Selected Heavy Metal and Organic Removal from Wastewater by Precipitation and Ozonation Processes

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Abstract

Experiments were conducted to precipitate dissolved copper, zinc, and lead from simulated wastewater solutions as solids which could then be separated by filtration. The precipitants used were hydrated lime, as a slurry and in powdered form, aqueous ammonium hydroxide, ferrous sulphide sludge, and carbon dioxide gas. These five different chemicals, singly or in combination, were used; at least one of which was highly successful in precipitating each of the metals, removing at least 99 % of that originally present. Copper and zinc were very effectively precipitated as the hydroxides with lime, whereas lead was not. Considering lead to be the most difficult metal to remove, four other chemical conditions were attempted for lead; these were ferrous sulphide alone, lime with ferrous sulphide, lime with carbon dioxide, and lime with ozone. The precipitation of lead with ferrous sulphide alone, was only partially successful with only 95 % removal. The other three combinations of chemicals precipitated more than 99 % of the soluble lead, giving excellent results. Furthermore, because lead is usually difficult to remove from solution, it is considered that the three new chemical combinations show strong promise for the removal of other heavy metals from wastewater solutions.

Experiments were also conducted to decompose the organic compounds, formaldehyde and pyridine, in simulated wastewater solutions in a mixed reactor, using ozone and UV radiation as oxidants. Although 200 ppm Total Organic Carbon content of each of those chemicals, and a mixture of both, were completely decomposed by ozone–

UV oxidation, the time taken for these decompositions ranged from about three to four hours. Such prolonged reaction times are considered too long for most wastewater treating processes. However, low concentrations of organic matter might be successfully treated using ozone/UV processes.

Résumé

Plusieurs essais ont été faits pour prélever des métaux lourds de solutions contenant soit du cuivre, du zinc, ou du plomb. Les résultats indiquent que le cuivre et le zinc précipitent facilement avec de la chaux, mais non le plomb. Considérant le plomb en tant que substance difficile a précipiter, quatre nouveaux agents ou combinaisons d'agents de précipitation furent essayés. Ces agents sont le sulfure ferreux, une combinaison de chaux et de sulfure ferreux, de chaux et de dioxide de carbone, et de chaux et d'ozone.

La précipitation du plomb avec le sulfure ferreux seul étais partiellement efficace, avec 95% de récupération. Les autres combinaisons précipitent plus de 99% du plomb soluble. En plus, par ce que le plomb est difficile à séparer de solution, on considère que les quatre combinaisons sont prometteuses pour la récupération d'autres métaux lourds de solution.

Des essais ont étés entrepris pour décomposer les produit organiques, fomaldéhyde et pyridine, d'une eaux synthétique dans un réacteur agité utilisant des oxydants tels que l'ozone et des rayons ultraviolet. Au moins 200 ppm de Carbone Organique Total de ces composés, et un mélange des deux, étaient complètement décomposés par la combinaison d'ozone et d'ultraviolet. Le temps requis pour ces décompositions était entre trois et quatre heures. Ces temps de traitement sont considérés trop longs pour un traitement industriel. Cependant de basses concentrations de matières

organiques pourraient être traitées utilisant une combinaison d'ozone et de rayons ultraviolets.

Acknowledgements

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Chapter 1.0 Introduction

The widespread availability of chemicals has brought benefits to almost all sectors of the economy, but experience has shown that there are significant hazards associated with some of these chemicals. Chemicals which are generally referred to as "hazardous" are being found more and more frequently in the environment. Their identification in trace quantities becomes easier as analytical measurement techniques become more sensitive. Strategies for avoidance of hazards related to chemical technology and manufacturing have not always been integrated into all plans for use of chemicals. Mistakes that have resulted in human illness, degradation of the ecosystem, and the necessity for costly cleanup efforts can be avoided (Thompson and McComas, 1987). For example, releasing industrial wastewaters that contain dissolved heavy metal ions into a sewer system or to open water may lead to severe problems as the heavy metals are apt to become widely dispersed in the environment. The heavy metals may be ab- and/or adsorbed by materials such as sewer water treatment plant sludges or by clay particles that float downstream in rivers and settle in harbour basins. Therefore, the waters become polluted with heavy metals to the point where these substances are regarded as a hazardous waste. While waste minimization goals are both necessary and desirable, most manufacturing operations still create waste products that ultimately need to undergo treatment to either destroy the wastes or render them harmless to the environment. There are numerous treatments applicable to hazardous wastes that can typically be categorized as chemical, physical, or biological in nature. Many such processes are already widely used to manage hazardous wastes and have broad acceptance from government, industry, and public alike. Combinations of these treatment technologies are often utilized to develop the most cost-effective and environmentally acceptable solutions to organic and inorganic waste management problems (Clark et al., 1977).

Determination of various treatment processes for wastewater depends on the compounds constituting the waste. Metals exist in wastewaters in many forms such as soluble, insoluble, inorganic, metal organic, free metal, reduced, oxidized, adsorbed, precipitated, and complexed. Toxic heavy metals of particular concern in treatment of industrial wastewaters include copper, zinc, cadmium, lead, nickel, silver, mercury, chromium, and iron. The metal processing, plating, and metal finishing industries are sources of such metal wastes (Peters and Ku, 1985) Organic wastes also play a significant role as water micropollutants since some of them are industrially used widely as pesticides, resin components, disinfectants, preservatives, bactericide, and synthetic reagents etc. (Shin et al., 1996). Substances belonging to the class of N-heterocyclic compounds act as examples of pesticides while aldehydes act as bactericides and preservatives etc. In this thesis, selected possible pollutants in the effluent streams from chemical plants will be considered as well as methods for treating these streams. Because the nature and chemical and biochemical properties of pollutants are extremely variable it was necessary to select a few possible pollutants and attempt to devise treatment processes for them rather than to consider all possible pollutants and treatment methods.

Treatment processes for metal removal must be selected to remove the existing form of the metal, or the metal must be converted to a suitable form compatible with the removal process. For soluble metals the process for removal from low concentrations in water frequently involves the addition of another, relatively innocuous chemical, which produces a highly insoluble stable precipitate. The formation of insoluble hydroxides, sulphides, and carbonates by a considerable number of metals allows the use of hydroxide and sulphide precipitation processes to be effective methods in the treatment of industrial wastewaters. Precipitation processes, for the removal of heavy–metal pollutants from aqueous solutions, were utilized in this work. The removal of dissolved copper, zinc, and lead (II) in dilute aqueous solutions were the metals chosen for treatment by the precipitation processes.

By far the most widely used industrial process for the removal of heavy metals from solution is that of chemical precipitation; approximately 75% of the electroplating facilities employ precipitation treatment using either hydroxide, carbonate, or sulphide treatment, or some combination to treat their wastewaters. The most commonly used precipitation technique is the hydroxide treatment due to its relative simplicity, low cost of precipitant (lime), and ease of pH control (Peters et al., 1985). The metals are removed by adding an alkali to adjust the wastewater pH to the point where metals exhibit minimum solubilities. The solubilities of the various metal hydroxides are minimized for a pH in the range of 8.0 to 11.0. The metal hydroxides can be removed by flocculation and sedimentation (Peters and Ku, 1987). Theoretically, hydroxide precipitation can result in very low residual metal concentrations for several metals, although it has several limitations. The optimum pH values for minimum solubility differ for different metals, which may limit the degree of metals removed when several different metals are precipitated simultaneously. Other constituents in the wastewater, particularly complexing agents, to some extent inhibit metal hydroxide precipitation. In addition, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems (Brantner and Cichon, 1981).

Carbonate and sulphide precipitation have been demonstrated to be more effective treatment techniques for certain heavy metal solutions than hydroxide precipitation (Peters and Ku, 1987). The advantages that carbonate precipitation theoretically has over hydroxide precipitation includes a lower metal carbonate solubility, a lower operating pH and a lower volume of significantly denser sludge (Brantner and Cichon, 1981). Sulphide precipitation is also an effective process for the treatment of industrial wastes containing highly toxic heavy metals. The attractive features of the sulphide process are the attainment of a high degree of metal removal over a broad pH range, a lower detention time required in the reaction tank because of the high reactivity of sulphides, and the feasibility of selective metal recovery (Bhattacharyya et al., 1980). Two different processes exist for sulphide precipitation of heavy metals, these are soluble sulphide precipitation (SSP) and insoluble sulphide precipitation (ISP), the difference being on how the sulphide is introduced into the wastewater. In the SSP process, sulphide is added in the form of a water soluble sulphide reagent such as sodium sulphide or sodium hydrosulphide (NaHS). In the ISP process, a slightly soluble ferrous sulphide (FeS) slurry is added to the wastewater to supply the needed sulphide ions. Since most of the heavy metals have sulphides less soluble than ferrous sulphide, they will displace the iron to form highly insoluble metal sulphides. Advantages of the ISP process include the absence of any detectable hydrogen sulphide (H_2S) gas. One disadvantage of this process is that ferrous ion is released and precipitated as the hydroxide in basic solutions. Another disadvantage of the process is the considerably larger than stoichiometric reagent consumption and large quantities of sludge being generated as a result of the conversion of the ferrous ion to ferric hydroxide formation (Peters and Ku, 1987). Economics may justify partial precipitation with lime to the solubility of the hydroxide, followed by separation of the solid, and then by a secondary treatment with sulphide for a further reduction of dissolved heavy metal.

For hydrocarbon pollutants in aqueous solutions, a recognized process for their removal is the chemical destruction of the hydrocarbon by oxidation. Oxidation can be considered to be a special case of incineration, since the ultimate reaction products of most organic materials treated by either process are carbon dioxide and water, or nitrogen oxide for organic compounds containing nitrogen. For this research project, ozone was the only oxidant considered because of its attractive property which is its eventual complete decomposition to form oxygen even in the presence of excess ozone. Oxidation in the presence of ultraviolet radiation by itself and in conjunction with ozonation was also studied. Pyridine and formaldehyde in dilute aqueous solution were utilized in the ozone, ultraviolet radiation (UV) experiments. A modification to ozone treatment for organic pollutants was also devised for the oxidation of soluble metal pollutants. The strong oxidizing properties of ozone were utilized to produce insoluble oxide or hydroxide precipitates of the metals.

1.1 Environmental Criteria for Copper, Zinc, and Lead

Health and Welfare Canada, and the Ontario Ministry of the Environment have established guidelines to support and protect the designated uses of water at a specified site. Table 1.1 lists the maximum acceptable concentrations of copper, zinc, and lead in drinking water, and for protection of aquatic life. These metal concentrations indicate the need for removal of the respective metals if found in plant effluent streams. However, the research involved in this study requires the treatment of metals that exist in solution in high concentrations (greater than 200 ppm), and the treatments to be presented are for primary treatment systems.

Table 1.1 Water Quality Criteria (Canadian Water Quality Guidelines, 1997).

Heavy Metal	Maximum acceptable concentration in drinking water	Guidelines for freshwater aquatic life
Copper	1.0 ppm	5 ppb
Zinc	5.0 ppm	5 ppb
Lead	0.05 ppm	0.03 ppm

Chapter 2.0 Scope of Research

The goal of this project was three fold: (1) to investigate the use of hydroxide and sulphide precipitation techniques in the treatment of the heavy metal ions, copper, zinc and lead (II) from aqueous solutions, (2) to decompose and hence remove the organic compounds, pyridine and formaldehyde using ozone, with and without UV radiation, and (3) to precipitate dissolved lead (II) ions in aqueous solution using ozone, an exploratory study.

2.1 Chemical Precipitation

Solutions of the metals were prepared from the soluble salts to produce approximately 200 ppm of the metal ions in aqueous solution. This concentration would be unacceptable in a wastewater discharge stream and therefore would require treatment. A removal rate of at least 95 % of this feed concentration would be considered a successful removal rate, and hence, was the minimum goal of the treatments used.

Precipitation reactions were conducted batch–wise in a stirred, glass reactor, essentially an Erlenmeyer flask of 300 mL capacity in each case, which was charged with 200 mL of solution. Lime was used in two forms as a precipitant – as a powdered solid and as a slurry of aqueous solid – added in excess, and in sufficient quantity to raise the pH to the required precipitation level (usually above pH 9) to precipitate all the metal ions present. Experiments were conducted at 25 °C and at 50 °C and all were duplicated. Samples were withdrawn at regular time intervals, usually 15 minutes, through a syringe–filter sampler. The samples were stabilized and subsequently analyzed. Aqueous ammonium hydroxide was another precipitant used for comparison treatment purposes conducted at 25 °C only. The dosage of NH_4OH was in a sufficient quantity to raise the solution pH above pH 8.

The same preparations of dissolved metal ions were treated with a sulphide precipitant. The precipitant in this case was a freshly prepared sludge of FeS and lime in water which was added to the reactor containing the metal ions. An excess of FeS sludge was used. Again samples were withdrawn and filtered at regular time intervals and stabilized for analysis. These latter experiments were duplicated and conducted at 25 °C and 50 °C. For the lead ion solutions using FeS sludge, the removal rate of the lead was well below the objective of 95 % removal. As a result, six variations of the sulphide precipitation process were utilized but conducted at 25 °C: (1) ammonium hydroxide was simultaneously added along with the FeS sludge to the dissolved lead sample, (2) ammonium hydroxide and FeS sludge were used consecutively as precipitants with filtration to remove precipitate after the first stage, (3) the same as in (2) except that the filtration after the first chemical addition was omitted. Another series of three experiments was conducted using powdered lime as the base precipitant instead of ammonium hydroxide. Otherwise the experiments were the same. For all the precipitation experiments the crystal morphology of the resulting precipitates was observed.

2.2 Ozonation

The organic compound concentrations were measured as a function of Total Organic Carbon (TOC) present in solution. Concentrations and desired removal rates of the organics and lead ion to be treated by ozonation were the same as those described in Sec. 2.1. The ozonation reactions were conducted batch–wise in a stirred, glass reactor, consisting of a 2 L capacity glass container which was charged with 500 mL of solution. All ozonation experiments were conducted at 25 °C only. Ozone was added to the reactor in two dosages of 3.5 mg/(L.min) and 6.0 mg/(L.min) with and without exposure to UV radiation. Samples were withdrawn at regular time intervals, usually 30 minutes, by a syringe sampler. The samples were subsequently analyzed.

For decomposition of pyridine, an experiment was conducted to determine the reaction time required to reduce more than 95 % TOC from solution utilizing 6.0 mg/(L.min) O_3 in the presence of UV radiation. The effects of ozonation on multi–organic systems were also studied. The multi–organic systems were comprised of pyridine and formaldehyde mixtures in aqueous solution. The concentrations of the mixtures to be treated were 200 ppm and 400 ppm TOC. The experiments were conducted for a reaction time up to five hours.

Lead ions were precipitated from solution by 6.0 mg/(L.min) O_3 with and without exposure to UV radiation. Treatment was at 25 °C for a reaction time of three hours. The lead ion solutions were pH adjusted by solid lime and aqueous ammonium hydroxide before treatment by ozonation.

Chapter 3.0 Theoretical Aspects

3.1 Chemical Precipitation

Let us first consider the equilibrium in pure water between a solid substance of very low solubility and the ions which form when a small amount of the solid dissolves. This process can be described by:

$$AB_2(s) \overset{K_{sp}}{\Leftrightarrow} A^{++} + 2B^{-} \quad (3.1\text{-}1)$$

The equilibrium between the solid and ionic concentrations (mol/L) is described by the solubility product:

$$K_{sp} = \frac{[A^{++}][B^{-}]^2}{[AB_2(s)]} \quad (3.1\text{-}2)$$

The activity of the solid phase is taken as unity, hence:

$$K_{sp} = [A^{++}]\,[B^{-}]^2 \quad (3.1\text{-}3)$$

The more common ionization or dissociation constant describes the relation between the concentrations of dissolved but undissociated salt and those of the ionized species. The ionization process can be described by:

$$CD_2 \Leftrightarrow C^{++} + 2D^- \qquad (3.1\text{-}4)$$

The ionization constant is given by:

$$K_i = \frac{\gamma_C\left[C^{++}\right]\gamma_D\left[D^-\right]^2}{\left[CD_2\right]} \qquad (3.1\text{-}5)$$

The activity coefficients γ_C, γ_D are taken to be equal to unity for approximate evaluations.

A number of different equilibria are usually involved during precipitation processes. First consider the treatment of a wastewater using lime to reduce the concentration of zinc. Let us also assume that the process for production of zinc involved dissolving it in sulphuric acid. Hence, along with dissolved ionized zinc, sulphate ion will also be present. When lime is added to such a solution undissolved, solid lime will be present. As the lime dissolves zinc hydroxide will form; but along with it calcium sulphate will also form as a precipitate. As the precipitation continues to completion, the concentrations of zinc and also of sulphate ions will be decreased. The quantity of lime will also be reduced. The sludge from this process will contain zinc hydroxide, calcium sulphate and residual lime. Please refer to Figure 3.1.

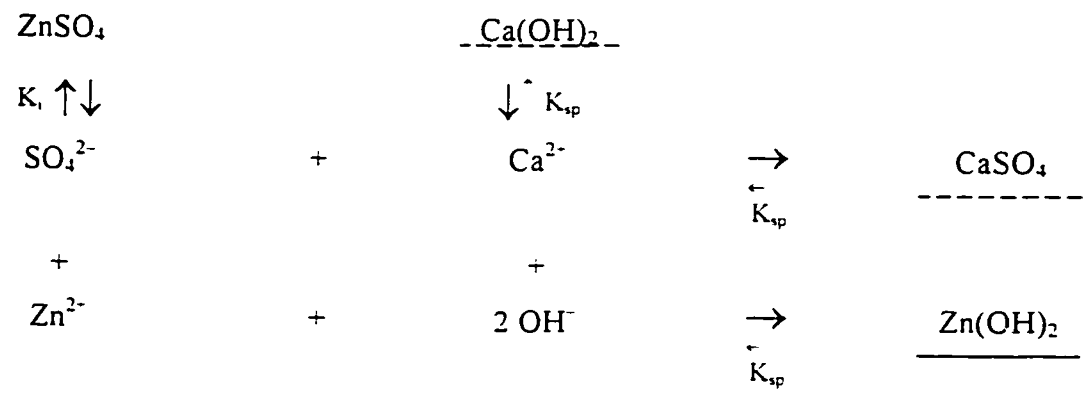


Figure 3.1 The Precipitation Reactions of Metal Ions using Lime (- - - - indicate slightly soluble compounds, _____ indicate insoluble compounds).

There are four different reactions taking place in the above precipitation The equilibrium values for three are described by solubility products, and one by an ionization constant. The slightly soluble solids, $Ca(OH)_2$ and $CaSO_4$ are indicated by a dashed line. This precipitation process is considered successful because the zinc is removed as an insoluble solid. The calcium is very plentiful in the earth's crust and is considered innocuous even if it is in a slightly soluble form. In contrast, if sodium or ammonium hydroxides were used to precipitate zinc or other metals, a much higher residual dissolved solids concentration would be left in the treated wastewater because sodium and ammonium salts are essentially all soluble.

In precipitation processes, chemicals that react with metal ions to form insoluble precipitates are added to the wastewater. The equilibrium between the solid precipitated metal compounds and the ions in solution follows the solubility product principle as governed by equations 3.1–6 through 3.1–9. The precipitates can be separated from the water by sedimentation or filtration. The solids most commonly generated are hydroxide and sulphide compounds (McLaughlin et al., 1995).

Examples:

$$ZnS \Leftrightarrow Zn^{2+} + S^{2-} \quad (3.1\text{–}6)$$

$$K_1 = [Zn^{2+}][S^{2-}] = 1.2 \times 10^{-23} \quad (3.1\text{–}7)$$

$$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2OH \quad (3.1\text{–}8)$$

$$K_2 = [Zn^{2+}][OH^-]^2 = 6.9 \times 10^{-17} \quad (3.1\text{–}9)$$

The equilibrium calculations involving precipitation using acid–base equilibria are generally less representative of the true situation because, generally, the rate of precipitation controls the extent of reaction since insufficient time is allowed to achieve equilibrium (Peters and Ku, 1988).

3.2 Hydroxide Precipitation

The lowest solubility limit of a metal ion may not be reached until the pH of the particular metal sludge is half to a whole unit above the pH where precipitation begins to occur. A good example is the divalent zinc ion. Most of the zinc metal will precipitate when a pH of 8.4 is reached. However, the maximum insolubility of the zinc cation is reached at pH 10. It is recognized that different crystal structures of zinc precipitate form at different pH values. Also, if the pH increases above pH = 12, the precipitated zinc hydroxide will become slightly more soluble. In this case a different form of hydroxide is produced. Therefore, a definite pH range is in order for practical reasons.

3.3 Sulphide Precipitation

Sulphide precipitation is another method for removing metals from metal finishing process wastewaters. Sulphide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation. The high reactivity of sulphides (S^{2-}, HS^{-}) with heavy metal ions and the insolubility of heavy metal sulphides over a broad pH range are attractive features compared with the hydroxide precipitation process. Sulphide precipitation can also achieve low metal solubilities in the presence of certain complexing and chelating agents (EPA Summary Report, 1980). Metal sulphides have much lower solubilities than metal hydroxides and are not amphoteric. Metal sulphide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges (Peters et al., 1984). However, there are potential dangers in the use of sulphide precipitation processes. A sulphide reagent coming into contact with an acidic waste stream can result in the evolution of toxic H_2S fumes. Therefore, it is essential that this precipitation be performed in a basic medium.

There are two sulphide precipitation processes; soluble sulphide precipitation (SSP) and insoluble sulphide precipitation (ISP). The main difference between the two processes is the means of introducing the sulphide ion into the wastewater. In the SSP process, the sulphide is added in the form of a water-soluble sulphide reagent such as Na_2S and NaHS. In the ISP process, a slightly soluble but non-toxic ferrous sulphide (FeS) slurry is added to the wastewater to supply the sulphide ions needed to precipitate the heavy metal contaminants. The technique involves an exchange of ions between iron sulphide (slightly soluble) and the sulphide of a heavy metal (much less soluble). The process operates on the principle that FeS will dissociate into ferrous ions and sulphide ions to the degree predicted by its solubility product. As sulphide ions are consumed, additional FeS will dissociate to maintain the equilibrium concentration of sulphide ions. In alkaline solutions, the ferrous ions will precipitate as ferrous hydroxides. Most heavy metals have sulphides less soluble than ferrous sulphide, thus they will precipitate as metal sulphides.

An advantage of the ISP process is the absence of any detectable H_2S odour because FeS has a low solubility in water. Therefore, the tendency of FeS to react with water and thereby generate H_2S gas is low as compared with an equivalent amount of a very soluble sulphide. The first reaction proceeds to a much lower degree than does the second reaction:

$$FeS(s) + 2H_2O \rightleftharpoons Fe^{2+} + 2OH^- + H_2S(g) \qquad (3.3-1)$$

$$Na^+ + HS^- + H_2O \rightleftharpoons OH^- + H_2S(g) + Na^+ \qquad (3.3-2)$$

It is important to recognize that, in the case of reaction (3.3−1), the amount of FeS added to the solution has no effect on the amount of H_2S in the air above it. This is true because once you have saturated a solution with an insoluble substance, like FeS, no more can dissolve. However, in the case of reaction (3.3−2) any increase in the amount of sulphide that would occur with poorly controlled addition of a soluble sulphide leads to an increase in the concentration of H_2S in the air (Schlauch and Epstein, 1977). Systems using soluble sulphides as precipitating agents do not have this advantage (Schlauch and Epstein, 1977).

3.4 Insoluble Sulphide Precipitation (ISP)

In the ISP process, the dissolved sulphide ions precipitate as a metal sulphide any metal with a sulphide solubility less than that of FeS. As shown in Table 3.1, the only heavy metal with a sulphide more soluble than FeS is manganese. In an alkaline solution, the ferrous ions generated in the dissociation of the FeS will precipitate as hydroxides. In order to maximize the driving force for the precipitation, a sulphide precipitant must be chosen having a sufficiently high equilibrium sulphide ion concentration. In practice, ferrous sulphide is the precipitant normally chosen because it has a comparatively higher solubility than have the heavy metals, and FeS is considered non–toxic.

Table 3.1 Solubility Product Constants at 25 °C (Benefield et al., 1982)

Compound	K_{sp}
MnS	7.0 x -16
FeS	4.0 x -19
ZnS	1.6 x -23
PbS	7.0 x -29
CuS	8.0 x -37
Fe_2S_3	1 x -88
$Zn(OH)_2$	4.5 x -17
$Fe(OH)_2$	1.8 x -15
$Fe(OH)_3$	6.0 x -38

Table 3.1 Solubility Product Constants at 25 °C Continued (Benefield et al., 1982).

Compound	K_{sp}
$Pb(OH)_2$	4.2 x -15
$Cu(OH)_2$	1.6 x -19
$CaSO_4$	2.5 x -05

The ISP process precipitates dissolved metals as sulphides by mixing the wastewater with an FeS slurry in a solid/liquid contact chamber. Since the FeS has very low solubility with a S^{2-} concentration of about 0.02 μg/L, emission of H_2S or contamination of the wastewater by sulphide ion is minimized (Kim, 1980). In practice, FeS, which is freshly prepared by mixing $FeSO_4$ and NaHS, is used. Using this method of preparation of FeS does not eliminate H_2S emissions entirely, hence some control measures are required in its production.

Furthermore, the addition of FeS is not automatically controlled in response to the quantity of dissolved metal; thus, the ISP process requires at least 50 % more than the stoichiometric amount of FeS. The following reactions occur when FeS is introduced into a solution initially made basic with lime and containing dissolved metals and metal hydroxide:

$$FeS \rightarrow Fe^{2+} + S^{2-} \tag{3.4–1}$$

$$M^{2+} + S^{2-} \rightarrow MS \downarrow \tag{3.4–2}$$

$$M(OH)_2 \rightarrow M^{2+} + 2(OH)^- \tag{3.4–3}$$

$$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2 \downarrow \tag{3 4–4}$$

It is important to note that the reactions (3.4–3) and (3.4–4) compete with each other in the removal of the metal ions but due to the lower solubility products for the metal sulphides, that is what precipitates. The addition of ferrous ions to the wastewater and their precipitation as ferrous hydroxide [$Fe(OH)_2$] results in a considerably larger quantity of solid waste from this process than from a conventional hydroxide precipitation process especially considering that calcium sulphate is often precipitated and an excess of lime and ferrous sulphide are usually provided (Kim, 1980). As with soluble sulphide precipitation processes, the ISP process achieves an almost complete conversion of previously precipitated metal hydroxides to the metal sulphides if enough time is permitted for the conversion to take place. As the precipitation is terminated, the slurry probably contains $CaSO_4$, $Fe(OH)_2$, $Fe(OH)_3$, MS, and unreacted $Ca(OH)_2$ and FeS. When the precipitation is first initiated, the dissolved metal will precipitate as the hydroxide (MOH) because of the relatively large concentrations of both the metal and the base. When the insoluble sulphide precipitant is added the MOH will be converted to MS (Peters and Ku, 1988).

The six main reactions which are involved in this process are shown in Figure 3.2. Yet another reaction, not shown in Fig. 3.2, is that involving the oxidation of ferrous ion to ferric ion if the precipitation is carried out in contact with air. Then the less soluble ferric hydroxide is also precipitated.

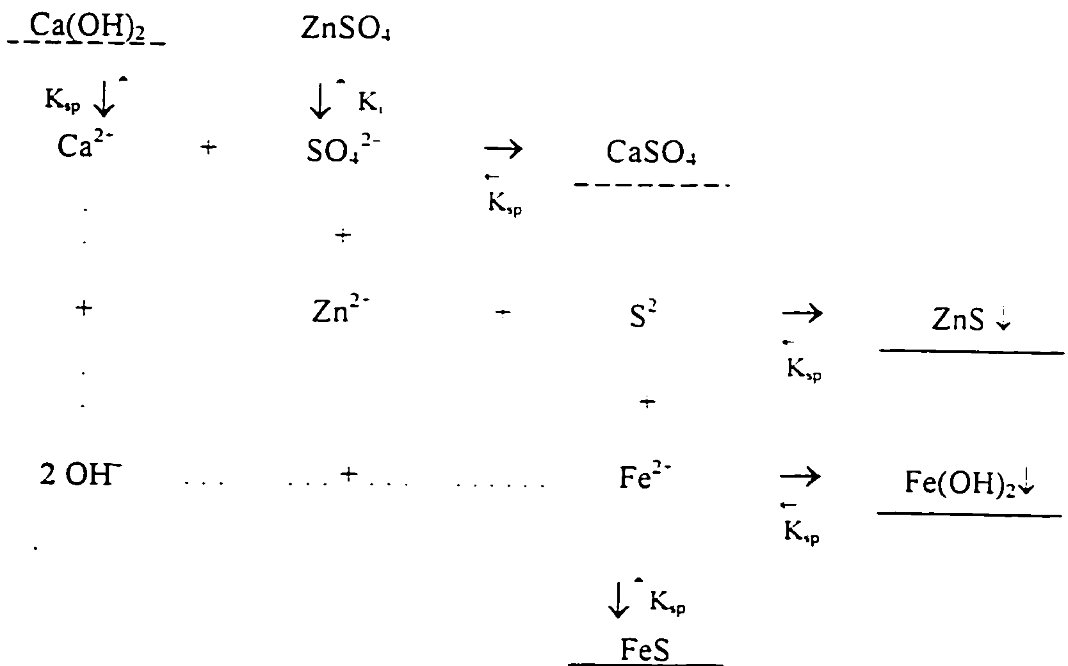


Figure 3.2 Precipitation of Zinc Ions and Related Reactions in Basic Slurry of Lime and Ferrous Sulphide (ISP) (- - - - indicate slightly soluble compounds, _____ indicate insoluble compounds).

3.5 pH Adjustment by CO_2

For this study, addition of CO_2 is used as a method for reducing the pH of treated wastewaters to produce the desired neutral solution. The elevated pH of lime treated effluents make it necessary to reduce the pH to permissible emission levels. It is clearly evident, however, that complete sludge removal is essential before the pH adjustment step is started. The most commonly used method for pH adjustment is by treatment with carbon dioxide (Brouzes, 1975). When CO_2 dissolves in water, it reacts with water to produce the hydrogen and bicarbonate ion (Chang and McCoy, 1993). The carbonate system is one of the major acid–conjugate base systems in natural waters. The chemical species that make up the carbonate system – gaseous CO_2, $CO_{2(g)}$, aqueous or dissolved CO_2, $CO_{2(aq)}$, carbonic acid, H_2CO_3, bicarbonate, HCO_3^-, carbonate CO_3^{2-}, and carbonate containing solids. The various components of the carbonate system are interrelated by the following equilibria (Snoeyink and Jenkins, 1980):

$$CO_2(g) \Leftrightarrow CO_2(aq); \qquad K = K_H = 10^{1.5} \tag{3.5-1}$$

In the above equation K_H is Henry's constant.

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3; \qquad K_1 = 10^{2.8} \tag{3.5-2}$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- ; \qquad K_2 = 10^{-3.5} \qquad (3.5\text{–}3)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}; \qquad K_3 = 10^{-10.3} \qquad (3.5\text{–}4)$$

The constants, K_i, are the respective equilibrium constants in reactions 3.5–2 through 3.5–4. Hence, any metal ions remaining in the treated solutions with post–carbonation treatment may combine with any anion formed by the carbonate system to form a metal carbonate precipitate. The formation of carbonic acid in a basic solution allows for the decrease in pH of the solution. Controlling the quantity of carbon dioxide fed to the treated solution controls the pH level of the resulting solution. It is apparent that as the carbonate ion concentration in the treated water is increased, some of the remaining metal ion will be precipitated as the carbonate. Hence, a final solids separation step may be necessary to remove the final sludge.

3.6 Ozonation

Ozone, a powerful oxidant, along with chlorine and hydrogen peroxide, are used commercially as oxidants in potable water and wastewater treatment plants. Ozone has the ability to oxidize a great number of organic and inorganic materials, especially those deemed to be hazardous. Some organic materials may be oxidized by ozone to produce CO_2 and water, or in the case of inorganic compounds, stable, insoluble metal oxide products. Oxidized products are less harmful than those produced by chlorination. Therefore, ozonation is attracting much attention for water treatment. Ozonation was chosen as the preferred method for the removal of pyridine, formaldehyde, and lead metal ions from wastewaters in this research.

Ozonation can achieve high purity levels of waters for even refractory pollutants. Ozone has a thermodynamic oxidation potential that is the highest of the common oxidants, 2.07 V. In principle, ozone should be able to oxidize inorganic substances to their highest stable oxidation states and organic compounds to carbon dioxide and water (Glaze et al., 1987). To be really effective however, the ozonation processes require the adoption of proper operating conditions chosen on the basis of the specific chemical properties and kinetic features of the systems under examination Ozone can react with organic substrates according to different chemical mechanisms ranging from ionic to radical pathways (Andreozzi et al., 1991).

