DEVELOPMENT OF A MATHEMATICAL MODEL FOR TREATMENT OF METAL FINISHING WASTEWATER

By

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DECLARATION

I (*NKOSINATHI WISEMAN MBONGWA, REG NO. 201175506082*) hereby declare that the contents of this thesis entitled **DEVELOPMENT OF A MATHEMATICAL MODEL FOR TREATMENT OF METAL FINISHING WASTEWATER** is the true reflection of my own work, and that this thesis has not been submitted, in whole or part, for a degree to any other University or Institution.

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January 2008

ABSTRACT

The waste generated by metal finishers is rated as the most toxic and harmful to the environment. Metal finishing wastewater consists of heavy metals, cyanides, acids and alkalis. Formal treatment of waste generated has not been of primary importance to metal finishers. It would be ideal to develop a generic model to assist finishers to predict the effectiveness of wastewater treatment. The model must be able to predict effectiveness of treatment based on a variety of equipment, chemicals and concentrations.

The model developed in this study allows the company to select relevant equipment, types of waste etc. The model allows a variation in chemical concentrations as it is accepted that metal finishers release chemicals with inconsistent concentrations. An illustration of the model is presented in Mat lab.

This model simulates the treatment process before the actual process takes place thus giving the treatment results, quantified amounts of reagents required, and residence time in each process unit. This makes it easier for metal finishers to conduct necessary adjustments on the treatment process so as to achieve effective and efficient treatment of metal ions and toxic substances in wastewater.

A mathematical model of a conventional process for treatment of metal finishing wastewater is developed. Wastewater from the electroplating industry is used to develop the model. This model is developed by using data from literature. Data that is collected includes:

- Reaction mechanisms that are involved in treatment of metal finishing wastewater.
- Reaction rate laws involved in the treatment of metal finishing wastewater.
- Design equations of engineering units involved in the treatment process.
- Typical characteristics of metal finishing wastewater.

- Optimum treatment conditions for different contaminants of metal finishing wastewater.
- Alternative technologies for treating metal finishing wastewater.

The model is developed by combining the mass transfer kinetics that take place inside the process units and the design equation of the process units. Reaction rates data is not readily available for usage in literature hence engineering mathematic skills have been employed to deduce usable information. The model is validated by putting typical real plant data from literature and observing the response of the model.

The model is simulated in Mat-Lab. The results of the model have shown the following:

- Variation of caustic amount required with changing input wastewater pH and changing caustic solution strength.
- Variation of treatment efficiencies with changing composition of wastewater and changing dose of treatment reagents.
- Adsorption of metal precipitate by alum to form bigger and settleable flocs.
- For sedimentation model, settling rates of different sized particles and water temperature is shown.

The applicability of the model to real situations is not overlooked, even though the models have not been tested on the real plant. There are high possibilities of difficulties in the applicability, since the study is developed purely from literature data.

Prior using the model, it is recommended that the model be validated with real plant data. The model may need to be fine-tuned to account for its limitations. The theoretical response of the model appears to be rational and logic. Hence, the model that is developed can be used to predict treatment efficiencies and effectiveness of metal finishing wastewater.

THIS THESIS IS DEDICATED TO MY
PARENTS (MY MOTHER AND MY LATE
FATHER) WHO HAVE BROUGHT ME
THIS FAR

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NOMENCLATURE

$[CN^-]$	Concentration of cyanide ions (mg/L)
$[Cr^{3+}]$	Concentration of chromium (III) (mg/L)
$[Cr^{6+}]$	Concentration of chromium (VI) (mg/L)
$[Fe^{2+}]$	Concentration of ferrous ions (mg/L)
$[H^+]$	Concentration of hydrogen ions (mg/L)
$[O_2]$	Dissolved oxygen concentration (mg/L)
$[OCl^-]$	Concentration of chlorite ions (mg/L)
$[OH^-]$	Concentration of hydroxyl ions (mg/L)
$[S^{4+}]$	Concentration of sulphate (IV) (mg/L)
A	Frequency factor (L/mgs)
a	Quadratic coefficient
b	Quadratic coefficient
c	Quadratic coefficient
C_f	Equilibrium concentration (mg/L)
C_i	Initial concentration (mg/L)
C_f	Equilibrium concentration (mg/L)
d	Diameter of particles (m)
d_b	Diameter of air bubble (m)
D_L	Diffusivity of gas in liquid (m^2/s)
E	Activation energy (KJ/mol)
F_A	Flowrate of specie A (mg/s)
g	Gravitational acceleration (m/s^2)
H	Height of tank (m)
k	Reaction rate constant (units depend on the order of reaction)
K_f	Freundlich capacity factor (mg/g). (L/mg)
M	Mass flowrate (g/s)
$M_{sorbent}$	Mass flowrate (mg/s)
n	Freundlich intensity
pH	Acidity or alkalinity

Q_G	Volume flowrate of gas (L/hr)
Q_{tot}	Total flowrate (L/hr)
R	Universal gas constant (J/mol.K)
$-r_A$	Reaction rate of specie A (mg/ L.s)
S or q_e	Mass of adsorbate per mass of adsorbent (mg/g)
T	Temperature (^OC)
V	Volume of tank (L)
X_A	Conversion of specie A (mg/s)
v	Settling velocity (m/s)
α	Mass transfer coefficient (s^{-1})
Θ	Ration of input reagent to basis specie
μ_L	Liquid viscosity (cm Poise)
ρ	Density of solids (g/L)
ρ_G	Density of gas (g/L)
ρ_s	Density of solids (g/L)
τ or t_R	Residence time (s)

CHAPTER 1- INTRODUCTION

This chapter explains the importance and benefits of this study. This chapter also expands on the current status of status and size of South African Metal Finishers. Challenges of treating wastewater in the metal finishing industry are explored. The research methodology that has been followed in this study is given in this chapter.

1.1 BACKGROUND

The metal finishing industry is a broad chemical sector that comprises of various types of surface finishers. These include electroplaters, powder coaters, galvanizers etc. All surface finishers deal with coating of surfaces of objects for; protection against atmospheric attack (e.g. corrosion); attractive finish; and protection of engineered units [1]. Electroplaters are considered to be the most technically sophisticated among metal finishers. Electroplaters comprise the largest group among the metal finishing sector, forming about 40 % in terms of numbers of companies [2].

In many industries, surface finishing is usually done in the final phase of production. This is typical in the production of metallic parts following their manufacture through various operations such as casting, shearing, forming, forging and drilling.

Electroplating is an electrodeposition of metal atoms onto the surface of a substrate. Electroplating is done in a series of sequential stages. The plating.process has three main stages which are: cleaning/preparation stage, plating stage and rinsing. All these stages generate waste. The characteristics of waste produced by each process depend on the operation and nature of the process bath.

The electroplating and anodizing industry are considered as the greatest consumers of water hence producing of the largest effluent load [3,4,5]. Wastewater from plating plants is generated from spent solvents, spent process solutions and sludge [6]. The largest waste comes from spent rinse water since about 80 % of the annual water intake of the plating industry is used for rinsing after plating [2,7].

Wastewater water from electroplating industry contains metal ions (Cr^{6+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} etc.), toxic substances (ammonia and cyanide), acid, alkaline, oil and grease at higher than permissible levels. This kind of waste is hazardous and toxic to the environment [2,8]. The accumulation of metal ions in the environment poses a serious threat to human health, living orgasms and ecological systems [9].

It is reported that there are no industrial statistical codes that cover these processes, size and the structures of South African Metal Finishing Industries (MFI) [2]. There are few surveys done to estimates the number of metal finishing industry in South Africa. One survey has shown that there are about 600 to 1200 finishers in South Africa [10].

Electroplating plants vary in size mostly been small to medium size enterprises. These enterprises are normally operated by staff of less than 50 and some have less than 10 employees. Some of the metal finisher operates in backyard shops.

1.2 CHALLENGES

Some electroplaters in South Africa do not treat their waste, whilst others manage waste treatment in a less than ideal manner[2]. Wastewater compositions and volumes are relatively unknown. This makes it difficult for platers to quantify the optimum amounts of treatment chemicals required to treat their wastewater. They dose the amounts that are thought to be enough. This leads to an improperly treated wastewater because of under dosing or overdosing of treatment chemicals.

Overdosing or under dosing results in high levels of metal ions, cyanide, ammonia, and high risk of serous secondary pollution caused by treatment reagent like chlorine. Secondary pollution hazards include excess metallic sludge than optimum, formation of chlorine sub-products etc [8,11]. If this improperly treated wastewater is released into rivers or into any surface water it could result in significant environmental impacts. If this wastewater is release to municipal sewers it causes problems to downstream treatment process, and sometimes these systems cannot treat such waste. Some of the problem caused by improperly treated waste to sewer systems [2]:

- They are not easily treated by sewer systems hence they occur in high levels in the effluent.
- They inhibit biological processes.
- A high level of metal ions limits municipalities' safe disposal and reuse.

1.3 STATUS OF WASTEWATER TREATMENT

There are many technologies that have been developed to treat wastewater from plating industry efficiently and effectively for reuse and/or to meet the permissible discharge levels. Conventional treatment which involves treatment by precipitation, coagulation settling, and filtration is a more dominant method. These conventional treatment processes are commonly used for the following reasons [11]:

- Comprises of simple equipments.
- It is convenient to operate.
- Capable of treating large volume of water containing high concentrations of metal ions.
- Low operational cost.

Usually the operation of metal finishing wastewater treatment plant is inefficient and poorly controlled. The inefficiencies are due to inaccurate management of wastewater. The availability of skills and tools to quantity treatment reagent doses also plays a significant role.

1.4 PROJECT OBJECTIVES and SCOPE

In this study a generic mathematical model is developed. This model will assist in predicting effluent composition of the treatment process from the influent composition. The model will also assist in quantifying the treatment reagents required to treat wastewater and residence time of equipment. The model allow for variation of process hardware in the treatment process. The model is design to cater for non rigid waste water concentration

This study provides a tool to solve the problem related to treatment of wastewater bearing metal ions from electroplating processes. This model runs the treatment process before the actual process takes place thus giving the treatment results, quantified amounts of reagents required, and residence time in each process unit. This makes it easier for metal finishers to conduct necessary adjustments on the treatment process so as to achieve effective and efficient treatment of metal ions and toxic substances in wastewater.

1.5 STUDY APPROACH

The model has been developed by using literature data of reaction rate kinetics, typical wastewater characteristics, reagents used for treatment etc. The literature sources used are water and wastewater treatment handbooks, current journal papers. The model is developed based on the possible and common conventional treatment process that has been reference from literature. Models are developed base on the equipment design equation and mass transfer taking place in that equipment. Treatment efficiencies of each equipment (specie conversion), residence time, and amounts of treatment reagents required in treatment equipments are determined from the mathematical expression developed. The mathematical model expression are run in excel spread sheet and programmed in Mat-Lab software. The model is run with single changing input variable and with multiple input variables changing. The change of multiple variables resembles real situations, where two or more variables can change at the same time.

1.6 THESIS OUTLINE

The outstanding chapters of this project report include the following concepts.

Chapter 1: This chapter presents objective and the importance of this study. This chapter also gives background and current status of South African Metal Finishers. Wastewater generation and challenges faced by South African Metal Finishers are discussed in this chapter. Lastly the chapter provides the study approach.

Chapter 2: This chapter presents literature review which gives background information on:

- Metal finishing industry processes and electroplating processes. Description of metal finishers and electroplaters. Challenges faced by metal finishing industries concerning their wastewater management. Nature of wastewater treatment facilities.
- Waste sources/ generation and nature of pollution in the electroplating industry.
- Electroplating wastewater treatment by conventional process. Challenges in conventional process application and treatment efficiencies.
- The objectives of this study.

Chapter 3: This chapter presents the study methodology. The following are presented in this chapter:

- The overall conventional treatment of metal finishing wastewater is described.
- Typical composition of wastewater from metal finishing industry.
- The method of developing mathematical models.

Chapter 4: This chapter gives the build-up of the mathematical model.

- Mass transfers and design equations are merged to give mathematical models that predict treatment efficiencies and residence time in equipment units. This chapter focuses on the development of following models: pH adjustment, cyanide removal and iron removal. This chapter also gives typical case scenarios of wastewater input to the model to illustrate the models flexibility and performance.

Chapter 5: This chapter gives the build-up of the mathematical model.

- Mass transfers and design equations are merged to give mathematical models that predict treatment efficiencies and residence time in equipment units. This chapter focuses on the development of following models: chromium removal, divalent metals (Ni^{2+},Cu^{2+}, Zn^{2+},Cd^{2+} etc) removal, coagulation and sedimentation. The chapter also gives typical case scenarios of wastewater to input to the model to illustrate the models flexibility and performance.

Chapter 6: In this chapter, typical metal finishing wastewater composition is put into the model to validate the model response. The response of treatment efficiencies with changing various process parameters is demonstrated. Models of pH adjustment, metal ions removal, flocculation and settling are presented. The chapter illustrate the response of the models to the change of a single parameter and multiple parameters.

Chapter 7: This chapter gives a comprehensive discussion and conclusion of the entire work. All assumptions made in the development of the models are accounted for. Factor that limits the applicability of the model to real plant situation are explained.

Chapter 8: References of literature data used in this study.

Chapter 9: This chapter gives all calculation methods done in this study, important figures and tables used in this study.

CHAPTER 2- LITURATURE REVIEW

This chapter gives a detailed introduction of the metal finishing industry. Distinguished classes of metal finishing industry are discussed in this chapter. The size and status of each metal finishing sector is given based on recent statistics. Activities that lead to waste generation in each metal finishing sector are discussed. This chapter also gives detailed information on the conventional wastewater treatment that is used in the metal finishing industry.

2.1. METAL FINISHING INDUSTRY

Metal finishing can be considered broad and comprises of a range of operations undertaken with the aim of protecting against corrosion. Metal finishing results in enhancing and strengthening metal, plastic products, general hardware, structural components, automotive parts, cans, and household products. The metal finishing sector encompasses different types of industries that treat metal or plastic surfaces; these include: electroplaters, electroless platers, galvanizers, spray painters, anodizers, etc. Metal finishing may be described as any operation applied to the surface of a metallic object, in order to enhance the properties of that surface.

The chemical processes used in the metal finishing industry generate significant amounts of toxic and hazardous waste, and can create potential environmental and health risks. Waste in the metal finishing industry comes from spills, leaks, drag-out and spent process baths. Spills refer to the process fluid that is released accidentally on the floors of the plant and end-up in the drain as waste. Drag-out refers to a bath solution that is wasted when it is carried over into rinse water. Refer to Figure 2.1, shows the stages involved in the metal finishing process. Wastewater from each stage is unique and similar to the bath fluid.

Surface preparation and cleaning is the first step in the metal finishing processes. Refer to Figure 2.2, shows the stages involved in the surface preparation and cleaning of work piece. Surface preparation and cleaning is done in order to ensure durability and effectiveness of coating. Cleaning is employed for the removal of grease, oil, or scale from the metal surface.

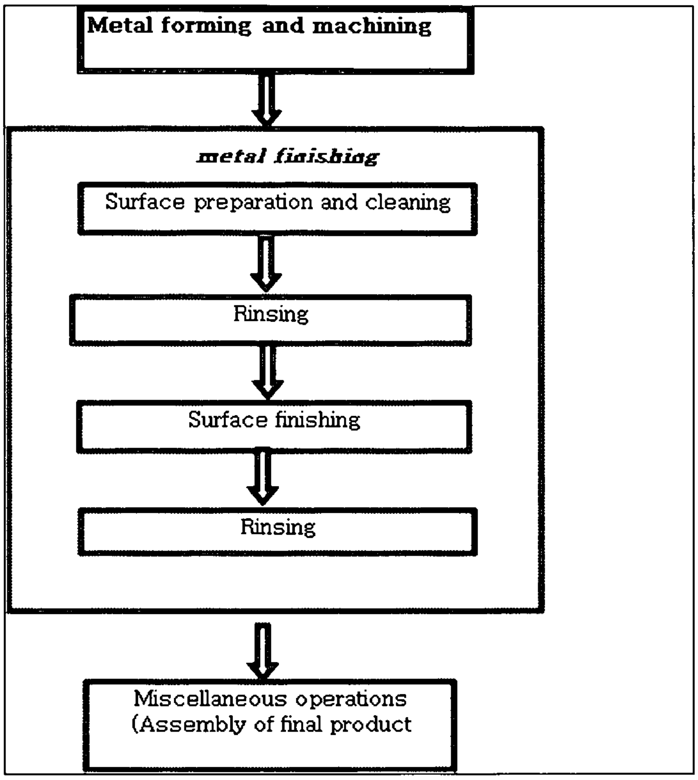

Figure 2.1: Work flow in the metal finishing industry[12]

Surface preparation and cleaning includes the following process which may vary from plant to plant depending on the cleaning specification requirements:

- ***Abrasive blasting:*** This is used for the removal of paint, rust and scale prior to painting or refinishing.

- ***Degreasing:*** This process removes oil/ grease. Organic solvents such as aliphatic petroleum, aromatic, oxygenated hydrocarbons and halogenated hydrocarbons are used to clean metal surfaces.
- ***Soaking in alkaline cleaners:*** This process removes oil, grease, soils and other residuals by employing alkaline hydroxide (e.g. NaOH) and carbonates. Organic/ inorganic additives that improve cleaning are also used. Surfactants are employed to increase the spreading and wetting properties of the solution. Alkaline soaking is done at elevated bath temperatures of about 50 to 90 ^{O}C.
- ***Acid cleaning and pickling:*** Acid cleaning removes oxides and scale from the metal surfaces. This process uses weak acid solutions in combination with wetting agents or detergents. Acid pickling is normally used for the preparation of metal surfaces for the final finishing operation. Sulfuric acid or hydrochloric acid is normally used for carbon steel. Hydrochloric acid or hydrofluoric acid is used to pickle stainless steel.
- ***Electrocleaning:*** This process uses the direct, reverse or periodic reverse electric current, in combination with an alkaline cleaning bath. Electrocleaning removes oil and also aids the activation of the metallic surface. The workpiece may be set as cathode or anode in the alkaline bath (e.g. <30 %wt NaOH solution). The temperature of these may be ambient or range between 40 to 80 ^{O}C. The electrocleaning process is recommended for the removal of particulate matter.
- ***Ultrasonic cleaning:*** This method may be used for removing particulate matter by creating a mechanical activity, which is usually combined with chemical activity to accelerate the cleaning medium process. The process may be carried out in aqueous or organic medium. Organic medium is ideal for the removal of finely divided solids particles. Ultrasonic cleaning is recommended for cleaning parts with complex geometry.

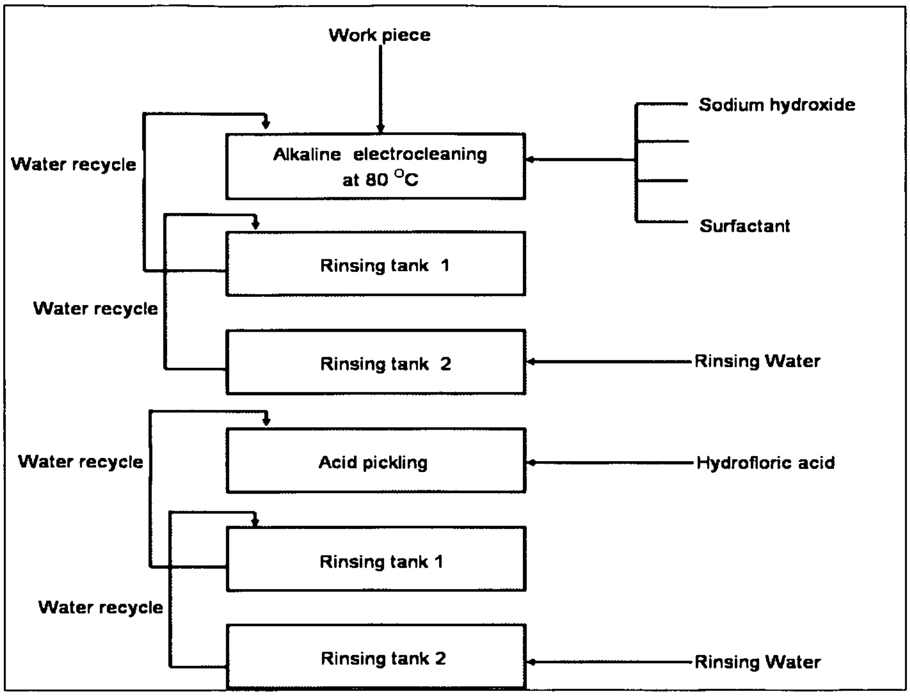

Figure 2.2: Typical process flow diagram of the preparation and cleaning stages[12]

The surface finishing stage follows after the preparation and cleaning stages. The surface finishing stage can be electroplating, galvanizing, spray painting, etc. For the purpose of this study electroplating is selected.

2.1.1. Size of metal finishing enterprises

Formally there were no industrial statistical codes (SIC) that cover the processes, size and the structures of South African metal finishing (MFI) [2, 13].Thus, there are recent surveys done in South Africa to determine the number and size of metal finishers in the country. The surveys have reported that metal finishing industry varies from small to medium size enterprises. The total number of employees in the metal finishing industry is reported to vary between 10 and 50 employees. Some of the enterprises are operated on the backyard and in-house. The estimated number of finishers in South Africa is between 600 and 1200.

The distribution of the these industries in South Africa, with a majority of firms in Gauteng, followed by KwaZulu Natal and the Western Cape and very few in Eastern Cape.

2.1.2. Challenges of wastewater treatment

Before 1996, metal finishers have always treated their waste in an appropriate manner, which resulted in stringent reactions by many boards to fight with the pollution of metal finishers. This reaction forced metal finishers to embark in boards of waste management. New local legislation (by- laws) were developed by municipalities, for example in 1998 Durban Metro (KwaZulu Natal) had a by-law that threatened local electroplaters. The reaction of national and local legislature forced metal finishers to treat the issue of their pollution seriously, and started to embark on Waste Minimization Clubs (WMC).

The most common method used by electroplaters in treating their metal bearing wastewater is a conventional method. The conventional method is used for the following reasons [11]:

- Comprises of simple engineering equipments.
- It is convenient to operate.
- Capable of treating large volumes of water containing high concentrations of metal ions.
- Low operational cost.

Surveys done by different authors from the year 2000 to 2004 have shown that even though metal finishers have wastewater treatment processes in place, there is lack of the ability to treat wastewater efficiently. Some electroplaters in South Africa do not treat their waste and some electroplaters treat theirs but in a less controlled and inappropriate manner[2]. Metal finishers do not know their wastewater composition and amounts that they produce from their processes. This makes it difficult for platers to quantify the optimum amounts of reagents to treat their wastewater. Generally, amounts of treatment reagents that are thought to be enough are dosed. This practice leads to an improperly treated wastewater because of under dosing or overdosing of treatment reagents.

Overdosing or under dosing results in high levels of metal ions, cyanide, ammonia, and a high risk of serious secondary pollution caused by a treatment reagent e.g. chlorine. Secondary pollution hazards include excess metallic sludge, formation of chlorine by-products, etc. [8,11]. If this improperly treated wastewater is released into rivers or any surface water it causes environmental impacts. If it is released into municipal sewers, it causes problems to the treatment process, and sometimes sewer systems can not treat such waste. The following are problems caused by improperly treated waste to sewer systems [2]:

- Metal ions are not easily treated by sewer systems; hence they occur in high levels in the effluent.
- Metal ions inhibit biological processes.
- A high level of metal ions limits municipalities' safe disposal and water reuse.

2.2. ELECTROPLATING INDUSTRY

Electroplaters are the most developed type of metal finishing industry and the largest group of metal finishers forming about 40 % in terms of numbers of firms [2]. Electroplaters deal with coating of surfaces of objects for protection against atmospheric attack (e.g. corrosion, attractive finish, untarnishable surfaces, purification of metals and protection of engineering units) [1].

Electroplating is an electrochemical process. The article to be coated is dipped into a bath of plating solution. An electric current is passed through the plating solution that causes the atoms from the solution to be deposited onto the article to be coated. The metal article to be coated constitutes the negative electrode, whereas the metal to be deposited comprises the electrode of opposite polarity [1].

2.2.1. Types of waste

Prior to the electroplating process, the metal article to be plated undergoes a series of cleaning stages to prepare it for plating. The cleaning stages are degreasing and pickling processes, with rinsing process after each cleaning stage. Each process produces a unique wastewater that is similar to the process bath, refer to Figure 2.3.

2.2.1.1. Alkaline waste from degreasing process

The metal article is dipped into a tank of a hot alkaline solution. The degreaser chemical usually used is sodium hydroxide. The alkaline solvent removes oil and grease from the metal surface and keeps it in a solution. After the degreaser tank, the metal proceeds to a series of rinse tanks. The purpose of rinse baths is to remove drag out from the surface of the article. Wastewater from the degreaser process contains oil, grease and alkaline solution which have to be removed before wastewater enters the downstream processes of the wastewater treatment plant.

Normally if the concentration of the alkali reagent, temperature and time of immersion is high the cleaning rate increases [1]. Strong alkaline reagents are used for steel. Non-etch cleaners are used for zinc and aluminum. Non-etch solutions have low free alkalinity. Typical cleaning temperatures range between 70 °C to 90 °C.

2.2.1.2. Acid waste from pickling/ acid process

Pickling is a method of cleaning by immersing the metal into an acid solution. The acid removes oxide, scale or corrosion products from the surface of the metal. The acid reacts with oxide to form metal salts. The metal article is dipped into a series of rinse tanks to remove drag out from the pickling tank. Wastewater from the pickling process has metal salts and acid which need to be treated.

The pickling process is mainly used for brass, copper, and copper alloys. Pickling with sulfuric acid is normally used for iron, steel, copper, brass, nickel-silver and other copper alloys [1]. Temperatures of pickling process are warmer temperatures of about 70 ^{o}C.

2.2.1.3. Metal ion bearing waste from electroplating process

Metal ions of the coating metal are dissolved in the plating solution. An electric current that is passed through this solution causes the deposition of atoms onto the surface of the metal to be coated. Plating of different articles is done at different conditions i.e. composition, temperature, pH, current density etc.

Generally, when the plating solution gets used, it is regenerated. When it has been regenerated a couple of times and cannot produce good quality work, it is disposed. The used up plating solution comes with metallic sludge that forms as a result of clustering of metal atoms in solution.

After plating, the metal article is dipped in a series of rinse tanks to remove the excess plating solution on the surface of the article. During the operation, plating solution is split on the floor and these spills end up in wastewater. Such spills have high levels of metal ions.

2.2.1.4. Rinsing process

Articles after each process come with excess process fluid on their surface called '*drag out*'. The drag out has a potential of contaminating the next process bath, hence rinsing with clean water is essential. Rinsing is normally carried out in a series of clean water baths. Rinse water loses its rinsing potential after being used for extended periods. The used-up rinse water requires regeneration by specific techniques depending on the contaminant to be removed.

In the electroplating industry, waste is generated in all processes involved and characteristics of wastes vary from one process to the next. Spills and leaks add to waste from plating industry. Usually, conventional methods are used to treat wastewater to achieve acceptable discharge levels or reuse.

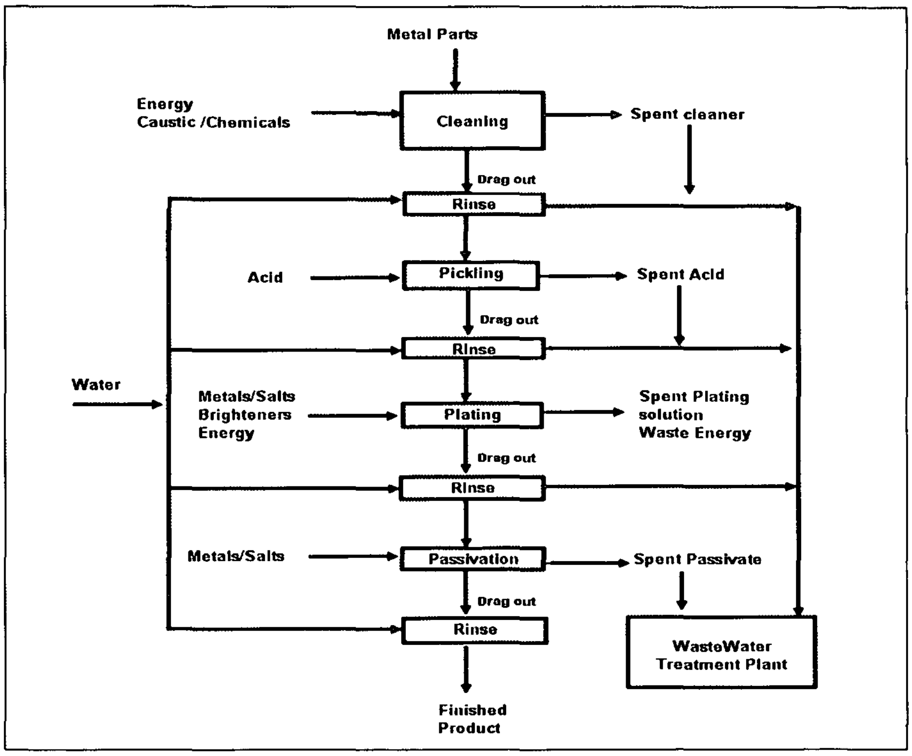

Figure 2.3: Utilization of raw material and production of wastewater in the electroplating industry[12]

2.3. STATUS OF WASTEWATER TREATMENT

Wastewater from electroplating industries has high levels of metal ions e.g. (Cr^{6+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} etc.), and toxic substances (ammonia and cyanide), acid, alkaline, oil and grease [13]. These substances pose environmental problems when released to the environment. Hence, waste release from the electroplating industry is monitored by legislature Acts, local by-laws and international Clean Water Acts, etc. All these acts have specified the required limits of discharge of metal ions and other toxic substances [3].

Generally, metal ions are removed by alkali precipitation methods. Two common alkali reagents used for hydroxide precipitation are lime and caustic. In the survey done for the national Association of Metal Platers and National Manufacturing Science, it has been shown that 84% of plant uses caustic and 5 % uses lime and 9 % uses a combination of both lime and caustic. Other alkalis used are magnesium hydroxide, sodium carbonate, bicarbonate. Magnesium hydroxide is used in conjunction with caustic or lime.

Sulfide precipitation is another technique that is used to precipitate metal ions out of plating wastewater. The use of sulfide precipitation method has a number of limitations and is commonly practiced method. This method generates significantly large volumes of sludge as compared to hydroxide treatment. Large volume of sludge is formed due to the liberation of ferric hydroxide, which adds to the sludge.

Metal ions are precipitated at the pH value where their solubility is minimal. This point of pH where solubility is minimal is called iso-electric point. The most common targeted pH for precipitation of mixed metal ions wastewater is 9.2, but could be in a range of 8.5 to 10. For a single metal ion wastewater, a pH of minimum solubility of that metal ion is used. Metal ions have different minimum solubility as shown in Appendix Figure 9.4 to Figure 9.5.

The difference in the nature of wastewater from different electroplating process makes it hard to mix waste and treat it simultaneously for metal removal [15,16]. Prior mixing, some wastewater requires pre-treatment. For example, the presence of cyanide or ammonia in wastewater requires pre-treatment for cyanide or ammonia removal before metal precipitation. Hexavalent chromium and iron require reduction and oxidation prior mixing with other waste [17,18,19,20].

The entire treatment process comprises of the following processes in a chronological manner; waste equalization process; neutralization process; coagulation and flocculation process; sedimentation process and filtration process [15,16,17].

