

## AN ABSTRACT OF THE THESIS OF

Ronald L. Adolf for the degree of Master of Science in Chemical Engineering presented  
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Lead Contaminated Wastewaters with Ozone

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Dr. Charles E. Wicks

Ozone was found to quickly reduce the concentration of lead in a prepared solution when the solution pH of said solution was greater than 7.0. When a solution having a pH of greater than 7.0 was filtered the concentration of lead was less than approximately 1.0 ppm. 1.0 ppm is the detection limit of the analytical instrumentation used in this study. The lead-II ions were observed to oxidize to lead-IV oxide until a minimum concentration was reached; the oxidation appears to follow first order, reversible reaction kinetics.

Mass transfer and pH seem to be the controlling factors of the reaction. No measurable amount of ozone was absorbed into the bulk solution indicating very low mass transfer rates. The oxidation of lead-II ions occurred only at pH values above 7.0. No oxidation was detected in an acidic medium ( i.e., when pH was less than 7.0).

**Preliminary Study on the Effect of pH on the  
Treatment of Lead Contaminated Wastewaters  
with Ozone**

**By**

**Ronald L. Adolf**

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## Nomenclature

$k$	Rate constant for the ozone oxidation of aqueous lead II, $\text{sec}^{-1}$
$[\text{Pb}^{\text{II}}]$	Lead concentration of bulk solution, $\text{mole}\cdot\text{L}^{-1}$
$[\text{Pb}^{\text{II}}]_0$	Initial lead concentration of solution, $\text{mole}\cdot\text{L}^{-1}$
$[\text{Pb}^{\text{II}}]_\infty$	Concentration of lead solution after long periods of ozonation, $\text{mole}\cdot\text{L}^{-1}$

## **Table of Contents**

<b>Introduction</b>	<b>1</b>
<b>Experimental</b>	<b>4</b>
Experimental Equipment	4
Experimental Procedure	9
Procedure for Data Analysis	16
<b>Results</b>	<b>17</b>
Expected Results	17
Observed Results	19
<b>Recommendation for Future Studies</b>	<b>30</b>
<b>Summary and Conclusions</b>	<b>32</b>
<b>References</b>	<b>36</b>
<b>Appendices</b>	<b>38</b>
Appendix A      Derivation of Kinetics Equation	38
Appendix B      Example Calculation of Ozone Concentration in Gas Stream	39
Appendix C      Tables of Run Data	40

## **List of Figures**

<b>Figure 1, Schematic of Reactor System</b>	<b>5</b>
<b>Figure 2, Reactor Diagram</b>	<b>6</b>
<b>Figure 3, Block Diagram of Reactor System</b>	<b>10</b>
<b>Figure 4, Run Number 8</b>	<b>21</b>
<b>Figure 5, Run 3</b>	<b>24</b>
<b>Figure 6, Run 4</b>	<b>25</b>
<b>Figure 7, Run 7</b>	<b>26</b>
<b>Figure 8, Run 8</b>	<b>27</b>
<b>Figure 9, Run 9</b>	<b>28</b>
<b>Figure 10, Run 10</b>	<b>29</b>

## List of Tables

Table 1	Data of Run 0	40
Table 2	Data of Run 1	41
Table 3	Data of Run 2	42
Table 4	Data of Run 3	43
Table 5	Data of Run 4	44
Table 6	Data of Run 5	45
Table 7	Data of Run 6	46
Table 8	Data of Run 7	47
Table 9	Data of Run 8	48
Table 10	Data of Run 9	49
Table 11	Data of Run 10	50



# PRELIMINARY STUDY ON THE EFFECT OF PH ON THE TREATMENT OF LEAD CONTAMINATED WASTEWATERS WITH OZONE

## Introduction

Ozone, a triatomic allotrope of oxygen, was discovered during the mid nineteenth century by people working with electrical equipment and was noted for its characteristic very pungent odor. Ozone is typically produced in the vicinity of electrical or corona discharges such as near lightning and electric motors.

The use of ozone in water treatment began at the turn of the century in France and Germany. In 1906 a municipal water treatment plant was built in Nice, France. The Bon Voyage plant is now considered to be the birth place of ozonation for water treatment since it had operated continuously until 1970<sup>1</sup>. After the success of this initial plant, many other water treatment plants have been constructed throughout the world. In 1977, a total of 1039 municipal water treatment plants incorporating ozonation were in operation or under construction, more than three quarters of which were located in Europe and more than half of which were located in France<sup>2</sup>. Only relatively recently has ozonation been applied in municipal water treatment in the United States.

Since its debut in France, ozone has been limited primarily to water treatment applications involving the removal of organic material from solution; a wealth of research has been performed in this field. Only within the last 15 years has ozone been applied to the removal of heavy metals from solution. Shambaugh and Melnyk<sup>3</sup> have shown that ozone can be used to effectively remove heavy metals, such as lead, mercury, and chromium from waste solutions to levels well below the acceptable Federal limits. Today, with growing concerns of heavy metal contamination of ground

water from industrial effluents, interest is developing in the application of ozone for treating these types of wastewaters.

The attractiveness of ozone for use in the removal of heavy metal ions from waste effluents stems from its extremely powerful oxidizing ability. Of the typical oxidants used for heavy metal treatment such as chlorine and chlorine dioxide, ozone's oxidizing ability is substantially more powerful, and has been shown capable of attacking even complexed metal ions<sup>4</sup>. The only chemical groups known to be more powerful than ozone in oxidizing ability are free radicals.

Some of the typical methods used for the treatment of heavy metal ions in wastewaters include such technologies as reverse osmosis, electrodialysis, and sedimentation of insoluble precipitates followed by filtration. Other methods are also available, but due to economic reasons the most commonly used methods for high volume output applications are those involving sedimentation followed by filtration. Oxidation to insoluble oxides via ozonation is included in these processes.

Some common oxidants used for heavy metal precipitation are chlorine dioxide and chlorine, chlorine dioxide being the stronger oxidizer of the two. Ozone, being relatively new to the heavy metal aspect of water treatment, is usually not used due to economic reasons, particularly due to the capital cost of the equipment. Ozone must be produced on-site and used immediately for it will decompose quickly back to normal oxygen, and ozone generation equipment capable of handling large volumes of wastewater is inherently expensive. Elaborate mixing devices and reactors must be employed to effectively introduce the ozone into the solution. These factors have contributed to the lack of ozonation in heavy metals removal.

Aside from the disadvantage of cost, ozone oxidation of heavy metals offers many characteristics which are advantageous compared to chlorine and chlorine dioxide oxidation. Most important is the ability of ozone to oxidize heavy metals rapidly. Netzer<sup>5</sup> and other researchers have shown that ozone can reduce very rapidly some

heavy metal concentrations by more than 99.0%. Due to the rapid decomposition of ozone in solution, no residual oxidant remains in solution downstream at the discharge, eliminating the need to treat output streams to reduce oxidant levels.

The objective of this research is aimed at a preliminary study of ozone and its applications on the removal of heavy metals from solution. Due to a limit on time and resources, only one heavy metal was studied, which was lead. Lead was chosen for some of its chemical characteristics and for economic reasons. This research was focused on the observable kinetics of oxidation of lead ions with ozone and the physical properties of the reaction environment that influence the rate and efficiency of oxidation.

A technique used in industry for the treatment of lead contaminated wastewaters involves increasing the hydroxide content of the solution, or increasing the pH. In alkaline solutions, lead-II ions form an insoluble lead-II hydroxide which is then filtered from the solution. An attempt was made to compare the efficiency of this technique with that of oxidation of lead by ozone followed by filtration.

## Experimental

### Experimental Equipment

The equipment and reactor for this experiment were designed to operate as a semi-batch type system. Semi-batch meaning that the lead solution operated as a batch process and the gas stream flowed continuously through the lead solution. There were several functions and physical properties that were required of the reactor and ozonation generation system. The primary physical property required was in the materials used in the construction of the reactor and the gas flow systems. All pieces of equipment that were in contact with ozone, either in the gas phase or liquid phase, were constructed out of ozone resistant materials. The most common materials used were PVC, stainless steel, glass, Teflon, and Tygon.

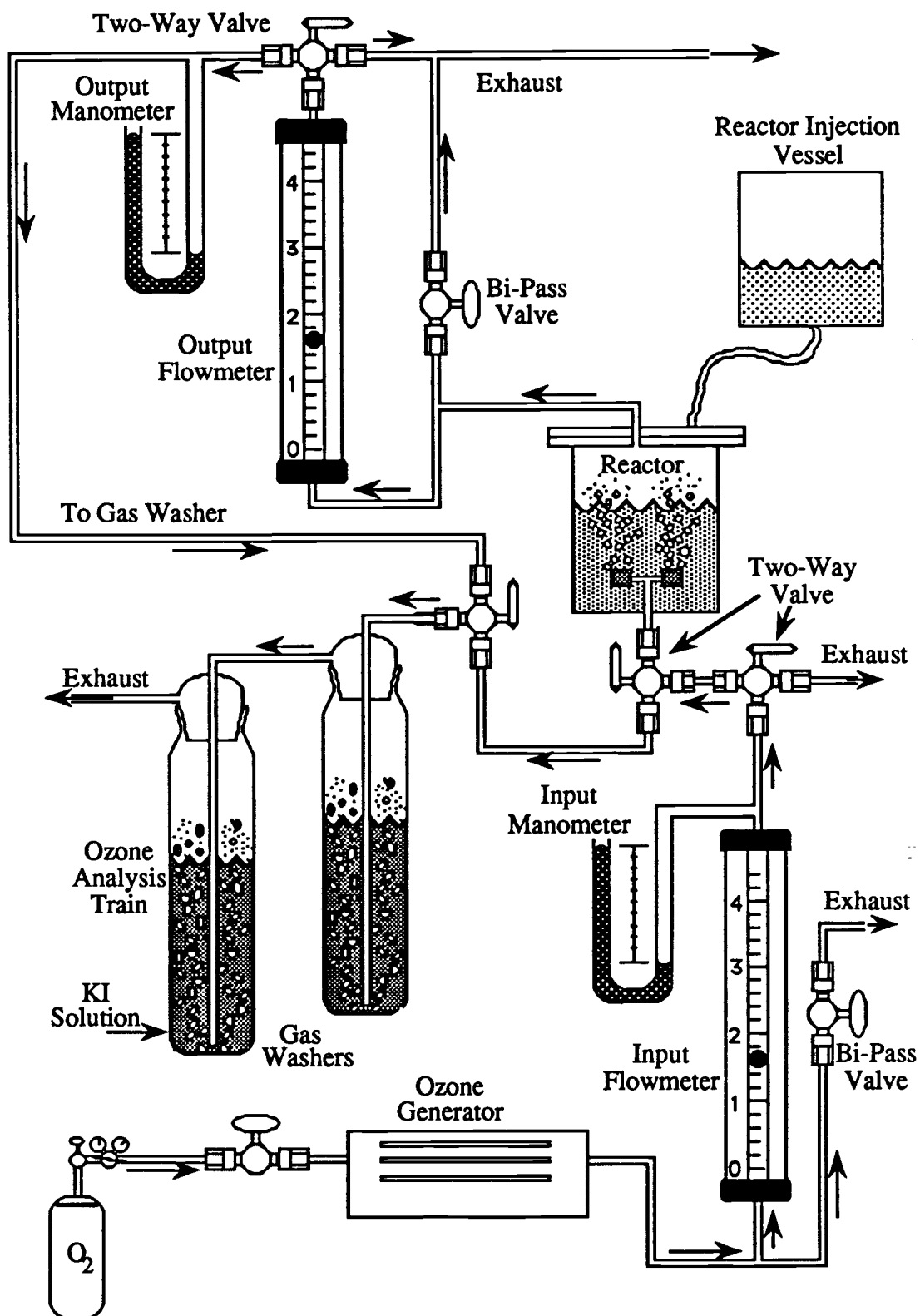
A schematic diagram of the reactor equipment is shown in Figure 1. The equipment was designed to maintain the reaction solution at a constant temperature, to allow for easy extraction of uniform samples representing bulk solution concentration, to disperse a constant flow of ozonated oxygen into the solution, and to maintain a thoroughly mixed solution in the reactor vessel. The equipment allowed for easy monitoring of temperature and gas flow rate.

