3-2             7.401e-007  1.818e-007    -6.131    -6.740
-0.610
             MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MgCO3             3.967e-008  4.357e-008    -7.401    -7.361
0.041
             Fe_diCO3          1.775e-009  1.949e-009    -8.751    -8.710
0.041
             NaCO3-            1.367e-009  9.987e-010    -8.864    -9.001
-0.136
             MnCO3             7.787e-010  8.551e-010    -9.109    -9.068
0.041
Ca             1.476e-001
             Ca+2              1.293e-001  3.499e-002    -0.888    -1.456
-0.568
             CaSO4             9.217e-003  1.012e-002    -2.035    -1.995
0.041
             CaHCO3+           9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             CaCO3             9.730e-006  1.068e-005    -5.012    -4.971
0.041
             CaHSO4+           2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             CaOH+             2.131e-009  1.557e-009    -8.672    -8.808
-0.136
Cl             2.367e-001
             Cl-               2.367e-001  1.559e-001    -0.626    -0.807
-0.181
             Fe_diCl+          1.316e-007  9.618e-008    -6.881    -7.017
-0.136
             MnCl+             5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             Fe_triCl+2        1.180e-008  3.368e-009    -7.928    -8.473
-0.545
             Fe_triCl2+        3.209e-009  2.345e-009    -8.494    -8.630
-0.136
             MnCl2             2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCl3-            1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             Fe_triCl3         3.329e-011  3.656e-011   -10.478   -10.437
0.041
Fe_di          2.681e-006
             Fe_di+2           1.567e-006  4.470e-007    -5.805    -6.350
-0.545
             Fe_diHCO3+        8.762e-007  6.403e-007    -6.057    -6.194
-0.136
             Fe_diCl+          1.316e-007  9.618e-008    -6.881    -7.017
-0.136
             Fe_diSO4          1.049e-007  1.152e-007    -6.979    -6.938
0.041
             Fe_diCO3          1.775e-009  1.949e-009    -8.751    -8.710
0.041
             Fe_diOH+          5.186e-011  3.790e-011   -10.285   -10.421
-0.136
             Fe_diHSO4+        3.831e-012  2.800e-012   -11.417   -11.553
-0.136
             Fe_di(HS)2        0.000e+000  0.000e+000  -276.293  -276.252
0.041
             Fe_di(HS)3-       0.000e+000  0.000e+000  -413.505  -413.641
-0.136
Fe_tri         1.583e-004
             Fe_tri(OH)2+      1.505e-004  1.100e-004    -3.823    -3.959
-0.136
             Fe_triOH+2        4.341e-006  1.238e-006    -5.362    -5.907
-0.545
             Fe_tri(OH)3       3.459e-006  3.798e-006    -5.461    -5.420
0.041
             Fe_triSO4+        1.556e-008  1.137e-008    -7.808    -7.944
-0.136
             Fe_tri+3          1.203e-008  7.153e-010    -7.920    -9.146
-1.226
             Fe_triCl+2        1.180e-008  3.368e-009    -7.928    -8.473
-0.545
             Fe_tri2(OH)2+4    6.232e-009  4.128e-011    -8.205   -10.384
-2.179
             Fe_triCl2+        3.209e-009  2.345e-009    -8.494    -8.630
-0.136
             Fe_tri3(OH)4+5    2.407e-009  9.483e-013    -8.619   -12.023
-3.405
             Fe_tri(OH)4-      1.271e-009  9.289e-010    -8.896    -9.032
-0.136
             Fe_tri(SO4)2-     4.935e-010  3.607e-010    -9.307    -9.443
-0.136
             Fe_triCl3         3.329e-011  3.656e-011   -10.478   -10.437
0.041
             Fe_triHSO4+2      3.945e-013  1.125e-013   -12.404   -12.949
-0.545
H(0)           0.000e+000
             H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K              5.270e-005
             K+                5.222e-005  3.440e-005    -4.282    -4.463
-0.181
             KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             KOH               2.912e-014  3.198e-014   -13.536   -13.495
0.041
Mg             9.719e-004
             Mg+2              8.365e-004  2.512e-004    -3.078    -3.600
-0.522
             MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
             MgHCO3+           5.761e-005  4.211e-005    -4.239    -4.376
-0.136
             MgCO3             3.967e-008  4.357e-008    -7.401    -7.361
0.041
             MgOH+             3.346e-010  2.445e-010    -9.475    -9.612
-0.136
Mn(2)          3.951e-007
             Mn+2              2.230e-007  5.922e-008    -6.652    -7.228
-0.576
             MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
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             MnCl+           5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             MnSO4           1.390e-008  1.527e-008    -7.857    -7.816
0.041
             MnCl2           2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCO3           7.787e-010  8.551e-010    -9.109    -9.068
0.041
             MnCl3-          1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             MnOH+           5.585e-013  4.082e-013   -12.253   -12.389
-0.136
Mn(3)          4.555e-017
             Mn+3            4.555e-017  2.709e-018   -16.342   -17.567
-1.226
Na             4.183e-004
             Na+             4.132e-004  2.951e-004    -3.384    -3.530
-0.146
             NaSO4-          2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             NaHCO3          2.165e-006  2.377e-006    -5.665    -5.624
0.041
             NaCO3-          1.367e-009  9.987e-010    -8.864    -9.001
-0.136
             NaOH            4.760e-013  5.227e-013   -12.322   -12.282
0.041
O(0)           3.828e-004
             O2              1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)          0.000e+000
             H2S             0.000e+000  0.000e+000  -137.957  -137.917
0.041
             HS-             0.000e+000  0.000e+000  -139.239  -139.426
-0.187
             S-2             0.000e+000  0.000e+000  -146.277  -146.912
-0.635
             Fe_di(HS)2      0.000e+000  0.000e+000  -276.293  -276.252
0.041
             Fe_di(HS)3-     0.000e+000  0.000e+000  -413.505  -413.641
-0.136
S(6)           1.579e-002
             CaSO4           9.217e-003  1.012e-002    -2.035    -1.995
0.041
             SO4-2           6.491e-003  1.450e-003    -2.188    -2.839
-0.651
             MgSO4           7.774e-005  8.537e-005    -4.109    -4.069
0.041
             NaSO4-          2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             HSO4-           7.129e-007  5.210e-007    -6.147    -6.283
-0.136
             KSO4-           4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             CaHSO4+         2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             Fe_diSO4        1.049e-007  1.152e-007    -6.979    -6.938
0.041
             Fe_triSO4+      1.556e-008  1.137e-008    -7.808    -7.944
-0.136
             MnSO4           1.390e-008  1.527e-008    -7.857    -7.816
0.041
             Fe_tri(SO4)2-   4.935e-010  3.607e-010    -9.307    -9.443
-0.136
             Fe_diHSO4+      3.831e-012  2.800e-012   -11.417   -11.553
-0.136
             Fe_triHSO4+2    3.945e-013  1.125e-013   -12.404   -12.949
-0.545

------------------------------Saturation indices------------------------------
---

             Phase               SI log IAP  log KT

             Anhydrite         0.07   -4.29   -4.36  CaSO4
             Aragonite         0.14   -8.20   -8.34  CaCO3
             Calcite           0.28   -8.20   -8.48  CaCO3
             CH4(g)         -138.48 -141.34   -2.86  CH4
             CO2(g)            0.55   -0.92   -1.47  CO2
             Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
             Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)           -41.21  -44.36   -3.15  H2
             H2O(g)           -1.51   -0.00    1.51  H2O
             H2S(g)         -136.92 -137.92   -1.00  H2S
             Halite           -5.92   -4.34    1.58  NaCl
             Hausmannite      -8.93   52.10   61.03  Mn3O4
             Manganite        -1.11   24.23   25.34  MnOOH
             O2(g)            -0.78   -3.68   -2.89  O2
             Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite        3.45   44.83   41.38  MnO2
             Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
             Sulfur         -101.59  -96.71    4.88  S

Reaction step 7.

WARNING: Element Fe_di has negative moles in solution, -5.710494e-006.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.  Kinetics defined in simulation 2.

