

University of Southern Queensland  
Department of Engineering and Built Environment

# **Pre-Treatment of Coal Seam Gas Produced Water**

A dissertation submitted by

**Byron Manthey**  
**0061003007**

In fulfilment of the requirements of

**Courses ENG4111 and 4112 Research Project**

Towards the degree of

**Bachelor of Engineering (Mechanical)**

Submitted: October 30, 2014

## Abstract

This research addresses pre-treatment of Coal Seam Gas produced formation water using coagulation as the primary means of pre-treatment. Produced formation water pre-treatment currently involves the use of filtration and natural settlement. After pre-treatment the water is treated to the required standard using reverse osmosis. Due to the high solids content of produced formation water, filter media is regularly damaged or impeded, reducing the efficiency of the filter. The need for pre-treatment is imperative, without effective pre-treatment an undesirable level of solids in the water will be allowed to pass directly to the reverse osmosis membranes, causing irreversible damage. Coagulation has been identified as the most suitable pre-treatment option. The coagulation process agglomerates suspended solids into large bodies, increasing the rate of natural settlement and enhancing the filtration efficiency of the water. The coagulants investigated in this research have been selected due to their proven effectiveness for pre-treatment processes of the desalination of seawater. The similarities between seawater and produced formation water identified the suitability of coagulants for selection and subsequent testing. Ferric Chloride and Ferric Sulphate have been identified as the most suitable coagulants for testing and analysis. Aluminium Sulphate has also been tested and analysed due to its wide spread use in water treatment. The produced formation water used for testing was collected from an initial coal seam gas well unload in the Surat basin, it provided a suitable representation of produced formation water quality. Jar testing was selected as the most effective method of testing and analysis and accounts for the primary means of testing in this research. The focus of initial testing was to first quantify the efficiency of the chosen coagulants, then to identify the range of dosage for optimisation. Initial testing proved all coagulants effectiveness, and identified the following ranges for optimisation, Aluminium sulphate 10 - 100 mg/L, Ferric Chloride 60 - 140 mg/L, and Ferric Sulphate 60 - 140 mg/L. Statistical analysis software Minitab was used to formulate the experimental designs, and the models required for optimisation analysis, based on two factors being dosage and pH. Surface response methodology was used to predict the optimum values of the parameters, with the minimum number experiments. The predicted results have been analysed and validated using analysis of variance. The analysis of optimisation was undertaken using overlain contour plots and provided a graphical representation of the optimal region. The results of optimisation indicated Aluminium Sulphate and Ferric chloride reduced turbidity at optimal conditions by 99%. Ferric chloride required 140 mg/L of coagulant, twice the dosage of Aluminium Sulphate. Although requiring twice the dosage, Ferric Chloride resulted in a third 0.273 mg/L of heavy metal residual, namely iron. This research has identified coagulation as being an effective means of pre-treatment of produced formation water.

**University of Southern Queensland**  
**Faculty of Health, Engineering and Sciences**  
**ENG4111/ENG4112 Research Project**

**Limitations of Use**

The Council of the University of Southern Queensland, its Faculty of Health, Engineering & Sciences, and the staff of the University of Southern Queensland, do not accept any responsibility for the truth, accuracy or completeness of material contained within or associated with this dissertation.

Persons using all or any part of this material do so at their own risk, and not at the risk of the Council of the University of Southern Queensland, its Faculty of Health, Engineering & Sciences or the staff of the University of Southern Queensland.

This dissertation reports an educational exercise and has no purpose or validity beyond this exercise. The sole purpose of the course pair entitled “Research Project” is to contribute to the overall education within the student’s chosen degree program. This document, the associated hardware, software, drawings, and other material set out in the associated appendices should not be used for any other purpose: if they are so used, it is entirely at the risk of the user.

## **Certification of Dissertation**

I certify that the ideas, designs and experimental work, results, analyses and conclusions set out in this dissertation are entirely my own effort, except where otherwise indicated and acknowledged.

I further certify that the work is original and has not been previously submitted for assessment in any other course or institution, except where specifically stated.

---

Byron Manthey  
0061003007

## Acknowledgments

I would like to thank my supervisor Dr. Vasantha Aravinthan for taking on the responsibility of supervising this dissertation. Vasantha, thank you for your patience, guidance, encouragement, persistence and expert advice throughout the past year, your contribution to the completion of this work cannot be appreciated enough. Friederike and Raed, thank you for your patience, advice and assistance in the labs, without your help and guidance this work would not have been possible.

Thank you to my friends Lachy and Shannon that have directly supported me throughout this work. Lachy, thanks for the advice and support. Shannon, thanks for the great friendship and allowing me to unwind with a few cold beers, even though you quit drinking on me for 12 weeks. I would like to thank all my friends for their support and understanding during this dissertation. Thank you, Tyson, Simon, Sam S, Sam P, Mitch and Luke. Each of you have provided support and encouragement, I am indebted to each of you.

I wish to thank my employer Australian Rig Construction, namely Guido, Al and Pete. Your support and understanding throughout the course of my study has been second to none. I sincerely thank you for all the opportunities and guidance you have given me over the past three years.

Finally I wish to thank my family. Mum and Dad thank you both for the never ending financial and emotional support, thank you for letting me forge my own pathways in life and being there to support me along the way and to catch me when I fall. Thank you to my brothers Nathan and Quinton, my two best friends. Quinton thanks for the support both emotional and financial. Nathan without your support, guidance and constant mentoring I would never have been able to accomplish what I have. To my two sisters, Amy and Sarah, you are both beautiful girls that have helped me to laugh and unwind. My amazing wife Jackie, thank you from the bottom of my heart for your love and support, you have always been there and supported me through thick and thin. I love you.

To those I have not mentioned but have been a part of this endeavour, I sincerely thank you.

## Contents

Abstract.....	i
Acknowledgments.....	iv
List of Figures .....	viii
List of Tables .....	ix
Nomenclature .....	x
Chapter 1 - Introduction .....	1
1.1 Aims and objectives .....	2
1.2 Scope of study .....	2
1.3 Dissertation outline .....	3
Chapter 2 – Literature Review .....	5
2.1 Coal Seam Gas Produced Water .....	5
2.1.1 Background of Coal Seam Gas Production .....	6
2.1.2 Background of Produced Formation Water.....	6
2.1.3 Produced Formation Water Quality and Treatment Options.....	7
2.1.4 Current Produced Formation Water Treatment and Associated Issues.....	8
2.1.5 Summary .....	9
2.2 Pre-treatment Technologies .....	11
2.3 Colloidal Mechanisms .....	11
2.4 Commonly Used Coagulants .....	12
2.4.1 Aluminium Based Coagulants .....	12
2.4.2 Iron Based Coagulants.....	13
2.4.3 Chitosan as a Coagulant .....	14
2.5 Selection of Coagulants Suitable for CSG Water Pre-Treatment.....	15
2.6 Use of Coagulants with Reverse Osmosis .....	16
2.7 Summary .....	19
Chapter 3 – Materials and Methodology.....	22
3.1 Jar Test.....	22
3.2 pH .....	23
3.3 Conductivity .....	24
3.4 Alkalinity.....	24
3.5 Turbidity .....	26

3.6	Atomic Absorption Spectrometry .....	27
3.7	Optimisation.....	28
3.8	Coagulant Preparation .....	29
3.9	Theory of Mathematics Used in This Research.....	29
Chapter 4 –Initial Testing Procedures and Water Characteristics.....		32
4.1	Settlement Rate .....	32
4.2	pH response.....	33
4.3	Initial Water Characteristics.....	35
Chapter 5 – Aluminium Sulphate as a Coagulant .....		36
5.1	Preliminary Experiments .....	36
5.2	Results and Discussion of preliminary experiment.....	37
5.3	Optimisation Experiments.....	37
5.4	Validation of the Model .....	39
5.5	Optimisation Analysis.....	42
5.6	The optimum Value.....	45
Chapter 6 – Ferric Chloride as a Coagulant .....		48
6.1	Preliminary Experiments .....	48
6.2	Results and Discussion of preliminary experiment.....	49
6.3	Optimisation Experiments.....	50
6.4	Validation of the Model .....	51
6.5	Optimisation Analysis.....	53
6.6	The optimum Value.....	56
Chapter 7 – Ferric Sulphate as a Coagulant .....		59
7.1	Preliminary Experiments .....	59
7.2	Results and Discussion of preliminary experiment.....	60
7.3	Optimisation Experiments.....	60
7.4	Validation of the Model .....	62
7.5	Optimisation Analysis.....	64
7.6	The optimum Value.....	67
Chapter 8 – Conclusion and Recommendations.....		70
8.1	Conclusion .....	70
8.2	Recommendations for Further Work.....	72

References .....	73
Appendix A: Project Specifications .....	75
Appendix B: Risk Management .....	77
Appendix C: Results of testing .....	79
Appendix D: Example Matlab Code .....	89



## List of Figures

Figure 2.1 - CSG extraction, (Aplng, 2014).....	5
Figure 2.2 - Particle size and treatment options, (Nghiem, L, 2011).....	8
Figure 2.3 - Negatively charged colloid, (water/Wastewater Distance Learning, 2011).....	12
Figure 2.4 - Reaction of Alum in water to be treated, (water/Wastewater Distance Learning, 2011).....	13
Figure 2.5 - Reaction of Al during Hydrolysis, (water/Wastewater Distance Learning, 2011).....	13
Figure 2.6 - Reaction of Ferric Salts, (water/Wastewater Distance Learning, 2011).....	14
Figure 2.7 - Solubility of Al in Seawater. James, EK & Johannes, H, (2011).....	17
Figure 2.8 - Solubility of Fe in seawater - James, EK & Johannes, H, (2011).....	18
Figure 3.1- Jar testing apparatus (Manthey, 2014).....	23
Figure 3.2 - Atomic Absorption Spectrometer. (Manthey, 2014).....	27
Figure 4.1 – Settlement Rate.....	33
Figure 4.2- Titration Curve.....	34
Figure 5.1 - Dosage vs. Turbidity Aluminium Sulphate.....	37
Figure 5.2 – Residual vs. % Predicted Turbidity Removal & Normal Probability.....	40
Figure 5.3 - Residual vs. Residual Al & Normal Probability.....	40
Figure 5.4 - Normal Distribution of Residual Turbidity and Residual Al.....	41
Figure 5.5– Surface and Contour Plots for Residual Turbidity.....	44
Figure 5.6 – Surface and Contour Plots for Residual Aluminium.....	44
Figure 5.7 – Overlaid Contour Plot of Residual Turbidity and Residual Aluminium.....	45
Figure 5.8 – Partial Derivative for Fitted Equations.....	46
Figure 5.9 – Point of Optimal Residual Turbidity & Residual Aluminium.....	47
Figure 6.1 - Dosage vs. Turbidity Ferric Chloride.....	49
Figure 6.2 – Residual vs. Predicted Residual (NTU) & Normal Probability.....	52
Figure 6.3 – Residual vs. Residual Al & Normal Probability.....	52
Figure 6.4 – Normal Distribution of Residual Turbidity and Residual Al.....	52
Figure 6.5 – Surface and Contour plots for Residual Turbidity.....	55
Figure 6.6 – Surface and Contour Plots for Residual Iron.....	55
Figure 6.7 – Overlaid Contour Plot of Residual Turbidity and Residual Iron.....	56
Figure 6.8 – Point of Optimal Residual Turbidity & Residual Iron.....	57
Figure 7.1 - Dosage vs. Turbidity Ferric Sulphate.....	60
Figure 7.2 – Residual vs. Predicted Turbidity & Normal Probability.....	62
Figure 7.3 - Residual vs. Predicted Residual Iron & Normal Probability.....	63
Figure 7.4 – Normal Distribution for Residual Turbidity and Residual Iron.....	64
Figure 7.5 – Surface and Contour Plots for Residual Turbidity.....	66
Figure 7.6 – Surface and Contour Plots for residual Iron.....	66
Figure 7.7 – Overlaid Contour Plot of Residual Turbidity and Residual Iron.....	67
Figure 7.8 – Point of Optimal Residual Turbidity & Residual Iron.....	68