A cross-sectional diagram for the reactor vessel is shown in Figure II. The reactor was constructed from a piece of 10 inch ID PVC pipe; its volume being approximately 5 liters. The top and bottom of the reactor are fabricated from flat PVC of a thickness of 1/2 inch. In to the top and bottom of the reactor were placed stainless pipe fittings to facilitate the necessary plumbing needed for the introduction and removal of gas, water and other items such as a thermometer, sampling system, etc.

The reactor heat exchanger was constructed from a 10 foot section of 1/4 inch stainless steel tubing wrapped into a coil. Temperature control is performed manually in the reactor by observing the solution temperature indicated on the mercury

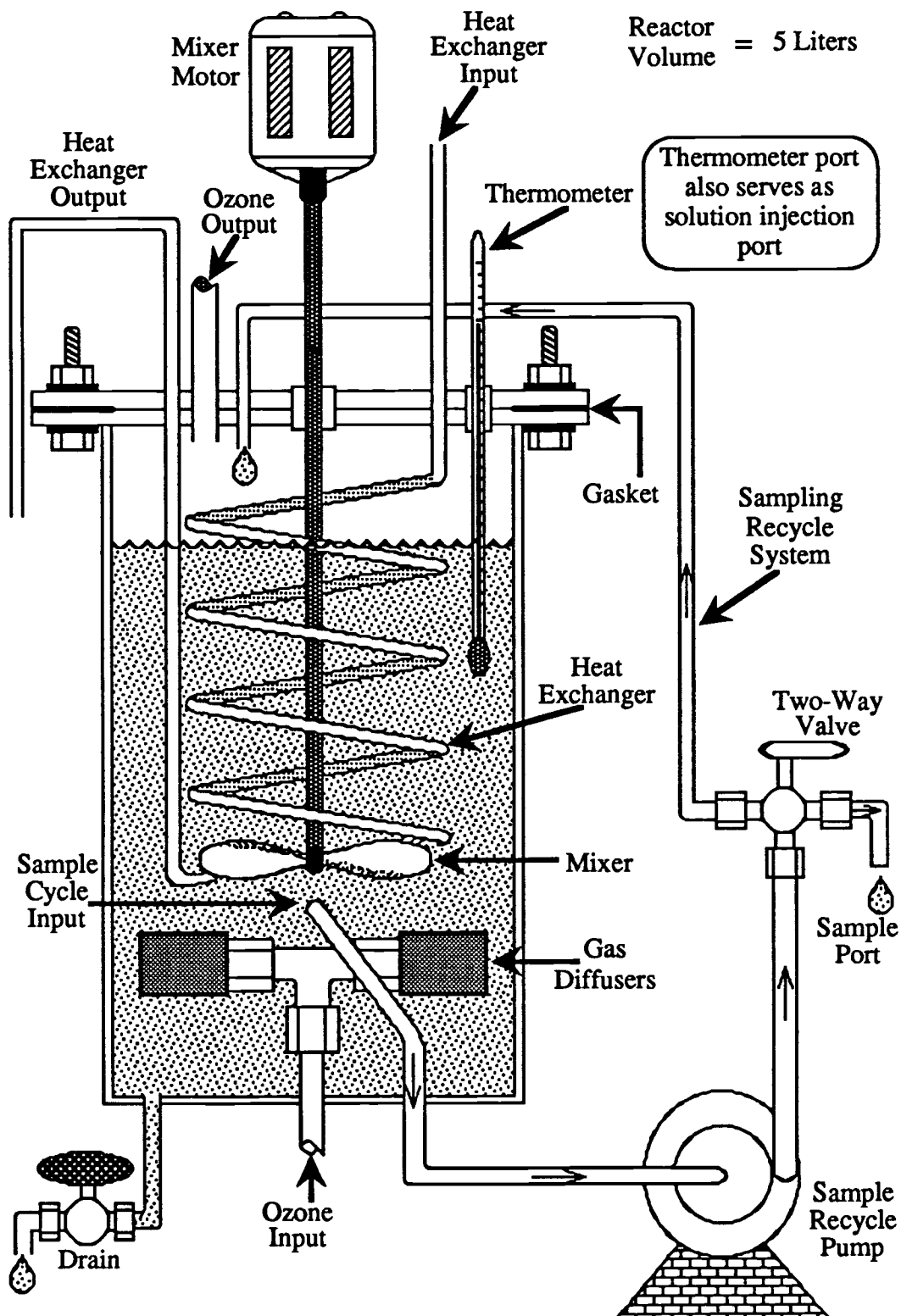
Schematic of Reactor System

Figure 1



Reactor Diagram

Figure 2



thermometer inserted into the reactor. Depending on the solution temperature, either hot or cold water could be pumped through the heat exchanger tubing until the desired solution temperature was reached.

Ozone rich oxygen was dispersed into the reactor through two sintered stainless steel diffusers mounted near the bottom of the tank. The diffusers, with a pore size of 60 microns, were mounted on a simple "T" pipe fitting. The exit gases were collected at the top of the reactor and routed to the exhaust.

A propellor type mixer was placed at a point two inches above the gas diffusers. The motor which drove the mixer was mounted above the top of the reactor, and its rpm could be monitored via a portable tachometer.

Sample collection operates through a recycle system which circulates the reactor solution through a sampling valve. The recycle pump draws the solution from the center of the reactor at a point approximately 1 inch directly above the gas diffusers. The solution is then pumped to a two-way valve which enables a sample to be drawn. With the two-way valve in the up position, the solution is returned to the top of the reactor. With the valve in the down position, the solution is routed to the sample port. The recirculating design was incorporated to minimize the discontinuities in sample data.

The ozone generator is of the parallel-plate type, and each plate had a diameter of approximately 4 inches. Operating voltages for this type of ozonator were on the order of 4000 to 7000 volts. 6500 volts was used in this research. Typical output concentrations for this ozonator were on the order of 0.1% by volume. Pure oxygen was used as a feed gas to increase the concentration of ozone in the output.

The flow rate of gases entering the reactor and leaving the reactor were measured and monitored with flow meters. Both the inlet flow meter and the outlet flow meter were also used in the analysis of the ozone concentration in the gas stream. A bypass valve, situated at each flow meter, allowed for the adjustment of the flow rate

to the ozone analysis system without effecting the flow rate of gas through the ozonator or from the reactor. U-tube type manometers were placed directly upstream from each flow meter such that pressure adjustment of indicated flow rates could be performed.

The ozone analysis system for the gas stream consisted of two gas washing bottles placed in series. Ozone rich gas could be routed from the flow meters to these bottles for concentration determination. The technique is described in detail in the Experimental Procedure section of this thesis.

The lead concentration of solution samples was measured by the use of a Perkin Elmer 4000 atomic adsorption spectrophotometer. Solution pH was measured via a Beckman  $\phi$ -21 portable pH meter. Other glassware used consisted of volumetric pipets and flasks.



## Experimental Procedure

The following text describes the procedure followed in the collection of data for this thesis. When reading this section it may be helpful for the reader to refer to the diagrams of the equipment contained in the Experimental Equipment section of this thesis. Figure 3 represents a block diagram of the experimental technique followed. Figure 3 may help the reader understand not only the experimental procedure but also the state of the solution and reaction at each phase of the experimental run.

### Solution preparation

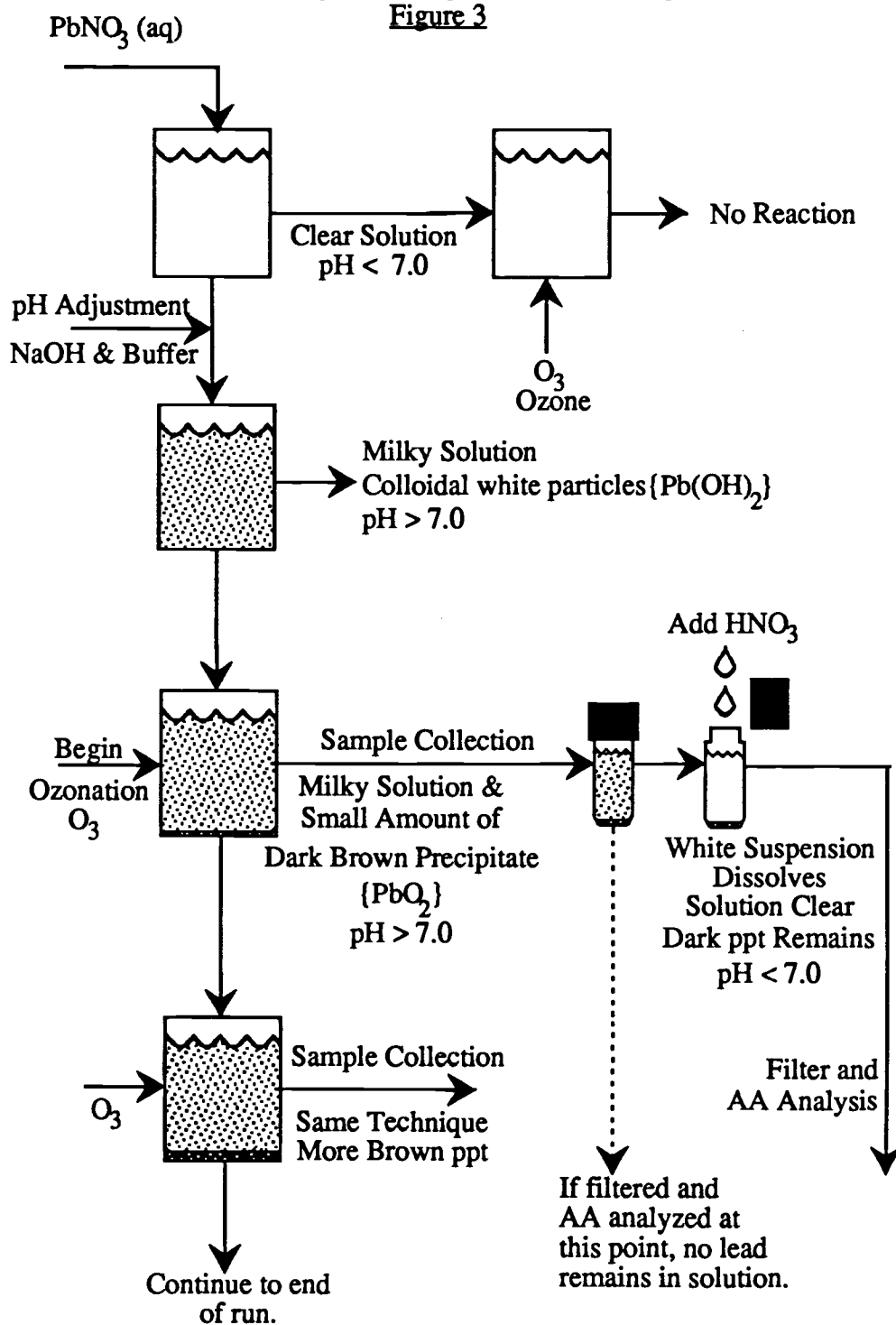
Test were conducted on pH buffered lead solutions; lead concentration was on the order of 100 mg/liter. The following paragraphs describe the process used to prepare the solutions prior to each run.