             Time step: 86400 seconds  (Incremented time: 172800 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox        -2.636e-006  9.998e-001   Fe_di
-1
                                                       Fe_tri
1

-------------------------------Phase assemblage-------------------------------
---

                                                     Moles in assemblage
             Phase               SI log IAP  log KT    Initial      Final
Delta

             O2(g)            -0.79   -3.68   -2.89 1.000e+001 1.000e+001-
6.591e-007

----------------------------Solution composition----------------------------
---

             Elements           Molality       Moles

             C                 1.389e-001  1.389e-001
             Ca                1.476e-001  1.476e-001
             Cl                2.367e-001  2.367e-001
             Fe_di             4.531e-008  4.531e-008
             Fe_tri            1.610e-004  1.610e-004
             K                 5.270e-005  5.270e-005
             Mg                9.719e-004  9.719e-004
             Mn                3.951e-007  3.951e-007
             Na                4.183e-004  4.183e-004
             S                 1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.432      Charge balance
                                       pe  =  15.170      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.066e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.983e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  3.342e-013
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  92
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587731e+001

----------------------------Distribution of species----------------------------
---

                                                          Log       Log
Log
             Species            Molality    Activity  Molality  Activity
Gamma

             H+                4.791e-006  3.697e-006    -5.320    -5.432
-0.113
             OH-               4.133e-009  2.684e-009    -8.384    -8.571
-0.187
             H2O               5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)          0.000e+000
             CH4               0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)           1.389e-001
             CO2               1.094e-001  1.201e-001    -0.961    -0.920
0.041
             HCO3-             2.035e-002  1.433e-002    -1.691    -1.844
-0.152
             CaHCO3+           9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             MgHCO3+           5.761e-005  4.210e-005    -4.239    -4.376
-0.136
             CaCO3             9.729e-006  1.068e-005    -5.012    -4.971
0.041
             NaHCO3            2.165e-006  2.377e-006    -5.665    -5.624
0.041
             CO3-2             7.400e-007  1.818e-007    -6.131    -6.741
-0.610
             MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MgCO3             3.967e-008  4.356e-008    -7.402    -7.361
0.041
             Fe_diHCO3+        1.481e-008  1.082e-008    -7.830    -7.966
-0.136
             NaCO3-            1.366e-009  9.986e-010    -8.864    -9.001
-0.136
             MnCO3             7.786e-010  8.550e-010    -9.109    -9.068
0.041
             Fe_diCO3          2.999e-011  3.293e-011   -10.523   -10.482
0.041
Ca             1.476e-001
             Ca+2              1.293e-001  3.499e-002    -0.888    -1.456
-0.568
             CaSO4             9.217e-003  1.012e-002    -2.035    -1.995
0.041
             CaHCO3+           9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             CaCO3             9.729e-006  1.068e-005    -5.012    -4.971
0.041
             CaHSO4+           2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             CaOH+             2.130e-009  1.557e-009    -8.672    -8.808
-0.136
Cl             2.367e-001
             Cl-               2.367e-001  1.559e-001    -0.626    -0.807
-0.181
             MnCl+             5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             Fe_triCl+2        1.200e-008  3.424e-009    -7.921    -8.465
-0.545
             Fe_triCl2+        3.263e-009  2.385e-009    -8.486    -8.623
-0.136
             MnCl2             2.331e-009  2.560e-009    -8.632    -8.592
0.041
             Fe_diCl+          2.224e-009  1.625e-009    -8.653    -8.789
-0.136
             MnCl3-            1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             Fe_triCl3         3.385e-011  3.718e-011   -10.470   -10.430
0.041
Fe_di          4.531e-008
             Fe_di+2           2.648e-008  7.553e-009    -7.577    -8.122
-0.545
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              Fe_diHCO3+        1.481e-008  1.082e-008    -7.830    -7.966
-0.136
              Fe_diCl+          2.224e-009  1.625e-009    -8.653    -8.789
-0.136
              Fe_diSO4          1.773e-009  1.947e-009    -8.751    -8.711
0.041
              Fe_diCO3          2.999e-011  3.293e-011   -10.523   -10.482
0.041
              Fe_diOH+          8.763e-013  6.404e-013   -12.057   -12.194
-0.136
              Fe_diHSO4+        6.474e-014  4.732e-014   -13.189   -13.325
-0.136
              Fe_di(HS)2        0.000e+000  0.000e+000  -278.065  -278.024
0.041
              Fe_di(HS)3-       0.000e+000  0.000e+000  -415.277  -415.413
-0.136
Fe_tri          1.610e-004
              Fe_tri(OH)2+      1.530e-004  1.118e-004    -3.815    -3.952
-0.136
              Fe_triOH+2        4.414e-006  1.259e-006    -5.355    -5.900
-0.545
              Fe_tri(OH)3       3.516e-006  3.861e-006    -5.454    -5.413
0.041
              Fe_triSO4+        1.582e-008  1.156e-008    -7.801    -7.937
-0.136
              Fe_tri+3          1.223e-008  7.273e-010    -7.913    -9.138
-1.226
              Fe_triCl+2        1.200e-008  3.424e-009    -7.921    -8.465
-0.545
              Fe_tri2(OH)2+4    6.442e-009  4.267e-011    -8.191   -10.370
-2.179
              Fe_triCl2+        3.263e-009  2.385e-009    -8.486    -8.623
-0.136
              Fe_tri3(OH)4+5    2.530e-009  9.966e-013    -8.597   -12.001
-3.405
              Fe_tri(OH)4-      1.292e-009  9.442e-010    -8.889    -9.025
-0.136
              Fe_tri(SO4)2-     5.018e-010  3.667e-010    -9.299    -9.436
-0.136
              Fe_triCl3         3.385e-011  3.718e-011   -10.470   -10.430
0.041
              Fe_triHSO4+2      4.012e-013  1.145e-013   -12.397   -12.941
-0.545
H(0)            0.000e+000
              H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K               5.270e-005
              K+                5.222e-005  3.440e-005    -4.282    -4.463
-0.181
              KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
              KOH               2.912e-014  3.198e-014   -13.536   -13.495
0.041
Mg              9.719e-004
              Mg+2              8.365e-004  2.512e-004    -3.078    -3.600
-0.522
              MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
              MgHCO3+           5.761e-005  4.210e-005    -4.239    -4.376
-0.136
              MgCO3             3.967e-008  4.356e-008    -7.402    -7.361
0.041
              MgOH+             3.346e-010  2.445e-010    -9.476    -9.612
-0.136
Mn(2)           3.951e-007
              Mn+2              2.230e-007  5.922e-008    -6.652    -7.228
-0.576
              MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
              MnCl+             5.147e-008  3.761e-008    -7.288    -7.425
-0.136
              MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
              MnCl2             2.331e-009  2.560e-009    -8.632    -8.592
0.041
              MnCO3             7.786e-010  8.550e-010    -9.109    -9.068
0.041
              MnCl3-            1.504e-010  1.099e-010    -9.823    -9.959
-0.136
              MnOH+             5.585e-013  4.082e-013   -12.253   -12.389
-0.136
Mn(3)           4.555e-017
              Mn+3              4.555e-017  2.710e-018   -16.341   -17.567
-1.226
Na              4.183e-004
              Na+               4.132e-004  2.951e-004    -3.384    -3.530
-0.146
              NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
              NaHCO3            2.165e-006  2.377e-006    -5.665    -5.624
0.041
              NaCO3-            1.366e-009  9.986e-010    -8.864    -9.001
-0.136
              NaOH              4.760e-013  5.227e-013   -12.322   -12.282
0.041
O(0)            3.828e-004
              O2                1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)           0.000e+000
              H2S               0.000e+000  0.000e+000  -137.957  -137.917
0.041
              HS-               0.000e+000  0.000e+000  -139.239  -139.426
-0.187
              S-2               0.000e+000  0.000e+000  -146.277  -146.912
-0.635
              Fe_di(HS)2        0.000e+000  0.000e+000  -278.065  -278.024
0.041
              Fe_di(HS)3-       0.000e+000  0.000e+000  -415.277  -415.413
-0.136
S(6)            1.579e-002
              CaSO4             9.217e-003  1.012e-002    -2.035    -1.995
0.041
              SO4-2             6.491e-003  1.450e-003    -2.188    -2.839
-0.651
              MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
              NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
              HSO4-             7.130e-007  5.211e-007    -6.147    -6.283
-0.136
              KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
              CaHSO4+           2.999e-007  2.192e-007    -6.523    -6.659
-0.136
              Fe_triSO4+        1.582e-008  1.156e-008    -7.801    -7.937
-0.136
              MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
              Fe_diSO4          1.773e-009  1.947e-009    -8.751    -8.711
0.041
              Fe_tri(SO4)2-     5.018e-010  3.667e-010    -9.299    -9.436
-0.136
              Fe_triHSO4+2      4.012e-013  1.145e-013   -12.397   -12.941
-0.545
              Fe_diHSO4+        6.474e-014  4.732e-014   -13.189   -13.325
-0.136