## List of Tables

<i>Table 2.1 - Statistical Analysis of raw water data for CSG wells, (Davey, A, et al ,2012)</i> .....	9
<i>Table 2.2 - Comparison between water</i> .....	15
<i>Table 2.3 - Comparison between seawater and CSG water</i> .....	16
<i>Table 2.4 - Dosages vs. turbidity removal, (Altaher, H, 2012)</i> .....	19
<i>Table 2.5 - Suitability Comparison of Coagulants</i> .....	20
<i>Table 2.6 - Suitability Comparison of Coagulant use with RO</i> .....	21
<i>Table 3.1- End-Point pH Values, (Eaton, A, et al 2005)</i> .....	25
<i>Table 3.2 - Alkalinity Relationships, (Eaton, A, et al 2005)</i> .....	25
<i>Table 4.1 – Settlement Rate</i> .....	32
<i>Table 4.2 - pH Response</i> .....	34
<i>Table 4.3 - Produced Formation Water Charateristic</i> .....	35
<i>Table 5.1 - Initial Results Aluminium Sulphate</i> .....	36
<i>Table 5.2 – Aluminium Sulphate Optimisation</i> .....	38
<i>Table 5.3 - Coefficient of Determination Values</i> .....	42
<i>Table 5.4 - ANOVA Response of Residual Turbidity</i> .....	42
<i>Table 5.5 – ANOVA Response Residual Aluminium</i> .....	43
<i>Table 5.6 – Point of Optimum</i> .....	46
<i>Table 5.7 – Optimal Conformational testing</i> .....	47
<i>Table 6.1 - Initial Ferric Chloride Results</i> .....	48
<i>Table 6.2 – Ferric Chloride Optimisation</i> .....	50
<i>Table 6.3 - Coefficient of Determination Values</i> .....	53
<i>Table 6.4 - ANOVA Response of Residual Turbidity</i> .....	54
<i>Table 6.5 – ANOVA Response of Residual Iron</i> .....	54
<i>Table 6.6 – Point of Optimum</i> .....	57
<i>Table 6.7 – Optimal Conformation Testing Results</i> .....	58
<i>Table 7.1 - Initial Ferric Sulphate Results</i> .....	59
<i>Table 7.2 – Ferric Sulphate Optimisation</i> .....	61
<i>Table 7.3 - Coefficient of Determination Values</i> .....	64
<i>Table 7.4– ANOVA Response Residual Turbidity</i> .....	65
<i>Table 7.5 – ANOVA Response Residual Iron</i> .....	65
<i>Table 7.6 – Point of Optimum</i> .....	68
<i>Table 7.7 - Optimal Conformational testing</i> .....	69
<i>Table 8.1 – Optimal Achieved Results for all Experiments Conducted</i> .....	71

## Nomenclature

The following abbreviations are used through-out the report:

<b>ANOVA</b>	Analysis of Variance
<b>CSG</b>	Coal Seam Gas
<b>CCD</b>	Central Composite Design
<b>DoE</b>	Design of Experiment
<b>MF</b>	Microfiltration
<b>MSDS</b>	Material Safety Data Sheet
<b>PFW</b>	Produced Formation Water
<b>PW</b>	Produced Water
<b>RM</b>	Rapid Mix
<b>RO</b>	Reverse Osmosis
<b>SG</b>	Specific Gravity
<b>SM</b>	Slow Mix
<b>St</b>	Settlement Time
<b>TDS</b>	Total Dissolved Solids
<b>UF</b>	Ultrafiltration
<b>RSM</b>	Response Surface Methodology

## Chapter 1 - Introduction

Coal seam Gas (CSG) is an attractive alternative to energy production when compared with conventional fossil fuels. Fossil fuels namely coal, have been in a steady decline since their age of inception. Coal seam gas offers an alternative to coal production, with the need for mining neglected. Instead a CSG well is drilled between 10 to 2000m, these wells are strategically placed throughout the coal seam to maximise yield. These wells allow CSG to rise to the surface, which is then collected and sent for further processing. Before the gas can freely flow to the surface, the water must first be removed from the coal seam. Coal seams are porous in nature and act as a natural aquifer for surface water. The CSG is held in the seam by hydrostatic pressure, once the well is drilled the seam is pressurised with compressed air. The CSG well is then unloaded, this unloading process brings water to the surface and aids in 'cleaning' of the well, this initial unload water is when the water is at its most polluted and requires the most treatment. The test water is high in solids, high in alkalinity, and high in pH. The initial unload water has been used extensively for testing through-out the course of this research. After the initial 'unload' a pump is placed in the bottom of the well and the water is continually removed, allowing gas production.

Once the CSG water has been extracted from the well, it is transported in gathering lines to a main feed line. The main feed line transports the water to a centralised holding and treatment location. The water is pumped into holding ponds then pre-treated. After pre-treatment the water is treated to a desired standard using reverse osmosis (RO). As identified by Davey, A, et al (2012) the current pre-treated processes being used are oxidisation, stripping, absorption, gas flotation, microfiltration (MF), ultrafiltration (UF), and media filtration. These processes are subjected to the same problems associated with reverse osmosis, being fouling of the filters/membranes, perceptible scaling, and irreversible damage to the filters/membranes. Once the water has been treated to a satisfactory level it is released into local catchments.

The conducted research has studied the effectiveness and suitability of coagulation as a suitable pre-treatment alternative. To be able to suitably identify the correct coagulant, the untreated water must be tested with special consideration towards solids content, pH and alkalinity. The main factor regarding the effective use of coagulants, is the test waters pH, this has had to be reduced to fall into the effective working envelope of the coagulant. The addition of chemicals to the pre-treated water must not have any adverse effects on the environment, the RO plant, and people associated or subjected to pre-treated or post treated water.

A detailed comparison between seawater, surface water, and CSG water has been conducted. This comparison shows the similar characteristics between CSG water and seawater. The comparison has enabled and influenced the selection of the coagulants.

Testing has focused on the optimisation of the best performing coagulant. Coagulants were first dosed in increasing dosages to identify the suitable working envelope. The key goal of the research is to identify the best performing coagulant that offers the best reduction in turbidity and solids.

## **1.1 Aims and objectives**

The overall aim of this project is to identify a suitable coagulant that offers the best performance for turbidity. The application of coagulant will be used as a pre-treatment process for Coal Seam Gas produced water.

The research objectives are as follows:

1. Acquire Coal Seam Gas water sample from an initial well unload in the Surat basin. Analyse the raw water characteristics, paying special attention to pH, alkalinity, turbidity, and total solids.
2. From the water characteristics and the comparison with sea-water select suitable coagulants.
3. Conduct preliminary jar test experiment to identify the effectiveness and required range of optimum dosage and pH required for maximum turbidity removal, and solids removal. Preliminary testing will also be used to optimise the mixing process, namely rapid mix (RM), slow mix (SM), and settle time (St).
4. Use statistical analysis technique Design of Experiment (DoE) to setup computational aid to find out the minimum number of tests needed to optimise the identified variables in point three.
5. Analyse the experimental data received for optimum parameters that can maximise the turbidity removal by deriving systematic mathematical models that adequately describe and predict the experimental phenomena using surface response methodology available in Mini tab software.
6. Identify the suitable coagulant by; critically evaluating the performance of the different coagulants, their effect on the environment-and their optimum range in the pre-treatment of CSG water using the results from points 4 and 5.

## **1.2 Scope of study**

The scope of this research will identify a suitable coagulant to be used as an alternative pre-treatment method for Coal Seam Gas produced water; this water is the feed water for the reverse osmosis process.

The research limitations include:

- CSG water characteristics are particular to the area of collection
- Coagulants were selected from their widespread use in sea-water desalination. Sea-water held the best comparative abilities with CSG produced water
- Only 3 coagulants will be used for testing being; Ferric Sulphate, Ferric Chloride, and Aluminium Sulphate.
- Flocculants/Coagulant aids have not been trialled for effectiveness when used in conjunction with coagulants.

### **1.3 Dissertation outline**

This dissertation covers 8 chapters. All chapters cover all the aspects of the chosen report. Detailed below is a short outline of each chapter.

#### ***Chapter 2- Literature Review***

This chapter identifies the need for pre-treatment of coal seam gas produced water. The reasons why coal seam gas produces water as part of the gas extraction process is also reviewed. The water characteristics are also investigated. The first part of Chapter 2 identifies the need for pre-treatment and the current treatment technologies. The current pre-treatment technologies aim to reduce the impurities of the water and improving its suitability for further treatment, namely reverse osmosis. Types and applications of coagulants have been discussed identifying their merits and weaknesses. Identified within the literature are the coagulants current uses and the results obtained from their use. The mechanisms of coagulation is also explained and the coagulants suitability when compared to sea water desalination. The research has identified gaps in the literature relating to this research, the lack thereof published research into pre-treatment of produced formation water using coagulation has been identified.

#### ***Chapter 3- Materials and Methodology***

This chapter details the materials and methodology used for the research testing. To be found in this chapter is the process adhered to when testing certain water characteristics. This chapter identifies the main testing platform being the jar test. This process is explained

in detail. The preparation of coagulants is also discussed. The optimisation process is explained utilising mathematical software Minitab.

#### ***Chapter 4 – Initial testing***

Chapter 4 details the initial water testing undertaken. This chapter identifies particular water characteristics and details the settlement rate of the water. Also detailed in this chapter is the waters response or buffering capability to the addition of acids. The content in this chapter underpins the necessity of this testing to ensure reliability in results of further testing.

#### ***Chapter 5 – Aluminium Sulphate as a Coagulant***

#### ***Chapter 6 – Ferric Chloride as a Coagulant***

#### ***Chapter 7 – Ferric Sulphate as a Coagulant***

Chapters 5, 6, and 7 detail the initial testing of each coagulant to identify its effectiveness and suitability. Initial testing has also revealed the optimal range of dosage for refinement testing. Surface response methodology was used to predict the optimum values of the parameters, for the least amount of required experiments. All results for experimentation have been input into statistical analysis software Minitab. Minitab was then used to generate quadratic regression models that have been used to generate 3d surface plots and overlain contour plots that address all variables and responses. Statistical analysis using analysis of variance (ANOVA) was applied to validate the models, predict the coefficients, and analysis the variance in each model. Finally the results are discussed and interpreted.

#### ***Chapter 8 – Conclusion and Recommendations***

Chapter 8 identifies the research's contribution to addressing gaps in literature regarding pre-treatment of produced formation water using coagulants. It also discusses and compares all obtained results. Further research is recommended for a better understanding of the conclusions made.

## Chapter 2 – Literature Review

This literature review identifies the need for coal seam gas (CSG) production water pre-treatment using coagulation and also critically reviews the current literature on coagulation applicable to water treatment. A background into CSG production, CSG produced water, CSG produced water treatment, and water quality testing results on CSG sample water are provided to quantify the material used throughout the project. Identification of the difference between CSG produced water, sea water, and surface water highlight the requirement for pre-treatment. Coagulants are described along with testing procedures, identification criteria for suitability of Coagulant, and the consequential effects of the project are assessed.

### 2.1 Coal Seam Gas Produced Water

Produced water or produced formation water (PFW) is a by-product of coal seam gas production. Coal seams are located at depths ranging from 10 to 2000 m, are porous in nature and are natural aquifers for underground water. To enable gas production of the coal seam, the hydrostatic pressure trapping the gas in the seams has to be reduced. This is accomplished by the reduction of water in the coal seam by pumping from the pre-drilled CSG well. Water quality and quantity varies from lease to lease and over time as water is extracted from the seam (Davey A et al, 2012). Figure 2.1 depicts the process of water and coal seam gas extraction from a CSG well.

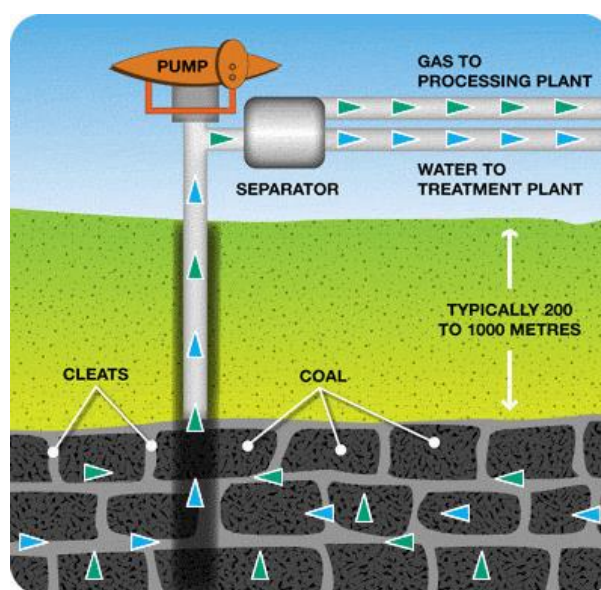


Figure 2.1 - CSG extraction, (Aplng, 2014)



### **2.1.1 Background of Coal Seam Gas Production**

CSG or Coal bed methane as it is known in America has become an important alternative to energy production. Many countries including but not limited to Australia, United States, Canada, China, and Russia are investing heavily into the CSG industry (Nghiem, et al 2011). This interest is due to the ever increasing cost associated with energy generation using fossil fuels and their decline, increases in global demand, and suitability as a more environmentally friendly alternative to current energy sources. Hamawand, I, et al, (2013), states that 'the estimated quantity of CSG worldwide is  $1.4 \times 10^{14} \text{ m}^3$ '. This amount highlights the fact that CSG is an attractive and significant alternative source for energy production.