The appropriate quantities of buffering agents were weighed and dissolved into two liters of distilled water. Each buffer consisted of an acid and base of the same chemical group. For example, a borate buffered solution was used frequently and consisted of roughly equal parts of sodium borate and boric acid, the sodium borate being the base. This solution was then placed into the reactor injection tank.

Fifty milliliters of 10000 mg/liter lead solution was diluted to two liters of volume and then added to the buffer solution in the reactor injection vessel giving a total volume of four liters ( The 10000 mg lead solution was prepared by dissolving the appropriate quantity of lead nitrate into a solution of 1 molar nitric acid). Upon addition of the lead nitrate solution to the buffer solution, the lead began to precipitate into very fine colloidal size particles of lead hydroxide. The solution was allowed to sit for at least one hour to allow an equilibrium to be reached between the lead ions and the lead-II hydroxide.

# Block Diagram of Experimental Technique

Figure 3



After equilibrium had been reached (or thought to have been reached), the pH of the solution was adjusted to the desired value by addition of a concentrated sodium hydroxide solution to the reactor injection vessel. The pH was measured with a Beckman pH meter. After adjustment of the pH, the solution was again allowed to come to equilibrium for one hour, after which the solution was placed into the reactor.

#### Start-up and run procedures

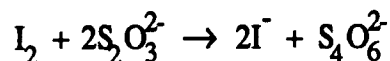
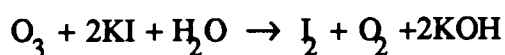
The following text describes the procedures for the start up and running of an experimental run. After placement of the lead solution into the reactor, the oxygen valve was opened and its flow adjusted to a flow meter reading of approximately 125 centimeters. (Note that the oxygen flow will decrease when the flow is routed to the reactor. Before the ozonator is turned on, one should check to make sure that the oxygen is routed to the exhaust.) The ozonator was then turned on and the voltage was adjusted to 6500 volts. Approximately twenty minutes were allowed to let the ozonator warm up.

The concentration of ozone in the gas stream was then measured using modified techniques described in Ozonation Manual for Water and Wastewater Treatment<sup>6</sup>.

These procedures were as follows;

Ozone reacts stoichiometrically with iodide ions to form free iodide.

One can determine the quantity of ozone in an air sample by bubbling the sample through a solution of potassium iodine and determining the quantity of free iodine formed from the reaction. The amount of free iodine formed can be determined by titrating the solution with sodium thiosulfate which reacts stoichiometrically to reduce the free iodine. These reactions are as follows:



Approximately 150 mL of 0.12 molar KI solution was placed into each of the two gas washing bottles. The ozone flow through the flow meter was adjusted by opening the bypass valve to allow some of the oxygen to escape such that the flowmeter indicated a reading of no greater than 60. Ozonated oxygen was then allowed to flow through the gas washer tube (removed from the gas washer bottles) for a few minutes prior to the gas analysis; this was done to eliminate dead time in the tube. The gas washer tube was then placed inside of the KI solution, and the flow was routed to the exhaust.

While simultaneously starting the stop watch, the ozone was then routed to the gas washing bottles; the flow and pressure were measured. At the appropriate time, flow to the gas washers was discontinued and the time was measured. The total volume of gas which passed through the gas washers was determined from the time of flow and flow rate.

The potassium iodide solutions from both gas washers were combined in an Erlenmeyer flask and acidified with 20ml of 1 normal sulfuric acid. The potassium iodide solution was then titrated with 0.0050 molar sodium thiosulfate. A few drops of starch indicator were added to the solution to help observe the end point.

From the volume of thiosulfate used, the quantity of free iodine produced could be calculated, and in turn the concentration of ozone in the gas stream could be determined.

Once the ozone concentration of the gas had been determined, the sampling recycle pump and the mixer motor were turned on. Mixer motor rpm, barometric pressure, and air temperature were then measured and recorded. An initial solution sample was taken, and the pH of the solution was measured.

The solution temperature was then measured and adjusted to 20 degrees Celsius. Temperature adjustment was performed manually by piping either hot or cold water through the heat exchanger, depending on the temperature of the reactor solution.

At this time the plumbing of the oxygen lines to the reactor was checked to make sure that every thing was hooked up correctly. All bypass valves were closed. The gas washing bottles were placed in position to measure the concentration of ozone in the exit stream. The reactor was at this time set up for the start of the experimental run. The procedures for the each sample run are described as follows:

Simultaneously, the stop watch was started and the two-way valve was flipped to route the oxygen to the reactor. The ozone/oxygen flow rate was adjusted to a flow meter reading of 100 centimeters. The temperature of the solution, the flow rate of oxygen into the reactor, the flow rate of oxygen out of the reactor and the pressure of the gas entering the reactor were then measured and recorded. The ozone concentration of the exit stream was measured using the technique described earlier; its concentration was recorded.

At the appropriate time, the two-way valve at the input flow meter was flipped to route the ozone to the exhaust. The time of ozonation was recorded. The residual ozone concentration in the solution was measured using techniques described in Standard Methods of the Examination of Water and Wastewater<sup>7</sup>. These techniques are outlined as follows:

Approximately 250 ml of solution was removed from the reactor, the volume of which was measured carefully, and was placed into one of the gas washing bottles. Air was piped through the gas washer bottle containing the solution and then into another gas washer bottle containing KI solution. This allowed the ozone to desorb from the sample solution into the passing air stream.

As the ozone entrained in the air stream passed through the KI solution, it reacted with the iodine ions to form free iodine. The quantity of ozone contained in the sample solution could then be determined using titration techniques described earlier. The concentration of ozone in the solution could then be easily calculated, details of which are shown in the appendix.

The 250 ml sample was then placed back into the reactor.

For solution sampling, two 20 ml samples were taken from the reactor and labeled. Two samples were taken to ensure that proper mixing was taking place in the reactor. The pH of the reactor solution was also recorded during sample collection.

These procedures were repeated for each sample collection period. Samples were usually collected at 1, 3, 5, 7, 12, 17, 22, 32, 42, and 60 min.

After the completion of all sample collections, the ozone concentration of the inlet gas stream was measured again as a test for fluctuations in the ozonator output.

Following this test, the equipment was shut down by first turning off the power supply to the ozonator. The oxygen tank was closed approximately 5 minutes after shutting off the power supply to the ozonator. This was done to flush any residual ozone out of the ozonator.

The reaction vessel was drained into the reactor injection vessel, and the volume of the remaining solution was measured and recorded. Before draining the reactor, the mixer motor and the sample recycle pump were turned off. The lead solution was filtered to remove all the precipitate, and the precipitate was stored. The solution was stored until analysis showed that the levels of lead remaining were low enough such that the solution could be discharged. The reactor was cleaned by filling it with tap

water by turning on the recycle pump and mixer motor and then by draining the reactor. This was repeated until the drained solution was clear. The process was repeated one more time with distilled water to remove any contaminants which might have been present in the tap water.

Sample analysis for lead concentration was performed on an atomic adsorption spectrophotometer. Standards for this analysis were prepared from lead nitrate solutions of known lead concentration.

### Procedure for Data Analysis

The data obtained for analysis consist of tables of the concentration of lead in solution at various times during the reaction. One table was obtained for each pH value studied. It was desired to present these data in the form of a graph of concentration versus the time of reaction with a best-fit curve representing the kinetics of the reaction through the data points. This was performed for all runs in which the data followed reasonably close to known reaction kinetics.

A non-linear regression analysis was performed for each set of data around the following equation which represented the expected reaction kinetics:

$$\frac{[\text{Pb}^{\text{II}}] - [\text{Pb}^{\text{II}}]_{\infty}}{[\text{Pb}^{\text{II}}]_0 - [\text{Pb}^{\text{II}}]_{\infty}} = e^{-kt} \quad [\text{A}]$$

The parameters obtained from regression analysis were the final lead concentration,  $[\text{Pb}^{\text{II}}]_{\infty}$ , and the reaction rate constant,  $k$ . The initial lead concentration,  $[\text{Pb}^{\text{II}}]_0$ , was obtained by extrapolating the data back to the zero time axis. Extrapolating to determine  $[\text{Pb}^{\text{II}}]_0$  was necessary due to the error in the measurement of lead concentration which made it difficult to measure  $[\text{Pb}^{\text{II}}]_0$  exactly. Equation [A] was then graphed through the data to give the reader an idea of the trend of the reaction. These steps were performed for each experimental run. Non-linear regression was performed using Statgraphics software on an IBM personal computer. The derivation of equation [A] is shown in the appendix of this thesis.



## Results

### Expected Results

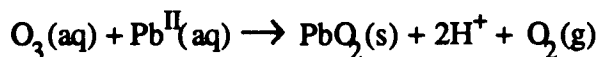
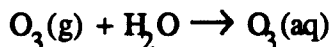
The initial purpose of this experiment and the ensuing research was threefold. First, we wanted to obtain an understanding of and experience in the use of ozone as a treatment technique for industrial wastewater effluents. Particularly, we wanted to study ozone's powerful oxidizing ability on solutions containing heavy metals. Lead was chosen because of its important role as a toxic pollutant, its availability in the form of salts and its ability to be easily precipitated as an oxide of lead IV.

The second purpose of this experiment was to attempt a study of the kinetics of the reaction between a lead solution and ozone in an effort to understand what considerations should be taken in the design of treatment plants incorporating ozone treatment. In particular, we wanted to determine the effect of the hydrogen ion (or pH) on the reaction rate. From these data, we hoped to make an assessment on the pH range at which a treatment plant should operate to optimize the reaction rate.

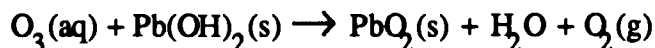
The third purpose of this research was to draw conclusions about whether ozone oxidation of lead solutions is a feasible treatment technique, and to make a comparison between ozone and commonly used treatment techniques. We also wanted to determine factors which might help in future design of ozone-type treatment plants.

