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Kinetics of Hydrogen Sulfide Oxidation in Sanitary Sewer Systems

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Kinetics of Hydrogen Sulfide Oxidation in Sanitary Sewer Systems

A Dissertation

Submitted to the Graduate Faculty of the
University of New Orleans
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Engineering and Applied Sciences

by

Karloren J. Guzmán

B.S.C.E., Universidad Santa Maria, 2000
M.S., University of New Orleans, 2003

May 2007

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To my beloved husband, Soli E. and adored kids, Daniel E. and Sebastian E.

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ABSTRACT

There is a need to evaluate different technologies such as FeCl_2 , H_2O_2 and O_2 addition as odor and corrosion control alternatives to determine required dosages and detention times. The goal of this research is to study the kinetics of H_2S removal using the techniques commonly employed in sanitary sewer systems to determine the effectiveness of each process. To achieve this objective a laboratory simulation of these chemicals additions was carried out using completely mixed BOD bottles as batch-reactors. The BOD reactor was filled with a 7 mg/L H_2S solution. FeCl_2 , 50%- H_2O_2 , O_2 and a combination of FeCl_2 and H_2O_2 were added to the reactors containing H_2S solution and the concentration of H_2S remaining was measured after certain reaction times. A rate expression based on experimental data was generated using the integration method. The rate constants (k) and the order of the reaction (n) were calculated from the concentration-time data. For a range of temperature of 12 °C and 14 °C and pH 7, the oxidation of H_2S with FeCl_2 adheres to second-order reaction kinetics. The removal of H_2S using H_2O_2 is well described by the third-order kinetic for a temperature range between 10 °C and 17 °C and pH 7. H_2S oxidation by the combination of FeCl_2 and H_2O_2 can be described by third-order reaction kinetic in a temperature range of 15-20°C and pH 7. The removal of H_2S injecting O_2 to force mains suggests a second-order reaction kinetic at 22.5 °C and pH 7. Summing up, FeCl_2 treatment requires the addition of large quantities to be effective. Also, O_2 injection was ineffective across the range of pure oxygen

investigated. Conversely, 50% H_2O_2 is the most effective chemical control strategy for the mitigation of H_2S investigated. Maximum percent H_2S removals using combination of FeCl_2 and H_2O_2 were in the 90s. In this case most of the H_2S is oxidized by H_2O_2 , which means that FeCl_2 addition does not have a significant effect on the removal of H_2O_2 . In every case, the initial concentration of the reactant used has a significant effect on the values of both k and $t_{1/2}$.

I. INTRODUCTION

1.1 Background

Wastewater is commonly known for its potential to create odor nuisances from a variety of sources, including odors escaping from sewer manholes and wastewater treatment facilities. Hydrogen sulfide (H_2S), a colorless gas detectable in very low concentrations and notable for both its toxicity and its ability to corrode various materials used in sewer and treatment plant construction, is a major source of odor in wastewater treatment systems with a characteristic rotten egg odor (Edwards, et al., 2000). For this reason, the need for economical and effective technologies for odor/corrosion prevention and control has always been prevalent, especially in flat areas, where H_2S generation in sewerage systems is more common.

There are many different types of control measures that can be used to treat sulfide compounds in the liquid phase before they can be emitted, or to remove them through chemical or biological action. Control methods can involve the addition of air or oxygen to decrease sulfide formation, and to oxidize existing sulfide. Another approach is the use of chemicals to halt sulfide production or react with sulfide in the liquid (WEF, 2004).

Significant amounts of sulfide generation occur in the existing sanitary sewer systems of the country creating several problems, including sewer corrosion and nuisance at the wastewater treatment plants. There are dozens of several effective methods for treating sulfide generation to control odor and corrosion problems

The objectives and logistics of an application often dictate selecting one technology over others. However, for reasons related to convenience and flexibility, oxygen injection and chemical oxidation using iron salts and hydrogen peroxide continue to grow in their scope of application (U.S. Peroxide, 2004a). Ferrous salts (FeCl_2) precipitate dissolved sulfide in wastewater. Hydrogen peroxide (H_2O_2) is a powerful, yet versatile, oxidant that is both safe and effective (U.S. Peroxide, 2004b). It can be added as a preventive measure to eliminate the anoxic conditions which favor the generation of H_2S . Similarly, pure oxygen has been successfully injected into sewage force mains for many years to maintain aerobic conditions in the sewer system. Oxygen with 90% purity can be produced locally with several economical and technical advantages as compared to other methods of controlling dissolved H_2S (Jordan, et al., 2003).

Despite the fact that these applications have been successfully used in some sewer systems at different locations in the country, there are some unanswered questions regarding the processes themselves and their cost as compared to other hydrogen sulfide technologies.

South Louisiana has experienced both nuisance odor problems and infrastructure degradation problems at different wastewater treatment plants. As an example, Jefferson Parish East Bank sewer systems have experienced substantial odor due to H_2S generation problems. Currently, American Water provides odor abatement activities at the two major feeder pumping stations using a liquid oxygen injection system with acceptable results (American Water, 2005).

Alternatively, the Sewerage and Water Board of New Orleans (SWBNO) is considering a new hydrogen sulfide control program (PRI-SCTM) proposed by US peroxide for the primary outer reach force main systems that eventually discharge into the East Bank Wastewater Treatment Plant (EBWWTP). It is based on the application of iron salts into the upper reach force main systems and injecting hydrogen peroxide in the force main pump station line.

The City of Baton Rouge/Parish of East Baton Rouge has experienced continuing problems with odors in the force main leading to the South wastewater treatment plant (SWWTP) and corrosion at the head works of the SWWTP. Attempts to mitigate the effects of H₂S have been made by both microbial addition and the current use of hydrogen peroxide. A study conducted by Louisiana State University analyzed several treatment alternatives to control the problem at the SWWTP including the addition of air, sodium hypochlorite (NaOCl), calcium nitrate (Ca(NO₃)₂), calcium hydroxide (Ca(OH)₂) and ferric chloride (FeCl₃) and to evaluate the current strategy of H₂O₂ additions. Attempts at H₂S mitigation from two different approaches were made. The first approach was to treat the entire force main to prevent formation of H₂S. The second approach targeted the destruction of H₂S prior to its arrival at the SWWTP. Study results indicate that NaOCl and H₂O₂ were the most effective chemical control strategies found for the mitigation of H₂S. Nonetheless, the quantity of each of these chemicals required to prevent the formation of H₂S is too large to be considered economically feasible. The current strategy of protecting appurtenances only by injecting a solution of 50% H₂O₂ is potentially effective, but the volume of H₂O₂ injected (100 to 300 gallons per day) is completely reduced within a period of 15 minutes in a rapid mixing scenario, which means that the consumption of H₂O₂ is rapid and the force main length for which the H₂O₂ remains effective is short. Concisely,

the H_2O_2 would likely be reduced before reaching the head works of the SWWTP (Sansalone, et al., 2000). According to this investigation, it was recommended that the City/Parish should further investigate the effectiveness of the H_2O_2 treatment regime. To do so, it is important to identify the kinetic expression that describes the H_2O_2 oxidation process, which was not determined in this study.

The application of kinetic principles to chemical processes attempts the study of rates and mechanisms of chemical reactions and the factors on which they depend. The oxidation kinetics are complicated, and the results of various studies are not in good agreement. Much of the interest in the oxidation of H_2S has been related to studies of anoxic (dissolved oxygen is not available) basins in natural waters (Millero, 2001). As demonstrate later, there is a lack of kinetic studies related to odor and corrosion control methods applicable to sanitary sewer systems, which are necessary to provide scientific justification for the selection of reaction times, types to chemicals to be added, and identification of reaction products.

Based on this background, it is important to conduct a kinetic study of hydrogen sulfide oxidation using the addition of ferrous iron salt, hydrogen peroxide and pure oxygen, to determine the effectiveness of each process, and to find out useful design parameters.

1.2 Objectives and Scope

The primary goal of this research project is to study the kinetics of hydrogen sulfide removal using the addition of ferrous chloride (FeCl_2), hydrogen peroxide (H_2O_2) and pure oxygen. These, according to Bowker (2004), are the most commonly used H_2S chemical control methods.

To achieve this objective a laboratory simulation of chemicals addition was carried out to determine process effectiveness and oxidation kinetics. Similarly, a batch-reactor kinetic study of hydrogen sulfide oxidation using pure oxygen was also performed to determine the reaction time and to identify the rate-limiting steps.

The specific objectives of this research project are the following:

- Determine the chemical addition (FeCl_2 and H_2O_2) process effectiveness.
- Determine the chemical dosages (ferrous chloride and hydrogen peroxide) and the minimum reaction times needed for hydrogen sulfide oxidation.
- Determine the reaction time and compare with the observation to others in the pure oxygen injection method performing a batch – reactor kinetic study of hydrogen sulfide oxidation using pure oxygen from laboratory cylinders.

- Determine the kinetic expression that describes the hydrogen sulfide oxidation process using FeCl_2 , H_2O_2 and pure oxygen using only integer values of reaction orders (n).

The results reported herein may assist municipalities in determining required dosages and detention times and evaluating chemicals addition and oxygen injection technologies as odor and corrosion control alternatives.

II. LITERATURE REVIEW

There is generally increasing public concern and intolerance of odors from wastewater facilities. Management of odor has become a significant activity as most facilities want to be good neighbors. Successful odor control requires proper planning, good management, intelligent design, and attentive operation and maintenance (WEF, 2004). In addition, U.S. EPA legislation concerning infrastructure maintenance related to corrosion prevention is also focusing attention on this environmental issue. Table 2.1 summarizes the key characteristics of H₂S gas.

Table 2.1: Characteristics of Hydrogen Sulfide^a (WEF, 2004)

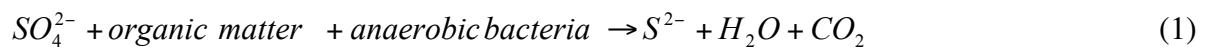
Molecular weight	34.08
Vapor pressure, -0.4 °C -25.5 °C	10 atm 20 atm
Specific Gravity (vs air)	1.19
Odor detection threshold	Approximately 1 ppm
Odor recognition threshold	Approximately 5 ppm
Odor character	Rotten eggs
Typical 8-hour weighted average exposure limit	10 ppm (varies by state agencies)
Imminent life threat	300 ppbv

^aIt should be noted that different sources report a range of values for odor detection or recognition thresholds of H₂S.

2.1 Process Occurring in Sewers under Sulfide Buildup Conditions

Hydrogen sulfide gas typically is formed in wastewater collection systems that are conducive to creating septic conditions, where this condition limits oxygen transfer to wastewater. Septic conditions occur in collection systems that have a flat grade or do not have the flow-through velocities to prevent the stagnation of fluid, thus allowing the septic conditions to occur. In general, septic conditions occur when bacteria use all of the available oxygen while decomposing nutrients such as sulfate and organic matter in wastewater for energy. Sewers with low velocities encourage the growth of anaerobic bacteria in a slime layer coating the sewer (Palmer, et al., 2000). These bacteria reduce sulfur compounds such as sulfate ion (SO_4^{2-}), which is naturally abundant in most waters, thereby producing sulfides (Harshman and Barnette, 1999). Under anaerobic (septic) wastewater conditions, sulfides cannot be oxidized. Therefore, they combine with hydrogen to produce hydrogen sulfide gas, creating the “rotten egg” odor associated with septic wastewater (Palmer, et al., 2000).

Although organic matter decomposition can contribute to H_2S production, sulfate (SO_4^{2-}) or thiosulfate reduction under anaerobic conditions is the most significant mechanism for H_2S generation in wastewater. Disulfovibrio bacteria, which are strict anaerobes, are responsible for the majority of the reduction of sulfate to sulfide, according to the following reactions:



Sulfate, organic matter and sulfate-reducing bacteria are present in virtually all wastewaters, yet sulfide generation does not always occur. The above reduction process will not take place if dissolved oxygen or another more thermodynamically favorable electron acceptor is present, e.g. nitrate (NO_3^-) (Prewitt, 2000). Proper design and maintenance can often prevent odors and corrosion associated with sulfide generation (U.S. EPA, 1985).

The sulfate content of the water supply is used to calculate an upper limit for dissolved hydrogen sulfide. The limit is 34/96 of the sulfate content in the water supply. This is based on molecular weights ($\text{SO}_4=96$, $\text{H}_2\text{S}=34$). For example, if water has an average sulfate content of 33 mg/L, the maximum dissolved H_2S would be 11.7 mg/L assuming no industrial sources and ignoring the minor contribution from human waste (Prewitt, 2000).

Most of the sulfate reduction in sewers occurs in the biological slime layer on the pipe wall or in the sludge and silt deposits on the pipe invert. The slime layer is the site of intense micro-biological action, and it is here where anaerobic conditions develop. Oxygen in wastewater diffuses into the slime layer producing an aerobic layer and an anaerobic zone. The depth to which oxygen will diffuse is dependent on the oxygen concentration in the wastewater as well as on temperature and concentration of organic matter, especially albumins (U.S. EPA, 1985).

Sulfide diffusing out of the zone where it is produced is at least in part biologically and chemically oxidized to thiosulfate ($\text{S}_2\text{O}_3^{2-}$) in the aerobic zone. If much oxygen is present, the sulfide will be oxidized there, but if the oxygen concentration in the stream approaches zero (i.e.,

< 0.1 mg/L) insufficient oxygen will be present in the slime to oxidize all the sulfide diffusing out of the anaerobic zone, and sulfide will enter the stream. Figure 2.1 shows a cross section view of the slime layer of a sewer.

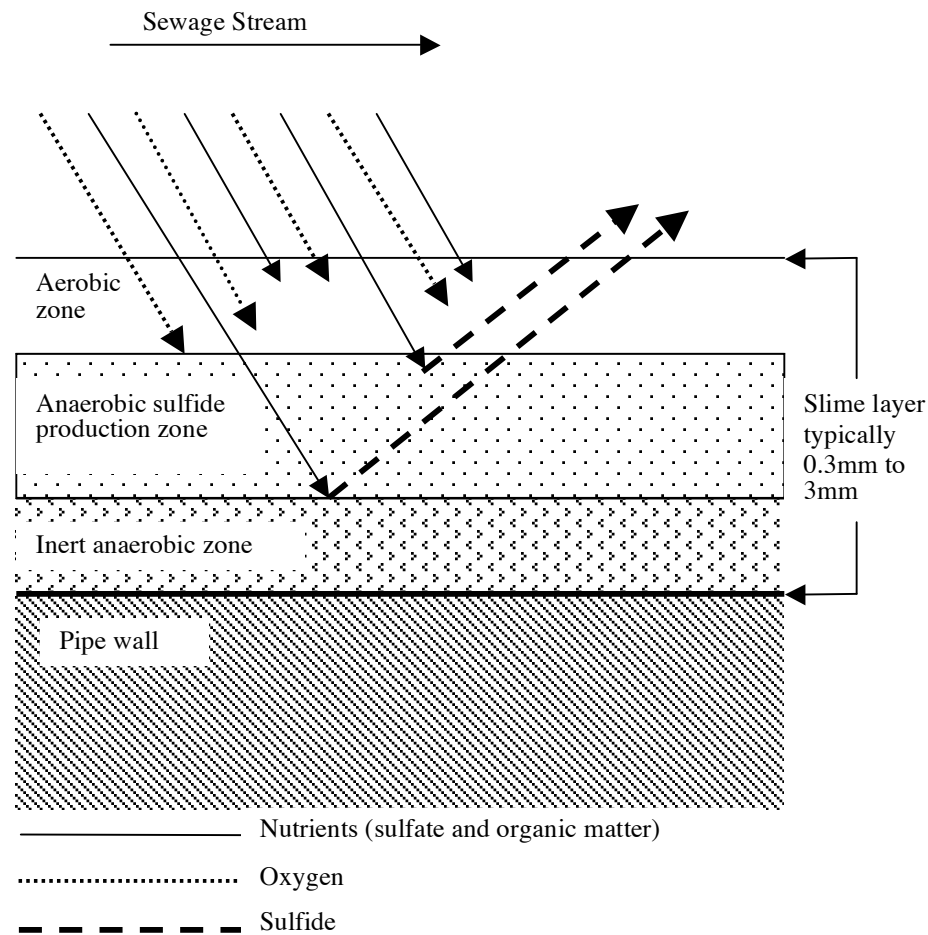


Figure 2.1: Cross Section of Slime Layer of a Sewer (Pomeroy, 1992)

Key parameters that affect sulfide generation include (WEF, 2004) the following:

- Concentration of organic material and nutrients,
- Sulfate concentration,

- Temperature,
- Dissolved oxygen, and
- Detention time

Changes in these parameters can affect the occurrence of odor by promoting both the production of odorous compounds and the transfer of such compounds to the gas phase. The characteristics of wastewater parameters affecting sulfide generation can be seen in Table 2.2.

Alkalinity affects the oxidation process of hydrogen sulfide and the resulting sulfur forms in solution. In essence, hydrogen sulfide gas is soluble in water as a nondissociated molecule and in a form of sulfide (S^{2-}) and hydrosulfide (HS^-) ions. The relative distribution of these species depends to a large extent on the pH (Sukyte, et al., 2002).



Table 2.2: Characteristics of Wastewater Parameters Affecting Sulfide Generation (U.S. EPA, 1985)

Parameter	Characteristics
Dissolved and total sulfides	Dissolved sulfides of 1.0 to 1.5 mg/L will typically result in an increase in odor. Dissolved sulfides are typically 70 to 90% of the total sulfides present.
pH	At lower pH values, weak acids such as H ₂ S can more easily be released to the atmospheres. A pH of 1 to 6 is conducive to sulfide generation and H ₂ S release.
BOD and dissolved oxygen	Wastewater with a high oxygen demand will rapidly take up available dissolved oxygen and can create anaerobic conditions will allow the formation of sulfides. Dissolved oxygen of at least 1.0 mg/L is desirable to prevent sulfide generation.
Sulfate	Sulfate will be reduced to sulfide under anaerobic conditions.
Temperature	Higher temperature favors biochemical generation of sulfides and lowers their solubility.

The pH of wastewater has an important role in determining the amount of molecular H₂S gas available to be released to the sewer atmosphere. Lower pH values favor the un-ionized H₂S, and thus result in greater potential for release of the gas from the liquid. In contrast, at higher pH values other sulfide forms (S⁻², HS⁻) predominate. Figure 2.2 shows this relationship at 25°C. Another major factor affecting H₂S release is turbulence. High levels of turbulence can dramatically increase H₂S emissions in collection systems such as drop manholes, junction chambers, aerated channels, clarifier weirs, etc.

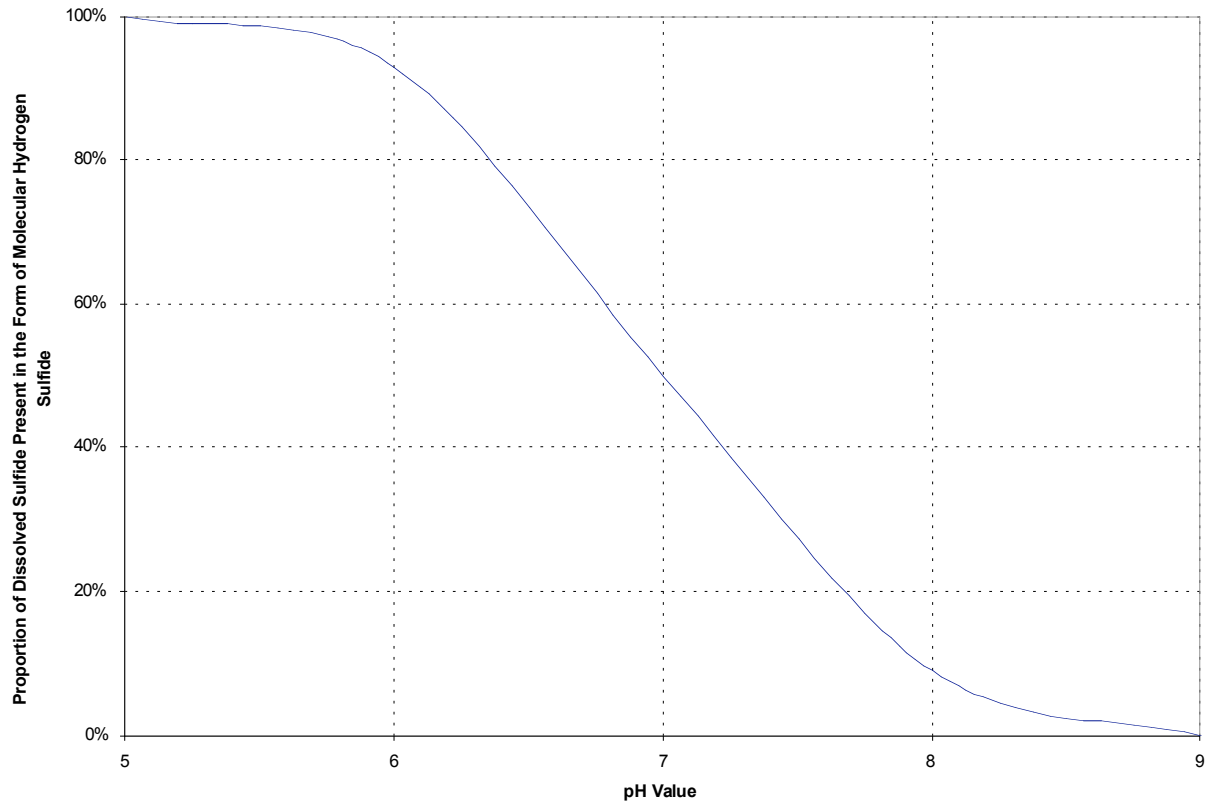


Figure 2.2: Relative Concentrations of Dissolved Molecular Hydrogen Sulfide (Thistlethwayte, 1972)

In wastewaters of normal pH values (6.5 to 8), sulfide may be present partly in solution as a mixture of H_2S and HS^- , and partly as insoluble metallic sulfides carried along as part of the suspended solids. In analyses of wastewater, a distinction is made between dissolved sulfide and insoluble sulfide. The sum of these forms is called total sulfide. The concentrations are normally expressed in terms of the sulfur content (Pomeroy, 1992).

The concentration of oxygen necessary to prevent any sulfide build-up may vary widely, depending upon a number of conditions. The velocity of the stream is one factor. At low velocity the motion of the water is not very efficient in carrying oxygen to the slime layer, and under

these conditions a higher oxygen concentration is necessary if sulfide is to be barred from the stream than when the stream is swift. In a typical case, it may be required to have 0.5 mg/L of dissolved oxygen to prevent sulfide build-up, but under certain conditions as much as 1.0 mg/L, or even more, may be required (Pomeroy, 1992). It is difficult to maintain these oxygen concentrations naturally, so supplemental sources of oxygen may be used (WEF, 2004).

In addition to odor, sulfide-induced corrosion of vulnerable materials used in pipelines and structures is a major concern in collection systems. One of the major expenditures in collection and treatment of municipal wastewater is the periodic replacement of the infrastructure, which is exacerbated, in warm climates. Much of the infrastructure is buried, necessitating costly excavation and installation of new pipes. Even though the design life is intended to be 25 to 50 years, often the systems can be employed only a fraction of this time (Speece, 2003d).

H₂S that escapes as a gas from solution due to the temperature difference between the sewage and the surrounding earth may be biologically oxidized on exposed moist surfaces to produce sulfuric acid (H₂SO₄) by the reaction:



This acid causes corrosive damage to vulnerable materials as metal and cement materials. Corrosion occurs downstream of the zone of H₂S formation, most severely at the crown of the pipe, where the acid collects, and leads to a weakening of the pipe (or structure), which

potentially collapses if left unattended (Palmer, et al., 2000). Figure 2.3 shows the release of H_2S gas in the interior of a sewer that causes odor and corrosion problems.

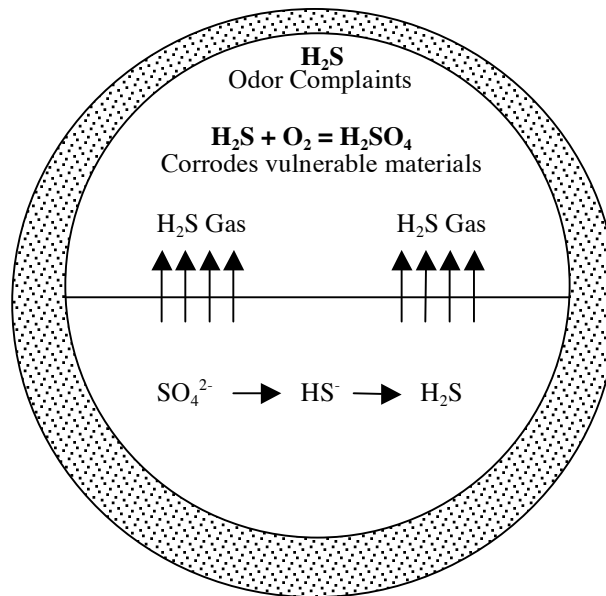


Figure 2.3: Process Occurring in Sewers under Sulfide Buildup Conditions

The potential for major economic loss arises from sulfuric acid attack of metal and cement materials in sewers and in pumping stations. It should be noted that in modern practice, small diameter sewer pipes are invariably made of plastic materials whereas the larger diameter lines (>800mm) are normally made of concrete (Lahav, et al., 2004)

2.2 Odor and Corrosion Control in Existing Wastewater Collection Systems

For existing systems, the most often used alternatives for controlling the formation and release of H_2S include:

- a. Improving the oxygen concentration to satisfy the oxygen demand of the bacteria:
 - compressed air injection
 - pure oxygen injection
- b. Chemical treatment, either to prevent sulfide generation or to destroy sulfide already present in the sewage stream, including the addition of:
 - chlorine
 - hydrogen peroxide
 - nitrates
 - metallic ions
 - lime

Pure oxygen injection systems feature a technology distinguished by its ability to achieve and maintain high dissolved oxygen (D.O.) levels. In contrast to many traditional water treatment options, it provides proactive prevention rather than reactive curve, precluding the formation of obnoxious hydrogen sulfide (H_2S) (Speece, 2003a).

Of the chemicals used by the wastewater industry to control sulfide, four find widespread use within collection systems: sodium hypochlorite, iron salts, hydrogen peroxide, and nitrates (calcium or sodium). The wide variability in treatment costs reflects the unique aspects of each chemical that may warranted for a particular application. Generally, economics is the dominant selection criterion. In that regard, there are two chemicals that provide the lowest theoretical costs: iron salts and hydrogen peroxide (Walton, et al., 2003).

2.2.1 Ferrous Iron Salt and Hydrogen Peroxide Addition

Iron salts are used by municipalities worldwide to control hydrogen sulfide within collection systems and to enhance primary clarification at treatment plants. The ferrous products control sulfide by converting volatile dissolved sulfide into non-volatile ferrous sulfide, which appears as a black precipitate.



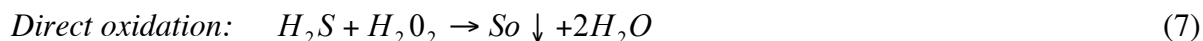
The theoretical chemical requirement is 1.7 kg Fe (or 3.7 kg FeCl₂) per kg-Sulfide. In addition to low cost, iron salts afford control of H₂S for several hours and are less impacted by the oxygen demand of the wastewater. To the extent that residual free iron (not FeS) is present at the plant headworks, primary clarification and digester H₂S control can be improved. However, the use of iron salts may pose problems related to solids production, alkalinity, and salinity, which can interfere with biodegradation of the waste (Edwards, et al., 2000). Table 2.3 shows the advantages and disadvantages of using iron salts for collection system sulfide control.

Hydrogen peroxide (H₂O₂) is also widely used within the municipal wastewater industry, though its utility is primarily for headworks treatment (to oxidize sulfide in the influent sewers) and less so for collection systems.

Table 2.3: Advantages and Disadvantages of using Iron Salts for H₂S Control (Walton, et al., 2003)

Advantages	Disadvantages
Affords long-duration control	Adverse by-products (solids, salinity, alkalinity)
Not impacted by O ₂ uptake rates	Diminishing returns at low sulfide levels
Provides plant benefits (clarification, digesters)	Depletion of dissolved oxygen

H₂O₂ controls sulfide by one of two mechanisms: direct oxidation of sulfide to elemental sulfur; and prevention of sulfide formation by supply of dissolved oxygen to the wastewater.



Where H₂O₂ is added to remove sulfide already present, the first reaction applies and the theoretical chemical requirement is 1.0 kg H₂O₂ per kg-Sulfide. Where H₂O₂ is added to prevent the downstream generation of sulfide, the second reaction applies and the theoretical chemical requirement is 4.0 kg H₂O₂ per kg-Sulfide. Generally 90% of the reaction between hydrogen peroxide and hydrogen sulfide takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes (Edwards, et al., 2000). Advantages and disadvantages of using H₂O₂ for hydrogen peroxide control are shown in Table 2.4.

Based on most water chemistry texts, elemental sulfur (S₀) is highly unstable. S₀ is only stable a relative low pH, which is not a typical condition of wastewater. Therefore, there is a big

concern regarding elemental sulfur (S_0) being generated in the direct oxidation of sulfide using hydrogen peroxide (Reaction 7).

Table 2.4: Advantages and Disadvantages of using Hydrogen Peroxide for H_2S Control (Walton, et al., 2003)

Advantages	Disadvantages
Adds no adverse by-products	Control for > 1-2 hours is costly
Oxygenates the waste water	Adversely affected by high O_2 uptake rates
	Special safety handling measures are needed

One of the latest commercial applications of the chemical oxidation technology is the proprietary technology called PRI-SCTM (Peroxide Regenerated Iron-Sulfide ControlTM, patent pending), developed by U.S. Peroxide. PRI-SCTM is a combination treatment that integrates iron salts with hydrogen peroxide (H_2O_2) in a synergistic fashion. The conceptual basis of PRI-SCTM is to use iron for primary sulfide control, and to use hydrogen peroxide to regenerate (oxidize) the spent iron from FeS – yielding free ferric/ ferrous iron and colloidal sulfur. The regenerated ferric iron affords subsequent control of sulfide further downstream (U.S. Peroxide, 2004d).

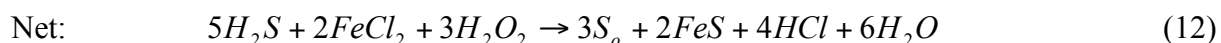
The literature presented by U.S. Peroxide (2004d) claims that the process occurs in three steps:

1. Precipitation of ferrous sulfide;
2. H_2O_2 oxidation of the FeS precipitates to yield elemental sulfur and free ferric hydroxide; and

3. Oxidation of additional sulfide by the ferric hydroxide to produce elemental sulfur and FeS.

The net reaction requires 0.67 kg Fe (or 1.45 kg FeCl₂) and 0.6 kg H₂O₂ per kg-Sulfide.

According to U.S. Peroxide (2004d), the reactions taking place are the following:



In practice, the PRI-SCTM process involves adding the ferrous iron salt at the upper reaches of the collection system and using hydrogen peroxide to regenerate the iron at one or more points downstream. U.S. Peroxide (2004d) claims that intermittent hydrogen peroxide injection serves to regenerate the capturing agent thereby allowing additional sulfide to be absorbed downstream.

Moreover, U.S. Peroxide, Inc (2004d) claims that PRI-SCTM technology provides cost benefits superior to either use iron salts or hydrogen peroxide alone, while allowing greater flexibility as to the placement of storage and dosing facilities. In addition to the benefits afforded by iron salts and H₂O₂ used independently, PRI-SCTM affords control of sulfides to very low levels (e.g., <0.1 mg/L) with minimal reaction time (within 1-2 minutes). Further, PRI-SCTM eliminates or greatly reduces the negative water quality impacts associated with using iron salts

alone. Table 2.5 shows the advantages and disadvantages of using PRI-SC™ technology for sulfide control.

Table 2.5: Advantages and Disadvantages of using PRI-SC™ for H₂S Control (Walton, et al., 2003).

Advantages	Disadvantages
Affords long-duration control	Small impacts on solids, alkalinity, and salinity
Not impacted by oxygen demand	
Provides plant benefits (clarification, digesters)	
Oxygenates the waste water	
Practical control to low sulfide levels	
Rapid oxidation reaction	

Walton, et al., (2003) have conducted a field trial at the Orange County Sanitation Districts using the PRI-SC™ technology. This study involved three major interceptors and the results show the PRI-SC™ technology met the control objectives at a significantly lower cost than other commonly used chemicals technologies. Further, much of the ferrous salt added in the collection for sulfide control was shown to be converted to hydrous ferric oxide at the treatment plant for enhanced clarification purposes.

Although U.S. Peroxide claims that the PRI-SC™ process has proved to be successful in some sewer systems, there are some unanswered questions regarding the process itself and its cost as compared to other hydrogen sulfide control technologies. One of the biggest concerns is

the identification of products being generated after each of the process steps such as the generation of elemental sulfur (S_0) because it is only possible at relative low pH.

Figure 2.4 gives the fields of stability for solid and dissolved forms of iron as function of pE and pH at 25°C and 1 atmosphere of pressure. The total activity of iron is fixed at 10^{-7} M, equivalent to 0.0056 mg/l. The other conditions specified are a total activity of sulfur species equivalent to 96 mg/L as SO_4^{2-} and a total activity of carbon dioxide species of 1,000 mg/L as HCO_3^- . Figure 2.4 shows that FeS_2 , not FeS , is predominant in a wide range of pH, which puts in doubt the products being generated in foregoing Reaction 9.

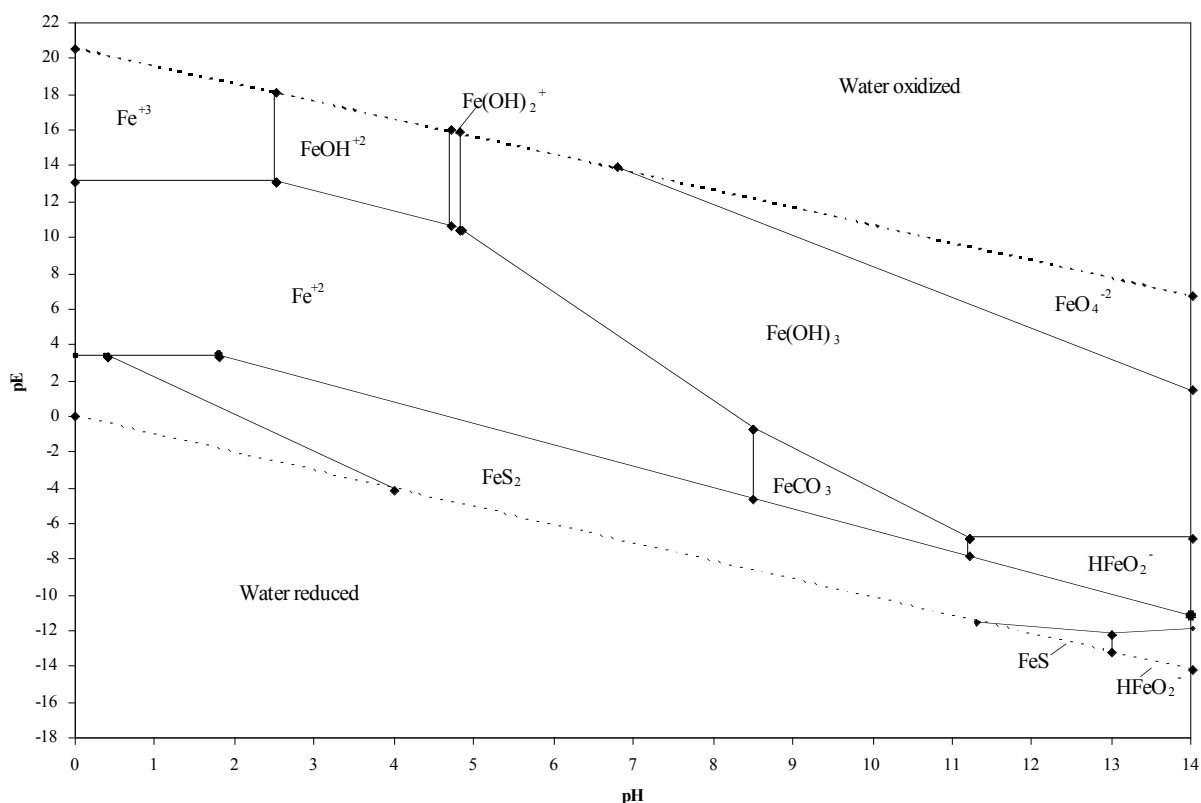


Figure 2.4: Iron System at 25°C and 1 atm of Pressure (Hem, 1975).

Figure 2.5 gives the final pE-pH diagram for $S_T = 10^{-2}$ M and $25^\circ\text{C}/1\text{ atm}$. It shows that elemental sulfur (S_0) is thermodynamically stable in a narrow wedge of pE values below pH 6. Also, Figures 3 and 4 demonstrate that S_0 and $\text{Fe}(\text{OH})_3$ can coexist at pE values which are incompatible with the pE produced by strong oxidants. Both statements are in contradiction with Reaction 7 and Reaction 10, mentioned previously. Also, $\text{Fe}(\text{OH})_3(\text{s})$ can oxidize H_2S only in the presence of an acid as is shown in the following reaction, which disagrees the products stated in aforementioned Reaction 11.

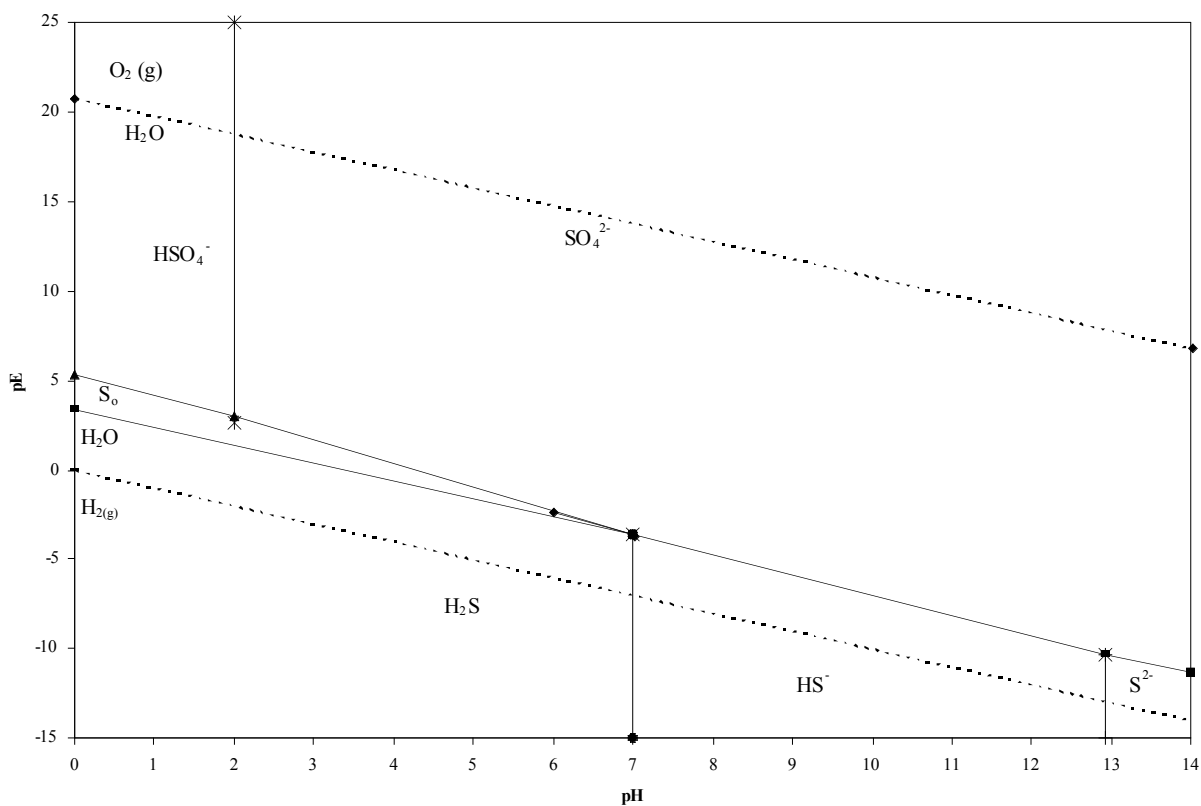
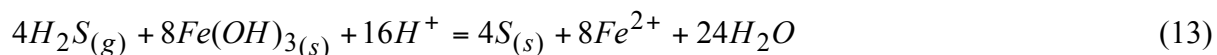


Figure 2.5: Sulfur System at 25°C and 1 atm of Pressure (Pankow, 1991).

2.2.1.1 Oxidation Kinetic Principles with Iron Salts

The application of kinetic principles to chemical processes attempts the study of rates and mechanisms of chemical reactions and the factors on which they depend. The oxidation kinetics are complicated, and the results of various studies are not in good agreement.

Only a few studies of the oxidation of hydrogen sulfide with Fe (III) (hydr) oxides have been conducted in environmental engineering, most of them related to seawater. Pyzik and Sommer (1981) have studied the reaction between hydrous iron oxides and aqueous sulfide species at estuarine conditions of pH, total sulfide, and ionic strength to determine the kinetics and formation mechanism of the initial iron sulfide. Total, dissolved and acid extractable sulfide, thiosulfite, sulfate, and elemental sulfur were determined by spectrophotometric methods. Polysulfides, S_4^{2-} and S_5^{2-} , were determined from ultraviolet absorbance measurements and equilibrium calculations, while product hydroxyl ion was determined from pH measurements and solution buffer capacity.

Elemental sulfur, as free and polysulfide sulfur, was 86% of the sulfide oxidation products; the remainder was thiosulfite. Rate expressions for the reduction and precipitation reactions were determined from analysis of electron balance and acid extractable iron monosulfide versus time respectively, by the initial rate method. The rate of iron reduction in moles/liter/minute was given by

$$\frac{d(\text{reduced Fe})}{dt} = k S_t^{0.5} (H^+)^{0.5} A_{FeOOH} \quad (14)$$

where S_t was the total dissolved sulfide concentration, (H^+) the hydrogen ion activity, both in moles/liter; and A_{FeOOH} the goethite (α -FeOOH) specific surface area in square meters/liter. The rate constant, k , was $0.017 \pm 0.002 \text{ m}^{-2}\text{min}^{-1}$. The exponents in this rate expression was rounded to 0.5 ml from the calculated regression slopes to account for 10-20% experimental error in the data.

The rate of iron monosulfide formation was determined by fitting data points of acid extractable iron sulfide concentration versus time to a second order polynomial equation. The rate expression for the precipitation reaction was

$$\frac{d(FeS)}{dt} = k S_t (H^+) A_{FeOOH} \quad (15)$$

where $d(FeS)/dt$ was the rate of precipitation of acid extractable iron monosulfide in moles/liter/minute, and $k = 82 \pm 18 \text{ M}^{-1}\text{L}^2\text{m}^{-2}\text{min}^{-1}$. Present results indicate first order for all three reactants.

Yao and Millero (1996) have determined the rates of oxidation of hydrogen sulfide by hydrous Fe (III) oxides as a function of pH (4.0-8.5), temperature (5-45°C), and ionic strength (0-4m) in seawater. The overall rate equation for the oxidation of sulfide with hydrous Fe (III) oxides can be expressed by

$$-\frac{d[H_2S]_T}{dt} = k [H_2S]_T^a [Fe(OH)_3(s)]^b \quad (16)$$

The order with respect to H_2S (a) was determined by fitting the data to various rate equations with different values of (a). Plots of $\ln[H_2S]_T$ versus time produce straight lines with the equivalent slope for different initial $[H_2S]_T$ concentrations, indicating that the reaction is first order with respect to H_2S . Similarly, the value of the reaction order with respect to $Fe(OH)_3(s)$ (b) at different concentrations have been determined to be the first order. The rate constant (k) for the H_2S oxidation by freshly precipitated $Fe(OH)_3(s)$ in seawater (pH=8.0) at $25^\circ C$ was found to be $1.48 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$.

It is difficult to directly compare Yao and Millero (1996) results with the earlier work of Pyzik and Sommer (1981), in which they monitored the rate of $FeS(s)$ formation and used a high initial concentration of H_2S .

The reaction kinetics of aqueous oxidation of H_2S by Fe^{3+} have been investigated by Tekin, et al., (1999) at $25^\circ C$ using a spectrophotometric method. Initially, a simple kinetic model first order with respect to H_2S and $FeOH^{2+}$ was tried to fit the kinetic data as is shown in the following rate expression

$$-\frac{d[Fe^{3+}]}{dt} = k[FeOH^{2+}][H_2S] \quad (17)$$

It has been found that a simple rate expression cannot explain the kinetic data because the study conducted at various reactant concentrations and pH revealed that the reaction proceeds to complex-series reactions involving polysulfides as intermediates products. Nonlinear regression

revealed that the reaction of each step is first order with respect to Fe^{3+} and hydrogen sulfide for the first step or polysulfides for the other steps. The complex dependency of rate constant values on pH suggests that various aquo complex of Fe^{3+} react with H_2S or HS^- with different rate constants. A mechanism involving the formation of free radicals has been proposed in the light of the kinetic model by Tekin, et al., (1999).

2.2.1.2 Oxidation Kinetic Principles with Hydrogen Peroxide

The oxidation of hydrogen sulfide, H_2S , with hydrogen peroxide, H_2O_2 , has been studied by a number of workers. The most extensive measurements in aqueous solution were made by Hoffmann (1977). His interest in the oxidation of H_2S by H_2O_2 was related to the use of H_2O_2 to eliminate odor in sewage waters and other anaerobic environmental systems. His studies were confined to low ionic strength solutions at 25 °C over a pH range of 2-8. The rate law for the oxidation of H_2S is

$$-\frac{d[\text{H}_2\text{S}]}{dt} = k_1[\text{H}_2\text{S}][\text{H}_2\text{O}_2] + \frac{k_2 K_{a1}[\text{H}_2\text{S}][\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad (18)$$

where K_{a1} is the first acid dissociation constant of H_2S , $k_2 = 29.0 \text{ M}^{-1} \text{ min}^{-1}$, and

$k_1 = 0.5 \text{ M}^{-1} \text{ min}^{-1}$. The rate law and other data indicate that the reaction proceeds via a nucleophilic displacement by sulfide on hydrogen peroxide with the formation of polysulfide intermediates.

Based on these studies, Hoffmann (1977) concluded that hydrogen peroxide appears to be an effective reagent for the control of hydrogen sulfide and its odor in aqueous systems. The optimal dosage of H_2O_2 for effective odor control is apparently two times the measured sulfide concentration. This stoichiometric excess is necessary to compensate for minor side reactions and for some decomposition. H_2O_2 should be added sufficiently far upstream of the odor or corrosion problem site to provide approximately a 15 min residence time (Raleigh, 1974). In sewage a minimum time of 15 min would be required for the reaction to go to completion. If $pH > 8$ a higher dosage of H_2O_2 will be required since the predominate product will be sulfate. In this case, a fourfold excess of peroxide will be needed for the reaction to go to completion.

Millero, et al., (1989) have studied the oxidation of H_2S with H_2O_2 as a function of pH (2-13), temperature (T) (5-45 °C), and ionic strength (I) (0-6m) in seawater and NaCl solutions. The rate constant, $k(\text{min}^{-1} M^{-1})$, in the following expression,

$$\frac{d[H_2S]_T}{dt} = -k[H_2S]_T[H_2O_2] \quad (19)$$

at pH equal 8, was found to be given by

$$\log k = 8.60 - 2052/T + 0.084I^{1/2} \quad (20)$$

The rate increased from $pH = 2$ to 8 due to the increased rate of oxidation of HS^- compared to H_2S . The rate constant for the oxidation of H_2S was found to be first order at every temperature. The rate constant for the oxidation of HS^- was found to be 12.0 ± 0.5 ,

36.2 ± 0.4 , and $211 \pm 5 \text{ min}^{-1}\text{M}^{-1}$, respectively, at 5, 25, and 45°C. Their results at 25°C from pH = 5 to 8 are in good agreement with the earlier findings of Hoffman (1977). At lower values of pH, Hoffmann (1977) results are faster than Millero, et al., (1989).

2.2.2 Pure Oxygen Injection Method

The pure oxygen injection method works by dissolving pure oxygen in wastewater to prevent formation of hydrogen sulfide and its resulting odor and corrosion. It is based upon providing prevention rather than reactive cure, precluding the formation of obnoxious hydrogen sulfide (H_2S) or else allowing aerobic metabolism to reduce them to innocuous end products (Speece, 2003a). Moreover, the cost of abating dissolved H_2S is higher after it has been discharged from a force main than abating it in a force main with oxygen (Prewitt, 2000). The oxygen injection method is commonly based on the Reaction 21 (Callaban, 1968). Then again, the generation of elemental sulfur (S_0) is a big concern because it is only possible at relative low pH.



The oxygen injection method provides dissolved oxygen for the aerobic life forms (bacteria), to prevent them from starting the sulfate reduction process, and by oxidizing existing sulfide in the wastewater to non-odorous sulfate compounds (Rush III, et al., 2002). An added benefit of increasing the DO concentration in force mains is the potential for some decrease in

the Biochemical Oxygen Demand (BOD) at the treatment plant influent (EWA, 2004). Table 2.6 shows the advantages and disadvantages of injecting pure oxygen for sulfide control.

Table 2.6: Advantages and Disadvantages of Injecting pure oxygen for H₂S Control (U.S. Peroxide, 2004c).

Advantages	Disadvantages
High dissolved oxygen levels are attainable	Efficient dissolution of oxygen into the water requires pressurization
Relatively low cost	Safety precautions
No chemical handling or storage	

The oxygen process involves adding dissolved oxygen into a force main at a pumping station to allow for adequate mixing and detention time. A force main with a long detention time in most cases is likely to generate dissolved H₂S. However, with oxygen injection, a force main can become a pressurized closed reactor to dissolve oxygen and oxidize dissolved sulfides. If dissolved sulfides exist at the beginning of a force main, the detention in the force main (at least 45 minutes) combined with dissolved oxygen will chemically oxidize the dissolved sulfides (MMBW, 1989). The oxygen is injected into high-pressure force mains where a driving force exists to dissolve 50-200 mg/L of oxygen (EWA, 2004). However, a small volume of gas is required to achieve an adequate oxygen transfer to maintain an aerobic condition because oxygen is very soluble in water. Unfortunately rising temperatures increase bacterial activity while D.O. solubility decreases, exacerbating odor generation problems under warm weather conditions (Speece, 2003a). The oxygen dosage depends on sulfide loading, but the typical design criterion

is usually between 15 and 35 mg oxygen per liter of wastewater (EWA, 2004). However, some prevention odor scenarios require much more elevated concentrations of D.O. to be added at the start to satisfy all of the oxygen demand throughout the plug flow process because there is no opportunity to supplement more D.O. at an intermediate point.

According to Riek and Gettings (1993), 4.81 pounds of oxygen are consumed per pound of sulfides oxidized due to respiration in the force main. The oxygen uptake rate of the wastewater is the rate at which microorganisms in the wastewater use the oxygen for respiration. The rate can be determined through sampling and analysis of the wastewater. A commonly used conservative value for oxygen uptake rate is 10 mg/L/hr for raw sewage streams (Rush III, et al., 2002). Besides, dissolved oxygen (DO) concentration in the range of at least 1-2 mg/L must be maintained to prevent the accumulation of H_2S in wastewater systems, according to research and field data on this subject (U.S. EPA, 1985). Therefore, a conservative method for estimating the desired oxygen output for a specific detention time in a force main should consider the dissolved sulfide reduction, the oxygen uptake rate and the desired residual dissolved oxygen. It is important to point out that longer force main detention times will result in higher oxygen requirements (Rush III, et al., 2002).

Oxygen can be delivered in liquid form and stored on-site in large tanks, which makes it expensive and inappropriate for many sites. Recently, a technology has been developed in which oxygen may be generated on site (Rush III, et al., 2002). It may be injected by several different methods, including sidestream U-tube injection or venturi induction. The utilization of air as an oxygen source may provide the most cost effective method for oxygen injection for wastewater

systems. High Purity Oxygen supplementation technology produces a very high D.O. concentration, achieves high oxygen absorption efficiency and requires low unit energy consumption per ton of D.O. added (Speece, 2003b).

For satisfactory prevention of H_2S only a few mg/L of dissolved oxygen in excess of the amount consumed in transit need be maintained. Therefore achievement of these concentrations using high purity oxygen will preclude H_2S generation in the bulk water and allow bacteria oxidation of H_2S flux from the sludge layer into the bulk water (Speece, 2003c).

Bowker (2004) claims that it is difficult to get the aqueous H_2S concentration below 0.5 mg/L (which is in equilibrium with about 150 ppm in the gas phase) using pure oxygen. Neither iron salts can get the aqueous sulfide concentration low enough (below 0.5 mg/L) to eliminate the corrosion problem present in sewer systems. However, hydrogen peroxide can achieve low sulfide concentrations but costs can be high. These chemicals cost \$0.60 to \$1.50 per pound of oxygen equivalent, or about 10 or more times the price of high purity oxygen, which costs only \$0.04 to \$0.15 per pound of O_2 depending of the usage rate (Speece, 2003a). In spite of these facts, iron salts are one of the chemical most commonly used to control hydrogen sulfide, followed by hydrogen peroxide and then oxygen injection with a low frequency of use (Bowker, 2004).

2.2.2.1 Oxidation Kinetic Principles with Dissolved Oxygen

The oxidation of hydrogen sulfide in natural waters using dissolved oxygen involves a complex mechanism that results in the formation of several reduced sulfur species (i.e., thiosulfate, sulfite, elemental sulfur, and polysulfide) as well as sulfate. The formation of the resultant products has been studied by a number of workers (Millero, 2001).

Chen and Morris (1972) have concluded from the universal existence of an induction period at all pH values and from the kinetic equation that the oxidation of sulfide by O_2 proceeds through a chain mechanism. Van't Hoff (differential) method has been used for estimation of the initial order of reaction. The initial rates were determined graphically from (ΣS^{2-}) versus time plot for various initial concentrations. For initial oxygen concentrations of 1.6 to $8.0 \times 10^{-4}M$ (5.12 to 25.6 mg/L) and initial sulfide concentrations of 0.5 to $2.0 \times 10^{-4}M$, reaction orders of sulfide and oxygen are 1.34 and 0.56 , respectively. Combination of these results leads to an overall empirical equation:

$$-\left[\frac{d(\Sigma S^{2-})}{dt}\right]_{t=0} = k(\Sigma S^{2-})_0^{1.34} (O_2)_0^{0.56} \quad (22)$$

Variations of rate parameter with pH show a very complex pattern. In acid solutions, $pH < 6$, where H_2S is the predominating sulfide species, the rate is very slow. The specific rate increases greatly as pH increases through 7 to a maximum of $pH 8.0$ or so, then decreases to a minimum near $pH 9$, increases again to a second maximum about equal to first near $pH 11$ and

finally decreases again in more alkaline solutions. According to Chen and Morris (1972), the half-time ($t_{1/2}$) for the oxidation of H_2S by O_2 is 50 hours at $25^\circ C$ and $pH=8.0$, which would make impractical to use pure O_2 for H_2S control.

O'Brien and Birkner (1977) have made kinetic studies of the oxygenation of the reduced sulfur species at pH values of 4, 7.55 and 10 using a model that suggested parallel reactions between reduced sulfur species and oxygen to form sulfite, thiosulfate, and sulfate. At pH 4 and 10 the reaction order was obtained by following the decrease in the $S(-II)_T$ concentration with time under conditions where oxygen was in excess. Reaction rate constants were calculated to be $0.524 M^{-1}min^{-1}$ and $2.24 M^{-1}min^{-1}$ at pH 4 and 10, respectively. The reaction was determined to be first order with respect to reduced sulfur at all pH values and nearly first order with respect to oxygen at pH 7.55.

At pH 7.55 the reaction order was evaluated by a differential analysis of the kinetic data, utilizing the method of initial rates. Initial rate of reaction was experimentally determined at initial reduced sulfur concentrations ranging from $2.2 \times 10^{-5} M$ to $1.21 \times 10^{-3} M$. A linear regression analysis yielded a value of 1.02 ± 0.008 for the order with respect to total reduced sulfur. For initial oxygen concentrations of 0.208 to $1.07 \times 10^{-3} M$, the order with respect to oxygen was 0.80 ± 0.25 . The overall reaction rate expression for the oxygenation of reduced sulfur species under the stated conditions can thus be written as:

$$-\frac{d[S(-II)_T]}{dt} = k[S(-II)_T]^{1.02}[O_2]^{0.80} \quad (23)$$

According to O'Brien and Birkner (1977), the half-time ($t_{1/2}$) for the oxidation of H_2S by O_2 is 37 hours for water and 27 hours for seawater at 25 °C and pH=8.0.

Millero, et al., (1987) have measured the values of k for the oxidation of H_2S in seawater as a function of pH (1-12), temperature, T , (5-65°C) and ionic strength, I , (0-6 M).

At p H 8.0, the overall rate constant (k) in

$$\frac{d[H_2S]_T}{dt} = k[O_2][H_2S]_T \quad (24)$$

can be determined from

$$\log k = 11.78 - (3.0 \times 10^3) / T + 0.44 I^{1/2} \quad (25)$$

At 25 °C and pH 8, the half time for the oxidation of H_2S with O_2 was found to be 50 ± 16 h in water and 26 ± 9 h in seawater. These results are in good agreement with the results of Chen and Morris (1972) and O'Brien and Birkner (1977).

Zhang and Millero (1993) have described the oxidation of H_2S in seawater as a first-order process with respect to both sulfide and oxygen. The order with respect to sulfide was determined by fitting the data to various rate equations with different values of the order of the reaction at 25 °C. The major products formed from the oxidation of H_2S were SO_3^{2-} , $S_2O_3^{2-}$, and

SO₄²⁻. The pH dependence of the product distribution has been attributed to the effect of pH on the rate of the individual reaction steps.

In summary, all their studies indicate that the rate equation for the oxidation of H₂S in water and seawater is given by

$$-\frac{d[H_2S]}{dt} = k[H_2S][O_2] \quad (26)$$

These results are in close agreement with the one obtained by O'Brien and Birkner (1977). Although some earlier workers (Chen and Morris, 1972) found the rates of the reaction to be other than first order with respect to H₂S and O₂.

From the hydraulic point of view, Lahav, et al., (2004) have measured the kinetics of hydrogen sulfide emission as a function of hydraulic parameters in the laboratory using methods adopted from flocculation theory as a function of energy input, and subsequently linked them with the actual head loss in a sewer. A flocculation unit was used to impart a selected velocity gradient (G) into the water, and sulfide concentration was measured with time. The process was repeated for a number of G values. Regression analysis was then used to fit the rate of hydrogen sulfide emission equation against G at $T=20\pm 2^\circ\text{C}$. The resulting rate equation is a function of easily measured parameters: total sulfide concentration, pH, width of flow, and cross-section area as shown in the following equation:

$$-d \frac{[S_T]}{dt} = KG^2 \cdot \frac{A_s}{V} \cdot [H_2S]_L \quad (27)$$

where S_T = total dissolved sulfide concentration (mol/L^{-1}); K = constant (ms^{-1}); A_s = surface area of liquid exposed to gas phase (m^2); V = volume of reactor or volume of flow; and $[H_2S]_L$ = hydrogen sulfide concentration in the aqueous phase (mol/L^{-1}). In order to use the hydrogen sulfide emission rate equation only to the total initial sulfide concentration and pH need to be measured, provided the slope of the sewer is known.

In summary, the oxidation of H_2S in natural waters has been studied by a number of workers. The oxidation kinetics are complicated, and the results of various studies are not in good agreement. As an example, based on the findings of Chen and Morris (1972) and O'Brien and Birkner (1977), who reported $t_{1/2}$ values ranging from 27h to 50h when use pure O_2 to oxidize H_2S , it would be impractical to use this method to control H_2S in sanitary sewer systems. However, there are several municipalities where this method has been used with success.

Based on this background, it is worthwhile studying the kinetics of hydrogen sulfide removal in sanitary sewer systems using the addition of ferrous iron salt, hydrogen peroxide and the pure oxygen to determine the effectiveness of each process, and to find out useful design parameters. Moreover, the results reported herein will assist municipalities in determining required dosages and detention times and evaluating different technologies such as ferrous chloride and hydrogen peroxide addition and pure oxygen injection as odor and corrosion control alternatives.

III. EXPERIMENTAL PHASE

3.1 Introduction

The methodology involved in developing the kinetics of hydrogen sulfide oxidation in sanitary sewer systems can be divided in two-phase bench scale studies. Each of these stages will be discussed in detail in the next sections.

- Sampling phase
- Laboratory Analysis

Both phases were in part developed at the University of New Orleans Schlieder Urban Environmental System Center (UNO SUESC) Analytical Laboratory located in the CERM Building at the University of New Orleans, New Orleans, LA. Also, a mobile laboratory was set up in Gainesville, FL to finish some experiments. Moreover, hydrogen sulfide oxidation experiments using oxygen injection were carried out in the Water Chemistry Laboratory of the University of Florida, Gainesville, FL.

3.2 Sampling Phase

3.2.1 Batch Reactors

To meet the objectives of this research, BOD bottles were used as reactors to eliminate the possibility of contact of the liquid with the atmospheric oxygen. These BOD bottles have a specially designed shoulder radius that sweeps all air from inside the bottle during filling. The interchangeable stoppers have a tapered bottom that also prevents air entrapment. The bottles have a flared mouth to form a water seal around the stopper that prevents air from being drawn into the bottle during incubation. The volume available for solution inside each of the bottles is 300 ml.

3.2.2 Degassed Reagent Water

Degassed reagent water was used to prepare sulfide standards and sample solutions through the whole experimental phase. In order to reduce the dissolved oxygen content of the water, nitrogen gas (N_2) was bubbled through distilled water for a minimum of twenty minutes for every liter. This water was stored in BOD bottles to avoid oxygen diffusion.

3.2.3 Hydrogen Sulfide (H_2S) Solution

The BOD reactor was filled with a hydrogen sulfide (H_2S) solution at concentrations around 7 mg/L, comparable to those found in wastewater treatment plants. The H_2S solution was

prepared using two different methods. First, a sulfide standard solution, 1000 ppm (Aqua Solutions) was diluted using deoxygenated water. The pH of the resultant solution was between 12 and 14; it was reduced to the wastewater pH level of 7.0 by adding a drop of 0.1 M HCl. Second, sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) crystals were dissolved using deoxygenated water. Preparation of sulfide standards followed the recommendations and procedures published in Method 4500- S^{2-} A of Standard Methods (AWWA, 1998).

3.2.4 Ferrous Iron Salt Addition

Iron salt (ferrous chloride – FeCl_2) at different concentrations was added simultaneously in several BOD bottles containing hydrogen sulfide solution. The concentrations of sulfide remaining after a given reaction time were measured to determine the sulfide consumption.

3.2.5 Hydrogen Peroxide (H_2O_2) Addition

Hydrogen peroxide (H_2O_2), 50% solution was added to the reactors containing H_2S solution and again the remaining concentration of hydrogen sulfide was measured after certain reaction times.

Furthermore, a combination of FeCl_2 and H_2O_2 was implemented in two different process steps. First, the iron salt was used to control a portion of the sulfide and then H_2O_2 was added to react with sulfide in the liquid and reach the upper limit for H_2S .

3.2.6 Pure Oxygen (O_2) Injection

A laboratory simulation of the pure oxygen injection system was performed by adding pure oxygen from laboratory cylinders using a BOD aerator to provide even bubble distribution in the batch reactor filled with a H_2S solution with a concentration around 7 mg/L. The effect of contact time on the hydrogen sulfide concentration remaining was observed. This experimental setup is schematically represented in Figure 3.1.

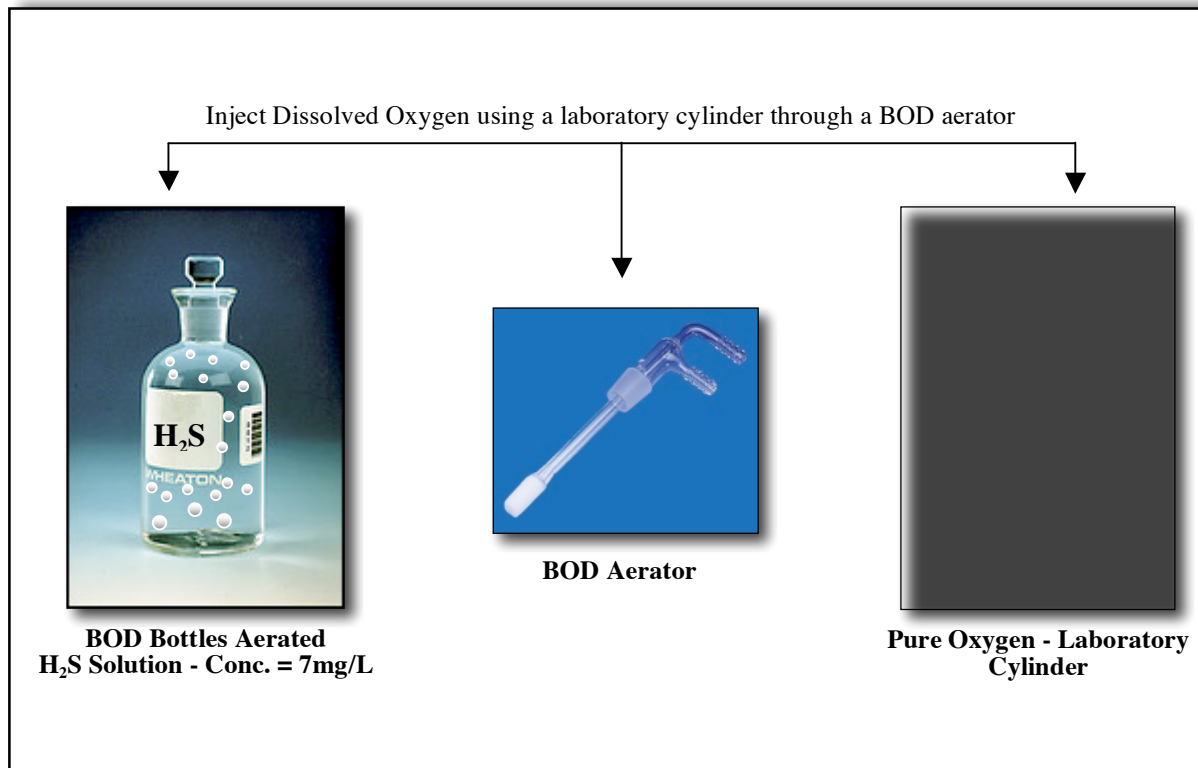


Figure 3.1: Laboratory simulation of the Pure Injection System

Dissolved Oxygen was measured using an YSI, Model 57, bench-top dissolved oxygen meter. Then the probe was introduced into every batch reactor filled with the H_2S solution until

the screen indicated stable values. The equipment was calibrated previously according to the instructions indicated.

3.3 Laboratory Analysis

3.3.1 Methylene Blue Method – Method 8131 (HACH Company, 1992)

Method 8131 - Methylene Blue Method recommended by Hach (Hach Company, 1992) adapted from Standard Methods for the Examination of Water and Wastewater (AWWA, 1998) was carried out to measure concentrations of sulfide remaining after a given reaction time. A portable datalogging spectrophotometer DR/2010, HACH was used. In this method the hydrogen sulfide reacts with N, N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. The method range is 0.005 to 0.8 mg/L. For this study, the H₂S solution was properly diluted using deoxygenated water due to the high sulfide levels, and then the result was multiplied by the dilution factor to find the concentration of the sample before it was diluted. These concentrations were expressed in mg/L S²⁻. Test results were measured at 665 nm. This method is schematically represented in Figure 3.2.

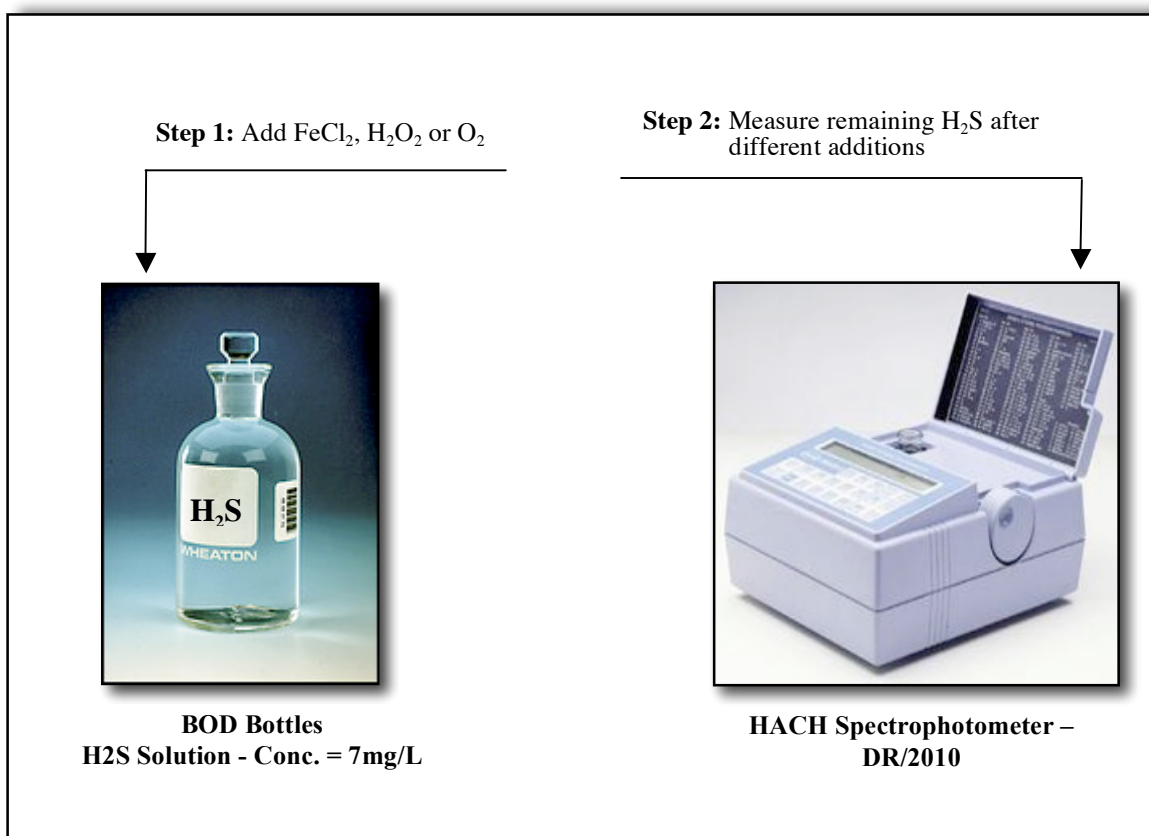


Figure 3.2: Methylene Blue Method – Method 8131 (HACH Company, 1992)

In order to have a more accurate H_2S concentration values using the Method 8131 - Methylene Blue Method (Hach Company, 1992), it was necessary to prepare a calibration curve (reading versus concentration). It is a graphical display of the functional relationship between the expected value of H_2S concentration of the observed signal to the analyte amount. Figure 3.3 shows the calibration curved used in this study.

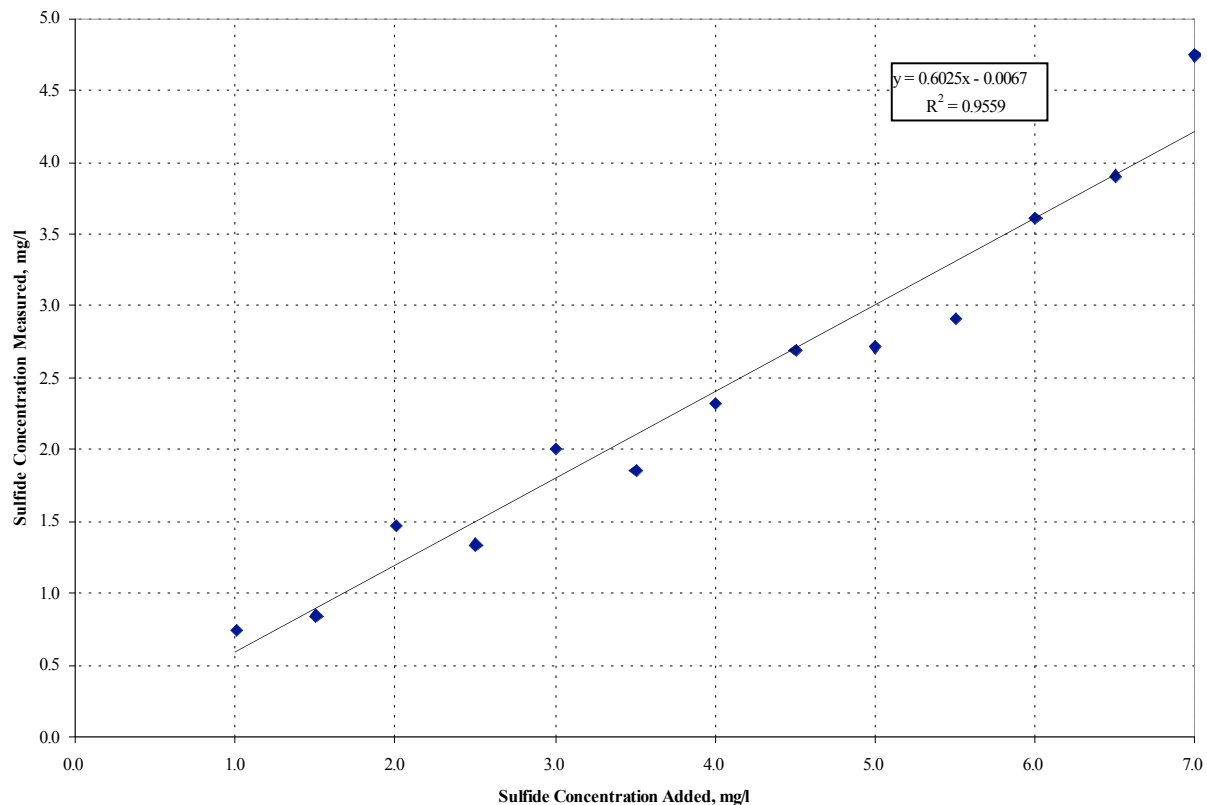


Figure 3.3: Calibration Curve (reading versus concentration)

3.3.2 Iodometric Method – Method 4500-S²⁻ F (Standard Methods, AWWA, 1998)

Later it was found that the Method 8131 - Methylene Blue Method (Hach Company, 1992) was underestimating the sulfide concentration. To solve this problem, an Iodometric Method was used to measure remaining sulfide concentration after the different chemicals are added at given reaction times. In the Iodometric Method, chlorine liberates free iodine from potassium iodide (KI) solutions at pH 8 or less. The liberated iodine and the solution containing sulfide is titrated with a standard solution thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) with starch as indicator as indicated in Method 4500-S²⁻ F of Standard Methods (AWWA, 1998). It is schematically represented in Figure 3.4.

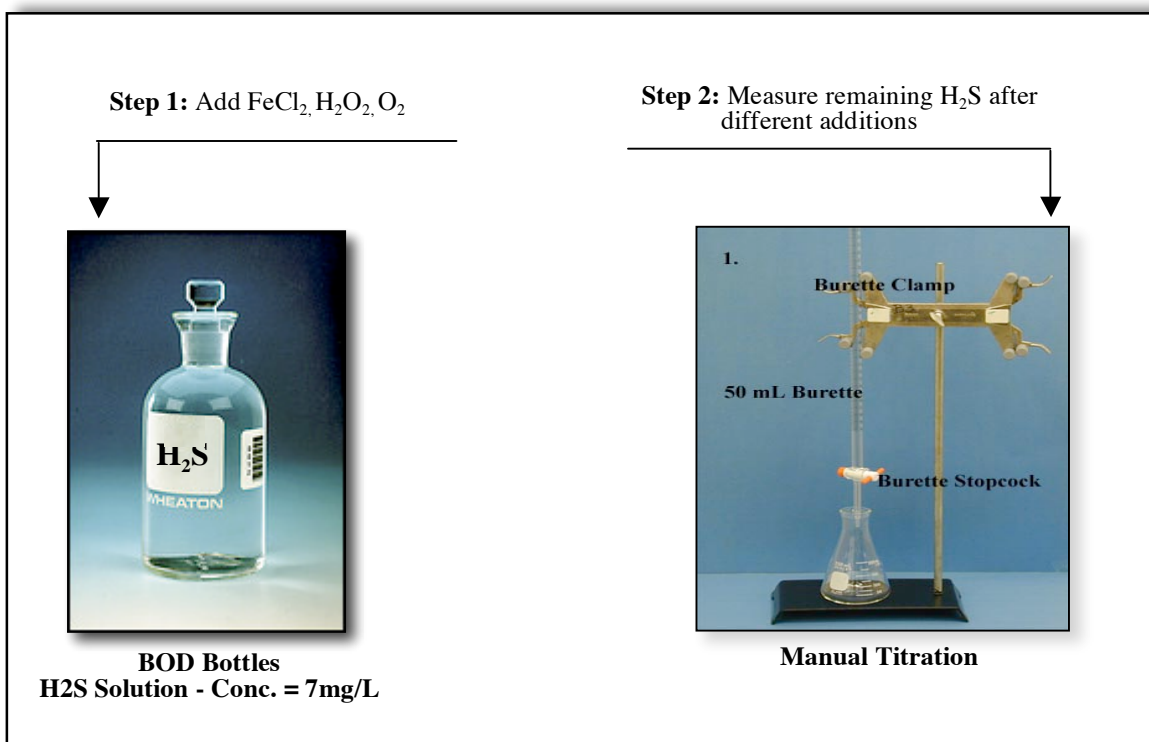


Figure 3.4: Iodometric Method - Method 4500-S²⁻ F (Standard Methods, 1998)

3.3.3 Ion-Selective Electrode Method – Method 4500-S²⁻ G (Standard Methods, AWWA, 1998)

It was found that addition of hydrogen peroxide (H_2O_2) and injection of pure oxygen (O_2) interferes with the iodometric method. For this reason, Ion-Selective Electrode Method – Method 4500-S²⁻ G (Standard Methods, AWWA, 1998) was implemented. The principle of this method is to relate the potential of a silver/sulfide ion selective electrode to the sulfide ion activity. An alkaline antioxidant reagent is added to samples and standards to inhibit oxidation of sulfide by oxygen and to provide a constant ionic strength and pH converting H_2S and HS^- forms of sulfur to S^{2-} (McKee et al., 1988). Use of the alkaline antioxidant reagent allows calibration in terms of total dissolved sulfide concentration. The representation of the Ion-Selective Electrode Method can be seen in Figure 3.5.

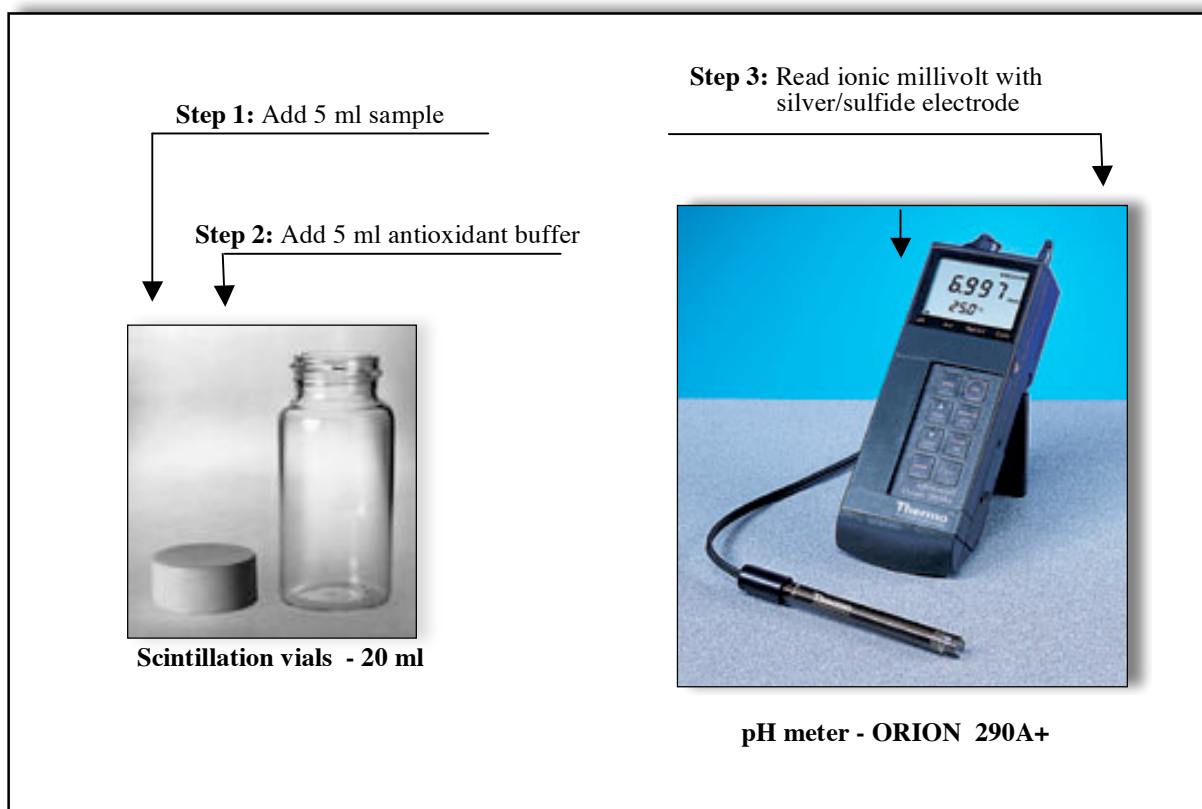


Figure 3.5: Ion-Selective Electrode Method – Method 4500-S²⁻ G (Standard Methods, 1998)

3.3.4 pH and Temperature

These two parameters were monitored through the experimental phase using an Orion pH meter, Model 420A+. An electrode was introduced into the batch reactors with the solution desired to be sampled until the screen indicated stable values. Previously, the equipment was calibrated according to the instructions given in the manual.

Temperature and pH changes may cause potentials to drift either upward or downward H₂S concentration. For this reason, a wastewater pH level around 7 was kept through all the experiments. Because all the experiments were performed in an outdoor laboratory without

temperature control, it was impossible to keep a constant temperature throughout the experimental phase, and the temperature ranged from 10 to 25°C. However, given the short duration of the experiments, the temperature in each individual experiment remained relatively constant.

3.3.5 Chemical Kinetics: Order of the reaction, rate constants and half-lives

A rate expression based on experimental data was generated using the integration method. The rate constants (k) and the order of the reaction (n) were calculated from the concentrations $[C]$ and time (t) of measurement. Graphs were constructed for their evaluation. A trend line was compared with data until get an acceptable fitting. If the fit was acceptable to within the errors of the experimental data, it was said that the proposed rate law was consistent with the data. If the fit was not good enough, another law was proposed and tested against the data.