CSG production in Queensland has dramatically increased from the lowly figure of 2PJ in 1997 to 234 PJ in 2011 this accounts for an increase of 11,600% in 14 years (Nghiem, et al 2011). The Surat basin accounts for a large percentage increase since its inception in CSG production in 2004.

### **2.1.2 Background of Produced Formation Water**

As previously mentioned, PFW is a by-product of CSG production. There is currently no viable option for CSG extraction without extraction of water. Due to these processes large amounts of PFW are produced throughout Australia with the national water commission estimating more than 7500 GL of PFW will be produced by the CSG industry in the next 50 years. Queensland alone is expected to account for 300 GL a year, which is the current water usage of the state (Davey A et al, 2012). During the initial commissioning of the well up to 600 kL of production water is produced in the first 24 hours. Water produced at the well site is transported to a central holding location for further treatment, namely desalination and/or sterilisation with a reverse osmosis plant. The preferred method of transportation for PFW is by high density polyethylene pipeline. A group of wells is connected to a main transportation pipeline. The produced CSG is transported in the same manner with feed lines from the well site connecting to a main supply line. The CSG is then transported to a centralised location for further processing (Davey, A, 2012).

### 2.1.3 Produced Formation Water Quality and Treatment Options

PFW in its natural form is unsuitable for domestic or agricultural use. It does not meet any standards for use in its current form. As stated by Abousnina, R, et al, (2014), 'CSG produced water is usually saline and is dominated by sodium', direct use of CSG produced water for irrigation will lead to soil structure damage; the increase of salinity level in soils make it difficult for vegetation to absorb water. CSG produced water is unsuitable to release directly into the natural environment. The produced formation water pumped from the coal seam which acts as a natural aquifer is high in suspended solids, dissolved solids and many minerals. In order to remove these particles of various sizes from the water, various treatment options are available. Table 2.2 identifies these various treatment options. The current treatment processes for CSG produced water, which contains high levels of suspended solids, dissolved solids, and turbidity, is pre-filtration followed by treatment using RO. After treatment the water is discharged into local streams, catchments, and other beneficial uses. In order for RO to be effective, pre-treatment needs to be improved to allow for a reduction in cost and man hours associated with pre-filter cleaning.

A substantial amount of solids in PFW are in colloidal form. A colloid is classified as a substance microscopically dispersed throughout another substance. The typical size range for colloids is between  $10^{-6}$  to  $10^{-9}$  m. Due to the small size of colloidal particles, they will not settle under gravitational forces alone. The amount of suspended solids, colloids, and dissolved solids all aid in increasing the turbidity of PFW, turbidity is a key testing parameter for water quality and is a measure of the degree to which water loses its transparency due to contaminants in the water. The particles will not amalgamate due to their electrical charge hence resulting in a repulsion force between particles (Abousnina, R, et al, 2014). This force keeps the particles in suspension in the substance. Figure 2.2 shows the size range of the colloids and suitable treatment process to remove the majority of the colloids.

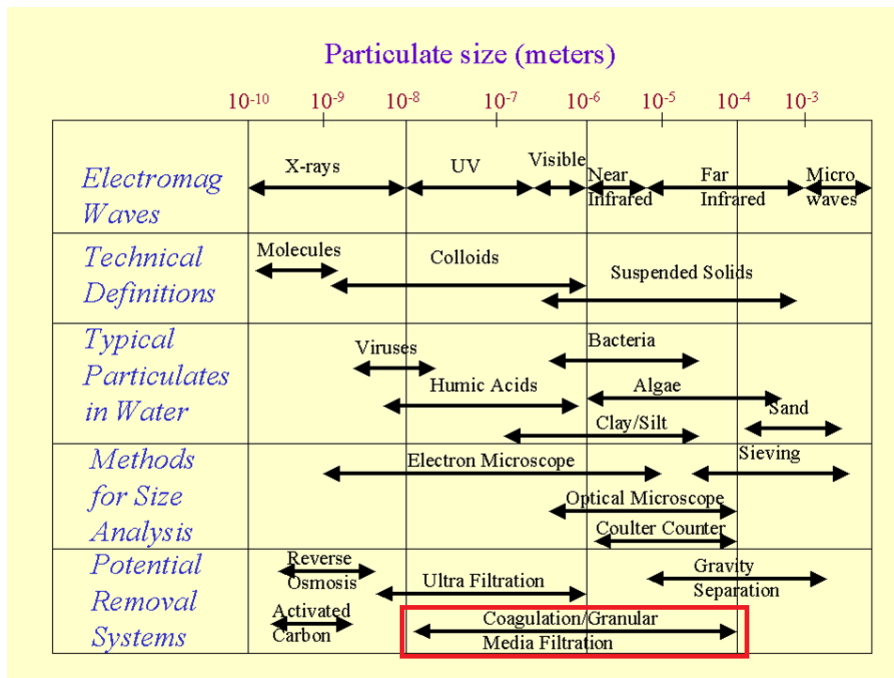


Figure 2.2 - Particle size and treatment options, (Nghiem, L, 2011)

#### 2.1.4 Current Produced Formation Water Treatment and Associated Issues

CSG produced water treatment is considered unique, this is due to a variety of quality characteristic (Abousnina, R, 2014). The current treatment process for PFW is namely reverse osmosis (RO) with the need for pre-treatment to avoid membrane fouling (Abousnina, R, 2014). Reverse osmosis is a water purification process that forces pressurised water through a series of membranes, these membranes allow water to pass through but retain molecules and ions. The resultant is water treated to a specified quality and standard and waste brine that is collected for further processing and treatment (Accepta, 2014). RO is a tried and tested method for water purification and is used worldwide for desalination to waste water treatment in industrial applications. Abousnina et al, (2014) states 'several feasibility studies were carried out for several desalination techniques, with RO considered the most competitive technology in terms of cost effect'. As depicted in Figure 2.2 reverse osmosis is capable of removing contaminations in water down to a very small size. This is because of the multitude of membranes used in a RO plant whereby, the membranes decrease in pore size depending on the required water quality. Therefore, the critical part of reverse osmosis plant is the membranes. The membranes equate to a 7% overall cost of the RO process but are considered a vital part of the process (Lenntech, 2014). It is therefore imperative to ensure the reliable operation of these membranes and to stop membrane fouling and damage.

Before the feed water reaches the RO plant, and the membranes, it is first pre-treated to remove suspended solids ranging in size from  $10^{-4}$  to  $10^{-8}$  meters. As stated by Davey, A, et al (2012), a variety of pre-treatment options are utilised, these being; oxidation, stripping, absorption, gas flotation, microfiltration (MF), Ultrafiltration (UF), and Media filtration. The difficulties faced with efficient pre-treatment of produced formation water are due to the facts of the varying qualities of the water. As stated by Davey, A, et al, (2012), 'water can vary vastly over a region', this fact is represented in Table 2.1. The variance in water quality and the fact water is transported to a centralised location for treatment means a multitude of filter options are required. The reason associated with the variance in water quality is due to the CSG wells water production rate varying dependant on the life of the well.

**Table 2.1 - Statistical Analysis of raw water data for CSG wells, (Davey, A, et al ,2012)**

Parameter	Dalby and Glenelg		Talinga		Moranbah	
	Typical	Maximum	Typical	Maximum	Typical	Maximum
<b>TDS (mg/L)</b>	3960	5360	3600	5300	5000	6450
<b>pH</b>	8.4	8.5	8.3	8.3	8.6	9.3
<b>Alkalinity (mg/L)</b>	885	1388	800	1600	838	2450
<b>Turbidity (NTU)</b>	16.5	110	12	40	n/a	n/a
<b>Total Suspended Solids (mg/L)</b>	30	150	20	46	30	30

Due to PFW having a high amount of suspended/colloidal solids and dissolved solids the pre-filtration and RO membranes are prone to fouling. The PFW is allowed to settle in containment ponds, however the time associated with this settlement is dependent on the amount of water being produced at the well sites. PFW can contain high levels of metal contaminants. These contaminants can lead to issues with oxidation and perceptible scaling on the RO membranes causing damage (Davey, A, 2012).

Pre-filtration of the RO plant feed water is currently used, but associated filter media will require regular cleaning and replacement. Due to these issues the cost associated with this option is high and the required man hours are also high.

### **2.1.5 Summary**

CSG produced water is high in contaminants and unsuitable for non-treated disposal, the current treatment process involves transporting the PFW to a centralised holding pond and treatment plant, and treating the water using pre-filtration and Reverse Osmosis. The issues associated with these water treatment processes have been discussed in the previous paragraph. There is only one conclusion to be drawn from these outcomes. That is, pre-treatment is necessary to ensure the reliable and longevity of issue free operation of the

reverse osmosis plant namely the RO membranes. The current pre-treatment options need refining or substitution.

The pre-treatment process that holds the best merits for a cost effective, easy application, safe and reliable operation is coagulation/flocculation. As depicted in Figure 2.2 coagulation/flocculation has the ability to remove contaminants in a range of sizes. If the correct dosage of coagulant/flocculent is established and adhered to the amount of coagulant/flocculent transferring to the RO feed water will be kept to a minimum hence reducing the possibility for perceptible scale build up and oxidation of the membrane.

## **2.2 Pre-treatment Technologies**

Pre-treatment of CSG water can involve the use of coagulation/flocculation, media filtration, ultra-filtration, electro-coagulation, and gravity separation. All the mentioned pre-treatments hold merit as an effective filtration process. However, media filtration and ultra-filtration require regular cleaning and filter replacement due to the high amounts of solids present in the water. The associated cost of electro-coagulation is high compared to other options. Gravity separation requires letting the solids settle, this is inappropriate due to the large amounts of settling time and the fact that not all solids will settle.

## **2.3 Colloidal Mechanisms**

The term coagulant is defined as 'to cause transformation of a liquid into or as if into a soft, semi-solid, or solid mass', Thefreedictionary (2014). For water treatment this transformation is the amalgamation of suspended/colloidal solids into a conglomeration known as 'flocs'. The increased size of the flocs enables gravitational forces to take effect causing them to settle (Gebbie, P, 2006). The first step in the treatment process is the addition of a predetermined amount of coagulant; this is determined from prior testing and dependent on the waters quality. Following the application of the coagulant, the water to be treated is rapidly mixed to disperse the coagulant evenly throughout the fluid. After this phase the mixing speed is then reduced to a more gentle mix. This process is aimed at allowing the newly forming flocs the opportunity to come into contact with each other. The floc is formed due to the coagulants ability to neutralise the electrical charge of the particles by the addition of a positively charged ion. This positively charged ion reduces the surface charge hence reducing the repulsion force between them and allowing Van Der Waals force to attract the particles together (Aravinthan, V, 2014). Figure 2.3 depicts a negatively charged colloid, the majority of colloids found in water are negatively charged. Once the gentle mixing phase has come to completion the flocs are allowed to settle. The rate and amount of settlement is proportional to time, therefore the longer you allow the more will settle.

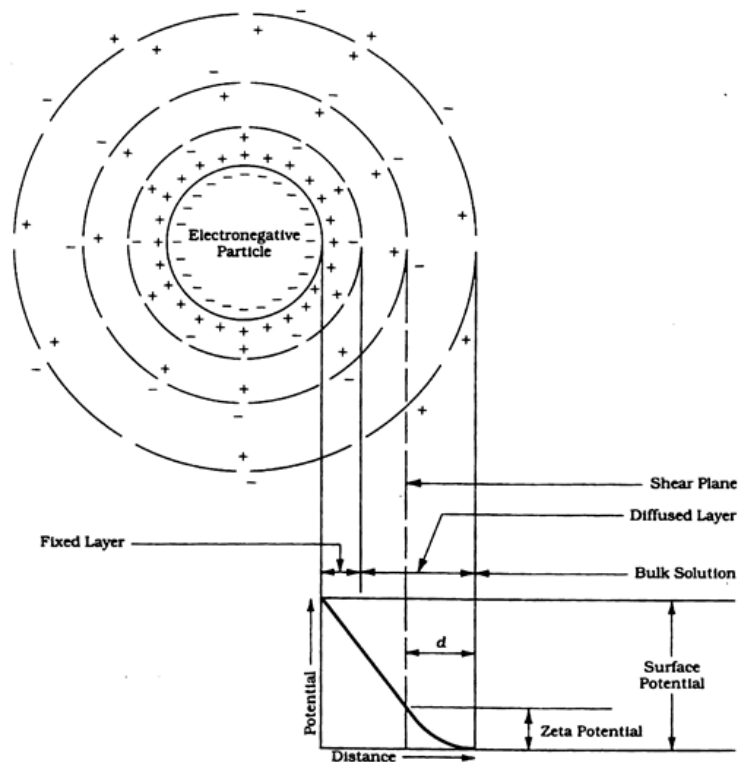


Figure 2.3 - Negatively charged colloid, (water/Wastewater Distance Learning, 2011)

## 2.4 Commonly Used Coagulants

Coagulation is the process of removing suspended solids in fluids, by the use of chemical compounds (Gebbie, P, 2006). Coagulants can be classified as inorganic or organic. The chemical compounds used are either metallic salts or polymers. Different types of water require different types of coagulants for effective coagulation. The most common used coagulants are salts of aluminium ( $\text{Al}^{3+}$ ) and iron ( $\text{Fe}^{3+}$ ), these salts react with water to achieve a particulate destabilisation (Aravinthan, V, 2014).