In the process studied, ozonated gas is bubbled through a reaction vessel containing the aqueous lead solution; the excess gas exits out the top of the reactor. Since the reaction conditions are heterogeneous, the ozone must follow a series of steps before it reaches the lead ions where the reaction occurs. First, the ozone must diffuse from the bulk phase of the gas bubble to the gas liquid interface. It must then traverse across the interface and be absorbed into the liquid phase where it reacts with lead-II

(probably with microparticulate Pb(II) hydroxide). The reaction between ozone and lead-II ions can be written as an oxidation-reduction reaction in the following form:



or



Mass transfer from the gas to the liquid will undoubtedly play a very important role in the reaction kinetics. The oxidation reaction is expected to be extremely fast in the well-mixed liquid phase, indicating that mass transfer will be the primary resistance and the rate-controlling step will be in the gas phase. All experimental parameters that effect mass transfer will have a large effect on the reaction rate and thus will be kept constant.

The hydrogen ion concentration ( or solution pH) is not expected to affect the reaction rate. However, the hydrogen ion concentration is expected to increase ( pH decrease) as the reaction proceeds since hydrogen ions are produced as a product. The decrease in solution pH will have an effect on the solubility of the lead-IV oxides and lead-II hydroxides in solution. A pH buffered solution will be used to control the hydrogen ion concentration during the experiment such that solubility changes resulting from pH changes can be ignored.

The lead ions were expected to react according to first order kinetics.

## Observed Results

One of the objectives of this study was to determine optimum condition at which to operate a treatment process for the removal of lead from a waste solution. In particular, the objective was to determine at what pH conditions of the waste solution will the removal lead be optimized.

It appears obvious that operation at a high ozone concentration in the feed gas stream and at conditions where mass transfer of the ozone into the solution are very high would produce the most efficient ozone contacting conditions at which treatment plants should operate. Indeed, numerous studies have been conducted on ozone contacting systems and high output ozonators<sup>8,9,10</sup>; accordingly, ozone contacting and mass transfer conditions were not considered in this study. The ozone concentration of the feed gas and mass transfer conditions were maintained constant with respect to experimental error in an attempt to eliminate their effects. Temperature effects were also ignored.

The reaction between lead and ozone was studied by following the lead concentration of the bulk solution as the reaction proceeded. As ozonated oxygen is bubbled into the reactor, the lead-II was oxidized to the very insoluble lead-IV oxide. The samples were then centrifuged to remove the precipitate before analysis.

The solution pH of each run was maintained at a relatively constant value through the incorporation of pH buffers. A buffer was necessary to counteract the production of hydrogen ions as the reaction proceeds. The pH values of the lead solutions studied in this project fell in the range between 8.5 to 10.5. Some tests were also performed at pH values below 7.0. A suitable buffer could not be found to maintain a constant pH for the range between 7.0 and 8.5. The process for the selection of a suitable buffer is outlined in the experimental section of this thesis.

At pH values in the acidic range of below 7.0, the lead-II solution was clear; no precipitate was visible. As the pH of the solution was increased to above 7.0 (or as the solution becomes basic), a milky white suspension appeared and was believed to be the result of the formation of a lead-II hydroxide. The lead-II hydroxide particles were extremely fine and were found to be very difficult to filter or settle completely out of solution. The equilibrium constant for the formation of the lead-II hydroxide at pH values above 7.0 is on the order of  $10^5$  indicating that the majority of the lead in a basic solution is in the form of the lead-II hydroxide<sup>6</sup>. Below a pH of 7.0 the hydroxide is converted to the lead-II ions and the solution remained clear.

As the ozone was bubbled through the solution a reaction involving the oxidation of lead-II to a lead-IV only occurred when the lead-II hydroxide was present in solution, or in other words, when the pH of the solution is above 7.0 or basic. No reaction was ever seen to occur in the acidic solution.

The ozone concentration of the bulk solution at the end of each sampling period was not detectable by the method used in this study. No detectable amount of ozone was ever found to have been absorbed into the bulk solution during an experimental run. This observation confirmed our earlier suspicion that the reaction is very highly mass transfer controlled.

The lead-IV oxide was a brown rust colored precipitate and was found to be very easily separated from the liquid by filtering or centrifuging. The lead-II hydroxide appeared to be attracted to or agglomerated to the lead IV oxide such that when this solution was filtered or settled before the addition of nitric acid, almost all of the lead was removed from the solution leaving only an undetectable amount behind in solution (Note that the detection limit for the atomic adsorption spectrophotometer used for analysis was on the order of 1mg/l or 1 ppm).

The lead concentrations of the samples were followed as a function of time (noting that the samples were acidified before analysis to redissolve any lead-II

hydroxide precipitate remaining). This typically produces a curve similar to that shown in Figure 4. An important feature of this curve is that, after long periods of ozonation, the lead concentration appears to approach a minimum non-zero value at which point the oxidation of lead-II proceeds no further, or at least very slowly. It should be pointed out at this time that when a sample solution was filtered without acidification, almost all of the lead was removed from the solution and only a negligible amount remained.

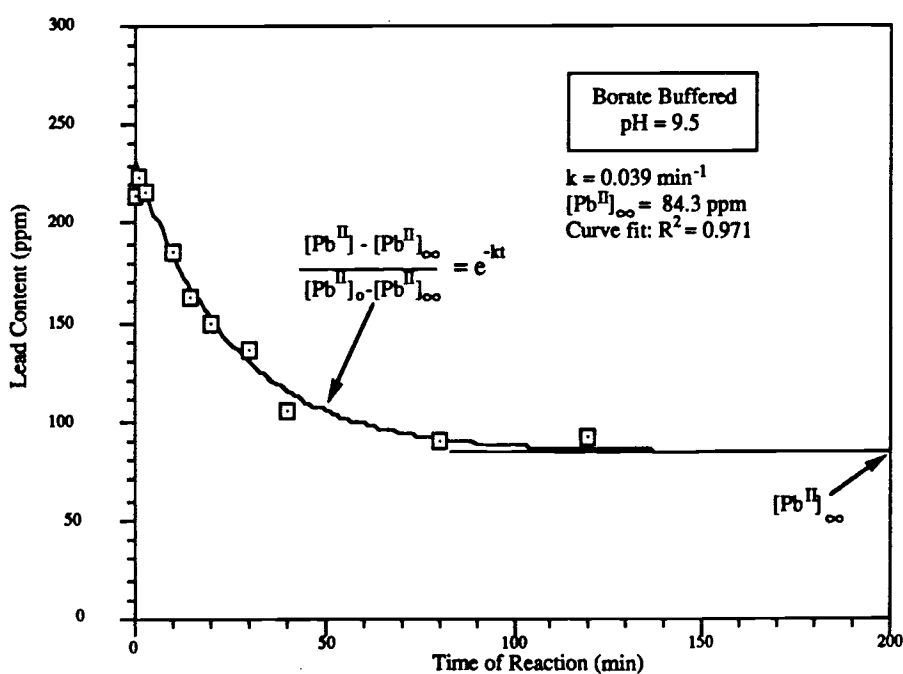


Figure 4, Run 8

At this point it should be emphasized that the oxidation of lead-II was found to only occur when the lead-II hydroxide precipitate was present in solution. No reaction between ozone and lead was ever seen to occur when only the lead-II ions were present in solution, such as the case where the solution is acidic and clear. It is not entirely understood why the reaction occurs only in the alkaline solutions. A possible explanation is that the ozone attacks only the lead-II hydroxide and not the lead-II ions. Recall that the majority of the lead-II in a basic solution or suspension is in the form of

the lead-II hydroxide, which would indicate that one would expect that the majority of the lead is also oxidized to lead-IV oxide by the ozone. By observation of Figure 4, it may be seen that the lead-II is usually not oxidized completely; rather, it is oxidized to a non-zero concentration level after a long time.

Another possible explanation is that the ozone oxidizes only the lead-II ions leaving the lead-II hydroxide precipitate unreacted. Once a sample has been removed from the reactor and acidified with nitric acid, the lead-II hydroxide precipitate dissociates to lead-II ions and hydroxide ions creating the appearance that the reaction approaches a minimum concentration. If a slow exists between the lead-II hydroxide precipitate and the lead-II ions, the reaction will be equilibrium controlled at long periods of ozonation.

The approach to a non-zero concentration after long periods of ozonation may also be a result of two forms of lead-II hydroxide being present in the solution. Two possibilities may be  $\text{Pb}_2\text{O}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$ , both of which are soluble in acidic solutions. These two forms of hydroxide will most likely react with ozone at different rates and kinetics. If one form of lead reacts significantly faster than the other, the kinetics of the fast reaction will dominate initially while the kinetics of the slower reaction would not appear for long periods of time, giving the appearance that a minimum has been reached. This is consistent with the fact that filtering the solution before acidification reduces the lead concentration to zero, providing that both hydroxides can be filtered with the same relative ease.

The reaction order in relation to the lead-II ions was determined by comparing the decrease in lead concentration in the bulk solution with what is expected for known reaction kinetic expressions. The expression that more closely follows the lead concentration decrease is first order reversible kinetics approaching a concentration at which point the net rate is zero. The following expressions represent these kinetics:

$$\text{Rate} = -\frac{d[\text{Pb}^{\text{II}}]}{dt} = k([\text{Pb}^{\text{II}}] - [\text{Pb}^{\text{II}}]_{\infty})$$

