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CATALYTIC WET AIR OXIDATION OF THERMO-MECHANICAL PULPING SLUDGE

by

Matthew Collyer

A Thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the
requirements for the Degree of
Master of Engineering

McGill

Department of Chemical Engineering
McGill University
Montréal, Canada

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ABSTRACT

Wet air oxidation (WAO) is a waste treatment process which involves the oxidation of organic and inorganic compounds at high temperature and pressure in the aqueous phase. Previous work has shown that WAO is technically feasible for the treatment of sludge from a thermo-mechanical pulping (TMP) mill. In an attempt to improve the degree of oxidation, and consequently reduce the overall cost, the use of different catalysts was investigated. Experiments were carried out in a stainless steel batch reactor using pure oxygen and sludge from the primary clarifier of a TMP mill. Various metal salts were screened in order to determine a suitable catalyst for the process. Further experiments were performed to study the effect of oxygen pressure, temperature, time of reaction, and catalyst concentration.

The screening experiments showed that the best catalyst was copper sulfate ($CuSO_4$). When using this catalyst, a 97.6% reduction in the chemical oxygen demand occurred compared to 76.5% reduction without catalyst at the same conditions.

The results indicate that the use of $CuSO_4$ significantly improves the treatment of TMP sludge by wet air oxidation.

RÉSUMÉ

L'oxydation à air humide est un processus de traitement des déchets qui comprends l'oxydation des matières organiques et inorganiques à haute température et pression dans la phase aqueuse. L'oxydation à air humide était prouvée faisable pour le traitment des boues venant d'une usine de pâte à papier thermo-méchanique. Afin d'améliorer le degré d'oxydation et de réduire les coûts, l'examen de plusieurs catalyseurs a été effectué. L'expérimentation a eu lieu dans un réacteur non-continu en utilisant l'oxygène pure et la boue récupérée d'un décanteur primaire d'une usine de pâte à papier thermo-méchanique. Certains sels métaliques ont été scrutés pour déterminer un catalyseur convenable. D'autre expérimentations ont été faites pour étudier l'effet de la pression d'oxygène, de la température, de la durée de la réaction, et de la concentration du catalyseur.

Les expérimentations ont démontré que le meilleur catalyseur était le sulfate de cuivre ($CuSO_4$). Une réduction de la demande chimique d'oxygène (DCO) de 97.6% a été atteinte comparée à une réduction de 76.5% sans catalyseur avec des conditions semblables.

Les résultats indiquent que $CuSO_4$ améliore notamment le traitement de la boue par le processus de l'oxydation à air humide.

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Without doubt, the work I performed for this thesis was aided and facilitated by many people. I would like to take the opportunity to show my appreciation to all those who helped me throughout this project:

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CHAPTER 1

INTRODUCTION

1.1 WET AIR OXIDATION

In the past two decades, the implementation of thermo-mechanical pulping (TMP) by the newsprint industry has been exceptional. Although TMP offers improvement in effluent quality compared to earlier technologies, parameters such as biological oxygen demand (BOD) and toxicity to fish are still at levels too substantial for untreated discharge to the environment. With consistently increasing public concern for environmental conservation, improved pollution control techniques will be necessary to comply to future government discharge regulations.

Due to this social pressure, a growing trend in the pulp and paper industry is to attain zero-effluent discharge or mill closure. This new interest has lead to a flourish of research into mill closure technologies such as evaporation, activated sludge, ultraviolet radiation treatment, ion exchange separation, and wet air oxidation (WAO). However, unlike the other closure technologies, WAO can be used effectively to treat highly concentrated organic waste streams. These waste streams can have solids contents as high as 10% (Randall and Knopp, 1990).

Current disposal techniques for the treatment of sludge from primary clarifiers of TMP mills consist of dewatering followed by landfilling or incineration, discharge to waterways, and deep well disposal. Of these, direct discharge is no longer acceptable and deep well injection is not practical. Typical TMP sludge has very high organic load with solids contents of around 3-6%. Consequently, WAO offers itself as a viable alternative to incineration and landfilling for the treatment of TMP sludge (Kubes, Lunn, and Keskin, 1993). Since suspensions can be effectively treated by WAO, expensive dewatering techniques which are necessary for incineration are not required. Finally, the quantity of ash produced by this method is far less than that by incineration, which implies reduced landfilling.

Wet air oxidation is described as the oxidation of aqueous suspensions or solutions of organic and inorganic materials at elevated temperature and pressure. During WAO, the reaction occurs in the liquid phase (Flynn, 1979). Dissolved oxygen initiates a free radical chain reaction by reacting with the organic compounds at weak C-H or O-H bonds, which creates hydroxyl and organic radicals (Li, Chen and Gloyna, 1991; Tufano, 1993; Shende and Mahajani, 1994). The reaction is exothermic and produces carbon dioxide, water, and residual low molecular weight organics (LMWO). The overall reaction for organic materials can be then be expressed as:

$$Organics + O_2 \rightarrow CO_2 + H_2O + LMWO \tag{1.1}$$

This reaction mechanism is discussed in more detail in Section 2.1.1.

Another product from WAO is small quantities of ash. Most of the inorganic material is oxidized and precipitates out of solution forming ash. The quantity of ash produced is dependent on oxidation temperature and the amount and type of inorganics present in the original waste (Kubes et al., 1993: Pradt, 1979).

Figure 1.1 shows a generalized flowsheet for the WAO process. Waste effluent containing the organic or inorganic materials to be oxidized is combined with compressed oxygen or air and enters the system. As previously mentioned, the products are ash, carbon dioxide, water and residual low molecular weight organics. The residual low molecular weight organics are commonly acetic acid and formic acid.

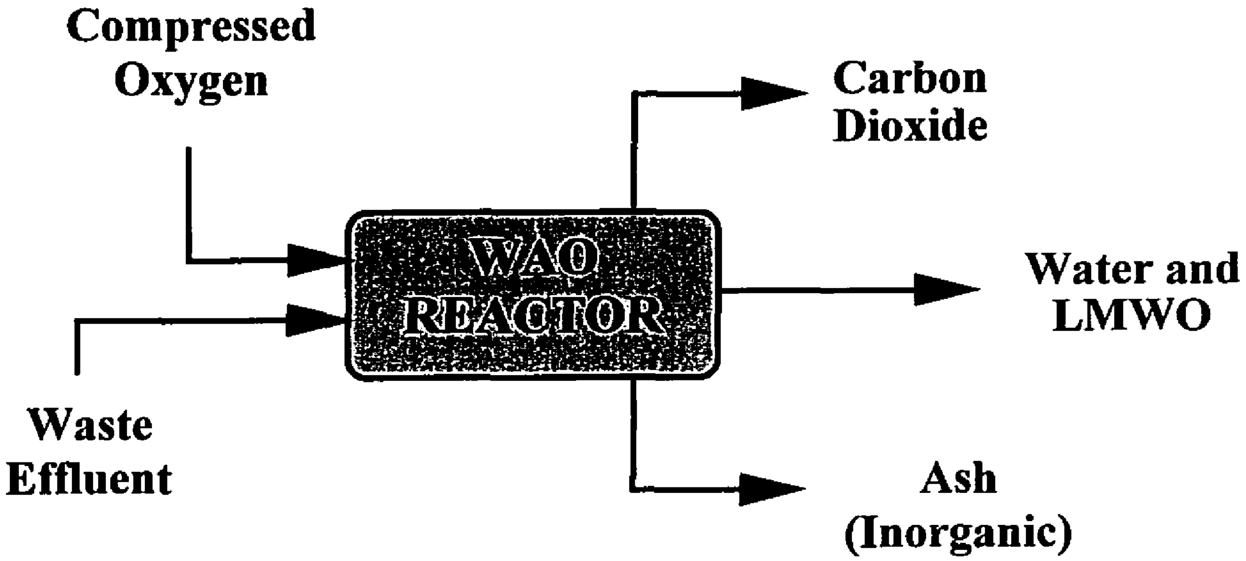


Figure 1.1 - Simplified Wet Air Oxidation Flowsheet

1.2 REVIEW OF THERMODYNAMICS AND RATE PROCESSES OF WAO

The degree of oxidation depends on several variables including oxygen to waste effluent ratio, system temperature, system pressure and time of reaction.

Temperature:

The wet oxidation of organic compounds proceeds slowly at temperatures less than 200°C, while at higher temperatures (250-320°C) it occurs rapidly for most substances (Li et al. 1991). In order to avoid entering a single phase region, the reaction temperature must remain below the critical temperature of water (374°C). As temperature increases, the solubility and diffusivity of oxygen in water increase (Geankoplis, 1983). Larger solubility and diffusivity result in a strong mass transfer driving force for oxidation. The formation of acetic acid and other LMWO as intermediate products varies inversely with the oxidation temperature (Kubes et al., 1993).

Pressure:

Operating pressures for different WAO processes vary over a wide range. However, it is necessary to remain in the two phase region. Oxygen necessary for oxidation dissolves into liquid water and reacts with the waste effluent during WAO. Consequently, without liquid water the waste will simply burn. Water also acts as an excellent heat transfer medium and will act as a heat sink through evaporation for the exothermic reaction.

Since the wet oxidation reaction requires the presence of the liquid phase, high operating pressure is necessary to prevent excessive evaporation. The total operating pressure includes the partial pressures of water vapour, oxygen, carbon dioxide and inert. It can be adjusted by changing the operating temperature or by adding more oxygen or inert. It should be noted that the minimum operating pressure must be greater than the water vapour pressure at the desired operating temperature (at 200°C the vapour pressure of water is 1.55 MPa). High pressure also increases both the quantity of oxygen that can be dissolved in water, as well as its rate of diffusion through the water (Geankoplis, 1983).

Oxygen Requirements:

In commercial applications, oxygen is commonly supplied by air and consequently does not add to the operating cost. However, in some situations the use of pure oxygen may be more favourable than air. By using pure oxygen the cost of compressing the nitrogen in the air is eliminated; hence the reactor volume is much smaller, and the ratio of steam to the quantity of non-condensable gases generated from the reactor is larger. Furthermore, smaller reactor volume implies reduced capital costs (Wilhelmi and Knopp, 1979).

In order to completely oxidize the waste effluent, a sufficient amount of oxygen must be supplied to the system. The theoretical amount of oxygen necessary can be determined by the chemical oxygen demand (COD) and volume of waste to be treated. COD is defined as the amount of oxygen required to oxidize the organic fraction of a sample which is susceptible to permanganate or dichromate oxidation (Ramalho, 1983). The COD method is fully explained in the following chapter. For the experimental system, the oxygen requirement calculation is described in Appendix A.

Reaction Time:

Zimmerman (1960) and other researchers claimed that the rate of the oxidation reaction significantly decreases after one hour at operating temperatures above 200°C. Figure 1.2 shows the variation of the percent material oxidized with time at different temperatures. At higher operating temperatures, the oxidation reaction seems to be over after the first half hour, however at lower temperatures the effect of reaction time is very significant.

1.3 APPLICATIONS, ADVANTAGES AND DISADVANTAGES

As previously mentioned, advantages associated with WAO over other waste technologies for the treatment of sludge are that no dewatering is required and reduced amounts of ash are formed. Furthermore, WAO offers the advantages of no air pollution problems and numerous applications.

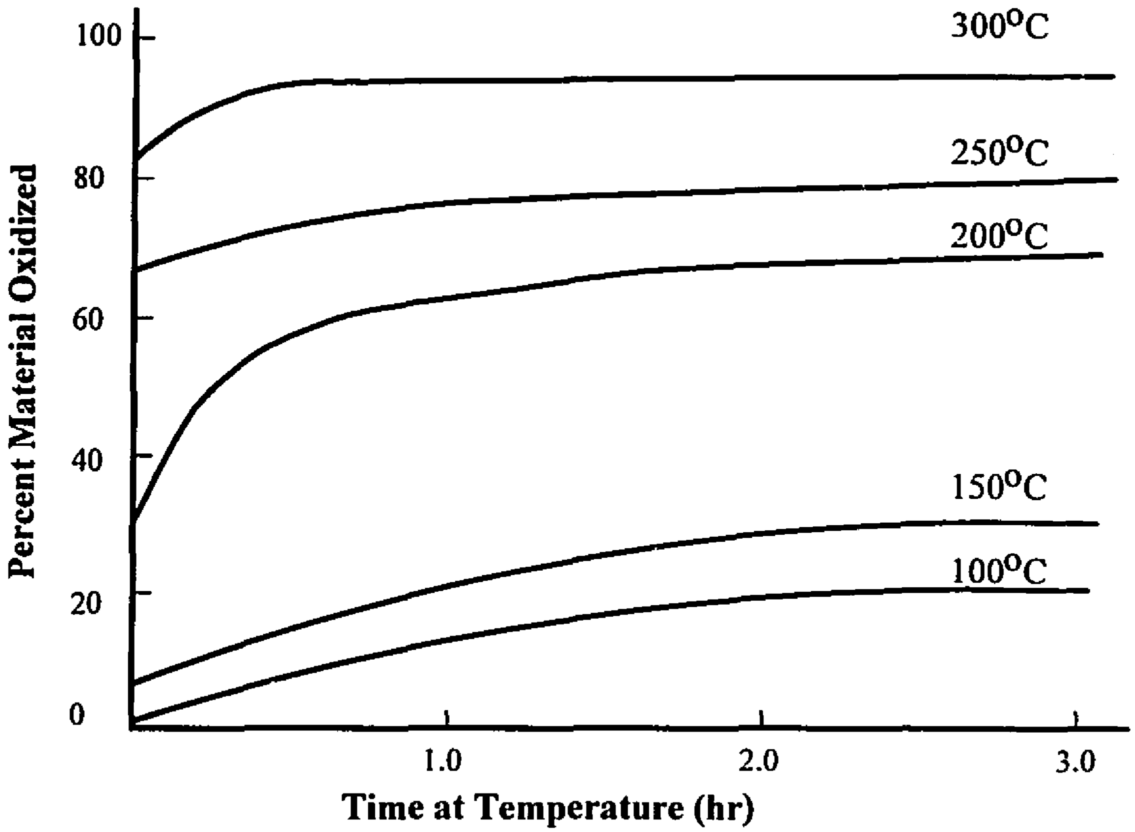


Figure 1.2 - Percent Material Oxidized vs. Time and Temperature

Since the process is operated in the aqueous phase, there is virtually no particulate emission, and the gas phase products consist mainly of carbon dioxide and nitrogen. Also, reaction conditions are not severe enough for the formation of nitrous oxides, while oxides of sulfur are immediately converted to soluble sulfate salts.

The applications of WAO are diverse (Zimmermann and Diddams, 1960; Pradt, 1972; Flynn and Flemmington, 1979; Wilhelmi and Knopp, 1979; Schaefer 1981; Foussard, Debellefontaine and Besombes-Vailhe, 1989). WAO has been proven to be an effective disposal technique for toxic and non-biodegradable effluents. Organic sludges containing high solids content (up to 10%) can be effectively treated by WAO (Randall and Knopp, 1980). Conversely, if the waste contains valuable inorganics, they can be recovered through WAO (Hanna and Jung, 1992). In the case of waste containing petroleum coke or other low-grade fuel, WAO can provide steam which can be used to generate energy (Hahn, Chowdhury and McLeod, 1985). WAO shows potential as a recovery process for the sulfur-free pulping technologies (ie: soda/oxygen/carbonate pulping) where cost advantages and environmental benefits exist (Foussard, et al., 1989).

Despite these advantages, WAO has the defects of (1) requiring high oxygen pressure as well as high temperature which results in higher capital and operating cost, and (2) partial oxidation leading to the formation of lower carboxylic acids such as acetic acid (Shogenji, 1968). The presence of acetic acid and other carboxylic acids is disadvantageous due to the corrosive nature of these compounds.

These disadvantages have attracted attention to catalytic wet air oxidation (CWAO). Ideally, the addition of a suitable catalyst to the WAO system is expected to increase the rate of oxidation, and improve the product distribution and selectivity by decreasing the amount of residual LMW organics. In meeting these criteria, CWAO would achieve the same degree of oxidation as WAO at lower operating temperatures and pressures. By reducing the operating pressure and temperature, costs of compression and heating will be decreased. More importantly, the capital cost will be significantly diminished with reduction of operating pressure. If the formation of acetic acid and other LMW acids is avoided, then less rigorous biological treatment will be necessary after CWAO. Also, corrosive problems associated with these acids will be avoided.

Since the oxidation occurs in the liquid phase, homogenous metal salt catalysts will be used. Unlike heterogeneous catalysts, soluble catalysts will not be affected by mass transfer disadvantages.

A disadvantage associated with the use of catalysts is the need for a separation process after wet oxidation in order to recover the catalyst. A homogenous or heterogeneous catalyst that is either too costly or too hazardous to the environment for discharge after WAO, will require advanced separation techniques. Also, catalyst in a closed cycle plant could cause fouling if the catalyst is not removed. For homogenous catalysts, a suitable separation technique for recovery is ion exchange.

1.4 ION EXCHANGE

Commonly, ion exchange is achieved by passing the solution through a column packed with a resin. The ion exchange resin consists of nearly insoluble large molecular weight organic polymers which are linked together in an open, permeable molecular structure. The polymers contain certain active groups of atoms that are capable of taking up ions from solutions and exchanging them for other similarly charged ions already on the resin. The open structure permits solvent molecules and ions to move freely within the solid. The active groups are always electrolytes, one ion of which is fixed to the resin while the other, of opposite charge, is mobile. The mobile ion is the ion that is exchanged. The relative strength of a resin in holding different types of ions depends on the nature of the resin, the ions, and the solvent. Cation exchange resins interchange positively charged ions, while anion exchangers exchange negative ions.

Figure 1.3 is a hypothetical schematic combining WAO with an ion exchange column for the recovery of a metal sulfate species. The metal sulfate is added to the sludge prior to WAO treatment. After WAO, the effluent containing the metal sulfate catalyst passes through the ion exchange column where the cation is separated and retained in the column. The metal sulfate is recovered by passing H_2SO_4 through the column and then returns to WAO for reuse.

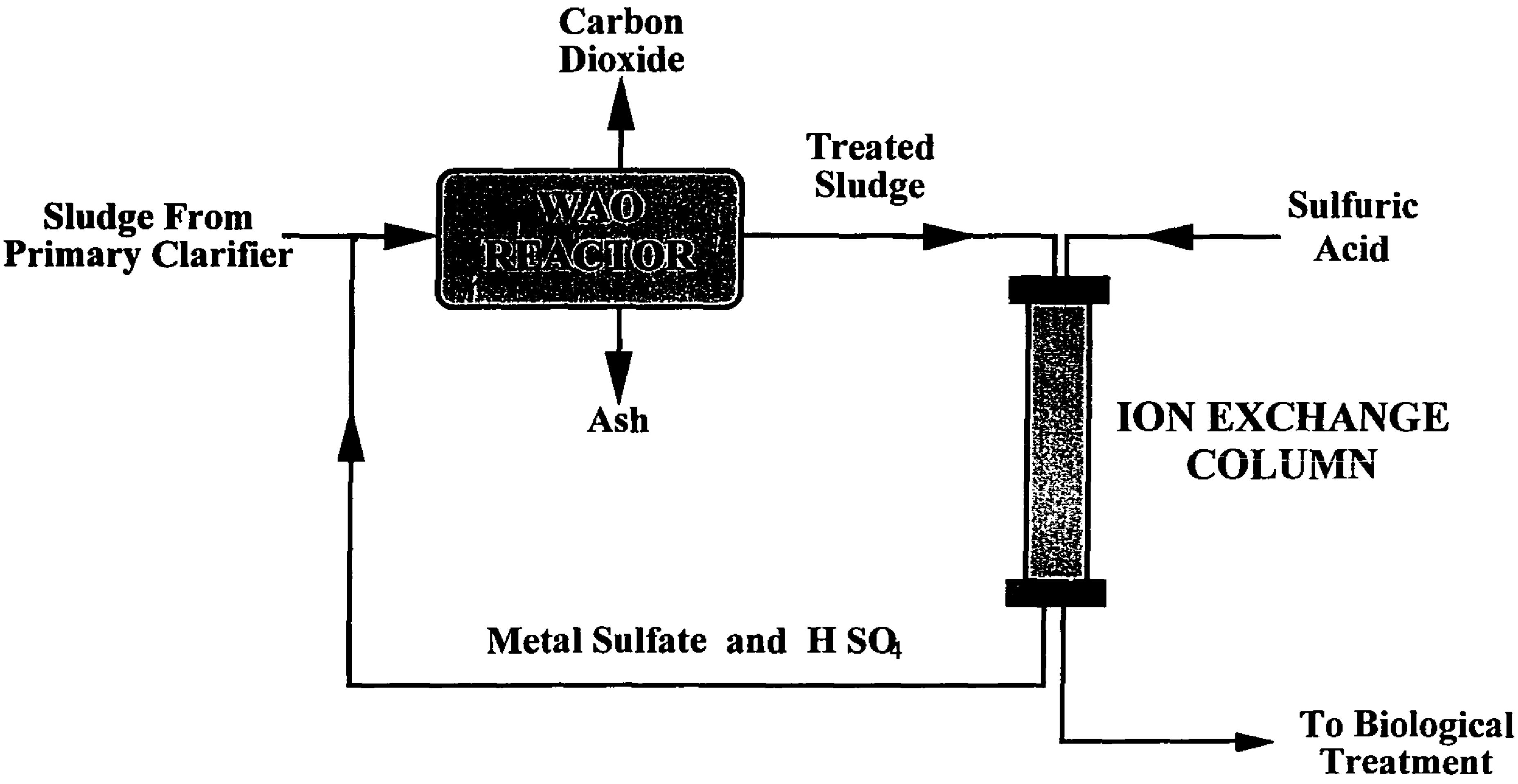


Figure 1.3 - Schematic for Ion Exchange and WAO

Advantages associated with ion exchange technology include low capital and operating cost. Also, as more mills attempt to achieve zero-discharge (mill closure), this technology will likely be employed for the removal of heavy metal electrolytes to avoid fouling. Consequently, ion exchange offers itself as a potential method for the removal of metal cations from the treated effluent after WAO.