### 2.4.1 Aluminium Based Coagulants

Aluminium Sulphate is the most widely used and commercially available coagulant used in water treatment worldwide (Gebbie, P, 2006). When Aluminium Sulphate is applied to water it reacts and produces positively charged ions. The effectiveness of Aluminium Sulphate is dependent on the pH range of the water to be treated. Aluminium Sulphate is suited to water with a pH range in-between 5.5 - 7.5. Water with higher pH ranges require a heavier dosage of Aluminium Sulphate with an equally heavier impact on associated cost of dosage. Because of the associated cost involved in large dosages, Aluminium Sulphate may

not be as suitable as Ferric salts. Figure 2.4 shows the occurred reaction with Aluminium Sulphate is applied to water.

*ALUM*

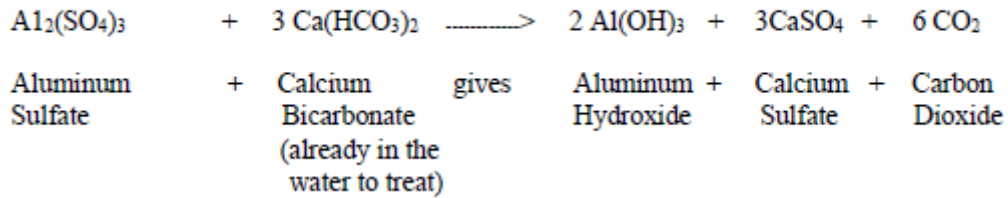


Figure 2.4 - Reaction of Alum in water to be treated, (water/Wastewater Distance Learning, 2011)

Aluminium Sulphate is renowned for its ability to buffer the waters initial pH, this is due to the occurred reaction during hydrolysis which also produces sulphuric acid, this reaction is depicted in Figure 2.5.

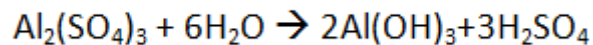


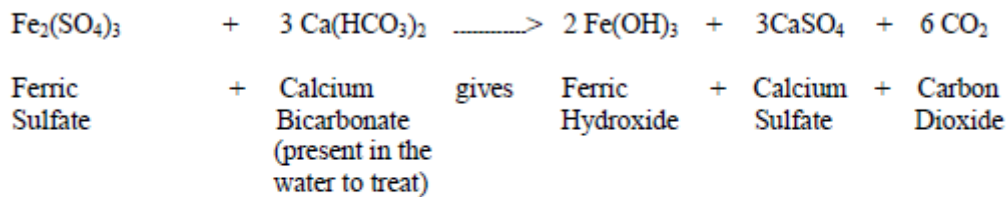
Figure 2.5 - Reaction of Al during Hydrolysis, (water/Wastewater Distance Learning, 2011)

### 2.4.2 Iron Based Coagulants

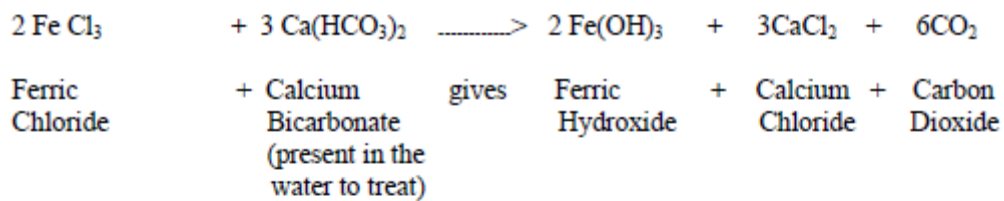
Iron based coagulants are normally cheaper and operate over a wider pH range than aluminium sulphate. Ferric Sulphate, Ferric Chloride, and Ferrous Sulphate are all iron based coagulants. Iron salts have a working envelope of pH between 5.5 and 8.5. Another advantage of the iron family of coagulants is that they contain no aluminium, which may have health implication to humans (Gebbie, P, 2006). One of the prevalent side effects of iron based coagulants is the reddish brown colour that can stain equipment effect water colour and look unsightly. The occurred reaction of ferric salts is depicted in Figure 2.6.



### *FERRIC SULFATE*



### *FERRIC CHLORIDE*



### *FERROUS SULFATE*

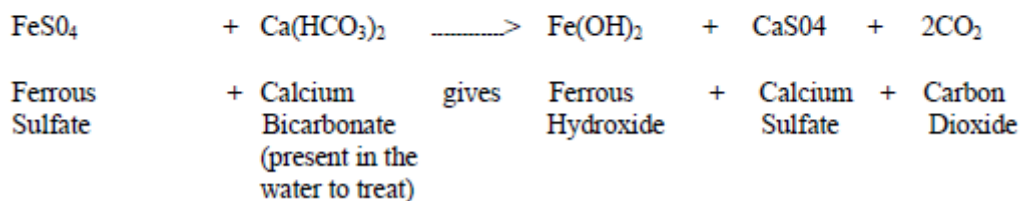


Figure 2.6 - Reaction of Ferric Salts, (water/Wastewater Distance Learning, 2011)

Ferric Salts including Ferric Chloride have been used extensively as coagulants solely or as a coagulant and flocculation process (Khai, EL & Tjoon, TT). The advantages of ferric based salts over Aluminium based salts are their ability to form stronger and heavier flocs over a broader pH range and their reduced problems associated with filtrate quality. Ferric coagulants when compared with Aluminium based coagulants do not possess the potential biological toxicity produced by residual aluminium in waste associated with the reverse osmosis process (Sanghyun, J, et al 2011).

### **2.4.3 Chitosan as a Coagulant**

Chitosan is a linear polysaccharide, made by treating crustacean shells with alkali sodium hydroxide, and is considered a natural polymer (Yogeshkumar, N, 2013). Being a natural polymer it holds some distinct advantages over other coagulants, the main being the hazardous residual caused by pre-treatment using metal based coagulants. Another

advantage chitosan holds is non-existent residual metal problems associated with other coagulants.

## 2.5 Selection of Coagulants Suitable for CSG Water Pre-Treatment

CSG produced water has specific and varying properties such as high pH, high alkalinity and high turbidity. Table 2.2 shows a comparison between seawater, surface water and PFW. This comparison highlights the similarities between seawater and PFW.

**Table 2.2 - Comparison between water**

	<b>Surface Water</b>	<b>Sea Water</b>	<b>PFW</b>
<b>pH</b>	6.5 – 8	7.5 – 8.3	9.3
<b>Turbidity</b>	20-30	500 - <1000	<1000
<b>Total Dissolved Solids (TDS) g/L</b>	>1	35	6.5

Table 2.3 shows the similarities in characteristics of seawater and PFW, these similarities have enabled the identification of suitable coagulants capable of pre-treating PFW. The Suitability of coagulants for CSG water pre-treatment therefore is based on two criteria;

- 1) Appropriateness for the characteristics for the water
- 2) Appropriateness of treated water by coagulants in reducing the fouling of RO membranes (as the pre-treated water from coagulation is fed directly to the RO plant).

**Table 2.3 - Comparison between seawater and CSG water**

<b>Ion</b>	<b>Seawater (worldwide average) mg/L</b>	<b>CSG Sample Mg/L</b>	<b>CSG Average</b>
<b>Chloride</b>	18980	3470	5000
<b>Sodium</b>	10556	2150	2500
<b>Sulphate</b>	2649	<10	8
<b>Magnesium</b>	1272	20.2	27
<b>Calcium</b>	400	143	150
<b>Potassium</b>	380	448	350
<b>Bicarbonate</b>	140	675	650
<b>Bromide</b>	65	n/a	n/a
<b>Borate</b>	26	n/a	n/a
<b>Strontium</b>	13	n/a	n/a
<b>Fluoride</b>	1	n/a	n/a
<b>TDS</b>	34482	6370	7500
<b>pH</b>	7.5-8.3	9.3	9

## **2.6 Use of Coagulants with Reverse Osmosis**

The use of coagulants and flocculants as a treatment and pre-treatment method for water treatment is widespread and has been justified above.

Issues regarding the use of Aluminium based salts as a coagulant are stated by (James, EK & Johannes, H, 2011); Alum and Poly-aluminium Chloride (PACl) raise concerns about precipitative scaling due to the high content of undissolved aluminium adhering to the RO membranes. Precipitative scaling is the side effects of water insoluble salts in the feed water, these salts adhere to the membranes of the reverse osmosis plant causing blockage and reduced flow rate, resulting in higher cost of operation and extended cleaning times. Addition of acids or anti-scalant solutions to the feed water can reduce membrane scaling, however increased dosage of acids and anti-scalants leads to reduce membrane efficiency resulting in higher operating cost (Lenntech, 2014).

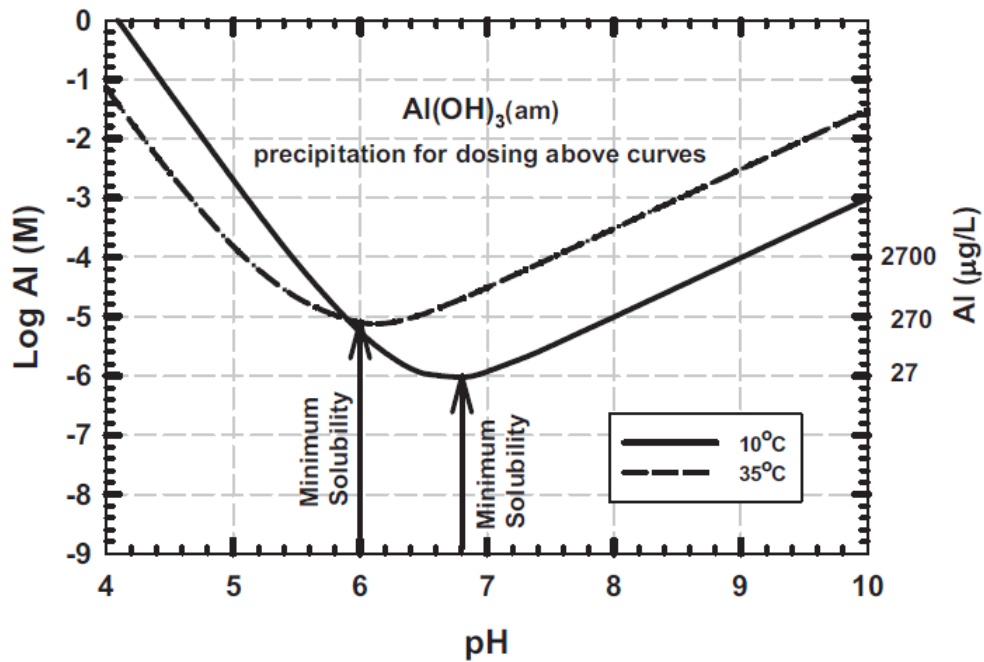


Figure 2.7 - Solubility of Al in Seawater. James, EK & Johannes, H, (2011)

As stated by James, EK & Johannes, H, (2011), Alum and PACl's have been thoroughly studied in the laboratory with the use of pilot scale RO plants, but have not been used in a full scale RO plant. The use of Alum based coagulants in real world conditions has not been implemented due to the high solubility of Al; the residual Al would carry over to the membranes leading to concentration and precipitative scaling. Due to the increased ionic strength of seawater compared to surface water, Al is more soluble. As Figure 2.7 shows, optimum pH conditions for the use of aluminium coagulants occurs at minimum solubility, thereby producing the maximum amount of precipitated solids for sweep floc and minimising residual soluble Al. Seawater pH is on average around 8 when compared to Figure 2.5. This higher pH requires higher dosage of Al, leading to more residual Al and more likelihood of precipitative scaling of the RO membranes.

Ferric chloride is more insoluble when compared with Al, leaving little to no residual of Fe in pre-treated water, and reducing the problems associated with precipitative scaling of membranes. Figure 2.8 when compared with Figure 2.7 shows Fe's suitability at higher pH's, reducing the amount of dosage required and falling closer to the minimal solubility range.