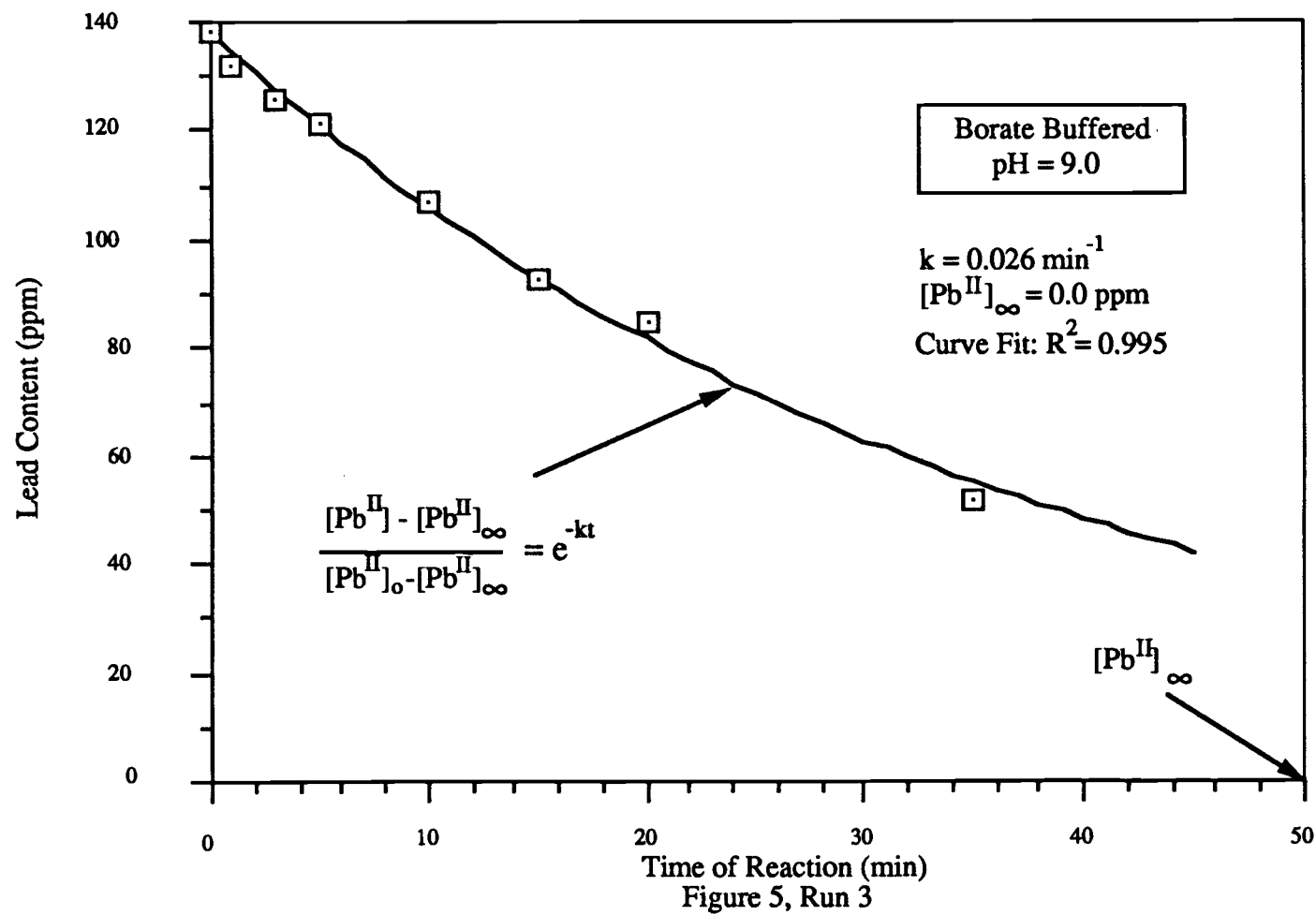
where  $[\text{Pb}^{\text{II}}]$  is the concentration of lead in the bulk solution. Solving the differential equation and observing concentration levels at the endpoint gives:

$$\ln \frac{[\text{Pb}^{\text{II}}] - [\text{Pb}^{\text{II}}]_{\infty}}{[\text{Pb}^{\text{II}}]_0 - [\text{Pb}^{\text{II}}]_{\infty}} = -kt$$

$[\text{Pb}^{\text{II}}]_{\infty}$  = Lead Concentration after long periods of ozonation

The derivation of this equation is shown in the appendix of this thesis . By non-linear regression analysis, this equation was fit to the data of each run; the data are presented in the appendix of this thesis. Regression analysis provided the parameters  $k$ , and  $[\text{Pb}^{\text{II}}]_{\infty}$ . These graphs are shown on the following pages.

Due to the scattering and experimental errors in the data presented, it is inconclusive how the pH effects the reaction rate in the alkaline range. It appears, though, that the pH does not influence the rate or that its influence is negligible. These statements also hold true for the effect of pH on the concentration after long periods of ozonation or  $[\text{Pb}^{\text{II}}]_{\infty}$ .