2.4. TYPICAL ENGINEERING EQUIPMENTS USED IN WATER TREATMENT

The types of equipments used in metal finishing wastewater treatment, depends on the method used. There are a number of methods that have been proposed to treat metal ion bearing wastewater. These methods include conventional method, ion-exchange method, reverse osmosis method etc.

The following are equipments involved in a conventional treatment process:

2.4.1. Equalizers

The characteristics of wastewater from metal finishing processes vary form time to time with changing parameter like concentrations of pollutants, temperature of wastewater etc. Equalizer is a hold up basin to dampen these fluctuations in the characteristics of wastewater. It maintains stable flows into the process. Normally, the equalizer tank is a large reservoir of concrete or steel. The content of the basin is continuously mixed by mechanical agitators. Equalizer tanks can either be constant volume (variable flow) or variable volume (constant out flow).

In the plating industry spills and disposal of spent plating solution occur frequently hence a method of reducing the effect of spills or shock loading events is to operate two complete mix basins in series. The first basin operate partially full to allow on-line storage of the spill volume, and the second basin operate at full volume [15].

2.4.2. Neutralizer

The process of neutralization is carried in a continuous stirred tank. The process precipitates dissolved metal ions. The reagents that are normally used for neutralization are caustic $(NaOH)$ or hydrated lime $(Ca(OH)_2)$. Lime is inexpensive but its use has a negative impact on the process. The negative impact of lime on the process includes: the formation of light weight sludge; and occur in powered forms which need to be dissolved in water and the dissolution is usually poor.

The technique of precipitation uses the advantage of decrease in solubility of metal ions with increase the in pH. Metal ions are precipitated at their lowest solubility point called iso-electric point. If the pH is increased beyond the iso-electric point, the metal hydroxide that has been formed dissolves back into the solution. Metal ions have different lowest solubility points (iso-electric points). Therefore for treatment of mixed streams of metal ions an optimum treatment pH has to determine for optimum removal of all metal ions present [17,18,19,20].

2.4.3. Coagulation and flocculation

Precipitates of metal ions and alkali reagent are small in size resulting in difficulties in separating them by sedimentation or by any liquid-solid separation technique. Small particles require long detention time in the sedimentation tanks, because of their low settling velocity.

Precipitates in water carry a negative charge on their surfaces, thus repel each other and remain dispersed. In water, particles are in a continuous motion known as Brownian motion. When coagulant is added into the water to neutralize, the repulsion forces between particles and attract them to form large flocs.

Coagulation or agglomeration of flocs into large particles is done in a continuous stirred tank. The tank is usually referred to as rapid mixer because it involves high speed mixing of flocculent with water. Coagulation is accomplished by using inorganic or organic coagulants, which can be cationic polymers or poly electrolytes. Common inorganic coagulants that are used include: aluminum salts-$Al_2(SO_4)_3$, sodium aluminates-($Na_2Al_2O_4$)) and iron sulfate- $Fe_2(SO_4)_3$ and ferric chlorine-Fe_2Cl_3. Inorganic coagulants have two mechanisms involved in their functioning. Firstly, the positive charge of the metal serves to neutralize the negative charge on the surface of flocs. Secondly, the metal hydroxide formed by the metals of the coagulants is gelatinous and tend to combine precipitated particles to bigger flocs [21,22].

The effectiveness of the inorganic coagulant depends on the water characteristics, mainly on pH and alkalinity. Aluminum salts are effective at a pH of 5.5 to 8.0, and iron salts and other salts are effective at a pH range of 8 to 10. In organic coagulants react with alkalinity in water, thus addition of lime or soda ash is when inorganic coagulants are used [21].

Likewise, organic polymers that are used for coagulation of particles neutralize the repulsion forces between particles in water. Polymers are long chain of organic compounds of high molecular weight. The main chains of these polymers carry positive charges. The positive charges attract negatively charged particles in water. For optimum dispersion of polymer and polymer/particle contact, initial mixing intensity is essential. The polymers require rapid and thorough mixing [21, 22].

2.4.4. Sedimentation

The process of sedimentation is carried in a huge tank, which is normally rectangular, square or circular in shape. The tank is designed such that its content is not affected by the influent or the effluent streams. The flows in the sedimentation tank are almost stationary. Sedimentation tanks are classified into two, horizontal flow and vertical flows. If the feed enters horizontally, the process is called horizontal sedimentation, and if it enters vertically, it is called vertical sedimentation. Sedimentation tanks are open, concrete or steel tanks and are equipped with a rake structure that collects sludge on the floor [21, 22, 23].

Sedimentation is the removal of agglomerated particles, whilst bigger size particles are allowed to settle down. Smaller particles take long to settle. Particles that settle down on the bottom of the sedimentation tank form a layer of mud sludge. Sludge is removed periodically through sludge drain valves. A sedimentation tank can be separated into 4 zones, depending on what happens on that section. These zones are the settling zone, inlet zone, zone sludge and outlet zone. The efficiency of sedimentation is affected by the following:

- By eddy currents which are set up by inertia of the incoming fluid.
- Wind –induced currents which basin is not covered.
- By convection currents that are thermal in origin.

The retention time or residence time in the sedimentation is the most important factor. Normally, sedimentation operates with a residence time of 2 to 4 hours [21,23].

2.4.5. Filtration

Filtration in the metal finishing wastewater plants is usually an optional stage, depending on the requirement of the final effluent. Filtration is put after sedimentation for the final polish of the effluent. Normally pressure filters are used. These are packed/ granular filters. Sand is normally used as a filter medium. The size of the bed is an important parameter in determining the operation of the filter, and the efficiency of the filter. The filter can be a constant rate filter or constant pressure filter [21,22,23].

2.5. CONCLUSION

The purpose of this chapter is to present the status of wastewater treatment in the metal finishing industry. It also expands on the processes of metal finishers that produce wastewater. From literature, it is seen that most electroplaters use conventional treatment method for its convenience and simplicity. Electroplaters do not know the treatment efficiencies and the effectiveness of their wastewater treatment plants. Thus, it will be ideal to develop a mathematical model that will assist metal finishers to determine treatment efficiencies and effectiveness. The model should be developed based on the conventional treatment process, since it is the commonly used method. The model is detailed in chapter 4 and 5, and the simulation of the model is shown in chapter 6.

CHAPTER 3- METHODOLOGY

This chapter gives details of all process that comprise the conventional treatment of metal finishing wastewater. Reagents that are commonly used for treatment of wastewater in each process stage are discussed. Reactions and design equations that are used in the development of each model are represented. The method followed in this study to develop mathematical models is described in this chapter.

3.1. INTRODUCTION

The purpose of this study is to develop a mathematical model to assist in predicting the treatment of metal ions in metal finishing wastewater plants. The mathematical models are developed by merging design equations of treatment units and mass transfers that take place in the treatment units. These models are developed base on the law of conservation of mass.

The reaction kinetics (i.e. involved in the treatment of metal finishing wastewater) and design equations of process units are well documented in literature. Some of the kinetics data is found in literature as raw data thus requires mathematical skills to convert it to usable data.

Metal finishing wastewater has metal ions (zinc, copper, nickel, chrome etc.) and toxic substances e.g. cyanide. It has been seen from literature that there are several methods that can be used to treat metal finishing waste. The conventional method is the commonly practiced method. Generally, the conventional treatment include: pH correction by acid /caustic, precipitation, flocculation, settling, and filtration. Thus, this study has only focused on the mathematical models of a conventional treatment process.

3.2. METHODOLOGY

3.2.1. Literature survey was covered to describe the following:

- Metal finishing industry processes and electroplating processes. Description of metal finishers and electroplaters. Challenges faced by metal finishing industries concerning their wastewater management. Characteristic of wastewater treatment metal finishing industry.
- Waste sources/ generation and nature of pollution in the electroplating industry.
- Electroplating wastewater treatment by conventional process. Challenges in conventional process application and treatment efficiencies.

3.2.2. Development of Mathematical Models

Review of literature for the required data for development of mass transfer models. This data included the following:

- Reaction mechanism
- Rate kinetic laws
- Design equations process units
- Required treatment condition of each pollutant (i.e. metal ion and cyanide)
- Typical methods that are adopted in the metal finishing wastewater plants (i.e. batch or continuous)
- Treatment reagents that are used with each pollutant (i.e. metal ion and cyanide)

Mathematical models of each process were developed by using the data that is gathered from literature. Some of this data was in an unusable form/ raw experimental data and had to be interpreted and converted to usable form using mathematical skills. Models of reaction vessels were modeled by merging the reaction rate kinetics with design expressions of process units. The sedimentation tank was model to show the settling rate of particles of various sizes.

3.2.3. Observe response of the model to inputs (single and multiple variables)

Typical characteristics of wastewater from the metal finishing wastewater were gathered from literature. This data was used as a guide to varying the inputs and selecting variable in the process. The response of the model was observed when more than one variable was change at the same time.

3.3. DESCRIPTION OF THE WASTEWATER TREATMENT PROCESS

Metal finishing industry is considered as a large producer of wastewater containing metal ions (e.g. Cr^{6+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+} etc.), toxic substances (ammonia and cyanide), acid, alkaline, oil and grease [13]. Wastewater composition corresponds to the composition of the baths of the plating process. Tabulated in Table 3.1 is the typical composition of plating bath solutions.

Table 3.1: Typical composition of planting process bath

Bath	Type of bath	Typical concentration	Units
Acid pickling	Hydrochloric acid (HCl)	<32 %wt	%wt
Alkaline cleaner	Sodium hydroxide Sodium carbonate	20- 30 20-50	%wt %wt
Nickel	Nickel sulfate Nickel chloride Boric acid	240 70 45	g/L g/L g/L
Chrome	Chromic acid with trivalent chromium	250 Cr^{6+} 5-7.5 Cr^{3+}	g/L g/L
Zinc	Sodium hydroxide Sodium carbonate	120 20	g/L g/L
Cyanide zinc	zinc chloride Potassium chloride	60 205	g/L g/L

Generally, the characteristics (i.e. flowrate, concentrations of metal ions and cyanide etc.) of metal finishing wastewater vary from time to time. Equalizer tanks are normally used to holdup wastewater. The equalizer tanks maintain stable flows and control fluctuations in the composition of the feed waste to the treatment process.

Typical equalizer tanks are large reservoirs of concrete or steel. The content of the basin is continuously stirred by mechanical agitators to maintain homogeneous condition.

The conventional treatment process includes the following stage in the treatment of metal finishing wastewater, refer to Figure 3.1.

- Acid and alkaline treatment.
- Pre-treatment of waste in cases of cyanide or ammonia presence.
- Metal ions removal, normally done by alkaline reagent e.g. $NaOH$ or $Ca(OH)_2$
- Sedimentation
- Filtration

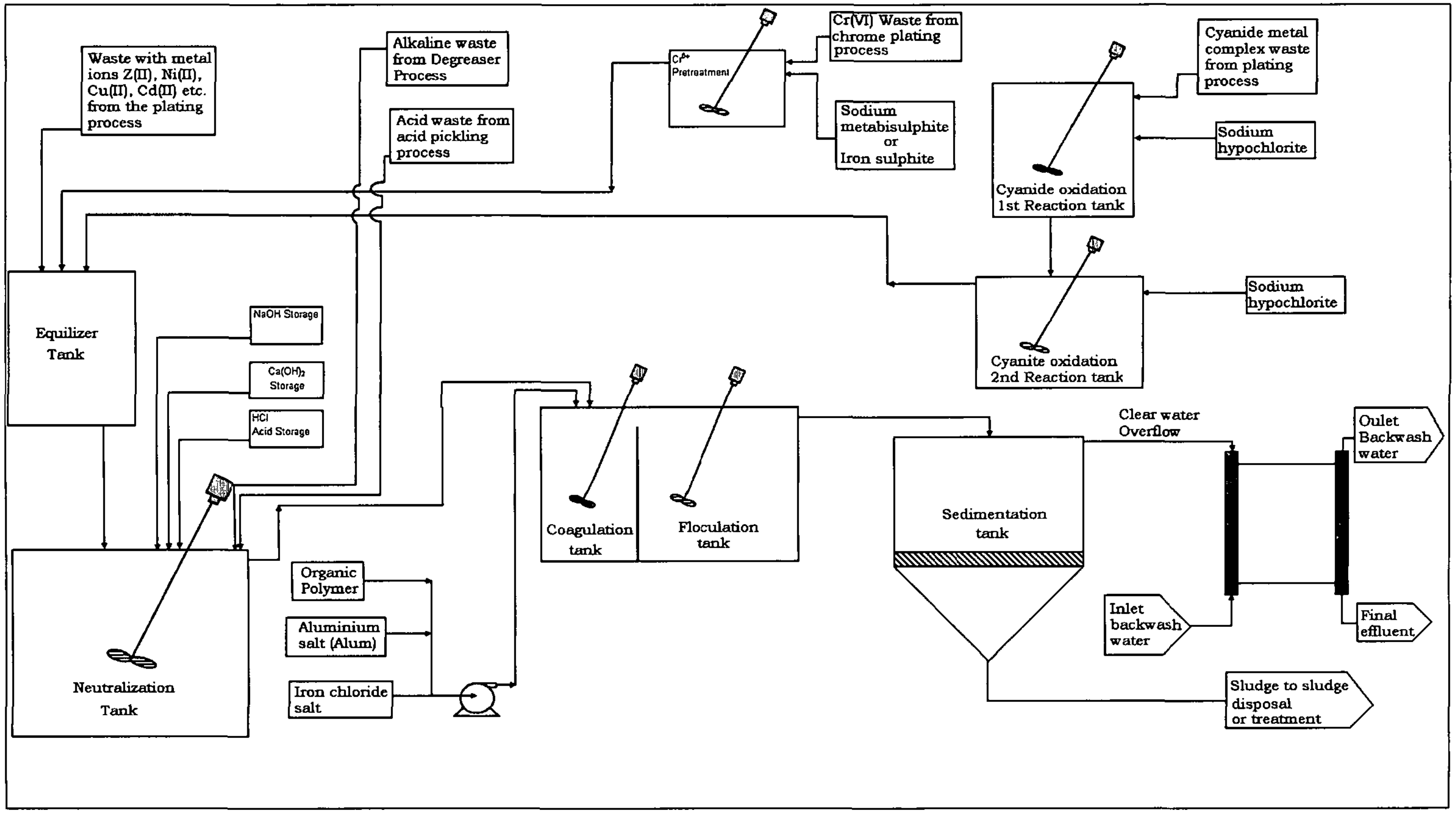

Figure 3.1: Conventional method for treating electroplating wastewater [17]

3.4. ACID AND ALKALINE WASTE TREATMENT

The acid and alkaline wastewater is generated in the acid pickling process and degreaser process, respectively. The two processes are carried in two separate units with rinsing done after each process. Clean water baths are used to rinse the articles that are to be plated.

The acidic wastewater from the acid pickling has high concentrations of dissolved metal ions. The metal ions are formed when the metal articles are dipped in the acid solutions to remove scale and rust, thus forming metal salts. For example, when an iron based article is pickled with hydrochloric acid, an iron chloride salts is formed. Usually, the acid content in waste is <15 %wt.

Alkaline wastewater is formed in the alkaline degreaser process, where the metal article is dipped into a weak alkaline solution of <15 %wt NaOH. The alkaline solution removes grease and oils on the surface of the article. The wastewater from the degreaser process contains emulsified oils and grease with alkaline pH because of sodium hydroxide.

Acidic and alkaline waste from the pickling and degreasing process is treated by pH adjustment. The acidic waste is treated by adding alkaline solution of sodium hydroxide (<30% NaOH). The alkaline waste is treated by weak solution of acid, usually <30 %wt NaOH. The treatment tanks are continuous stirred tanks that are equipped with pH and Oxidation Reduction Potential (ORP) online analyzers. The pH and ORP are used to optimize treatment reaction.

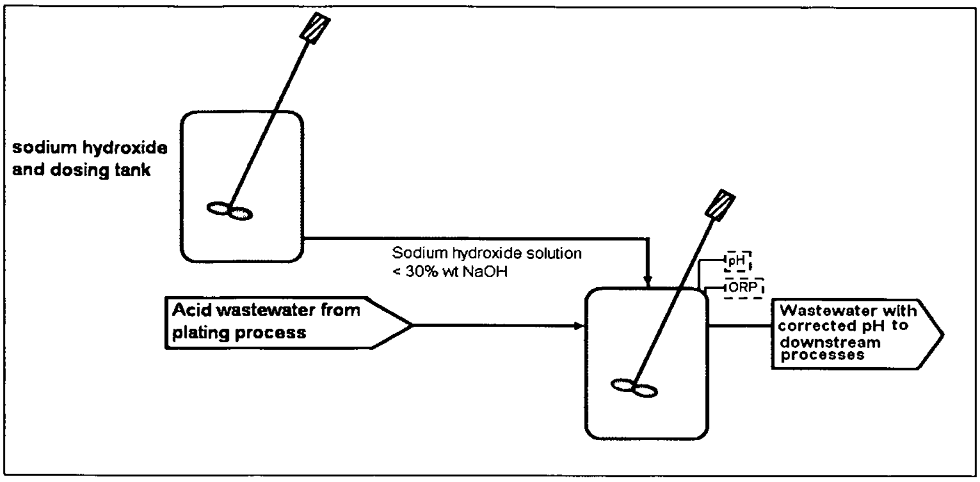

Figure 3.2: Acid and alkaline treatment process [18]

3.5. METAL ION WASTES TREATMENT

Chemical precipitation is used to remove metal ions such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+} and Fe^{2+} etc. from wastewater. Metal precipitation is achieved by using a precipitant which can be lime or caustic. The choice of the precipitant depends on a number of factors including cost; total dissolved solids criteria; sludge production; carbonate and non-carbonate hardness; and chemical stability. Metal precipitation is carried in a continuously stirred tank. The precipitate of metal ions are small flocs and require agglomeration which is achieved by using coagulants like ferric chloride ($FeCl_3$) or Alum ($Al_2(SO_4)_3$, polymers etc [18].

Metal ions occur in different states in wastewater and behave differently to treatment by an alkaline reagent. Some of metal ions e.g. chromium hexavalent and iron, require special pre-treatment prior precipitation. The discrepancy in the response of these metal ions to an alkaline reagent makes it difficult to treat mixed streams of metal ions. Thus treating mixed metal ions stream requires a selection of an optimum condition to achieve optimum removal of all metal ions.

3.5.1. Cyanide treatment

Cyanide is known for its toxicity and environmental unfriendly. Cyanide in the presence of hydrogen ions forms a deadly acid called prussic acid (hydrogen cyanide).

Cyanide presence in metal finishing wastewater disturbs the treatment of other metals like copper, zinc, iron etc. The strong and resistive negative charge of cyanide attracts the positively charged metal ions and keeps them in a solution.

The cyanide-metal complexes cannot be directly treated by an alkaline precipitation method. Cyanide is converted to less toxic cyanite by alkali-oxidation. Normally, chlorination at high pH of about 10 to 11 or sodium hypochlorite is used to oxidize cyanide to cyanite. Cyanite is further oxidized to carbon dioxide and nitrogen by alkali-oxidation in the second stage as shown in the figure 3.3 below. Cyanide treatment is carried in series of two continuously mixed tanks. The first tank converts cyanide to cyanite and the second tank convert cyanite to carbon dioxide and nitrogen. The second process is carried at pH 8.

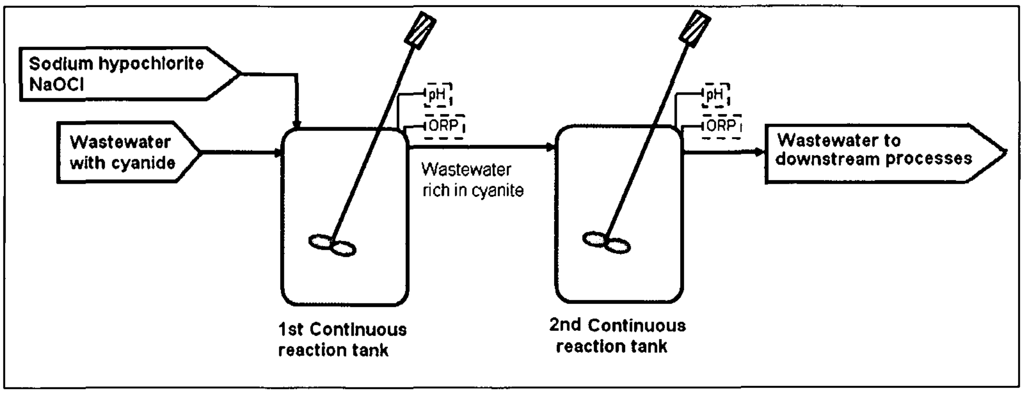

Figure 3.3: Double stage cyanide oxidation process [18]

3.5.2. Chromium (VI) treatment

Chromium in solutions occurs as chromium (VI), and at this state it is stable and resists precipitation by lime or caustic. Prior to precipitation Chromium (VI) is reduced to chromium (III). Normally, the reduction of chromium (VI) is achieved by using sodium metabisulphite at low pH of about 1.5 to 3. Iron sulphide and sulfur dioxide can also be used to reduce chromium (VI).

The reduction of chromium (VI) is carried in a continuous stirred tank, refer to figure 3.4 below. The tank is equipped with an online pH and Oxidation Reduction Potential (ORP) analyzers. The pH and ORPO are used to optimize the reaction conditions.

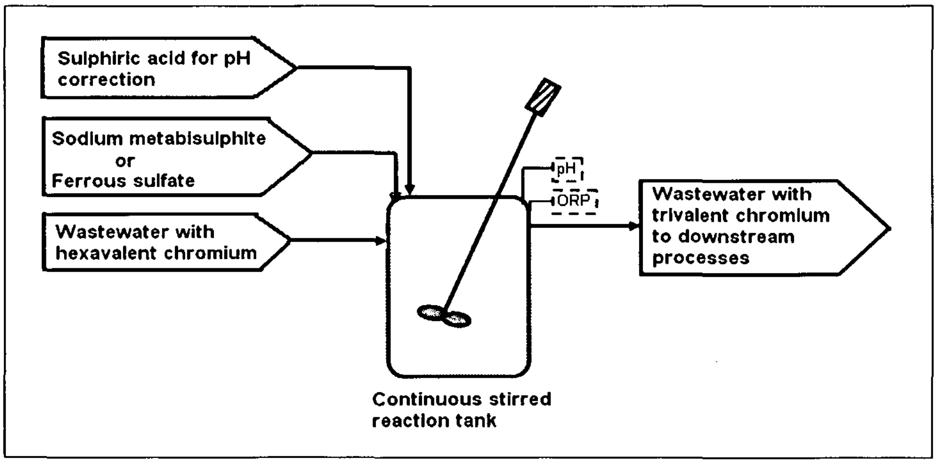

Figure 3.4: Chromium (IV) reduction process [18]

3.5.3. Iron treatment

Iron in a low pH solution (pH > 6) occurs as ferrous ions. In this form it is stable and soluble. It can not be precipitated by lime or caustic.

Ferrous ions are precipitated by elevating the pH, normally to a pH of 7.5, through addition of alkaline reagent (NaOH and $Ca(OH)_2$) and aeration. Aeration supplies oxygen, which oxidize ferrous ions to ferric ions. The ferric ions are readily precipitated by alkali reagents.

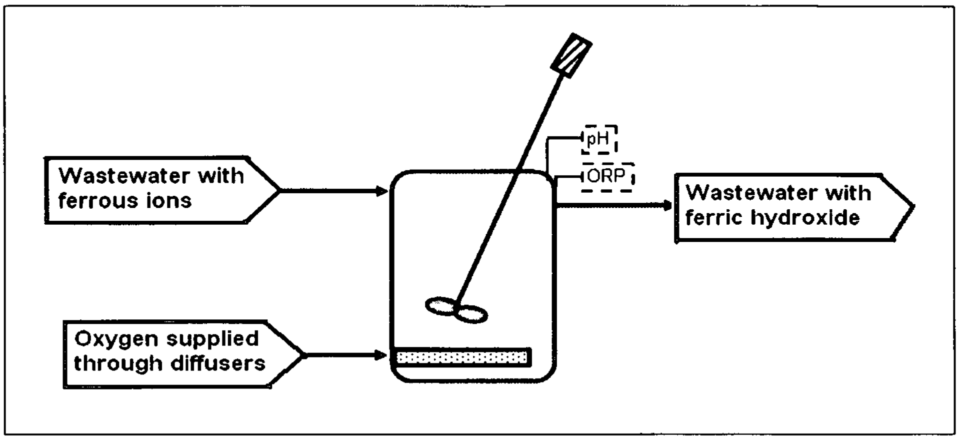

Figure 3.5: Ferrous ions oxidation process [18]

3.5.4. Treatment of other metal ions (zinc, copper, cadmium and nickel)

Metals like copper, zinc, nickel and cadmium are readily precipitated by addition of alkali reagent (NaOH and $Ca(OH)_2$). These metals simply form their corresponding metal hydroxide when treated with an alkali reagent.

The precipitation of metal ions is carried in neutralizers, refer to figure 3.6. The neutralizer is a continuous stirred tank in which metals are precipitated. In the neutralizer, the pH of wastewater bearing metal ions is adjusted to a pH of low solubility of the metal ions carried in wastewater. Acid or alkali reagents may be added to adjust the pH. If an alkali reagent is added, it reacts with water acidity hence increasing the concentration of hydroxide ions. The hydroxide ions attract the metal ions and form metal precipitates.

Metal hydroxide precipitates are small flocs which can be agglomerated by coagulation and flocculation. The agglomerated flocs can be separated by settling.

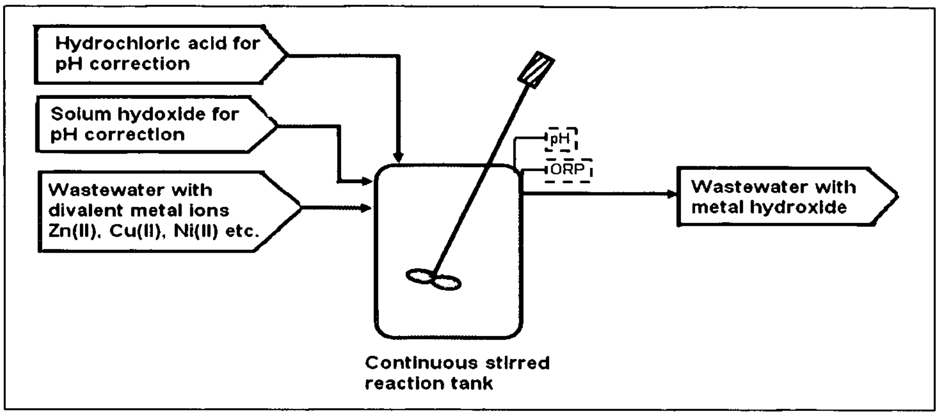

Figure 3.6: Divalent metal ions precipitation process [18]

3.6. EQUIPMENT SPECIFICATION

3.6.1. Precipitation and pretreatment tanks

The conventional treatment process for metal finishing wastewater use continuously stirred tanks. There are reactions that take place in these tanks, hence are considered to be Continuous Stirred Tank Reactors (CSTR), See figure3.7 below. Usually the CSTR are round or square in shape with mechanical agitators. The content of these tanks is assumed to be instantaneously mixed and uniform throughout the tank. The residence time of the tank content depends on the geometry of the tank.

The reactions that take place in the CSTR are described by their reaction rate laws. These reaction laws are determined from literature. The rate laws are merged with the mass transfers that take place in the reactor to yield the design equations of the units.

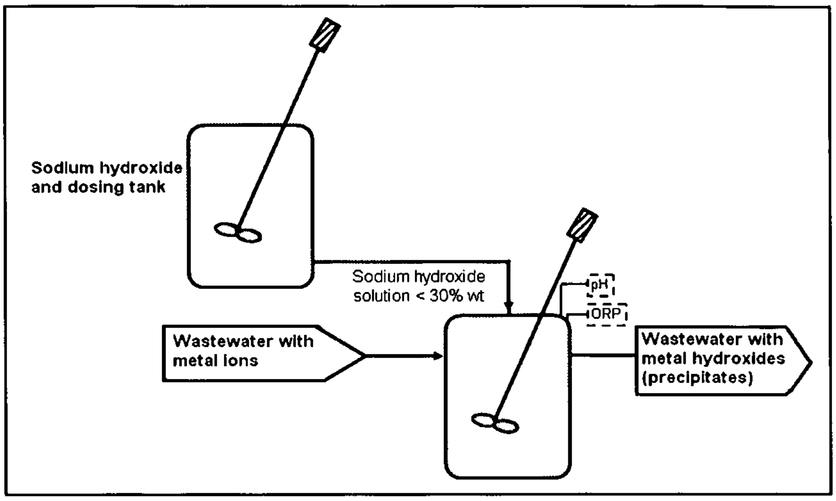

Figure 3.7: Typical continuous stirred tank reactor [18]

The design equation of a reaction tank is similar to that of a continuous stirred tank reactor (CSTR) and is as follow [24]:

$$V = \frac{F_A X_A}{-r_A} \qquad \text{.......................(3.5.1)}$$

Where V = volume of the tank (m^3)

F_A = flowrate of Specie A (or any specie of concern) (kg/s)

X_A = conversion of specie A (any specie of concern)

$-r_A$ = reaction rate (concentration per time)

3.6.2. Coagulation and flocculation

Coagulation using alum involves a fast reaction of hydrolysis of alum forming alum hydroxide. The alum is added into a rapidly mixed tank. This tank is considered as a continuous stirred reactor (CSTR) hence its design equation is similar to equation 3.5.1.

Alum hydrolysis as follows [25]:

$$Al^{3+} \xrightarrow{k_1} Al(OH)^{2+} \xrightarrow{k_2} Al(OH)_2^{+} \xrightarrow{k_3} Al(OH)_3 \xrightarrow{k_4} Al(OH)_4^{-} \qquad \text{....................(3.5.2)}$$

The coagulation rate can be determined from the following expression 3.5.3. This expression 3.5.3 is developed from mass balance on the reaction mechanism.

$$\frac{d[Al_2(SO_4)_3]}{dt} = k[\ [Al_2(SO_4)_3] - [Al(OH)_3]] \qquad \text{........................(3.5.3)}$$

The process of coagulation is followed by flocculation, which is carried in a slowly mixed tank. This tank promotes agglomeration of flocs by adsorption on the hydrolyzed Alum (coagulant). The adsorption is assumed to follow Freudlich isotherm. The Freundlich isotherm is reported to characterize most adsorption processes rather well under conditions present in most water treatment systems. The shortfall of the Freundlich isotherm is that it fails to consider that there may be a limited amount of adsorption sites on the surface of the solid. The lack of further site may prevent adsorption under conditions in which equilibrium is reached. The model uses the equilibrium relationship between the adsorbent and the adsorbate at a fixed temperature.