1.5 STRUCTURE OF THESIS

The purpose of this work is to find a catalyst that will increase the degree of oxidation and favorably alter the selectivity and product distribution by decreasing the amount of residual LMW organics.

The structure of the thesis is as follows; Chapter 2 presents a literature review on CWAO, Chapter 3 consists of the objectives for the thesis, Chapter 4 describes the methods and materials used throughout experimentation, and Chapter 5 presents and discusses the results. The conclusions are found in Chapter 6, followed by the references in Chapter 7. A series of appendices is included at the end of the thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 WET AIR OXIDATION

Originally developed in the mid-1940s as a way to recover vanillin from spent pulping liquor, WAO is becoming more and more extensively applied (Foussard, Debellefontaine, and Besombes-Vilhe, 1989). WAO has been commonly used to oxidize sewage sludge and treat manufacturing process wastewater. However, further applications include implementation to environmental control, resource recovery, and energy-related applications (Schaefer, 1981). In the pulp and paper industry, WAO offers an effective method for treating waste sludge in order to achieve complete mill closure.

Several patents covering conditions to give high degrees of oxidation for a broad range of waste liquors including pulp mill liquors were obtained by Zimmerman (Zimmerman and Diddams, 1960). The Zimmerman process operates on the principle that aqueous suspensions or solutions of organic materials can react with the oxygen contained in a gas such as compressed air or pure oxygen, at conditions of elevated temperature (150-370°C) and pressure (2-20 MPa) (Flynn and Flemmington, 1979).

The basic flowsheet for <u>continuous</u> WAO is shown in Figure 2.1 (Zimmerman and Diddams, 1960; Werthemann, 1992; Wilhelmi and Knopp, 1979). Waste enters the system by a high pressure pump and is mixed with compressed air or pure oxygen. The waste and air mixture is preheated by passing through a heat exchanger in order to achieve a temperature high enough to support oxidation. The mixture then enters the reactor where oxygen in the air reacts with organic matter in the waste. The reaction is exothermic, and the heat generated further raises the temperature of the reaction mixture to the design temperature. The gas and liquid phases are separated after the reactor, and the liquid passes through the heat exchanger heating the incoming material (Pradt, 1979). The process

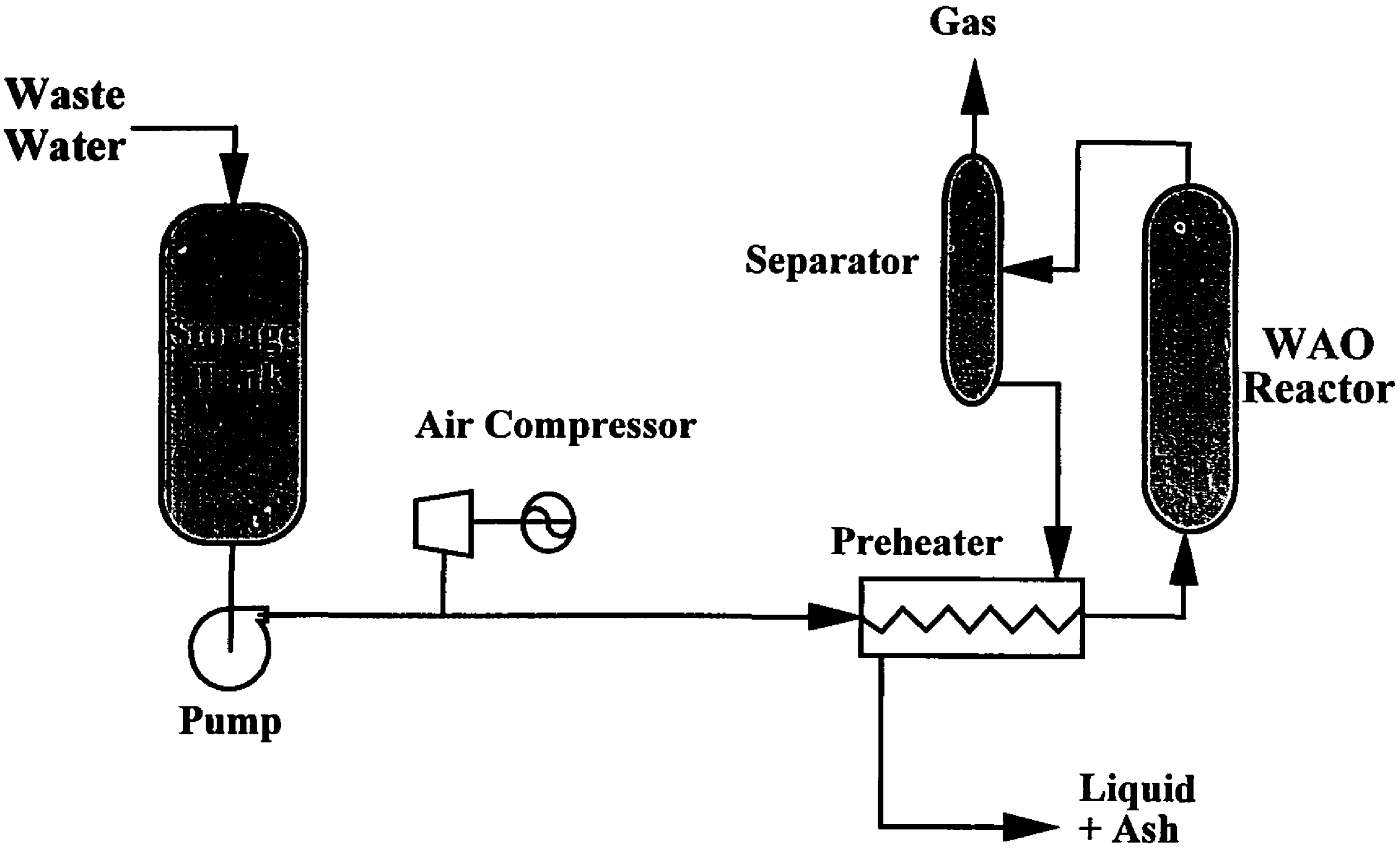


Figure 2.1 - Industrial Wet Air Oxidation System

converts organic compounds to mainly carbon dioxide and water, while inorganic materials to their highest state of oxidation (ie. sulfite to sulfate). Residual compounds produced by WAO are generally LMW organics, such as acetic and formic acid, which are readily biodegradable by conventional treatment methods (Randall and Knopp, 1980). The formation of residual ash does occur but depends on the quantity and type of inorganics present in the waste water. The ash consists of insoluble metal oxides and carbonates which precipitate out of solution.

2.1.1 Reaction Mechanism

As previously mentioned, the generalized reaction for organic compounds undergoing WAO is that organics react with oxygen to form mainly carbon dioxide and water.

The destruction of organics by WAO techniques is known to be free radical chain reactions (Li et al., 1991; Tufano, 1993; Shende and Mahajani, 1994). Free-radicals in the absence of initiators are commonly formed by the reaction of oxygen with the weakest C-H bonds of the oxidized organic compound as shown in Eqs. 2.1 and 2.2.

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet \tag{2.1}$$

$$RH + HO_2^\bullet \rightarrow R^\bullet + H_2O_2 \tag{2.2}$$

where R denotes the organic functional group. It should be noted that free radicals are also formed by the reaction of oxygen with an O-H bond as in the case of the WAO of phenols (Shibaeva, Metelitsa and Denisov, 1969). The common product of Eq. 2.2 is hydrogen peroxide which further decomposes to generate hydroxyl radicals.

$$H_2O_2 + M \rightarrow 2HO^\bullet \tag{2.3}$$

The term M can be either a homogeneous or heterogeneous species (Hoare, Protheroe and Walsh, 1958).

The oxidation of organic compounds by hydroxyl radicals, as shown in Eq. 2.4, follows a hydrogen abstraction mechanism by removing a hydrogen atom to form an organic radical ($R^\bullet$). The organic radical reacts with oxygen (Eq. 2.5) to form an organic peroxy radical ($ROO^\bullet$) (Emanuel, Denisov and Maizus, 1984). The organic peroxy radical further abstracts a hydrogen atom from the organic compound, producing an organic hydroperoxide (ROOH) and another organic radical (Eq. 2.6).

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O \tag{2.4}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{2.5}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{2.6}$$

The organic hydroperoxides formed are relatively unstable and decompose to form subsequent intermediates with lower carbon numbers. These reactions continue rapidly until the formation of acetic and formic acid. Both acids are eventually converted into carbon dioxide and water but at lower rates (Li et al., 1991).

2.2 CATALYTIC WET AIR OXIDATION

Catalytic wet air oxidation is the same process as conventional wet oxidation process except that a catalyst is added to the waste. In CWAO, organic compounds are more rapidly and more thoroughly decomposed to carbon dioxide and water, resulting in the formation of smaller amounts of low molecular weight acids. By increasing the rate of oxidation in the presence of a catalyst, the process may be operated at a lower temperature, lower pressure and reduced reaction time. Consequently, for the same degree of oxidation, CWAO will result in lower capital and operating costs.

Effect of Catalyst on WAO Mechanism:

According to Sheldon and Kochi (1981) metal species can act as catalysts or inhibitors during the initiation stage of free radical chain reactions. As previously mentioned by Equation 2.3, the decomposition of hydrogen peroxide to generate hydroxyl radicals is increased by the presence of a homogeneous or heterogeneous species, M, which is commonly a metal species acting as a catalyst resulting in chain initiation. Not only does the metal species react with H_2O_2, it also reacts with other organic substrates producing free radicals which continue on through the propagation and termination stages (Sheldon, Kochi, 1981):

$$M^{n+} + H_2O_2 \rightarrow M^{(n-1)+} + HO_2^{\bullet} + H^{+} \qquad (2.7)$$

$$M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + HO^{\bullet} + HO^{-} \qquad (2.8)$$

$$M^{n+} + {>}CHOH \rightarrow M^{(n-1)+} + {>}\dot{C}OH + H^{+} \qquad (2.9)$$

The addition of a catalyst will increase the rate of formation of hydroxyl and organic radicals. Consequently, the oxidation rates of reaction will be increased during CWAO.

Previous Work:

The majority of previous work on CWAO has been performed on specific compounds. Amongst them are phenol, aldehydes, various alcohols, and low molecular weight organic acids such as formic and oxalic acid (Baldi, Goto, Chow and Smith, 1974; Sadana and Katzer, 1974; Imamura, Hirano, and Kawabata, 1982; Debellefontaine, Foussard, Besombes-Vilhe and Chakchouk, 1991). Industrial scale studies on CWAO have been reported on effluents from breweries, rum distillery wastes, pharmaceutical effluents, and coal gasifier waste-water (Munoz, Pedraja, and Colon, 1981; Chowdhury and Ross, 1981; Hanh, Chowdhury and McLeod, 1985; Werthemann, 1992).

In earlier work Baldi et al. (1974) used CuO-ZnO for the oxidation of formic acid, and Levec and Smith (1976) used ferric oxide for oxidation of acetic acid. Also, Lebedev, Manakov and Litovka (1974) examined the kinetics of the oxidation of butyraldehyde catalyzed by cobalt(II) and copper(II) acetates.

Sadana and Katzer (1974) studied the oxidation of phenol with CuO and MnO_2 at 0.01-1.72 MPa (1-17 atm) and 100-150°C. They used a continuously stirred batch reactor to determine the kinetics of the wet oxidation of phenol over supported copper (II) oxide. The reaction seemed to undergo a period of relatively slow activity, called an induction period, before making a transition to a faster constant activity regime. The activity quickly dropped off before completion. They found that larger catalyst particle size resulted in lower activation energies in the constant activity regime.

Imamura et al. (1982) have studied the wet oxidation of oxalic acid using a Co/Bi (5/1) complex oxide catalyst at temperatures between 112-160°C. In the case of oxidation without catalyst, 27% reduction in total organic carbon (TOC) was observed at 140°C in just 20 minutes. In catalytic oxidation using the Co/Bi complex oxide catalyst, about 32% TOC removal was observed at 140°C. Increasing the temperature to 160°C resulted in a 90% TOC reduction. They also observed that the use Co/Bi oxide catalyst resulted in reduced formation of lower molecular weight acids than without catalyst.

Debellefontaine et al. (1991) found that the oxidation of phenol in water with oxygen and hydrogen peroxide in the presence of Fe^{2+} at 160°C was more effective than WAO without catalyst at 220°C. The process yielded mainly biodegradable carboxylic acids.

Ferrous sulfate was used as a homogenous catalyst in the treatment of groundwater with hydrogen peroxide (instead of oxygen) by the National Institute of Applied Science and IDE Environment (1993). Results at 0.51 MPa and 150°C were comparable to conventional WAO at 10.13 MPa and 300°C for the same COD load.

Ferric chloride was found to be an effective catalyst in the WAO of rum distillery waste according to Munoz et al. (1981). They observed that pressure in the range of 3.4 to

13.8 MPa did not influence the rate of reaction. Without the catalyst, charring of carbohydrate compounds present in the waste water was observed, however, with $FeCl_3$ no charring occurred.

For the treatment of toxic waste, Randall and Knopp (1980) used cupric sulfate as a catalyst for the detoxification of certain toxic compounds. In catalyzed oxidation of acrylonitrile, 2-chlorophenol, and pentachlorophenol at 275°C, the catalyst had little effect on the reduction of toxicity for acrylonitrile, but almost a four-fold increase on the reduction of toxicity for 2-chlorophenol and pentachlorphenol. With the cupric catalyst effective destruction of these more slowly reacting compounds was observed. The products were generally low molecular weight compounds, such as formic and acetic acid.

Cupric sulfate was also used as a homogeneous catalyst for the WAO of glyoxalic and oxalic acid by Shende and Mahajani (1994). They found cupric sulfate to be a very effective catalyst in destroying glyoxalic and oxalic acid. Without the catalyst, they observed a reduction in the chemical oxygen demand (COD) of 54% after 5 hours at 160°C and 0.69 MPa oxygen partial pressure. However, under the same operating conditions, they obtained a 93% COD reduction using 1.25 mmol/L $CuSO_4$.

Chowdhury and Ross (1975) investigated the oxidation of effluents from the centrifuges of a Coors brewery using hydrogen peroxide as the oxidizing agent. The waste water was rich in carbohydrate and proteins with COD loads of approximately 6000 mg/L. Cu^{2+} and Fe^{2+} in the presence of hydrogen peroxide were found to be very effective in reducing the COD of the waste water at 200°C. They observed that neither pH (between 2.8 and 7.0) nor oxygen pressure was found to be very influential in catalytic wet-oxidation although they exerted considerable influence during the experiments without catalyst.

Hahn et al.(1985) investigated the effectiveness of CWAO for scrub water from a moving bed research coal gasifier. Various industrial catalysts with active elements ranging from Ni, Pd, Pt, Cu, Fe, and Ag were tested. The rate of reaction was doubled when using catalysts over runs without catalyst. Total carbon conversion of about 90% at 10 min was achieved using a Cu-catalyst (39%Cu, wt.).

Finally, Ciba-Geigy currently operates several WAO systems in southern Germany for the treatment of toxic wastes from the pharmaceutical industry. Werthemann (1992) found that ionic catalysts such as Cu^{2+} accelerated the rate of degradation of organic and inorganic compounds.

Table 2.1 summarizes the catalysts aforementioned in this section.

TABLE 2.1:

Summary of Catalysts Cited

Cation	Catalyst	Type	Reference
Cupric (Cu^{2+})	$CuSO_4$ $Cu(CH_3COO)_2$ Cu^{2+}-H_2O_2	Homogeneous	Randall and Knopp (1980) Manakov and Litovka (1974) Chowdhury and Ross (1975)
Cupric	CuO-Mn_2 CuO-ZnO	Heterogeneous	Sadana and Katzer (1974) Baldi et al. (1974)
Ferrous (Fe^{2+})	Fe^{2+}-H_2O_2 $FeSO_4$	Homogeneous	Debellfontaine et al. (1991) N.I.A.S. (1993)
Ferric	Fe_2O_3	Heterogeneous	Levec and Smith (1976)
Ferric (Fe^{3+})	$FeCl_3$	Homogeneous	Munoz et al. (1981)
Cobalt	Co/Bi Complex	Heterogeneous	Imamura et al. (1982)
Cobalt (Co^{2+})	$Co(CH_3COO)_2$	Homogeneous	Manakov and Litovka (1974)
Ni, Pd, Pt, Cu. Fe. Ag Mixture	Industrial Catalysts	Heterogeneous	Hahn et al. (1985)

Finally it should be noted that experiments using heterogenous solid catalyst (the oxides of the metal salts investigated in this thesis), were tested during the same time period by Volstad (1994). Volstad's results show that CuO resulted in the largest improvement over other catalysts at the same operating conditions. Cupric oxide yielded a COD reduction of 96.3%, while without catalyst the reduction in COD was 76.5%. These results are presented and discussed more thoroughly in Section 5.1.1.

CHAPTER 3

OBJECTIVES

The principal objective of this thesis is to improve the degree of oxidation of thermo-mechanical pulping (TMP) sludge during wet air oxidation by finding a suitable catalyst. The secondary objectives are; to characterize the improvement in the degree of oxidation by varying the systems operating conditions (temperature, pressure and catalyst concentration), and to recover the catalyst after WAO.

These goals are to be fulfilled by:

- using a high pressure stainless batch reactor at the Pulp and Paper Research Centre, McGill University, for the WAO of TMP sludge.
- selecting various catalysts and testing them at similar operating parameters.
- characterizing the improvement due to the most suitable catalyst for WAO of TMP sludge by studying the effects of temperature, pressure and catalyst concentration on the degree of oxidation.
- attempt to recover the most suitable catalyst by using a bench scale ion exchange column at Paprican in Pointe Claire.

CHAPTER 4

EXPERIMENTAL PROCEDURES AND CALCULATIONS

4.1 MATERIALS

The **waste effluent** used for experimentation is sludge collected in the primary clarifier of a thermo-mechanical pulping (TMP) mill in south eastern Quebec. All waste streams from the mill pass through the primary clarifier prior to biological treatment, consequently the sludge contains a wide variety of compounds which include lignin, celluiose, wood fibres, carboxylic acids, carbonates, and resins. The sludge is an opaque aqueous suspension with a solids content of approximately 4.02% by weight and a pH of about 4.6. Other sludge characteristics are presented in Table 4.1.

TABLE 4.1:

Sludge Characteristics

Chemical Oxygen Demand	40,000 mg/L
Total Solids	4.02%
Total Organic	37.6 g/L
Total Inorganics	2.6 g/L
pH	4.6
Acetic Acid Concentration	0.31 g/L
Total Organic Carbon - liquid phase	63 ppm

Samples were obtained in late May, 1994, and were stored in 5 gallon containers and refrigerated at 3°C.

Compressed **oxygen** from a cylinder with a minimum purity of 99.5% was used for oxidation. Oxygen was supplied by Matheson.

The **catalysts** used for this thesis research were all soluble in water at room temperature. Their chemical formulas and molecular weights are included in Table 4.2.

Although ferric chloride was cited as an effective catalyst for WAO in Chapter 2, it was not used. The chloride ion is extremely corrosive under the operating conditions; this may result in reactor damage and possible failure. Also, there exists a growing tendency in the pulp and paper industry to eliminate the use of chlorine compounds as much as possible.