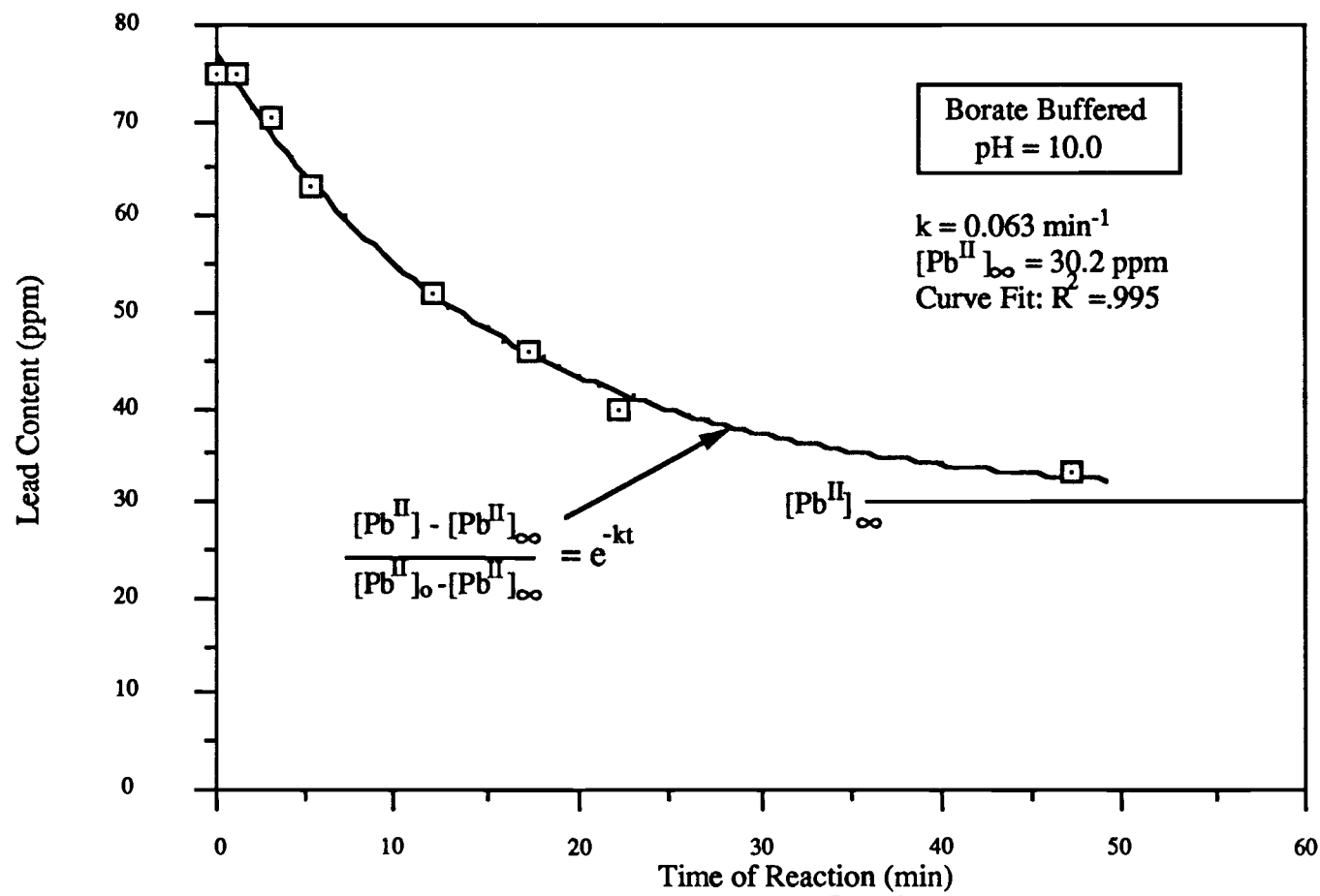


Figure 6, Run 4

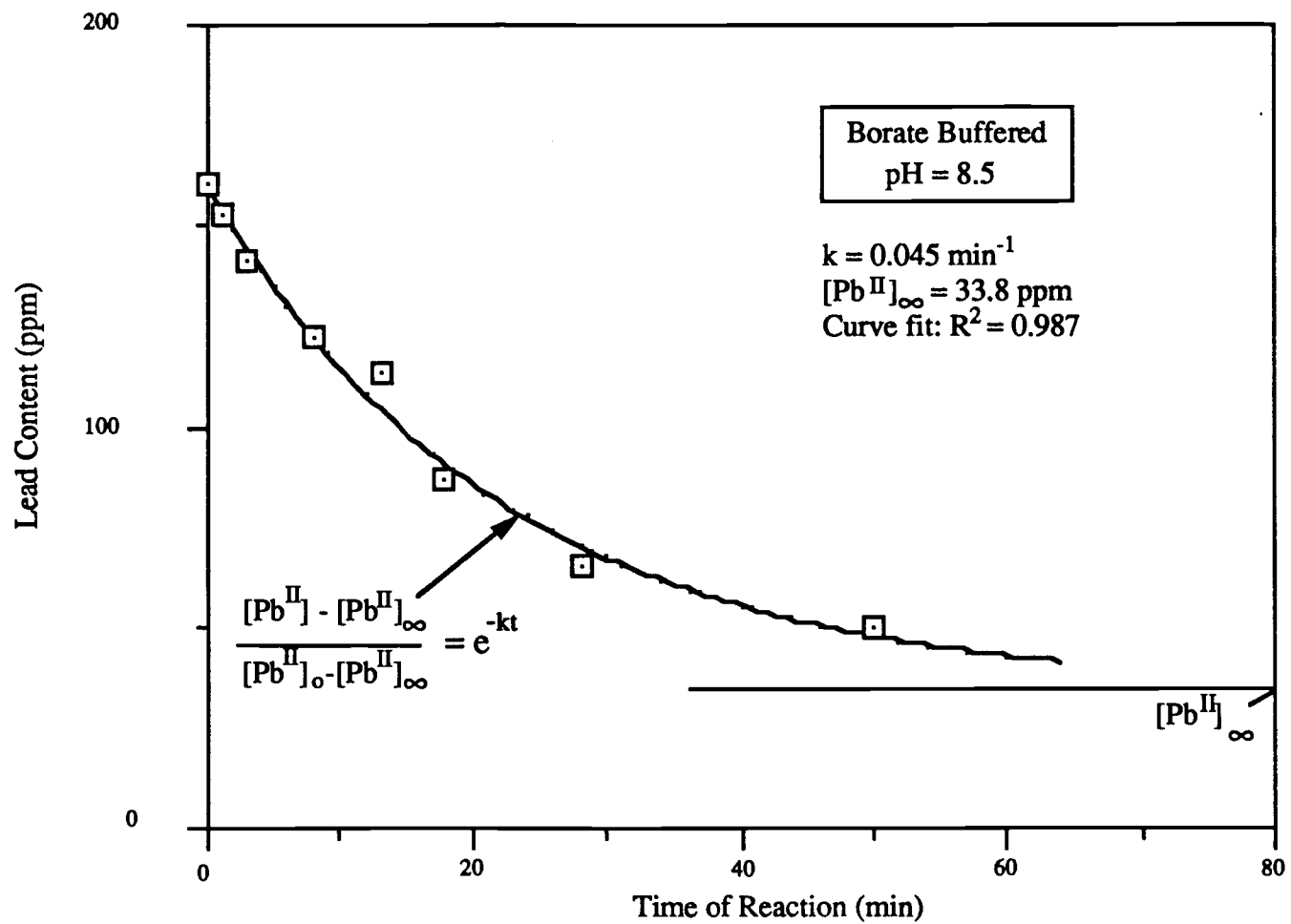
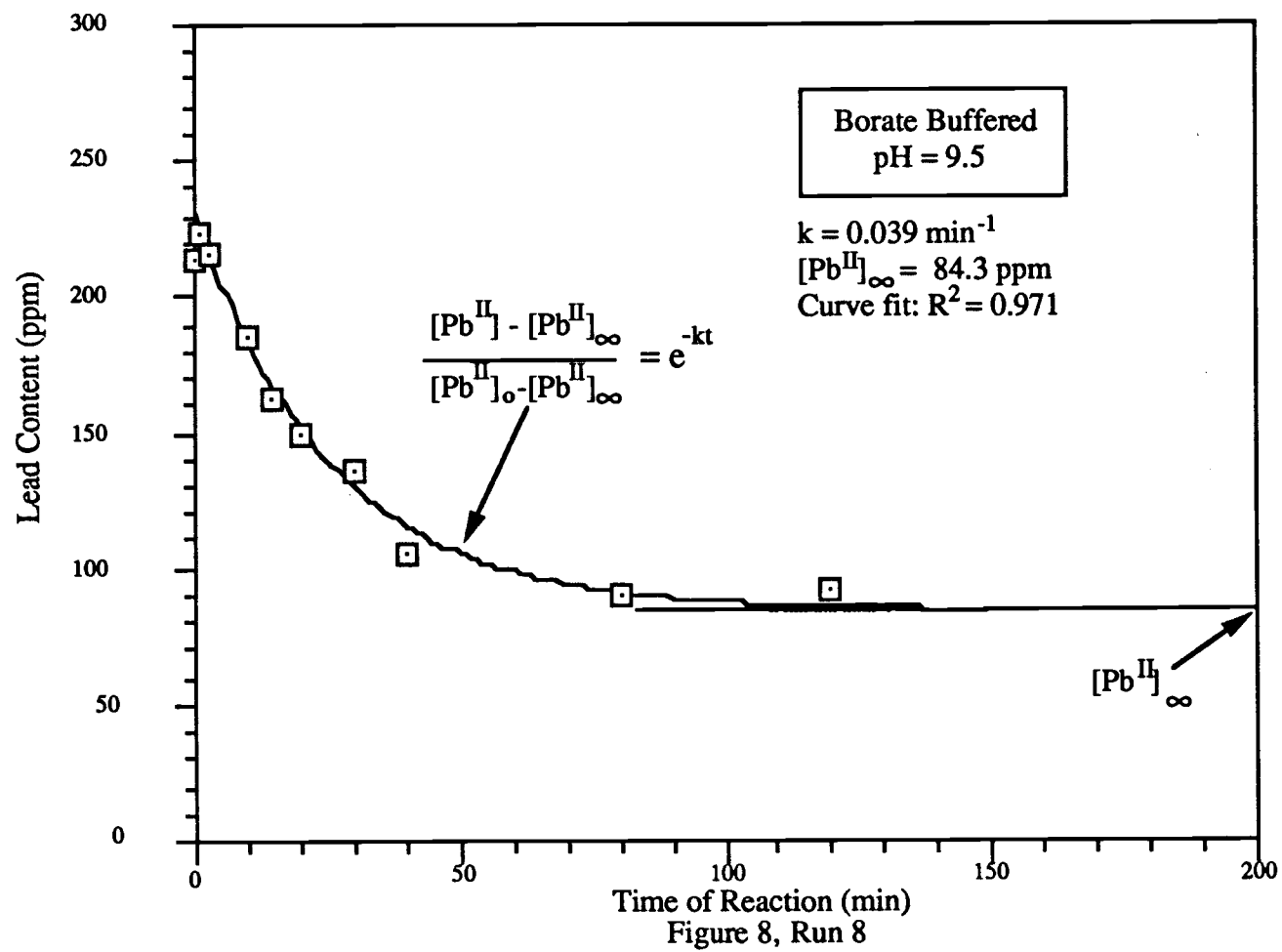
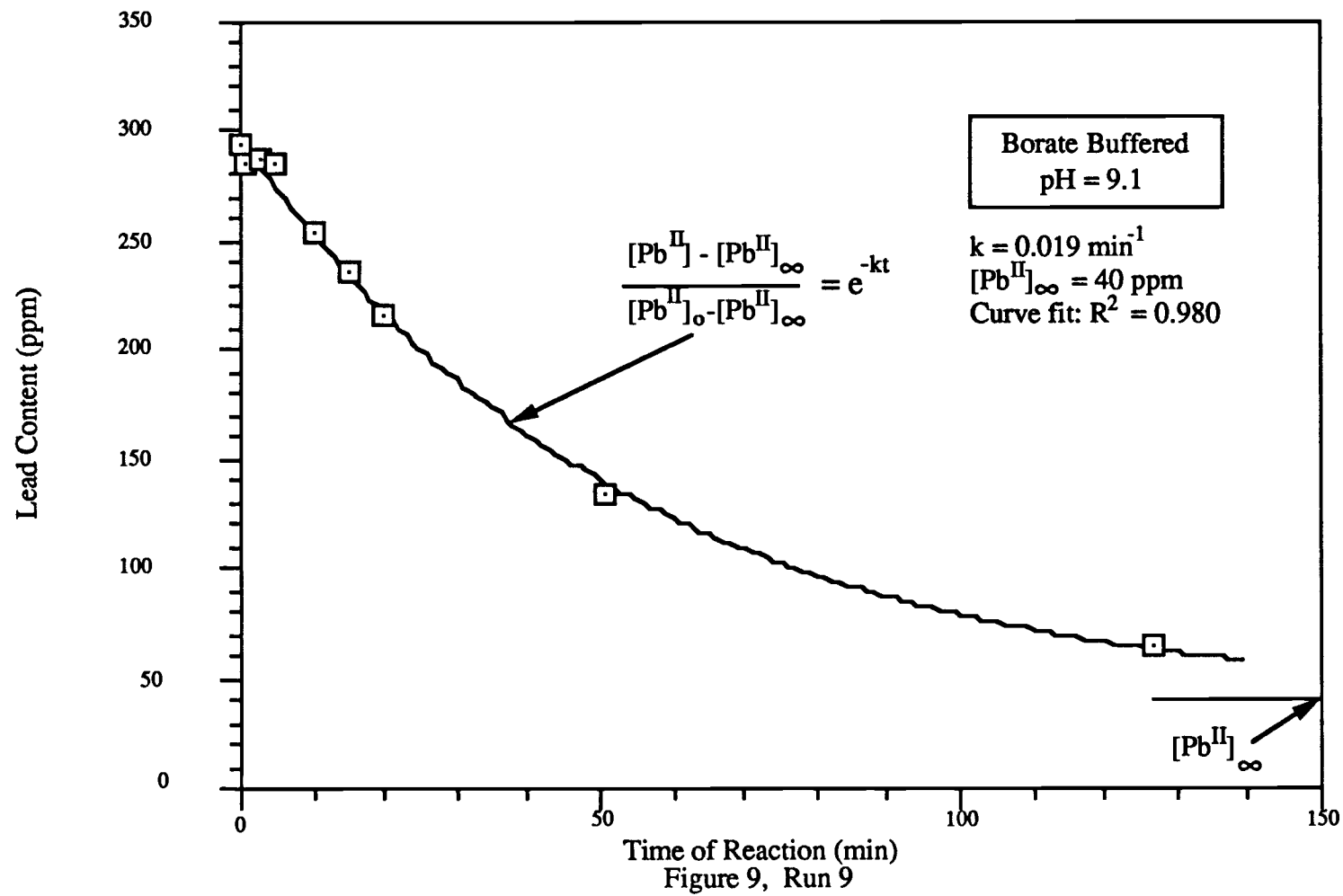
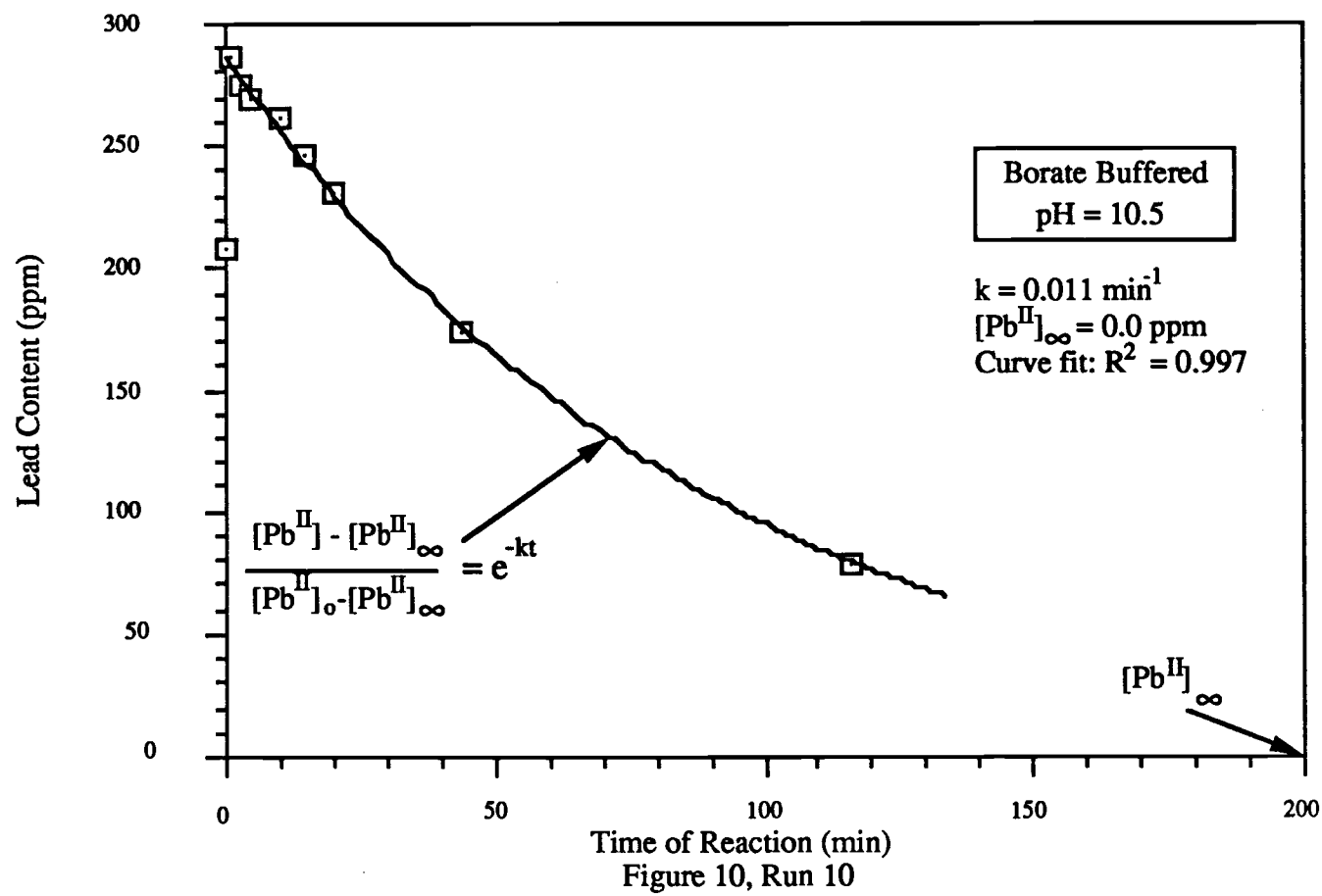


Figure 7, Run 7







### Recommendations for Future Studies

A number of recommendations are presented here as an aid to people who wish to continue research on the removal of lead and other heavy metals by ozonation.