3.7 Ozone Generation

Ozone is made by rupturing the stable oxygen molecule, forming two oxygen fragments, which can combine with oxygen molecules to form ozone:

$$O_2 \Leftrightarrow 2[O] \qquad (3.7\text{-}1)$$

$$2[O] + 2O_2 \Leftrightarrow 2O_3 \tag{3.7-2}$$

Nature generates ozone continuously by means of sunlight acting upon oxygen in the atmosphere, or intermittently by lightning passing through the air. This latter, natural process is simulated in the production of commercial ozone by passing high voltage electrical discharges through air or oxygen (Rice and Browning, 1980).

3.8 Ozone Decomposition

The stability of dissolved ozone (or its half-life) is readily affected by pH, ultraviolet (UV) light, ozone concentration, and the concentration of radicals, $OH^{\bullet}$, formed during ozone generation. Ozone decomposition is first order with respect to both ozone and hydroxide ions producing oxygen as the final product (Langlais et al., 1991). The overall rate equation is:

$$-\frac{d[O_3]}{dt} = k[O_3][OH^-] \tag{3.8-1}$$

where

$$k = \frac{k'}{[OH^-]} \tag{3.8-2}$$

and k' is the pseudo first–order rate constant for a given pH value.

This mechanism makes oxidation especially attractive because ozone decomposes to form oxygen. When the mechanisms are initiated by the presence of hydroxide ion, and when organic substances are present, the hydroxyl radical is the agent which does most of the chemical destruction because it is so reactive (Gordon et al., 1988). Hence, it is apparent that to continue this form of oxidation, ozone must be continuously added to the wastewater during the oxidation process. In an aqueous solution, ozone may act on various compounds in the following two ways: 1) by direct reaction with the molecular ozone, and 2) by indirect reaction with the radical species that are formed when ozone decomposes in water, (Hoigne and Bader, 1978), to be explained in Sec 3 9

3.9 Ozone/Ultraviolet Radiation Process

The combination of ultraviolet radiation and ozone is a powerful source of hydroxyl radicals via hydrogen peroxide formation and photolysis (Peyton and Glaze, 1988). The combination of ozonation with UV radiation is promising because of the necessity to form $OH^{\bullet}$ radicals to oxidize the required hydrocarbon. The UV radiation dissociates ozone into an oxygen molecule and oxygen atom. The latter reacts with water to produce $OH^{\bullet}$ radicals (Ikemizu et al., 1987).

$$O_3 \xrightarrow{h\nu} O_2 + O^{\bullet} \tag{3.9-1}$$

$$O^{\bullet} + H_2O \longrightarrow 2OH^{\bullet} \tag{3.9-2}$$

There is a synergistic effect between ozone and UV radiation. The UV radiation acts as a catalyst by enhancing the oxidation rate of organics being destroyed. The production of the hydroxyl free radical by the reaction of UV radiation and ozone is responsible for this increased reaction rate (Francis, 1987). It is also possible for another radical to form; the hydroperoxide ion, HO_2^- (Paillard et al., 1987) according to the following equations:

$$O_3 + H_2O \xrightarrow{h\nu} O_2 + H_2O_2 \tag{3.9-3}$$

$$H_2O_2 + H_2O \Leftrightarrow HO_2^- + H_3O^+ \tag{3.9-4}$$

Thus a compound could be oxidized either by a direct means, such as molecular ozone or UV radiation, or by an indirect method based on a radical mechanism producing $OH^{\bullet}$ radicals. In essence, it appears that the O_3/UV and O_3/H_2O_2 processes are one and the same; in the former, one is forming hydrogen peroxide in situ, rather than adding it from an external source. In this thesis, only the O_3/UV process is considered because of the interest in observing the decomposition rates of UV radiation, with and without ozone, on water treatment processes. The reactions produced when UV radiation is combined with ozone are complex and the oxidation process is likely to be a mixture of photoexcitation, ozonation, and reactions with the free radicals produced from the photolysis of ozone. The work to be described in this thesis does not attempt to evaluate the mechanisms of the UV–ozone process. Its main purpose is to investigate whether the oxidation rate by ozonation can be increased with the combination of UV and ozone to give a higher total oxidation rate, or synergistic effect, than is possible by either oxidizing agent alone.

3.10 Ozone Reaction with Inorganics

The reaction with inorganic compounds found in water generally follows a first–order kinetic law with respect to both ozone and the oxidizable compound. The ozone disappearance rate can be expressed by equations of the following form, where [M] represents the concentration of the inorganic pollutant:

$$-\frac{d[O_3]}{dt} = k_{O_3}[O_3][M] \qquad (3.10\text{–}1)$$

Metals which can exist in solution in more than one valence state generally can be oxidized to their higher (or highest) state by means of ozone. For example, iron (II) is quantitatively oxidized to iron (III), which then hydrolyzes to produce the easily flocculated $Fe(OH)_3$, and which can then be readily separated from solution (Rice, 1980).

$$O_3^- + Fe^{2+} + H_2O \longrightarrow O_2 + Fe^{3+} + 2OH^- \qquad (3.10\text{–}2)$$

If these oxidized metal ions or their hydrolysis products are insoluble in water, ozonation will allow their direct conversion to filterable compounds. Hydroxides of many of these metals are insoluble, thus conducting ozonation in a basic pH range should allow their removal from solution.

Chapter 4.0 Analytical Equipment

Descriptions of the analytical instruments and methods for determination of the concentrations of the heavy metals, organic compounds and ozone used in this study are presented in this chapter. These include the Atomic Absorption Spectrophotometer (AAS) and pH electrode sensor used in the heavy metal removal experiments. Also included for the organic compound analyses was a Total Organic Carbon (TOC) analyzer and a Gas Chromatograph (GC) analyzer.

4.1 Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectroscopy is used for the determination of dissolved metals in all types of water samples. For analysis, a sample is aspirated into a flame and atomized at high temperature. A light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. The lamps used to provide the light beam are called hollow cathode lamps and made of, or lined with, the element of interest and filled with an inert gas. These lamps, when subjected to a current, emit the spectrum of the desired element together with that of the filler gas. Each element has its own characteristic absorption wavelength and, therefore, lamps composed of each element are employed. In AAS, the element of interest in the sample is not excited, but is merely dissociated from its chemical bonds in an unionized state. The element is then capable of absorbing radiation from the light source. The amount of radiation absorbed in the flame is proportional to the concentration of the element present in the flame and this principle is the basis of AAS. This principle follows what is commonly known as the Beer Lambert law. Furthermore, chemical interferences are often experienced and are caused by the inability of the flame to atomize the desired compound in the sample because the flame temperature is not sufficiently high to dissociate the metal compound. Therefore, in this situation, the flame mixture must be altered to remove the chemical interferences associated with the respective metal ions in solution. In this thesis, the air–acetylene flame was utilized for the detection of zinc, lead, copper, sodium and iron metal ions. The only metal ion that did not utilize this flame mixture was calcium, which required a nitrous oxide–acetylene flame. The nature of these chemical interferences with the AAS analysis did not allow the possibility of performing analysis for combinations of two or more heavy metals at the same time.

4.2 pH Electrode Sensor

The concept of pH is a means of quantitatively expressing the degree of effective acidity or alkalinity or the hydrogen ion concentration. It is important to note that the pH electrode used in the ISP process was different than the one used for the hydroxide process. The pH probe used in the hydroxide treatment process was a Low Maintenance Triode Electrode containing a Ag/AgCl filling solution. The reference materials, Ag/AgCl, and combination electrodes are incompatible with samples containing sulphides. Sulphides would cause reactions with the silver fillings, coating the sensing bulb, and damaging the electrode. Therefore, for pH measurements in the ISP process, a special Ross

Combination Electrode with an internal filling solution of 3M KCl and an automatic temperature compensation probe was utilized.

4.3 Total Organic Carbon (TOC) Analyzer

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. The TOC analysis is independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by biochemical or chemical processes. To determine the quantity of organically bound carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively. The TOC methods utilize heat, and oxygen, ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide. The CO_2 formed by the TOC analyzer is measured directly by a nondispersive infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample. A small, constant volume of the aqueous solution is fed into an electrically heated quartz glass tube whose interior surface is coated with a catalyst. Nitrogen gas, containing a small amount of air, is allowed to flow through the heated tube. As the sample is blown into the heated chamber it vapourizes instantly and any hydrocarbon is oxidized quickly yielding the regular products of complete combustion. A CO_2 detector provides a recording of a CO_2–peak whose height is proportional to the organic present in the sample.

4.4 Gas Chromatograph (GC)

In gas chromatography a mobile phase (a carrier gas) and a stationary phase (column packing) are used to separate individual compounds. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven, and detector are maintained. Stationary–phase material and concentration, column length and diameter, oven temperature, carrier gas flow, and detector type are the controlled variables. When the sample solution is introduced into the column, the organic compounds are vapourized and moved through the column by the carrier gas, usually helium. They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phase for the different components.

The organic samples used in the ozonation experiments, pyridine and formaldehyde, alone and in combination, were analyzed using a GC. The particular GC model was selected because it contained a flame ionization detector (FID). The FID is highly sensitive to organic carbon–containing compounds. The detector consists of a hydrogen/air diffusion flame burning at the end of a jet. The response of the detector is directly proportional to the total mass entering the detector per unit time and is independent of the concentration of the carrier gas. For the separation and detection of pyridine and formaldehyde, a specific column of type 10% Fluorad FC–431 on Chromasorb W–HP 80/100 was utilized. Refer to the Appendix B for the parameters set for the GC operation. The results generated by the GC were provided by a recorder.

These results were used solely as qualitative measurements to observe the decrease in peak size of the organic compounds in the aqueous solution during the oxidation experiments using ozone. The GC was strictly utilized only to provide an immediate guide to the approximate efficiency of the ozonation treatment while the experiments were being performed. Quantitative results were based on TOC analysis The GC analysis were rapid and could be performed while the experiments were in progress, while the TOC analysis were performed later in another location.

Chapter 5.0 Preparation of Solutions and Reagents

In this chapter details of the methods for preparing the synthetic wastewater test solutions are given along with the methods for preparing the several reagents used in forming the precipitates which are part of the experimental treatment process. The actual quantities of the chemicals and volumes of solutions are given. The handling of lime precipitant was a special problem because it is only slightly soluble and hence needed to be prepared as a slurry. Similarly, the ferrous sulphide precipitant was an aqueous slurry which needed to be basic at all times to prevent evolution of H_2S gas. As a precaution the preparation of ferrous sulphide was accomplished in the fume hood.

5.1 Preparation of Wastewater Solutions

Stock solutions of approximately 200 ppm of each metal ion were prepared in volumes of 205 mL from soluble metal salts using deionized, distilled water. This water was prepared by treating distilled water with an ion exchanger. The total volume of solution remaining to be treated was 200 mL, in each case after a 5 mL sample of wastewater was extracted for an initial analysis by AAS. The following quantities added to form 205 mL of solution of Cu^{2+}, Zn^{2+}, and Pb^{2+} metal ion in the solutions were 0.161 g $CuSO_4 \bullet 5H_2O$, 0.180 g $ZnSO_4 \bullet 7H_2O$, and 0.0655 g $Pb(NO_3)_2$, respectively. These quantities were carefully weighed out and charged to the water in the 300 mL Erlenmeyer flasks which would subsequently serve as treatment reactors.

5.1.1 Preparation of Aqueous Lime, $Ca(OH)_2$, Slurry

The function of the aqueous lime slurry could be considered two fold. to raise the pH level of the treated wastewater to a value of about 11, and to precipitate all the metal ion present. The lime dosage actually used was in excess of the stoichiometric quantity equivalent to the concentration of metal ion in solution and was selected to be 50 % above this stoichiometric quantity for all three metal ions to ensure as complete a removal of the metals as possible. For all the hydroxide experiments, the quantity of lime was based on a treatment volume of 25 mL of lime slurry to be added to the wastewater solutions. The aqueous lime slurries were prepared prior to the beginning of the experiments by dispersing the appropriate mass of lime in a 100 mL water slurry mixture from which 25 mL was used for treatment of one sample of wastewater. The aqueous lime slurry was added to the wastewater solutions by means of a modified 25 mL pipette. The modification to a normal 25 mL pipette involved cutting off the capillary end of the pipette so that well mixed slurry could be drawn into it rapidly before any settling of the solid occurred.

5.1.2 Preparation of Solid $Ca(OH)_2$ and Aqueous NH_4OH Precipitants

Because the use of the lime slurry tended to dilute the wastewater samples, solid lime was added to perform the precipitation for comparison of the results. For solid hydrated lime treatment, the quantity of lime added was determined from preliminary trial and error experiments performed to determine the appropriate amount of lime necessary to raise the pH of the metal stock solutions to the pH range where the respective metals exhibit their minimum solubilities. This method was also used to determine the amount of liquid ammonium hydroxide required for treatment of the waste metal ions in solution. The mass of solid $Ca(OH)_2$ added to the wastewater solutions was 0.0420 g, 0.0440 g, and 0.0200 g for Cu^{2-}, Zn^{2-}, Pb^{2-} treatments, respectively. These values indicated that no excess lime was added to raise the solution pH of the copper and zinc ions to be treated. However, the lead ion treatments required 50 % excess solid lime to raise their solution pH. Again, by trial and error the quantity of NH_4OH was determined to raise the pH of the wastewater samples to the point of maximum precipitation.

Aqueous ammonium hydroxide was added to the wastewater solutions by means of an eppendorf pipette. The amount of 200 μL NH_4OH was added to all the stock metal waste solutions for treatment. In this case, the excess amount of base was at least 30 % above the stoichiometric requirements.

5.1.3 Preparation of FeS Sludge Precipitant

The ISP process involved the production of FeS sludge in preparation for the treatment of wastewaters. The FeS sludge was freshly prepared by mixing $FeSO_4$ and NaHS. The dosage of NaHS and $FeSO_4$ was determined by a stoichiometric determination of the amount required to produce the desired quantity of FeS necessary to remove the specific metal ion while still providing an excess amount of 50 %. Separate 100 mL solutions of NaHS and $FeSO_4$ were prepared in glass flasks. Preparation of the NaHS solution requires that the pH of the water it was added to was in the basic range to prevent production of H_2S gas. To prevent and overcome H_2S gas generation, 0.200 g solid $Ca(OH)_2$ was added to the designated hydrosulphide flask solution to maintain an approximate pH 11 prior to NaHS addition. The quantity of NaHS determined was then weighed and added to this basic water solution in a fume hood. Both the NaHS and $FeSO_4$ solutions were stirred vigorously for five minutes. After mixing was complete, the NaHS solution was transferred to a Erlenmeyer glass flask and mixed at 400 rpm. To this hydrosulphide solution, the ferrous sulphate solution was slowly added forming a concentrated slurry of FeS instantaneously. The mixing speed was increased to 1000 rpm and allowed to continue for an additional five minutes.

5.2 Preparation for Ozonation Experiments

Since pure liquids of pyridine, C_5H_5N, and formaldehyde, HCHO, were provided, calculated equivalent concentrations of 200 ppm of the total organic carbon content were prepared for both chemicals. The resulting solutions were analyzed and dilutions were made as required to obtain the approximate total organic carbon concentration desired of 200 ppm TOC in C_5H_5N and HCHO Thus, it was determined that for a water solution of 500 mL, the amount of C_5H_5N, and HCHO was 175 µL, and 435 µL, respectively. The pyridine and formaldehyde solutions, with a concentration of 400 ppm TOC to be treated, were prepared by doubling the amounts of C_5H_5N and HCHO and subsequently analyzing the solutions to ensure accuracy in the preparations. The heavy metal waste stock solutions to be treated by ozonation were prepared by mass as described previously, but for a solution volume of 500 mL. Furthermore, it should be noted that TOC is equivalent to the total organic carbon, in ppm of organic carbon. TOC is not equal to the concentration of pyridine and formaldehyde. However, 60 % removal of TOC of either chemical is equivalent to 60 % removal of pyridine or of formaldehyde.

Ozone gas was produced by utilizing an ozone generator. However, the production of ozone was problematic because of certain limiting operating parameters. The limiting parameters were resistance and current. Ozone is produced by passing a high–voltage electrical discharge through oxygen gas. Hence, a resistivity meter was utilized to control the amount of current. The ozonation experiments were modified to suite the limitations of the ozone generator.

5.2.1 Ozone Utilization Rate

The method described is a semi–batch method which involves determination of ozone consumption during continuous addition of gaseous ozone to a batch reactor. The results obtained in this method depend upon the mass–transfer characteristics of the reactor. The ozone utilization rate is determined by the oxidation of KI in acid solution followed by titration with standard sodium thiosulphate ($Na_2S_2O_3$). The following reactions occur:

$$2KI + O_3 + H_2O \Leftrightarrow O_2 + 2KOH + I_2 \qquad (5.2.1-1)$$

$$2Na_2S_2O_3 + I_2 \Leftrightarrow 2NaI + Na_2S_4O_6 \qquad (5.2.1\text{–}2)$$

Therefore, the total quantity of ozone dissolved during the time of the test (2 minutes) is calculated using the following equation:

$$M_{O_3} = M_{I_2} = \frac{M_{S_2O_3^{2-}} \cdot V_{S_2O_3^{2-}}}{2 \cdot V_{solution}} \qquad (5.2.1\text{–}3)$$

In the above equation, M and V are molarity, and volume of the compound measured, in mol/(L.min) and L, respectively.

The chemicals required for the titrimetric analysis of ozone were the oxidation–reduction reagents potassium iodide (KI), sodium thiosulphate ($Na_2S_2O_3$), sulphuric acid, and starch indicator solution. A 2% KI solution was prepared by dissolving 10 g KI in 400 mL distilled water. A 0.005 N $S_2O_3^{2-}$ solution was prepared by dissolving 0.395 g thiosulphate in 500 mL distilled water. In addition 2N sulphuric acid was prepared by diluting 56 mL of concentrated acid to 1 L of aqueous solution.

First, the ozone generated under steady–state was passed into a 200 mL solution containing 2% KI for two minutes. Then 10 mL of 2N H_2SO_4 was added to this solution and titrated with standardized 0.005N $Na_2S_2O_3$ until the yellow iodine colour almost disappeared. To this solution 1 to 2 mL starch indicator solution was added and the titration was continued just until the blue colour disappeared. The absorption rate of ozone (M_{O_3}) was then calculated using equation 5.2.1–3. When the ozone utilization rate was determined, the ozone was then fed to the treatment reactor to decompose the organic compounds and precipitate the heavy metals again using the same volume of reacting solution (0.500 L) and ozone generation conditions.

Chapter 6.0 Experimental Aspects

In this chapter, the experimental procedures and equipment are presented for both the precipitation and ozonation research studies. In the first series of experiments, the potentially polluting soluble metals are removed by precipitation to form highly insoluble hydroxide or sulphide precipitates. In the second series of experiments an attempt is made to oxidize the soluble metals to form the metal oxides using ozone. Finally, soluble organic pollutants are removed by decomposition with ozone and UV radiation singly or in combination.

6.1 Hydroxide Precipitation

The hydroxide precipitation experiments were conducted in a continuously stirred, batch reactor. The reactor consisted of a 300 mL glass Erlenmeyer flask charged with 200 mL of test solution, a gas dispersion tube, and a calibrated variable speed mixer with a glass agitator. Experiments in which one specific metal was precipitated were duplicated. Mixing was initiated at a fixed speed and the 25 mL of treatment lime slurry was added to the reactor. For all performed experiments the mixing speed was kept constant at 1000 rpm. The time at which the treatment precipitant was added to the reactor was recorded and 10 mL samples of solution containing some precipitated solids were extracted every 15 minutes for the first hour and every hour after the first hour throughout the duration of the experiment. The experiments were performed for a total reaction time period of two hours. This two hour time period was the maximum allowed due to practical considerations. The treated samples were extracted using gas tight syringes fitted with membrane syringe filter units for filtration of the formed precipitate. The resulting samples were then preserved with 1 μL nitric acid and refrigerated until analysis of the residual metal ion concentration was conducted by AAS. Since all nitrates are soluble, HNO_3 was used to acidify samples to pH less than 2.0 to prevent post–precipitation of the residual metal ion between the time the sample was taken and subsequently analyzed. During each sample extraction from the wastewater solution, the pH, temperature and colour of the solution was observed and recorded. At the end of each experiment, the residual treated wastewater solution was filtered using a vacuum filter and a sample of the solution was acquired for AAS analysis. The above–mentioned experimental procedure was used for Cu^{2+}, Zn^{2+}, and Pb^{2+} precipitation by aqueous and solid calcium hydroxide, and aqueous ammonium hydroxide. The amount of solid $Ca(OH)_2$ required was determined by initial experimentation necessary to raise the pH of the stock wastewater solutions close to the minimum solubility points of the metals. Then, carbon dioxide gas was fed to the treated, filtered solution. The rate of CO_2 gas flow was not controlled or monitored because the sole objective at this point was to reduce the pH of the solution. Instead, during carbonation of the solutions, the pH was monitored until it was within the neutral range, pH 6–7. At this stage, a sample was extracted from the solution and analyzed as previously mentioned. One study was conducted for the removal of Pb^{2+} by aqueous $Ca(OH)_2$ where the flow of CO_2 gas was controlled at 0.10 mL/s and the mixing speed reduced to 400 rpm. The flow of CO_2 was determined by use of a bubble meter. For each unit pH decrease in the solution, a sample was extracted and analyzed accordingly. These experiments were conducted at room temperature and at 50 °C. Experiments conducted at 50 °C were performed by immersing the reactors in a constant temperature water bath and repeating the experimental process as mentioned above. See Figure 6.1 for a schematic diagram of the hydroxide precipitation process.

6.2 Insoluble Sulphide Precipitation (ISP)

The heavy metal wastewater stock solutions of Cu^{2+}, Zn^{2+}, and Pb^{2+} were prepared and analyzed as described in Section 5.1. The ISP process involved the production of FeS sludge for the treatment of the wastewater solutions. While still being mixed, the fresh FeS sludge produced was transferred to the reactor containing the wastewater solution to be treated. A volume of 25 mL of well mixed sludge was used to treat the wastewater. The experiments were conducted in the same manner as those for the hydroxide precipitation processes, that is, in a 300 mL continuously stirred batch reactor. The temperature at which all the sulphide precipitation experiments were conducted was 25 °C only although the experiments were duplicated. Samples were drawn and filtered but were not acidified before analysis. Nor were they carbonated. A variation of the ISP process was introduced for the treatment of lead wastewater because the results of the initial treatment were only partially successful. These variations included raising the pH of the lead wastewater solution before the addition of the FeS sludge using first NH_4OH and then $Ca(OH)_2$. See Figure 6.2 for the schematic diagram of the ISP process.

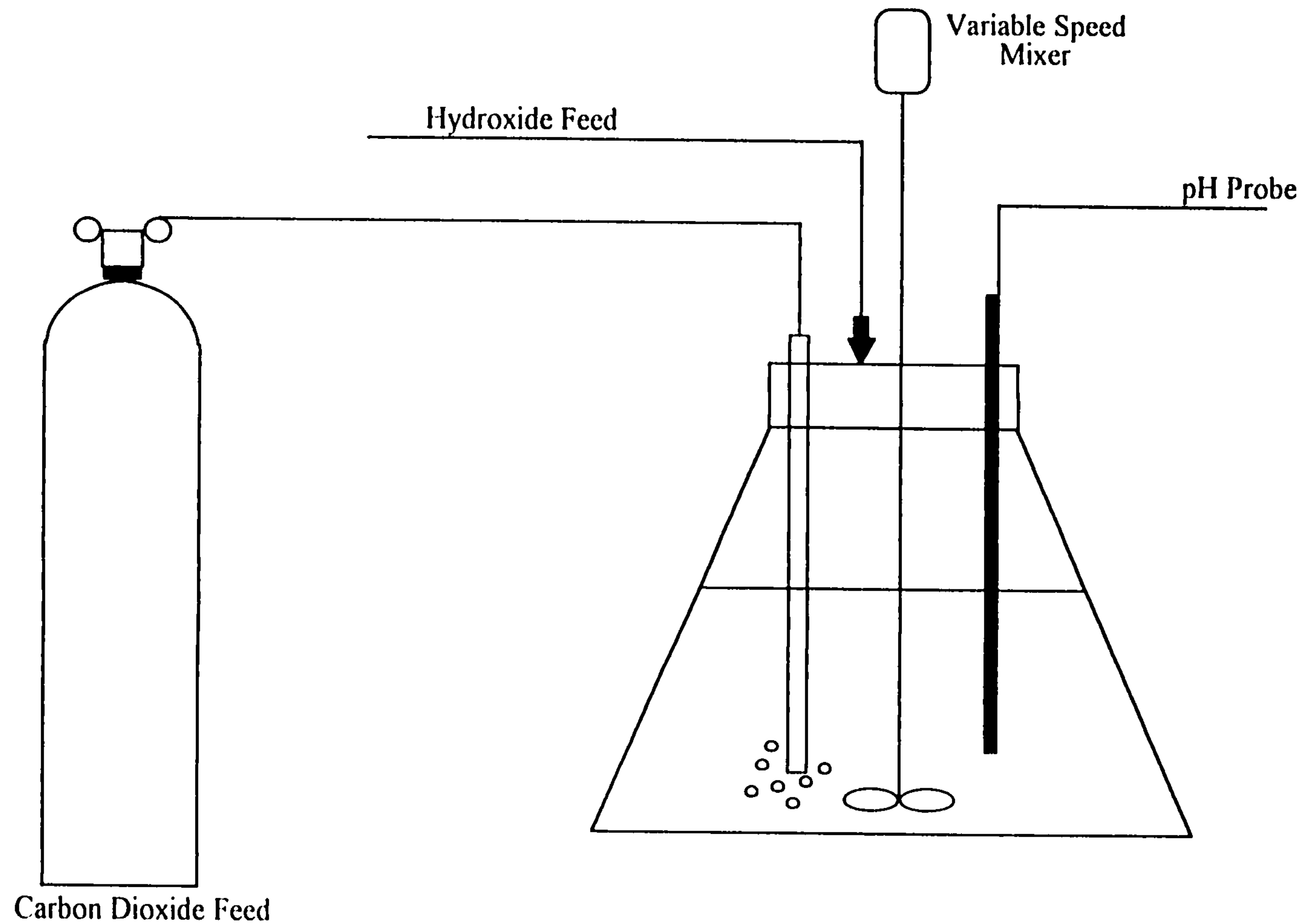


Figure 6.1 Schematic Diagram for the Hydroxide Process

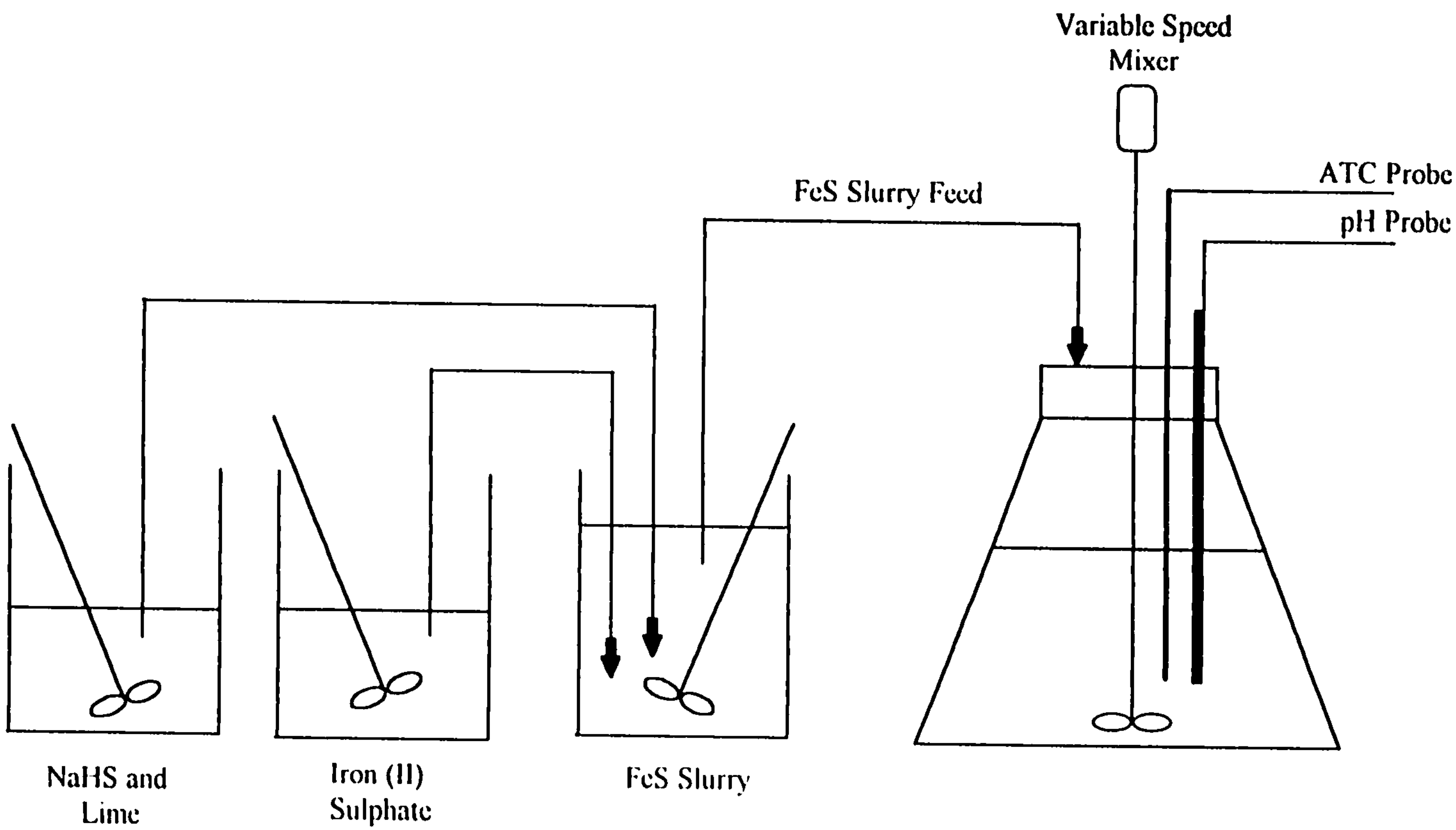


Figure 6.2 Schematic Diagram for the Insoluble Sulphide Precipitation Process.

6.2.1 Two–stage Precipitation of Lead with NH_4OH and Sulphide Sludge

Three experiments were conducted involving the addition of 300 μL NH_4OH to the lead–containing wastewater solution. The first experiment involved the addition of NH_4OH simultaneously with the FeS sludge. The second experiment involved the addition of NH_4OH initially to the lead wastewater where mixing occurred for 15 minutes after which the resulting solution was filtered and the concentration of the residual lead ion in solution was determined by AAS analysis. The FeS sludge was then prepared to 50 % more than the equivalent stoichiometric amount of Pb^{2+} left in solution and added to the residual partially treated wastewater solution. The third experiment was conducted in the same manner as that of the second experiment, except the residual solution was not filtered after NH_4OH had been added and mixed for 15 minutes The experimental methodology for this precipitation is essentially the same as outlined earlier for the ISP process.

6.2.2 Two–stage Precipitation of Lead with Solid Lime and Sulphide Sludge

Similar to the modified processes for lead precipitation utilizing NH_4OH, three experiments were conducted utilizing solid lime in the amount of 0.200 g as the base for raising the pH of the lead ion solutions. The three experiments were performed using an exactly analogous procedure as that using NH_4OH as the base.

6.3 Ozonation of Organics, and Dissolved Metals

The same equipment was used for all experiments utilizing ozone. The equipment arrangement is shown in Figure 6.3. A continuously stirred, batch reactor was employed to hold the 500 mL volume of organic wastewater to be treated. The physical specifications for the glass housing for the reactor is provided in Appendix B. As the experiments progressed, 10 mL samples of wastewater solution were extracted every 30 minutes until the end of the experiment. The duration of an experiment varied between three to six hours depending on the investigation under study. Samples were withdrawn from the reactor utilizing the opening made in the cork sealer housing the thermocouple Oxygen was fed to the ozone generator at a constant flow rate of 40 L/min as measured at atmospheric pressure and controlled in the system at a pressure of 10 psig. The flow rate of oxygen was determined using a wet test meter. The rate of ozone generation was determined by directing the ozone–oxygen flow fed to a 2% KI solution. After reaction of the ozone with the KI solution for 2 min, the ozone–oxygen flow was fed to the reactor. Ozone was dispensed into the reactor by means of a gas dispersion tube. Exhaust gases from the reactor were fed to a KI scrubber to ensure the complete removal of ozone before being vented to the atmosphere. The reactor also contained a glass stirrer designed specifically for the reactor.