------------------------------Saturation indices------------------------------
---

              Phase               SI log IAP  log KT

              Anhydrite         0.07   -4.29   -4.36  CaSO4
              Aragonite         0.14   -8.20   -8.34  CaCO3
              Calcite           0.28   -8.20   -8.48  CaCO3
              CH4(g)         -138.48 -141.34   -2.86  CH4
              CO2(g)            0.55   -0.92   -1.47  CO2
              Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
              Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
              H2(g)           -41.21  -44.36   -3.15  H2
              H2O(g)           -1.51   -0.00    1.51  H2O
              H2S(g)         -136.92 -137.92   -1.00  H2S
              Halite           -5.92   -4.34    1.58  NaCl
              Hausmannite      -8.93   52.10   61.03  Mn3O4
              Manganite        -1.11   24.23   25.34  MnOOH
              O2(g)            -0.79   -3.68   -2.89  O2
              Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
              Pyrolusite        3.45   44.83   41.38  MnO2
              Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
              Sulfur         -101.59  -96.71    4.88  S

Reaction step 8.

WARNING: Element Fe_di has negative moles in solution, -2.872895e-008.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.971399e-009.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -3.030945e-009.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -2.415059e-009.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.478622e-009.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -7.499156e-010.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -3.589512e-011.
              Erroneous mole balance occurs as moles are added to produce
zero moles.
              Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
              May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.   Kinetics defined in simulation 2.

              Time step: 172800 seconds  (Incremented time: 345600 seconds)

              Rate name       Delta Moles Total Moles   Reactant
Coefficient

              Fe_di_ox        -4.530e-008  9.998e-001   Fe_di
-1
                                                        Fe_tri
1

------------------------------Phase assemblage------------------------------
---

                                                      Moles in assemblage
              Phase               SI log IAP  log KT    Initial      Final
Delta

              O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001-
1.132e-008
```

```
----------------------------Solution composition----------------------------
---

             Elements           Molality       Moles

             C                1.389e-001  1.389e-001
             Ca               1.476e-001  1.476e-001
             Cl               2.367e-001  2.367e-001
             Fe_di            1.298e-011  1.298e-011
             Fe_tri           1.610e-004  1.610e-004
             K                5.270e-005  5.270e-005
             Mg               9.719e-004  9.719e-004
             Mn               3.951e-007  3.951e-007
             Na               4.183e-004  4.183e-004
             S                1.579e-002  1.579e-002

---------------------------Description of solution--------------------------
---

                                        pH  =   5.432     Charge balance
                                        pe  =  15.170     Adjusted to redox
equilibrium
                          Activity of water  =   0.991
                             Ionic strength  =  4.066e-001
                         Mass of water (kg)  =  1.000e+000
                   Total alkalinity (eq/kg)  =  2.983e-002
                        Total CO2 (mol/kg)  =  1.389e-001
                        Temperature (deg C)  =  25.000
                    Electrical balance (eq)  = -1.264e-009
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                                 Iterations  = 236
                                    Total H  = 1.110421e+002
                                    Total O  = 5.587731e+001

---------------------------Distribution of species---------------------------
---

                                                         Log       Log
Log
             Species            Molality    Activity  Molality  Activity
Gamma

             H+               4.791e-006  3.697e-006    -5.320    -5.432
-0.113
             OH-              4.133e-009  2.684e-009    -8.384    -8.571
-0.187
             H2O              5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)           0.000e+000
             CH4              0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)            1.389e-001
             CO2              1.094e-001  1.201e-001    -0.961    -0.920
0.041
             HCO3-            2.035e-002  1.433e-002    -1.691    -1.844
-0.152
             CaHCO3+          9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             MgHCO3+          5.761e-005  4.210e-005    -4.239    -4.376
-0.136
             CaCO3            9.729e-006  1.068e-005    -5.012    -4.971
0.041
             NaHCO3           2.165e-006  2.377e-006    -5.665    -5.624
0.041
             CO3-2            7.400e-007  1.818e-007    -6.131    -6.741
-0.610
             MnHCO3+          1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MgCO3            3.967e-008  4.356e-008    -7.402    -7.361
0.041
             NaCO3-           1.366e-009  9.986e-010    -8.864    -9.001
-0.136
             MnCO3            7.786e-010  8.550e-010    -9.109    -9.068
0.041
             Fe_diHCO3+       4.243e-012  3.101e-012   -11.372   -11.509
-0.136
             Fe_diCO3         8.593e-015  9.436e-015   -14.066   -14.025
0.041
Ca              1.476e-001
             Ca+2             1.293e-001  3.499e-002    -0.888    -1.456
-0.568
             CaSO4            9.217e-003  1.012e-002    -2.035    -1.995
0.041
             CaHCO3+          9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             CaCO3            9.729e-006  1.068e-005    -5.012    -4.971
0.041
             CaHSO4+          2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             CaOH+            2.130e-009  1.557e-009    -8.672    -8.808
-0.136
Cl              2.367e-001
             Cl-              2.367e-001  1.559e-001    -0.626    -0.807
-0.181
             MnCl+            5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             Fe_triCl+2       1.201e-008  3.425e-009    -7.921    -8.465
-0.545
             Fe_triCl2+       3.264e-009  2.385e-009    -8.486    -8.622
-0.136
             MnCl2            2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCl3-           1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             Fe_triCl3        3.386e-011  3.719e-011   -10.470   -10.430
0.041
             Fe_diCl+         6.373e-013  4.658e-013   -12.196   -12.332
-0.136
Fe_di           1.298e-011
             Fe_di+2          7.587e-012  2.164e-012   -11.120   -11.665
-0.545
             Fe_diHCO3+       4.243e-012  3.101e-012   -11.372   -11.509
-0.136
             Fe_diCl+         6.373e-013  4.658e-013   -12.196   -12.332
-0.136
             Fe_diSO4         5.081e-013  5.580e-013   -12.294   -12.253
0.041
             Fe_diCO3         8.593e-015  9.436e-015   -14.066   -14.025
0.041
             Fe_diOH+         2.511e-016  1.835e-016   -15.600   -15.736
-0.136
             Fe_diHSO4+       1.855e-017  1.356e-017   -16.732   -16.868
-0.136
             Fe_di(HS)2       0.000e+000  0.000e+000  -281.608  -281.567
0.041
             Fe_di(HS)3-      0.000e+000  0.000e+000  -418.820  -418.956
-0.136
Fe_tri          1.610e-004
             Fe_tri(OH)2+     1.530e-004  1.118e-004    -3.815    -3.951
-0.136
             Fe_triOH+2       4.415e-006  1.259e-006    -5.355    -5.900
-0.545
             Fe_tri(OH)3      3.517e-006  3.862e-006    -5.454    -5.413
0.041
             Fe_triSO4+       1.583e-008  1.157e-008    -7.801    -7.937
-0.136
             Fe_tri+3         1.223e-008  7.275e-010    -7.913    -9.138
-1.226
             Fe_triCl+2       1.201e-008  3.425e-009    -7.921    -8.465
-0.545
             Fe_tri2(OH)2+4   6.446e-009  4.269e-011    -8.191   -10.370
-2.179
             Fe_triCl2+       3.264e-009  2.385e-009    -8.486    -8.622
-0.136
             Fe_tri3(OH)4+5   2.532e-009  9.974e-013    -8.597   -12.001
-3.405
             Fe_tri(OH)4-     1.292e-009  9.444e-010    -8.889    -9.025
-0.136
             Fe_tri(SO4)2-    5.020e-010  3.668e-010    -9.299    -9.436
-0.136
             Fe_triCl3        3.386e-011  3.719e-011   -10.470   -10.430
0.041
             Fe_triHSO4+2     4.013e-013  1.145e-013   -12.397   -12.941
-0.545
H(0)            0.000e+000
             H2               0.000e+000  0.000e+000   -44.396   -44.355
0.041
K               5.270e-005
             K+               5.222e-005  3.440e-005    -4.282    -4.463
-0.181
             KSO4-            4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             KOH              2.912e-014  3.198e-014   -13.536   -13.495
0.041
Mg              9.719e-004
             Mg+2             8.365e-004  2.512e-004    -3.078    -3.600
-0.522
             MgSO4            7.774e-005  8.537e-005    -4.109    -4.069
0.041
             MgHCO3+          5.761e-005  4.210e-005    -4.239    -4.376
-0.136
             MgCO3            3.967e-008  4.356e-008    -7.402    -7.361
0.041
             MgOH+            3.346e-010  2.445e-010    -9.476    -9.612
-0.136
Mn(2)           3.951e-007
             Mn+2             2.230e-007  5.922e-008    -6.652    -7.228
-0.576
             MnHCO3+          1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MnCl+            5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             MnSO4            1.390e-008  1.527e-008    -7.857    -7.816
0.041
             MnCl2            2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCO3            7.786e-010  8.550e-010    -9.109    -9.068
0.041
             MnCl3-           1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             MnOH+            5.585e-013  4.082e-013   -12.253   -12.389
-0.136
Mn(3)           4.555e-017
             Mn+3             4.555e-017  2.710e-018   -16.341   -17.567
-1.226
Na              4.183e-004
             Na+              4.132e-004  2.951e-004    -3.384    -3.530
-0.146
             NaSO4-           2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             NaHCO3           2.165e-006  2.377e-006    -5.665    -5.624
0.041
             NaCO3-           1.366e-009  9.986e-010    -8.864    -9.001
-0.136
             NaOH             4.760e-013  5.227e-013   -12.322   -12.282
0.041
O(0)            3.828e-004
             O2               1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)           0.000e+000
             H2S              0.000e+000  0.000e+000  -137.957  -137.917
0.041
             HS-              0.000e+000  0.000e+000  -139.239  -139.426
-0.187
             S-2              0.000e+000  0.000e+000  -146.277  -146.912
-0.635
             Fe_di(HS)2       0.000e+000  0.000e+000  -281.608  -281.567
0.041
             Fe_di(HS)3-      0.000e+000  0.000e+000  -418.820  -418.956
-0.136
S(6)            1.579e-002
             CaSO4            9.217e-003  1.012e-002    -2.035    -1.995
0.041
             SO4-2            6.491e-003  1.450e-003    -2.188    -2.839
-0.651
             MgSO4            7.774e-005  8.537e-005    -4.109    -4.069
0.041
             NaSO4-           2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             HSO4-            7.130e-007  5.211e-007    -6.147    -6.283
-0.136
             KSO4-            4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             CaHSO4+          2.999e-007  2.192e-007    -6.523    -6.659
-0.136
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             Fe_triSO4+       1.583e-008  1.157e-008    -7.801    -7.937
-0.136
             MnSO4            1.390e-008  1.527e-008    -7.857    -7.816
0.041
             Fe_tri(SO4)2-    5.020e-010  3.668e-010    -9.299    -9.436
-0.136
             Fe_diSO4         5.081e-013  5.580e-013   -12.294   -12.253
0.041
             Fe_triHSO4+2     4.013e-013  1.145e-013   -12.397   -12.941
-0.545
             Fe_diHSO4+       1.855e-017  1.356e-017   -16.732   -16.868
-0.136