The adsorption modeling equation is [26]:

$$amount\ adsorbed = S = \frac{(c_f - c_i)v_{solution}}{m_{sorbent}} \qquad \text{.........................(3.5.4)}$$

Where q_e = adsorbent (i.e solid) phase concentration after equilibrium, mg adsorbate/g adsorbent

c_f *and* c_i = initial and equilibrium (residual) concentration of the sorbate in solution, respectively

V = volume of waste contacted with the sorbent (L)

But q_e is represented as follow in the Freundlich model express [26]:

$$q_e = K_f C_e^n \qquad \text{……………………(3.5.5)}$$

Where: q_e = adsorbent (i.e. solid) phase concentration after equilibrium, mg adsorbate/g adsorbent

K_f = Freundlich capacity factor $(mg_{absorbate} / g_{adsorbent})(L_{water} / mg_{adsorbate})$

n = Freundlich intensity parameter

C_e = Concentration of solute in solution at equilibrium (mg/L)

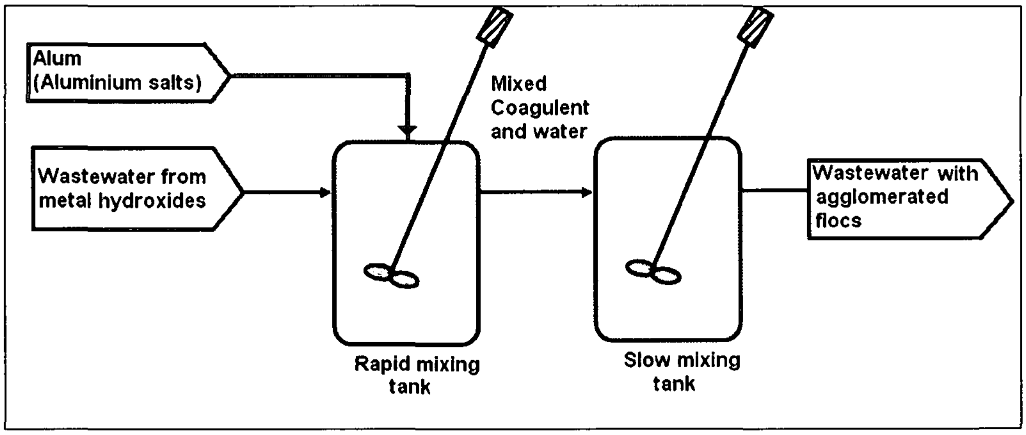

Figure3.8: Coagulation and flocculation system [17]

3.6.3. Sedimentation tank

Sedimentation is used to separate flocs from water. Prior sedimentation flocs are flocculated to enhance their settling in the sedimentation tank. The most important parameters in the sedimentation tank are the residence time and the settling velocity. Different authors have empirically determined these two parameters, assuming a discrete particle that is moving at a same horizontal speed with water [26,27,28].

The settling velocity of flocs depends on the density of water which is affected by the temperature. Thus an expression that will take into account the effect of water temperature was developed by Hazen. The Hazen's equation is applicable to a particle size ranging from 0.1 to 1.0 cm [26,27,28].

$$v = 60.6\frac{(\rho_s - \rho)}{\rho} \times \frac{3T + 70}{100} d \qquad \text{.........................(3.5.6)}$$

Where v = Settling velocity in m/s

ρ_s = Mass density of the particle in kg/m^3

ρ = Mass density of the water in kg/m^3

d = Diameter of particles in m

T = Temperature of liquid in ^{o}C

The residence time required for settling of particles of a certain size can be determined from the settling velocity, using the following equation [26,27,28]:

$$\mathrm{Re}\,sidence\ time = t_R = \frac{H_{clarify}}{V_{settling}} \qquad \text{......................(3.5.7)}$$

$$\mathrm{Re}\,sidence\ time = t_R = \frac{H}{v}$$

Where t_R = Residence time in seconds

H = Height of the clarifier in meters

v and V= Settling velocity in m/s

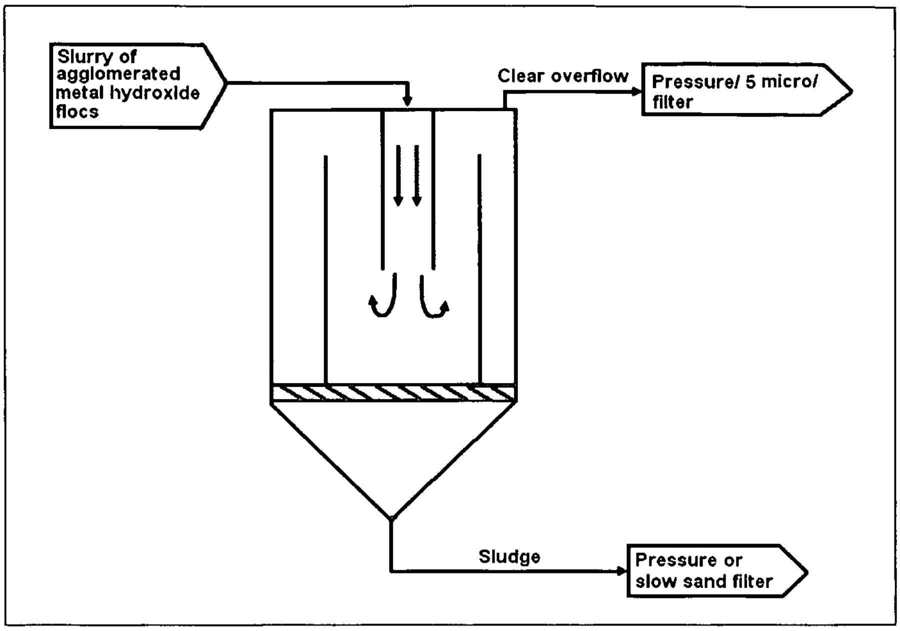

Figure 3.9: Sedimentation tank [28]

3.7. CONCLUSION

The chapter has presented details of treatment of metal finishing waste and the engineering equipments used in the treatment processes. This chapter has also discussed the approach that has been implemented to develop mathematical models. Detailed models are developed in chapter 4 and 5.These model are built by combining the design equations and the mass transfers that take place inside the equipments.

CHAPTER 4- DEVELOPMENT OF MATHEMATICAL MODELS I

This charter covers the development of mathematical models for pH adjustments, cyanide and iron treatment. Reaction mechanisms and design equations are provided in this chapter. Typical scenarios are provided to illustrate the functioning of the models.

4.1 INTRODUCTION

This chapter illustrates the development and applicability of the mathematical models of pH adjustment, cyanide and iron treatment. The models are developed by using reaction mechanisms and design equations of process hardware.

Practically, wastewater treatment plant may include removal of more than one contaminant but the models are presented separately. This chapter also illustrates practical situations in which the models can be applied.

4.2 pH ADJUSTMENT

4.2.1 Reaction mechanisms of pH adjustment and pH determining equation

In a wastewater treatment plants, the incoming pH of wastewater from the acid and degreaser rinse water is known within a band of operation. Thus, if pH is changed to a certain pH value, the change in hydrogen ion concentration can be determined.

The pH correction is carried in a continuous stirred tank, which is considered as a CSTR. Normally sodium hydroxide of <10 %wt or hydrochloric acid <10 %wt are used interchangeable, depending on the requirements of the neutralization process. The reaction mechanism when sodium hydroxide and hydrochloric acid are used is as follows [18,26,28]:

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad \text{.........................(4.2.1)}$$

The pH of a solution is defined by [18,26,28]:

$$pH = -\log\left[H^{+}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2.2)$$

The equation that predicts the change in pH of a solution is shown in equation (4.2.3). The concentration of acid/alkali added is represented as $[H^{+}]_2$.

$$\frac{\left[H^{+}\right]_2}{\left[H^{+}\right]_1} = 10^{-\left[pH_2 - pH_1\right]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2.3)$$

4.2.2 Typical applicability of the model

Assuming that wastewater from acid pickling rinse tank has 500mg/L of hydrogen ions. The required pH for the treatment of metal ions in the next process is 8.5. The pH is adjusted by adding a solution of 10 %wt sodium hydroxide. The volume of wastewater is 2000 L/hr. The reaction takes place in a continuous stirred tank. The reaction takes the above mechanism (4.2.1).

The change of pH to 8.5 is caused by the change of concentration of hydrogen ions [H⁺]. This change is brought by the reaction of hydrogen ions and the hydroxyl ions. The moles of hydroxyl ions required are equal to the moles of change in hydrogen ions.

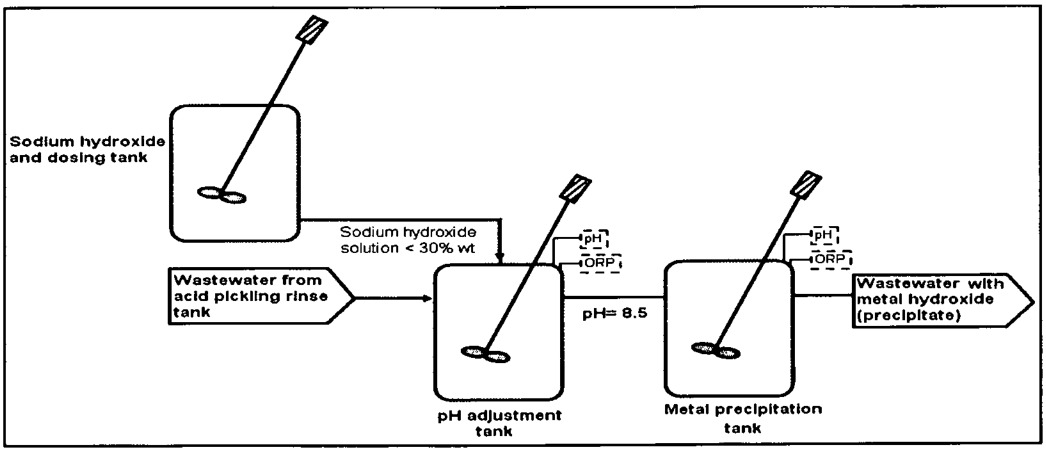

Figure 4.1: Adjustment of pH in metal finishing wastewater treatment

Feed data required as input to the model:

$Concentration\ of\ hydrogen\ ions = 500\ mg / L$

$pH_{outlett} = 8.5$

$a)$
$$\begin{aligned}[H^+]_{inlet} &= (500 / RMM_{H^+}) / 1000 \\ &= 0.496\ mol / L\end{aligned}$$

Model solution:

$b)$
$$\begin{aligned}pH_{inlet} &= -\log[H^+]_{inlet} \\ &= -\log(0.496) \\ &= 0.3045\end{aligned} \quad \Leftrightarrow \quad \begin{aligned}[H^+]_{inlet} &= 10^{-0.3045} \times 1.008 \times 1000 \\ &= 499.9891\ mg / L\end{aligned}$$

Hydrogen ions concentration in the outlet from tank.

$c)$
$$\begin{aligned}[H^+]_{outlet} &= (10^{-pH_{outlet}}) \times (RMM_{H^+}) \times 1000 \\ &= (10^{-8.5}) \times (1.008) \times 1000 \\ &= 3.19 \times 10^{-6} \quad mg / L\end{aligned}$$

$d)$
$$\begin{aligned}\Delta[H^+] &= \left|[H^+]_{inlet} - [H^+]_{outlet}\right| \\ &= 499.9891 - 3.19 \times 10^{-6} \\ &\approx 499.9891 \quad mg / L\end{aligned}$$

$e)$
$$\begin{aligned}Converssion\ of\ [H^+] &= \frac{\Delta[H^+]}{[H^+]_{inlet}} \\ &= \frac{499.9891}{499.9891} \\ &= 1\end{aligned}$$

$$f)\qquad Mass\,[H^+]reacted = X \times [H^+] \times \frac{Q_{tot}}{3600}$$

$$= 1 \times 499.9891 \times \frac{2000}{3600}$$

$$= 277.7717 \quad mg/s$$

From the neutralization reaction (4.2.1), that 36 g of hydrochloric acid requires 40 g of sodium hydroxide.

$$g)\qquad Mass\ NaOH\ required = (40/36) \times Mass\,[H^+]reacted$$

$$= 1.1111 \times 277.7717$$

$$= 308.6321 \quad mg/s$$

$$h)\qquad Total\ mass\ NaOH\ stream = Mass\ NaOH\ required/(10\%)$$

$$= 3086.321 \ mg/s$$

4.3 CYANIDE TREATMENT

4.3.1 Reaction mechanism, rate laws and equipment design equation

Cyanide in water interferes with the treatment of metal ions e.g. iron, zinc, nickel, copper, cadmium etc. Cyanide forms metal-complexes which remain dissolved and do not respond to precipitation by sodium hydroxide or any precipitation reagent. Cyanide has to be removed before metal treatment stages.

Cyanide is removed by a double stage oxidation process using sodium hypochlorite as an oxidant. The first stage reaction oxidizes cyanide to cyanite. This reaction is carried in a continuous stirred tank, which can be considered as a CSTR. The second reaction further oxidizes cyanite to carbon dioxide and nitrogen. This reaction is carried in a continuous stirred tank, which is also considered as a CSTR.

For the purpose of this study only the first stage reaction is detailed. The design equation of this reaction tank is developed based on the following assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed.
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

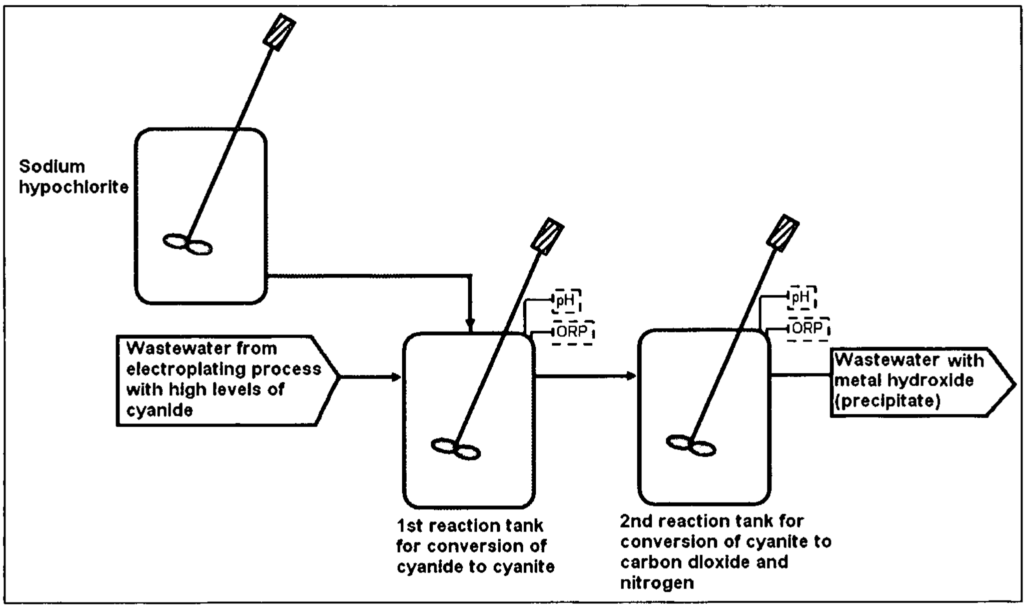

Figure 4.2: Double stage cyanide treatment process [18].

The design equation of the reaction tank is shown below in equation (4.3.1) [24]:

$$V = \frac{F_{CN^{-1}} X_{CN^{-1}}}{-r_{CN^{-1}}} \qquad \text{..........................} (4.3.1)$$

Where: V = volume of the tank (m^3)

F_{CN} = flowrate of cyanide (kg/s)

X_{CN} = conversion of cyanide

$-r_{CN}$ = reaction rate

The pH of the first reaction tank is maintained at a pH range of 8.5 to 11.5. Normally, the pH is corrected by adding sodium hydroxide (10 %wt). The pH in the second tank is usually elevated to 10.5 or 11.

The following is the reaction mechanisms of the first stage [18,29,30,31]:

Cyanide oxidation to cyanite reaction:

$$NaCN + NaOCl \rightarrow NaCNO + NaCl \qquad \text{.................(4.3.2)}$$

The reaction rate law expression for the oxidation of cyanide by hypochlorite ions (CN-) at 25 °C is [30,31]:

$$\frac{d[CN^-]}{dt} = \left(k_1 + \frac{k_2}{[OH^-]}\right)[CN^-][OCl^-] \qquad \text{.................(4.3.3)}$$

Where: $[CN^-]$ = cyanide concentration, mg/L

$[OCl^-]$ = hypochlorite ions (or sodium hypochlorite) concentration, mg/L

From expression (4.3.3) it can seen that the rate is first order with respect to cyanide and hypochlorite. This equation shows an inverse proportionality of hypochlorite to pH (i.e. $[OH^-]$). The rate constants in expression (4.3.3) are not applicable at high pH, hence an expression to incorporate the pH in the rate law has to be developed.

The dependency of rate to the pH has been deduced from the data given by the EPA memo of 1994. This paper has given the reaction data of cyanide and hypochlorite at different pH conditions. The rate law expression and the rate constant have been determined by using the integral data analysis method. The relationship of pH and rate constant is found to be:

$$k = 0.0031pH - 0.0207 \qquad \text{.........................(4.3.4)}$$

The rate constant expression shows a direct proportionality to rate to pH. The reaction increases due to formation of more reactive hypochlorous acid (HOCl) at high pH. The hypochlorite acid (OCl^-) concentration decreases at high pH [30].

The rate constant in equation (4.3.3) is substituted by equation (4.3.4), yielding the following rate expression"

$$-\frac{d[CN^-]}{dt} = (0.0031\,pH - 0.0207)[CN^-][OCl^-] \qquad \text{.................(4.3.5)}$$

4.3.2 Development of a mathematical model to predict the cyanide oxidation

Substitute the rate expression (4.3.5) into the design expression (4.3.1), yields the following expression:

$$V = \frac{F_{CN^-} X_{CN^-}}{(0.0031pH - 0.0207)[CN^-][OCl^-]} \qquad \text{.................(4.3.6)}$$

Let: $0.0031pH - 0.0207 = k$

Now putting initial conditions (feed conditions) and using the stoichiometric table, refer to appendix B, table 9.4, yields the following:

$$V = \frac{F_{CN^-} X_{CN^-}}{(k)[CN^-]^2_{init}(1 - X_{CN^-})(\Theta - X_{CN^-})} \qquad \text{....................(4.3.7)}$$

Making X_{CN^-} the subject of the above expression (4.3.8) in the above equation. Gives the following expression:

$$V\left(k\left[CN^-\right]^2_{init}\right)\left(\Theta - X_{CN^-} - \Theta X_{CN^-} + X^2_{CN^-}\right) = F_{CN^-} X_{CN^-} \qquad \text{.................(4.3.8)}$$

Let:

$$Vk\left[CN^-\right]^2_{init} = K$$

Substituting K into the above expression (4.3.8) and rearranging the resulting expression yields the following expression:

$$K\,X^2_{init} - \left(K + K\,\Theta + F_{CN^-}\right)X_{CN^-} + K\Theta = 0 \qquad \text{...........................(4.3.9)}$$

The above quadratic expression (4.3.9) can be used to determine conversion of cyanide to cyanite, refer to the solution provided in section 4.3.3.

To determine the residence time inside the treatment tank, the conversion from the above expression (4.3.1.9) is substituted in expression (4.3.8). The cyanide flowrate is replaced by the product of the concentration and inlet volumetric flowrate.

$$V = \frac{\left[CN^-\right]_{init} Q_{ini}\, X_{CN^-}}{(k)\left[CN^-\right]^2_{init}\left(1 - X_{CN^-}\right)\left(\Theta - X_{CN^-}\right)} \qquad \text{..........................(4.3.10)}$$

Rearranging the above expression (4.3.10) making the residence time the subject of the equation, gives an expression that can be used to predict treatment time required:

$$\frac{V}{Q_{init}} = \tau = \frac{X_{CN^-}}{(k)\left[CN^-\right]_{init}\left(1 - X_{CN^-}\right)\left(\Theta - X_{CN^-}\right)} \qquad \text{..........................(4.3.11)}$$

4.3.3 Typical applicability of the model

Wastewater form an electroplating process has high levels of cyanide of about 25 mg/L and a pH of 7. The pH is adjusted to 10.5 by using appropriate amount of sodium hydroxide. The temperature of water is approximately 24 ^{O}C. The average wastewater flowrate is 2000L/hr. Wastewater is fed into a series of two continuous stirred reactor tanks. The inlet cyanide ratio to sodium hypochlorite to the first reaction tank is 1.2.

The model requires the following input variable to predict the treatment efficiencies of cyanide oxidation to cyanite and reaction space-time:

Feed data require as input to the model:

- Feed flow rate = 2000 L/hr
- Cyanide feed concentration = 25 mg/L
- Feed ratio of hypochlorite to cyanide = 0.9
- Volume of tank = 140 L
- Density of water = ρ_L = 1000 g/L
- pH after correction (gives the concentration of hydroxyl group) = 10.5
- Reaction rate constant
    - ✓ $k = 0.0031pH - 0.0207$
      $= 0.0119\, s^{-}$

Model solution:

Substitute the known variables into expression 4.3.10. This expression is in a form of a quadratic equation with the following coefficients: see detailed calculations in *appendix.9.1.14*

$$a = K = 5111.464\, mg^2 / L s$$

$$b = \left(K + K\Theta + F_{CN^-}\right) = -11319.921\, mg^2 / L s$$

$$c = K\Theta = 6133.757\, mg^2 / L s$$

The conversion of cyanide to cyanite is:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$X = \frac{(11319.921) \pm \sqrt{(-11319.921)^2 - (4 \times 5111.464 \times 6133.757)}}{2 \times 5111.464}$$

$$X = 0.95 \quad or \quad > 1$$

The second root is greater than 1, hence does not represents the conversion.

The residence time in the reaction tank to achieve such conversion is determined by equation (4.3.12):

$$\frac{V}{Q_{init}} = \tau = \frac{0.95}{(0.0119) \times 25 \times (1 - 0.95)(1.2 - 0.95)}$$

$$\frac{V}{Q_{init}} = \tau = 255\, s$$

$$= 4.2 \text{ min}$$

Note: Reverse calculation of conversion is possible. If the residence time is determined from the ratio of the tank volume and feed flow, equation (4.3.12) can be solved for conversion.

The parameters that affect the conversion are the volume of reaction tank, cyanide input concentration and the flow rate. The impact of these parameters is detailed in chapter 6 which show the model in Mat Lab.

4.4 IRON TREATMENT

4.4.1 Reaction mechanisms, rate law and equipment design equation

Iron in solution occurs as dissolved ferrous ions at pH below 6.5 and in the absence of oxygen. The ferrous ions cannot be removed by direct precipitation with sodium hydroxide. Prior precipitation ferrous ions require oxidation to ferric ions. Usually, oxygen is used as an oxidizing agent, which is supplied through diffusers or aeration.

The reaction tank is considered to be a Continuous Stirred Tank Reactor (CSTR). The design equation is developed based on these assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed.
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

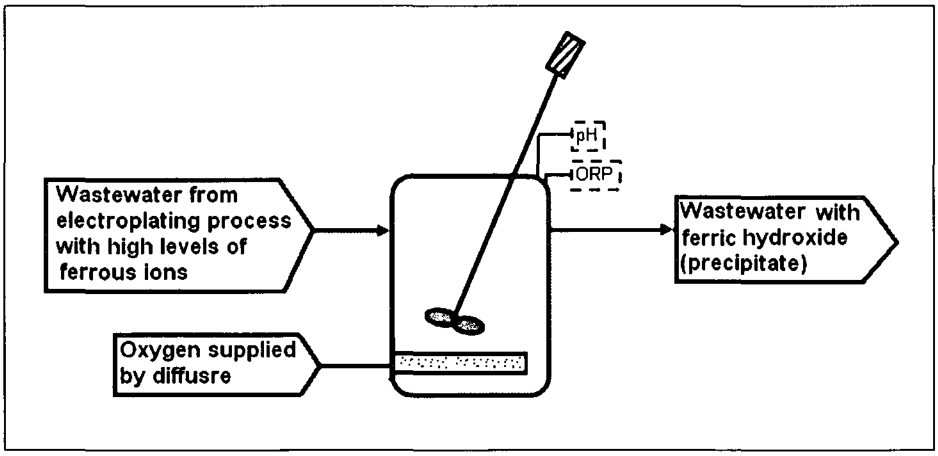

Figure 4.3: Iron treatment process [18].

The design equation of a reaction tank is shown in equation (4.4.1) below [24]:

$$V = \frac{F_{Fe^{2+}} X_{Fe^{2+}}}{-r_{Fe^{2+}}} \qquad \text{...} (4.4.1)$$

Where: V = volume of the tank (m^3)

$F_{Fe^{2+}}$ = flowrate of ferrous ions (kg/s)

$X_{Fe^{2+}}$ = conversion of ferrous ions

$-r_{Fe^{2+}}$ = reaction rate

The reaction tank is maintained at a pH > 7 for optimum oxidation of ferrous ions to ferric ions. Sodium hydroxide solution (>10 %wt) is added to adjust the pH and aids precipitation of ferric hydroxide flocs.

The oxidation of a ferrous ion requires a transfer of one electron to the oxidizing agent from Fe (II) ions, changing its oxidation state to Fe (III). When molecular oxygen is used, four (4) electrons are required to reduce the molecule of oxygen. The first step in the 4 electron transfer is a rate determining step1. This reaction is shown in equation (4.4.2) below [32]:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \qquad \text{.................} (4.4.2)$$

The reactions of iron in water are complex but the table (4.1) below gives some of the approximated reactions, showing a complete series of iron hydrolysis in water. Table 4.2, shows the rate kinetic data of iron hydrolysis.

Iron (II)(aq) species	**Stoichiometric reaction**
Aqua ions	$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$
Mono- hydroxo solution	$4Fe(OH)^+ + O_2 + 4H^+ \rightarrow 4Fe(OH)^{2+} + 2H_2O$
Di-hydroxo solution complex	$4Fe(OH)_{2\,(aq)} + O_2 + 4H^+ \rightarrow 4Fe(OH)_2^+ + 2H_2O$
Surface Fe(II) complex	$4XFeOFe^+ + O_2 + 4H^+ \rightarrow 4XFeFe^{2+} + 2H_2O$
Surface Fe(II) hydroxo complex	$4XFeOFeOH + O_2 + 4H^+ \rightarrow 4XFeOFeOH^+ + 2H_2O$

Table 4.1: Reaction of dissolved and adsorbed ferrous species [32].

Fe(II) species	**2nd-order rate constant (k_i)**	**Units**
Fe^{2+}	7.9×10^{-6}	l/(mol.s)
$Fe(OH)^+$	25.1	l/(mol.s) d
$Fe(OH)_{2\,(aq)}$	$7.94 \times 10^{+6}$	l/(mol.s) d
$XFeOFe^+$	5.01	l/(mol.s) d
XFeOFeOH	5.01	l/(mol.s) d

Table 4.2: Rate constants for oxidation of the dissolved and adsorbed Fe(II) species including parameters: k = second order rate constant for reaction rate law expression [32].

The reaction rate of iron oxidation in aqueous solutions is [32]:

$$-r_{Fe^{3+}} = -\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][O_2] \qquad \text{..................(4.4.3)}$$

Where: $\frac{-d[Fe^{2+}]}{dt}$ = rate of depletion of Fe (II) ions;

k = rate constant;

$[Fe^{2+}]$ = concentration of Fe (II) ions;

$[O_2]$ = concentration of oxygen.

4.4.2 Development of a mathematical model for iron oxidation and precipitation

Combining the above design expression (4.4.1) with the rate law expression (4.4.3) yields:

$$V = \frac{F_{Fe^{2+}} X_{Fe^{2+}}}{K\left[Fe^{2+}\right]\left[O_2\right]} \qquad \text{......................... (4.4.4)}$$

Mass transfer of oxygen:

Oxygen in water diffuses due to concentration gradient. The oxygen flux is proportional to the deficit of oxygen. Oxygen deficit is the difference between the concentration of dissolved oxygen at saturation and the concentration of the dissolved oxygen in the reactor. The linear mass transfer coefficient is proportional to the diffusion coefficient of oxygen and the surface area of the reactor that is in contact with air. It is inversely proportional to the film thickness of water in the reactor. Once oxygen diffuses in water it then reacts with iron converting from ferric iron to ferrous iron. The oxygen mass transfer expression is shown in equation (4.4.5) [32,26,28]:

$$\frac{dc_{O_2}}{dt} = \alpha(C_{equil} - C_{O_2}) \qquad \text{.........................(4.4.5)}$$

Where $\frac{dC_{O_2}}{dt}$ = rate of change of oxygen concentration in water with respect to time (mg/L.s)

α = linear mass transfer coefficient (s^{-1})

C_{O_2} *and* C_{O_2} = saturation concentration at pressure conditions as in the reactor and instantaneous oxygen concentration in the reactor, respectively (mg/L)

The extent of aeration depends on the residence time of an air bubble in the reaction tank. The longer the residence time the better the aeration of water. Form the above equation

(4.4.4), the concentration of oxygen can be determined as a function of residence time. This relationship of residence time and oxygen transfer is shown in the following integration.

This expression (4.4.4) is in a form of separable first order differential equation, it can be integrated by separating variables: The integration is as follows:

$$\frac{dc_{O_2}}{dt} = \alpha(C_{equil} - C_{O_2})$$

Rearranging the above equation (4.4.4) by separating variables and integrating the arranged expression.

$$\int \frac{dc_{O_2}}{\left(C_{equil} - C_{O_2}\right)} = \int \alpha \, dt$$

$$-LN\left(C_{equil} - C_{O_2}\right) = \alpha t + A$$

Making C_{O_2} the subject of the equation and solving the integrating constant A using initial conditions. Initial conditions are such that the oxygen content in the water is low approximately zero for acidic acid pickling waste with ferrous ions and time is zero.

Therefore initial conditions

$$t = 0 \quad and \quad CO_2 \approx 0$$

$$C_{O_2} = C_{equil} - e^{-(\alpha t + A)}$$

Substituting the initial conditions into the integrated expression give the following expression. This expression can be solved to determine the integration constant (A).

$$0 = C_{equil} - e^{-A}$$

$$A = Ln\left(C_{equil}\right)$$

$$e^{-A} = C_{equil}$$

Substituting A into the expression of C_{O_2} :

$$C_{O_2} = C_{equil} - \left[\frac{1}{e^{\alpha t + A}}\right]$$

$$C_{O_2} = C_{equil} - \left[\frac{1}{e^{\alpha t} e^{-LnC_{equil}}}\right]$$

$$C_{O_2} = C_{equil} - \left[\frac{C_{equil}}{e^{\alpha t}}\right]$$

$$C_{O_2} = C_{equil}\left(1 - e^{-\alpha t}\right) \qquad \text{........................(4.4.6)}$$

C_{O_2} is the concentration of oxygen at a certain residence time of an air. This reacts with ferrous iron. Hence, substituting the above expression (4.4.6) into the model equation (4.4.4) gives the following expression:

$$V = \frac{F_{Fe^{2+}}\, X}{k\,[Fe^{2+}]\,(1 - X)\left[C_{equil}\left(1 - e^{-\alpha t}\right)\right]} \qquad \text{...........................(4.4.7)}$$

The above equation (4.4.7) is a mathematical model for prediction of iron oxidation. The conversion from this expression can be used to determine the output composition of the outlet stream from the reaction tank.

4.4.3 Determination of an air bubble residence time

The mass transfer coefficient is dependent on the size of the air bubble that is diffused and the contact time of bubble and water etc. A set of equations that can be used is shown in this section, with their limitations. The mass transfer coefficient is determined as follows [28]:

Calderbrook and Moo-Young empirical correlation for single free rising air particle.

$$\frac{K_L}{D_L} = \frac{2.0}{d} + 0.31\left[\frac{(\rho_L - \rho_G}{\mu_L D_L}\right]^{1/3} \qquad \text{..........................(4.4.8)}$$

The above expression (4.4.8) is for bubble diameter less than 1mm.

$$\frac{K_L}{D_L} = 0.42\left(\frac{\mu_L}{\rho_L D_L}\right)^{1/2}\left[\frac{\rho_L(\rho_L - \rho_G)g}{\mu_L^2}\right]^{1/3} \qquad \text{.........................(4.4.9)}$$

The above equation (4.4.9) is for bubble diameter greater than 2.5 mm.