TABLE 4.2:

List of Catalysts and Molecular Weights

Catalyst	**Molecular Formula**	**Molecular Weight (g/mol)**
cupric sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	249.68
cupric acetate monohydrate	$(CH_3COO)_2Cu \cdot H_2O$	199.65
cupric chloride	$CuCl_2$	13.44
ferrous sulfate heptahydrate	$FeSO_4 \cdot 7H_2O$	278.02
silver sulfate	Ag_2SO_4	311.80
aluminum sulfate	$Al_2SO_2 \cdot (14\text{-}18)H_2O$	342.14
manganese sulfate monohydrate	$MnSO_4 \cdot H_2O$	169.01
cobalt sulfate heptahydrate	$CoSO_4 \cdot 7H_2O$	281.10

The **cation exchange resin** used in the ion exchange column is the acid sulfonated AG 50W crosslinked resin from Bio-Rad. *AG 50W-X8* resin consists of the resin matrix, styrene divinylbenzene, to which $-SO_3^-H^+$ is attached as the functional group (Figure 4.1). The H^+ of this sulfonic group is the mobile electrolyte and is exchanged for other cations in the sample. Bio-Rad suggests the use of this resin for the removal of inorganic and organic compounds with positive charges.

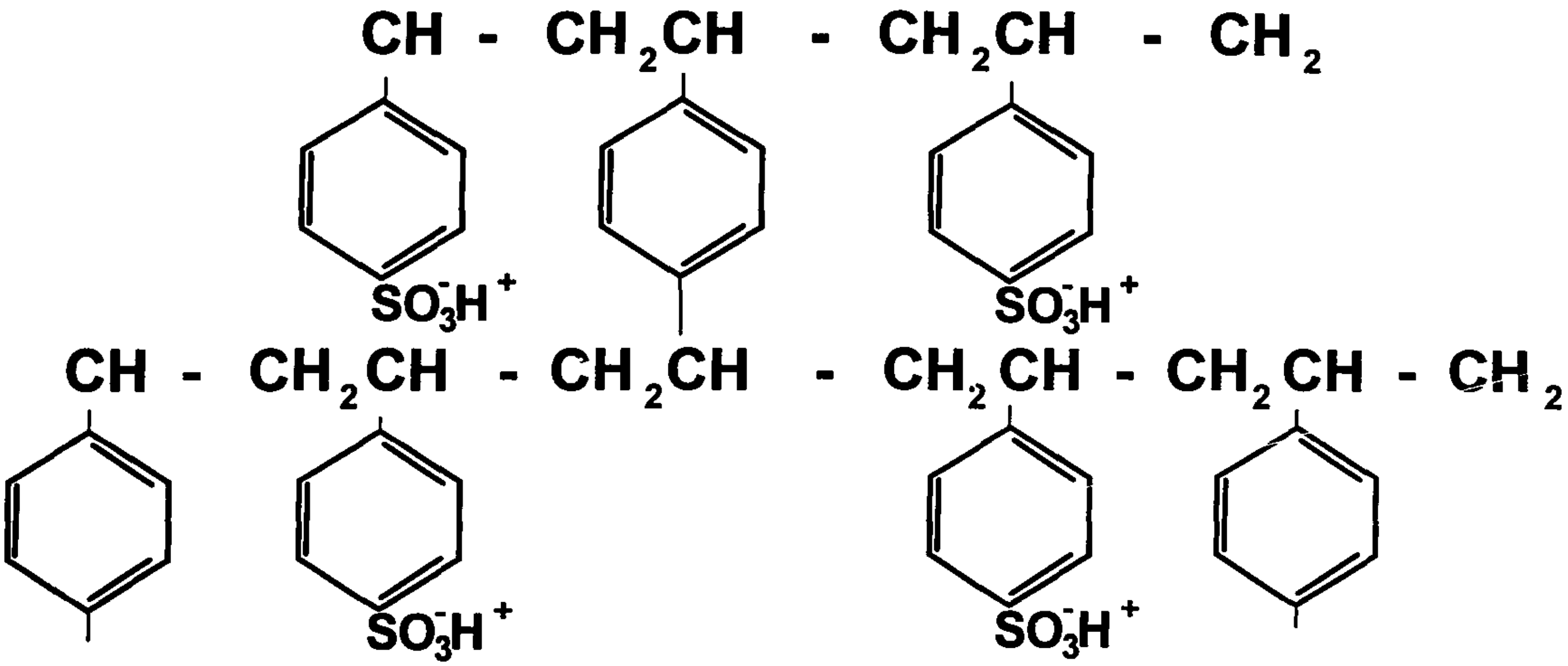


Figure 4.1 - AG 50W Crosslinked Acidic Cation Exchange Resin

4.2 DATA ANALYSIS AND ANALYTICAL PROCEDURES

In order to quantitatively analyze the effect of different operating conditions on the degree of oxidation for WAO, two analytical methods, the Chemical Oxygen Demand and Solids Content Analysis, were used. Also for the ion exchange column experiments, absorption spectroscopy was used to analyze the concentration of cupric sulfate.

4.2.1 Chemical Oxygen Demand

The most significant criterion to compare and evaluate different sets of experiments is the reduction in chemical oxygen demand (COD). As previously stated, COD is defined as the amount of oxygen required to oxidize the organic fraction of a sample which is susceptible to permanganate or dichromate oxidation (Ramalho, 1983).

Two different standard methods were used to measure the COD. For both methods the COD is defined as the milligrams of oxygen consumed by one litre of sample under the conditions of the test. Both methods result in the same COD values for similar samples; however they offer different advantages.

The first method, CPPA Standard H.3 (Canadian Pulp and Paper Association, 1993), applies to samples with suspended organic solids, and was used for the determination of the COD of the untreated sludge. Under strongly acidic conditions, organic matter in the test specimen is oxidized by open refluxing with a known amount of potassium dichromate. At the end of the reflux period excess dichromate is determined by titration with ferrous ammonium sulfate using Ferroin indicator. The standard deviation of a set of synthetic samples was found to range from 6.5 to 10.8% of the average COD value.

The second method, Standard 5220.C (Standard Methods Committee, 1990), is more economical in the use of reagents, but requires homogeneous samples for reproducible results. This method was used for treated effluent (after WAO), and involves the same reaction and reagents as the previously mentioned standard. Its only difference is that refluxing is performed under closed conditions, consequently, volatile organic compounds are more completely oxidized because of longer contact with the oxidant. As a result, precision is increased, and the range of standard deviation of a set of synthetic samples varies from 4.8 to 5.6%.

4.2.2 Solids Content

The method used for solids determination is CPPA Standard H.1 (Canadian Pulp and Paper Association, 1993). This standard determines the total, fixed and volatile fractions of suspended and dissolved solids and settleable solids in pulp and paper mill effluents.

Total solids is the sum of the total suspended solids and total dissolved solids. The total suspended solids is determined by weighing the oven dried precipitate from the filtration of a representative sample volume of the effluent. The total dissolved solids is measured by drying a known volume of the filtrate from this same filtration. For determination of the organic and inorganic fractions, the dried precipitate and filtrate are placed inside a furnace at 550°C until constant weight is achieved.

4.2.3 Other Analysis

For some selected experiments, Total Organic Carbon (TOC) and the concentration of acetic acid were determined at the Paprican Analytical Laboratory in Pointe Claire. The Technicon Auto Analyzer #2 was used to measure TOC, while Dionex Ion Chromatography was used to determine the concentration of acetic acid.

4.2.4 Concentration of Cupric Sulfate (Ion Exchange Experiments)

The samples were analyzed for copper by a Perkin-Elmer UV visible spectrophotometer (Lamda 3B). Maximum absorption occurs at 808 nm (Cotton and Wilkinson). In Appendix D, Figure D.1 shows the absorption spectrum for a 35 mmol/L sample of cupric sulfate pentahydrate in water. Figure D.2 shows the calibration curve for different concentrations of cupric sulfate. The relationship between absorption and cupric sulfate concentration (mmol/L) is:

$$Concentration = 87.4 \times Absorption + 0.096 \qquad (4.1)$$

4.3 EXPERIMENTAL APPARATUS

A schematic of the WAO system is shown in Figure 4.2.

The laboratory rocking autoclave consists of a stainless steal bomb, autoclave shell and rocking mechanism. The bomb is a small pressure vessel having a threaded opening and a volume of 1.4 litres. The lid, which seals the bomb, is screwed onto the threaded opening. The sealed bomb is placed inside the autoclave shell, which contains a 1600W heating coil. Together the bomb and shell are rocked back and forth approximately thirty degrees in order to achieve mixing. The rocking mechanism is primarily a small motor connected to the autoclave shell by a shaft. To improve the degree of mixing, the shaft length was shortened, causing the bomb to pass through the horizontal position.

Two 1/4" O.D. thick-walled tubes are connected to the bomb via two inlets. The tubes, called the charging line and the discharging line, are spiraled several times to absorb the motion of the autoclave and thereby prevent stress fatigue. Valves isolate the spiraled section of the tubing and bomb (hereafter called the high pressure side) from the rest of the tubing (low pressure side). The valves on the charging line permit desired amounts of compressed oxygen or argon to enter the bomb through one of the inlets. While on the discharge line, a valve operates as a pressure release and connects the other bomb inlet to the discharge vessel.

A pressure gauge and rupture disc assembly is connected on the high pressure side of the charging and discharging lines. The rupture disc has a burst pressure of 24.8 Mpa.

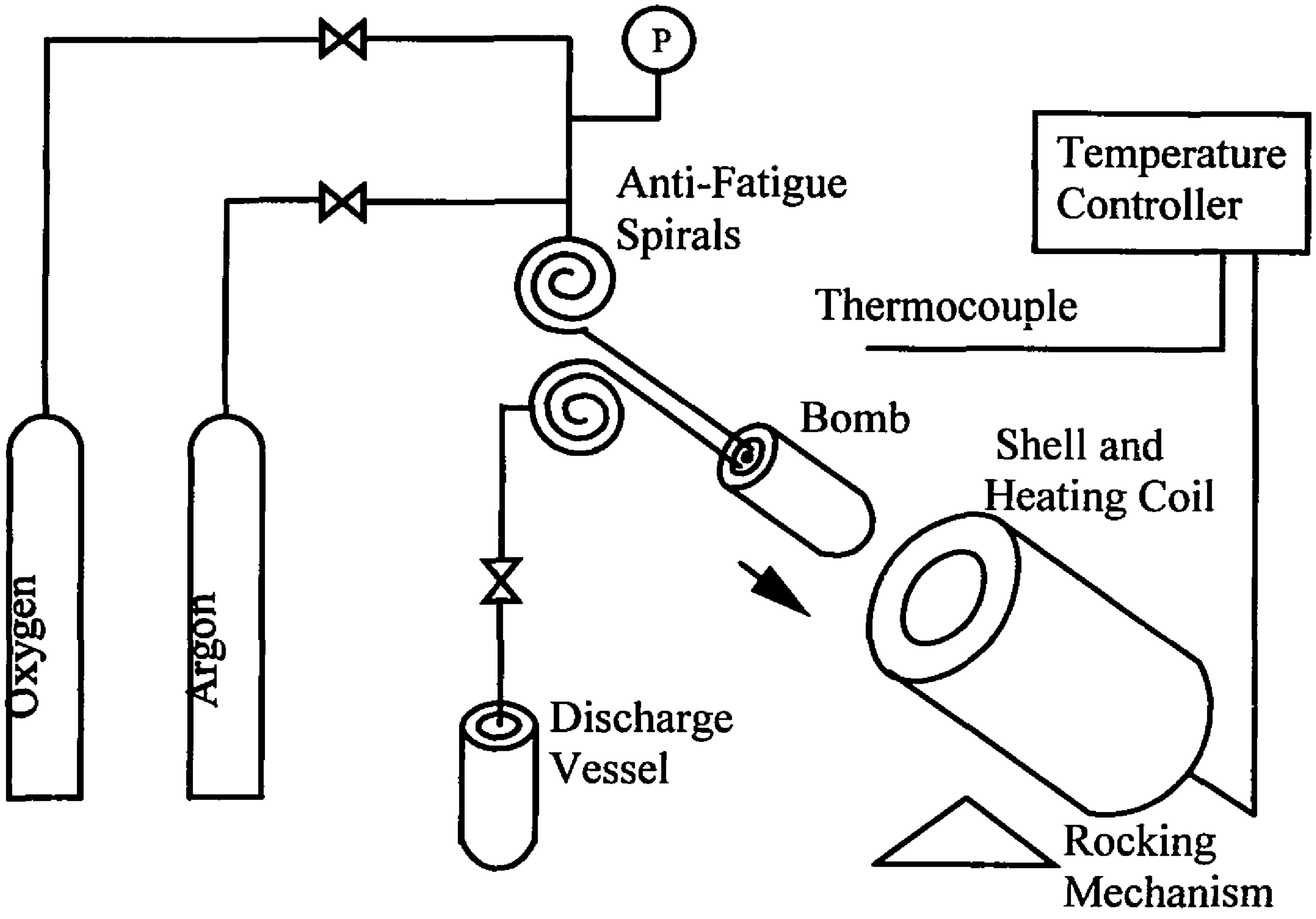


Figure 4.2 - Experimental Wet Air Oxidation Flowsheet

The entire high pressure portion of the autoclave is surrounded by a double wall grate cage for further safety.

Temperature is monitored via a tap in the bomb lid which allows a thermocouple to be in contact with the vessel's contents. The thermocouple is connected to the temperature controller which in turn sends a signal to the heater using proportional control.

Some design limitations should be noted and clarified: there exists no mechanism for sampling at high pressure; there are no means for cooling the reactor rapidly; heating up time to the desired operating temperature is significant; and mixing is not complete. Although the system is not perfectly mixed, it was optimized under the design limitations by studying the effect of moving the location of the bomb with respect to its pivot point. This was achieved by observing the dispersion of drops dye inside a clear plexiglas bomb.

4.4 WET AIR OXIDATION PROCEDURE

The bomb is filled with a calculated amount of effluent and catalyst such that the experiment will remain in the liquid-vapour region at the desired operating temperature and pressure (see Appendix A - Initial Calculations). The cap is fitted over the lid and is then screwed tight to the bomb (see Figure 4.3). The bomb is carefully sealed by applying equal torque to the ten retention bolts, and then placed inside the autoclave shell.

The charging and discharging lines are then connected to the inlets of the bomb and fastened tightly.

The bomb is then pressurized with a desired amount of oxygen (see Appendix A). If the sum of the vapour and oxygen partial pressures calculated at the operating temperature is less than the desired total operating pressure, then the bomb is further pressurized with an inert gas (argon) such that the desired operating pressure is achieved. All valves are closed, isolating the high pressure side from the rest of the apparatus.

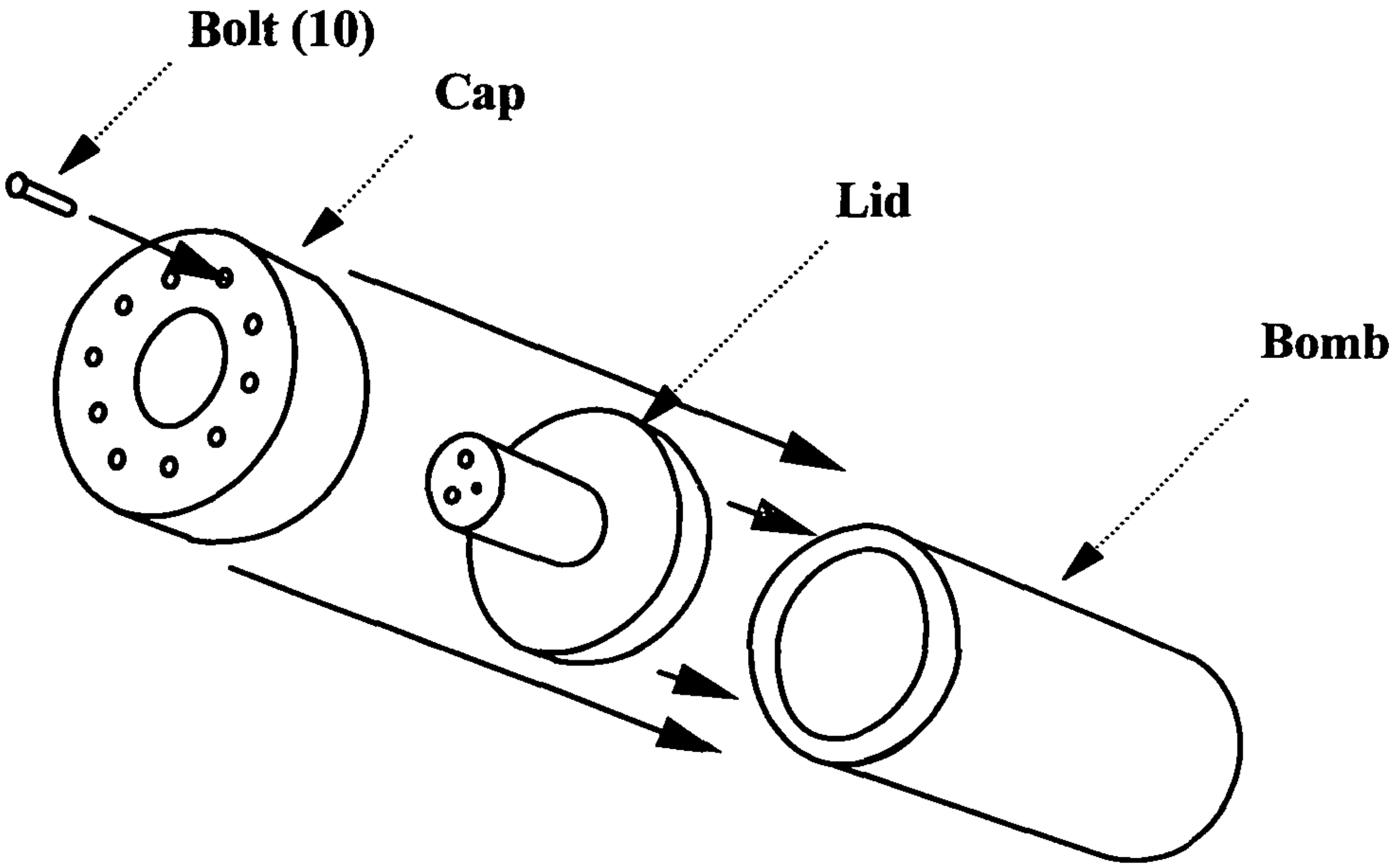


Figure 4.3 - Stainless Steel Bomb Sealing Procedure.

The rocking mechanism and the heater are then activated and a timer is started. The pressure and temperature inside the bomb are recorded at subsequent time intervals. For most experiments, the reactor is turned off at a specified temperature and the system is allowed to proceed without additional energy input. This method for controlling different sets of experiments has proven itself successful in achieving similar conditions from one experiment to another. Also, when the system has cooled to a set temperature (10-15°C below the maximum temperature), a fan is turned on to cool the system by convection. The rocking mechanism is turned off at another set temperature (20-30°C below the maximum operating temperature, T_{max}) in order to further standardize experimental conditions.

After allowing the system to cool to room temperature, the pressure is released to the discharge vessel. The bomb is disconnected from the two inlet lines and disassembled. Effluent and catalyst are removed. The effluent is then analyzed accordingly.

4.5 EXPERIMENTAL PROGRAM

The experimental program was divided into two sections: (1) evaluation of various catalysts for the WAO of pulp and paper sludge, and (2) characterization using the selected catalyst in order to determine the extent of improvement in the degree of oxidation under different operating conditions.

4.5.1 Phase (1): Evaluation of the Catalysts

For the determination of the best catalyst, temperature, total pressure, oxygen pressure, volume of effluent, and concentration of catalyst were held constant throughout experimentation. Initial oxygen charging pressure, p_{oi}, was fixed at 5.72 MPa. The volume of waste effluent, V_e, was held constant at 400 mL. The concentration of catalyst added was 10 mmol/L. In order to standardize the set of experiments, the heater was turned off at 185°C and the system was allowed to proceed without additional heating. Under these conditions, the maximum operating temperature achieved ranged from 208-214°C while maximum total operating pressure varied from 10.98-12.03 MPa from one experiment to the next. After the system cooled down to 200°C the cooling fan was activated. After cooling to 185°C the rocker was deactivated and the system was allowed to return to room temperature. Figure 4.4 shows typical temperature and pressure profiles with time for this type of experiment. An experiment without catalyst was also performed under the same conditions for comparison.

4.5.2 Phase (2): Characterization

After the most promising catalyst was selected, the extent of improvement in the degree of oxidation under different operating conditions was characterized. The temperature, pressure, length of time at the maximum operating and concentration of catalyst were varied in this section of experimentation.

Temperature Experiments:

In order to study the effect of temperature on the degree of oxidation, the maximum operating temperature, T_{max}, was varied from 164-315°C for both experiments with and without catalyst. Throughout these experiments, the maximum operating pressure, P_{max}, ranged from 10.75-11.68 MPa. The effluent volume was held constant at 400 mL except for the high temperature reactions (301°C and 315°C) which employed less effluent (175 mL) due to specific volume of effluent restraints, and oxygen requirements. Catalyst concentration was held constant at 10 mmol/L.