The UV lamp employed was a specifically designed high intensity lamp for the photochemical reactions in the combined O_3/UV treatment processes. The lamp was designed with a round glass taper for sealing to the aperture of the reactor's glass housing

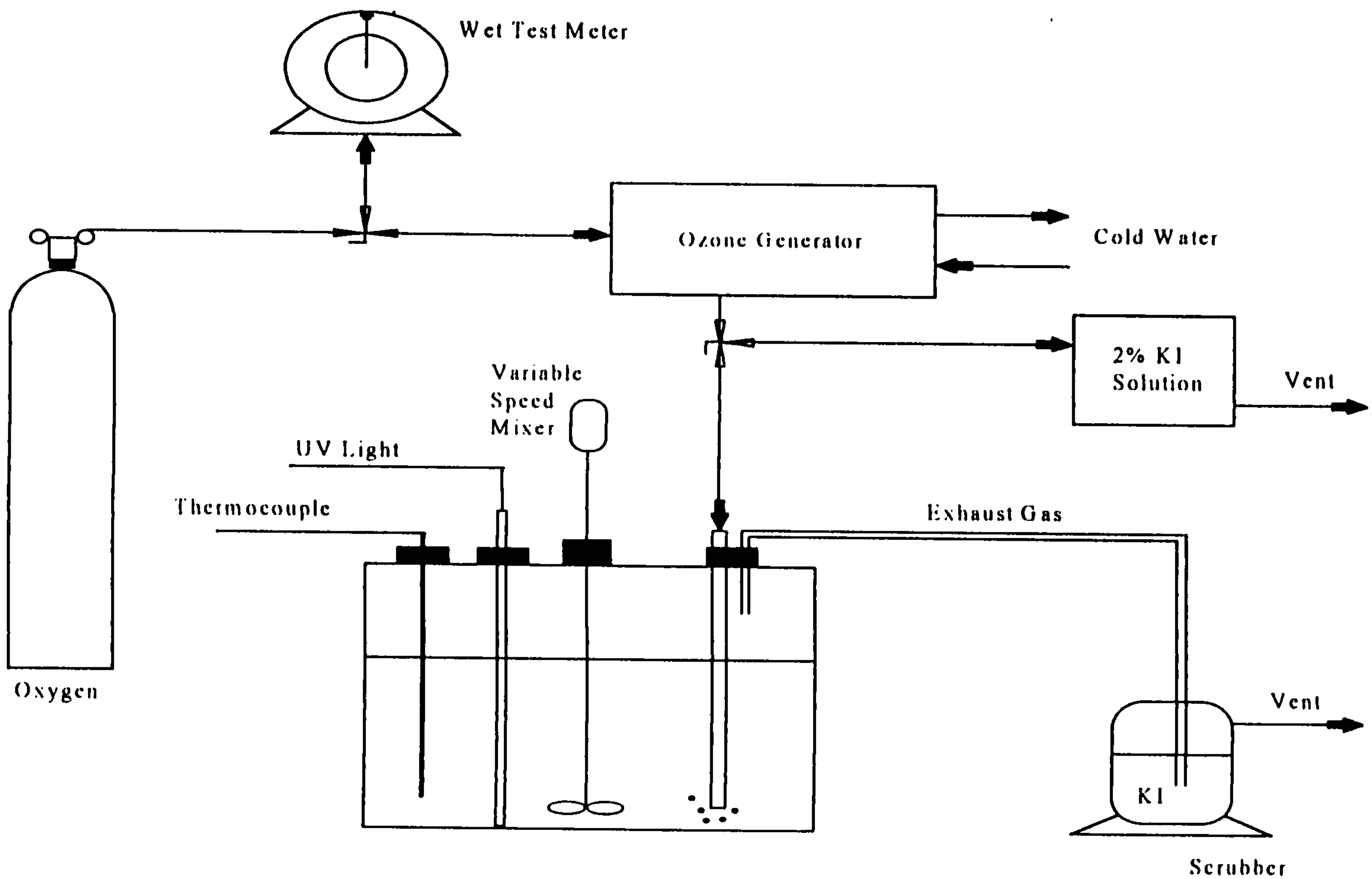


Figure 6.3 Schematic Diagram for the Ozone/UV Process.

lid. The light intensity from the UV lamp was 5000 $\mu W/s^2$ and primary emission was 254 nm for a required 8.0 inch lighted length. The UV lamp was specially ordered from UVP, Inc, California, USA. The mixing speed for all wastewater treated by ozonation was constant at 570 rpm. The operating temperature of the ozonation experiments was at room temperature. However, this temperature was not maintained completely constant with treatment processes involving exposure to UV radiation because of heat generated by the UV lamp. The heat generated increased the temperature of the solutions during experimentation. However, the temperature profile was the same for all the experiments involving UV radiation.

6.3.1 Organic Decomposition

The wastewater investigations involved the decomposition of the organic compounds, pyridine and formaldehyde. Experiments were conducted to decompose these compounds using three types of oxidation procedures: ozone only, UV radiation only, and the ozone/UV combination. Treatment included decomposition of pyridine alone, formaldehyde alone, and a combination of pyridine and formaldehyde. Treated water samples were extracted at regular time intervals and subsequently analyzed for total organic carbon (TOC) content. Furthermore, the treated samples were also analyzed by a Gas Chromatograph (GC) as the experiments progressed. Quantitative results were based on TOC analysis only. Preservation of the treated organic water samples, if necessary, were performed by covering them with parafilm and refrigerating them until the TOC analysis could be performed.

6.3.2 Metal Precipitation by Ozonation

The procedure for metal precipitation by ozone and UV radiation was the same as that outlined for the hydrocarbon decomposition. The metal ion in the wastewater to be precipitated was lead. Experiments for lead removal were conducted first with ozone only and then with the ozone/UV combination. Adjustments of pH were made to the wastewaters prior to treatment using solid $Ca(OH)_2$ and aqueous NH_4OH. Immediately following the addition of these chemicals to the metal ion wastewater in the reactor, the flow of ozone and/or exposure to UV radiation was started. Samples were extracted every 30 minutes for a duration of three hours. Samples were analyzed for pH and the residual metal ion concentration. Analysis and preservation of metal samples were the same as detailed in Section 6.1.

Chapter 7.0 Results and Discussion

This section presents the results and observations of the wastewater treatment techniques addressed in the objectives of this thesis. Solutions containing heavy metal ions were treated using different reagents to produce hydroxide and sulphide precipitates. Experiments were also performed to produce precipitates using ozonation processes. Solutions containing organic compounds were treated by combinations of ozone and UV radiation, alone and together, to destroy the organic compounds The quantitative results were based on the average values obtained from duplicated experimental runs performed for each treatment method. Detailed experimental results are listed in Appendices D and E. The results of the precipitation experiments with copper, zinc and lead metal ions by the precipitants $Ca(OH)_2$, NH_4OH, and FeS from aqueous solutions will be presented first.

7.1 Precipitation of Cu^{2+} as the Hydroxide using Lime and NH_4OH

Figure 7.1 shows the effect of the four variations in hydroxide precipitation of dissolved copper in the two hour time interval on the percentage removal of copper. After 15 min, more than 99.5 % of the Cu^{2+} was removed by all the hydroxide treatments. The removal rates of Cu^{2+} were approximately equivalent, varying from 99.8 to 99.9 % and maintaining steady–state values after 30 min, except for the treatment by aqueous $Ca(OH)_2$ at 50 °C for which the removal fraction for Cu^{2+} was 99.6 %. It is apparent that all four hydroxide precipitation methods are highly effective for copper. Although the

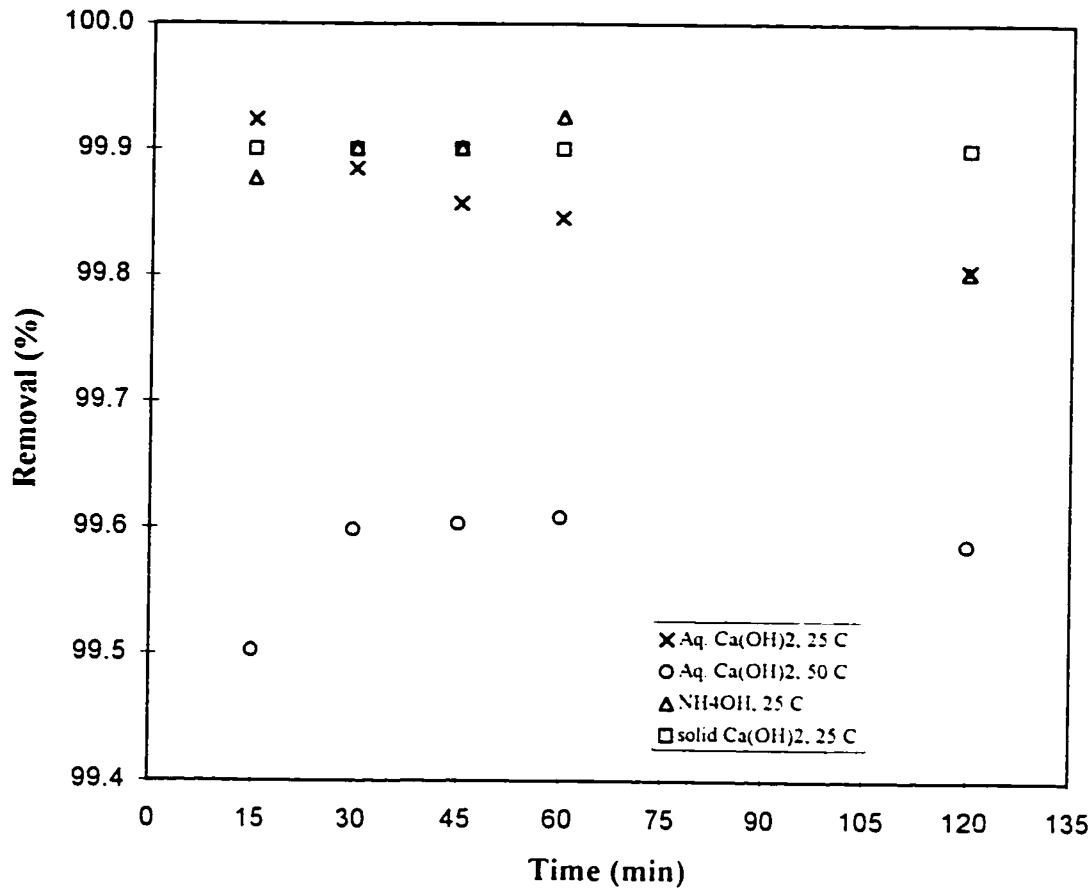


Figure 7.1. Removal of Copper Ions by Hydroxide Precipitation.

rates were very similar in value, the residual concentration of Cu^{2+} left in solution after treatment at 50 °C was 0.9 ppm as opposed to 0.4 ppm at 25 °C. It was better to operate the aqueous lime treatments at 25 °C for two reasons: it was a more energy efficient system requiring little or no additional thermal energy, and it resulted in the highest fractional removal rate for the dissolved copper.

Figure 7.2 shows the pH stability in each of the treatment processes involved in the precipitation of Cu^{2+}. When comparing the pH values for the aqueous lime treatments at the different operating temperatures, the pH decreased from 10.7 to 10.3 at 25 °C while treatment at 50 °C yielded pH decreases from 8.7 to 7.8 by the end of the experiments. Operating the aqueous lime treatments at a higher temperature decreased the solution pH thus moving copper away from its minimum solubility point possibly causing some resolubilization of the copper hydroxide precipitates previously formed. Thus, the copper ion concentration in solution increased within two hours, corroborating the decline in removal values shown in Fig. 7.1. The calcium concentrations as shown in Fig. 7.3 appeared to be scattered for treatments by aqueous lime while maintaining constant values for solid lime treatment. Aqueous lime treatment at 25 °C caused a continuous decrease in Ca^{2+} concentration indicating that some calcium ions were being precipitated out of solution probably as Cu^{2+}– Ca^{2+} solid complexes observed by the precipitate colour changes to be described in Sec 7.1.1.

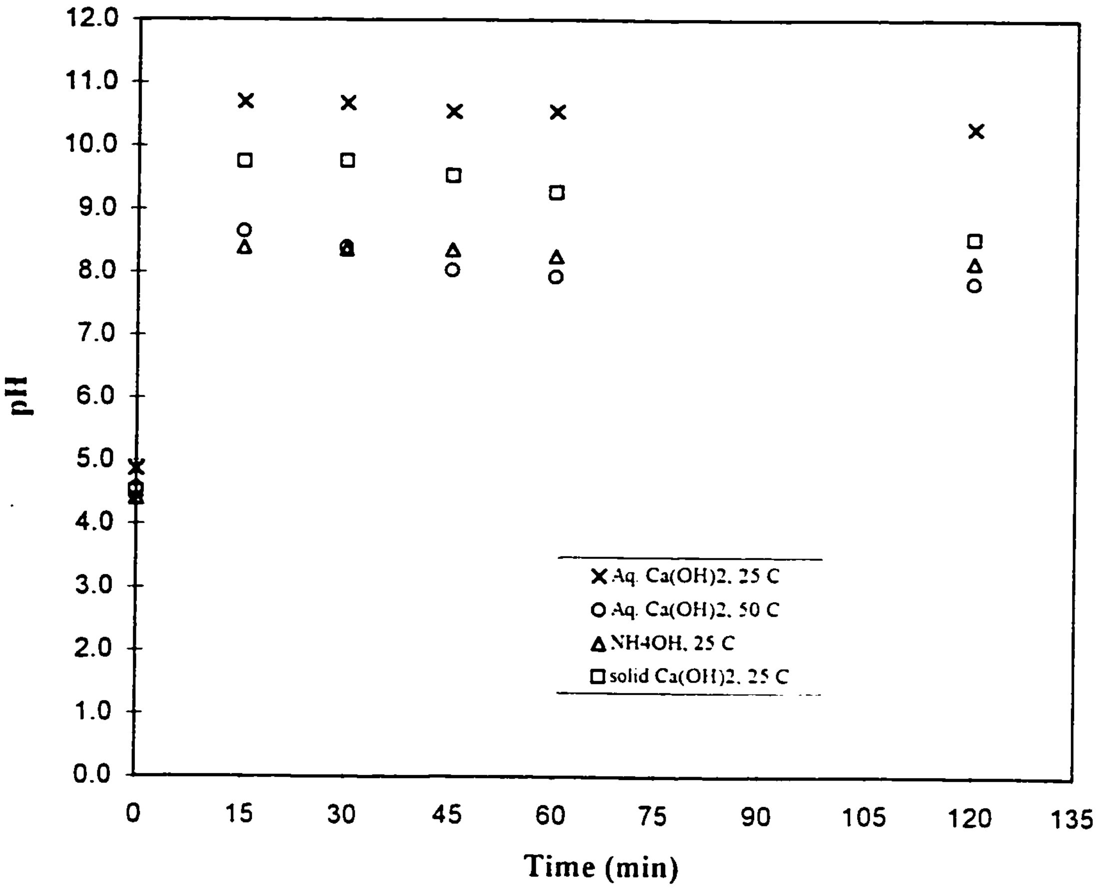


Figure 7.2. Variation of pH during the Removal of Copper Ions by Hydroxide Precipitation.

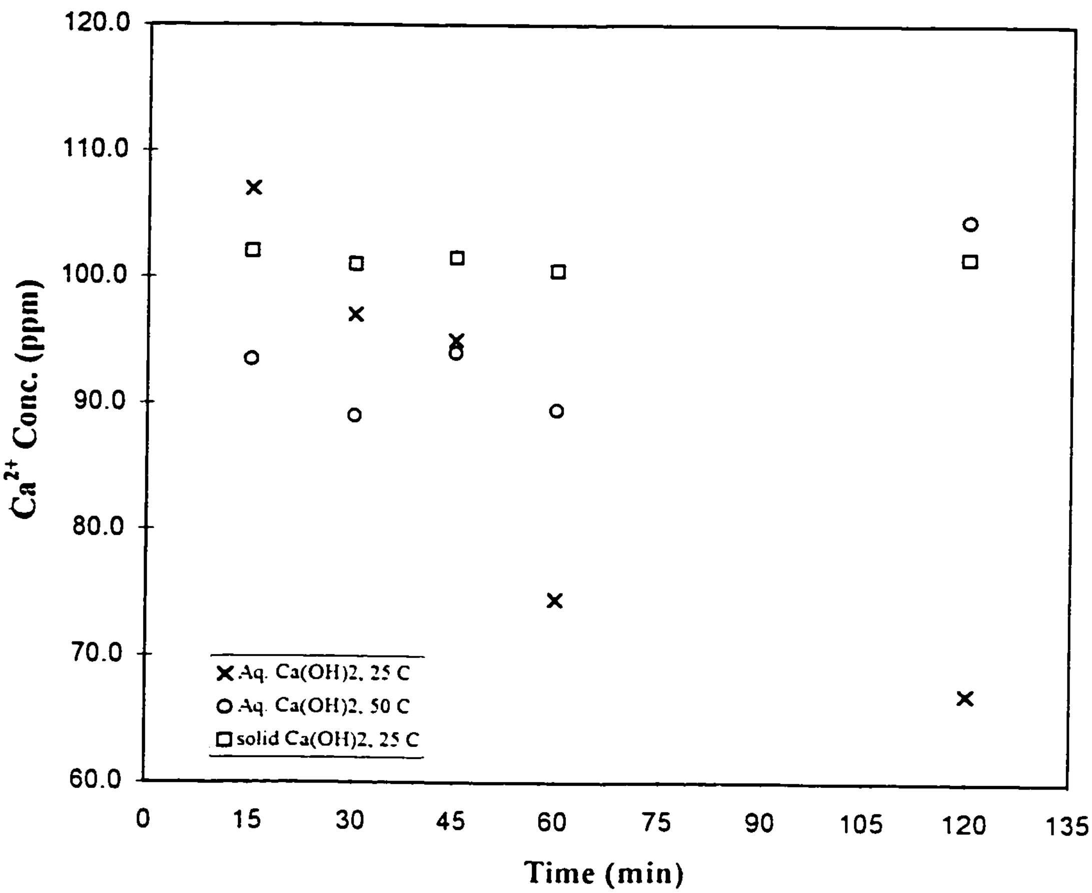


Figure 7.3. Variation of the Dissolved Ca^{2-} Concentration during the Removal of Copper Ions by Hydroxide Precipitation.

It is clear from the measurements made, that while the copper was very effectively removed, it was replaced, to some extent, by soluble calcium. The overall process is considered successful, however, because soluble calcium occurs most abundantly in all natural waters and is completely innocuous.

7.1.1 The Nature of the Solution and Precipitates during Precipitation of $Cu(OH)_2$

The copper stock solutions were colourless before the respective treatments began. Treatments by aqueous $Ca(OH)_2$ and NH_4OH at 25 °C turned the solutions blue during mixing, and formed tiny blue gelatinous particles of precipitate that remained suspended in solution and settled very slowly. However, treatment at 50 °C by aqueous $Ca(OH)_2$ formed granular brown precipitates that settled very fast. On the other hand, addition of solid $Ca(OH)_2$ formed a cloudy white/light blue solution which consequently formed large blue gelatinous flocs that settled very quickly Vacuum filtration of the hydroxide precipitates did not significantly affect the residual Cu^{2+} concentration in any of the treated systems except for treatments using aqueous $Ca(OH)_2$ where the residual concentrations of Cu^{2+} increased by only 0.5 ppm. This increase may have resulted from the decrease in temperature and solution pH which may have resolubilized some copper precipitates during the filtration process.

Post–carbonation treatment of the resulting aqueous lime treated solutions was utilized to provide a final, neutral pH of the treated solutions. This treatment did not affect residual Cu^{2+} concentrations. The solutions were colourless after carbonation with no visible precipitate being formed. Carbonation reduced the residual Ca^{2+} concentration of the solutions by only an average of 2 ppm.

7.2 Precipitation of Cu^{2+} as the Sulphide using FeS as a Precipitant

Figure 7.4 demonstrates the results of the removal of Cu^{2+} obtained by insoluble iron sulphide precipitation performed at 25 °C and 50 °C. The treatment with FeS was unsuccessful in precipitating more than 95 % Cu^{2+} at both operating temperatures. In fact, the maximum removals of Cu^{2+}, even after 120 minutes of contact with the FeS precipitant, were 67.7 %, and 71.6 %, at 25 °C, and 50 °C, respectively. The removal rates increased slightly (~ 2%) for both system temperatures from the initial rates and appeared to be slightly higher for the operating temperatures of 50 °C when compared with that at 25 °C. However, the difference in removal rates were minimal (~ 4 %). The slight increase in metal ion removal at the higher temperature may indicate that the FeS dissociates more at that temperature and, hence, supplies more sulphide ions for precipitation.

In Fig. 7.5, it may be observed that the pH of the solutions decreased by a pH of about 0.4 over the two hour reaction time period. The solutions remained acidic. The fact that the pH values were less than 4.3 indicated the deviation of copper from its minimum solubility point (pH 8.5 to 10). Thus, the solution pH had a significant influence on the quality of the treatment obtained. Therefore, in order to achieve higher removals of Cu^{2+}

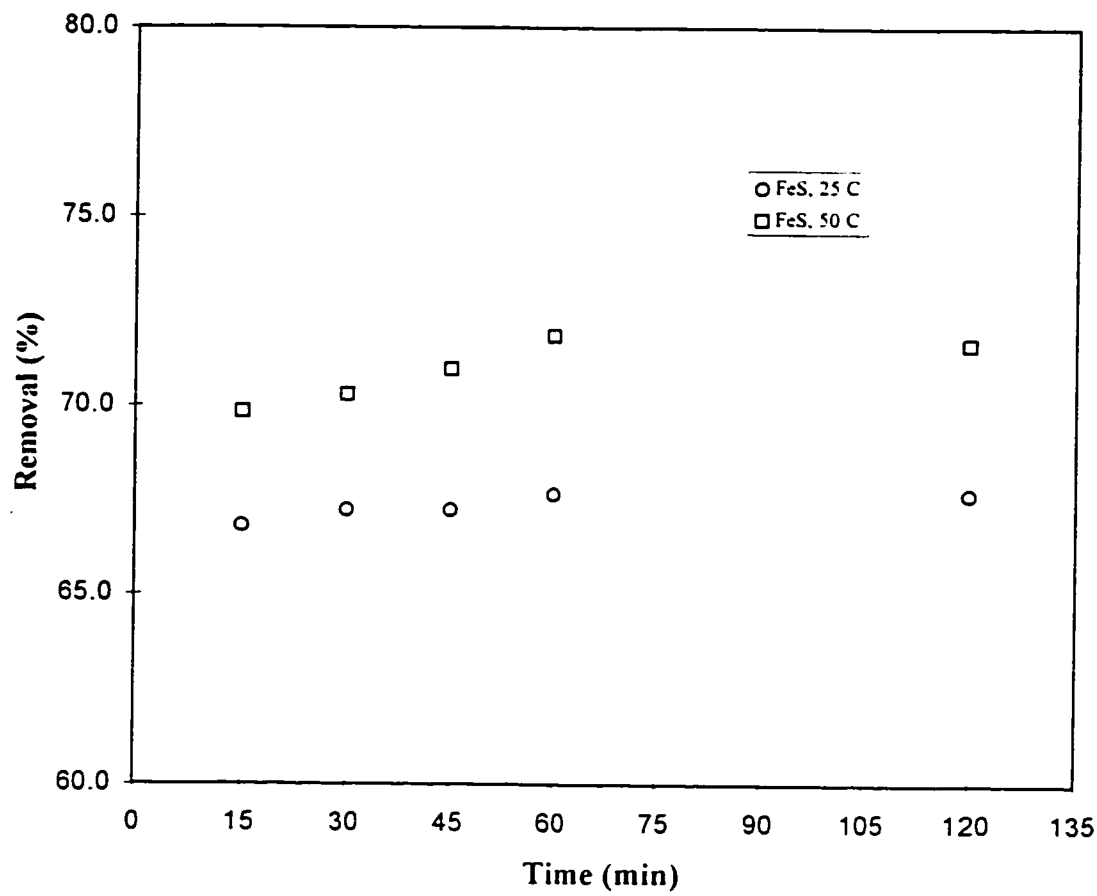


Figure 7.4. Removal of Copper Ions by ISP.

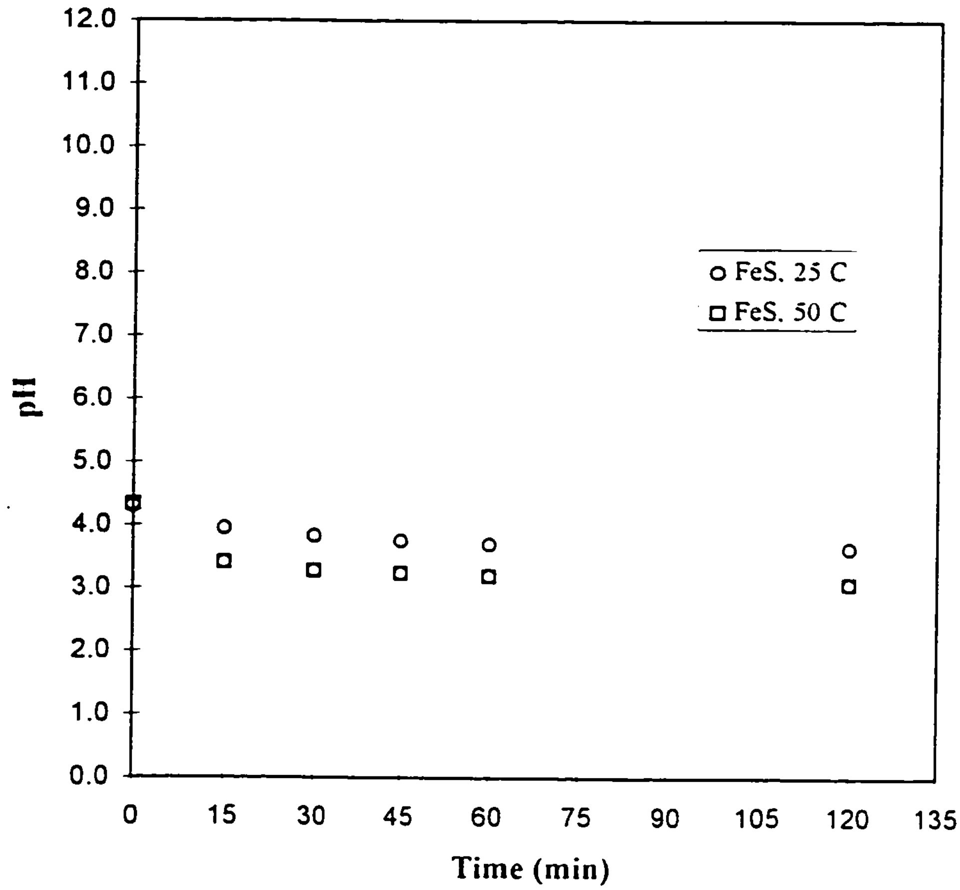


Figure 7.5. Variation of pH during the Removal of Copper Ions by ISP.

within the parameters of the treatment system, the dosage of FeS should have been increased.

The pH of the resulting solutions also affected the Fe^{2-} concentration in solution as shown in Fig. 7.6. After 30 min, the concentration remained fairly constant. The low pH of the treated copper ion solution did not provide sufficient hydroxyl ions to precipitate Fe^{2-} out from solution, thus retaining the high concentrations of Fe^{2-}. The observed increase in Fe^{2-} concentration within the first 30 min of treatment indicated that FeS was still dissociating into the solution during that time

In retrospect, a successful treatment system for Cu^{2-} could probably be devised using FeS as a precipitant. It would involve two precipitants used at the same time lime and FeS. The purpose of the lime would be to increase the pH, thereby increasing the OH concentration to precipitate some of the Fe^{2-} and some of the Cu^{2-}. As a result of the removal of Fe^{2-}, additional FeS would dissociate to increase the S^{2} concentration. Some Ca^{2-} would precipitate in a reaction with SO_4^{2-} present in the solution. Gradually, the Fe^{2-} present would precipitate as the $Fe(OH)_2$, and $Cu(OH)_2$ would be converted to CuS because CuS is less soluble than $Cu(OH)_2$. Unfortunately, the problem associated with the slow reaction rate for the precipitation of CuS because of the low concentration of S^{2} was unforeseen before the experiments began.

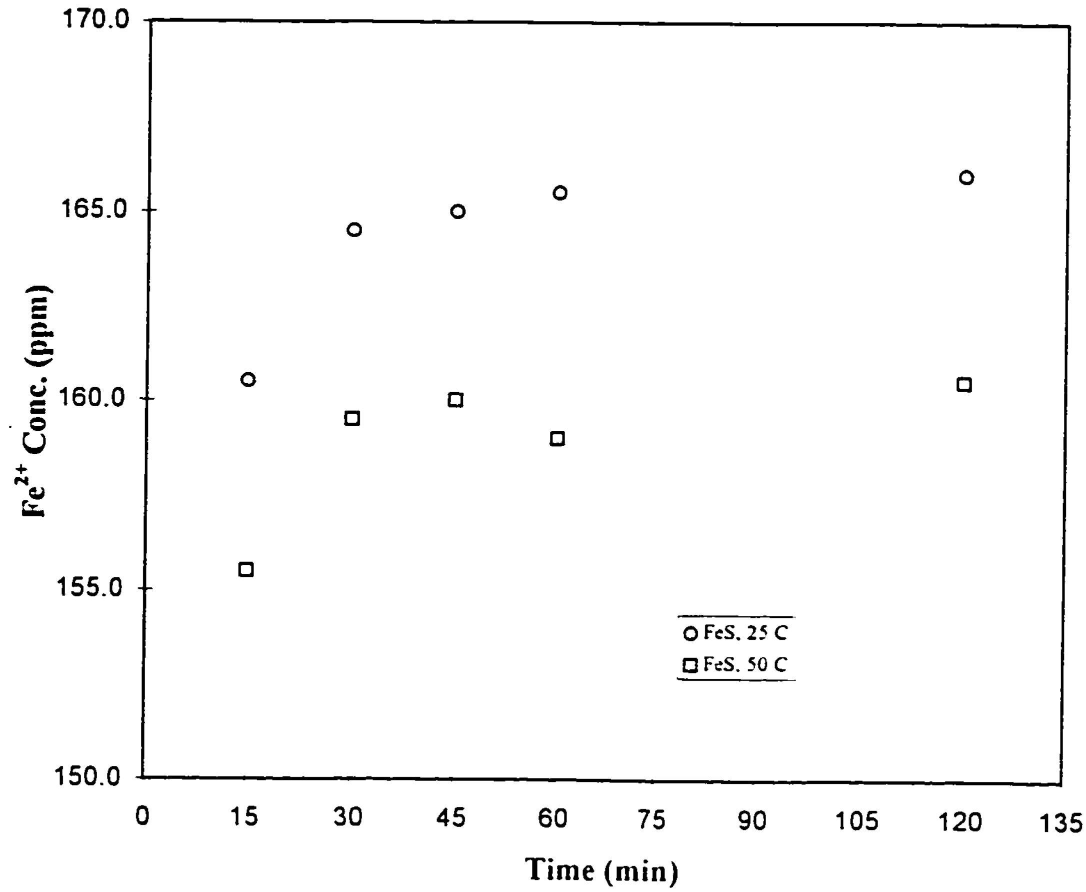


Figure 7.6. Variation of the Dissolved Fe^{2-} Concentration during the Removal of Copper Ions by ISP.

7.2.1 The Nature of the Precipitates during Precipitation of CuS by the ISP Process

The FeS sludge used as a reagent appeared as a homogeneous black precipitate. Upon addition of the FeS to the colourless Cu^{2+} stock solution, the solution turned dark with the formation of additional olive green particles which tended to settle. The colour of the copper sulphide precipitate was the same throughout all the experiments and did not change with operating temperature. No change in the characteristics of the treated solution was observed after vacuum filtration.

7.3 Summary of Hydroxide and Sulphide Precipitation of Cu^{2+}

Figure 7.7 summarizes and compares the removal efficiencies of the different hydroxide and sulphide treatments used in the chemical precipitation of copper metal ions with their respective pH after a two hour treatment. The best removal of Cu^{2+} is obtained by hydroxide formation at an operating temperature of 25 °C. Both solid and aqueous lime treatments are equally effective so that a choice would depend on the economic feasibility of the process. The removal of Cu^{2+} by aqueous and solid lime treatments was 99.8 % at a pH of 10.3, and 99.9 % at a pH of 8.5, respectively, at 25 °C.

7.4 Precipitation of Zn^{2+} as the Hydroxide using Lime and NH_4OH

Figure 7.8 shows the effect of the four variations in hydroxide precipitation of dissolved zinc in the two hour time interval on the percentage removal of soluble zinc.