A summary of the relationship in a differential form to calculate the order of a reaction in a batch reactor is given below

$$\frac{d[C]}{dt} = -k[C]^n \quad (29)$$

If $n \neq 1$, the differential form can then be integrated

$$-k \int_0^t dt = \int_{C_0}^C \frac{dc}{C^n}$$

$$-kt = \frac{C^{-n+1}}{-n+1} \Big|_{C_0}^C$$

$$-kt = \frac{1}{1-n} (C^{1-n} - C_0^{1-n})$$

This gives the final form

$$C^{1-n} = C_0^{1-n} + (n-1)kt \quad (30)$$

The best value of n for a reaction can be determined by preparing a regression analysis from concentration-time data using software such as Datafit or Microsoft Office Excel.

Microsoft Office Excel was the one used to analyze the results of this investigation.

Similarly, half-life ($t_{1/2}$) of the reactions was calculated. Half-life is the time period required to reduce the reactant to half of its original value. It is a useful way of specifying the extent of a reaction.

For a first order reaction it turns out that the half-life is independent of the initial concentration

$$t_{1/2} = \frac{\ln 2}{k} \quad (31)$$

For a second order reaction, this half-life does depend on the initial concentration

$$t_{1/2} = \frac{1}{k[C_0]} \quad (32)$$

3.3.6 The Arrhenius Rate Law

Arrhenius Law is an expression that shows the dependence of the rate constant (k) of chemical reactions on the temperature T (in Kelvin) and activation energy E_a . Arrhenius rate law can be written as

$$k = A \exp(-E_a/RT) \quad (33)$$

where A is the pre-exponential factor expressed in the same units as k , E_a is the activation energy of the reaction expressed in kJ mol^{-1} and R is the universal gas constant. The values of both the activation energy and the frequency factor for any reaction can be determined experimentally by measuring the rate of the reaction at several different temperatures. Then, by taking the logarithm of both sides of Equation 33, the following equations are obtained:

$$\ln k = \ln A - (-E_a/R)(1/T) \quad (34)$$

$$\log k = \log A - (-E_a/2.303R)(1/T) \quad (35)$$

These equations show that a plot of either the natural logarithm (\ln) or the common logarithm (\log) of the rate constant against the reciprocal of the absolute temperature will give a linear plot whose slope contains only the activation energy of the reaction, E_a , and known constants. The intercept of the plot is the logarithm of the frequency factor A .

IV. RESULTS AND DISCUSSION

The results and analysis carried out along the course of this research study are presented in this chapter, according to the sequence of experiments performed in this investigation. All the results reported herein were gathered using the Ion-Selective Electrode Method – Method 4500-S2- G (Standard Methods, AWWA, 1998).

4.1 Ferrous Iron Salt Addition

Different concentrations of ferrous chloride (FeCl_2) were added to approximately 7 mg/L of H_2S in solution, and several reaction times were used, namely 0, 10, 30, 60 and 90 minutes, to observe the H_2S remaining in the reactor. Raw data obtained during the experimental phase was analyzed in order to characterize the kinetic behavior of the reaction using the integrated rate law.

A relationship between the remaining concentration of H_2S and detention time using a dosage of 1.45 kg FeCl_2 /kgS can be seen in Figure 4.1. This indicates around 37% of H_2S oxidation at 90 minutes.

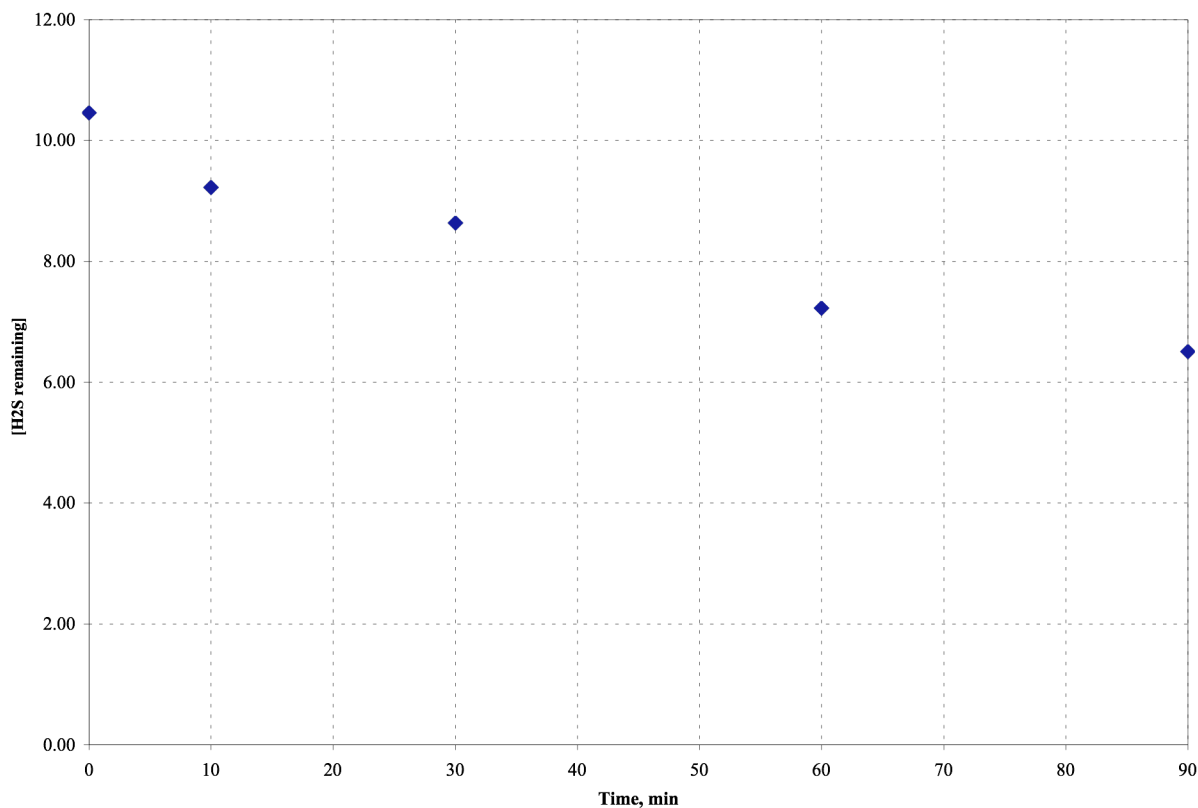


Figure 4.1: H₂S remaining after 1.45 kg FeCl₂/kgS addition

Then, a best-fit test to determine the reaction order was performed by preparing characteristics plots from concentration-time data. Thus, $\ln[C]$ versus t , and $1/C$ versus t , were plotted to test first-and second-order reactions, respectively. The slope of the straight line was used to determine the rate constant for the reaction (k). The plot with the best coefficient of multiple determination (R^2) was selected to represent the reaction kinetics.

A second-order kinetic expression best described the observed data relating to the concentration of H₂S remaining at different reaction times after 1.45 kg FeCl₂/kgS addition. The best-fit equation is:

$$\frac{1}{[C]} = 0.0006t + 0.0985 \quad (36)$$

Where t = time corresponding to concentration measurement (min) and $[C] = \text{H}_2\text{S}$ concentration.

The linear regression analysis of the first-order reaction yields a coefficient of determination, R^2 , equal to 0.973. However, the best-fit function for the second-order reaction produced a R^2 equal to 0.986 and a rate constant (k) of $0.0006 \text{ Lmg}^{-1}\text{min}^{-1}$. Figure 4.2 illustrates the test of second order kinetics relative to the observed data. The time period ($t_{1/2}$) required to reduce the H_2S concentration to half of its original value was calculated using the aforementioned equation 32, and it was found to be equal to 159.34 min.

The pH of the H_2S solution was 12.30, which was reduced to 7.5 by adding 0.1M HCl. A constant temperature ranging between 12°C and 14°C was maintained in the solution.

Based on the results gathered along the course of this research, H_2S oxidation ranges in the order of 37% to 98% with a reaction time of 90 minutes. However, the quantity of FeCl_2 required to oxidize H_2S is too large to be considered feasible. The oxidation of H_2S by FeCl_2 can be described as a second order process with respect to both H_2S and FeCl_2 at temperatures ranging between 12°C and 14°C . Earlier workers (Pyzik and Sommer (1981), Yao and Millero (1996)) found the rates of the reaction to be first order with respect to H_2S and FeCl_2 . However, it is important to point out that most of the studies of the oxidation of H_2S with iron salts have been related to seawater. Also, different methods to determine the reaction order were used by

these earlier researchers. Pyzik and Sommer (1981) studied the reaction between hydrous iron oxides and aqueous sulfide species at estuarine conditions by spectrophotometric methods. Rate expressions for the reduction and precipitation reactions were determined from analysis of electron balance and acid extractable iron monosulfide versus time respectively, by the initial rate method. On the other hand, Yao and Millero (1996) determined the order of the reaction by fitting the concentration data to various rate equations.

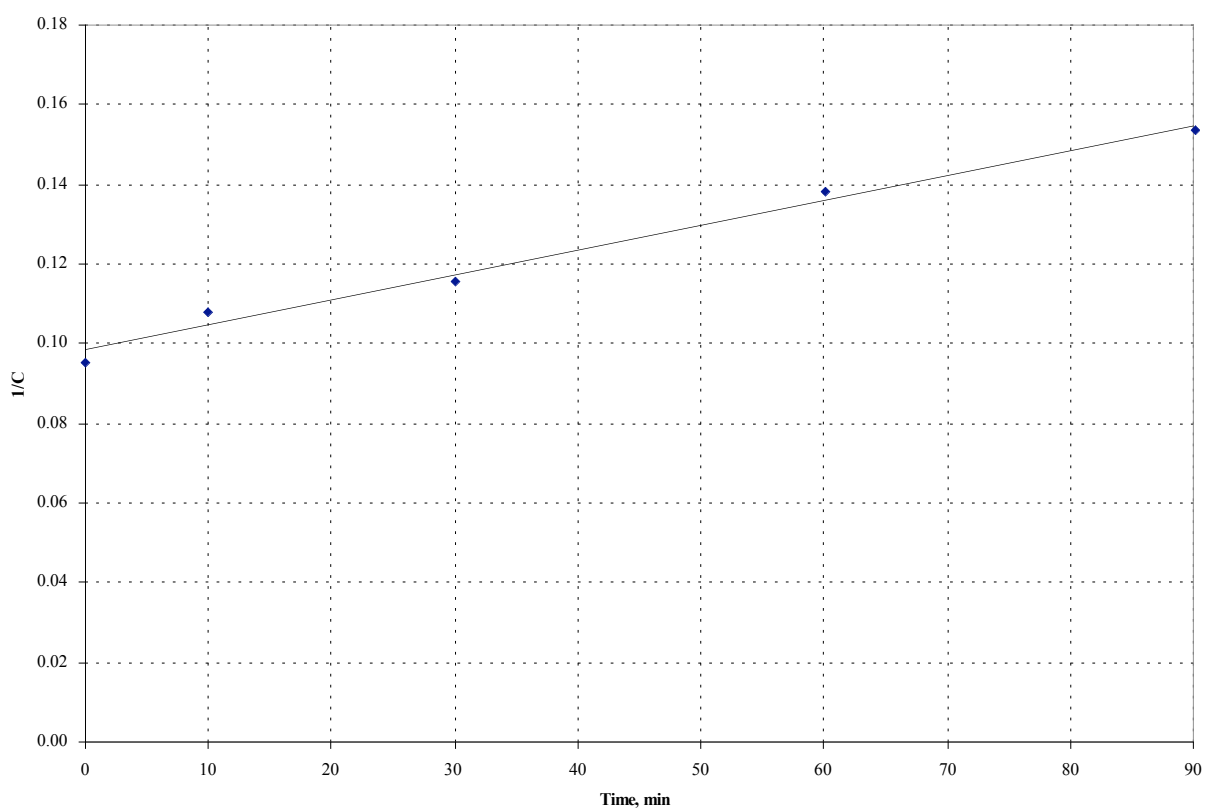


Figure 4.2: Test of Second-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS – pH=7.50

Similar experiments were carried out using different FeCl₂ concentrations, namely 2.90 kg FeCl₂/kgS, 3.70 kg FeCl₂/kgS, 5.00 kg FeCl₂/kgS and 10.0 kg FeCl₂/kgS. A summary of these results and complete analysis worksheets can be found in Appendix A. Additional

experiments were carried out along the experimental phase for FeCl₂ addition at different reaction times. These results can be viewed in Appendix B, including concentration-time data from experiments and characteristic kinetics plots.

Table 4.1 summarizes the parameters obtained in the linear regression analysis, including coefficient of multiple determination (R^2), rate constants (k) and half-lives for FeCl₂ addition at different concentrations.

Table 4.1: Linear Regression Analysis Parameters for FeCl₂ Addition

FeCl ₂ Concentration	Coefficient of Determination, (R^2)	Rate Constant, (k)	Half-life, ($t_{1/2}$)
1.45 kgFeCl ₂ /kgS	0.986	0.0006 Lmg ⁻¹ min ⁻¹	159.34 min
2.90 kgFeCl ₂ /kgS	0.863	0.0013 Lmg ⁻¹ min ⁻¹	77.78 min
3.70 kgFeCl ₂ /kgS	0.972	0.0057 Lmg ⁻¹ min ⁻¹	21.53 min
5.00 kgFeCl ₂ /kgS	0.966	0.0087 Lmg ⁻¹ min ⁻¹	12.45 min
10.00 kgFeCl ₂ /kgS	0.974	0.0631 Lmg ⁻¹ min ⁻¹	1.98 min

Figure 4.3 presents a plot of the half-lives as a function of the initial concentrations of FeCl₂. It can be seen that FeCl₂ concentration should be greater than 5 in order to mitigate H₂S with feasible detention times. This indicates that large dosages of FeCl₂ are required to control effectively the H₂S generation.

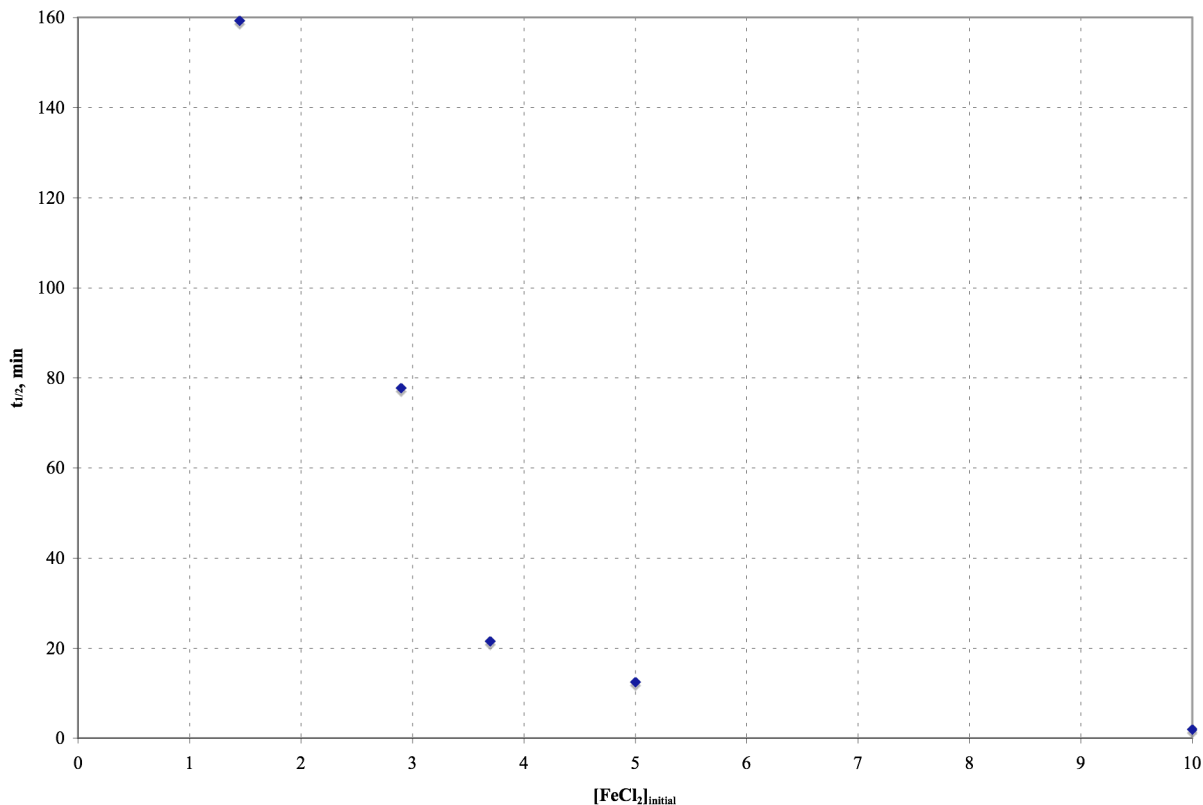


Figure 4.3: Half-lives ($t_{1/2}$) for FeCl_2 addition at different initial concentrations

Figure 4.4 shows the effect of the initial concentration of FeCl_2 on the second-order rate constants (k). This figure shows that the rate constant (k) is significantly affected by the initial concentration of FeCl_2 . Thus, a seven-fold increase in the initial concentration of FeCl_2 (from 1.45 to 10 kg FeCl_2 /kg S) resulted in a 105-fold increase in the value of k . However, since the temperature was not kept constant from one experiment to the next, it is difficult to ascertain what proportion of the change in the constant k is due to a change in temperature, and what proportion is due to the change in the initial reactant concentration.

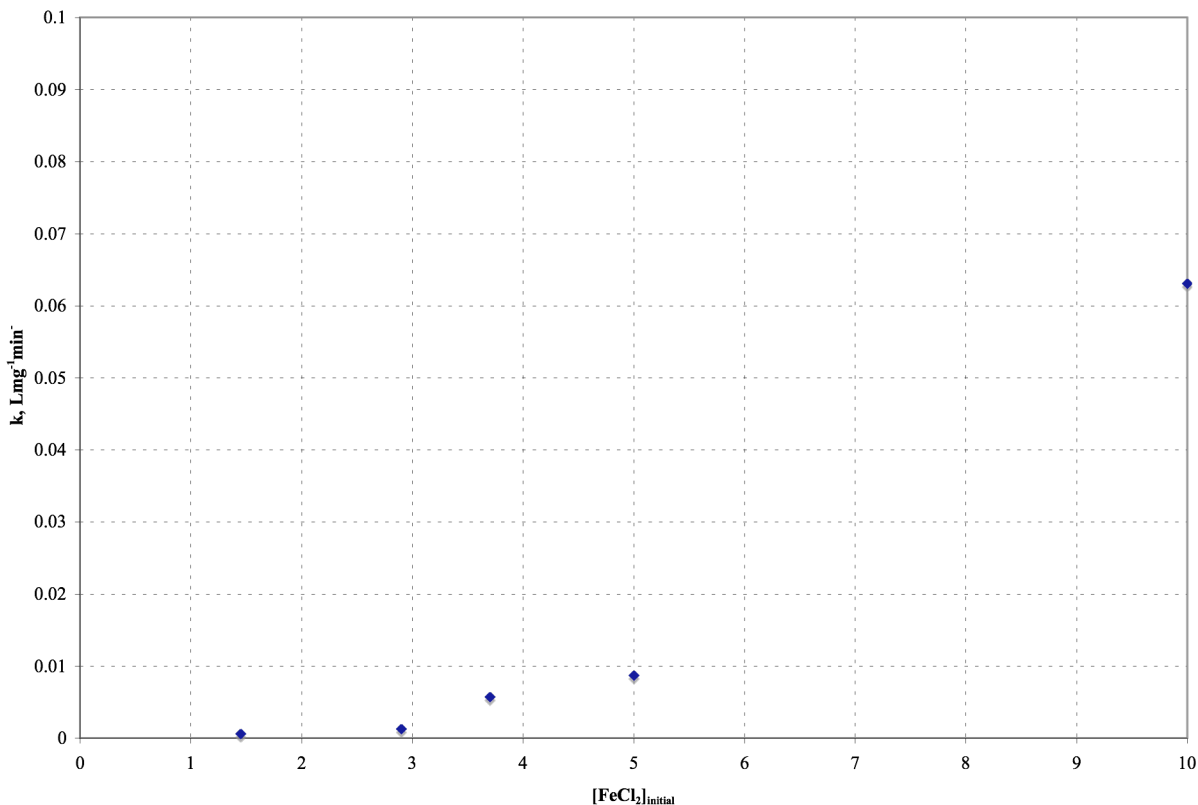


Figure 4.4: Rate constants (k) for FeCl_2 addition at different initial concentrations

4.2 Hydrogen Peroxide (H_2O_2) Addition

To determine the existence of a relationship between the oxidation of H_2S and the addition of 50% standard grade hydrogen peroxide (H_2O_2) at different reaction times, five different concentrations of H_2O_2 were added to H_2S solutions, namely 0.05, 0.10, 0.30, 0.60 and 1.00 kg H_2O_2 /kgS. The initial pH of the H_2S solution was equal to 13.20. It was kept around 7.80 within the BOD reactor using 0.1M HCl.

Figure 4.5 is a representative typical graph that illustrates the observed concentration of H_2S remaining at different detention times after 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$ addition. This indicates about 96% of H_2S oxidation at 60 minutes.

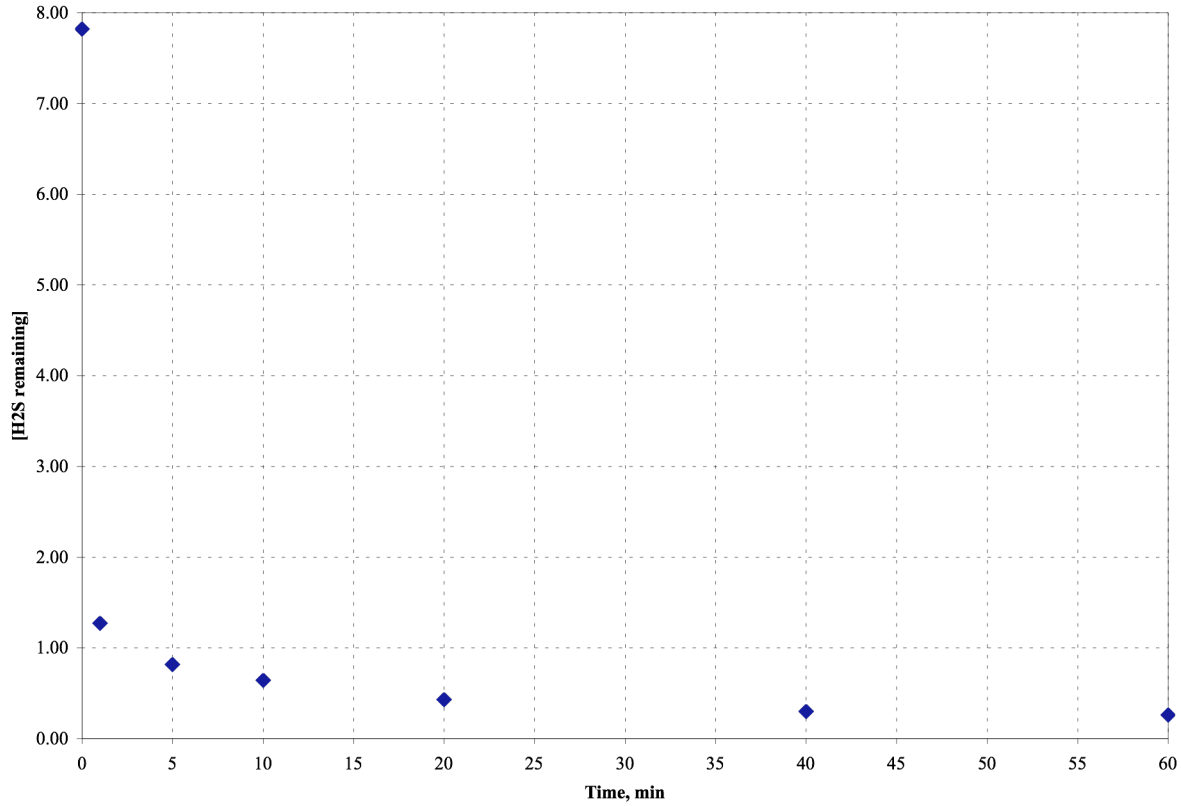


Figure 4.5 H_2S remaining after 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$ addition

Similar plots for each initial hydrogen concentration. The linear regression analysis produced a coefficient of determination (R^2) equal to 0.5539 and 0.9226 for first and second-order kinetics, respectively. A third order kinetic expression best described the observed data. The best-fit linearized function is:

$$\frac{1}{[C]^2} = 0.2517t + 0.2236 \quad (37)$$

The best-fit function produced a coefficient of multiple determination, R^2 , equal to 0.994 and a rate constant (k) of $0.126 \text{ Lmg}^{-1}\text{min}^{-1}$. Figure 4.6 illustrates the respective plot. The value of $t_{1/2}$ is 0.19 min, which was calculated using equation 37.

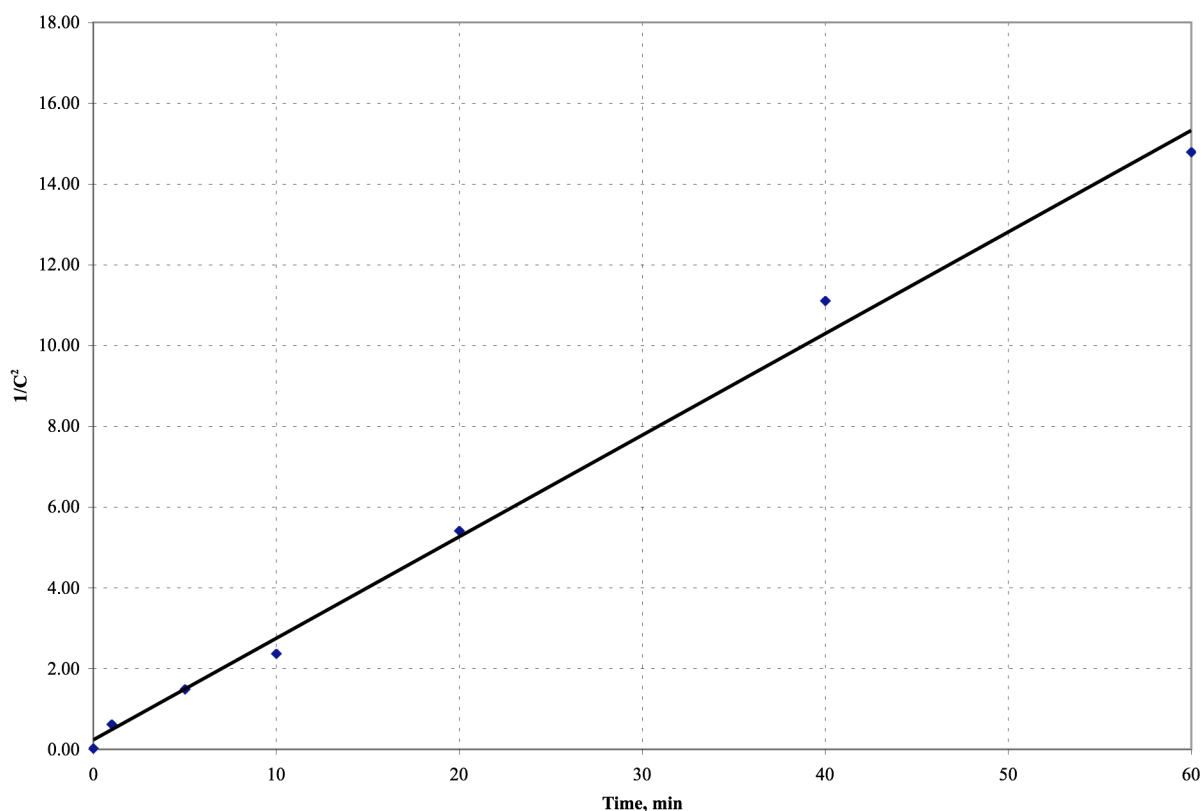


Figure 4.6: Test of Third-Order Kinetics corresponding to 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$ – pH = 7.80

Raw data corresponding to the addition of different initial concentrations of H_2O_2 , namely 0.05, 0.10, 0.30, 0.60 and 1.00 kg $\text{H}_2\text{O}_2/\text{kgS}$ can be viewed in Appendix C. Also, a table summary of results and analysis of the data, including test of first, second and third-order kinetics can be viewed in Appendix C. Additional graphs and linear regression analysis can be seen in Appendix D.

Table 4.2 lists the coefficient of multiple determination (R^2), rate constants (k) and half-lives ($t_{1/2}$) for H_2O_2 addition at different concentrations.

Table 4.2: Linear Regression Analysis Parameters for H_2O_2 Addition

H_2O_2 Concentration	Coefficient of Determination, (R^2)	Rate Constant, (k)	Half-life, ($t_{1/2}$)
0.05 kg H_2O_2 /kgS	0.992	0.0024 L ² mg ⁻² min ⁻¹	18.45 min
0.10 kg H_2O_2 /kgS	0.994	0.2517 L ² mg ⁻² min ⁻¹	0.19 min
0.30 kg H_2O_2 /kgS	0.977	0.5514 L ² mg ⁻² min ⁻¹	0.05 min
0.60 kg H_2O_2 /kgS	0.971	1.1939 L ² mg ⁻² min ⁻¹	0.04 min
1.00 kg H_2O_2 /kgS	0.981	38.873 L ² mg ⁻² min ⁻¹	0.0008 min

The half-lives ($t_{1/2}$) corresponding to different H_2O_2 concentrations are presented in Figure 4.7. It can be clearly seen that the half-lives ($t_{1/2}$) have relative low values, which implies that H_2O_2 is effective for controlling odors with relative low dosages.

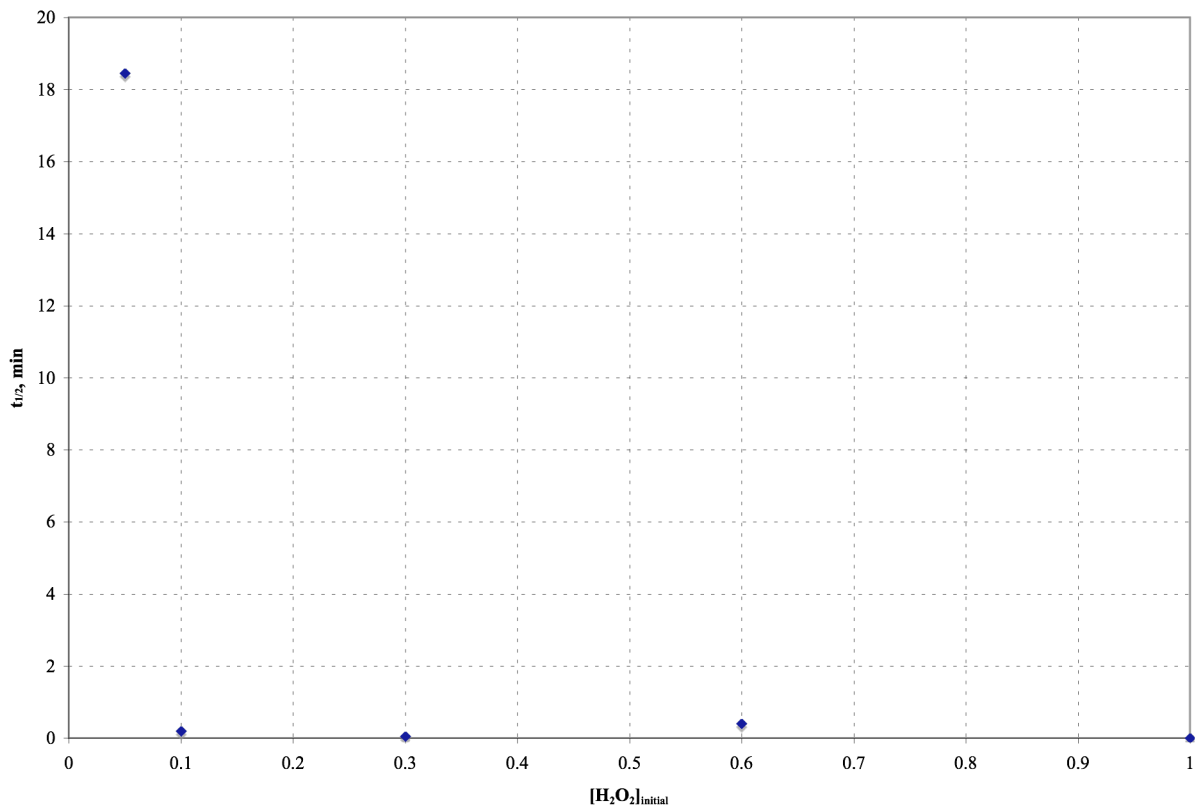


Figure 4.7: Half-lives ($t_{1/2}$) for H_2O_2 addition at different initial concentrations

Figure 4.8 shows the rate constants (k) corresponding to different H_2O_2 concentrations. This figure shows that the rate constant (k) increases proportionally with the initial concentration of H_2O_2 through an initial concentration of 0.6 kg H_2O_2 /kg S. After this, the initial concentration of this oxidant has a dramatic effect on the kinetic constant, which increases 32 times when the initial concentration changes from 0.6 to 1.0 kg H_2O_2 /kg S. Again, changes in k may also be due to the temperature variation from one experiment to the next.

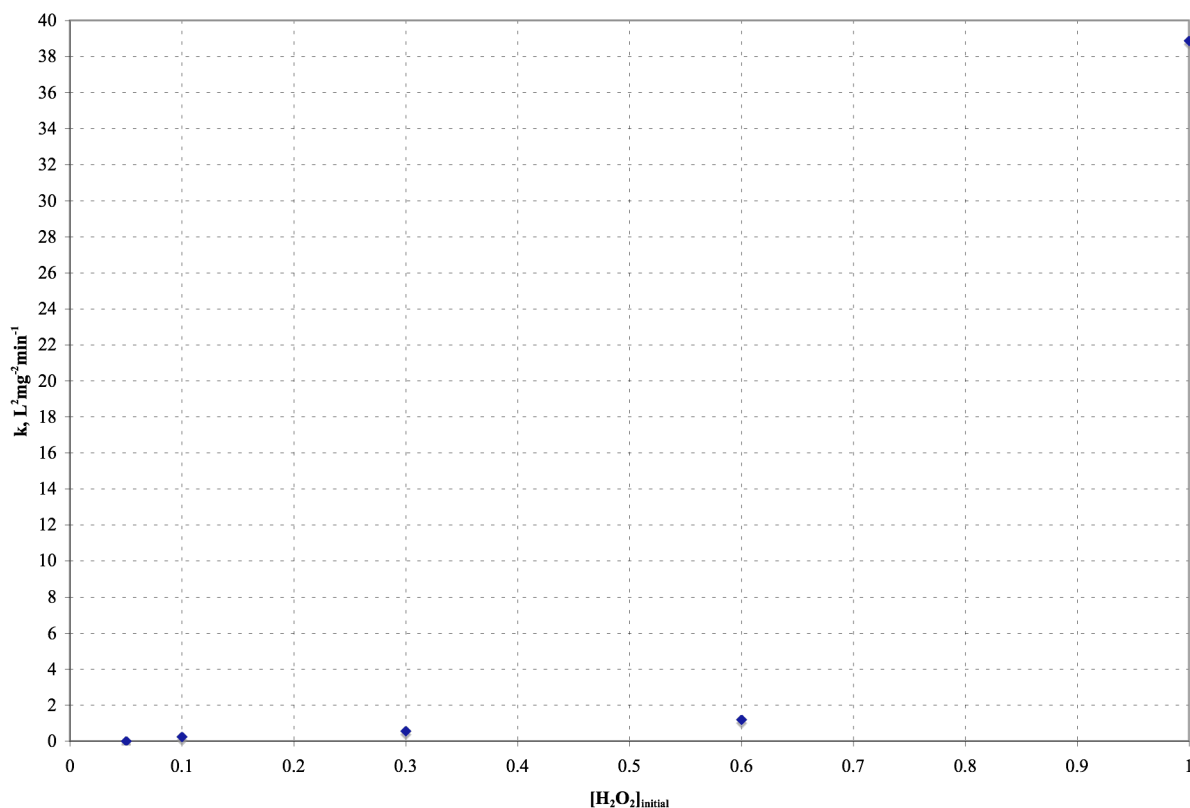


Figure 4.8: Rate constants (k) for H_2O_2 addition at different initial concentrations

It can be concluded that H_2S oxidation by 50% H_2O_2 is a method potentially effective achieving removals from about 70% to 99%. Besides, it can be said that 90% of this removal takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes. This statement is consistent with Edwards', et al., (2000) and Hoffmann's (1977) claims. On the other hand, the reaction rate for the H_2S oxidation was found to be third order with respect to the concentration of H_2S remaining in the temperature range between 10°C and 17°C and at a pH nearly 7, which disagrees with the earlier findings of Hoffmann (1977) and Millero, et al., (1989). Such differences could be due to the analytical method used to determine the sulfide concentration. Thus, Hoffmann's (1977) studied the kinetics of the oxidation of H_2S using potentiometric titration with AgNO_3 . Kinetic data were obtained using a silver sulfide

membrane electrode. On the other hand, Millero, et al., (1989) determined the rate of the reaction using a modified methylene blue technique. The absorbance of the methylene blue was determined at 670 nm with a Cary 2200 spectrophotometer.

4.3 Combination of Ferrous Iron Salt (FeCl_2) and Hydrogen Peroxide (H_2O_2)

Similar to the FeCl_2 and H_2O_2 experiments, the oxidation of hydrogen sulfide (H_2S) was investigated using the addition of FeCl_2 and H_2O_2 combined. For the oxidation of H_2S using a dosage of H_2O_2 , two detention times were used, namely 1 minute and 5 minutes. In other words, FeCl_2 was added to the H_2S solution in two different concentrations 1.45 and 2.90 kg FeCl_2 /kgS with reactions times ranging from 0 to 30 minutes. Then, H_2O_2 was added at three different concentrations, namely 0.10, 0.30 and 0.60 kg H_2O_2 /kgS to the remaining H_2S solution using as reaction times 1 and 5 minutes. The dosages and reaction times used in the experimental phase were based on the PRI-SC process. According to U.S. Peroxide, (2004d), one of the benefits of the combined treatment in comparison to either chemical alone is to control sulfide attaining less than 0.1 mg/L levels of dissolved sulfides with minimal reaction times of less than 5 minutes. Similarly, the PRI-SC process requires 1.45 kg FeCl_2 /kgS and 0.60 kg H_2O_2 /kgS for sulfide control.

Figure 4.9 shows the H_2S remaining after 1.45 kg FeCl_2 /kgS and 0.60 kg H_2O_2 /kgS addition as a function of time. It can be clearly seen that the maximal removal of H_2S at 31 minutes is equal to 98.7%. Here, the reaction time used for H_2O_2 was equal to 1 minute. The pH was reduced using 0.1 M HCl from 12.5 to 7.20. The temperature was kept at 16.0°C.

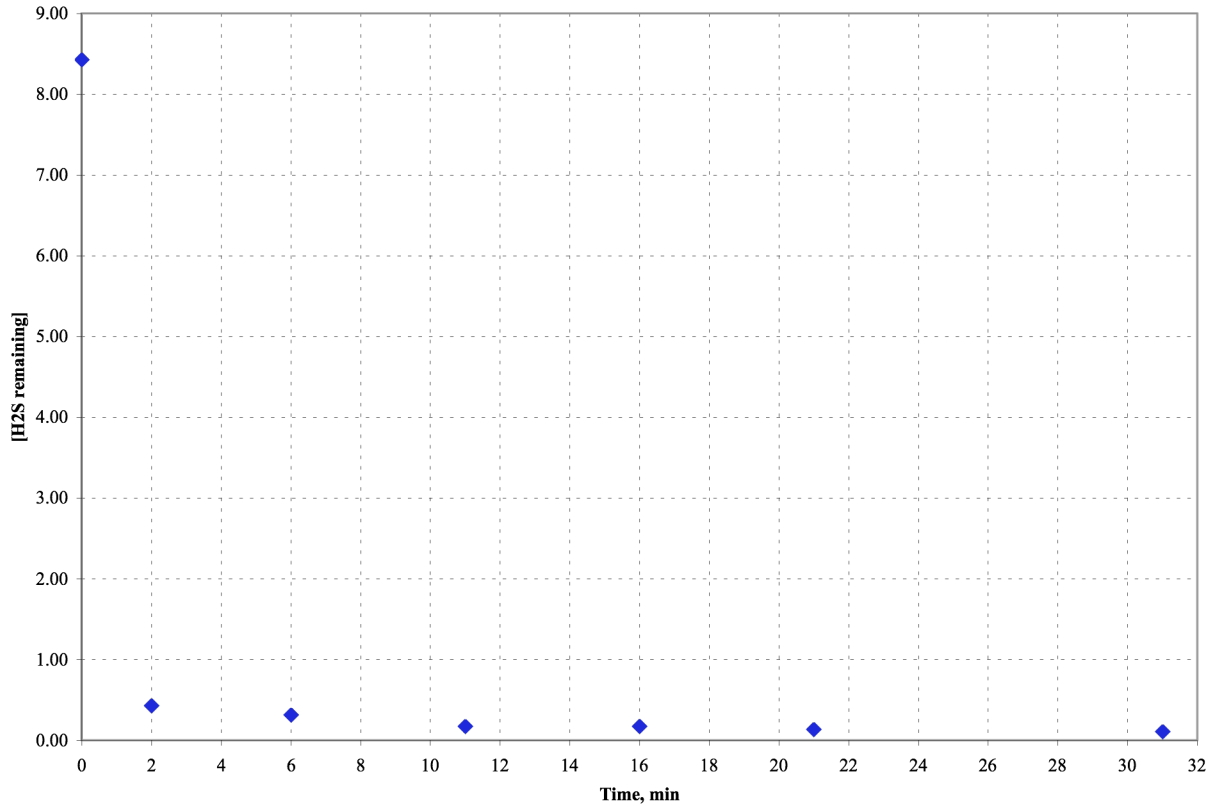


Figure 4.9: H₂S remaining after 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS addition

Then, a best fit to determine the order of the kinetic was performed by preparing characteristic kinetic plots from concentration-time data. Test of first and second order kinetics yield a coefficient of determination (R^2) of 0.525 and 0.920, respectively. A third-order kinetic best described the observed data relating to the concentration of H₂S remaining at different reaction times after 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS addition. In that order, the values of R^2 , k and $t_{1/2}$ obtained were 0.976, 1.306 L²mg⁻²min⁻¹ and 0.02 min. The best-fit line is shown by equation (38), which is schematically represented in Figure 4.10. Equation (38) was used to calculate the values of half-lives $t_{1/2}$.

$$\frac{1}{[C]^2} = 2.612t + 1.3129 \quad (38)$$

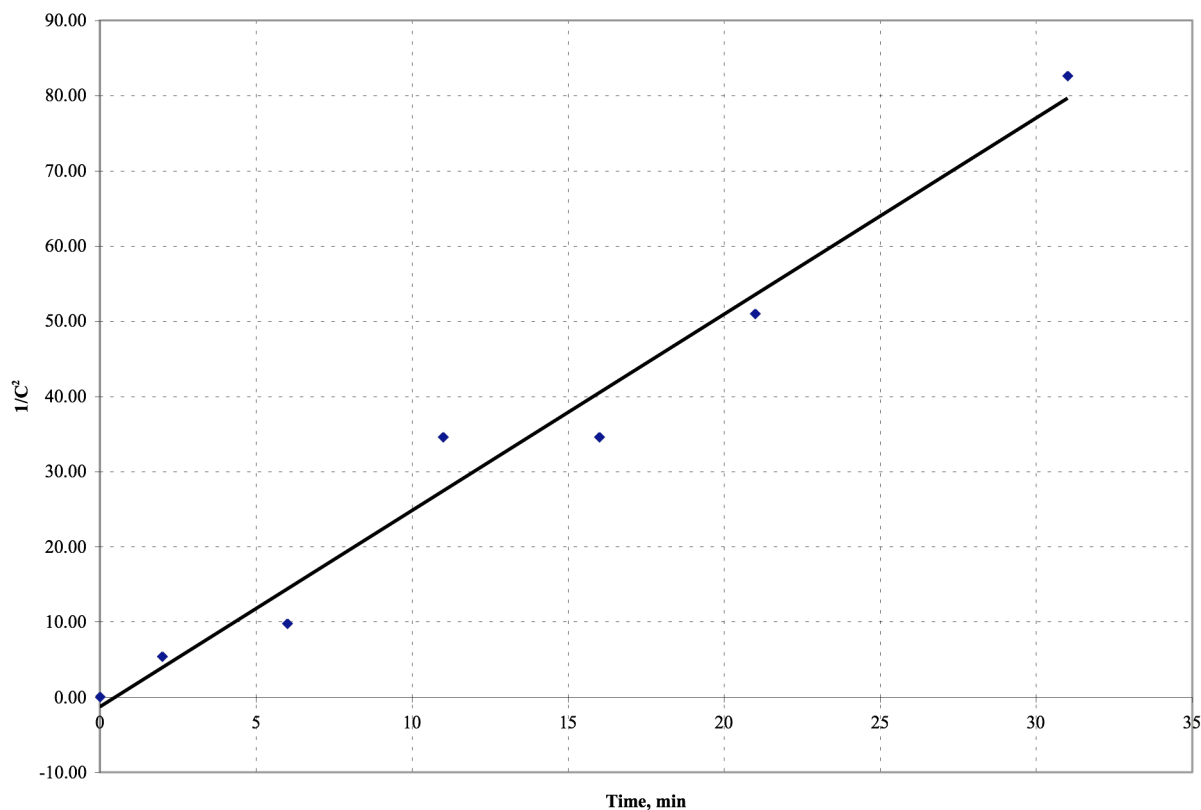


Figure 4.10: Test of Third-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS – pH= 7.20

Table 4.3 lists the coefficient of determination (R^2), rate constant (k), (obtained from a linear regression analysis) and half-life for the addition of FeCl₂ combined with H₂O₂ for the oxidation of H₂S with a H₂O₂ detention time of 1 minute. Raw data, results summary table and characteristic kinetics plots of H₂S oxidation using a combination of FeCl₂ and H₂O₂ for remaining graphs can be reviewed in Appendix E. All the experiments were carried out with a temperature range from 16 to 22°C.

Table 4.3: Linear Regression Analysis Parameters for FeCl₂ and H₂O₂ AdditionH₂O₂ Reaction Time = 1 min

FeCl ₂ Concentration	H ₂ O ₂ Concentration	Coefficient of Determination, (R^2)	Rate Constant, (k)	Half-life, ($t_{1/2}$)
1.45 kg FeCl ₂ /kgS	0.10 kg H ₂ O ₂ /kgS	0.984	0.089 L ² mg ⁻² min ⁻¹	0.26 min
1.45 kg FeCl ₂ /kgS	0.30 kg H ₂ O ₂ /kgS	0.941	0.227 L ² mg ⁻² min ⁻¹	0.14 min
1.45 kg FeCl ₂ /kgS	0.60 kg H ₂ O ₂ /kgS	0.976	1.306 L ² mg ⁻² min ⁻¹	0.02 min
2.90 kg FeCl ₂ /kgS	0.10 kg H ₂ O ₂ /kgS	0.970	0.636 L ² mg ⁻² min ⁻¹	0.04 min
2.90 kg FeCl ₂ /kgS	0.30 kg H ₂ O ₂ /kgS	0.964	1.595 L ² mg ⁻² min ⁻¹	0.02 min
2.90 kg FeCl ₂ /kgS	0.60 kg H ₂ O ₂ /kgS	0.983	3.921 L ² mg ⁻² min ⁻¹	0.01 min

Similarly, Figure 4.11 is a representative graph that presents the H₂S remaining concentration after using a dosage of 1.45 kg FeCl₂/kgS combined with 0.60 kg H₂O₂/kgS against time. It can be noticed that the H₂S concentration at 35 minutes using this combination method decreases around 99% of the initial value. In this case, a reaction time equal to 5 minutes for the H₂O₂ oxidation was used. The pH of the H₂S solution was 12.30, which was reduced to 7.2 by adding 0.1 M HCl. A constant temperature of 18.6°C was maintained in the solution. The remaining graphs can be seen in Appendix E.

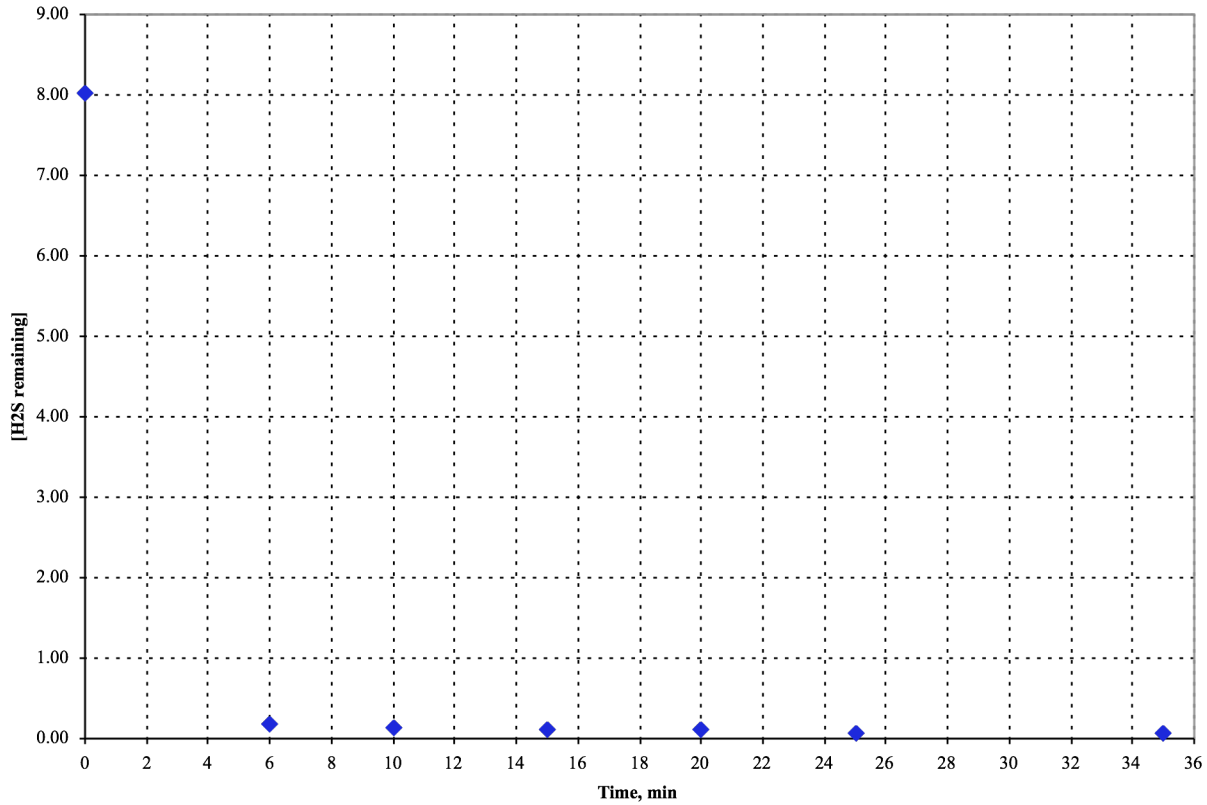


Figure 4.11: H₂S remaining after 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS addition

A linear regression analysis produced a best-fit line of trial for third-order kinetics well described by equation (39). Application of the aforementioned equation (36) is illustrated in Figure 4.12. The linear regression analysis produced a coefficient of determination (R^2) of 0.501 for first-order kinetics and 0.859 for second-order kinetics. For third order kinetics, the R^2 is 0.922, and the rate constant (k) is $2.387 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$. The time period ($t_{1/2}$) required to reduce the H₂S concentration to half of its original value was determined using equation (39). It was found to be equal to 0.01 minutes.

$$\frac{1}{[C]^2} = 4.774t + 2.8953 \quad (39)$$

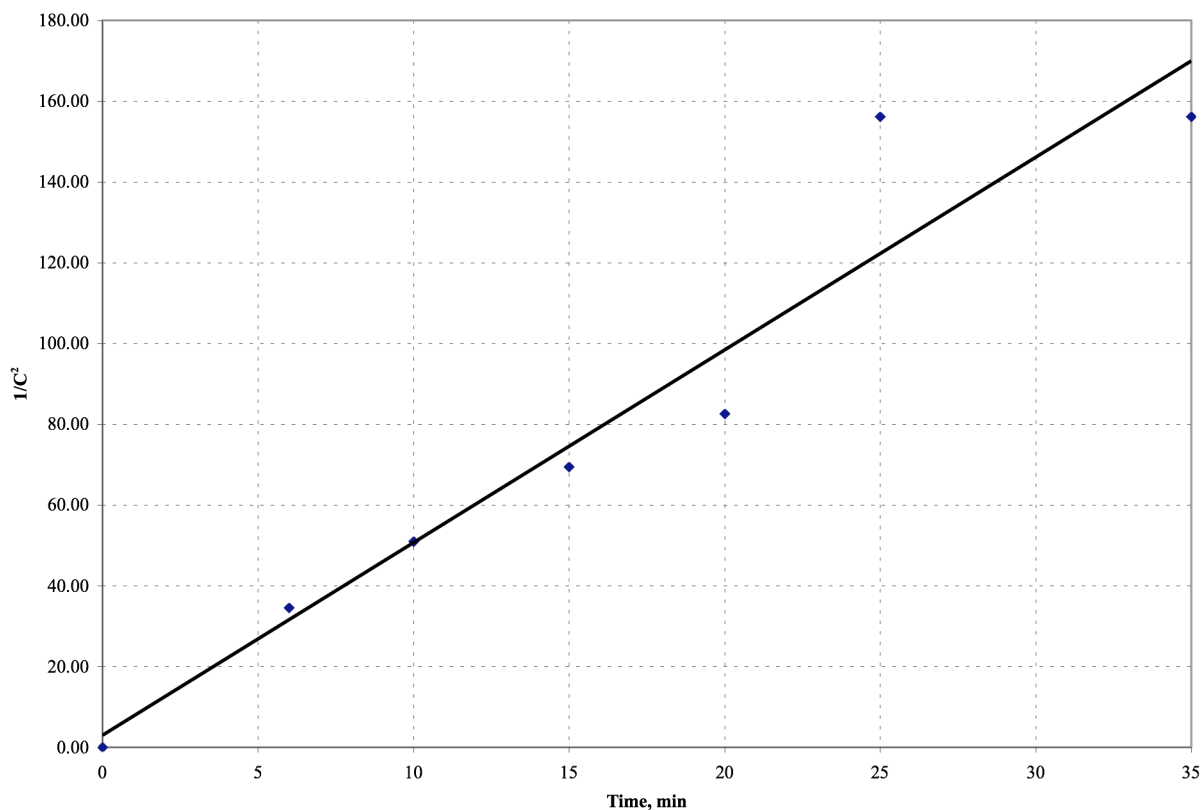


Figure 4.12: Test of Third-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS – pH= 7.20

Similarly, Table 4.4 records the linear regression analysis parameters for the addition of FeCl₂ and H₂O₂ with a reaction time of 5 minutes. Appendix E contains the experiment's data including results summary table and characteristic kinetic plots. All the experiments were gathered in a temperature range of 15-20°C.

Table 4.4: Linear Regression Analysis Parameters for FeCl₂ and H₂O₂ AdditionH₂O₂ Reaction Time = 5 min

FeCl ₂ Concentration	H ₂ O ₂ Concentration	Coefficient of Determination, (R^2)	Rate Constant, (k)	Half-life, ($t_{1/2}$)
1.45 kg FeCl ₂ /kgS	0.10 kg H ₂ O ₂ /kgS	0.994	0.506 L ² mg ⁻² min ⁻¹	0.05 min
1.45 kg FeCl ₂ /kgS	0.30 kg H ₂ O ₂ /kgS	0.978	0.717 L ² mg ⁻² min ⁻¹	0.03 min
1.45 kg FeCl ₂ /kgS	0.60 kg H ₂ O ₂ /kgS	0.922	2.387 L ² mg ⁻² min ⁻¹	0.01 min
2.90 kg FeCl ₂ /kgS	0.10 kg H ₂ O ₂ /kgS	0.974	1.230 L ² mg ⁻² min ⁻¹	0.02 min
2.90 kg FeCl ₂ /kgS	0.30 kg H ₂ O ₂ /kgS	0.984	5.406 L ² mg ⁻² min ⁻¹	0.007 min

The results obtained in this research indicate a maximum H₂S removal of around 90% using FeCl₂ and H₂O₂ combination. It is important to mention that most of the H₂S is oxidized by H₂O₂. Both reaction times used for H₂O₂, namely 1 and 5 minutes achieve high H₂S removal with relative low half-life values ranging from 0.26 to 0.007 minutes. However, the experiments carried out during the experimental phase suggest that the addition of FeCl₂ does not have a significant effect on the percent H₂S removal. The claim made by U.S. Peroxide about the efficacy of this process could not be substantiated in this investigation. However, as stated before, changing the initial concentration of FeCl₂ significantly affects both the third-order kinetic constant k , and the $t_{1/2}$. It can be seen a 7-fold increase in k by simply doubling the concentration of FeCl₂ and a 5-times reduction on $t_{1/2}$. In other words, the addition of FeCl₂ does not affect the H₂S removal but it has a chemical effect on the reaction. On the other hand, the variation on the value of k can be also attributed to the difference in temperature in which each experiment was performed. The research presented herein demonstrates that for H₂S oxidation by FeCl₂ and

H₂O₂ combination, the rate of H₂S removal can be adequately described by third-order reaction kinetics.

4.4 Pure Oxygen (O₂) Injection

In order to evaluate the effectiveness of the pure oxygen (O₂) method, H₂S oxidation was determined at different reaction times, namely 0, 30, 60, 90, 120 and 150 minutes. Pure oxygen (O₂) was injected to the H₂S solution at concentrations of 5, 10, 15, and 20 kg O₂/kgS.

Figure 4.13 illustrates a representative relationship between the remaining concentration of H₂S and different reaction times using a dosage of 20 kg O₂/kgS. In this case, 150 minutes reaction time yields an average value of 51% H₂S oxidation. The pH and temperature kept in the batch reactor during this experiment were 7.80 and 22.5°C, respectively. The remaining graphs can be seen in Appendix F.

The best-fit line of the trial for second-order kinetics is schematically represented in Figure 4.14, and its equation is well described by (40). The linear regression analysis produced an R² of 0.858 and 0.921 for first and second order kinetics, respectively. The slope of the best-fit line (rate constant, *k*) for H₂S remaining after 20 kg O₂/kgS addition is 0.0007 Lmg⁻¹min⁻¹. The half-life (*t*_{1/2}) of the reaction is equal to 174.0 min.

$$\frac{1}{[C]} = 0.0007t + 0.1432 \quad (40)$$

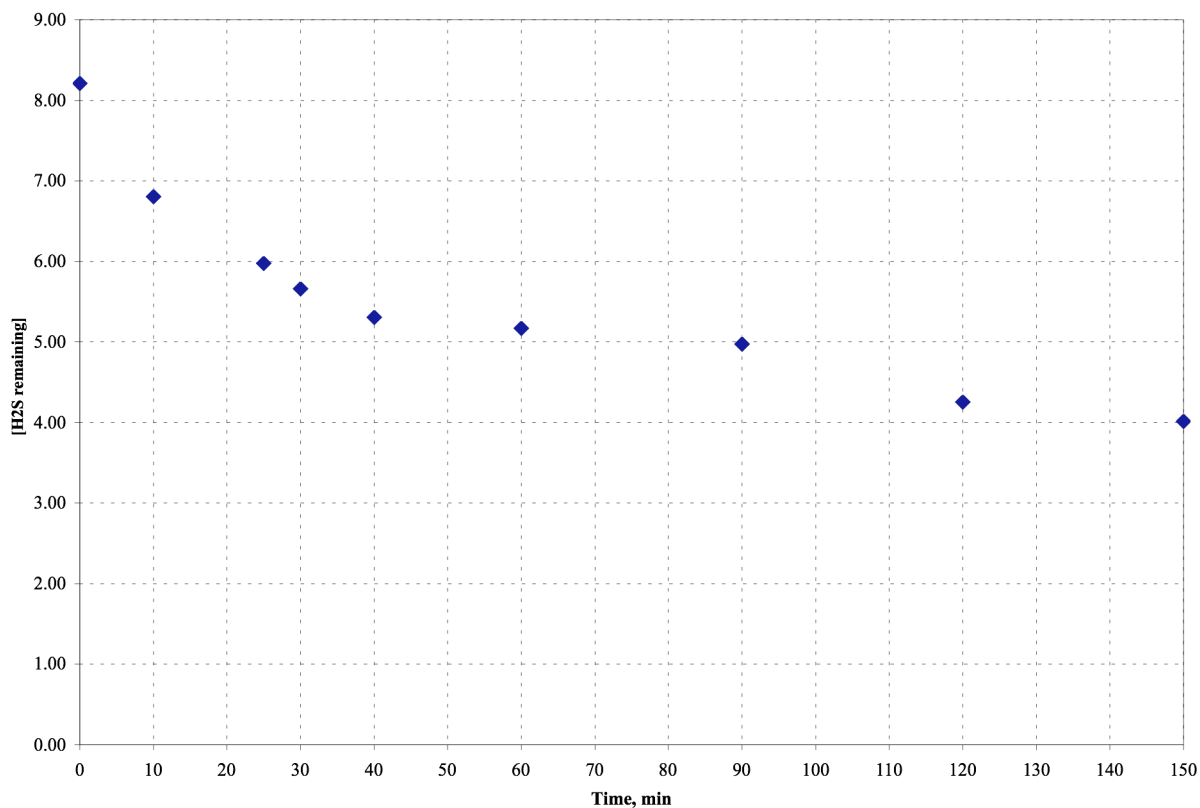


Figure 4.13: H₂S remaining after 20 kg O₂/kgS addition

Linear regression analysis parameters for O₂ injection are listed in Table 4.5 including the coefficient of determination (R^2), rate constant (k), (obtained from a linear regression analysis) and half-lives ($t^{1/2}$). Raw data, a table summary of results and analysis of the data, including test of first and second order kinetics can be viewed in Appendix F.

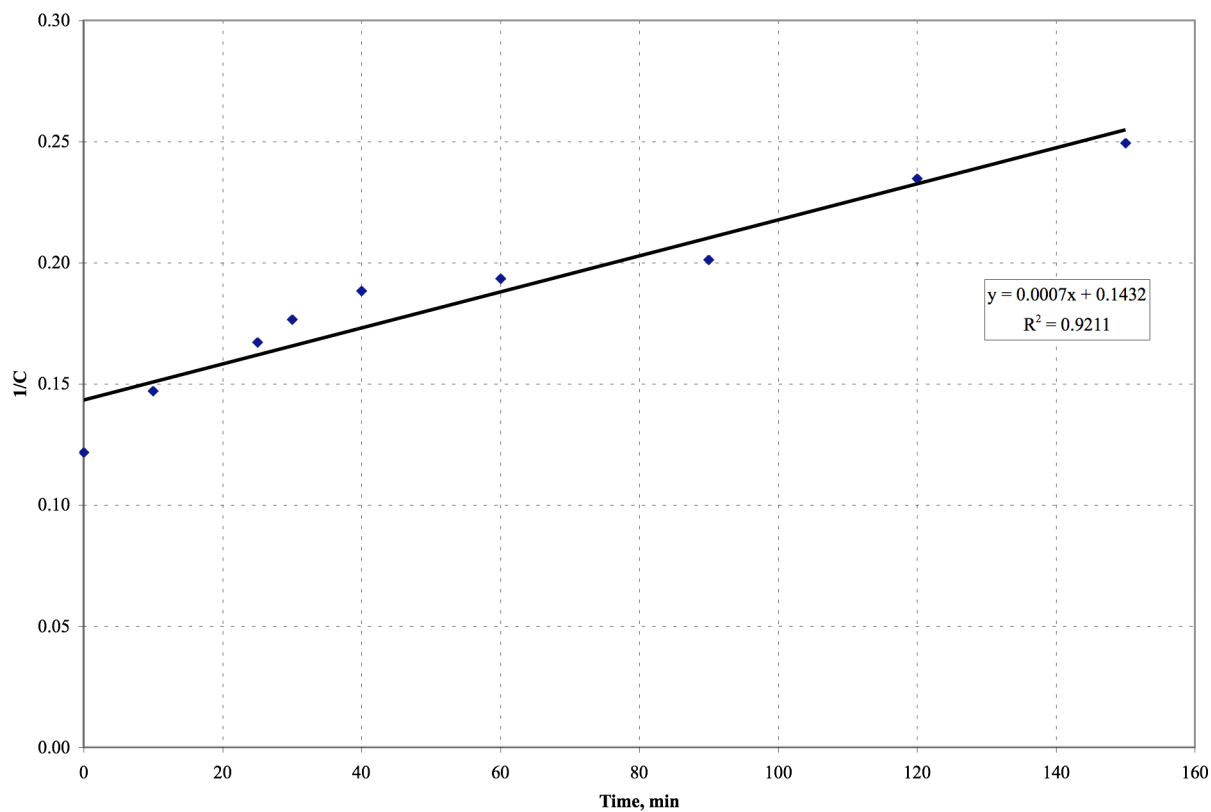


Figure 4.14: Test of Second-Order Kinetics corresponding to 20 kg O₂/kgS – pH=7.80

Table 4.5: Linear Regression Analysis Parameters for O₂ Injection

O ₂ Concentration	Coefficient of Determination, (R^2)	Rate Constant, (k)	Half-life, ($t_{1/2}$)
5 kg O ₂ /kgS	0.913	0.0002 Lmg ⁻¹ min ⁻¹	783.70 min
10 kg O ₂ /kgS	0.926	0.0004 Lmg ⁻¹ min ⁻¹	434.78 min
15 kg O ₂ /kgS	0.977	0.0004 Lmg ⁻¹ min ⁻¹	271.74 min
20 kg O ₂ /kgS	0.921	0.0007 Lmg ⁻¹ min ⁻¹	174.00 min

Figure 4.15 shows the half-lives ($t_{1/2}$) corresponding to different O_2 concentrations. It can be noticed that the half-lives ($t_{1/2}$) necessary to oxidize H_2S are relatively high, which implies that O_2 dosages should be reasonably high in order to mitigate H_2S with practical detention times. This indicates that it is difficult to get the H_2S concentration low enough to eliminate odor and corrosion problems using pure oxygen injection.

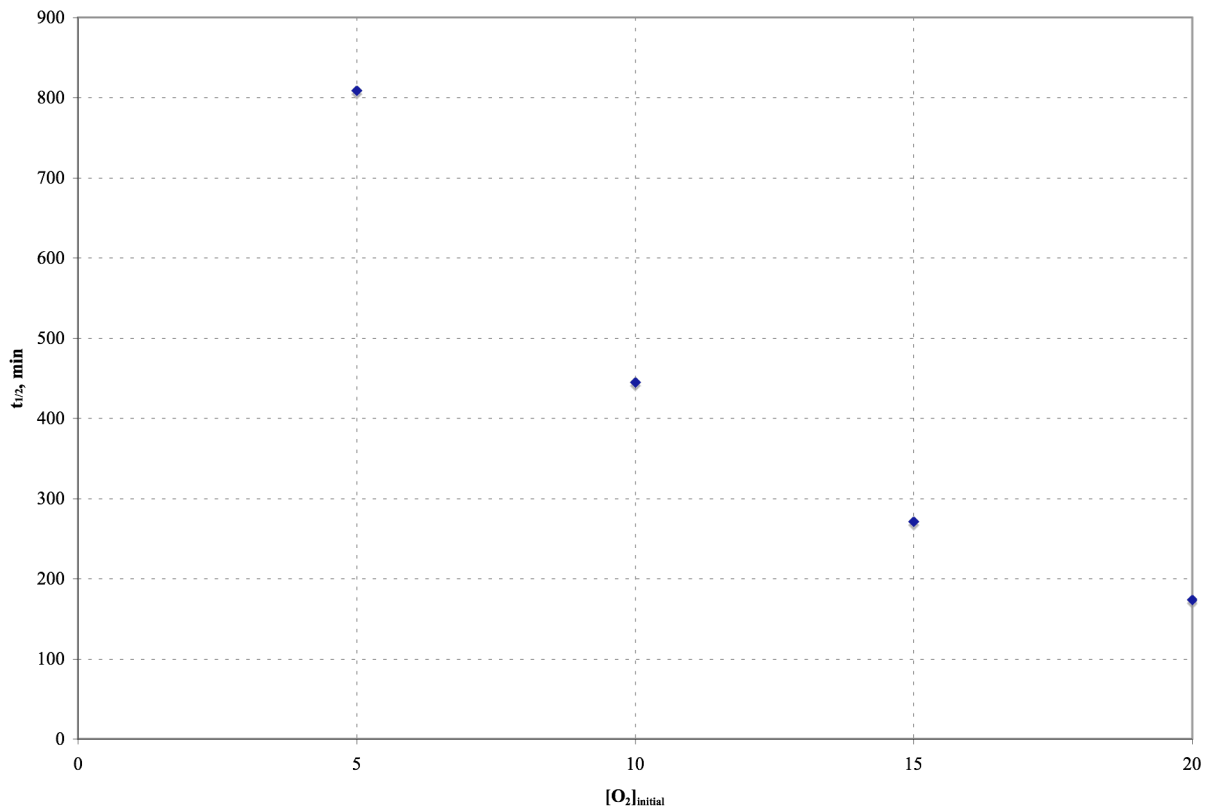


Figure 4.15: Half-lives ($t_{1/2}$) for O_2 addition at different initial concentrations

The rate constant (k) corresponding to the addition of O_2 at different concentrations is depicted in Figure 4.16. It can be noticed that the value of k increases with the concentration of O_2 , which means that the slope of the line is defined by the value of the rate constant (k).

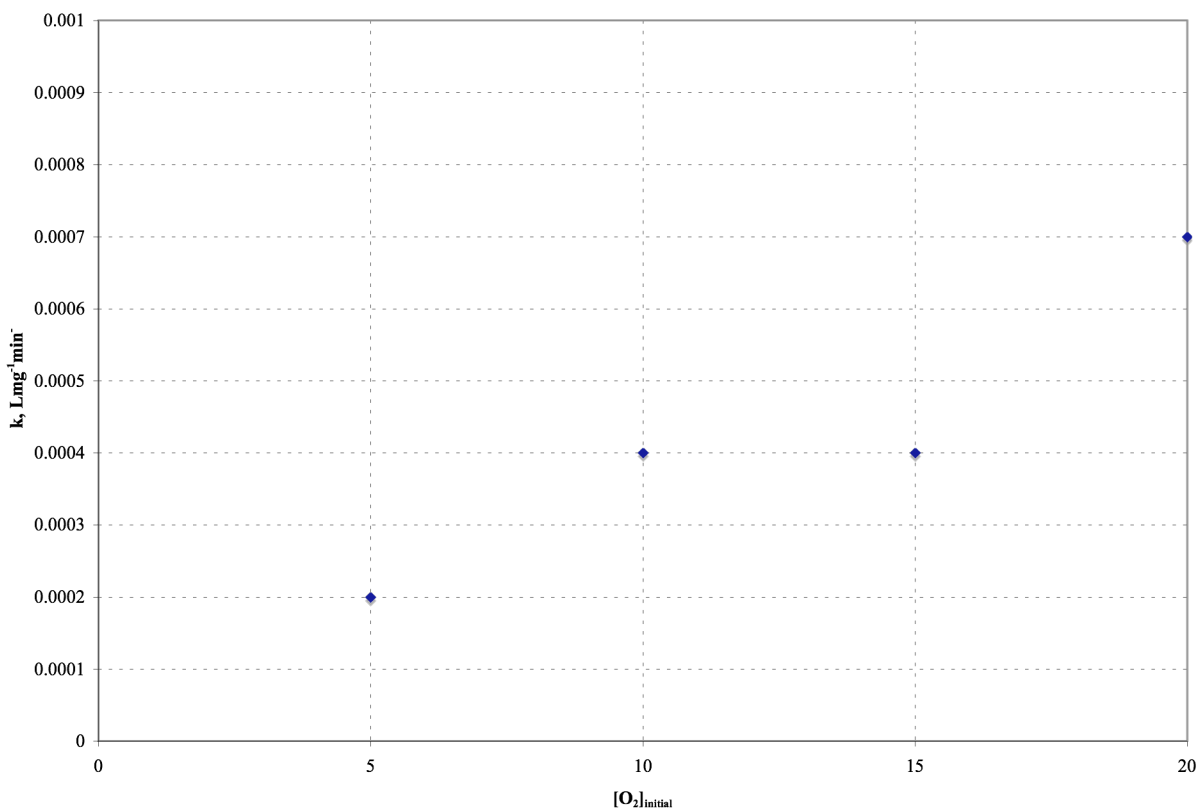


Figure 4.16: Rate constants (k) for O_2 addition at different initial concentrations

These results are not in good agreement with the one obtained by Chen and Morris (1972), O'Brien and Birkner (1977) and Zhang and Millero (1993). According to Chen and Morris (1972) at all pH values and 25 °C, the reaction orders of sulfide and oxygen are 1.35 and 0.56, respectively. These researchers used Van't Hoff (differential) method for the estimation of the initial order of reaction. The initial rates were determined graphically from a concentration versus time plot for various initial concentrations. On the other hand, O'Brien and Birkner (1977) and Zhang and Millero (1993) found the rate of the reaction to be the first order with respect H_2S and O_2 at 25 °C and pH 8. O'Brien and Birkner (1977) used a model that suggested parallel reactions between reduced sulfur species and oxygen. Based on the pH values, two different models were used for these researchers. First, the reaction order was obtained by

following the decrease in the $S(-II)_T$ concentration with time under conditions where oxygen was in excess and then the reaction order was evaluated by a differential analysis of the kinetic data, utilizing the method of initial rates. Zhang and Millero (1993) determined the reaction order by fitting the data to various rate equations with different values of the order of the reaction. However, the investigation reported herein suggests a second-order reaction at 22.5°C and pH around 7. Similarly, the $t_{1/2}$ values reported herein ranges from 174 min (3h) to 784 min (13h), which again are in disagreement with Chen and Morris (1972) and O'Brien and Birkner (1977) findings. Their studies suggest $t_{1/2}$ values ranging from 27h to 50h. It is important to note that all the earlier kinetic studies were measured in water and seawater.

Based on the results of this research, it can be concluded that injection of pure oxygen was ineffective for the mitigation of H_2S across a range of 5-20 kg O_2 /kgS. Since the oxygen demand was significantly greater than the supply provided by the injection, the H_2S solution was not oxidized within reasonable reaction times.

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the research presented in this dissertation:

1. For a range of temperature of 12°C and 14°C and pH around 7, the oxidation of hydrogen sulfide with FeCl_2 adheres to second-order reaction kinetics, which disagrees with the observations of Pyzik and Sommer (1981) and Yao and Millero (1996)
2. The removal of hydrogen sulfide using H_2O_2 is well described by the third-order rate equation for a range of temperature between 10°C and 17°C and over a pH nearly 7, which disagrees with the earlier findings of Hoffmann (1977) and Millero, et al., (1989).
3. Hydrogen sulfide oxidation by the combination of FeCl_2 and H_2O_2 can be adequately described by a third-order reaction kinetic in a temperature range of 15-20°C and pH 7.
4. The removal of H_2S injecting pure oxygen (O_2) to force mains suggests a second-order reaction kinetic at 22.5°C and pH around 7, which again is not in good agreement with the results of O'Brien and Birkner (1977) and Zhang and Millero (1993).
5. It was possible to control odors generated by H_2S using FeCl_2 addition. Nonetheless, this treatment requires large quantities of FeCl_2 to be effective, which is not considered feasible. The maximal removal achieved by FeCl_2 was 98%, using a relative high dosage of 10 kg FeCl_2 /kgS. When lower dosages were used, the $t_{1/2}$ obtained reach values up to 159 min (2.65 h).
6. H_2O_2 (50%) is the most effective chemical control strategy for the mitigation of H_2S investigated, with relative low half-lives ($t_{1/2}$) ranging from 0.0008min to 18.45min and dosages of 0.05 kg H_2O_2 /kgS to 1.00 kg H_2O_2 /kgS, respectively.

7. Maximum percent H_2S removals using combination of FeCl_2 and H_2O_2 were in the 90s. It is important to mention that most of the H_2S is oxidized by H_2O_2 . For the concentrations and reaction times used for FeCl_2 addition, this chemical does not have a significant effect on the H_2S removal. Both reaction times used for H_2O_2 , namely 1 and 5 minutes achieve high H_2S removal with relative low half-life values ranging from 0.26 to 0.007 minutes.
8. The half-life ($t_{1/2}$) range for the oxidation of H_2S by O_2 is equal to 174min (13h) – 784min (2.9h) corresponding to dosages from 5 kg O_2 /kgS to 20 kg O_2 /kgS, respectively. O_2 injection was ineffective across the range of pure oxygen investigated. Since the oxygen demand was significantly greater than the supply provided by the injection, the H_2S solution was not oxidized within reasonable reaction times.
9. In all cases the initial concentration of the reactant used had a significant effect on the value of both the kinetic constant and the half-life. The actual magnitude of this effect could not be established because of the temperature variation from one experiment to the next.
10. Although temperature changes may cause a variation on the value of the kinetic constant, such changes would not affect the kinetic expression. Due to limitations of the experimental setup, the dependence of k on the temperature could not be determined in this research.

The following are recommendations for future research projects:

1. Addition of chemicals as FeCl_2 and H_2O_2 should be applied to an operational, full-scale sanitary sewer system in order to evaluate the complexity of hydrogen sulfide generation and the uniqueness of the sanitary sewer biology.
2. A study of pure oxygen injection process effectiveness to operational wastewater treatment systems should be conducted in order to determine the effect of force main detention times on chemical dosages for hydrogen sulfide oxidation.
3. In order to further evaluate the effectiveness of the pure oxygen (O_2) method, pure oxygen (O_2) should be injected to the H_2S solution at concentrations higher than 20 kg O_2/kgS .
4. Rate constants versus temperature plots should be prepared to determine the activation energy and the pre-exponential factor, which define the dependence of the rate constant (k) of the chemical reaction on the temperature variation.