Safety should be of prime consideration for anyone working in this field. Specifically, the proper venting of excess ozone gas, the disposal and handling of heavy metal precipitates and solutions, the operation of high voltage ozonators, and the proper handling of chemicals used in the experiment should be known and understood before operation of equipment. The entire reactor equipment used in this experiment should be placed under a vented hood to prevent the leakage of ozone into breathing air. Heavy metal precipitates should be filtered and stored for proper disposal.

There is no doubt that the most efficient and economical ozone treatment plants will be designed according to the kinetics of oxidation by ozone and the mass transfer of ozone into solution. Therefore, initial research should focus on attention on the kinetics of oxidation of heavy metals by ozone. The next logical step for the continuation of this research may be the determination of compositions of the lead precipitates encountered during the various phases of the reaction sequence. The knowledge of these compositions would be a great help in the determination of accurate kinetics schemes for the reactions involved.

Often in industry, heavy metals occur not as free ions, but are complexed with various organic complexing agents. Other researchers have shown that the ozone oxidation of complexed lead is much more difficult than uncomplexed lead<sup>3</sup>. Studies may be performed in this area as a companion to studies performed for uncomplexed lead.

Some researchers have conducted studies on the combination of ozone with ultraviolet light for applications on the removal of many organic wastes and have reported considerable success<sup>2,13,14</sup>. It may be worth while to study the effect of ultraviolet light on the reaction of lead with ozone, particularly with complexed lead.

From the experience obtained in this research, it is known that pH control is, at best, very difficult. Only one buffer was found that could adequately control pH in the range where a reaction occurs. The development of adequate pH control will be necessary for studies in kinetics of ozonation and in the design of treatment processes involving ozone. This would be an excellent topic of research for this field.

The ultimate goal of any research in ozone oxidation of heavy metals is the application of ozone in industrial scale treatment plants. Future studies in ozonation may focus attention on the introduction of ozonation into the design of practical wastewater treatment equipment. One important area of research will be in the design of continuous treatment systems.

## Summary and Conclusions

Ozone was seen to effectively reduce the concentration of dissolved lead to below 1mg/liter so long as the solution pH and precipitate removal techniques are consistent with those presented in this thesis (1mg/liter was the detection limit of the apparatus used for lead concentration analysis in this thesis). Specifically, the solution pH must be maintained in the alkaline range above 7.0 for oxidation of lead-II to occur. The optimum pH range is believed to be between 8.0 and 10.0.

For water treatment purposes, filtration or sedimentation of the precipitate must precede any adjustments of pH or introduction of acid. Filtration or sedimentation not only removes the insoluble lead-IV oxide, produced in the oxidation reaction, filtration also removes the lead-II hydroxide precipitate formed due to pH changes. Because lead-II hydroxide dissociates to ions in an acidic solution, the solution pH must be maintained above 7.0 for filtration of precipitate species to be most effective.

The atomic adsorption spectrophotometer used for solution analysis was capable of measuring lead concentrations no less than 1 mg/liter (ppm). The maximum allowable discharge concentration limit for lead as published by the Environmental Protection Agency is 50 mg/liter (ppb)<sup>11</sup>, which is well below the capabilities of the analysis apparatus used in in this thesis.

It is therefore inconclusive from the data presented in this thesis whether ozone will effectively reduce levels of lead ions to below acceptable EPA discharge limits. However, ozonation was seen to be considerably more effective at reducing solution lead levels than that seen by the sedimentation of lead-II hydroxide produced from pH



change alone. The lead -IV oxide produced by ozonation appeared to actually aid in the removal of the lead-II hydroxide during the filtration or settling steps.

A by-product of the oxidation of lead-II by ozone is the by-production of hydrogen ions. The production of hydrogen ions causes an unbuffered solution to decrease in pH as the reaction proceeds. Even with pH buffers, it was found to be very difficult to control the solution pH as the ozonation reaction proceeded. Many pH buffers were tested in the course of this research, most of which failed either in the control of the solution pH or in how they affected the oxidation of lead. The only buffer tested which could maintain a constant pH at a range above 7.0 without interfering with the reaction was the boric acid/ sodium borate buffer. The dissociation constant, or  $pK_a$ , for the boric acid is 9.14<sup>16</sup>, which limits the effectiveness of this buffer to a pH range between approximately 8.0 and 10.2. For pH values below 7.0, citric acid/ sodium citrate buffered solutions performed well. No other buffer tested was found to be suitable for this research.

In the study of the reaction kinetics of the oxidation of lead-II by ozone, an attempt was made in this thesis to observe only the oxidation reaction between the lead-II in solution (or suspension) to the lead-IV oxide precipitate. The technique was performed by measuring the concentration of the lead-II remaining in the solution at various times during the reaction (note that the samples were filtered or centrifuged before analysis). In order to eliminate the effect of precipitation of lead-II hydroxide, the lead-II hydroxide precipitate was re-ionized before analysis by the acidification of the sample solution. The only precipitate thus remaining in the sample before filtering was the lead-IV oxide. In reading the portion of this thesis concerning oxidation kinetics, one should be aware of the procedure of re-acidification of the sample solutions before analysis to re-ionize the lead-II hydroxide.

The oxidation of lead-II by ozone was found to be influenced very strongly by the pH of the solution. No reaction between lead and ozone was seen to occur in an

acidic solution, where the pH was below 7.0. Oxidation was only seen to occur when the solution was alkaline or the pH was above 7.0. Above a pH of 7.0, the oxidation reaction rate appeared to be independent of the pH of the solution.

It appears that the oxidation of lead-II in an alkaline solution by ozone is a complex reaction which may involve a sequence of steps or competing reactions. By observation of Figure 4 in this thesis, it is noticed that the lead concentration of the solution decreases according to what appears first-order, reversible kinetics approaching a minimum concentration level at which point the reaction appears to stop.

At this point it should be mentioned that the data in this research were obtained by using very low concentrations of ozone. These concentrations were on the order of .01 to .02% by volume of ozone in the input stream. Conditions of the reaction, such as mass transfer limitations, which exist at these concentrations, may not occur at the high concentrations of ozone typically produced in high powered ozonators. These ozonators can typically produce concentrations on the order of 2.0 to 3.0% by volume of ozone from oxygen.

Through the course of this research, it was noticed that the off-gasses from the reactor contained a large amount of the ozone that was present in the feed gas. Evidence for this is seen from the data of each run included in the appendix of this thesis. Only a fraction of the ozone produced in the ozonator actually reacted with the lead in solution, indicating that a redesign of the reactor used for this research might improve the transfer of ozone to the solution.

In light of the evidence presented here in this thesis, some possible recommendations can be made concerning the design of ozone water treatment equipment for the removal of lead ions. First, the introduction of ozone into solution should be performed under high mass transfer conditions, such as high pressure and rapid, very turbulent mixing. Many research articles have been published on the design of mixing equipment specific to applications involving ozone<sup>8,9,10</sup>. The off gasses,

which invariably will contain high concentrations of ozone, should be recycled or used in a pre-ozonation stage of the system proposed by some researchers in the field<sup>12</sup>.

Second, the pH of the lead solution must be maintained above 7.0 and should be between 8.0 and 10.0. Settling or filtering should occur prior to any pH reduction or acid addition. Times required for oxidation will be dependent on the specific reactor and the concentration of ozone produced from the ozonator.

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## **APPENDICES**

## Appendix A

### Derivation of Kinetics Equation

Ignoring the effects of mass transfer, for first order reversible kinetics in solution, the lead-II reacts until it reaches a minimum concentration after long periods of ozonation according to the following equation:

$$\frac{d[Pb^{II}]}{dt} = -k \left( [Pb^{II}] - [Pb^{II}]_{\infty} \right)$$

$[Pb^{II}]_{\infty}$  = Lead Concentration after long periods of ozonation

Solving for this differential equation as follows gives:

$$\int_{[Pb^{II}]_0}^{[Pb^{II}]} \frac{d[Pb^{II}]}{([Pb^{II}] - [Pb^{II}]_{\infty})} = -k \int_0^t dt$$

which then becomes:

$$\frac{[Pb^{II}] - [Pb^{II}]_{\infty}}{[Pb^{II}]_0 - [Pb^{II}]_{\infty}} = e^{-kt}$$

## Appendix B

### Example Calculation of Ozone Concentration in Gas Stream

This example outlines the procedure for calculation of ozone concentration in the initial input gas stream of Run #7. Calculations for all other runs including output gas concentrations and solution concentration follow the same procedure.

Oxygen flow (measured)	=	0.76Liters/min
Total time of flow	=	1.08 min
Total volume of gas tested	=	(0.76Liters/min)X(1.08min) = 0.82Liters
Titrate volume of Sodium Thiosulfate(0.0050Molar)	=	13.843mL
Moles of Ozone titrated	=	(0.0050mol/liter)X(0.013843L)X (1mole titrate/2 mole ozone) =3.46X10 <sup>-5</sup> mol Titrate
Ozone Concentration of Gas	=	(3.46X10 <sup>-5</sup> mol)/(0.82Liters) =4.25X10 <sup>-5</sup> mol/Liter



**Appendix C**  
**Tables of Run Data**

Run number 0  
Boric acid buffered

Barometer	762.0 mm Hg	Ozonator volts	6500
Water Temp.	18. deg C	Ozone concentration determination of input gas	Initial final
pH	8.65	Flow reading	40 43
Oxygen Flow	2.4 l/min	Oxygen flow	.94 l/min .97 l/min
Mixer RPM	1715	Total time	1. min 1. min
initial sample # = 1		Titrate volume	13.24 ml 16.75 ml
initial volume	5000. ml	Ozone moles/L	3.56E-05 4.37E-05
final volume	---	Vol %	0.091 % 0.108 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
1	0.0 min	75. ppm	8.65	ml	moles/liter	liter/min	min
2	1	78.	8.71	---			
3	3	77.	8.75	---			
4	5	70.	8.51	3.82	2.12E-05	0.91	0.5
5	10	68.	8.42	2.921	1.43E-05	1.03	0.5
6	15	37.	8.34	3.25	1.37E-05	1.2	0.50
7	21	1.	8.29	3.15	1.22E-05	1.12	0.58
8	42	0.	8.24	---			

Data of Run 0  
Table 1

Run number1  
Boric acid buffered

pH Drop

Barometer 753.4  
Water Temp. 20. deg C  
pH 7.8  
Oxygen Flow 2.4 l/min  
Mixer RPM 1705  
initial sample # = 51  
initial volume 4000. ml  
final volume ---