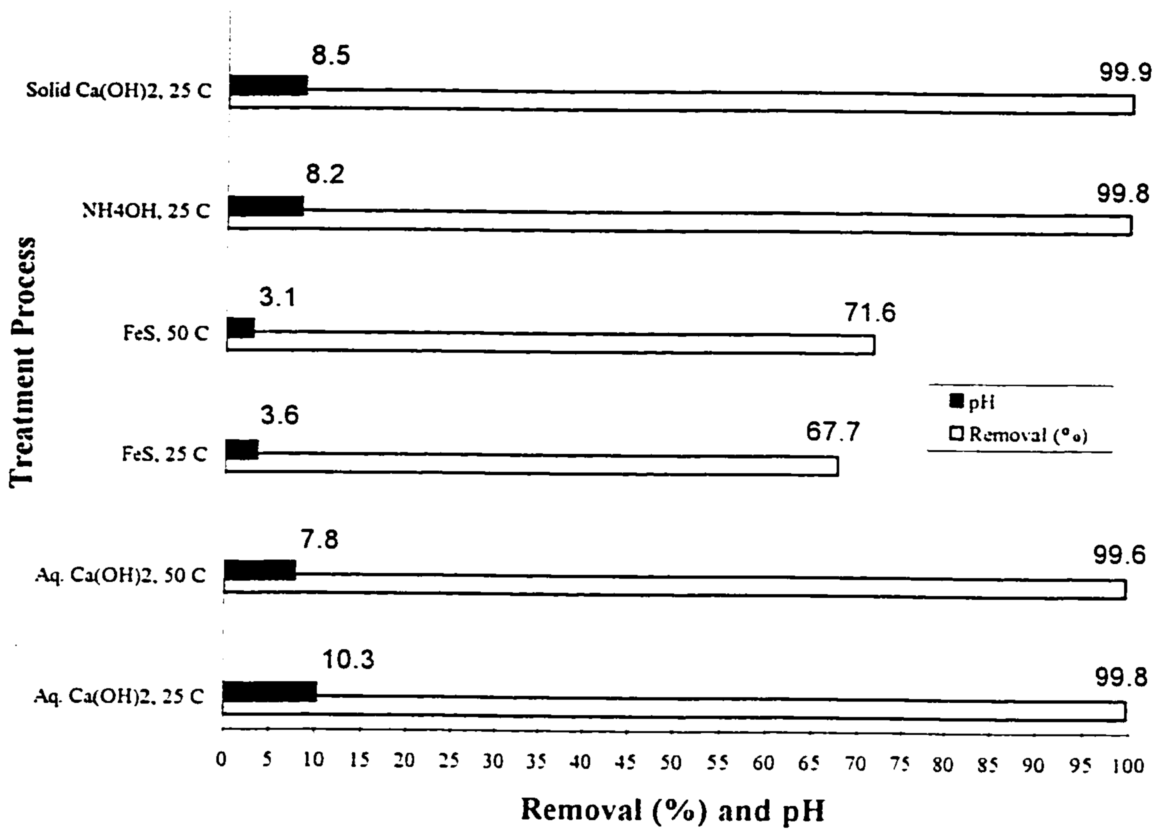


Figure 7.7. Comparison of the Processes in the Removal of Copper Ions after 2 hr Treatment.

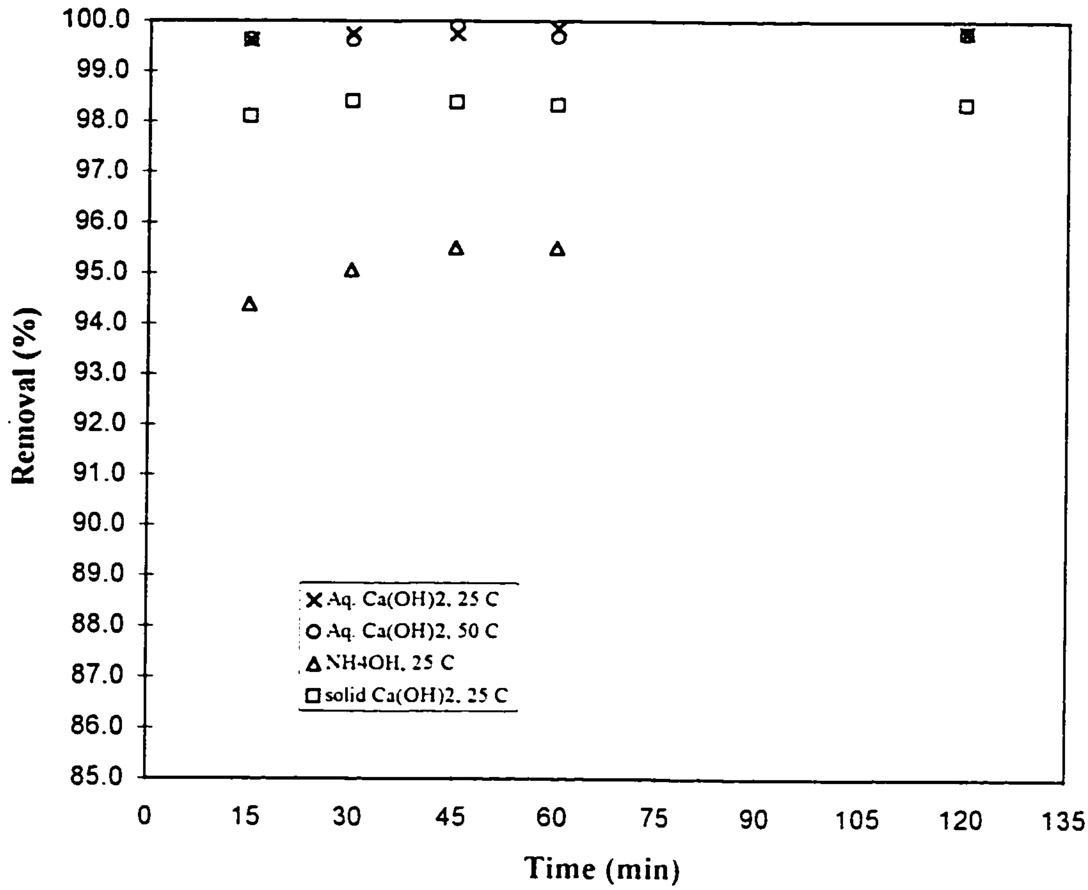


Figure 7.8. Removal of Zinc Ions by Hydroxide Precipitation.

After 15 min, more than 98 % of the Zn^{2+} was removed by the aqueous, and solid lime, treatments at 25 °C leading to 99.6 % and 98.1% Zn^{2+} removal, respectively after two hours. The removal rates remained at these values for the duration of the experiment. Aqueous lime treatments at 50 °C resulted in essentially the same fractional removal of Zn^{2+} as at 25 °C. Treatment by NH_4OH resulted in a Zn^{2+} removal of 94.4 % after 15 min; this fractional removal rate increased marginally to 95.5 % after 60 min. It is clear that soluble zinc is very effectively removed by precipitation as the hydroxide, especially using an aqueous lime slurry as the precipitant.

Figure 7.9 shows the change in pH for the four treatment processes in the precipitation on Zn^{2+}. In all the four cases, the pH decreased marginally with time. As expected, for the treatment by aqueous lime, the pH was higher at 25 °C than at 50 °C. However, in spite of the lower pH attained in the precipitation at 50 °C, the removal of Zn^{2+} was as high as that obtained at 25 °C. Thus, $Zn(OH)_2$ appears to exhibit a minimum solubility in a pH range from 9.1 to 10.7. The pH values resulting from the NH_4OH and solid lime treatment processes were lower than those of the aqueous lime treatments. The lower pH values indicated that the solubility of Zn^{2+} was greater at this lower pH than at a higher pH. Thus, in order to have achieved the maximum removal of zinc ions from solution, the pH must be controlled at higher levels such as in the range, $9 < pH < 11$, by increasing the dosage of NH_4OH or $Ca(OH)_2$ to achieve a higher solution pH. The calcium ion concentrations in solution are shown in Figure 7.10. As for the treatment of soluble copper solutions, the precipitation of zinc as the hydroxide using lime, leaves an appreciable concentration of innocuous calcium in solution.

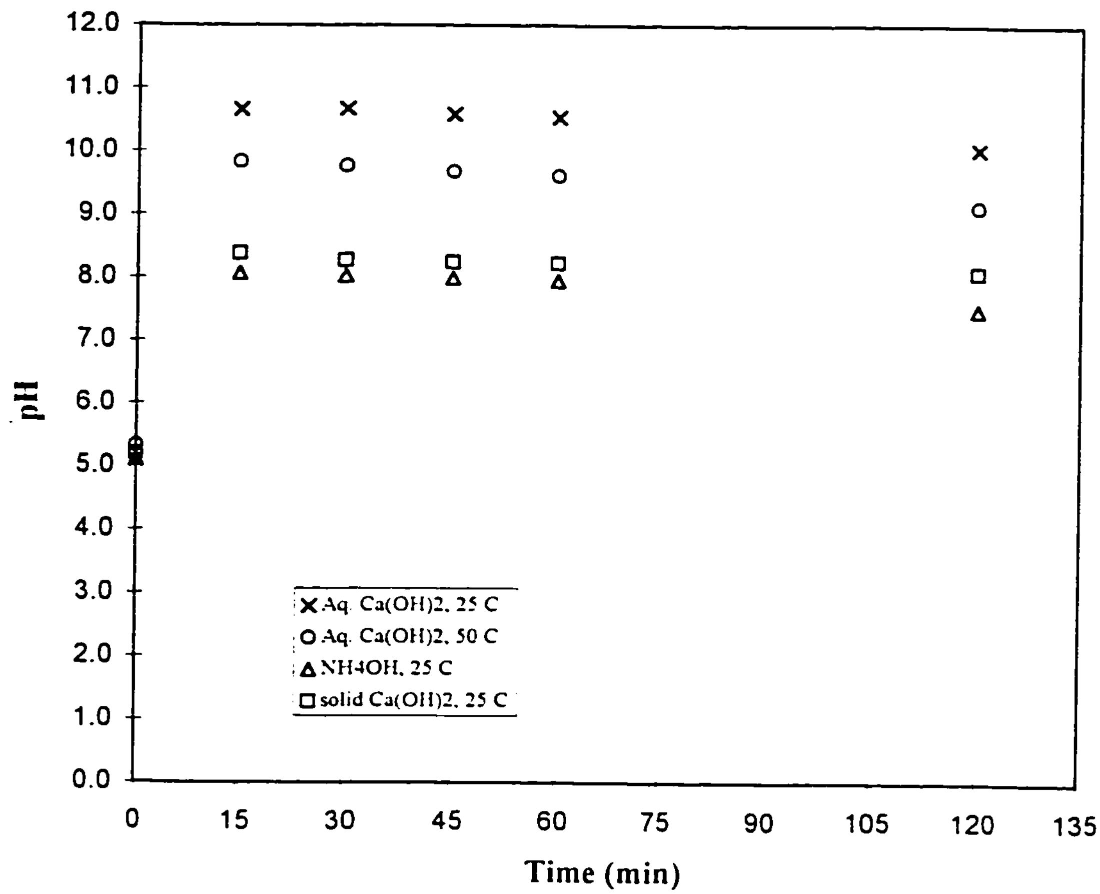


Figure 7.9. Variation of pH during the Removal of Zinc Ions by Hydroxide Precipitation.

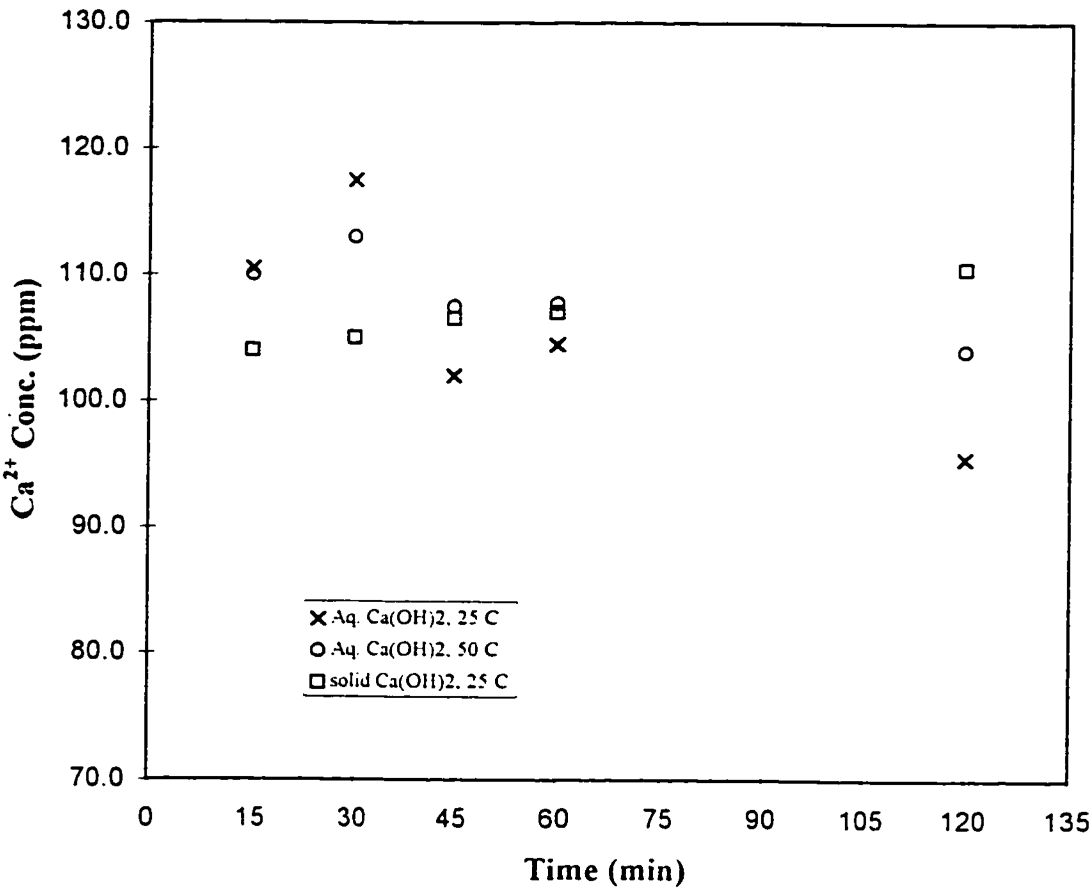


Figure 7.10. Variation of the Dissolved Ca^{2-} Concentration during the Removal of Zinc Ions by Hydroxide Precipitation.

7.4.1 Characteristics of the Precipitates Resulting from the Precipitation of Zn^{2+} as the Hydroxide

The zinc stock solutions were colourless before treatment. Addition of the hydroxide compounds produced gelatinous white precipitates that formed large flocs which settled quickly. Aqueous lime treatment at 50 °C produced white but more granular, precipitates. The increase in temperature appeared to alter the morphology of the precipitates, changing the crystal structure. Post–carbonation of the zinc ion solutions treated by aqueous $Ca(OH)_2$ decreased the pH to approximately 6.0 without affecting the residual zinc concentration. No visible precipitates were observed in this latter process.

7.5 Precipitation of Zn^{2+} as the Sulphide using FeS as a Precipitant

Figure 7.11 demonstrates the results for the precipitation of Zn^{2+} obtained by using the insoluble sulphide precipitation (ISP) method for temperatures of 25 °C and 50 °C. The results indicate that the precipitant, FeS, was unsuccessful in removing more than 95 % Zn^{2+} at both operating temperatures. However, increasing the system temperature to 50 °C marginally increased the removal rates of zinc. As discussed previously, it is possible that more sulphide ions were being supplied by the dissociation of FeS at the higher temperature. For the FeS treatment at 25 °C and at 50 °C, it was observed that after 30 min of treatment, there was an increase in zinc ion removal rates, or equivalently, a decrease in zinc ion concentration as the treatment time progressed. This temporary decrease in concentration may have been due to the changes in crystalline structure of the

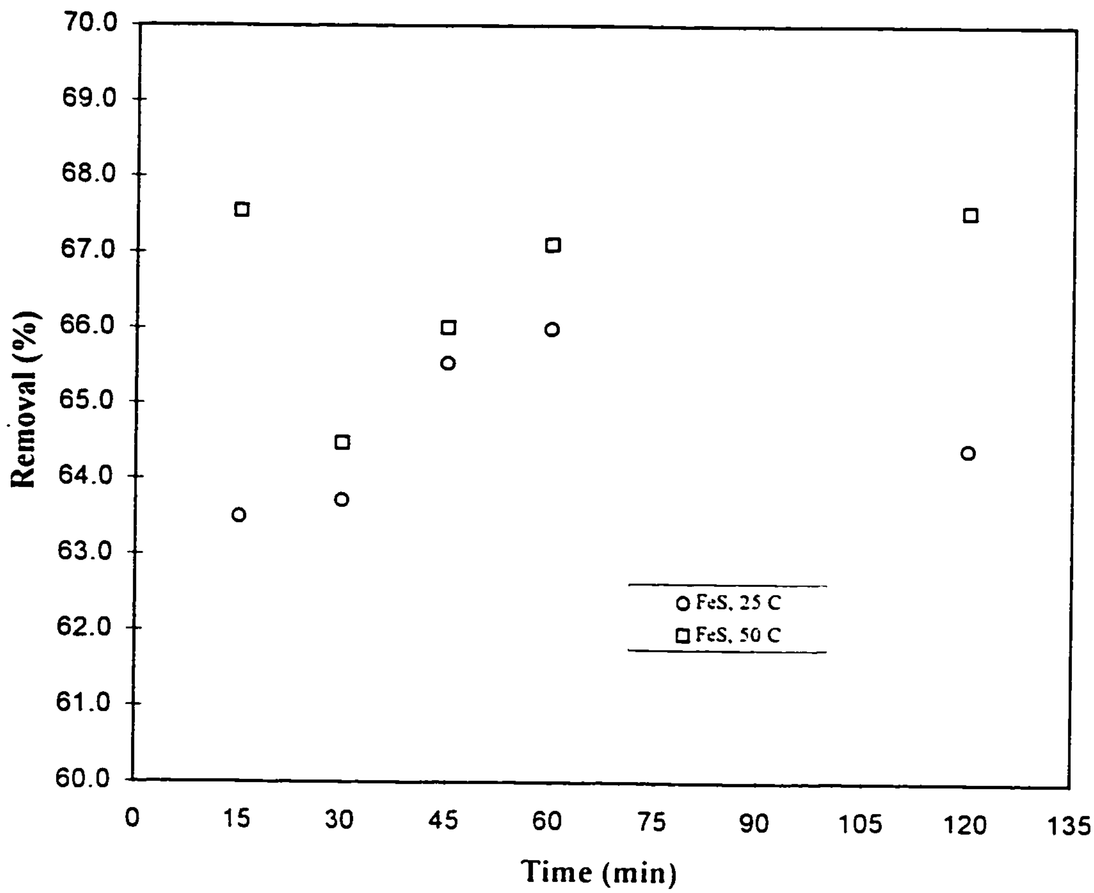


Figure 7.11. Removal of Zinc Ions by ISP.

zinc sulphide precipitates being formed. As noted earlier, changes in colour and size of the precipitates were observed.

The pH of the solutions containing zinc and FeS decreased by an average pH reading of 0.5 from their initial values over the two hour reaction period as indicated in Fig. 7.12. The pH of the treated solutions were lower than 6.0, (acidic), thus not providing suitable conditions for dissociation of FeS to facilitate precipitation of the ZnS present in the wastewater. It is indicated that sulphides of zinc are soluble in acidic solutions.

The concentrations of Fe^{2+}, as shown in Fig. 7.13, decreased slightly over the total experimental time. The acid nature of the solutions, with a pH less than 6.0, did not provide OH^- for the possible precipitation of Fe^{2+}. Had the solution been basic, the Fe^{2+} concentration may have been significantly reduced. As with the dissolved copper in solution, a combined aqueous lime–ferrous sulphide precipitant would probably have been successful as a wastewater treatment process.

7.5.1 The Nature of the Precipitates during Precipitation of ZnS by the ISP Processes

For the FeS treatment of the solution containing zinc at 50 °C, the solution appeared orange/brown with the precipitation of orange particles in the form of large flocs during the first 60 min of reaction. At the end of the experiment, the final precipitated particles became larger and appeared to be more gelatinous in nature. For the FeS treatment at 25 °C, the precipitate appeared black and gave an olive green tint to the

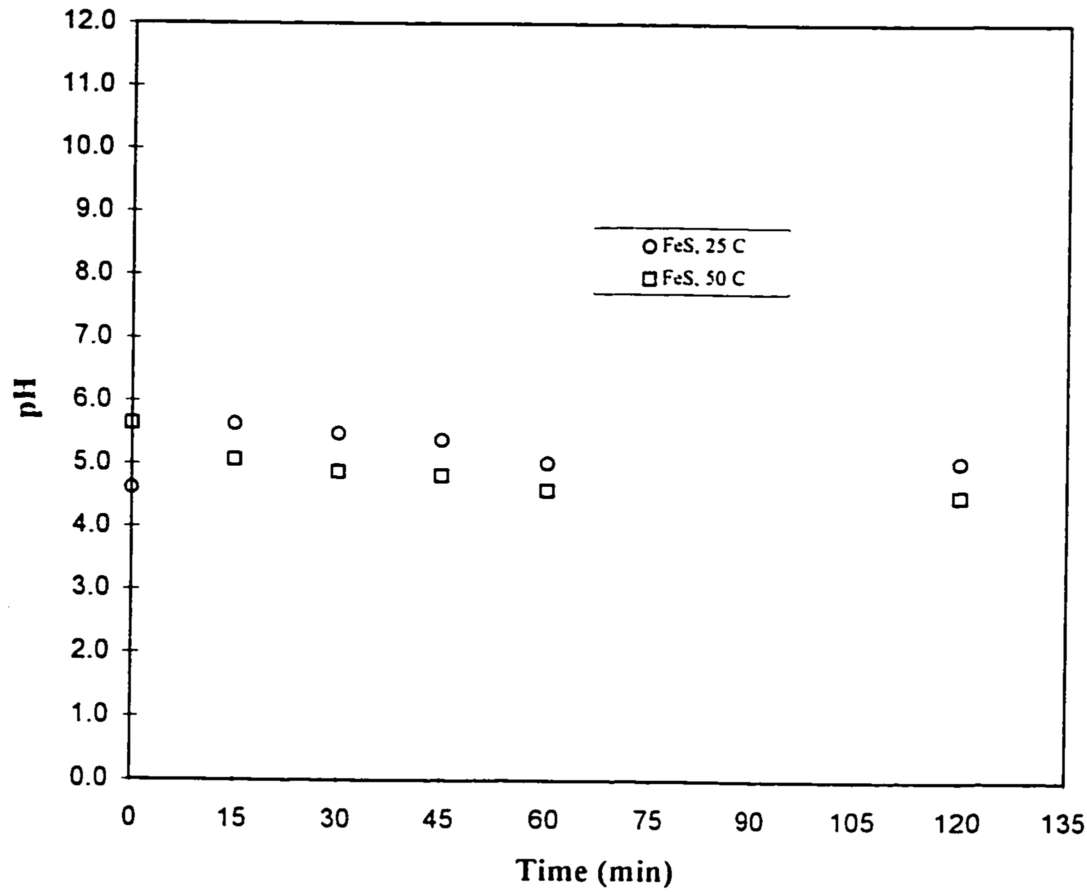


Figure 7.12. Variation of pH during the Removal of Zinc Ions by ISP.

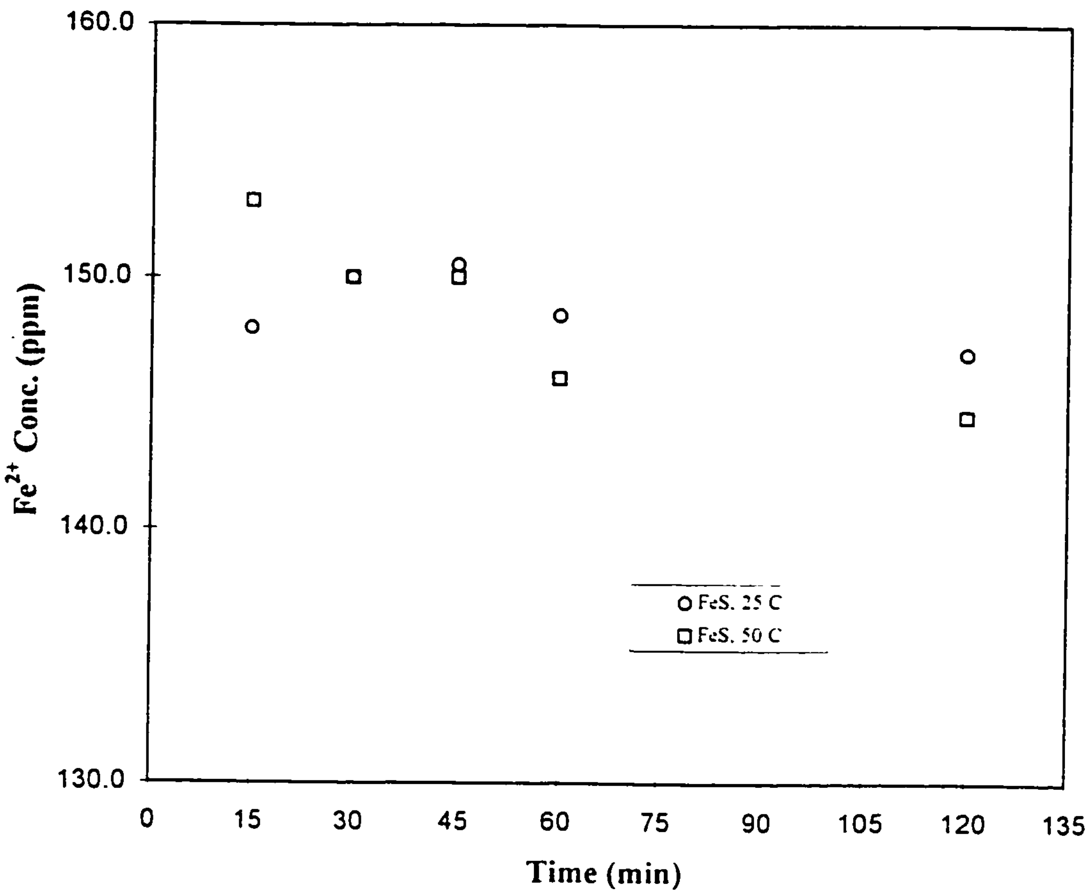


Figure 7.13. Variation of the Dissolved Fe^{2+} Concentration during the Removal of Zinc Ions by ISP.

solution. After 30 min, olive/green particles were observed to form, which later turned dark brown at the end of the experiment. The variation in colour probably resulted from changes in the crystalline structure of the precipitate formed.

7.6 Summary of Hydroxide and Sulphide Precipitation of Zn^{2+}

Figure 7.14 summarizes and compares the removal efficiencies of the different processes involved in the precipitation of Zn^{2+} with their respective pH values after a reaction time of two hours. The best removal of Zn^{2+} is achieved by aqueous lime treatment at 25 °C, and 50 °C, with removal rates for both temperatures of 99.8 % at pH 10, and pH 9.1, respectively. Furthermore, the hydroxide treatment processes were much better at removing Zn^{2+} from solution than FeS at the dosages and methods utilized. It appears that modifications to the FeS process are required before it can be successful. The FeS process potentially has an advantage over hydroxide precipitation because the metal sulphides are less soluble than the hydroxides.

7.7 Precipitation of Pb^{2+} as the Hydroxide, or Carbonate using Lime and Dispersed CO_2 Gas

Figure 7.15 shows the effect of the four variations in hydroxide precipitation on the percentage removal of Pb^{2+}. Unlike the excellent removal of Cu^{2+} and Zn^{2+} by hydroxide precipitation, the percentage removal of lead by the lime and NH_4OH removed only between 20 % and 60 % of the lead, far short of the removal of 95 % Pb^{2+} desired. Only after two hours of treatment by aqueous and solid lime was the removal of lead

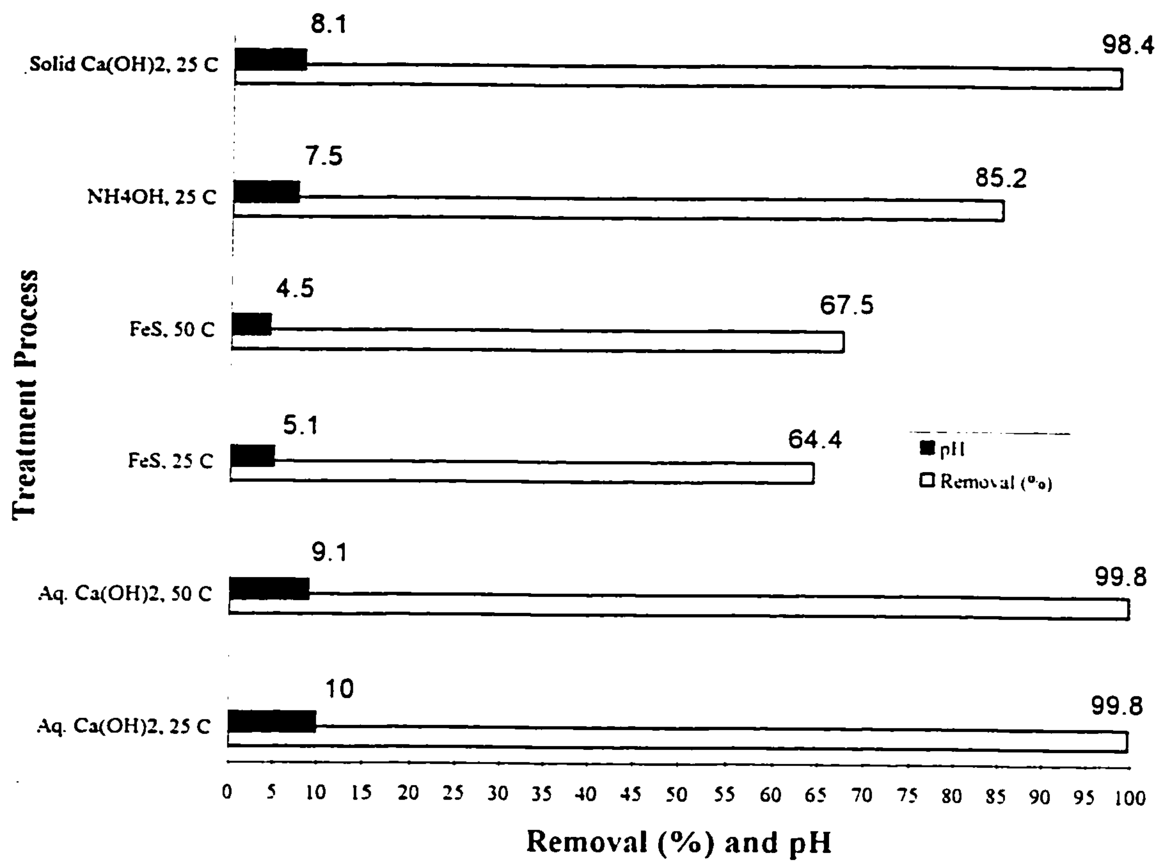


Figure 7.14. Comparison of the Processes in the Removal of Zinc Ions after 2 hr Treatment.

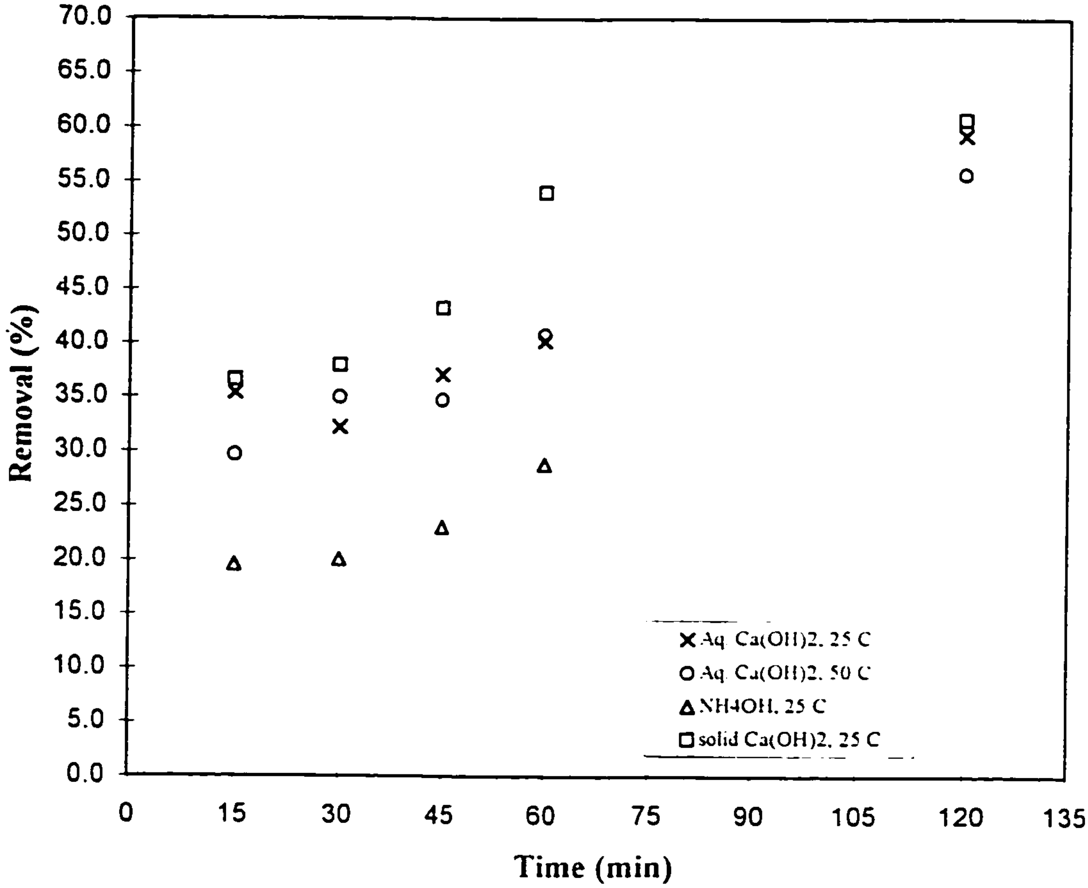


Figure 7.15. Removal of Lead Ions by Hydroxide Precipitation.

approximately 60 %. The pH of the treated solution remained relatively stable throughout the reaction period as depicted in Figure 7.16. Varying the temperature of the systems had no significant effect on the removal rate when using lime. However, the pH of the solutions were lower for the aqueous lime treatment at 50 °C, than at 25 °C. Lead removal by NH_4OH yielded a removal of only 28.8 % after 60 min at a pH of 10.2. The low removals of lead indicated the high solubility of lead hydroxide at pH greater than 9.0. It appears possible, that because lead is amphoteric, its chemical nature may have produced soluble lead–hydroxyl complexes in the presence of excess amounts of OH^- at the high pH values. The concentrations of Ca^{2+} in the treated solutions remained constant for treatment by solid lime as shown in Figure 7.17. Aqueous lime treatment varied the concentration of Ca^{2+} slightly indicating that some Pb^{2+}–Ca^{2+} complexes may have formed. An exploratory experiment was performed to see if prolonged contact between lime and Pb^{2+} would precipitate more of the lead. The treatment by solid $Ca(OH)_2$ was carried out for a period of twelve hours to determine if the reactions would reach chemical equilibrium in the precipitation of all the lead. The result was that the concentration of Pb^{2+} was reduced to a surprisingly low level of 0.3 ppm at pH 7.8 indicating a removal of 99.9 %, while the Ca^{2+} concentration remained constant at 47.0 ppm also after 12 hours (refer to Table D–39 and D–40). This last result suggests that the rate of precipitation of Pb^{2+} as a hydroxide is too slow for practical purposes even though the equilibrium reached after a prolonged period of time is favourable.