Depending on the desired operating temperature, different initial oxygen charging pressures were used ranging from 3.65 to 7.79 MPa in order to maintain a constant maximum operating pressure. To achieve similar operating conditions for these experiments, the heater was turned off at 20°C bellow the desired maximum operating temperature. The cooling fan and rocking mechanism were respectively activated and deactivated at set temperatures depending on the maximum operating temperature.

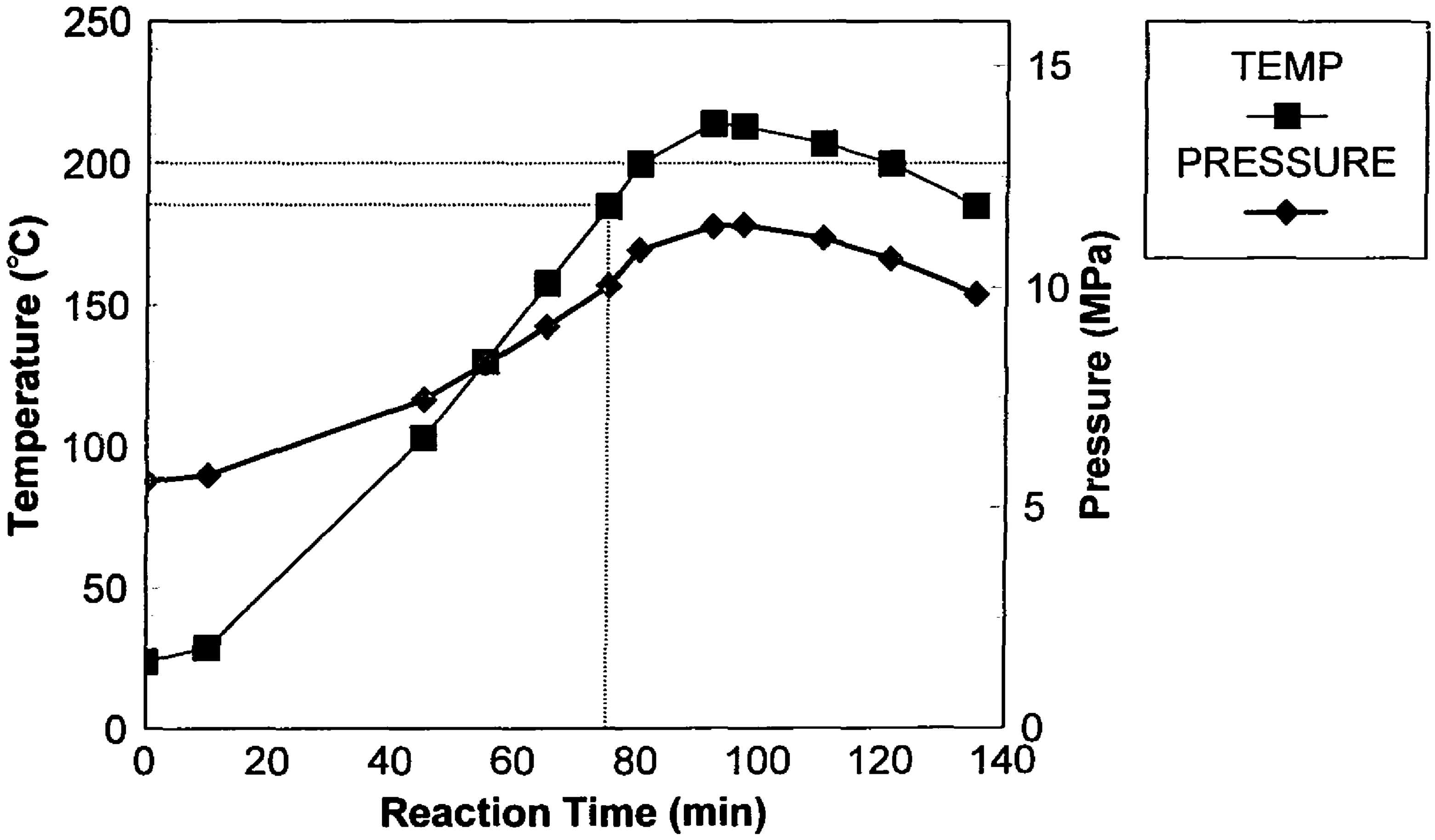


Figure 4.4 - Typical Temperature and Pressure Profiles

Length of Time at Maximum Operating Temperature:

The effect of length of time at the maximum operating temperature, t, on COD reduction was examined. Experiments with and without catalyst were performed for two different times (5 and 60 min). For the two experiments with t=5 min, the procedure outlined in Section 4.5.1 was followed. For the other two experiments at t=60 min, the temperature was maintained to within two degrees of the maximum operating temperature by manual control for one hour. Otherwise the same procedure was followed (Section 4.5.1).

Pressure Experiments:

Total operating pressure varied from 4.38 to 15.44, by changing the initial oxygen charging pressure. Experiments were performed with and without catalyst (10 mmol/L) under similar operating conditions for comparison. Effluent volume was held constant at 400 mL. The experimental method described in Section 4.5.1 to achieve the same temperature profiles was followed. This resulted in maximum operating temperatures ranging from 210-216°C between different experiments.

Concentration Experiments:

The concentration of the catalyst was varied from 0 to 20 mmol/L. Otherwise, the same method was followed as described in Section 4.5.1. Using this procedure resulted in maximum operating temperatures and maximum operating pressures ranging from 211-214°C and 11.17-11.72 MPa respectively.

A complete listing of all experiments performed is shown in Appendix B.

4.6 ION EXCHANGE EQUIPMENT AND METHODOLOGY

Experimentation was performed using the laboratory bench scale exchange column apparatus at Paprican, Pointe Claire. Figure 4.5 depicts the configuration for the system.

The exchange column is packed with the ion exchange resin (AG 50W-X8). This is prepared by slurrying the resin with deionized water and then pouring the slurry into the column. After allowing the resin to settle, the column is equilibrated to the desired conditions. The volume of the exchange column is approximately 300 mL and the void fraction for the packed column is 0.40.

Three storage columns exist; a feed column, a regeneration column, and a deionized water column. For the purpose of this experiment, the feed column contained the sample which consisted of 10 mmol/L of the chosen metal sulfate catalyst dissolved in aqueous solution. The regeneration column contained the eluant - a solution of sulfuric acid in water (1 M). Flow rates were maintained constant at 120 mL/min and driven by compressed nitrogen lines connected to the tops of each storage column. The deionized water and sulfuric acid solution enter the top of packed column (downstroke) while the metal sulfate feed solution enters at the bottom (upstroke). Valves are adjusted to allow for the appropriate flow configuration.

The experimental procedure includes three cycles; rinse, separation, and regeneration cycles.

- Rinse Cycle: The packed column is rinsed before each separation and regeneration cycle. Approximately 75 mL of deionized H_2O is passed through the column during this stage.
- Separation Cycle: The desired amount of the cupric sulfate solution is upstroked trough the column. Samples of around 50 mL are taken at the exit of the column. During this stage the metal cation is exchanged with H^+. The exchange metal cations are bound to the matrix and retained on the column.

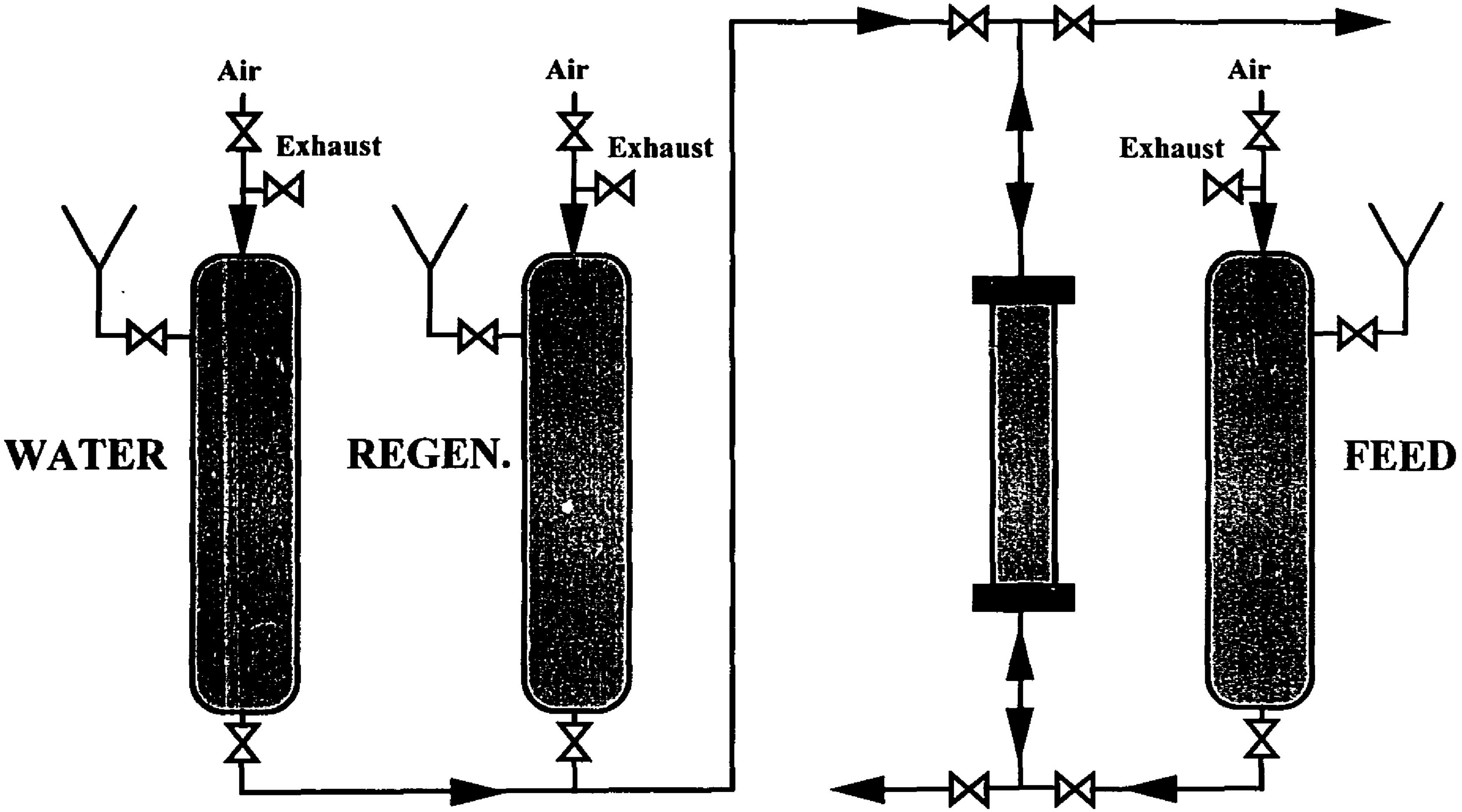


Figure 4.5 - Ion Exchange Column Bench Configuration

- Regeneration Cycle: The sulfuric acid eluant is downstroked through the column to recover the bound cupric cations. During this stage H^+ is exchanged with the metal cation. 50 mL samples are taken. Sufficient eluant is passed through the column until all catalyst is removed from the column.

CHAPTER 5

RESULTS AND DISCUSSION

In this chapter the results of the experimental program are presented and discussed. The first section of this chapter accounts for the results from catalyst screening experiments and includes a discussion of the effects of different catalysts on the reduction of COD and total solids. The results from the second phase of the experimental program are presented in Section 5.2. In this section, the effects of temperature, pressure and catalyst concentration on the COD reduction and total solids reduction are discussed. Both experiments with and without the catalyst are compared. The final section presents the ion exchange column results for the recovery of the most suitable catalyst tested.

In Appendix B, Table B1 presents a complete listing of all experiments, showing operating conditions and other pertinent parameters.

5.1 PHASE ONE EXPERIMENTAL RESULTS: *CATALYST SCREENING*

These experiments were conducted as described in Section 4.5.1 using 10 mmol catalyst per liter waste effluent before pressurization. All catalysts were soluble in water at room temperature.

All experiments were analyzed using COD and total solids reduction. For selected experiments, an organic and inorganic solids analysis was performed.

5.1.1 Effect of Catalyst on COD Reduction

Figure 5.1 shows the effect of different catalysts on the percent COD reduction under similar operating conditions (see Table C1 in Appendix C).

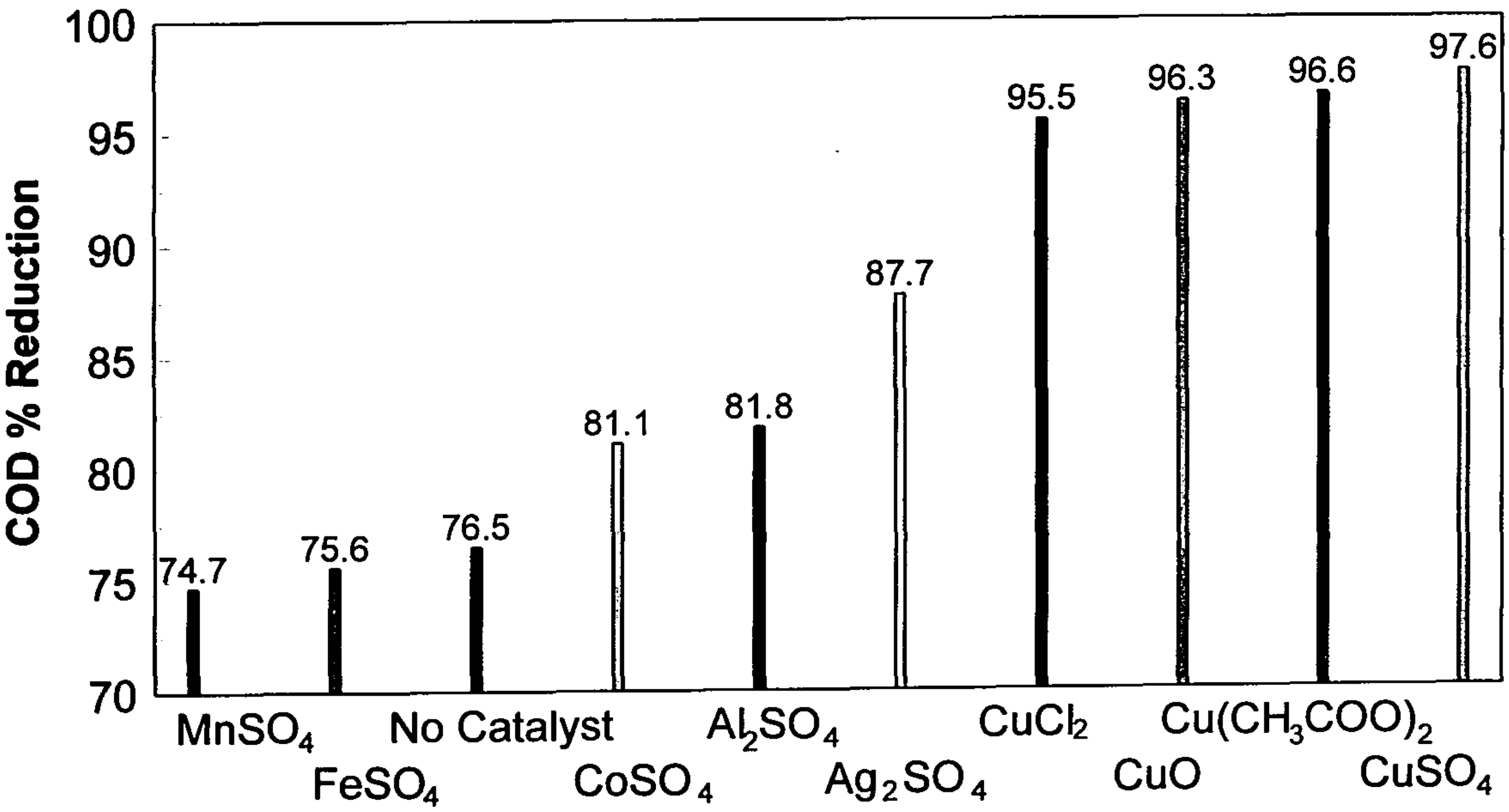


Figure 5.1 - Effect of Different Catalyst on the Percent COD Reduction
(T=200°C, P=10.34 MPa, concentration of catalyst =10mmol/L)

Improvement in the degree of oxidation was exhibited when using cobalt sulfate, aluminum sulfate, silver sulfate and the copper (II) species. The best reduction was achieved when cupric sulfate was used. The results show that without a catalyst, the COD Reduction was found to be 76.5% while the use of cupric sulfate yielded a 97.6% COD reduction.

Cobalt sulfate, aluminum sulfate and silver sulfate all had varying degrees of improvement for the oxidation of the TMP sludge. Amongst these, silver sulfate, a catalyst used to achieve complete oxidation in COD measurement methods, yielded the highest COD reduction of 87.7%. This reduction is significantly less than that obtained when using the copper containing catalysts.

Figure 5.1 also includes the COD reduction the presence of CuO which is insoluble at room temperature. This experiment was performed by Volstad (1994) while screening heterogeneous metal oxides under similar operating conditions. Table 5.1 shows the reduction in COD results obtained by Volstad when using the various oxides of the metal salts (all experiments were performed at conditions similar to the method presented in Section 4.5.1 except that the amount of catalyst used varied according to surface area).

Table 5.1

COD Reduction Using Metal Oxides (Volstad, 1994)

Metal Oxide Catalyst	Moles of Metal Oxide Added Per Litre (mmol/L)	% COD Reduction
CuO	10	96.3%
Co_3O_4	3.4	76.6%
Fe_2O_3*	1.7	74.7%
Al_2O_3*	3.2	73.4%
MnO_2*	94.7	49.2%

* Metal oxide inhibits oxidation reaction at experimental conditions tested.

As mentioned in Chapter 2, cupric oxide offered the best improvement (96.3%) over other metal oxides tested. It should be noted that unlike the other homogenous catalysts, cupric oxide became soluble at higher temperatures and remained partially soluble after cooling. This behaviour would demand a series of separation techniques for the recovery of the partially soluble copper (II) (one for the recovery of CuO and another for the recovery of soluble cupric cations).

Figure 5.1 also shows that the addition of ferrous sulfate and manganese sulfate had negative effects on the COD reduction. These results are in agreement with the results obtained by Volstad (1994) when using their respective oxides, although the molar amounts of the oxide catalyst used were different. The molar quantities varied in order to maintain a constant catalyst surface area throughout the experiments.

Under these experimental conditions, ferrous sulfate oxidizes from a 2+ state to 3+, resulting in the production of ferric oxide and ferric sulfate (aq.). This reaction consumes oxygen. However, the amount consumed is calculated to be only 77 mg/L and consequently does not contribute to the observed inhibition.

Statistical Assessment of Results:

The following is a statistical analysis to distinguish between different pairs of results and thus rank the catalysts.

To determine the reproducibility of the results, three replicates were performed for experiments with no catalyst and with cupric sulfate. The COD reductions for the individual experiments are shown in Table 5.2 (see Appendix C, Table C1).

TABLE 5.2

Reproducibility of Results

Experiment (*)	**Catalyst**	**T_{max} (^0C)**	**P_{max} (MPa)**	**% COD Reduction**
12	None	212	11.34	76.2
13	None	212	11.44	76.4
16	None	212	11.44	76.8
o2	$CuSO_4$	211	11.17	97.3
o12	$CuSO_4$	214	11.72	97.8
o21	$CuSO_4$	212	11.58	97.8

* See Appendix B

The 95% confidence intervals for the ensemble means with no catalyst (μ_{none}) and with cupric sulfate (μ_{CuSO_4}) are:

$$75.71 \le \mu_{none} < 77.22 \tag{5.1}$$

$$96.91 \le \mu_{CuSO_4} < 98.3 \tag{5.2}$$

To distinguish between the effect of different catalysts, it is assumed that the variance occurring from one experiment to the next is the same. For the experiments without catalyst the variance is 0.0933%, while for the experiments with cupric sulfate the variance was 0.0833%. Comparison of these variances with a null hypothesis of $\sigma_A^2=\sigma_B^2$, shows that they are not significantly different (see Appendix E). Consequently, the aforementioned assumption is valid.

This assumption enables the analysis of the experimental results by pooling the variances and testing the ensemble "means" (see Appendix E). It can be shown that when the difference between two experiments is less than 1.28 %, then they are statistically the same ($\alpha=0.05$).

By comparing the COD reduction for all of the experiments, the best catalysts are found to be those containing copper (II). Table 5.3 shows the ranking of the catalysts tested according to the aforementioned assumption.