------------------------------Saturation indices------------------------------
---

             Phase               SI log IAP  log KT

             Anhydrite         0.07   -4.29   -4.36  CaSO4
             Aragonite         0.14   -8.20   -8.34  CaCO3
             Calcite           0.28   -8.20   -8.48  CaCO3
             CH4(g)         -138.48 -141.34   -2.86  CH4
             CO2(g)            0.55   -0.92   -1.47  CO2
             Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
             Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)           -41.21  -44.36   -3.15  H2
             H2O(g)           -1.51   -0.00    1.51  H2O
             H2S(g)         -136.92 -137.92   -1.00  H2S
             Halite           -5.92   -4.34    1.58  NaCl
             Hausmannite      -8.93   52.10   61.03  Mn3O4
             Manganite        -1.11   24.23   25.34  MnOOH
             O2(g)            -0.78   -3.68   -2.89  O2
             Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite        3.45   44.83   41.38  MnO2
             Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
             Sulfur         -101.59  -96.71    4.88  S

Reaction step 9.

WARNING: Element Fe_di has negative moles in solution, -8.232164e-012.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -5.648819e-013.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -8.685081e-013.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -6.920311e-013.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -4.236973e-013.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -2.148874e-013.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.028570e-014.
             Erroneous mole balance occurs as moles are added to produce
zero moles.
             Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
             May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.   Kinetics defined in simulation 2.

             Time step: 172800 seconds  (Incremented time: 518400 seconds)

             Rate name       Delta Moles Total Moles   Reactant
Coefficient

             Fe_di_ox       -1.298e-011  9.998e-001   Fe_di
-1
                                                      Fe_tri
1

-------------------------------Phase assemblage-------------------------------
---

                                                    Moles in assemblage
             Phase               SI log IAP  log KT    Initial      Final
Delta

             O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001-
3.196e-012

-----------------------------Solution composition-----------------------------
---

             Elements           Molality       Moles

             C                1.389e-001  1.389e-001
             Ca               1.476e-001  1.476e-001
             Cl               2.367e-001  2.367e-001
             Fe_di            3.720e-015  3.720e-015
             Fe_tri           1.610e-004  1.610e-004
             K                5.270e-005  5.270e-005
             Mg               9.719e-004  9.719e-004
             Mn               3.951e-007  3.951e-007
             Na               4.183e-004  4.183e-004
             S                1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                       pH  =   5.432      Charge balance
                                       pe  =  15.170      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.066e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.983e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -1.265e-009
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                               Iterations  = 233
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587731e+001

----------------------------Distribution of species----------------------------
---

                                                            Log       Log
Log
             Species           Molality    Activity  Molality  Activity
Gamma