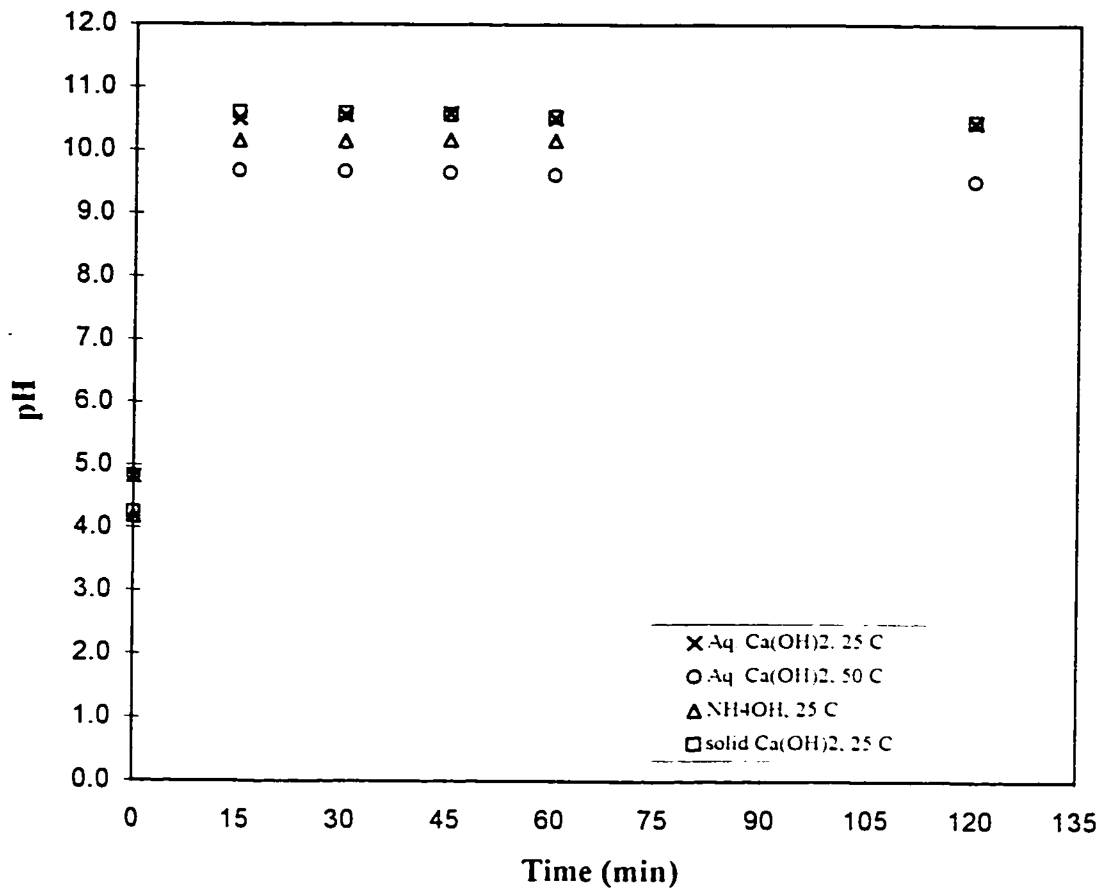


Figure 7.16. Variation of pH during the Removal of Lead Ions by Hydroxide Precipitation.

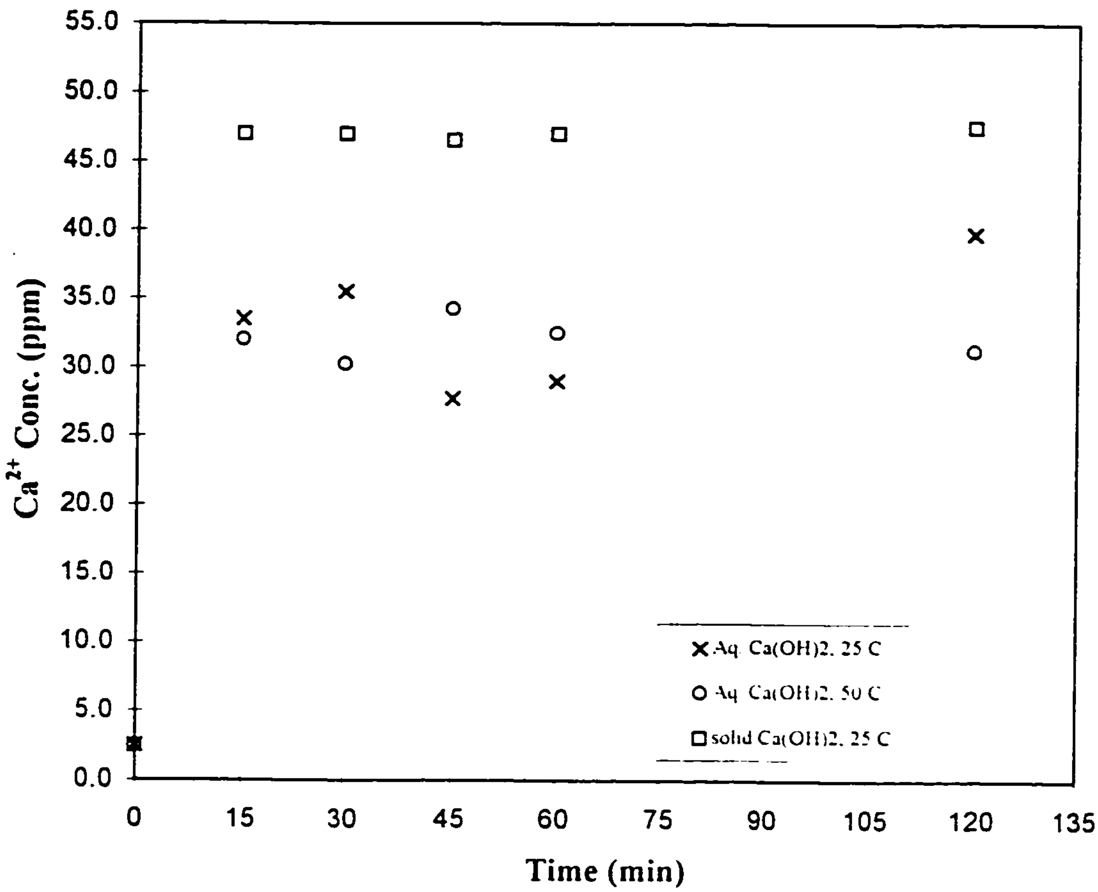


Figure 7.17. Variation of Soluble Calcium Ion Concentration during the Removal of Lead Ions by Hydroxide Precipitation

7.7.1 The Nature of the Solution and Precipitate during Precipitation of Lead as a Hydroxide

The lead stock solution was colourless before treatment. Aqueous lime treatment at 25 °C caused tiny white granular particles to form in about 15 min. After 45 min, the particles agglomerated to generate larger particles that appeared as a white cloud which did not settle. However, vacuum filtration was able to separate the cloudy precipitate from solution. Aqueous lime treatment at 50 °C produced larger white particles that were observed to grow in size throughout the experiments and settle readily. After 30 min of treatment, an "oily" layer was observed on the surface of the solution. Although the precipitate settled quickly, the "oily" surface remained. During subsequent treatments, this "oily" film appeared again and again. Treatment with NH_4OH produced a gelatinous white precipitate during mixing which quickly became granular and settled. An "oily" layer was again observed after 15 min of treatment. Treatment by solid lime led to the formation of tiny white particles that settled very slowly with no "oily" layer observed in the first hour of treatment. After one hour of treatment the "oily" layer became evident and the particles remained tiny but still settled.

One condition of successful wastewater treatment is to obtain a neutral treated solution. For the copper and zinc hydroxide processes, gaseous CO_2 gas was used to reduce the pH to a neutral value. When this was attempted with the lead–lime solutions, a further precipitate was formed, most likely lead carbonate. For this reason, further experiments were conducted using CO_2 gas dispersed in the lead solution.

7.7.2 Post–carbonation with CO_2 of Pb^{2+} Solution Previously Treated with Lime

The formation of a significant additional quantity of precipitate to the soluble lead solution initially treated with lime was unexpected. It was not clear whether the additional precipitation formed when CO_2 gas was dispersed in the aqueous lime–lead hydroxide slurry, was formed because the lead carbonate was less soluble than the lead hydroxide, or simply because the pH was reduced. Yet, the solubility products of the two possible precipitates indicated that the hydroxide was much less soluble under comparable conditions.

To explore whether the more complete removal rates for the lead could be achieved, additional experiments were devised. First, at both 25 °C and 50 °C, experiments were conducted by bubbling CO_2 gas through a dispersing tube into the lead solution containing lime and lead precipitate, taking samples and pH readings initially, after 15 min, and again after 30 min of treatment.

Post–carbonation of the aqueous lime treated solutions dramatically reduced the lead concentration to provide increased removals of 90 % Pb^{2+} at pH 5.5 as shown in Tables 7.1 and 7.2. However, further addition of CO_2 reducing the pH to 4.7 resolubilzed the precipitates, and decreased the removal of Pb^{2+}.

Table 7.1 Post–carbonation of Pb^{2+} Precipitation by Aqueous $Ca(OH)_2$ at 25 °C.

CO_2 Addition	pH	Pb^{2+} Concentration (ppm)	Ca^{2+} Concentration (ppm)	Pb^{2+} Removal (%)
No addition	10.4	83.5	39.8	59.3
Initial	5.7	22.3	25.3	89.1
Final	4.6	64.0	27.3	68.8

Table 7.2 Post–carbonation of Pb^{2+} Precipitation by Aqueous $Ca(OH)_2$ at 50 °C.

CO_2 Addition	pH	Pb^{2+} Concentration (ppm)	Ca^{2+} Concentration (ppm)	Pb^{2+} Removal (%)
No addition	9.5	87.5	31.3	55.7
Initial	5.5	16.0	28.0	91.9
Final	4.7	35.5	24.5	82.0

Immediate addition of CO_2 formed a cloudy white precipitate that developed a pink tint before becoming white. The Ca^{2+} concentration did not vary during these post–carbonation steps indicating the likely formation of lead carbonate precipitates. On investigation of lead chemistry, it appears that the white precipitate may have been "white lead" or hydrocerussite [$2PbCO_3 \bullet Pb(OH)_2$] which tends to form in alkaline solutions. Increasing the reaction temperature had no significant impact on the initial addition of CO_2, however when CO_2 addition was terminated at 25 °C the concentration of Pb^{2+} increased almost three times more than when CO_2 was first added. These dramatic changes in lead concentration indicated a large influence of pH on the minimum solubility of the lead. Hence, one–step carbonation was not recommended to lower the pH to achieve maximum removal of Pb^{2-}

Thus, a further experiment was devised in which the lead would be treated by aqueous lime for 30 min, filtered and then CO_2 gas would be fed at a controlled rate, 0.10 mL/s, decreasing the pH by approximately one unit only, each time, before sampling. The residual lead concentration in solution by this post–treatment is presented in Tables 7.3 and 7.4.

Table 7.3 Pb^{2-} Precipitation by Aqueous $Ca(OH)_2$ and Rate Controlled Post–CO_2 Treatment at 25 °C.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Pb^{2+} Removal (%)
0	4.4	207.0	2.5	
15	10.9	91.0	43.0	56.0
30	10.9	97.0	41.0	53.1
After filtration	10.8	53.0	40.5	74.4
CO_2 Addition				
	10.0	2.5	41.5	98.8
	9.0	2.0	42.5	99.0
	8.0	2.5	42.5	98.8
	7.0	4.5	44.0	97.8
	6.0	9.0	43.5	95.7
	5.5	9.0	41.5	95.7

Table 7.4 Pb^{2+} Precipitation by Aqueous $Ca(OH)_2$ and Rate Controlled Post-CO_2 Treatment at 50 °C.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Pb^{2+} Removal (%)
0	4.8	209.0	2.5	
15	9.4	86.5	37.5	58.6
30	10.0	86.0	37.0	58.9
After filtration	10.1	54.0	37.5	74.2
CO_2 Addition				
	9.1	4.0	35.5	98.1
	7.8	1.0	34.5	99.5
	7.0	1.0	36.0	99.5
	5.9	4.5	36.0	97.8

As observed in Tables 7.3 and 7.4, the removal fractions of Pb^{2+} were greater than 97 % with controlled addition of CO_2 gas for pH values greater than 7.0. Below pH 7.0, resolubilization of the lead precipitates began to occur. Thus, the pH of the lead carbonated system must be maintained in a pH range between 7.0 and 9.0 for maximum removal of Pb^{2+} at 25 °C and 50 °C. The concentration of Ca^{2+} was nearly constant whereas that of Pb^{2+} dropped sharply, indicating that the precipitates were most likely composed of lead complexes as speculated earlier. Before CO_2 was added, the treated lime solution was filtered. A dramatic decrease in Pb^{2+} was observed during this filtration step; approximately 15 % more Pb^{2+} was removed from solution during filtration. This decrease indicated that the chemical precipitation of lead was still in progress during filtration. This would suggest that precipitation of lead is a relatively slow process, perhaps limited in rate by the diffusion of Pb^{2+} ions to the crystallization sites. As a result, it appears possible that as the solution passed through a filter cake of precipitate, deposition of lead ions continued on particles already there. These additional experiments were successful in defining a process capable of removing Pb^{2-} from waste solution.

7.8 Precipitation of Pb^{2+} as the Sulphide using FeS and a Combination of FeS and a Base

Figure 7.18 shows the effect of the FeS precipitation treatment on the removal of Pb^{2-}. After 15 min, the removal of lead was 95.2 % at a pH of 7.5, and 93.4 % at a pH of 6.6, for FeS treatments at 25 °C, and 50 °C, respectively. A continuing decline in the removal rates was observed for longer treatment periods. Removal rates at 50 °C were lower than removal rates at 25 °C. This lower removal rate was associated with a decrease in pH over the same time period as depicted in Fig. 7.19. As the solution pH became more acidic, the precipitate resolubilized. Figure 7.20 shows the effect of the FeS precipitation treatment on the concentration of Fe^{2+}. The removal of lead by FeS in an acidic medium was found to be effective for a 15 min treatment only at 25 °C whereas the residual Fe^{2-} concentration in the solution being treated gradually decreased, the concentration of Pb^{2-} increased. There is no obvious explanation why this should occur.

7.8.1 The Nature of the Precipitates during Precipitation of Pb^{2+} by the ISP Processes

Upon addition of the FeS slurry to the lead waste solution, the solution appeared black during mixing. For treatment at 25 °C, the particles were tiny, granular and dark brown and some remained suspended without settling. Settling of the precipitate was

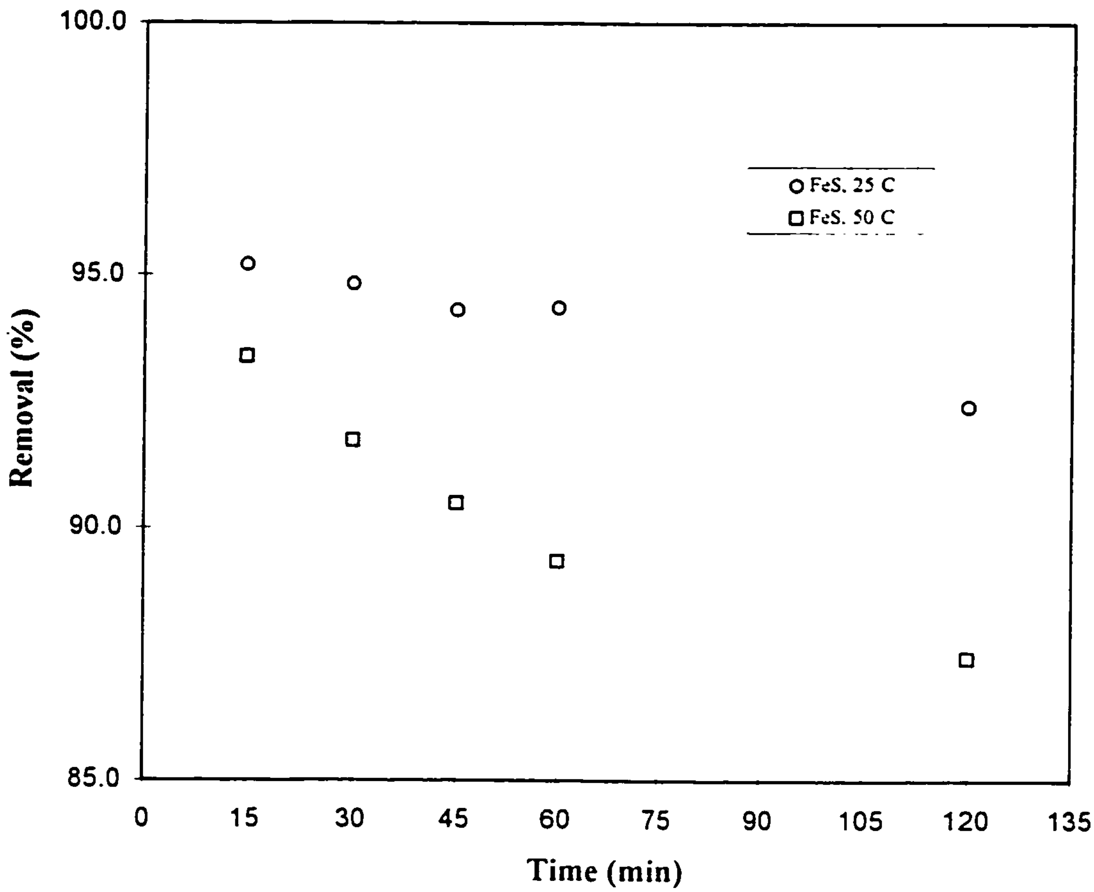


Figure 7.18. Removal of Lead Ions by ISP.

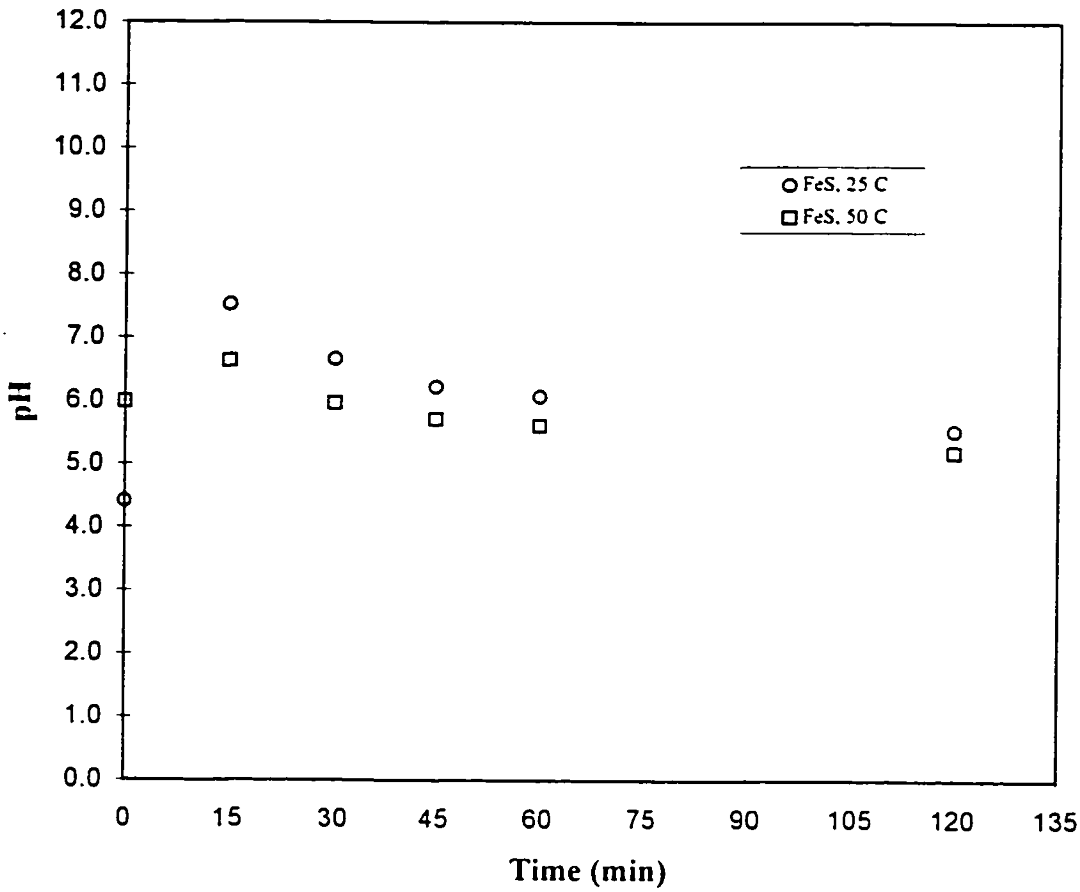


Figure 7.19. The Solution pH during the Removal of Lead Ions by ISP.

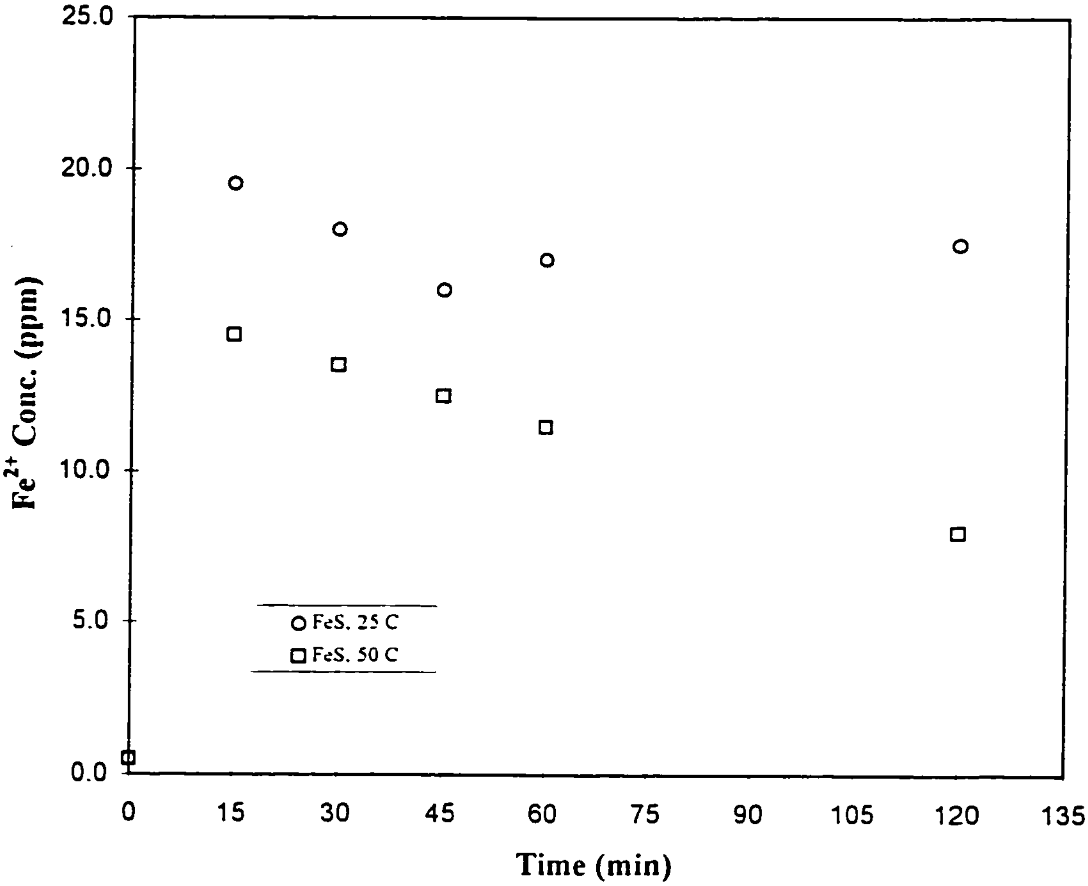


Figure 7.20. The Fe^{2-} Concentration in Solution during the Removal of Lead Ions by ISP.

slow. Treatment at 50 °C yielded tiny granular brown particles which formed brown flocs after two hours that settled quickly. The treated solution did not produce any additional precipitate after filtration on standing. Because none of the sulphide precipitation products of Pb^{2+} are brown, it is assumed that the brown particles were FeS dispersed throughout the solution.

7.9 Combined Hydroxide–Insoluble Sulphide Precipitation of Pb^{2+}

Encouraged by the success of a two–stage process for removing Pb^{2+} by a lime–CO_2 process, a two–stage base–FeS treatment was devised in an attempt to improve the Pb^{2+} removal percentage using FeS. Essentially, this would allow for the investigation into the precipitation of lead as the sulphide at high pH values. The experiment consisted of adding a sufficient quantity of base to the Pb^{2+} solution to yield a pH value of about 10.5. After being stirred for 15 min, the precipitate was removed by filtration. Next, a sufficient amount of FeS was added to precipitate the Pb^{2+} as the sulphide Samples were withdrawn, and readings taken at regular time intervals. The hydroxide compounds used were NH_4OH and solid lime. The combined treatment results are presented in Tables 7.5 to 7.10. The differences in the treatment methods were the time at which the hydroxide compound was introduced for treatment. The hydroxides basically acted as pH adjusters for FeS treatment.

Table 7.5 Pb^{2+} Precipitation by 300 μL NH_4OH and FeS at 25 °C; FeS Added after 15 min Preceded by Filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Pb^{2+} Removal (%)
0	4.2	198.5		
Add NH_4OH	10.2			
15	10.4	137.0		31.0
Filtration	10.5	149.0		24.9
8.7 mmol/L FeS added				
15	10.5	0.2	<0.1	99.9
30	10.4	< 0.2	<0.1	99.9
45	10.6	< 0.2	<0.1	99.9
60	10.5	< 0.2	<0.1	99.9
120	10.5	< 0.2	<0.1	99.9
After filtration	10.5	< 0.2	<0.1	99.9

Table 7.6 Pb^{2+} Precipitation by 300 μL NH_4OH Followed by Addition of FeS after 15 min at 25 °C; No Filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Pb^{2+} Removal (%)
0	4.2	195.5		
Add NH_4OH	10.4			
15	10.4	153.0		21.7
8.7 mmol/L FeS added				
15	10.5	0.7	<0.1	99.6
30	10.4	0.2	<0.1	99.9
45	10.5	0.2	<0.1	99.9
60	10.4	0.1	<0.1	99.9
120	10.4	<0.1	<0.1	99.9
After filtration	10.4	< 0.2	<0.1	99.9

Table 7.7 Pb^{2+} Precipitation by 300 μL NH_4OH and FeS Added Simultaneously at 25 °C.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Pb^{2+} Removal (%)
0.0	4.0	213.0	---	
15.0	10.6	<0.2	<0.1	99.9
30.0	10.4	<0.2	<0.1	99.9
45.0	10.4	<0.2	<0.1	99.9
60.0	10.3	<0.2	<0.1	99.9
120.0	10.3	<0.2	<0.1	99.9
720.0	9.7	0.3	0.5	99.9
After filtration	9.7	<0.2	<0.2	99.9

Table 7.8 Pb^{2+} Precipitation by 0.200 g $Ca(OH)_2$ and FeS at 25 °C, FeS Added After 15 min Preceded by Filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Pb^{2+} removal (%)
0	4.7	213.0	---	---	
0.200 g $Ca(OH)_2$ added					
15	11.2	132.0	---	52.0	38.0
8.1 mmol/L FeS added after filtering solution					
30	11.5	<0.1	<0.3	95.0	99.9
45	11.4	<0.1	<0.3	92.5	99.9
60	11.4	1.4	<0.3	92.5	99.4
120	11.2	1.2	<0.3	86.0	99.5
After filtration	11.2	0.7	<0.3	83.0	99.7

Table 7.9 Pb^{2+} Precipitation by 0.200 g $Ca(OH)_2$ Followed by Addition of FeS after 15 min at 25 °C; No Filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Pb^{2+} removal (%)
0	4.6	213.0	---	---	
0.200 g $Ca(OH)_2$ added					
15	11.1	135.5	---	52.0	36.4
8.1 mmol/L FeS added without filtering solution					
30	11.4	0.9	<0.3	99.5	99.6
45	11.4	1.0	<0.3	98.5	99.6
60	11.4	1.0	<0.3	98.5	99.6
120	11.3	0.9	<0.3	90.5	99.6
After filtration	11.3	1.3	<0.3	88.5	99.4

Table 7.10 Pb^{2+} Precipitation by 0.200 g $Ca(OH)_2$ and FeS Added Simultaneously at 25°C

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Pb^{2+} removal (%)
0	4.7	217.0	---	---	
15	10.6	0.2	<0.3	86.0	99.9
30	10.6	0.1	<0.3	85.0	99.9
45	10.5	<0.1	<0.3	87.0	99.9
60	10.5	<0.1	<0.3	85.5	99.9
120	10.1	<0.1	<0.3	82.0	99.9
After filtration	10.0	<0.1	<0.3	79.0	99.9

The removal of Pb^{2+} obtained by the combined NH_4OH–FeS treatment in only 15 min is excellent. Almost all the lead was removed from the solution in addition to the precipitation of Fe^{2+}. The iron ions were precipitated most likely as ferrous hydroxide. The order in which NH_4OH was added played no role in the removal efficiency of the lead in the various treatment methods. It was more convenient to perform the experiments by adding the treatment chemicals simultaneously.

For the treatment described in Table 7.7, no precipitate was observed upon addition of NH_4OH. Upon the subsequent addition of FeS, brown granular particles were observed with the formation of an "oily" surface film. The precipitate settled quickly. For treatment described in Table 7.8, upon addition of FeS, the solution turned grey with some white particles visible in the presence of an "oily" layer. After 15 min, the particles all appeared to be brown and granular. Addition of FeS and NH_4OH simultaneously formed tiny brown particles that settled slowly. However, no "oily" layer was observed by this treatment method.

The results for combined FeS–$Ca(OH)_2$ treatments also provided excellent removals of Pb^{2+} as well as Fe^{2+} with almost all the lead being precipitated within 15 min when the precipitants were added simultaneously. The Ca^{2+} concentration remained essentially constant throughout all the treatments. For treatment with FeS and $Ca(OH)_2$ added simultaneously to the waste solution, the particles formed were tiny, granular and brown with the formation of a dark olive solution. No "oily" layer was observed. For treatment with $Ca(OH)_2$ added prior to FeS, the precipitate formed was brown, which consequently formed a brown solution in the presence of an "oily" layer on the surface of the solution.

Although a very thin "oily" layer on top of the solution containing lead appeared incongruous, it did indeed occur a number of times so that some explanation is necessary. The "oily" layer became visible only with lead–containing solutions which had a base, lime or ammonium hydroxide, added to them. Only one lead–containing chemical forms an oily liquid; it is lead tetrachloride ($PbCl_4$) and its colour is supposed to be yellow. Maybe because of the very small amount of the "oily" liquid, its colour was not actually apparent. Nor is the source of the chloride ion in the solutions. However, the small amount of chloride ion necessary to make a surface film could easily be an impurity in one or other of the chemicals or reagents. For the lack of a more definitive explanation, this is the most likely source of the "oily" layer.