TABLE 5.3

Ranking of Catalysts

Rank	Catalyst	% COD Reduction
1	Cupric Sulfate	97.6
	Cupric Acetate	96.6
	Cupric Oxide	96.3
	Cupric Chloride	95.5
5	Silver Sulfate	87.7
6	Aluminum Sulfate	81.8
	Cobalt Sulfate	81.1
8	Ferrous Sulfate*	75.6
	Manganese Sulfate*	74.7

*** Inhibits oxidation reaction at experimental conditions tested.**

Effect of the Anion:

Cupric sulfate, cupric acetate, and cupric chloride were tested to determine the effect of the anion. According to the developed statistical criteria, only the sulfate and chloride anions resulted in statistically different COD reductions within this group (difference > 1.28%).

After the cupric chloride experiment, it was observed that the reactor had undergone severe corrosion. In particular, the surfaces of the lid and bomb which form the seal had to be refinished before further experimentation could be performed. This severe corrosion can explain cupric chloride's poorer performance when compared to the results obtained using cupric sulfate. Under acidic conditions, chloride is extremely corrosive toward metal surfaces. Consequently, the corrosion of the stainless steel reactor results in the production of Fe^{3+}. According to Volstad (1994) ferric oxide, which becomes partially soluble at these reaction conditions, was found to inhibit the degree of oxidation during WAO. As a result, the COD reduction is lower. The corrosive nature of $CuCl_2$ leaves the catalyst undesirable for WAO.

Although cupric acetate results in COD reduction comparable to cupric sulfate, it has an additional drawback. The addition of acetate will add to the overall organic load, increasing the COD and thus requiring further treatment. The effect of acetate on the initial COD through the addition of 10 mmol cupric acetate per litre of sludge, increases the COD by 640 mg/L or 1.6%. Consequently, in an industrial setting, the addition of cupric acetate would not be practical as a catalyst for WAO.

The effect of the three anions tested on the degree of oxidation is almost negligible. Consequently, it can be concluded that the principal active catalytic component is the cupric cation. According to the COD reduction and the aforementioned disadvantages associated with $CuCl_2$, $Cu(CH_3COO)_2$, and CuO, the best catalyst is $CuSO_4$.

Sources of Error:

Although the variance between experiments is relatively low, the following is a discussion of the sources of error resulting from experimentation and chemical analysis.

As mentioned in Chapter 4, one source of error comes from the COD method Standard 5220.C (Standards Method Committee, 1990) which states a standard deviation of 4.8 to 5.6% for synthetic samples. Three replicate COD measurements were conducted for experiment "o2" (see Appendix C - Table C1). The results were 1120, 1090 and 1070 mg/L which corresponds to a standard deviation of 27.6 mg/L or 2.5%. The variance reported in the statistical analysis section for the three replicate experiments is 0.0833%, but refers to the percent COD reduction - not the COD. Consequently, the variance due to the Standard 5220.C COD measurement converted to percent COD reduction is 0.0048%, which is much less than 0.0833% (see Appendix E). The remaining portion or error must therefore come from the WAO experimental procedure.

The most important source of error is from the control mechanism of the reactor. As mentioned, the heater is turned off at set temperatures in order to achieve a desired maximum operating temperature, T_{max}. For three identical experiments using $CuSO_4$, T_{max} varied from 211-214°C. An experiment which peaks at 214°C will remain above 200°C for approximately five minutes longer then an experiment peaking at 211°C. In the most extreme case the two experiments with T_{max}=211°C and the other at 214°C result in a COD difference of around 200 mg/L out of 1000 mg/L, i.e. 20%. Consequently, the error associated with the experimental method contributes significantly to the overall error.

Other less significant sources of error are: measurement error for the volume of sludge (+/- 5 mL would affect the initial COD load by +/-200 mg/L or +/- 0.5%), measurement error for the amount of catalyst added (+/- 0.005 g), and error from the pressure gauge (+/- 0.034 MPa). In Section 5.2, it will be shown that the effect of the error arising from the mass of catalyst added and pressure readings are negligible.

5.1.2 Effect of Catalyst on Total Solids Reduction

Figure 5.2 shows the effect of different catalysts on the reduction of total solids, which is the sum of the dissolved and suspended solids. The untreated sludge had a total solids content of 40.18 g/L, of which 2.00 g/L were dissolved solids and 38.18 g/L were suspended solids. The largest total solids reduction occurs when using cupric sulfate, which coincides with the results of the COD reduction. The reduction in total solids without catalyst was 85.3% while with cupric sulfate the reduction was 95.6%. The total solids after treatment when using cupric sulfate was found to be 1.79 g/L which is equivalent to 0.179% solids content (see Appendix C - Table C2). The original untreated sludge had a solids content of 4.02%.

Other catalysts showed varying degrees of improvement in the destruction of solids relative to the non-catalyzed experiment. Only $MnSO_4$ inhibited the reduction of

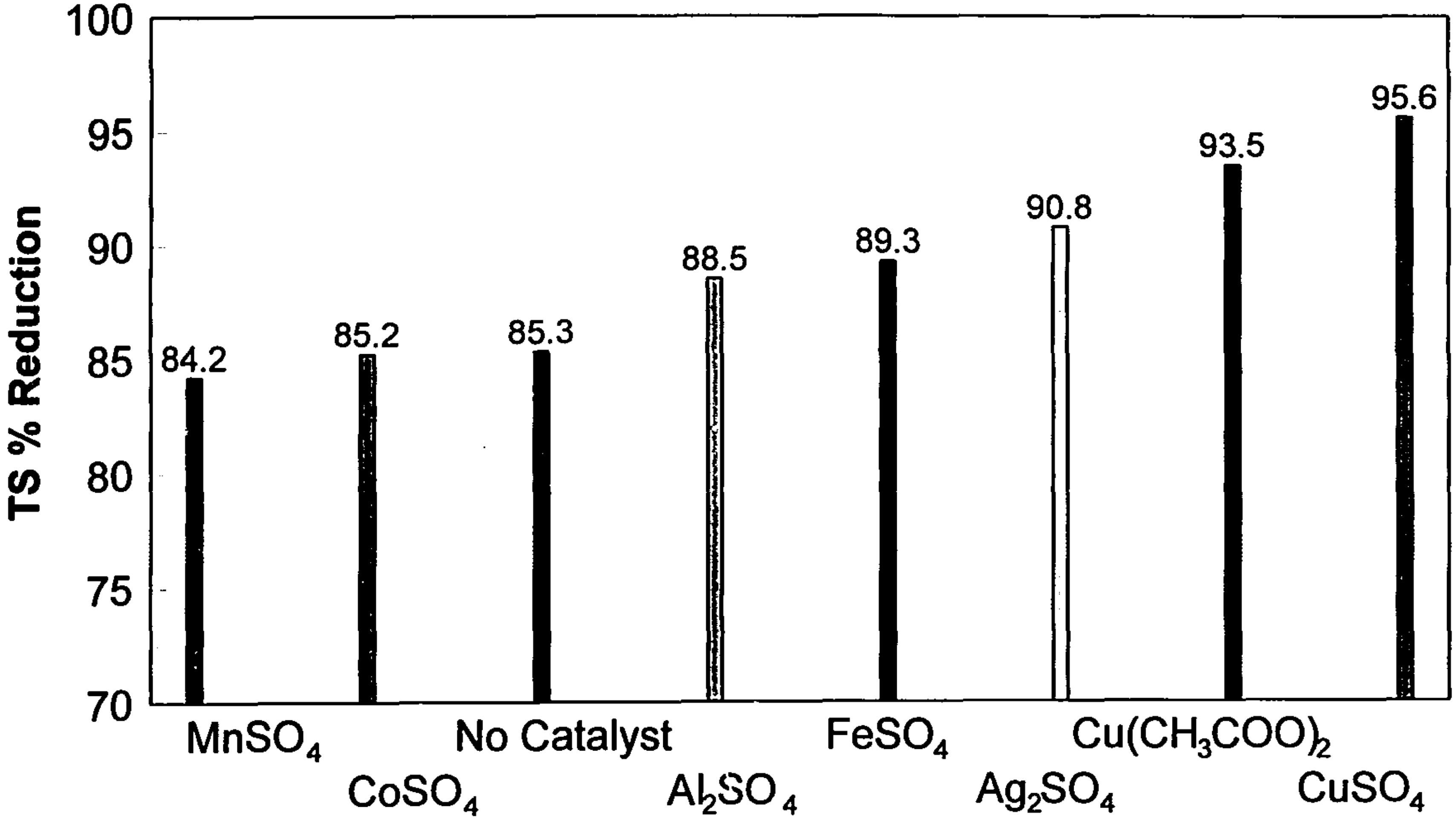


Figure 5.2 - Effect of Different Catalyst on the Percent Total Solids Reduction
(T=200^0 C, P=10.34 MPa, concentration of catalyst =10mmol/L)

solids. The ranking of the catalyst according to total solids reduction is the same as that presented by the COD analysis, except for $FeSO_4$ which showed an improvement of approximately 4% over non-catalyzed runs.

An analysis of the inorganic and organic components for untreated sludge, treated sludge without a catalyst, and treated sludge using cupric sulfate is presented later in Section 5.2.1.

After comparing the COD and the total solids reduction for experiments using different homogenous catalysts, it can be concluded that catalysts containing copper (II) offer the best improvement over the other metal salts. Cupric sulfate does not add to the organic load (unlike $Cu(CH_3COOH)_2$), it is completely soluble at the concentrations tested (unlike CuO) and it does not significantly increase the corrosion of the reactor (unlike $CuCl_2$). Consequently, cupric sulfate was chosen as the catalyst for further experimentation.

5.2 PHASE TWO EXPERIMENTAL RESULTS: *CHARACTERIZATION*

The second phase of experimentation consists of a characterization of the extent of improvement using the best catalyst, cupric sulfate, compared to experiments without catalyst. The parameters which were varied include maximum operating temperature (164-315°C), maximum operating pressure (4.38-15.44 MPa), catalyst concentration (0-20 mmol/L) and length of reaction time at the maximum operating temperature (5 and 60 min). All samples were tested for COD, while selected experiments were analyzed for solids content, acetic acid concentration and total organic carbon (TOC).

5.2.1 Effect of Reaction Time on COD Reduction

Initial experimentation was performed to understand the effect of length of reaction time at the maximum temperature on the COD reduction for experiments with and without cupric sulfate. Table 5.4 shows the COD reduction after operating for 5 and

60 minutes at the maximum operating temperature. For these four experiments, the maximum operating pressure was kept between 11.17 to 11.72 MPa (see Appendix B).

TABLE 5.4

Effect of Time at T_{max}

Experiment (*)	$[CuSO_4]$ (mmol/L)	T_{max} (^{o}C)	Time at T_{max} (min)	% COD Reduction
12	0	212	5	76.2
o12	10	214	5	97.8
7	0	214	60	87.0
o1	10	215	60	99.5

* See Appendix B.

Experiments with increased time at the maximum operating temperature result in further destruction of organic matter. For experiments without cupric sulfate catalyst the COD reduction improved from 76.2% to 87.0% after one hour at T_{max}. For cupric sulfate catalyzed runs, the COD reduction improved from 97.8% to 99.5%. Finally, the addition of $CuSO_4$ has a greater effect on the COD reduction than increasing the time at T_{max} to 60 minutes.

5.2.2 Effect of Operating Temperature

Reduction of COD:

Figure 5.3 shows the effect of maximum operating temperature on the percent COD reduction while all other parameters were held constant (see Table C3 in Appendix C). The solid line represents experiments which used cupric sulfate, while the dotted line is for experiments without catalyst. The greatest improvement between experiments with and without catalyst is around 200°C where the COD reduction increases by approximately 20%.

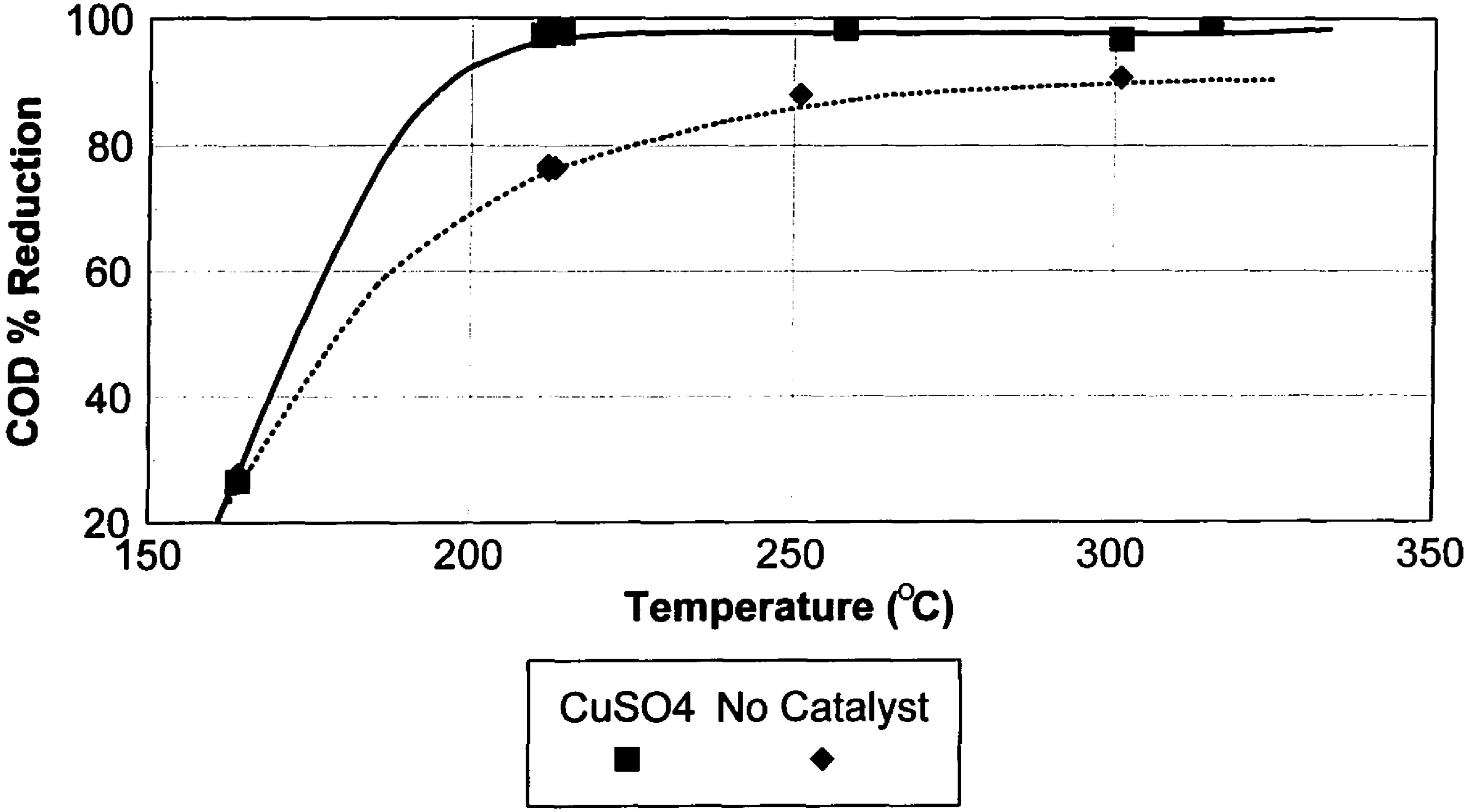


Figure 5.3 - Effect of Temperature on Percent COD Reduction
(P=10.34 MPa, concentration of cupric sulfate =10 mmol/L)

At temperatures greater than 210°C, cupric sulfate catalyzed experiments result in COD reductions of greater than 97%, while experiments without catalyst only yield 90% reduction at temperatures greater than 300°C.

The increased COD reduction observed when using cupric sulfate, suggests that the catalyst aids the oxidation of LMW organics like acetic acid. Table 5.5 shows the effect of maximum operating temperature on the acetic acid concentration with and without catalyst (see Table C6 in Appendix C).

TABLE 5.5

Concentration of Acetic Acid at Different Temperatures (P=10.34 MPa)

Exp.	Cupric Sulfate (mmol/L)	T_{max} (°C)	Acetic Acid (g/L)	COD Due to Acetic Acid (mg/L)*	Measured Total COD (mg/L)
16	0	212	3.71	3960	9270
21	0	301	3.16	3370	3720
o12	10	214	2.76	2940	890
o24	10	301	1.24	1320	1330

* See Appendix F for calculation of the COD due to Acetic Acid.

A comparison of the measured COD with the calculated COD due to acetic acid for experiment "o12" shows a discrepancy, in that the calculated COD value due to acetic acid is larger than the measured COD. However, the measured COD results from three experiments performed at the same conditions as those in experiment "o12" result in a standard deviation of only 0.29% (see Appendix E). Consequently, the error is most likely found in the acetic acid measurement.

Table 5.5 clearly shows that increased temperature reduces the quantity of acetic acid produced in experiments without catalyst. More importantly, comparison of the concentration of acetic acid for experiments with and without catalyst at the same temperature demonstrates the effect of the cupric cation on the selectivity. At 300°C the concentration of acetic acid was reduced from 3.16 g/L to 1.24 g/L. The cupric sulfate improves the selectivity of the WAO reactions by aiding in the oxidation of low molecular weight organics.

Total Solids Reduction:

Table 5.6 shows the total solids reduction for the same four experiments listed in Table 5.5 (see Appendix C, Table C6).

TABLE 5.6

Total Solid Reduction at Different Temperatures (P=10.34 MPa)

Exp.	**Cupric Sulfate Concentration (mmol/L)**	**T_{max} (^{o}C)**	**%Total Solids Reduction**	**% Organic Solids Reduction**	**% Inorganic Solids Reduction**
16	0	212	85.3	89.3	25.5
21	0	301	95.6	98.0	53.8
o12	10	214	95.6	97.3	69.5
o24	10	301	96.9	98.2	77.5

The reduction of solids by 96.9% (exp. o24) corresponds to a solids concentration after oxidation of 0.12% solids (wt/wt). The original untreated sludge had a consistency of 4.02%. With increasing temperature, the total solids reduction increases for both experiments with and without catalyst. The effect of the catalyst is more noticeable at lower temperatures (about 212^{o}C) where total solids reduction increases from 85.3% without catalyst to 95.6% with catalyst.

Table 5.6 also shows that the reductions in organic and inorganic (ash) solids contents increased with increasing temperature and with the addition of cupric sulfate. The decrease in inorganic solids due to temperature can be the result of the decomposition of carbonates to carbon dioxide. According to Gould (1962) the stability of carbonates decreases as temperature increases.

To demonstrate the effect of the catalyst on the solids reduction, Figure 5.4 presents the concentration of inorganic and organic solids for the untreated sludge, treated sludge without catalyst (exp. 16) and treated sludge with catalyst (exp. o12). This figure shows that the addition of cupric sulfate causes further improvement in reducing the amount of ash created. The quantity of inorganic solids decreased from 2.56 g/L to 1.91 g/L without catalyst and to 0.78 g/L with cupric sulfate. This implies that more inorganic carbon is converted to CO_2 when cupric sulfate is used as a catalyst.

As expected, Figure 5.4 also shows that the addition of cupric sulfate reduces the organic solids content over experiments without catalyst. The reduction of organic solids for experiments without catalyst was 89.3% (4.01 g/L) while with cupric sulfate it was 97.3% (1.01 g/L).

Analysis of the total organic carbon (TOC) for experiments 16 and o12 yielded values of 293 mg/L and 96 mg/L, respectively (Table C6, Appendix C). The use of $CuSO_4$ resulted in a 67.2% improvement in TOC when comparing these experiments with and without catalyst. It should be noted that TOC only measures the dissolved organic carbon (liquid phase) and does not account for any organic carbon present as suspended solids. Consequently, the addition of cupric sulfate causes further reduction of dissolved organic solids.

Summary

As the maximum operating temperature increases the degree of oxidation during WAO is improved for both experiments with and without catalyst. The addition of cupric sulfate results in improved COD and total solids reduction, and lower acetic acid concentrations over experiments without catalyst. Cupric sulfate also reduces the quantity of ash produced. The benefits from adding cupric sulfate at 200°C are more significant than the improvement which occurs from increasing the operating temperature to 300°C without a catalyst.