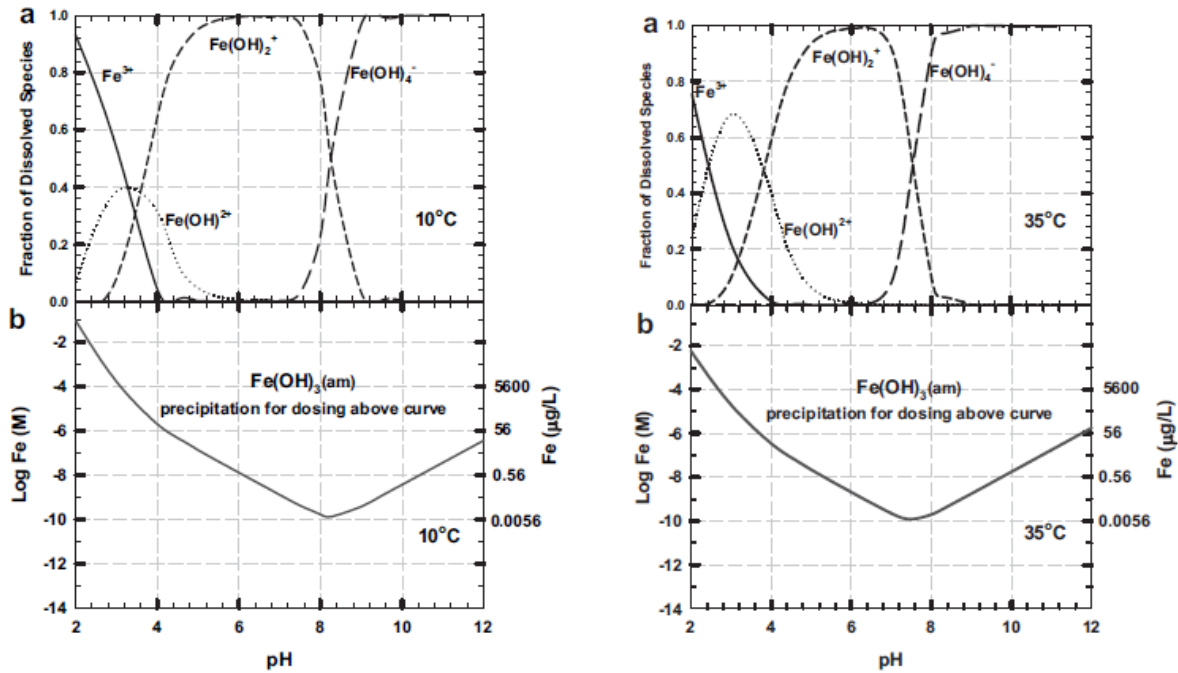


Figure 2.8 - Solubility of Fe in seawater - James, EK & Johannes, H, (2011)

Sanghyun, J, et al, (2011) identified from testing the performance of two coagulants used for coagulation in seawater. The coagulants being tested for comparison are Ferric Chloride and Poly Ferric Silicate. In the conducted study, five different dosages of Ferric Chloride were used from 0.5 -4.0 mg/L, and three different dosages of Poly Ferric Silicate ranging from 0.4-1.2 mg/L. Jar testing was performed using 1L jars, initial rapid mixing was at 120 rpm for 2 minutes followed by slow mixing at 60 rpm for 20 minutes and 30 minutes of settling time. Results from the testing indicated that poly ferric silicate at a dosage of 1.2 mg/L accounted for a 60% removal of turbidity whereas ferric chloride at all dosage ranges accounted for an increase in turbidity of seawater from 0.5-0.7 to 1.3 NTU.

A study conducted by Altaher, H, (2012), identified the use of chitosan as a possible coagulant for seawater, as a pre-treatment process for reverse osmosis. The study conducted compared chitosan with commercially available coagulants alum and ferrous sulphate. Chitosan was dosed at an amount of 6 to 60 mg/L and a substantially higher dosage of 180 to 360 mg/L. The highest achieved turbidity removal was achieved using alum at an extremely high dosage of 1200 mg/L. Table 2.4 shows the coagulant, dosage and achieved turbidity removal.

**Table 2.4 - Dosages vs. turbidity removal, (Altaher, H, 2012)**

<b>Coagulant</b>	<b>Dosage mg/L</b>	<b>Turbidity Removal %</b>
<b>Chitosan</b>	6 - 60	95.8 - 97.6
<b>Chitosan</b>	180 - 360	Turbidity deterioration
<b>Alum</b>	1200	98
<b>Ferrous Sulphate</b>	120	89

As can be seen from the Table 2.4 chitosan out performed Alum and Ferrous Sulphate on a dosage vs. turbidity removal basis, when trialled in laboratory testing. All samples were tested using jar testing methods with a rapid mixing time of 5 minutes at 250 rpm, followed by 30 minutes of mixing at 50 rpm then left to settle for 30 minutes. After settling the treated water was removed to a level 2cm above the floc, and filtered using a sand filter.

Although this study identifies the effectiveness of chitosan as a coagulant, it does not take into account the possible issues associated with the use of chitosan as a coagulant for pre-treatment of feed water to a RO plant. Chitosan being a natural polymer, organic in nature will influence the growth of algae and provide it with a nutrient source for it to flourish, this may lead to algae blooms on the RO membranes.

## **2.7 Summary**

As identified in the above sections, seawater desalination and subsequent pre-treatment holds the best comparative ability to CSG produced water. Because of the similarities between seawater and CSG produced water, coagulant selection will be based on these similarities. The selection of coagulant for PFW pre-treatment is based on optimum pH requirements for the coagulants and also the pH of the waters, Table 2.5.

**Table 2.5 - Suitability Comparison of Coagulants**

	<b>PFW pH (8.0 - 9.5)</b>	<b>Seawater pH (7.5 - 8.3)</b>
<b>Aluminium Sulphate pH (5.5 – 7.5)</b>	Not suitable	Not suitable
<b>Poly Aluminium Chloride pH (4.5 – 9.5)</b>	Suitable	Suitable
<b>Ferric Sulphate pH (5.5 – 8.5)</b>	Suitable, may require pH reduction.	Suitable
<b>Ferric Chloride pH (5.5 – 8.5)</b>	Suitable, may require pH reduction.	Suitable
<b>Chitosan pH (6.5 – 8.5)</b>	Suitable, may require pH reduction.	Suitable

The second criterion is the suitability of the coagulants for use with Reverse Osmosis namely the associated risk of damage or fouling of the membrane, Table 2.6. Table 2.5 and Table 2.6 form the summarisation of selection Criteria for the suitability of Coagulants. From these criterions and before mentioned issues in previous sections, Ferric Sulphate, Aluminium Sulphate and Ferric Chloride will be used for pre-treatment testing of PFW. Their performance and suitability will be tested with special attention payed towards maximum turbidity removal, lowest dosage and maximum solids removal. This will be the key testing criteria for effectiveness and efficiency of the coagulant.

**Table 2.6 - Suitability Comparison of Coagulant use with RO**

	<b>PFW pH (8-9.5)</b>	<b>Seawater pH (7.5 – 8.3)</b>
<b>Aluminium Sulphate pH (5.5 – 7.5)</b>	Not suitable	Not suitable
<b>Poly Aluminium Chloride pH (4.5 – 9.5)</b>	Not Suitable Issue with precipitative scaling	Not Suitable Issue with precipitative scaling
<b>Ferric Sulphate pH ( 5.5 – 8.5)</b>	Suitable	Suitable
<b>Ferric Chloride pH (5.5 – 8.5)</b>	Suitable	Suitable
<b>Chitosan pH (6.5 – 8.5)</b>	Suitable	Suitable



## Chapter 3 – Materials and Methodology

The ability to be able to suitably select a coagulant and a coagulant aid for the use in water treatment lies in the ability to be able to accurately and correctly measure certain aspects of the water. As there are many different ways each aspect can be tested one would expect a difference between acquired values. To accurately quantify the results depending on the chosen test method the publication 'standard methods for the examination of water and waste water' Eaton, A, et al, (2005) sets out a standard testing procedure, below each test is explained in detail.

Before each measurement is undertaken the water must first be dosed with an amount of coagulant, this amount will be optimised after testing of a range of dosages. Testing of the suitability and effectiveness of coagulants and coagulant aids will be undertaken using a standardised jar test.

### 3.1 Jar Test

Jar testing is a testing procedure aimed at simulating a full scale treatment environment. It will provide an environment where the effectiveness of coagulants/flocculants can be assessed. Jar test apparatuses usually are made up of six test beakers each with their own stirrer, this enables users to systematically increase the dosage of coagulant/flocculent in each beaker. The six beakers offer the opportunity of six individual tests run concurrently. Once the coagulant/flocculent is added the sample is rapidly mixed at a pre-determined speed for a set time. Once this process is complete a more gentle mixing process takes place. This process is aimed at enabling that newly formed flocs to come into contact with each other. Once the dosage and stirring phases are complete the dosed test water is allowed to settle for a predetermined time.

#### Procedure

1. Six beakers of 1 L are filled with 'raw' water.
2. Prepare coagulant; syringes can be used to allow quick application.
3. Set times on mixing apparatus, rapid mix two minutes, gentle mix 15 minutes, settle time of 30 minutes.
4. Apply stirrers into test jars.
5. Dose water with coagulants, an assistant may be required to ensure dosage is done in a timely manner.
6. Start mixing program.

7. Once completed remove stirrers from test water.
8. Using a syringe fitted with a length of plastic tubing, remove 100ml of water below the 800 ml mark on the beaker. Take care not to disrupt the flocs.
9. This water will be used for the below mentioned testing.



Figure 3.1- Jar testing apparatus (Manthey, 2014)

## 3.2 pH

pH measurement is one of the most important and commonly used tests in chemistry. Many water treatment processes are pH dependent including but not limited to, coagulation, water softening, alkalinity, and precipitation. pH measurement gives an indication of the water's acidity or basic nature. The electrometric pH meter consists of a potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. When the electrode is immersed in the test solution the circuit is completed and a pH reading is displayed to three decimal places on the unit's screens.

### Procedure

1. Ensure the calibration of the testing probe with the use of calibration fluid.
2. Wash probe with demineralised water and dry off residual leftover water.
3. Immerse probe in fluid to be tested.
4. Ensure fluid is stirred at a gentle speed or the probe is used to stir the fluid.
5. Wait for reading on display to register the ready symbol.
6. Record the data.

### **3.3 Conductivity**

Conductivity is a measure of the test waters ability to carry an electric charge; this is due to the presence of ions and on their total concentration, mobility and valence. Waters conductance is a useful measure to use for the measurement of total dissolved solids of the test water. The conductivity meter used is a small portable device, consisting of a probe and a display screen. Once the machine has been calibrated to a standard test solution the probe is immersed in the fluid to be tested with the results displayed on the screen, the units displayed will typically be in Siemens.

#### **Procedure**

1. Ensure the calibration of the unit with the use of a calibration fluid.
2. Wash probe with demineralised water and dry off residual water.
3. Immerse probe in fluid to be tested.
4. Ensure fluid is stirred at gentle speed or the probe is used to stir the fluid.
5. Wait for reading on display to register the ready symbol.
6. Record data.

### **3.4 Alkalinity**

Alkalinity is the measure of a waters capacity to neutralise acids (Eaton, A, et al, 2005). It is the sum of all titratable bases. The measured values may vary significantly as a resultant of the end pH of the substance. The identification of specific substances in the tested water can only be interpreted when the specific chemical composition of the substance is known. Alkalinity measurement proves useful in the treatment of water and waste water as it is a primary function of carbonate, bi-carbonate and hydroxide content, because of this fact it is taken as an indication of the concentration of the before mentioned components. The measured value may also include borates, phosphates, silicates and other bases if present. To determine the levels of carbonate, bi-carbonate and hydroxide present in water the titration method is used, this method involves the measurement of the sample waters pH and dosage with standard acid. Eaton, A, et al (2005), states that Hydroxyl ions present in sample water react with standard acids thus effecting the pH. The End point pH is the resultant of a titration curve, the end point pH are the points of inflection at which the curvature changes from convex to concave or vice versa. Table 3.1 provides end point pH values, this table also coincide with Table 3.2 explained below. Titration is defined as the determining of sample alkalinity from volume of sample acid required to titrate a portion to a designated pH (Eaton, A, et al 2005).

**Table 3.1- End-Point pH Values, (Eaton, A, et al 2005).**

Test Condition	End Point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity - mg CaCO <sub>3</sub> /L		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, Phosphates known or suspected	4.5	8.3
Routine or automated analysis	4.5	8.3
Industrial waste or complex system	4.5	8.3

**Table 3.2 - Alkalinity Relationships, (Eaton, A, et al 2005).**

Result of Titration	Hydroxide Alkalinity as CaCO <sub>3</sub>	Carbonate Alkalinity as CaCO <sub>3</sub>	Bicarbonate Concentration as CaCO <sub>3</sub>
P = 0	0	0	T
P < 0.5T	0	2P	T - 2P
P = 0.5T	0	2P	0
P > 0.5T	2P-T	2(T-P)	0
P = T	T	0	0

\*Key: P – phenolphthalein alkalinity; T – total alkalinity

## **Procedure**

1. Preparation of Reagents; Sodium carbonate solution, approximately 0.05N, sulphuric acid dilute 200.00 mL 0.1N standard acid to 1000mL distilled water.
2. Prepare sample water in 100.0 mL beaker.
3. Using Table 3.1 add reagents until phenolphthalein alkalinity is reached, record dosage of reagents.
4. Using Table 3.1 add reagents until total alkalinity is met, record amount of reagent added.
5. Using Table 3.2 use selected reference equations to determine hydroxide alkalinity, carbonate alkalinity and bicarbonate concentration.