7.10 Summary of Hydroxide and Sulphide Precipitation of Pb^{2+}

Figure 7.21 summarizes and compares the removal efficiencies of the different treatment compounds and methods involved in the precipitation of Pb^{2+} within a two hour reaction time period. The best removal of lead ions were obtained by a combined iron sulphide–hydroxide treatment. The only disadvantage of the combined treatment was the high resulting solution pH which was 11. A post–carbonation treatment with CO_2, after initial addition of lime, provided an adequate removal with the advantage of controlling

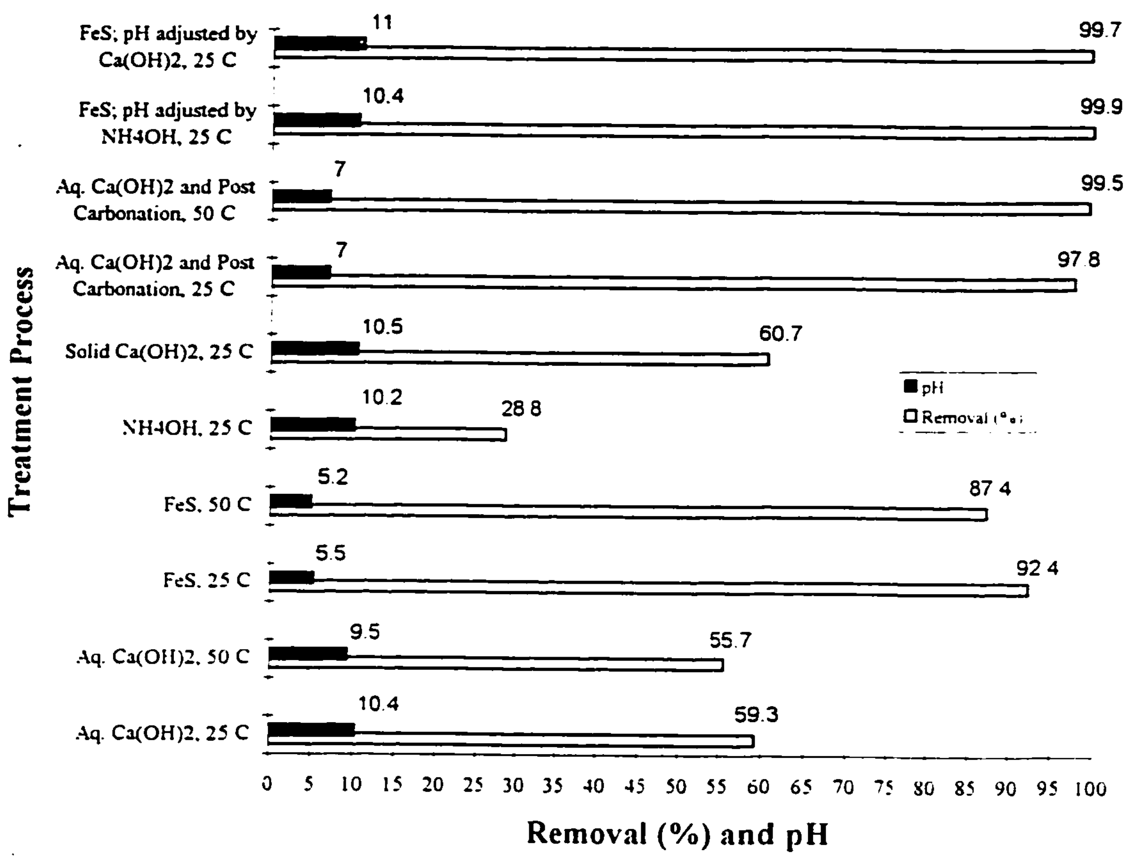


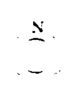
Figure 7.21. Comparison of the Processes in the Removal of Lead Ions after 2 hr Treatment.

the resulting pH of the solution. Treatment by NH_4OH alone led to an insufficient removal of Pb^{2+} within the two–hour period, with a removal fraction of only 29.0 %.

7.11 Decomposition of Pyridine and Formaldehyde by UV Radiation and Ozone, Singly and Together

The decomposition experiment with pyridine and formaldehyde in aqueous solutions by ozone both in combination with, and without, exposure to UV radiation were conducted. For all ozonation experiments, only two dosages of ozone were utilized; these were 3.5 and 6.0 mg/(L.min). The UV radiation intensity was constant throughout all the experiments. The effects of temperature and pH were not studied in these decomposition experiments. Actual data of the results for these experiments are given in Appendix E.

7.11.1 Decomposition of Pyridine

Initial investigations into the decomposition of pyridine, , were conducted over a time period of three hours. The ozone was dispersed continuously through the solution and/or the solution was continuously irradiated by UV radiation for that time period. All aqueous solutions of pyridine were colourless before treatment. Small samples of solution were frequently taken and analyzed by GC to qualitatively monitor the pyridine concentration. The GC retention time of pyridine was observed to be 9.50 min. The rate of reduction of pyridine in the solutions by the various treatment methods was quantitatively determined by TOC analysis of samples taken at regular time intervals. The results are shown in Figure 7.22. It is evident from this figure that none of the treatments of the pyridine solutions was satisfactory; that is, none decomposed at least 95 % TOC of the pyridine within a three hour reaction period.

During the treatments, the colour of the solutions remained colourless except for treatment by UV radiation alone. Treatments by UV alone produced a light yellow tint after 30 min before forming a yellow/green solution. The colour changes may be attributed to complex compound formations during treatment. However, there was no indication of the presence of these compounds from the GC. The GC only showed the reduction in the pyridine peak area throughout the experiment. This reduction was also observed for all the other treatment processes. For the treatments where ozone alone was involved, the solutions probably remained colourless because ozone reacted with pyridine by adding across the carbon–carbon double bond resulting in the production of colourless compounds which did not interact further with ozone (Gordon et al., 1988).

The rate of reduction of TOC during ozone treatments were similar for the two different ozone dosages applied. The increase in ozone dosage did not play any significant role in enhancing the decomposition of pyridine. For ozone dosages of 3.5 mg/(L.min) and 6.0 mg/(L.min) the reduction in TOC was 32.0 and 30.0 %, respectively, after three hours. Thus, in comparing the two processes, it appeared that the decomposition rate was not limited by the ozone rate so that even the lower rate provided an excess of ozone.

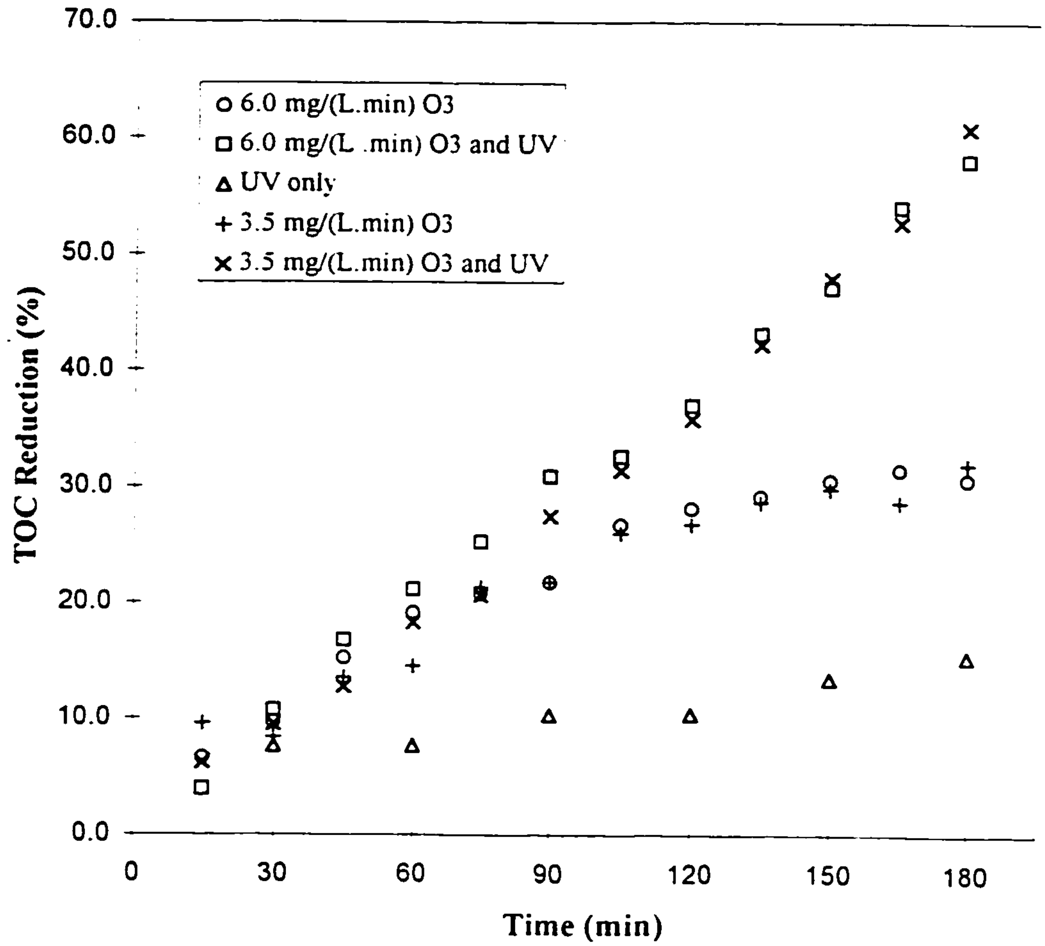


Figure 7.22. Decomposition of Pyridine by Ozone with and without Exposure to UV Radiation as Indicated in the Legend.

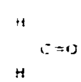
On the other hand, for ozone treatments in the presence of UV radiation, the TOC was reduced significantly by up to 60 % of its initial value. The best treatment for removal of pyridine in three hours was found to be the ozone treatment in combination with UV Again, the ozone dosage was not a significant factor in the experiments because the decomposition rates were similar for both rates of 3.5, and 6.0 mg/(L.min), O_3; the corresponding TOC reduction of pyridine was 60.9 %, and 58.1 %, respectively. When comparing the ozone treatment with and without UV radiation, the decomposition rates differed for each treatment method. The combined O_3/UV system produced rates of decomposition faster than those of ozone and UV treatments alone; thus, there was a synergistic effect.

Experiments performed in the absence of UV radiation were conducted at constant room temperature. However, in the presence of UV radiation, the temperature of the solutions being treated increased with time as expected by an average of 6.9 °C by the end of the experiment because of the heat generated by the UV lamp. The treatment of pyridine wastewaters by UV radiation alone fell far short of achieving the desired TOC removal of at least 95 %. The total TOC removed after three hours of treatment was 15.4 %. This result indicated that only a slight degree of oxidation of pyridine occurred, i.e. pyridine was not photolyzed directly with much efficiency.

Figure 7.22 also demonstrated that the decomposition rate of the ozone/UV systems appeared to be nearly linear with time; i.e. first order. In the pyridine treatment with ozone alone, a plateau in rate of reduction was obtained. This trend may indicate the production of refractory compounds (Francis, 1987). The resulting bond cleavage of ozone with the carbon–carbon double bonds may have formed intermediate oxidation products which did not interact further with ozone, thus decomposition of the pyridine was reduced or terminated completely (Gordon et al., 1988). Furthermore, the possibility that ozone reacted directly with pyridine rather than forming the highly reactive $OH^{\bullet}$ radicals may have caused the rates of oxidation to be slower by the ozone treatment alone. The pH of the pyridine solution before treatment was approximately 7.10, thus not producing the environment necessary to generate the key reactive hydroxyl radicals which are stronger oxidizing agents than is free ozone. In theory, at elevated pH levels, the hydroxyl free radical reactions dominate over the direct ozone (Rice, 1980). At low pH, ozone acts as the free ozone molecule, usually oxidizing at slower rates than at elevated pH (Rice, 1980). Therefore, only partial oxidation of pyridine occurs by treatment with ozone alone. On the other hand, the limitations associated with the characteristics of the ozone system at neutral pH levels, are apparently overcome by the presence of UV light in combination with ozone which yields a high number of $OH^{\bullet}$ radicals which accelerate the destruction of the organic species in water (Glaze et al., 1987). To oxidize pyridine, the cyclic structure must be broken first, requiring a great deal of energy. Since pyridine is a nitro–containing compound, upon ozonation NO_2^- is formed (Jun and Baozhen, 1989). This formation of NO_2^- shows that the ozone molecule attacks the nitro group in pyridine first, causing it to split off and open the ring. The separated NO_2^- can be further oxidized by ozone to NO_3^- (Andreozzi et al., 1991). This oxidation makes NO_2 act as scavengers for the free radicals in solution, thus decreasing the number of free radicals available for destruction of the organic constituent and may even terminate the radical chain reactions

(Fronk, 1987). For the ozonation experiments UV radiation provides additional energy believed to be ample for producing substantially more and additional types of free radicals. Thus it appeared that total oxidation might have been possible with an ozone/UV combined system. Hence, another experiment was performed to determine the reaction time to reduce the TOC content to desired levels. The GC peak area for pyridine was observed throughout the treatment and when the peak completely disappeared the reaction was terminated. The result for the rate of reduction of TOC (pyridine) by a combined O_3/UV treatment is presented in Figure 7.23 for which the total reaction time was six hours. The decomposition of pyridine by 6.0 mg/(L.min) O_3 with UV was successful in achieving a 99.2 % reduction in pyridine after a treatment period of six hours. The decomposition rate appeared to be linear. In conclusion, pyridine dissolved in water can only be fully degraded by means of an ozone/UV process, using a long treatment time.

7.11.2 Decomposition of Formaldehyde

Investigations into the decomposition of formaldehyde, , were conducted over a time period of three hours. All aqueous solutions of HCHO were colourless before treatment. Here also, GC analysis was used to observe the disappearance of formaldehyde. Accurate determinations were obtained by sampling at frequent time intervals and subsequent TOC analysis. The GC retention time of HCHO was observed to be 3.75 min. The results of the rate of decomposition of formaldehyde are shown in Figure 7.24. The combined ozone/UV treatments produced satisfactory results in that at least 95 %

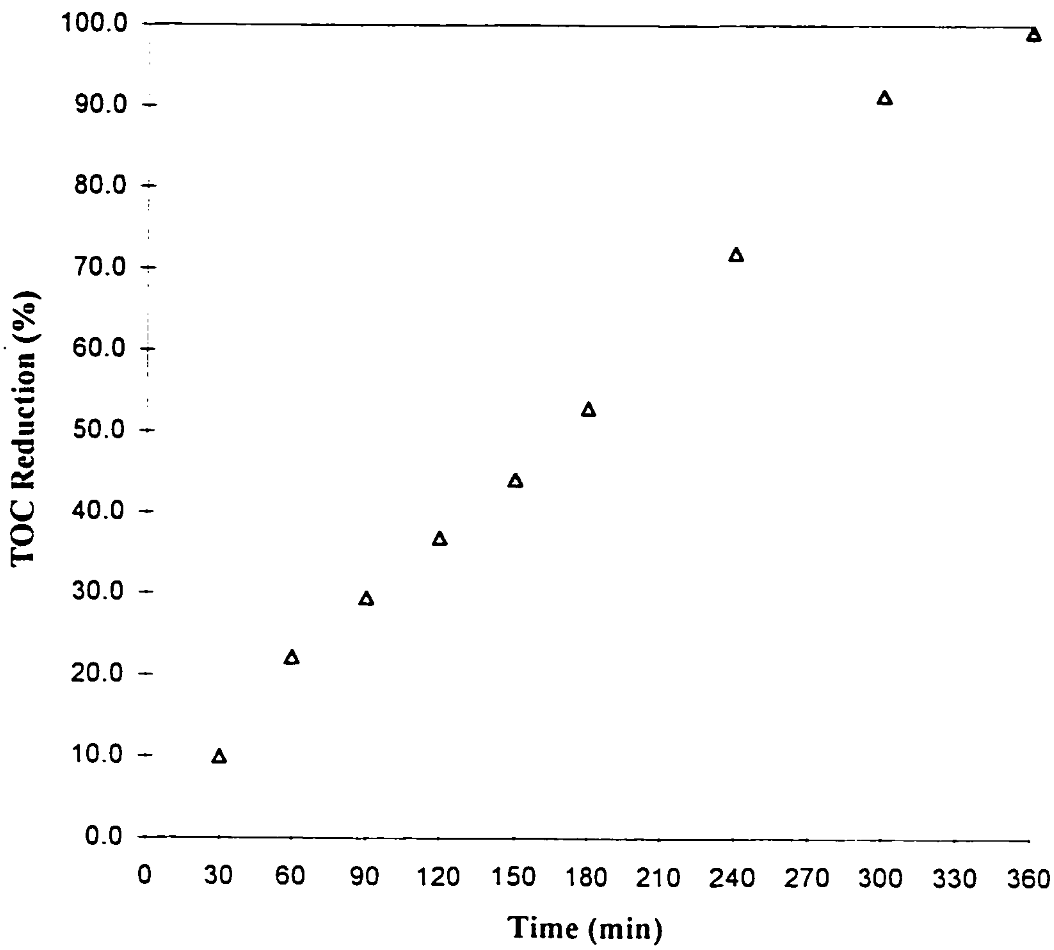


Figure 7.23. Decomposition of 200 ppm TOC of Pyridine by 6.0 mg/(L.min) O_3 in Combination with UV Radiation for Six Hours.

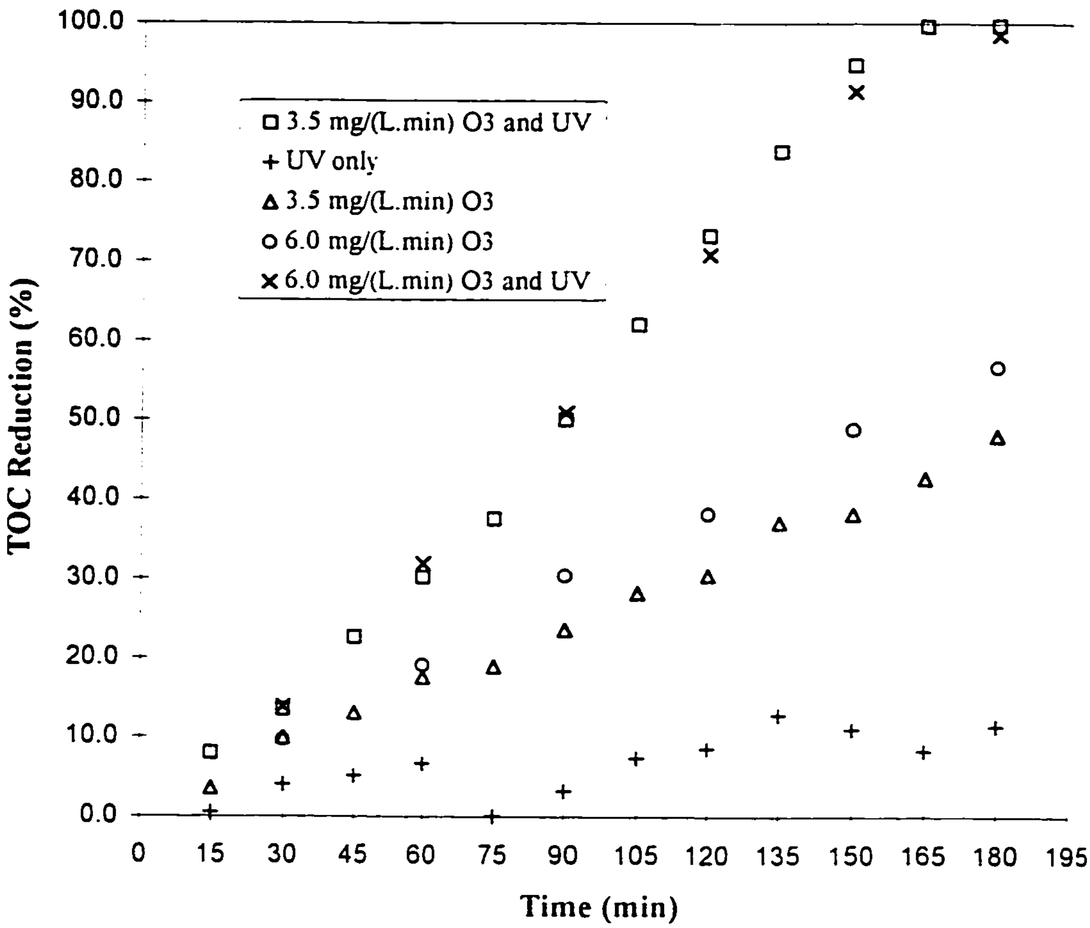


Figure 7.24. Decomposition of Formaldehyde by O_3 with and without Exposure to UV Radiation.

decomposition of formaldehyde was achieved within a three hour reaction time period. Actually using the TOC analysis, a decomposition of 99.7 % was obtained in 165 minutes. Decomposition by ozone alone reduced the TOC levels by 56.7 %, and 48.0 %, for ozone dosages of 6.0 mg/(L.min) and 3.5 mg/(L.min), respectively, within the three hour treatment. For these ozone treatments, the rates of decomposition for both ozone dosages were essentially linear; however, the decomposition rate was higher for the higher ozonation rate.

The formaldehyde was decomposed at essentially the same rate for the combined ozone/UV treatment for the two different ozone doses. This result indicated that for combined UV/ozone processes, a lower ozonation rate is sufficient for decomposition of HCHO when used in conjunction with UV radiation. For oxidation of HCHO by ozone alone, however, significantly higher ozone dosages are required. The presence of UV in the combined treatment systems seems to act as a catalyst in breaking up the HCHO double bond.

Formaldehyde decomposition by UV radiation alone only reduced the TOC (formaldehyde) content by 11.4 % at the end of the three hour experiment. In all the experiments, the solutions remained colourless throughout the treatment period. During the ozone/UV treatments, the pH of the treated formaldehyde solutions decreased slightly from 5.40 to 4.54. These pH values are averaged for all the ozone/UV experiments. This pH decrease probably indicated that CO_2 was formed as a product of decomposition (Shin et al., 1996). In conclusion, for the formaldehyde solution of about 200 ppm TOC, essentially complete TOC reduction or decomposition was obtained with the combined ozone/UV system of treatment in 165 minutes. It is noted also, that formaldehyde is considerably easier to oxidize using ozone/UV radiation than is pyridine.

7.11.3 Decomposition of Both Pyridine and Formaldehyde Together in Aqueous Solution, by Ozone and UV Radiation

Mixtures of approximately equal TOC values of pyridine and formaldehyde were oxidized by ozonation and UV radiation using solutions with 200 and 400 ppm TOC. Solutions with concentrations of 200 ppm TOC were treated for four hours while those of 400 ppm TOC were treated for five hours. The results of the rate of reduction of TOC from these mixtures is shown in Figure 7.25 and 7.26. The results shown in Figure 7.25 indicate that in the initial test with 200 ppm TOC in the mixture, the TOC value was reduced by 99.2 % in 240 min for a treatment by 6.0 mg/(L.min) ozone in combination with UV radiation. The rates of TOC reduction are smaller but appear to be linear with time for the ozone/UV treatment with a reduced ozone dosage. The treatment with 3.5 mg/(L.min) O_3/UV yielded a reduction of 94.3 % TOC after 240 min. Treatment with 6.0 mg/(L.min) O_3 alone yielded a TOC reduction of 66.5 %, which is greater than either of those obtained for the pure organic compounds. There appears to be a synergistic effect of decomposition of two compounds at the same time. The decomposition rate for the ozone treatment alone appears to be linear for the first 120 min of treatment, then the rate is reduced gradually as observed for the oxidation of pyridine previously presented

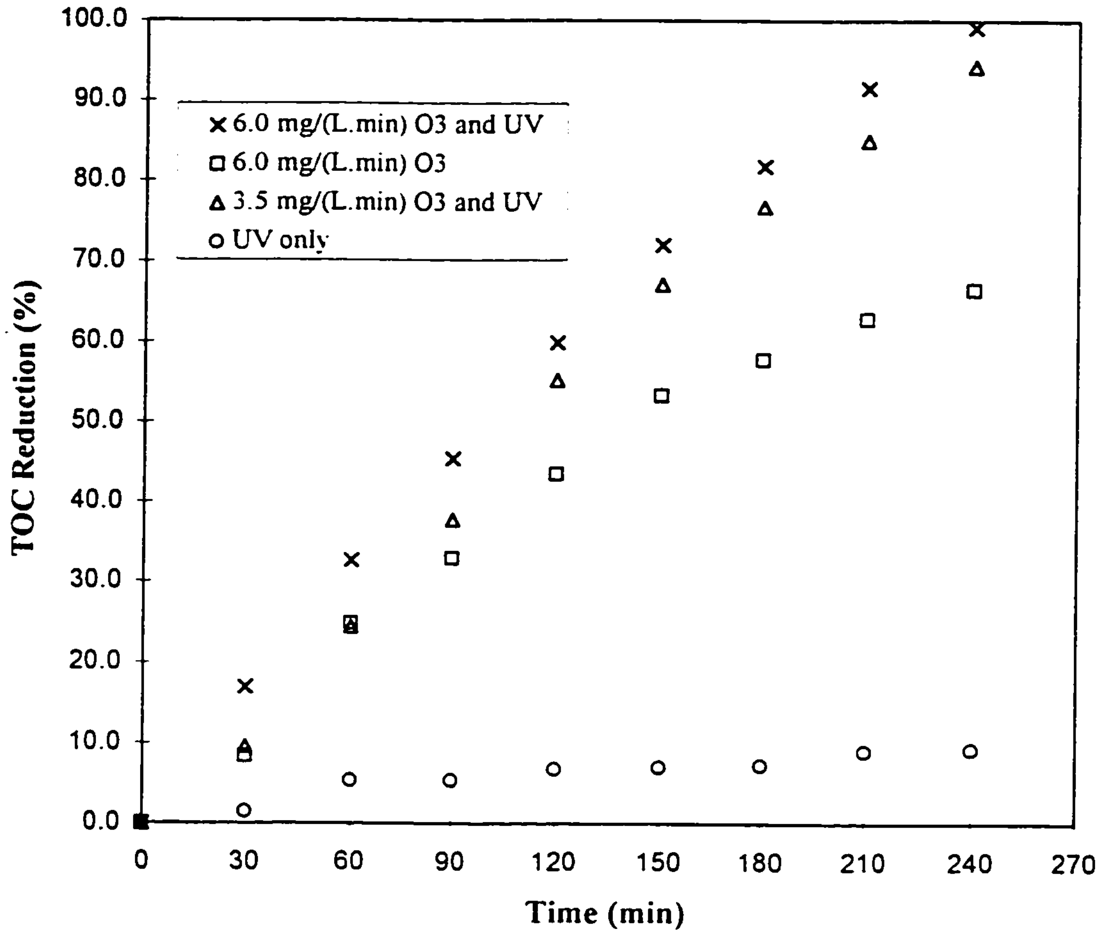


Figure 7.25. Decomposition of 200 ppm TOC for Pyridine/Formaldehyde Mixture by Ozonation and UV Radiation.

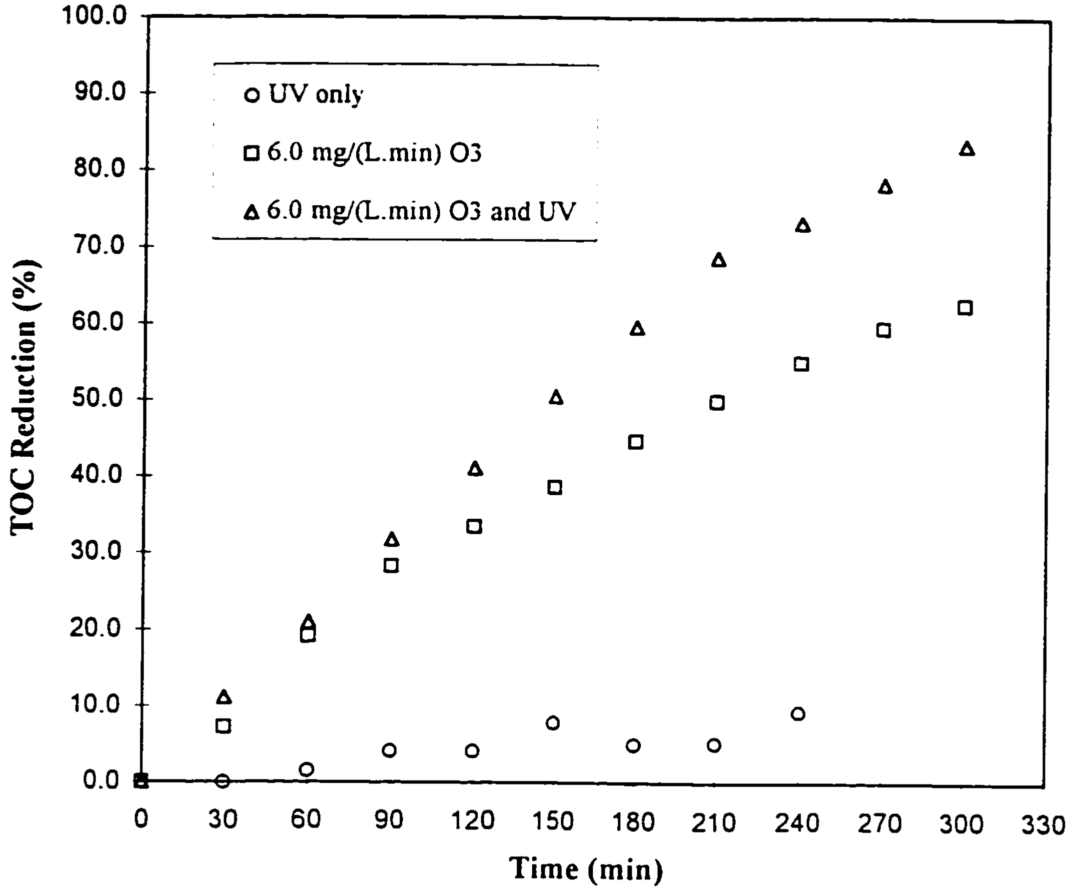


Figure 7.26. Decomposition of 400 ppm TOC for Pyridine/Formaldehyde Mixture by Ozonation and UV Radiation.

The average initial pH of the mixture was 6.9 which decreased to pH 3.0 at the conclusion of the experiment, further indicating the formation of CO_2 in solution. The effect of UV radiation alone on the decomposition of this multi–organic system was negligible as only a reduction in TOC of 9.3 % occurred after four hours of treatment.

Several observations can be made on inspection of the decomposition rates of the mixed compounds in aqueous solution. It would appear that even in solution, formaldehyde tended to be decomposed at a faster rate than did pyridine. Upon observation of the GC chart, the formaldehyde peak always disappeared before the pyridine peak. This more rapid disappearance indicated the ease with which formaldehyde could be oxidized in relation to that for pyridine due to their respective chemical structures.

Another observation concerns the decomposition rates with the high rate of ozone and UV radiation for both formaldehyde and pyridine, singly and together, at the two concentrations in solution, 200 and 400 ppm TOC. Essentially all the pyridine at 200 ppm was decomposed in six hours; essentially all the formaldehyde at 200 ppm was decomposed in 2.75 hours. If it is assumed that each organic compound required a fixed amount of ozone to decompose it while assisted by UV radiation, it should be possible to estimate how much ozone, or time of exposure to ozone, would be required for different concentrations of the organic. In the situation of a solution composed of 400 ppm of total organic contaminant, it would then require about 6.0 hr + 2.75 hr or 8.75 hours of exposure to the high dose of ozone with UV radiation to decompose this concentrated mixture. While this experiment was not actually performed, extrapolation of Fig. 7.26 to some 525 minutes would be required for complete decomposition of this solution. Further, if a 200 ppm mixture contains 100 ppm of each organic, the time for decomposition would be 3.0 hr + 1.37 hr or 4.37 hours or half the time for each chemical. The actual time for decomposition of the 200 ppm TOC mixture of the two chemicals was four hours. Thus, it would appear that the decomposition is approximately related to the quantity of ozone utilized.

It is also observed that the rate of decomposition in most of the experiments decreases as time progresses. One could consider that the rate of decomposition is influenced by the reduced concentration of residual organic left in solution after much of it was decomposed. This effect seems unlikely, though, because, when starting with a 400 ppm mixed solution, the rate of decomposition of the second half of the organic when 200 ppm are remaining, is much lower than for the situation when starting with a 200 ppm solution of pyridine alone. There are two variables which were not kept constant during these experiments; they are the temperature and pH. As the solution temperature rose steadily during the reaction, one would expect an increase in decomposition, not a reduction. Further, the temperature change was only a few degrees On the other hand, the pH changed very significantly from approximately 7 to as low as 3. It seems likely that the higher acidity of the aqueous solutions may have contributed to the reduced reaction rates during the later stages of treatment. Perhaps the acidity influenced the stability of the free radicals attacking the molecular structure of the organics.