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APPENDIX A

Appendix A-1. Results Summary - Ion Selective Electrode Method - FeCl₂ Addition

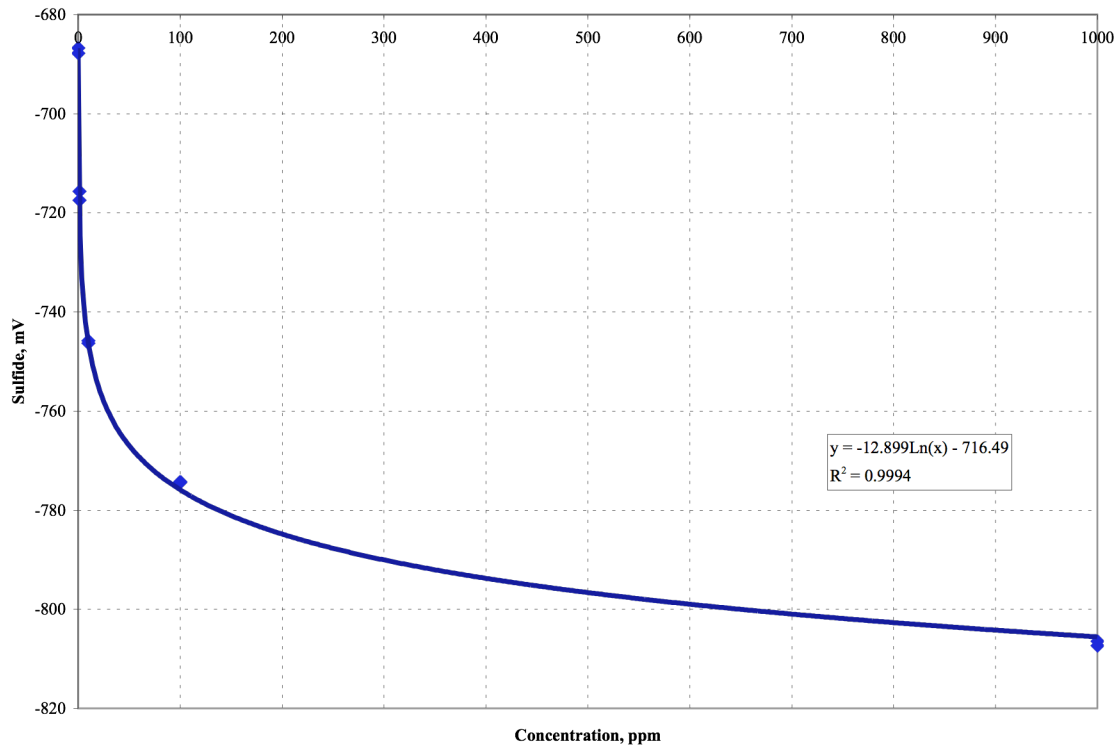
Time, min	FeCl ₂ Concentration, kgFeCl ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	1.45	10.46	100.00	0.00
10	1.45	9.23	88.24	11.76
30	1.45	8.64	82.60	17.40
60	1.45	7.23	69.12	30.88
90	1.45	6.51	62.24	37.76
0	2.90	9.89	100.00	0.00
10	2.90	6.36	64.31	35.69
30	2.90	5.42	54.80	45.20
60	2.90	4.79	48.43	51.57
90	2.90	4.28	43.28	56.72
0	3.70	8.15	100.00	0.00
10	3.70	3.86	47.36	52.64
30	3.70	2.94	36.07	63.93
60	3.70	1.85	22.70	77.30
90	3.70	1.54	18.90	81.10
0	5.00	9.23	100.00	0.00
10	5.00	3.95	42.80	57.20
30	5.00	3.19	34.56	65.44
60	5.00	1.80	19.50	80.50
90	5.00	1.06	11.48	88.52
0	10.0	8.01	100.00	0.00
10	10.0	1.17	14.61	85.39
30	10.0	0.82	10.24	89.76
60	10.0	0.28	3.50	96.50
90	10.0	0.17	2.12	97.88

Appendix A-2. Standard Curve Data for 1.45 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



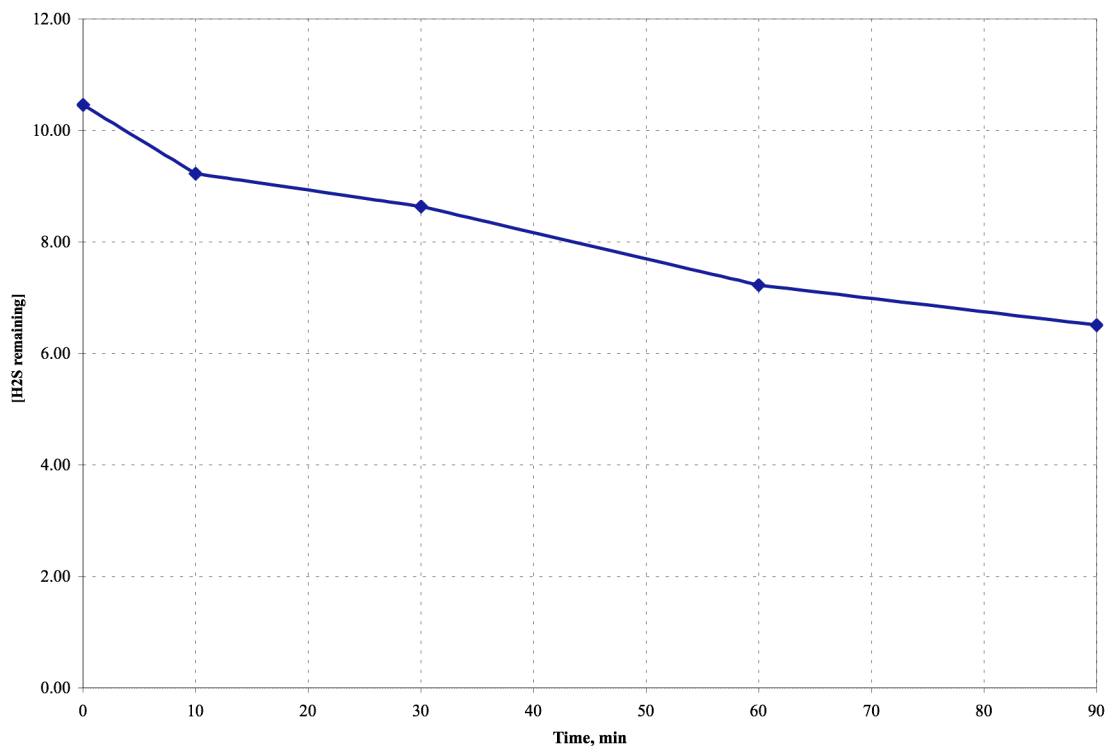
Appendix A-3. Standard Curve for 1.45 kg FeCl₂/kgS Addition

Appendix A-4. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS Addition

Date: 2/3/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂S Initial Concentration: 10.46 mg/L
 Initial pH: 12.30
 pH after HCl addition: 7.50

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-746.0	2.287774246	9.85	10.46	14.0
	b		-747.5	2.40406233	11.07		14.0
2	a	10	-744.9	2.202496318	9.05	9.23	14.0
	b		-745.4	2.241259012	9.41		14.0
3	a	30	-744.4	2.163733623	8.70	8.64	14.0
	b		-744.2	2.148228545	8.57		14.0
4	a	60	-742.3	2.000930305	7.40	7.23	14.0
	b		-741.7	1.954415071	7.06		14.0
5	a	90	-740.5	1.861384603	6.43	6.51	14.0
	b		-740.8	1.88464222	6.58		14.0
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix A-5. H₂S remaining after 1.45 kg FeCl₂/kgS Addition

Appendix A-6. Linear Regression Analysis corresponding to 1.45 FeCl₂/kgS – pH = 7.50

Date: 2/3/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS

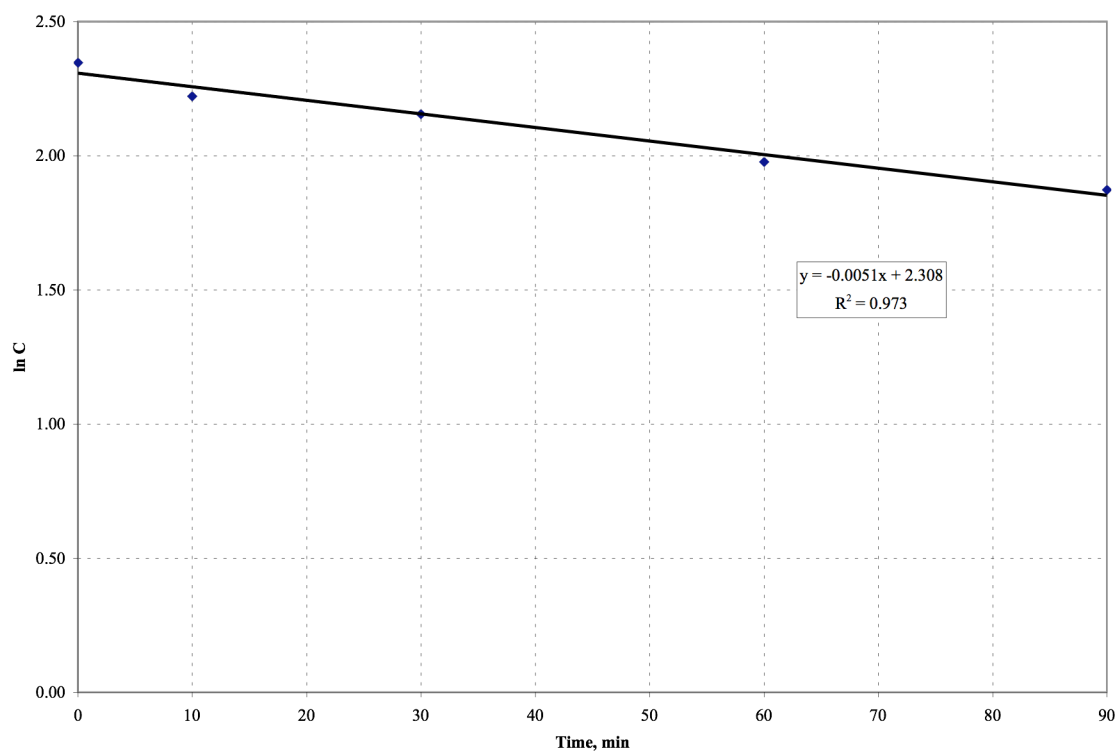
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	10.46	2.3475585	0.0956023	0.0091398	0.0008738	0.0000835	0.0000080	0.0000008	0.0000001
10	9.23	2.2224590	0.1083424	0.0117381	0.0012717	0.0001378	0.0000149	0.0000016	0.0000002
30	8.64	2.1564026	0.1157407	0.0133959	0.0015505	0.0001795	0.0000208	0.0000024	0.0000003
60	7.23	1.9782390	0.1383126	0.0191304	0.0026460	0.0003660	0.0000506	0.0000070	0.0000010
90	6.51	1.8733395	0.1536098	0.0235960	0.0036246	0.0005568	0.0000855	0.0000131	0.0000020

$$t_{1/2} = \frac{1}{k[C_0]}$$

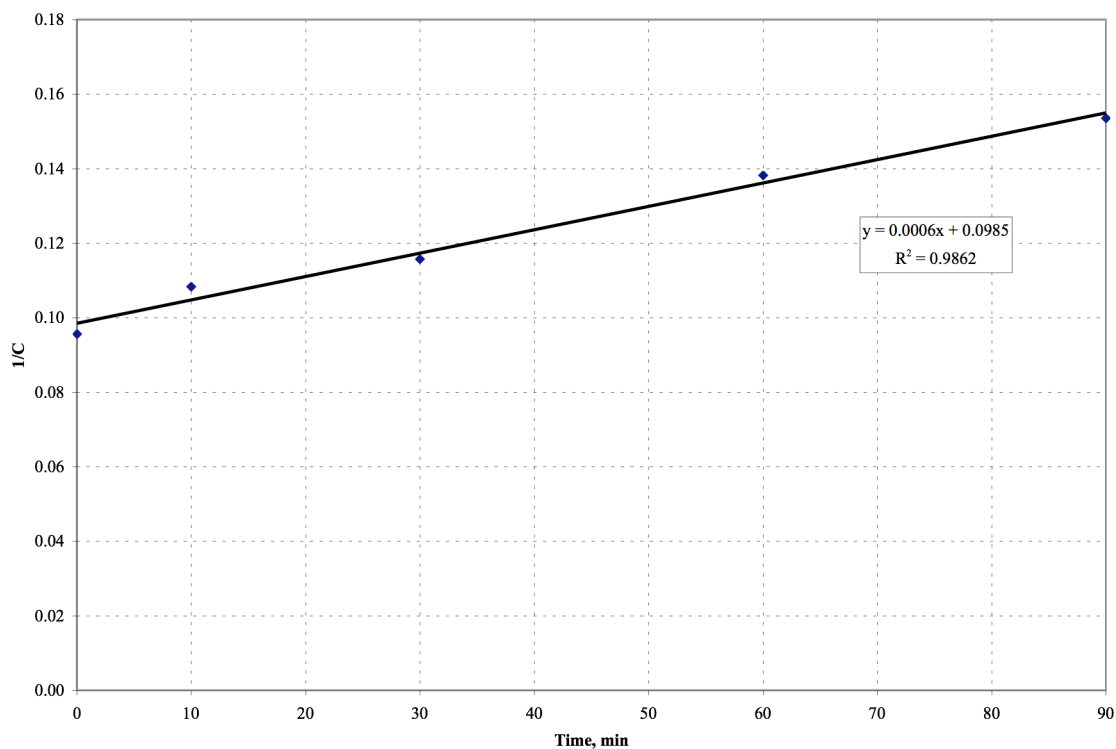
$$k = 0.0006 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_0 = 10.46 \text{ mg/L}$$

$$t_{1/2} = 159.34 \text{ min}$$



Appendix A-7. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS



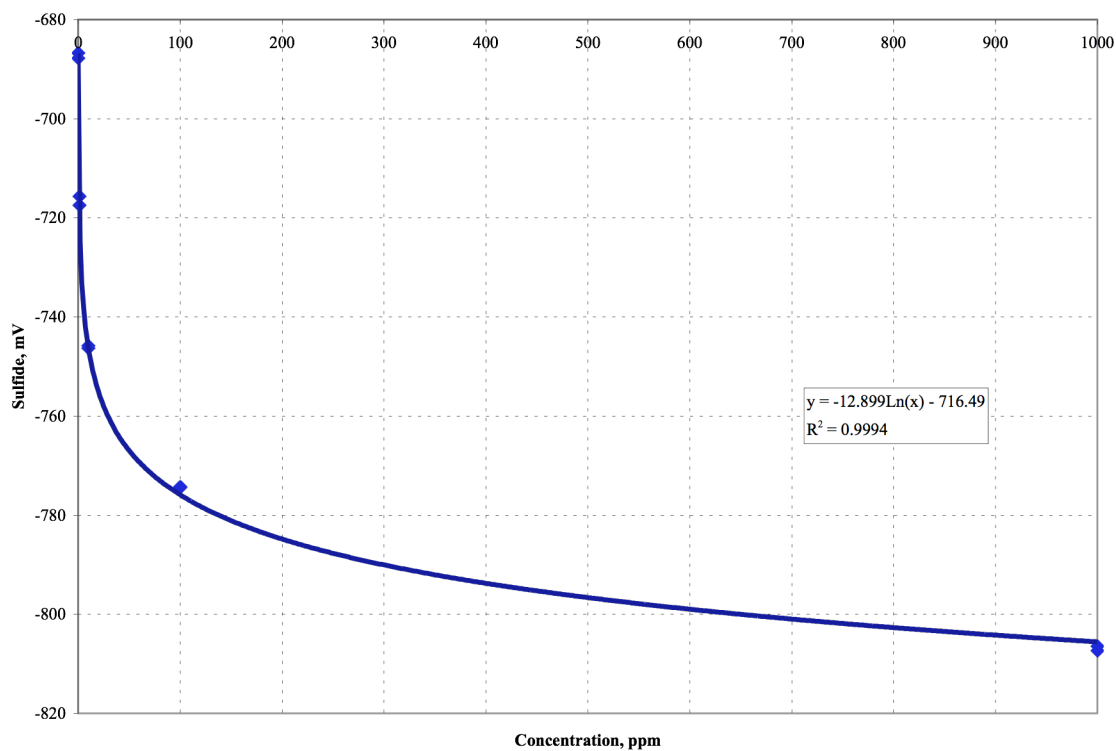
Appendix A-8. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS

Appendix A-9. Standard Curve Data for 2.90 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



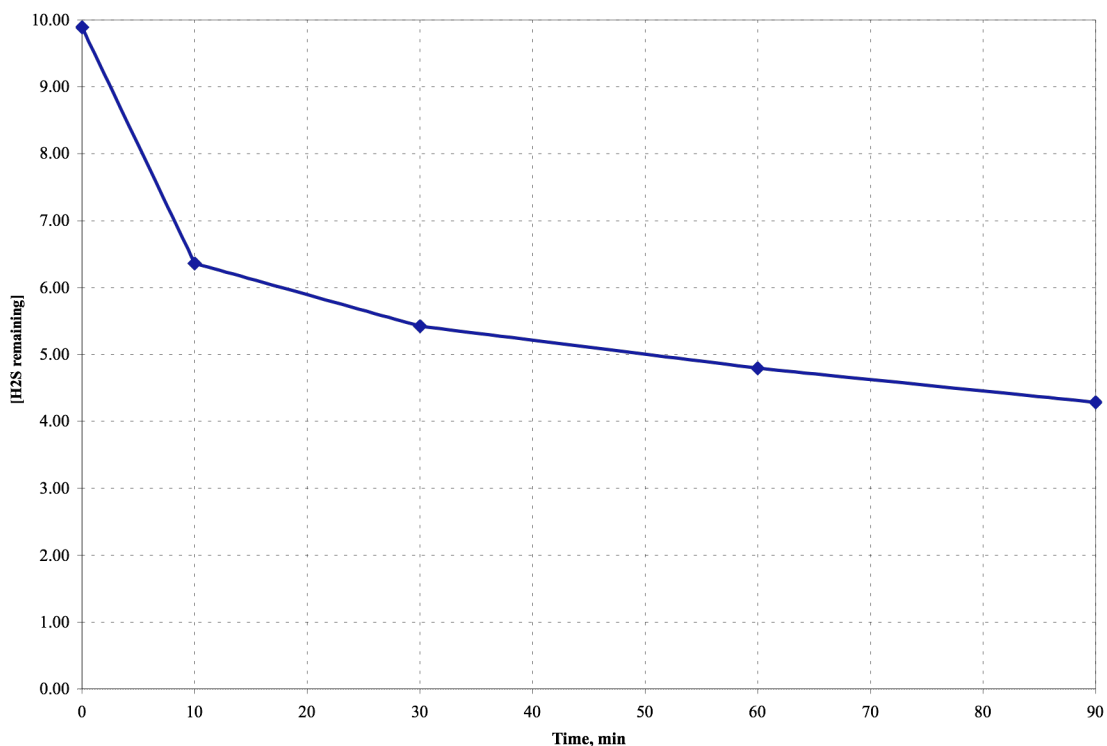
Appendix A-10. Standard Curve for 2.90 kg FeCl₂/kgS Addition

Appendix A-11. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS Addition

Date: 2/3/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂S Initial Concentration: 9.89 g
 Initial pH: 12.30
 pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-745.9	2.280021707	9.78	9.89	13.2
	b		-746.2	2.303279324	10.01		13.2
2	a	10	-740.6	1.869137142	6.48	6.36	13.2
	b		-740.1	1.830374448	6.24		13.2
3	a	30	-738.2	1.683076207	5.38	5.42	13.2
	b		-738.4	1.698581285	5.47		13.2
4	a	60	-736.7	1.566788123	4.79	4.79	13.2
	b		-736.7	1.566788123	4.79		13.2
5	a	90	-735.7	1.489262734	4.43	4.28	13.2
	b		-734.8	1.419489883	4.14		13.2
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix A-12. H₂S remaining after 2.90 kg FeCl₂/kgS Addition

Appendix A-13. Linear Regression Analysis corresponding to 2.90 FeCl₂/kgS – pH = 7.80

Date: 2/3/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS

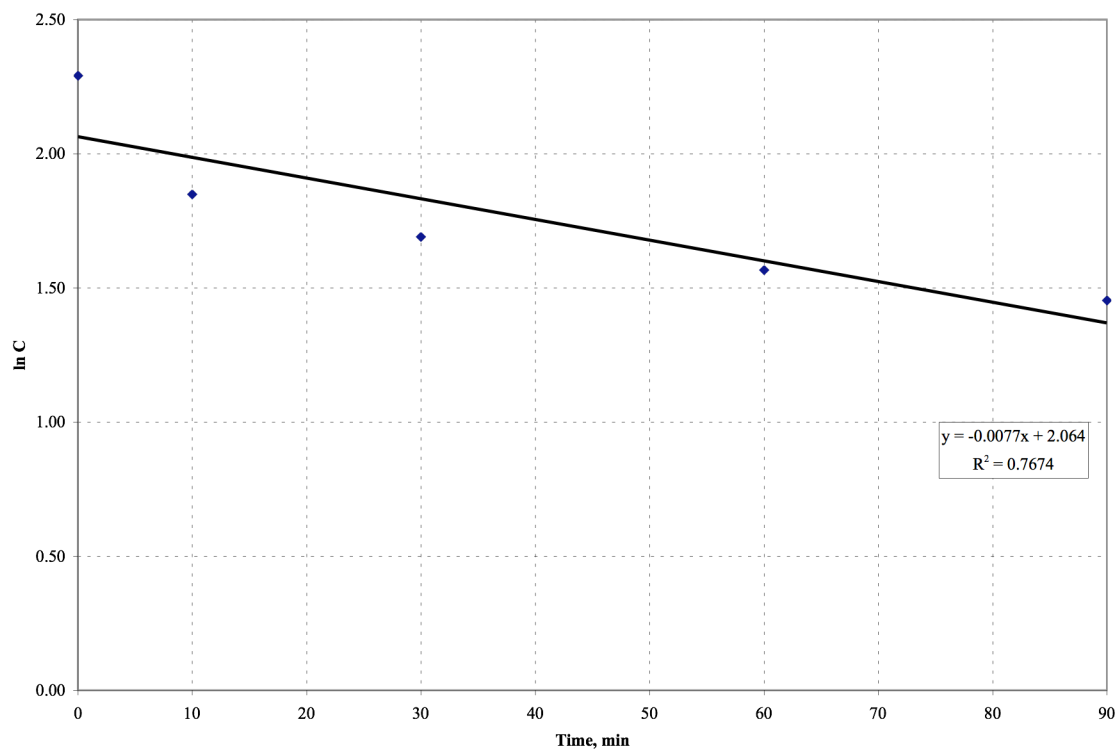
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	9.89	2.2915241	0.1011122	0.0102237	0.0010337	0.0001045	0.0000106	0.0000011	0.0000001
10	6.36	1.8500284	0.1572327	0.0247221	0.0038871	0.0006112	0.0000961	0.0000151	0.0000024
30	5.42	1.6900958	0.1845018	0.0340409	0.0062806	0.0011588	0.0002138	0.0000394	0.0000073
60	4.79	1.5665304	0.2087683	0.0435842	0.0090990	0.0018996	0.0003966	0.0000828	0.0000173
90	4.28	1.4539530	0.2336449	0.0545899	0.0127547	0.0029801	0.0006963	0.0001627	0.0000380

$$t_{1/2} = \frac{1}{k[C_o]}$$

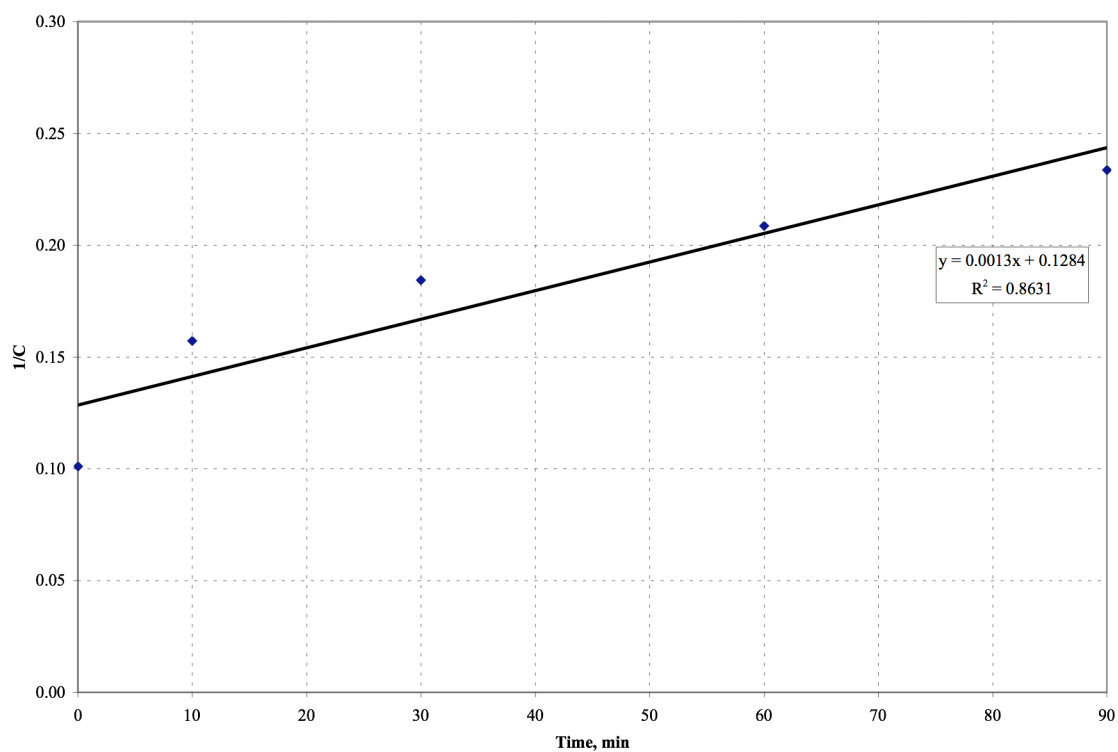
$$k = 0.0013 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_o = 9.89 \text{ mg/L}$$

$$t_{1/2} = 77.78 \text{ min}$$



Appendix A-14. Test of First-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS



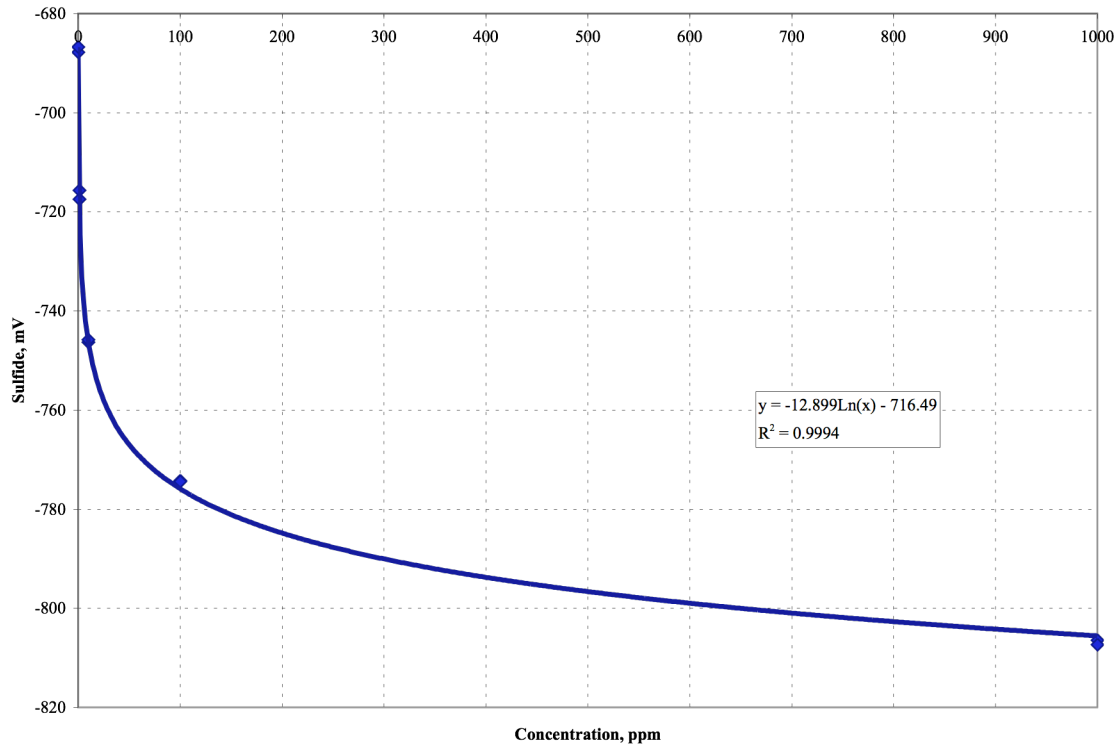
Appendix A-15. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS

Appendix A-16. Standard Curve Data for 3.70 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



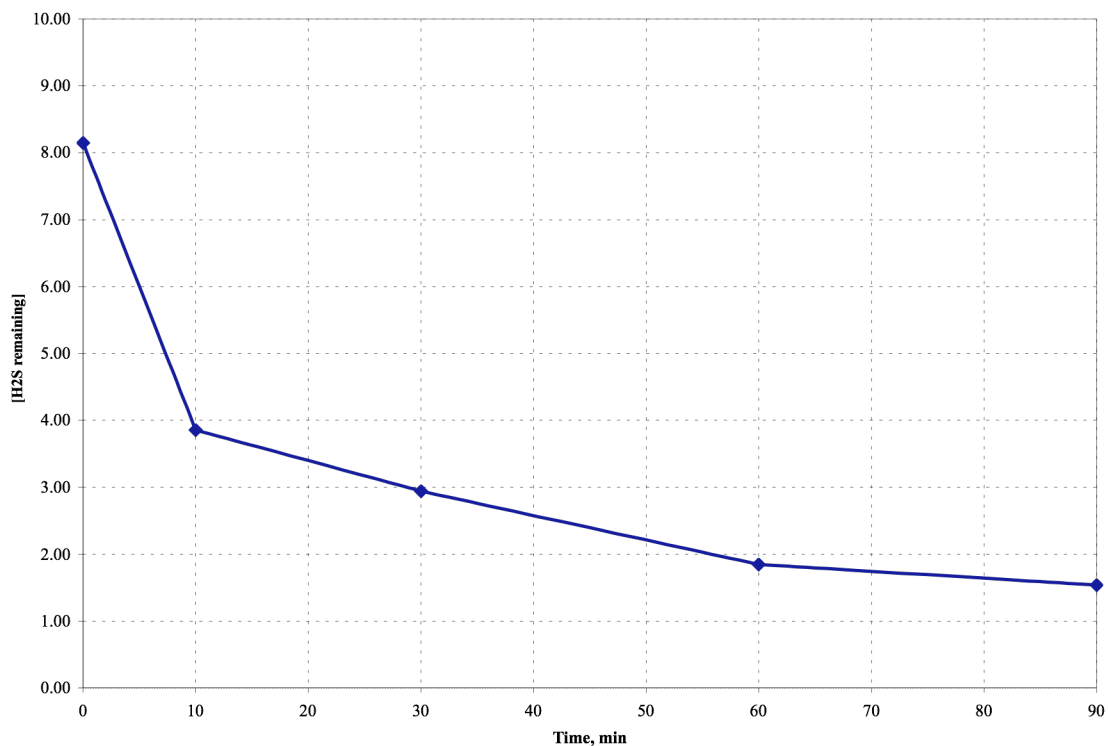
Appendix A-17. Standard Curve for 3.70 kg FeCl₂/kgS Addition

Appendix A-18. Ion Selective Electrode Method Data for 3.70 kg FeCl₂/kgS Addition

Date: 2/4/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 3.70 kgFeCl₂/kgS
 H₂S Initial Concentration: 8.15 mg/L
 Initial pH: 12.30
 pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-743.4	2.086208233	8.05	8.15	11.2
	b		-743.7	2.10946585	8.24		11.2
2	a	10	-733.8	1.341964493	3.83	3.86	11.2
	b		-734.0	1.357469571	3.89		11.2
3	a	30	-730.3	1.07062563	2.92	2.94	11.2
	b		-730.5	1.086130708	2.96		11.2
4	a	60	-724.8	0.644235987	1.90	1.85	11.2
	b		-724.0	0.582215676	1.79		11.2
5	a	90	-721.8	0.411659819	1.51	1.54	11.2
	b		-722.3	0.450422513	1.57		11.2
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix A-19. H₂S remaining after 3.70 kg FeCl₂/kgS Addition

Appendix A-20. Linear Regression Analysis corresponding to 3.70 FeCl₂/kgS – pH = 7.80

Date: 2/4/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 3.70 kgFeCl₂/kgS

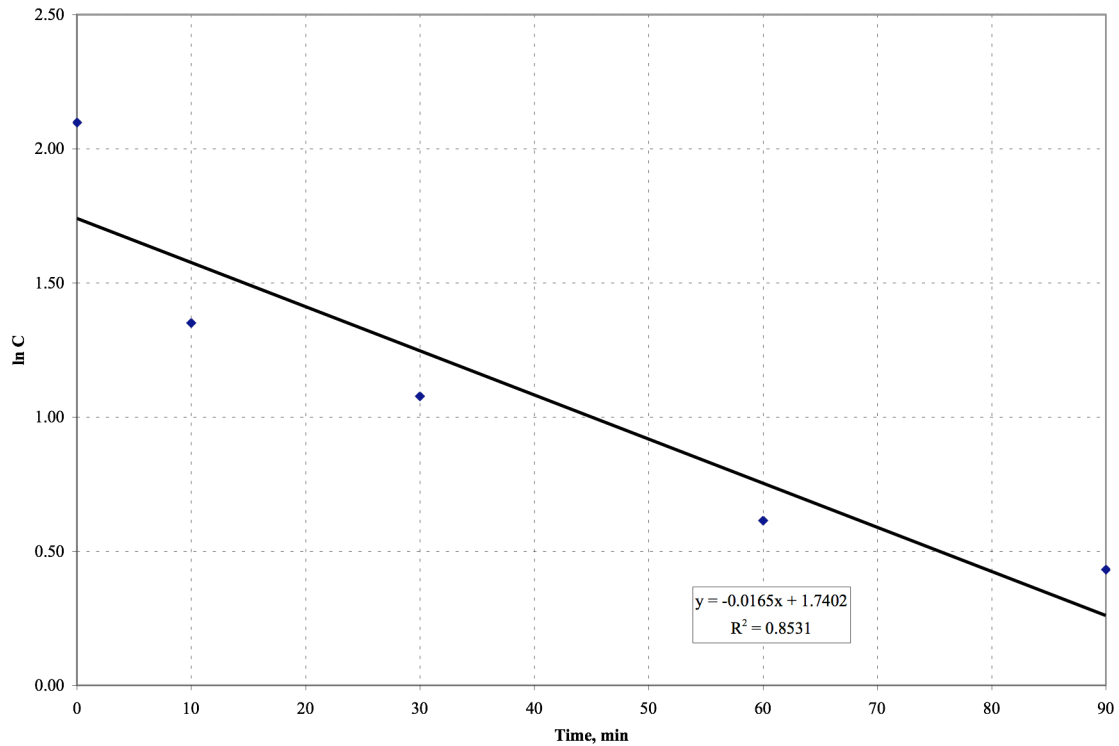
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.15	2.0980179	0.1226994	0.0150551	0.0018473	0.0002267	0.0000278	0.0000034	0.0000004
10	3.86	1.3506672	0.2590674	0.0671159	0.0173875	0.0045045	0.0011670	0.0003023	0.0000783
30	2.94	1.0784096	0.3401361	0.1156925	0.0393512	0.0133848	0.0045526	0.0015485	0.0005267
60	1.85	0.6151856	0.5405405	0.2921841	0.1579373	0.0853715	0.0461468	0.0249442	0.0134834
90	1.54	0.4317824	0.6493506	0.4216563	0.2738028	0.1777940	0.1154507	0.0749680	0.0486805

$$t_{1/2} = \frac{1}{k[C_0]}$$

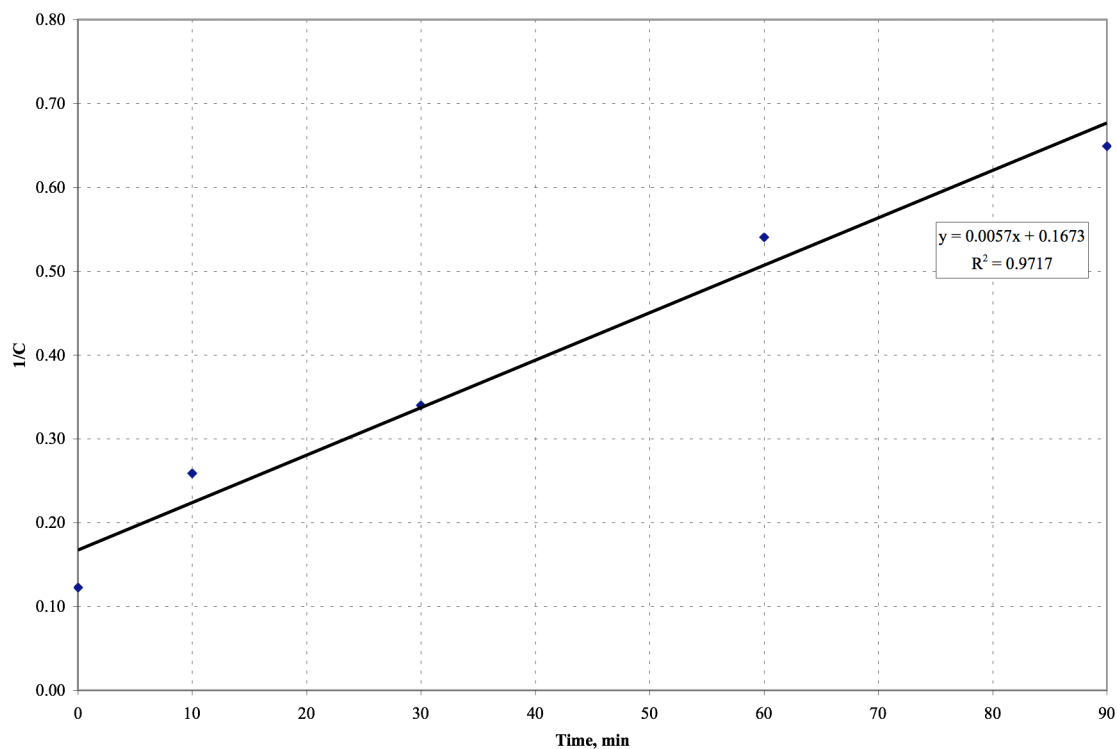
$$k = 0.0057 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_0 = 8.15 \text{ mg/L}$$

$$t_{1/2} = 21.53 \text{ min}$$



Appendix A-21. Test of First-Order Kinetics corresponding to 3.70 kg FeCl₂/kgS



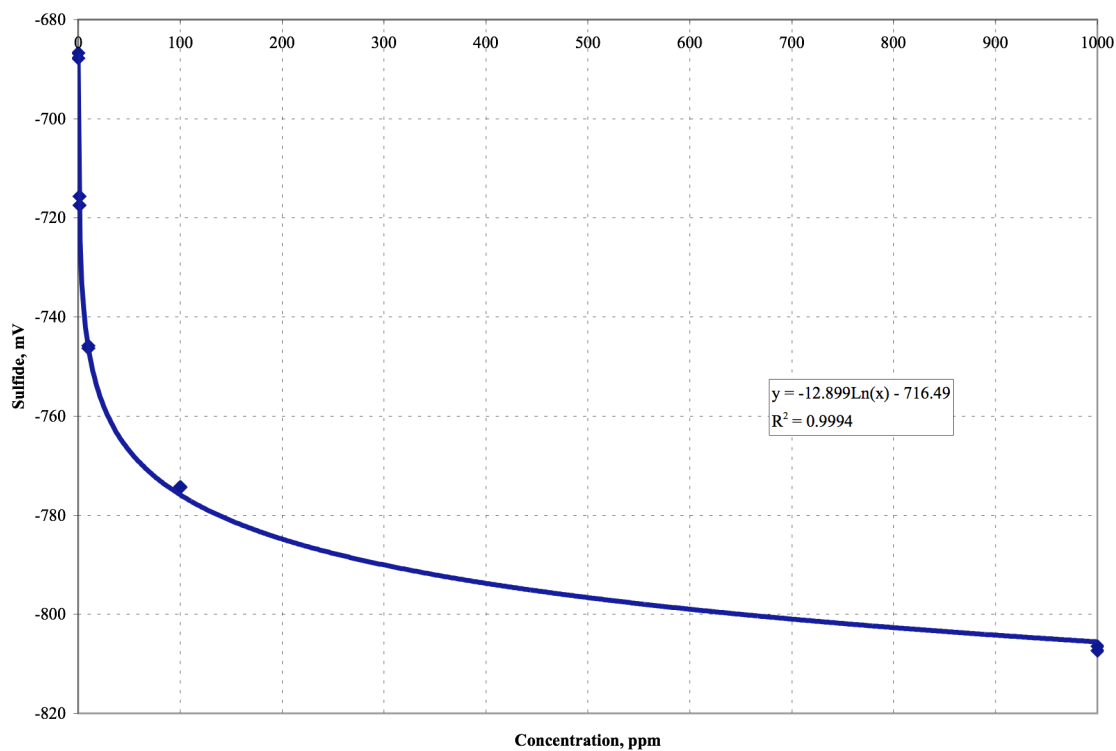
Appendix A-22. Test of Second-Order Kinetics corresponding to 3.70 kg FeCl₂/kgS

Appendix A-23. Standard Curve Data for 5.00 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



Appendix A-24. Standard Curve for 5.00 kg FeCl₂/kgS Addition

Appendix A-25. Ion Selective Electrode Method Data for 5.00 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

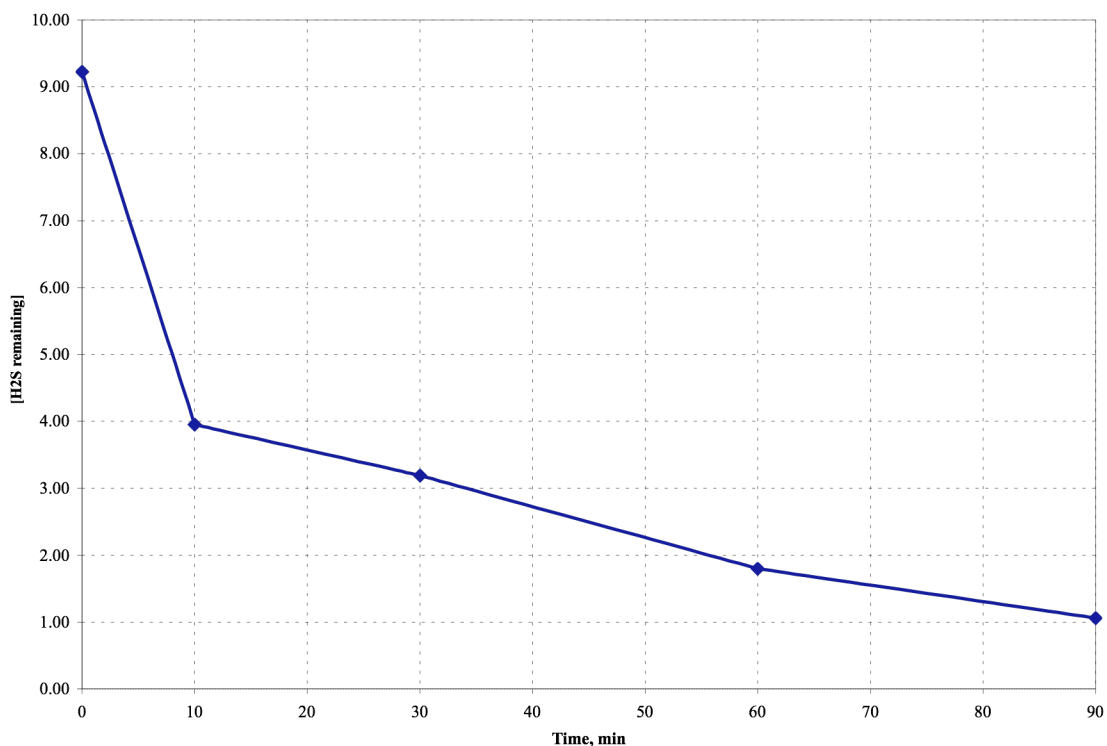
FeCl₂ Concentration: 5.00 kgFeCl₂/kgS

H₂S Initial Concentration: 9.23 mg/L

Initial pH: 12.30

pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-744.9	2.202496318	9.05	9.23	12.1
	b		-745.4	2.241259012	9.41		12.1
2	a	10	-734.7	1.411737344	4.10	3.95	12.1
	b		-733.7	1.334211954	3.80		12.1
3	a	30	-731.5	1.163656097	3.20	3.19	12.1
	b		-731.4	1.155903558	3.18		12.1
4	a	60	-723.8	0.566710598	1.76	1.80	12.1
	b		-724.3	0.605473293	1.83		12.1
5	a	90	-716.0	-0.037987441	0.96	1.06	12.1
	b		-718.3	0.140320955	1.15		12.1
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix A-26. H₂S remaining after 5.00 kg FeCl₂/kgS Addition

Appendix A-27. Linear Regression Analysis corresponding to 5.00 FeCl₂/kgS – pH = 7.80

Date: 2/3/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 5.00 kgFeCl₂/kgS

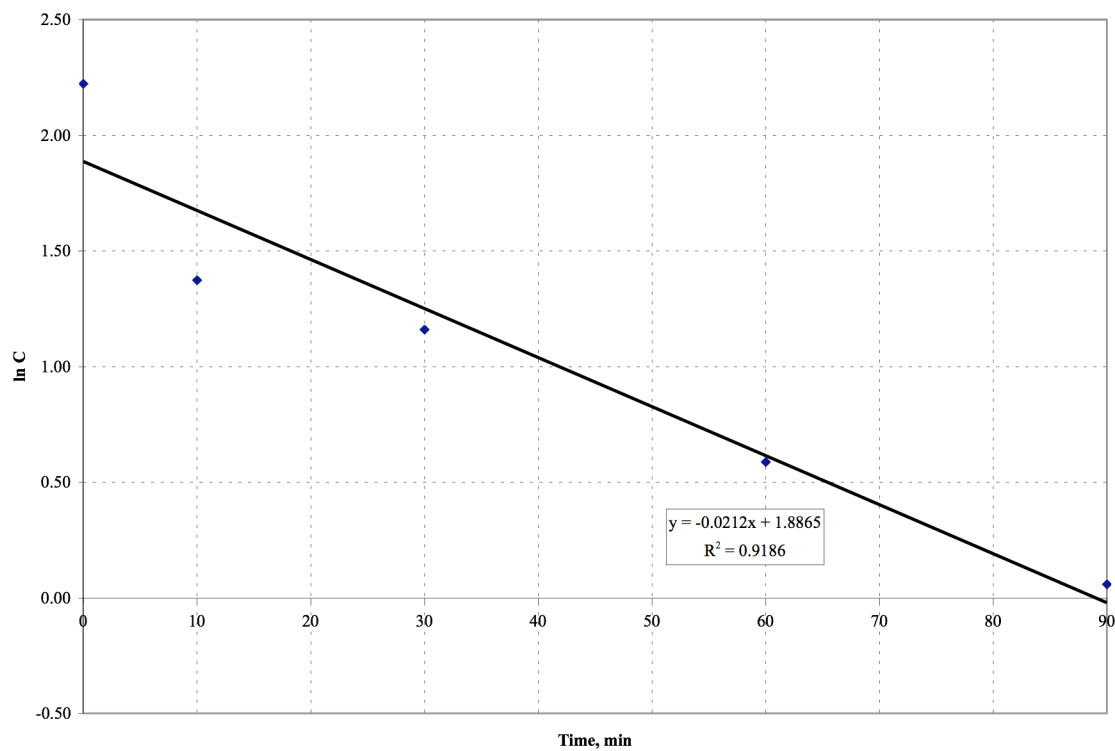
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	9.23	2.2224590	0.1083424	0.0117381	0.0012717	0.0001378	0.0000149	0.0000016	0.0000002
10	3.95	1.3737156	0.2531646	0.0640923	0.0162259	0.0041078	0.0010400	0.0002633	0.0000667
30	3.19	1.1600209	0.3134796	0.0982695	0.0308055	0.0096569	0.0030272	0.0009490	0.0002975
60	1.80	0.5877867	0.5555556	0.3086420	0.1714678	0.0952599	0.0529221	0.0294012	0.0163340
90	1.06	0.0582689	0.9433962	0.8899964	0.8396193	0.7920937	0.7472582	0.7049605	0.6650571

$$t_{1/2} = \frac{1}{k[C_o]}$$

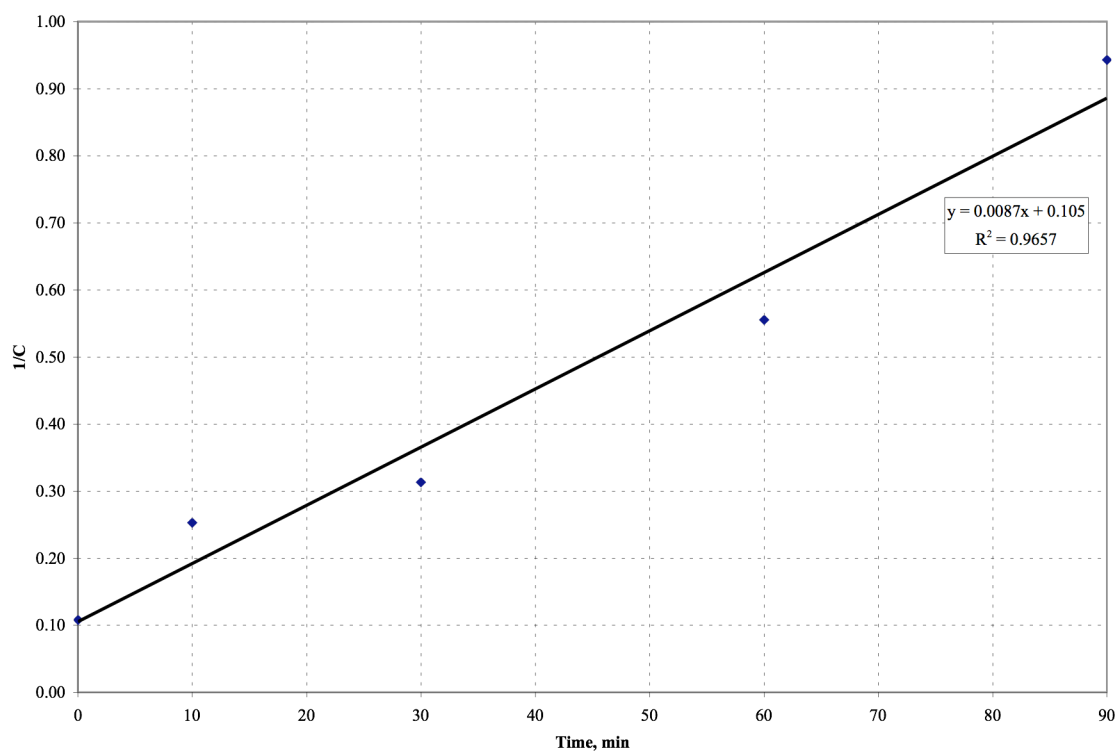
$$k = 0.0087 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_o = 9.23 \text{ mg/L}$$

$$t_{1/2} = 12.45 \text{ min}$$



Appendix A-28. Test of First-Order Kinetics corresponding to 5.00 kg FeCl_2/kgS



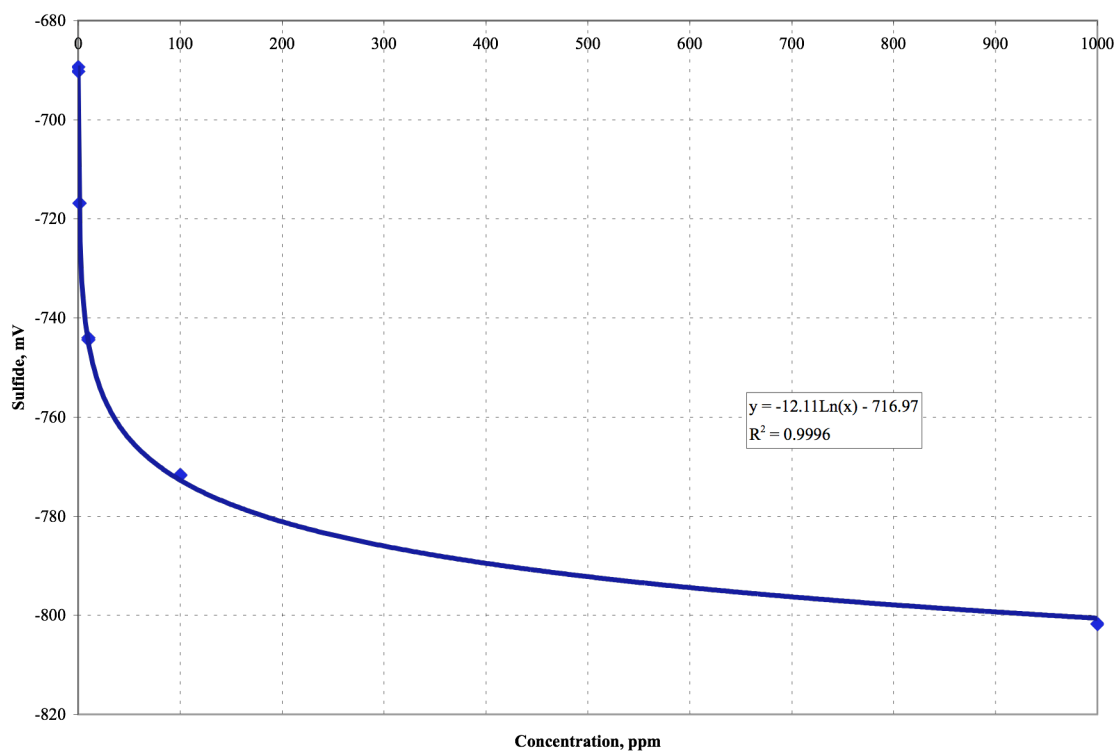
Appendix A-29. Test of Second-Order Kinetics corresponding to 5.00 kg FeCl_2/kgS

Appendix A-30. Standard Curve Data for 10.00 kg FeCl₂/kgS Addition

Date: 2/4/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.7	12.4	13.5
	b	1000	-801.8	12.4	13.5
2	a	100	-771.6	12.4	13.5
	b	100	-771.8	12.4	13.5
3	a	10	-744.4	12.4	13.5
	b	10	-744.0	12.4	13.5
4	a	1	-716.9	12.4	13.5
	b	1	-716.8	12.4	13.5
5	a	0.1	-690.2	12.4	13.5
	b	0.1	-689.3	12.4	13.5

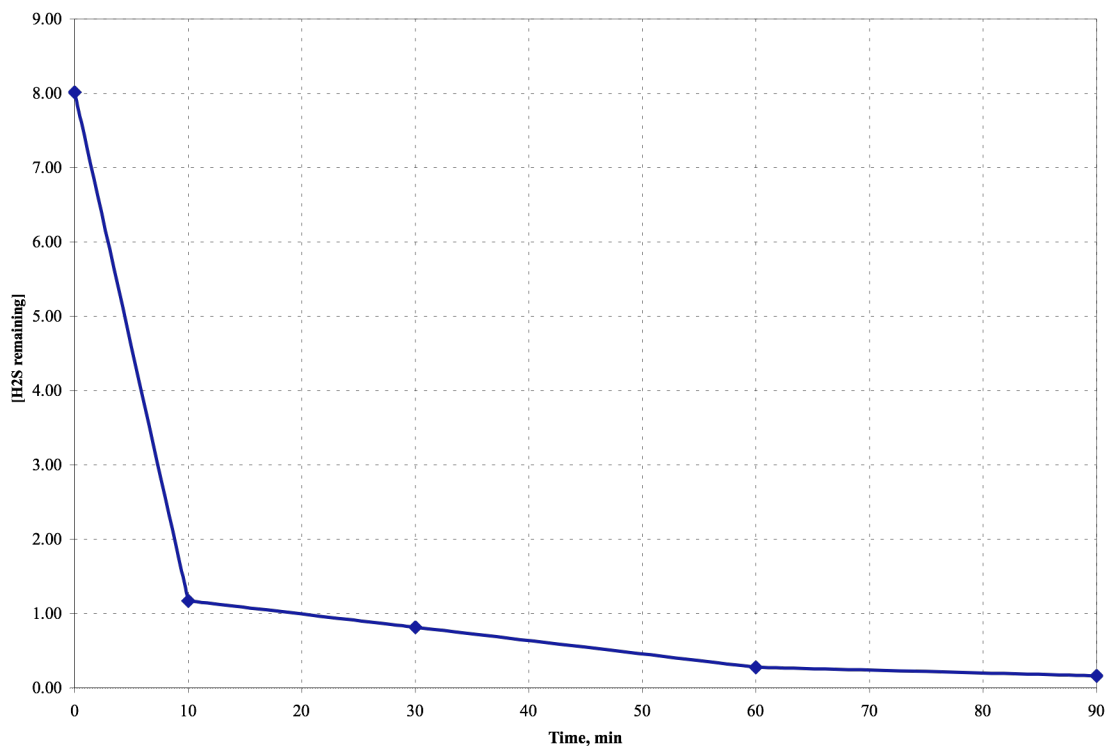


Appendix A-31. Standard Curve for 10.00 kg FeCl₂/kgS Addition

Appendix A-32. Ion Selective Electrode Method Data for 10.00 kg FeCl₂/kgS Addition

Date: 2/4/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 10.00 kgFeCl₂/kgS
 H₂S Initial Concentration: 8.01 mg/L
 Initial pH: 12.40
 pH after HCl addition: 7.00

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-741.4	2.01734104	7.52	8.01	12.5
	b		-742.9	2.141205615	8.51		12.5
2	a	10	-719.0	0.167630058	1.18	1.17	12.5
	b		-718.8	0.151114781	1.16		12.5
3	a	30	-714.9	-0.170933113	0.84	0.82	12.5
	b		-714.1	-0.23699422	0.79		12.5
4	a	60	-701.0	-1.318744839	0.27	0.28	12.5
	b		-701.8	-1.252683732	0.29		12.5
5	a	90	-695.0	-1.814203138	0.16	0.17	12.5
	b		-695.4	-1.781172585	0.17		12.5
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix A-33. H₂S remaining after 10.00 kg FeCl₂/kgS Addition

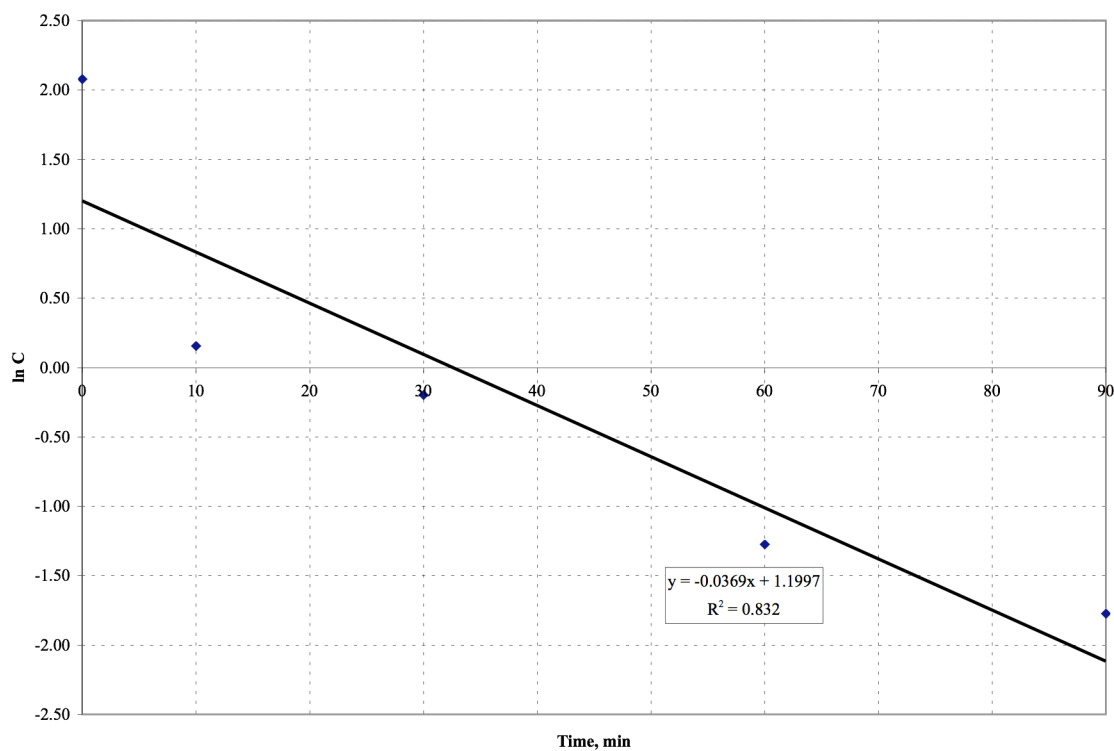
Appendix A-34. Linear Regression Analysis corresponding to 10.00 FeCl₂/kgS – pH = 7.00

Date: 2/4/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 10.00 kgFeCl₂/kgS

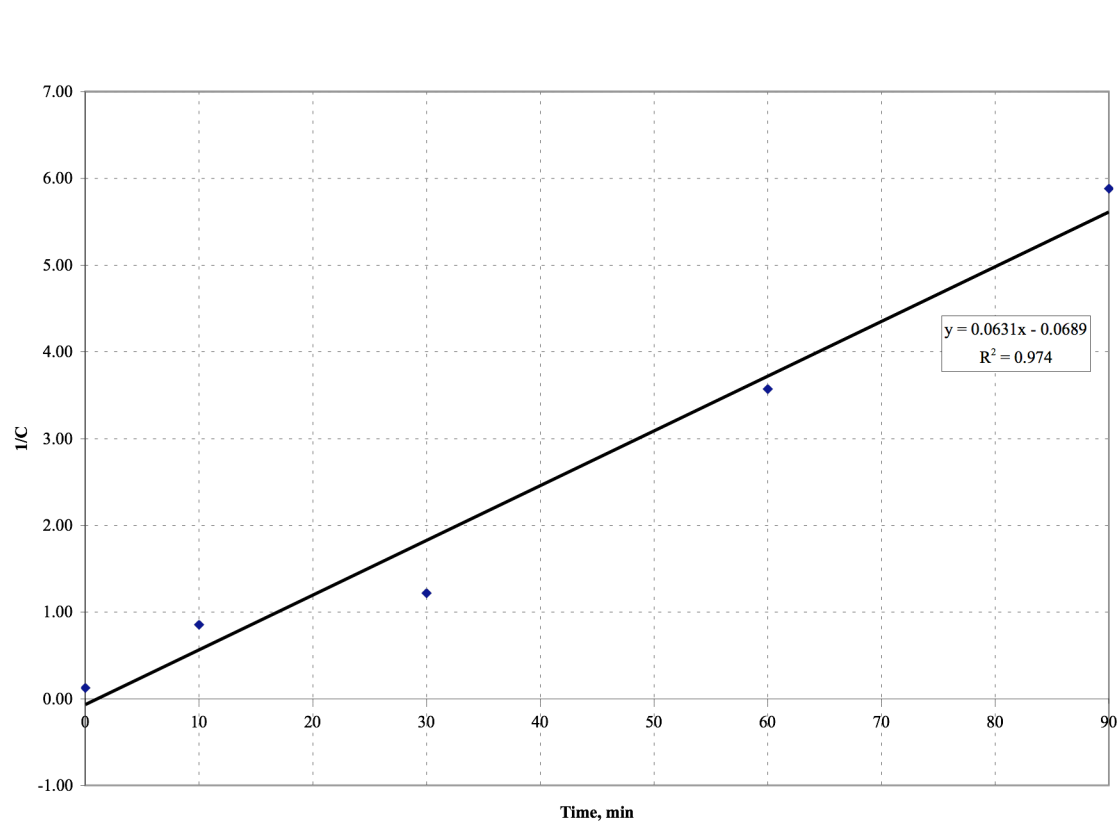
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.01	2.08069	0.12484	0.01559	0.00195	0.00024	0.00003	0.00000	0.00000
10	1.17	0.15700	0.85470	0.73051	0.62437	0.53365	0.45611	0.38984	0.33320
30	0.82	-0.19845	1.21951	1.48721	1.81367	2.21179	2.69731	3.28940	4.01147
60	0.28	-1.27297	3.57143	12.75510	45.55394	162.69263	581.04510	2075.16107	7411.28954
90	0.17	-1.77196	5.88235	34.60208	203.54162	1197.30367	7042.96278	41429.19281	243701.13416

$$t_{1/2} = \frac{1}{k[C_o]}$$

k= 0.0631 Lmg⁻¹min⁻¹
C_o= 8.01 mg/L
t_{1/2}= 1.98 min



Appendix A-35. Test of First-Order Kinetics corresponding to 10.00 kg FeCl₂/kgS



Appendix A-36. Test of Second-Order Kinetics corresponding to 10.00 kg FeCl_2/kgS

APPENDIX B

Appendix B-1. Additional Results Summary - Ion Selective Electrode Method - FeCl₂ Addition

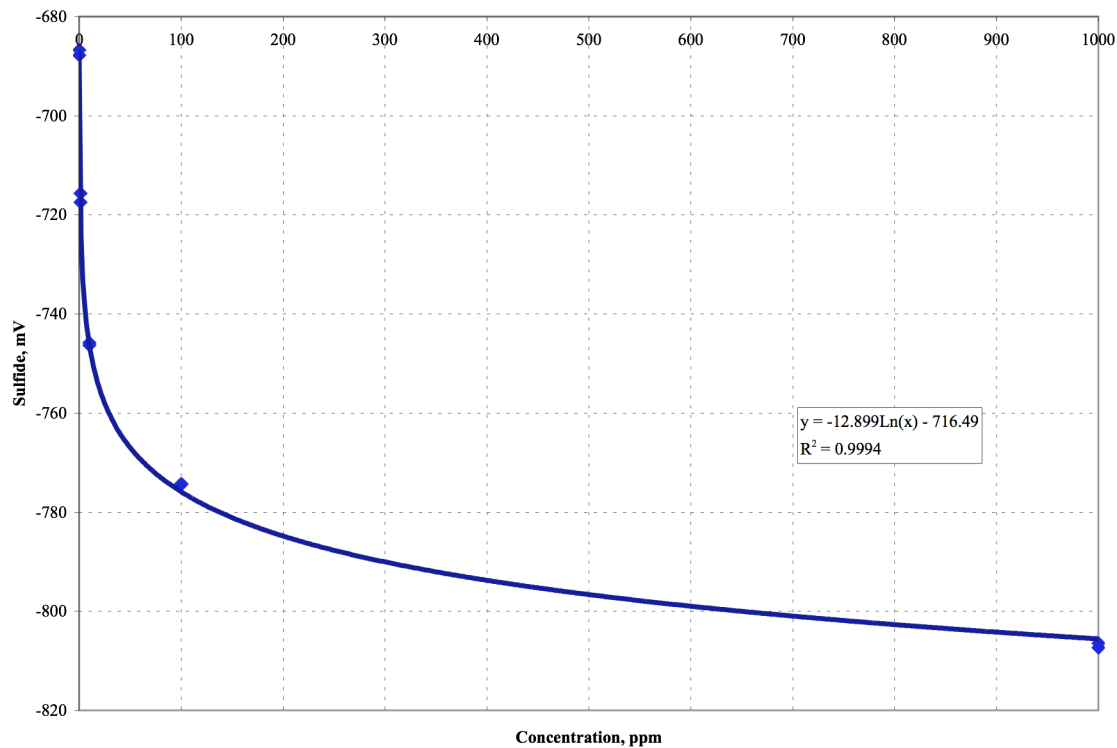
Time, min	FeCl ₂ Concentration, kgFeCl ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	1.45	9.55	100.00	0.00
10	1.45	8.44	88.38	11.62
30	1.45	7.82	81.88	18.12
60	1.45	7.06	73.93	26.07
90	1.45	6.38	66.81	33.19
0	2.90	6.15	100.00	0.00
10	2.90	3.71	60.33	39.67
30	2.90	3.34	54.31	45.69
40	2.90	3.15	51.22	48.78
60	2.90	2.86	46.50	53.50
90	2.90	2.62	42.60	57.40
0	2.90	8.05	100.00	0.00
10	2.90	4.83	60.00	40.00
30	2.90	4.50	55.90	44.10
60	2.90	4.38	54.41	45.59
90	2.90	3.34	41.49	58.51
0	3.70	7.43	100.00	0.00
10	3.70	3.42	46.03	53.97
30	3.70	2.74	36.88	63.12
60	3.70	1.76	23.69	76.31
90	3.70	1.64	22.07	77.93
0	5.00	5.39	100.00	0.00
10	5.00	2.15	39.89	60.11
20	5.00	1.78	33.02	66.98
30	5.00	1.77	32.84	67.16
40	5.00	1.68	31.17	68.83
60	5.00	1.55	28.76	71.24
90	5.00	0.65	12.06	87.94
0	5.00	7.43	100.00	0.00
10	5.00	2.63	35.40	64.60
30	5.00	2.26	30.42	69.58
60	5.00	1.52	20.46	79.54
90	5.00	0.85	11.44	88.56
0	10.0	8.44	100.00	0.00
10	10.0	0.97	11.49	88.51
30	10.0	0.57	6.75	93.25
60	10.0	0.09	1.07	98.93
90	10.0	0.04	0.47	99.53

Appendix B-2. Standard Curve Data for 1.45 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



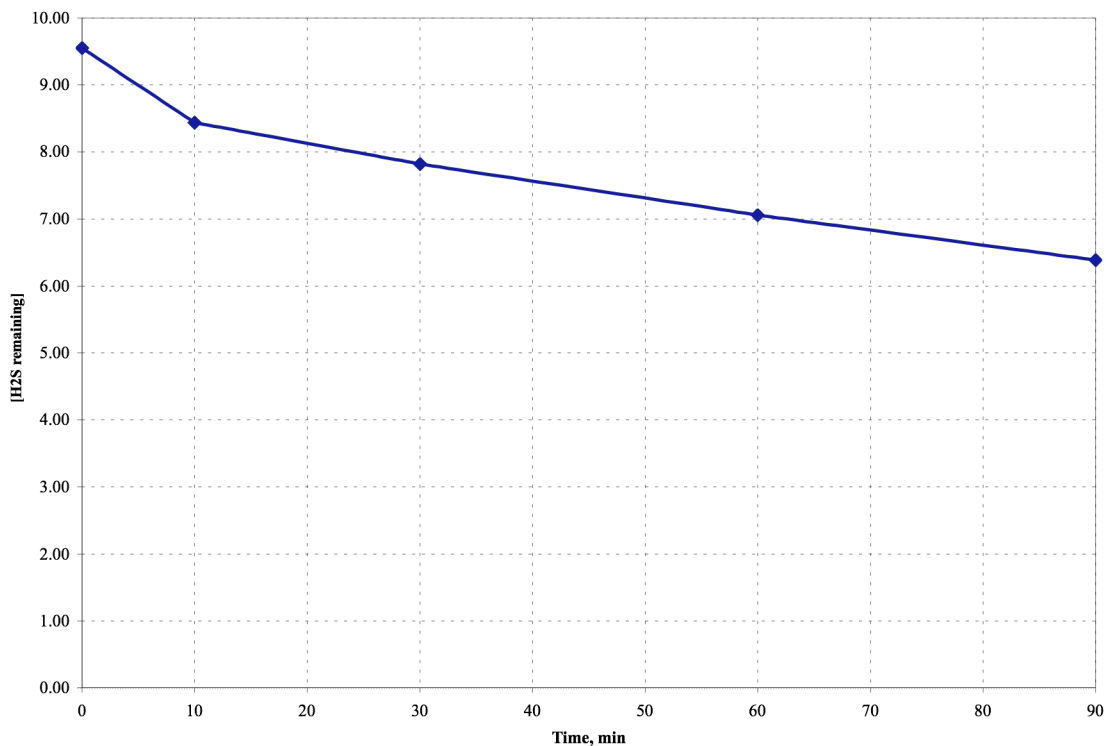
Appendix B-3. Standard Curve for 1.45 kg FeCl₂/kgS Addition

Appendix B-4. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS Addition

Date: 2/3/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂S Initial Concentration: 9.55 mg/L
 Initial pH: 12.30
 pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-745.5	2.249011551	9.48	9.55	13.4
	b		-745.7	2.264516629	9.63		13.4
2	a	10	-743.9	2.124970928	8.37	8.44	13.4
	b		-744.1	2.140476006	8.50		13.4
3	a	30	-742.2	1.993177766	7.34	7.82	13.4
	b		-743.8	2.117218389	8.31		13.4
4	a	60	-741.6	1.946662532	7.01	7.06	13.4
	b		-741.8	1.96216761	7.11		13.4
5	a	90	-740.2	1.838126987	6.28	6.38	13.4
	b		-740.6	1.869137142	6.48		13.4
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix B-5. H₂S remaining after 1.45 kg FeCl₂/kgS Addition

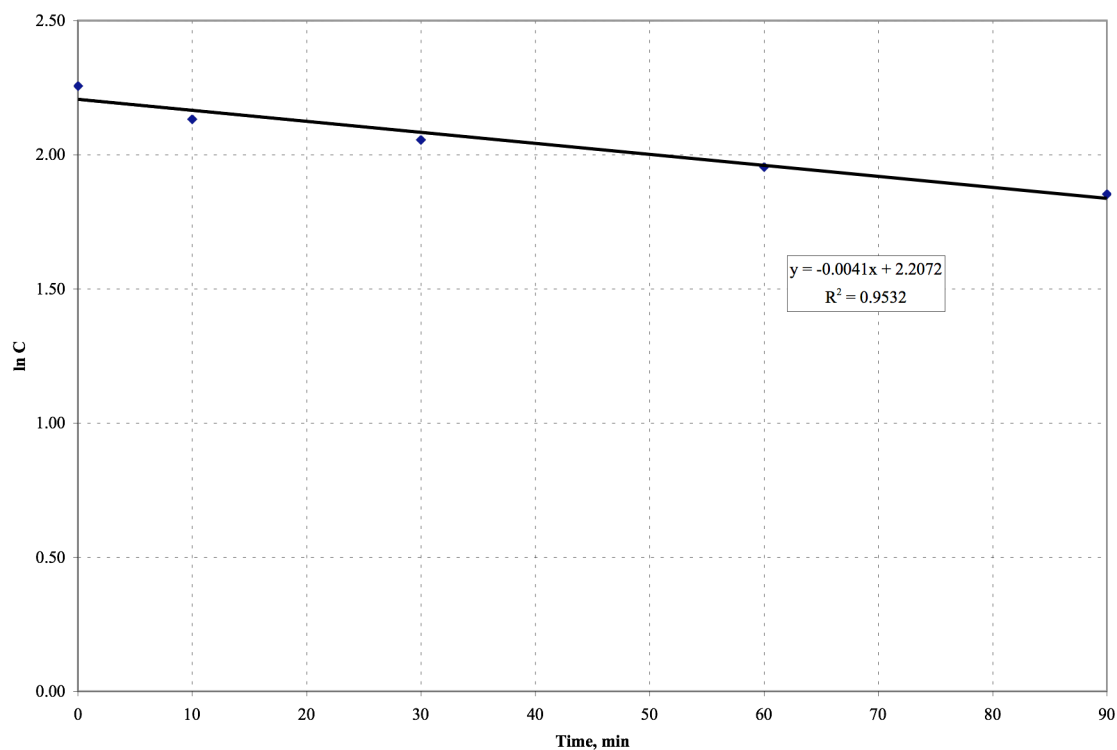
Appendix B-6. Linear Regression Analysis corresponding to 1.45 FeCl₂/kgS – pH = 7.80

Date: 2/3/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS

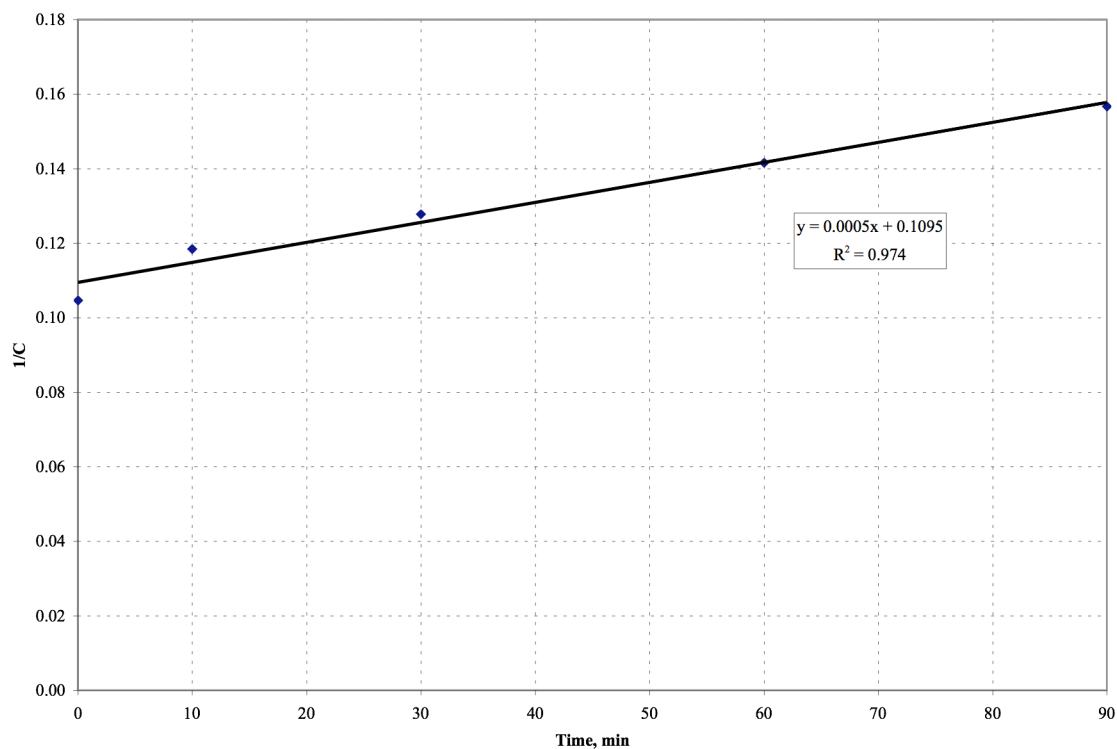
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	9.55	2.2565412	0.1047120	0.0109646	0.0011481	0.0001202	0.0000126	0.0000013	0.0000001
10	8.44	2.1329823	0.1184834	0.0140383	0.0016633	0.0001971	0.0000234	0.0000028	0.0000003
30	7.82	2.0566846	0.1278772	0.0163526	0.0020911	0.0002674	0.0000342	0.0000044	0.0000006
60	7.06	1.9544451	0.1416431	0.0200628	0.0028418	0.0004025	0.0000570	0.0000081	0.0000011
90	6.38	1.8531681	0.1567398	0.0245674	0.0038507	0.0006036	0.0000946	0.0000148	0.0000023

$$t_{1/2} = \frac{1}{k[C_0]}$$

k = 0.0005 Lmg⁻¹min⁻¹
 C₀ = 9.55 mg/L
 t_{1/2} = 209.42 min



Appendix B-7. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS

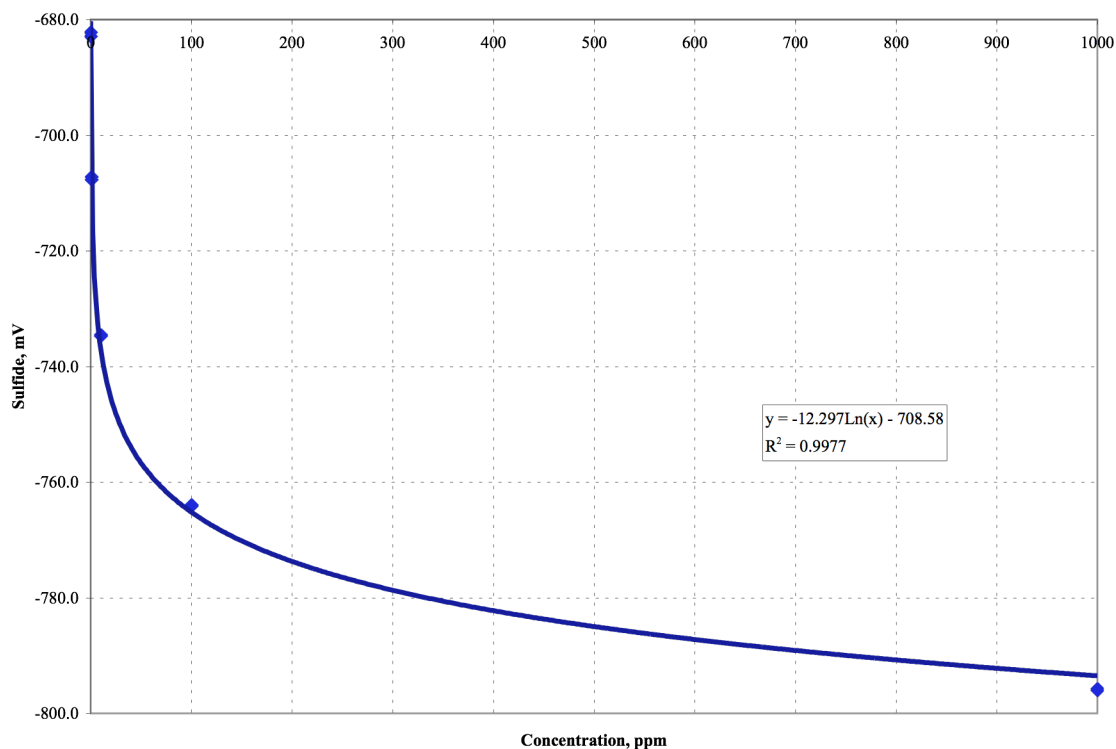


Appendix B-8. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS

Appendix B-9. Standard Curve Data for 2.90 kg FeCl₂/kgS Addition

Date: 8/3/06
Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S2-	Sulfide, mV	pH	Temperature, °C
1	a	1000	-796.0	12.6	14.0
	b	1000	-795.7	12.6	14.0
2	a	100	-764.1	12.6	14.0
	b	100	-763.9	12.6	14.0
3	a	10	-734.7	12.6	14.0
	b	10	-734.5	12.6	14.0
4	a	1	-707.7	12.6	14.0
	b	1	-707.2	12.6	14.0
5	a	0.1	-682.9	12.6	14.0
	b	0.1	-682.2	12.6	14.0

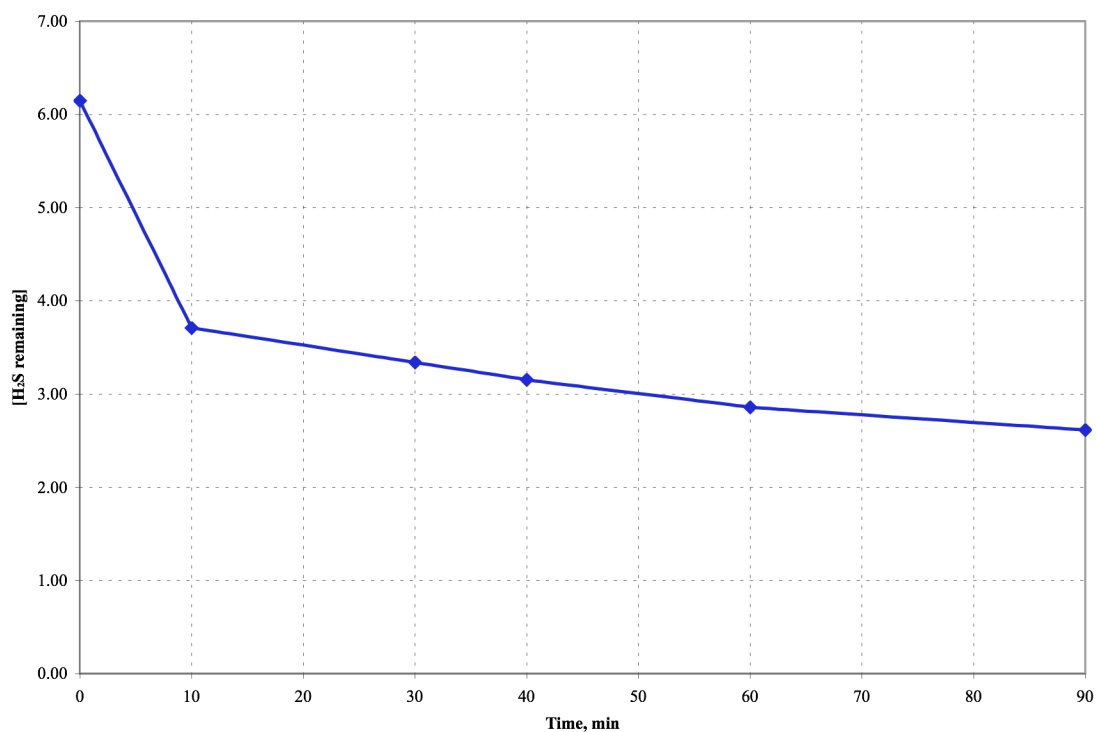


Appendix B-10. Standard Curve Data for 2.90 kg FeCl₂/kgS Addition

Appendix B-11. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS Addition

Date: 8/3/06
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.9 kgFeCl₂/kgS
 H₂S Initial Concentration: 6.15 mg/L
 Initial pH: 12.80
 pH after HCl addition: 7.20

Analysis	Replicates	Time, min	Concentration, mg/L, S ²⁻				pH after buffer addition	Temperature, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L		
1	a	0	-730.9	1.816110659	6.15	6.15	12.64	14.0
	b		-730.9	1.816110659	6.15		12.64	14.0
2	a	10	-724.6	1.303498779	3.68	3.71	12.63	14.0
	b		-724.8	1.319772172	3.74		12.63	14.0
3	a	30	-723.4	1.205858421	3.34	3.34	12.71	14.0
	b		-723.4	1.205858421	3.34		12.71	14.0
4	a	40	-722.7	1.148901546	3.15	3.15	12.68	14.0
	b		-722.7	1.148901546	3.15		12.67	14.0
5	a	60	-721.5	1.051261188	2.86	2.86	12.70	14.0
	b		-721.5	1.051261188	2.86		12.70	14.0
6	a	90	-720.4	0.961757526	2.62	2.62	12.62	14.0
	b		-720.4	0.961757526	2.62		12.62	14.0
7	a							
	b							
8	a							
	b							
9	a							
	b							
10	a							
	b							



Appendix B-12. H₂S remaining after 2.90 kg FeCl₂/kgS Addition

Appendix B-13. Linear Regression Analysis corresponding to 2.90 FeCl₂/kgS – pH = 7.20