## **3.5 Turbidity**

As previously mentioned turbidity is the measure of the cloudiness of the water or the amount of transparency. Many factors can affect turbidity such as, colloids, clay, silt, and organic or inorganic matter. The Nephelometric method is based on a comparison of the amount of light that is scattered in a test sample of water against a standard reference solution under the same conditions (Eaton, A, et al 2005). Typically the test unit is a small unit consisting of a display screen and a chamber to hold the vials of test solution. The chamber contains a light source and an instrument for recording the amount of scattered light. The unit should be checked for calibration with the supplied test solutions before use.

## **Procedure**

1. Calibrate the unit using test solution.
2. Gather sample water in supplied vials.
3. Ensure the outside of the vial is clean of residue or any contaminants that may affect the reading.
4. Place the vial into the test chamber ensure the chamber lid is placed on the unit.
5. Test the solution using the test button.
6. Record the reading.
7. Re-do three times to ensure reliability of test.

### 3.6 Atomic Absorption Spectrometry

Atomic absorption spectrometry is the process of aspirating a fluid into an open source of flame, the result is the atomisation of the fluid (Eaton, A, et al 2005). A light beam is directed through the flame and is reflect to a detector that measures the amount of light absorbed by the atomised element. The amount of energy absorbed is proportional to the amount of that element in the liquid. Extraction/Air-Acetylene flame method is best suited to deterioration of iron, lead, cadmium, zinc, silver, and chromium. This method involves chelation with ammonium pyrrolide dithiocarbamate and extraction into methyl isobutyl ketone, followed by aspiration into an air-acetylene flame Eaton, A, et al (2005).

#### Procedure

1. Follow safe work practices and operation manual to set up machine, selecting suitable bulb to record iron concentration.
2. Prepare solutions for testing.
3. Select at least three suitable concentrations of standard metal solutions, these solutions will ensure the accuracy of the test machine.
4. Apply test samples to auto selector and run the machine according machine operation guidelines

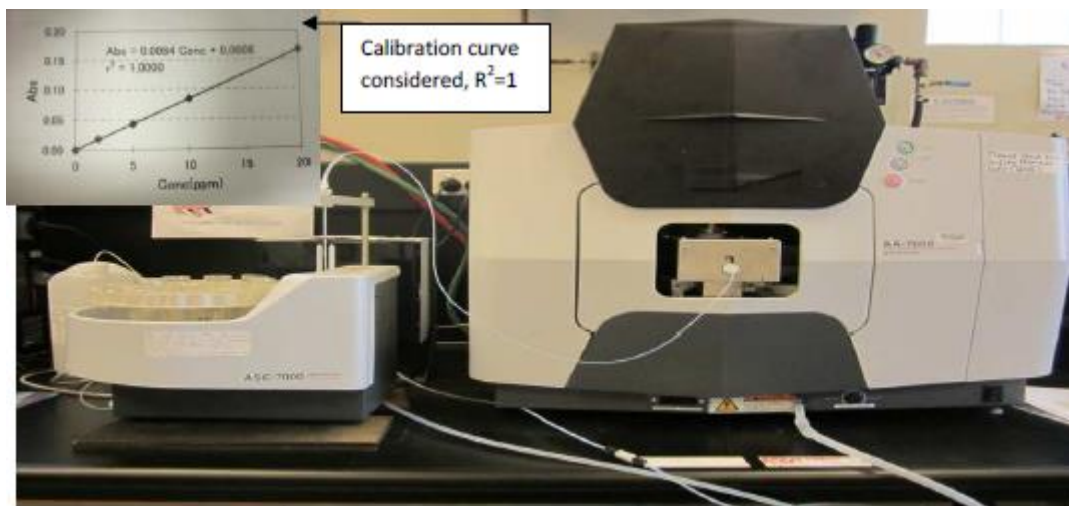


Figure 3.2 - Atomic Absorption Spectrometer. (Manthey, 2014)

### 3.7 Optimisation

Response surface method (RSM) and experimental design have been used as an alternative to conventional testing and refinement methods. These processes have been used to optimise the process. Experimental design is a systematic method that enables prediction of the optimum values of the effective parameters, with the minimum number of experiments (Amir et al, 2009). The computational design of experiment software Minitab has been used for optimisation. A central composite design comprised (CCD) of 4 axial points, 4 factorial points, and 5 replicates at the centre point has been chosen as depicted in figure 3.3. Mathematical model equations have been derived from the results using Minitab. In these equations the efficiency of turbidity reduction has been expressed as a second order function with two variables, being dosage and pH. The predicted response from the generated model has been compared with experimental results.

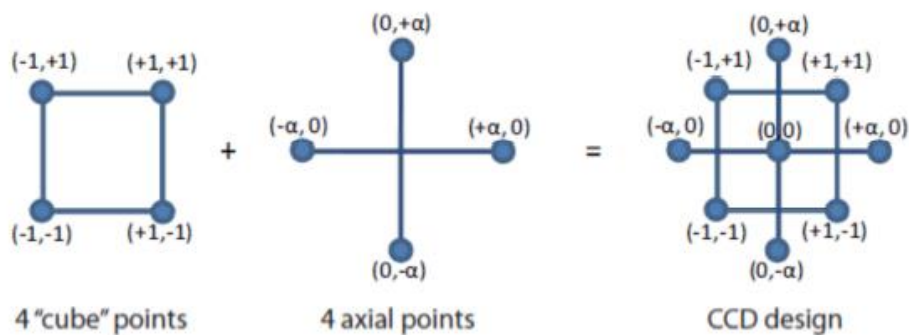


Figure 3.3 - Central Composite Design (CCD) (Trinh & Kang, 2010)

#### Procedure

1. Using Minitab select – Stat, DOE, Response Surface, and Create Surface Response Design.
2. Select required design, factors and type of design.
3. Conduct experiments using experimental values,
4. Predict values using Minitab,
5. Determine residual using Equation 3.1.

*Tested NTU – Experimental NTU*

**(3.1)**

### **3.8 Coagulant Preparation**

Three coagulants have been selected for experimentation these coagulants are;

#### **1. Aluminium sulphate.**

Aluminium Sulphate was sourced from Sigma-Aldrich. The Alum solution was prepared by dissolving 10 g of Alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) in one litre of distilled water. This produced a stock solution of 10 g/L. when 1 mL is added to a 1 litre solution it is equal to 10 mg/L (Bina et al 2009)

#### **2. Ferric Chloride.**

Ferric chloride was provided by Omega chemicals as a stock solution. The stock solution had a concentration of 42% Ferric chloride. The provided MSDS indicated the specific gravity (SG) of Ferric chloride from this SG the amount of stock solution was determined. 17.5 ml of stock solution was added to 982.5 mL of distilled water to produce a solution with a concentration of 10g/L.

#### **3. Ferric Sulphate.**

Ferric Sulphate was provided by Omega chemicals as a stock solution. The stock solution had a concentration of 45% Ferric Sulphate. The provided MSDS indicated the specific gravity (SG) of Ferric Sulphate, from this SG the amount of stock solution was determined. 14.0 ml of stock solution was added to 986.0 mL of distilled water to produce a solution with a concentration of 10 g/L.

### **3.9 Theory of Mathematics Used in This Research**

Experimental design is a systematic approach that enables the prediction of optimum values of the effective parameters, with the minimum number of experiments (Amir et al. 2009). The traditional approach of experimentation is to test one variable at a time, while maintaining the other variables as constants and studying the effects on the response variable. This method is not capable of detecting the interactions between the variables, variables acting together may behave in different ways than that of when acting alone. The



most common and consider basic type of experiment based on statistical approach is the Box-Wilson design. This design is widely used for fitting of second order models. The Box-Wilson design serves as a basis for deriving a mathematical model of a chemical or physical process. Equation 3.2 can be applied to transform a real value into a coded value according to a determinate experimental design (Bezerra et al. 2008).

$$x_{coded} = \left[ \frac{x_{actual} - x_{center}}{\frac{x_{center} - x_{min}}{\sqrt{k}}} \right] \quad (3.2)$$

Where  $k$  is the number of variables

The number of experiments can be determined by Equation 3.3.

$$N = 2^k + 2k + 1 \quad (3.3)$$

Equation 3.4 is used to determine the number of terms in the polynomial.

$$\text{Number of terms} = \frac{(k+1)(k+2)}{2} \quad (3.4)$$

Response surface methodology (RSM) is a combination of mathematical and statistical techniques that are used for analysis where the dependant variable is influenced by severable variables. A suitable approximation of the dependant variable is the first step of RSM. Equation 3.5 is the first order model if the response is modelled well by a linear function of the independent variables.

$$y = B_0 + B_1x_1 + B_2x_2 \dots \dots \dots + B_kx_k + \varepsilon \quad (3.5)$$

Equation 3.6 can be used when curvature is present in the system.

$$y = B_0 + \sum_{i=1}^k B_i x_i + \sum_{i=1}^k B_{ii} x_i^2 + \sum_i \sum_j B_{ij} x_i x_j + \varepsilon \quad (3.6)$$

Where  $i < j$

$B_0, B_i, B_{ii}, B_{ij}$  are parameters of the regression coefficients to be estimated from the collected data from the experiments and coded variables. The least square method estimates the parameters in the approximated polynomials, RSM is then conducted in terms of the fitted surface. If the fitted surface is an adequate approximation, then the analysis of the fitted surface will be an equivalent approximation of the actual system (Montgomery, 2001).

## Chapter 4 –Initial Testing Procedures and Water Characteristics

This chapter will analyse and discuss the results obtained from initial testing. Initial testing was conducted to determine specific water characteristics, settlement rates, suitability of coagulants and the waters pH response. The presentation of results in this chapter will first focus on the settlement rate and the pH response of the PFW. The efficiency of selected coagulants will be analysed to determine their suitability and efficiency of turbidity removal and included in each coagulants chapter. Also include in Chapter 4 is the water characteristic particular to the water used for testing.

### 4.1 Settlement Rate

The settlement rate of Produced Formation Water has been analysed to determine the settlement rate of the large amounts of undissolved impurities in the water. The majority of these undissolved impurities will settle under gravitational force alone as can be seen in Table 4.1 and Figure 4.1.

Table 4.1 – Settlement Rate

Time (hr.)	Average Turbidity (NTU)
0	1032
0.5	453
1.0	235
1.5	163
2.0	127
2.5	95.5
3.0	82.6
3.5	70.1
24	15.1

Initial testing has been conducted at a level of turbidity between 127 and 163 NTU, this falls between settlement times of one to one and a half hours. In this time period the turbidity has been reduced by 85%. This Turbidity level has been determined to be an appropriate

level for testing to suitably determine the effectiveness of the selected coagulants. As can be seen in figure 13 at a turbidity of 170 NTU, the rate of settlement will not negatively impact the results observed in the jar tests.