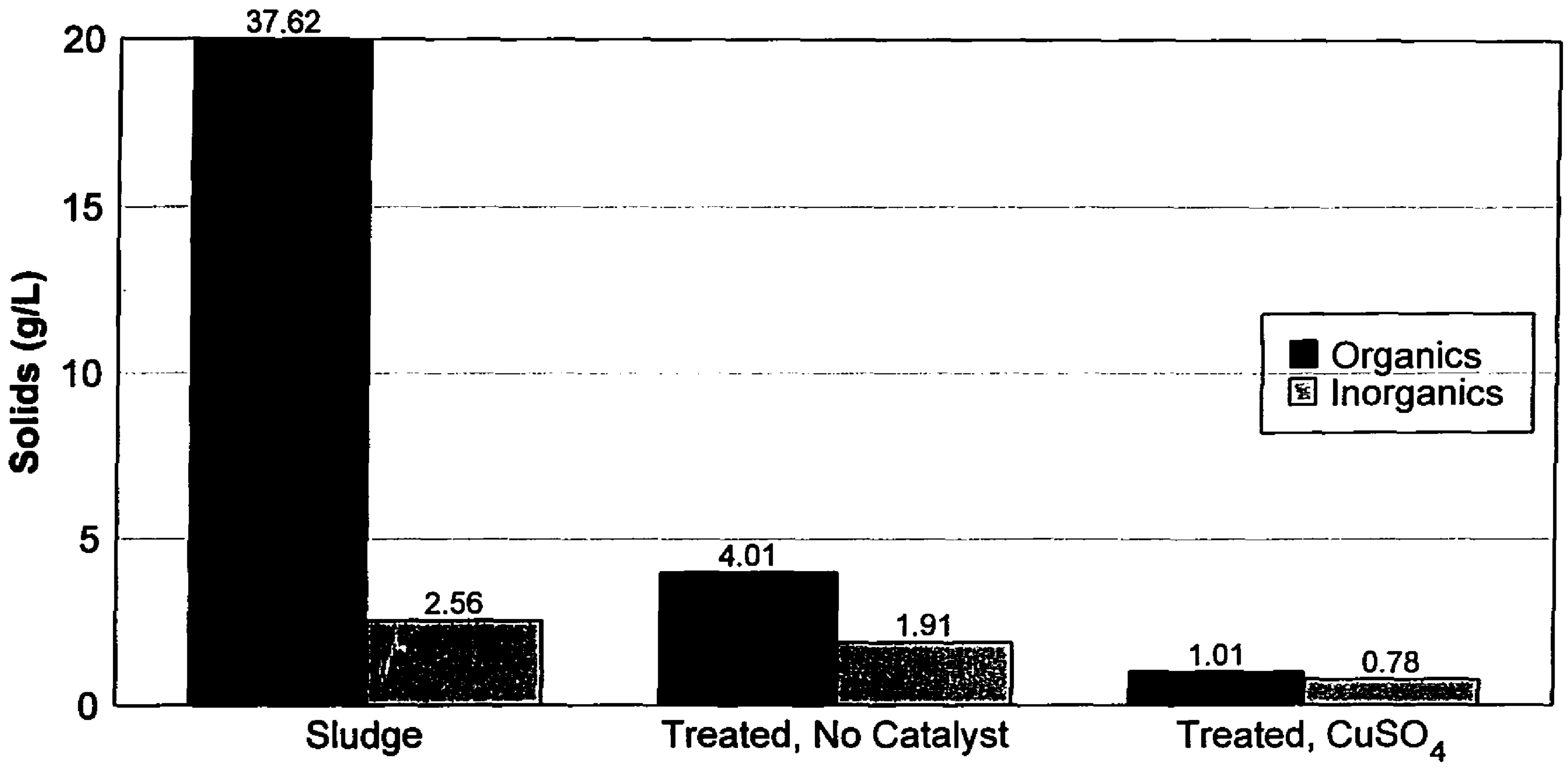


Figure 5.4 - Analysis of Organic and Inorganic Solids
(T=200 ^{0} C, P=10.34 MPa, concentration of catalyst =10mmol/L)

5.2.3 Effect of Catalyst Concentration on COD Reduction

The effect of varying the cupric sulfate concentration from 1-20 mmol/L on the COD reduction is shown in Figure 5.5 (Appendix C, Table C4). For these experiments the maximum operating temperature and pressure were kept between 211 to 214°C and 11.17-11.72 MPa, respectively. Figure 5.5 shows that the effect of cupric sulfate even at concentrations as low as 1 mmol/L is significant. The COD reduction undergoes a sharp increase after 1 mmol/L of cupric sulfate is added. At the highest concentration tested (20 mmol/L) there were no signs of inhibition caused by cupric sulfate.

5.2.4 Effect of Operating Pressure

Reduction of COD

Figure 5.6 shows the results for experiments with and without catalyst at different maximum total pressures. For these experiments the maximum operating temperature was kept between 210-216°C. All other variables were held constant. The maximum pressure was varied from 4.38 to 15.44 MPa (Appendix C, Table C5). The solid line represents cupric sulfate experiments while the doted line is for experiments without catalyst. The total operating pressure includes the partial pressures of water vapour, oxygen, and carbon dioxide. At 200°C the contribution of water vapour to the total pressure is 1.55 MPa. Since the maximum temperature is held constant from one experiment to the next, the total operating pressure is controlled by changing the initial oxygen charging pressure at the beginning of each experiment (see Appendix A - Initial Calculations).

The use of the cupric sulfate catalyst shows an improvement on the COD reduction of approximately 20% throughout the range of pressures tested.

At the lower pressure (5 MPa) the presence of char was observed. This is due to pyrolysis which occurs in the absence or reduced concentration of oxygen and results in the production of char. However, at these lower pressures, the initial oxygen charging pressure is still larger than the theoretical oxygen requirements. At the lowest maximum

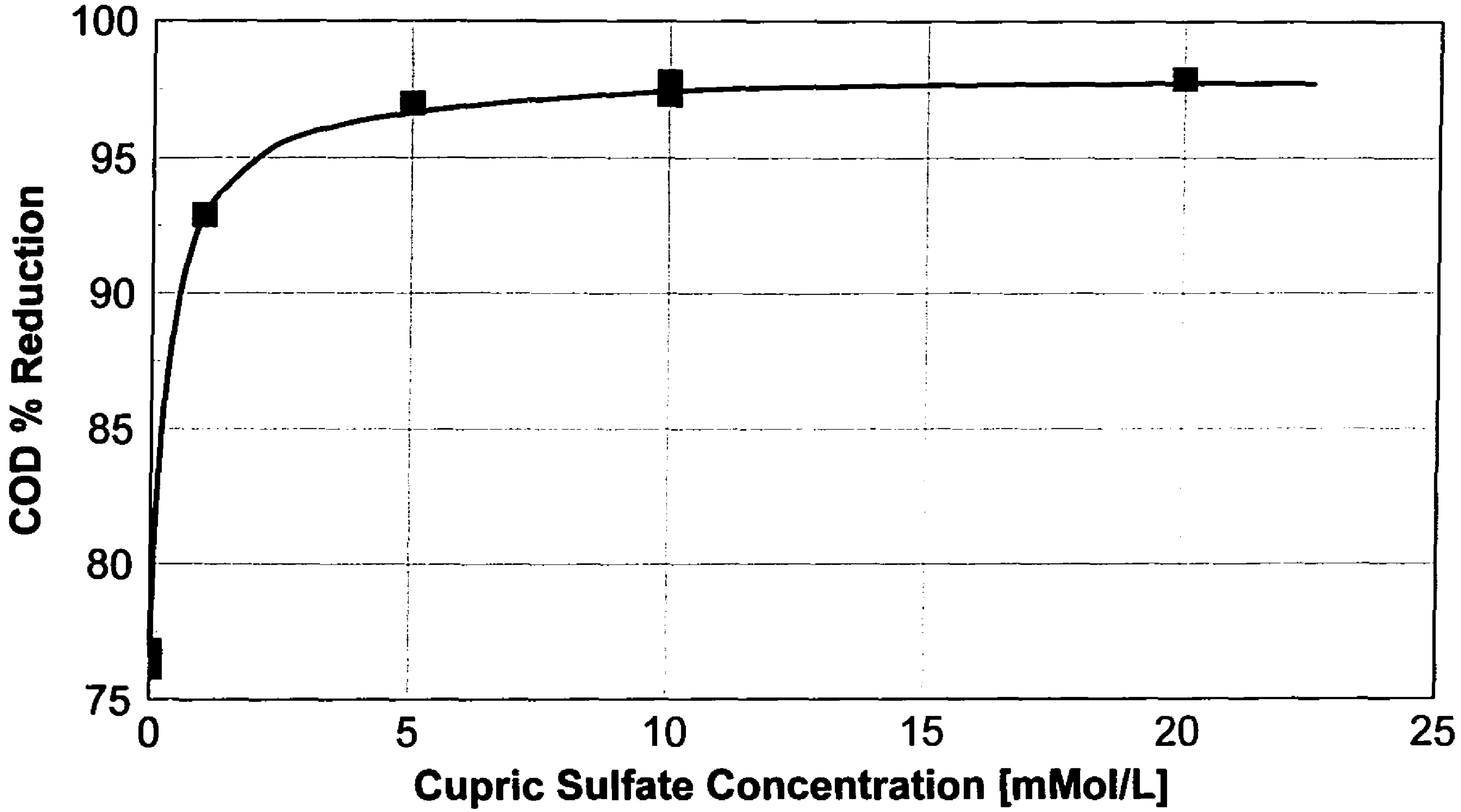


Figure 5.5 - Effect of Catalyst Concentration on Percent COD Reduction
(T=200 °C, P=10.34 MPa)

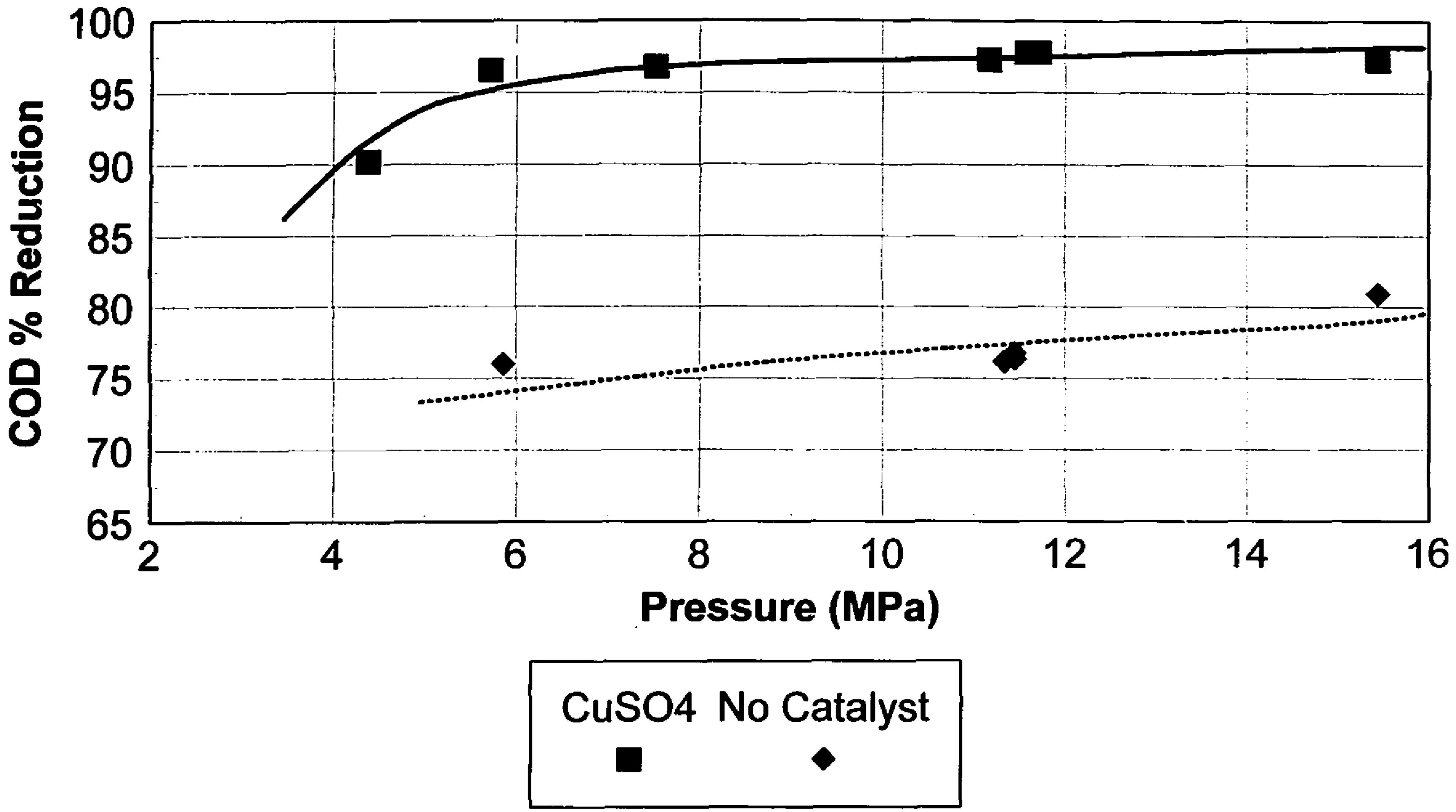


Figure 5.6 - Effect of Pressure on Percent COD Reduction
(T=200 ^{0}C, concentration of cupric catalyst =10 mmol/L)

pressure (4.38 MPa) there is 31% excess oxygen. Consequently, not enough oxygen is getting into the liquid phase, limiting the rates of oxidation. The solubility of oxygen in water increases with increasing pressure (Perry, 1984). With better mixing, the amount of O_2 entering the liquid phase may be increased, lowering the pressure at which char forms.

At higher pressures (P_{max}>6 MPa) the COD reduction levels off around 97.5%. Since the effect of increasing the total pressure by increasing the oxygen partial pressure becomes negligible, the system is no longer dependent on the solubility of oxygen at the specified temperature and catalyst concentration.

Total Solids Reduction

An analysis of the solids content at three different operating pressures is presented in Table 5.7 (Appendix C, Table C6).

TABLE 5.7

Total Solids Reduction at Different Pressures (T=200°C)

Exp.	Cupric Sulfate Concentration (mmol/L)	Pres. (MPa)	%Total Solids Reduction	% Organic Solids Reduction	% Inorganic Solids Reduction
16	0	11.45	85.3	89.3	25.5
o20	10	5.65	93.7	96.0	59.8
o12	10	11.72	95.6	97.3	69.5
o16	10	15.44	95.3	97.4	64.4

At the lower pressures (5.65 MPa) the total solids reduction when using $CuSO_4$ is much greater than the experiment without catalyst at higher pressure (11.45 MPa). The effect of pressure is negligible when increasing from 11.72 MPa to 15.44 MPa, which agrees with the COD reduction results. Consequently, lower operating pressures can be used for WAO with cupric sulfate.

The maximum operating pressure has little affect on the COD reduction and total solids reduction at pressures above 6 MPa. At pressures below 6 MPa, the oxidation rates decrease due to the solubility of oxygen in water.

5.2.5 COD Reduction at Highest Maximum Temperature and Pressure

Other experiments conducted which offer some interest are experimentation at highest T_{max} and P_{max}. Table 5.8 shows two experiments performed under the most rigorous operating conditions.

TABLE 5.8

COD Reduction at Highest T_{max} and P_{max}

Experiment (*)	**$[CuSO_4]$ (mmol/L)**	**T_{max} (^{o}C)**	**P_{max} (MPa)**	**% COD Reduction**
12 -control	0	212	11.34	76.2
o12 - control	10	214	11.72	97.8
14	0	310	14.89	91.9
o19A	10	315	15.17	99.1

* See Appendix B.

Further reduction in COD at the highest temperature and pressure is due to the increase in T_{max} only. As demonstrated in the previous section, P_{max} does not affect the COD reduction.

Also, at temperatures greater than 300°C, the degree of oxidation for experiments without catalyst is less than 92% COD reduction. This is in agreement with results obtained by Lunn (1992) who observed a maximum reduction of 92% at 320°C after treating sludge from a CTMP mill. Lunn used the same experimental apparatus employed for this thesis. Finally, the addition of cupric sulfate shows greater improvement in the COD reduction than the effect of increasing the maximum operating temperature from 212°C to 310°C.

5.3 RECOVERY OF CUPRIC SULFATE CATALYST

The following section presents the results obtained for the recovery of cupric sulfate using a cationic exchange column. It should be noted that the objective was to determine the feasibility of recovering the copper (II) catalyst using ion exchange. This part of the thesis was not intended to be an in-depth study on the separation of cupric ions by ion exchange.

Two separation and regeneration experiments were performed. Table 5.9 shows the results of two separation runs A and B (see Appendix D). Throughout the length of each experiment, samples of approximately 50 mL were collected as the cupric sulfate solution passed through the exchange column.

Table 5.9

Separation of Catalyst

Run A		Run B	
Sample Volume (mL)*	**Concentration Cu^{++} (mmol/L)**	**Sample Volume (mL)***	**Concentration Cu^{++} (mmol/L)**
50-100	0.27	50-100	-0.08
100-150	0.36	100-150	-0.08
150-200	-0.34	150-200	0.53
200-250	0.10	350-400	-0.25
---	---	800-850	0.10
---	---	3400-3450	-0.25

* Sample volume: 50-100 mL implies that a 50 mL sample was taken after 50 mL of cupric sulfate had passed through the column. 100-150 mL implies that 50 mL sample was taken after 100 mL of $CuSO_4$ had passed through.

The total volume of 10 mmol/L cupric sulfate solution treated for each run was 275 mL and 5000 mL for Run A and Run B respectively. None of the samples recorded showed significant amounts of the cupric ion, and are all within the error associated with spectroscopic unit.

According to Bio-Rad, the AG-50W resin has an exchange capacity of 1.7 milliequivalents per milliliter of hydrated resin (E_c). Consequently, the total exchange capacity (E_T) can be calculated by:

$$E_T = E_c \times V_r \tag{5.3}$$

where V_r is the volume of the hydrated resin (300 mL). As a result, the total exchange capacity is 510 milliequivalents or 0.510 moles of cupric ion. After treating 5 L of 10 mmol/L cupric sulfate solution, 50 mmol of cupric ions had been retained in the bottom portion of the column (the colour changed from its initial reddish-brown to a dark blue colour). This is significantly less than the total exchange capacity and thus accounts for the negligible amounts of cupric sulfate found in the results. A total exchange capacity of 510 milliequivalents implies that over 50 L of the cupric sulfate solution could be theoretically treated with this laboratory bench top exchange column.

Table 5.10 shows the results during the regeneration cycles. Run C and Run D are the respective regeneration cycles associated with the separation runs A and B (see Appendix D).

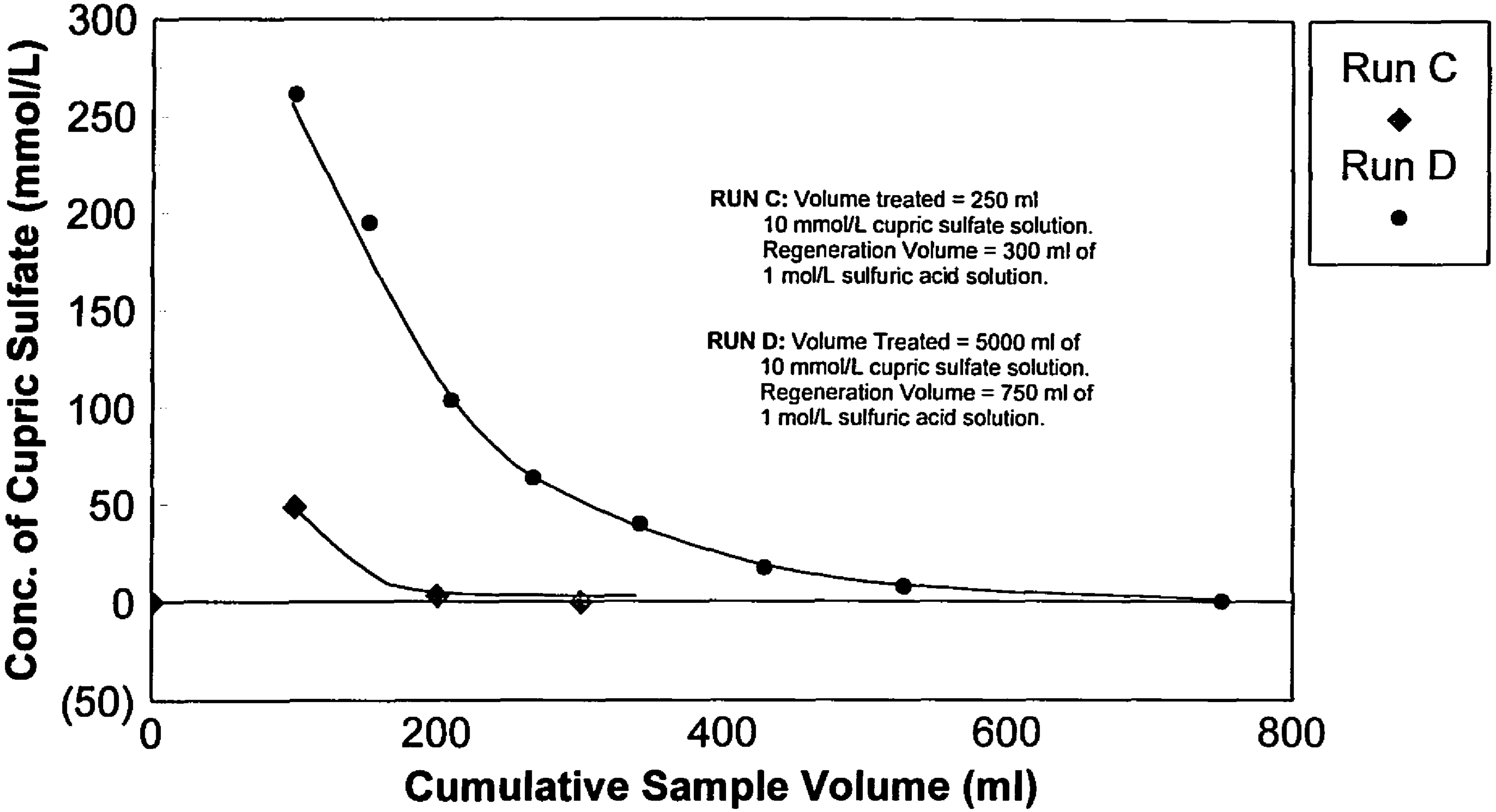
Table 5.10

Regeneration of Catalyst

Run C		Run D	
Sample Volume (mL)	Concentration Cu^{++} (mmol/L)	Sample Volume (mL)	Concentration Cu^{++} (mmol/L)
50-100	48.61	0-100	261.46
150-200	2.98	100-152	195.03
250-300	-0.34	152-209	103.68
---	---	209-267	63.47
---	---	267-341	39.78
---	---	341-429	17.40
---	---	429-527	7.79
---	---	527-750	0.36

For Run C, the cupric sulfate catalyst was fully recovered after only 250 mL of sulfuric acid (1M) had passed through the column. The large majority of the catalyst was recovered in the first 100 mL of the eluant. During Run D, the cupric sulfate catalyst was recovered after 750 mL of sulfuric acid (1M) had passed through the column. Figure 5.7 plots the concentration of the cupric ion in each regeneration stage sample versus the cumulative volume of the samples.