The UV radiation treatment process alone did not oxidize the organic mixtures as effectively as O_3/UV treatments. The rate of decomposition is slower in comparison to the other treatment processes. Therefore, regardless of the reaction mechanisms by which the ultraviolet–catalyzed ozonation reactions proceeded, there can be no doubt that the ozone/UV combination caused oxidation to proceed more rapidly than did the use of ozone alone or UV radiation systems alone.

7.12 Oxidation of Dissolved Lead using Ozone and UV Radiation, Separately and Together

As previously presented, removal of copper and zinc metal ions were removed successfully by chemical precipitation. Although precipitation of zinc was not completely achieved, it was not treated by ozonation because it only exists in one valence state in solution and would be unreactive when exposed to ozone oxidation (Rice, 1980). Only lead metal ion was not successfully removed by the single chemical precipitation techniques investigated in this thesis. Thus, the precipitation of lead was investigated using ozone both with, and without, exposure to UV radiation and by adjusting the pH of the solution using solid $Ca(OH)_2$ and aqueous NH_4OH The results of the rates of removal of approximately 200 ppm Pb^{2-} from the wastewater solutions by the various ozonation treatment processes over a three hour period are demonstrated in Figure 7.27. This figure shows the successful removal of more than 97 % Pb^{2-} from the solution. The rate of precipitation by the ozonation treatments was faster than by any of the chemical precipitation systems investigated previously.

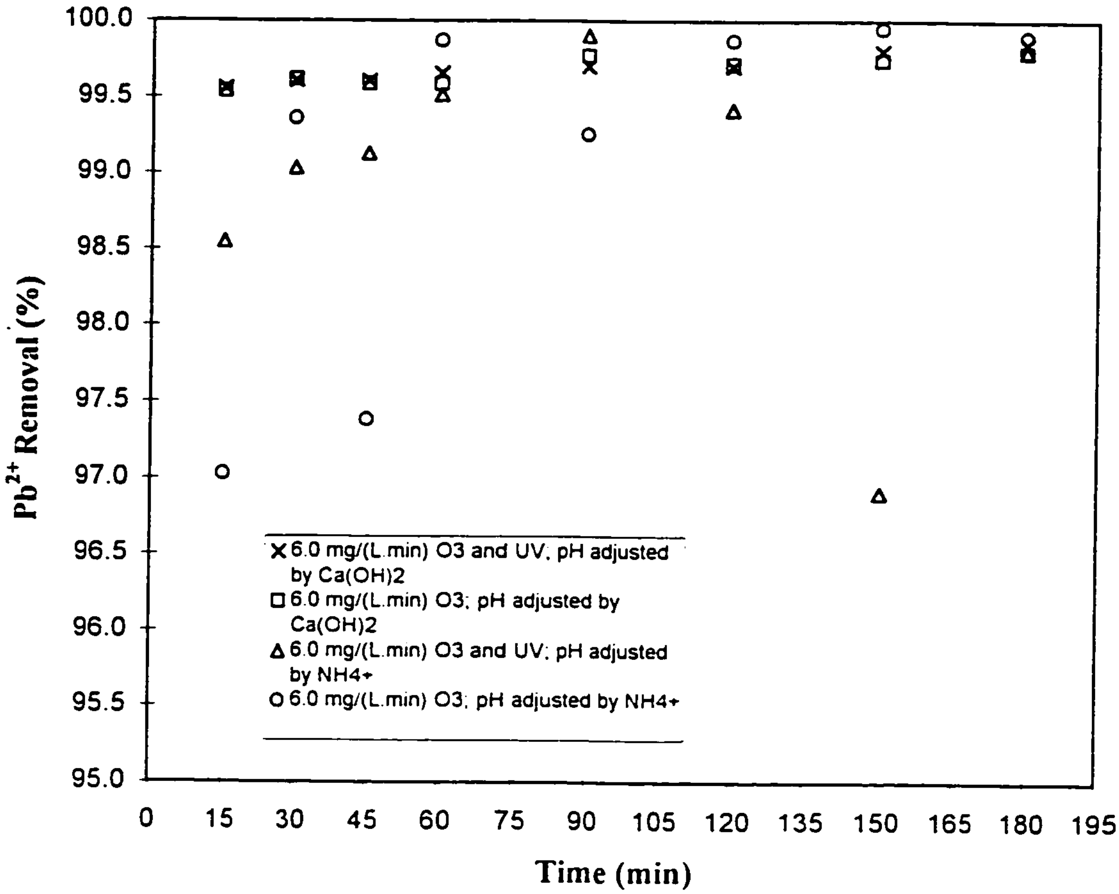


Figure 7.27. Lead Metal Ion Precipitation by Ozonation with pH Adjustment using $Ca(OH)_2$ and NH_4OH.

After just 15 min of treatment by the ozonation systems, with and without UV radiation, but using lime as a base, the removal of Pb^{2+} was more than 99.5 %. At the end of the three hour treatment period, it was clear that almost all the lead ions had been precipitated from the solution. The Pb (II) was oxidized to Pb (IV) to produce compounds of various oxidation states.

7.12.1 Effect of $Ca(OH)_2$ Addition

For lead treatment by ozonation involving the pH adjustment by $Ca(OH)_2$, the use of UV radiation had no effect in the removal efficiency of Pb^{2+} Hence, it was possible that ozone is the rate controlling factor, and UV radiation had little influence on the oxidation rate. During ozonation, the pH of the solution declined while the concentration of Ca^{2+} decreased by an average of 39 % by the end of the three hour experiments. The decrease in pH indicated that probably calcium precipitated out of the solution as a complex of lead and calcium. Furthermore, calcium only exists in solution in one valence state and could not have been oxidized by ozone. The Pb^{2+} solution before ozonation treatment was colourless. The solutions turned yellow upon immediate addition of O_3 and combined O_3/UV. After 15 min, the solutions turned orange during mixing forming tiny suspended precipitates which settled slowly. After 60 min of treatment, the solutions turned brown during mixing forming dark orange precipitates. The observed colours of the resulting precipitates indicated the formation of complex oxide and hydroxide compounds of lead at its highest oxidation state of +4. The colour changes of the precipitates give a clue as to the compounds: $Pb(OH)_2$ (white), PbO (yellow), Pb_2O_3 (orange–yellow), Ca_2PbO_4 calcium orthoplumbate (red–brown), and PbO_2 (brown).

7.12.2 Effect of NH_4OH Addition

For removal of lead ions using NH_4OH for pH adjustments, and utilizing ozone with and without UV radiation, the colours observed for the precipitates in the treated solutions were similar to those of the solutions using lime, except for the formation of brown precipitates after 90 min of treatment. The lack of brown precipitates indicated that the final oxidation state for lead achieved with lime was not achieved with NH_4OH.

Ozone is an effective means of reducing the lead concentration of lead–bearing wastewater, when lime is used for pH adjustment. Its effectiveness is comparable to that using a two–stage lime–carbonation precipitation treatment. It is apparent that alternate methods of treatment can sometimes be devised and the one that is ultimately used usually depends on financial considerations.

Chapter 8.0 Conclusions

The conclusions will be listed in two sections, based on the experimental results obtained, and followed by a summary for the uses of this research.

8.1 Chemical Precipitation

1) Precipitation of Cu^{2+} and Zn^{2+} (more than 99 % metal ion removed) as the hydroxides was more effective in removing the metals than treatment by FeS (not more than 70 % metal removed).
2) In an acidic medium, FeS was not effective for the precipitation of Cu^{2+} and Zn^{2+}.
3) Increasing the precipitation temperature from 25 °C to 50 °C had no significant effect on precipitation of Cu^{2+}, Zn^{2+}, and Pb^{2+} as the hydroxides
4) For maximum removal efficiency of Cu^{2+} and Zn^{2+} the pH must be controlled within a narrow range, $8.5 < pH < 10$.
5) Maximum removal of Cu^{2+} and Zn^{2+} with hydroxide and insoluble sulphide precipitation was achieved in 15 minutes for the treatment dosages specified.
6) Insoluble sulphide precipitation was more effective (95 % ion removed) in the precipitation of Pb^{2+} than hydroxide precipitation (60 % metal ion removal) within a two hour reaction time period.
7) Insoluble sulphide precipitation of Pb^{2+} produced better removal rates at 25 °C, 95 % metal ion removal, than at 50 °C, 93% metal ion removal.

8) A combined OH^-–FeS precipitation technique was effective in removing more than 95 % of each Pb^{2+} and Fe^{2+} in 30 minutes.

9) For the combined OH^-–FeS precipitation treatment, the method in which the hydroxide compound was added was not significant in improving the removal rates of Pb^{2+}; it was more convenient to add the hydroxide and FeS simultaneously.

10) Post–precipitation treatments using one–step carbonation was not as effective as incremental addition of CO_2 for the removal of Pb^{2+}, because the precipitate tended to resolubilize when the solution pH deviated from the minimum solubility point.

11) The FeS treatment of Cu^{2+}, Zn^{2+}, and Pb^{2+} produced high concentrations of iron ions in the treated solutions.

12) The ISP process using FeS for the treatment of Pb^{2+} was effective over the pH range 5–11 with maximum effectiveness shown for pH > 10.0.

8.2 Ozonation

1) Combined ozone/UV systems should be utilized to produce radicals that are highly reactive to achieve total oxidation of organic species in wastewater.

2) Pyridine and formaldehyde both as pure solutions and as mixtures were not photolyzed directly with much efficiency when being treated by UV radiation alone.

3) Pyridine decomposition by ozonation required a treatment of six hours in the presence of UV radiation to remove more than 99 % TOC in solution.

4) For pyridine decomposition, increasing the ozone dosage from 3.5 mg/(L.min) to 6.0 mg/(L.min) had no significant effect on the reduction rates of TOC in any of the ozonation systems.

5) Total reduction in TOC content was achieved in the decomposition of HCHO in 165 minutes utilizing a combined O_3/UV treatment.

6) For decomposition of HCHO, increasing ozone dosage from 3.5 mg/(L.min) to 6.0 mg/(L.min) had no effect on the reduction rates of TOC in the combined O_3/UV processes.

7) Essentially total TOC reduction for a multi–organic system of 200 ppm C_5H_5N/HCHO was obtained by the O_3/UV system after four hours of treatment.

8) A TOC reduction by 83.5 % for the multi-organic system of 400 ppm C_5H_5N/HCHO was obtained by the O_3/UV system after four hours of treatment.

9) More than 97 % of lead ions were precipitated after 15 minutes of treatment utilizing a pH adjusted ozone treatment.

10) UV radiation had no significant effect on the removal of lead ions from solution.

11) More than three hours of treatment time is required, using ozone even when assisted by UV radiation, to decompose organic contaminants.

8.3 General Conclusions

There are many different metal contaminants in wastewater depending on the industrial source; hence, there can be no single system of treatment for a wide range of metals. Essentially the major contribution of this work is defining five different variations in treatment processes which can be utilized for the removal of dissolved metals by precipitation where the concentration of the metals are high; 200 ppm. These treatment processes are:

1) Use of lime slurry alone to precipitate metals as the hydroxide.
2) Use of FeS slurry to precipitate metals as the sulphide in an acidic medium.
3) Use of a combination of lime and FeS slurry to precipitate the metals and additional chemicals as the sulphide along with ferrous hydroxide.
4) Use of combination of lime and dispersed carbon dioxide gas to precipitate the metals as the carbonate or hydroxide–carbonate complex.
5) Use of lime and ozone to precipitate the metals as various oxide forms.

This research was mainly exploratory; hence, by defining possible methods of treatment for metals in wastewater, two or more of these methods could be used to determine which is the most suitable for the metal or metals concerned.

Insofar as the ozone/UV treatment for organic contaminants is concerned, it appears that the decomposition of even relatively simple hydrocarbons, while possible, takes a good deal more time than is normally practical.

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APPENDIX A

List of Chemicals

A Chemicals

- Cupric sulphate ($CuSO_4 \bullet 5H_2O$), min. assay 99.5%, BDH Inc.
- Zinc sulphate ($ZnSO_4 \bullet 7H_2O$), min. assay 99.5%, BDH Inc.
- Lead nitrate ($Pb(NO_3)_2$), min. assay 100.2%, BDH Inc.
- Hydrated lime ($Ca(OH)_2$), Fisher Scientific.
- Ammonium hydroxide (NH_4OH), min. assay 28.0%–30.0%, Fisher Scientific.
- Carbon dioxide gas, Air Products Inc.
- Hydrochloric acid (HCl), min. assay 36.5%–38.0%, BDH Inc
- Copper Standard, 1000 ppm Cu^{2+} in 1% HCl, A.A standard, VWR.
- Zinc Standard, 1000 ppm Zn^{2+} in 5% HNO_3, A.A standard, VWR.
- Lead Standard, 1000 ppm Pb^{2+} in 5% HNO_3, A.A standard, VWR.
- Calcium Standard, 1000 ppm Ca^{2+} in 1% HNO_3, A.A standard, VWR.
- Iron Standard, 1000 ppm Fe^{2+} in 1% HCl, A.A standard, VWR.
- Sodium Standard, 1000 ppm Na^{+} in 1% HCl, A.A standard, VWR.
- Sulphuric acid (H_2SO_4), min. assay 95.0%–98.0%, BDH Inc.
- Iron (II) sulphate ($FeSO_4 \bullet 7H_2O$), min. assay 99.0%, Fisher Scientific.
- Sodium hydrosulphide hydrate (NaHS), Aldrich Chemicals.
- Internal Filling Solution (3M KCl), Orion Research
- Pyridine (C_5H_5N), Fisher Scientific.
- Formaldehyde solution (HCHO), 37% wt., 10%–15% methanol, Fisher Scientific.

- Oxygen gas, compressed, zero grade, Air Products Inc.
- Helium gas, compressed, zero grade, Air Products Inc.
- Hydrogen gas, compressed, zero grade, Air Products Inc.
- Acetylene gas, compressed, zero grade, Air Products Inc.
- Nitrous oxide gas, compressed, zero grade, Air Products Inc.
- Potassium iodide (KI), min. assay 99.0%, BDH Inc.
- Sodium thiosulphate ($Na_2S_2O_3$), assay 100.1%, Fisher Scientific.
- Starch indicator solution, 1% wt/v, VWR Scientific.

APPENDIX B

List of Equipment with Specifications and Parameters

B–1 Equipment

- Atomic absorption spectrophotometer, Varian Spectra AA•250 Plus.
- pH meter, Orion Research, model 230A.
- Variable speed mixer (drive for mixer), Cole Parmer Instrument and Equipment Company.
- Glass mixer (for lime and ISP process), Glass Blowing Shop, University of Ottawa, 7.0 in. length w/ 3.5 cm impeller diameter.
- Glass mixer (for ozonation process), Glass Blowing Shop, University of Ottawa, 10.0 in. length w/ 3.5 in. impeller diameter
- Thermocouple, Barnant Type T, model 100.
- Stopwatch, Fisher Scientific.
- Gas tight syringes, Hamilton Inc., Teflon Luerlock, 10 ml.
- Membrane syringe filter units. Chromatographic Specialties Inc., 25 mm diameter, 5.0 μm pore size diameter.
- Eppendorf pipette, Gilson, 200 μL and 1 mL.
- Bubble meter.
- pH probe, Orion Research, Low Maintenance Triode, model 9107.
- pH probe, Orion Research, Ross Combination Electrode, model 8102.
- Automatic Temperature Compensation Probe, Orion Research, model 917005 ATC.
- Vacuum filter, VWR Scientific, glass funnel w/ support.

- Prefilter paper, Millipore Ltd, nominal retention ≅ 2 μm.
- Stir bars, Labcor Inc., 1" x $\frac{5}{16}$" w/ spinning ring.
- Gas Dispersion tubes, ACE Glass Inc., 300 mm pore fritted ware.
- Pipette (for ISP process), Kimble, modified, 25 mL w/ 3.0 mm orifice diameter.
- Ozone generator, OREC model 0305–0.
- UV lamp, UVP Inc., Pen-Ray PCQ immersion lamp, 8.0 in. lighted length, 20.0–24.0 mm taper length, λ = 254 nm, 5000 $\mu W/s^2$ light intensity, 90% radiation emitted.
- Power supply (for UV lamp operation), UVP Inc., 115 V / 60 Hz @ 26 mAmps.
- Total organic carbon analyzer, Folio Instruments, model DC–190.
- Gas Chromatograph, Varian Aerograph Series 1400.
- GC column, Chromatographic Specialties, 10% Fluorad FC–431 on Chromasorb W–HP 80/100.
- Ion exchanger, Zenopure, Quatra 90LC.
- Scrubber, volumetric flask, 200 mL.
- Housing for the ozonation process reactor, glass container, Univ. of Ottawa ware; 2 L volume; 7.0 in. height; 1 in. lid thickness; three, 23 ½ mm x 1 ¼ in., open ports on lid; center port fitted with a 4 in. Teflon end-cap w/ bearing to support the stirring rod.

- Cork sealers (for ozone glass housing port openings), punctured to fit relevant equipment, 24 mm diameter.

B–2 Equipment Parameters

The operating parameters for the GC and ozone generator are specified in this section.

B–2.1 GC Parameters

The temperature settings were constant for all ozonation experiments:

Column temperature: 120 °C

Injector temperature: 160 °C

Detector temperature: 200 °C

Table B–2.1 Gas Pressure and Flow Rate Settings for all Ozonation Experiments

Gas	Pressure (psig)	Flow rate of gas (cm^3/min)
Helium	40.0	30
Hydrogen	18.0	40
Air	20.0	300

B–2.2 Ozone Generator Parameters

- The following parameters were constant for ozone production: At a system pressure of 10 psig the oxygen flow rate was 40.0 L/min.

- Settings for maximum ozone production: resistance 0 %, current 0.55 Amps

- Settings for minimum ozone production: resistance 6 %, current 0.45 Amps

APPENDIX C

Sample Calculations

C Sample Calculations for the Production of $FeS_{(s)}$

The sample calculation presented is for the production of FeS sludge for the removal of 200 ppm Cu^{2+} from water using the ISP process.

1) By unit conversion of ppm to mmol, the amount of Cu^{2+} in solution to be treated is 0.63 mmol in a 200 mL solution $CuSO_4 \bullet 5H_2O$, i.e.,

$$200\ \text{mg/L}\left(\frac{1\ \text{mmol}\ Cu^{2+}}{63.546\ \text{mg}}\right)\left(\frac{200\ \text{mL}}{1000\ \text{mL}}\right) = 0.63\ \text{mmol}\ Cu^{2+}$$

2) The amount of 25 mL FeS sludge required is 1.5 times the theoretical equivalent of 200 ppm Cu^{2+} in solution to be treated.

$$FeS(s) + Cu^{2+}(aq) \Leftrightarrow CuS(s) + Fe^{2+}(aq) \qquad (C-1.1)$$

$$C_1V_1 = 1.5\,[C_2V_2] \qquad (C-1.2)$$

where C and V are the concentration and volume of compounds in mmol and mL, respectively. Therefore,

$$C_1(25\ \text{mL}) = 1.5(0.63\ \text{mmol}\ Cu^{2+})$$

$$C_1 = 37.8\ \text{mmol/L FeS}$$

3) From the stoichiometric ratio of FeS to Cu^{2+} in equation C−1.1, the required concentration of 25 mL FeS is 37.8 mmol/L.

4) To produce FeS the following reaction occurs:

$$FeSO_4(aq) + NaHS(aq) \Leftrightarrow FeS(s) + H^+(aq) + SO_4^{2-}(aq) + Na^+(aq) \qquad (C-1.3)$$

5) From equation C−1.3, the stoichiometric ratio of compounds is NaHS : $FeSO_4$: FeS : : 1:1. Thus the required concentration of Fe^{2-} and HS^- is 37.8 mmol/L for each component.

6) Hence, the calculated amount of $FeSO_4 \bullet 5H_2O$ is 1.051 g per 100 mL solution.

7) Also the calculated amount of NaHS is 0.212 g per 100 mL solution.

8) Thus, to produce the required dosage of FeS sludge, dilution effects of adding the two reagents implies doubling their relevant mass per solution. Therefore, 2.102 g and 0.424 g of $FeSO_4 \bullet 5H_2O$ and NaHS, respectively, must be added to individual 100 mL water solutions to form 37.8 mmol/L FeS.

APPENDIX D

Raw Experimental Data for Chemical Precipitation Processes

D Structure for Presentation of the Raw Experimental Data

1). Treatment of Cu^{2-}, Zn^{2-}, and Pb^{2-} by aqueous $Ca(OH)_2$ slurry are presented in Tables D–1 through D–12.

2) Treatment of Pb^{2-} by aqueous $Ca(OH)_2$ slurry followed by post–CO_2 gas addition are presented in Tables D–13 through D–16.

3) Treatment of Cu^{2-}, Zn^{2-}, and Pb^{2-} by FeS sludge are presented in Tables D–17 through D–30.

4) Treatment of Cu^{2-}, Zn^{2-}, and Pb^{2-} by aqueous NH_4OH are presented in Tables D–29 through D–34.

5) Treatment of Cu^{2-}, Zn^{2-}, and Pb^{2-} by solid $Ca(OH)_2$ are presented in Tables D–35 through D–40.

6) Combined Hydroxide–Insoluble Sulphide Precipitation of Pb^{2-} is presented in Tables D–41 through D–52.

Table D-1. Cu^{2+} Precipitation by 40.9 mg/L $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.8	214.0	2.5	22.9	
15	10.7	0.1	112.0	24.6	99.9
30	10.8	0.3	100.0	24.3	99.9
45	10.6	0.4	95.0	25.5	99.8
60	10.6	0.3	73.0	25.1	99.9
120	10.3	0.5	74.0	24.9	99.8
After filtration	9.9	0.4	72.0	22.8	99.8
CO_2 addition	5.4	0.7	67.0	22.8	99.7

Table D-2. Cu^{2+} Precipitation by 40.9 mg/L $Ca(OH)_2$; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.9	219.0	2.5	22.9	
15	10.7	0.2	102.0	24.7	99.9
30	10.6	0.2	94.0	24.8	99.9
45	10.5	0.3	95.0	25.4	99.9
60	10.5	0.4	76.0	24.9	99.8
120	10.2	0.4	60.0	24.7	99.8
After filtration	10.1	0.6	67.0	22.7	99.7
CO_2 addition	5.2	0.7	64.0	22.8	99.7

Table D-3. Cu^{2+} Precipitation by 39.3 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.6	223.0	2.5	51.9	
15	8.8	1.3	86.0	52.6	99.4
30	8.5	0.8	94.0	50.0	99.6
45	8.1	0.9	89.0	52.4	99.6
60	8.0	0.8	91.0	50.5	99.6
120	8.0	0.9	103.0	52.4	99.6
After filtration	6.3	1.5	84.0	31.1	99.3
CO_2 addition	5.3	1.5	60.0	31.3	99.3

Table D-4. Cu^{2+} Precipitation by 39.3 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.6	193.0	2.5	50.5	
15	8.5	0.8	101.0	53.9	99.6
30	8.3	0.9	84.0	51.7	99.5
45	8.0	0.8	99.0	53.3	99.6
60	7.8	0.8	88.0	50.9	99.6
120	7.7	0.9	106.0	52.3	99.6
After filtration	6.9	1.5	77.0	33.9	99.2
CO_2 addition	5.5	1.4	96.0	28.3	99.3

Table D-5. Zn^{2+} Precipitation by 37.4 mg/L $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.0	203.0	2.5	23.2	
15	10.7	0.8	119.0	23.7	99.6
30	10.7	0.5	121.0	23.7	99.8
45	10.6	0.5	110.0	23.8	99.7
60	10.5	0.3	102.0	23.9	99.9
120	9.8	0.2	93.5	24.9	99.9
After filtration	9.4	1.1	97.5	24.1	99.5
CO_2 addition	5.7	1.2	163.0	23.9	99.4

Table D-6. Zn^{2+} Precipitation by 37.4 mg/L $Ca(OH)_2$; Temp ~ 25 °C, Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.2	203.0	2.5	23.3	
15	10.7	0.8	102.0	23.9	99.6
30	10.7	0.5	114.0	24.1	99.7
45	10.6	0.5	94.0	24.2	99.8
60	10.6	0.3	107.0	24.2	99.9
120	10.3	0.7	97.5	25.5	99.7
After filtration	10.2	1.1	94.5	23.8	99.4
CO_2 addition	6.2	1.2	96.0	23.7	99.4

Table D-7. Zn^{2+} Precipitation by 38.1 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.3	208.0	2.5	51.9	
15	9.9	0.5	113.0	50.9	99.8
30	9.8	1.1	117.0	49.8	99.5
45	9.7	0.1	115.0	51.5	100.0
60	9.7	1.0	96.5	52.2	99.5
120	9.1	0.5	104.0	51.8	99.8
After filtration	9.1	0.5	98.0	50.0	99.7
CO_2 addition	6.6	0.2	86.5	53.7	99.9

Table D-8. Zn^{2+} Precipitation by 38.1 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.4	206.0	2.5	52.8	
15	9.8	1.0	107.0	49.7	99.5
30	9.7	0.5	109.0	49.5	99.8
45	9.6	0.3	100.0	50.8	99.9
60	9.6	0.3	119.0	50.0	99.8
120	9.1	0.5	104.0	52.7	99.8
After filtration	9.1	0.5	96.0	48.3	99.8
CO_2 addition	5.9	0.5	84.0	52.4	99.8

Table D-9. Pb^{2+} Precipitation by 11.9 mg/L $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.9	205.0	2.5	22.9	
15	10.5	123.0	32.0	23.5	40.0
30	10.6	146.0	35.5	23.5	28.8
45	10.6	131.0	28.0	23.6	36.1
60	10.5	129.0	26.5	23.7	37.1
120	10.4	83.5	38.0	24.0	59.3
After filtration	10.4	100.0	33.5	22.8	51.2
CO_2 initial	6.0	13.5	28.0	23.1	93.4
CO_2 final	4.6	60.0	30.0	23.2	70.7

Table D-10. Pb^{2+} Precipitation by 11.9 mg/L $Ca(OH)_2$; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.8	205.0	2.5	22.7	
15	10.5	142.0	35.0	23.5	30.7
30	10.5	132.0	35.5	23.8	35.6
45	10.6	127.0	27.5	23.8	38.0
60	10.5	116.0	31.5	24.0	43.4
120	10.5	--------	41.5	24.6	--------
After filtration	10.4	<50	33.5	22.8	--------
CO_2 initial	5.3	31.0	22.5	22.9	84.9
CO_2 final	4.6	68.0	24.5	23.0	66.8

Table D-11. Pb^{2+} Precipitation by 11.4 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.8	203.0	2.5	50.4	
15	9.8	122.0	30.5	51.8	39.9
30	9.8	111.0	27.5	49.6	45.3
45	9.7	124.0	31.0	50.8	38.9
60	9.7	103.0	36.0	49.9	49.3
120	9.6	72.0	30.5	50.1	64.5
After filtration	9.7	63.0	30.5	49.3	69.0
CO_2 initial	5.8	11.0	33.0	49.9	94.6
CO_2 final	4.7	44.0	21.5	49.4	78.3

Table D-12. Pb^{2+} Precipitation by 11.4 mg/L $Ca(OH)_2$; Temp ~ 50 °C; Run2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.85	192	2.5	50.4	
15	9.6	156	33.5	49.7	18.8
30	9.58	146	33	49.6	24.0
45	9.54	134	37.5	51.3	30.2
60	9.52	131	29	50.3	31.8
120	9.47	103	32	50.6	46.4
After filtration	9.53	86	36	49.7	55.2
CO_2 initial	5.18	21	23	49.4	89.1
CO_2 final	4.6	27	27.5	49.7	85.9

Table D-13. Pb^{2+} Precipitation by 11.9 mg/L $Ca(OH)_2$ and Post-CO_2 Treatment; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.3	205.0	2.5	22.5	
15	10.8	92.0	44.0	23.4	55.1
30	10.9	96.0	44.0	23.5	53.2
After filtration	10.9	48.0	45.0	23.2	76.6
$C0_2$ addition; 0.10 mL/s @ 400 rpm					
	10.0	4.0	44.0	23.4	98.0
	9.0	3.0	46.0	23.4	98.5
	8.0	3.0	46.0	23.4	98.5
	7.0	5.0	45.0	23.4	97.6
	6.0	9.0	44.0	23.4	95.6
	5.5	9.0	43.0	24.6	95.6

Table D-14. Pb^{2-} Precipitation by 11.9 mg/L $Ca(OH)_2$ and Post-CO_2 Treatment; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.6	209.0	2.5	22.6	
15	10.9	90.0	42.0	23.5	56.9
30	10.9	98.0	38.0	23.7	53.1
After filtration	10.8	58.0	36.0	23.2	72.2
$C0_2$ addition; 0.10 mL/s @ 400 rpm					
	10.0	1.0	39.0	23.4	99.5
	9.0	1.0	39.0	23.4	99.5
	8.0	2.0	39.0	23.3	99.0
	7.0	4.0	43.0	23.6	98.1
	6.0	9.0	43.0	24.1	95.7
	5.5	9.0	40.0	24.5	95.7

Table D-15. Pb^{2+} Precipitation by 12.1 mg/L $Ca(OH)_2$ and Post-CO_2 Treatment; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.8	212.0	2.5	50.1	
15	9.3	88.0	36.0	50.2	58.5
30	10.0	90.0	37.0	52.4	57.5
After filtration	10.0	53.0	40.0	50.4	75.0
$C0_2$ addition; 0.13 mL/s @ 400 rpm					
	9.3	1.0	33.0	50.1	99.5
	7.6	1.0	30.0	50.1	99.5
	7.0	1.0	34.0	50.1	99.5
	5.6	6.0	37.0	50.1	97.2

Table D-16. Pb^{2+} Precipitation by 12.1 mg/L $Ca(OH)_2$ and Post-CO_2 Treatment; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.8	206.0	2.5	50.1	
15	9.5	85.0	39.0	50.0	58.7
30	10.1	82.0	37.0	50.0	60.2
After filtration	10.1	55.0	35.0	50.0	73.3
$C0_2$ addition; 0.13 mL/s @ 400 rpm					
	9.0	7.0	38.0	50.6	96.6
	8.0	1.0	39.0	50.6	99.5
	7.0	1.0	38.0	50.1	99.5
	6.1	3.0	35.0	50.1	98.5

Table D-17. Cu^{2+} Precipitation by 44.7 mmol/L FeS ; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.2	240.0	0.5	23.9	
15	4.0	88.0	160.0	25.1	64.7
30	3.8	86.0	165.0	25.2	65.5
45	3.7	87.0	166.0	25.3	65.1
60	3.7	85.0	166.0	25.3	65.9
120	3.6	84.0	168.0	25.5	66.3
After filtration	3.7	88.0	156.0	25.5	64.7

Table D-18. Cu^{2+} Precipitation by 44.7 mmol/L FeS ; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.4	233.0	0.5	23.6	
15	3.9	69.0	161.0	24.8	70.4
30	3.9	69.0	164.0	25.0	70.4
45	3.8	68.0	164.0	25.2	70.8
60	3.7	68.0	165.0	25.3	70.8
120	3.6	69.0	164.0	25.5	70.4
After filtration	3.6	69.0	162.0	25.5	70.4

Table D-19. Cu^{2+} Precipitation by 41.9 mmol/L FeS ; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Cu^{2-} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.3	229.0	0.5	50.2	
15	3.4	64.0	155.0	50.3	72.1
30	3.3	64.0	160.0	50.5	72.1
45	3.3	63.0	161.0	50.7	72.5
60	3.2	61.0	160.0	50.4	73.4
120	3.1	62.0	160.0	49.9	72.9
After filtration	3.1	65.0	162.0	49.9	71.6

Table D-20. Cu^{2+} Precipitation by 41.9 mmol/L FeS ; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Cu^{2-} removal (%)
0	4.3	215.0	0.5	50.4	
15	3.4	70.0	156.0	50.7	67.4
30	3.2	68.0	159.0	50.5	68.4
45	3.2	66.0	159.0	50.5	69.3
60	3.2	64.0	158.0	50.4	70.2
120	3.1	64.0	161.0	50.1	70.2
After filtration	3.1	65.0	162.0	50.1	69.8

Table D-21. Zn^{2+} Precipitation by 40.6 mmol/L FeS ; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	4.6	221.0	0.5	23.7	
15	5.6	78.0	148.0	24.6	64.7
30	5.5	84.0	151.0	24.8	62.0
45	5.4	78.0	152.0	25.0	64.7
60	5.0	75.0	150.0	25.1	66.1
120	5.0	78.0	148.0	25.2	64.7
After filtration	5.1	79.0	148.0	23.9	64.3

Table D-22. Zn^{2+} Precipitation by 40.6 mmol/L FeS ; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	4.7	220.0	0.5	23.6	
15	5.7	83.0	148.0	24.5	62.3
30	5.5	76.0	149.0	24.8	65.5
45	5.4	74.0	149.0	24.9	66.4
60	5.1	75.0	147.0	24.6	65.9
120	5.1	79.0	146.0	25.2	64.1
After filtration	5.2	74.0	145.0	24.0	66.4