Where: d = bubble diameter

D_L = diffusivity of gas in liquid

μ_L = liquid viscosity

ρ_L = liquid density

ρ_G = gas density

K_L = m/s

$$a = \frac{(number\ of\ bubble)(area\ per\ bubble)}{reactor\ volume} \qquad \text{.....................(4.4.10)}$$

$$a = \frac{Q_G\, t\, 6}{V\, d}$$

Where: Q_G = volumetric flow rate of air.

t = residence time of air bubble.

V = volume of tank.

Residence time is the ratio of reactor height and the velocity of an air bubble. Time is given by the following expression [28]:

$$t = \frac{h}{\upsilon} \qquad (4.4.11)$$

Where: h = height of the reactor.
υ = velocity of the rising air bubble.

The rising velocity of an isolated air bubble is determined in a same manner as the velocity of an isolated falling particle postulated by Stoke' Law.

For laminar flow (Reynolds number < 1) with particle diameter (d) < 0.013 cm. The velocity of air bubble rising is given by [28]:

$$\upsilon = \frac{g}{18\mu_L}(\rho_L - \rho_G)d^2 \qquad \text{........................}(4.4.12)$$

Where: g = gravitational acceleration

For turbulent flow (Reynolds number > 1000) with particle diameter (d) > 0.30 cm. The velocity of air bubble rising is given by [28]:

$$\upsilon = 1.82\left[\frac{(\rho_L - \rho_G)dg}{\rho_L}\right]^{1/2} \qquad \text{........................}(4.4.13)$$

Fine diffusers with a diameter range at 0.2 cm, the velocity expression is [28]:

$$\upsilon = \left[0.072g(\rho_L - \rho_L)d^{1.6}\,\rho_L^{-0.4}\,\mu_L^{-0.6}\right]^{0.714} \qquad \text{........................}(4.4.14)$$

Hence the mass transfer coefficient is given by [28]:

$$\alpha = K_L a \qquad \text{.........................(4.4.15)}$$

4.4.4 Typical applicability of the model

Wastewater from the acid pricking process has iron chloride at acidic pH of 4. The pH is adjusted to 8.5 by using appropriate amount of sodium hydroxide. The temperature of water is 24 ^{O}C. The flowrate of wastewater is 1000L/hr. This wastewater is fed into a continuous stirred tank that is considered as a CSTR. This tank is continuously aerated by the supply of air through diffuser that produces 0.3 cm air bubbles. The flowrate of air is one third of wastewater flowrate.

Feed data required as input to the model:

- Feed flow rate = Q = 1000 L/hr
- Feed iron (II) concentration = $[Fe^{2+}]_{init}$ = 20 mg/L
- Volume of tank = V_T = 475 L
- Height of tank = 2 m
- Air flow rate = Q_{Air} = (1/3) x wastewater flowrate
- Equilibrium concentration of oxygen at STP = 8 mg/L
- Density of water = ρ_L = 1000 g/L
- Density of air = ρ_{Air} = 1.29 g/L
- Diffusivity of air = D = 0.000204 m^2/s
- Viscosity of water = μ_L = 0.001 cPoise
- Diameter of air bubbles from pore DIA of diffuser = d = 0.3 cm
- Gravitational acceleration = g = 9.81m/s^2
- Rate constant = $k = 12.55\ L/mol.s$ or $k = 2.2471\ L/mg.s$
- pH of the solution after pH adjustment = 8.5
- Temperature of reaction tank = 25^{O}C= 288 K

Model solution:

These are the constants determined from the input parameters.

Oxygen mass transfer coefficient:

Use all the known input parameters to solve for K_L in expression (4.4.9)

$$K_L = 0.0598\, m/s$$

Use all the known input parameters to solve for KL in expression (4.4.10)

$$a = 1.1078\, m^{-1}$$

Determine the mass transfer coefficient from equation (4.4.15).

$$K_L a = \alpha = 0.0662\, s^{-1}$$

Determine velocity of a rising air bubble from equation (4.4.13) and the bubble residence time from equation (4.4.11)

$$\upsilon = 1.82\left[\frac{(1000-1.29)(0.0001\times 9.81)}{1000}\right]^{1/2}$$

$$\upsilon = 0.057\, m/s$$

Residence time of the air bubble is:

$$t = \frac{2}{0.057}$$

$$t = 35.1\, s$$

Determine the conversion from equation (4.4.7) conversion of Fe^{2+} to Fe^{3+}

$$X = \frac{17.044 \times \left(1 - e^{-(0.0662 \times 35.1)}\right)}{5.556 + 17.044 \times \left(1 - e^{-(0.0662 \times 35.1)}\right)}$$

$$X = 0.74$$

Residence time water in the reaction tank is:

$$\tau = \frac{0.74}{2.2411 \times 10^{-4}\,(1 - 0.74) \times 8 \times \left(1 - e^{-(0.539 \times 35.1)}\right)}$$

$$\tau = 29 \text{ min}$$

The response of the model to multiple variable inputs is shown in Mat-Lab program in chapter 6.

4.5 CONCLUSION

This chapter has focused mainly on the models of pre-treatment processes that are essential before treatment of metal ions. This chapter has presented three models: pH adjustment, cyanide treatment and iron treatment. Typical cases where the model can be applied have also been presented in this chapter. After cyanide treatment and pH adjustment, metal bearing wastewater can be treated for metal precipitation. An integrated model is presented in Mat-Lab in chapter 6.

CHAPTER 5-DEVELOPMENT OF MATHEMATICAL MODELS II

This charter covers the development of mathematical models for hexavalent chromium reduction, trivalent chromium precipitation, other metal ions precipitation, flocculation and sedimentation. Reaction mechanisms and design equation are provided in this chapter. Typical scenarios are provided to illustrate the functioning of the models.

5.1 MODEL DEVELOPMENT PROCEDURE

This chapter illustrates the development and applicability of the mathematical models of chromium (VI) reduction, chromium (III) precipitation, divalent metal precipitation, flocculation and settling of flocs. The models are developed by using reaction mechanisms and design equations of process hardware.

Practically, wastewater treatment plant may include removal of more than one contaminant but the models are presented separately. This chapter also illustrates practical situations in which the models can be applied.

5.2 HEXAVALENT CHROMIUM TREATMENT

5.2.1 Reaction mechanism, rate laws and equipment design equation

Chrome at high pH solutions occur as hexavalent chromium. In this state (Cr^{6+}) it cannot be removed by direct precipitation thus requires reduction to trivalent chromium. The trivalent chromium (Cr^{3+}) can be removed by precipitation techniques. Normally, hexavalent chromium is reduced by metabisulphite at acidic conditions.

Chromium reduction is carried in a continuous stirred tank, which is considered as a continuous stirred tank reactor (CSTR). The mixing is achieved by mechanical agitators. The design equation is developed based on these assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

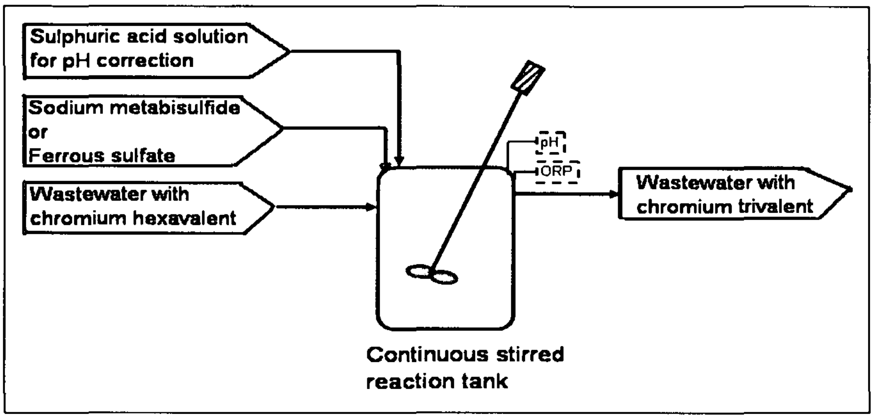

Figure 5.1: Hexavalent chromium reduction process [18].

The design equation of the reaction tank is as follows [24]:

$$V = \frac{F_{Cr^{6+}} X_{Cr^{6+}}}{-r_{Cr^{6+}}} \qquad \text{..........................(5.2.1)}$$

Where:
V = volume of the tank (m^3)
$F_{Cr^{6+}}$ = flowrate of hexavalent chromium (kg/s)
$X_{Cr^{6+}}$ = conversion of hexavalent chromium
$-r_{Cr^{6+}}$ = reaction rate

The reaction pH is maintained at 2 by continuous addition of sulfuric acid. A ratio of feed chromium (VI) to metabisulphite of 5 is maintained for optimum reduction of chromium (VI). The reaction of hexavalent chromium and metabisulphite is as follows [18,33,34,35]:

$$2CrO_3 + 3Na_2SO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Na_2(SO_4) + 3H_2O \qquad (5.2.2)$$

The reaction rate of hexavalent chromium reduction to trivalent chromium is a function of the concentration of hexavalent chromium, metabisulfite, temperature and pH. The reaction rate is first order with respect to hexavalent chromium concentration and sulphite concentration [34,35]. The following equation (5.2.3) shows the rate expression:

$$r_{Cr^{6+}} = \frac{d[Cr^{6+}]}{dt} = K[Cr^{6+}][S^{4+}] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.2.3)$$

Where : $-r_{Cr^{6+}}$ =reaction rate;

K = Lumped reaction rate constant that considers the pH effect;

$[Cr^{6+}]$ = Concentration of hexavalent chromium ions;

$[S^{+4}]$ = Concentration of sulphite ions

The lumped reaction rate constant has been determined from experimental data provided by Martin et al. 1999. This data shows different reaction rate that are determined at various pH and temperature conditions. Chromium (VI) reduction reaction of hexavalent chromium exhibited high dependence on pH, showing an inverse proportionality to pH.

A mathematical representation of the relationship of the reaction rate and pH has been determined using the linear regression method. The lumped reaction constant (K) takes into account the effect of pH to the reaction rate.

From the data given by Martin *et.al* 1999, the set of data at pH 2 and temperature has been selected as reference point. The ratio of the rate constant values $(k_i / k_{reference})$ is plotted against pH, from this plots a relationship of pH and rate constant (K) has been deduced. The K factor in the rate expression (5.2.3) can be approximated by the following expression:

$$K = A\left\lfloor \exp\left\lfloor - {}^{E}\!/_{RT} \right\rfloor \right\rfloor \times 84.794\, pH^{-4.368} \qquad \text{.......................... (5.2.4)}$$

Where: E = Activation energy

A = Frequency factor

R = Universal gas constant

T = Temperature of water

The data that shows the relationship of rate constant and temperature has been used to determine the constant for the Arrhenius law. The magnitude of the activation energy (E) and the frequency factor (A) were determine from the plot of $-Ln\,k$ and $1/T$. This relationship is determined from the liner regression of Arrhenius expression. Refer to appendix for detailed calculations [35].

$$A = 5.692 \times 10^{10}\ L\,mg^{-1}\ s^{\bar{1}}$$

$$E = 74.6301\, kJ / mol$$

Chromium (VI) reduction reaction takes place in a continuous stirred tank (CSTR) [18].

5.2.2 Development of a mathematical model to predict the chromium (VI) reduction

Substitute the rate expression (5.2.3) into the design equation (5.2.1) yields the following expression:

$$V = \frac{F_{C^{6+}} X}{K[Cr^{6+}][S^{4+}]} \qquad \text{.........................(5.2.5)}$$

Where $K = A \exp\left\lfloor - {}^{E}\!/_{RT} \times 0.3952\, pH^{-4.4259} \right\rfloor$

Now putting initial conditions and using the stoichiometric, *refer to appendix B, table 9.4.*

$$V = \frac{F_{Cr^{3+},init}\,X}{K\left[Cr^{6+}\right]^{2}_{init}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{.........................(5.2.6)}$$

Where: $\Theta_{SO_4^-/Cr^{6+}}$ is the ratio of initial sulphite and initial hexavalent chromium

Rearrange expression (5.2.6) by making a quadratic expression.

$$\frac{3VK\left[Cr^{6+}\right]^{2}_{init}}{2}X^{2} - \left(\frac{3VK\left[Cr^{6+}\right]^{2}_{init}}{2} + \Theta_{S^{+4}/Cr^{6+}}VK\left[Cr^{6+}\right]^{2}_{init} + F_{Cr^{6+}init}\right)X + \Theta_{S^{+4}/Cr^{6+}}VK\left[Cr^{6+}\right]^{2}_{init} = 0 \quad \text{... (5.2.7)}$$

These are the boundaries of the root that represents conversion of chromium (VI):

X: $0 \leq X \geq 1$

The above expression (5.2.7) can be solved by a quadratic expression to determine its roots. The root that satisfies the boundaries is the conversion of hexavalent chromium to trivalent chromium. This conversion can be used to predict the outlet composition and the residence time.

To determine the residence time required to achieve specific conversions substitute the following expression 5.2.8 into expression 5.2.7, and make (V/Q) the subject of the formulation.

$$F_{Cr^{6+}} = Q \times \left[Cr^{6+}\right] \qquad \text{..........................(5.2.8)}$$

Q= flowrate of wastewater

$\left[Cr^{6+}\right]$ = concentration of hexavalent chromium

Substitute expression (5.2.8) into the above expression (5.2.6) gives the following expression,

$$V = \frac{Q\left[Cr^{6+}\right]_{init} X}{K\left[Cr^{6+}\right]_{init}^{2}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{.................(5.2.9)}$$

Rearranging the above expression by making V/Q the subject of the expression

$$\frac{V}{Q} = \tau = \frac{X}{K\left[Cr^{6+}\right]_{init}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{................(5.2.10)}$$

5.2.3 Typical applicability of the model

Wastewater from chrome single stage rinse water has a pH of 4 and a temperature of 20 ^{O}C. The pH is adjusted to 2.6 by adding sulfuric acid. Wastewater flowrate to the treatment process is 1000 L/hr with 45 mg/L of chromium (VI) and negligible chromium (II) concentration.. It is an industrial practice for the effective reduction of chromium to put 5:1 ratio of metabisulfite to hexavalent chromium.

The model requires the following input variables to predict the conversion of chrome, residence time and output composition.

Feed data required as input to the model:

- Feed flow rate $= Q$ = 1000 L/hr
- Chrome (VI) concentration = $\left[Cr^{6+}\right]_{init}$ = 45 mg/L
- Volume of tank = V_T = 365 L

- Ratio of metabisulphite to chrome (VI) = $\Theta_{S^{4+}/Cr^{6+}} = 5$
- pH = 2.6
- Activation energy = E = 7.46*10^4 J/mol
- Universal gas constant = $A = 74600\ J/mol$
- Frequency factor = $A = 5.69 \times 10^{10}\ Lmg^{-1}s^{-1}$
- Temperature of reaction tank = 20^{O}C= 288 K

Model Solution:

Parameters determined from the input conditions:

$K = 0.0036\, s^{-1}$

Use expression (5.2.7) to solve for chromium (VI) conversion to chromium (III). Expression (5.2.7) is in a form of a quadratic expression. The solution has two roots. The root that represents conversion falls with the boundaries. The following are the coefficients of the quadratic equation (5.2.7):

$$a = \frac{3VK\left[Cr^{6+}\right]^2_{init}}{2} = 3986435\, mg/s$$

$$b = \left(\frac{3VK\left[Cr^{6+}\right]^2_{init}}{2} + \Theta_{S^{+4}/Cr^{6+}} VK\left[Cr^{6+}\right]^2_{init} + F_{Cr^{6+}init} \right) = -172871\, mg/s$$

$$c = \Theta_{S^{+4}/Cr^{6+}} VK\left[Cr^{6+}\right]^2_{init} = 1328812\, mg/s$$

Refer to appendix 9.1.1.2 for detailed calculations

From these parameters, equation (5.2.6) can be solved for determination of Cr^{6+} reduction to Cr^{3+} using the quadratic expression.

Use the general quadratic expression:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$3986.435X^2 - 17287.1X + 13288.12 \quad = 0$$

$$X = 0.999 \quad OR \quad 3.340$$

The second root is greater than 1 hence it does not represent the conversion, since it fall outside the boundaries of the conversion.

From the conversion, it is seen that 99.8 % of input chromium (VI) is converted to chromium (III). This conversion can be used to determine the required time for such conversion, and the output concentration.

To determine residence time substitute the above conversion into equation (5.2.9).

$$\frac{V}{Q} = \tau = \frac{0.998}{0.0036(20)\ (1-0.998)\left(5-\left(\frac{3}{2}\times 0.998\right)\right)}$$

$$\tau = 33 \text{ min}$$

This means that to achieve 99.9 % conversion of 45 mg/L of Cr(VI), wastewater must be inside the tank for about 30 minutes. The residence time depends on the input flowrate and the size of the reaction tank. The influence of the multiple variables is shown in Mat-Lab program in chapter- 6.

5.3 TRIVALENT CHROMIUM TREATMENT

5.3.1 Reaction mechanism, rate laws and equipment design equation

After the reduction of hexavalent chromium, the most dominant chrome specie in wastewater is the trivalent chrome specie.

Wastewater rich in chromium (III) is treated in a separate continuous stirred tank, for precipitation of chromium (III). This waste is acidic in nature because of the sulfuric acid that is added in the reaction to keep the pH less than 3. Sodium hydroxide is added in the second reaction tank to increase the pH to 8.5 and precipitates trivalent chromium. The solubility of trivalent chromium decreases with increasing pH. If the pH increases beyond 8.5, chromium (III) solubility increases [18,29].

The reaction tank is considered a CSTR, with mixing achieved by mechanical agitators. The design equation of the reaction tank is developed based on following assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed.
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

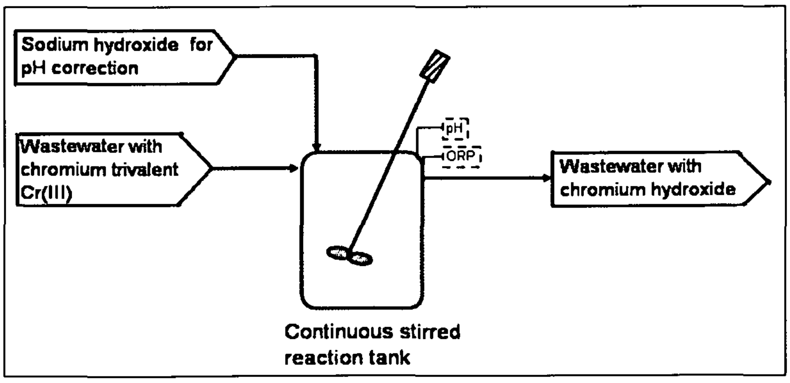

Figure 5.2: Trivalent chromium precipitation process [18].

The design equation of a reaction tank is as follows [24]:

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{-r_{Cr^{3+}}} \qquad \text{.................(5.3.1)}$$

Where: V = volume of the tank (m^3)
$F_{Cr^{3+}}$ = flowrate of trivalent chromium (kg/s)
$X_{Cr^{3+}}$ = conversion of trivalent chromium
$-r_{Cr^{3+}}$ = reaction rate

The optimum pH for chromium (III) precipitation is 7.5 to 8. The ratio of feed trivalent chromium to sodium hydroxide that is fed to the reaction tank is maintained at 3. The reaction mechanism when trivalent chromium is precipitated by sodium hydroxide is as follows [18,26]:

$$Cr^{3+} + 3NaOH \Leftrightarrow Cr(OH)_3 + 3Na^+ \qquad \text{.................(5.3.2)}$$

OR

$$Cr^{3+} + 3OH^- \underset{k_{sp}}{\overset{k_1}{\Leftrightarrow}} Cr(OH)_3 \downarrow$$

When the reaction pH is perfectly monitored and kept at the optimum pH, only the forward reaction is favored [15], thus the reaction rate is:

Assuming the reaction is elementary:

$$r_{Cr^{3+}} = k\ \left[Cr^{3+}\right]\left[OH^-\right]^3 \qquad \text{.................(5.3.3)}$$

Where: k = rate constant;
$\left[Cr^{3+}\right]$ *and* $\left[OH^-\right]$ = concentration of trivalent chromium and hydroxyl group, respectively (mg/L)

5.3.2 Development of a mathematical model to predict the chromium (III) precipitation oxidation

Combining the reaction rate expression (5.3.3) with the rate the design equation (5.3.1) yields the following expression:

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k\left[Cr^{3+}\right]\left[OH^{-}\right]^{3}} \qquad \text{..................(5.3.4)}$$

Substituting initial conditions using stoichiometric table, *refer to Appendix B table 9.4,* yield the following expression:

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k\left[Cr^{3+}\right]\left[\left[Cr^{3+}\right]^{3}\left(\Theta_{OH^{-}/Cr^{3+}} - 3X\right)^{3}\right]} \qquad \text{..................(5.3.5)}$$

The above expression (5.3.5) is a mathematical model that can be used to predict the conversion and residence time. The above expression is a third degree polynomial which can be solved by trial an error method.

5.3.3 Typical applicability of the model

Wastewater from the chromium reduction stage flows at a flowrate of 1000 L/hr and 10 mg/L of trivalent chromium. This wastewater is treated in a continuous stirred tank that can be considered as a CSTR. Sodium hydroxide is added to precipitate trivalent chromium is at stoichiometric quantities.

The model requires the following to predict the treatment precipitation of trivalent chromium, reaction space-time, composition of the output from the reaction tank:

Feed data required as input to the model:

- Feed flow rate =Q = 1000 L/hr
- Chrome (VI) concentration = $\left[Cr^{3+}\right]_{init}$ = 9.98 mg/L
- Volume of tank = V_T = 140 L
- Ratio of sodium hydroxide to chrome (III) = $\Theta_{OH^-/Cr^{3+}}$ = 3
- pH = 8.1
- Temperature of reaction tank = 25^{O}C= 288 K
- Reaction rate constant = 1.5x10^{-5} s^{-1}

The conversion expression (5.3.5) is solved by a trail and error method, by substituting the all kwon properties and equating the right hand side and the left hand side of the equation. The conversion is assumed between 0 and 1. Table 5.1 shows a typical result, where conversion is assume between 0.65 and 0.75.

Iteration of conversion (X)	***LHS of the equation***	***RHS of the equation***
X		
0.65	6.969	3.072
0.7	5.974	5.253
0.75	4.979	9.726

Table 5.1: Sample of trial and error solution for chromium (III) conversion to chromium hydroxide

It can bee seen that the root to equation (5.3.4) is between 0.7 and 0.75. This root represents the percentage of chromium (III) precipitation. A detailed model response to multiple variables is show in Mat-Lab in chapter 6.

5.4 NICKEL, COPPER, ZINC, AND CADMIUM TREATMENT

5.4.1 Reaction mechanism, rate laws and equipment design equation

These metals in solution occur in divalent oxidation state e.g. Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} etc. These metal ions respond easily to precipitation by sodium hydroxide, in the absence of cyanide or ammonia. In mixed metal streams, optimum treatment conditions are selected for optimum removal of all metal ions present [18].

Metal ions are treated with sodium hydroxide in a continuous stirred tank, which can be considered as a CSTR. Hydrochloric acid of 10 %wt can be used to correct the pH if the reaction mixture is higher than required. The design equation is developed based on the following assumptions:

- The feed and outlet are at steady state.
- The tank content is perfectly mixed
- There is no accumulation inside the reaction tank.
- There are no dead zones in the reaction tank.

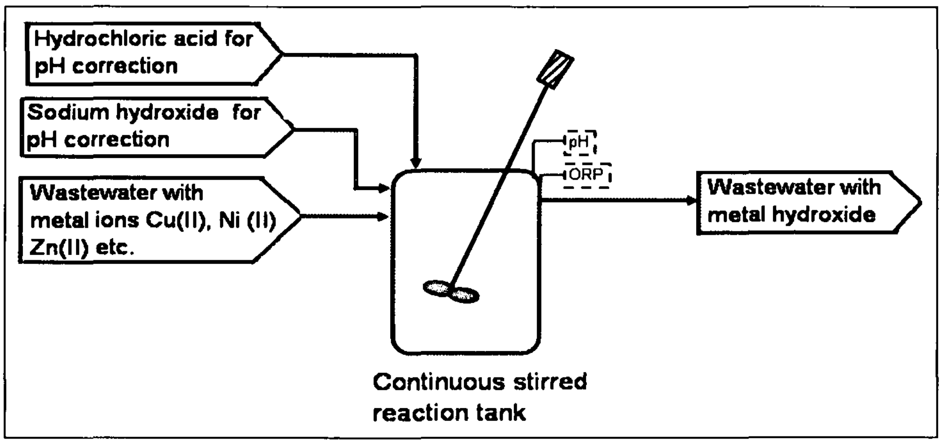

Figure 5.3: Nickel, copper, zinc, or cadmium treatment process [18].

The design equation of a reaction tank is as follows [24]:

$$V = \frac{F_{M^{2+}} X_{M^{2+}}}{-r_{M^{2+}}} \qquad \text{..........................(5.4.1)}$$

Where: V = volume of the tank (m^3)
$F_{M^{2+}}$ = flowrate of metal ion of concern (kg/s)
$X_{M^{2+}}$ = conversion of metal ion of concern
$-r_{M^{2+}}$ = reaction rate

The reaction when sodium hydroxide is used to precipitate metal ions is as follow [18]:

$$M^{2+} \;+\; 2NaOH \underset{k_{reverse}}{\overset{k_{forward}}{\Leftrightarrow}} M(OH)_2 \;+\; 2Na^{+} \qquad \text{..............(5.4.2)}$$

Where: M is a metal specie

The optimum treatment conditions for each are metal specie is [18,36,28,29].

- *Nickel optimum treatment pH is 10.58*
- *Copper optimum treatment pH is 8.5*
- *Zinc optimum treatment pH is 10*
- *Cadmium optimum treatment pH is 11*

For mixed metal stream an optimum pH of 9 can be used [15,31]:

The reaction rate precipitation of metal ions is:

Assuming the reaction is maintained at an optimum pH where the forward reaction is favored and is elementary. The reaction rate is equal to the solubility constant.

$$-r_{M^{2+}} = k_{forward}\left[M^{2+}\right]\left[NaOH\right]^2 \qquad \text{..........................(5.4.3)}$$

5.4.2 Development of a mathematical model to predict the metal precipitation

Substituting the rate expression (5.4.3) into the design equation (5.4.1) of the reaction tank (CSTR), yields the following expression:

$$V = \frac{F_{M^{2+}}X_{M^{2+}}}{k_{forward}\left[M^{2+}\right]\left[NaOH\right]^2} \qquad \text{..........................(5.4.4)}$$

Substituting initial conditions using stoichiometric balance, *refer to Appendix B, table 9.4,* yield the following expression:

$$V = \frac{F_{M^{2+}}X_{M^{2+}}}{k_{forward}\left[M^{2+}\right]^3(1-X)\left(\Theta_{M^{2+}/M^{2+}}-2X\right)^2} \qquad \text{..........................(5.4.5)}$$

The conversion ($X_{M^{2+}}$) can be determined by trial and error method. Rearrange the above expression :

$$(1-X)\left(\Theta_{NaOH/M^{2+}}-2X\right)^2 = \frac{F_{M^{2+}}X_{M^{2+}}}{k_{forward}\left[M^{2+}\right]^3 V} \qquad \text{..........................(5.4.6)}$$

The space time (residence time) is given by substituting this expression

$$F_{Cr^{6+}} = Q\times\left[M^{2+}\right] \qquad \text{..........................(5.4.7)}$$

Q = flowrate of wastewater

$\left[M^{2+}\right]$ = concentration of metal ions in the feed.

Substituting expression (5.4.7) into expression (5.4.5) gives the following expression,

$$\tau = \frac{X_{M^{2+}}}{k_{forward}\left[M^{2+}\right]^{2}(1-X)\left(\Theta_{M^{2+}/M^{2+}}-2X\right)^{2}} \qquad \text{..........................(5.4.8)}$$

This is a mathematical model to predict the precipitation of metal ions.

5.4.3 Typical applicability of the model

The application of this model is the same as the one discussed for the chromium (III) precipitation. Expression (5.4.6) can be solved by trial and error method. The conversion from expression (5.4.6) is used to determine the residence time.

A typical case scenario is a cyanide free wastewater from single cupper rinse water. This waste has 50 mg/L of copper and a flow at 1000 L/hr. Sodium hydroxide is added in the precipitation tank to adjust the pH to 10.

Use equation (5.4.6) to determine the conversion of copper (II) to copper hydroxide. This equation is a third degree polynomial which can be solved by trial and error method.

The following solutions have been generated from the trial and error method:

Assumed X (conversion)	**LHS**	**RHS**
0.85	1.35E-02	2.68E-03
0.9	4.00E-03	2.83E-03
0.9732	7.70E-05	3.06E-03

Table 5.2: Sample of the trial and error solution for copper (II) conversion to copper hydroxide.

From the above table 5.4.1, it can be seen that the solution is between 0.85 and 0.9.

5.5 COAGULATION AND FLOCCULATION

5.5.1 Reaction mechanism, rate laws and equipment design equation

For the purpose of the study, only the alum reactions are considered since alum is the most used coagulant. Alum in water hydrolyzes form aluminum hydroxide flocs, which are slightly gelatinous in nature. These flocs trap colloidal matter in water forming large flocs. Alum reacts in a series of reactions with water. Equation 5.5.1 shows an overaal reaction for alum hydrolysis [25]:

$$Al_2(SO_4)_3 + 6H_2O \underset{k_{reverse}}{\overset{k_{fforward}}{\Longleftrightarrow}} 2Al(OH)_3 \downarrow + H_2SO_4 \qquad \text{............(5.5.1)}$$

It hydrolysis as this:

$$Al^{3+} \xrightarrow{k_1} Al(OH)^{2+} \xrightarrow{k_2} Al(OH)_2^{+} \xrightarrow{k_3} Al(OH)_3 \xrightarrow{k_4} Al(OH)_4^{-} \qquad \text{........(3.5.2)}$$

Assuming that the pH of the water is maintained at a pH value that favors the formation of aluminum hydroxide, that is pH slightly above 7.5. The rate of hydrolysis affects the formation of flocs in the way that before flocs are formed once aluminum hydroxide is formed. The rate of conversion of alum to alum hydroxide can be described by this expression (3.5.3):

$$\frac{d[Al_2(SO_4)_3]}{dt} = k[\,[Al_2(SO_4)_3] - [Al(OH)_3]\,] \qquad \text{....................(3.5.3)}$$

This reaction takes place in a tank considered a CSTR with the following a design expression [24]:

$$V = \frac{F_A X_A}{-r_A} \qquad \text{....................(3.5.1)}$$

Where V = volume of the tank (m^3)

F_A = flowrate of Specie alum (kg/s)

X_A = conversion of alum.

$-r_A$ = reaction rate of alum (concentration per time)

Substituting the rate expression (3.5.3) into expression (3.5.1) yields the following expression.

5.5.2 Development of a mathematical model to predict the metal precipitation

$$V = \frac{F_{Alum} X_{Alum}}{k\left[[Al_2(SO_4)_3] - [Al(OH)_3^2][H_2SO_4]\right]} \quad \text{.................(5.5.2)}$$

Assuming the pH is perfectly maintained at an optimum pH favoring the forward reaction of formation of alum hydroxide.