             H+               4.791e-006  3.697e-006    -5.320    -5.432
-0.113
             OH-              4.133e-009  2.684e-009    -8.384    -8.571
-0.187
             H2O              5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)          0.000e+000
             CH4              0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)           1.389e-001
             CO2              1.094e-001  1.201e-001    -0.961    -0.920
0.041
             HCO3-            2.035e-002  1.433e-002    -1.691    -1.844
-0.152
             CaHCO3+          9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             MgHCO3+          5.761e-005  4.210e-005    -4.239    -4.376
-0.136
             CaCO3            9.729e-006  1.068e-005    -5.012    -4.971
0.041
             NaHCO3           2.165e-006  2.377e-006    -5.665    -5.624
0.041
             CO3-2            7.400e-007  1.818e-007    -6.131    -6.741
-0.610
             MnHCO3+          1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MgCO3            3.967e-008  4.356e-008    -7.402    -7.361
0.041
             NaCO3-           1.366e-009  9.986e-010    -8.864    -9.001
-0.136
             MnCO3            7.786e-010  8.550e-010    -9.109    -9.068
0.041
             Fe_diHCO3+       1.216e-015  8.885e-016   -14.915   -15.051
-0.136
             Fe_diCO3         2.462e-018  2.704e-018   -17.609   -17.568
0.041
Ca             1.476e-001
             Ca+2             1.293e-001  3.499e-002    -0.888    -1.456
-0.568
             CaSO4            9.217e-003  1.012e-002    -2.035    -1.995
0.041
             CaHCO3+          9.085e-003  6.396e-003    -2.042    -2.194
-0.152
             CaCO3            9.729e-006  1.068e-005    -5.012    -4.971
0.041
             CaHSO4+          2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             CaOH+            2.130e-009  1.557e-009    -8.672    -8.808
-0.136
Cl             2.367e-001
             Cl-              2.367e-001  1.559e-001    -0.626    -0.807
-0.181
             MnCl+            5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             Fe_triCl+2       1.201e-008  3.425e-009    -7.921    -8.465
-0.545
             Fe_triCl2+       3.264e-009  2.385e-009    -8.486    -8.622
-0.136
             MnCl2            2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCl3-           1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             Fe_triCl3        3.386e-011  3.719e-011   -10.470   -10.430
0.041
             Fe_diCl+         1.826e-016  1.335e-016   -15.738   -15.875
-0.136
Fe_di          3.720e-015
             Fe_di+2          2.174e-015  6.202e-016   -14.663   -15.207
-0.545
             Fe_diHCO3+       1.216e-015  8.885e-016   -14.915   -15.051
-0.136
             Fe_diCl+         1.826e-016  1.335e-016   -15.738   -15.875
-0.136
             Fe_diSO4         1.456e-016  1.599e-016   -15.837   -15.796
0.041
             Fe_diCO3         2.462e-018  2.704e-018   -17.609   -17.568
0.041
             Fe_diOH+         7.195e-020  5.258e-020   -19.143   -19.279
-0.136
             Fe_diHSO4+       5.316e-021  3.885e-021   -20.274   -20.411
-0.136
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                 Fe_di(HS)2        0.000e+000  0.000e+000  -285.150  -285.110
0.041
                 Fe_di(HS)3-       0.000e+000  0.000e+000  -422.363  -422.499
-0.136
Fe_tri             1.610e-004
                 Fe_tri(OH)2+      1.530e-004  1.118e-004    -3.815    -3.951
-0.136
                 Fe_triOH+2        4.415e-006  1.259e-006    -5.355    -5.900
-0.545
                 Fe_tri(OH)3       3.517e-006  3.862e-006    -5.454    -5.413
0.041
                 Fe_triSO4+        1.583e-008  1.157e-008    -7.801    -7.937
-0.136
                 Fe_tri+3          1.223e-008  7.275e-010    -7.913    -9.138
-1.226
                 Fe_triCl+2        1.201e-008  3.425e-009    -7.921    -8.465
-0.545
                 Fe_tri2(OH)2+4    6.446e-009  4.269e-011    -8.191   -10.370
-2.179
                 Fe_triCl2+        3.264e-009  2.385e-009    -8.486    -8.622
-0.136
                 Fe_tri3(OH)4+5    2.532e-009  9.974e-013    -8.597   -12.001
-3.405
                 Fe_tri(OH)4-      1.292e-009  9.444e-010    -8.889    -9.025
-0.136
                 Fe_tri(SO4)2-     5.020e-010  3.668e-010    -9.299    -9.436
-0.136
                 Fe_triCl3         3.386e-011  3.719e-011   -10.470   -10.430
0.041
                 Fe_triHSO4+2      4.013e-013  1.145e-013   -12.397   -12.941
-0.545
H(0)               0.000e+000
                 H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K                  5.270e-005
                 K+                5.222e-005  3.440e-005    -4.282    -4.463
-0.181
                 KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
                 KOH               2.912e-014  3.198e-014   -13.536   -13.495
0.041
Mg                 9.719e-004
                 Mg+2              8.365e-004  2.512e-004    -3.078    -3.600
-0.522
                 MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
                 MgHCO3+           5.761e-005  4.210e-005    -4.239    -4.376
-0.136
                 MgCO3             3.967e-008  4.356e-008    -7.402    -7.361
0.041
                 MgOH+             3.346e-010  2.445e-010    -9.476    -9.612
-0.136
Mn(2)              3.951e-007
                 Mn+2              2.230e-007  5.922e-008    -6.652    -7.228
-0.576
                 MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
                 MnCl+             5.147e-008  3.761e-008    -7.288    -7.425
-0.136
                 MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
                 MnCl2             2.331e-009  2.560e-009    -8.632    -8.592
0.041
                 MnCO3             7.786e-010  8.550e-010    -9.109    -9.068
0.041
                 MnCl3-            1.504e-010  1.099e-010    -9.823    -9.959
-0.136
                 MnOH+             5.585e-013  4.082e-013   -12.253   -12.389
-0.136
Mn(3)              4.555e-017
                 Mn+3              4.555e-017  2.710e-018   -16.341   -17.567
-1.226
Na                 4.183e-004
                 Na+               4.132e-004  2.951e-004    -3.384    -3.530
-0.146
                 NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
                 NaHCO3            2.165e-006  2.377e-006    -5.665    -5.624
0.041
                 NaCO3-            1.366e-009  9.986e-010    -8.864    -9.001
-0.136
                 NaOH              4.760e-013  5.227e-013   -12.322   -12.282
0.041
O(0)               3.828e-004
                 O2                1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)              0.000e+000
                 H2S               0.000e+000  0.000e+000  -137.957  -137.917
0.041
                 HS-               0.000e+000  0.000e+000  -139.239  -139.426
-0.187
                 S-2               0.000e+000  0.000e+000  -146.277  -146.912
-0.635
                 Fe_di(HS)2        0.000e+000  0.000e+000  -285.150  -285.110
0.041
                 Fe_di(HS)3-       0.000e+000  0.000e+000  -422.363  -422.499
-0.136
S(6)               1.579e-002
                 CaSO4             9.217e-003  1.012e-002    -2.035    -1.995
0.041
                 SO4-2             6.491e-003  1.450e-003    -2.188    -2.839
-0.651
                 MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
                 NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
                 HSO4-             7.130e-007  5.211e-007    -6.147    -6.283
-0.136
                 KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
                 CaHSO4+           2.999e-007  2.192e-007    -6.523    -6.659
-0.136
                 Fe_triSO4+        1.583e-008  1.157e-008    -7.801    -7.937
-0.136
                 MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
                 Fe_tri(SO4)2-     5.020e-010  3.668e-010    -9.299    -9.436
-0.136
```

```
                 Fe_triHSO4+2      4.013e-013  1.145e-013   -12.397   -12.941
-0.545
                 Fe_diSO4          1.456e-016  1.599e-016   -15.837   -15.796
0.041
                 Fe_diHSO4+        5.316e-021  3.885e-021   -20.274   -20.411
-0.136

------------------------------Saturation indices-----------------------------
---

                 Phase               SI log IAP  log KT

                 Anhydrite         0.07   -4.29   -4.36  CaSO4
                 Aragonite         0.14   -8.20   -8.34  CaCO3
                 Calcite           0.28   -8.20   -8.48  CaCO3
                 CH4(g)         -138.48 -141.34   -2.86  CH4
                 CO2(g)            0.55   -0.92   -1.47  CO2
                 Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
                 Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
                 H2(g)           -41.21  -44.36   -3.15  H2
                 H2O(g)           -1.51   -0.00    1.51  H2O
                 H2S(g)         -136.92 -137.92   -1.00  H2S
                 Halite           -5.92   -4.34    1.58  NaCl
                 Hausmannite      -8.93   52.10   61.03  Mn3O4
                 Manganite        -1.11   24.23   25.34  MnOOH
                 O2(g)            -0.78   -3.68   -2.89  O2
                 Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
                 Pyrolusite        3.45   44.83   41.38  MnO2
                 Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
                 Sulfur         -101.59  -96.71    4.88  S

Reaction step 10.

WARNING: Element Fe_di has negative moles in solution, -2.358917e-015.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.618662e-016.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -2.488700e-016.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.983007e-016.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.214100e-016.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -6.157574e-017.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -2.947357e-018.
                 Erroneous mole balance occurs as moles are added to produce
zero moles.
                 Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
                 May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.      Kinetics defined in simulation 2.

                 Time step: 172800 seconds  (Incremented time: 691200 seconds)

                 Rate name       Delta Moles Total Moles   Reactant
Coefficient

                 Fe_di_ox        -3.886e-015  9.998e-001   Fe_di
-1
                                                           Fe_tri
1

-------------------------------Phase assemblage------------------------------
---

                                                        Moles in assemblage
                 Phase               SI log IAP  log KT    Initial      Final
Delta

                 O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001
1.048e-013

-----------------------------Solution composition----------------------------
---

                 Elements           Molality       Moles

                 C                 1.389e-001  1.389e-001
                 Ca                1.476e-001  1.476e-001
                 Cl                2.367e-001  2.367e-001
                 Fe_di             1.066e-018  1.066e-018
                 Fe_tri            1.610e-004  1.610e-004
                 K                 5.270e-005  5.270e-005
```

```
               Mg                 9.719e-004  9.719e-004
               Mn                 3.951e-007  3.951e-007
               Na                 4.183e-004  4.183e-004
               S                  1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---

                                        pH  =   5.432      Charge balance
                                        pe  =  15.170      Adjusted to redox
equilibrium
                          Activity of water  =   0.991
                           Ionic strength  =  4.066e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.983e-002
                    Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -1.265e-009
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                               Iterations  = 233
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587731e+001

----------------------------Distribution of species----------------------------
---

                                                    Log       Log
Log
               Species            Molality   Activity  Molality  Activity
Gamma

               H+                 4.791e-006  3.697e-006    -5.320    -5.432
-0.113
               OH-                4.133e-009  2.684e-009    -8.384    -8.571
-0.187
               H2O                5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)            0.000e+000
               CH4                0.000e+000  0.000e+000  -141.384  -141.343