Ozonator volts 6500  
Ozone concentration determination  
of input gas Initial final  
Flow reading 43 ---  
Oxygen flow 1. l/min ---  
Total time 1. min ---  
Titrate volume 14.26 ml ---  
Ozone moles/L 3.61E-05 ---  
Vol % 0.087 ---

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
51	0.0 min	127. ppm	7.80	ml	moles/liter	liter/min	min
52	1	128. ppm	7.57	---			
53	3	125. ppm	7.58	3.47		0.72	0.5
54	5	120. ppm	7.28	3.44	1.87E-05	0.93	0.5
55	10	118. ppm	6.98	5.49	1.98E-05	1.05	0.67
56	16	108. ppm	6.02	4.77	2.14E-05	1.13	0.50

Data of Run 1  
Table 2

Run number 2  
Boric acid buffered

Barometer	751.1	Ozonator volts	6500
Water Temp.	20. deg C	Ozone concentration determination	
		of input gas	Initial final
pH	8.5	Flow reading	48 41
Oxygen Flow	2.4 l/min	Oxygen flow	1.08 l/min .93 l/min
Mixer RPM	1725	Total time	1. min 1. min
initial sample # = 20		Titrate volume	13.175 ml 11.825 ml
initial volume	5000. ml	Ozone moles/L	3.09E-05 3.22E-05
final volume	3500. ml	Vol %	0.070 % 0.084 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
20	0.0 min	122. ppm	8.57	ml	moles/liter	liter/min	min
21	1	126	8.62	---			
22	3	122	8.69	3.781	2.04E-05	0.94	0.5
23	5	125.5	8.58	2.87	1.32E-05	1.1	0.5
24	10	121	8.47	2.85	1.36E-05	1.06	0.5
25	10	109.5	---	---			
26	15	86.5	8.4	2.58	1.26E-05	1.04	0.50
27	20	79.5	8.5	6.42	2.26E-05	1.08	0.67
28	---	67	7.35	4.158		1.08	0.5

Data of Run 2  
Table 3

Run number 3  
Boric acid buffered

Barometer	750.5	Ozonator volts	6500
Water Temp.	20. deg C	Ozone concentration determination	
		of input gas	Initial final
pH	9.06	Flow reading	52 49
Oxygen Flow	2.4 l/min	Oxygen flow	1.15 l/min 1.11 l/min
Mixer RPM	1721	Total time	1. min 1. min
initial sample # = 31		Titrate volume	15.661 ml 14.951 ml
initial volume	5000. ml	Ozone moles/L	3.45E-05 3.41E-05
final volume	4000. ml	Vol %	0.073 0.075

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
31	0.0 min	138. ppm	9.06	ml	moles/liter	liter/min	min
32	1	132.5	9.23	---			
33	3	126	9.17	---			
34	3	129	9.26	restart			
35	5	121.5	9.14	---			
36	10	107	9.14	2.01	1.20E-05	0.85	0.50
37	15	92.5	9.07	2.499	1.58E-05	0.8	0.50
38	20	85	8.96	1.99	1.44E-05	0.7	0.50
39	35	52	9	3.23	1.78E-05	0.92	0.5

Data of Run 3  
Table 4

Run number 4  
Boric acid buffered

Barometer	772.9	Ozonator volts	6500
Water Temp.	20. deg C	Ozone concentration determination	
		of input gas	Initial final
pH	10	Flow reading	43 35
Oxygen Flow	2.4 l/min	Oxygen flow	.96 l/min .79 l/min
Mixer RPM	1697	Total time	1. min 1. min
initial sample # = 41		Titrate volume	14.275 ml 11.51 ml
initial volume	5000. ml	Ozone moles/L	3.76E-05 3.69E-05
final volume	4000. ml	Vol %	0.0926 % 0.1103 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
41	0.0 min	75	10.14	ml	moles/liter	liter/min	min
42	1.00	75	9.99	---			
43	3.00	70.5	---	---			
44	5.17	63	9.96	---			
45	12.17	52	9.46	5.21	4.39E-05	0.6	0.5
46	17.17	46	9.81	4.673	2.23E-05	1.06	0.50
47	23.17	40	9.6	2.301	1.76E-05	0.66	0.50
48	47.17	33	9.81	2.155	1.36E-05	0.8	0.5

Data of Run 4  
Table 5

Run number 5  
Barbatol buffered

Buffer reacted with ozone and did not maintain pH
--

Barometer	766.7	Ozonator volts	6500
Water Temp.	20. deg C	Ozone concentration determination	
pH	7.55	of input gas	initial final
Oxygen Flow	2.4 l/min	Flow reading	54 ---
Mixer RPM	1720	Oxygen flow	1.22 l/min ---
initial sample # = 50		Total time	1. min ---
initial volume	4000. ml	Titrate volume	20.332 ml ---
final volume	----	Ozone moles/L	4.22E-05 ---
		Vol %	0.0824 % ---

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
50	0.0 min	82.3 ppm	7.65	ml	moles/liter	liter/min	min
51	1	81.5	7.74	---			
52	3	79.75	7.59	---			
53	5	76	7.34	---			
54	10	68	7.01	0	0.00E+00	1.2	1
55	15	57.5	6.34	3.64	4.19E-06	1.1	2

Data of Run 5  
Table 6

Run number 6  
Boric acid buffered

pH Drop  
Lead concentration too high to measure.

Barometer	264.7	Ozonator volts	6500
Water Temp.	19.8 deg C	Ozone concentration determination	
		of input gas	Initial final
pH	8.71	Flow reading	35 ---
Oxygen Flow	2.4 l/min	Oxygen flow	.85 l/min ---
Mixer RPM	1740	Total time	1. min ---
initial sample # = 60		Titrate volume	14.885 ml ---
initial volume	4000. ml	Ozone moles/L	4.43E-05 ---
final volume	---	Vol %	0.360 % ---

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
				ml	moles/liter	liter/min	min
60	0.0 min	off scale	8.71	ml			
61	1	off scale	8.75	---			
62	3	off scale	8.34	---		---	
63	5	off scale	8.52	3.623	2.11E-05	0.87	0.5
64	10	off scale	8.2	1.1	5.80E-06	0.96	0.5
65	15	off scale	7.76	1.76	9.58E-06	0.93	0.50
66	20	97	7.2	6.34	1.46E-05	1.1	1.00

Data of Run 6  
Table 7



Run number 7  
Boric acid buffered

Barometer 770.6  
Water Temp. 20. deg C  
pH 8.5  
Oxygen Flow 2.4 l/min  
Mixer RPM 1740  
initial sample # = 70  
initial volume 4000. ml  
final volume 3500. ml

Ozonator volts 6500  
Ozone concentration determination  
of input gas Initial final  
Flow reading 34 42  
Oxygen flow .76 l/min .95 l/min  
Total time 1.08 min 1. min  
Titrate volume 13.843 ml 11.13 ml  
Ozone moles/L 4.25E-05 2.96E-05  
Vol % 0.123 % 0.074 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
70	0.0 min	161	8.62	ml	moles/liter	liter/min	min
71	1	153	8.73	---			
72	3	141.5	8.63	---			
73	8	122.5	8.59	3.6	1.70E-05	1.07	0.5
74	13	114	8.56	2.6	1.34E-05	0.98	0.5
75	18	86.5	8.49	4.95	2.47E-05	0.98	0.52
76	28	64.5	8.2	3.75	2.13E-05	0.92	0.48
77	50	50	8.18	11.12	5.02E-05	1.12	0.5

Data of Run 7  
Table 8

Run number 8

Boric acid buffered

Barometer 761  
 Water Temp. 20. deg C  
 pH 9.46  
 Oxygen Flow 2.4 l/min  
 Mixer RPM 1744  
 initial sample # = 100  
 initial volume 4000. ml  
 final volume 3500. ml

Ozonator volts 6500  
 Ozone concentration determination  
 of input gas initial final  
 Flow reading 35 -----  
 Oxygen flow .82 l/min -----  
 Total time 1. min -----  
 Titrate volume 9.812 ml -----  
 Ozone moles/L 3.03E-05 -----  
 Vol % 0.089 % -----

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
80	0.0 min	214.5	9.46	ml	moles/liter	liter/min	min
81	1.05	223.5	9.67	---			
82	3.05	229.5	9.76	---			
83	5.05	215	9.56	---			
84	10.05	184.5	9.67	2.99	8.50E-06	0.89	1
85	15.05	161	9.59	5.9	1.34E-05	1.11	1
86	20.05	150	9.62	6.09	2.20E-05	1.4	0.5
87	30.05	135.5	9.53	4.67	1.79E-05	1.28	0.52
88	40.05	104	9.61	5.521	2.33E-05	1.2	0.5
89	80.05	90		5.428	2.18E-05	1.26	0.5
810	120.05	91					

Data of Run 8  
 Table 9

Run number 9  
Boric acid buffered

Barometer	762	Ozonator volts	6500
Water Temp.	20. deg C	Ozone concentration determination	
pH	8.96	of input gas	initial final
Oxygen Flow	2.4 l/min	Flow reading	55 62
Mixer RPM	1765	Oxygen flow	1.22 l/min 1.36 l/min
initial sample # = 90		Total time	1.25 min 1. min
initial volume	4000. ml	Titrate volume	18.55 ml 14.89 ml
final volume	3450. ml	Ozone moles/L	3.08E-05 2.77E-05
		Vol %	0.0484 % 0.0488 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
=====	=====	=====	=====	=====	=====	=====	=====
90	0.0 min	293.5	8.96	ml	moles/liter	liter/min	min
91	1	285	8.75(9.12)*	---			
92	3	287.5	9.17	---			
93	5	285	9.16	---			
94	10	254.5	9.16	9.2	1.72E-05	1.35	1
95	15	236.5	9.18	6.95	1.64E-05	1.07	1
96	20	217	9.12	9.22	1.77E-05	1.32	1
97	51	133.5	9.1	9.39	2.00E-05	1.19	1

Data of Run 9  
Table 10

Run number 10  
Boric acid buffered

Barometer 758.5  
Water Temp. 20. deg C  
pH 10.75  
Oxygen Flow 2.4 l/min  
Mixer RPM 1744  
initial sample # = 100  
initial volume 4000. ml  
final volume 3500. ml

Ozonator volts 6500  
Ozone concentration determination  
of input gas initial final  
Flow reading 72 40  
Oxygen flow 1.59 l/min .92 l/min  
Total time 1. min 1. min  
Titrate volume 18.96 ml 9.49 ml  
Ozone moles/L 3.02E-05 2.61E-05  
Vol % 0.0457 % 0.0683 %

Sample#	time of run	lead content	solution pH	Ozone analysis of output gas		oxygen flow	Time of flow
				Titrate Vol	Ozone conc		
100	0.0 min	280.5	10.75	ml	moles/liter	liter/min	min
101	1	287	10.72	---			
102	3	275	10.69	---			
103	5	270	10.66	---			
104	10	261	10.64	8.98	1.42E-05	1.6	1
105	15	246	10.54	9.04	1.59E-05	1.44	1
106	20	231	10.46	11.11	1.95E-05	1.44	1
107	44	174.5	10.32	11.22	1.87E-05	1.52	1

Data of Run 10  
Table 11