Substitute the initial conditions i.e. feed conditions in to the above expression (5.5.2) using stoichiometric table given in appendix B, table 9.4. The above expression becomes:

$$V = \frac{F_{Alum} X_{Alum}}{k\left[[Al_2(SO_4)_3]_{init}(1 - X_{Alum})\right]} \quad \text{..................(5.5.3)}$$

Flocculation

The above expression can predict the size of the coagulation tank required and the time required for effective coagulation.

Flocculation precedes coagulation. Flocculation takes place in a slowly stirred tank. In this tank there is no reaction taking place, only adsorption takes place of precipitates to grow them into settle-able flocs[29,37].

$$q_e = \frac{\left(c_{init} - c_{equili}\right)v_{solution}}{m_{sorbent}} \qquad \text{.....................(5.5.4)}$$

Where: S = amount of the added sorbent on the dry basis (g)

c_{init} *and* c_{equil} = initial and equilibrium (residual) concentration of the sorbate in solution, respectively

V = volume of waste contacted with the sorbent (L)

m = mass of adsorbent (g)

Assuming that the adsorption of chromium hydroxide follows the Freundlich isotherm. The Freundlich isotherm equation 3.5.4 becomes[29,37]:

$$q_e = K_f C_{equil}^{1/n} = \frac{mass\ adsorbate\ (kg)}{mass\ adsorbent\ (kg)} = \frac{mass\ Cr(OH)_3\ adsorbed}{mg\ Al(OH)_3} \qquad \text{........(5.5.4)}$$

Hence:

$$K_f\ C_{equil}^{1/n} = \frac{\left(c_{init} - c_{equil}\right)V_{solution}}{m_{sorbent}} \qquad \text{.........................(5.5.5)}$$

Where: C_{equil} = initial and equilibrium (residual) concentration of the sorbate in solution, respectively

K_f = Freundlich capacity factor (mg adsorbate/ g adsorbent)(L/ mg adsorbate)$^{1/n}$

$1/n$ = Freundlich intensity parameter

To determine C_{equil} (i.e.the exit concentration of chrome in water) rearrange the above equation (5.5.5) to give the following expression:

$$K_f\ m\ C_{equil}^{1/n} \quad + \quad V\ C_{equil} \quad = \quad V\ C_{init} \qquad \text{...........................(5.5.6)}$$

The left hand side in the above expression (5.5.6) must be equal to the right hand side:

The boundaries of C_{equil} are:

$$0 \leq C_{equil} \geq C_{init}$$

Considering the removal of chromium hydroxide flocs

Mass of chromium hydroxide removed is:

$$M_{Cr(OH)_3}\ removed = q_e \times mg\ Al(OH)_3 \qquad \text{..........................(5.5.7)}$$

5.6 SEDIMENTATION

5.6.1 Empirical settling characteristics

For the purpose of this study, the Hazen's equation has been used [26,28]:

$$v = 60.6\frac{(\rho_s - \rho)}{\rho}\times\frac{3T + 70}{100}d \qquad \text{........................ (3.5.5)}$$

The rate of settling of particle can be determined from this expression (3.5.5). The rate of settling can be used to determine the residence time required for the parcticle.

The residence time of particle of this size is determined as follow [26,28]:

$$\mathrm{Re}\,sidence\ time = t_R = \frac{H}{v} \qquad \text{..........................(3.5.6)}$$

The solid mass balance around the settler is:

$$M_{ini} - M_{aett} = M_{out} \qquad \text{(5.6.1)}$$

Using volumetric flow and concentration to represent mass in equation (5.6.1) yields the following expression:

$$Q_{in} C_{in} - v.A_{s,sett}.C_{in} = Q_{out}\, C_{out} \qquad \text{(5.6.2)}$$

The output mass from the settler is equal to the inlet mass minus the mass of settled solids, therefore the above expression becomes:

$$Q_{in} C_{in} - v.A_{s,sett}.C_{in} = \left(Q_{ini} - \frac{v.A_{s,sett}.C_{in}}{\rho_{solids}} \right) C_{out} \qquad \text{(5.6.3)}$$

Rearranging the above expression (5.6.3) yield an expression for output concentration from the settler:

$$C_{out} = \frac{Q_{in} C_{in} - v.A_{s,sett}.C_{in}}{\left(Q_{ini} - \frac{v.A_{s,sett}.C_{in}}{\rho_{solids}} \right)} \qquad \text{(5.6.4)}$$

5.6.2 Typical applicability of the model

Assuming that waste from the flocculation tank has agglomerated flocs with a diameter of 0.001cm, and the density of flocs is 2419.99 g/L. The settler height is 9m.

Feed data required as input to the model:

a) ρ_s = 2419.99 g/L

b) ρ = 998 g/L

c) $T = 25\ ^{O}\mathrm{C}$

d) $d = 0.001\mathrm{cm}$

e) $H = 9\ \mathrm{m}$

Using Hazen's equation (3.5.5) of sedimentation to predict the settling rate.

$$v = 60.6\frac{(2419.99 - 998)}{998} \times \frac{3 \times 25 + 70}{100}(0.00001)$$

$$v = 0.00117\ m/s$$

The residence time of particle of this size is:

$$t_R = \frac{9}{0.00117}$$

$$t_R = 7692.308\ s = 2.14\ h$$

The out put concentration of the overflow can be determined from equation (5.6.4).

5.7 CONCLUSION

This chapter has illustrated the models of chrome pre-treatment, metal ions precipitation reactions processes, agglomeration of flocs and settling. Typical cases where the model can be applied have also been presented in this chapter. Integrated models are simulated in Mat-Lab in chapter 6.

CHAPTER 6- RESULTS AND DISCUSSION

This chapter presents Mat-Lab simulation of mathematical models. The models of pH adjustment shows how caustic requirements change with changing pH of wastewater. Mathematical models of treatment of cyanide, chromium, iron, copper, zinc and nickel are presented in this chapter. All models are presented using typical case scenarios in the treatment process.

6.1 INTRODUCTION

The mathematical models presented in this thesis were programmed using Mat-Lab. This chapter presents the results of the basic mathematical models. Typical wastewater conditions were used as input to the model. The composition of wastewater was varied in typical ranges that were referenced from literature.

The impact of variations in input conditions, concentrations, compositions, time, flowrates etc, is illustrated in the models. The impact of these variations on treatment efficiencies is illustrated in a form graphs. In overall this chapter illustrates the importance of the models by illustrating the following:

- Treatment efficiencies at varying wastewater composition or hardware size.
- Treatment reagent required at varying feed waste composition or treatment hardware size.
- Time required for treatment at varying feed waste composition or treatment hardware size.
- Optimum treatment condition at varying feed waste composition or treatment hardware size.

6.2 pH ADJUSTMENT

The first model that is shown is the pH adjustment model. The simulation shows the relationship between caustic amount required and the pH of wastewater. The simulation also shows how the pumping requirements increase with the strength of caustic solution.

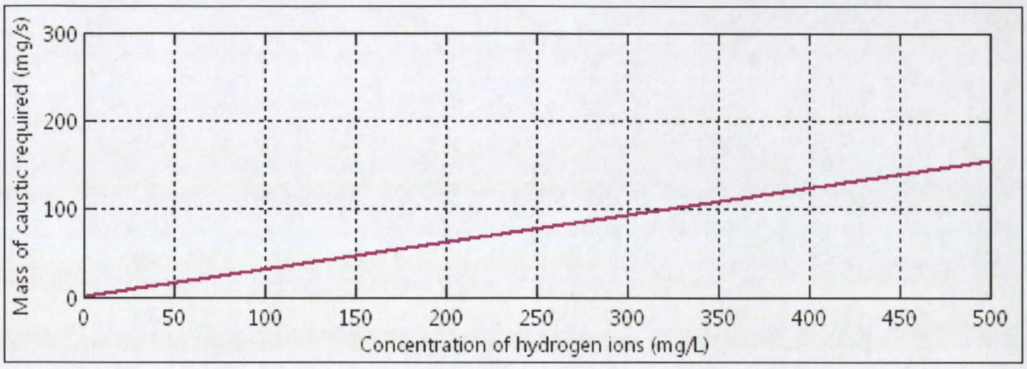

Figure 6.1: Caustic required with changing concentration of hydrogen ions

Figure 6.1, shows the relationship of caustic mass with hydrogen ions concentration in typical wastewater. From this plot, it is evident that the amount of caustic required increases with the increases in hydrogen ions, showing a linear relationship.

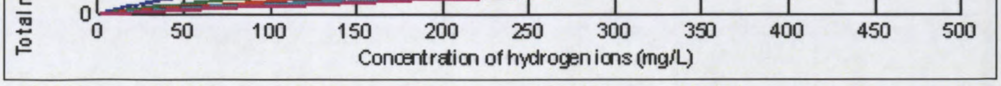

Figure6.2: Impact of caustic strength on the dosing requirements

Figure 6.2, shows the Mat Lab results for treating a varying acid wastewater (load and acidic strength) using various concentrations of caustic This relationship shows that the caustic flowrate is high for 10% wt NaOH and minimum for 50% wt NaOH. The discrepancy in the amount of caustic stream flowrate that is required at different %wt solution decreases between 30% and 50% wt NaOH. This shows that using low concentration of caustic can results in high pumping requirements. The 30% solution is optimum, since high concentrations can results in corrosion of process equipments.

The pH adjustment model can be seen to respond logically to the varying inputs wastewater conditions. Hence the model can be used to predict required amounts of caustic or acid for pH adjustment, based on the condition of input waste.

6.3 CYANIDE TREATMENT MODEL

Cyanide is treated by sodium hypochlorite. The treatment involves cyanide oxidation. This reaction is favored by high pH. The composition of wastewater from metal finishing industry is inconsistent. The following simulation represents the experiences that can take place in the treatment process. Figure 6.3 below illustrates the response of the model to changing wastewater composition.

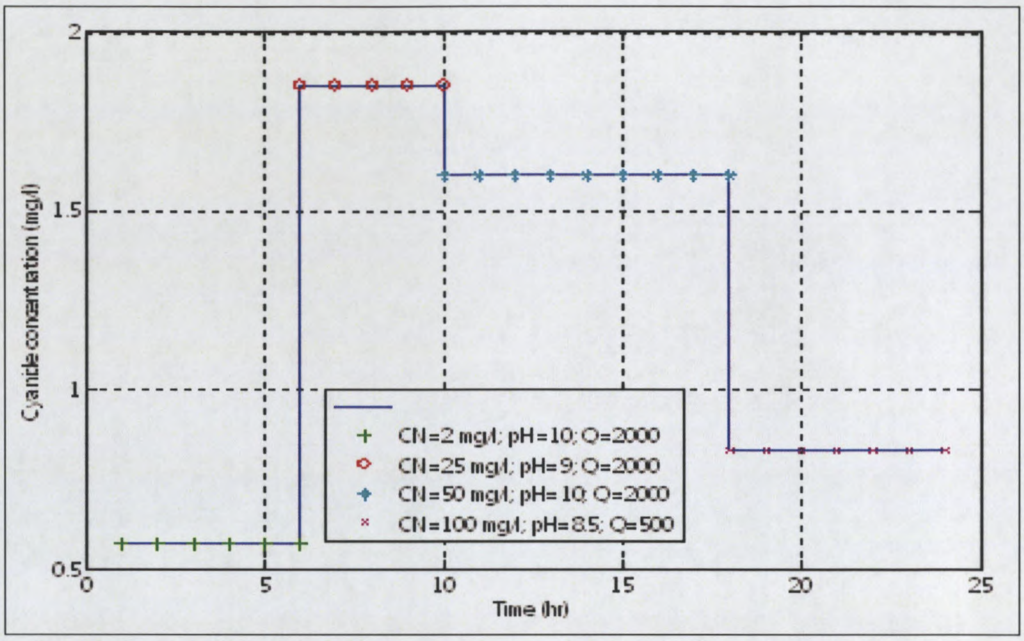

Figure 6.3: Variation of cyanide output concentration with time at different feed conditions

Figure 6.3 illustrates cyanide treatment over a period of a day. It was assumed that various changes are experienced in terms of the incoming wastewater over the day's operations. For the first five hours the incoming wastewater flowrate was 2000 L/hr, pH was 10 and cyanide concentration was 2 mg/L. From the figure 6.3, it can be seen that the output cyanide concentration was 0.6 mg/L. Thus, it can be stated that the plant was effective during that time.

After the first five hours, the feed wastewater concentration of cyanide changed to 25 mg/L. The pH also changed to 9.0 with the flowrate constant at 2000 L/hr. These conditions remained unchanged for the five hours. The output cyanide concentration was 1.8 mg/L. The effectiveness of the process decreased at such condition. The plant was ineffective at these conditions.

A step change in concentration is experienced after ten hours but the flowrate of wastewater remained unchanged. The concentration of cyanide changed to 50 mg/L and the pH changed to 10. These conditions remained unchanged for eight hours. At these conditions, the effectiveness improves than that of the late conditions due to increase in pH. The plant is ineffective since the output concentration of cyanide is greater than 1 mg/L.

After the eighteen hours, the composition of wastewater changed to a flowrate of 500 L/hr, 100 mg/L cyanide concentration and pH of 8.5. These conditions persist for six hours. The treatment efficiency improved at these conditions.

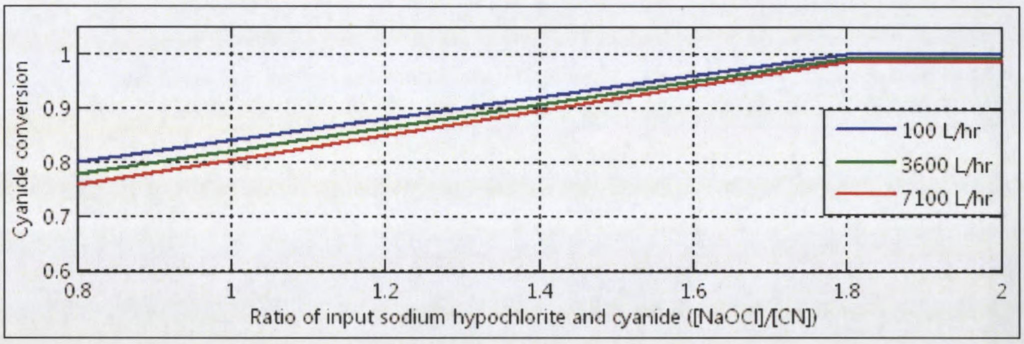

Figure 6.4: Variation of cyanide conversion with changing feed ratio of NaOCl/CN at different wastewater flowrates, pH=9.0 and [CN] =150 mg/L

Figure 6.4, shows the variation of cyanide conversion with changing ratio of NaOCl/CN at different wastewater flowrates. The pH is kept constant at 9.0. The feed concentration of cyanide is kept constant at 150 mg/L. The wastewater flowrate varies from 100 to 7100 L/hr at intervals of 3500 L/hr. The cyanide conversion increases with increasing ratio of NaOCl/CN. The conversion reaches one (1) at the ratio of 1.8 for all flowrates. This shows that there would be an excess sodium hypochlorite if the feed ration of NaOCl/CN increases beyond 1.8. Therefore a ration of 1.8 is sufficient for effective oxidation of cyanide.

The conversion decreases with increasing flowrate. The decrease in conversion is shown by taking a fixed NaOCl/CN dose and pH at different flowrates. The decrease in conversion with increasing flowrate is due the decrease residence time of wastewater inside the reactor.

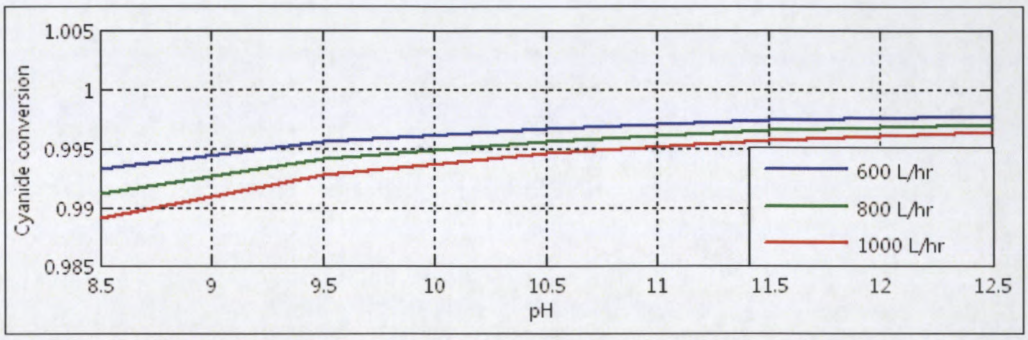

Figure 6.5: Variation of cyanide conversion with changing pH at different wastewater flowrates input NaOCl/CN= 1.2 and [CN] =150 mg/L

Figure 6.5, shows the relationship of pH with cyanide conversion at different wastewater flowrates. Cyanide feed concentration and ration of NaOCl/CN are constant at 150 mg/L and 1.2, respectively. The flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The pH varies from 8.5 to 12.5. Cyanide conversion increases with increasing pH. The increase of conversion with increasing pH is due to the high reactive specie of sodium hypochlorite (i.e. hypochlorous specie) that forms at high pH. At low pH the dominant specie of sodium hypochlorite is the hypochlorite specie. The hypochlorite specie is less reactive than the hypochlorous specie.

The cyanide conversion decreases with increasing flowrate. The decrease in cyanide conversion with increasing flowrate is shown by taking a fixed pH for different flowrates. This is due to the decrease in residence time with increasing flowrate.

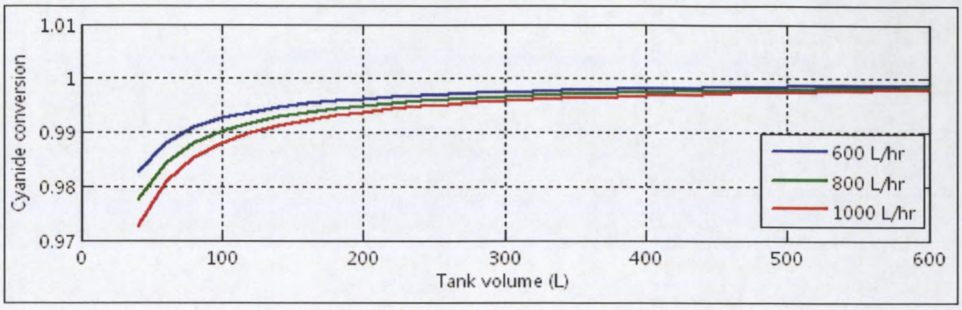

Figure 6.6: Variation of cyanide conversion with changing volume of treatment tank at different wastewater flowrates, pH=9.0 and feed ratio of NaOCl/CN =1.2 and feed [CN] =150 mg/L

Figure 6.6, shows the variation of cyanide conversion with changing reaction tank volume at different wastewater flowrate. The tank volume is varied from 50 to 600 L. Input cyanide concentration is kept constant at 150 mg/L. the ratio of NaOCl/CN is constant at 1.2 and the pH is 9. The cyanide conversion increases with increasing tank volume. The wastewater residence time in the treatment tank decreases as the flowrate increases, thus resulting in reduced treatment efficiencies.

The model of cyanide responds in accordance with literature. The model provides a prompt alert to a process operator that indicates the composition of final effluent from input conditions.

6.4 IRON TREATMENT MODEL

Iron is treated by aeration at slightly alkaline pH. The optimum pH of iron treatment is 7.5. Wastewater from metal finishing industry is inconsistent. The following simulation represents the experiences that can take place in the treatment process. Figure 6.7, below illustrates the response of the model to changing wastewater composition.

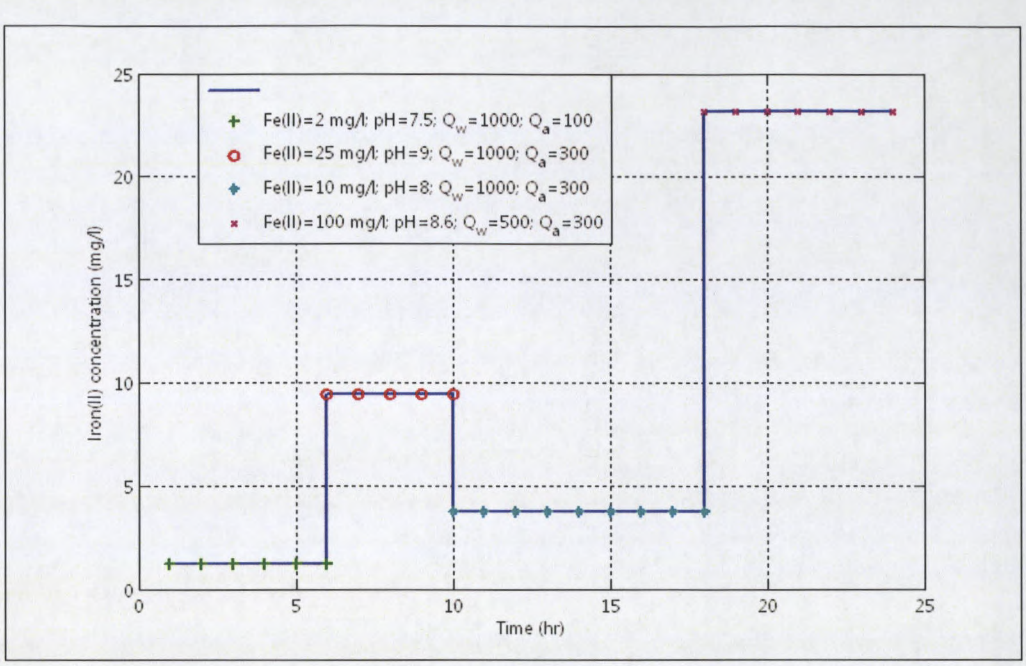

Figure 6.7: Variation of iron (II) output with time

Figure 6.7 illustrates iron treatment over a period of a day. It was assumed that various changes are experienced in terms of the incoming wastewater over the day's operations. For the first five hours the incoming wastewater flowrate was 1000 L/hr. The air flowrate was set in proportion to the concentration of iron (II) in the input wastewater. During the first five hours of the day iron concentration was 2 mg/L and the air flowrate was 100 L/hr. The pH of wastewater was 7.5. At such input wastewater compositions and air flowrate the output concentration of iron (II) is greater that 1 mg/L .Thus it can be stated that the treatment plant was not effective. This may point out that the air flowrate needs to be increased so as to increase the plant effectiveness.

After the first five hours, the composition of input wastewater changed. The iron (II) concentration increased to 25 mg/L, pH was 9. The flowrate of wastewater remained at 1000 L/hr. The flowrate of air changed to 300 L/hr, to compensate the increase in iron(II) concentration. The treatment plant was not effective since the output ion was more than 1 mg/L. This means the air flowrate must be increased more than 300 L/hr or residence time of wastewater must be increased.

After ten hours, the concentration of iron (II) in the feed wastewater decreased to 10 mg/L. The wastewater flowrate remained unchanged at 1000 L/hr at a pH of 8. The flowrate of air was set at 300 L/hr. The output concentration of iron (II) is 4 mg/L, showing that the plant effectiveness could increase if the flowrate of air is increased beyond 300 L/hr. Since the output concentration of iron (II) is greater that 1 mg/L the plant at these conditions is ineffective. Therefore, necessary adjustment must be conducted before wastewater exit the treatment plant. These adjustments include increasing air flowrate and changing residence time of wastewater.

In the last 6 hours of the day the flowrate of wastewater decreased to 500 L/hr and the pH changed to 8.6. The air flowrate remained unchanged at 300 L/hr while a dramatic increase iron (II) concentration was experienced. The iron concentration increased to 100 mg/L. At such input wastewater composition the effectiveness of the plant decrease drastically. This shows that there are required adjustments that need to be conducted to increase plant effectiveness.

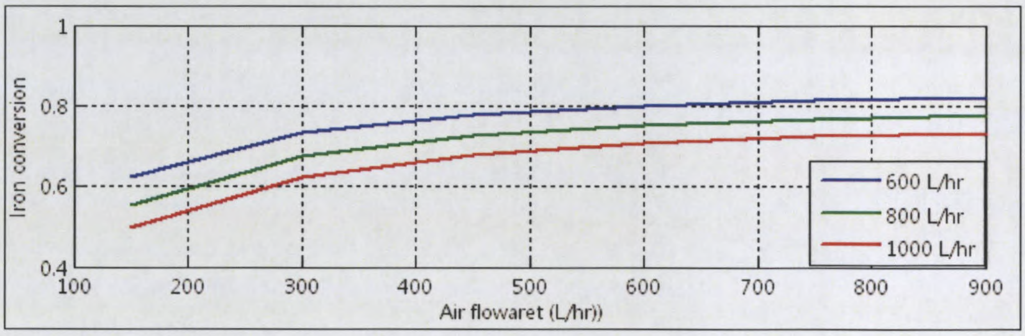

Figure 6.8: Variation of iron (II) conversion with changing air flowrate at different wastewater flowrates, feed iron concentration = 150 mg/L and pH=8.5

Figure 6.8, shows the relationship of iron conversion with air flowrate at different wastewater flowrates. The feed flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The air flowrate changes from 150 to 900 L/hr. The pH and feed iron concentration are 8.5 and 150 mg/L, respectively. The conversion increases with an increase in air flowrate. The conversion decreases with increasing flowrate at constant pH and feed iron concentration.

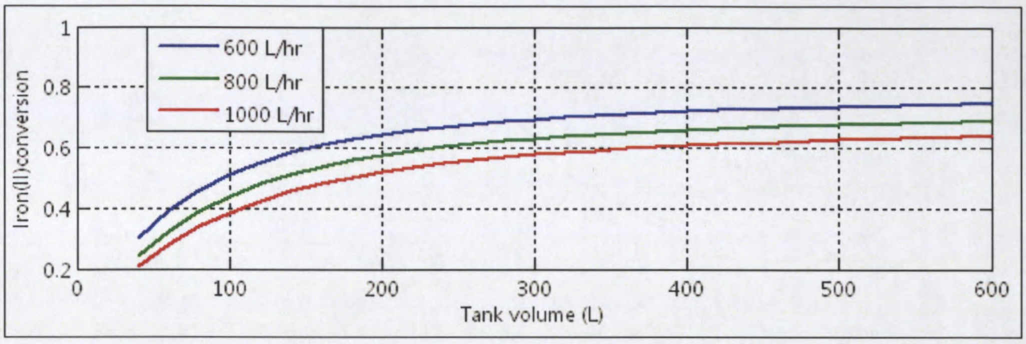

Figure 6.9: Variation of iron (II) conversion with changing tank volume at different flowrates, feed iron concentration =150 mg/L, pH =8.5, air flowrate=300 L/hr

Figure 6.9, shows the variation of iron (II) conversion with tank volume at different wastewater flowrates. The tank volume is varied from 50 to 600 L. Input iron concentration is150 mg/L, air flowrate is 300 L/hr and the pH is 8.5. The iron conversion increases with increasing tank volume. The wastewater residence time is low at small tank volume, thus the reaction time is not sufficient for optimum conversion of iron(II). From this it can be concluded that the low concentration will require smaller size tank than high concentrations.

The conversion decreases with increasing wastewater flowrate. The decrease of conversion with wastewater can be shown in the above figure 6.3 by taking a fixed point of tank volume at different wastewater flowrates. The model shows the size of the treatment unit that is ideal for wastewater with such characteristic.

6.5 CHROMIUM TREATMENT MODEL

Chrome wastewater form metal finishing has high levels of soluble chromium (VI). Chromium (VI) is treated by reduction with metabisulphite reagent. The reaction is favored by acidic pH. Usually, sulfuric acid is used to decreases the pH to 2.6. The wastewater from the metal finishing industry is inconsistent. The following simulation represents the experiences that can take place in the treatment process. Figure 6.10 below, illustrates the response of the model to changing wastewater compositions.

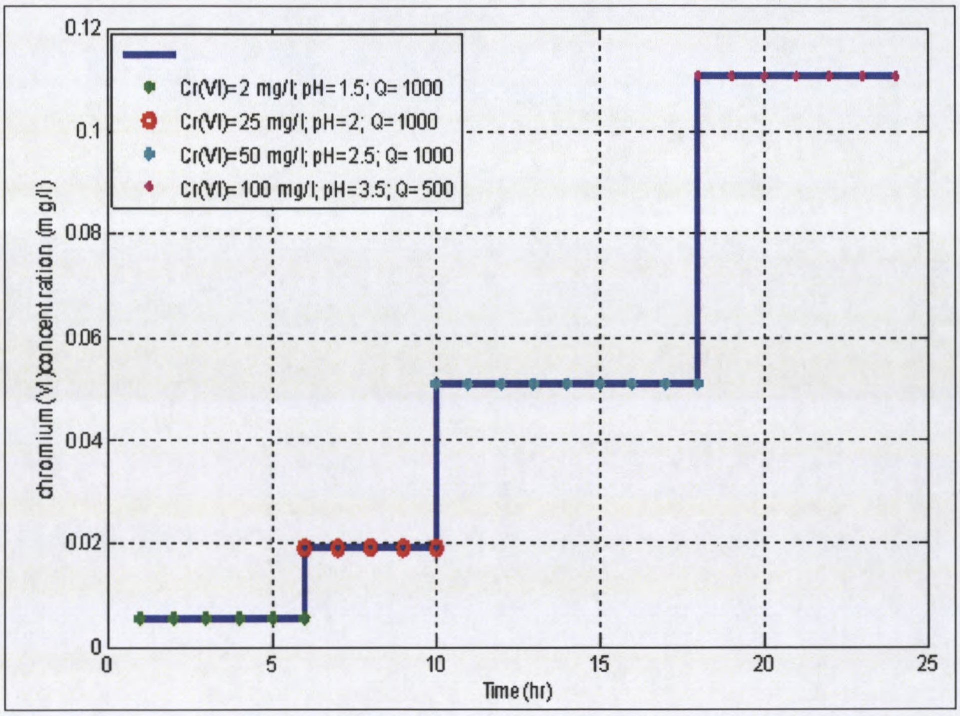

Figure 6.10: Variation of chromium (VI) conversion output with time

Figure 6.10 illustrates chromium (VI) treatment over a period of a day. It was assumed that variations are experienced in terms of the incoming wastewater over the day's operations. For the first five hours the incoming wastewater flowrate was 1000 L/hr, pH was 1.5 and chromium (VI) concentration was 2 mg/L. From figure 6.10, it can be concluded that the output wastewater concentration was less tan 0.001. Thus it can be stated that the plant was effective.

After the first five hours the concentration of chromium (VI) in the feed wastewater changed to 25 mg/L. The flowrate remained unchanged at 1000 L/hr, at a pH of 2. These conditions remained unchanged for the five hours. From figure 6.10, it can be concluded that the effectiveness of the plant decreased since the output chromium (VI) increased to 0.02 mg/L. The plant can be considered effective since the output chromium (VI) concentration is 0.02 mg/L which is less than 1 mg/L.

A step change in chromium (VI) concentration is experienced after ten hours but the flowrate of wastewater remained unchanged. The concentration of chromium (VI) changed to 50 mg/L and the pH changed to 2.5. These conditions remained unchanged for eight hours. At these conditions, the plant effectiveness decreased. The output chromium (VI) concentration increased to 0.05 mg/L. The plant can be considered effective since the output chromium concentration is less than 1 mg/L.