0.041
C(4)             1.389e-001
               CO2                1.094e-001  1.201e-001    -0.961    -0.920

0.041
               HCO3-              2.035e-002  1.433e-002    -1.691    -1.844

-0.152
               CaHCO3+            9.085e-003  6.396e-003    -2.042    -2.194

-0.152
               MgHCO3+            5.761e-005  4.210e-005    -4.239    -4.376

-0.136
               CaCO3              9.729e-006  1.068e-005    -5.012    -4.971

0.041
               NaHCO3             2.165e-006  2.377e-006    -5.665    -5.624

0.041
               CO3-2              7.400e-007  1.818e-007    -6.131    -6.741

-0.610
               MnHCO3+            1.035e-007  7.562e-008    -6.985    -7.121

-0.136
               MgCO3              3.967e-008  4.356e-008    -7.402    -7.361

0.041
               NaCO3-             1.366e-009  9.986e-010    -8.864    -9.001

-0.136
               MnCO3              7.786e-010  8.550e-010    -9.109    -9.068

0.041
               Fe_diHCO3+         3.484e-019  2.546e-019   -18.458   -18.594

-0.136
               Fe_diCO3           7.056e-022  7.748e-022   -21.151   -21.111

0.041
Ca               1.476e-001
               Ca+2               1.293e-001  3.499e-002    -0.888    -1.456

-0.568
               CaSO4              9.217e-003  1.012e-002    -2.035    -1.995

0.041
               CaHCO3+            9.085e-003  6.396e-003    -2.042    -2.194

-0.152
               CaCO3              9.729e-006  1.068e-005    -5.012    -4.971

0.041
               CaHSO4+            2.999e-007  2.192e-007    -6.523    -6.659

-0.136
               CaOH+              2.130e-009  1.557e-009    -8.672    -8.808

-0.136
Cl               2.367e-001
               Cl-                2.367e-001  1.559e-001    -0.626    -0.807

-0.181
               MnCl+              5.147e-008  3.761e-008    -7.288    -7.425

-0.136
               Fe_triCl+2         1.201e-008  3.425e-009    -7.921    -8.465

-0.545
               Fe_triCl2+         3.264e-009  2.385e-009    -8.486    -8.622

-0.136
               MnCl2              2.331e-009  2.560e-009    -8.632    -8.592

0.041
               MnCl3-             1.504e-010  1.099e-010    -9.823    -9.959

-0.136
               Fe_triCl3          3.386e-011  3.719e-011   -10.470   -10.430

0.041
               Fe_diCl+           5.233e-020  3.824e-020   -19.281   -19.417

-0.136
Fe_di            1.066e-018
               Fe_di+2            6.230e-019  1.777e-019   -18.206   -18.750

-0.545
               Fe_diHCO3+         3.484e-019  2.546e-019   -18.458   -18.594

-0.136
               Fe_diCl+           5.233e-020  3.824e-020   -19.281   -19.417

-0.136
               Fe_diSO4           4.172e-020  4.582e-020   -19.380   -19.339

0.041
               Fe_diCO3           7.056e-022  7.748e-022   -21.151   -21.111

0.041
               Fe_diOH+           2.062e-023  1.507e-023   -22.686   -22.822

-0.136
               Fe_diHSO4+         1.523e-024  1.113e-024   -23.817   -23.953

-0.136
               Fe_di(HS)2         0.000e+000  0.000e+000  -288.693  -288.653

0.041
               Fe_di(HS)3-        0.000e+000  0.000e+000  -425.906  -426.042

-0.136
Fe_tri           1.610e-004
               Fe_tri(OH)2+       1.530e-004  1.118e-004    -3.815    -3.951

-0.136
               Fe_triOH+2         4.415e-006  1.259e-006    -5.355    -5.900

-0.545
               Fe_tri(OH)3        3.517e-006  3.862e-006    -5.454    -5.413

0.041
               Fe_triSO4+         1.583e-008  1.157e-008    -7.801    -7.937

-0.136
               Fe_tri+3           1.223e-008  7.275e-010    -7.913    -9.138

-1.226
               Fe_triCl+2         1.201e-008  3.425e-009    -7.921    -8.465

-0.545
               Fe_tri2(OH)2+4     6.446e-009  4.269e-011    -8.191   -10.370

-2.179
               Fe_triCl2+         3.264e-009  2.385e-009    -8.486    -8.622

-0.136
               Fe_tri3(OH)4+5     2.532e-009  9.974e-013    -8.597   -12.001

-3.405
               Fe_tri(OH)4-       1.292e-009  9.444e-010    -8.889    -9.025

-0.136
               Fe_tri(SO4)2-      5.020e-010  3.668e-010    -9.299    -9.436

-0.136
               Fe_triCl3          3.386e-011  3.719e-011   -10.470   -10.430

0.041
               Fe_triHSO4+2       4.013e-013  1.145e-013   -12.397   -12.941

-0.545
H(0)             0.000e+000
               H2                 0.000e+000  0.000e+000   -44.396   -44.355

0.041
K                5.270e-005
               K+                 5.222e-005  3.440e-005    -4.282    -4.463

-0.181
               KSO4-              4.794e-007  3.504e-007    -6.319    -6.455

-0.136
               KOH                2.912e-014  3.198e-014   -13.536   -13.495

0.041
Mg               9.719e-004
               Mg+2               8.365e-004  2.512e-004    -3.078    -3.600

-0.522
               MgSO4              7.774e-005  8.537e-005    -4.109    -4.069

0.041
               MgHCO3+            5.761e-005  4.210e-005    -4.239    -4.376

-0.136
               MgCO3              3.967e-008  4.356e-008    -7.402    -7.361

0.041
               MgOH+              3.346e-010  2.445e-010    -9.476    -9.612

-0.136
Mn(2)            3.951e-007
               Mn+2               2.230e-007  5.922e-008    -6.652    -7.228

-0.576
               MnHCO3+            1.035e-007  7.562e-008    -6.985    -7.121

-0.136
               MnCl+              5.147e-008  3.761e-008    -7.288    -7.425

-0.136
               MnSO4              1.390e-008  1.527e-008    -7.857    -7.816

0.041
               MnCl2              2.331e-009  2.560e-009    -8.632    -8.592

0.041
               MnCO3              7.786e-010  8.550e-010    -9.109    -9.068

0.041
               MnCl3-             1.504e-010  1.099e-010    -9.823    -9.959

-0.136
               MnOH+              5.585e-013  4.082e-013   -12.253   -12.389

-0.136
Mn(3)            4.555e-017
               Mn+3               4.555e-017  2.710e-018   -16.341   -17.567

-1.226
Na               4.183e-004
               Na+                4.132e-004  2.951e-004    -3.384    -3.530

-0.146
               NaSO4-             2.934e-006  2.144e-006    -5.533    -5.669

-0.136
               NaHCO3             2.165e-006  2.377e-006    -5.665    -5.624

0.041
               NaCO3-             1.366e-009  9.986e-010    -8.864    -9.001

-0.136
               NaOH               4.760e-013  5.227e-013   -12.322   -12.282

0.041
O(0)             3.828e-004
               O2                 1.914e-004  2.102e-004    -3.718    -3.677

0.041
S(-2)            0.000e+000
               H2S                0.000e+000  0.000e+000  -137.957  -137.917

0.041
               HS-                0.000e+000  0.000e+000  -139.239  -139.426

-0.187
               S-2                0.000e+000  0.000e+000  -146.277  -146.912

-0.635
               Fe_di(HS)2         0.000e+000  0.000e+000  -288.693  -288.653

0.041
               Fe_di(HS)3-        0.000e+000  0.000e+000  -425.906  -426.042

-0.136
S(6)             1.579e-002
               CaSO4              9.217e-003  1.012e-002    -2.035    -1.995

0.041
               SO4-2              6.491e-003  1.450e-003    -2.188    -2.839

-0.651
               MgSO4              7.774e-005  8.537e-005    -4.109    -4.069

0.041
               NaSO4-             2.934e-006  2.144e-006    -5.533    -5.669

-0.136
               HSO4-              7.130e-007  5.211e-007    -6.147    -6.283

-0.136
               KSO4-              4.794e-007  3.504e-007    -6.319    -6.455

-0.136
               CaHSO4+            2.999e-007  2.192e-007    -6.523    -6.659