Date: 8/3/06
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 2.90 kgFeCl₂/kgS

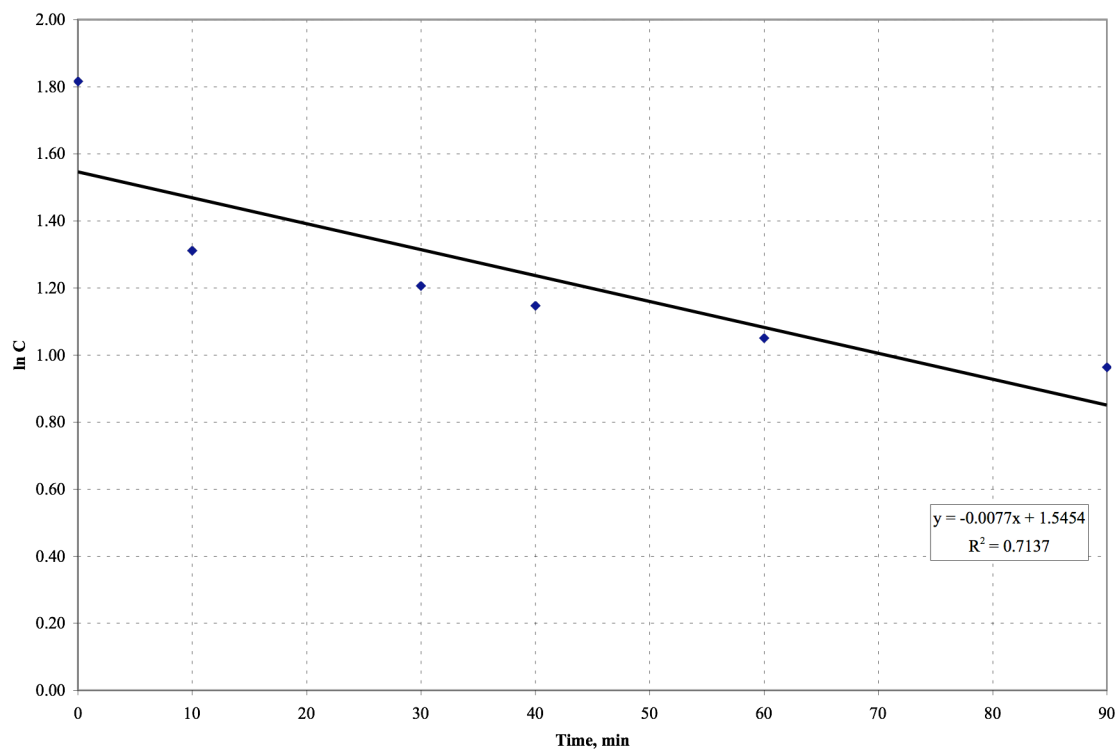
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.15	1.8164521	0.1626016	0.0264393	0.0042991	0.0006990	0.0001137	0.0000185	0.0000030
10	3.71	1.3110319	0.2695418	0.0726528	0.0195830	0.0052784	0.0014228	0.0003835	0.0001034
30	3.34	1.2059708	0.2994012	0.0896411	0.0268386	0.0080355	0.0024058	0.0007203	0.0002157
40	3.15	1.1474025	0.3174603	0.1007811	0.0319940	0.0101568	0.0032244	0.0010236	0.0003250
60	2.86	1.0508216	0.3496503	0.1222554	0.0427466	0.0149464	0.0052260	0.0018273	0.0006389
90	2.62	0.9631743	0.3816794	0.1456792	0.0556027	0.0212224	0.0081002	0.0030917	0.0011800

$$t_{1/2} = \frac{1}{k[C_0]}$$

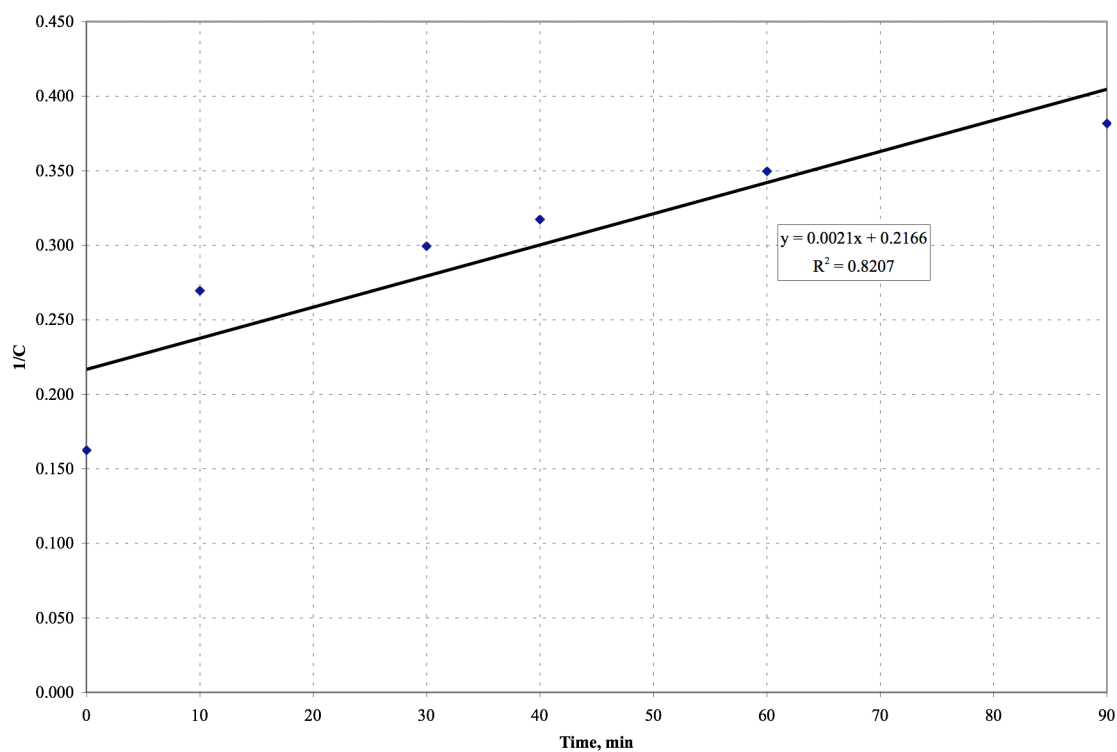
$$k = 0.0021 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_0 = 6.15 \text{ mg/L}$$

$$t_{1/2} = 77.43 \text{ min}$$



Appendix B-14. Test of First-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS



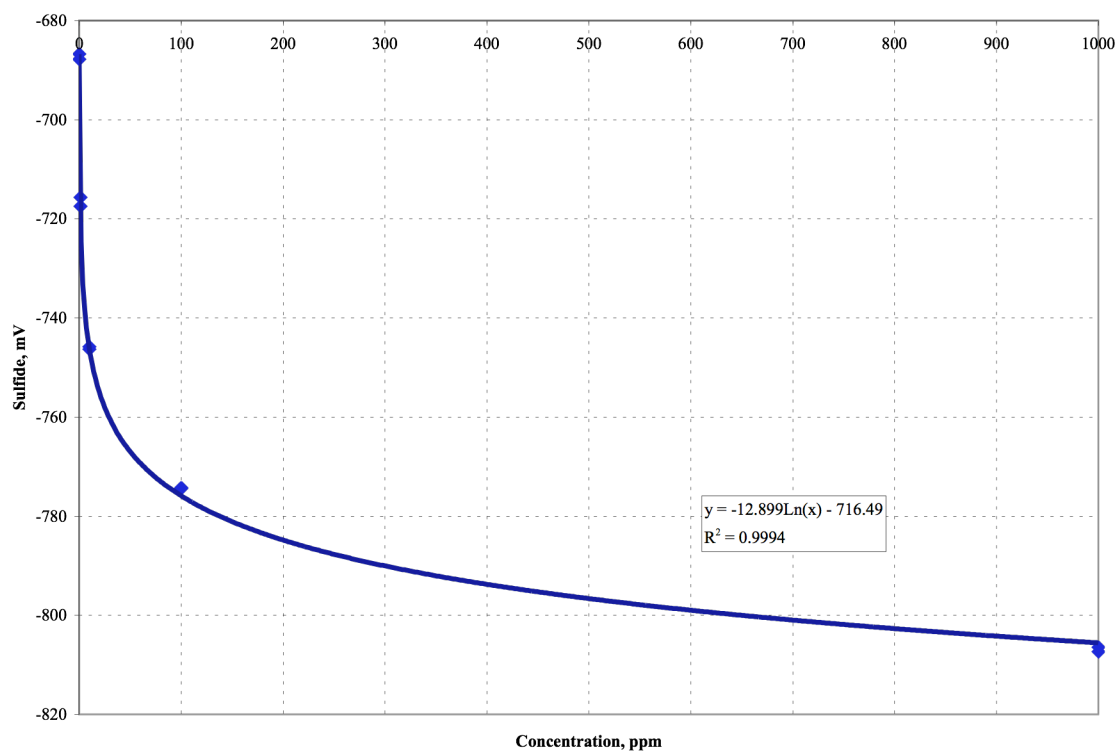
Appendix B-15. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS

Appendix B-16. Standard Curve Data for 2.90 kg FeCl₂/kgS Addition

Date: 2/3/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



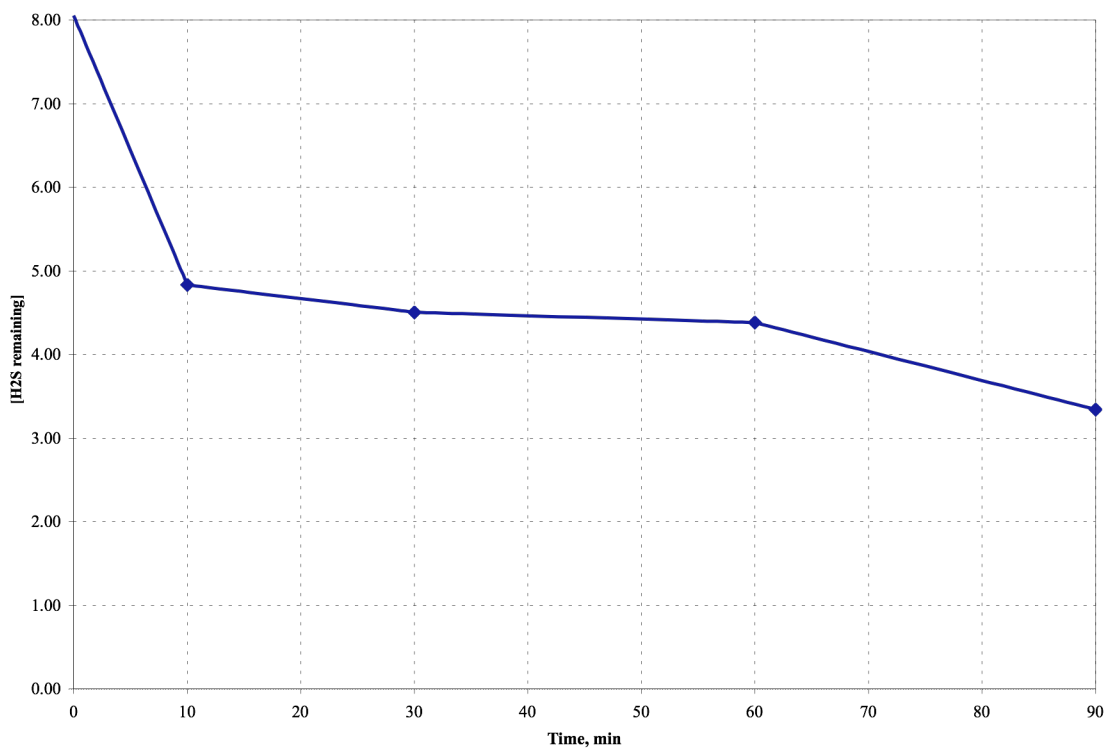
Appendix B-17. Standard Curve for 2.90 kg FeCl₂/kgS Addition

Appendix B-18. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS Addition

Date: 2/3/07
Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
H₂S Initial Concentration: 8.05 mg/L
Initial pH: 12.30
pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-743.4	2.086208233	8.05	8.05	12.7
	b		-743.4	2.086208233	8.05		12.7
2	a	10	-736.4	1.543530506	4.68	4.83	12.7
	b		-737.2	1.605550818	4.98		12.7
3	a	30	-736.1	1.520272889	4.57	4.50	12.7
	b		-735.7	1.489262734	4.43		12.7
4	a	60	-735.7	1.489262734	4.43	4.38	12.7
	b		-735.4	1.466005117	4.33		12.7
5	a	90	-731.7	1.179161175	3.25	3.34	12.7
	b		-732.4	1.233428948	3.43		12.7
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix B-19. H₂S remaining after 2.90 kg FeCl₂/kgS Addition

Appendix B-20. Linear Regression Analysis corresponding to 2.90 FeCl₂/kgS – pH = 7.80

Date: 2/3/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS

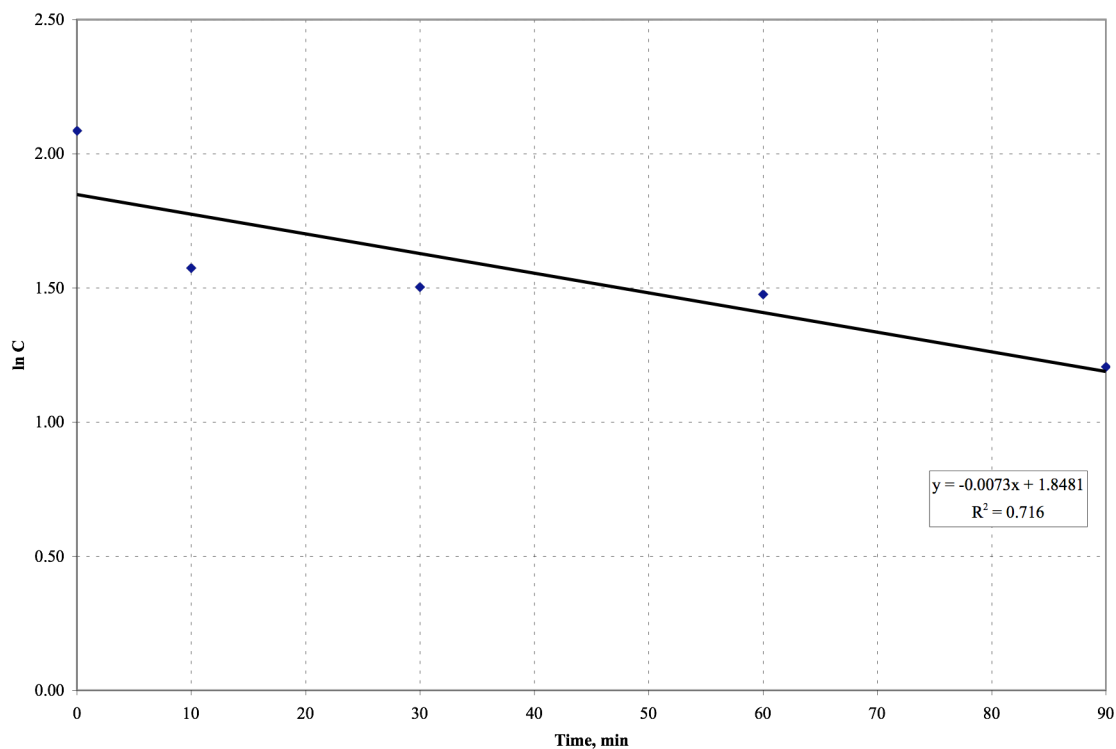
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.05	2.0856721	0.1242236	0.0154315	0.0019170	0.0002381	0.0000296	0.0000037	0.0000005
10	4.83	1.5748465	0.2070393	0.0428653	0.0088748	0.0018374	0.0003804	0.0000788	0.0000163
30	4.50	1.5040774	0.2222222	0.0493827	0.0109739	0.0024387	0.0005419	0.0001204	0.0000268
60	4.38	1.4770487	0.2283105	0.0521257	0.0119008	0.0027171	0.0006203	0.0001416	0.0000323
90	3.34	1.2059708	0.2994012	0.0896411	0.0268386	0.0080355	0.0024058	0.0007203	0.0002157

$$t_{1/2} = \frac{1}{k[C_0]}$$

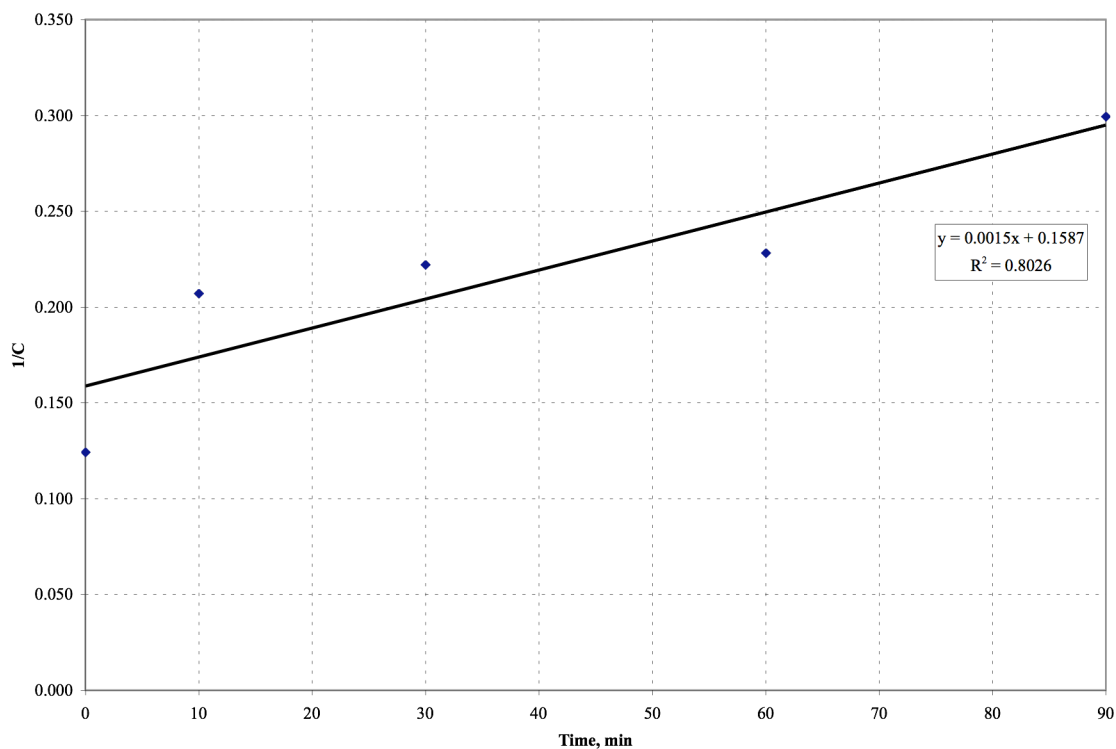
$$k = 0.0015 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_0 = 8.05 \text{ mg/L}$$

$$t_{1/2} = 82.82 \text{ min}$$



Appendix B-21. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS

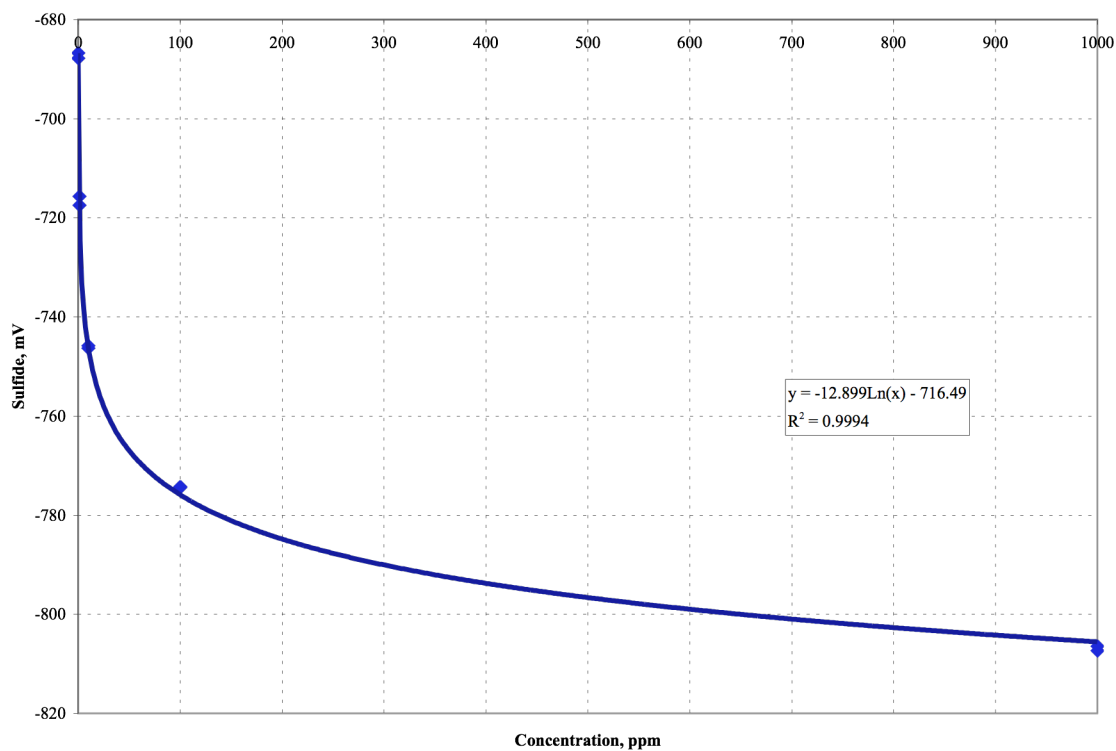


Appendix B-22. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS

Appendix B-23. Standard Curve Data for 3.70 kg FeCl₂/kgS Addition

Date: 2/3/07
Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-806.4	12.3	18.4
	b	1000	-807.3	12.3	18.4
2	a	100	-774.2	12.3	18.4
	b	100	-774.4	12.3	18.4
3	a	10	-746.3	12.3	18.4
	b	10	-745.8	12.3	18.4
4	a	1	-717.4	12.3	18.4
	b	1	-715.6	12.3	18.4
5	a	0.1	-687.8	12.3	18.4
	b	0.1	-686.7	12.3	18.4



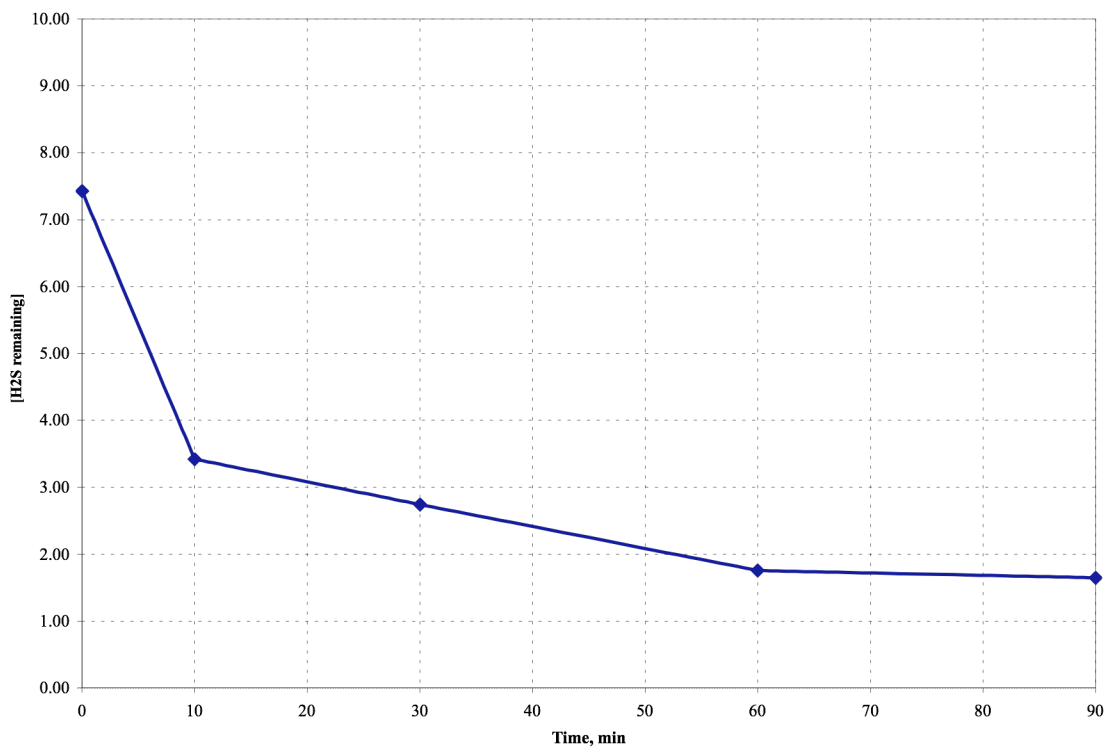
Appendix B-24. Standard Curve for 3.70 kg FeCl₂/kgS Addition

Appendix B-25. Ion Selective Electrode Method Data for 3.70 kg FeCl₂/kgS Addition

Date: 2/4/07
Method: Ion Selective Electrode Method

FeCl₂ Concentration: 3.70 kgFeCl₂/kgS
H₂S Initial Concentration: 7.43 mg/L
Initial pH: 12.30
pH after HCl addition: 6.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-742.0	1.977672688	7.23	7.43	12.8
	b		-742.7	2.031940461	7.63		12.8
2	a	10	-732.6	1.248934026	3.49	3.42	12.8
	b		-732.1	1.210171331	3.35		12.8
3	a	30	-729.0	0.969842623	2.64	2.74	12.8
	b		-730.0	1.047368013	2.85		12.8
4	a	60	-723.6	0.55120552	1.74	1.76	12.8
	b		-723.9	0.574463137	1.78		12.8
5	a	90	-722.5	0.465927591	1.59	1.64	12.8
	b		-723.3	0.527947903	1.70		12.8
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix B-26. H₂S remaining after 3.70 kg FeCl₂/kgS Addition

Appendix B-27. Linear Regression Analysis corresponding to 3.70 FeCl₂/kgS – pH = 6.80

Date: 2/4/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 3.70 kgFeCl₂/kgS

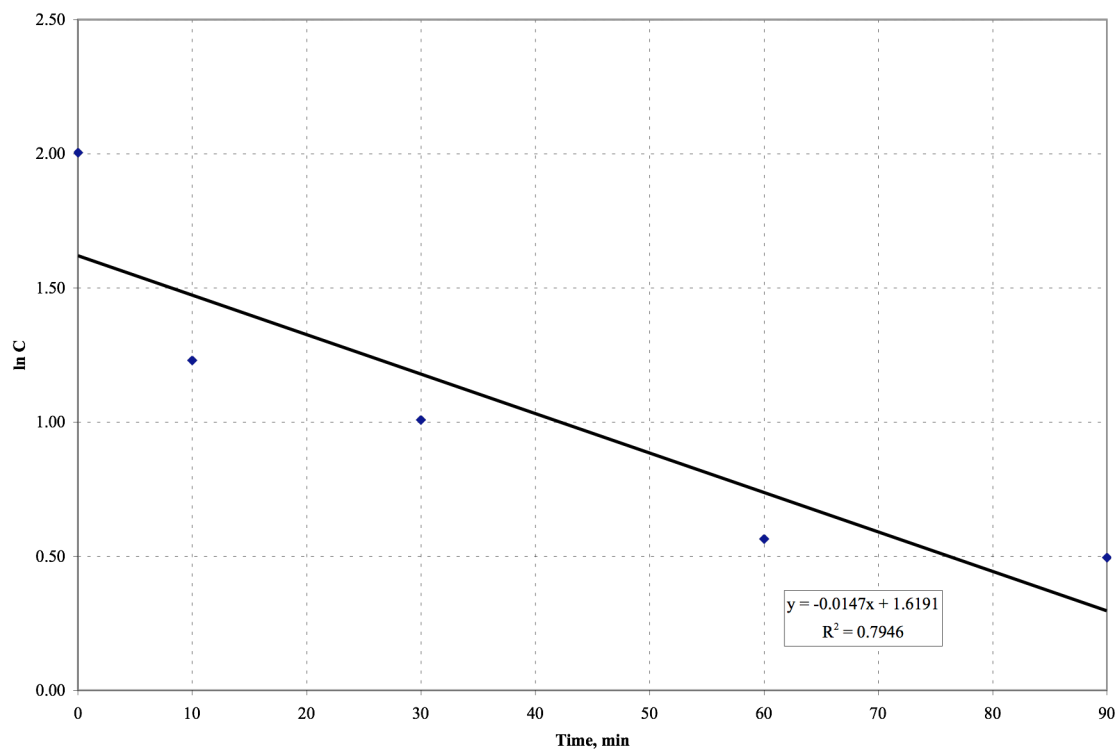
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.43	2.0055259	0.1345895	0.0181143	0.0024380	0.0003281	0.0000442	0.0000059	0.0000008
10	3.42	1.2296406	0.2923977	0.0854964	0.0249989	0.0073096	0.0021373	0.0006249	0.0001827
30	2.74	1.0079579	0.3649635	0.1331984	0.0486125	0.0177418	0.0064751	0.0023632	0.0008625
60	1.76	0.5653138	0.5681818	0.3228306	0.1834265	0.1042196	0.0592157	0.0336453	0.0191166
90	1.64	0.4946962	0.6097561	0.3718025	0.2267088	0.1382371	0.0842909	0.0513969	0.0313396

$$t_{1/2} = \frac{1}{k[C_o]}$$

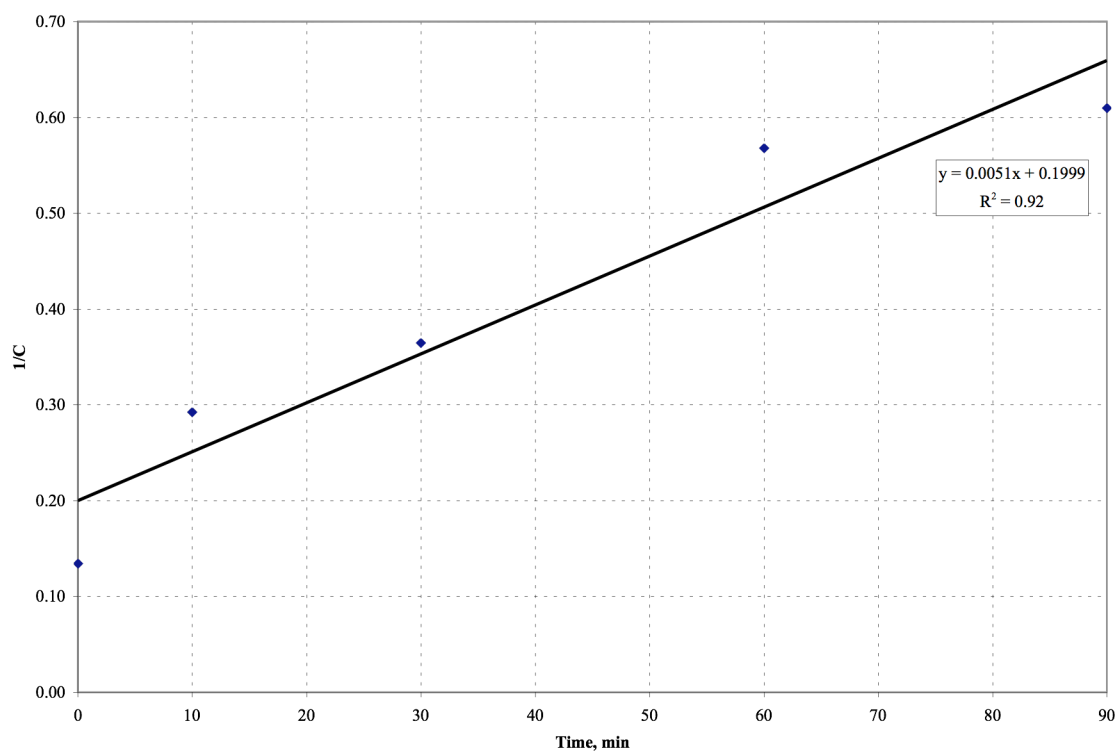
$$k = 0.0051 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_o = 7.43 \text{ mg/L}$$

$$t_{1/2} = 26.39 \text{ min}$$



Appendix B-28. Test of First-Order Kinetics corresponding to 3.70 kg FeCl_2/kgS



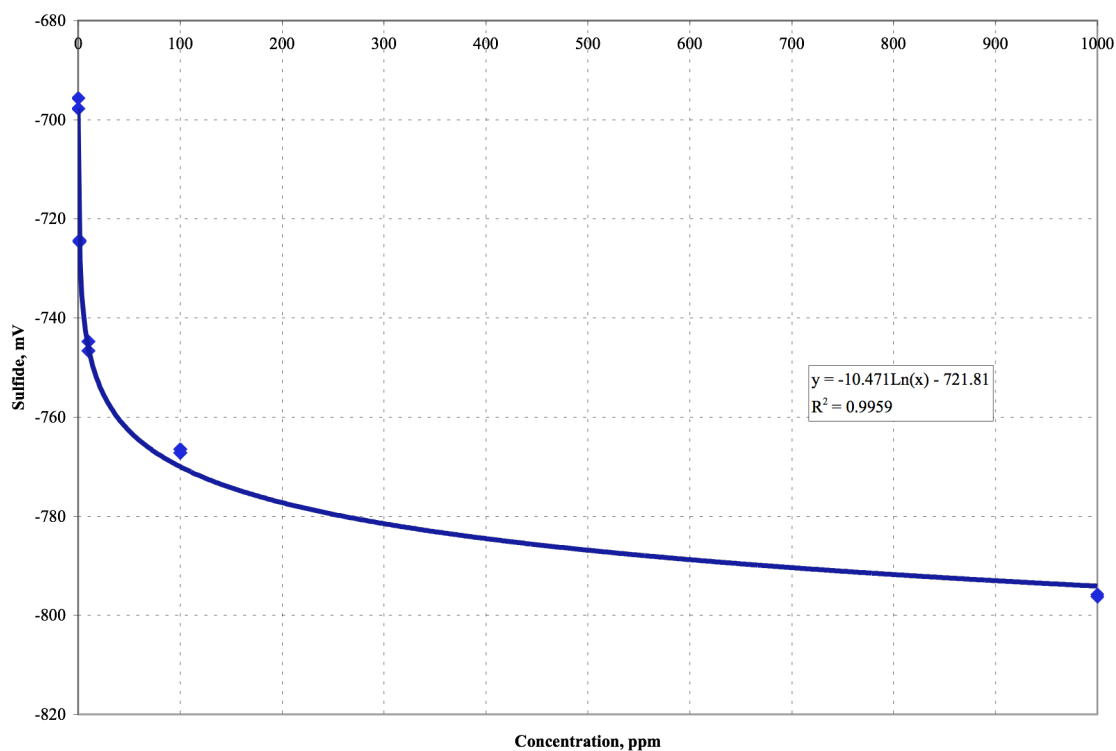
Appendix B-29. Test of Second-Order Kinetics corresponding to 3.70 kg FeCl_2/kgS

Appendix B-30. Standard Curve Data for 5.00 kg FeCl₂/kgS Addition

Date: 12/19/06

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-796.2	12.6	13.5
	b	1000	-795.8	12.6	13.5
2	a	100	-766.5	12.6	13.5
	b	100	-767.2	12.6	13.5
3	a	10	-744.7	12.6	13.5
	b	10	-746.6	12.6	13.5
4	a	1	-724.3	12.6	13.5
	b	1	-724.6	12.6	13.5
5	a	0.1	-697.7	12.6	13.5
	b	0.1	-695.6	12.6	13.5



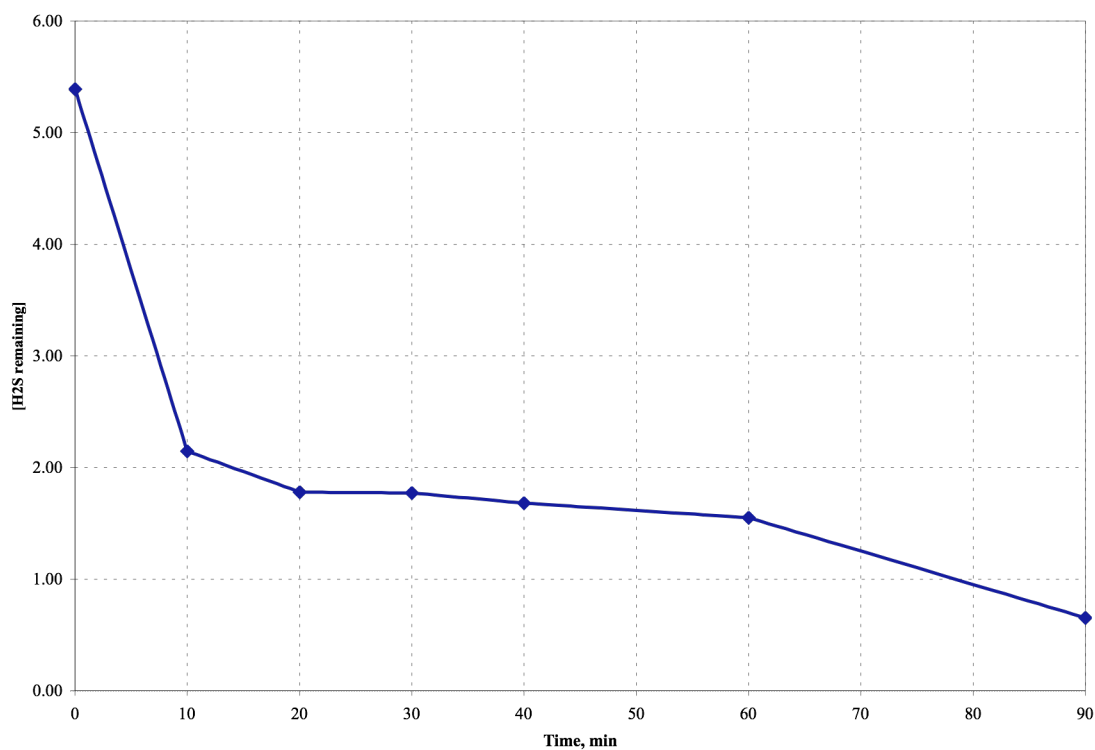
Appendix B-31. Standard Curve for 5.00 kg FeCl₂/kgS Addition

Appendix B-32. Ion Selective Electrode Method Data for 5.00 kg FeCl₂/kgS Addition

Date: 12/19/06
Method: Ion Selective Electrode Method

FeCl₂ Concentration: 5.00 kgFeCl₂/kgS
H₂S Initial Concentration: 5.39 mg/L
Initial pH: 12.00
pH after HCl addition: 7.71

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-739.6	1.69897813	5.47	5.39	12.5
	b		-739.3	1.670327571	5.31		12.5
2	a	10	-730.1	0.791710438	2.21	2.15	12.5
	b		-729.5	0.734409321	2.08		12.5
3	a	20	-727.9	0.581606341	1.79	1.78	12.5
	b		-727.8	0.572056155	1.77		12.5
4	a	30	-727.9	0.581606341	1.79	1.77	12.5
	b		-727.7	0.562505969	1.76		12.5
5	a	40	-727.4	0.53385541	1.71	1.68	12.5
	b		-727.1	0.505204851	1.66		12.5
6	a	60	-726.1	0.409702989	1.51	1.55	12.5
	b		-726.7	0.467004107	1.60		12.5
7	a	90	-724.6	0.266450196	1.31	0.65	12.5
	b		724.6	-138.1348486	0.00		12.5
8	a						
	b						
9	a						
	b						



Appendix B-33. H₂S remaining after 5.00 kg FeCl₂/kgS Addition

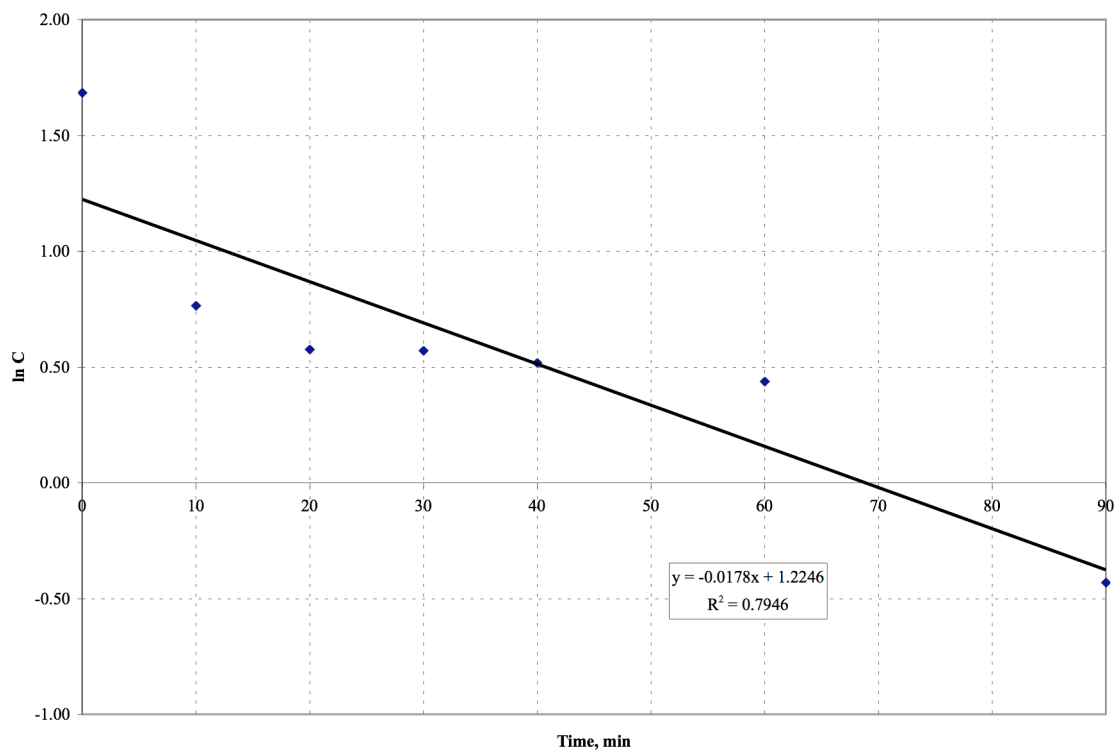
Appendix B-34. Linear Regression Analysis corresponding to 5.00 FeCl₂/kgS – pH = 7.71

Date: 12/19/06
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 5.00 kgFeCl₂/kgS

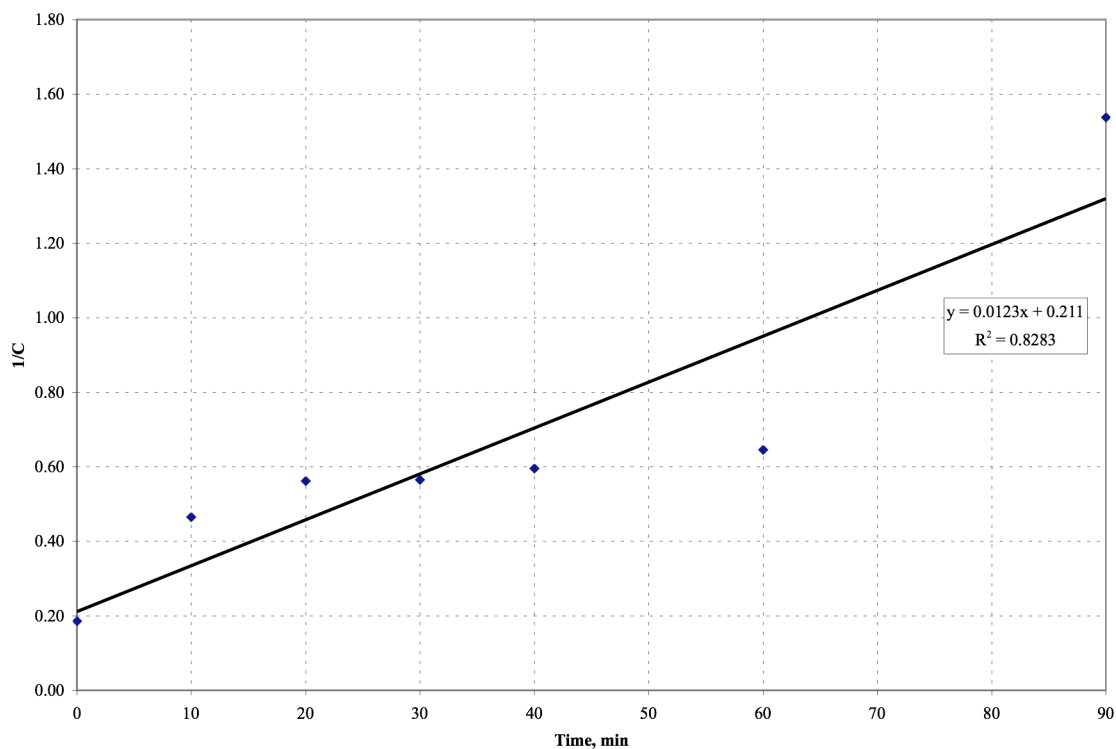
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	5.39	1.6845454	0.1855288	0.0344209	0.0063861	0.0011848	0.0002198	0.0000408	0.0000076
10	2.15	0.7654678	0.4651163	0.2163332	0.1006201	0.0468000	0.0217675	0.0101244	0.0047090
20	1.78	0.5766134	0.5617978	0.3156167	0.1773128	0.0996139	0.0559629	0.0314398	0.0176628
30	1.77	0.5709795	0.5649718	0.3191931	0.1803351	0.1018842	0.0575617	0.0325207	0.0183733
40	1.68	0.5187938	0.5952381	0.3543084	0.2108979	0.1255344	0.0747229	0.0444779	0.0264749
60	1.55	0.4382549	0.6451613	0.4162331	0.2685375	0.1732500	0.1117742	0.0721124	0.0465241
90	0.65	-0.4307829	1.5384615	2.3668639	3.6413291	5.6020447	8.6185304	13.2592775	20.3988885

$$t_{1/2} = \frac{1}{k[C_0]}$$

$k = 0.0123 \text{ Lmg}^{-1}\text{min}^{-1}$
 $C_0 = 5.39 \text{ mg/L}$
 $t_{1/2} = 15.08 \text{ min}$



Appendix B-35. Test of First-Order Kinetics corresponding to 5.00 kg FeCl₂/kgS



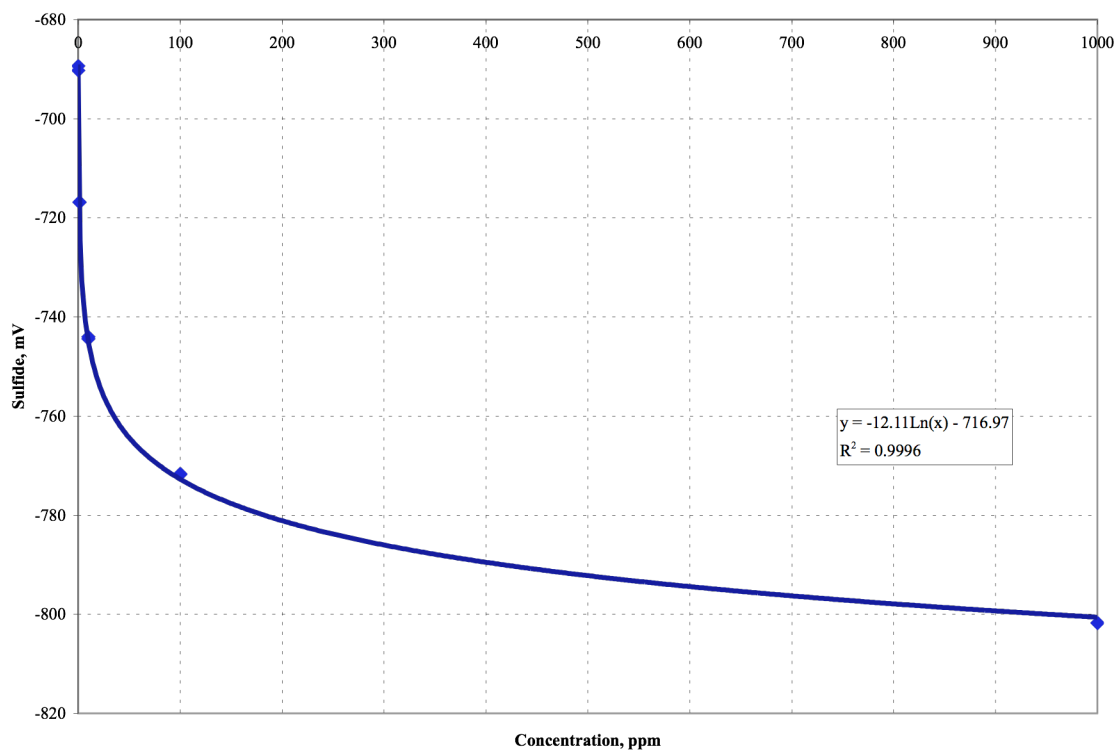
Appendix B-36. Test of Second-Order Kinetics corresponding to 5.00 kg FeCl_2/kgS

Appendix B-37. Standard Curve Data for 5.00 kg FeCl_2/kgS Addition

Date: 2/4/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S^{2-}	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.7	12.4	13.5
	b	1000	-801.8	12.4	13.5
2	a	100	-771.6	12.4	13.5
	b	100	-771.8	12.4	13.5
3	a	10	-744.4	12.4	13.5
	b	10	-744.0	12.4	13.5
4	a	1	-716.9	12.4	13.5
	b	1	-716.8	12.4	13.5
5	a	0.1	-690.2	12.4	13.5
	b	0.1	-689.3	12.4	13.5



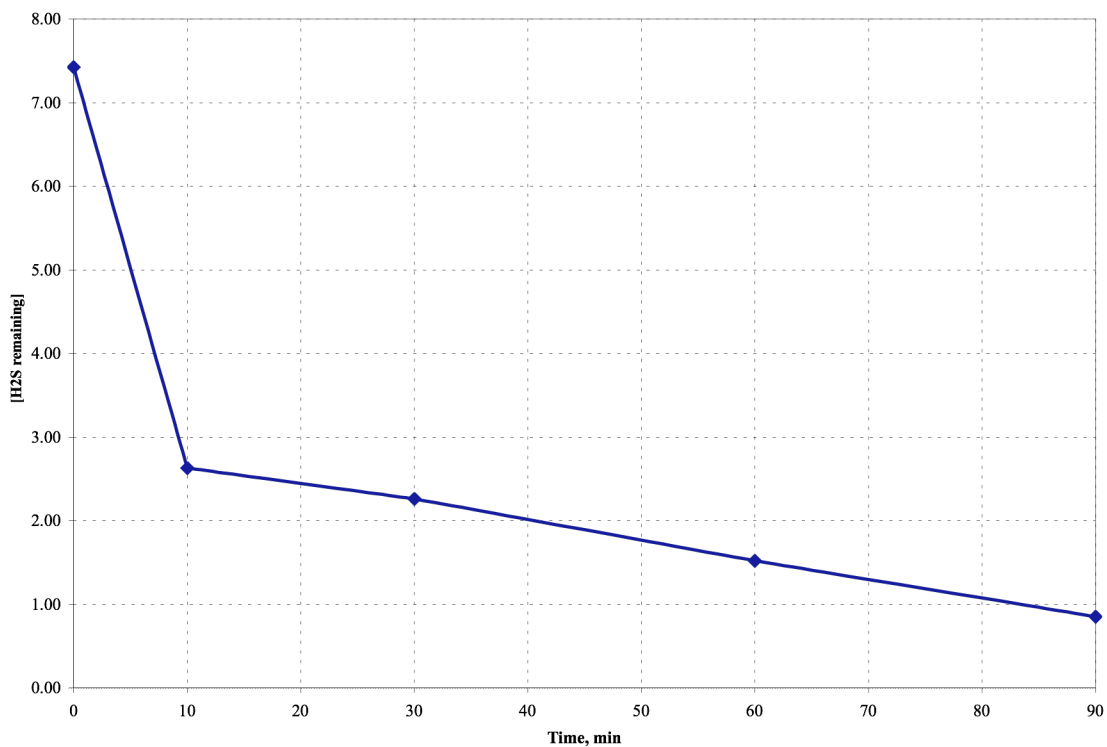
Appendix B-38. Standard Curve for 5.00 kg FeCl₂/kgS Addition

Appendix B-39. Ion Selective Electrode Method Data for 5.00 kg FeCl₂/kgS Addition

Date: 2/4/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 5.00 kgFeCl₂/kgS
 H₂S Initial Concentration: 7.43 mg/L
 Initial pH: 12.40
 pH after HCl addition: 7.00

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-741.2	2.000825764	7.40	7.43	13.0
	b		-741.3	2.009083402	7.46		13.0
2	a	10	-727.8	0.89430223	2.45	2.63	13.0
	b		-729.5	1.034682081	2.81		13.0
3	a	30	-726.8	0.811725846	2.25	2.26	13.0
	b		-726.9	0.819983485	2.27		13.0
4	a	60	-722.9	0.489677952	1.63	1.52	13.0
	b		-721.1	0.341040462	1.41		13.0
5	a	90	-713.3	-0.303055326	0.74	0.85	13.0
	b		-716.5	-0.0388109	0.96		13.0
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix B-40. H₂S remaining after 5.00 kg FeCl₂/kgS Addition

Appendix B-41. Linear Regression Analysis corresponding to 5.00 FeCl₂/kgS – pH = 7.00

Date: 2/4/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 5.00 kgFeCl₂/kgS

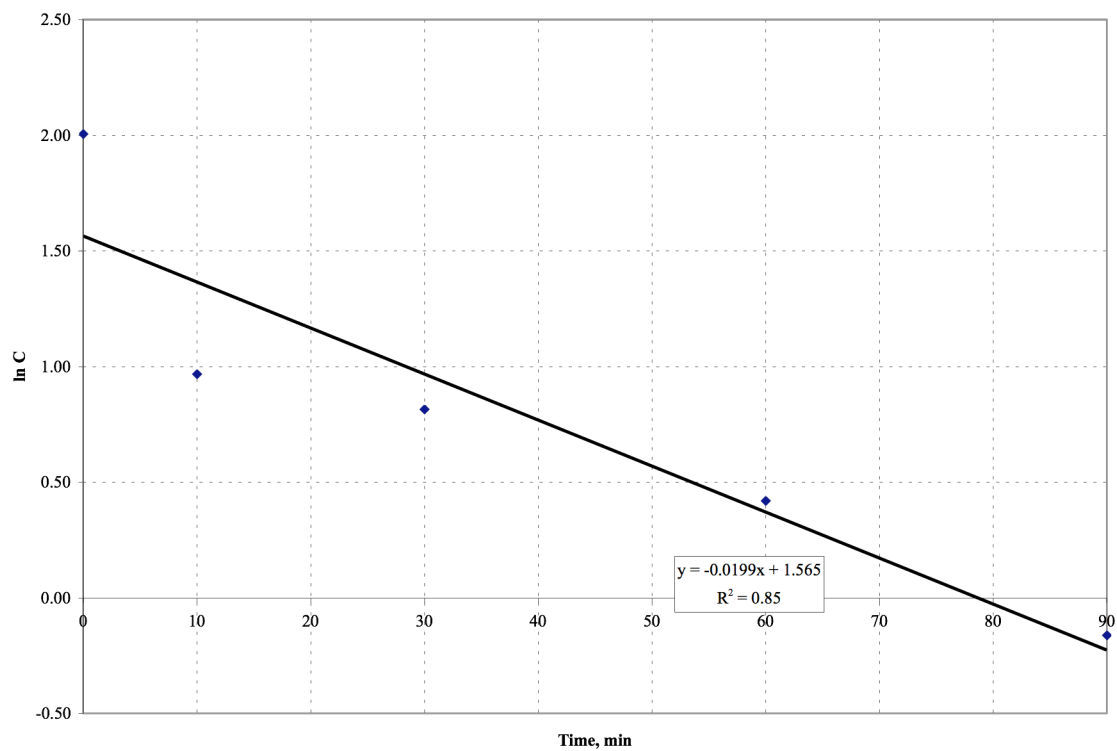
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.43	2.0055259	0.1345895	0.0181143	0.0024380	0.0003281	0.0000442	0.0000059	0.0000008
10	2.63	0.9669838	0.3802281	0.1445734	0.0549709	0.0209015	0.0079473	0.0030218	0.0011490
30	2.26	0.8153648	0.4424779	0.1957867	0.0866313	0.0383324	0.0169612	0.0075050	0.0033208
60	1.52	0.4187103	0.6578947	0.4328255	0.2847536	0.1873379	0.1232486	0.0810846	0.0533451
90	0.85	-0.1625189	1.1764706	1.3840830	1.6283330	1.9156859	2.2537481	2.6514683	3.1193745

$$t_{1/2} = \frac{1}{k[C_o]}$$

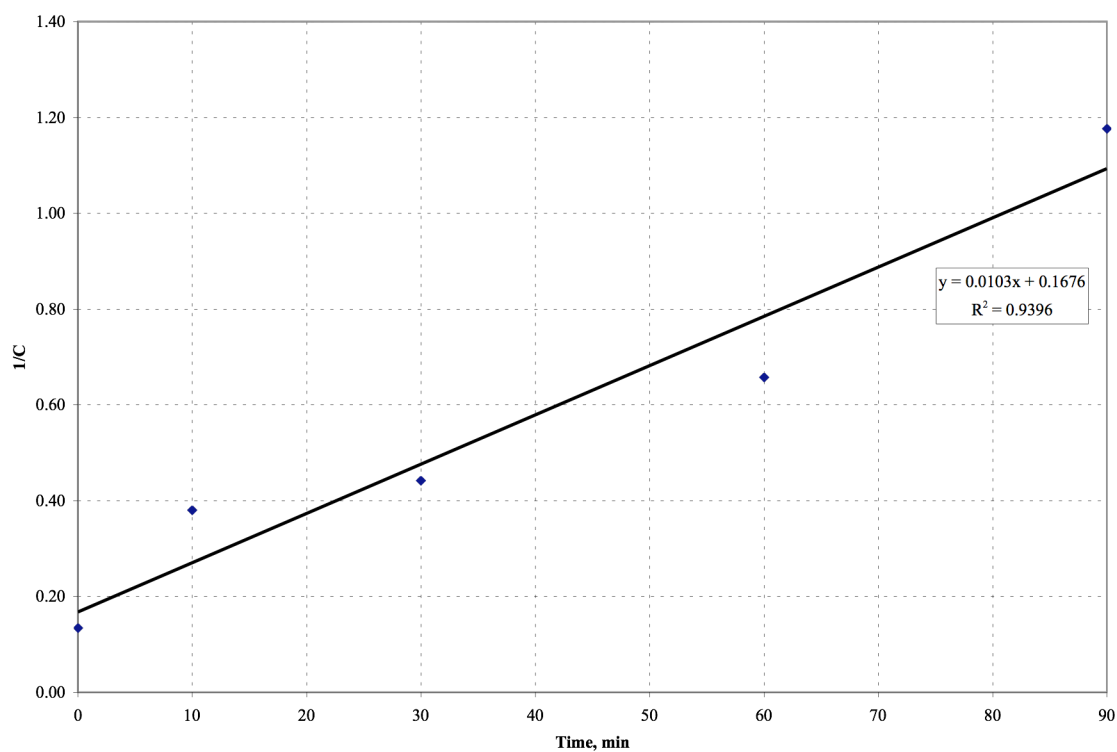
$$k = 0.0103 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_o = 7.43 \text{ mg/L}$$

$$t_{1/2} = 13.07 \text{ min}$$



Appendix B-42. Test of First-Order Kinetics corresponding to 5.00 kg FeCl_2/kgS



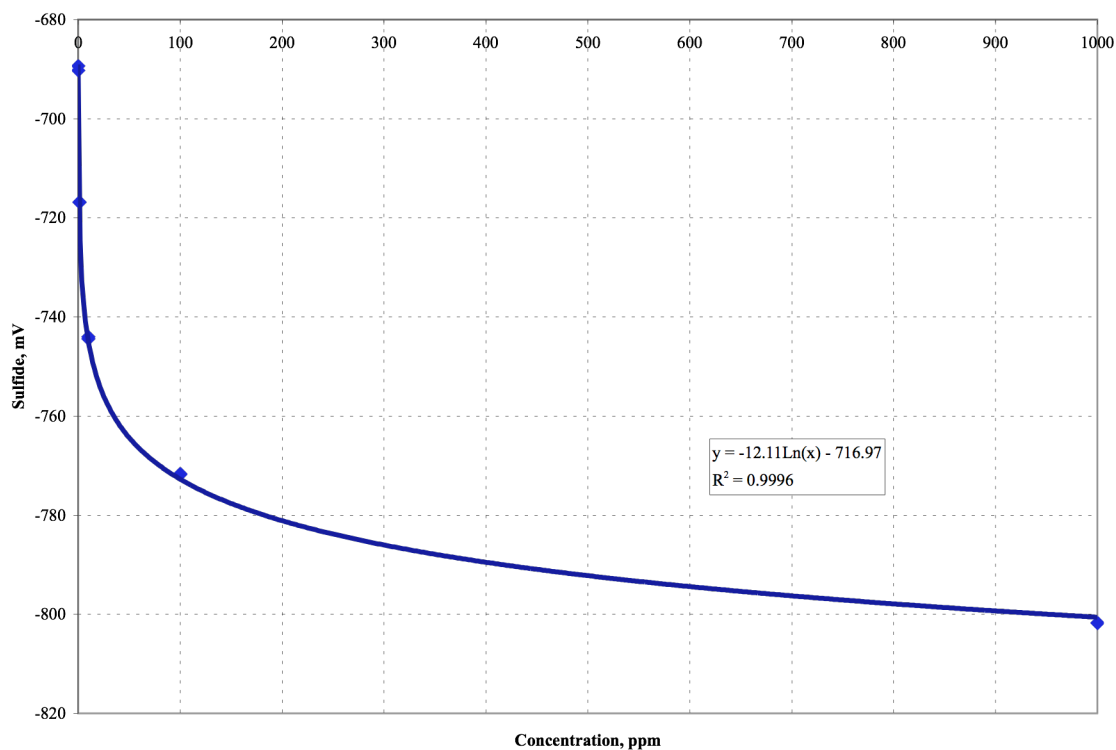
Appendix B-43. Test of Second-Order Kinetics corresponding to 5.00 kg FeCl_2/kgS

Appendix B-44. Standard Curve Data for 10.00 kg FeCl₂/kgS Addition

Date: 2/4/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.7	12.4	13.5
	b	1000	-801.8	12.4	13.5
2	a	100	-771.6	12.4	13.5
	b	100	-771.8	12.4	13.5
3	a	10	-744.4	12.4	13.5
	b	10	-744.0	12.4	13.5
4	a	1	-716.9	12.4	13.5
	b	1	-716.8	12.4	13.5
5	a	0.1	-690.2	12.4	13.5
	b	0.1	-689.3	12.4	13.5



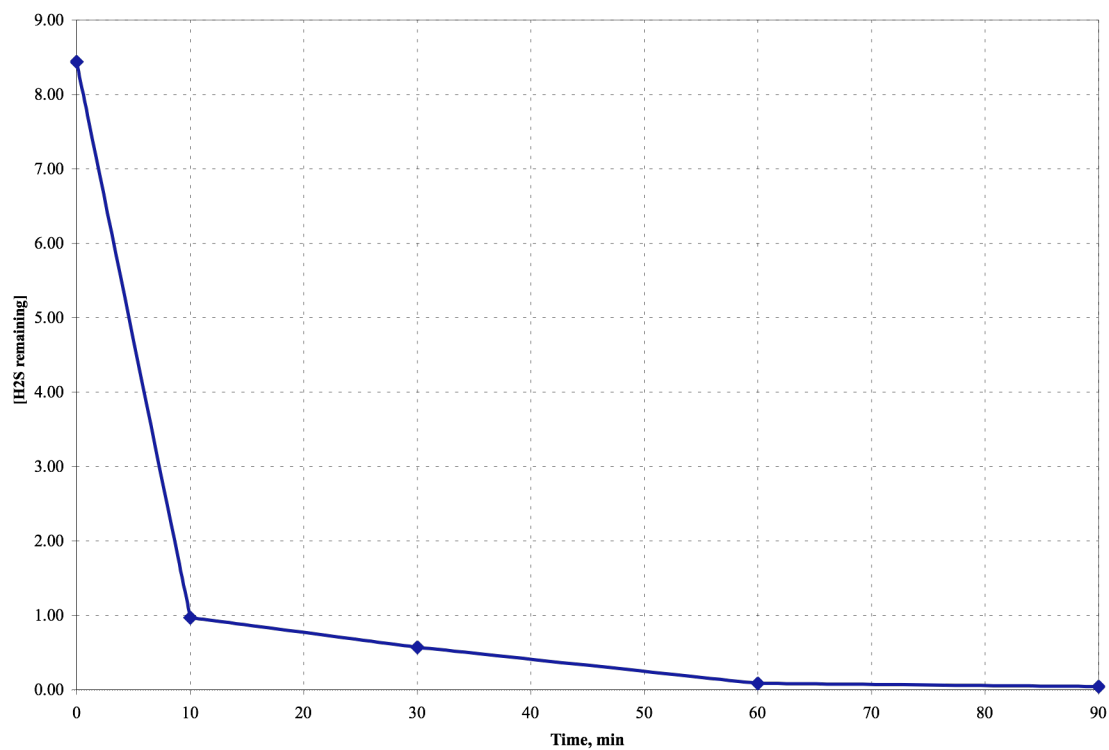
Appendix B-45. Standard Curve for 10.00 kg FeCl₂/kgS Addition

Appendix B-46. Ion Selective Electrode Method Data for 10.00 kg FeCl₂/kgS Addition

Date: 2/4/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 10.00 kgFeCl₂/kgS
 H₂S Initial Concentration: 8.44 mg/L
 Initial pH: 12.40
 pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-742.6	2.1164327	8.30	8.44	12.4
	b		-743.0	2.149463254	8.58		12.4
2	a	10	-716.7	-0.022295623	0.98	0.97	12.4
	b		-716.5	-0.0388109	0.96		12.4
3	a	30	-709.9	-0.583815029	0.56	0.57	12.4
	b		-710.6	-0.526011561	0.59		12.4
4	a	60	-687.7	-2.417010735	0.09	0.09	12.4
	b		-687.5	-2.433526012	0.09		12.4
5	a	90	-677.9	-3.22625929	0.04	0.04	12.4
	b		-679.1	-3.12716763	0.04		12.4
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix B-47. H₂S remaining after 10.00 kg FeCl₂/kgS Addition

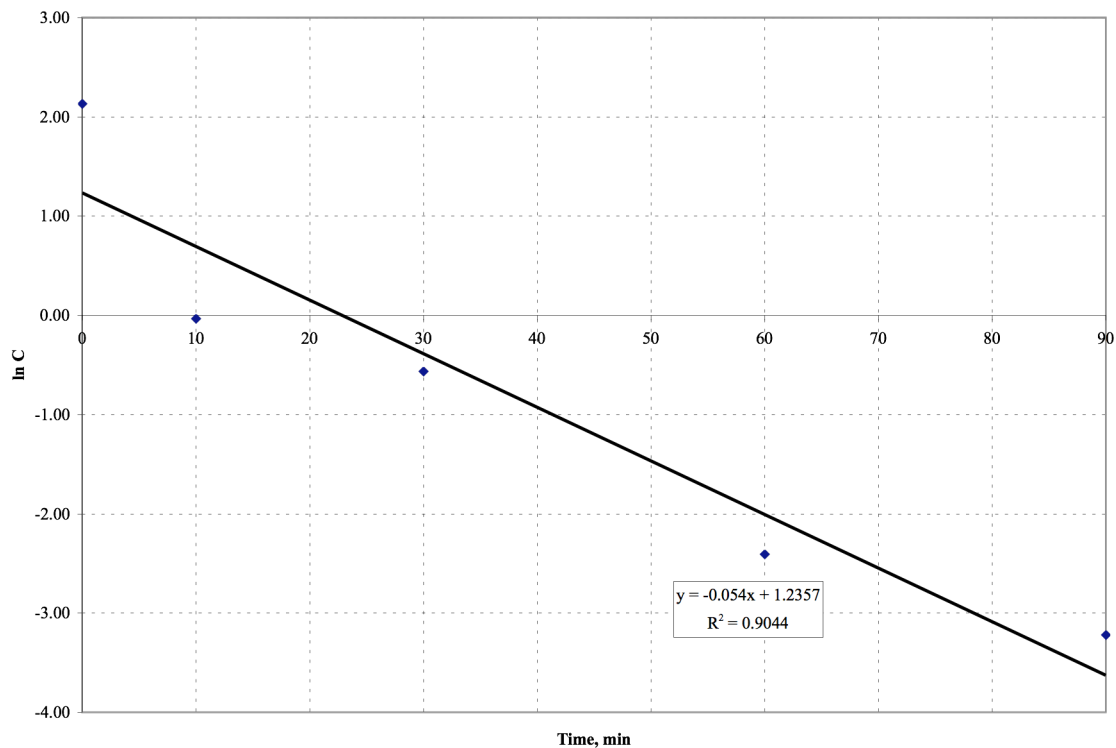
Appendix B-48. Linear Regression Analysis corresponding to 10.00 FeCl₂/kgS – pH = 7.80

Date: 2/4/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 10.00 kgFeCl₂/kgS

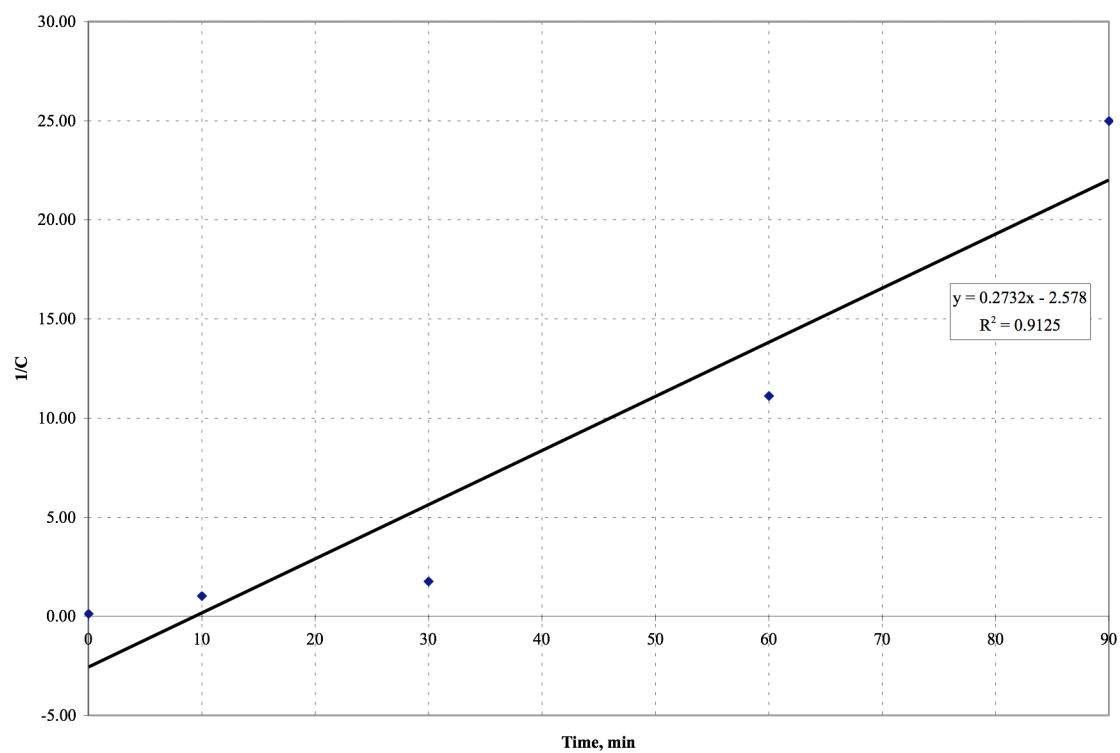
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.44	2.1329823	0.1184834	0.0140383	0.0016633	0.0001971	0.0000234	0.0000028	0.0000003
10	0.97	-0.0304592	1.0309278	1.0628122	1.0956827	1.1295698	1.1645049	1.2005205	1.2376500
30	0.57	-0.5621189	1.7544	3.0779	5.3998	9.4733	16.6198	29.1575	51.1536
60	0.09	-2.4079456	11.1111	123.4568	1371.7421	15241.5790	169350.8781	1881676.4232	20907515.8129
90	0.04	-3.2188758	25.0000	625.0000	15625.0000	390625.0000	9765625.0000	244140625.0000	6103515625.0000

$$t_{1/2} = \frac{1}{k[C_o]}$$

$k = 0.2732 \text{ Lmg}^{-1}\text{min}^{-1}$
 $C_o = 8.44 \text{ mg/L}$
 $t_{1/2} = 0.43 \text{ min}$



Appendix B-49. Test of First-Order Kinetics corresponding to 10.00 kg FeCl₂/kgS



Appendix B-50. Test of Second-Order Kinetics corresponding to 10.00 kg FeCl_2/kgS

APPENDIX C

Appendix C-1. Results Summary - Ion Selective Electrode Method – H₂O₂ Addition

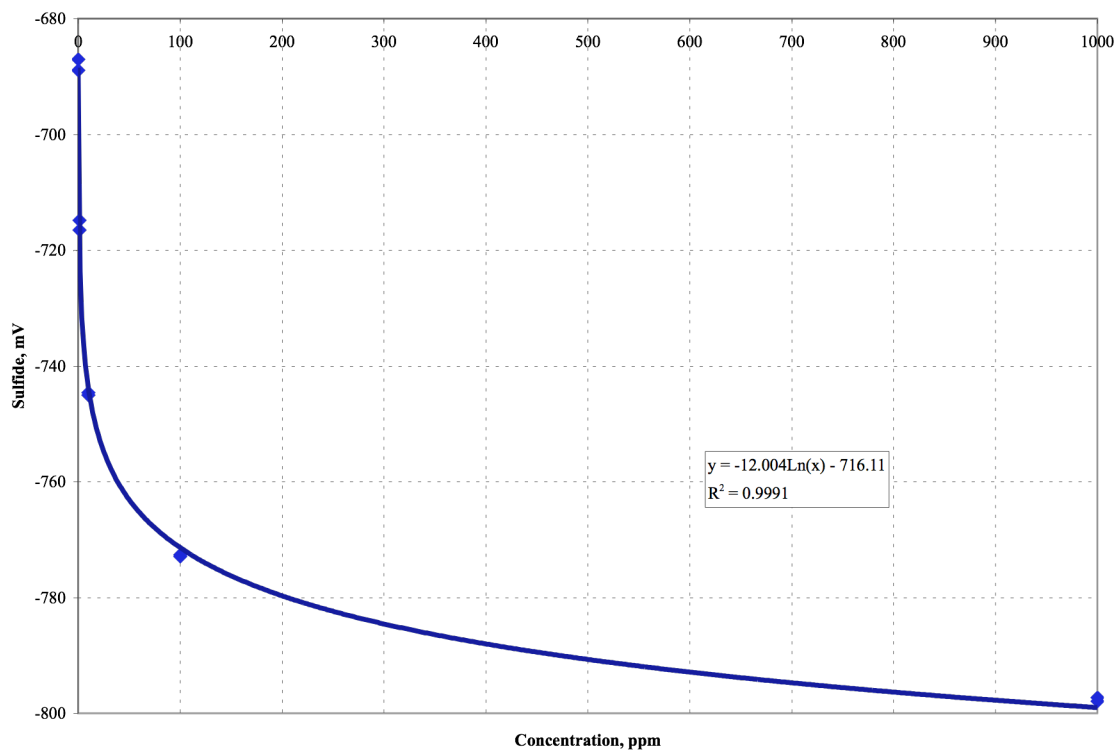
Time, min	H ₂ O ₂ Concentration, kgH ₂ O ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	0.10	7.82	100.00	0.00
1	0.10	1.27	16.24	83.76
5	0.10	0.82	10.49	89.51
10	0.10	0.65	8.31	91.69
20	0.10	0.43	5.50	94.50
40	0.10	0.30	3.84	96.16
60	0.10	0.26	3.32	96.68
0	0.05	8.23	100.00	0.00
0.5	0.05	7.75	94.17	5.83
2	0.05	6.56	79.71	20.29
10	0.05	5.79	70.35	29.65
20	0.05	4.02	48.85	51.15
30	0.05	3.27	39.73	60.27
60	0.05	2.51	30.50	69.50
0	0.30	10.60	100.00	0.00
1	0.30	0.44	4.15	95.85
5	0.30	0.38	3.58	96.42
10	0.30	0.33	3.11	96.89
20	0.30	0.26	2.45	97.55
40	0.30	0.19	1.79	98.21
60	0.30	0.17	1.60	98.40
0	0.60	7.90	100.00	0.00
1	0.60	0.42	5.32	94.68
5	0.60	0.32	4.05	95.95
10	0.60	0.28	3.54	96.46
20	0.60	0.21	2.66	97.34
40	0.60	0.13	1.65	98.35
60	0.60	0.12	1.52	98.48
0	1.00	9.63	100.00	0.00
0.5	1.00	0.39	4.05	95.95
1	1.00	0.13	1.35	98.65
5	1.00	0.08	0.83	99.17
10	1.00	0.05	0.52	99.48

Appendix C-2. Standard Curve Data for 0.10 kg H₂O₂/kgS Addition

Date: 2/6/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-797.9	13.2	17.0
	b	1000	-797.3	13.25	17.0
2	a	100	-772.9	13.2	17.0
	b	100	-772.6	13.2	17.0
3	a	10	-745.0	13.2	17.0
	b	10	-744.6	13.2	17.0
4	a	1	-716.5	13.2	17.0
	b	1	-714.8	13.2	17.0
5	a	0.1	-687.0	13.2	17.0
	b	0.1	-688.9	13.2	17.0



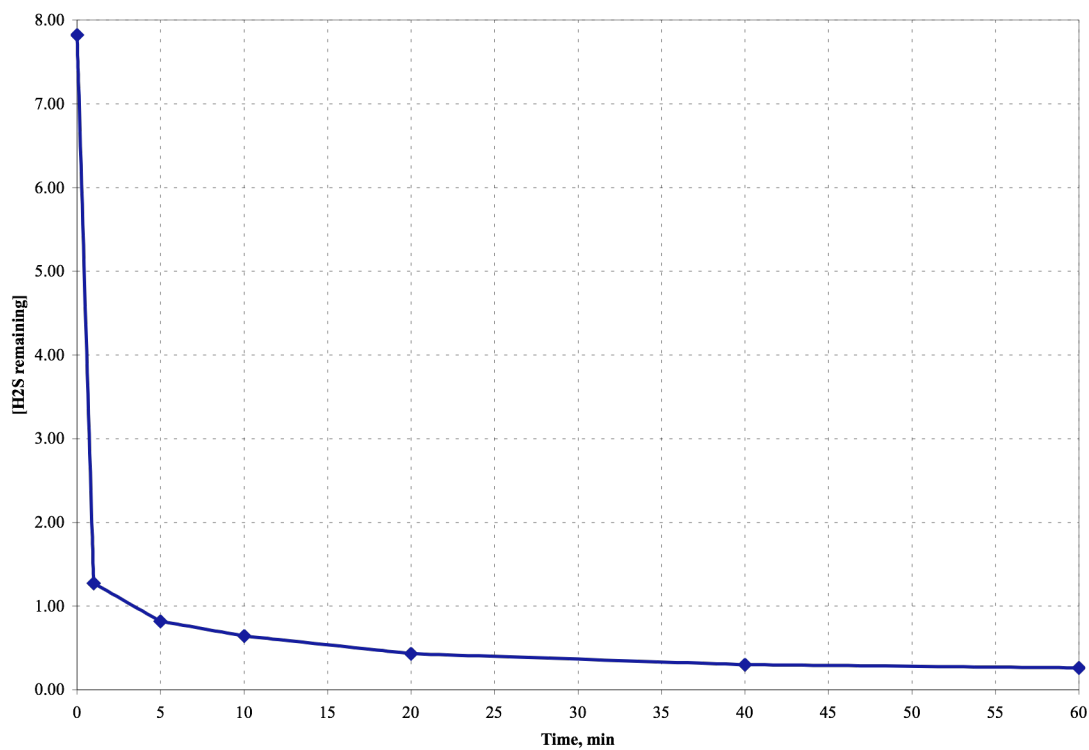
Appendix C-3. Standard Curve for 0.10 kg H₂O₂/kgS Addition

Appendix C-4. Ion Selective Electrode Method Data for 0.10 kg H₂O₂/kgS Addition

Date: 2/6/06
Method: Ion Selective Electrode Method

H₂O₂ Concentration: 0.10 kgH₂O₂/kgS
H₂S Initial Concentration: 7.82 mg/L
Initial pH: 13.20
pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-740.5	2.031822726	7.63	7.82	17.0
	b		-741.1	2.081806065	8.02		17.0
2	a	1	-717.7	0.132455848	1.14	1.27	17.0
	b		-720.2	0.34071976	1.41		17.0
3	a	5	-714.8	-0.10913029	0.90	0.82	17.0
	b		-712.4	-0.309063645	0.73		17.0
4	a	10	-694.7	-1.783572143	0.17	0.65	17.0
	b		-717.5	0.115794735	1.12		17.0
5	a	20	-704.9	-0.933855382	0.39	0.43	17.0
	b		-707.1	-0.750583139	0.47		17.0
6	a	40	-706.4	-0.808897034	0.45	0.30	17.0
	b		-694.0	-1.841886038	0.16		17.0
7	a	60	-700.5	-1.300399867	0.27	0.26	17.0
	b		-699.4	-1.392035988	0.25		17.0
8	a						
	b						
9	a						
	b						