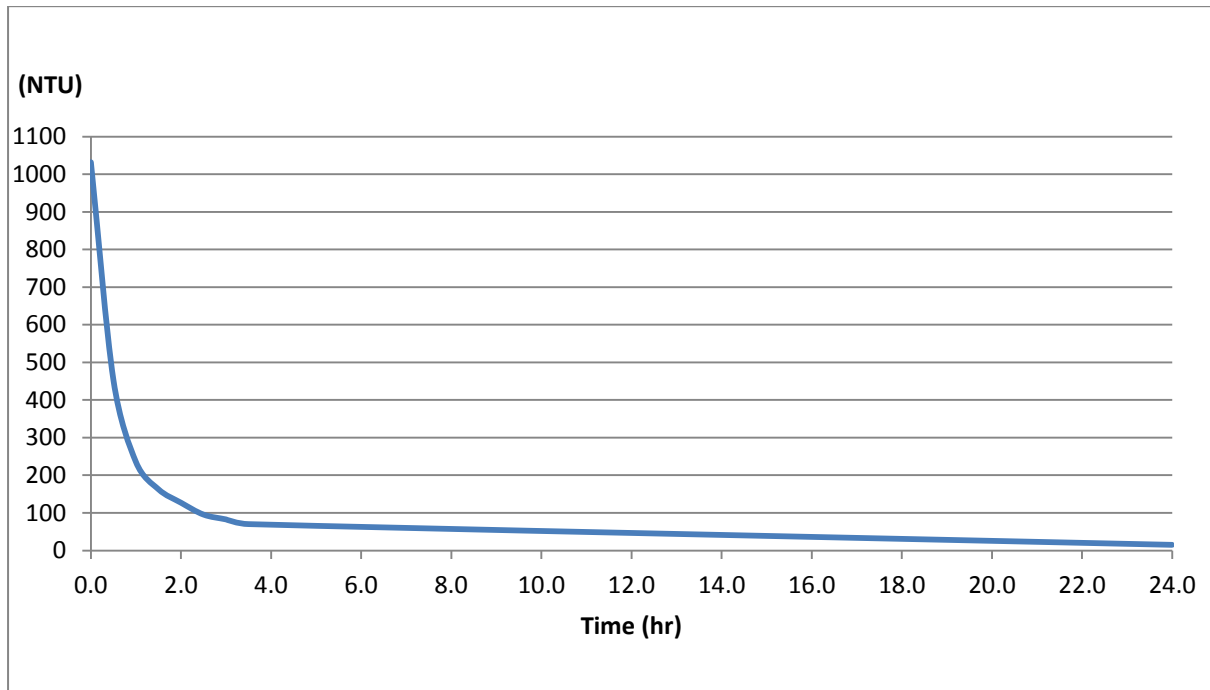


Figure 4.1 – Settlement Rate

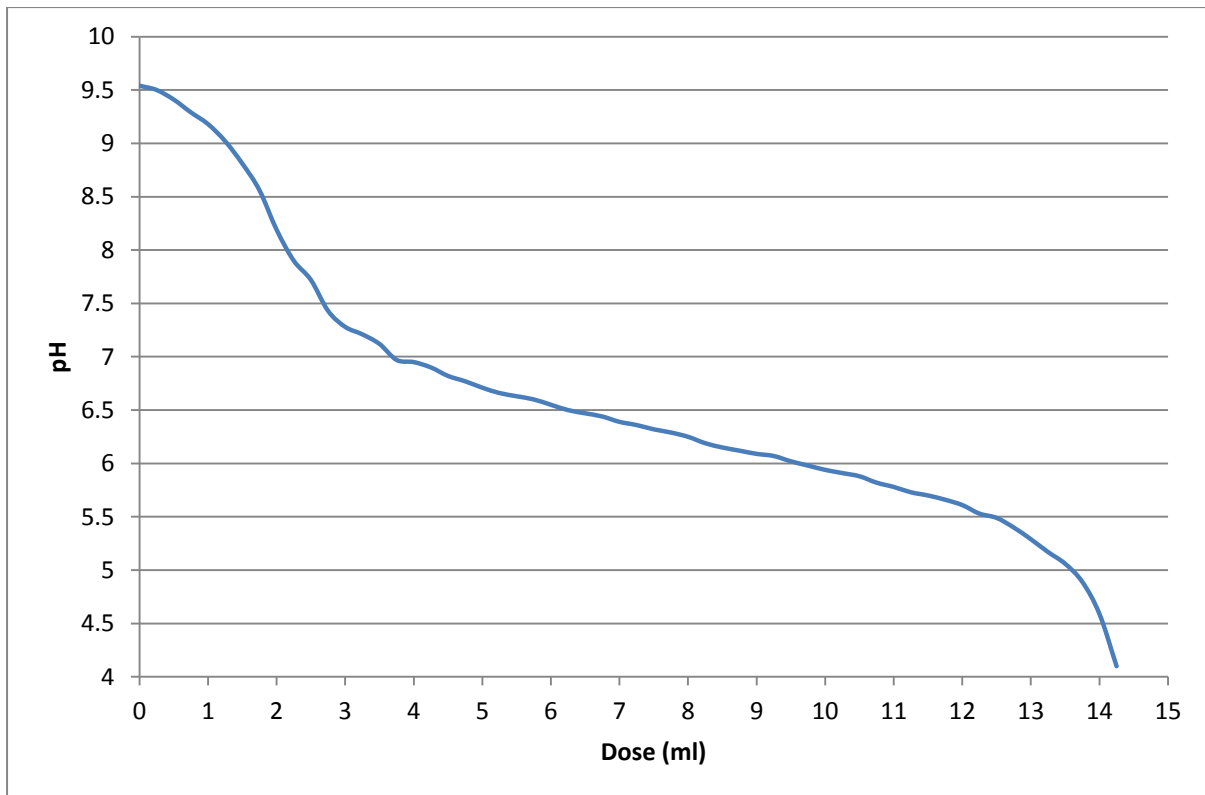
## 4.2 pH response

As detailed in Chapter 2 ferrous and alum based coagulants are more effective in their specific pH windows. The experimental values produced by Minitab require that it is imperative to be able to successfully alter the pH level of the water as required. Depicted in Figure 4.1 a titration curve has been developed from the results of pH reduction seen in Table 4.2.

**Table 4.2 - pH Response**

pH	Dose	pH	Dose	pH	Dose	pH	Dose	pH	Dose	pH	Dose	pH	Dose	pH	Dose	pH	Dose
9.54	0	8.56	1.75	7.12	3.50	6.66	5.25	6.39	7.00	6.12	8.75	5.88	10.5	5.53	12.25	4.59	14.00
9.50	0.25	8.19	2.00	6.97	3.75	6.63	5.50	6.36	7.25	6.09	9.00	5.82	10.75	5.49	12.5	4.10	14.25
9.41	0.50	7.9	2.25	6.95	4.00	6.60	5.75	6.32	7.50	6.07	9.25	5.78	11.00	5.40	12.75		
9.29	0.75	7.72	2.50	6.9	4.25	6.55	6.00	6.29	7.75	6.02	9.50	5.73	11.25	5.29	13.00		
9.18	1.00	7.43	2.75	6.82	4.50	6.5	6.25	6.25	8.00	5.98	9.75	5.70	11.5	5.17	13.25		
9.02	1.25	7.28	3.00	6.77	4.75	6.47	6.50	6.19	8.25	5.94	10.00	5.66	11.75	5.06	13.50		
8.81	1.50	7.21	3.25	6.71	5.00	6.44	6.75	6.15	8.50	5.91	10.25	5.61	12.00	4.89	13.75		

The process of pH reduction was undertaken with 0.5 normality sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). A one litre sample of PFW was collected and acid was added in increments of 0.25 ml. the resulting pH of each addition of acid was recorded. This collected data has produced the below titration curve. Table 4.2 will aid in determining the required amount of acid to be dosed to the samples to reduce the pH to the required level.



**Figure 4.2- Titration Curve**

### 4.3 Initial Water Characteristics

Initial water characteristics have been tabulated in Table 4.3 below. These characteristics give an indication of the quality of produced formation water particular to the Surat Basin. The testing was conducted by Mt Kynoch water treatment laboratories Toowoomba.

**Table 4.3 - Produced Formation Water Characteristic**

Method	Analysis	Units	LOR	Results
QP-KYN-009	Suspended Solids	mg/L	2	16500
ALS	Exchangeable Cations	meq/100g	0.001	20.5
ALS	Sulphate	mg/kg	1	270
ALS	Chloride	mg/kg	1	3470
QP-KYN-001	pH	Units		9.3
QP-KYN-002	Conductivity	uS/cm	1	10600
QP-KYN-017	Total Hardness	mg/L CaCO <sub>3</sub>	1	440
QP-KYN-015	Total Alkalinity	mg/L CaCO <sub>3</sub>	2	981
QP-KYN-090	Molybdate Reactive Silica	mg/L	1	3.1
QP-KYN-014	Total Iron	mg/L	0.01	14.2
QP-KYN-014	Total Magnesium	mg/L	0.01	1.39
QP-KYN-016	Calcium	mg/L	1	143
Derived	Magnesium	mg/L	2	20.2
QP-KYN-014	Sodium	mg/L	0.5	2150
QP-KYN-014	Potassium	mg/L	0.1	448
QP-KYN-058	Sulphate	mg/L SO <sub>4</sub>	1	<10
QP-KYN-058	Chloride	mg/L	1	3010
QP-KYN-058	Nitrate	mg/L NO <sub>3</sub>	1	10.7
QP-KYN-022	Phosphate	mg/L PO <sub>3</sub>	0.02	0.03
QP-LSB-A013	Temporary Hardness	mg/L CaCO <sub>3</sub>	1	440
QP-LSB-A013	Bicarbonate Alkalinity	mg/L CaCO <sub>3</sub>	1	675
QP-LSB-A013	Carbonate Alkalinity	mg/L CaCO <sub>3</sub>	2	306
QP-LSB-A013	Hydroxide Alkalinity	mg/L CaCO <sub>3</sub>	2	<2
QP-LSB-A013	Free Carbon Dioxide	mg/L	0.1	0.7
QP-LSB-A013	Total Dissolved Ions	mg/L	1	6790
QP-LSB-A013	Total Dissolved Solids	mg/L	1	6370
QP-LSB-A013	Figure of Merit	n/a	0.1	0.1
QP-LSB-A013	Saturation Index	n/a	n/a	2.84
QP-LSB-A013	Residual Alkalinity	Meg/L CaCO <sub>3</sub>	n/a	11.0
QP-LSB-A013	Sodium Absorption Ratio	n/a	0.1	44.6

## Chapter 5 – Aluminium Sulphate as a Coagulant

This chapter includes the results and discussion for all experiments carried out at a set level of turbidity of 150 NTU ( $\pm 20$  NTU). These experiments utilised Aluminium Sulphate at a concentration of 10mg/L as the primary and sole coagulant. Aluminium Sulphate has been chosen to be tested due to its widespread use in water treatment. This will form a basis for comparison between other coagulants.

### 5.1 Preliminary Experiments

Preliminary experiments were undertaken to first identify the coagulants suitability, and to give an indication of the optimal range of dosage for the coagulant. As can be seen in Figure 5.1 the level of turbidity has started to decrease in effectiveness. It is also to be noted that no pH reduction was undertaken in the preliminary experiments. As identified in the literature the optimum pH range for Aluminium Sulphate is in the range of 5 to 7 (Trinh & Kang 2010). This initial testing will form the basis for the refinement testing detailed below. As detailed in Table 5.1 the initial experiments were conducted with the range of dosage of 10mg/L to 100 mg/L. the results of the initial testing have indicated that the optimum range will be between 60 mg/L and 100 mg/L. To obtain sufficient results, pH reduction will be utilised to allow the coagulant to work within its desired envelop of optimum performance.

Table 5.1 - Initial Results Aluminium Sulphate

Jar	Dosage (mg/L)	Turbidity (NTU)	pH
Initial	0	170	9.50
1	10	47.2	9.40
2	20	42.8	9.40
3	40	24.4	9.40
4	60	15.1	9.35
5	80	6.7	9.30
6	100	5.9	9.25

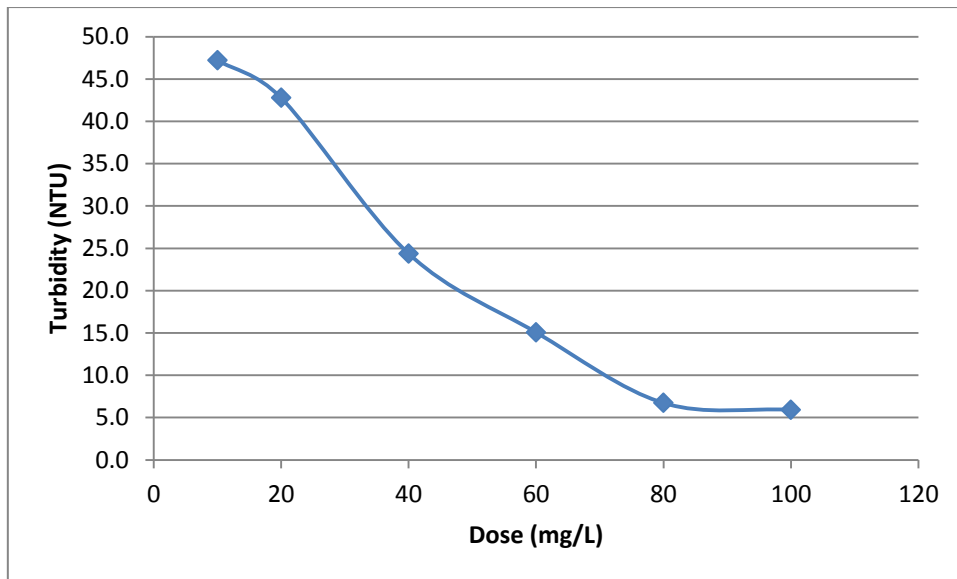


Figure 5.1 - Dosage vs. Turbidity Aluminium Sulphate

## 5.2 Results and Discussion of preliminary experiment

As can be seen in Figure 5.1 even with no pH reduction, and alum working outside of its optimum pH range it is still an effective coagulant for this type of water. A dosage of 100 mg/L accounted for a turbidity removal of 96.5 %. This preliminary testing has formed a basis for refinement using the mathematical modelling software Minitab. The pH range has been set between the range of 5 and 9.3 with dosages ranging from 10 to 100 mg/L. These ranges of pH and dosages fall in line with the optimum working conditions for alum as identified by literature (Trinh & Kang, 2010).