-0.136
               Fe_triSO4+         1.583e-008  1.157e-008    -7.801    -7.937

-0.136
               MnSO4              1.390e-008  1.527e-008    -7.857    -7.816

0.041
               Fe_tri(SO4)2-      5.020e-010  3.668e-010    -9.299    -9.436

-0.136
               Fe_triHSO4+2       4.013e-013  1.145e-013   -12.397   -12.941

-0.545
               Fe_diSO4           4.172e-020  4.582e-020   -19.380   -19.339

0.041
               Fe_diHSO4+         1.523e-024  1.113e-024   -23.817   -23.953

-0.136
```

```
-----------------------------Saturation indices-----------------------------
---

            Phase               SI log IAP  log KT

            Anhydrite         0.07   -4.29   -4.36  CaSO4
            Aragonite         0.14   -8.20   -8.34  CaCO3
            Calcite           0.28   -8.20   -8.48  CaCO3
            CH4(g)         -138.48 -141.34   -2.86  CH4
            CO2(g)            0.55   -0.92   -1.47  CO2
            Dolomite         -1.45  -18.54  -17.09  CaMg(CO3)2
            Gypsum            0.28   -4.30   -4.58  CaSO4:2H2O
            H2(g)           -41.21  -44.36   -3.15  H2
            H2O(g)           -1.51   -0.00    1.51  H2O
            H2S(g)         -136.92 -137.92   -1.00  H2S
            Halite           -5.92   -4.34    1.58  NaCl
            Hausmannite      -8.93   52.10   61.03  Mn3O4
            Manganite        -1.11   24.23   25.34  MnOOH
            O2(g)            -0.78   -3.68   -2.89  O2
            Pyrochroite     -11.57    3.63   15.20  Mn(OH)2
            Pyrolusite        3.45   44.83   41.38  MnO2
            Rhodochrosite    -2.84  -13.97  -11.13  MnCO3
            Sulfur         -101.59  -96.71    4.88  S

Reaction step 11.

WARNING: Element Fe_di has negative moles in solution, -6.759450e-019.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -4.638259e-020.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -7.131341e-020.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -5.682284e-020.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -3.478989e-020.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -1.764446e-020.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
WARNING: Element Fe_di has negative moles in solution, -8.445617e-022.
            Erroneous mole balance occurs as moles are added to produce
zero moles.
            Usually caused by KINETICS, REACTION, or diffuse layer
calculation.
            May be due to large time steps in early part of KINETICS
simulation or negative concentrations in the diffuse layer.
Using solution 1.
Using pure phase assemblage 1.
Using kinetics 1.          Kinetics defined in simulation 2.

Kinetics 1.   Kinetics defined in simulation 2.

            Time step: 172800 seconds  (Incremented time: 864000 seconds)

            Rate name       Delta Moles Total Moles   Reactant
Coefficient

            Fe_di_ox        0.000e+000  9.998e-001   Fe_di
-1
                                                     Fe_tri
1

-----------------------------Phase assemblage-----------------------------
---

                                                   Moles in assemblage
            Phase               SI log IAP  log KT    Initial      Final
Delta

            O2(g)            -0.78   -3.68   -2.89 1.000e+001 1.000e+001
1.243e-013

----------------------------Solution composition----------------------------
---

            Elements           Molality       Moles

            C                1.389e-001  1.389e-001
            Ca               1.476e-001  1.476e-001
            Cl               2.367e-001  2.367e-001
            Fe_di            3.055e-022  3.055e-022
            Fe_tri           1.610e-004  1.610e-004
            K                5.270e-005  5.270e-005
            Mg               9.719e-004  9.719e-004
            Mn               3.951e-007  3.951e-007
            Na               4.183e-004  4.183e-004
            S                1.579e-002  1.579e-002

----------------------------Description of solution----------------------------
---
```

```
                                       pH  =   5.432      Charge balance
                                       pe  =  15.170      Adjusted to redox
equilibrium
                        Activity of water  =   0.991
                           Ionic strength  =  4.066e-001
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.983e-002
                       Total CO2 (mol/kg)  =  1.389e-001
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -1.265e-009
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                               Iterations  = 233
                                  Total H  = 1.110421e+002
                                  Total O  = 5.587731e+001

----------------------------Distribution of species----------------------------
---

                                                          Log       Log
Log
            Species          Molality    Activity  Molality  Activity
Gamma

            H+              4.791e-006  3.697e-006    -5.320    -5.432
-0.113
            OH-             4.133e-009  2.684e-009    -8.384    -8.571
-0.187
            H2O             5.551e+001  9.911e-001     1.744    -0.004
0.000
C(-4)         0.000e+000
            CH4             0.000e+000  0.000e+000  -141.384  -141.343
0.041
C(4)          1.389e-001
            CO2             1.094e-001  1.201e-001    -0.961    -0.920
0.041
            HCO3-           2.035e-002  1.433e-002    -1.691    -1.844
-0.152
            CaHCO3+         9.085e-003  6.396e-003    -2.042    -2.194
-0.152
            MgHCO3+         5.761e-005  4.210e-005    -4.239    -4.376
-0.136
            CaCO3           9.729e-006  1.068e-005    -5.012    -4.971
0.041
            NaHCO3          2.165e-006  2.377e-006    -5.665    -5.624
0.041
            CO3-2           7.400e-007  1.818e-007    -6.131    -6.741
-0.610
            MnHCO3+         1.035e-007  7.562e-008    -6.985    -7.121
-0.136
            MgCO3           3.967e-008  4.356e-008    -7.402    -7.361
0.041
            NaCO3-          1.366e-009  9.986e-010    -8.864    -9.001
-0.136
            MnCO3           7.786e-010  8.550e-010    -9.109    -9.068
0.041
            Fe_diHCO3+      9.982e-023  7.295e-023   -22.001   -22.137
-0.136
            Fe_diCO3        2.022e-025  2.220e-025   -24.694   -24.654
0.041
Ca            1.476e-001
            Ca+2            1.293e-001  3.499e-002    -0.888    -1.456
-0.568
            CaSO4           9.217e-003  1.012e-002    -2.035    -1.995
0.041
            CaHCO3+         9.085e-003  6.396e-003    -2.042    -2.194
-0.152
            CaCO3           9.729e-006  1.068e-005    -5.012    -4.971
0.041
            CaHSO4+         2.999e-007  2.192e-007    -6.523    -6.659
-0.136
            CaOH+           2.130e-009  1.557e-009    -8.672    -8.808
-0.136
Cl            2.367e-001
            Cl-             2.367e-001  1.559e-001    -0.626    -0.807
-0.181
            MnCl+           5.147e-008  3.761e-008    -7.288    -7.425
-0.136
            Fe_triCl+2      1.201e-008  3.425e-009    -7.921    -8.465
-0.545
            Fe_triCl2+      3.264e-009  2.385e-009    -8.486    -8.622
-0.136
            MnCl2           2.331e-009  2.560e-009    -8.632    -8.592
0.041
            MnCl3-          1.504e-010  1.099e-010    -9.823    -9.959
-0.136
            Fe_triCl3       3.386e-011  3.719e-011   -10.470   -10.430
0.041
            Fe_diCl+        1.500e-023  1.096e-023   -22.824   -22.960
-0.136
Fe_di         3.055e-022
            Fe_di+2         1.785e-022  5.092e-023   -21.748   -22.293
-0.545
            Fe_diHCO3+      9.982e-023  7.295e-023   -22.001   -22.137
-0.136
            Fe_diCl+        1.500e-023  1.096e-023   -22.824   -22.960
-0.136
            Fe_diSO4        1.196e-023  1.313e-023   -22.922   -22.882
0.041
            Fe_diCO3        2.022e-025  2.220e-025   -24.694   -24.654
0.041
            Fe_diOH+        5.908e-027  4.318e-027   -26.229   -26.365
-0.136
            Fe_diHSO4+      4.365e-028  3.190e-028   -27.360   -27.496
-0.136
            Fe_di(HS)2      0.000e+000  0.000e+000  -292.236  -292.195
0.041
            Fe_di(HS)3-     0.000e+000  0.000e+000  -429.448  -429.585
-0.136
Fe_tri        1.610e-004
            Fe_tri(OH)2+    1.530e-004  1.118e-004    -3.815    -3.951
-0.136
            Fe_triOH+2      4.415e-006  1.259e-006    -5.355    -5.900
-0.545
            Fe_tri(OH)3     3.517e-006  3.862e-006    -5.454    -5.413
0.041
            Fe_triSO4+      1.583e-008  1.157e-008    -7.801    -7.937
-0.136
```