Figure 5.8 shows the results of a mass balance for Runs B and D (see Appendix D). In this figure the percent mass of the cupric ions recovered is plotted versus the cumulative regeneration sample volumes. The mass of the cupric ions entering the packed column during the separation stage, M_{in}, is 3.18 g. The mass of the cupric ions recovered during the regeneration stage, M_{out}, is 3.25 g. The difference between these two values is 2.2%, which is less than the error associated with the spectroscopic method.



RUN C: Volume treated = 250 ml
10 mmol/L cupric sulfate solution.
Regeneration Volume = 300 ml of
1 mol/L sulfuric acid solution.

RUN D: Volume Treated = 5000 ml of
10 mmol/L cupric sulfate solution.
Regeneration Volume = 750 ml of
1 mol/L sulfuric acid solution.

Figure 5.7 - Sample Concentration of Cupric Sulfate During Regeneration
(Run C and D)

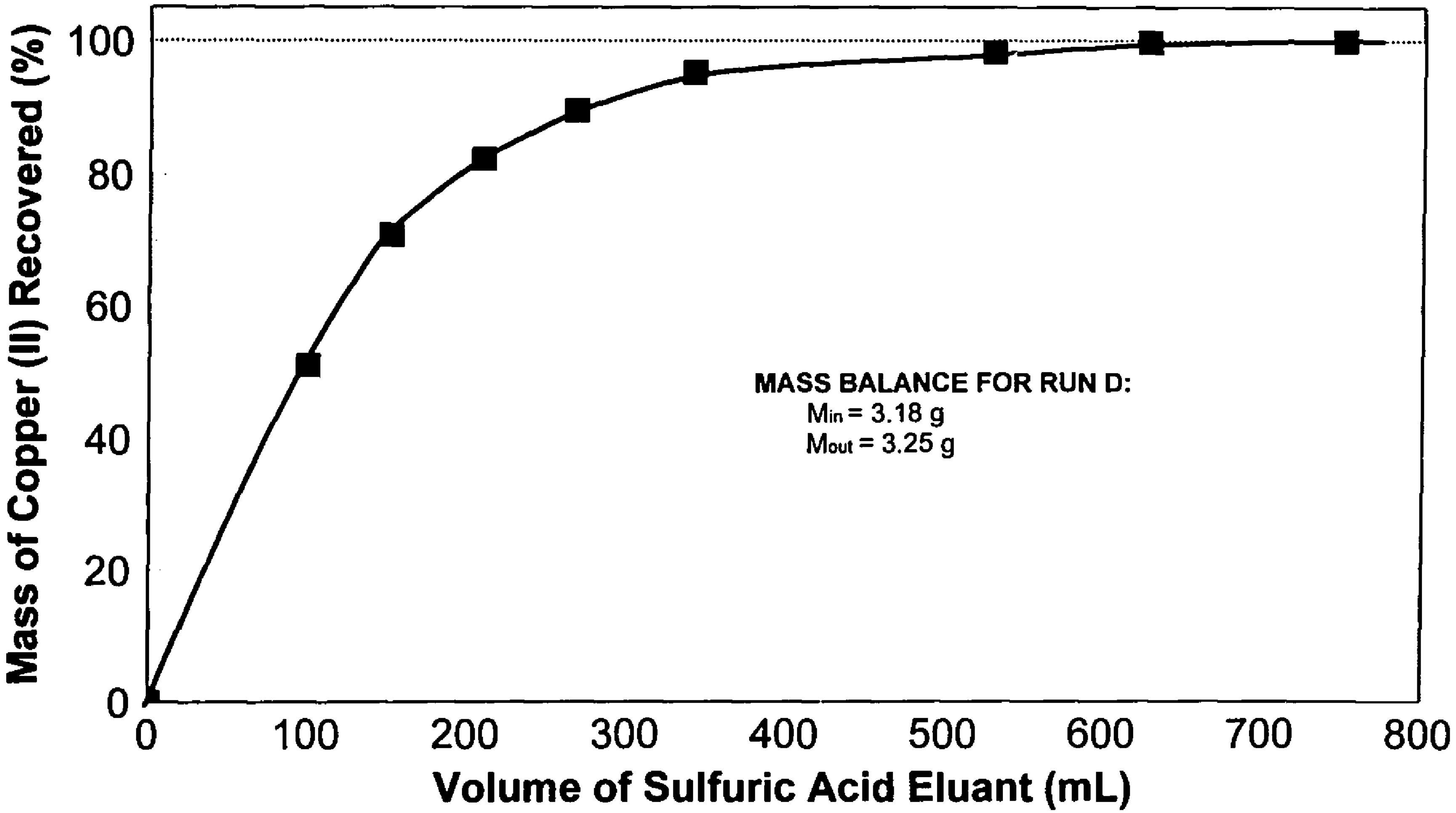


Figure 5.8 - Percent Copper (II) Recovered: Mass Balance
(Run D)

Summary

These results show that *AG 50W-X8* is an effective cationic resin for the removal of cupric ions from an aqueous solution of cupric sulfate. Further tests using the WAO treated pulp mill sludge are scheduled to be performed in September, 1995.

The eluant containing the recovered cupric sulfate catalyst can then be returned to the WAO system. Residual sulfuric acid still remaining in the exiting eluant stream should improve the conditions under which WAO occurs. If desired, the H_2SO_4 can be neutralized with lime prior to returning to the WAO reactor.

5.4 SUMMARY OF RESULTS:

- The addition of copper (II) species results in the best improvement in the degree of oxidation over other catalysts tested according to COD measurements and total solids analysis. $CuSO_4$ was used for further experimentation because it does not add to the organic load of the sludge and it does not cause noticeable corrosion.
- The addition of $CuSO_4$ has a greater effect on the COD reduction than increasing the time of reaction at the maximum operating temperature from 5 to 60 min.
- As the maximum operating temperature increases there is greater reduction in COD. The greatest improvement due to the addition of $CuSO_4$ occurred at approximately 200°C. The COD reduction without catalyst was 76.5%, while with $CuSO_4$ 97.6% COD reduction occurred.
- The effect of maximum operating pressure has negligible effect on the COD reduction when $P_{max} \geq 6$ MPa. At pressures lower than 6 MPa, the production of char is observed and the COD reduction decreased.
- The effect of catalyst concentration of the COD reduction is negligible at concentrations greater than 5 mmol/L. At lower concentrations, COD reduction decreases with decreasing catalyst concentration.

- *AG 50W-X8* is an effective resin for the removal of Cu^{++}. $CuSO_4$ can be recovered by this ion exchange resin and reused for WAO.

CHAPTER 6

CONCLUSIONS

The degree of oxidation of TMP sludge during wet air oxidation is significantly improved with the use of copper (II) species such as cupric sulfate, cupric acetate, cupric oxide or cupric chloride. Several other metal salts; ferrous sulfate, aluminum sulfate, silver sulfate, cobalt sulfate, and manganese sulfate were also tested but showed poorer results for the reduction of COD than the copper (II) species. The best result from the screening experiments showed that when using $CuSO_4$ there was 97.6% reduction in the COD occurred compared to 76.5% without catalyst at the same conditions. Cupric sulfate was used for further experimentation because it offered the least adverse effects (less corrosion than $CuCl_2$, completely soluble unlike CuO).

As the maximum operating temperature increased, the degree of oxidation increased. The effect of $CuSO_4$ is the most noticeable at operating temperatures around 200°C. The production of low molecular weight organics decrease with increasing oxidation temperature and with the addition of cupric sulfate. Analysis of the concentration of acetic acid showed that the effect of the cupric sulfate catalyst at lower temperatures was greater than that occurring at higher temperatures without catalyst. COD reduction also showed this phenomenon.

The degree of oxidation is not dependent on the concentration of cupric sulfate when greater than 5 mmol/L. At catalyst concentrations of less than 1 mmol/L, the COD reduction decreases rapidly.

The maximum operating pressure does not significantly effect the degree of oxidation when $P_{max}>6$ MPa. At lower pressures, pyrolysis occurs and the rate of oxidation is limited by the solubility of oxygen in water.

AG 50W-X8, an ion exchange resin, proved to be very effective for the recovery of copper (II) cation. Results showed that almost 100% of the copper used can be recovered during ion exchange separation. Regeneration with H_2SO_4 abstracts the cupric cation, which results in the complete regeneration of the cupric sulfate catalyst.

CHAPTER 7

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APPENDIX A

INITIAL CALCULATIONS

A.1 INITIAL CHARGING PRESSURE

Prior to each experiment, the initial charging pressures must be determined so that the desired total operating pressure is achieved during the experiment and so enough oxygen is present for complete oxidation. The initial charging pressure depends upon the operating temperature and pressure, and the volume of waste effluent.

First, the desired maximum temperature (T) and pressure (P) is chosen.

Choose a volume of effluent (V_e) such that the system will remain in the two phase region. The aqueous phase should not be allowed to evaporate completely, otherwise the organic compounds will burn. This is done by referring to a standard steam table. First of all, the specific volume of the effluent (v_e) is;

$$v_e = \frac{V_t}{\rho_e \times V_e} \tag{A.1}$$

where V_e is the volume of the waste effluent, ρ_e is the density of the effluent (0.9985 kg/L) and V_t is the volume of the bomb (1.4 L). The value for the specific volume of the effluent should be checked by using vapour-liquid phase data for water as a guide line. The assumption that the specific volume of effluent is comparable to that of a pure water system is weak, consequently, the value should be well within the two phase specific volume limits for H_2O at the maximum operating temperature. Otherwise a new volume should be chosen.

At the specified desired maximum temperature obtain the partial pressure of vapour (p_w). Subtract the vapour partial pressure from the total desired pressure (P). This is the partial pressure component due to oxygen (p_o) and carbon dioxide (p_c) and can be expressed as;

$$p_{oc} = P - p_w \tag{A.2}$$

where $p_{oc} = p_o + p_c$. The contribution from the partial pressure of carbon dioxide is assumed to be negligible. Consequently, one can determine the initial oxygen charging pressure (p_{oi}) by using the ideal gas law such that;

$$p_{oi} = \frac{p_{oc} \times T_i}{T} \tag{A.3}$$

where T_i is room temperature and T is the desired maximum temperature. The previous assumption and that of idealiality have shown to be valid for the calculation procedure.

A.2 THEORETICAL OXYGEN REQUIREMENTS

Before proceeding, one must check if enough initial oxygen is present for complete oxidation of the organic and inorganic matter. The theoretical amount of oxygen required can be expressed as a function of the COD and mass;

$$M_o = COD \times V_e \tag{A.4}$$

where M_o is the mass of oxygen (mg), V_e is the volume of waste effluent (L), and COD is the chemical oxygen demand (mg/L) of the waste effluent. The specific volume of O_2 (v_o) is defined as;

$$v_o = \frac{V_t - V_e}{M_o} \tag{A.5}$$

where V_t is the total volume of the bomb, which is 1.4 L. Consequently, the theoretical initial oxygen charging pressure (p_{to}) is;

$$p_{to} = \frac{R \times T_i}{v_o} \tag{A.6}$$

where R is the gas constant. This value, p_{to}, should be compared with the initial charging pressure, p_{oi}, obtained according to the desired operating conditions. Through experimentation, it was found that at least 80% excess oxygen was necessary to avoid pyrolysis. This is due to solubility limitations which is discussed in Chapter 5. Consequently, for more complete oxidation:

$$p_{oi} > 1.8 \times p_{to} \tag{A.7}$$

APPENDIX B

LISTING OF OPERATING CONDITIONS FOR ALL EXPERIMENTS

Experiment	Catalyst	Initial Oxygen Pressure (MPa)	Initial Argon Pressure (MPa)	Pmax (MPa)	Tmax (degC)	Time at Tmax (min)	Ve (mL)	% Excess Oxygen	Notes
1	none	1.03	4.55	15.17	250	60	800	10.0	char formation
2	none	4.48	1.10	12.61	255	60	800	20.0	char formation
3	none	5.51	0	10.20	220	60	800	26.8	char formation
4	none	2.07	5.45	10.06	211	60	400	63.5	less char formed, HV
5	none	3.58	0	9.82	249	60	400	183.5	HV
6	none	3.86	0	10.75	249	60	400	192.5	HV
7	none	5.72	0	11.24	215	60	400	346.5	
8	none	0.97	0	11.10	301	60	175	105.0	HV
9	none	5.72	0	14.27	250	60	400	192.5	
10	none	3.58	0	10.75	251	0	400	192.5	HV
11	none	3.58	0	11.17	256	60	400	192.5	HV
12	none	5.72	0	11.34	212	0	400	346.5	
13	none	5.72	0	11.44	212	0	400	346.5	HV
14	none	2.31	0	14.89	310	0	400	84.0	
15	none	3.45	0	7.58	216	0	400	171.5	small amount of char formation
16	none	5.72	0	11.44	212	0	400	346.5	
17	none	7.93	0	15.44	214	0	400	521.5	
18	none	2.38	0	5.86	214	0	400	84.0	char formation
19	none	3.45	0	7.10	215	0	400	171.5	
20	none	7.10	0	9.79	164	0	400	430.0	plugged pressure gauge
21	none	0.97	0	10.34	301	0	175	105.0	
o1	10 mmol/L cupric sulfate	5.72	0	11.17	215	60	400	346.5	
o2	10 mmol/L cupric sulfate	5.72	0	11.17	211	0	400	346.5	
o3	10 mmol/L cobalt sulfate	5.72	0	11.37	212	0	400	346.5	
o4	10 mmol/L manganesse sulfate	5.72	0	11.31	208	0	400	346.5	
o5	10 mmol/L aluminum sulfate	5.72	0	11.03	212	0	400	346.5	
o6	10 mmol/L ferrous sulfate	5.72	0	10.98	208	0	400	346.5	
o7	10 mmol/L cupric acetate	5.72	0	11.62	214	0	400	346.5	
o8	1 mmol/L cupric chloride	5.72	0	11.58	214	0	400	346.5	severe corrosion observed
o9	10 mmol/L silver sulfate	5.72	0	12.03	214	0	400	346.5	
o10	10 mmol/L cupric chloride	5.72	0	11.37	213	0	400	346.5	corrosion less severe than in Exp o8
o11	1 mmol/L cupric sulfate	5.72	0	11.58	214	0	400	346.5	
o12	10 mmol/L cupric sulfate	5.72	0	11.72	214	0	400	346.5	
o13	10 mmol/L cupric sulfate	3.45	0	7.51	212	0	400	171.5	
o14	5 mmol/L cupric sulfate	5.72	0	11.44	212	0	400	346.5	
o15	20 mmol/L cupric sulfate	5.72	0	11.65	214	0	400	346.5	
o16	10 mmol/L cupric sulfate	7.93	0	15.44	213	0	400	521.5	
o17	10 mmol/L cupric sulfate	3.72	0	11.24	258	0	400	192.5	
o18	10 mmol/L cupric sulfate	5.72	0	11.31	206	0	400	346.5	loss of pressure (leakage)
o19a	10 mmol/L cupric sulfate	2.34	0	15.17	315	0	400	84.0	
o19b	10 mmol/L cupric sulfate	0.62	0	11.58	315	0	175	32.0	
o20	10 mmol/L cupric sulfate	2.38	0	5.72	212	0	400	84.0	small amount of char formation
o21	10 mmol/L cupric sulfate	5.72	0	11.58	212	0	400	346.5	
o22	10 mmol/L cupric sulfate	7.03	0	11.68	164	0	400	430.0	
o23	10 mmol/L cupric sulfate	1.62	0	4.38	210	0	400	31.0	char formation
o24	10 mmol/L cupric sulfate	0.97	0	11.31	301	0	175	105.0	

* HV - experiment performed by Hans Volstad (1994)

APPENDIX C

TABULATED EXPERIMENTAL RESULTS - WET AIR OXIDATION

PHASE ONE: SCREENING TESTS

Table C1: Effect of Catalyst on COD Reduction

T=200degC, P=10.34 MPa, [catalyst]=10mmol/L, Excess Oxygen=346.5%, Ve=400ml

Exp	Catalyst	Tmax (degC)	Pmax (MPa)	pH	COD (mg/L)	% Reduction	
o3	CoSO4	212	11.37	2.65	8056, 7049	79.8, 82.3	
o4	MnSO4	208	11.31	2.57	10108	74.7	
o5	Al2SO4	212	11.03	2.3	7281	81.8	
o6	FeSO4	208	10.98	2.24	9748	75.6	
o7	CuAcetat	214	11.62	3.80	1397, 1369	96.5, 96.6	
o9	Ag2SO4	214	12.03	2.60	4934	87.7	
o10	CuCl2	213	11.37	4.31	1799	95.5	
o2	CuSO4	211	11.17	4.01	1123, 1092, 1068	97.2, 97.3, 97.3	
o12	CuSO4	214	11.72	4.28	887	97.8	**Average**
o21	CuSO4	212	11.58	4.13	890	97.8	**97.6**
12	None	212	11.34	2.47	9538, 9563	76.2, 76.1	
13	None	212	11.44	2.64	9439	76.4	**Average**
16	None	212	11.44	2.51	9800, 8740	75.5, 78.1	**76.5**

Table C2: Effect of Catalyst on Solids Reduction

T=200degC, P=10.34 MPa, [catalyst]=10mmol/L, Excess Oxygen=346.5%, Ve=400ml

Exp	Catalyst	Tmax (degC)	Pmax (MPa)	Total Solids (mg/L)	% Solids Red.	Total Organic (mg/L)	% Org. Red.	Total Inorganic (mg/L)	% Inorg. Red.
o3	CoSO4	212	11.37	5946	85.2%	5010	86.7%	936	63.4%
o4	MnSO4	208	11.31	6355	84.2%	5501	85.4%	854	66.6%
o5	Al2SO4	212	11.03	4630	88.5%	4033	89.3%	597	76.7%
o6	FeSO4	208	10.98	4297	89.3%	3789	89.9%	508	80.2%
o7	CuAcetate	214	11.62	2614	93.5%	1511	96.0%	1103	56.9%
o9	Ag2SO4	214	12.03	3687	90.8%	3515	90.7%	172	93.3%
o10	CuCl2	213	11.37	—	—	—	—	—	—
o2	CuSO4	211	11.17	—	—	—	—	—	—
o12	CuSO4	214	11.72	1786	95.6%	1003	97.3%	782	69.5%
o21	CuSO4	212	11.58	—	—	—	—	—	—
12	None	212	11.34	—	—	—	—	—	—
13	None	212	11.44	—	—	—	—	—	—
16	None	212	11.44	5915	85.3%	4007	89.3%	1908	25.5%
Sludge	n/a	n/a	n/a	40180	n/a	37620	n/a	2560	n/a