For the last eight hours of the day, the flowrate of wastewater change to 500 L/hr with a pH of 3 and chromium (VI) concentration of 100 mg/L. From figure 6.10 it can be seen that the plant effectiveness significantly decreased. The output chromium (VI) concentration increased beyond 0.1 mg/L. Even though the output concentration of chromium (VI) increase, the plant can be considered effective at these conditions, since the output concentration of chromium is less than 1 mg/L.

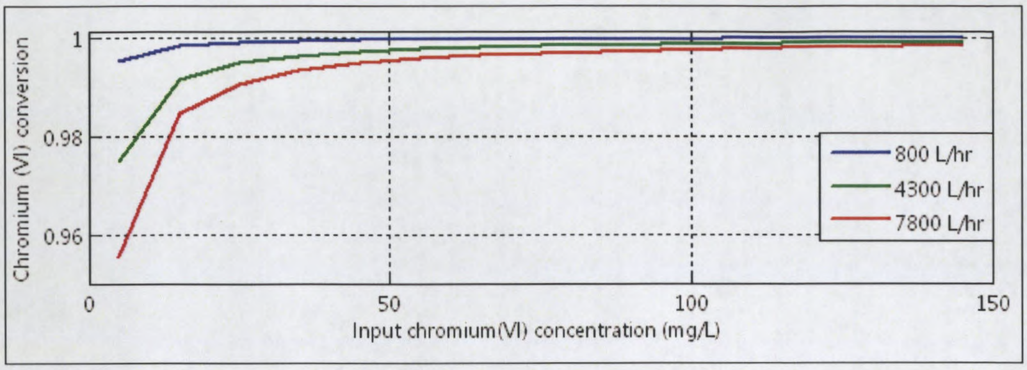

Figure 6.11: Variation of chromium (VI) conversion with changing input chromium (VI) at feed S (IV)/Cr (VI) =5, reaction pH= 2.5 and Temperature = 20 ^{o}C

Figure 6.11, shows the relationship of chromium (VI) conversion with changing feed chromium (VI) concentrations at different waste flowrates. Chromium (VI) varies from 5 mg/L to 150 mg/L. The pH and feed ratio of S (IV)/Cr (VI) are constant at 2.5 and 5, respectively. Wastewater varies from 800 to 7800 L/hr at intervals of 3500 L/hr. The conversion of chromium increases with increasing concentration of chromium (VI) in the feed wastewater. This is due to that the reaction rate is directly proportional to concentration of chromium (VI). At high chromium (VI) concentrations, the reaction rate is high and sufficient to give appreciable conversions at a given residence time. Whilst at low chromium (VI) concentration the reaction rate is not sufficient to give an appreciable conversion at a given residence time.

At constant chromium concentration, the conversion decreases with increasing flowrate. Low flowrate have sufficient time inside the reactor to have optimum conversion. High flowrate have less residence time resulting in low conversion.

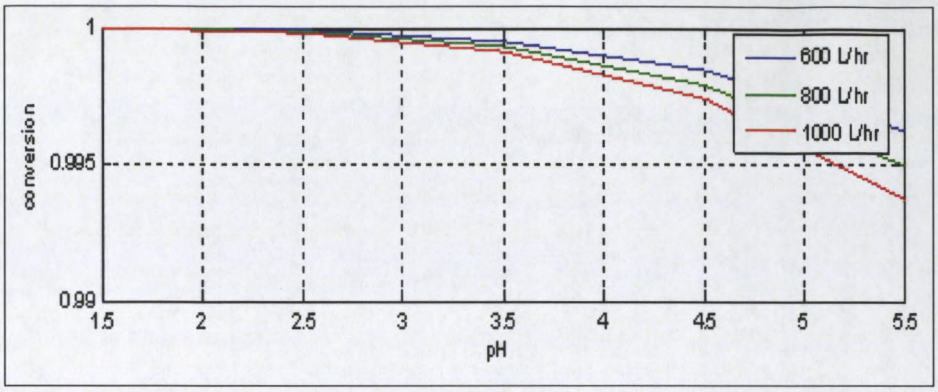

Figure 6.12: Variation of chromium (VI) with changing pH at different wastewater flowrate, ratio of metabisulphite to chromium (VI) =5, Temperature= 20 ^{o}C and input chromium (VI) = 150 mg/L

Figure 6.12, shows the relationship of chromium (VI) conversion with changing pH at different wastewater flowrates. The pH is varied from 1.5 to 5.5. Wastewater flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The concentration of chromium(VI) and ratio of S (IV)/Cr (VI) are constant at 150 mg/L and 5, respectively. Chromium conversion decreases with decreasing pH.. The conversion decreases with increasing wastewater flowrate.

6.6 COPPER TREATMENT MODEL

6.6.1 Copper Precipitation Model

Copper in metal finishing wastewater occur as divalent ions. These ions are removed by direct pH adjustment. The pH is adjusted to a minimum solubility point. At the minimum solubility point copper form copper (II) hydroxide precipitates. The optimum pH is 8.5.

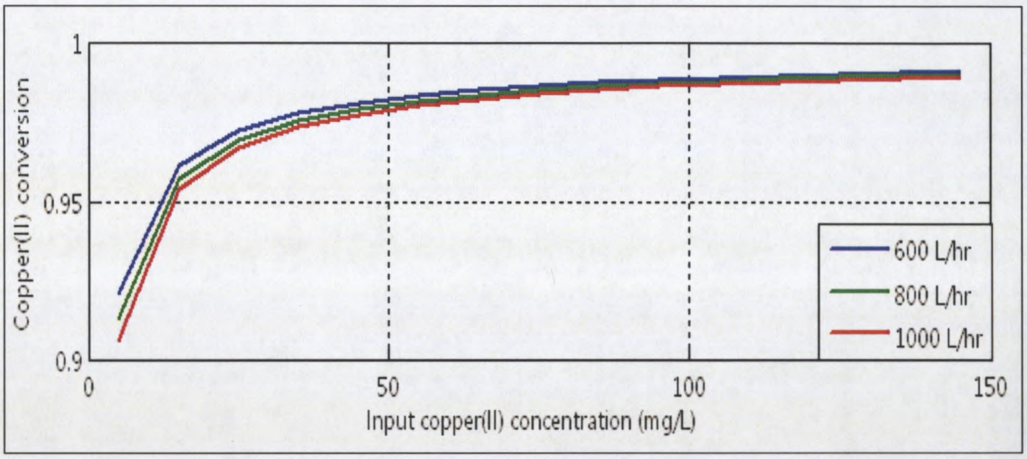

Figure 6.13: Variation of copper (II) conversion with changing feed copper (II) concentration at different wastewater flowrate and pH =8.5

Figure 6.13, shows the relationship of copper (II) conversion with feed concentration of copper (II) at different flowrates. The flowrate is varied from 600 to 1000 L/hr at intervals of 200 L/hr. Copper (II) concentration varies from 5 to 150 mg/L. The pH is constant at 8.5. The copper (II) conversion increases with increasing feed copper (II) concentration. The increase of conversion with increasing copper (II) concentration is due to that the reaction rate is directly proportional to concentration of copper (II). At high copper (II) concentrations, the reaction rate is high and sufficient to give an appreciable conversion at a given residence time. At low copper (II) concentration the reaction rate is not sufficient to give an appreciable conversion at a given residence time.

At constant copper (II) concentration, the conversion decreases with increasing flowrate. Low flowrates have sufficient time inside the reactor to have optimum conversion. High flowrates have less residence time resulting in low conversions.

6.6.2 Copper hydroxide flocculation

Small copper precipitate particles are agglomerated into big settable flocs by alum. Alum is added in water and quickly hydrolyzes to aluminum hydroxide. The optimum pH for alum is 8.5. The aluminum hydroxide is gelatinous, thus traps the small size precipitate of copper by adsorption. The adsorption of copper precipitates is described by the Freundlich model.

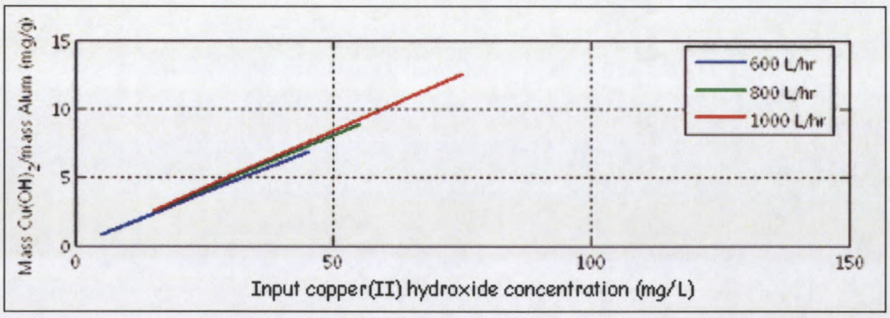

Figure 6.14: Variation of mass of adsorbate per mass of adsorbent (q_e) with changing concentration of copper hydroxide precipitate at different wastewater flowrates and alum dose of 2.5 mg/L

Figure 6.14, shows the relationship of copper (II) hydroxide concentration and amount of copper (II) hydroxide precipitate adsorbed by alum at different wastewater flowrates. Wastewater flowrate is varied from 600 to 1000 L/hr at intervals of 200 L/hr. The alum dose and pH are 2.5 and 8.5, respectively. The amount adsorbed by alum is directly proportional to the feed concentration of copper (II) hydroxide, shows a linear relationship. The amount adsorbed by alum increases with increasing wastewater flowrate. Low concentrations of copper (II) hydroxide at high flowrates require high alum doses.

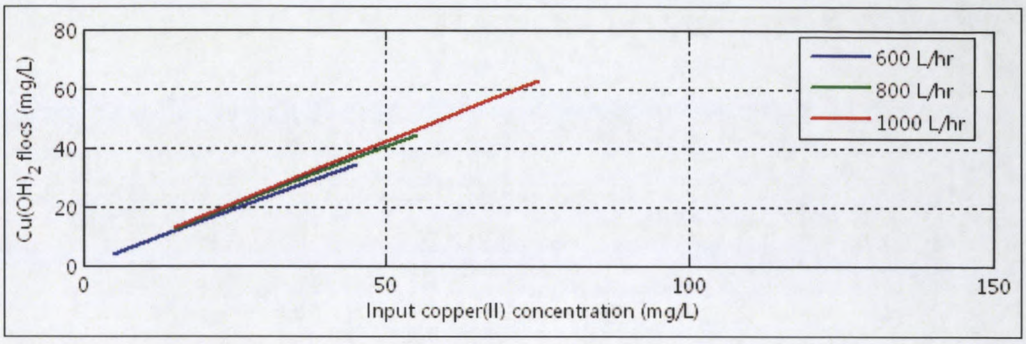

Figure 6.15: Variation of copper hydroxide flocs with changing concentration of copper hydroxide precipitate after flocculation at different flowrates and constant alum dose of 2.5 mg/L

Figure 6.15, shows the relationship of concentration of copper (II) hydroxide flocs and input copper hydroxide precipitate adsorbed by alum at different wastewater flowrates. Copper (II) hydroxide precipitate concentration varies from 5 to 150 mg/L. Wastewater flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The alum dose is constant at 2.5 mg/L. The concentration of copper (II) hydroxide flocs increase with increasing feed concentration of copper (II) hydroxide precipitate. The concentration of copper (II) hydroxide flocs increases with increasing wastewater flowrate.

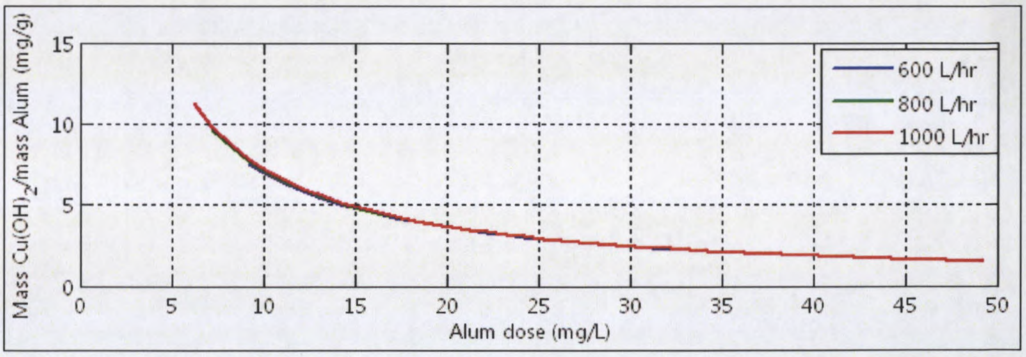

Figure 6.16: Variation of mass adsorbate per mass adsorbent with changing alum dose at different wastewater flowrate after flocculation at different flowrates

Figure 6.16, shows the variation in the mass of q_e (copper (II) hydroxide adsorbed per alum mass) with changing alum dose. The alum dose varies from 2.5 to 50 mg/L. There is no adsorption at low alum dosages. The flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The feed wastewater upstream had a concentration of 150 mg/L of copper (II) ions. The adsorption starts at an alum dose of 6 mg/L for the flowrate of 1000 L/hr. For the flowrates of 600 and 800 L/hr adsorption starts at an alum dose of approximately 7 and 9, respectively. The amount of copper (II) hydroxide precipitate adsorbed per gram of alum decreases with increasing dose.

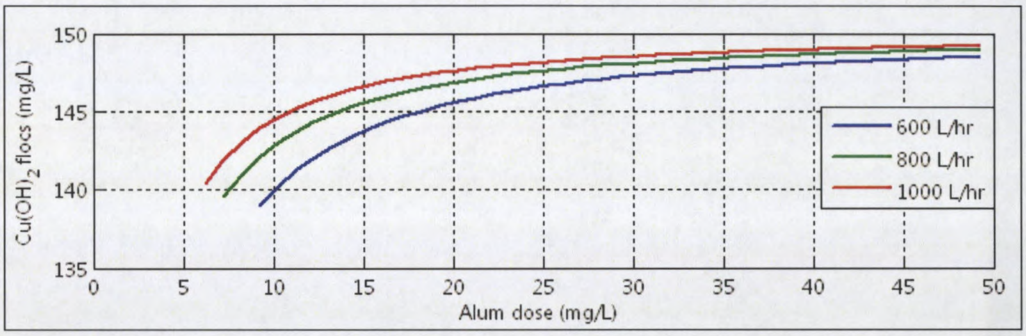

Figure 6.17: Variation of copper hydroxide flocs with changing alum dose at different flowrates

Figure 6.17, shows the variation of copper (II) hydroxide flocs with changing alum dose at different flowrates. The alum dose varies from 2.5 to 50 mg/L. The flowrate is varied from 600 to 1000 L/hr at intervals of 200 L/hr. The feed copper (II) ion upstream is 150 mg/L. The concentration of copper (II) hydroxide flocs increases with increasing alum dose. The concentration of flocs increases with increasing flowrate.

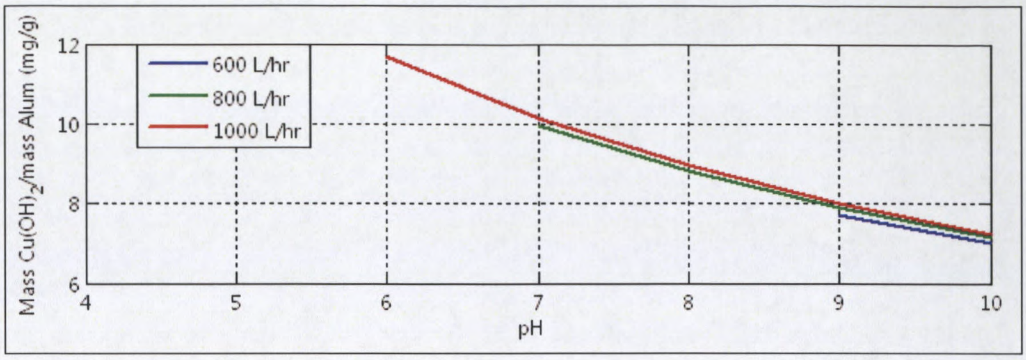

Figure 6.18: Variation of mass adsorbate per mass adsorbent with changing pH at different wastewater flowrate and alum dose = 2.5 mg/L after flocculation at different flowrates

Figure 6.18, shows the variation of q_e (mass of copper (II) hydroxide precipitate per mass of alum) with pH at different wastewater flowrates. The pH varies from 4 to 10 mg/L. The flowrate varies from 600 to 1000 L/hr at interval of 200 L/hr. The feed concentration of copper upstream is 150 mg/L .There is no adsorption at low pH between 4 and 6. The adsorption starts at a pH of 6 for wastewater flowrate of 1000 L/hr. For wastewater flowrates of 600 and 800 L/hr adsorption starts at a pH dose of 7 and 9, respectively. The amount of copper (II) hydroxide precipitate adsorbed per gram of alum decreases with increasing pH. Flocculation by alum is favored by high pH. Usually, a pH of 8.5 is used.

6.6.3 Copper hydroxide flocs settling

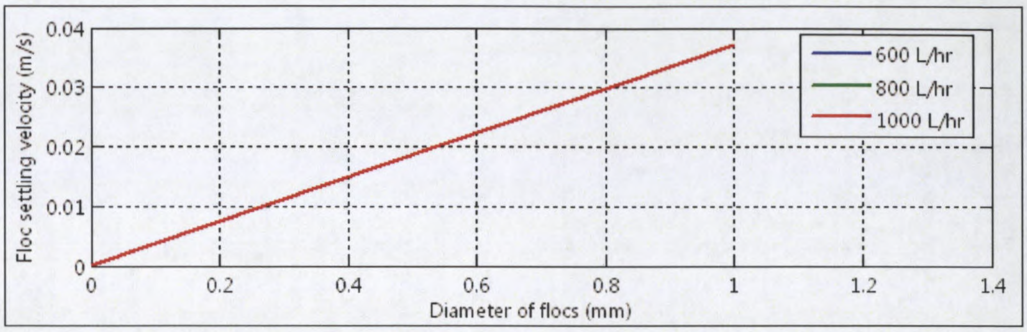

Figure 6.19: Variation of settling velocity with changing particle diameter (mm) at different flowrates and water temperature of 25 °C.

Figure 6.19, shows the variation of floc settling velocity with changing diameter of particles at different flowrates. The flowrate is varied from 600 to 1000 L/hr at intervals of 200 L/hr. The temperature of water is 25 °C. The diameter represents the size of the particle. The settling rate of flocs is independent of wastewater flowrate. The settling velocity is directly proportional to the size of particles. The settling velocity increases linearly with increasing particle size.

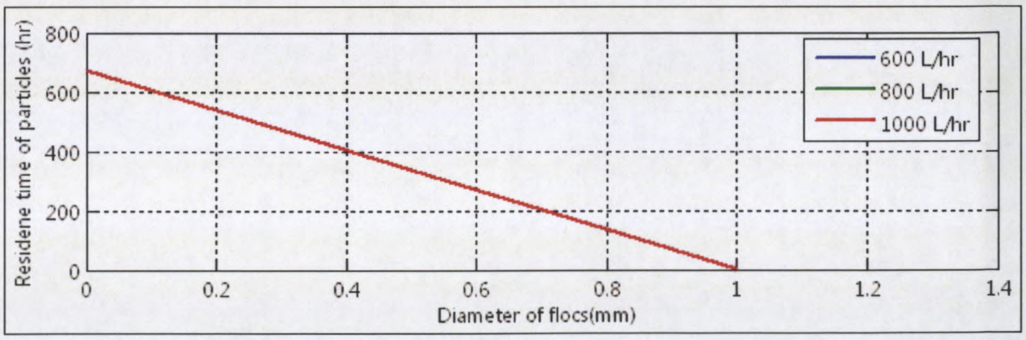

Figure 6.20: Variation of particle residence time with changing particle diameter (mm)

Figure 6.20, shows the variation of floc residence time with changing diameter (i.e. size) of particles at different flowrates. The flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The temperature of water is 25 °C. The floc residence time is independent of wastewater flowrate. The residence time is inversely proportional to particle diameter. The floc residence time decreases linearly with increasing particle diameter.

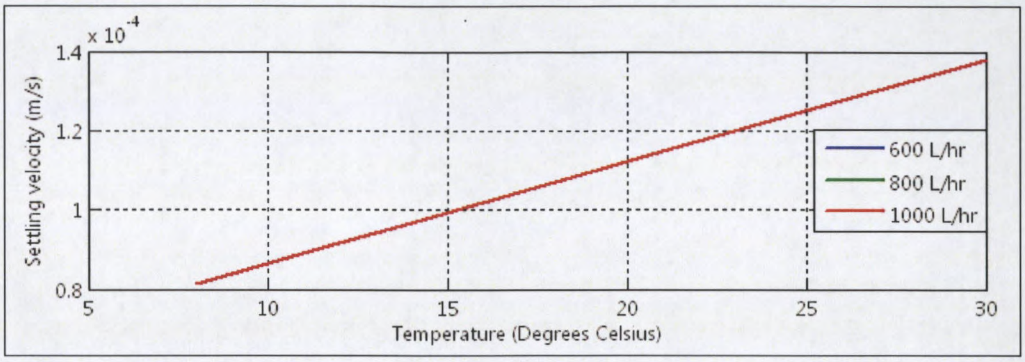

Figure 6.21: Variation of settling velocity with changing water temperature

Figure 6.21, shows the variation of floc settling velocity with changing temperature of water at different flowrates. The temperature of water varies from 8 to 30 ^{o}C. The flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The settling velocity of flocs is independent of wastewater flowrate. The settling velocity is directly proportional to the temperature of water. The settling velocity increases linearly with increasing temperature of water.

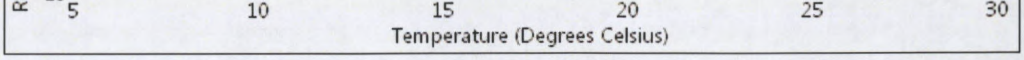

Figure 6.22: Variation of particle residence time with changing water temperature

Figure 6.22, shows the variation of floc residence time with changing temperature of water at different flowrates. The temperature of water varies from 8 to 30 ^{o}C. The flowrate varies from 600 to 1000 L/hr at intervals of 200 L/hr. The floc residence time is independent of wastewater flowrate. The floc residence time is inversely proportional to the water temperature. The floc residence time decreases linearly with increasing temperature.

6.7 CONCLUSION

The model is developed based on literature data and typical experiences in treatment plant. The model shows to respond rationally to the varying input data. The models may require fine tuning before being applicable to real plant situations. In overall, the models show an appreciable potential of predicting treatment efficiencies.

CHAPTER 7- CONCLUSSION AND RECOMMENDATIONS

This chapter provides an overall executive summary of this study. This chapter presents: the methodology followed in this research; findings; assumptions made in the development and limitation of the models is presented in this chapter.

7.1 SUMMARY

This study provides a generic mathematical model to assist in predicting treatment efficiencies of metal finishing wastewater. The models use feed wastewater characteristics and design configuration of process units to predict treatment efficiencies. The model allows the company to select relevant equipment, types of waste and optimum treatment conditions. Furthermore, the models allow for a variation in chemical concentrations since electro-platers release chemicals with inconsistent concentrations. An illustration of the models is presented in Mat-Lab in Chapter 6.

The Models are developed from literature values. Typical metal finishing wastewater compositions from literature is used to develop the models. Output results of the models observed from the Mat-Lab have a logic response to varying wastewater composition and treatment chemical doses.

Since the models are developed from literature values it is recommended that the model be validated with real plant data. This kind of validation will show the necessity of fine-tuning the models for their applicability to real plant situations.

7.2 RESEARCH METHODOLOGY

Mathematical models of conventional treatment of metal finishing wastewater are developed. The electroplating wastewater is selected for the development of the model. Literature data has been used to develop the mathematical model. The following is the set of data that has been collected and used:

- Reaction mechanisms and rate laws that are involved in the treatment of metal finishing wastewater.
- Design equations and process flow diagrams of the treatment plants.
- Typical characteristics of metal finishing wastewater.
- Optimum treatment conditions for different contaminants of the metal finishing wastewater.
- Alternative technologies for treating metal finishing wastewater.

The model is developed by combining the mass transfer kinetics that take place inside the process units and the design equation of the process units. Reaction rates data is not readily available for usage in literature hence engineering mathematic skills have been employed to deduce usable information. The model is validated by putting real plant data from literature and observing the response of the model.

7.3 DISCUSSION OF RESULTS

The simulation of models in Mat-Lab is presented in chapter 6. The following is deduced from model results:

- There is a significant relationship between caustic and the concentration of hydrogen ions. Caustic required is directly proportional to the hydrogen concentration in wastewater. The caustic strength is inversely proportional to the caustic required at constant concentration of hydrogen ions.

- The models have been tested for response to continuously changing composition of wastewater. The models have shown a sensible response to continuously changing wastewater composition. This shows that the models can be used to predict output conditions from input conditions.

- Treatment efficiencies have been evaluated with change doses of treatment reagents. Treatment efficiencies have shown to increase with increasing doses of treatment reagents. The increase in efficiency reaches an optimum efficiency, after which any further increase in the doses of treatment reagent results in no change in the efficiency. Similarly, treatment efficiencies have also shown to increase with the increasing metal ions in wastewater for a fixed volume of treatment tank. The increase in efficiency reaches an optimum point, after which any increase in the input concentration results in no change in the efficiencies and large amounts of un-reacted species in the output stream.

- The adsorption of metal precipitate by alum to form bigger and settleable flocs have been simulated. The results have shown the amount of precipitate that is absorbed increases with increasing alum dose. The increase reaches an optimum point at which any further increase results in no increases in the amount absorbed. The alum dose is dependent of the flowrate it increases with increasing flowrate. Alum has shown to work optimally at high pH of 8.5 to 9.

- It has been deduced from the sedimentation models that the settling rate increases with increasing size of particles and water temperature.

7.4 ASSUMPTIONS MADE IN THE DEVELOPMENT OF THE MODEL

7.4.1 Treatment equipments

The mathematical models of reaction tanks are developed based on the following assumptions:

- The reaction tanks are considered as continuous stirred tank reactors (CSTR).
- The mass is conserved from one process unit to the next
- Energy loss and gain is negligible.
- Complex and reversible reactions of metal precipitation are held at the optimum pH point that favors forward reactions i.e. the reaction rate is only a function of

the reactants. Precipitation reactions are considered to be elementary and stoichiometric amounts are fed in to the reaction tanks.

- The concentrations of species inside the reaction tank are equal to the concentrations in the output streams.
- Process equipment size is referenced from literature.
- Wastewater characteristics are referenced from literature.
- Coagulation is assumed to be a very quick reaction of hydrolysis of aluminum metal salt (Alum) forming gelatinous flocs. Alum is used in the model because it is reported to be the commonly used coagulant. The reaction is assumed to be elementary and dependant on the concentration of aluminum hydroxide. The hydrolysis reaction of alum is assumed to be carried in an optimum pH above 7.
- Flocculation is assumed to occur by adsorption of metal precipitate by gelatinous aluminum hydroxide which grows the metal precipitate into bigger flocs. The adsorption is assumed to follow Freudlich isotherm. The Freundlich isotherm is reported to characterize most adsorption processes rather well under conditions present in most water treatment systems. The shortfall of the Freundlich isotherm is that it fails to consider that there may be a limited amount of adsorption sites on the surface of the solid, the lack of further site may prevent adsorption under conditions in which equilibrium is reached.

Sedimentation tank that is used in the model is a vertical flow sedimentation tank, since this is a more typical sedimentation tank. To determine the settling rate of particles, a discrete particle is assumed i.e. the particle is not affected by other particles in the water. The discrete particle is assumed to be moving at a same horizontal speed as the water. The only forces acting on the particle is the gravity force and the frictional force opposing settling. The settling rate is determined using the Hazen's equation since it covers a wide range of particle size. Moreover the Hazen's equation includes temperature of water which plays a significant role in the settling rate. The performance of the settler is affected by the temperature during seasonal changes. The particles with settling velocity greater or equal to the settling rate of the average particle will settle.

7.4.2 Reaction conditions

The reaction of cyanide oxidation takes place in very alkaline conditions; typical pH is 10.5 with 1.5 ratio of cyanide to sodium hypochlorite. When sodium hypochloric acid is added in water it forms hypochlorite (OCl^-) and hypochlorous acid (HOCl). The former reacts with cyanide, the rate law and rate law constant reported in literature.

Chromium reduction is carried at a pH of 2.6. The industrial input ratio of sodium metabisulphite to hexavalent chromium is 5. The reaction rate is affected by the pH of the reaction. The rate expression that incorporates pH has been derived from the reaction data provided in literature.

Iron is treated in an aerated tank where air is supplied through diffuser. The air bubble size is equal to the diameter of the diffuser pores. The oxidation of iron is carried at a pH of 7.5. The equilibrium concentration of oxygen at a fixed temperature and pressure is a constant. The reaction rate of law and the rate constant are determined from literature. The concentration of dissolved oxygen is approximately zero and changes inside the reaction tank.

Precipitation reactions are assumed to be elementary with sodium hydroxide fed in stoichiometric amounts to the metal ions to be removed. The reaction mixture is assumed to be perfectly mixed and held at an optimum pH, to favor the forward reaction. The rate law constant is assumed to be equal to the solubility of metal hydroxide.

7.5 LIMITATION AND RECOMMENDATION OF THE MODELS

The applicability of the models to real situations is not overlooked. The difficulties in the applicability of the models are bound to exist, since the models are developed purely on literature data. The following are sources of the difficulties:

- The model is based on theoretical values.

- Precipitation reaction rate laws do not take into account the effect of pH. These reactions are modeled based on the assumption that they take place at optimized fixed pH.
- The effect of temperature is not taken into account in reaction rate laws of treatment of copper (II), iron (II), cyanide coagulation and flocculation.
- The iron reaction rate is dependent on pH but the model has been developed based on the rate that does not include pH dependency.
- The rate laws from literature might be different from the plant situation.
- The model of copper (II) precipitation has modern two solutions which sometimes are all close to one another. Mat-Lab model fails to run in cases where two solution.

The theoretical response of the model appears to be rational and logic. Hence, the models that are developed can be used to predict treatment efficiencies and effectiveness of metal finishing wastewater. Prior using the models for prediction of wastewater output, it is recommended that the model be validated with real plant data. The models may need to be fine-tuned to account for their limitations.

CHAPTER 8- REFERENCES

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CHAPTER 9- APPENDIX

This chapter presents all calculations, tables and figures that are relevant to the study. This chapter also shows engineering mathematical methods that have been applied in the development of mathematical models.

9.1 APPENDIX A - CALCULATIONS OF MATHEMATICAL MODELS

9.1.1 Model Development and Sample of Calculation

9.1.1.1 pH Adjustment

Assuming that wastewater from acid pickling rinse tank has 500mg/L of hydrogen ions. The required pH for the treatment of metal ions in the next process is 8.5. The pH is adjusted by adding a solution of 10 %wt sodium hydroxide. The volume of wastewater is 2000 L/hr. The reaction takes place in a continuous stirred tank and follows mechanism (4.2.1).

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad \text{..........................(4.2.1)}$$

The change of pH to 8.5 is caused by the change of concentration of hydrogen ions [H^+]. This change is brought by the reaction of hydrogen ions and the hydroxyl ions. The moles of hydroxyl ions required are equal to the moles of change in hydrogen ions.