Appendix C-5. H₂S remaining after 0.10 kg H₂O₂/kgS Addition

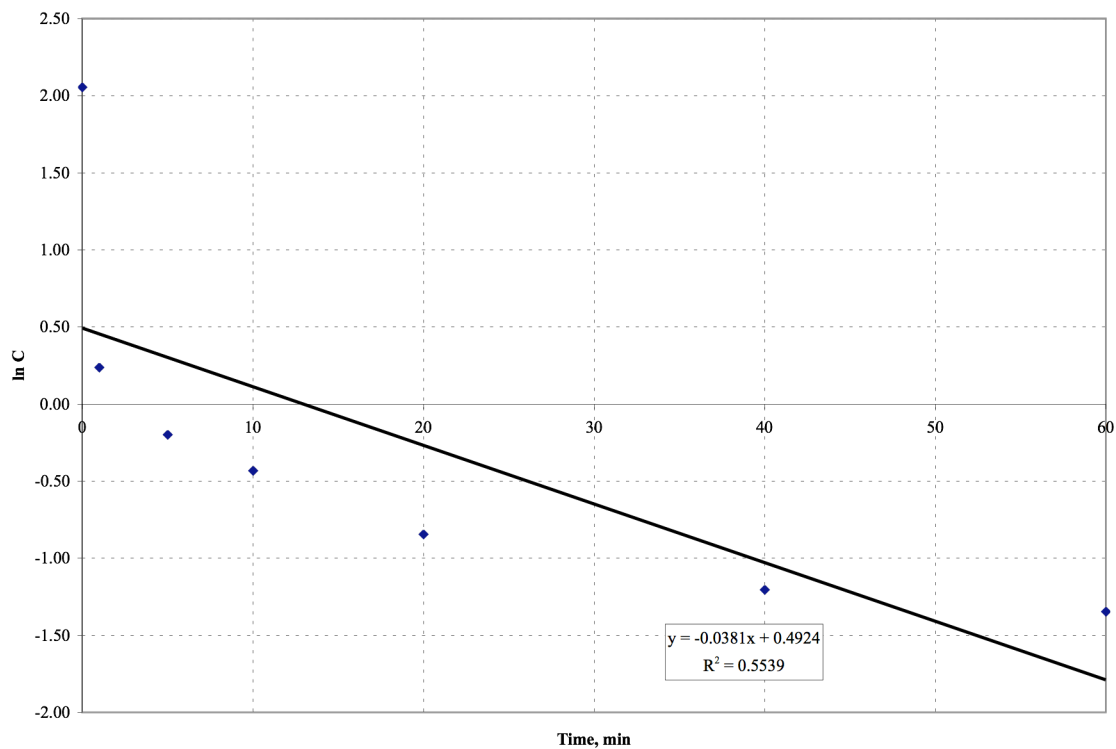
Appendix C-6. Linear Regression Analysis corresponding to 0.10 H₂O₂/kgS – pH = 7.80

Date: 2/6/07
 Method: Ion Selective Electrode Method
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS

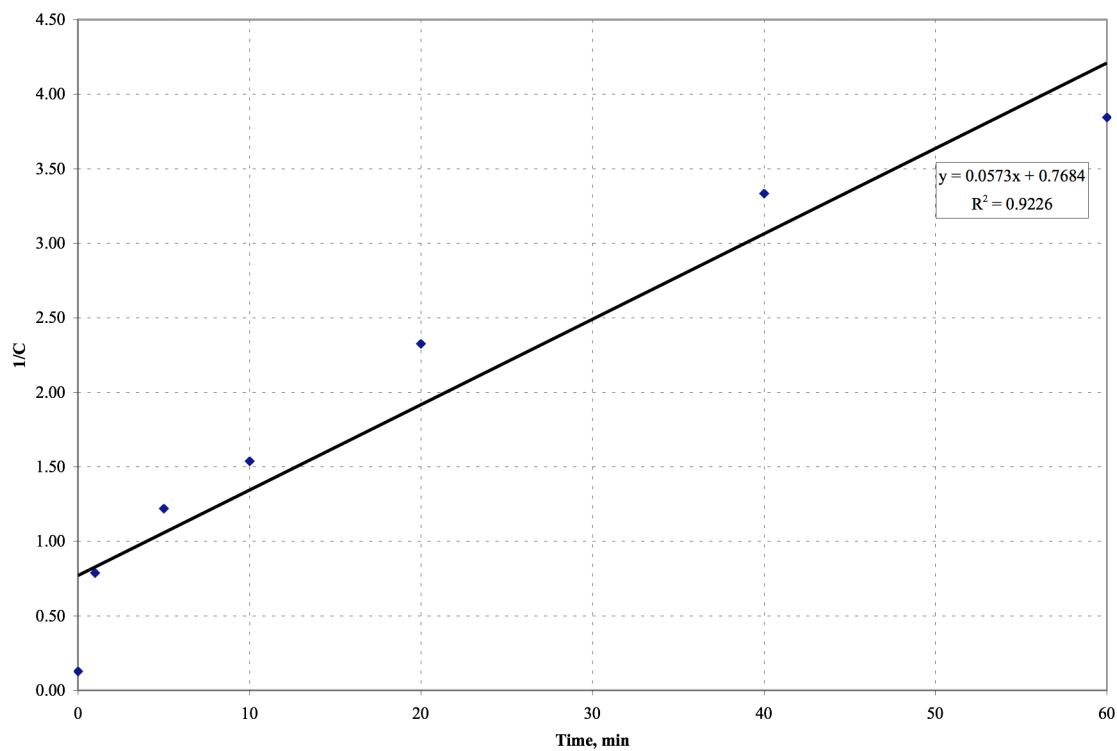
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.82	2.0566846	0.1278772	0.0163526	0.0020911	0.0002674	0.0000342	0.0000044	0.0000006
1	1.27	0.2390169	0.7874016	0.6200012	0.4881900	0.3844015	0.3026784	0.2383294	0.1876610
5	0.82	-0.1984509	1.2195122	1.4872100	1.8136707	2.2117936	2.6973092	3.2894015	4.0114652
10	0.65	-0.4307829	1.5384615	2.3668639	3.6413291	5.6020447	8.6185304	13.2592775	20.3988885
20	0.43	-0.8439701	2.3255814	5.4083288	12.5775089	29.2500207	68.0233039	158.1937301	367.8923956
40	0.30	-1.2039728	3.3333333	11.1111111	37.0370370	123.4567901	411.5226	1371.7421	4572.4737
60	0.26	-1.3470736	3.8461538	14.7928994	56.8957670	218.8298729	841.6533573	3237.1282974	12450.4934515

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

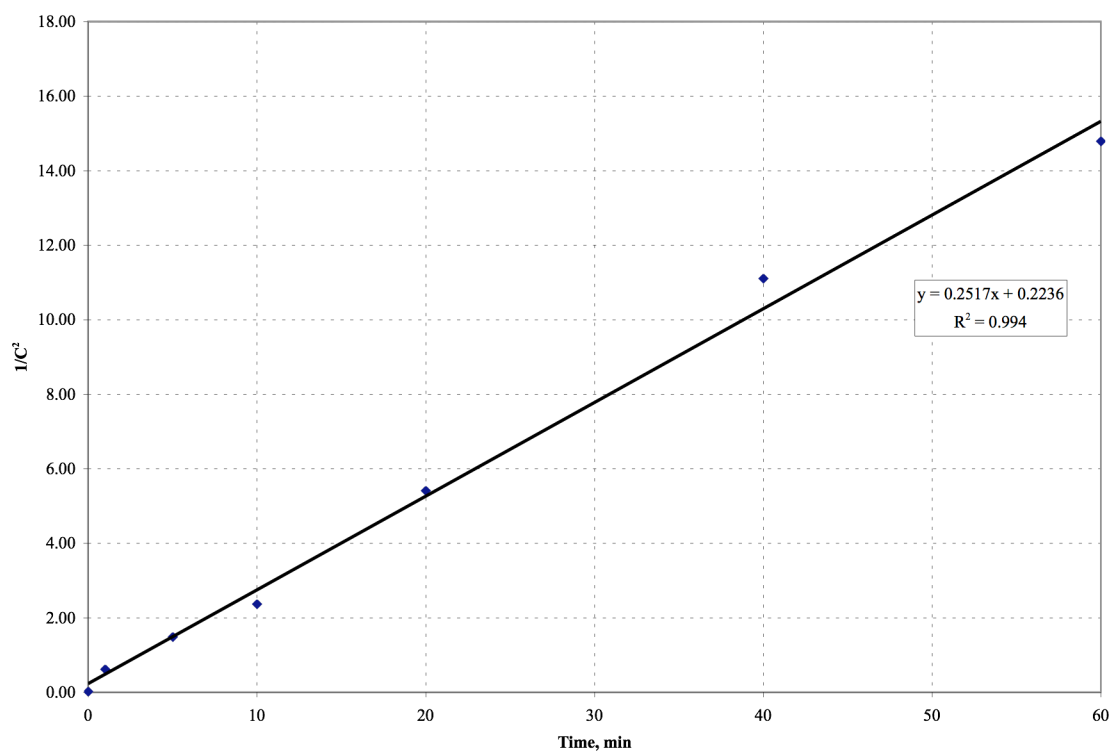
k = 0.126 L²mg⁻²min⁻¹
 C₀ = 7.82 mg/L
 C = 3.91 mg/L
 t_{1/2} = 0.19 min



Appendix C-7. Test of First-Order Kinetics corresponding to 0.10 kg H₂O₂/kgS



Appendix C-8. Test of Second-Order Kinetics corresponding to 0.10 kg H_2O_2 /kgS



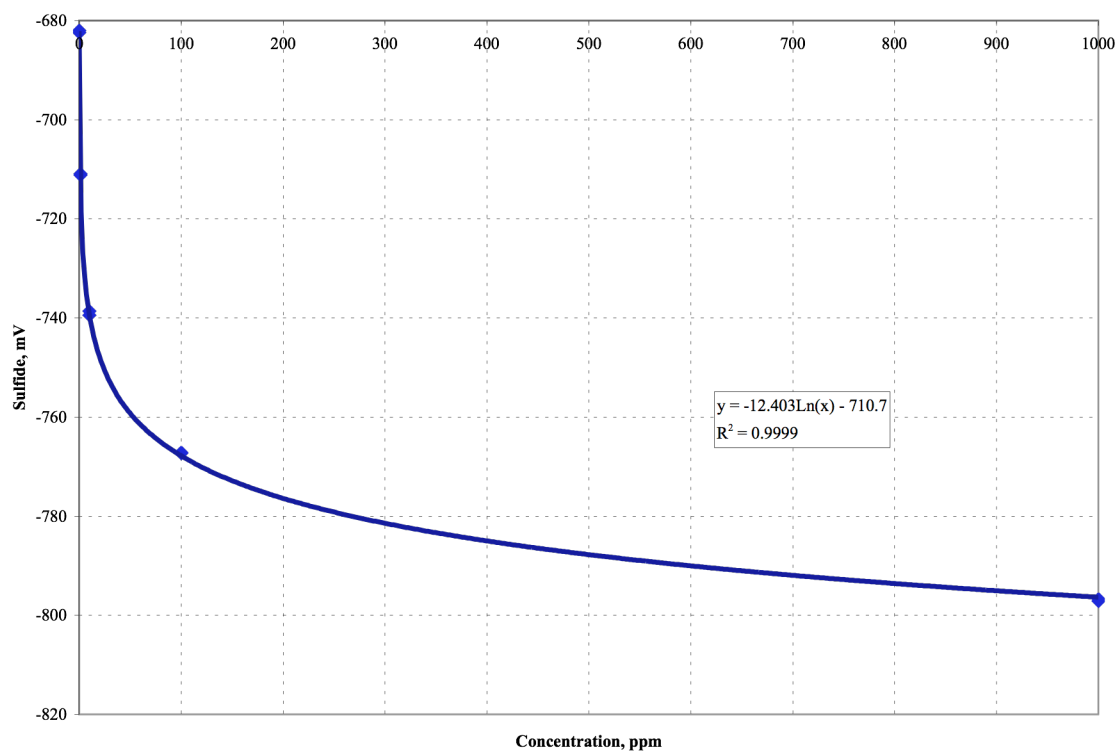
Appendix C-9. Test of Third-Order Kinetics corresponding to 0.10 kg H_2O_2 /kgS

Appendix C-10. Standard Curve Data for 0.05 kg H₂O₂/kgS Addition

Date: 11/8/06

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-797.1	12.6	25.0
	b	1000	-796.7	12.6	25.0
2	a	100	-767.3	12.6	25.0
	b	100	-767.1	12.6	25.0
3	a	10	-739.4	12.6	25.0
	b	10	-738.6	12.6	25.0
4	a	1	-710.9	12.6	25.0
	b	1	-711.1	12.6	25.0
5	a	0.1	-682.4	12.6	25.0
	b	0.1	-682.0	12.6	25.0



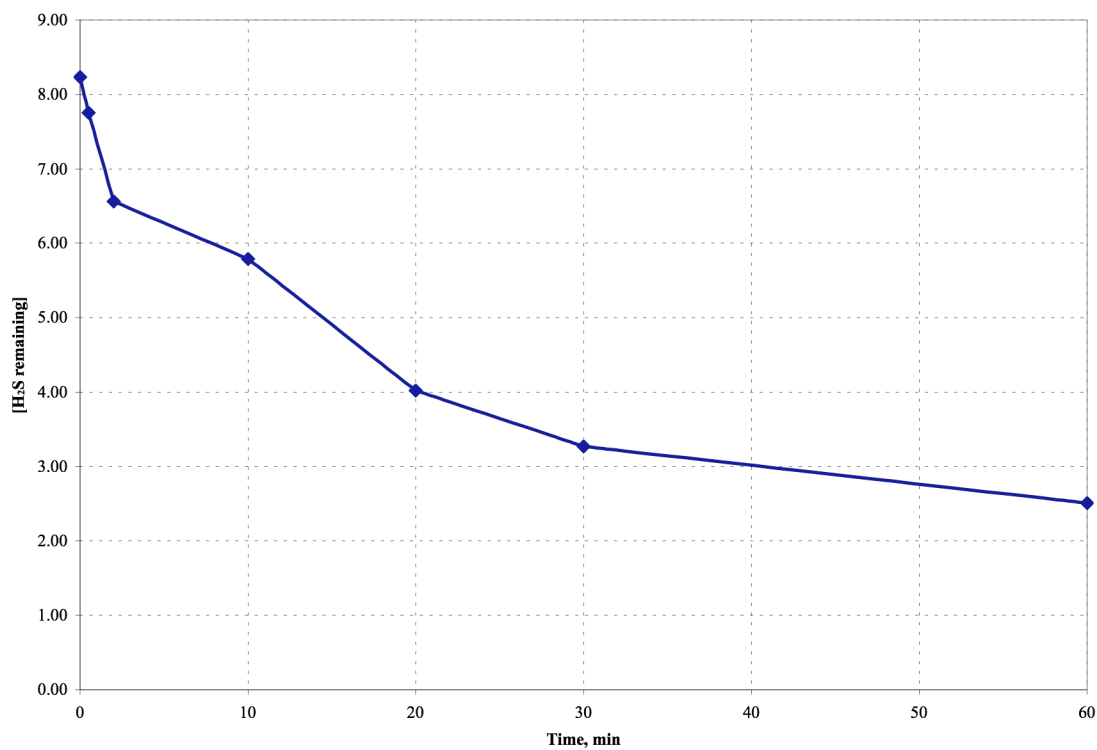
Appendix C-11. Standard Curve for 0.05 kg H₂O₂/kgS Addition

Appendix C-12. Ion Selective Electrode Method Data for 0.05 kg H₂O₂/kgS Addition

Date: 11/8/06
Method: Ion Selective Electrode Method

H₂O₂ Concentration: 0.05 kgH₂O₂/kgS
H₂S Initial Concentration: 8.23 mg/L
Initial pH: 12.50
pH after HCl addition: 7.20

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-736.8	2.104329598	8.20	8.23	15.0
	b		-736.9	2.112392163	8.27		15.0
2	a	0.5	-736.0	2.039829074	7.69	7.75	15.0
	b		-736.2	2.055954205	7.81		15.0
3	a	2	-733.1	1.806014674	6.09	6.56	15.0
	b		-734.9	1.951140853	7.04		15.0
4	a	10	-734.4	1.910828025	6.76	5.79	15.0
	b		-730.2	1.572200274	4.82		15.0
5	a	20	-728.5	1.43513666	4.20	4.02	15.0
	b		-727.4	1.34644844	3.84		15.0
6	a	30	-725.2	1.169071999	3.22	3.27	15.0
	b		-725.6	1.201322261	3.32		15.0
7	a	60	-723.1	0.999758123	2.72	2.51	15.0
	b		-721.0	0.830444247	2.29		15.0
8	a						
	b						
9	a						
	b						



Appendix C-13. H₂S remaining after 0.05 kg H₂O₂/kgS Addition

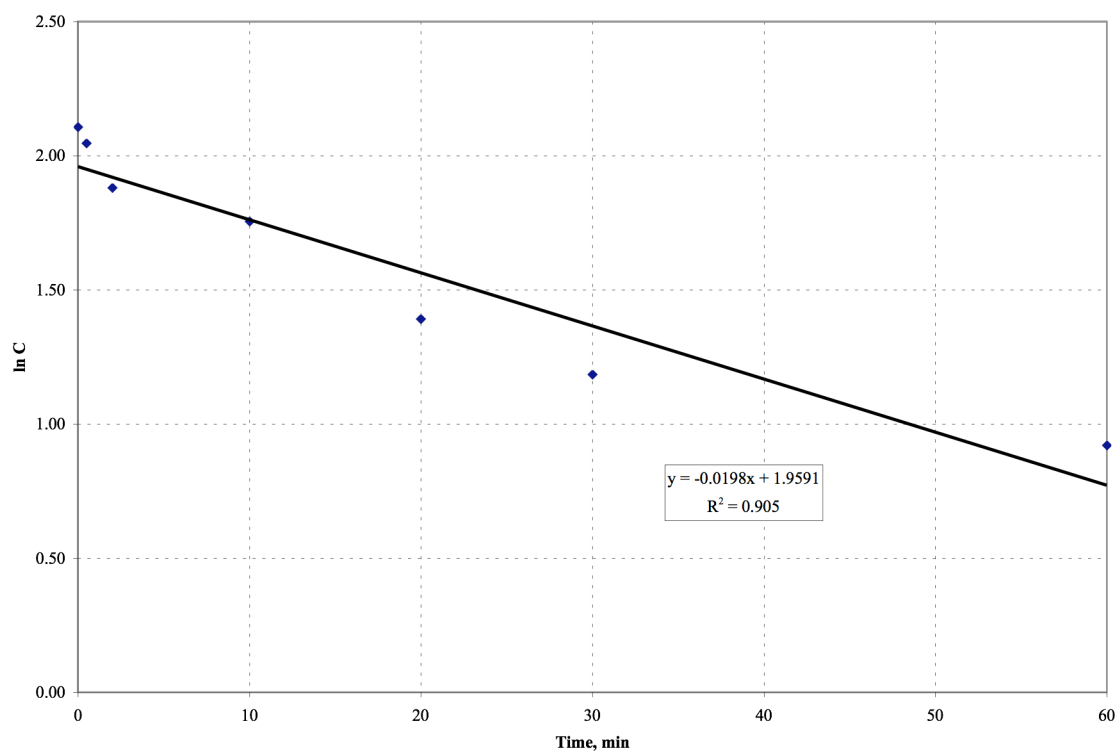
Appendix C-14. Linear Regression Analysis corresponding to 0.05 H₂O₂/kgS – pH = 7.20

Date: 11/8/06
 Method: Ion Selective Electrode Method
 H₂O₂ Concentration: 0.05 kgH₂O₂/kgS

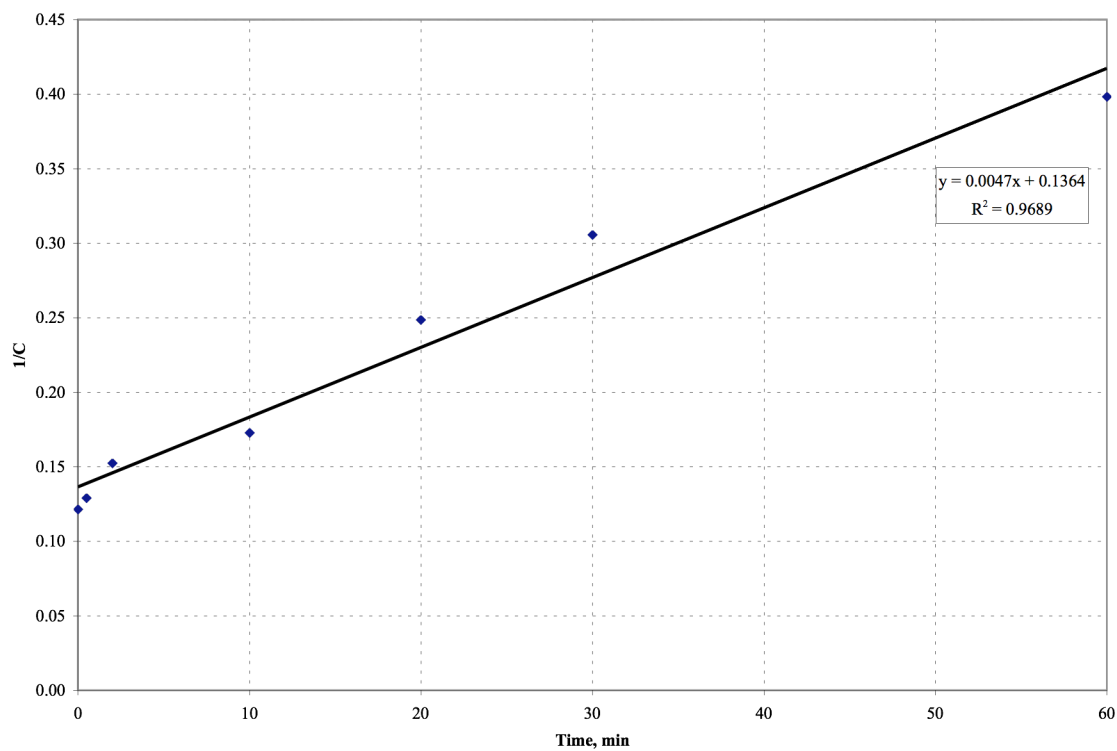
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.23	2.1077860	0.1215067	0.0147639	0.0017939	0.0002180	0.0000265	0.0000032	0.0000004
0.5	7.75	2.0476928	0.1290323	0.0166493	0.0021483	0.0002772	0.0000358	0.0000046	0.0000006
2	6.56	1.8809906	0.1524390	0.0232377	0.0035423	0.0005400	0.0000823	0.0000125	0.0000019
10	5.79	1.7561323	0.1727116	0.0298293	0.0051519	0.0008898	0.0001537	0.0000265	0.0000046
20	4.02	1.3912819	0.2487562	0.0618797	0.0153929	0.0038291	0.0009525	0.0002369	0.0000589
30	3.27	1.1847900	0.3058104	0.0935200	0.0285994	0.0087460	0.0027	0.0008	0.0003
60	2.51	0.9202828	0.3984064	0.1587276	0.0632381	0.0251945	0.0100376	0.0039991	0.0015933

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

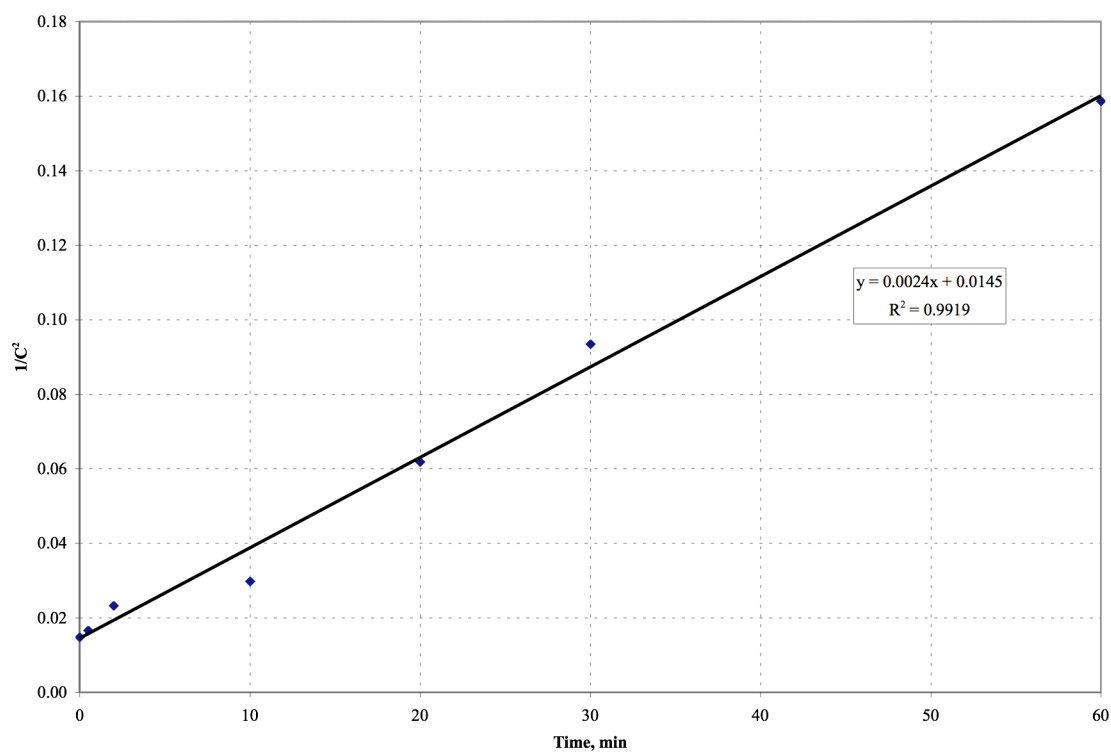
$k = 0.0012 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$
 $C_0 = 8.23 \text{ mg/L}$
 $C = 4.12 \text{ mg/L}$
 $t_{1/2} = 18.45 \text{ min}$



Appendix C-15. Test of First-Order Kinetics corresponding to 0.05 kg H₂O₂/kgS



Appendix C-16. Test of Second-Order Kinetics corresponding to 0.05 kg H_2O_2 /kgS



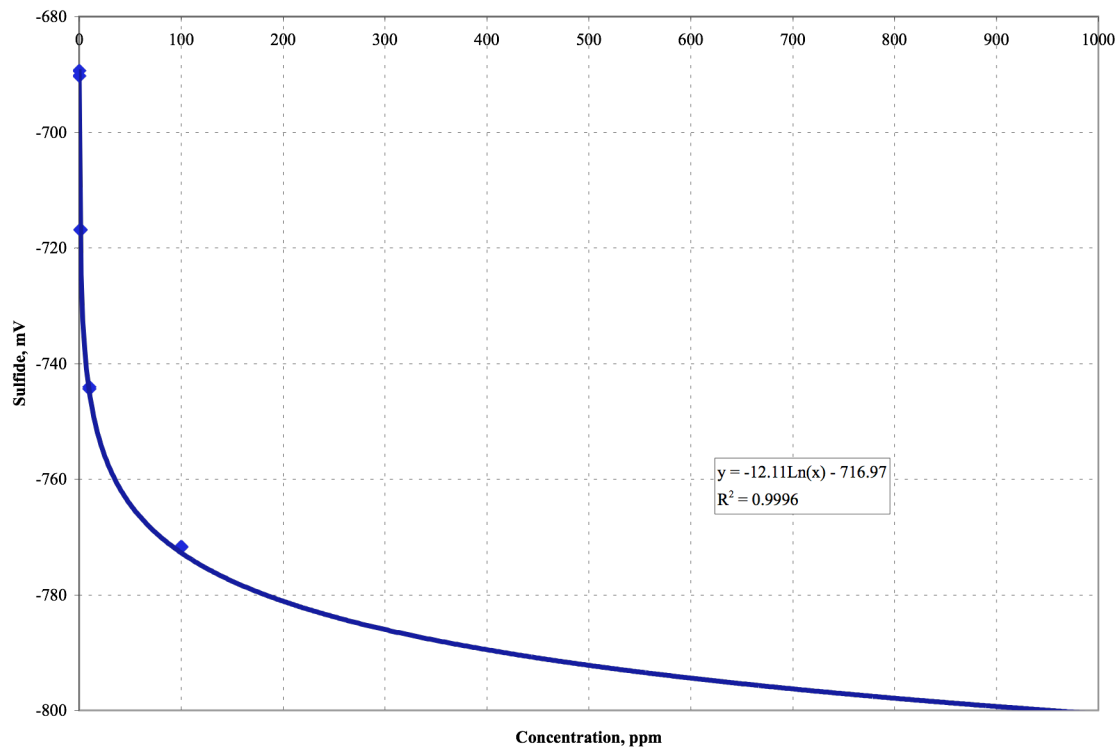
Appendix C-17. Test of Third-Order Kinetics corresponding to 0.05 kg H_2O_2 /kgS

Appendix C-18. Standard Curve Data for 0.30 kg H₂O₂/kgS Addition

Date: 2/4/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.7	13.5	12.4
	b	1000	-801.8	13.5	12.4
2	a	100	-771.6	13.5	12.4
	b	100	-771.8	13.5	12.4
3	a	10	-744.4	13.5	12.4
	b	10	-744.0	13.5	12.4
4	a	1	-716.9	13.5	12.4
	b	1	-716.8	13.5	12.4
5	a	0.1	-690.2	13.5	12.4
	b	0.1	-689.3	13.5	12.4



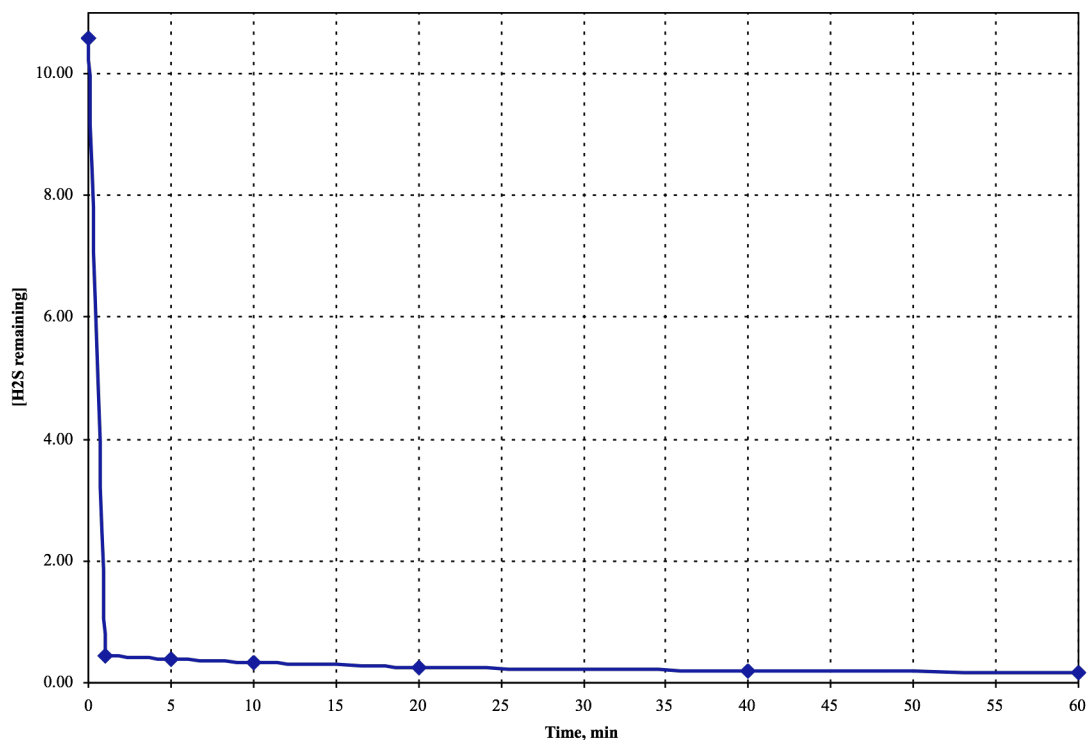
Appendix C-19. Standard Curve for 0.30 kg H₂O₂/kgS Addition

Appendix C-20. Ion Selective Electrode Method Data for 0.30 kg H₂O₂/kgS Addition

Date: 2/5/06
Method: Ion Selective Electrode Method

H₂O₂ Concentration: 0.30 kgH₂O₂/kgS
H₂S Initial Concentration: 10.60 mg/L
Initial pH: 13.50
pH after HCl addition: 6.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-745.2	2.331131296	10.29	10.60	10.6
	b		-745.9	2.388934765	10.90		10.6
2	a	1	-707.7	-0.765483072	0.47	0.44	10.6
	b		-706.1	-0.897605285	0.41		10.6
3	a	5	-705.8	-0.9223782	0.40	0.38	10.6
	b		-704.7	-1.013212221	0.36		10.6
4	a	10	-704.4	-1.037985136	0.35	0.33	10.6
	b		-703.0	-1.153592073	0.32		10.6
5	a	20	-701.0	-1.318744839	0.27	0.26	10.6
	b		-699.9	-1.40957886	0.24		10.6
6	a	40	-698.3	-1.541701073	0.21	0.19	10.6
	b		-695.2	-1.797687861	0.17		10.6
7	a	60	-689.5	-2.268373245	0.10	0.17	10.6
	b		-699.2	-1.467382329	0.23		10.6
8	a						
	b						
9	a						
	b						



Appendix C-21. H₂S remaining after 0.30 kg H₂O₂/kgS Addition

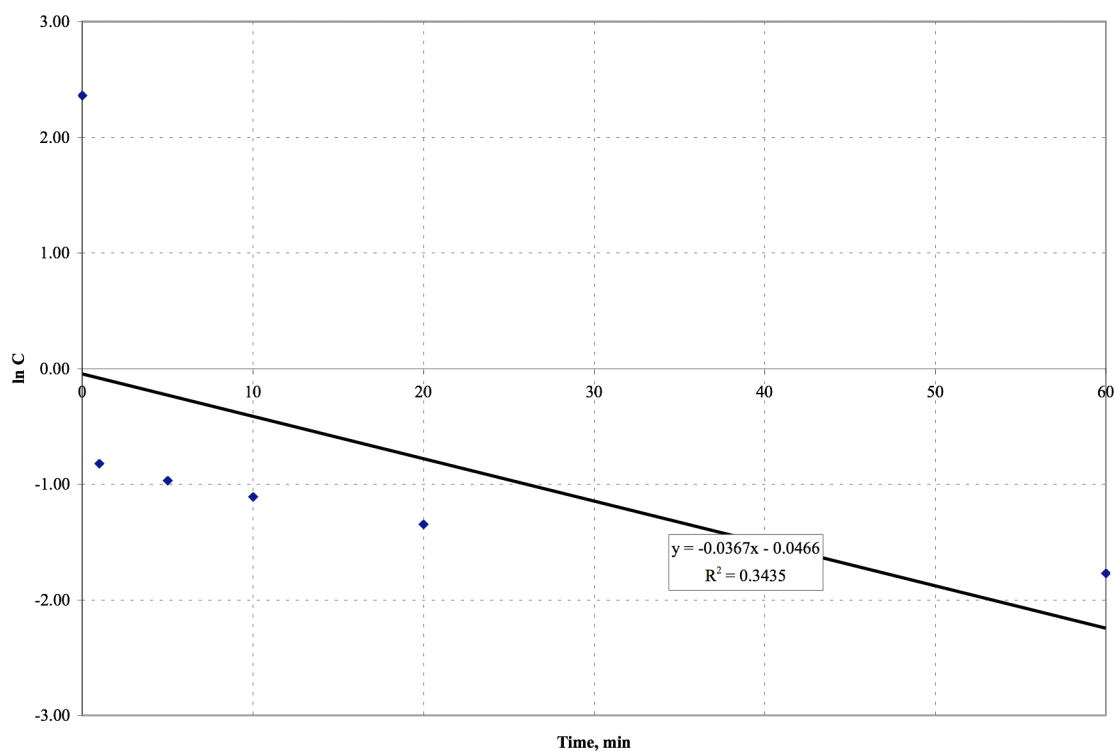
Appendix C-22. Linear Regression Analysis corresponding to 0.30 H₂O₂/kgS – pH = 6.80

Date: 2/5/07
 Method: Ion Selective Electrode Method
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

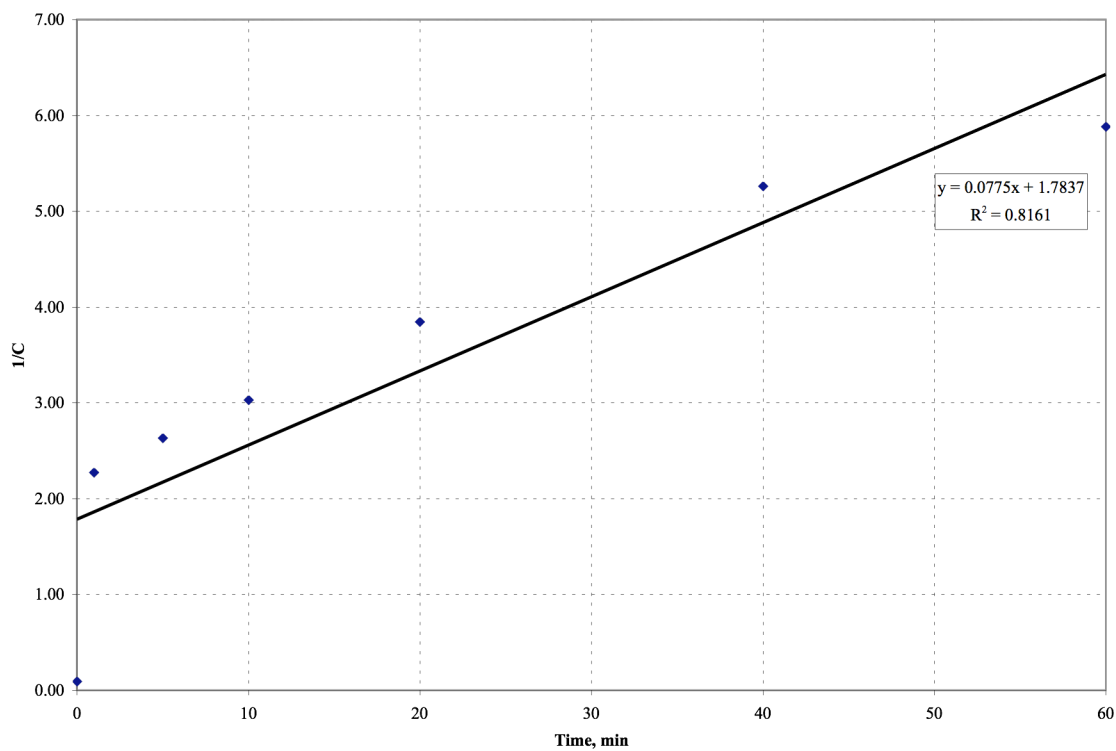
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	10.60	2.3608540	0.0943396	0.0089000	0.0008396	0.0000792	0.0000075	0.0000007	0.0000001
1	0.44	-0.8209806	2.2727273	5.1652893	11.7392938	26.6802131	60.6368480	137.8110181	313.2068593
5	0.38	-0.9675840	2.6315789	6.9252078	18.2242309	47.9585025	126.2065854	332.1225933	874.0068244
10	0.33	-1.1086626	3.0303030	9.1827365	27.8264741	84.3226488	255.5231782	774.3126613	2346.4020038
20	0.26	-1.3470736	3.8461538	14.7928994	56.8957670	218.8298729	841.6533573	3237.1282974	12450.4934515
40	0.19	-1.6607312	5.2631579	27.7008310	145.7938475	767.3360395	4038.6107	21255.8460	111872.8735
60	0.17	-1.7719568	5.8823529	34.6020761	203.5416243	1197.3036721	7042.9627772	41429.1928073	243701.1341605

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

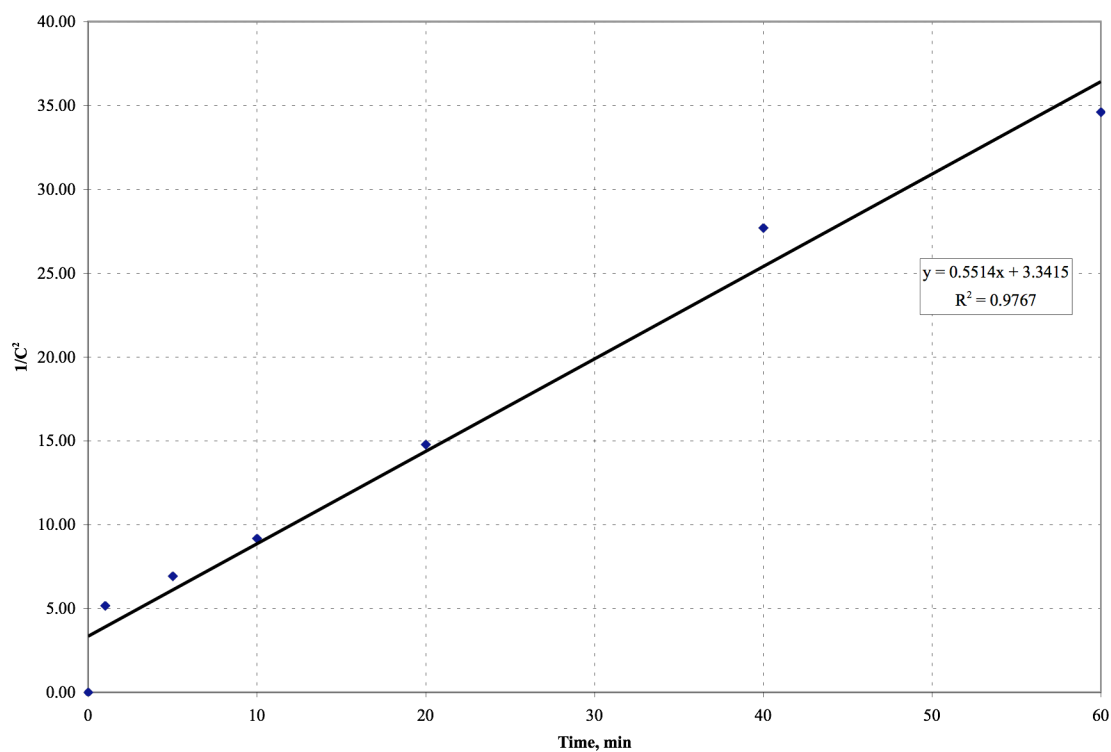
k = 0.2757 L²mg⁻²min⁻¹
 C₀ = 10.60 mg/L
 C = 5.30 mg/L
 t_{1/2} = 0.05 min



Appendix C-23. Test of First-Order Kinetics corresponding to 0.30 kg H₂O₂/kgS



Appendix C-24. Test of Second-Order Kinetics corresponding to 0.30 kg H_2O_2 /kgS



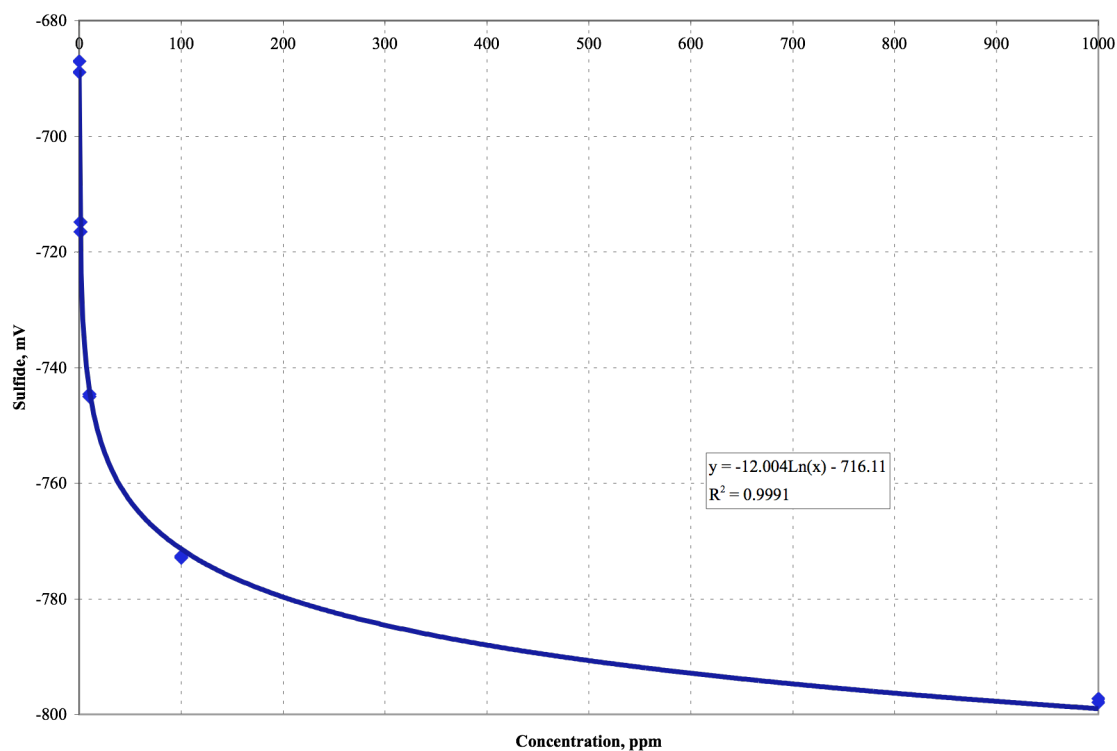
Appendix C-25. Test of Third-Order Kinetics corresponding to 0.30 kg H_2O_2 /kgS

Appendix C-26. Standard Curve Data for 0.60 kg H₂O₂/kgS Addition

Date: 2/6/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-797.9	13.2	17.0
	b	1000	-797.3	13.25	17.0
2	a	100	-772.9	13.2	17.0
	b	100	-772.6	13.2	17.0
3	a	10	-745.0	13.2	17.0
	b	10	-744.6	13.2	17.0
4	a	1	-716.5	13.2	17.0
	b	1	-714.8	13.2	17.0
5	a	0.1	-687.0	13.2	17.0
	b	0.1	-688.9	13.2	17.0



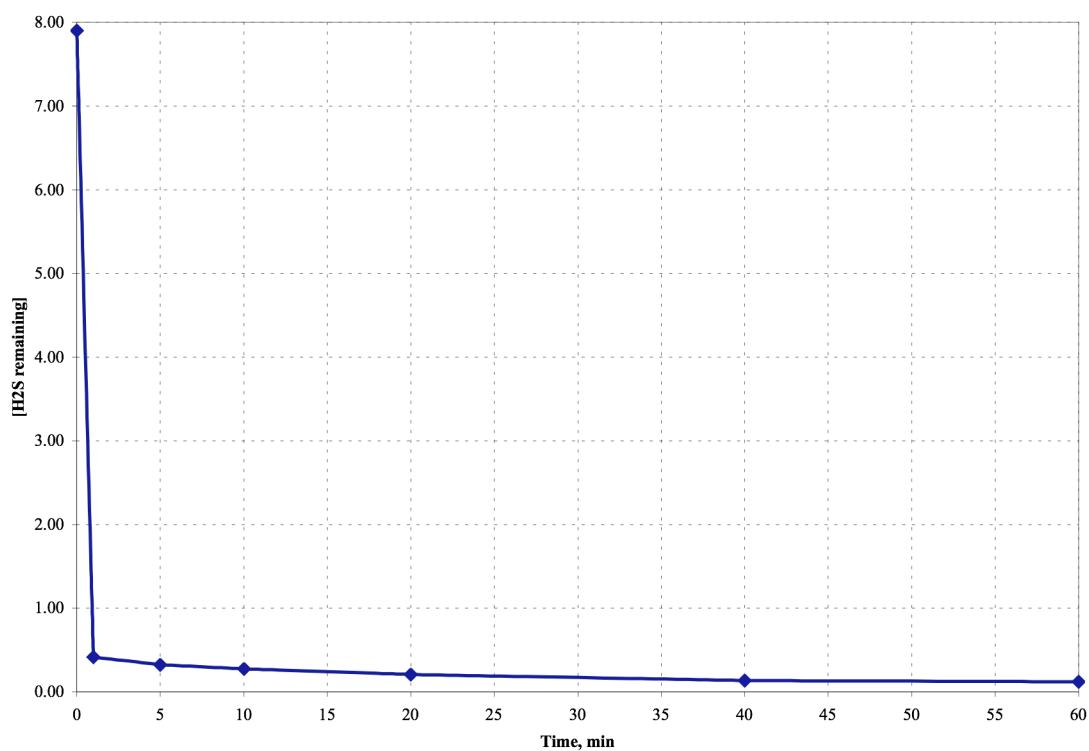
Appendix C-27. Standard Curve for 0.60 kg H₂O₂/kgS Addition

Appendix C-28. Ion Selective Electrode Method Data for 0.60 kg H₂O₂/kgS Addition

Date: 2/6/06
Method: Ion Selective Electrode Method

H₂O₂ Concentration: 0.60 kgH₂O₂/kgS
H₂S Initial Concentration: 7.90 mg/L
Initial pH: 13.20
pH after HCl addition: 6.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-740.3	2.015161613	7.50	7.90	14.4
	b		-741.5	2.115128291	8.29		14.4
2	a	1	-706.5	-0.800566478	0.45	0.42	14.4
	b		-704.7	-0.950516495	0.39		14.4
3	a	5	-705.9	-0.850549817	0.43	0.32	14.4
	b		-697.8	-1.525324892	0.22		14.4
4	a	10	-700.7	-1.283738754	0.28	0.28	14.4
	b		-700.7	-1.283738754	0.28		14.4
5	a	20	-698.2	-1.492002666	0.22	0.21	14.4
	b		-696.3	-1.650283239	0.19		14.4
6	a	40	-689.8	-2.19176941	0.11	0.13	14.4
	b		-693.7	-1.866877707	0.15		14.4
7	a	60	-692.8	-1.941852716	0.14	0.12	14.4
	b		-688.4	-2.308397201	0.10		14.4
8	a						
	b						
9	a						
	b						



Appendix C-29. H₂S remaining after 0.60 kg H₂O₂/kgS Addition

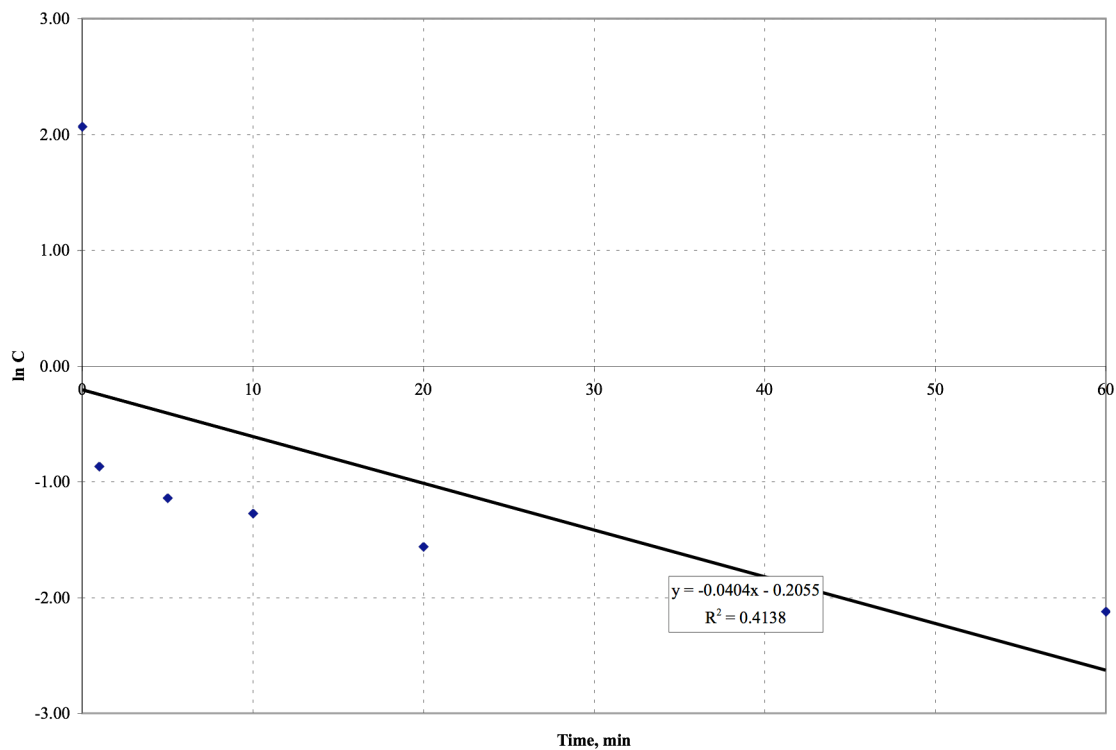
Appendix C-30. Linear Regression Analysis corresponding to 0.60 H₂O₂/kgS – pH = 6.80

Date: 2/6/07
 Method: Ion Selective Electrode Method
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS

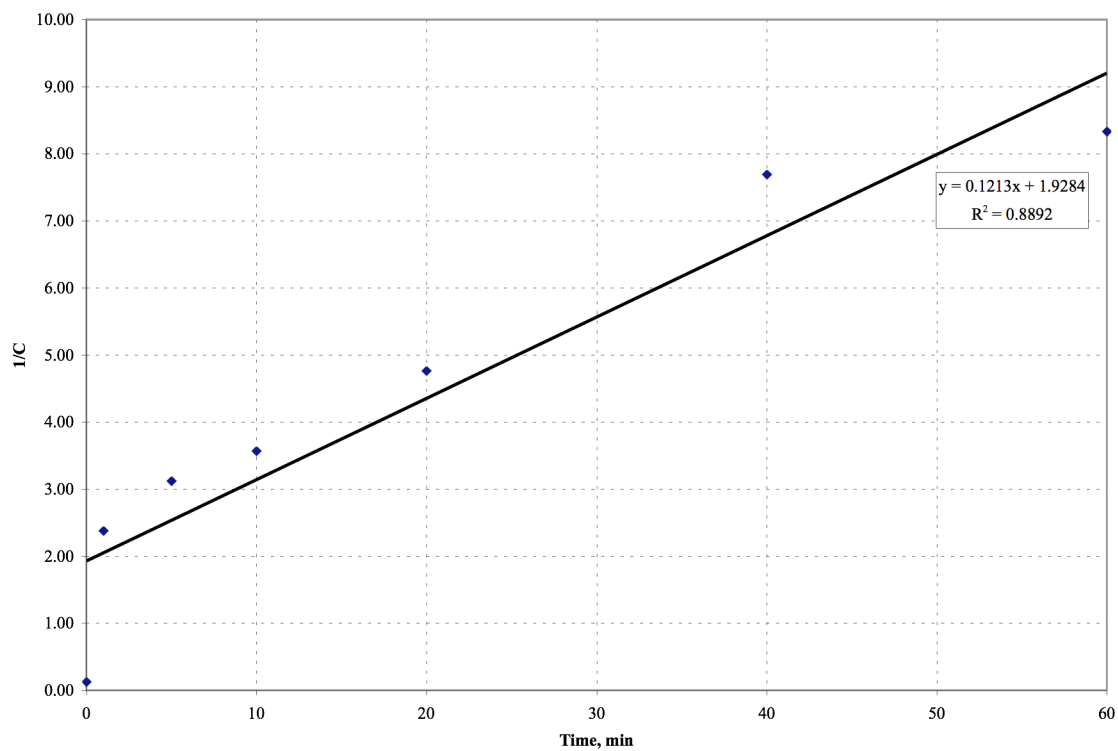
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.90	2.0668628	0.1265823	0.0160231	0.0020282	0.0002567	0.0000325	0.0000041	0.0000005
1	0.42	-0.8675006	2.3809524	5.6689342	13.4974625	32.1368154	76.5162272	182.1814933	433.7654603
5	0.32	-1.1394343	3.1250000	9.7656250	30.5175781	95.3674316	298.0232239	931.3225746	2910.3830457
10	0.28	-1.2729657	3.5714286	12.7551020	45.5539359	162.6926281	581.0451003	2075.1610723	7411.2895441
20	0.21	-1.5606477	4.7619048	22.6757370	107.9796998	514.1890467	2448.5192702	11659.6155724	55521.9789164
40	0.13	-2.0402	7.6923	59.1716	455.1661	3501.2780	26932.9074	207176.2110	1593663.1618
60	0.12	-2.1203	8.3333	69.4444	578.7037	4822.5309	40187.7572	334897.9767	2790816.4723

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

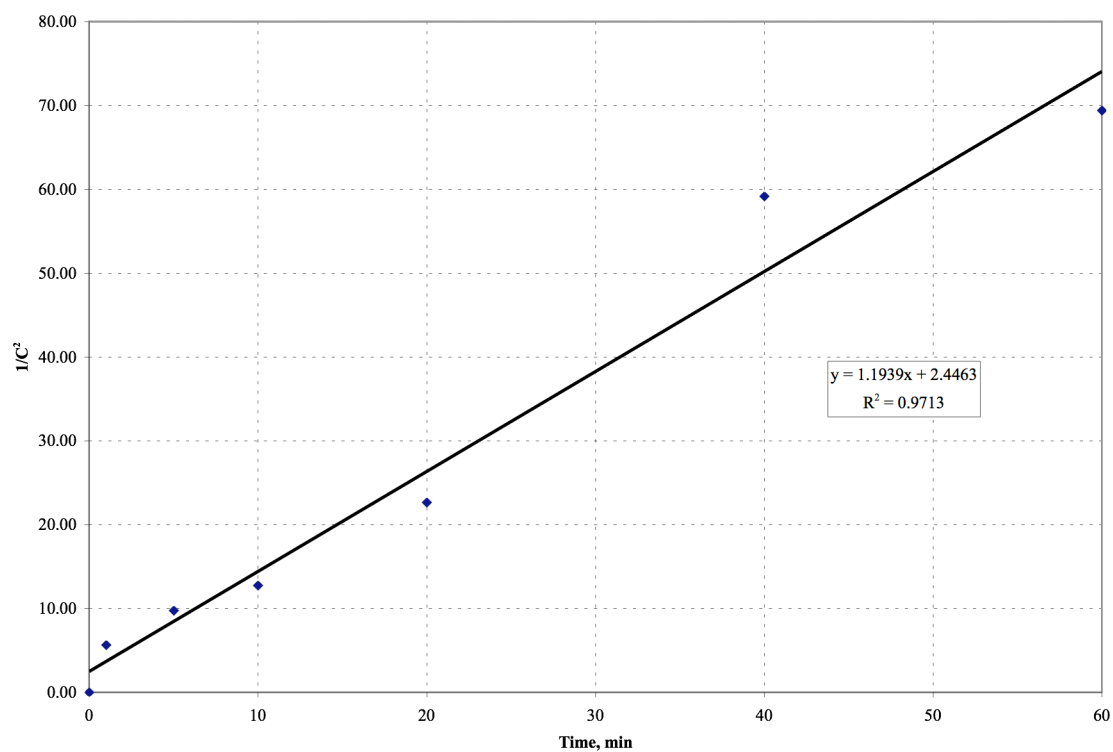
k = 0.5970 L²mg⁻²min⁻¹
 C₀ = 7.90 mg/L
 C = 3.95 mg/L
 t_{1/2} = 0.04 min



Appendix C-31. Test of First-Order Kinetics corresponding to 0.60 kg H₂O₂/kgS



Appendix C-32. Test of Second-Order Kinetics corresponding to 0.60 kg H_2O_2 /kgS



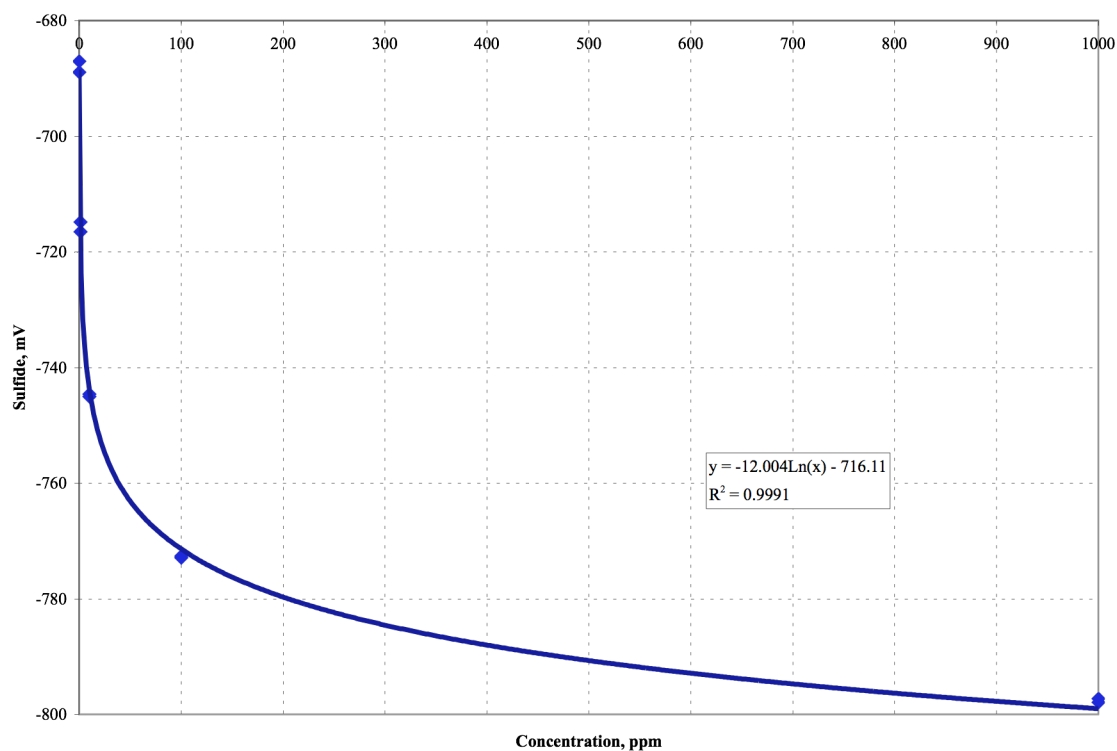
Appendix C-33. Test of Third-Order Kinetics corresponding to 0.60 kg H_2O_2 /kgS

Appendix C-34. Standard Curve Data for 1.00 kg H₂O₂/kgS Addition

Date: 2/6/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-797.9	13.2	17.0
	b	1000	-797.3	13.25	17.0
2	a	100	-772.9	13.2	17.0
	b	100	-772.6	13.2	17.0
3	a	10	-745.0	13.2	17.0
	b	10	-744.6	13.2	17.0
4	a	1	-716.5	13.2	17.0
	b	1	-714.8	13.2	17.0
5	a	0.1	-687.0	13.2	17.0
	b	0.1	-688.9	13.2	17.0



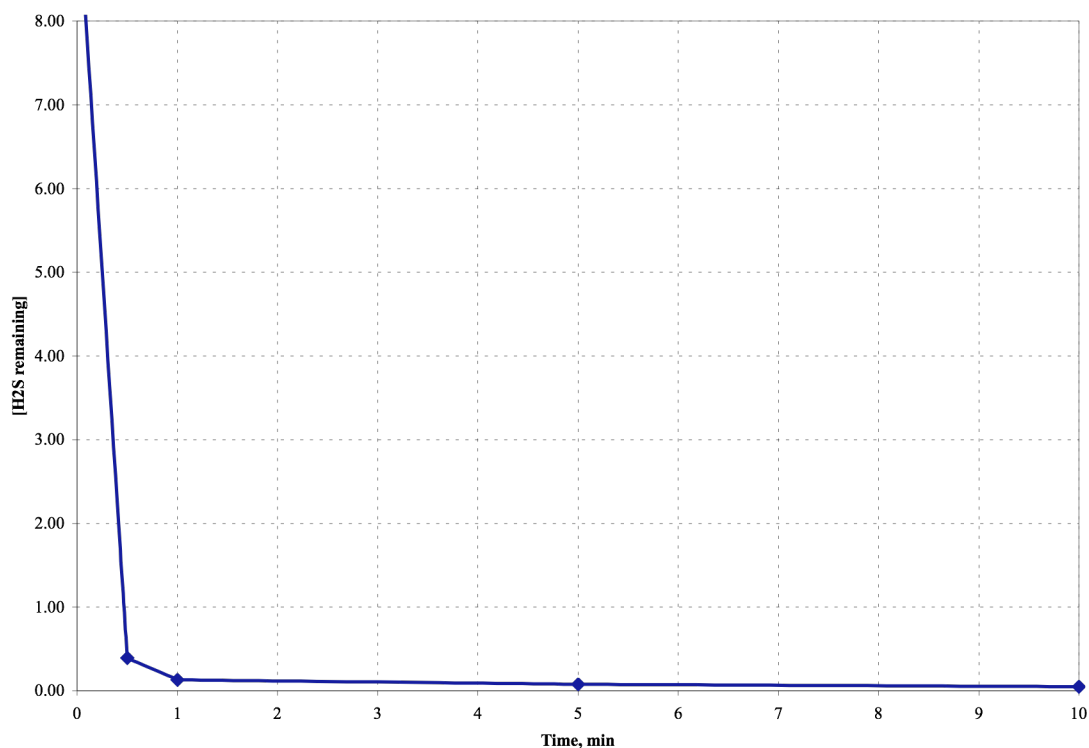
Appendix C-35. Standard Curve for 1.00 kg H₂O₂/kgS Addition

Appendix C-36. Ion Selective Electrode Method Data for 1.00 kg H₂O₂/kgS Addition

Date: 2/6/06
Method: Ion Selective Electrode Method

H₂O₂ Concentration: 1.00 kgH₂O₂/kgS
H₂S Initial Concentration: 9.63 mg/L
Initial pH: 13.20
pH after HCl addition: 7.50

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-743.0	2.240086638	9.39	9.63	10.3
	b		-743.6	2.290069977	9.88		10.3
2	a	0.5	-705.5	-0.883872043	0.41	0.39	10.3
	b		-704.2	-0.992169277	0.37		10.3
3	a	1	-692.3	-1.983505498	0.14	0.13	10.3
	b		-690.8	-2.108463845	0.12		10.3
4	a	5	-685.0	-2.591636121	0.07	0.08	10.3
	b		-685.4	-2.558313895	0.08		10.3
5	a	10	-685.5	-2.549983339	0.08	0.05	10.3
	b		-665.1	-4.249416861	0.01		10.3
6	a						
	b						
7	a						
	b						
8	a						
	b						
9	a						
	b						



Appendix C-37. H₂S remaining after 1.00 kg H₂O₂/kgS Addition

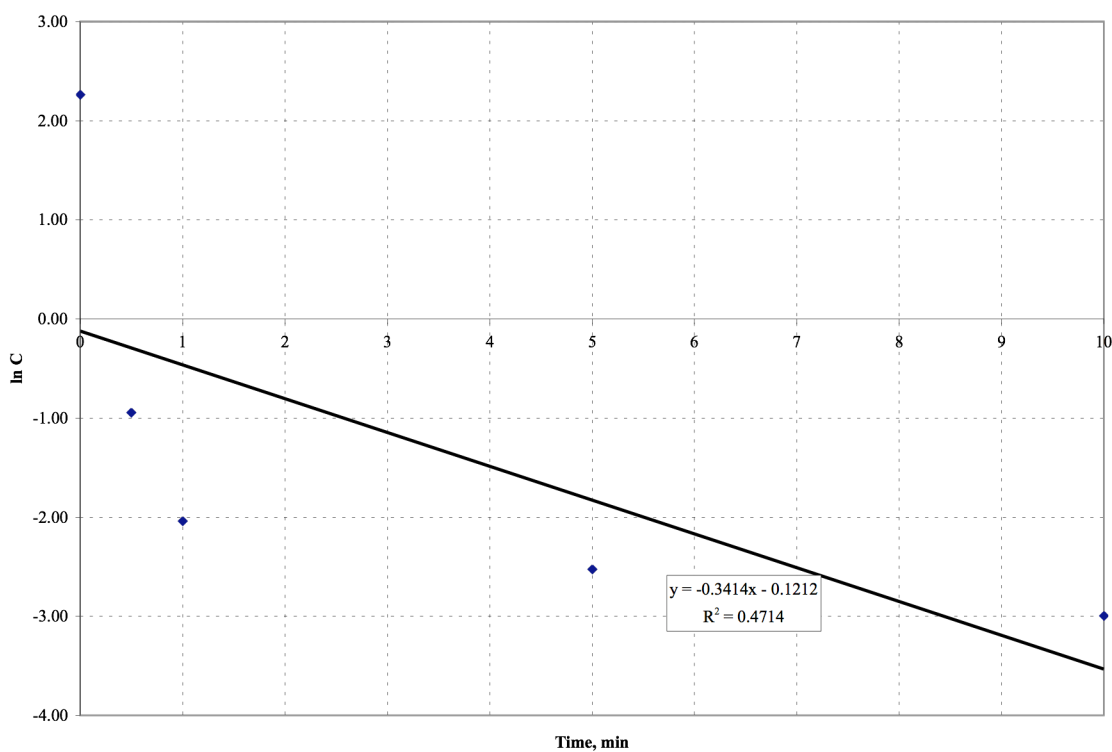
Appendix C-38. Linear Regression Analysis corresponding to 1.00 H₂O₂/kgS – pH = 7.50

Date: 2/6/07
Method: Ion Selective Electrode Method
H₂O₂ Concentration: 1.00 kgH₂O₂/kgS

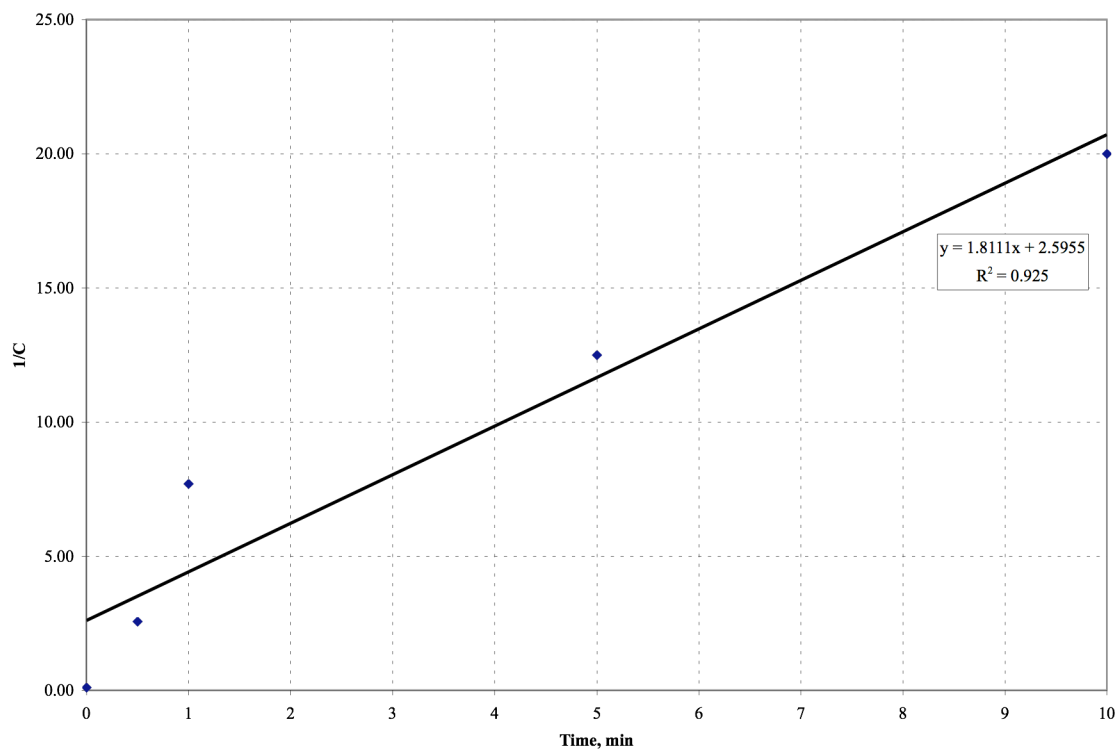
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	9.63	2.2649	0.1038	0.0108	0.0011	0.00011628	0.00001207	0.00000125	0.00000013
0.5	0.39	-0.9416	2.5641	6.5746	16.8580	43.2257	110.8350	284.1923	728.6983
1	0.13	-2.0402	7.6923	59.1716	455.1661	3501.2780	26932.9074	207176.2110	1593663.1618
5	0.08	-2.5257	12.5000	156.2500	1953.1250	24414.0625	305175.7813	3814697.2656	47683715.8203
10	0.05	-2.9957	20.0000	400.0000	8000.0000	160000.0000	3200000.0000	64000000.0000	1280000000.0000

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

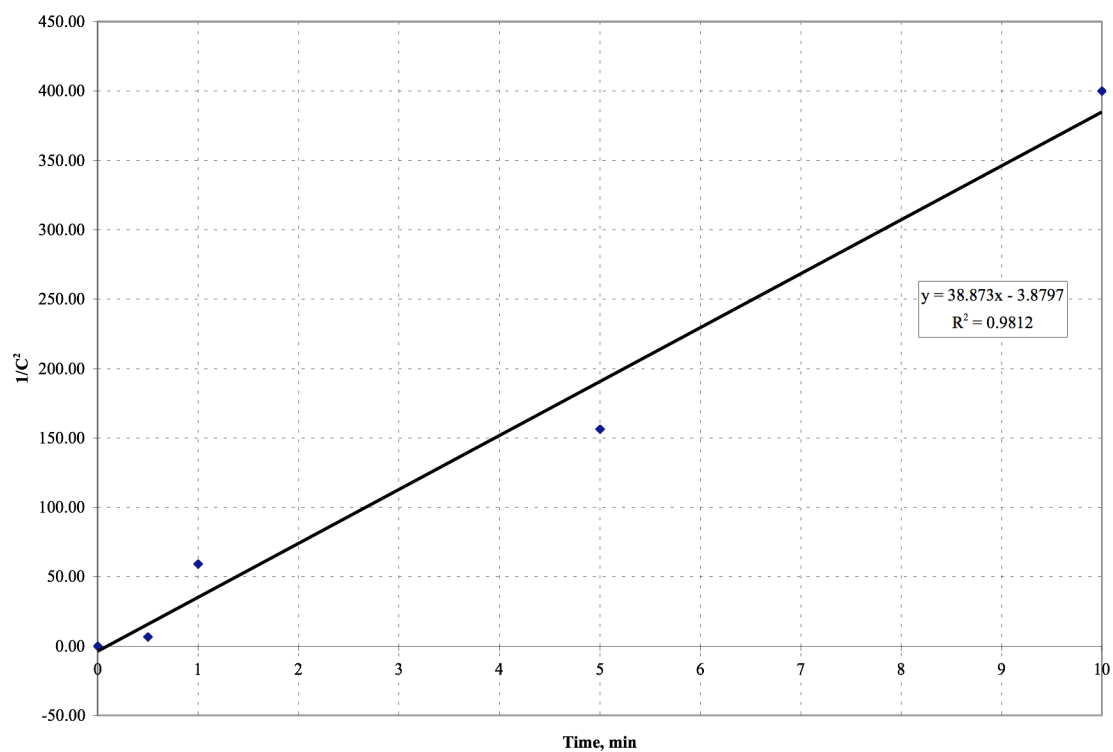
k = 19.4365 L²mg⁻²min⁻¹
C₀ = 9.63 mg/L
C = 4.82 mg/L
t_{1/2} = 0.0008 min



Appendix C-39. Test of First-Order Kinetics corresponding to 1.00 kg H₂O₂/kgS



Appendix C-40. Test of Second-Order Kinetics corresponding to 1.00 kg H_2O_2 /kgS



Appendix C-41. Test of Third-Order Kinetics corresponding to 1.00 kg H_2O_2 /kgS

APPENDIX D

Appendix D-1. Results Summary - Ion Selective Electrode Method – H₂O₂ Addition

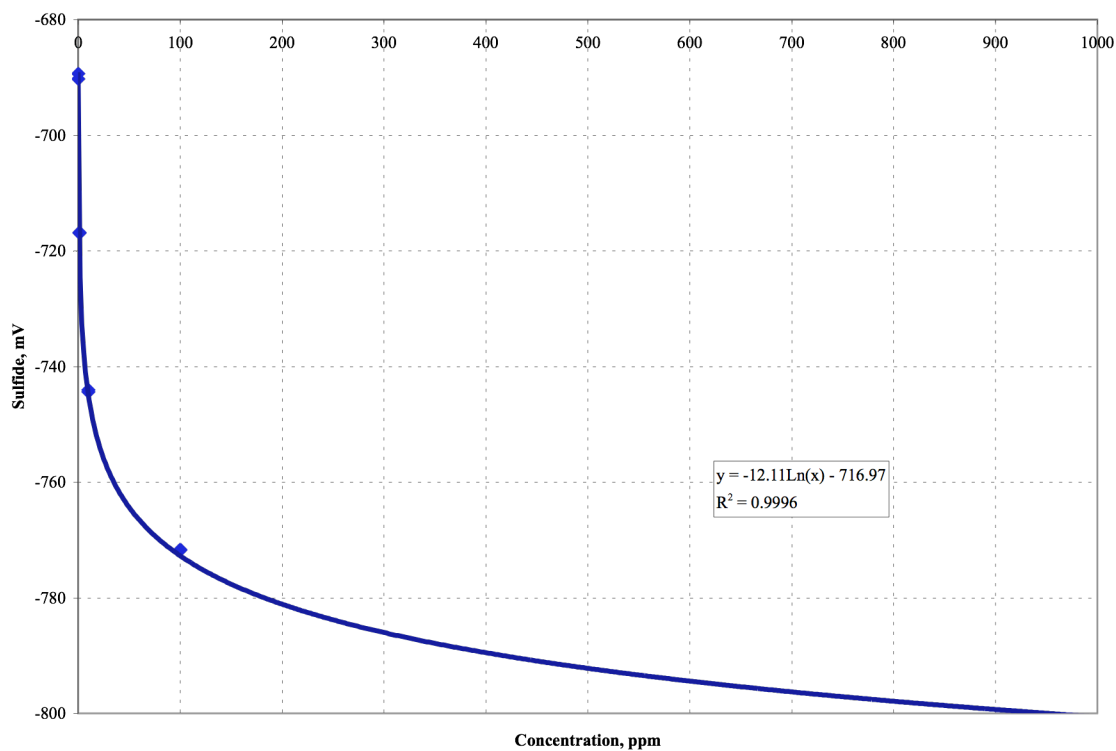
Time, min	H ₂ O ₂ Concentration, kgH ₂ O ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	0.30	8.78	100.00	0.00
1	0.30	0.51	5.81	94.19
5	0.30	0.39	4.44	95.56
10	0.30	0.33	3.76	96.24
20	0.30	0.28	3.19	96.81
40	0.30	0.22	2.51	97.49
60	0.30	0.18	2.05	97.95

Appendix D-2. Standard Curve Data for 0.30 kg H₂O₂/kgS Addition

Date: 2/4/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.7	13.5	12.4
	b	1000	-801.8	13.5	12.4
2	a	100	-771.6	13.5	12.4
	b	100	-771.8	13.5	12.4
3	a	10	-744.4	13.5	12.4
	b	10	-744.0	13.5	12.4
4	a	1	-716.9	13.5	12.4
	b	1	-716.8	13.5	12.4
5	a	0.1	-690.2	13.5	12.4
	b	0.1	-689.3	13.5	12.4



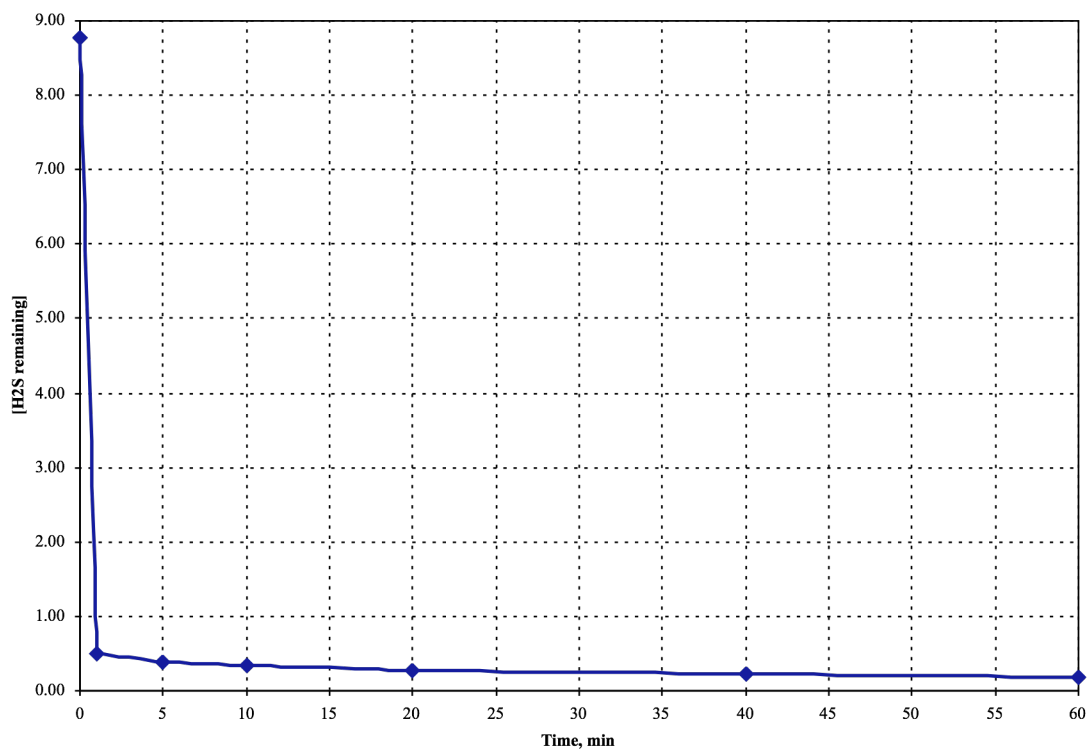
Appendix D-3. Standard Curve for 0.30 kg H₂O₂/kgS Addition

Appendix D-4. Ion Selective Electrode Method Data for 0.30 kg H₂O₂/kgS Addition

Date: 2/5/06
 Method: Ion Selective Electrode Method

H₂O₂ Concentration: 0.30 kgH₂O₂/kgS
 H₂S Initial Concentration: 8.78 mg/L
 Initial pH: 13.50
 pH after HCl addition: 7.20

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-742.5	2.108175062	8.23	8.78	11.2
	b		-744.0	2.232039637	9.32		11.2
2	a	1	-708.6	-0.691164327	0.50	0.51	11.2
	b		-708.8	-0.67464905	0.51		11.2
3	a	5	-705.5	-0.947151115	0.39	0.39	11.2
	b		-705.7	-0.930635838	0.39		11.2
4	a	10	-704.2	-1.054500413	0.35	0.33	11.2
	b		-703.2	-1.137076796	0.32		11.2
5	a	20	-701.4	-1.285714286	0.28	0.28	11.2
	b		-701.5	-1.277456647	0.28		11.2
6	a	40	-698.6	-1.516928159	0.22	0.22	11.2
	b		-698.7	-1.50867052	0.22		11.2
7	a	60	-700.3	-1.376548307	0.25	0.18	11.2
	b		-690.5	-2.185796862	0.11		11.2
8	a						
	b						
9	a						
	b						