PHASE TWO: CHARACTERIZATION

Table C3: Effect of Temperature on COD Reduction

P=10.34 MPa, [Cupric sulfate]=10mmol/L

Exp	Tgoal (degC)	Tmax (degC)	Pmax (MPa)	pH	COD (mg/L)	% Reduction	% Excess Oxygen	Effluent Vol. (ml)
With Catalyst								
o22	150	164	11.68	2.33	29303	26.7	430	400
o2	200	211	11.17	4.01	1123, 1092, 1068	97.2, 97.3, 97.3	346.5	400
o12	200	214	11.72	4.28	887	97.8	346.5	400
o21	200	212	11.58	4.13	890	97.8	346.5	400
o17	250	258	11.24	4.31	581	98.5	192.5	400
o24	300	301	11.31	4.17	1330	96.7	105	175
o19B	315	315	11.58	4.89	360	99.1	84	175
Without Catalyst								
20*	150	164	9.79	2.49	28869	27.8	430	400
12	200	212	11.34	2.47	9538, 9563	76.2, 76.1	346.5	400
13	200	212	11.44	2.64	9439	76.4	346.5	400
16	200	212	11.44	2.51	9800, 8740	75.5, 78.1	346.5	400
10	250	251	10.75	3.11	4803	88	192.5	400
21	300	301	10.34	3.89	3720	90.7	105	175

*Pressure gauge plugged around T=110 celcius, and popped later giving Pmax=9.79 MPa

Table C4: Effect of Catalyst Concentration on COD Reduction

T=200degC, P=10.34 MPa, Excess Oxygen=346.5%, Ve=400ml

Exp	Catalyst Conc. (mmol/L)	Tmax (degC)	Pmax (MPa)	pH	COD (mg/L)	% Reduction	
12	0	212	11.34	2.47	9538, 9563	76.2, 76.1	
13	0	212	11.44	2.64	9439	76.4	**Average**
16	0	212	11.44	2.51	9800, 8740	75.5, 78.1	**76.5**
o11	1	214	11.58	4.28	2837	92.9	
o14	5	212	11.44	3.90	1217	97	
o2	10	211	11.17	4.01	1123, 1092, 1068	97.2, 97.3, 97.3	
o12	10	214	11.72	4.28	887	97.8	**Average**
o21	10	212	11.58	4.13	890	97.8	**97.6**
o15	20	214	11.65	3.87	827	97.9	

Table C5: Effect of Total Pressure on COD Reduction

T=200degC, [Cupric sulfate]=10mmol/L, Ve=400ml

Exp	Pgoal (MPa)	Tmax (degC)	Pmax (MPa)	pH	COD (mg/L)	% Reduction	% Excess Oxygen
With Catalyst							
o23	4.14	210	4.38	3.20	3908	90.2	31.00
o20	5.17	212	5.72	3.72	1376	96.6	84.00
o13	6.89	212	7.51	3.44	1260	96.8	171.50
o2	10.34	211	11.17	4.01	1123, 1092, 1068	97.2, 97.3, 97.3	346.50
o12	10.34	214	11.72	4.28	887	97.8	346.50
o21	10.34	212	11.58	4.13	890	97.8	346.50
o16	13.79	213	15.44	4.17	1085	97.3	521.50
Without Catalyst							
18	5.17	214	5.86	2.41	9016	77.5	84.00
15	6.89	216	7.58	2.43	7000	82.5, 78.3	171.50
12	10.34	212	11.34	2.47	9538, 9563	76.2, 76.1	346.50
13	10.34	212	11.44	2.64	9439	76.4	346.50
16	10.34	212	11.44	2.51	9800, 8740	75.5, 78.1	346.50
17	13.79	214	15.44	2.72	4314	80.9	521.50

Table C6: Analysis of Solids

Total, Organic and Inorganic Solids; Acetic Acid; Total Organic Carbon (TOC)

Exp	Catalyst	Tmax (degC)	Pmax (MPa)	Total Solids (mg/L)	% Solids Red.	Total Organic (mg/L)	% Org. Red.	Total Inorganic (mg/L)	% Inorg. Red.	Acetic Acid (mg/L)	TOC* (mg/L)
Sludge	None	n/a	n/a	40180	n/a	37620	n/a	2560	n/a	314	63
21	None	301	11.34	1781	95.6%	741	98.0%	1184	53.8%	3164	118
o24	CuSO4	301	11.31	1243	96.9%	667	98.2%	576	77.5%	1243	72
16	None	212	11.44	5915	85.3%	4007	89.3%	1908	25.5%	3706	293
o12	CuSO4	214	11.72	1786	95.6%	1003	97.3%	782	69.5%	2760	96
o20	CuSO4	212	5.72	2549	93.7%	1521	96.0%	1028	59.8%	2551	104
o16	CuSO4	213	15.44	1885	95.3%	974	97.4%	911	64.4%	2652	97

* TOC only measures organic carbon in aqueous phase

APPENDIX D

SPECTROSCOPIC ANALYSIS OF ION EXCHANGED SAMPLES

System Specifications:
Method of Sampling: Roughly 50ml samples were taken at a desired intervals.
Sample Solution: 10 mmol/L cupric sulfate aqueous solution.
Eluant: 1 M sulfuric acid solution.
Rinse Solution: De-ionized water.
Flow Rates (all solution) = 120 ml/min or 7.2 L/hr.
Nitrogen Pressure = 184 kPa
Volume of Column = 300 ml
Void Fraction = 40%
Exchange Resin: AG 50-X8 crosslinked exchange resin
Exchange Capacity = 1.7 milliequivalents/mL of hydrated resin

Figure D.1 shows the apbsorption spectrum for a 35 mmol/L solution of cupric sulfate.

Figure D.2 shows the calibration curve for the determination of cupric sulfate.

Table D1 - UV Visible Spectrophotometer Data for Ion Exchange

Sample No.	Run A (ABS.)	(mMol/L)	Run B (ABS.)	(mMol/L)	Run C (ABS.)	(mMol/L)	Run D (ABS.)	(mMol/L)
1	0.002	0.270105	-0.002	-0.07955	0.555	48.60927	2.99	261.4589
2	0.003	0.357517	-0.002	-0.07955	0.033	2.979895	2.23	195.0253
3	-0.005	-0.34178	0.005	0.532343	-0.005	-0.34178	1.185	103.6792
4	0	0.09528	-0.004	-0.25437	---	---	0.725	63.46941
5	---	---	0	0.09528	---	---	0.454	39.78059
6	---	---	-0.004	-0.25437	---	---	0.198	17.40297
7	---	---	---	---	---	--	0.088	7.787587
8							0.003	0.357517
Total Vol. (ml)	275		5000		325		750	

Run A: Separation Stage - 10 mMol/L CuSO4 passed through the column. 50ml samples taken at 75, 125, 175, 225ml.
Run B: Separation Stage - same as Run A, except last 3 samples were at 375, 825, 3425ml
Run C: Regeneration Stage - 1 mol/L H2SO4 passed through column. Samples at 75, 175, 275ml
Run D: Regeneration Stage - same as Run C. Samples at 0, 100, 150, 200, 250, 350, 450.

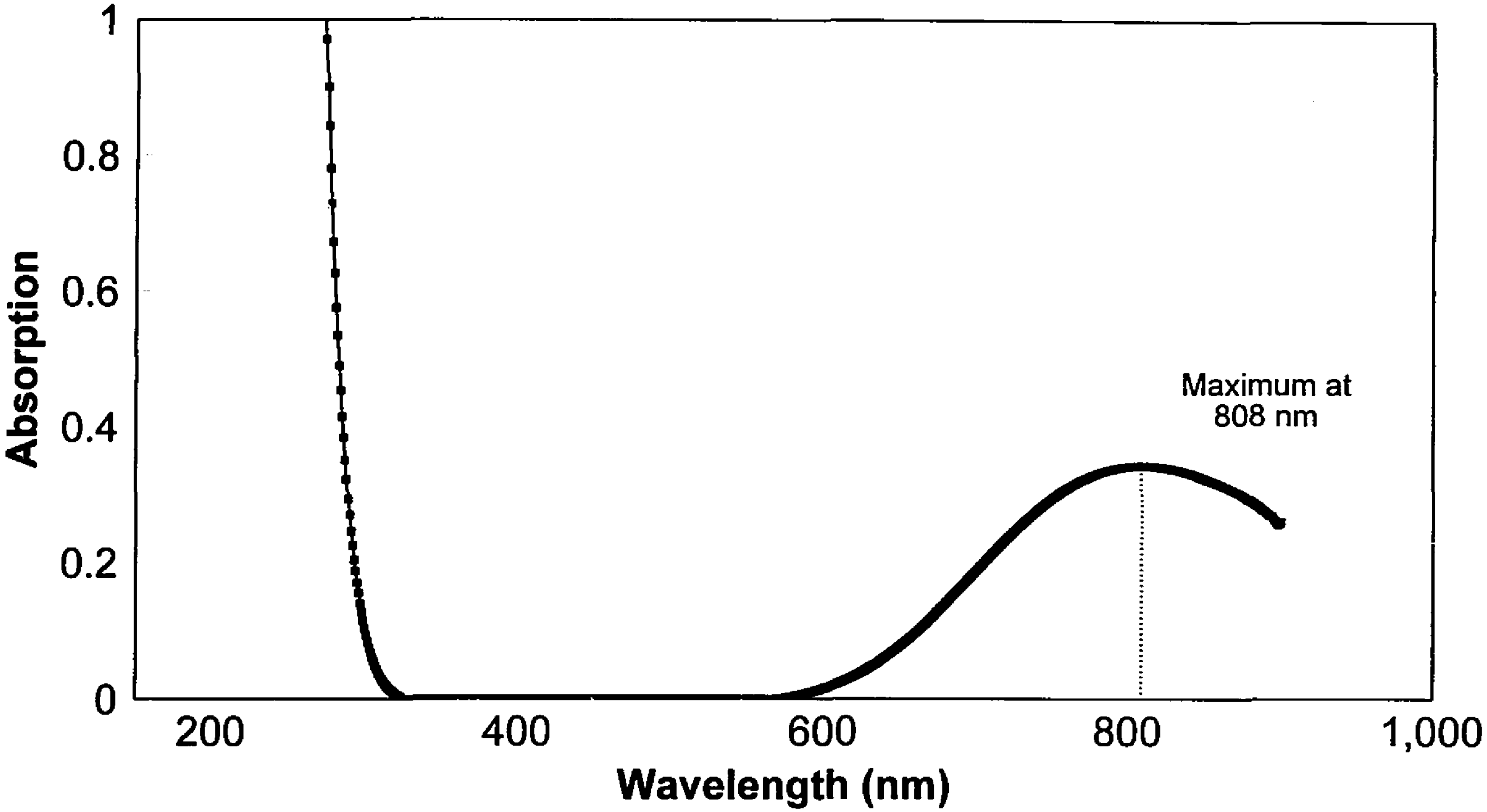
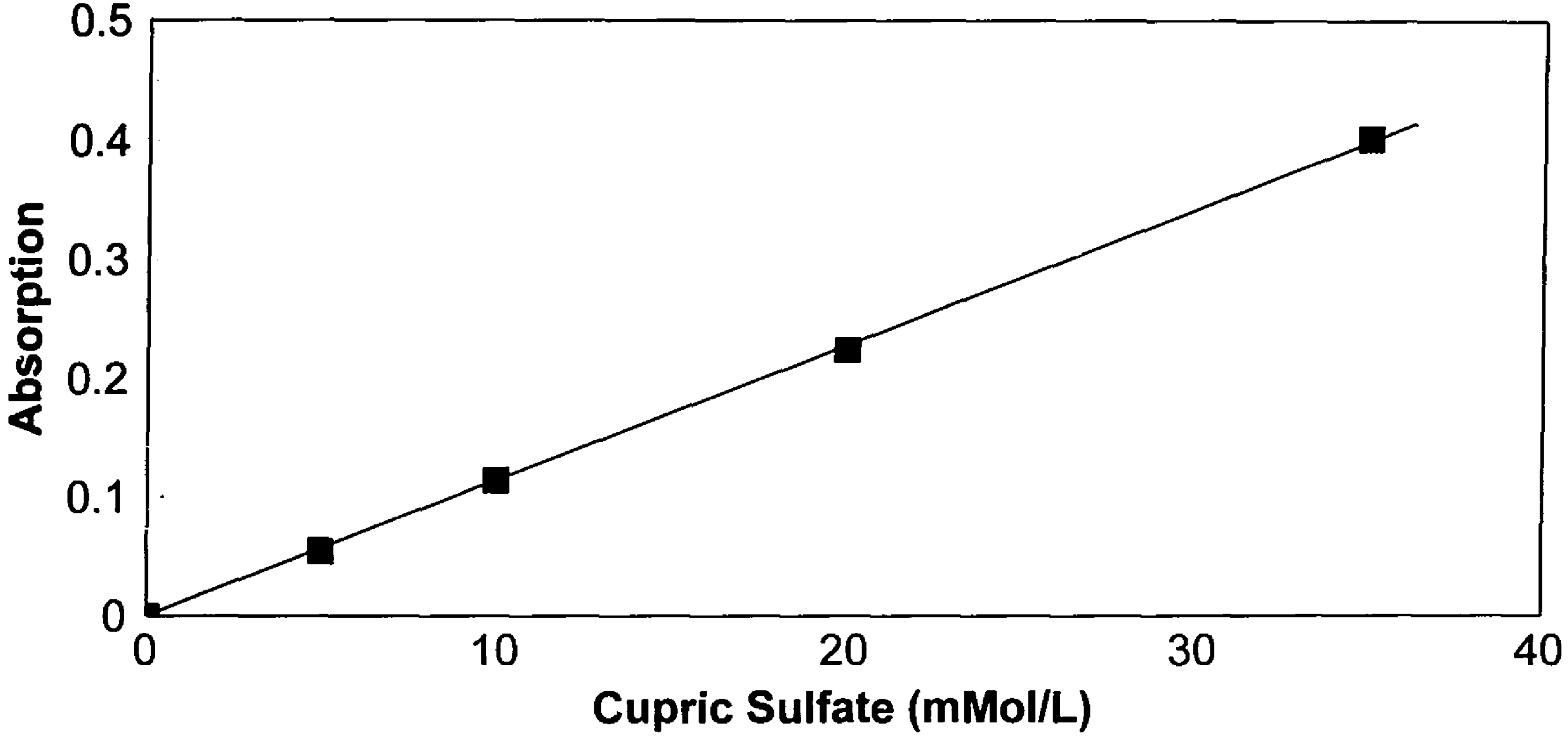


Figure D.1 - Absorption Spectrum for Cupric Sulfate Solution
(concentration of cupric sulfate = 35 mmol/L)



Regression Analysis:
Absorption=0.01144(Concentration)-0.0011
R-Square=0.99981

Figure D.2 - Calibration Curve for Cupric Sulfate at 808 nm

D.1 MASS BALANCE FOR COPPER

Since no copper is generated the mass balance for copper is:

$$M_{in} = M_{out} \tag{D.1}$$

and

$$M_{in} = V_{treated} \times C_{in} \times GMW \tag{D.2}$$

and

$$M_{out} = \sum_{i=1} \left[GMW \times V_{SAMi} \times C_{SAMi} \right] \tag{D.3}$$

where $V_{treated}$ is the volume of $CuSO_4$ solution treated, V_{SAMi} is the regeneration sample volume for sample i, C_{SAMi} is the cupric cation concentration for regeneration sample i, M_{in} is the mass of copper entering the packed column during the separation stage, and M_{out} is the mass of the copper exiting the column during the regeneration stage. C_{in} = 10 mmol/L and is the concentration of the prepared cupric sulfate sample. GMW=63.546 g/mol and is the molecular weight of copper.

For runs B and D, $V_{treated}$=5.0 L. Consequently, M_{in}=3.18 g and M_{out}=3.25 g. The difference between these two values is 2.2%, which is less then the error associated with the spectroscopic method. Table D.2 shows the values obtained for the mass of cupric cation recovered (Figure 5.8 shows the percent mass of cupric cation recovered versus the cumulative regeneration sample volume).

Table D.2
Mass of Cupric Cation Recovered

Sample Volume (mL)	Concentration of Cu^{++} (mmol/L)	Mass of Cupric Cation Recovered (g)	Percent Recovered (%)
100	261.46	1.66	51.07
52	195.03	0.64	70.88
57	103.68	0.38	82.42
58	63.47	0.23	89.61
74	39.78	0.19	95.36
88	17.40	0.10	98.35
98	7.79	0.05	99.84
223	0.36	0.005	100.00

APPENDIX E

STATISTICS- SAMPLE CALCULATIONS

Calculation of the Variance for a Sample:

The variance of a sample set is defined as:

$$\sigma_x^2 \equiv s_x^2 = \frac{1}{n-1}\sum_i \left(x_i - \bar{x}\right)^2 n_i$$

where σ^2_x is the sample variance, n is the number of experiments, $\bar{x}$ is the ensemble mean, and x_i's are the sample values. For the three replicates using $CuSO_4$ at 200°C:

i	x_i
1	97.3
2	97.8
3	97.8
$\bar{x}$	97.63

$$s_x^2 = 0.0833\%$$

Calculation of the 95% Confidence Interval:

The 95% confidence interval for an ensemble mean is:

$$\bar{x} - t_{1-\alpha/2(\nu=n-1)} s_{\bar{x}} \le \mu_x < \bar{x} + t_{1-\alpha/2(\nu=n-1)} s_{\bar{x}}$$

where $s_{\bar{x}} = \left(\frac{s_x^2}{n}\right)^{1/2}$

Therefore, for the three copper sulfate replicates at 200°C:

$$97.63 - 4.303(0.167) \le \mu_x < 97.63 + 4.303(0.167)$$

$$96.91 \le \mu_x < 98.3$$

Comparison of Sample Variances:

Two sample variances are similar if the hypothesis $\sigma^2_A = \sigma^2_B$ is satisfied. For the three replicates involving non-catalyzed and catalyzed runs, $\sigma^2_A = 0.0933\%$ and $\sigma^2_B = 0.0833\%$ (Himmelblau, 1990, pg.65). Therefore:

$$H_0:\ \sigma^2_A = \sigma^2_B$$

$$H_1:\ \sigma^2_A \ne \sigma^2_B$$

$$\alpha = 0.05$$

$$Statistic:\ F_{0.975(2,2)} = 39.0$$

$$Critical Value:\ \frac{s^2_A}{s^2_B} = \frac{0.0933}{0.0833} = 1.120$$

$$Conclusion:\ C.V. < Stat.$$

$$\therefore\ accept\ \ hypothesis$$

Comparison of Two Ensemble Means:

If the variances of two samples are the statistically the same, then the ensemble means can be tested for significance (H_0: $\mu_A = \mu_B$) as follows:

Pool the variances:

$$s^2_p = \frac{(n_A - 1)s^2_A + (n_b - 1)s^2_B}{(n_A - 1) + (n_B - 1)}$$

$$s^2_p = \frac{2(0.0933) + 2(0.0833)}{2 + 2}$$

$$s^2_p = 0.0883$$

From Example 3.6-2 of Himmelblau (1990): when $\sigma^2_A \approx \sigma^2_B$ a test can be made based on the hypothesis $\mu_A = \mu_B$:

$$H_0:\ \mu_A = \mu_B$$

$$H_1:\ \mu_A \neq \mu_B$$

$$\alpha = 0.05$$

$$\textit{Statistic:}\quad t_{(1-\alpha/2)(\upsilon = n_A + n_B - 2)} s_p \left(\frac{n_A + n_B}{n_A n_B}\right)^{1/2} = t_{0.975(2)} (0.0883)^{1/2} \left(\frac{4}{4}\right)^{1/2} = 1.279$$

$$\textit{Critical Value:}\quad \left|\bar{x}_A - \bar{x}_B\right|$$

$$\textit{Conclusion:}\quad \textit{if}\quad C.V. < Stat.\quad \textit{accept}\quad \textit{hypothesis}$$

Therefore any two % COD reductions are similar if their difference is less than 1.279%.

Conversion of Variance - From COD to Percent COD

As reported in Section 5.1.1 the standard deviation for three COD measurements for the same experiment was 27.6 mg/L. For the three experiments the variance of 0.0833% refers to the percent COD reduction and not COD. Consequently, the standard deviation for the three COD measurements must be divided by the initial COD (40,000 mg/L). This yields a standard deviation of 0.069% or a variance of 0.0048%.

APPENDIX F

ACETIC ACID CONVERSION TO COD

The balanced oxidation reaction for acetic acid and oxygen is:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad \text{(F.1)}$$

Consequently, the oxygen consumed in this reaction can be calculated as follows:

$$\text{Oxygen Consumed [mg/L]} = \frac{(2 \times 32 \times \text{Mass of Acetic Acid})}{60} \qquad \text{(F.2)}$$