Feed data required input to the model:

a) $Concentration\ of\ hydrogen\ ions\ input = 500\ mg/L$

$pH_{outlet} required = 8.5$

$$\left[H^+\right]_{inlet} = \left(500 / RMM_{H^+}\right)/1000$$
$$= 0.496\, mol/L$$
$$pH_{inlet} = -\log\left[H^+\right]_{inlet} \quad \Leftrightarrow \quad \left[H^+\right]_{inlet} = 10^{-0.3045} \times 1.008 \times 1000$$
$$= -\log(0.496) \qquad = 499.9891\, mg/L$$
$$= 0.3045$$

Model Solution:

Hydrogen ions concentration in the outlet from the reaction tank:

b)

$$\left[H^+\right]_{outlet} = \left(10^{-pH_{outlet}}\right) \times \left(RMM_{H^+}\right) \times 1000$$
$$= \left(10^{-8.5}\right) \times (1.008) \times 1000$$
$$= 3.19 \times 10^{-6} \quad mg/L$$

c)

$$\Delta\left[H^+\right] = \left|\left[H^+\right]_{inlet} - \left[H^+\right]_{outlet}\right|$$
$$= 499.9891 - 3.19 \times 10^{-6}$$
$$\approx 499.9891 \quad mg/L$$

d)

$$Converssion\ of\ \left[H^+\right] = \frac{\Delta\left[H^+\right]}{\left[H^+\right]_{inlet}}$$
$$= \frac{499.9891}{499.9891}$$
$$= 1$$

e)

$$Mass\ \left[H^+\right] reacted = X \times \left[H^+\right] \times \frac{Q_{tot}}{3600}$$
$$= 1 \times 499.9891 \times \frac{2000}{3600}$$
$$= 277.7717 \quad mg/s$$

From the neutralization reaction (4.2.1), it can be concluded that 36 g of hydrochloric acid requires 40 g of sodium hydroxide.

$$
\begin{aligned}
f)\ \textit{Mass NaOH required} &= (40/36)\times \textit{Mass}\left[H^{+}\right]\textit{reacted} \\
&= 1.1111\times 277.7717 \\
&= 308.6321\,mg/s \\
\textit{Toatal mass NaOH stream} &= \textit{Mass NaOH required}/(10\%) \\
&= 3086.321\,mg/s
\end{aligned}
$$

The pH adjustment depends on the requirement of the process, i.e. sodium hydroxide or hydrochloric acid can be used interchangeable. Hydrochloric acid is used to decrease the pH, while sodium is used to increase the pH.

9.1.1.2 Hexavalent chromium reduction

Wastewater from chromium (VI) rinse water tanks has a pH of 4 and a temperature of 25 ^{O}C. The required pH for effective reduction hexavalent chromium is 2.6. Feed flowrate into the treatment tank is 100L/hr. Prior addition of the reducing agent the pH is corrected to optimum pH for the reduction of hexavalent chromium. It is an industrial practice for the effective reduction of chromium to put 5:1 ratio of metabisulphite to hexavalent chromium. The model predicts the treatment efficiencies the conversion, space time, output concentration of all species that are in the reaction tank.

Feed data required as input to the model:

- Feed flowrate = Q = 100L/hr
- Chrome (VI) concentration = $\left[Cr^{6+}\right]_{init}$ = 20 mg/L
- Volume of tank = V_T = 140 L
- Ratio of metabisulphite: chromium (VI) = $\Theta_{S^{4+}/Cr^{6+}}$ = 5
- pH = 2.6
- Activation energy = E = $7.46\text{x}10^{4}$ J/mol

- Universal gas constant = R = 8.3044 J/K. mol
- Frequency factor = A = 5.69x10^{10} L.mg^{-1}.s^{-1}
- Temperature of reaction tank = 25 ^{o}C= 288 K

Model solution:

$$K = A \times \exp\left[-E/RT\right] \times 84.794 \times pH^{-4.368}$$

$$K = 5.69 \times 10^{10} \times \exp\left[-74.6 \times 10^{4} /(8.3144 \times 298)\right] \times 84.794 \times 2.6^{-4.368} \qquad ....(5.2.4)$$

$$K = 0.00624\, s^{-1}$$

Using expression 5.2.7 to determine conversion of chromium (VI) to chromium (III).

$$\frac{3VK\left[Cr^{6+}\right]_{init}^{2}}{2} X^{2} - \left(\frac{3VK\left[Cr^{6+}\right]_{init}^{2}}{2} + \Theta_{S^{+4}/Cr^{6+}} VK\left[Cr^{6+}\right]_{init}^{2} + F_{Cr^{6+}init} \right) X + \Theta_{S^{+4}/Cr^{6+}} VK\left[Cr^{6+}\right]_{init}^{2} = 0 \quad ..... (5.2.7)$$

Substituting the known variables into the above expression gives the following quadratic expression:

$$523.747\, X^{2} - 2271.514 X + 1745.823 \quad = 0$$

The above expression is a quadratic expression which can be solved by a quadratic equation below (9.1.1), giving two solutions of X.

Coefficients of the above quadratic expression are:

$a = 523.747$

$b = 2271.514$

$c = 1745.823$

Substitute these coefficients into the general solution for a quadratic expression.

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$X_1 = 3.339 \quad and \quad X_2 = 0.999$$

Boundaries of X :

$$0 \leq X \geq 1$$

The root that falls within the boundaries of X is the conversion.

The following equation is used to determine the residence time. If the ratio of the tank and flowrate (i.e. V_{tank}/Q_{input}) is made the subject of equation (5.2.6) results in the residence time expression.

$$V = \frac{F_{Cr^{3+},init}\, X}{K\left[Cr^{6+}\right]^2_{init}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{................(5.2.6)}$$

Substitute $F_{Cr^{6+}} = Q \times \left[Cr^{6+}\right]$ into the above expression giving the following

$$V = \frac{Q\left[Cr^{6+}\right]_{init} X}{K\left[Cr^{6+}\right]^2_{init}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{...........................(5.2.9)}$$

Rearranging the above expression (5.2.9) making V/Q the subject of the expression

$$\frac{V}{Q} = \tau = \frac{X}{K\left[Cr^{6+}\right]^2_{init}(1-X)\left(\Theta_{S^{+4}/Cr^{6+}} - \frac{3}{2}X\right)} \qquad \text{..................(5.2.10)}$$

Substitute the known variables into the above expression (5.2.10).

$$\frac{V}{Q}=\tau=\frac{0.998}{0.00624(20)^2\ (1-0.998)\left(5-\left(\frac{3}{2}\times 0.998\right)\right)}$$

$$\tau = 254.16\, s = 4.24 \text{ min}$$

The above result from expression (5.2.10) is the time required to achieve a conversion of 0.998.

Output concentrations of all other species that enter the reduction tank can be predicted from the conversion. The following are the output concentrations of hexavalent chromium, trivalent chromium and metabisulphite.

- **Hexavalent chromium**

$$\left[Cr^{6+}\right]=\left[Cr^{6+}\right]_{init}\left(1-X_{Cr^{6+}}\right)$$

$$\left[Cr^{6+}\right]=20\left(1-0.998\right)$$

$$\left[Cr^{6+}\right]=0.032\, mg/L$$

- **Trivalent chromium**

$$\left[Cr^{3+}\right]=\left[Cr^{6+}\right]_{init}\left(\frac{1}{2}X_{Cr^{6+}}\right)$$

$$\left[Cr^{3+}\right]=20\left(0.5\times 0.998\right)$$

$$\left[Cr^{3+}\right]=9.98\, mg/L$$

- **Sodium metabisulphite**

$$\left[S^{4+}\right]=\left[Cr^{6+}\right]_{init}\left(\Theta_{S^{4+}/Cr^{6+}}-\frac{3}{2}X_{Cr^{6+}}\right)$$

$$\left[S^{4+}\right]=20\left(5-\left(\frac{3}{2}\times 0.998\right)\right)$$

$$\left[S^{4+}\right]=70.06\, mg/L$$

Wastewater from chromium (VI) reduction tank is reach in reach in chromium (VI). Trivalent chromium can be precipitated by pH adjustment using caustic.

9.1.1.3Trivalent chromium precipitation

Wastewater from chromium reduction has trivalent chromium as a dominant metal ions species. This wastewater is treated in a continuous stirred tank that can be considered as a CSTR. Sodium hydroxide is added to precipitate trivalent chromium. The ratio of feed of sodium hydroxide/chromium (III) is at stoichiometric quantities. Assuming steady state operation the mass into the tank from the chromium tank is equal and no significant change on the volume flowrate.

Development of the model:

To predict this treatment the precipitation efficiencies are determined as follow:

Substitute initial conditions in expression (5.3.4) below (as in appendix B, table 9.2). Solve the left had side and the right hand side by trial and error in the resulting expression (5.3.5).

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k\left[Cr^{3+}\right]\left[OH^{-}\right]^{3}} \qquad \text{..(5.3.4)}$$

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k\left[Cr^{3+}\right](1-X)\left[\left[Cr^{3+}\right]^{3}_{3init}\left(\Theta_{OH^{-}/Cr^{3+}} - 3X\right)^{3}\right]} \qquad \text{................(5.3.5)}$$

$$V\,k\left[Cr^{3+}\right]^{4}(1-X) = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{\left[\left(\Theta_{OH^{-}/Cr^{3+}} - 3X\right)^{3}\right]}$$

for solutions of X

$LHS = RHS$

And $0 \le X \ge 1$

Using trial and error method to solve for X, the left hand side must be equal to the right hand side for the right solution of X and X must fall with the following boundaries:

$0 \leq X \geq 1$

Feed data required as input to the model:

- Feed flowrate $= Q$ = 100 L/hr
- Chromium (VI) concentration = $[Cr^{3+}]_{init}$ = 9.98 mg/L
- Volume of the tank = V_T = 140 L
- Ratio of sodium hydroxide to chrome (III) = $\Theta_{OH^-/Cr^{3+}} = 3$
- pH = 8.1
- Temperature of reaction tank = $25^{O}C$= 288 K
- Reaction rate constant = $1.5x10^{-5}\ s^{-1}$

Model solution:

Substituting all the known variables and assume conversion between 0and 1(i.e. range of conversion is 0 to 1) gives following table 9.1 and figure 9.1 where the conversion is where the two plots intersects.

Conversion (X)	LHS	RHS
0.1	410.046	0.097
0.2	277.989	0.194
0.7	15.187	0.679
0.8	4.500	0.776
0.9	0.562	0.873
1	0.000	0.970

***Table 9.1*:** Solution to trail and error method for determination of the extent of trivalent chromium precipitation.

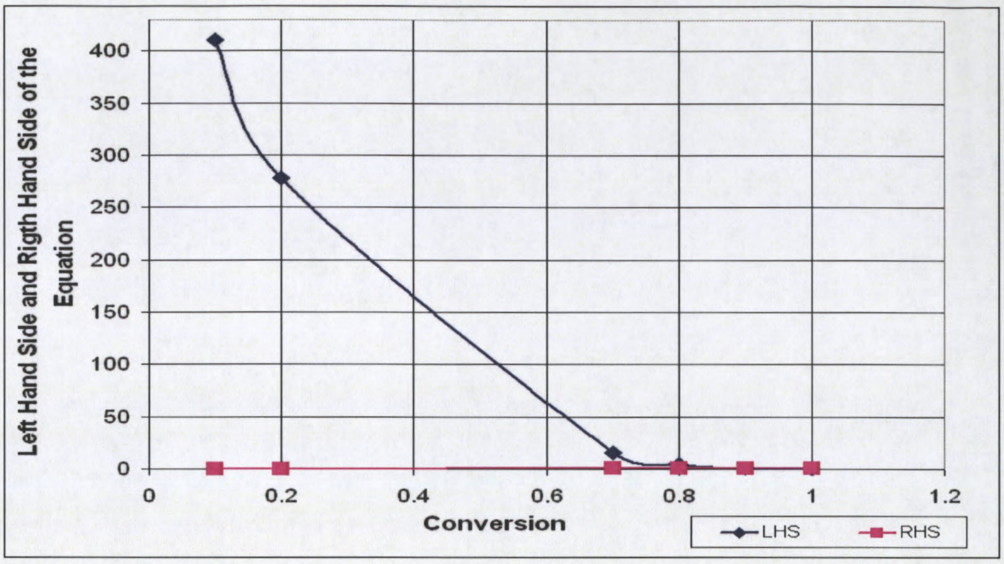

Figure 9.1: Solution of the trail and error method for determination of trivalent chromium precipitation

From figure 9.1 above, it can be concluded that the conversion is approximately 0.9. This conversion can be used to determine time required to treat wastewater.

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k\left[Cr^{3+}\right]\left[\left[Cr^{3+}\right]^{3}\left(\Theta_{OH^{-}/Cr^{3+}} - 3X\right)^{3}\right]}$$

$$\tau = \frac{X_{Cr^{3+}}}{k\left[\left[Cr^{3+}\right]^{3}\left(\Theta_{OH^{-}/Cr^{3+}} - 3X\right)^{3}\right]}$$

$$\tau = \frac{0.9}{(1.5\times10\text{^}-5)(9.98)^{3}\,(3-3\times0.9)^{3}}$$

$$\tau = 2235.61\,s = 37.26\text{ min}$$

This is the time it would take to achieve a conversion of 0.9.

The exit concentrations can be determined from this conversion. These are the concentration of trivalent chromium, sodium hydroxide and chromium hydroxide.

- ✓ **Trivalent chromium**

$$\left[Cr^{3+}\right]=\left[Cr^{3+}\right]^{i}_{init}\left(1-X_{Cr^{3+}}\right)$$

$$\left[Cr^{3+}\right]=9.98\left(1-0.9\right)$$

$$\left[Cr^{3+}\right]=0.998\,mg/L$$

- ✓ **Sodium hydroxide (hydroxyl ions)**

$$\left[OH^{-}\right]=\left[Cr^{3+}\right]\left(\Theta_{OH^{-}/Cr^{3+}}-3X_{Cr^{3+}}\right)$$

$$\left[OH^{-}\right]=9.98\left(3-3\times0.9\right)$$

$$\left[OH^{-}\right]=2.994\,mg/L$$

- ✓ **Chromium hydroxide**

$$\left[Cr(OH)_3\right]=\left[Cr^{3+}\right]_{init}\left(\Theta_{Cr(OH)_3/Cr^{3+}}-X_{Cr^{3+}}\right)$$

$$\left[Cr(OH)_3\right]=\left[Cr^{3+}\right]_{init}X_{Cr^{3+}}$$

$$\left[Cr(OH)_3\right]=9.98\times0.9$$

$$\left[Cr(OH)_3\right]=8.982\,mg/L$$

9.1.1.4 Cyanide treatment

Wastewater form an electroplating process has high levels of cyanide of about 25 mg/L and a pH of 7. The pH is corrected to 11 by using appropriate amount of alkaline reagent (sodium hydroxide). The temperature of water is approximately 24 ^{o}C. The flow of wastewater is 100L/hr. This wastewater is fed into two continuous stirred reactor tanks that are connected in series. The inlet cyanide ratio to feed sodium hypochlorite is 0.95. The first tank is for the oxidation of cyanide to less toxic cyanite. The model can predict treatment efficiencies the conversion, space-time, output concentration of all species that are in the reaction tank.

The following model presents the development and solution to the model of cyanide oxidation to cyanite.

Feed data required as input to the model:

- Feed flowrate $= Q$ = 100 L/hr
- Cyanide concentration = $[CN^-]_{init}$ = 25 mg/L
- $[NaOCl]/[NaCN] = 0.9$
- Volume of tank = V_T = 140 L
- Height of tank is = H_t = 0.48 m
- Diameter of tank = 0.611 m
- Density of water = ρ_L = 1000 g/L
- pH after correction = 11
- Temperature of reaction tank = 25°C= 288 K

Development of the model and the solution of the model:

The concentration of hydroxide ions $[OH^-]$ is:

$$pH + pOH = 14$$

But:

$$pH = -\log[H^+] \qquad and \qquad pOH = [OH^-]$$

$$[OH^-] = 10^{(pH-14)} \times RMM_{OH^-} \times 1000$$

$$[OH^-] = 10^{(11-14)} \times 17.008 \times 1000$$

$$[OH^-] = 1.7008\, mg / L$$

Cyanide oxidation is reported to be pH dependent, showing an increasing rate with increasing pH. The pH dependency is incorporated in the rate constant expression (4.3.5)

The design equation of cyanide treatment tank is:

$$V = \frac{F_{CN^{-1}} X_{CN^{-1}}}{-r_{CN^{-1}}} \qquad \text{.....................................(4.3.1)}$$

The reaction rate law of cyanide oxidation is:

$$-\frac{d\left[CN^{-}\right]}{dt} = k\left[CN^{-}\right]\left[OCl^{-}\right] \qquad \text{.....................................(4.3.5)}$$

Where k is the rate law constant and is dependent on pH. The dependency of k to pH is defined by the following expression (4.3.4):

$$k = 0.0031pH - 0.0207 \qquad \text{.....................................(4.3.4)}$$

Substituting the rate law into the design equation and putting initial conditions gives the following expression (4.3.7):

$$V = \frac{F_{CN^{-}} X_{CN^{-}}}{(k)\left[CN^{-}\right]_{init}^{2}\left(1 - X_{CN^{-}}\right)\left(\Theta - X_{CN^{-}}\right)} \qquad \text{.....................................(4.3.7)}$$

Substituting the rate constant expression (4.3.4) into the above expression (4.3.7) gives the following expression:

$$V = \frac{F_{CN^{-}} X_{CN^{-}}}{(0.0031pH - 0.0207)\left[CN^{-}\right]\left[OCl^{-}\right]}$$

Making X the subject of the above expression and grouping like terms gives the following expression.

$$V\left(k\left[CN^{-}\right]_{init}^{2}\right)\left(\Theta - X_{CN^{-}} - \Theta X_{CN^{-}} + X_{CN^{-}}^{2}\right) = F_{CN^{-}} X_{CN^{-}} \qquad \text{..................(4.3.8)}$$

Let:

$$Vk\left[CN^{-}\right]_{init}^{2} = K$$

Grouping like terms in the above expression:

$$K\,X_{init}^{2}-\left(K+K\,\Theta+F_{CN^{-}}\right)X_{CN^{-}}+K\Theta=0 \qquad \text{.........................(4.3.9)}$$

The above expression is a quadratic with following coefficients. It is solved by a quadratic expression.

$$a=K=1179.161\,mg^{2}\,/\,L\,s$$

$$b=\left(K+K\,\Theta+F_{CN^{-}}\right)=-2241.1\,mg^{2}\,/\,L\,s$$

$$c=K\Theta=1061.245\,mg^{2}\,/\,L\,s$$

The conversion of cyanide to cyanite is:

$$X=\frac{-b\pm\sqrt{b^{2}-4ac}}{2a}$$

$$X=\frac{(2241.1)\pm\sqrt{(2241.1)^{2}-(4\times1179.161\times1061.245)}}{2\times1179.161}$$

$$X_{1}=0.895 \qquad or \qquad X_{2}=1.006$$

The second root is greater than one, hence does not represents the conversion.

To determine the residence time inside the treatment tank, the conversion from the above expression (4.3.9) is substituted in expression (4.3.8). The cyanide flowrate is replaced by the product of cyanide concentration and inlet volumetric flowrate.

$$V=\frac{\left[CN^{-}\right]_{init}Q_{ini}\,X_{CN^{-}}}{(k)\left[CN^{-}\right]_{init}^{2}\left(1-X_{CN^{-}}\right)\left(\Theta-X_{CN^{-}}\right)} \qquad \text{.........................(4.3.10)}$$

Rearranging the above expression (4.3.10) making the residence time the subject of the equation, gives an expression that can be used to predict treatment time required:

$$\frac{V}{Q_{init}}=\tau=\frac{X_{CN^-}}{(k)[CN^-]_{init}(1-X_{CN^-})(\Theta-X_{CN^-})} \qquad \text{..........................(4.3.11)}$$

$$\tau=\frac{0.895}{0.0134(25)^2(1-0.895)(0.9-0.895)}$$

$\tau=5068.633\,s$

$\tau=84\text{ min}$

Note in real plant treatment process, the first stage oxidation is usually shorter than this, it take about 25 minute. Therefore if the tank is oversized for such flowrate, since the residence time is greater than 25 minute.

- ***Cyanide output concentration***

$[CN^-]=[CN^-]_{init}(1-X)$

$=25(1-0.895)$

$=2.625\,mg/L$

- ***Sodium hypochlorite output concentration***

$[NaOCl]=[CN^-]_{init}(\Theta-X)$

$=25(0.9-0.895)$

$=0.126\,mg/L$

- ***Cyanite output concentration***

The cyanite concentration in the feed is approximately zero; therefore the ration θ is zero in the expression below.

$[Cyanite]=[CN^-]_{init}(\Theta+X)$

$=25(0+0.895)$

$=22.375\,mg/L$

- ***Sodium chloride output concentration***

The sodium chloride concentration in the feed is approximately zero; therefore the ratio θ is zero in the expression below.

$$
\begin{aligned}
[NaCl] &= [CN^-]_{init}(\Theta + X) \\
&= 25(0+0.895) \\
&= 22.375\ mg/L
\end{aligned}
$$

9.1.1.5 Iron treatment

Wastewater form the acid pickling process has iron chloride at acidic pH of 4 and the pH is corrected by using appropriate amount of alkaline reagent (sodium hydroxide). The pH is set to 7 with the temperature of water corrected from high temperatures to 24 °C. The flow of wastewater is 100L/hr. This wastewater is fed into a continuous stirred tank that is considered as a CSTR. This tank is continuous aerated by the supply of air through diffusers. The supplied oxygen oxidizes the ferrous iron to ferric iron. The model predicts treatment efficiencies the conversion, residence time, output concentration of all species that are in the reaction tank.

Feed data required as input to the model:

- Feed flowrate = Q = 100 L/hr
- Iron (II) concentration = $[Fe^{2+}]_{init}$ = 20 mg/L
- Volume of tank = V_T = 140 L
- Height of tank = H_t = 1.5 m
- Air flowrate = Q_{Air} = 70 L/hr
- Equilibrium concentration of oxygen = 8 mg/L
- Density of water = ρ_L = 1000 g/L
- Density of air = ρ_{Air} = 1.29 g/L
- Diffusivity of air = D = 0.000203 m^2/s

- Viscosity of water = μ_L = 0.001 cPoise
- Diameter of air bubbles = d = 0.3 cm
- Gravitational acceleration = g = 9.81m/s^2
- Rate constant in l/g.s = (12.55 l/mol.s) /RMM = 2.241x10^{-4} L/mg.s
- pH = 7.0
- Temperature of reaction tank = 25°C= 288 K

Development of the model and the solution of the model:

Reaction mechanism involved in the oxidation is:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \qquad \text{..............} (4.4.2)$$

The rate law expression of ferrous reduction is as follow, with the reaction rate constant being a constant determined from literature for the above reaction.

$$-r_{Fe^{3+}} = -\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][O_2] \qquad \text{..............................} (4.4.3)$$

The design equation of the oxidation tank is similar to that of a CSTR, therefore is:

$$V = \frac{F_{Fe^{2+}} X_{Fe^{2+}}}{-r_{Fe^{2+}}} \qquad \text{...}(4.4.1)$$

Substituting the reaction rate into the design equation (4.4.1):

$$V = \frac{F_{Fe^{2+}} X_{Fe^{2+}}}{K[Fe^{2+}][O_2]} \qquad \text{...} (4.4.4)$$

In the tank, the concentration of oxygen changes as the tank is continuously aerated. The change of oxygen with time can be assimilated by the mass transfer equation, which is as follow:

$$\frac{dc_{O_2}}{dt} = \alpha(C_{equil} - C_{O_2}) \qquad \text{...} \ (4.4.5)$$

Integrating the above mass transfer equation and using initial conditions where the concentration of oxygen in the tank mixture is zero and time is zero, yields the following expression:

$$C_{O_2} = C_{equil}\left(1 - e^{-\alpha t}\right)$$

Substitute the above equation into the design equation in order to replace the concentration of oxygen.

$$V = \frac{F_{Fe^{2+}} X}{k\,[Fe^{2+}]\,(1 - X)\left[C_{equil}\left(1 - e^{-\alpha t}\right)\right]} \qquad \text{..............................} \ (4.4.7)$$

Represent the iron concentration in the above expression in terms of initial concentration of ferrous iron that enters the reaction tank, as in the stoichiometric table in appendix B, table 9.4. Expression (4.4.7) becomes the following expression:

$$V = \frac{F_{Fe^{2+}} X}{k\,[Fe^{2+}]_{init}\,(1 - X_{Fe^{2+}})\left[C_{equil}\left(1 - e^{-\alpha t}\right)\right]}$$

Making X the subject of the equation in the above expression gives the following expression:

$$X_{Fe^{2+}} = \frac{Vk\left[F^{2+}\right]_{init} C_{equil}(1-e^{-\alpha t})}{[Fe^{2+}]_{init} + Vk\left[F^{2+}\right]_{init} C_{equil}(1-e^{-\alpha t})}$$

The residence time of the air bubble is equal to‘t’ in the above expression inside the tank.

Assuming turbulent flow conditions (Reynolds number > 1000) with particle diameter (d) > 0.30 cm. The velocity a rising of air bubble is:

$$\upsilon = 1.82\left[\frac{(\rho_L - \rho_G)dg}{\rho_L}\right]^{1/2} \qquad \text{.........................(4.4.13)}$$

$$\upsilon = 1.82\left[\frac{(1000-1.29)(0.003\times 9.81)}{1000}\right]^{1/2}$$

$$\upsilon = 0.0987\ m/s$$

Bubble residence time

$$t = \frac{h}{\upsilon} \qquad (4.4.11)$$

$$t = \frac{1.5}{0.0987}$$

$$t = 15.198\ s$$

The conversion in this reaction tank is:

$$X = \frac{Vk\left[Fe^{2+}\right]_{init} C_{equil}(1-e^{-\alpha t})}{F_{Fe^{2+}} + Vk\left[Fe^{2+}\right]_{init} C_{equil}(1-e^{-\alpha t})}$$

The above expression is derived from expression 4.4.7, by making the conversion (X) the subject of the expression.

Now substitute all known properties into expression 4.4.7, yields the following expression to determine the iron(II) conversion

$$X = \frac{140\times 2.2411\times 10^{-4}\times 20\times 8(1-e^{-\alpha\times 15.198})}{(20\times 0.0278)+140\times 2.2411\times 2.2411\times 10^{-4}\times 20\times 8(1-e^{-\alpha\times 15.198})}$$

$$X = \frac{5.020064(1-e^{-\alpha\times 15.198})}{5.56\times 10^{-1}+5.020064(1-e^{-\alpha\times 15.198})}$$

The mass transfer coefficient is given by the product of K_L and a. These parameters are determined as follow:

K_L is determined from expression (4.4.9):

$$\frac{K_L}{D_L} = 0.42\left(\frac{\mu_L}{\rho_L D_L}\right)^{1/2}\left[\frac{\rho_L(\rho_L-\rho_G)g}{\mu_L^2}\right]^{1/3} \qquad \text{..........................(4.4.9)}$$

$$\frac{K_L}{D_L} = 0.42\left(\frac{0.001}{1000\times 0.000203}\right)^{1/2}\left[\frac{1000\,(1000-1.29)9.81}{0.001^2}\right]^{1/3}$$

$$K_L = 0.42\times(7.019\times 10^{-2})(2.1398\times 10^{4})(0.000203)$$

$$K_L = 0.128\ m/s$$

a is determined from expression (4.4.10):

$$a = \frac{(number\ of\ bubble)\,(area\ per\ bubble)}{reactor\ volume} \qquad \text{..........................(4.4.10)}$$

$$a = \frac{Q_G t 6}{Vd}$$

$$a = \frac{0.0194\times 15.198\times 6}{140\times 0.003}$$

$$a = 4.212\ m^{-1}$$

Therefore the mass transfer coefficient is:

$$K_L a = \alpha = 0.128\times 4.212$$

$$\alpha = 0.539\ s^{-1} \qquad \text{...............................(4.4.15)}$$

Hence the conversion of ferrous iron to ferric iron is:

$$X = \frac{5.020064(1 - e^{-\alpha \times 15.198})}{5.56 \times 10^{-1} + 5.020064(1 - e^{-\alpha \times 15.198})}$$

$$X = \frac{5.020064(1 - e^{-(0.539 \times 15.198)})}{5.56 \times 10^{-1} + 5.020064 \times (1 - e^{-(0.539 \times 15.198)})}$$

$$X = \frac{5.0062}{5.56 \times 10^{-1} + 5.0062}$$

$$X = 0.900$$

Wastewater residence time in the reaction tank is:

$$\frac{V}{v_o} = \tau = \frac{X_{Fe^{2+}}}{k(1 - X_{Fe^{2+}})C_{equil}(1 - e^{-\alpha t})}$$

$$\tau = \frac{0.9}{2.2411 \times 10^{-4}(1 - 0.9) \times 8 \times (1 - e^{-(0.539 \times 15.198)})}$$

$$\tau = 5021.247\ s = 83.678\ \text{min}$$

The ferric ions formed are hydrolyzed by water at high pH forming ferric iron hydroxide. The formation and consumption of other chemical species that enter the reactor is determined from the conversion using the stoichiometric table as shown in *appendix B, table9.4.*

9.1.1.6 Copper treatment

9.1.1.6.1 Precipitation of copper (II) ions

Copper occur as divalent ions in solution. The solubility of copper decreases with increasing pH. The minimum solubility of copper is at a pH of 8.5.

Copper is treated by direct precipitation with caustic. The reaction takes place in a continuous stirred tank. These precipitates are flocculated and settled in the sedimentation tanks. Alum is a commonly used flocculent.

Development of the model:

To predict this treatment the precipitation efficiencies are determined as follow:
The reaction of copper hydroxide formation is assumed elementary, with the following rate law:

$$r_{Cr^{3+}} = k\ [Cr^{3+}][OH^-]^3 \qquad \text{.................(5.3.3)}$$

The design equation of the reaction tank:

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k[Cr^{3+}][OH^-]^3} \qquad \text{.................(5.3.4)}$$

Substituting the rate law expression (5.3.3) into the design equation (5.3.4) and substituting the initial conditions give the following expression (5.3.5):

$$V = \frac{F_{Cr^{3+}} X_{Cr^{3+}}}{k[Cr^{3+}]\left[[Cr^{3+}]^3 \left(\Theta_{OH^-/Cr^{3+}} - 3X\right)^3\right]} \qquad \text{.................(5.3.5)}$$

Equating two sides (i.e. LHS and RHS) of the above expression and solving them by trial and error method.

$$(1-X)(\Theta_{OH/Cu^{2+}} - 2X)^2 = \frac{F_{Cu^{2+}} X_{Cu^{2+}}}{k[Cu^{2+}]^3 V}$$

for solutions of X
$LHS = RHS$
And $0 \le X \ge 1$

Using trial and error method to solve for X, the left hand side must be equal to the right hand side. For the right solution of the conversion, X must fall with the following boundaries.

$0 \leq X \geq 1$

Feed data required as input to the model:

- Feed flowrate $= Q$ = 1000 L/hr
- Copper concentration = $\left[Cu^{2+}\right]_{init}$ =50 mg/L
- Volume of tank = V_T = 140 L
- Ratio of sodium hydroxide to chrome (III) = $\Theta_{OH^-/Cu^{2+}} = 2$
- pH = 8.5
- Temperature of reaction tank = 25°C= 288 K
- Reaction rate constant = 0.022 $L^2.mg^{-1}.s^{-1}$

Model solution:

Substituting all the known variables and assume conversion between 0 and 1, gives following table 9.2 and figure 9.2, the conversion is where the two plots intersects.