Appendix D-5. H₂S remaining after 0.30 kg H₂O₂/kgS Addition

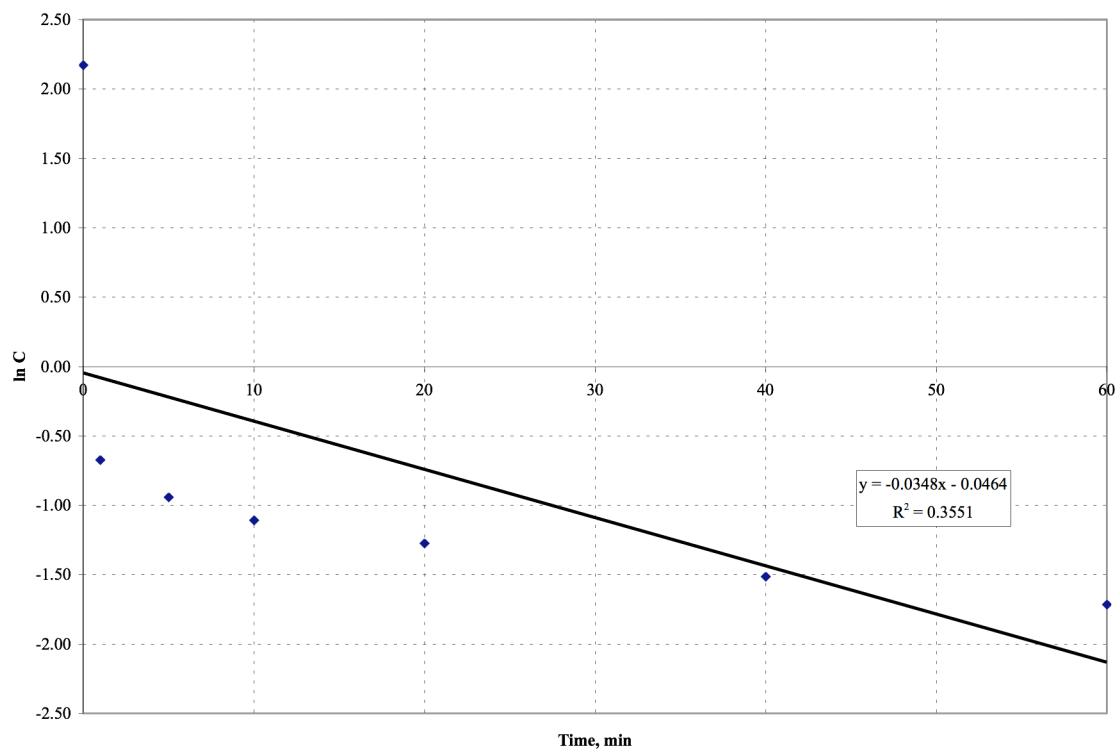
Appendix D-6. Linear Regression Analysis corresponding to 0.30 H₂O₂/kgS – pH = 7.20

Date: 2/5/07
Method: Ion Selective Electrode Method
H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

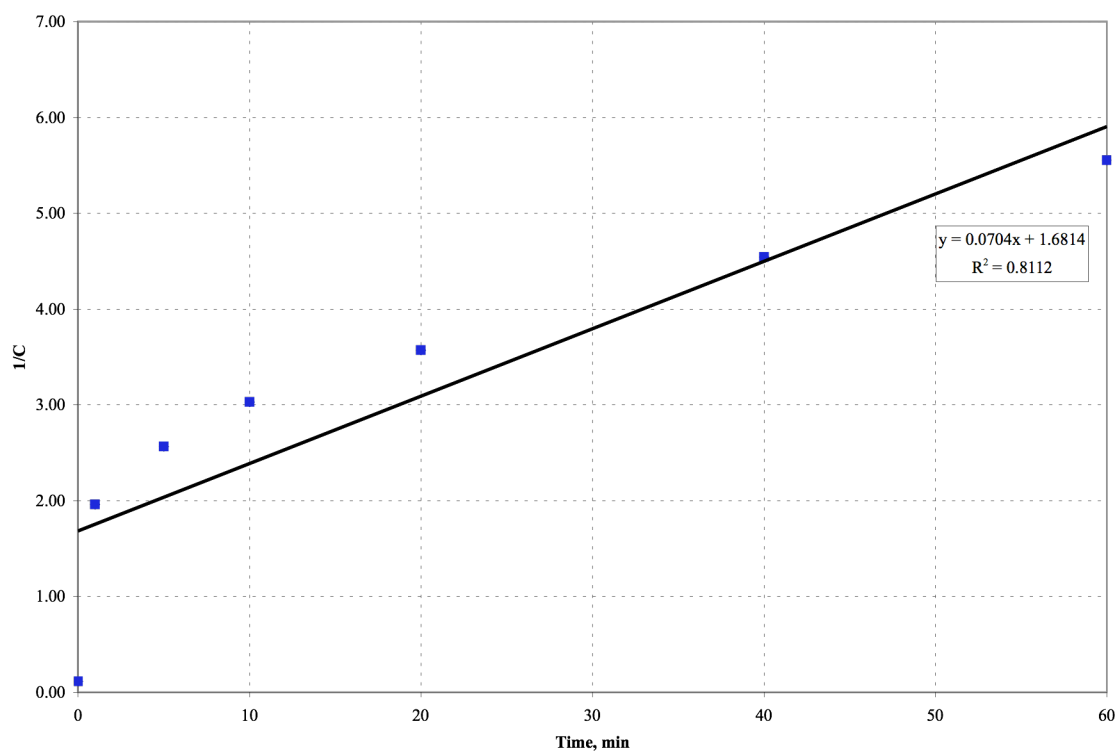
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.78	2.1724764	0.1138952	0.0129721	0.0014775	0.0001683	0.0000192	0.0000022	0.0000002
1	0.51	-0.6733446	1.9607843	3.8446751	7.5385787	14.7815268	28.9833859	56.8301685	111.4317029
5	0.39	-0.9416085	2.5641026	6.5746220	16.8580050	43.2256539	110.8350100	284.1923334	728.6982907
10	0.33	-1.1086626	3.0303030	9.1827365	27.8264741	84.3226488	255.5231782	774.3126613	2346.4020038
20	0.28	-1.2729657	3.5714286	12.7551020	45.5539359	162.6926281	581.0451003	2075.1610723	7411.2895441
40	0.22	-1.5141277	4.5454545	20.6611570	93.9143501	426.8834096	1940.3791	8819.9052	40090.4780
60	0.18	-1.7147984	5.5555556	30.8641975	171.4677641	952.5986892	5292.2149401	29401.1941119	163339.9672881

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

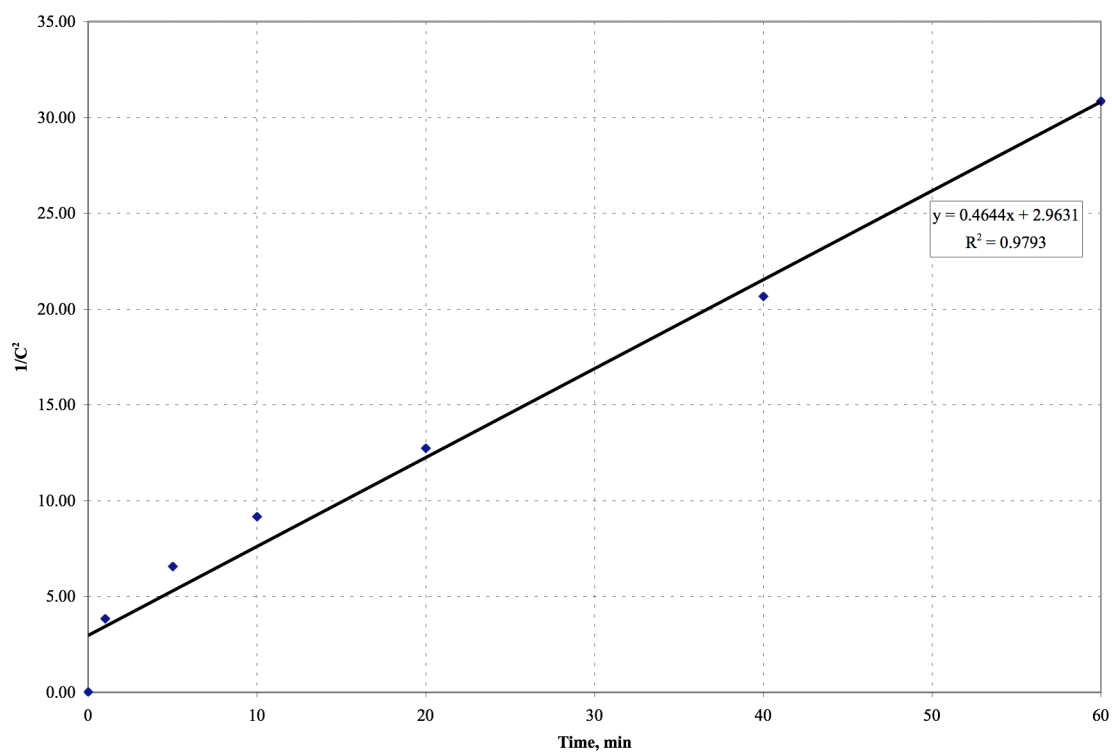
k= 0.2322 L²mg⁻²min⁻¹
C₀= 8.78 mg/L
C= 4.39 mg/L
t_{1/2}= 0.08 min



Appendix D-7. Test of First-Order Kinetics corresponding to 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



Appendix D-8. Test of Second-Order Kinetics corresponding to 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



Appendix D-9. Test of Third-Order Kinetics corresponding to 0.30 kg H₂O₂/kgS

APPENDIX E

Appendix E-1. Results Summary - Ion Selective Electrode Method – FeCl₂ and H₂O₂ Addition

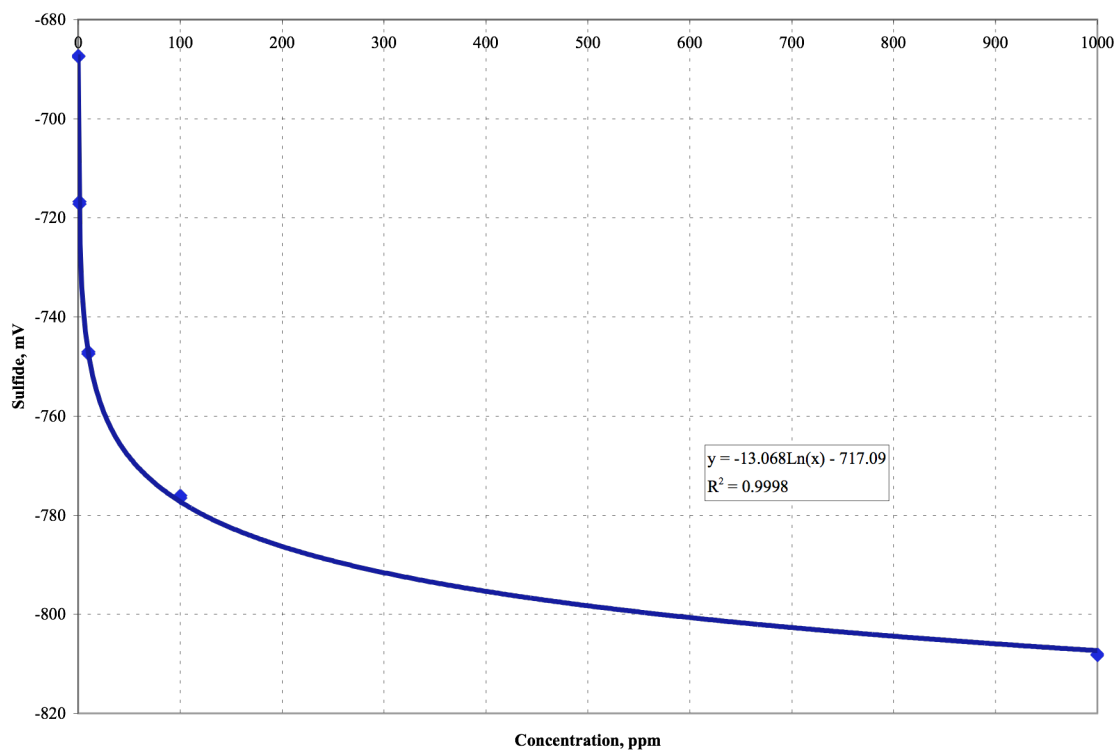
Time, min	Time, min	FeCl ₂ Concentration, kgFeCl ₂ /kgS	H ₂ O ₂ Concentration, kgH ₂ O ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	0	1.45	0.60	8.43	100.00	0.00
1	1	1.45	0.60	0.43	5.10	94.90
5	1	1.45	0.60	0.32	3.80	96.20
10	1	1.45	0.60	0.17	2.02	97.98
15	1	1.45	0.60	0.17	2.02	97.98
20	1	1.45	0.60	0.14	1.66	98.34
30	1	1.45	0.60	0.11	1.30	98.70
0	0	1.45	0.10	8.08	100.00	0.00
1	1	1.45	0.10	1.16	14.36	85.64
2	1	1.45	0.10	0.96	11.88	88.12
5	1	1.45	0.10	0.80	9.90	90.10
10	1	1.45	0.10	0.67	8.29	91.71
15	1	1.45	0.10	0.56	6.93	93.07
20	1	1.45	0.10	0.50	6.19	93.81
0	0	1.45	0.30	6.91	100.00	0.00
1	1	1.45	0.30	0.69	9.99	90.01
5	1	1.45	0.30	0.48	6.95	93.05
10	1	1.45	0.30	0.43	6.22	93.78
15	1	1.45	0.30	0.39	5.64	94.36
20	1	1.45	0.30	0.30	4.34	95.66
0	0	2.9	0.10	7.55	100.00	0.00
1	1	2.9	0.10	0.62	8.21	91.79
5	1	2.9	0.10	0.58	7.68	92.32
10	1	2.9	0.10	0.35	4.64	95.36
15	1	2.9	0.10	0.25	3.31	96.69
20	1	2.9	0.10	0.20	2.65	97.35
30	1	2.9	0.10	0.16	2.12	97.88
0	0	2.9	0.30	6.97	100.00	0.00
1	1	2.9	0.30	0.28	4.02	95.98
5	1	2.9	0.30	0.26	3.73	96.27
10	1	2.9	0.30	0.22	3.16	96.84
15	1	2.9	0.30	0.15	2.15	97.85
20	1	2.9	0.30	0.12	1.72	98.28
30	1	2.9	0.30	0.10	1.43	98.57
0	0	2.9	0.60	6.70	100.00	0.00
1	1	2.9	0.60	0.39	5.82	94.18
5	1	2.9	0.60	0.20	2.99	97.01
10	1	2.9	0.60	0.12	1.79	98.21
15	1	2.9	0.60	0.09	1.34	98.66
20	1	2.9	0.60	0.08	1.19	98.81
0	0	1.45	0.60	8.03	100.00	0.00
1	5	1.45	0.60	0.17	2.12	97.88
5	5	1.45	0.60	0.14	1.74	98.26
10	5	1.45	0.60	0.12	1.49	98.51
15	5	1.45	0.60	0.11	1.37	98.63
20	5	1.45	0.60	0.08	1.00	99.00
30	5	1.45	0.60	0.08	1.00	99.00
0	0	1.45	0.10	8.05	100.00	0.00
1	5	1.45	0.10	0.39	4.84	95.16
5	5	1.45	0.10	0.31	3.85	96.15
10	5	1.45	0.10	0.25	3.11	96.89
15	5	1.45	0.10	0.22	2.73	97.27
20	5	1.45	0.10	0.19	2.36	97.64
30	5	1.45	0.10	0.17	2.11	97.89
0	0	1.45	0.30	7.76	100.00	0.00
1	5	1.45	0.30	0.35	4.51	95.49
5	5	1.45	0.30	0.22	2.84	97.16
10	5	1.45	0.30	0.19	2.45	97.55
15	5	1.45	0.30	0.18	2.32	97.68
20	5	1.45	0.30	0.16	2.06	97.94
30	5	1.45	0.30	0.14	1.80	98.20
0	0	2.9	0.10	7.54	100.00	0.00
1	5	2.9	0.10	0.28	3.71	96.29
5	5	2.9	0.10	0.25	3.32	96.68
10	5	2.9	0.10	0.20	2.65	97.35
15	5	2.9	0.10	0.14	1.86	98.14
20	5	2.9	0.10	0.13	1.72	98.28
30	5	2.9	0.10	0.11	1.46	98.54
0	0	2.9	0.30	6.51	100.00	0.00
1	5	2.9	0.30	0.10	1.54	98.46
5	5	2.9	0.30	0.09	1.38	98.62
10	5	2.9	0.30	0.08	1.23	98.77
15	5	2.9	0.30	0.07	1.08	98.92
20	5	2.9	0.30	0.06	0.92	99.08
30	5	2.9	0.30	0.05	0.77	99.23

Appendix E-2. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



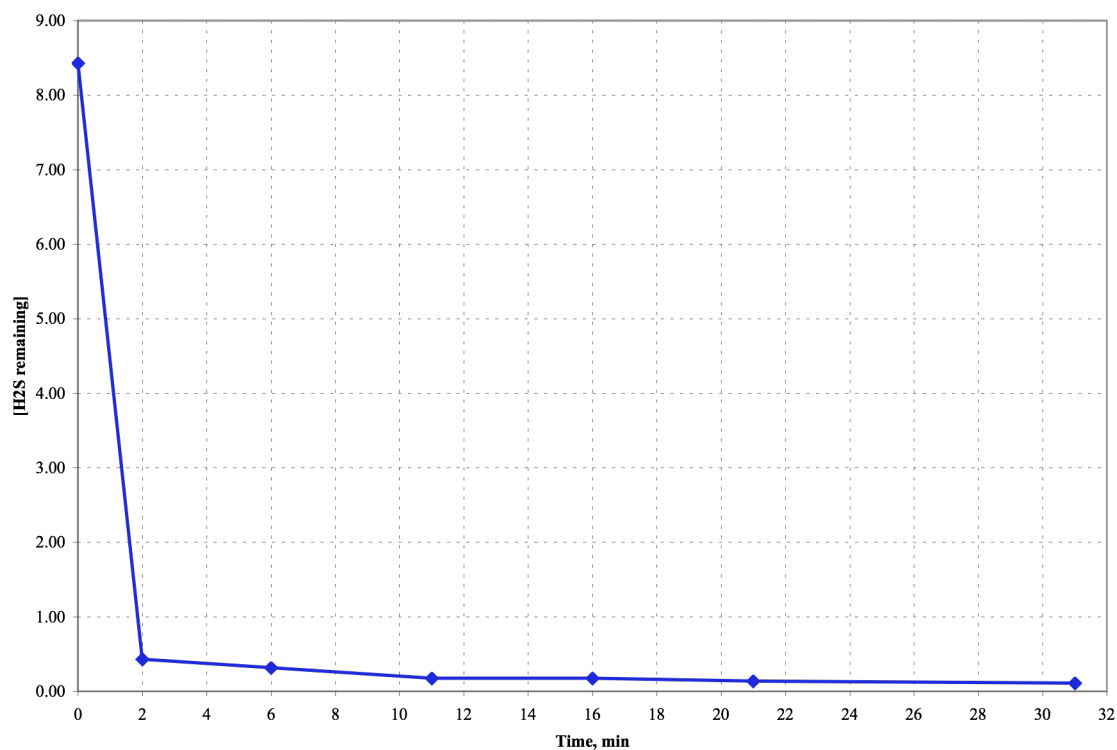
Appendix E-3. Standard Curve for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Appendix E-4. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/8/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS
 H₂S Initial Concentration: 8.43 mg/L
 Initial pH: 12.50
 pH after HCl Addition: 7.20

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-744.9	2.128099174	8.40	8.43	16.0
	b				-745.0	2.135751454	8.46		16.0
2	a	1	1	2	-697.4	-1.506734007	0.22	0.43	16.0
	b				-711.1	-0.458371595	0.63		16.0
3	a	5	1	6	-698.9	-1.391949801	0.25	0.32	16.0
	b				-704.6	-0.955769819	0.38		16.0
4	a	10	1	11	-695.7	-1.636822773	0.19	0.17	16.0
	b				-692.4	-1.889348026	0.15		16.0
5	a	15	1	16	-690.6	-2.027089073	0.13	0.17	16.0
	b				-696.9	-1.544995409	0.21		16.0
6	a	20	1	21	-684.7	-2.478573615	0.08	0.14	16.0
	b				-695.2	-1.675084175	0.19		16.0
7	a	30	1	31	-687.2	-2.287266605	0.10	0.11	16.0
	b				-688.6	-2.18013468	0.11		16.0



Appendix E-5. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Appendix E-6. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS – pH = 7.20

Date: 2/8/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS

Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.43	2.1318	0.1186	0.0141	0.0017	0.0001980	0.0000235	0.0000028	0.0000003
2	0.43	-0.8440	2.3256	5.4083	12.5775	29.2500	68.0233	158.1937	367.8924
6	0.32	-1.1394	3.1250	9.7656	30.5176	95.3674	298.0232	931.3226	2910.3830
11	0.17	-1.7720	5.8824	34.6021	203.5416	1197.3037	7042.9628	41429.1928	243701.1342
16	0.17	-1.7720	5.8824	34.6021	203.5416	1197.3037	7042.9628	41429.1928	243701.1342
21	0.14	-1.9661	7.1429	51.0204	364.4315	2603.0820	18593.4432	132810.3086	948645.0616
31	0.11	-2.2073	9.0909	82.6446	751.3148	6830.1346	62092.1323	564473.9301	5131581.1823

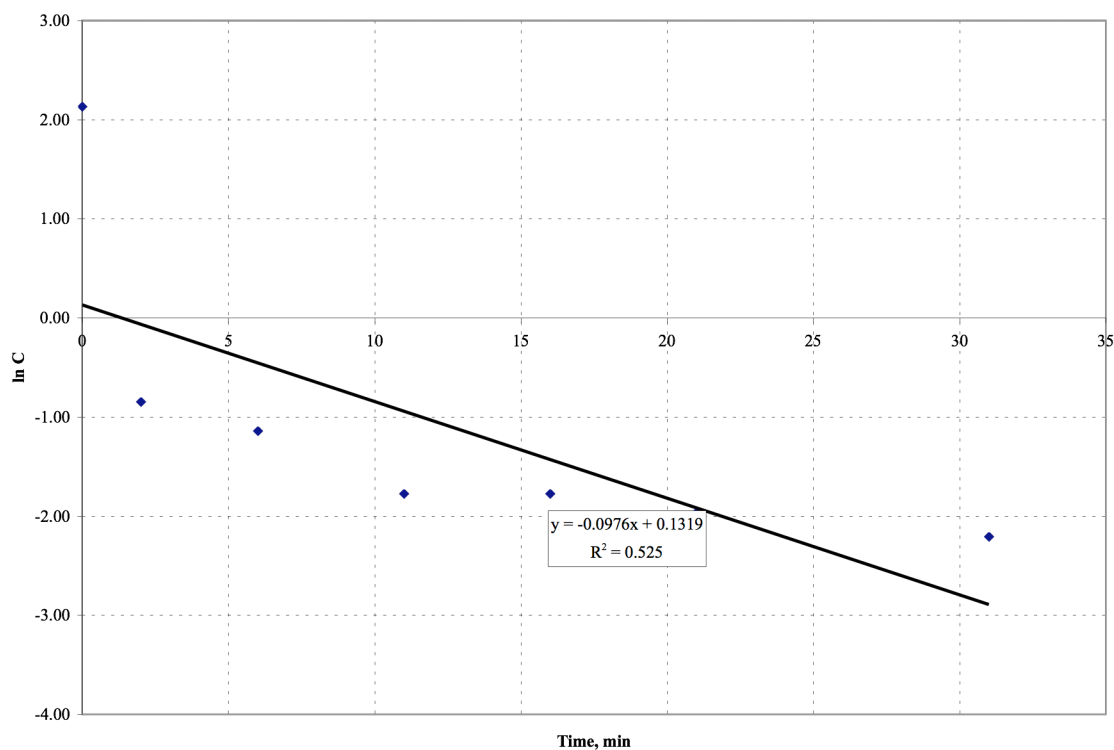
$$\frac{1}{[C]^n} = \frac{1}{[C_0]^n} + 2kt$$

$$k = 1.3060 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$$

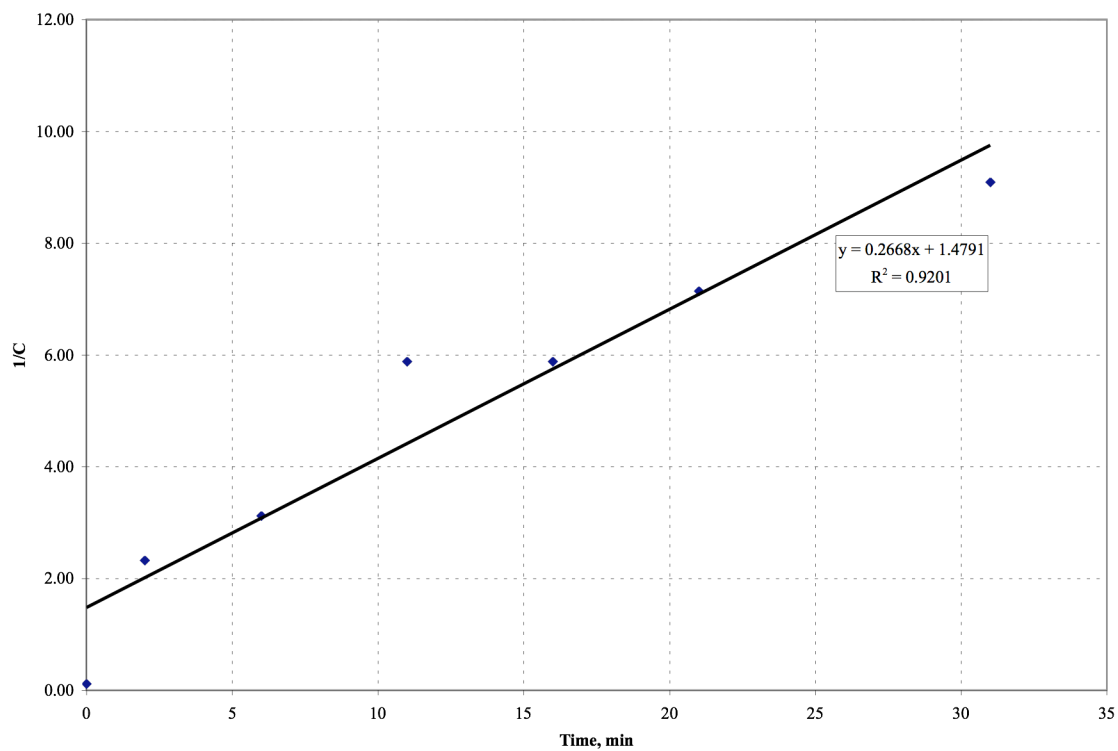
$$C_0 = 8.43 \text{ mg/L}$$

$$C = 4.22 \text{ mg/L}$$

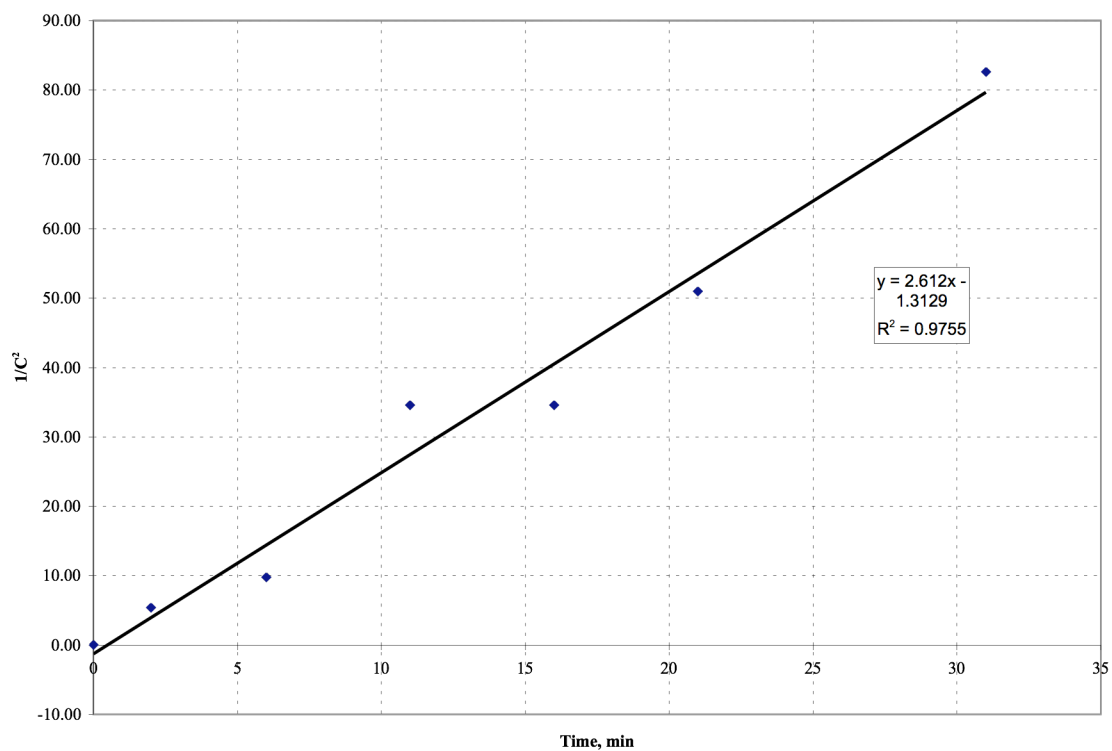
$$t_{1/2} = 0.02 \text{ min}$$



Appendix E-7. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS



Appendix E-8. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$



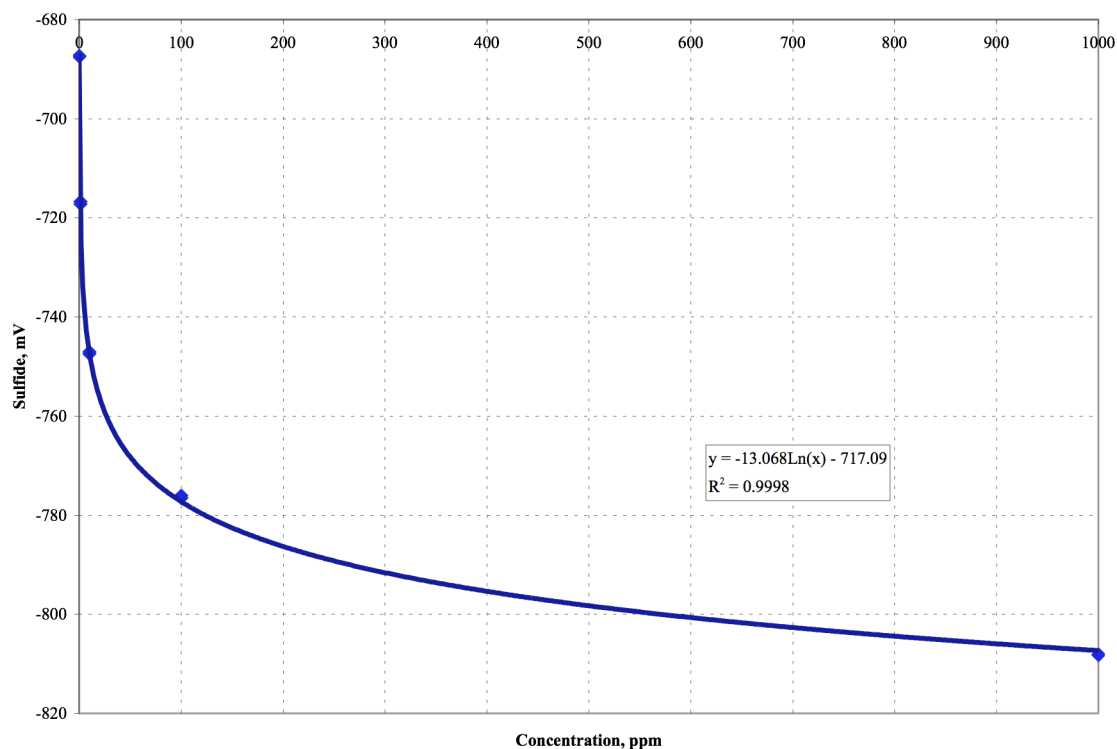
Appendix E-9. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-10. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



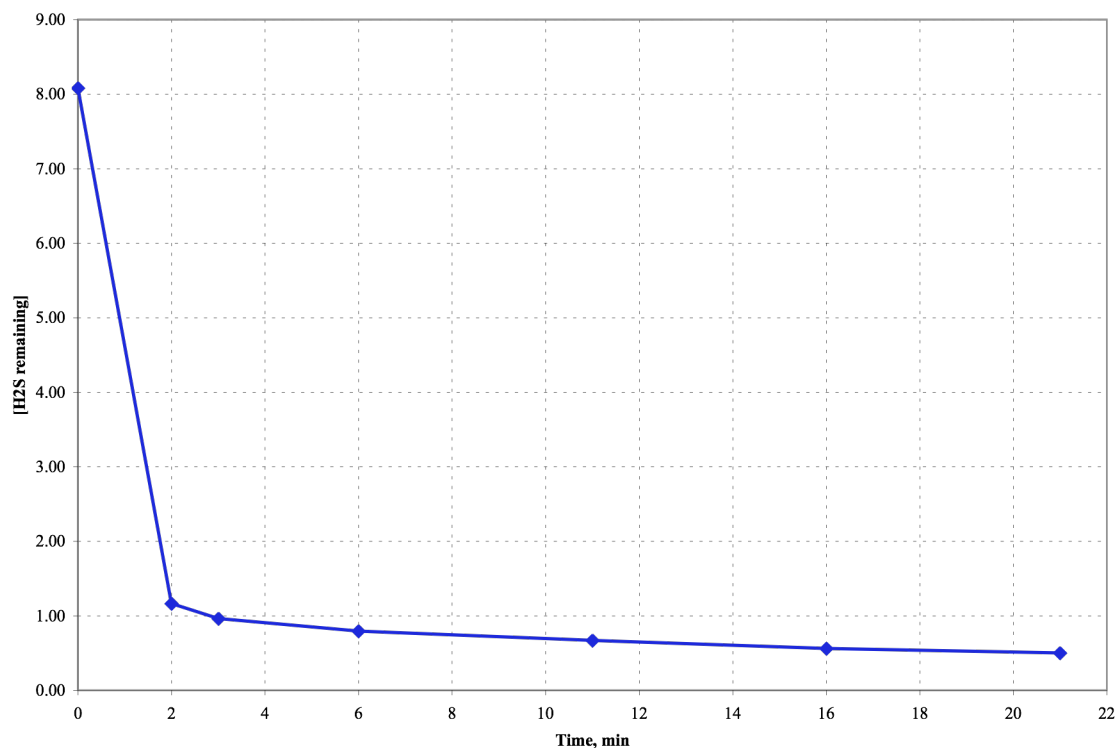
Appendix E-11. Standard Curve for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Appendix E-12. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/8/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS
 H₂S Initial Concentration: 8.08 mg/L
 Initial pH: 12.50
 pH after HCl Addition: 7.00

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-744.3	2.082185491	8.02	8.08	21.5
	b				-744.5	2.097490052	8.15		21.5
2	a	1	1	2	-719.3	0.169115396	1.18	1.16	21.5
	b				-718.8	0.130853994	1.14		21.5
3	a	2	1	3	-716.9	-0.014539333	0.99	0.96	21.5
	b				-716.2	-0.068105295	0.93		21.5
4	a	5	1	6	-714.1	-0.228803183	0.80	0.80	21.5
	b				-714.1	-0.228803183	0.80		21.5
5	a	10	1	11	-711.9	-0.397153352	0.67	0.67	21.5
	b				-711.8	-0.404805632	0.67		21.5
6	a	15	1	16	-710.6	-0.496632997	0.61	0.56	21.5
	b				-708.4	-0.664983165	0.51		21.5
7	a	20	1	21	-707.2	-0.75681053	0.47	0.50	21.5
	b				-708.8	-0.634374043	0.53		21.5
8	a								
	b								



Appendix E-13. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Appendix E-14. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS – pH = 7.00

Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS

Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.08	2.0894	0.1238	0.0153	0.0019	0.0002	0.00002904	0.00000359	0.00000044
2	1.16	0.1484	0.8621	0.7432	0.6407	0.5523	0.4761	0.4104	0.3538
3	0.96	-0.0408	1.0417	1.0851	1.1303	1.1774	1.2264	1.2775	1.3308
6	0.80	-0.2231	1.2500	1.5625	1.9531	2.4414	3.0518	3.8147	4.7684
11	0.67	-0.4005	1.4925	2.2277	3.3249	4.9625	7.4067	11.0548	16.4997
16	0.56	-0.5798	1.7857	3.1888	5.6942	10.1683	18.1577	32.4244	57.9007
21	0.50	-0.6931	2.0000	4.0000	8.0000	16.0000	32.0000	64.0000	128.0000

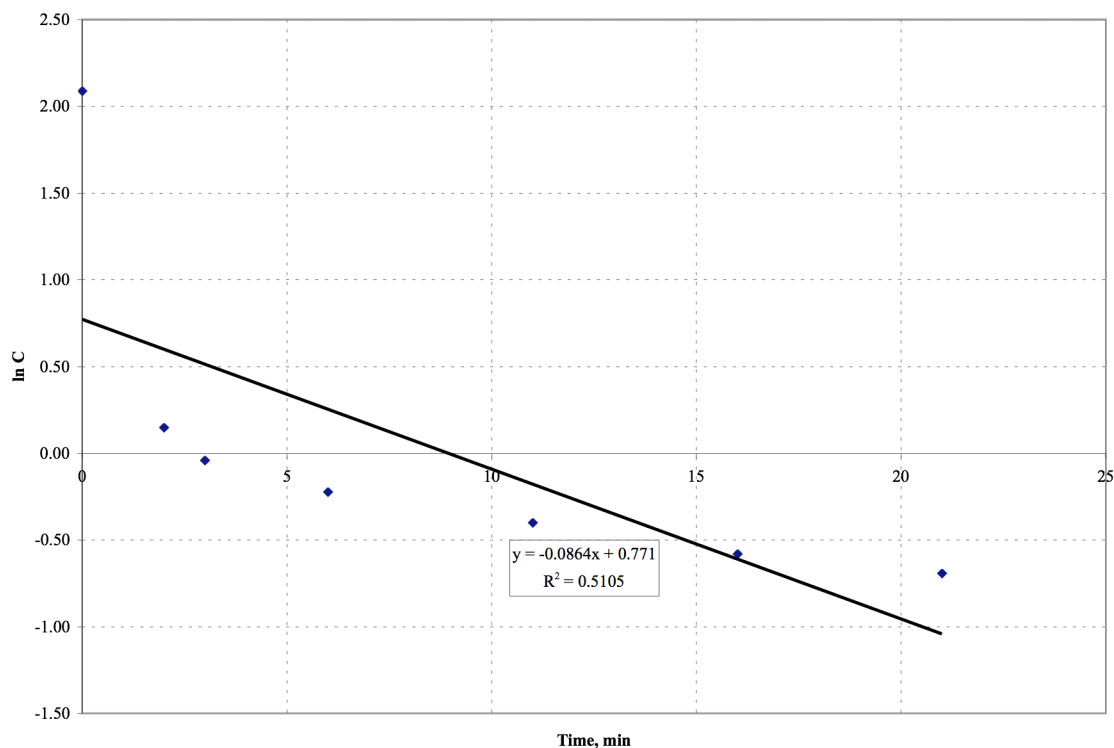
$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

$$k = 0.0887 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$$

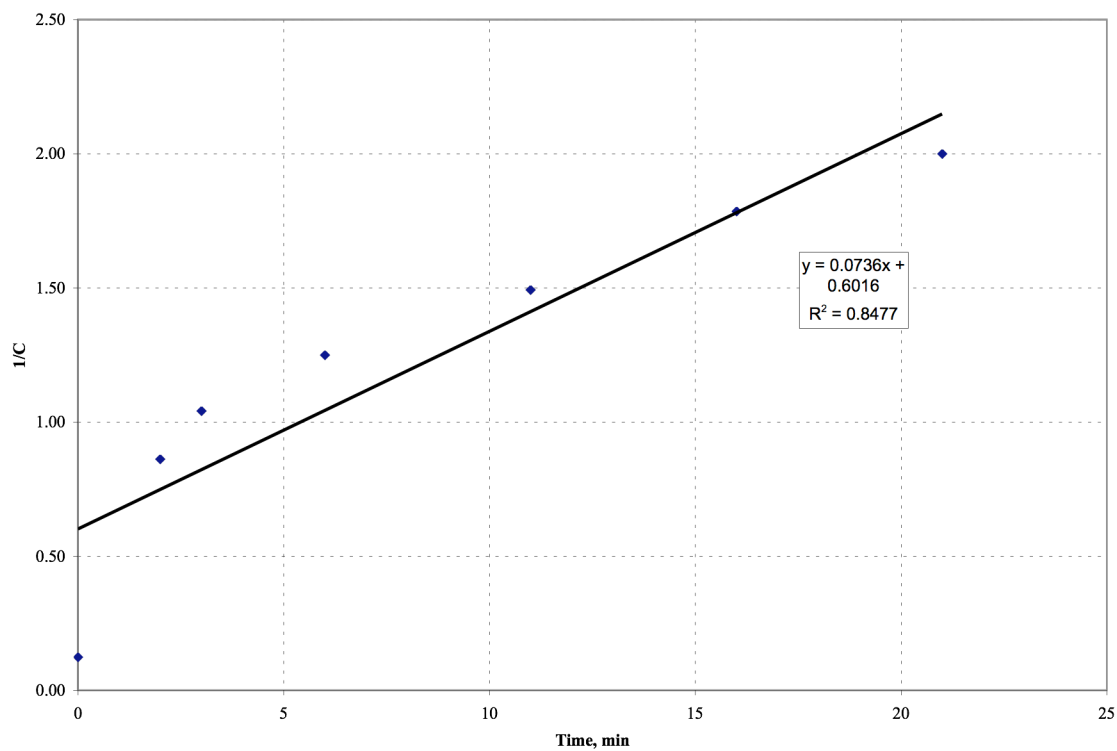
$$C_0 = 8.08 \text{ mg/L}$$

$$C = 4.04 \text{ mg/L}$$

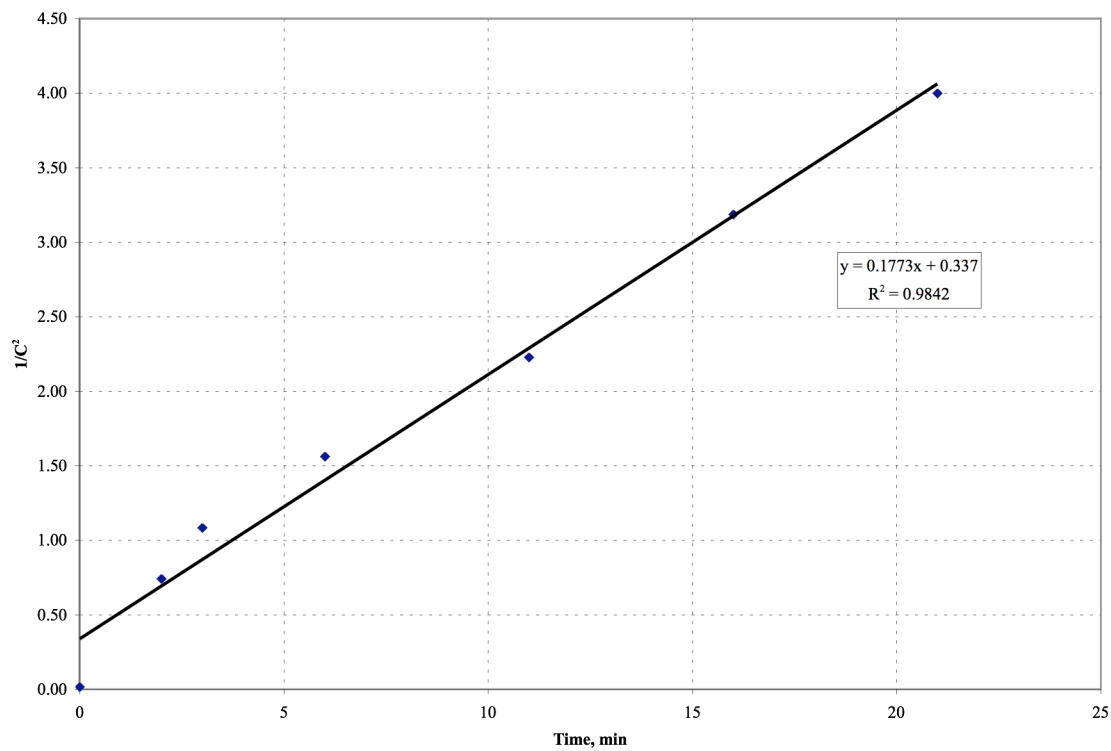
$$t_{1/2} = 0.259 \text{ min}$$



Appendix E-15. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS



Appendix E-16. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$



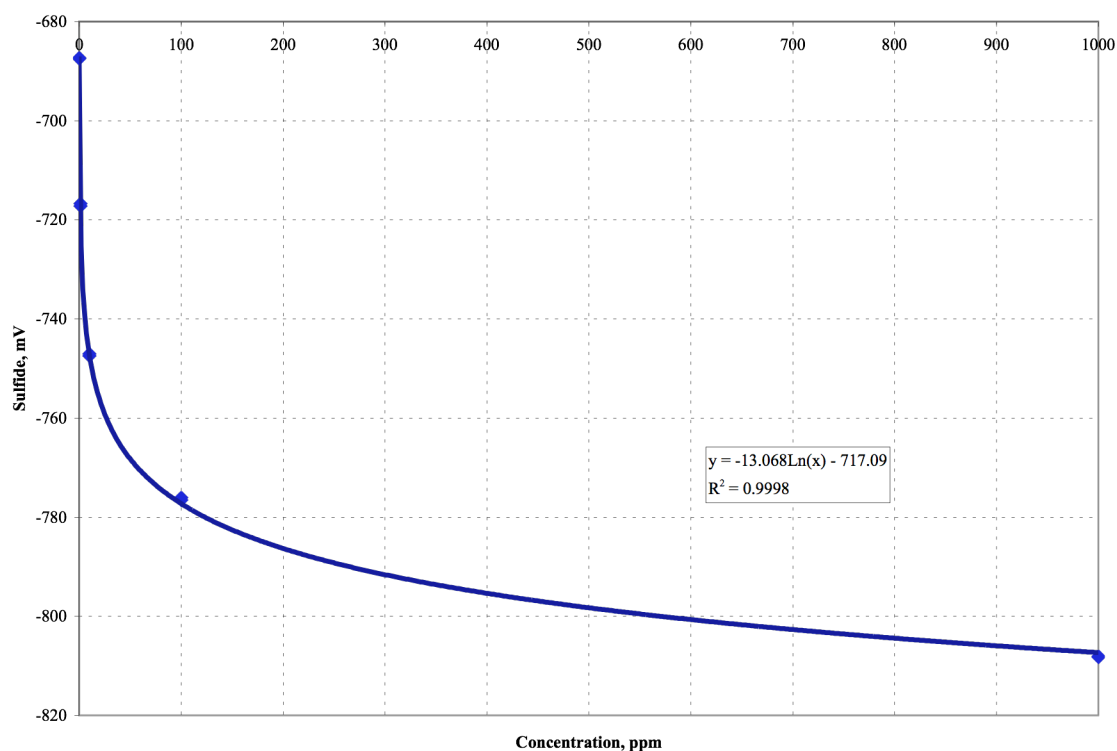
Appendix E-17. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-18. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



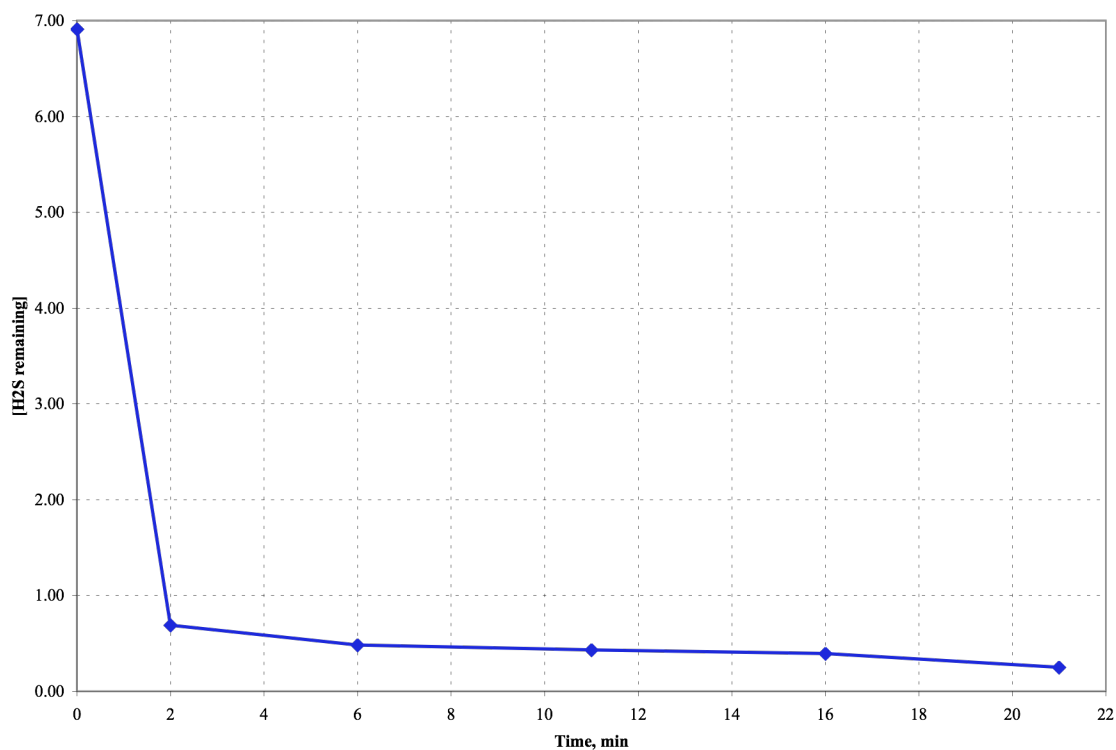
Appendix E-19. Standard Curve for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Appendix E-20. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/8/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS
 H₂S Initial Concentration: 6.91 mg/L
 Initial pH: 12.50
 pH after HCl Addition: 6.80

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-742.0	1.906183043	6.73	6.91	19.7
	b				-742.7	1.959749005	7.10		19.7
2	a	1	1	2	-711.9	-0.397153352	0.67	0.69	19.7
	b				-712.5	-0.351239669	0.70		19.7
3	a	5	1	6	-708.0	-0.695592287	0.50	0.48	19.7
	b				-707.2	-0.75681053	0.47		19.7
4	a	10	1	11	-705.3	-0.902203857	0.41	0.43	19.7
	b				-706.9	-0.779767371	0.46		19.7
5	a	15	1	16	-705.1	-0.917508418	0.40	0.39	19.7
	b				-704.8	-0.940465259	0.39		19.7
6	a	20	1	21	-699.9	-1.315426997	0.27	0.25	19.7
	b				-698.1	-1.453168044	0.23		19.7
7	a								
	b								



Appendix E-21. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Appendix E-22. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS – pH = 6.80

Date: 2/8/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.91	1.9330	0.1447	0.0209	0.0030	0.0004	0.000063	0.000009	0.000001
2	0.69	-0.3711	1.4493	2.1004	3.0441	4.4117	6.3937	9.2663	13.4294
6	0.48	-0.7340	2.0833	4.3403	9.0422	18.8380	39.2459	81.7622	170.3379
11	0.43	-0.8440	2.3256	5.4083	12.5775	29.2500	68.0233	158.1937	367.8924
16	0.39	-0.9416	2.5641	6.5746	16.8580	43.2257	110.8350	284.1923	728.6983
21	0.30	-1.2040	3.3333	11.1111	37.0370	123.4568	411.5226	1371.7421	4572.4737

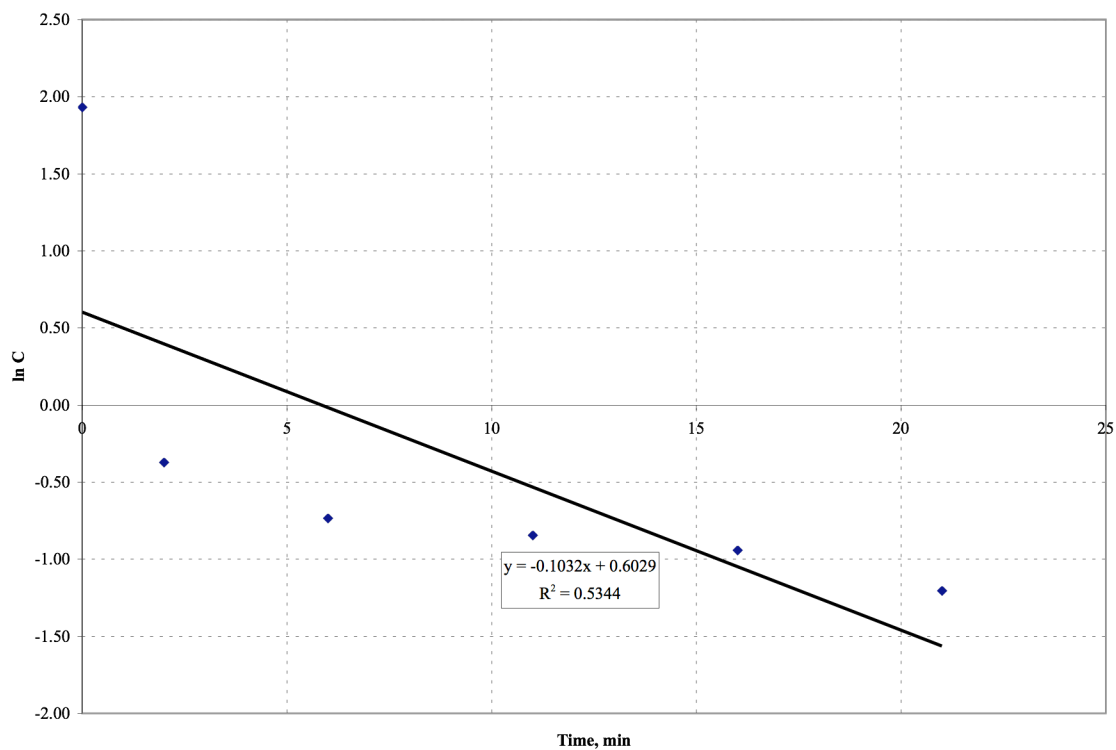
$$\frac{1}{[C]^n} = \frac{1}{[C_0]^n} + 2kt$$

$$k = 0.2273 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$$

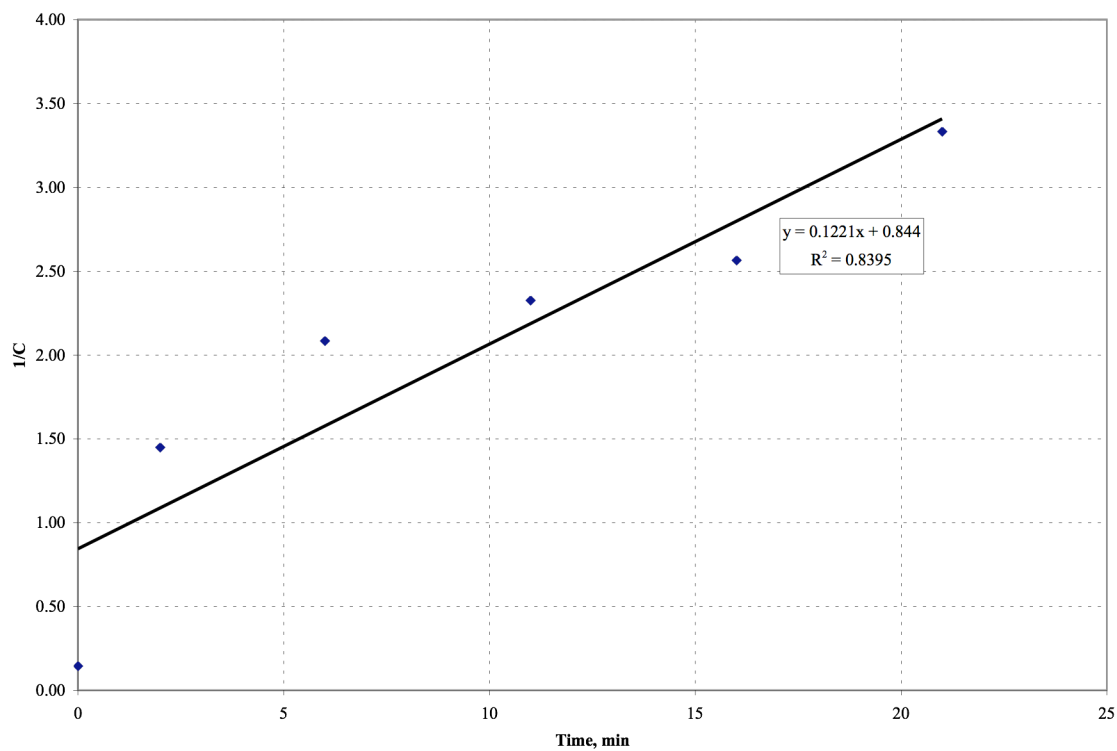
$$C_0 = 6.91 \text{ mg/L}$$

$$C = 3.46 \text{ mg/L}$$

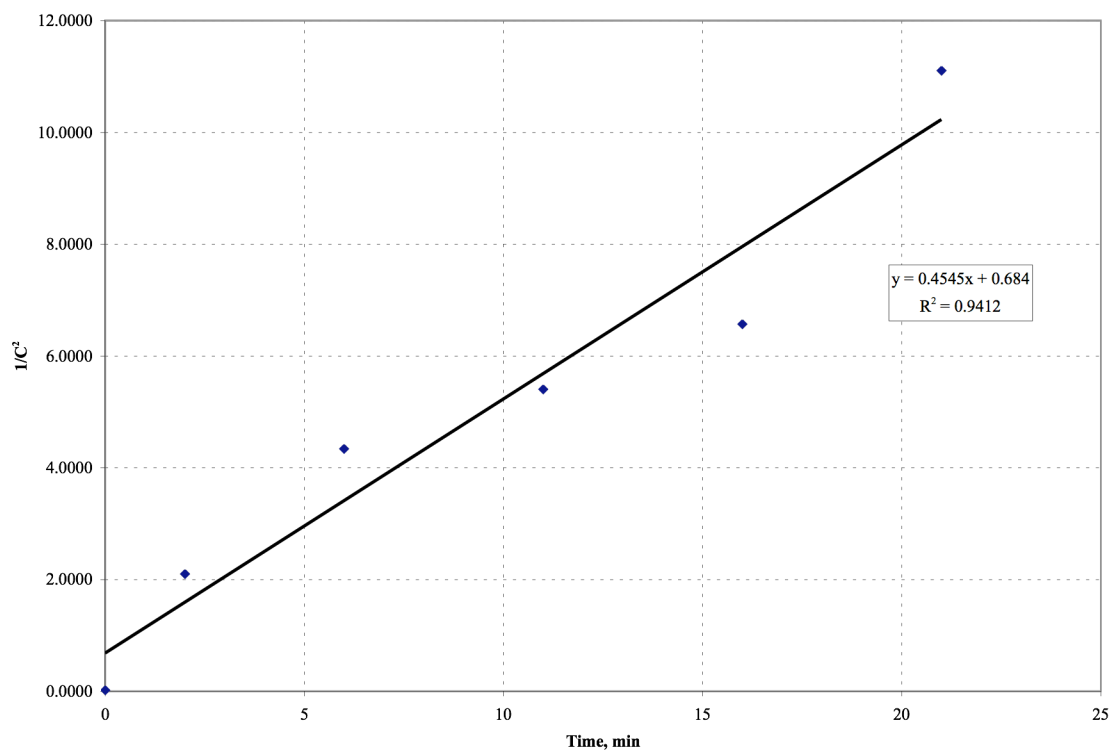
$$t_{1/2} = 0.14 \text{ min}$$



Appendix E-23. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS



Appendix E-24. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



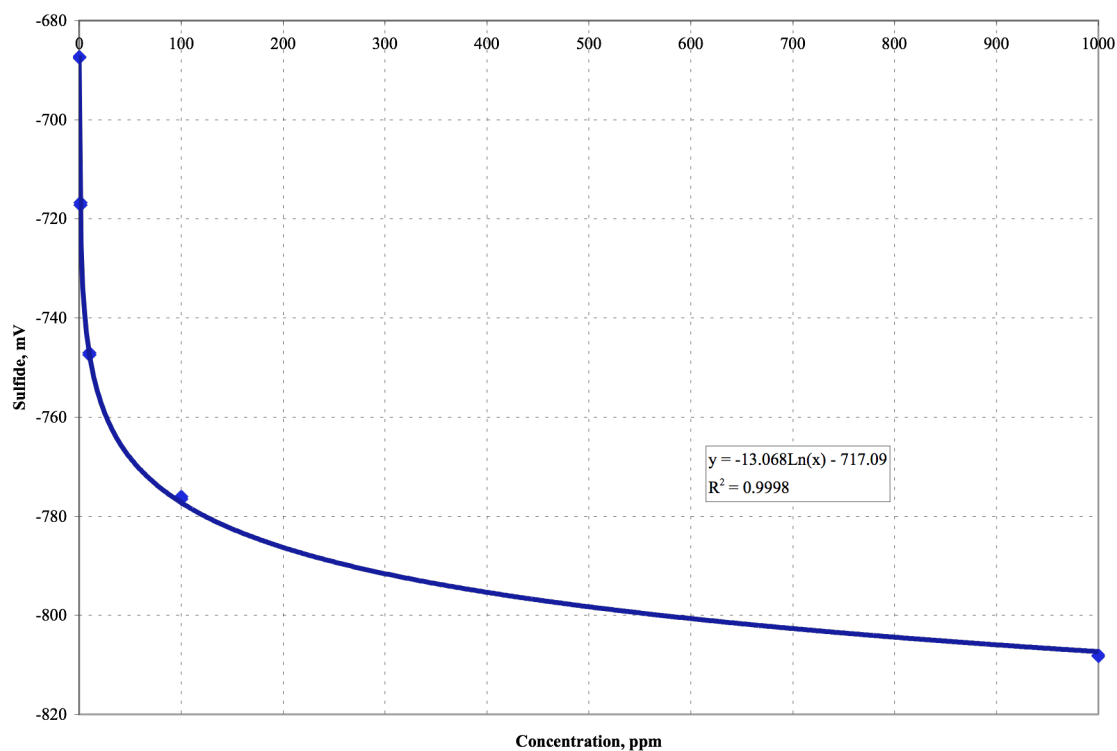
Appendix E-25. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-26. Standard Curve Data for 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



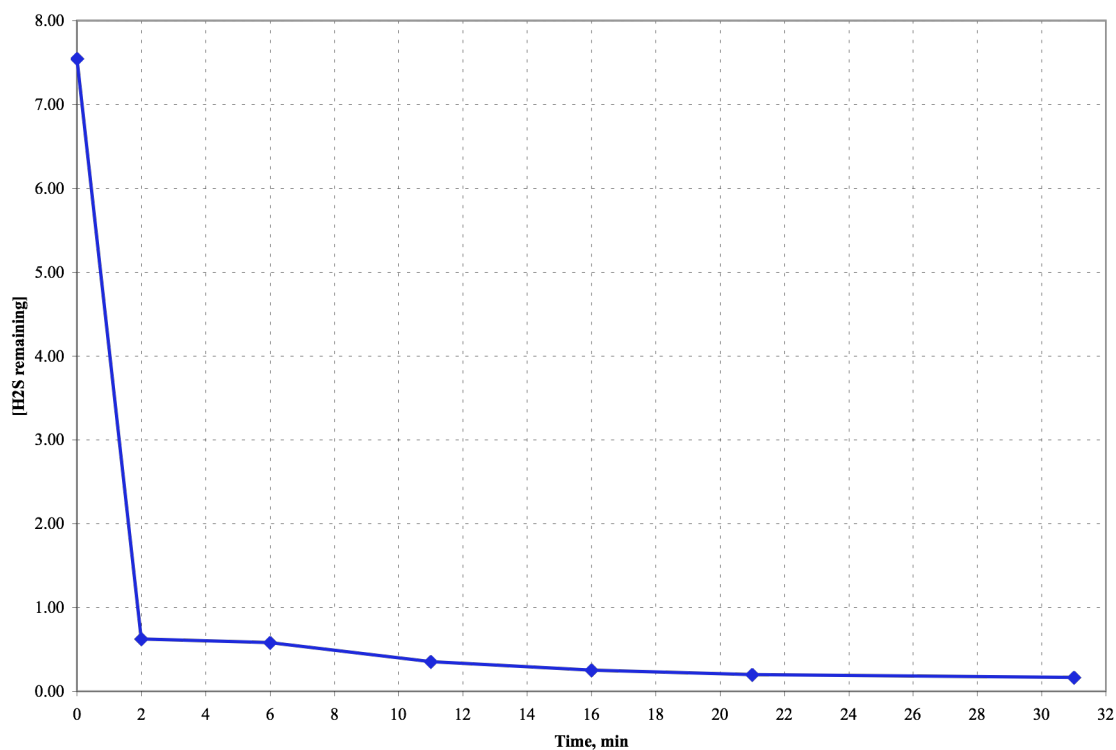
Appendix E-27. Standard Curve for 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Appendix E-28. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/8/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS
 H₂S Initial Concentration: 7.55 mg/L
 Initial pH: 12.50
 pH after HCl Addition: 7.00

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-743.2	1.998010407	7.37	7.55	17.6
	b				-743.8	2.043924089	7.72		17.6
2	a	1	1	2	-711.6	-0.420110193	0.66	0.62	17.6
	b				-710.1	-0.534894399	0.59		17.6
3	a	5	1	6	-709.3	-0.596112642	0.55	0.58	17.6
	b				-710.5	-0.504285277	0.60		17.6
4	a	10	1	11	-699.4	-1.353688399	0.26	0.35	17.6
	b				-706.7	-0.795071931	0.45		17.6
5	a	15	1	16	-696.8	-1.552647689	0.21	0.25	17.6
	b				-700.8	-1.246556474	0.29		17.6
6	a	20	1	21	-693.8	-1.7822161	0.17	0.20	17.6
	b				-697.5	-1.499081726	0.22		17.6
7	a	30	1	31	-694.3	-1.743954699	0.17	0.16	17.6
	b				-692.5	-1.881695745	0.15		17.6



Appendix E-29. H₂S remaining after 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

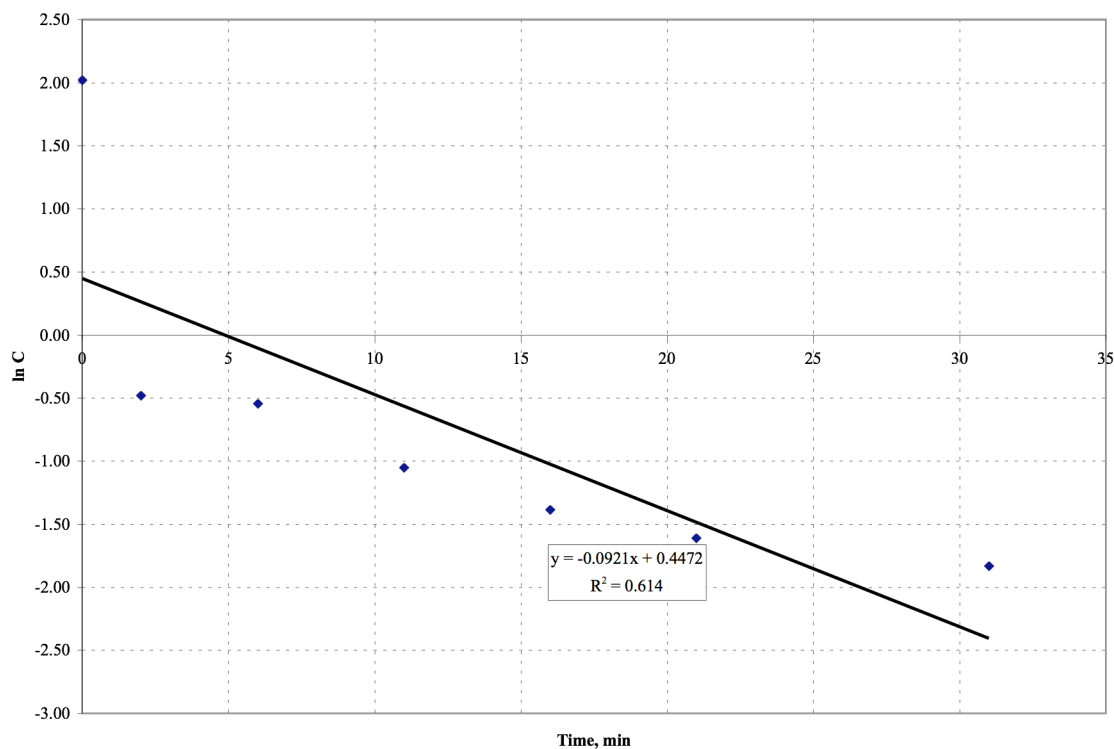
Appendix E-30. Linear Regression Analysis corresponding to 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS – pH = 7.00

Date: 2/8/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS

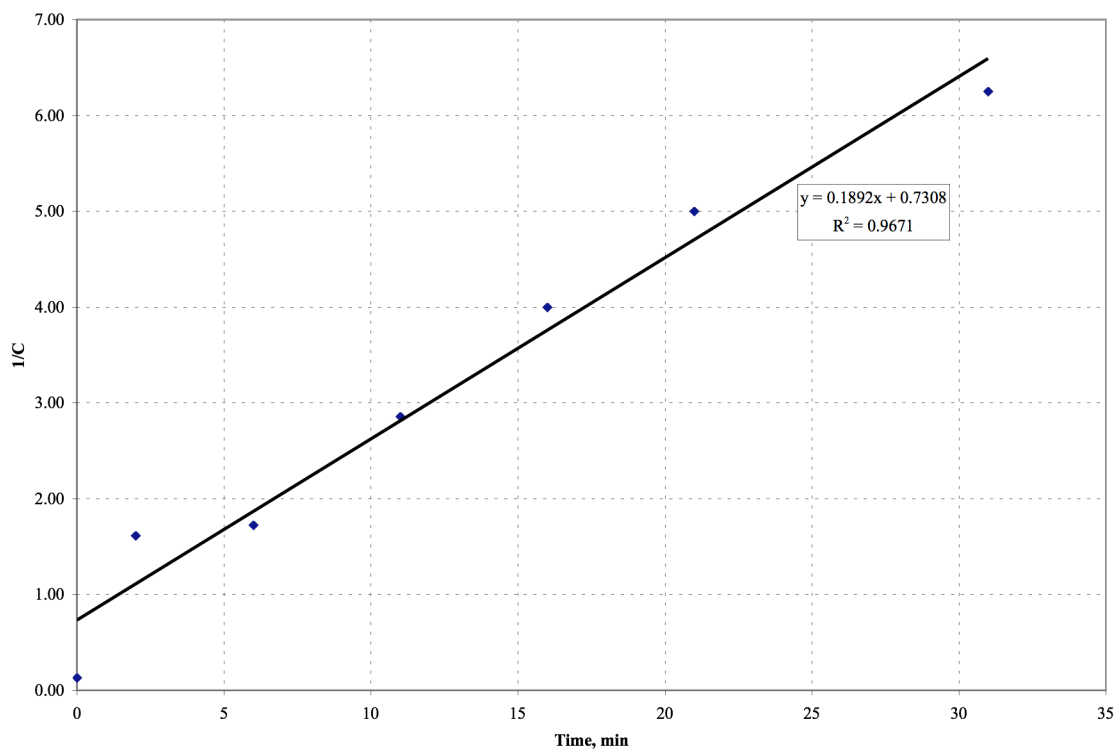
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.55	2.0215	0.1325	0.0175	0.0023	0.00030776	0.00004076	0.00000540	0.00000072
2	0.62	-0.4780	1.6129	2.6015	4.1959	6.7676	10.9154	17.6056	28.3961
6	0.58	-0.5447	1.7241	2.9727	5.1253	8.8367	15.2356	26.2683	45.2902
11	0.35	-1.0498	2.8571	8.1633	23.3236	66.6389	190.3969	543.9910	1554.2601
16	0.25	-1.3863	4.0000	16.0000	64.0000	256.0000	1024.0000	4096.0000	16384.0000
21	0.20	-1.6094	5.0000	25.0000	125.0000	625.0000	3125.0000	15625.0000	78125.0000
31	0.16	-1.8326	6.2500	39.0625	244.1406	1525.8789	9536.7432	59604.6448	372529.0298

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

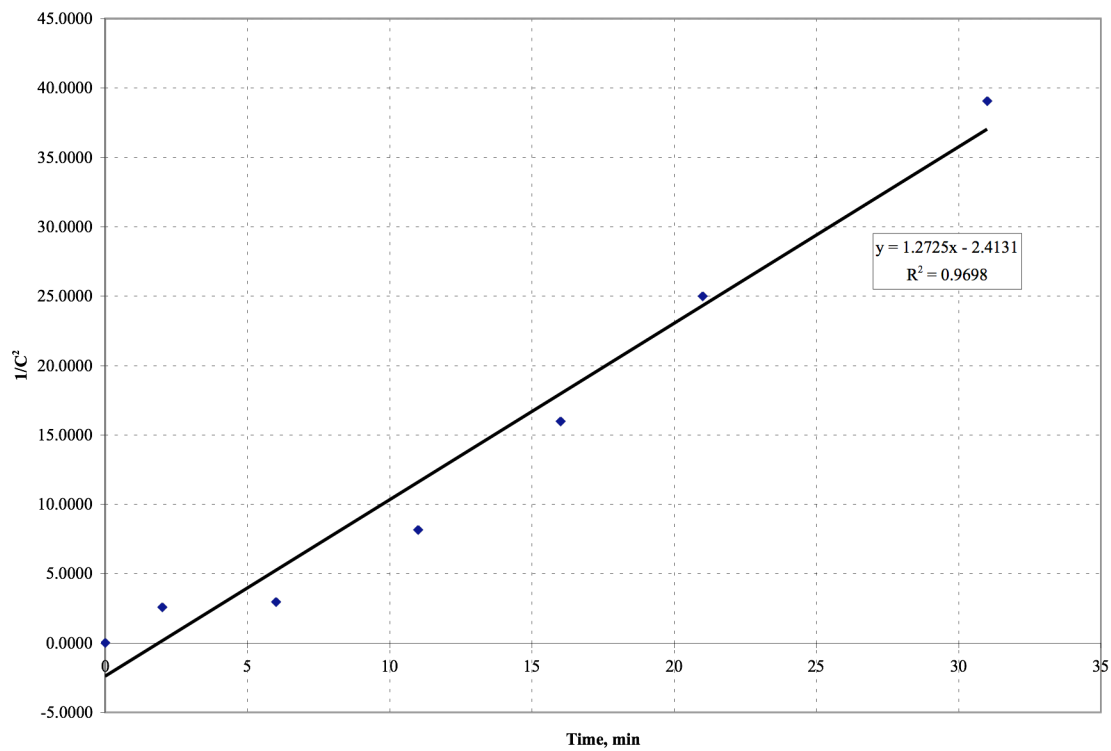
k= 0.6363 L²mg⁻²min⁻¹
 C₀= 7.55 mg/L
 C= 3.78 mg/L
 t_{1/2}= 0.04 min



Appendix E-31. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS



Appendix E-32. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$



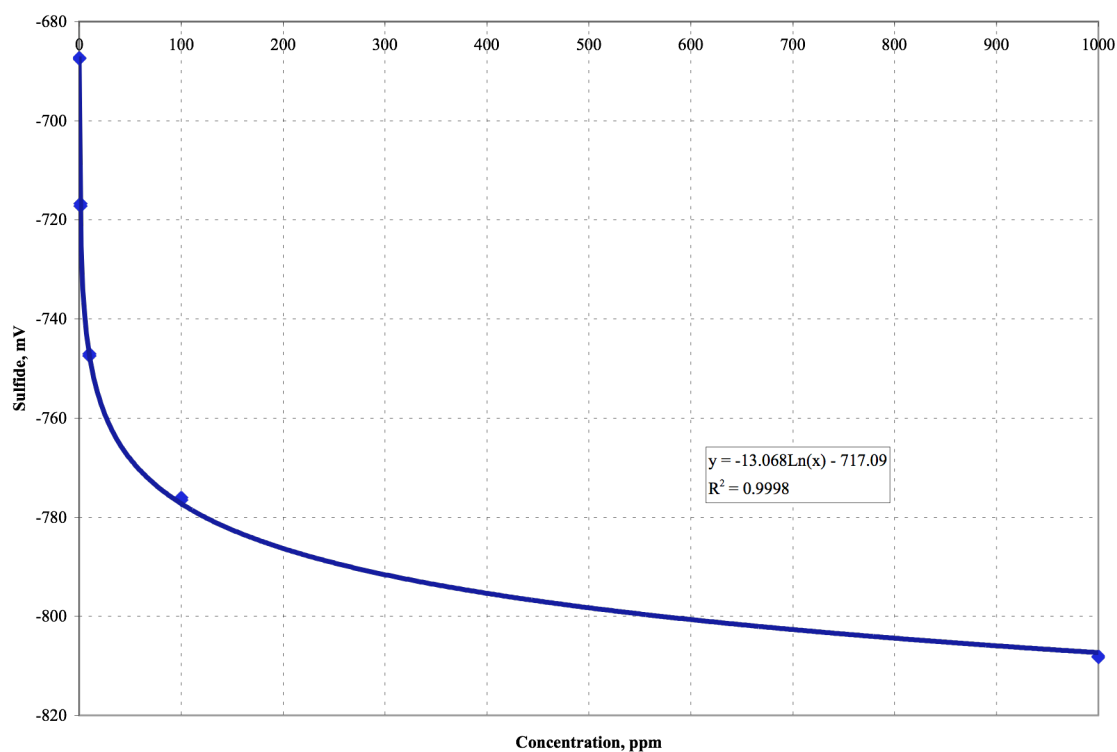
Appendix E-.33 Test of Third-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-34. Standard Curve Data for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



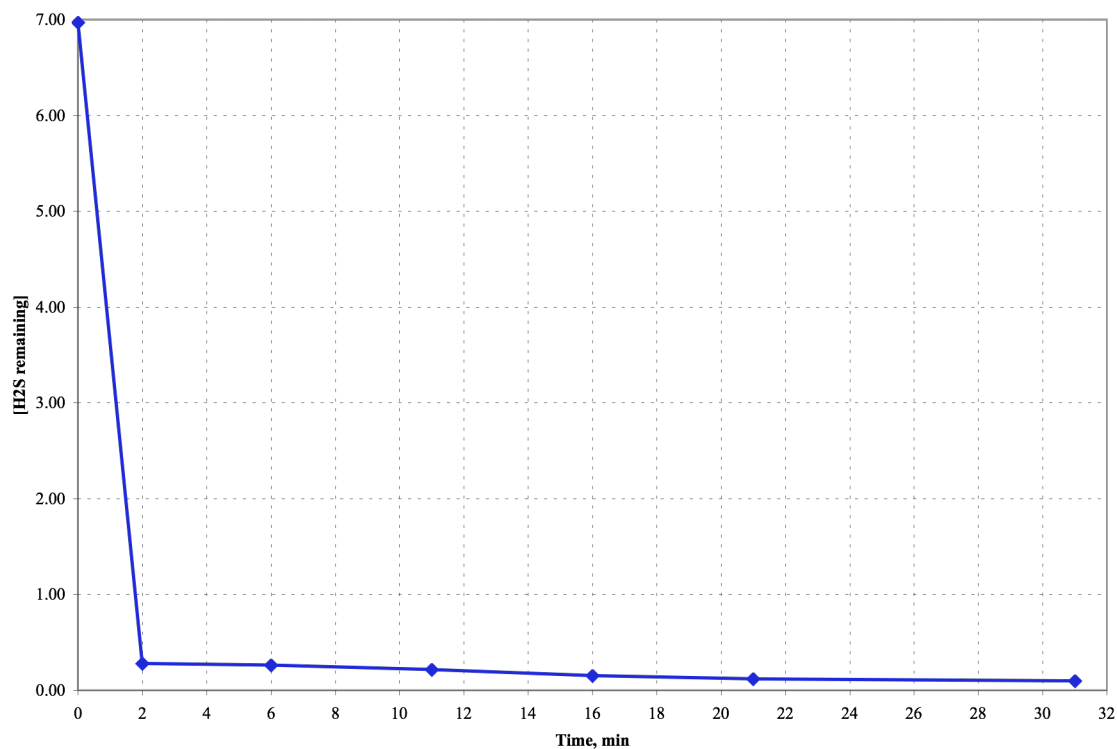
Appendix E-35. Standard Curve for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Appendix E-36. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/8/07
Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
H₂O₂ Concentration: 0.30 kgH₂O₂/kgS
H₂S Initial Concentration: 6.97 mg/L
Initial pH: 12.50
pH after HCl Addition: 7.20

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-741.8	1.890878482	6.63	6.97	17.8
	-743.1				1.990358127	7.32	17.8		
2	a	1	1	2	-699.8	-1.323079278	0.27	0.28	17.8
	-700.9				-1.238904193	0.29	17.8		
3	a	5	1	6	-699.0	-1.384297521	0.25	0.26	17.8
	-700.3				-1.284817876	0.28	17.8		
4	a	10	1	11	-691.7	-1.942913988	0.14	0.22	17.8
	-701.0				-1.231251913	0.29	17.8		
5	a	15	1	16	-695.6	-1.644475054	0.19	0.15	17.8
	-688.7				-2.1724824	0.11	17.8		
6	a	20	1	21	-688.9	-2.157177839	0.12	0.12	17.8
	-689.2				-2.134220998	0.12	17.8		
7	a	30	1	31	-687.1	-2.294918886	0.10	0.10	17.8
	-686.2				-2.363789409	0.09	17.8		



Appendix E-37. H₂S remaining after 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