Table D-23. Zn^{2+} Precipitation by 41.9 mmol/L FeS ; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.7	239.0	0.5	50.6	
15	5.1	85.0	155.0	50.3	59.1
30	4.9	92.0	150.0	51.3	55.8
45	4.9	89.0	150.0	50.3	57.2
60	4.6	86.0	147.0	50.5	58.7
120	4.5	83.0	146.0	51.6	60.1
After filtration	4.6	89.0	142.0	49.9	57.2

Table D-24. Zn^{2+} Precipitation by 41.9 mmol/L FeS ; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.6	217.0	0.5	50.4	
15	5.0	63.0	151.0	50.7	69.4
30	4.9	70.0	150.0	51.2	66.0
45	4.8	66.0	150.0	51.3	68.0
60	4.6	64.0	145.0	50.6	68.9
120	4.5	65.0	143.0	50.8	68.4
After filtration	4.6	67.0	140.0	50.0	67.5

Table D-25. Pb^{2+} Precipitation by 12.4 mmol/L FeS ; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.5	208.0	0.5	23.1	
15	7.5	9.0	20.0	24.8	95.7
30	6.8	9.4	18.0	24.2	95.5
45	6.3	11.0	16.0	24.5	94.7
60	6.1	10.1	15.0	24.8	95.1
120	5.6	14.8	17.0	25.2	92.9
After filtration	5.5	12.9	17.0	24.0	93.8

Table D-26. Pb^{2+} Precipitation by 12.4 mmol/L FeS ; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.3	219.0	0.5	23.1	
15	7.5	11.5	19.0	24.8	94.7
30	6.6	12.7	18.0	24.4	94.2
45	6.2	13.3	16.0	24.7	93.9
60	6.0	14.0	19.0	24.9	93.6
120	5.5	17.6	18.0	25.3	92.0
After filtration	5.5	17.8	18.0	23.7	91.9

Table D-27. Pb^{2+} Precipitation by 12.4 mmol/L FeS ; Temp ~ 50 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	6.0	213.0	0.5	51.2	
15	6.7	13.8	15.0	50.2	93.5
30	6.0	17.8	14.0	50.8	91.6
45	5.7	21.5	13.0	50.7	89.9
60	5.6	23.8	12.0	50.7	88.8
120	5.1	27.0	9.0	50.0	87.3
After filtration	5.3	30.0	9.0	49.6	85.9

Table D-28. Pb^{2-} Precipitation by 12.4 mmol/L FeS ; Temp ~ 50 °C; Run 2

Time (min)	pH	Conc. of Pb^{2-} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2-} removal (%)
0	6.0	216.0	0.5	50.0	
15	6.6	14.6	14.0	50.8	93.2
30	5.9	17.7	13.0	50.5	91.8
45	5.7	19.3	12.0	50.6	91.1
60	5.6	21.9	11.0	50.5	89.9
120	5.3	27.0	7.0	50.3	87.5
After filtration	5.3	25.0	7.0	50.1	88.4

Table D-29. Cu^{2+} Precipitation by 200 μL NH_4OH; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.3	179.0	23.4	
15	8.4	0.3	24.8	99.8
30	8.4	0.2	25.1	99.9
45	8.4	0.3	25.1	99.8
60	8.2	0.2	25.5	99.9
720	8.0	0.2	25.1	99.9
After filtration	8.0	0.2	24.4	99.9

Table D-30. Cu^{2+} Precipitation by 200 μL NH_4OH; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.5	226.0	23.4	
15	8.4	0.2	24.6	99.9
30	8.4	0.2	24.5	99.9
45	8.4	0.1	25.0	100.0
60	8.3	0.1	25.2	100.0
720	8.3	0.6	24.8	99.7
After filtration	8.2	0.6	24.2	99.7

Table D-31. Zn^{2+} Precipitation by 200 μL NH_4OH; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.0	224.0	23.4	
15	7.9	12.0	24.3	94.6
30	7.9	12.0	24.4	94.6
45	7.9	12.0	24.7	94.6
60	7.8	12.0	24.7	94.6
720	7.4	32.0	25.2	85.7
After filtration	7.3	32.0	24.8	85.7

Table D-32. Zn^{2+} Precipitation by 200 μL NH_4OH; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.2	221.0	23.4	
15	8.2	13.0	24.7	94.1
30	8.2	10.0	25.0	95.5
45	8.1	8.0	25.1	96.4
60	8.1	8.0	25.5	96.4
720	7.6	34.0	24.9	84.6
After filtration	7.5	34.0	24.8	84.6

Table D-33. Pb^{2+} Precipitation by 300 μL NH_4OH; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.1	215.0	24.3	
15	10.1	165.0	24.6	23.3
30	10.1	166.0	24.7	22.8
45	10.2	160.0	25.0	25.6
60	10.2	147.0	25.2	31.6
After filtration	10.2	140.0	25.0	34.9

Table D-34. Pb^{2+} Precipitation by 300 μL NH_4OH; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.3	219.0	24.2	
15	10.2	184.0	24.6	16.0
30	10.2	181.0	24.8	17.4
45	10.2	174.0	25.0	20.5
60	10.1	162.0	25.0	26.0
After filtration	10.1	162.0	25.0	26.0

Table D-35. Cu^{2+} Precipitation by 0.042g $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.5	227.0	-----	23.4	
15	9.4	<0.1	101.0	24.3	99.9
30	9.7	<0.1	101.0	24.0	99.9
45	9.5	<0.1	103.0	24.4	99.9
60	9.3	<0.1	100.0	24.8	99.9
120	8.5	<0.1	102.0	25.5	99.9
720	7.5	0.2	109.0	25.3	99.9
After filtration	7.5	0.2	110.0	25.1	99.9

Table D-36. Cu^{2+} Precipitation by 0.043g $Ca(OH)_2$; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Cu^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Cu^{2+} removal (%)
0	4.6	169.0	----	23.5	
15	10.1	<0.1	103.0	23.8	99.9
30	9.8	<0.1	101.0	24.1	99.9
45	9.6	<0.1	100.0	24.3	99.9
60	9.2	<0.1	101.0	24.5	99.9
120	8.6	0.1	101.0	24.4	99.9
720	7.6	0.2	108.0	25.1	99.9
After filtration	7.6	0.2	110.0	25.1	99.9

Table D-37. Zn^{2+} Precipitation by 0.044g $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.2	210.0	-----	23.3	
15	8.6	2.0	105.0	24.3	99.0
30	8.5	0.7	105.0	25.0	99.7
45	8.5	0.8	107.0	24.8	99.6
60	8.4	1.0	106.0	25.3	99.5
120	8.1	2.9	108.0	25.2	98.6
720	7.1	9.0	114.0	26.9	95.7
After filtration	7.1	9.0	115.0	26.4	95.7

Table D-38. Zn^{2+} Precipitation by 0.045g $Ca(OH)_2$; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Zn^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Zn^{2+} removal (%)
0	5.2	211.0	-----	23.4	
15	8.1	6.0	103.0	24.0	97.2
30	8.0	6.0	105.0	24.4	97.2
45	8.0	6.0	106.0	24.2	97.2
60	8.0	6.0	108.0	24.2	97.2
120	8.1	4.0	113.0	24.1	98.1
720	7.1	7.0	115.0	26.0	96.7
After filtration	7.1	8.0	115.0	25.5	96.2

Table D-39. Pb^{2+} Precipitation by 0.021g $Ca(OH)_2$; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.2	213.0	-----	23.4	
15	10.4	137.0	42.0	23.6	35.7
30	10.3	143.0	43.0	23.6	32.9
45	10.3	135.0	42.0	23.9	36.6
60	10.3	115.0	42.0	24.3	46.0
120	10.2	110.0	42.0	24.6	48.4
720	7.8	0.3	45.0	24.5	99.9
After filtration	7.8	0.5	45.0	24.4	99.8

Table D-40. Pb^{2+} Precipitation by 0.020g $Ca(OH)_2$; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.3	217.0	-----	23.5	
15	10.8	136.0	52.0	23.6	37.3
30	10.8	124.0	51.0	24.0	42.9
45	10.8	109.0	51.0	24.4	49.8
60	10.8	83.0	52.0	24.8	61.8
120	10.8	59.0	53.0	25.2	72.8
720	7.8	0.2	49.0	25.0	99.9
After filtration	7.6	0.2	49.0	24.4	99.9

Table D-41. Pb^{2+} Precipitation by 8.7 mmol/L FeS after Filtration; Temp ~25 °C; Run 1 pH adjusted by 300 μL NH_4OH

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.3	200.0	—	23.5	
NH_4OH add.	10.2	—	—	23.4	
15	10.4	140.0	—	23.5	30.0
Filtration	10.5	143.0	—	23.4	28.5
8.7 mmol/L FeS added					
15	10.5	0.2	<0.1	24.6	99.9
30	10.5	0.1	<0.1	24.8	99.9
45	10.6	<0.2	<0.1	25.0	99.9
60	10.5	<0.2	<0.1	25.0	99.9
120	10.5	<0.2	<0.1	25.5	99.9
After filtration	10.5	<0.2	<0.1	25.0	99.9

Table D-42. Pb^{2+} Precipitation by 8.7 mmol/L FeS after Filtration; Temp ~25 °C; Run 2 pH adjusted by 300 μL NH_4OH

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.1	197.0	—	23.4	
NH4OH add.	10.2	—	—	23.5	
15	10.4	134.0	—	23.9	32.0
Filtration	10.5	155.0	—	23.7	21.3
8.7 mmol/L FeS added					
15	10.5	0.1	<0.1	24.9	99.9
30	10.4	<0.2	<0.1	25.1	99.9
45	10.5	<0.2	<0.1	25.3	99.9
60	10.5	<0.2	<0.1	25.6	99.9
120	10.5	<0.2	<0.1	26.5	99.9
After filtration	10.5	<0.2	<0.1	24.9	99.9

Table D-43. Pb^{2+} Precipitation by 8.7 mmol/L FeS, No Filtration after pH adjusted; Temp ~25 °C; pH adjusted by 300 µL NH_4OH; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0.0	4.2	196.0	---	23.6	
NH4OH add.	10.4	---	---	23.9	
15.0	10.4	147.0	---	24.2	25.0
8.7 mmol/L FeS added					
15.0	10.5	1.2	<0.1	25.0	99.4
30.0	10.5	0.2	<0.1	25.3	99.9
45.0	10.5	0.1	<0.1	25.6	99.9
60.0	10.4	0.1	<0.1	25.8	99.9
120.0	10.5	<0.2	<0.1	26.4	99.9
After filtration	10.5	<0.2	<0.1	25.1	99.9

Table D-44. Pb^{2+} Precipitation by 8.7 mmol/L FeS, No Filtration after pH adjusted; Temp ~25 °C; pH adjusted by 300 µL NH_4OH; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0.0	4.3	195.0	---		
NH4OH add.	10.4	---	---	23.4	
15.0	10.5	159.0	---	23.6	18.5
8.7 mmol/L FeS added					
15.0	10.5	0.2	<0.1	24.3	99.9
30.0	10.4	0.2	<0.1	24.5	99.9
45.0	10.5	0.2	<0.1	24.7	99.9
60.0	10.4	0.1	<0.1	24.8	99.9
120.0	10.4	0.1	<0.1	25.3	99.9
After filtration	10.4	<0.2	<0.1	24.5	99.9

Table D-45. Pb^{2+} Precipitation by 11.6 mmol/L FeS and 300 μL NH_4OH; Temp ~ 25 °C; Run 1

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0.0	4.0	215.0	---	23.8	
15.0	10.6	<0.2	<0.1	24.6	99.9
30.0	10.4	<0.2	<0.1	24.8	99.9
45.0	10.4	<0.2	<0.1	24.5	99.9
60.0	10.3	<0.2	<0.1	25.1	99.9
120.0	10.3	<0.2	<0.1	24.8	99.9
720.0	9.5	0.4	0.9	24.9	99.8
After filtration	9.5	<0.2	<0.2	23.6	99.9

Table D-46. Pb^{2-} Precipitation by 11.6 mmol/L FeS and 300 μL NH_4OH; Temp ~ 25 °C; Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0.0	4.0	211.0	---	23.9	
15.0	10.6	<0.2	<0.1	24.5	99.9
30.0	10.5	<0.2	0.7	24.6	99.9
45.0	10.4	<0.2	<0.1	24.8	99.9
60.0	10.4	0.1	0.9	24.9	99.9
120.0	10.4	<0.2	<0.1	25.1	99.9
720.0	9.8	0.1	<0.1	24.7	99.9
After filtration	9.8	<0.2	0.1	24.5	99.9

Table D-47. Pb^{2+} Precipitation by 8.1 mmol/L FeS; Temp ~ 25 °C; Run 1; pH adjusted by $Ca(OH)_2$ FeS added after filtering pH adjusted solution.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.7	208.0	---	---	22.9	
0.200 g $Ca(OH)_2$ added						
15	11.2	125.0	---	52.0	23.7	39.9
8.1 mmol/L FeS added after filtering solution						
30	11.5	<0.1	<0.3	95.0	24.2	99.9
45	11.4	<0.1	<0.3	93.0	24.5	99.9
60	11.4	0.1	<0.3	93.0	24.8	99.9
120	11.2	0.1	<0.3	86.0	24.8	99.9
After filtration	11.2	0.9	<0.3	86.0	24.3	99.6

Table D-48. Pb^{2+} Precipitation by 8.1 mmol/L FeS; Temp ~ 25 °C; Run 2; pH adjusted by $Ca(OH)_2$ FeS added after filtering pH adjusted solution.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.8	218.0	---	---	22.9	
0.200 g $Ca(OH)_2$ added						
15	11.2	139.0	---	52.0	23.7	36.2
8.1 mmol/L FeS added after filtering solution						
30	11.5	0.2	<0.3	95.0	24.2	99.9
45	11.4	0.1	<0.3	92.0	24.5	99.9
60	11.4	2.6	<0.3	92.0	24.8	98.8
120	11.3	2.2	<0.3	86.0	24.8	99.0
After filtration	11.2	0.5	<0.3	80.0	24.3	99.8

Table D-49. Pb^{2+} Precipitation by 8.1 mmol/L FeS; Temp ~ 25 °C; Run 1; pH adjusted by $Ca(OH)_2$ FeS added after pH adjusted without filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.6	214.0	—	—	23.0	
0.200 g $Ca(OH)_2$ added						
15	11.1	137.0	—	52.0	23.9	36.0
8.1 mmol/L FeS added without filtering solution						
30	11.4	0.8	<0.3	98.0	24.8	99.6
45	11.4	0.8	<0.3	98.0	25.2	99.6
60	11.4	0.9	<0.3	100.0	25.6	99.6
120	11.2	0.8	<0.3	91.0	25.4	99.6
After filtration	11.3	0.9	<0.3	88.0	24.3	99.6

Table D-50. Pb^{2+} Precipitation by 8.1 mmol/L FeS; Temp ~ 25 °C; Run 1; pH adjusted by $Ca(OH)_2$ FeS added after pH adjusted without filtration.

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.7	212.0	—	—	23.2	
0.200 g $Ca(OH)_2$ added						
15	11.1	134.0	—	52.0	23.8	36.8
8.1 mmol/L FeS added without filtering solution						
30	11.5	1.0	<0.3	101.0	24.3	99.5
45	11.4	1.1	<0.3	99.0	24.4	99.5
60	11.4	1.0	<0.3	97.0	24.8	99.5
120	11.3	0.9	<0.3	90.0	25.0	99.6
After filtration	11.3	1.7	<0.3	89.0	23.8	99.2

Table D-51. Pb^{2+} Precipitation by 12.6 mmol/L FeS and 0.200 g $Ca(OH)_2$ Together, Temp ~ 25 °C; Run 1

. Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.7	217.0	—	—	22.8	
15	10.6	0.2	<0.3	87.0	25.0	99.9
30	10.7	0.1	<0.3	86.0	25.3	99.9
45	10.6	<0.1	<0.3	86.0	25.3	99.9
60	10.6	<0.1	<0.3	86.0	25.4	99.9
120	10.3	<0.1	<0.3	82.0	25.8	99.9
After filtration	10.2	<0.1	<0.3	82.0	25.8	99.9

Table D-52. Pb^{2+} Precipitation by 12.6 mmol/L FeS and 0.200g $Ca(OH)_2$ Together, Temp ~ 25 °C, Run 2

Time (min)	pH	Conc. of Pb^{2+} (ppm)	Conc. of Fe^{2+} (ppm)	Conc. of Ca^{2+} (ppm)	Temp. (°C)	Pb^{2+} removal (%)
0	4.7	217.0	—	—	23.0	
15	10.6	0.2	<0.3	85.0	25.5	99.9
30	10.6	0.1	<0.3	84.0	25.7	99.9
45	10.5	<0.1	<0.3	88.0	25.8	99.9
60	10.4	<0.1	<0.3	85.0	25.9	99.9
120	10.0	<0.1	<0.3	82.0	26.1	99.9
After filtration	9.7	<0.1	<0.3	76.0	26.1	99.9

APPENDIX E

Raw Experimental Data for Ozonation Processes

E Structure for Presentation of the Raw Experimental Data

1) Decomposition of pyridine by O_3 and UV radiation, singly and in combination, are presented in Tables E–1 through E–8.

2) Decomposition of formaldehyde by O_3 and UV radiation, singly and in combination, are presented in Tables E–9 through E–15.

3) Decomposition of 200 ppm TOC pyridine and formaldehyde, as a mixture, by O_3 and UV radiation, singly and in combination, are presented in Tables E–16 through E–19.

4) Decomposition of 400 ppm TOC pyridine and formaldehyde, as a mixture, by O_3 and UV radiation, singly and in combination, are presented in Tables E–20 through E–23.

5) Oxidation of Dissolved Lead using O_3 and UV radiation, separately and together, after the wastewater solution pH had been adjusted are presented in Tables E–24 through E–29.

Table E-1. Pyridine Decomposition by 6.0 mg/(L.min) O_3.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	23.8	203.8	0.0
15	24.2	190.4	6.6
30	24.3	184.1	9.7
45	24.3	172.7	15.3
60	24.3	164.8	19.1
75	24.3	161.5	20.8
90	24.4	159.4	21.8
105	24.2	149.4	26.7
120	24.2	146.5	28.1
135	24.2	144.4	29.1
150	24.1	141.6	30.5
165	24.1	139.7	31.5
180	24.1	141.4	30.6

Table E-2. Pyridine Decomposition by 6.0 mg/(L.min) O_3 and UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.1	206.7	0.0
15	23.6	198.7	3.9
30	24.8	184.6	10.7
45	25.9	172.0	16.8
60	26.5	163.1	21.1
75	27.1	154.6	25.2
90	27.2	142.9	30.9
105	27.4	139.4	32.6
120	27.8	130.3	37.0
135	28.2	117.5	43.2
150	28.4	109.3	47.1
165	28.4	94.9	54.1
180	28.9	86.6	58.1

Table E-3. Pyridine Decomposition by UV only (Run 1).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	21.6	217.4	0.0
15	23.1	212.9	2.1
30	24.6	193.3	11.1
45	25.8	203.4	6.4
60	26.9	199.8	8.1
75	27.4	193.4	11.0
90	28.4	193.5	11.0
105	28.9	192.0	11.7
120	29.4	195.3	10.2
135	29.7	190.0	12.6
150	29.9	187.3	13.8
165	30.1	190.3	12.5
180	30.1	180.6	16.9

Table E-4. Pyridine Decomposition by UV only (Run 2).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.2	203.0	0.0
30	25.1	195.0	3.9
60	27.3	188.5	7.1
90	28.6	183.4	9.7
120	29.5	181.4	10.6
150	30.0	176.5	13.1
180	30.3	174.9	13.8

Table E-5. Pyridine Decomposition by 3.5 mg/(L.min) O_3.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.6	193.9	0.0
15	22.7	175.4	9.5
30	23.1	177.7	8.4
45	23.3	167.6	13.6
60	23.4	165.7	14.5
75	23.4	152.6	21.3
90	23.2	151.7	21.8
105	23.3	143.5	26.0
120	23.0	142.0	26.8
135	22.9	138.3	28.7
150	22.9	136.1	29.8
165	22.9	138.3	28.7
180	22.9	131.9	32.0

Table E-6. Pyridine Decomposition by 3.5 mg/(L.min) O_3 and UV

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.1	202.9	0.0
15	23.6	190.3	6.2
30	26.1	183.7	9.5
45	26.5	177.0	12.8
60	27.0	165.8	18.3
75	27.4	161.0	20.7
90	28.1	147.2	27.5
105	28.5	139.2	31.4
120	28.8	130.3	35.8
135	29.1	117.2	42.2
150	29.3	105.6	48.0
165	29.4	95.8	52.8
180	29.5	79.3	60.9

Table E-7. Pyridine Decomposition by 6.0 mg/(L.min) O_3 and UV (Run 1).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	21.9	206.9	0.0
30	24.9	178.2	13.9
60	26.1	154.7	25.2
90	27.1	139.4	32.6
120	26.9	123.8	40.2
150	27.4	106.3	48.6
180	27.1	86.0	58.5
240	27.5	41.2	80.1
300	28.4	1.5	99.3
360	27.3	1.2	99.4

Table E-8. Pyridine Decomposition by 6.0 mg/(L.min) O_3 and UV (Run 2).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.8	192.8	0.0
30	25.6	181.7	5.8
60	27.1	156.3	18.9
90	27.9	142.6	26.0
120	28.3	128.6	33.3
150	28.4	117.3	39.2
180	28.8	102.3	46.9
240	28.8	70.9	63.2
300	28.5	33.4	82.7
360	27.8	2.0	99.0

Table E-9. Formaldehyde Decomposition by 3.5 mg/(L.min) O_3.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.4	194.6	0.0
15	22.5	187.7	3.5
30	22.8	175.3	9.9
45	22.9	169.2	13.1
60	23.0	160.4	17.6
75	23.3	157.7	19.0
90	23.3	148.7	23.6
105	23.4	139.6	28.3
120	23.5	135.3	30.5
135	23.7	122.3	37.2
150	23.7	120.3	38.2
165	23.7	111.6	42.7
180	23.7	101.2	48.0

Table E-10. Formaldehyde Decomposition by UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	24.0	197.5	0.0
15	25.3	196.6	0.5
30	26.4	189.6	4.0
45	27.5	187.4	5.1
60	28.0	184.3	6.7
75	28.8	198.7	0.1
90	29.3	191.1	3.2
105	29.6	182.9	7.4
120	29.6	180.5	8.6
135	29.8	172.1	12.9
150	30.0	175.8	11.0
165	30.1	181.2	8.3
180	30.1	175.0	11.4

Table E-11. Formaldehyde Decomposition by 3.5 mg/(L.min) O_3 and UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.4	197.9	0.0
15	24.3	182.2	7.9
30	25.4	171.3	13.4
45	26.4	153.2	22.6
60	27.1	138.3	30.1
75	27.7	123.7	37.5
90	28.3	98.8	50.1
105	28.6	75.3	62.0
120	28.9	53.0	73.2
135	29.1	32.0	83.8
150	29.2	10.5	94.7
165	29.2	0.8	99.6
180	29.2	0.6	99.7

Table E-12. Formaldehyde Decomposition by 6.0 mg/(L.min) O_3 (Run1).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.6	200.6	0.0
30	23.3	181.1	9.7
60	23.8	160.3	20.1
90	23.9	139.1	30.7
120	23.9	123.1	38.6
150	24.0	104.2	48.1
180	23.8	85.5	57.4

Table E-13. Formaldehyde Decomposition by 6.0 mg/(L.min) O_3 (Run2).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	23.3	202.7	0.0
30	23.9	183.0	9.7
60	23.9	166.0	18.1
90	24.0	141.6	30.1
120	23.9	126.4	37.6
150	24.1	102.0	49.7
180	24.4	89.1	56.1

Table E-14. Formaldehyde Decomposition by 6.0 mg/(L.min) O_3 and UV (Run1).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.4	196.1	0.0
30	25.2	167.3	14.7
60	26.7	125.0	36.3
90	27.7	87.7	55.3
120	27.8	46.2	76.4
150	28.2	4.3	97.8
180	28.6	1.1	99.4

Table E-15. Formaldehyde Decomposition by 6.0 mg/(L.min) O_3 and UV (Run2).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.8	192.3	0.0
30	25.4	167.2	13.1
60	26.8	139.4	27.5
90	27.6	102.9	46.5
120	27.9	66.9	65.2
150	28.6	29.1	84.9
180	28.9	4.6	97.6

Table E-16. Pyridine and Formaldehyde Decomposition by 6.0 mg/(L.min) O_3 and UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	23.0	196.1	0.0
30	25.3	162.9	16.9
60	26.1	132.1	32.6
90	27.1	107.0	45.4
120	27.8	78.7	59.9
150	27.9	54.8	72.0
180	27.9	35.5	81.9
210	28.2	16.5	91.6
240	27.9	1.5	99.2

Table E-17. Pyridine and Formaldehyde Decomposition by 6.0 mg/(L.min) O_3.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	21.9	193.5	0.0
30	23.0	177.2	8.4
60	23.6	145.5	24.8
90	23.5	129.8	32.9
120	23.8	109.3	43.5
150	23.8	90.4	53.3
180	23.8	81.7	57.8
210	23.6	71.9	62.9
240	23.8	64.8	66.5

Table E-18. Pyridine and Formaldehyde Decomposition by 3.5 mg/(L.min) O_3 and UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.0	197.4	0.0
30	24.6	178.4	9.6
60	26.4	149.2	24.4
90	27.3	123.0	37.7
120	27.9	88.3	55.3
150	27.8	64.9	67.1
180	27.9	45.9	76.8
210	28.1	29.6	85.0
240	28.3	11.3	94.3

Table E-19. Pyridine and Formaldehyde Decomposition by UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.0	203.1	0.0
30	24.6	200.1	1.5
60	25.9	192.1	5.4
90	26.9	192.1	5.4
120	27.8	189.3	6.8
150	28.1	188.8	7.0
180	28.8	188.3	7.3
210	29.0	184.8	9.0
240	28.8	184.2	9.3

Table E-20. Pyridine and Formaldehyde Decomposition by UV.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	22.9	398.7	0.0
30	25.5	398.7	0.0
60	27.1	392.7	1.5
90	28.1	382.5	4.1
120	28.8	382.3	4.1
150	29.1	367.5	7.8
180	29.2	378.7	5.0
210	29.9	378.0	5.2
240	29.5	361.4	9.4

Table E-21. Pyridine and Formaldehyde Decomposition by 6.0 mg/(L.min) O_3.

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	21.3	383.5	0.0
30	22.6	355.9	7.2
60	23.2	310.2	19.1
90	23.3	275.1	28.3
120	23.3	255.1	33.5
150	23.4	235.6	38.6
180	23.2	212.3	44.6
210	23.1	192.2	49.9
240	23.1	172.5	55.0
270	23.0	155.5	59.5
300	23.4	143.6	62.6

Table E-22. Pyridine and Formaldehyde Decomposition by 6.0 mg/(L.min) and UV (Run 1).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	21.8	387.6	0.0
30	24.6	344.3	11.2
60	26.4	306.3	21.0
90	27.6	264.5	31.8
120	28.4	228.2	41.1
150	28.8	191.8	50.5
180	28.8	156.3	59.7
210	29.0	121.3	68.7
240	28.7	103.5	73.3
270	28.4	83.8	78.4
300	28.6	64.1	83.5

Table E-23. Pyridine and Formaldehyde Decomposition by 6.0 mg/(L.min) and UV (Run 2).

Time (min)	Temp. (°C)	avg. TOC (ppm)	TOC Reduction (%)
0	25.1	352.1	0.0
30	27.1	350.1	0.6
60	29.0	302.0	14.2
90	29.5	273.6	22.3
120	29.3	239.6	32.0
150	29.3	213.5	39.4
180	29.3	179.2	49.1
210	29.3	145.4	58.7
240	29.3	125.1	64.5

Table E-24. Lead Precipitation by 6.0 mg/(L.min) O_3 and UV; pH adjustment with $Ca(OH)_2$

Time (min)	Temp. (°C)	pH	Pb^{2+} conc. (ppm)	Ca^{2+} conc. (ppm)	Pb^{2+} Removal (%)
0	23.1	5.0	203.0	----	0.0
$Ca(OH)_2$ addtion					
0	23.6	11.8	151.0	153.0	25.6
O_3/UV treatment					
15	24.0	11.8	0.9	144.0	99.6
30	24.9	11.8	0.8	138.0	99.6
45	25.8	11.7	0.8	132.0	99.6
60	26.5	11.7	0.7	127.0	99.7
90	27.3	11.6	0.6	115.0	99.7
120	27.8	11.5	0.6	105.0	99.7
150	28.3	11.4	0.4	93.0	99.8
180	28.9	11.4	0.3	86.0	99.9

Table E-25. Lead Precipitation by 6.0 mg/(L.min) O_3; (Run 1).
pH adjustment with $Ca(OH)_2$

Time (min)	Temp. (°C)	pH	Pb^{2+} conc. (ppm)	Ca^{2+} conc. (ppm)	Pb^{2+} Removal (%)
0.0	23.3	5.1	197.0	----	0.0
$Ca(OH)_2$ addtion					
0.0	23.6	11.7	131.0	160.0	33.5
O_3 treatment					
15.0	23.8	11.8	1.0	157.0	99.5
30.0	23.9	11.8	0.9	151.0	99.5
45.0	24.0	11.7	0.9	146.0	99.5
60.0	24.2	11.7	0.9	139.0	99.5
90.0	23.8	11.6	0.4	130.0	99.8
120.0	24.2	11.6	0.7	119.0	99.6
150.0	24.2	11.5	0.6	108.0	99.7
180.0	24.1	11.5	0.4	97.0	99.8

Table E-26. Lead Precipitation by 6.0 mg/(L.min) O_3; (Run 2).
pH adjustment with $Ca(OH)_2$

Time (min)	Temp. (°C)	pH	Pb^{2+} conc. (ppm)	Ca^{2+} conc. (ppm)	Pb^{2+} Removal (%)
0	22.1	5.1	191.0	----	0.0
$Ca(OH)_2$ addtion					
0	22.2	11.7	176.0	153.0	7.9
O_3 treatment					
15	22.6	11.8	0.8	146.0	99.6
30	22.8	11.8	0.6	142.0	99.7
45	22.9	11.7	0.7	136.0	99.6
60	23.0	11.7	0.7	133.0	99.6
90	22.9	11.6	0.5	126.0	99.7
120	23.1	11.6	0.4	116.0	99.8
150	23.3	11.5	0.4	109.0	99.8
180	23.6	11.5	0.4	99.0	99.8

Table E-27. Lead Precipitation by 6.0 mg/(L.min) O_3 and UV; pH adjustment with NH_4^-

Time (min)	**Temp. (°C)**	**pH**	**Pb^{2+} conc. (ppm)**	**Pb^{2+} Removal (%)**
0.0	22.0	4.9	207.0	0.1
NH_4OH addition				
0.0	22.1	10.1	183.0	11.6
O_3/UV treatment				
15.0	24.5	9.6	3.0	98.6
30.0	25.4	9.2	2.0	99.0
45.0	26.2	8.6	1.8	99.1
60.0	26.8	7.0	1.0	99.5
90.0	27.4	5.5	0.2	99.9
120.0	27.9	4.9	1.2	99.4
150.0	28.0	4.6	6.4	96.9
180.0	28.1	4.4	0.4	99.8

Table E-28. Lead Precipitation by 6.0 mg/(L.min) O_3; (Run 1) pH adjustment with NH_4^+

Time (min)	Temp. (°C)	pH	Pb^{2+} conc. (ppm)	Pb^{2+} Removal (%)
0.0	25.4	5.1	196.0	0.1
NH_4OH addition				
0.0	25.4	10.1	181.0	7.7
O_3 treatment				
15.0	25.2	9.6	5.2	97.3
30.0	25.1	9.3	2.3	98.8
45.0	25.0	9.0	3.1	98.4
60.0	24.9	8.2	0.2	99.9
90.0	24.4	6.0	1.1	99.4
120.0	24.3	5.0	<0.1	99.9
150.0	23.9	4.7	0.1	99.9
180.0	23.6	4.6	0.3	99.8

Table E-29. Lead Precipitation by 6.0 mg/(L.min) O_3; (Run 2) pH adjustment with NH_4^+

Time (min)	Temp. (°C)	pH	Pb^{2+} conc. (ppm)	Pb^{2+} Removal (%)
0	24.6	5.0	194.0	0.1
750 μL NH_4OH addition				
0	24.6	9.7	153.0	21.1
O_3 treatment				
15	24.4	8.3	6.4	96.7
30	24.2	6.6	0.2	99.9
45	24.0	6.1	7.1	96.3
60	23.8	5.6	0.3	99.8
90	23.5	5.1	1.8	99.1
120	23.3	4.8	0.4	99.8
150	23.3	4.7	<0.1	99.9
180	23.2	4.6	0.1	99.9

IMAGE EVALUATION TEST TARGET (QA-3)

1.0 1.1 1.25 1.4 1.6 1.8 2.0 2.2 2.5 2.8 3.2 3.6 4.0 4.5 5.0

150mm

6"

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