Conversion (X)	LHS	RHS
0.6	2.56E-01	2.15E-05
0.65	1.72E-01	2.32E-05
0.7	1.08E-01	2.50E-05
0.75	6.25E-02	2.68E-05
0.8	3.20E-02	2.86E-05
0.85	1.35E-02	3.04E-05
0.9	4.00E-03	3.22E-05
0.9794	3.50E-05	3.50E-05
1	0	3.58E-05

Table 9.2: Solution to the trail and error method for determination of the extent of divalent copper precipitation.

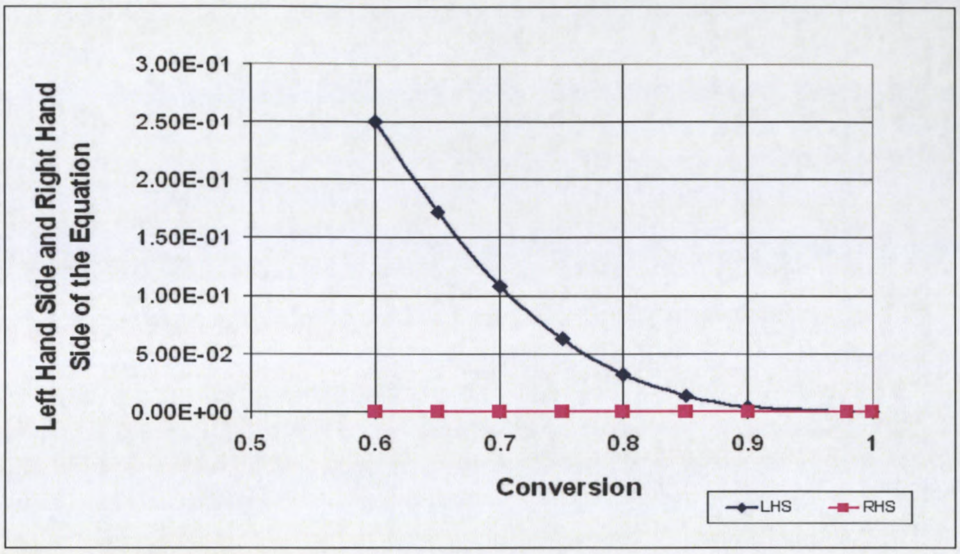

Figure 9.2: Solution of the trail and error method for determination the extent of divalent copper precipitation

From the above plot of the conversion is at 0.9794. This conversion can be used to determine time required to treat waste for such conversion.

$$V = \frac{F_{Cu^{2+}} X_{Cu^{2+}}}{k\,[Cu^{2+}]\,(1-X)([Cu^{2+}]^2(\Theta_{OH^-/Cu^{2+}} - 2X)^2)}$$

$$\tau = \frac{X_{Cu^{2+}}}{k[Cu^{2+}](1-X)[Cu^{2+}](\Theta_{OH^-/Cu^{2+}})^2}$$

$$\tau = 0.9794/0.022(50^2)(1-0.9794)(2-2X)$$

$$\tau = 509\ s = 8.49\ \text{min}$$

This is the time it would take to achieve a conversion of 0.9794.

The exit concentrations can be determined from this conversion. These are the concentration of copper (II) ions, sodium hydroxide and copper hydroxide.

- ***Copper(II) ions***

$$[Cu^{2+}]=[Cu^{2+}]_{init}(1-X_{Cu^{2+}})$$
$$=50(1-0.9794)$$
$$=1.03\ mg/L$$

- ***Sodium hydroxide(i.e. hydroxyl ions)***

$$[OH^-]=[Cu^{2+}]_{init}(\Theta_{OH^-/Cu^{2+}}-X_{Cu^{2+}})$$
$$=50(2-0.9794)$$
$$=2.06\ mg/L$$

- ***Copper hydroxide***

$$[OH^-]=[Cu^{2+}]_{init}(\Theta_{Cu(OH)_2/Cu^{2+}}+X_{Cu^{2+}})$$
$$=50(0+0.9794)$$
$$=78.97\ mg/L$$

8.1.1.6.2 Flocculation of copper hydroxide flocs

The conversion of alum sulphite to aluminum hydroxide for the formation of flocs.

Feed data require as input the model:

- Feed flowrate $=Q$ = 1000 L/hr
- Alum concentration = $[Al_2(SO_4)_3]_{init}$ = 2.5 mg/L
- Volume of tank = V_T = 7366.071 L
- pH = 8.5
- Temperature of reaction tank = 25°C= 288 K
- Reaction rate constant = 0.015 s^{-1}

$$V=\frac{F_{Alum}X_{Alum}}{k[[Al_2(SO_4)_3]-[Al(OH)_3^2][H_2SO_4]]} \qquad \text{.................(5.5.2)}$$

$$X_{Alum} = \frac{F_{Alum} X_{Alum}}{Vk[Al_2(SO_4)_3]_{init} - F_{Alum}}$$

$$X_{Alum} = \frac{7366.071 \times 0.015 \times 2.5}{(7366.071 \times 0.015 \times 2.5) + ((1000/3600) \times 2.5)}$$

$$X_{Alum} = 0.998$$

The reaction time for coagulation is:

$$\tau = \frac{F_{Alum} X_{Alum}}{k\left[[Al_2(SO_4)_3]_{init}(1 - X_{Alum})\right]}$$

$$\tau = \frac{((1000/3600) \times 2.5)(0.998)}{0.015 \times 2.5 \times (1 - 0.998)}$$

$$\tau = 9240.74\, s = 154.012 \text{ min}$$

Assuming that the adsorption follows Freundlich isotherm

Feed data required as input data to the model:

$$K_f = 6.61\, (mg/g)(L/mg)^{1/n}$$
$$1/n = 0.8$$

Model solution:

Mass of adsorbent ($Al(OH)_3$)

$$\begin{aligned} m &= Alum\ dose \times X \times (Q/3600) \\ &= 2.5 \times 2 \times 0.956 \times (1000/3600) \\ &= 1.328\, mg/L \end{aligned}$$

The ratio of copper hydroxide adsorbed per mass of alum hydroxide (i.e. q_e) can be determined by the following equation below. Both of these equations have equilibrium concentration of copper hydroxide. The equilibrium concentration of copper hydroxide is the concentration that remains dissolved in solution after adsorption.

$$q_e = K_f C_{equil}^{1/n} = \frac{mass\ adsorbate\ (kg)}{mass\ adsorbent\ (kg)} = \frac{mass\ Cr(OH)_3\ adsorbed}{mg\ Al(OH)_3} \qquad \text{........(5.5.4)}$$

$$q_e = \frac{C_{init} - C_{equil}}{m\tau}$$

Equating the above equations results in the following expression; this equation can be solved by trial and error method. The equilibrium concentration of copper is assumed and substituted into the following expression; the left hand side equals the right hand side for the right solution of equilibrium concentration (C_{eq}). See table 9.3 and figure 9.3 for the solution.

$$q_e = \frac{C_{init} - C_{eq}}{m\tau} = K_f C_{eq}^{1/n}$$

Output Copper(II) conc. (C_{equil})	**LHS**	**RHS**
mg/L	*mg/s*	*mg/s*
48.970	0.000	148.823
44.073	3.535	136.793
39.176	7.069	124.492
29.382	14.139	98.899
24.989	17.310	86.881
19.598	21.201	71.531
14.691	24.743	56.803
9.794	28.278	41.067
4.755	31.915	23.036
0.000	35.347	0.000

Table 9.3: Solution of the trial and error method of determining the equilibrium copper hydroxide after adsorption with alum

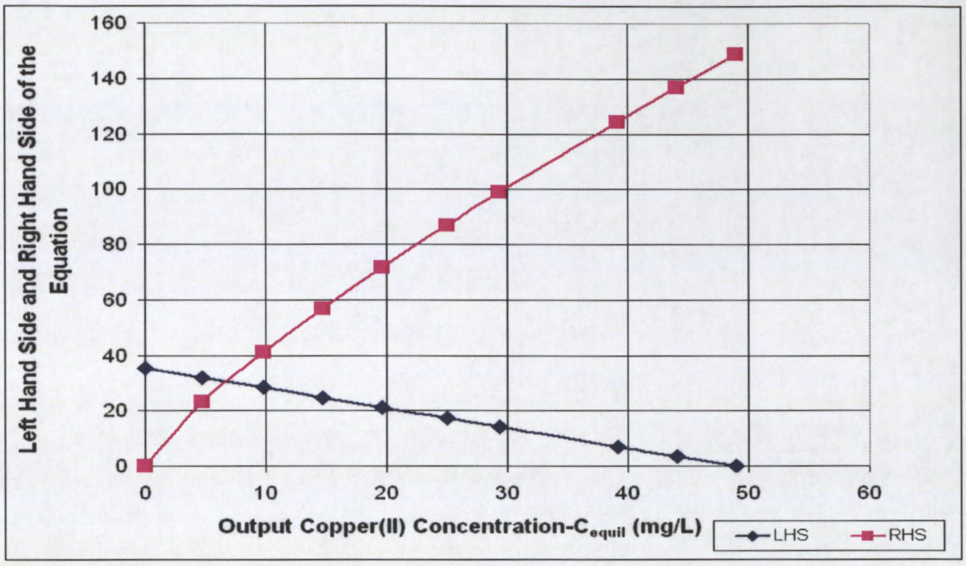

Figure 9.3: Solution of the trial and error method for determination of equilibrium concentration of copper hydroxide after adsorption with alum

From the above solution (see table 9.3 and figure 9.3), it can be seen that the equilibrium concentration of copper hydroxide is 6.7 mg/L

The mass of copper hydroxide adsorbed per mass of alum is determined as follows:

$$q_e = \frac{([Cu(OH)] - [Cu(OH)]_{eq}) \times V}{m}$$

$$q_e = \frac{(48.97 - 6.7) \times (1000/3600)}{1.328}$$

$$q_e = 8.842\ mg/g$$

The mass of copper hydroxide adsorbed is:

$$\begin{aligned} M_{adsorbed} &= q_e \times m \\ &= 8.842 \times 1.328 \\ &= 11.742\ mg/s \end{aligned}$$

Concentration of copper hydroxide

$$[Cu(OH)_2] = \frac{M_{adsorbed}}{(Q/3600)}$$

$$= \frac{11.742}{(1000/3600)}$$

$$= 42.2712\ mg/L$$

9.1.1.6.3 Sedimentation

Using Hazen's equation of sedimentation to predict the settling rate.

Feed data require as input to the model:

- ρ_s = 1419.99 g/L
- ρ = 998 g/L
- T = 25 °C
- d = 0.001cm
- H = 9 m
- Tank cross sectional area =A_{sc}=4.526 m^2

$$v = 60.6\frac{(\rho_s - \rho)}{\rho} \times \frac{3T+70}{100} d \qquad \text{..........................(3.5.6)}$$

$$v = 60.6\frac{(1419.99 - 998)}{998} \times \frac{3 \times 25 + 70}{100}(0.00001)$$

$$v = 0.000372\ m/s$$

The residence time of particle of this size is determined as follow:

$$\text{Re}\,sidence\ time = t_R = \frac{H}{v} \qquad \text{...........................(3.5.6)}$$

$$t_R = \frac{9}{0.000372}$$

$$t_R = 24223.13\,s = 6.73\,h$$

The output concentration from the clarify is:

$$C_{out} = \frac{Q_{in} C_{in} - v.A_{s,sett}.C_{in}}{\left(Q_{ini} - \frac{v.A_{s,sett}.C_{in}}{\rho_{solids}} \right)} \qquad \text{............................(5.6.4)}$$

$$C_{out} = \frac{(1000/3600)(42.2712) - (0.000372 \times 4.526 \times 42.2714 \times 1000)}{\left((1000/3600) - \frac{(0.000372 \times 4.526 \times 42.2712 \times 1000)}{998 \times 1000} \right)}$$

$$C_{out} = \frac{11.742 - 71.171}{0.2778 - 0.0000713}$$

$$C_{out} = -213.982\,mg\,/\,L$$

The negative sign in the concentration means that particles of that size will not appear in the overflow.

9.1.2 Excel-Spreadsheet calculations

9.1.2.1 Cyanide model

Input							
Inlet Wastewater flowrate	Q	100	l/h		**RMM of Species**		
Inlet CN$^-$ Concentration	[CN$^-$]	25	mg/l		NaOCl	74	g/mol
pH		11			NaCN	69	g/mol
Temperature	T	24	^{0}C		NaCNO	85	g/mol
Diameter	d_T	0.611	m				
Height	H_T	0.48	m				
Vol. of Neutralizer	V_T	140.7954	L				
Surface are of tank	A_{rs}	0.2933	m^2				
Density of wastewater		1010	g/L				
[OH$^-$]		17.008	mg/l				
[NaCNO]/[NaOCl]		0.9					
Reaction rate constant	k	0.0134	L/mgs				

9.1.2.2 Chromium (VI) model

Input						
Feed waste	Q	1000	L/h	***RMM of species***		
Chrome(VI) conc.	$[Cr^{6+}]_{init}$	45	mg/L	CrO_3	100	g/mol
pH		2.6		Na_2SO_3	126.05	g/mol
Tank height	H_T	0.6	m	H_2SO_4	98.086	g/mol
Tank diameter	d_T	0.88	m	$Cr_2(SO_4)_3$	328.07	g/mol
Tank volume	V_T	365.074	L	Na_2SO_4	142.05	g/mol
Ratio of metabisulphite to chrome(VI)	$Q_{S4+/Cr6+}$	5		H_2O	18.016	g/mol
Ratio of sulfuric acid to chrome(VI)	$Q_{H2SO4/Cr6+}$	5.4751		Density of wastewater	1000	g/L
Activation energy	E	74600	J/mol			
Universal gas constant	R	8.3044	J/K.mol			
Frequency factor	A	5.69E+10	L/mg.s			
Temperature	T	20	^{o}C			
Feed waste	Q	1000	L/h			
Output						
Reaction rate constant	K	0.0036	s^{-1}			
quadratic coefficient 1	a	3986.435				
quadratic coefficient 2	b	-17287.052				
quadratic coefficient 3	c	13288.1167				
Conversion	X_1	3.338				
	X_2	0.999				
	21.90	min	min			

Out put concentrations			
Chrome(VI) concentration	$[Cr^{6+}]_{init}$	0.0604	mg/L
Sodium metabisulphite	S^{4+}	157.5905	mg/L
Suphuric acid	H_2SO_4	178.9714	mg/L
Chrome(III) concentration	$[Cr^{6+}]_{init}$	22.4698	mg/L
Sodium sulphate	Na_2SO_4	67.4095	mg/L
output ph		2.7388	

9.1.2.3 Iron (II) model

Input			
Feed flowrate	Q	1000	L/h
Iron(II) concentration	$[Fe^{2+}]$	78	mg/L
pH		8.5	
Temperature of the reaction tank	T	222	^{o}C
Tank height	H_T	2	m
Tank diameter	d_T	0.55	m
Tank volume	V_T	475.357	L
Airflowrate	Q_{Air}	333.3333	L/h
equilibrium oxygen concentration	$[O_2]$equil	8	mg/L
Density of water	ρ_{water}	1000	g/L
Density of air	ρ_{air}	1.29	g/L
Diffusivity of air	d_T	3.34E-02	m^2/s
Viscosity of water	m_w	0.001	cPoise
Diameter of an air bubble	d	0.0001	m
Gravitational acceleration	g	9.81	m^2/s
Reaction rate constant	k	0.00023	L/mg.s
Output			
Mass transfer coefficient			
	K_L/D_L	22.9707	
	K_L	0.7673	m/s
Velocity of a rising air bubble	v_{Air}	0.057	m/s

RMM of species		
Fe^{2+}	55.85	g/mol
O_2	32	g/mol
H_2SO_4	98.086	g/mol
H_2O	18.016	g/mol
H^+	1.008	g/mol
H_2O	18.016	g/mol
Density of wastewater	1000	g/L
Molar volume water	25.6	cm^3/g.mole
y_{H2O}	2.26	

Residence of an air bubble	t	35.1079	s
	a	0.4103	m^{-1}
Mass transfer coefficient (Kla)	a	0.3148	s^{-1}
Conversion	X	0.755	
Residence time	τ	1711.2857	s
		28.5214	min
		0.4754	h

Output concentrations			
Ferrous ions	$[Fe^{2+}]$	19.1346	mg/L
Oxygen	$[O_2]$	14.7163	mg/L
Ferric hydroxide	$[Fe(OH)_3]$	58.8654	mg/L
Hydrogen ions	$[H^+]$	117.7308	mg/L

9.1.2.4 Copper (II) model

Input							
Feed flowrate	Q	1000	L/h		***RMM of species***		
Copper (II) concentration	$[Cu^{2+}]$	50	mg/L		Cu^{2+}	63.55	g/mol
pH		8.5			NaOH	39.998	g/mol
$Q_{NaOH/Ni(II)}$		2			Cu(OH)	97.566	g/mol
Tank height	H_T	0.78	m		Na^+	22.99	g/mol
Tank diameter	d_T	0.48	m		H+	1.008	g/mol

Tank volume	V_T	141.2023	L		Density of wastewater	1000	g/L
Solubility constant	k	0.022					
Temperature of the reaction tank	T	25	^0C				

Output			
Iteration of conversion (X)			
X	*LHS*	*RHS*	
0.05	3.43E+00	1.79E-06	
0.6	2.56E-01	2.15E-05	
0.75	6.25E-02	2.68E-05	
0.85	1.35E-02	3.04E-05	
0.9	4.00E-03	3.22E-05	
0.9794	3.50E-05	3.50E-05	
1	0	3.58E-05	
Conversion	X	0.9794	
Space time	t	8.4876	min

Out put concentrations			
Copper(II)	$[Cu^+]$	1.03	mg/L
Sodium hydroxide	[NaOH]	2.06	mg/L
Copper hydroxide	$[Cu(OH)_2]$	48.97	mg/L
Sodium ions	$[Na^+]$	97.94	mg/L

9.1.2.5 Coagulation of alum

Input			
Feed wastewater	Q	1000	L/hr
Alum concentration	$[Al_2(SO_4)_3]$	2.5	mg/L
Tank height	H_T	1.5	m
Tank diameter	d_T	2.5	m
Tank volume	V_T	7366.071	L
pH		7.7	
Temperature	T	25	^oC
Reaction rate constant	k	0.015	s^{-1}
Output			
Conversion of alum to alum hydroxide	X	0.998	
Space (residence) time	t	7366.0714	s
		122.7679	min
Out put concentrations			
Alum sulphate	$[Al_2(SO_4)_3$	0.0063	mg/L
Alum hydroxide	$[Al(OH)_3]$	4.9875	mg/L

9.1.2.6 Copper (II) hydroxide flocculation

Input			
Freundlich capacity factor	K_f	6.618	
Freundlich intensity parametr	1/n	0.8	
mass of adsorbent ($Al(OH)_3$)	m	1.385405938	g/s
Output Copper (II) conc. In solution (C_{equil})	**LHS**	**RHS**	
mg/L	*mg/s*	*mg/s*	
48.970	0.000	148.823	
39.176	7.069	124.492	
29.382	14.139	98.899	
19.598	21.201	71.531	
9.794	28.278	41.067	
0.000	35.347	0.000	
Output Copper(II) conc. in solution (C_{equil})		6.7	mg/L
mass adsorbate (mg)/ mass adsorbent	q_e	8.4753	mg/g
mass $Cu(OH)_2$ adsorbed	M_{abs}	11.7417	mg/s
concentration of chromium flocs		42.27	mg/L

9.1.2.7 *Copper flocs settling*

Input			
Feed wastewater flowrate	Q	1000	L/h
Density of chromium hydroxide flocs	ρ_g	1419.99	g/L
Density of water	ρ_w	998	g/L
Diameter of copper hydroxide flocs	d_p	0.00001	m
		0.001	cm
Height of settler	H_T	9	m
Diameter of settler	d_T	2.4	m
Cross sectional area of settler	$A_{s,sett}$	4.5257	m^2
Volume of settler	V_T	40.7314	m^3
Temperature of wastewater	T	25	^{O}C
Output			
Settling velocity	v	0.000372	m/s
Residence time	τ	24223.1303	s
		6.7287	h
overflow concentration of flocs		-213.6472	mg/L

9.2 APPENDIX B – GRAPH AND FIGURES USED IN THIS STUDY

9.2.1 Stoichiometric table for reaction

Considered a generalized reaction:

$$aA \;+\; bB \;+\; cC \;\rightarrow\; dD \;+\; eE \;+\; fF$$

Table 9.4 shows the generalized reaction's stoichiometric balance. This table can be applied in any engineering units where there is a reaction taking place.

Specie	**Concentration**
	mg/L
A	$[C_A] = [C_A]_{init}(1 - X)$
B	$[C_B] = [C_A]_{init}(\Theta_{B/A} - b/a\,X)$
C	$[C_C] = [C_A]_{init}(\Theta_{C/A} - c/a\,X)$
D	$[C_D] = [C_A]_{init}(\Theta_{D/A} + d/a\,X)$
E	$[C_E] = [C_A]_{init}(\Theta_{E/A} + e/a\,X)$

Table 9.4: Generalized stoichiometric table for a reaction [24].

Where: $[C_A]_{init}$ = input concentration of basis species A (mg/L)

$[C_A]$ = output concentration of basis species A (mg/L)

$\Theta_{i/A}$ = ratio of input specie i over basis specie A

a, b, c, d = stoichiometric coefficient

X = conversion of basis specie A

Table 9.5, illustrates typical local discharge standards of metal finishers. Metal finishers to monitor and reduce the discharge of contaminates in the environment.

Pollutant	**Units**	**Limit**
Temperature	^{0}C	44
Electrical conductivity	mS/m	500 at 25 ^{0}C
pH		>5
Substances not in solution	mg/L	2000
Cynogen compounds (as HCN)	mg/L	20
Sulphide, hydrosulphides and polysulphides (as S)	mg/L	50
Sulphate in solution (as SO_4)	mg/L	1800
Anionic surface active agents	mg/L	500
Copper (as Cu)	mg/L	10
Nickel (as Ni)	mg/L	10
Zinc	mg/L	10
Cadmium (as Cd)	mg/L	2.5
Chromium (as Cr)	mg/L	20
Lead (as Pb)	mg/L	2.5
Arsenic	mg/L	2.5
Cobalt (as Co)	mg/L	20

Table 9.5: Discharge standards for the Johannesburg Municipality (abridged) [38].

Table 9.6 and table 9.7 show sample test results of waste before and after treatment.

SI. No.	***units***	**Parameters**	**Before Treatment**	**After treatment**
1.		PH	2.40	6.83
2.	*mg/l*	T.S.S.	250.00	40.00
3.	*mg/l*	Oil & Grease	11.00	N.T.
4.	^{o}C	Temperature	29	30
5.	*mg/l*	Total Chromium	0.39	0.10
6.	*mg/l*	Hexavalent Chromium	0.17	N.T.
7.	*mg/l*	Zinc	0.63	0.25
8.	*mg/l*	Iron	6.79	1.09
9.	*mg/l*	Nickel	0.37	N.T.
10.	*mg/l*	Copper	N.T.	N.T.
11.	*mg/l*	Cadmium	1.48	0.52
12.	*mg/l*	Cyanide	0.13	0.076
13.	*mg/l*	Lead	0.01	N.T.
14.	*mg/l*	Ammoniacal-N	1.36	N.T.
15.	*mg/l*	Total Res. Chlorine	23.21	N.T
16.	*mg/l*	Total Metal	9.67	1.96

Table 9.6: Typical wastewater treatment efficiencies of zinc plating waste treatment plant[39].

SI. No.	**units**	**Parameters**	**Before Treatment**	**After treatment**
1.		PH	5.60	6.98
2.	mg/L	T.S.S.	100.00	50.00
3.	mg/L	Oil & Grease	8.00	4.00
4.	^0C	Temperature	25	26
5.	mg/L	Total Chromium	0.19	0.08
6.	*mg/l*	Hexavalent Chromium	0.07	N.T.
7.	*mg/l*	Iron	N.T.	N.T
8.	*mg/l*	Nickel	5.82	1.75
9.	*mg/l*	Copper	12.94	1.46
10.	*mg/l*	Cadmium	0.03	0.01
11.	*mg/l*	Cyanide	N.T.	N.T.
12	*mg/l*	Lead	N.T	N.T
13	*mg/l*	Ammoniacal-N	N.T.	N.T.
14.	*mg/l*	Total Res. Chlorine	15.58	N.T.
15.	*mg/l*	Total Metal	19.03	3.30

Table 9.7: Typical wastewater treatment efficiencies of a Nickel, Brass. Copper plating waste treatment plant[39].

Figure 9.4 and 9.5 illustrate the variation metal ion's solubility with changing pH.

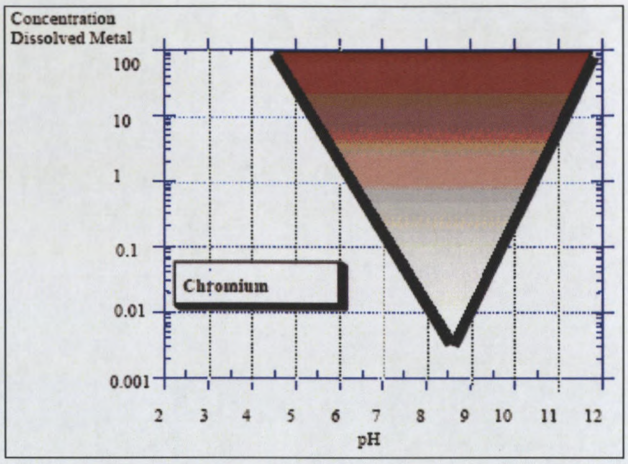

Figure 9.4: The relationship of chromium solubility and pH [18].

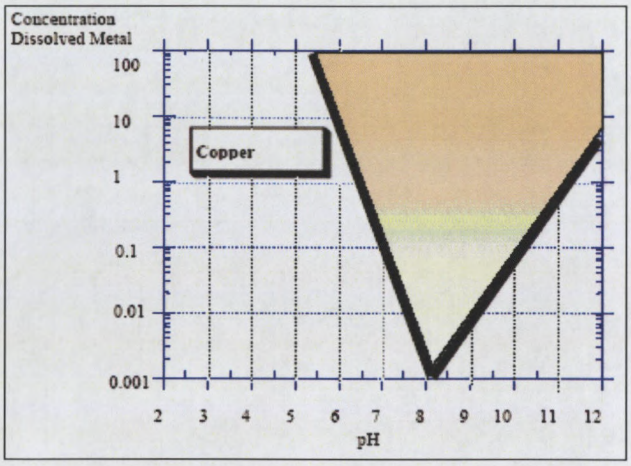

Figure 9.5: The relationship of copper solubility and pH [18].

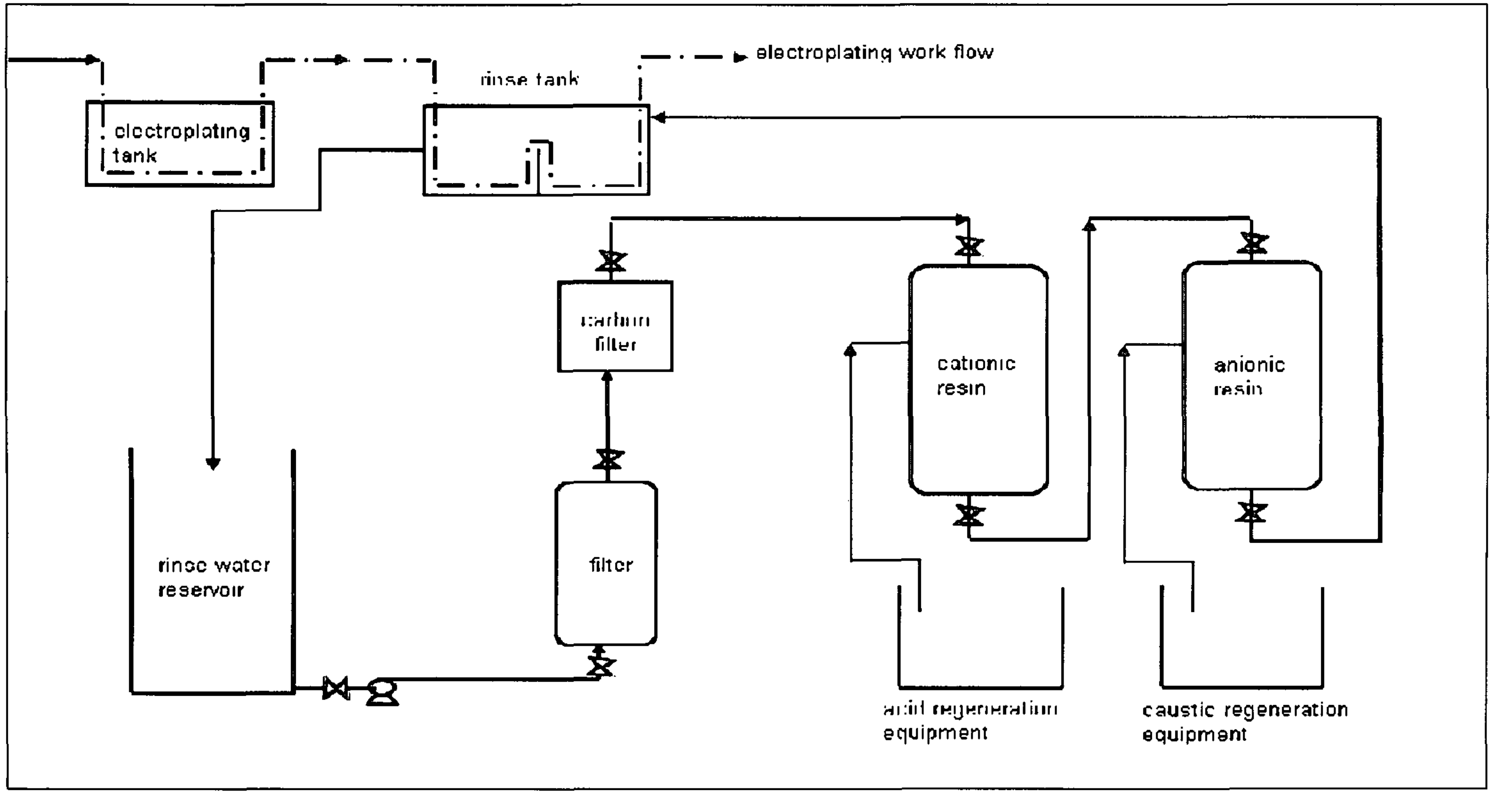

Figure 9.6: Ion exchanger process for treating Electroplating wastewater treatment [40,41].

9.3 APPENDIX C – MATHEMATICAL METHODS

9.3.1 Integration by separating variables

A first order equation that can be written in the form:

$$dy / dx = g(x) / h(y) \qquad \text{........................(9.3.1)}$$

where: $g(x)$ is a function of x

$f(y)$ is a function of y

Expression 8.3.1 can be rearranged by grouping same variables as follows:

$$h(y)\,dy = g(x)\,dx \qquad \text{...........(9.3.2)}$$

Expression 8.3.2 can be integrated as follows:

$$\int h(y)\,dy = \int g(x)\,dx \qquad \text{..................(9.3.3)}$$

Equation 8.3.3 defines y implicitly as a function of x but in some cases y can be solved in terms of x.

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DEVELOPMENT OF A MATHEMATICAL MODEL FOR TREATMENT OF METAL FINISHING WASTEWATER

2008

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