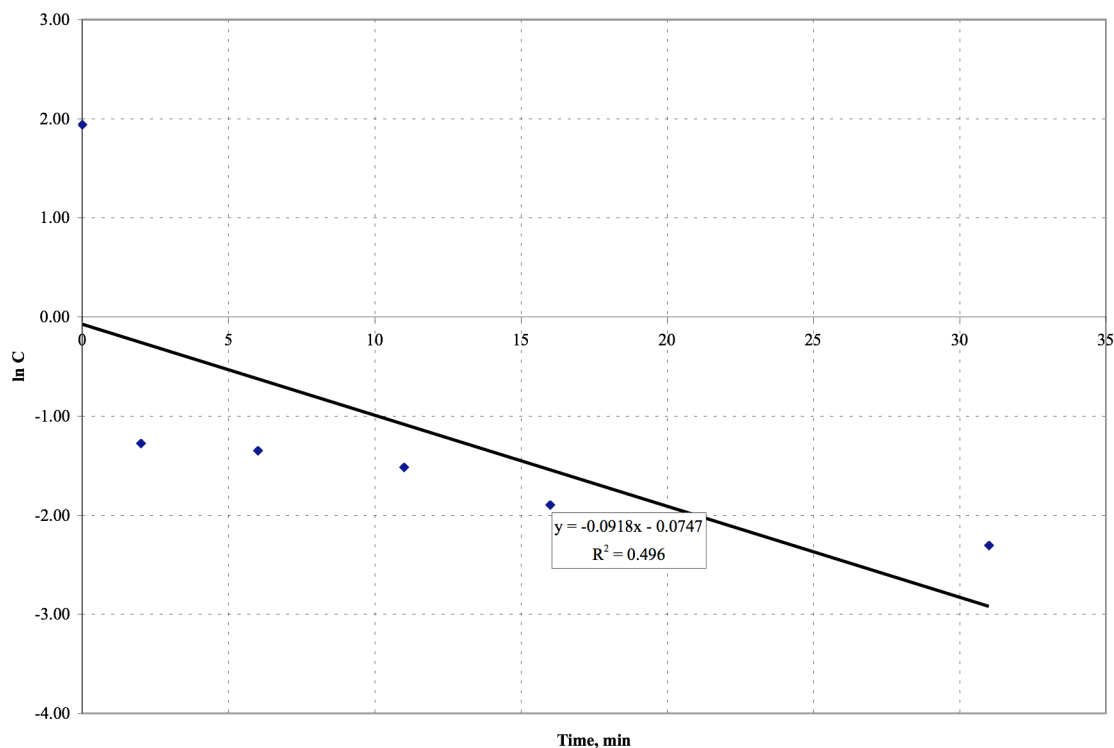
Appendix E-38. Linear Regression Analysis corresponding to 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS – pH = 7.20

Date: 2/8/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

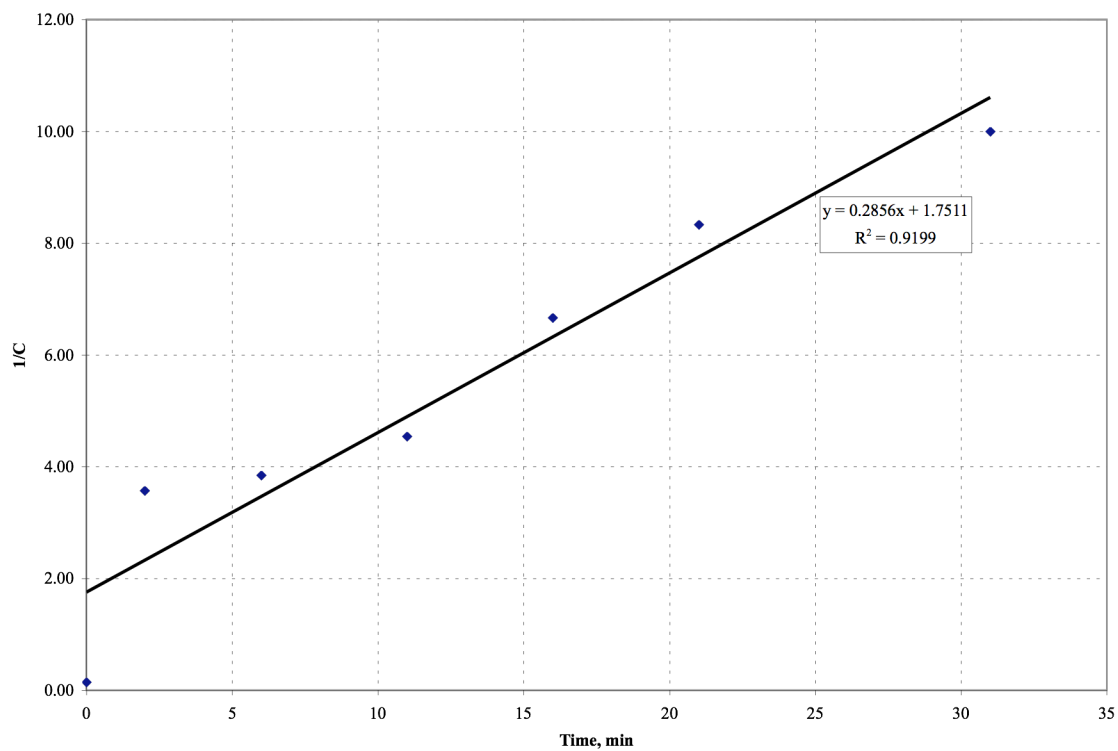
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.97	1.9416	0.1435	0.0206	0.0030	0.0004	0.0000608	0.0000087	0.0000013
2	0.28	-1.2730	3.5714	12.7551	45.5539	162.6926	581.0451	2075.1611	7411.2895
6	0.26	-1.3471	3.8462	14.7929	56.8958	218.8299	841.6534	3237.1283	12450.4935
11	0.22	-1.5141	4.5455	20.6612	93.9144	426.8834	1940.3791	8819.9052	40090.4780
16	0.15	-1.8971	6.6667	44.4444	296.2963	1975.3086	13168.7243	87791.4952	585276.6347
21	0.12	-2.1203	8.3333	69.4444	578.7037	4822.5309	40187.7572	334897.9767	2790816.4723
31	0.10	-2.3026	10.0000	100.0000	1000.0000	10000.0000	100000.0000	1000000.0000	10000000.0000

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

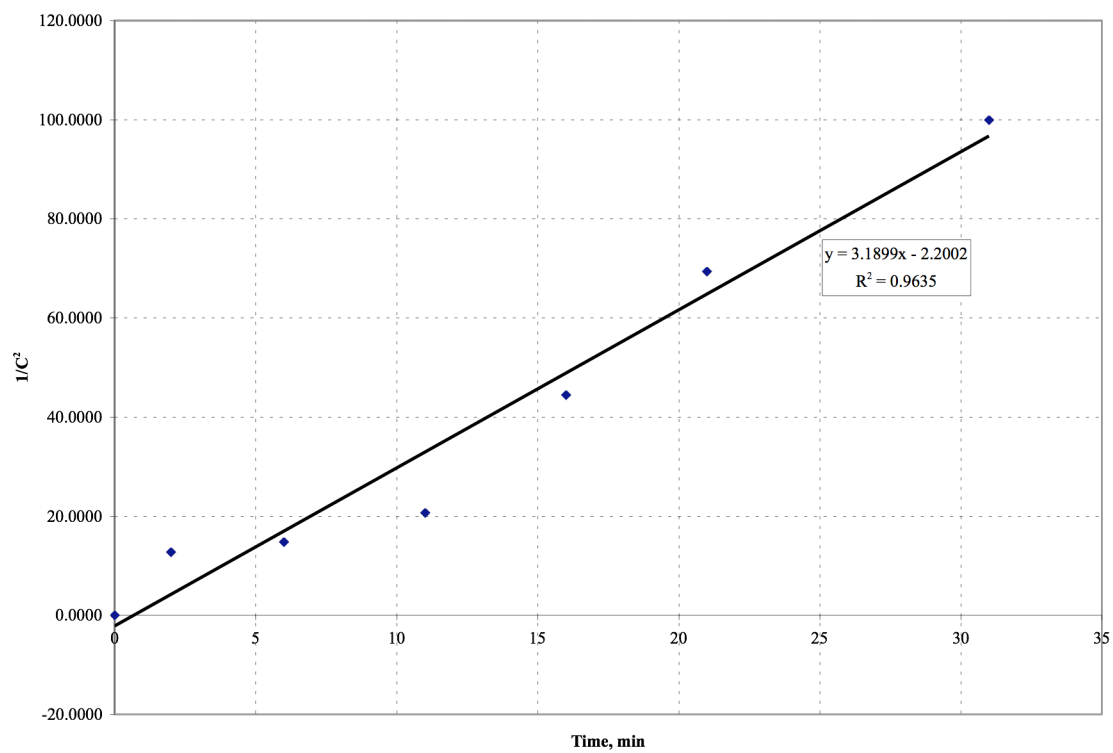
k= 1.5950 L²mg⁻²min⁻¹
 C₀= 6.97 mg/L
 C= 3.49 mg/L
 t_{1/2}= 0.02 min



Appendix E-39. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS



Appendix E-40. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



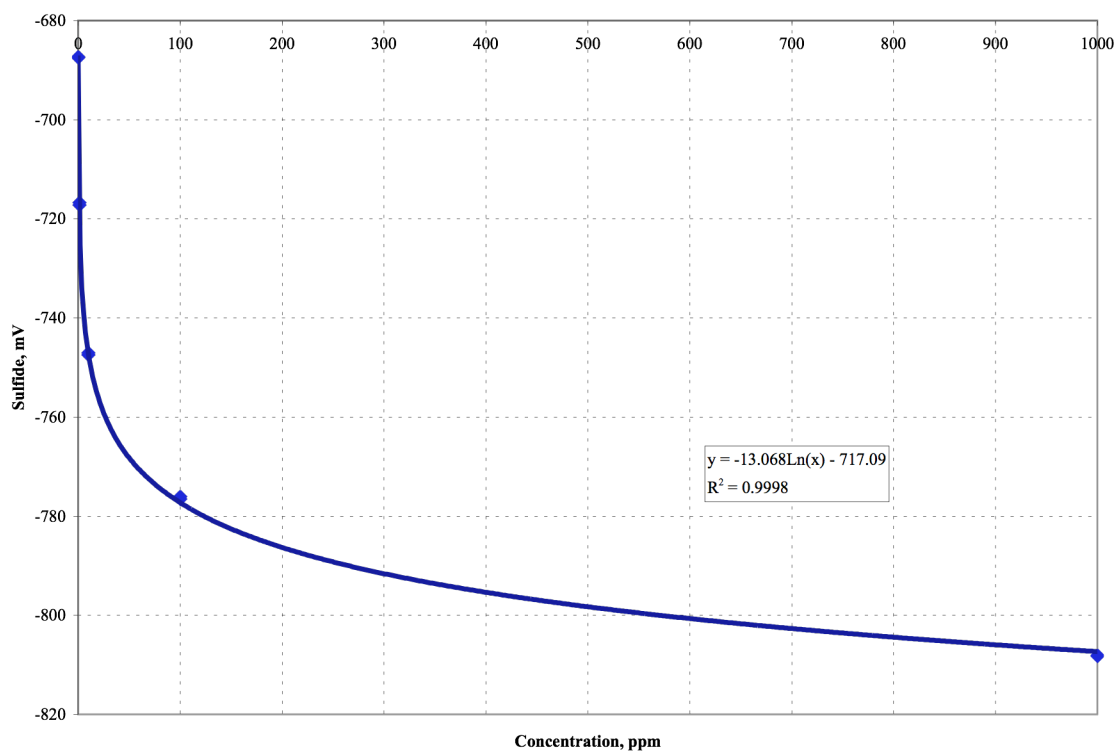
Appendix E-41. Test of Third-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-42. Standard Curve Data for 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/8/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-808.2	12.5	21.5
	b	1000	-808.1	12.5	21.5
2	a	100	-776.0	12.5	21.5
	b	100	-776.5	12.5	21.5
3	a	10	-747.4	12.5	21.5
	b	10	-747.0	12.5	21.5
4	a	1	-717.2	12.5	21.5
	b	1	-716.7	12.5	21.5
5	a	0.1	-687.4	12.5	21.5
	b	0.1	-687.3	12.5	21.5



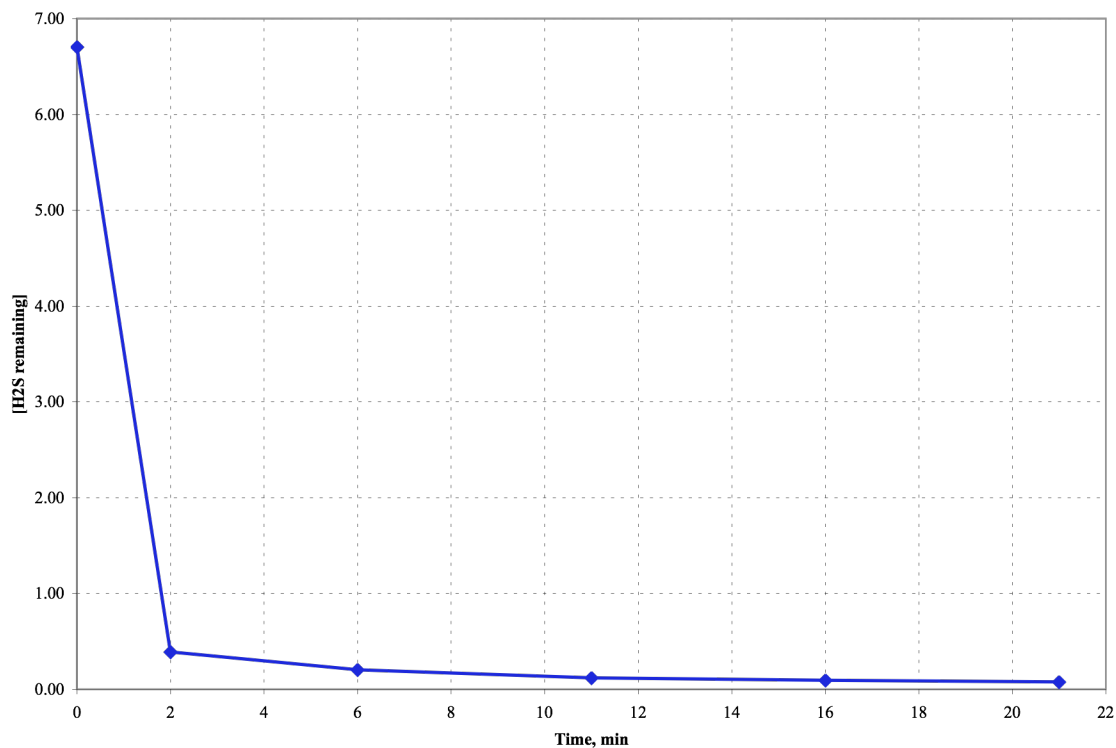
Appendix E-43. Standard Curve for 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Appendix E-44. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/9/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS
 H₂S Initial Concentration: 6.70 mg/L
 Initial pH: 12.50
 pH after HCl Addition: 6.80

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-741.6	1.875573921	6.52	6.70	21.6
	b				-742.3	1.929139884	6.88		21.6
2	a	1	1	2	-704.5	-0.9634221	0.38	0.39	21.6
	b				-704.9	-0.932812978	0.39		21.6
3	a	5	1	6	-696.4	-1.5832568	0.21	0.20	21.6
	b				-695.9	-1.621518212	0.20		21.6
4	a	10	1	11	-688.1	-2.218396082	0.11	0.12	21.6
	b				-689.8	-2.088307316	0.12		21.6
5	a	15	1	16	-685.6	-2.409703092	0.09	0.09	21.6
	b				-686.5	-2.340832568	0.10		21.6
6	a	20	1	21	-683.7	-2.555096419	0.08	0.08	21.6
	b				-683.5	-2.570400979	0.08		21.6



Appendix E-45. H₂S remaining after 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Appendix E-46. Linear Regression Analysis corresponding to 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS – pH = 6.80

Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS

Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.70	1.9021	0.1493	0.0223	0.0033	0.0004963	0.0000741	0.0000111	0.0000016
2	0.39	-0.9416	2.5641	6.5746	16.8580	43.2257	110.8350	284.1923	728.6983
6	0.20	-1.6094	5.0000	25.0000	125.0000	625.0000	3125.0000	15625.0000	78125.0000
11	0.12	-2.1203	8.3333	69.4444	578.7037	4822.5309	40187.7572	334897.9767	2790816.4723
16	0.09	-2.4079	11.1111	123.4568	1371.7421	15241.5790	169350.8781	1881676.4232	20907515.8129
21	0.08	-2.5257	12.5000	156.2500	1953.1250	24414.0625	305175.7813	3814697.2656	47683715.8203

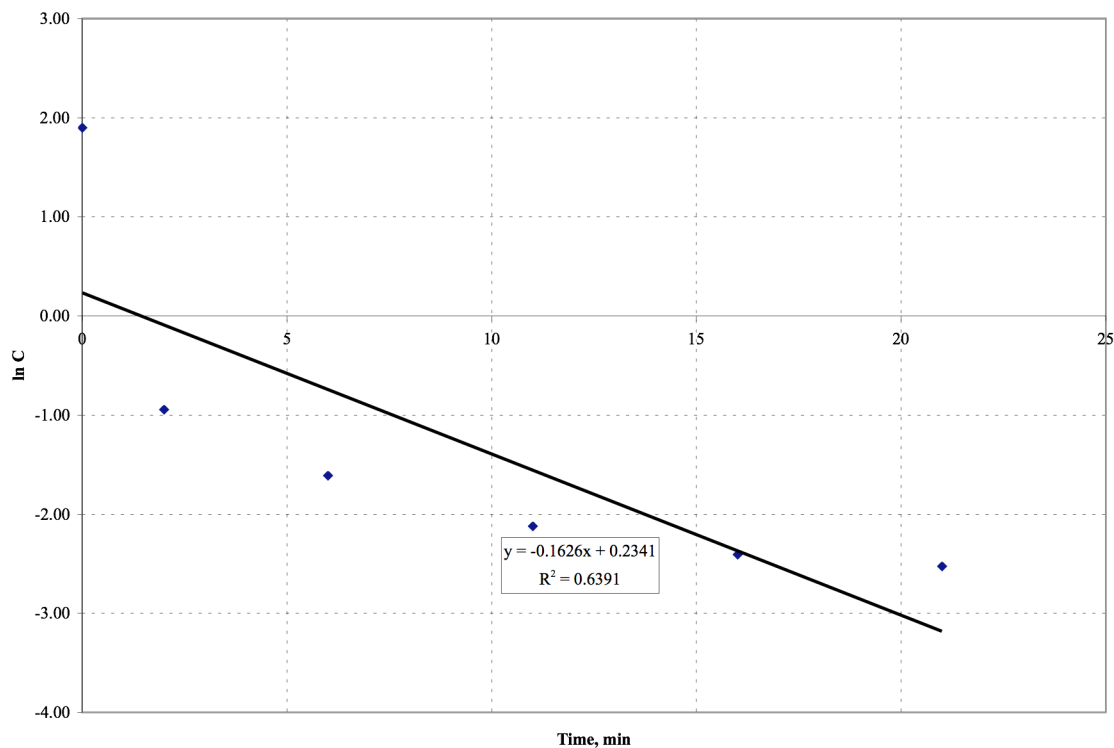
$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

$$k = 3.9214 \text{ L}^2\text{mg}^{-2}\text{min}^{-1}$$

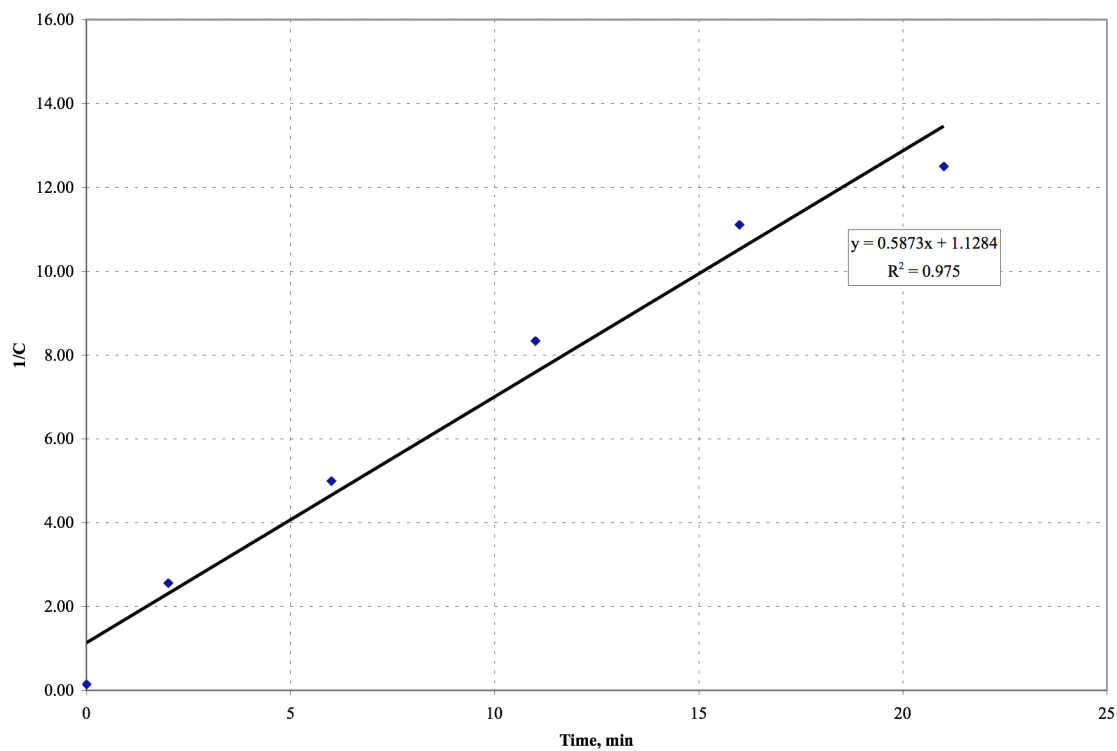
$$C_0 = 6.70 \text{ mg/L}$$

$$C = 3.35 \text{ mg/L}$$

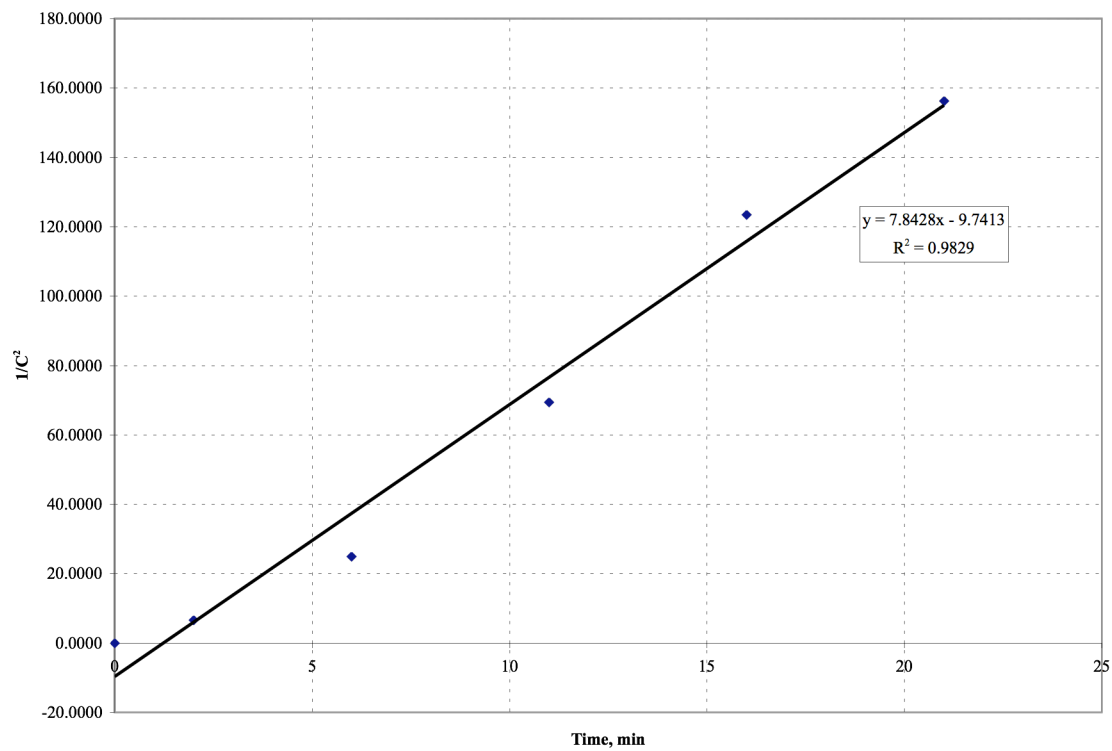
$$t_{1/2} = 0.01 \text{ min}$$



Appendix E-47. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS



Appendix E-48. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$



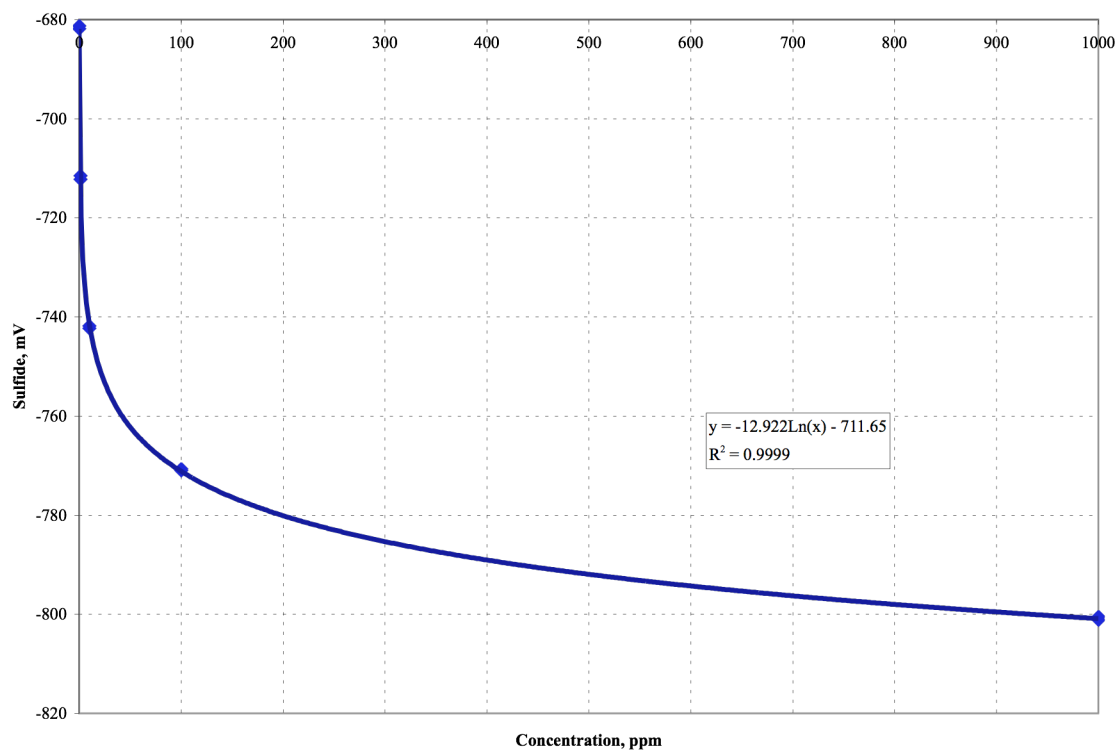
Appendix E-49. Test of Third-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-50. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/9/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.1	12.3	21.6
	b	1000	-800.5	12.3	21.6
2	a	100	-770.6	12.3	21.6
	b	100	-771.0	12.3	21.6
3	a	10	-742.3	12.3	21.6
	b	10	-741.8	12.3	21.6
4	a	1	-712.2	12.3	21.6
	b	1	-711.5	12.3	21.6
5	a	0.1	-681.8	12.3	21.6
	b	0.1	-681.2	12.3	21.6



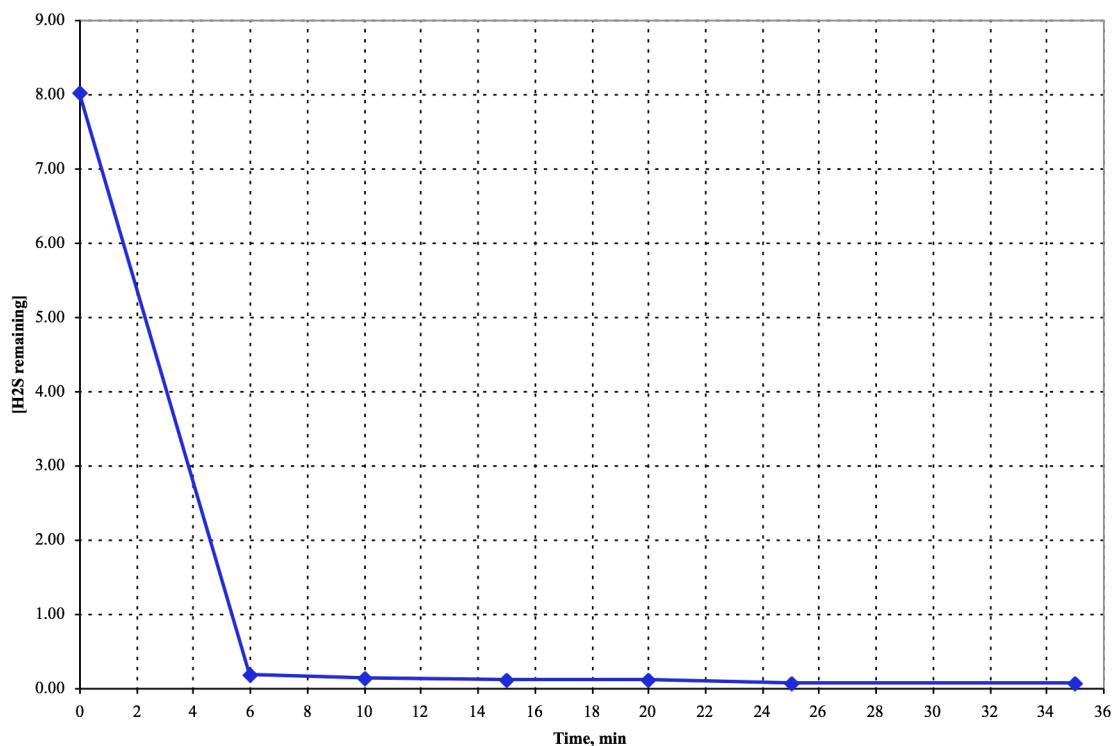
Appendix E-51. Standard Curve for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Appendix E-52. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

Date: 2/10/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/lbS
 H₂O₂ Concentration: 0.60 kgH₂O₂/lbS
 H₂S Initial Concentration: 8.03 mg/L
 Initial pH: 12.30
 pH after HCl Addition: 7.20

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-738.0	2.039158025	7.68	8.03	18.6
	b				-739.1	2.124284167	8.37		18.6
2	a	1	5	6	-688.0	-1.830212041	0.16	0.17	18.6
	b				-689.9	-1.683175979	0.19		18.6
3	a	5	5	10	-687.8	-1.845689522	0.16	0.14	18.6
	b				-685.1	-2.054635505	0.13		18.6
4	a	10	5	15	-683.6	-2.170716607	0.11	0.12	18.6
	b				-684.3	-2.116545426	0.12		18.6
5	a	15	5	20	-683.6	-2.170716607	0.11	0.11	18.6
	b				-683.0	-2.217149048	0.11		18.6
6	a	20	5	25	-679.3	-2.503482433	0.08	0.08	18.6
	b				-678.0	-2.604086055	0.07		18.6
7	a	30	5	35	-677.6	-2.635041015	0.07	0.08	18.6
	b				-679.1	-2.518959913	0.08		18.6



Appendix E-53. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS Addition

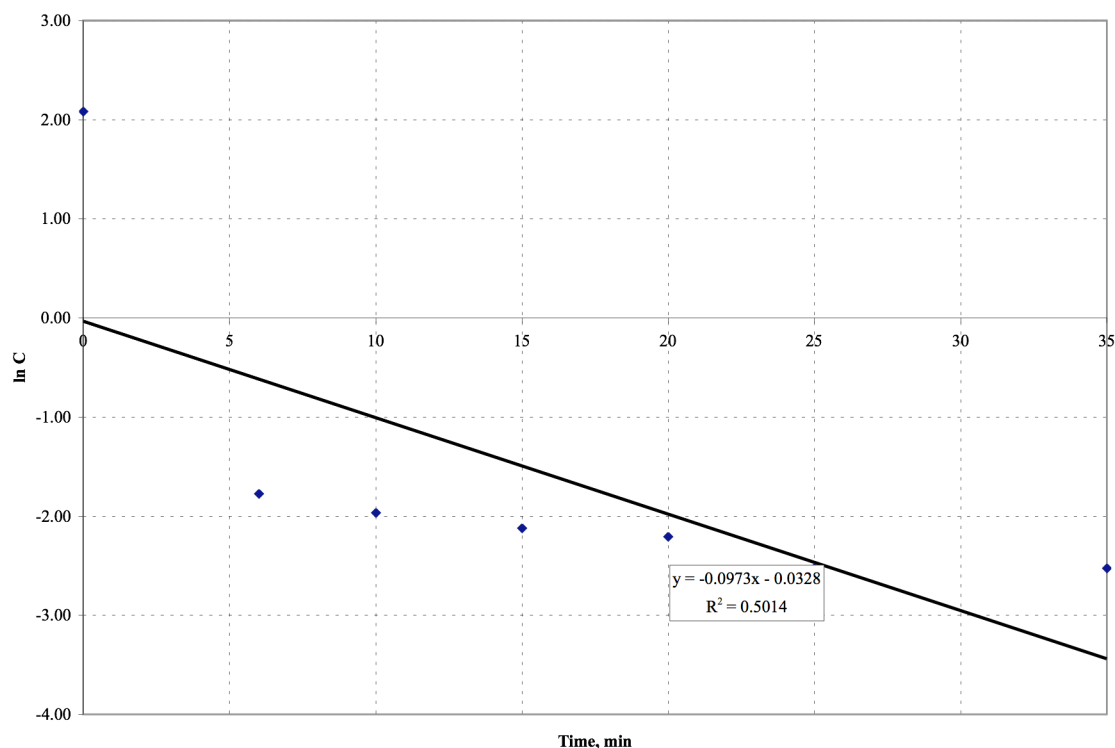
Appendix E-54. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS – pH = 7.20

Date: 2/10/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.60 kgH₂O₂/kgS

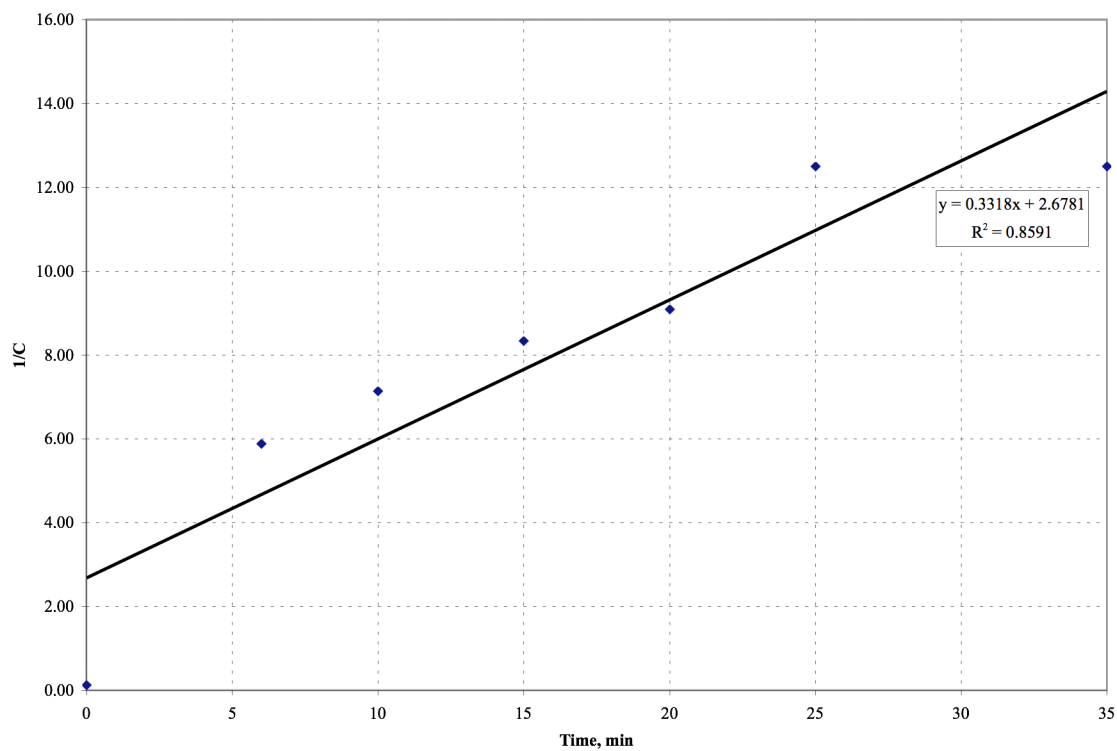
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.03	2.0832	0.1245	0.0155	0.0019	0.00024051	0.00002995	0.00000373	0.00000046
6	0.17	-1.7720	5.8824	34.6021	203.5416	1197.3037	7042.9628	41429.1928	243701.1342
10	0.14	-1.9661	7.1429	51.0204	364.4315	2603.0820	18593.4432	132810.3086	948645.0616
15	0.12	-2.1203	8.3333	69.4444	578.7037	4822.5309	40187.7572	334897.9767	2790816.4723
20	0.11	-2.2073	9.0909	82.6446	751.3148	6830.1346	62092.1323	564473.9301	5131581.1823
25	0.08	-2.5257	12.5000	156.2500	1953.1250	24414.0625	305175.7813	3814697.2656	47683715.8203
35	0.08	-2.5257	12.5000	156.2500	1953.1250	24414.0625	305175.7813	3814697.2656	47683715.8203

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

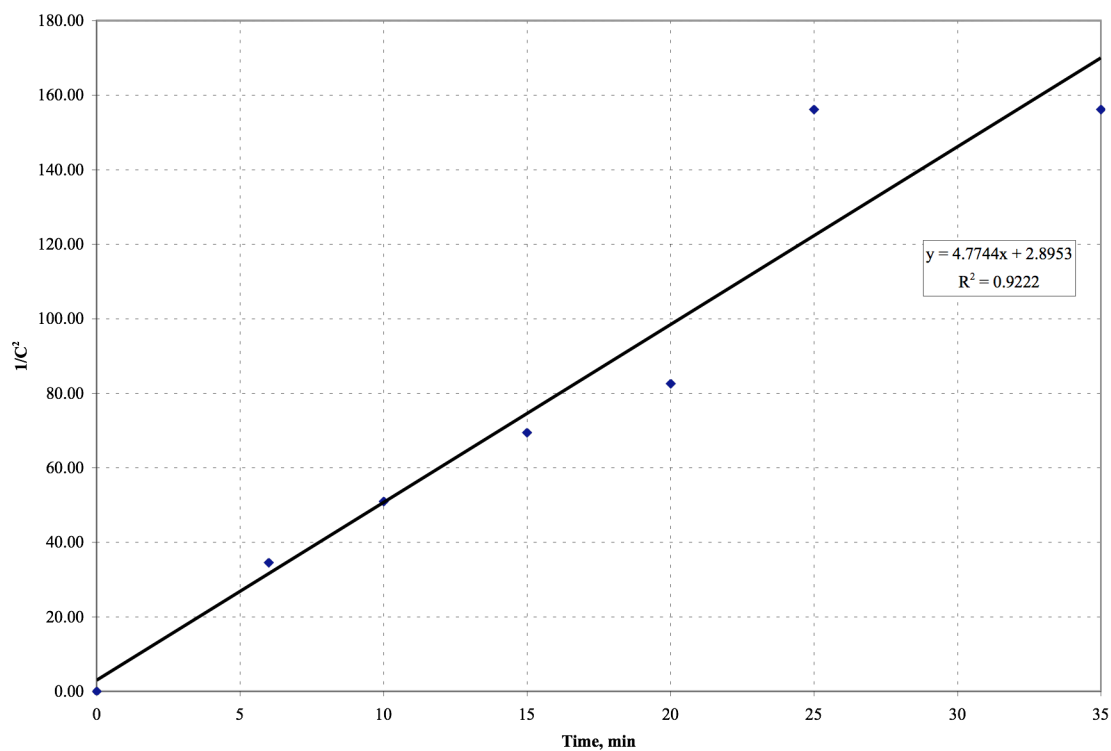
k = 2.3872 L²mg⁻²min⁻¹
 C₀ = 8.03 mg/L
 C = 4.02 mg/L
 t_{1/2} = 0.01 min



Appendix E-55. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.60 kg H₂O₂/kgS



Appendix E-56. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$



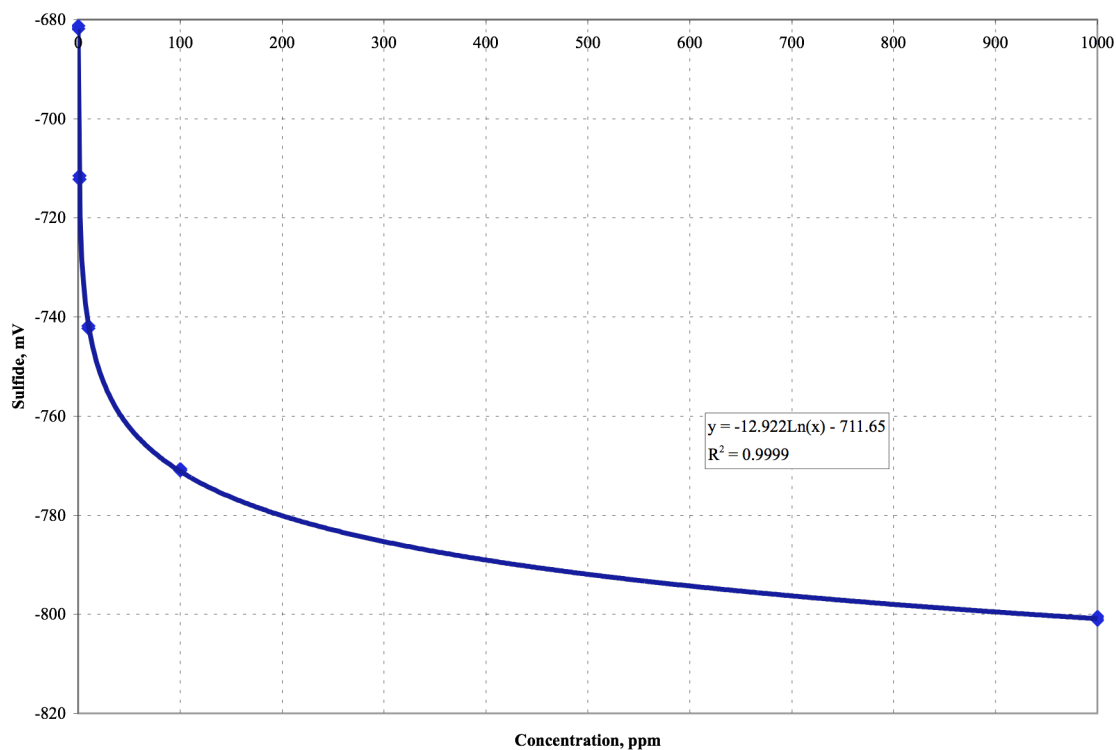
Appendix E-57. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.60 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-58. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/9/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.1	12.3	21.6
	b	1000	-800.5	12.3	21.6
2	a	100	-770.6	12.3	21.6
	b	100	-771.0	12.3	21.6
3	a	10	-742.3	12.3	21.6
	b	10	-741.8	12.3	21.6
4	a	1	-712.2	12.3	21.6
	b	1	-711.5	12.3	21.6
5	a	0.1	-681.8	12.3	21.6
	b	0.1	-681.2	12.3	21.6



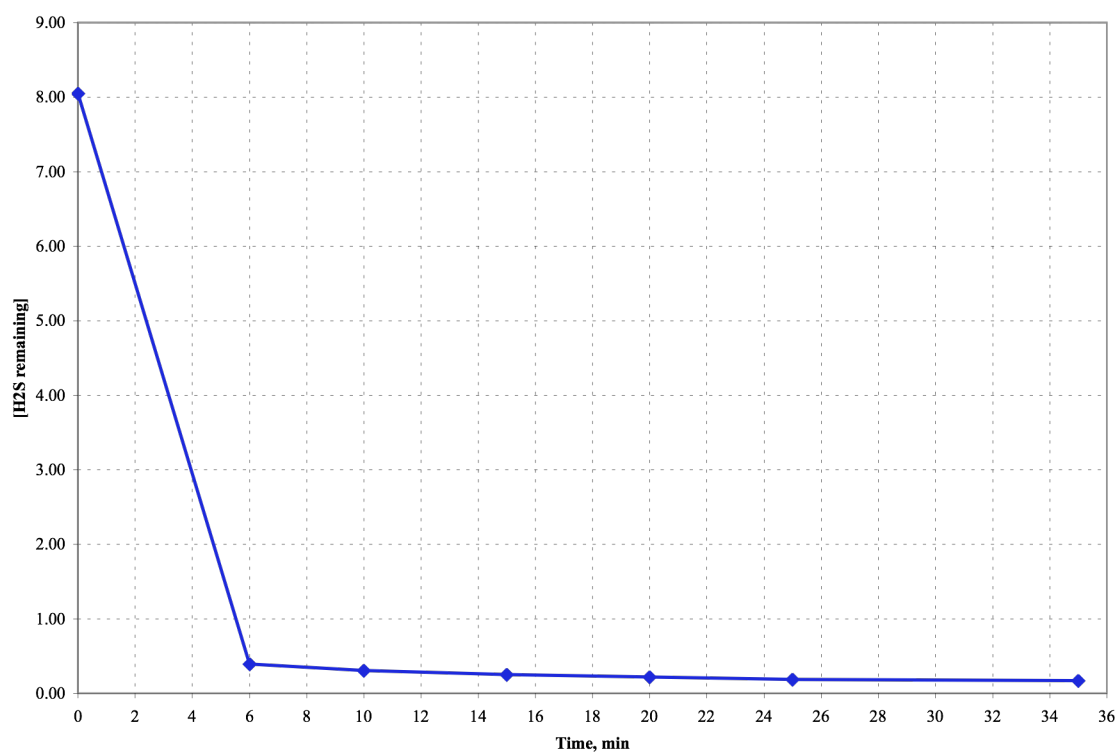
Appendix E-59. Standard Curve for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Appendix E-60. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/9/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/lbS
 H₂O₂ Concentration: 0.10 kgH₂O₂/lbS
 H₂S Initial Concentration: 8.05 mg/L
 Initial pH: 12.30
 pH after HCl Addition: 6.80

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-738.4	2.070112986	7.93	8.05	15.2
	-738.8				2.101067946	8.17	15.2		
2	a	1	5	6	-700.1	-0.893824485	0.41	0.39	15.2
	-699.1				-0.971211887	0.38	15.2		
3	a	5	5	10	-697.5	-1.095031729	0.33	0.31	15.2
	-695.1				-1.280761492	0.28	15.2		
4	a	10	5	15	-693.7	-1.389103854	0.25	0.25	15.2
	-693.9				-1.373626374	0.25	15.2		
5	a	15	5	20	-691.8	-1.536139916	0.22	0.22	15.2
	-692.2				-1.505184956	0.22	15.2		
6	a	20	5	25	-689.1	-1.7450859	0.17	0.19	15.2
	-690.6				-1.629004798	0.20	15.2		
7	a	30	5	35	-687.3	-1.884383222	0.15	0.17	15.2
	-689.9				-1.683175979	0.19	15.2		



Appendix E-61. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

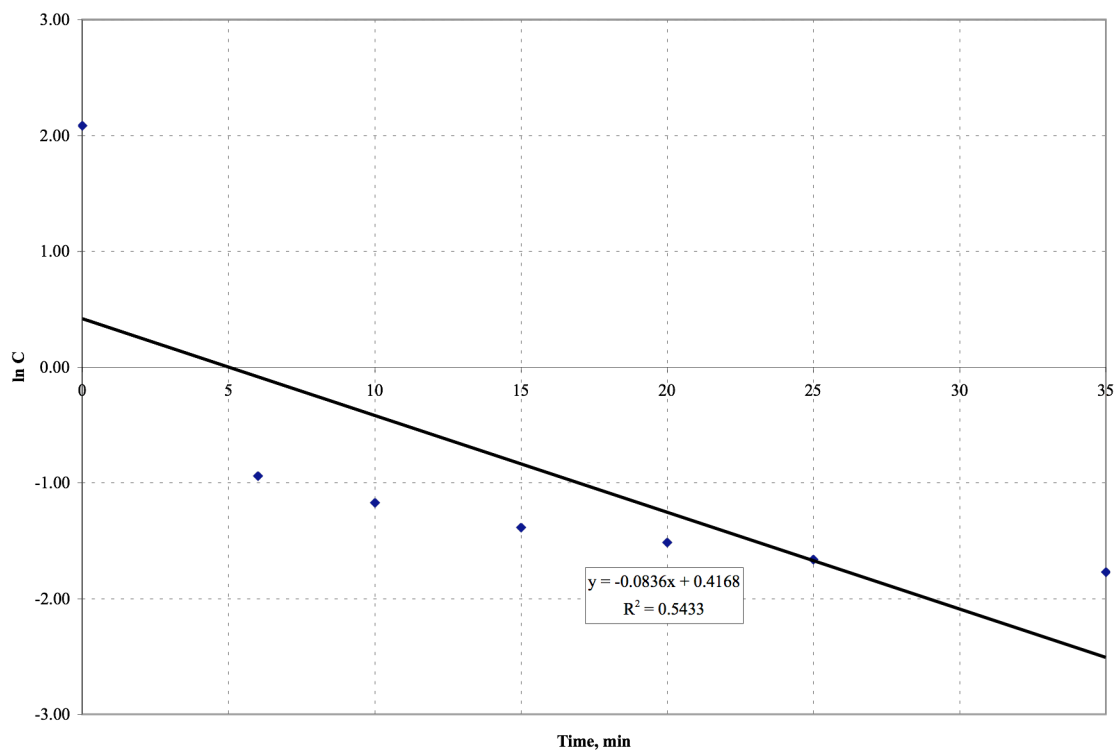
Appendix E-62. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS – pH = 6.80

Date: 2/9/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS

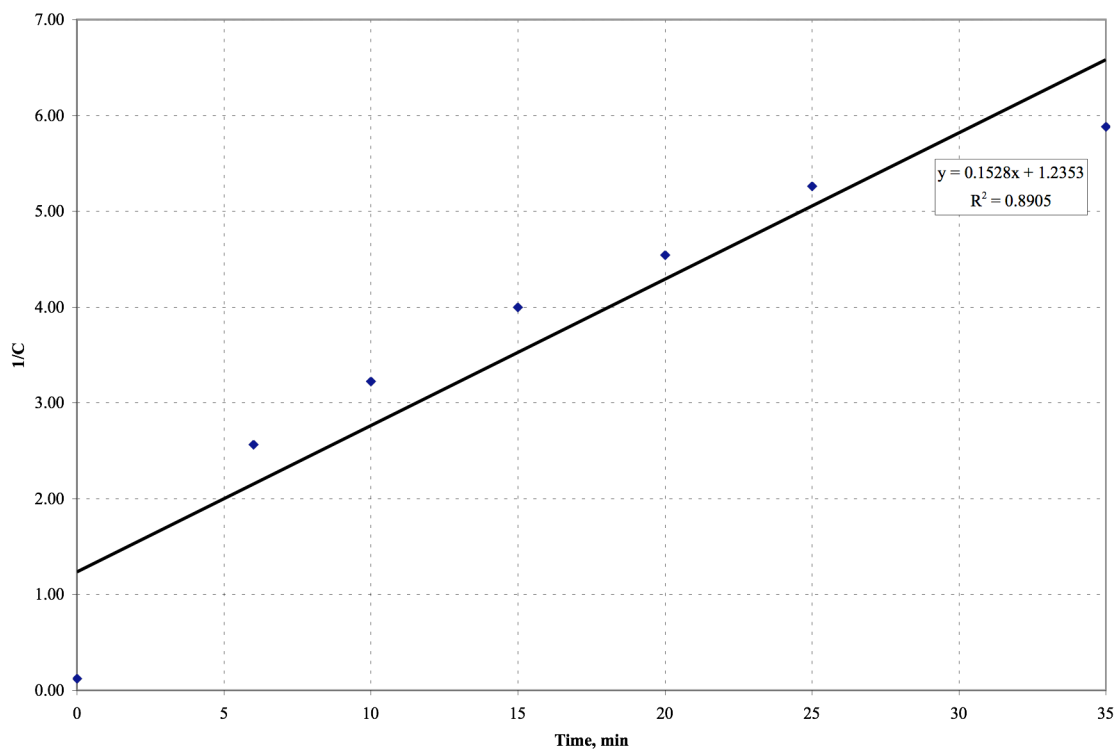
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.05	2.0857	0.1242	0.0154	0.0019	0.00023813	0.00002958	0.00000367	0.00000046
6	0.39	-0.9416	2.5641	6.5746	16.8580	43.2257	110.8350	284.1923	728.6983
10	0.31	-1.1712	3.2258	10.4058	33.5672	108.2812	349.2943	1126.7559	3634.6964
15	0.25	-1.3863	4.0000	16.0000	64.0000	256.0000	1024.0000	4096.0000	16384.0000
20	0.22	-1.5141	4.5455	20.6612	93.9144	426.8834	1940.3791	8819.9052	40090.4780
25	0.19	-1.6607	5.2632	27.7008	145.7938	767.3360	4038.6107	21255.8460	111872.8735
35	0.17	-1.7720	5.8824	34.6021	203.5416	1197.3037	7042.9628	41429.1928	243701.1342

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

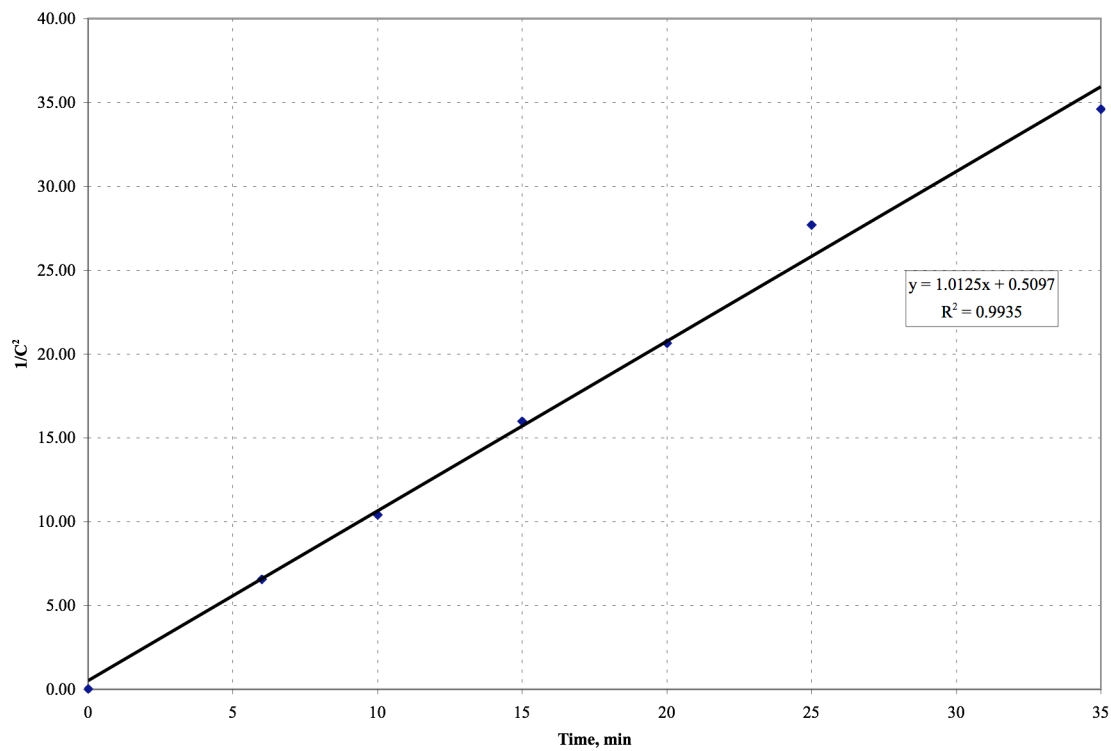
k = 0.5063 L²mg⁻²min⁻¹
 C₀ = 8.05 mg/L
 C = 4.03 mg/L
 t_{1/2} = 0.05 min



Appendix E-63. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS



Appendix E-64. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$



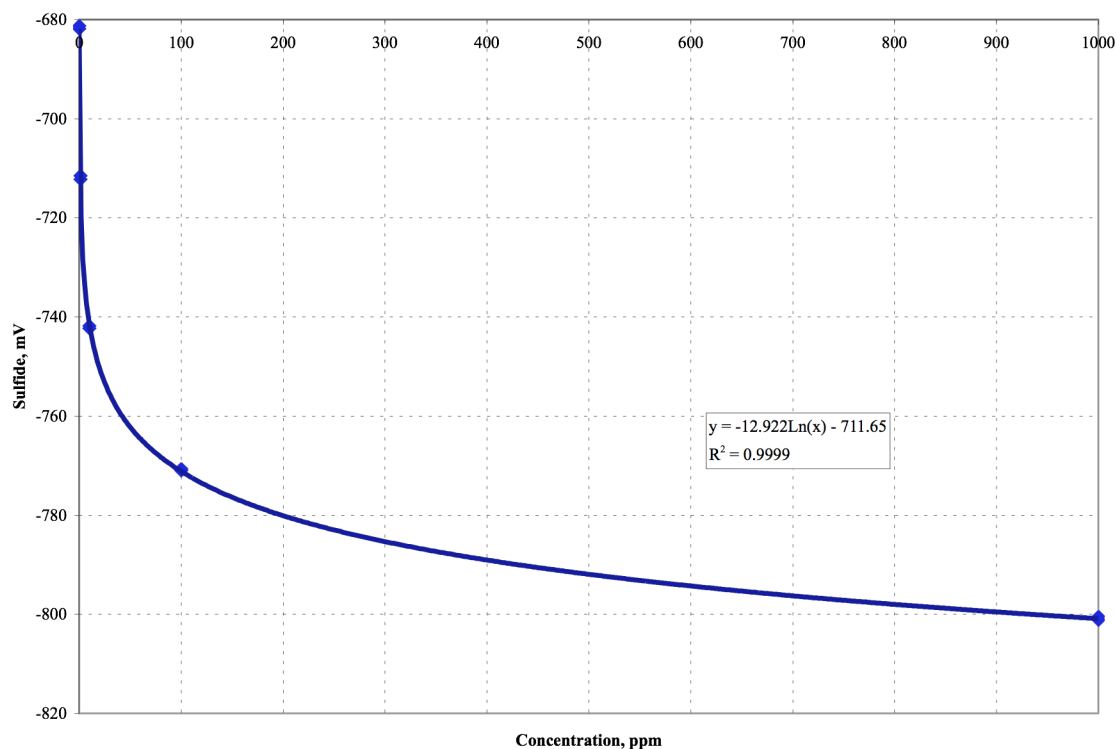
Appendix E-65. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-66. Standard Curve Data for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/9/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.1	12.3	21.6
	b	1000	-800.5	12.3	21.6
2	a	100	-770.6	12.3	21.6
	b	100	-771.0	12.3	21.6
3	a	10	-742.3	12.3	21.6
	b	10	-741.8	12.3	21.6
4	a	1	-712.2	12.3	21.6
	b	1	-711.5	12.3	21.6
5	a	0.1	-681.8	12.3	21.6
	b	0.1	-681.2	12.3	21.6



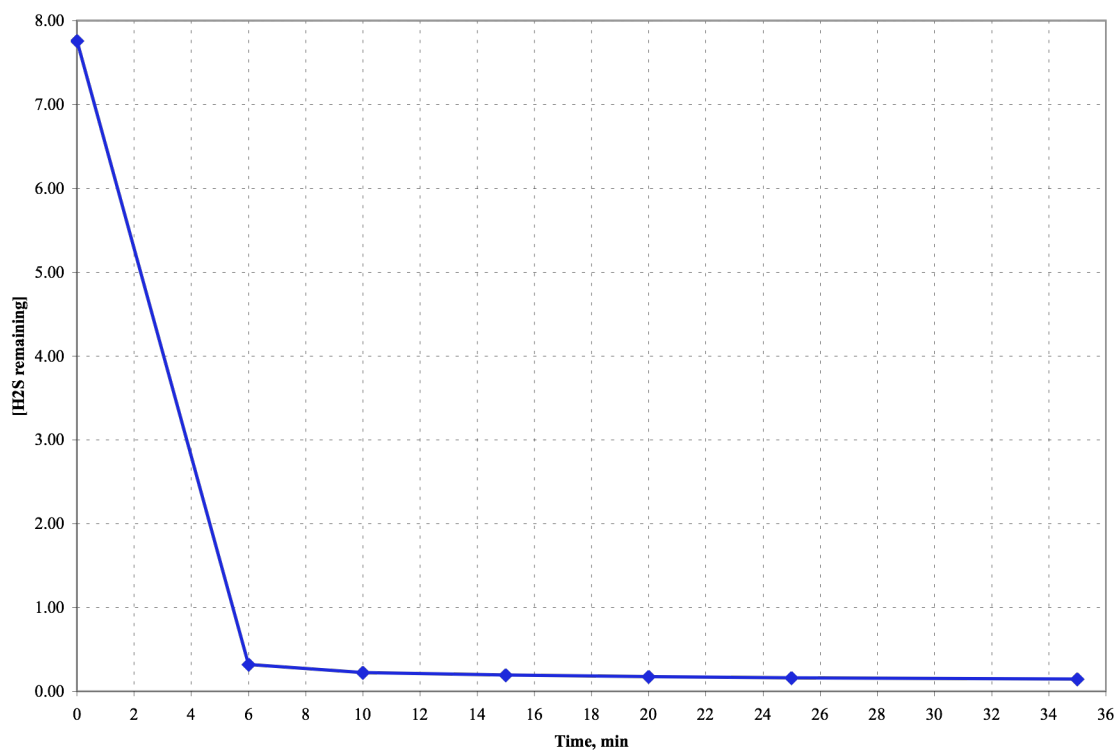
Appendix E-67. Standard Curve for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Appendix E-68. Ion Selective Electrode Method Data for 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/10/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 1.45 kgFeCl₂/lbS
 H₂O₂ Concentration: 0.30 kgH₂O₂/lbS
 H₂S Initial Concentration: 7.76 mg/L
 Initial pH: 12.30
 pH after HCl Addition: 7.20

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-737.3	1.984986844	7.28	7.76	16.7
	b				-738.9	2.108806686	8.24		16.7
2	a	1	5	6	-696.6	-1.16468039	0.31	0.32	16.7
	b				-697.2	-1.118247949	0.33		16.7
3	a	5	5	10	-692.1	-1.512923696	0.22	0.22	16.7
	b				-692.4	-1.489707476	0.23		16.7
4	a	10	5	15	-689.9	-1.683175979	0.19	0.19	16.7
	b				-690.7	-1.621266058	0.20		16.7
5	a	15	5	20	-689.4	-1.72186968	0.18	0.18	16.7
	b				-688.9	-1.76056338	0.17		16.7
6	a	20	5	25	-687.0	-1.907599443	0.15	0.16	16.7
	b				-689.1	-1.7450859	0.17		16.7
7	a	30	5	35	-686.8	-1.923076923	0.15	0.14	16.7
	b				-686.4	-1.954031884	0.14		16.7



Appendix E-69. H₂S remaining after 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

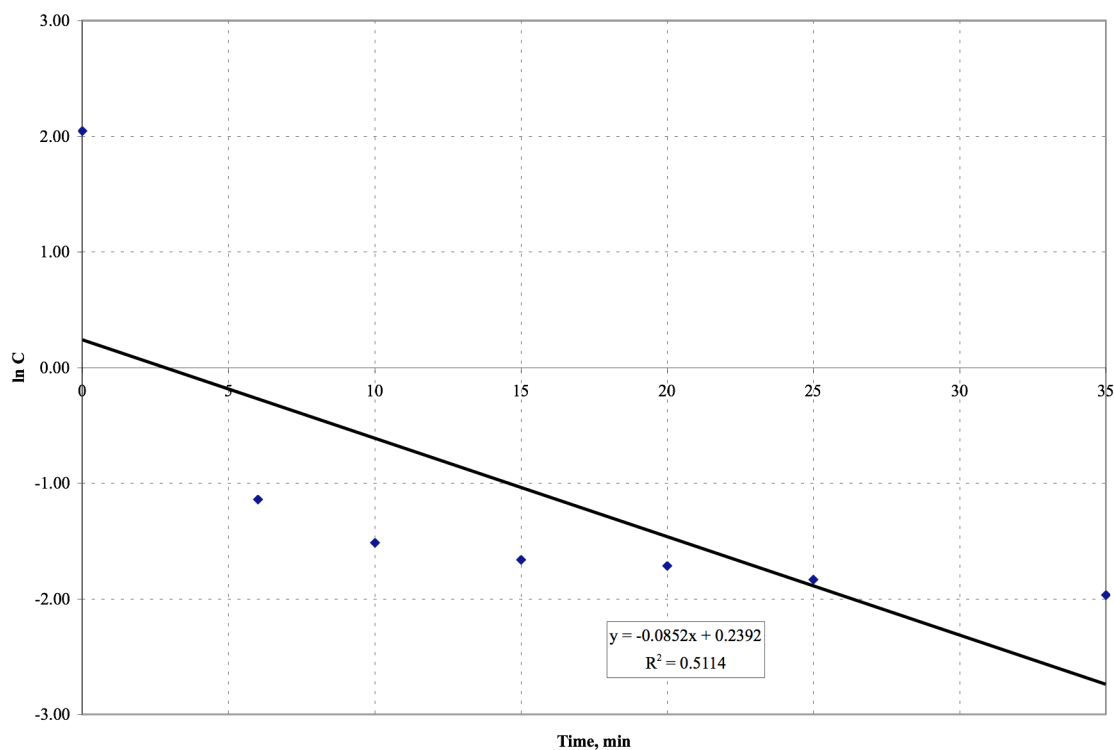
Appendix E-70. Linear Regression Analysis corresponding to 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS – pH = 7.20

Date: 2/10/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 1.45 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

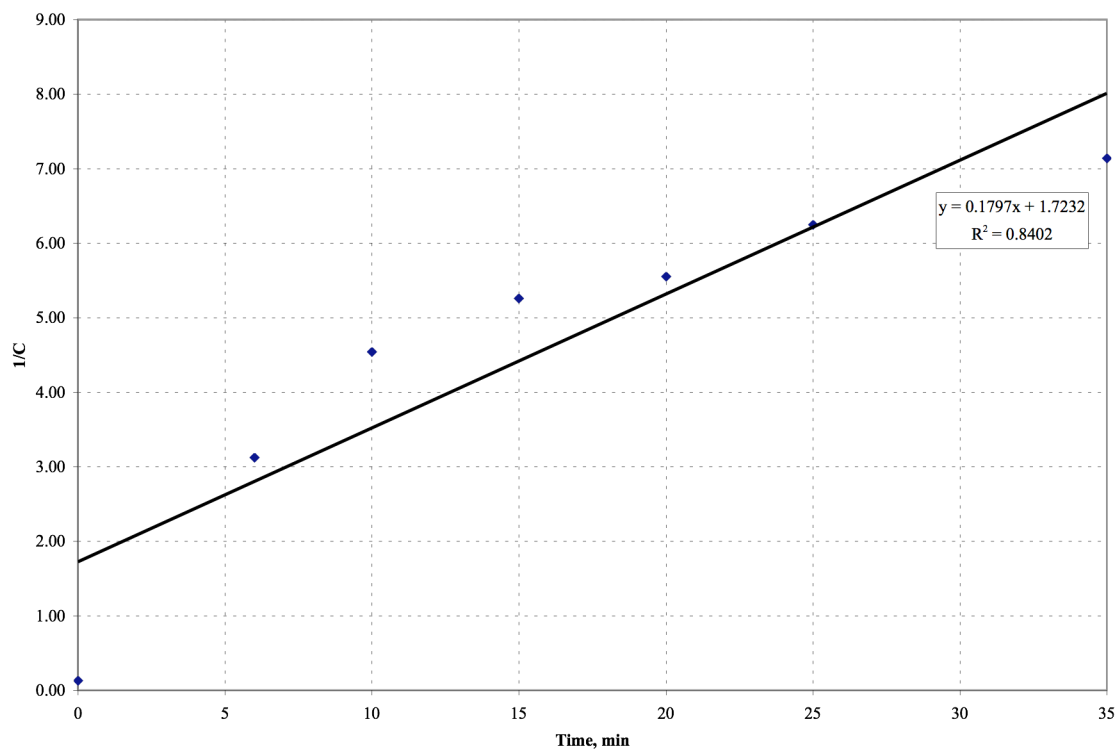
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.76	2.0490	0.1289	0.0166	0.0021	0.00027577	0.00003554	0.00000458	0.00000059
6	0.32	-1.1394	3.1250	9.7656	30.5176	95.3674	298.0232	931.3226	2910.3830
10	0.22	-1.5141	4.5455	20.6612	93.9144	426.8834	1940.3791	8819.9052	40090.4780
15	0.19	-1.6607	5.2632	27.7008	145.7938	767.3360	4038.6107	21255.8460	111872.8735
20	0.18	-1.7148	5.5556	30.8642	171.4678	952.5987	5292.2149	29401.1941	163339.9673
25	0.16	-1.8326	6.2500	39.0625	244.1406	1525.8789	9536.7432	59604.6448	372529.0298
35	0.14	-1.9661	7.1429	51.0204	364.4315	2603.0820	18593.4432	132810.3086	948645.0616

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

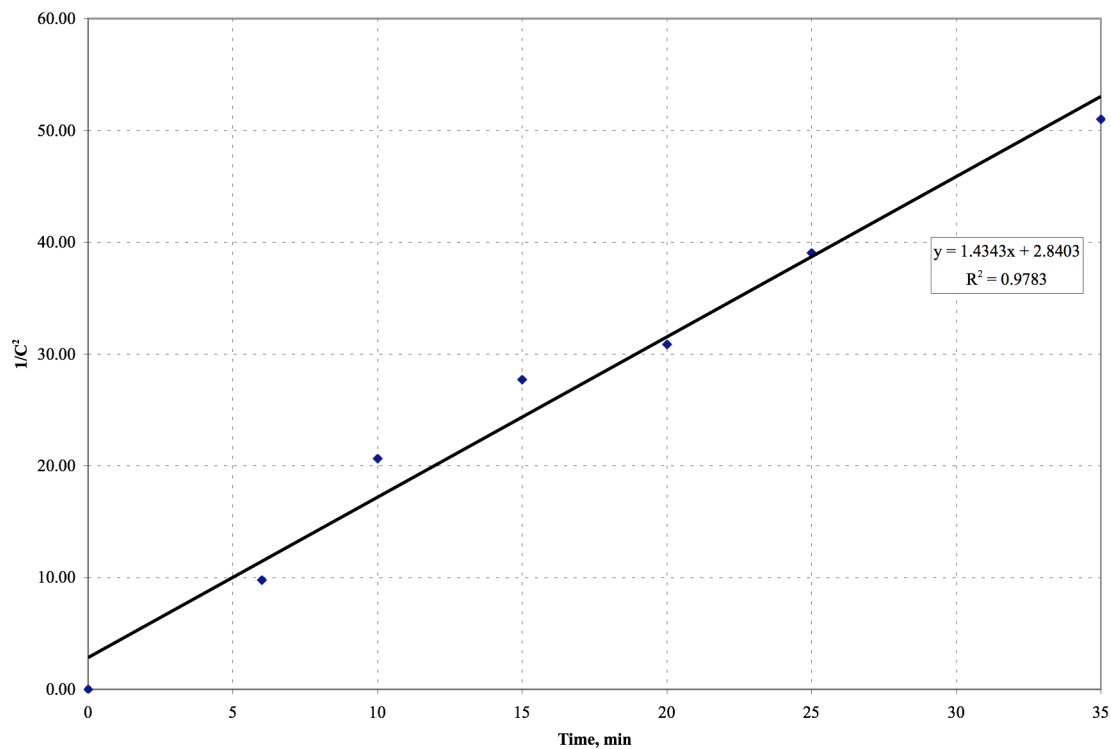
k = 0.7172 L²mg⁻²min⁻¹
 C₀ = 7.76 mg/L
 C = 3.88 mg/L
 t_{1/2} = 0.03 min



Appendix E-71. Test of First-Order Kinetics corresponding to 1.45 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS



Appendix E-72. Test of Second-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



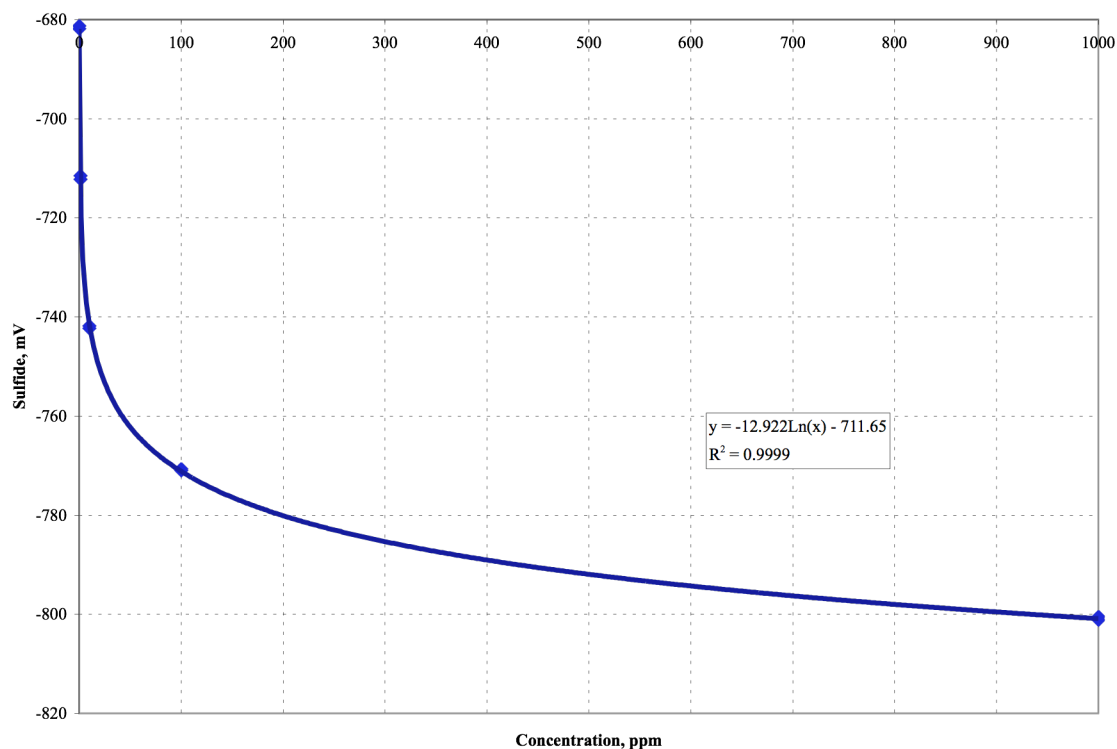
Appendix E-73. Test of Third-Order Kinetics corresponding to 1.45 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-74. Standard Curve Data for 29.0 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/9/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.1	12.3	21.6
	b	1000	-800.5	12.3	21.6
2	a	100	-770.6	12.3	21.6
	b	100	-771.0	12.3	21.6
3	a	10	-742.3	12.3	21.6
	b	10	-741.8	12.3	21.6
4	a	1	-712.2	12.3	21.6
	b	1	-711.5	12.3	21.6
5	a	0.1	-681.8	12.3	21.6
	b	0.1	-681.2	12.3	21.6

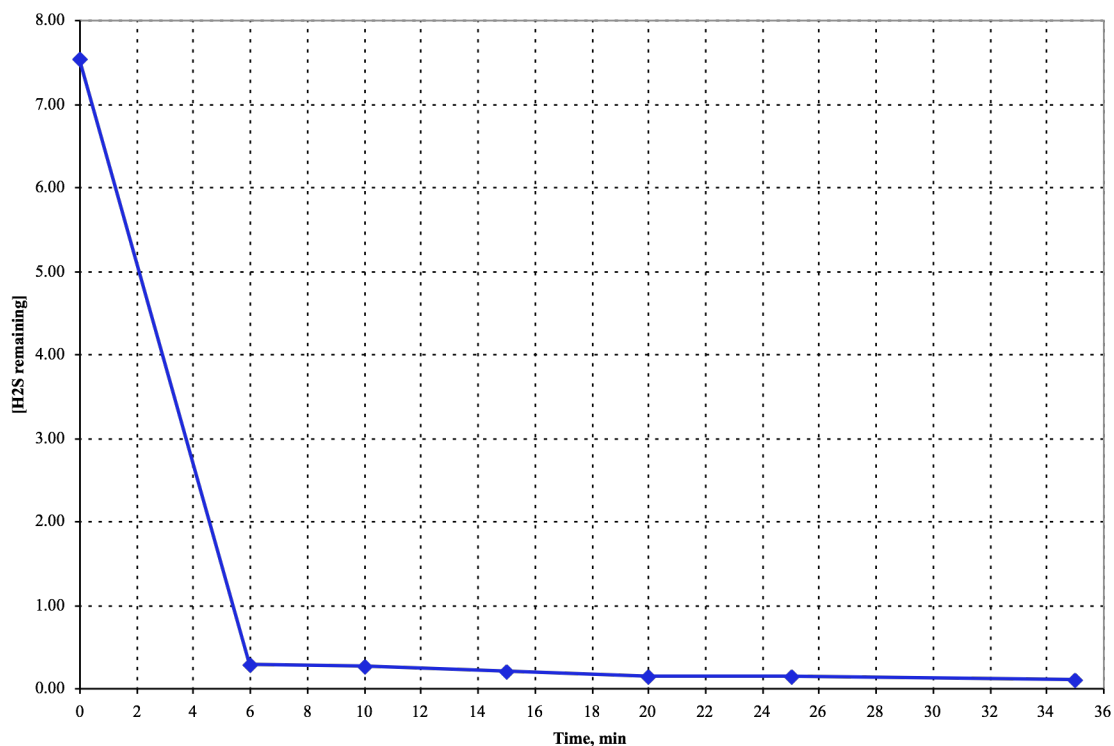


Appendix E-75. Standard Curve for 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Appendix E-76. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

Date: 2/10/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/lbS
 H₂O₂ Concentration: 0.10 kgH₂O₂/lbS
 H₂S Initial Concentration: 7.54 mg/L
 Initial pH: 12.30
 pH after HCl Addition: 7.80

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-737.2	1.977248104	7.22	7.54	17.7
	b				-738.3	2.062374245	7.86		17.7
2	a	1	5	6	-696.1	-1.203374091	0.30	0.28	17.7
	b				-693.9	-1.373626374	0.25		17.7
3	a	5	5	10	-694.2	-1.350410153	0.26	0.25	17.7
	b				-693.7	-1.389103854	0.25		17.7
4	a	10	5	15	-690.9	-1.605788578	0.20	0.20	17.7
	b				-691.0	-1.598049837	0.20		17.7
5	a	15	5	20	-685.3	-2.039158025	0.13	0.14	17.7
	b				-687.5	-1.868905742	0.15		17.7
6	a	20	5	25	-683.6	-2.170716607	0.11	0.13	17.7
	b				-687.2	-1.892121963	0.15		17.7
7	a	30	5	35	-683.3	-2.193932828	0.11	0.11	17.7
	b				-682.2	-2.279058969	0.10		17.7



Appendix E-77. H₂S remaining after 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS Addition

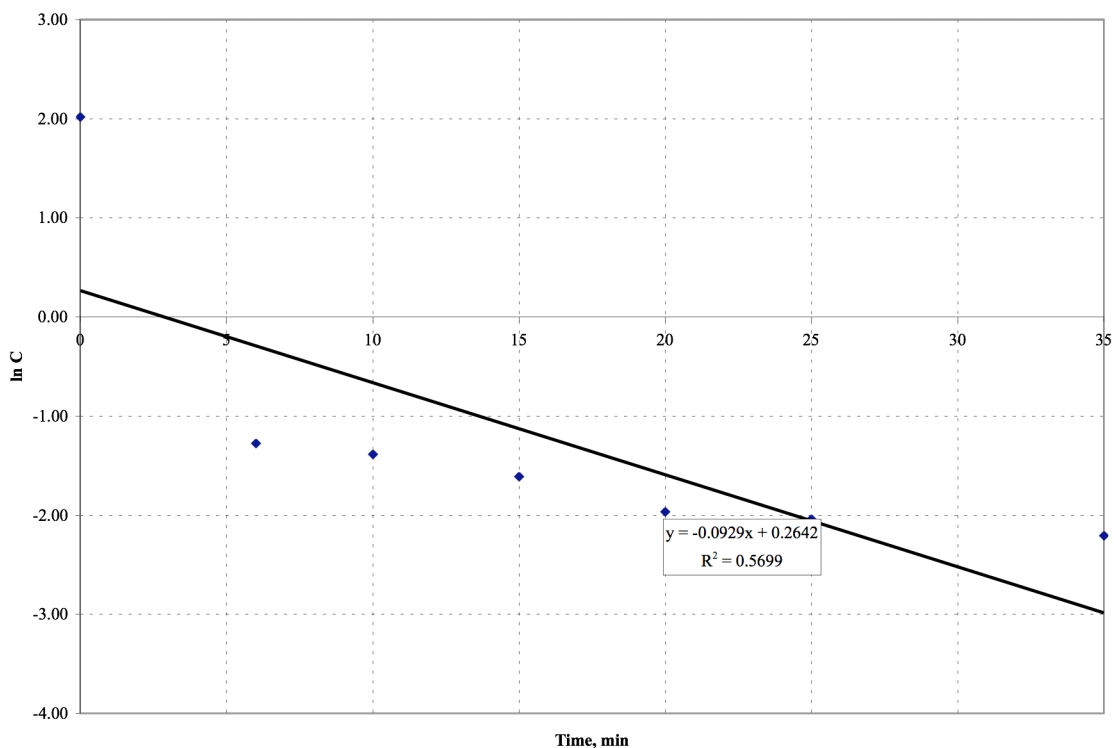
Appendix E-78. Linear Regression Analysis corresponding to 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS – pH = 7.80