```
             Fe_tri+3          1.223e-008  7.275e-010    -7.913    -9.138
-1.226
             Fe_triCl+2        1.201e-008  3.425e-009    -7.921    -8.465
-0.545
             Fe_tri2(OH)2+4    6.446e-009  4.269e-011    -8.191   -10.370
-2.179
             Fe_triCl2+        3.264e-009  2.385e-009    -8.486    -8.622
-0.136
             Fe_tri3(OH)4+5    2.532e-009  9.974e-013    -8.597   -12.001
-3.405
             Fe_tri(OH)4-      1.292e-009  9.444e-010    -8.889    -9.025
-0.136
             Fe_tri(SO4)2-     5.020e-010  3.668e-010    -9.299    -9.436
-0.136
             Fe_triCl3         3.386e-011  3.719e-011   -10.470   -10.430
0.041
             Fe_triHSO4+2      4.013e-013  1.145e-013   -12.397   -12.941
-0.545
H(0)           0.000e+000
             H2                0.000e+000  0.000e+000   -44.396   -44.355
0.041
K              5.270e-005
             K+                5.222e-005  3.440e-005    -4.282    -4.463
-0.181
             KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             KOH               2.912e-014  3.198e-014   -13.536   -13.495
0.041
Mg             9.719e-004
             Mg+2              8.365e-004  2.512e-004    -3.078    -3.600
-0.522
             MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
             MgHCO3+           5.761e-005  4.210e-005    -4.239    -4.376
-0.136
             MgCO3             3.967e-008  4.356e-008    -7.402    -7.361
0.041
             MgOH+             3.346e-010  2.445e-010    -9.476    -9.612
-0.136
Mn(2)          3.951e-007
             Mn+2              2.230e-007  5.922e-008    -6.652    -7.228
-0.576
             MnHCO3+           1.035e-007  7.562e-008    -6.985    -7.121
-0.136
             MnCl+             5.147e-008  3.761e-008    -7.288    -7.425
-0.136
             MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
             MnCl2             2.331e-009  2.560e-009    -8.632    -8.592
0.041
             MnCO3             7.786e-010  8.550e-010    -9.109    -9.068
0.041
             MnCl3-            1.504e-010  1.099e-010    -9.823    -9.959
-0.136
             MnOH+             5.585e-013  4.082e-013   -12.253   -12.389
-0.136
Mn(3)          4.555e-017
             Mn+3              4.555e-017  2.710e-018   -16.341   -17.567
-1.226
Na             4.183e-004
             Na+               4.132e-004  2.951e-004    -3.384    -3.530
-0.146
             NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             NaHCO3            2.165e-006  2.377e-006    -5.665    -5.624
0.041
             NaCO3-            1.366e-009  9.986e-010    -8.864    -9.001
-0.136
             NaOH              4.760e-013  5.227e-013   -12.322   -12.282
0.041
O(0)           3.828e-004
             O2                1.914e-004  2.102e-004    -3.718    -3.677
0.041
S(-2)          0.000e+000
             H2S               0.000e+000  0.000e+000  -137.957  -137.917
0.041
             HS-               0.000e+000  0.000e+000  -139.239  -139.426
-0.187
             S-2               0.000e+000  0.000e+000  -146.277  -146.912
-0.635
             Fe_di(HS)2        0.000e+000  0.000e+000  -292.236  -292.195
0.041
             Fe_di(HS)3-       0.000e+000  0.000e+000  -429.448  -429.585
-0.136
S(6)           1.579e-002
             CaSO4             9.217e-003  1.012e-002    -2.035    -1.995
0.041
             SO4-2             6.491e-003  1.450e-003    -2.188    -2.839
-0.651
             MgSO4             7.774e-005  8.537e-005    -4.109    -4.069
0.041
             NaSO4-            2.934e-006  2.144e-006    -5.533    -5.669
-0.136
             HSO4-             7.130e-007  5.211e-007    -6.147    -6.283
-0.136
             KSO4-             4.794e-007  3.504e-007    -6.319    -6.455
-0.136
             CaHSO4+           2.999e-007  2.192e-007    -6.523    -6.659
-0.136
             Fe_triSO4+        1.583e-008  1.157e-008    -7.801    -7.937
-0.136
             MnSO4             1.390e-008  1.527e-008    -7.857    -7.816
0.041
             Fe_tri(SO4)2-     5.020e-010  3.668e-010    -9.299    -9.436
-0.136
             Fe_triHSO4+2      4.013e-013  1.145e-013   -12.397   -12.941
-0.545
             Fe_diSO4          1.196e-023  1.313e-023   -22.922   -22.882
0.041
             Fe_diHSO4+        4.365e-028  3.190e-028   -27.360   -27.496
-0.136

-----------------------------Saturation indices-----------------------------
---

             Phase              SI log IAP  log KT

             Anhydrite        0.07   -4.29   -4.36  CaSO4
             Aragonite        0.14   -8.20   -8.34  CaCO3
             Calcite          0.28   -8.20   -8.48  CaCO3
             CH4(g)        -138.48 -141.34   -2.86  CH4
             CO2(g)           0.55   -0.92   -1.47  CO2
             Dolomite        -1.45  -18.54  -17.09  CaMg(CO3)2
             Gypsum           0.28   -4.30   -4.58  CaSO4:2H2O
             H2(g)          -41.21  -44.36   -3.15  H2
             H2O(g)          -1.51   -0.00    1.51  H2O
             H2S(g)        -136.92 -137.92   -1.00  H2S
             Halite          -5.92   -4.34    1.58  NaCl
             Hausmannite     -8.93   52.10   61.03  Mn3O4
             Manganite       -1.11   24.23   25.34  MnOOH
             O2(g)           -0.78   -3.68   -2.89  O2
             Pyrochroite    -11.57    3.63   15.20  Mn(OH)2
             Pyrolusite       3.45   44.83   41.38  MnO2
             Rhodochrosite   -2.84  -13.97  -11.13  MnCO3
             Sulfur        -101.59  -96.71    4.88  S

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End of simulation.
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Reading input data for simulation 3.
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End of run.
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END
```

B-3: PHREEQC Partial Output File

```
     Days           Fe(2)          Fe(3)           pH        si_Fe(OH)3(a)
 0.0000e+000    1.6100e+002    0.0000e+000    5.4344e+000    -9.9990e+001
 1.1574e-003    1.6023e+002    7.6792e-001    5.4344e+000    -9.9990e+001
 5.7870e-003    1.5720e+002    3.7999e+000    5.4344e+000    -9.9990e+001
 4.1667e-002    1.3558e+002    2.5417e+001    5.4341e+000    -9.9990e+001
 1.6667e-001    8.1085e+001    7.9915e+001    5.4333e+000    -9.9990e+001
 4.1667e-001    2.9106e+001    1.3189e+002    5.4326e+000    -9.9990e+001
 1.0000e+000    2.6813e+000    1.5832e+002    5.4322e+000    -9.9990e+001
 2.0000e+000    4.5311e-002    1.6095e+002    5.4322e+000    -9.9990e+001
 4.0000e+000    1.2984e-005    1.6100e+002    5.4322e+000    -9.9990e+001
 6.0000e+000    3.7205e-009    1.6100e+002    5.4322e+000    -9.9990e+001
 8.0000e+000    1.0661e-012    1.6100e+002    5.4322e+000    -9.9990e+001
 1.0000e+001    3.0549e-016    1.6100e+002    5.4322e+000    -9.9990e+001
```

Appendix C. Iron Standards Calculations

Table C-1: Standards Calculations

Formula Weight, FeCl3 (g/mol)	270.32
Molar Weight, Fe (g/mol)	55.847
Actual Weight of Compound*, FeCl3 (g)	0.495
Volume of flask (L)	1
Desired Conc. (mg/L)	100
Desired Mass	100
Mass of Compound to produce desired [Fe] (mg)	484.0367

Table C-2: Iron Standards

Stand. [C]	Vol.(mL)	Actual Vol (mL)*	Actual Dilution (ppm)
1	0.977852	1	1.02265
2	1.955704	2	2.0453
5	4.88926	5	5.11325
8	7.822816	8	8.1812
50	48.8926	50	51.1325

*measured quantity