Date: 2/10/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.10 kgH₂O₂/kgS

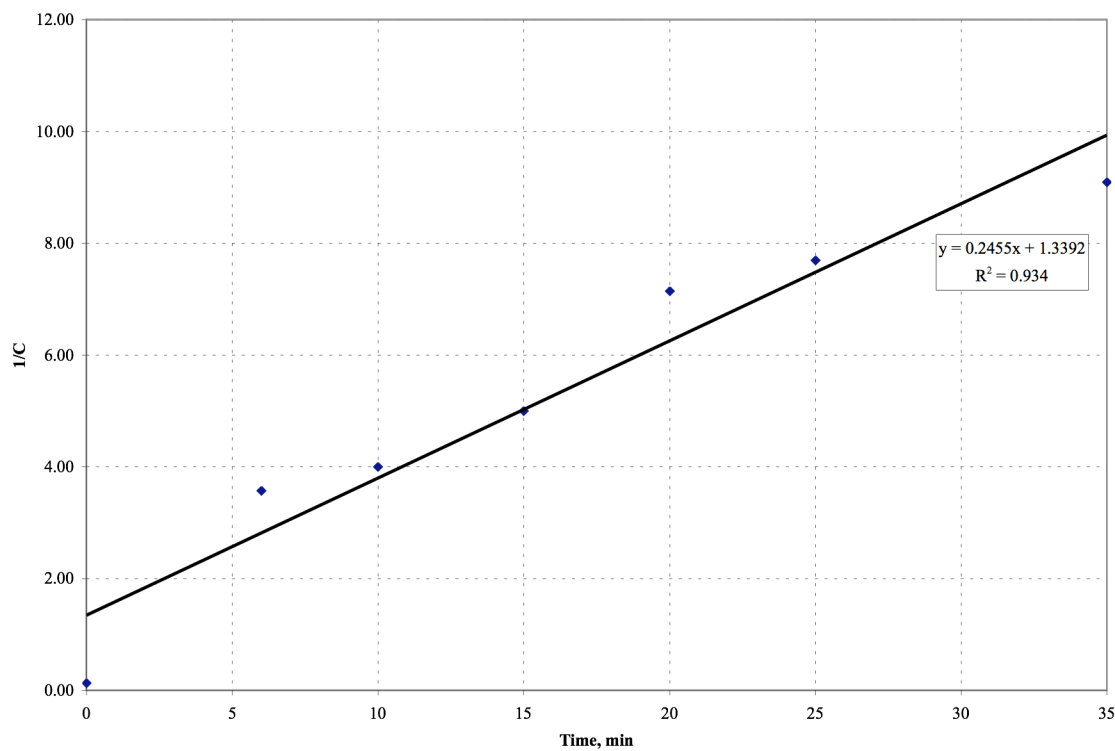
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	7.54	2.0202	0.1326	0.0176	0.0023	0.0003094	0.0000410	0.0000054	0.0000007
6	0.28	-1.2730	3.5714	12.7551	45.5539	162.6926	581.0451	2075.1611	7411.2895
10	0.25	-1.3863	4.0000	16.0000	64.0000	256.0000	1024.0000	4096.0000	16384.0000
15	0.20	-1.6094	5.0000	25.0000	125.0000	625.0000	3125.0000	15625.0000	78125.0000
20	0.14	-1.9661	7.1429	51.0204	364.4315	2603.0820	18593.4432	132810.3086	948645.0616
25	0.13	-2.0402	7.6923	59.1716	455.1661	3501.2780	26932.9074	207176.2110	1593663.1618
35	0.11	-2.2073	9.0909	82.6446	751.3148	6830.1346	62092.1323	564473.9301	5131581.1823

$$\frac{1}{[C]^t} = \frac{1}{[C_0]^t} + 2kt$$

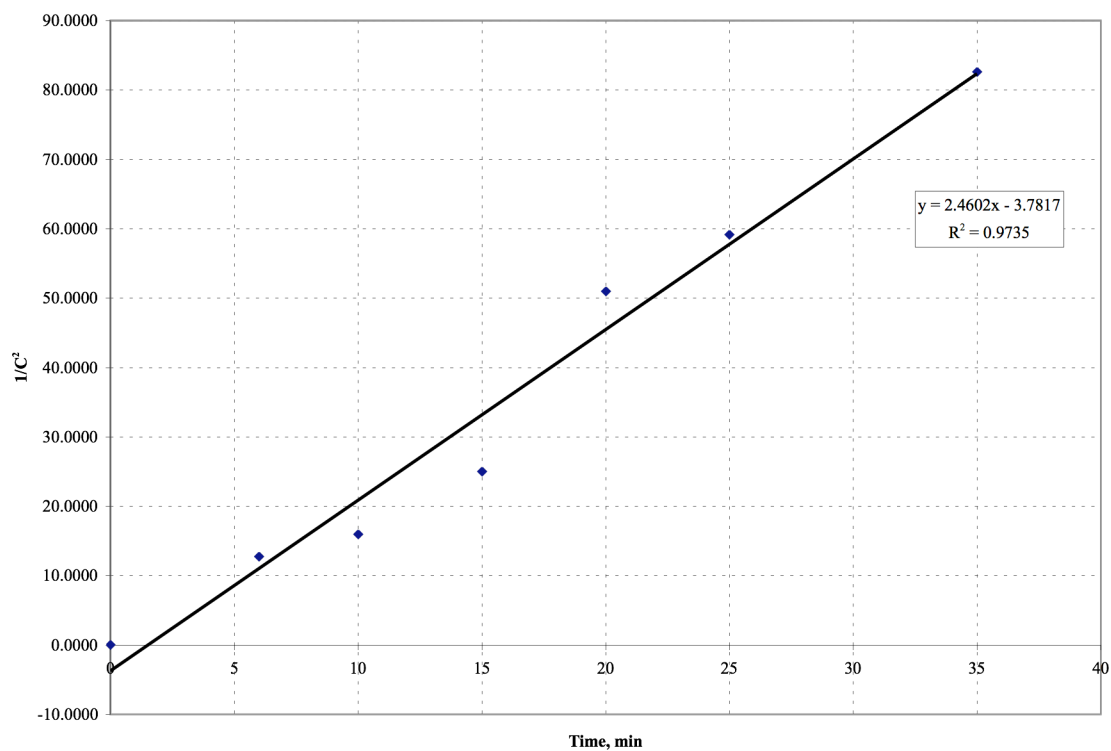
k = 1.2301 L²mg⁻²min⁻¹
 C₀ = 7.54 mg/L
 C = 3.77 mg/L
 t_{1/2} = 0.02 min



Appendix E-79. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS and 0.10 kg H₂O₂/kgS



Appendix E-80. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$



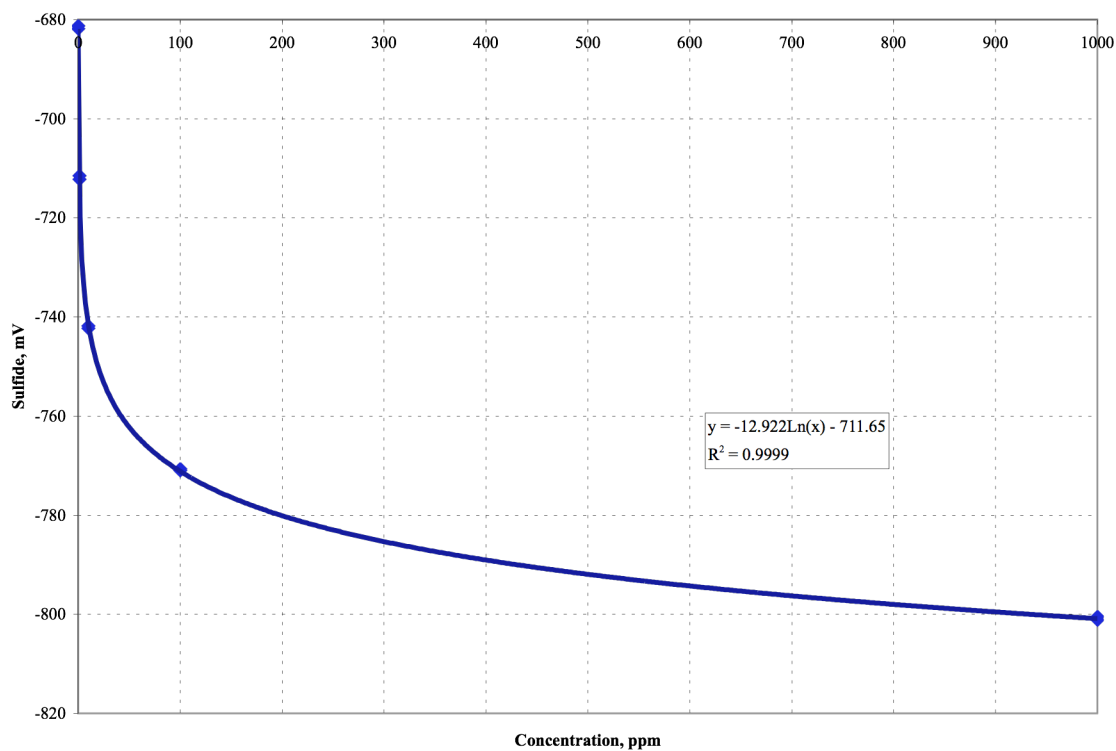
Appendix E-81. Test of Third-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.10 kg $\text{H}_2\text{O}_2/\text{kgS}$

Appendix E-82. Standard Curve Data for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/9/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-801.1	12.3	21.6
	b	1000	-800.5	12.3	21.6
2	a	100	-770.6	12.3	21.6
	b	100	-771.0	12.3	21.6
3	a	10	-742.3	12.3	21.6
	b	10	-741.8	12.3	21.6
4	a	1	-712.2	12.3	21.6
	b	1	-711.5	12.3	21.6
5	a	0.1	-681.8	12.3	21.6
	b	0.1	-681.2	12.3	21.6



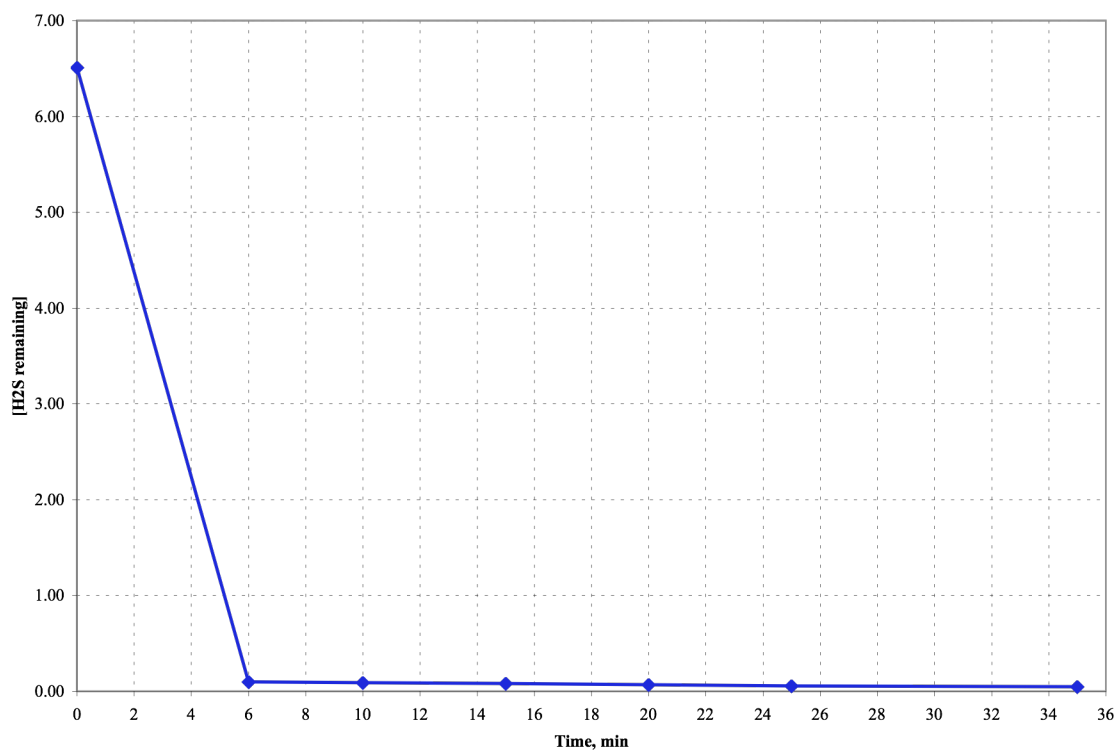
Appendix E-83. Standard Curve for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Appendix E-84. Ion Selective Electrode Method Data for 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

Date: 2/9/07
 Method: Ion Selective Electrode Method

FeCl₂ Concentration: 2.90 kgFeCl₂/lbS
 H₂O₂ Concentration: 0.30 kgH₂O₂/lbS
 H₂S Initial Concentration: 6.51 mg/L
 Initial pH: 12.30
 pH after HCl Addition: 7.20

Sample	Replicates	Adding FeCl ₂ & H ₂ O ₂							Temp, °C
		FeCl ₂ Time, min	H ₂ O ₂ Time, min	Total Time, min	Concentration, mg/L S ²⁻				
					Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Total Sulfide, mg/L	
1	a	0	0	0	-735.5	1.845689522	6.33	6.51	18.9
	b				-736.2	1.899860703	6.68		18.9
2	a	1	5	6	-682.4	-2.263581489	0.10	0.10	18.9
	b				-680.1	-2.441572512	0.09		18.9
3	a	5	5	10	-680.6	-2.402878811	0.09	0.09	18.9
	b				-679.9	-2.457049992	0.09		18.9
4	a	10	5	15	-679.5	-2.488004953	0.08	0.08	18.9
	b				-678.7	-2.549914874	0.08		18.9
5	a	15	5	20	-677.7	-2.627302275	0.07	0.07	18.9
	b				-676.5	-2.720167157	0.07		18.9
6	a	20	5	25	-674.7	-2.859464479	0.06	0.06	18.9
	b				-673.8	-2.92911314	0.05		18.9
7	a	30	5	35	-672.5	-3.029716762	0.05	0.05	18.9
	b				-670.8	-3.161275344	0.04		18.9



Appendix E-85. H₂S remaining after 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS Addition

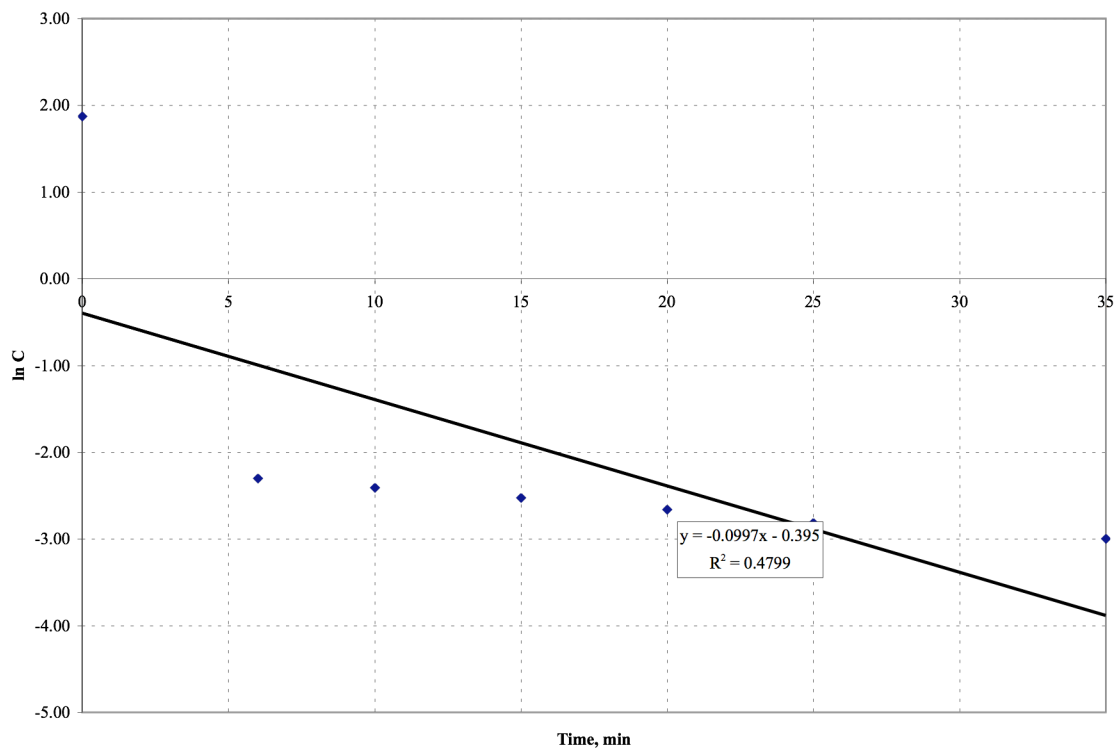
Appendix E-86. Linear Regression Analysis corresponding to 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS – pH = 7.20

Date: 2/9/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 2.90 kgFeCl₂/kgS
 H₂O₂ Concentration: 0.30 kgH₂O₂/kgS

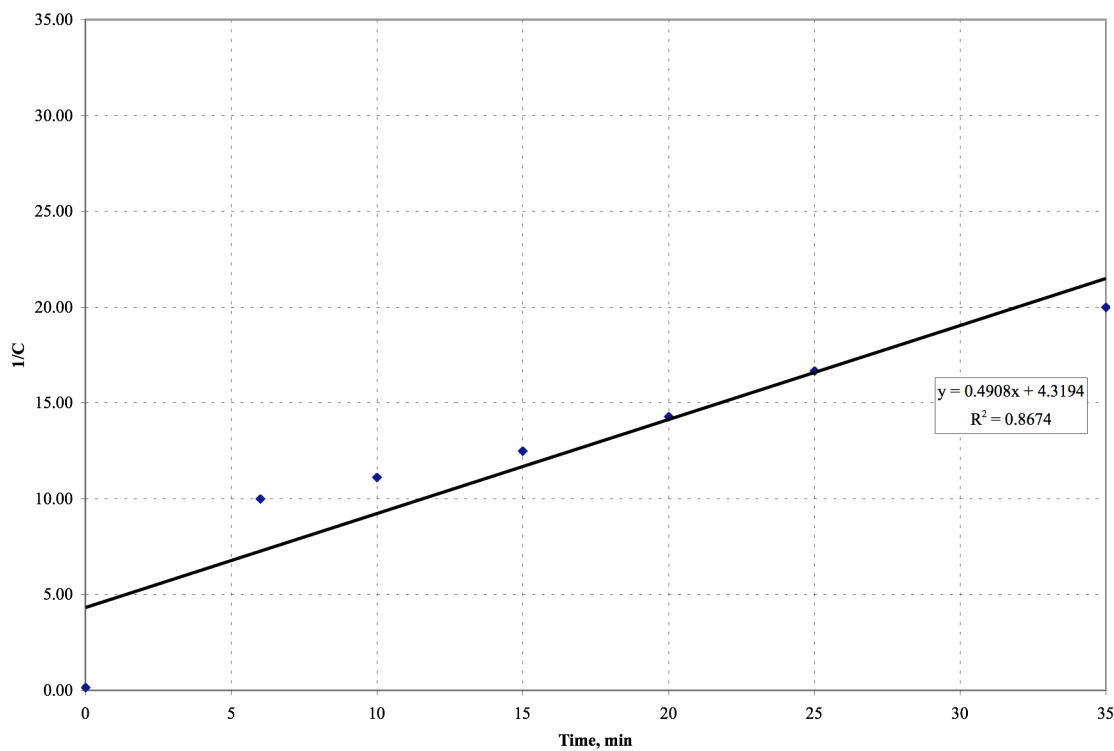
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.51	1.8733	0.1536	0.0236	0.0036	0.0006	0.0000855	0.0000131	0.0000020
6	0.10	-2.3026	10.0000	100.0000	1000.0000	10000.0000	100000.0000	1000000.0000	10000000.0000
10	0.09	-2.4079	11.1111	123.4568	1371.7421	15241.5790	169350.8781	1881676.4232	20907515.8129
15	0.08	-2.5257	12.5000	156.2500	1953.1250	24414.0625	305175.7813	3814697.2656	47683715.8203
20	0.07	-2.6593	14.2857	204.0816	2915.4519	41649.3128	594990.1827	8499859.7523	121426567.8902
25	0.06	-2.8134	16.6667	277.7778	4629.6296	77160.4938	1286008.2305	21433470.5075	357224508.4591
35	0.05	-2.9957	20.0000	400.0000	8000.0000	160000.0000	3200000.0000	64000000.0000	1280000000.0000

$$\frac{1}{[C]^2} = \frac{1}{[C_0]^2} + 2kt$$

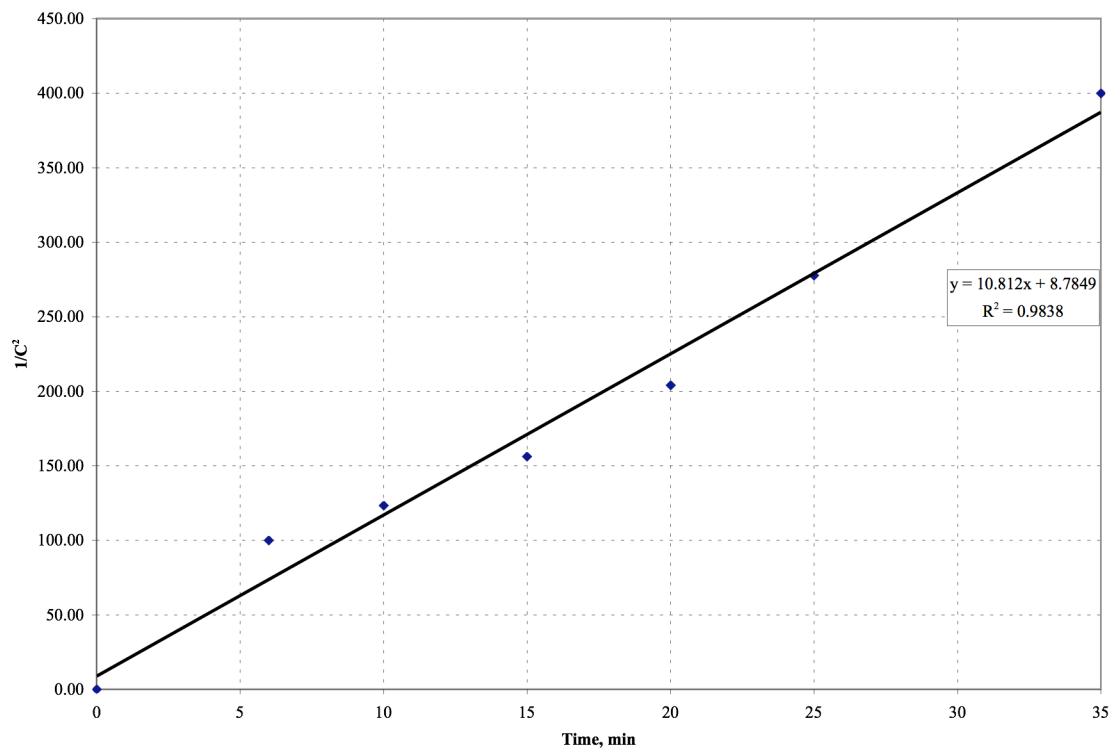
k= 5.4060 L²mg⁻²min⁻¹
 C₀= 6.51 mg/L
 C= 3.26 mg/L
 t_{1/2}= 0.007 min



Appendix E-87. Test of First-Order Kinetics corresponding to 2.90 kg FeCl₂/kgS and 0.30 kg H₂O₂/kgS



Appendix E-88. Test of Second-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$



Appendix E-89. Test of Third-Order Kinetics corresponding to 2.90 kg FeCl_2/kgS and 0.30 kg $\text{H}_2\text{O}_2/\text{kgS}$

APPENDIX F

Appendix F-1. Results Summary - Ion Selective Electrode Method – O₂ Addition

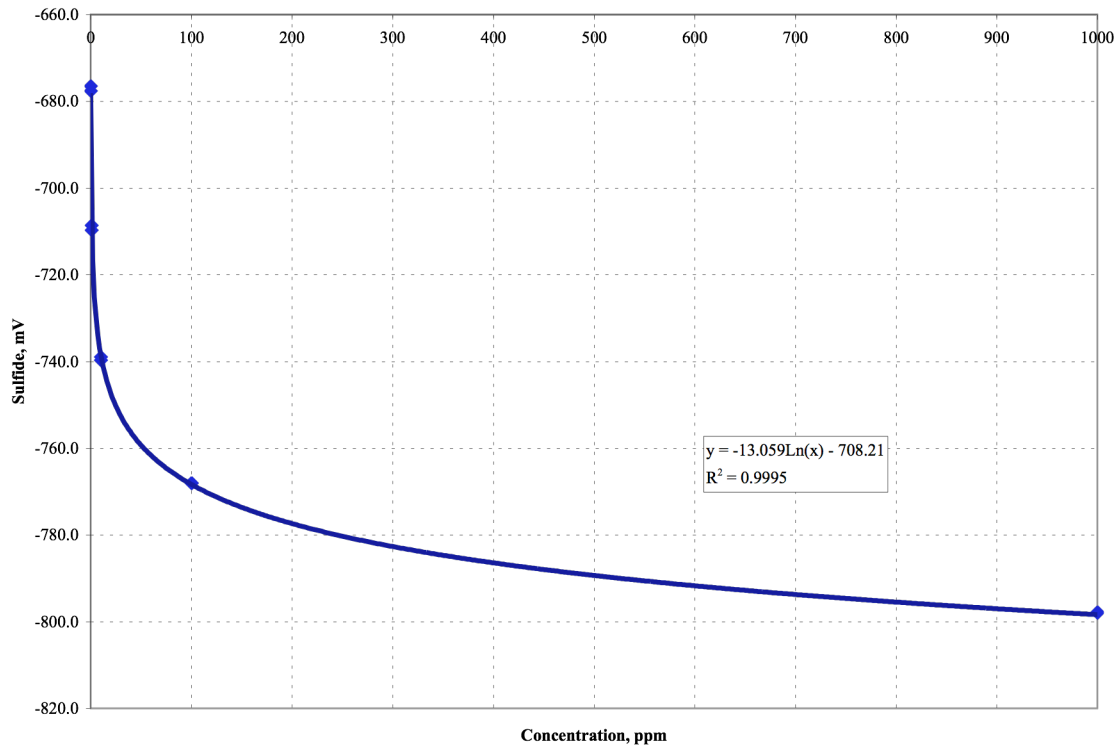
Time, min	O ₂ Concentration, kgO ₂ /kgS	H ₂ S Concentration, mg/L	H ₂ S Remaining Concentration, %	H ₂ S Oxidation, %
0	20.00	8.21	100.00	0.00
10	20.00	6.80	82.83	17.17
25	20.00	5.98	72.84	27.16
30	20.00	5.65	68.82	31.18
40	20.00	5.30	64.56	35.44
60	20.00	5.16	62.85	37.15
90	20.00	4.97	60.54	39.46
120	20.00	4.25	51.77	48.23
150	20.00	4.02	48.96	51.04
0	15.00	9.20	100.00	0.00
10	15.00	8.24	89.57	10.43
25	15.00	8.12	88.26	11.74
30	15.00	7.94	86.30	13.70
40	15.00	7.72	83.91	16.09
60	15.00	7.12	77.39	22.61
90	15.00	6.89	74.89	25.11
120	15.00	6.24	67.83	32.17
150	15.00	5.93	64.46	35.54
0	10.00	5.75	100.00	0.00
10	10.00	5.33	92.70	7.30
25	10.00	5.17	89.91	10.09
30	10.00	5.05	87.83	12.17
40	10.00	4.92	85.57	14.43
60	10.00	4.55	79.13	20.87
90	10.00	4.45	77.39	22.61
120	10.00	4.32	75.13	24.87
150	10.00	4.17	72.52	27.48
0	5.00	6.38	100.00	0.00
10	5.00	6.11	95.77	4.23
25	5.00	5.91	92.63	7.37
30	5.00	5.79	90.75	9.25
40	5.00	5.68	89.03	10.97
60	5.00	5.51	86.36	13.64
90	5.00	5.30	83.07	16.93
120	5.00	5.20	81.50	18.50
150	5.00	5.15	80.72	19.28

Appendix F-2. Standard Curve Data for 20.0 kg O₂/kgS Addition

Date: 3/26/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-798.0	12.4	21.0
	b	1000	-797.8	12.4	21.0
2	a	100	-768.0	12.4	21.0
	b	100	-768.1	12.4	21.0
3	a	10	-739.7	12.4	21.0
	b	10	-738.9	12.4	21.0
4	a	1	-709.7	12.4	21.0
	b	1	-708.6	12.4	21.0
5	a	0.1	-677.6	12.4	21.0
	b	0.1	-676.4	12.4	21.0



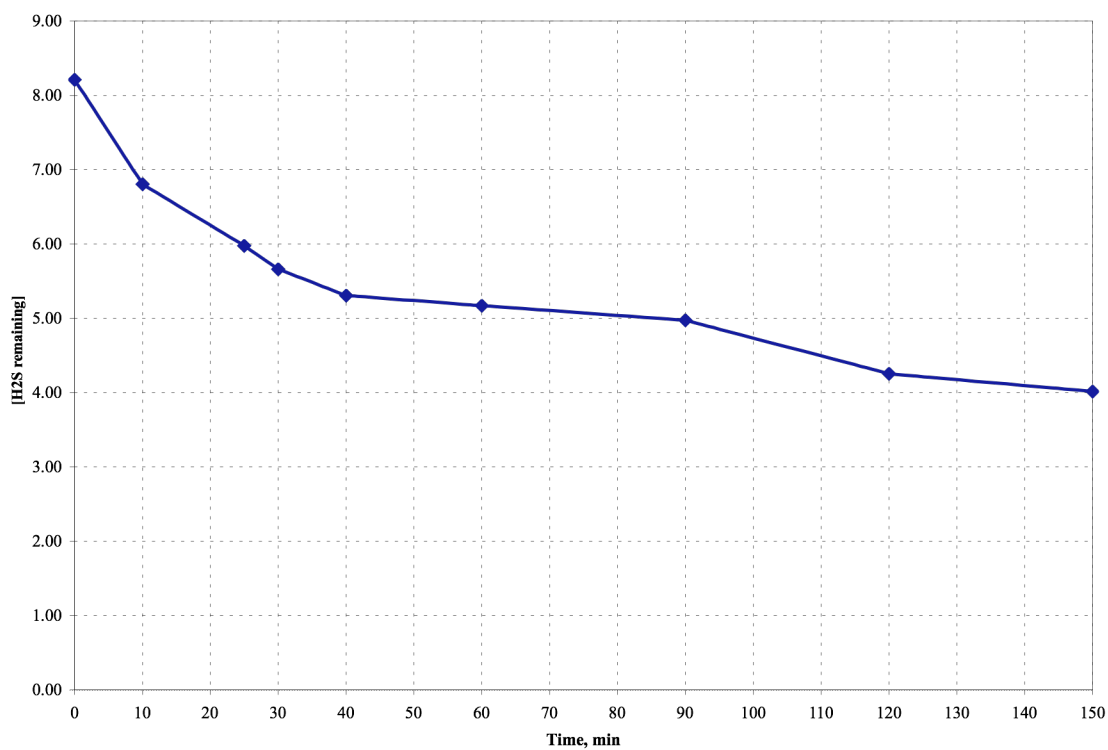
Appendix F-3. Standard Curve for 20.0 kg O₂/kgS Addition

Appendix F-4. Ion Selective Electrode Method Data for 20.0 kg O₂/kgS Addition

Date: 3/26/07
Method: Ion Selective Electrode Method

O₂ Concentration: 20.00 kgO₂/kgS
H₂S Initial Concentration: 8.21 mg/L
Initial pH: 12.40
pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-735.7	2.105061643	8.21	8.21	22.5
	b		-735.7	2.105061643	8.21		22.5
2	a	10	-733.3	1.921280343	6.83	6.80	22.5
	b		-733.2	1.913622789	6.78		22.5
3	a	25	-731.0	1.745156597	5.73	5.98	22.5
	b		-732.1	1.829389693	6.23		22.5
4	a	30	-731.0	1.745156597	5.73	5.66	22.5
	b		-730.7	1.722183934	5.60		22.5
5	a	40	-729.6	1.637950839	5.14	5.31	22.5
	b		-730.4	1.699211272	5.47		22.5
6	a	60	-729.1	1.599663068	4.95	5.17	22.5
	b		-730.2	1.683896164	5.39		22.5
7	a	90	-728.6	1.561375297	4.77	4.97	22.5
	b		-729.7	1.645608393	5.18		22.5
8	a	120	-727.9	1.507772417	4.52	4.26	22.5
	b		-726.3	1.385251551	4.00		22.5
9	a	150	-725.9	1.354621334	3.88	4.01	22.5
	b		-726.8	1.423539322	4.15		22.5



Appendix F-5. H₂S remaining after 20.0 kg O₂/kgS Addition

Appendix F-6. Linear Regression Analysis corresponding to 20.0 kg O₂/kgS – pH = 7.20

Method: Ion Selective Electrode Method
FeCl₃ Concentration: 20 kgO₂/kgS

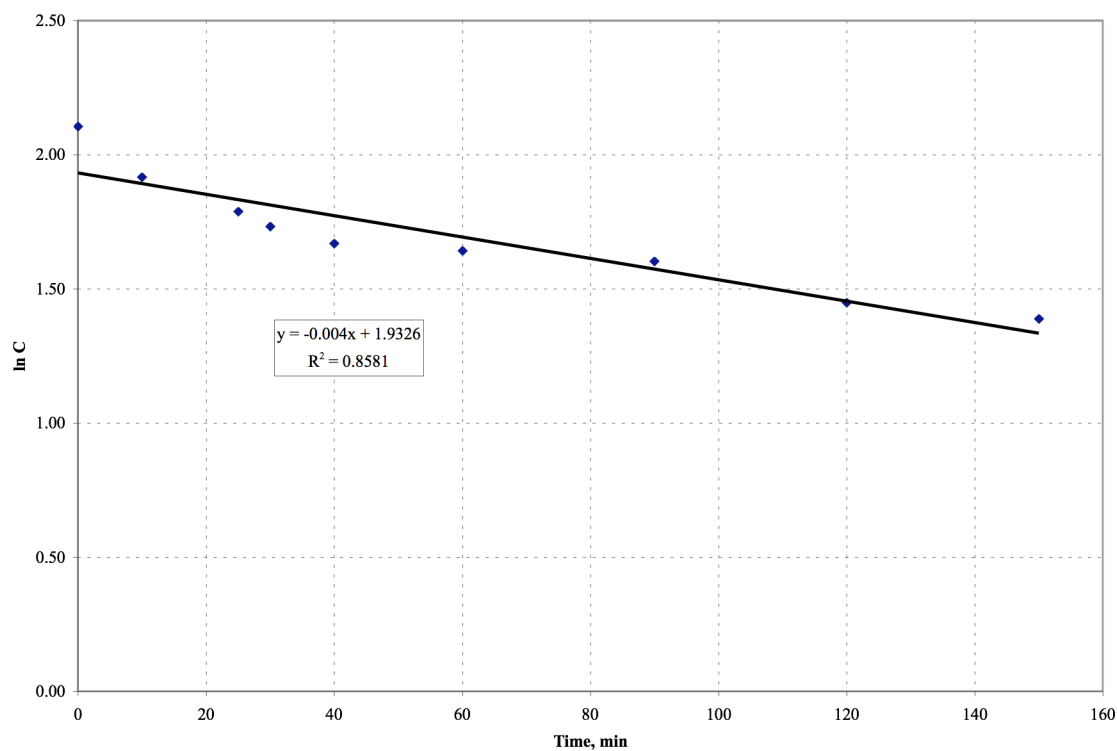
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	8.21	2.1054	0.1218	0.0148	0.0018	0.0002	0.00002681	0.00000327	0.00000040
10	6.80	1.9169	0.1471	0.0216	0.0032	0.0005	0.0001	0.0000	0.0000
25	5.98	1.7884	0.1672	0.0280	0.0047	0.0008	0.0001	0.0000	0.0000
30	5.66	1.7334	0.1767	0.0312	0.0055	0.0010	0.0002	0.0000	0.0000
40	5.31	1.6696	0.1883	0.0355	0.0067	0.0013	0.0002	0.0000	0.0000
60	5.17	1.6429	0.1934	0.0374	0.0072	0.0014	0.0003	0.0001	0.0000
90	4.97	1.6034	0.2012	0.0405	0.0081	0.0016	0.0003	0.0001	0.0000
120	4.26	1.4493	0.2347	0.0551	0.0129	0.0030	0.0007	0.0002	0.0000
150	4.01	1.3888	0.2494	0.0622	0.0155	0.0039	0.0010	0.0002	0.0001

$$t_{1/2} = \frac{1}{k[C_0]}$$

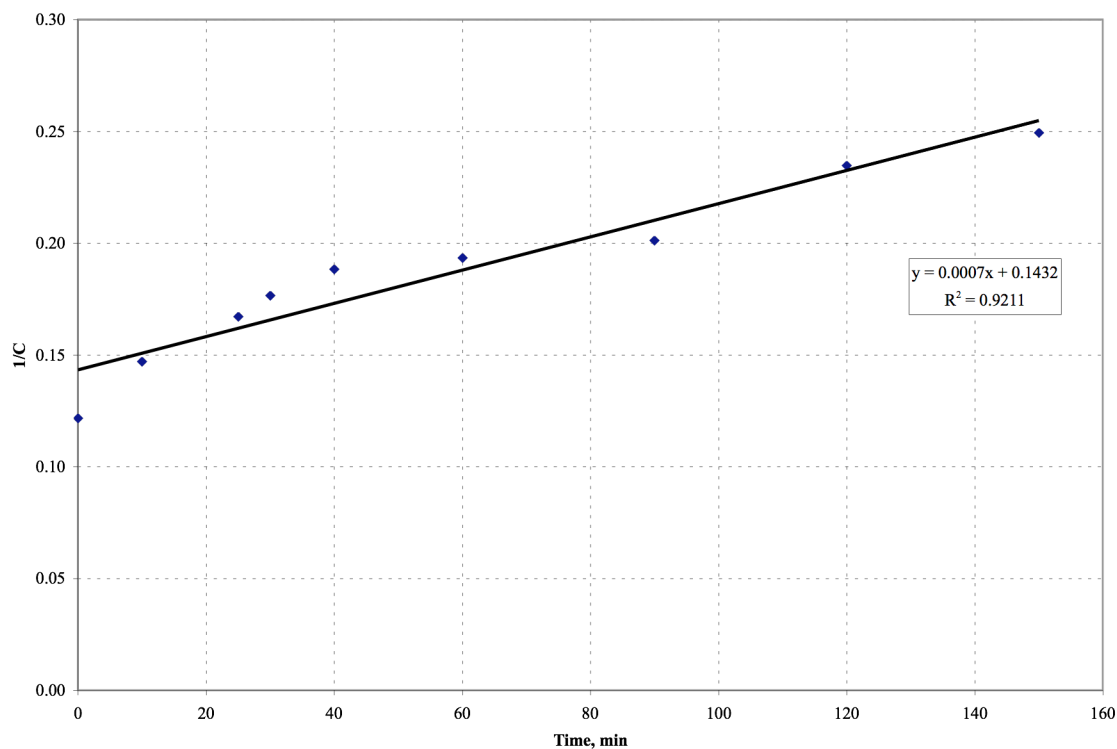
$$k = 0.0007 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_0 = 8.21 \text{ mg/L}$$

$$t_{1/2} = 174.00 \text{ min}$$



Appendix F-7. Test of First-Order Kinetics corresponding to 20.0 kg O₂/kgS

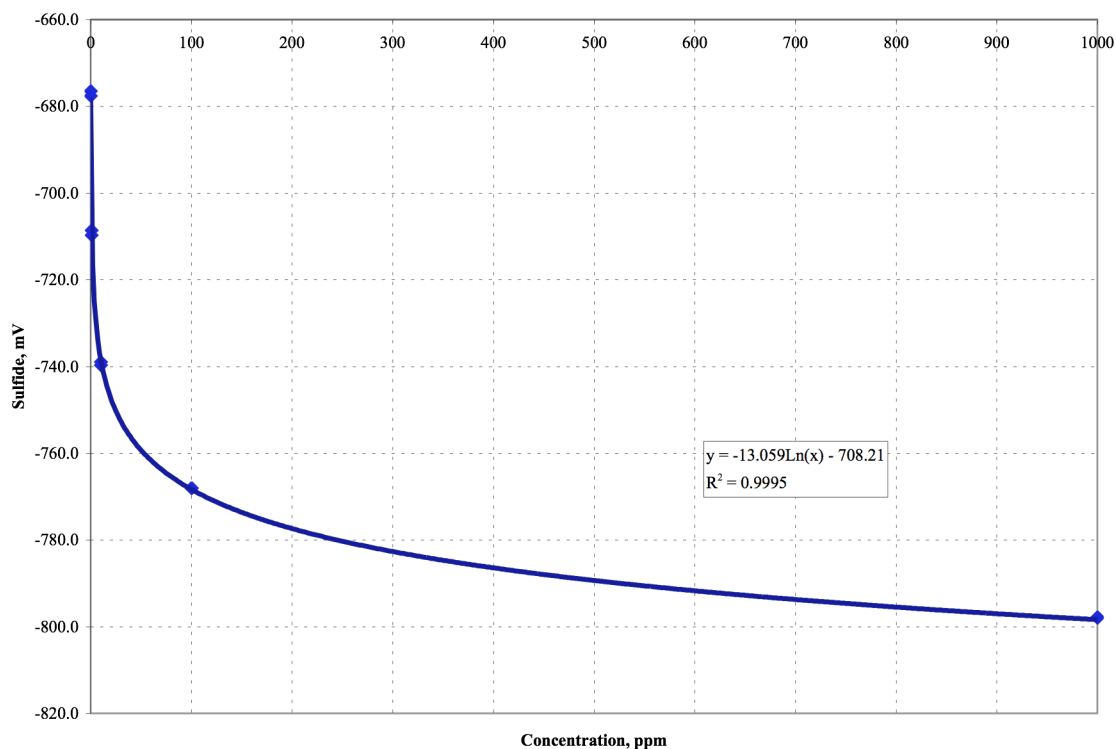


Appendix F-8. Test of Second-Order Kinetics corresponding to 20.0 kg O₂/kgS

Appendix F-9. Standard Curve Data for 15.0 kg O₂/kgS Addition

Date: 3/26/07
Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-798.0	12.4	21.0
	b	1000	-797.8	12.4	21.0
2	a	100	-768.0	12.4	21.0
	b	100	-768.1	12.4	21.0
3	a	10	-739.7	12.4	21.0
	b	10	-738.9	12.4	21.0
4	a	1	-709.7	12.4	21.0
	b	1	-708.6	12.4	21.0
5	a	0.1	-677.6	12.4	21.0
	b	0.1	-676.4	12.4	21.0



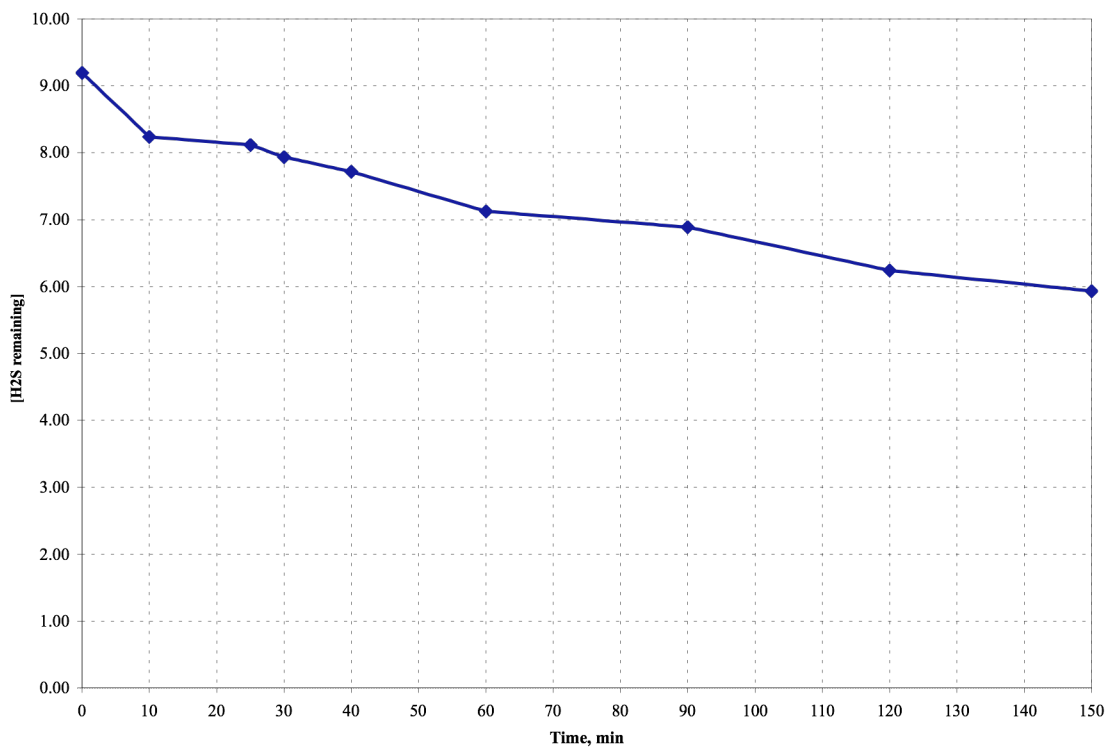
Appendix F-10. Standard Curve for 15.0 kg O₂/kgS Addition

Appendix F-11. Ion Selective Electrode Method Data for 15.0 kg O₂/kgS Addition

Date: 3/26/07
 Method: Ion Selective Electrode Method

O₂ Concentration: 15.00 kgO₂/kgS
 H₂S Initial Concentration: 9.20 mg/L
 Initial pH: 12.50
 pH after HCl addition: 7.80

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-738.1	2.288842944	9.86	9.20	22.5
	b		-736.2	2.143349414	8.53		22.5
2	a	10	-735.9	2.120376752	8.33	8.24	22.5
	b		-735.6	2.097404089	8.14		22.5
3	a	25	-735.2	2.066773872	7.90	8.12	22.5
	b		-735.9	2.120376752	8.33		22.5
4	a	30	-734.7	2.028486102	7.60	7.94	22.5
	b		-735.8	2.112719197	8.27		22.5
5	a	40	-734.8	2.036143656	7.66	7.72	22.5
	b		-735.0	2.051458764	7.78		22.5
6	a	60	-733.8	1.959568114	7.10	7.12	22.5
	b		-733.9	1.967225668	7.15		22.5
7	a	90	-733.9	1.967225668	7.15	6.89	22.5
	b		-732.9	1.890650126	6.62		22.5
8	a	120	-732.9	1.890650126	6.62	6.24	22.5
	b		-731.3	1.76812926	5.86		22.5
9	a	150	-731.9	1.814074585	6.14	5.93	22.5
	b		-731.0	1.745156597	5.73		22.5



Appendix F-12. H₂S remaining after 15.0 kg O₂/kgS Addition

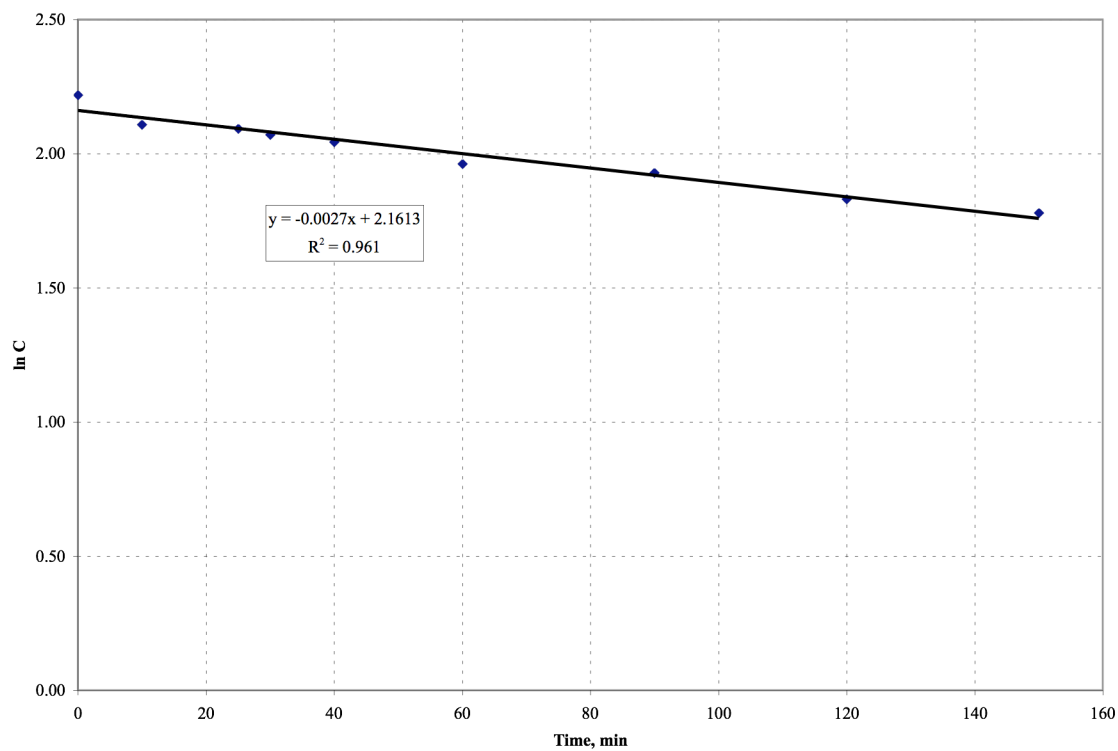
Appendix F-13. Linear Regression Analysis corresponding to 15.0 kg O₂/kgS – pH = 7.20

Date: 3/26/07
Method: Ion Selective Electrode Method
FeCl₂ Concentration: 15 kgO₂/kgS

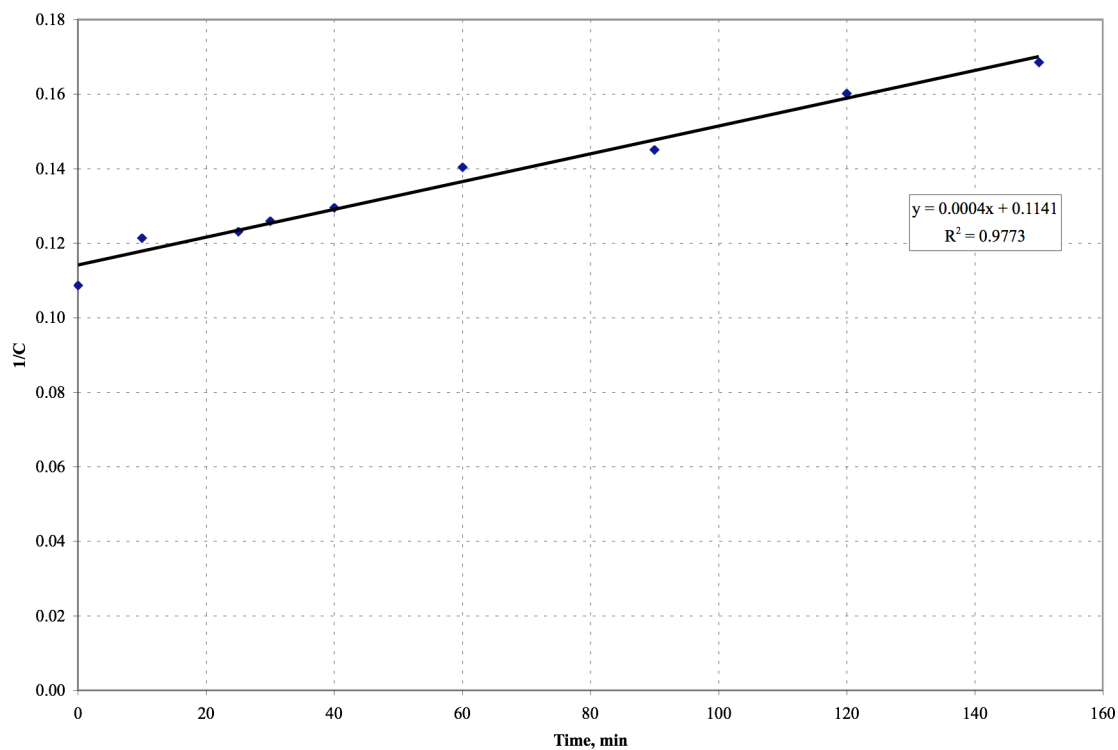
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	9.20	2.2192	0.1087	0.0118	0.0013	0.0001	0.00001517	0.00000165	0.00000018
10	8.24	2.1090	0.1214	0.0147	0.0018	0.0002	0.0000	0.0000	0.0000
25	8.12	2.0943	0.1232	0.0152	0.0019	0.0002	0.0000	0.0000	0.0000
30	7.94	2.0719	0.1259	0.0159	0.0020	0.0003	0.0000	0.0000	0.0000
40	7.72	2.0438	0.1295	0.0168	0.0022	0.0003	0.0000	0.0000	0.0000
60	7.12	1.9629	0.1404	0.0197	0.0028	0.0004	0.0001	0.0000	0.0000
90	6.89	1.9301	0.1451	0.0211	0.0031	0.0004	0.0001	0.0000	0.0000
120	6.24	1.8310	0.1603	0.0257	0.0041	0.0007	0.0001	0.0000	0.0000
150	5.93	1.7800	0.1686	0.0284	0.0048	0.0008	0.0001	0.0000	0.0000

$$t_{1/2} = \frac{1}{k[C_0]}$$

k= 0.0004 Lmg⁻¹min⁻¹
C₀= 9.20 mg/L
t_{1/2}= 271.74 min



Appendix F-14. Test of First-Order Kinetics corresponding to 15.0 kg O₂/kgS



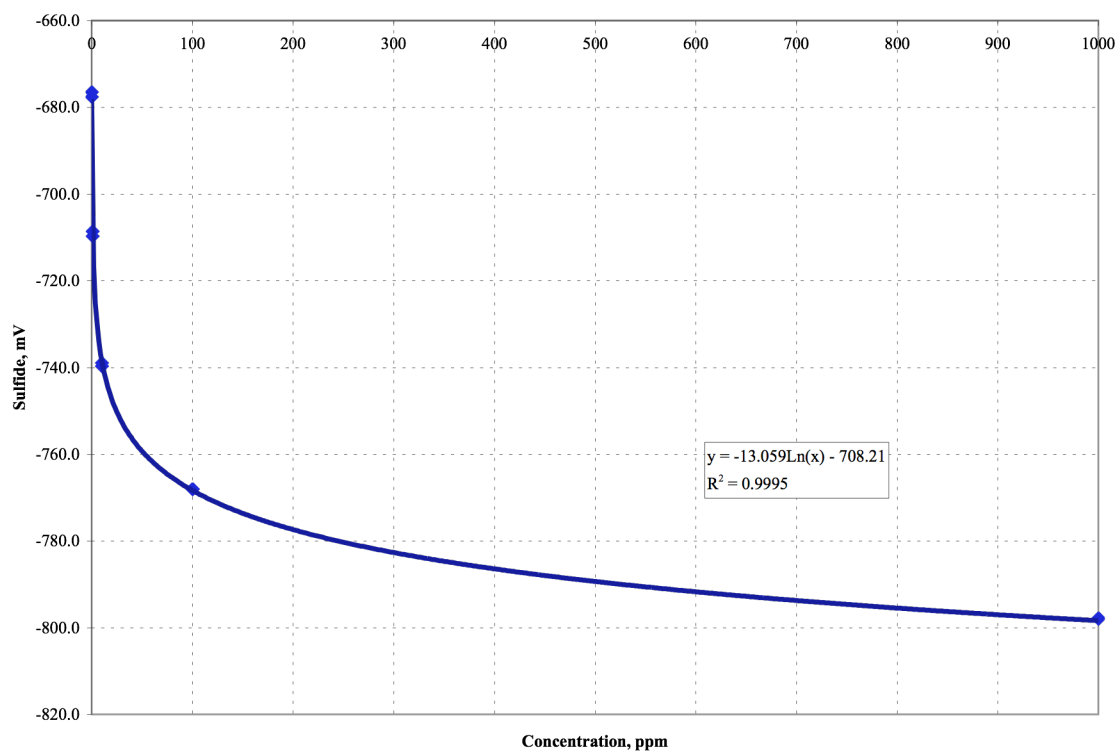
Appendix F-15. Test of Second-Order Kinetics corresponding to 15.0 kg O₂/kgS

Appendix F-16. Standard Curve Data for 10.0 kg O₂/kgS Addition

Date: 3/26/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-798.0	12.4	21.0
	b	1000	-797.8	12.4	21.0
2	a	100	-768.0	12.4	21.0
	b	100	-768.1	12.4	21.0
3	a	10	-739.7	12.4	21.0
	b	10	-738.9	12.4	21.0
4	a	1	-709.7	12.4	21.0
	b	1	-708.6	12.4	21.0
5	a	0.1	-677.6	12.4	21.0
	b	0.1	-676.4	12.4	21.0



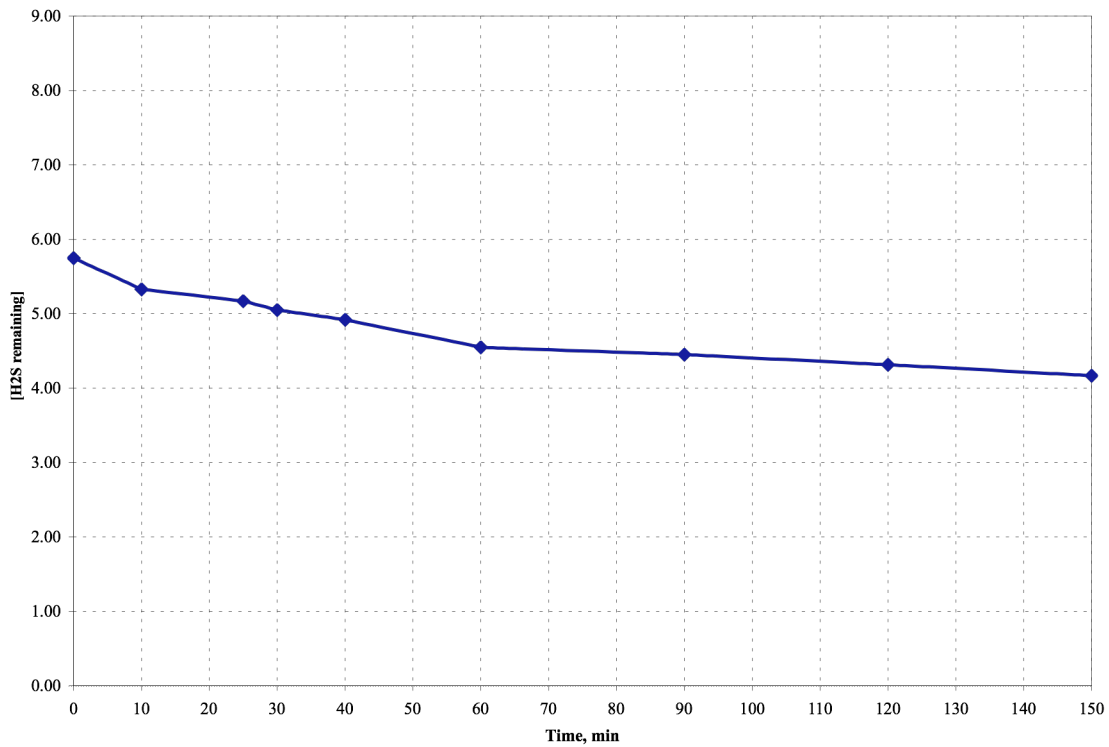
Appendix F-17. Standard Curve for 10.0 kg O₂/kgS Addition

Appendix F-18. Ion Selective Electrode Method Data for 10.0 kg O₂/kgS Addition

Date: 3/26/07
Method: Ion Selective Electrode Method

O₂ Concentration: 10.00 kgO₂/kgS
H₂S Initial Concentration: 5.75 mg/L
Initial pH: 12.10
pH after HCl addition: 6.20

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-731.2	1.760471705	5.82	5.75	22.5
	b		-730.9	1.737499043	5.68		22.5
2	a	10	-729.8	1.653265947	5.22	5.33	22.5
	b		-730.3	1.691553718	5.43		22.5
3	a	25	-730.1	1.676238609	5.35	5.17	22.5
	b		-729.2	1.607320622	4.99		22.5
4	a	30	-729.8	1.653265947	5.22	5.05	22.5
	b		-728.9	1.584347959	4.88		22.5
5	a	40	-728.4	1.546060188	4.69	4.92	22.5
	b		-729.6	1.637950839	5.14		22.5
6	a	60	-728.1	1.523087526	4.59	4.55	22.5
	b		-727.9	1.507772417	4.52		22.5
7	a	90	-728.0	1.515429972	4.55	4.45	22.5
	b		-727.4	1.469484647	4.35		22.5
8	a	120	-727.7	1.492457309	4.45	4.32	22.5
	b		-726.9	1.431196876	4.18		22.5
9	a	150	-726.9	1.431196876	4.18	4.17	22.5
	b		-726.8	1.423539322	4.15		22.5



Appendix F-19. H₂S remaining after 10.0 kg O₂/kgS Addition

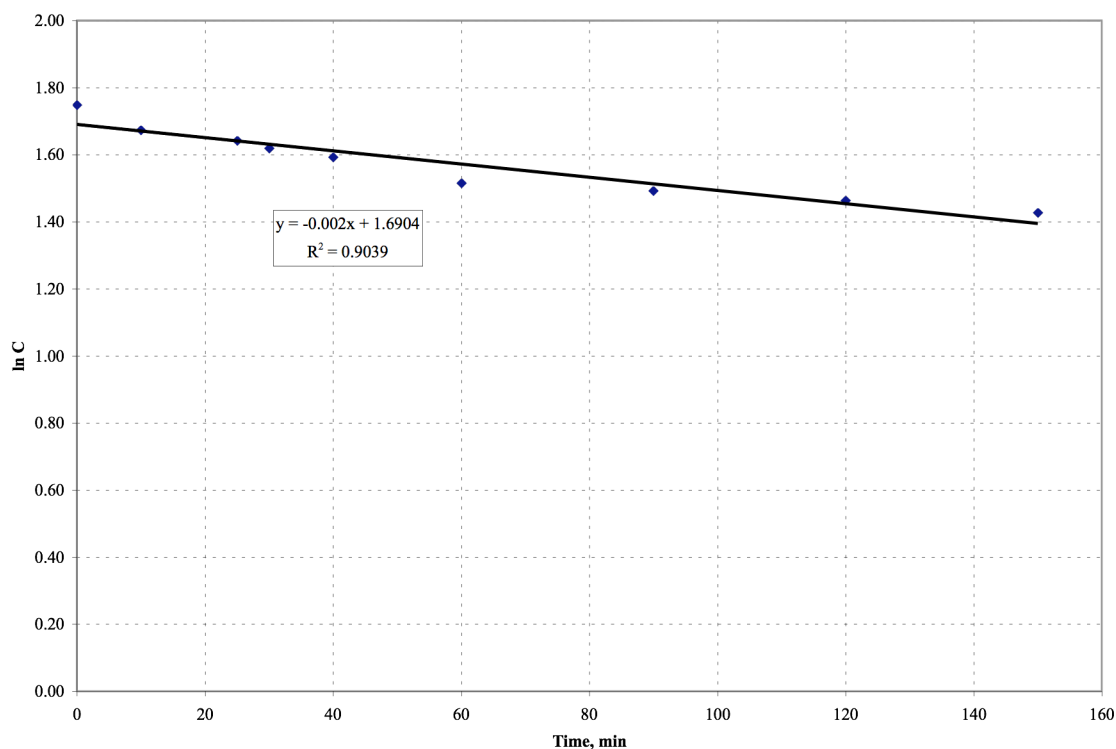
Appendix F-20. Linear Regression Analysis corresponding to 10.0 kg O₂/kgS – pH = 6.20

Date: 3/26/07
 Method: Ion Selective Electrode Method
 FeCl₂ Concentration: 10 kgO₂/kgS

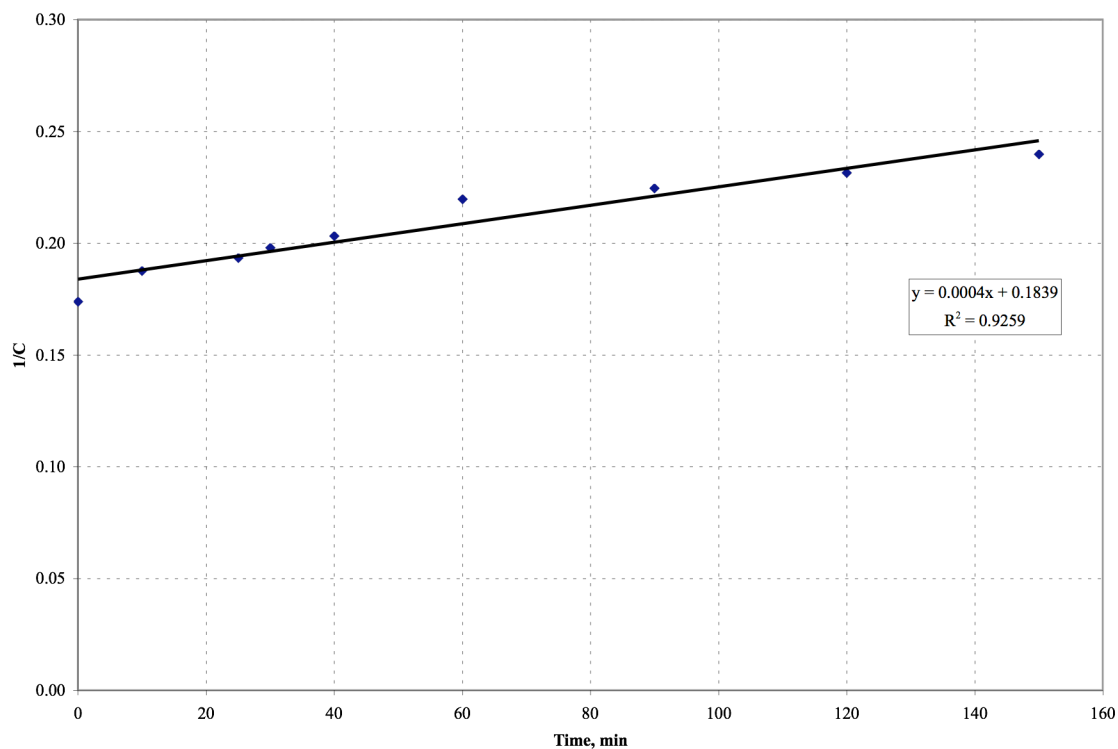
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	5.75	1.7492	0.1739	0.0302	0.0053	0.0009	0.00015910	0.00002767	0.00000481
10	5.33	1.6734	0.1876	0.0352	0.0066	0.0012	0.0002	0.0000	0.0000
25	5.17	1.6429	0.1934	0.0374	0.0072	0.0014	0.0003	0.0001	0.0000
30	5.05	1.6194	0.1980	0.0392	0.0078	0.0015	0.0003	0.0001	0.0000
40	4.92	1.5933	0.2033	0.0413	0.0084	0.0017	0.0003	0.0001	0.0000
60	4.55	1.5151	0.2198	0.0483	0.0106	0.0023	0.0005	0.0001	0.0000
90	4.45	1.4929	0.2247	0.0505	0.0113	0.0026	0.0006	0.0001	0.0000
120	4.32	1.4633	0.2315	0.0536	0.0124	0.0029	0.0007	0.0002	0.0000
150	4.17	1.4279	0.2398	0.0575	0.0138	0.0033	0.0008	0.0002	0.0000

$$t_{1/2} = \frac{1}{k[C_0]}$$

k = 0.0004 Lmg⁻¹min⁻¹
 C₀ = 5.75 mg/L
 t_{1/2} = 434.78 min



Appendix F-21. Test of First-Order Kinetics corresponding to 10.0 kg O₂/kgS



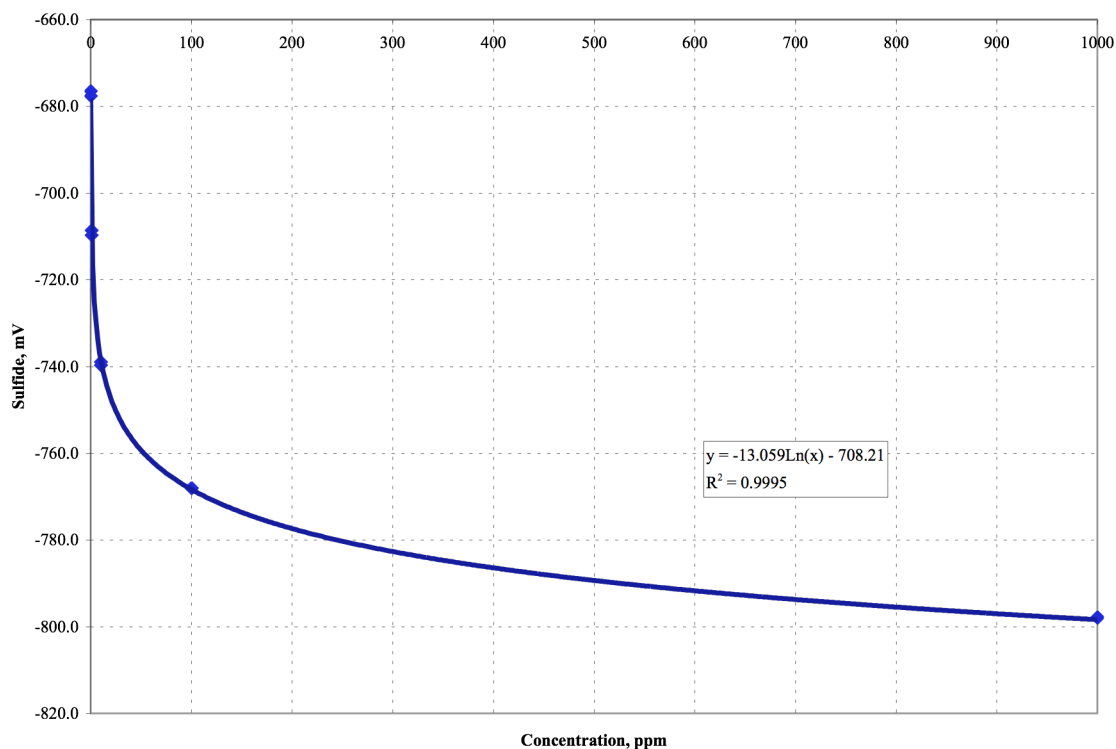
Appendix F-22. Test of Second-Order Kinetics corresponding to 10.0 kg O₂/kgS

Appendix F-23. Standard Curve Data for 5.0 kg O₂/kgS Addition

Date: 3/26/07

Method: Ion Selective Electrode Method

Analysis	Replicates	Concentration, ppm S ²⁻	Sulfide, mV	pH	Temperature, °C
1	a	1000	-798.0	12.4	21.0
	b	1000	-797.8	12.4	21.0
2	a	100	-768.0	12.4	21.0
	b	100	-768.1	12.4	21.0
3	a	10	-739.7	12.4	21.0
	b	10	-738.9	12.4	21.0
4	a	1	-709.7	12.4	21.0
	b	1	-708.6	12.4	21.0
5	a	0.1	-677.6	12.4	21.0
	b	0.1	-676.4	12.4	21.0



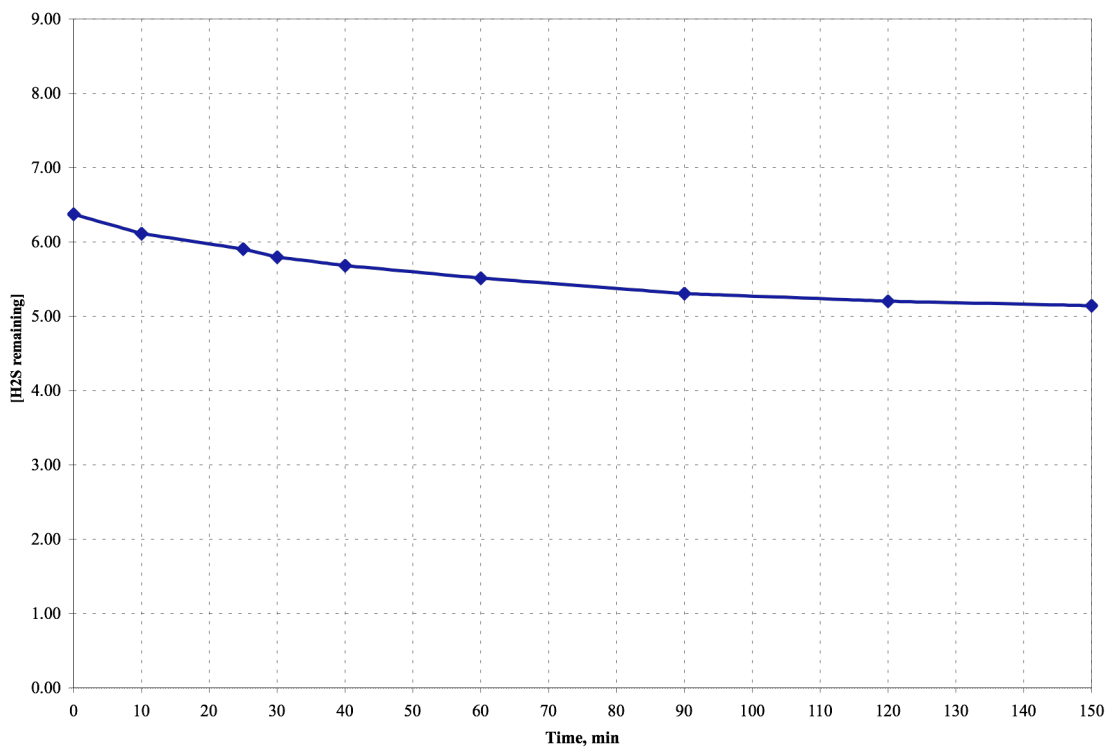
Appendix F-24. Standard Curve for 5.0 kg O₂/kgS Addition

Appendix F-25. Ion Selective Electrode Method Data for 5.0 kg O₂/kgS Addition

Date: 3/26/07
 Method: Ion Selective Electrode Method

O₂ Concentration: 5.00 kgO₂/kgS
 H₂S Initial Concentration: 6.38 mg/L
 Initial pH: 12.70
 pH after HCl addition: 7.20

Sample	Replicates	Time, min	Concentration, mg/L S ²⁻				Temp, °C
			Sulfide, mV	Sulfide Equation	Sulfide, mg/L	Sulfide Average, mg/L	
1	a	0	-732.7	1.875335018	6.52	6.38	22.5
	b		-732.1	1.829389693	6.23		22.5
2	a	10	-731.6	1.791101922	6.00	6.11	22.5
	b		-732.1	1.829389693	6.23		22.5
3	a	25	-731.0	1.745156597	5.73	5.91	22.5
	b		-731.8	1.80641703	6.09		22.5
4	a	30	-730.9	1.737499043	5.68	5.79	22.5
	b		-731.4	1.775786814	5.90		22.5
5	a	40	-730.9	1.737499043	5.68	5.68	22.5
	b		-730.9	1.737499043	5.68		22.5
6	a	60	-730.6	1.71452638	5.55	5.51	22.5
	b		-730.4	1.699211272	5.47		22.5
7	a	90	-729.9	1.660923501	5.26	5.30	22.5
	b		-730.1	1.676238609	5.35		22.5
8	a	120	-729.8	1.653265947	5.22	5.20	22.5
	b		-729.7	1.645608393	5.18		22.5
9	a	150	-729.4	1.62263573	5.07	5.15	22.5
	b		-729.8	1.653265947	5.22		22.5



Appendix F-26. H₂S remaining after 5.0 kg O₂/kgS Addition

Appendix F-27. Linear Regression Analysis corresponding to 5.0 kg O₂/kgS – pH = 7.20

Method: Ion Selective Electrode Method
FeCl₃ Concentration: 5 kgO₂/kgS

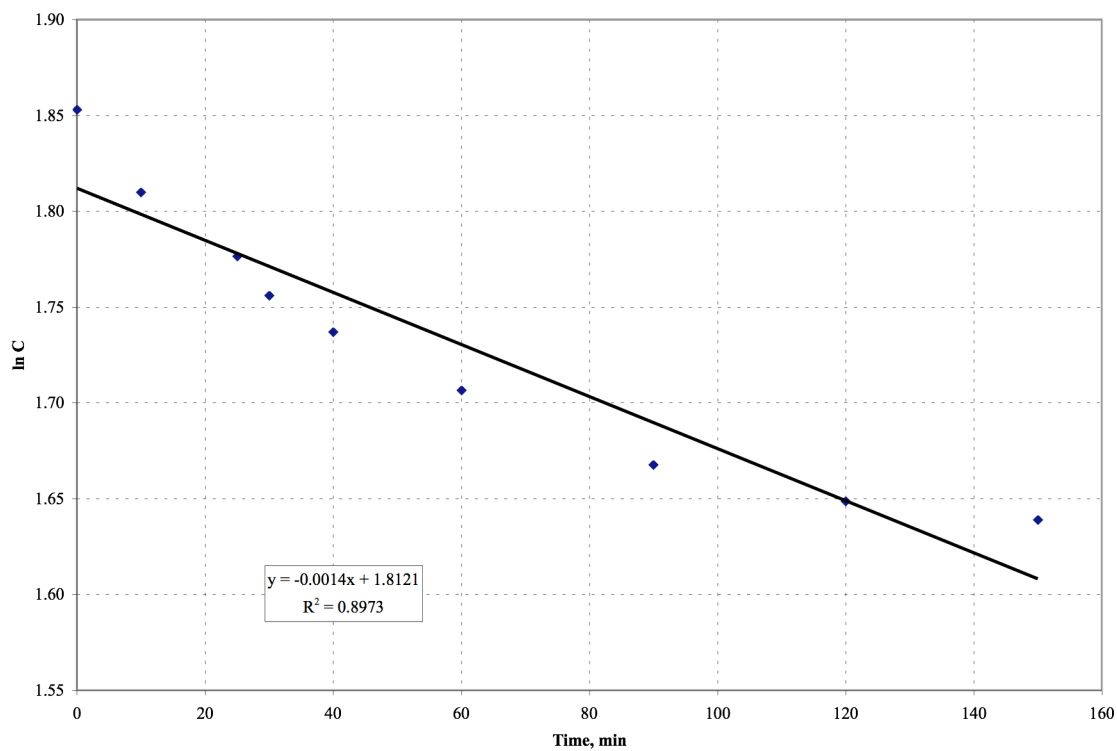
Time, min	Concentration, mg/L	ln C	1/C	1/C ²	1/C ³	1/C ⁴	1/C ⁵	1/C ⁶	1/C ⁷
0	6.38	1.8532	0.1567	0.0246	0.0039	0.0006	0.00009460	0.00001483	0.00000232
10	6.11	1.8099	0.1637	0.0268	0.0044	0.0007	0.0001	0.0000	0.0000
25	5.91	1.7766	0.1692	0.0286	0.0048	0.0008	0.0001	0.0000	0.0000
30	5.79	1.7561	0.1727	0.0298	0.0052	0.0009	0.0002	0.0000	0.0000
40	5.68	1.7370	0.1761	0.0310	0.0055	0.0010	0.0002	0.0000	0.0000
60	5.51	1.7066	0.1815	0.0329	0.0060	0.0011	0.0002	0.0000	0.0000
90	5.30	1.6677	0.1887	0.0356	0.0067	0.0013	0.0002	0.0000	0.0000
120	5.20	1.6487	0.1923	0.0370	0.0071	0.0014	0.0003	0.0001	0.0000
150	5.15	1.6390	0.1942	0.0377	0.0073	0.0014	0.0003	0.0001	0.0000

$$t_{1/2} = \frac{1}{k[C_o]}$$

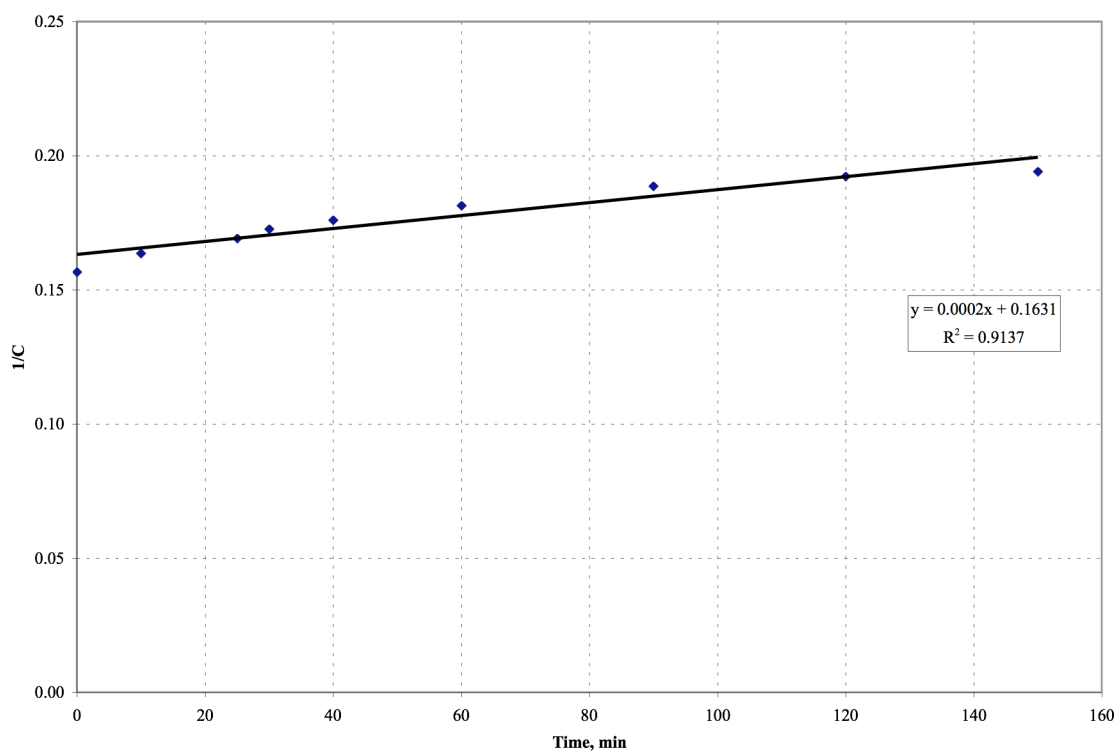
$$k = 0.0002 \text{ Lmg}^{-1}\text{min}^{-1}$$

$$C_o = 6.38 \text{ mg/L}$$

$$t_{1/2} = 783.70 \text{ min}$$



Appendix F-28. Test of First-Order Kinetics corresponding to 5.0 kg O₂/kgS



Appendix F-29. Test of Second-Order Kinetics corresponding to 5.0 kg O₂/kgS

VITA

Karloren José Guzmán-Lozada was born in Maturín, Venezuela on January 25, 1978. She graduated from “Alejandro de Humboldt” high school in 1994. She obtained her Civil Engineer degree in November 2000 from Santa Maria University in Lechería, Venezuela. In spring 2002, she entered the graduate program at University of New Orleans pursuing a Master of Science in Environmental Engineering and conducted research on the effect of shear stress on sediment transport in PVC sewer pipes until December 2003. From January 2004 to May 2007, the author pursued her PhD at the same institution as a graduate assistant. Her academic emphasis has been in the areas of water and wastewater processes, hydraulic, and sewer systems design criteria and she is a registered engineering intern in the state of Louisiana.