## 5.3 Optimisation Experiments

Thirteen observed responses have been used to compute the model using the least square method. Minitab has been used to generate required dosage at the required pH level. With these dosage and pH level 13 jar tests were conducted. An initial rapid mix speed of 90 rpm for two minutes enabled the coagulant to be evenly dispersed in the one litre jars. After this rapid mix phase a slow mix of 30 rpm for 15 minutes was utilised, after this the solution was allowed to settle for 30 minutes. After settlement the turbidity, pH, residual aluminium, and conductivity were tested. Each experiment has been replicated to ensure the reproducibility of the results. All results have been averaged and tabulated in Table 5.2.



Table 5.2 – Aluminium Sulphate Optimisation

	Coded Variable	Real Variables		Experimental Results				
	X <sub>1</sub>	Dose (mg/L)	pH	Residual Turbidity (NTU)	Predicted Residual Turbidity (NTU)	% Turbidity Removal (NTU)	Residual Aluminium (mg/L)	Predicted Residual Aluminium (mg/L)
1	0	55.0	7.2	1.92	2.09	98.76	1.1196	0.8930
2	-1	55.0	5.0	2.44	2.40	98.58	1.5444	1.5503
3	0	55.0	7.2	2.11	2.25	98.67	0.8363	0.8930
4	1	23.2	8.7	15.80	16.84	90.04	2.7481	2.2094
5	0	55.0	7.2	2.50	2.88	98.30	0.8363	0.8930
6	1	86.8	8.7	1.97	3.82	97.74	3.4916	2.8444
7	-1	10.0	7.2	9.57	12.45	92.63	1.0133	1.2858
8	1	86.8	5.6	1.17	1.38	99.19	0.9425	0.7814
9	0	55.0	7.2	3.07	2.72	98.39	0.8363	0.8930
10	0	55.0	7.2	3.01	2.66	98.43	0.8365	0.8930
11	1	23.2	5.6	3.09	5.04	97.01	1.6506	1.5985
12	-1	100.0	7.2	1.19	1.33	99.22	0.7301	1.1567
13	-1	55.0	9.3	4.36	4.56	97.31	2.7481	3.4414

The turbidity response and Residual Aluminium have been correlated with the two initial factors (dosage and pH). This correlation has enabled the computation of a quadratic regression model represented in Equations 5.1, and 5.2. Included with Equations 5.1 and 5.2 are the  $R^2$  and  $R^2_{ADJ}$  values computed by Minitab. The coefficients of dose or pH represent the effects on that particular factor. The coefficients of the two factors, (dose x pH) and all of those of second order (dose<sup>2</sup> and pH<sup>2</sup>), represent the interaction between the factors and the quadratic effect. A positive or negative sign in front of each term will indicate if the term is either synergistic or antagonistic.

**Residual Turbidity (NTU) =**

$$7.4 - 0.062 * Dose - 1.33 * pH + 0.002548 * Dose^2 + 0.378 * pH^2 - 0.0483 * Dose * pH \quad (5.1)$$

$$(R^2=91.85\%, R^2_{ADJ}=86.03\%)$$

**Residual Aluminium (mg/L) =**

$$18.99 - 0.0729 * Dose - 4.93 * pH + 0.000162 * Dose^2 + 0.3468 * pH^2 + 0.0075 * Dose * pH \quad (5.2)$$

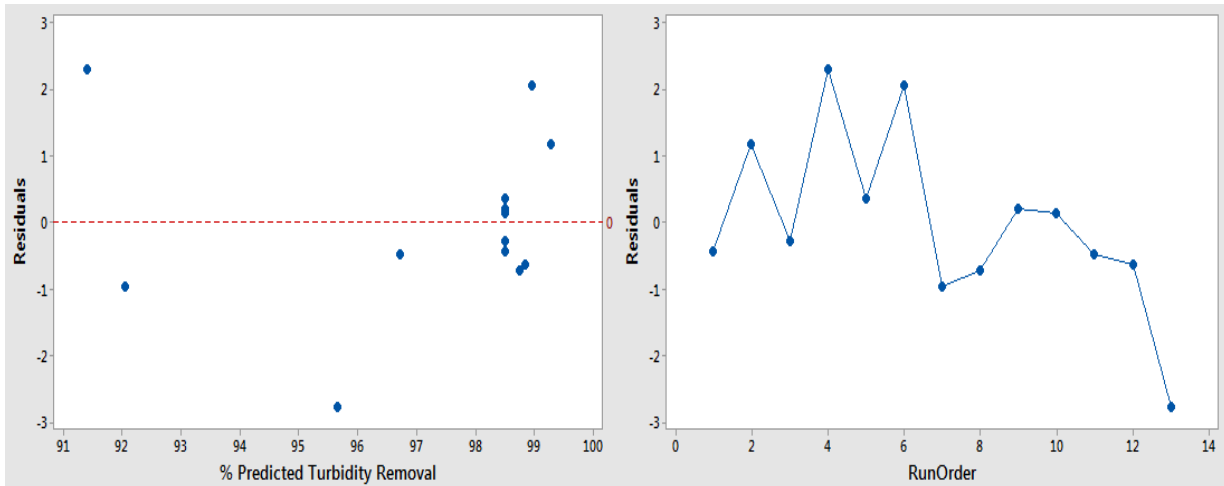
$$(R^2=84.85\%, R^2_{ADJ}=74.02\%)$$

These quadratic regression models have been used to predict values for turbidity removal and residual aluminium detailed in Table 5.2. These values form the basis for the validation of the mathematical model.

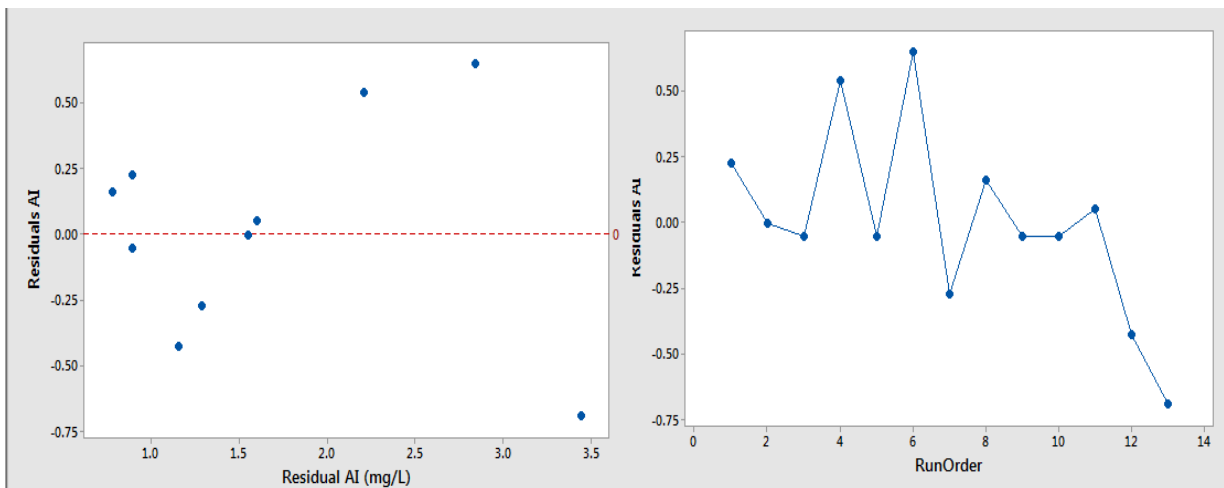
## 5.4 Validation of the Model

To ensure the reliability and validation of the model it is necessary to check the fitted model (Trinh & Kang 2010). This checking of the model is to ensure it provides an adequate approximation to the actual system. Graphical and numerical models have been used as the primary tool to confirm the validation of the model. The graphical models depicted in Figures 5.2 and 5.3 characterise the nature of residuals in the model. The residuals are the values calculated using Equation 5.3 and defined as the difference between the actual value and the fitted value.

$$Turbidity - Predicted Turbidity \quad (5.3)$$



**Figure 5.2 – Residual vs. % Predicted Turbidity Removal & Normal Probability**



**Figure 5.3 - Residual vs. Residual AI & Normal Probability**

As can be seen in Figures 5.2 and 5.3 the residuals have been used to examine the functional part of the model and to ensure its sufficiency. The right hand plot in Figures 5.2 and 5.3 are residual vs. run order. Upon examination of these two plots it is clear there is no obvious pattern in the model. This implies that the residuals of the model are randomly distributed. Figure 5.4 is the residuals plotted against a theoretical normal distribution. The residual points should fall in a straight line. Deviation from this line would indicate a non-normal distribution. From interpretation of Figures 5.2 - 5.4 it is safe to assume that the assumption of normality for the model has been satisfied.

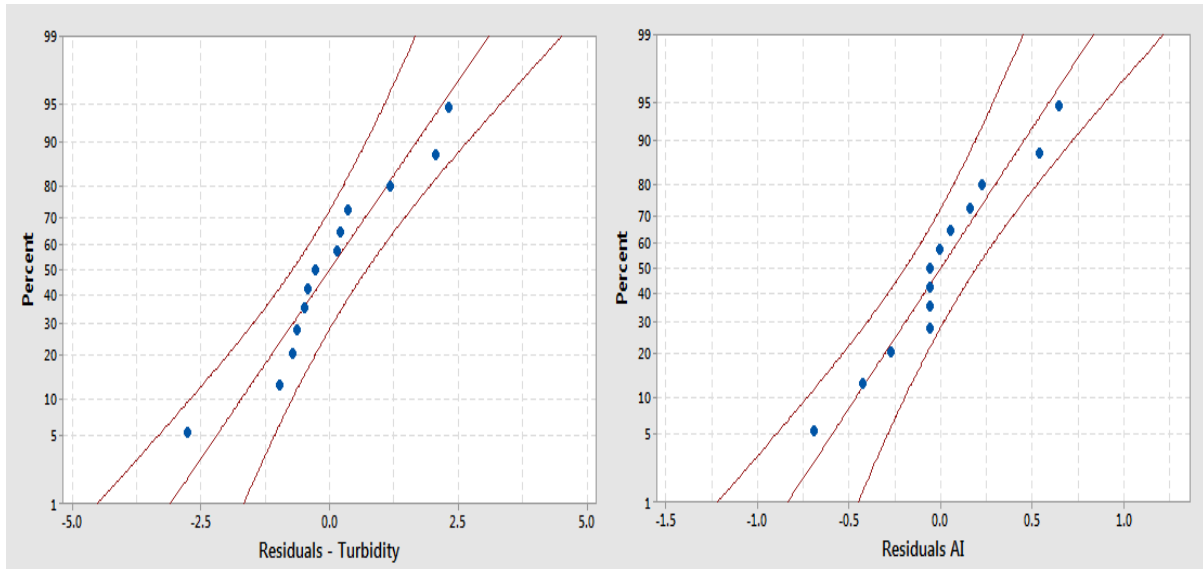


Figure 5.4 - Normal Distribution of Residual Turbidity and Residual Al

The models have been checked using a numerical method using the coefficient of determination ( $R^2$ ),  $R^2$  adjusted ( $R^2_{ADJ}$ ). To calculate the coefficient of determination the following equations have been used.

$$R^2 = 1 - \frac{SS_{Residual}}{SS_{Residual} + SS_{model}} \quad (5.4)$$

$$R^2_{ADJ} = 1 - \frac{n-1}{n-p} (1 - R^2) \quad (5.5)$$

Where:

SS = Sum of Squares.

n = number of experiments.

p = number of predictors (terms).

Table 5.3 illustrated below shows the values for  $R^2$  and  $R^2_{ADJ}$  for the surface response model developed. The  $R^2$  values for Turbidity and residual aluminium are above or very close to 90%, furthermore the  $R^2_{ADJ}$  values fall within a close margin of the  $R^2$  values. This indicates a satisfactory adjustment of the quadratic model when compared to the experimental values. The regression models closely represent the Turbidity and residual aluminium values to a satisfactory level.

**Table 5.3 - Coefficient of Determination Values**

	$R^2$	$R^2_{ADJ}$
<b>Residual Turbidity</b>	91.85%	86.03%
<b>Residual Aluminium</b>	84.85%	74.02%

## 5.5 Optimisation Analysis

Analysis of variance (ANOVA) has been used for the graphical analysis of the gained data. Tables 5.4 and 5.5 present the ANOVA calculated by Minitab, the data in Table 5.4 corresponds to residual turbidity and Table 5.5 corresponds to residual aluminium. As depicted in table 5.4 and 5.5, the degrees of freedom that governs each term of the model is depicted by d.f, the F-statistic (F-value) is used for comparison of the factors of total deviation. The p-value is the probability of the F-value.

**Table 5.4 - ANOVA Response of Residual Turbidity**

Residual Turbidity								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Turbidity</b>				Constant	1	2.521	3.24	0.014
				Dose	1	-5.731	-6.59	0.000
				pH	1	3.058	3.51	0.010
Regression	5	15.78	0.001	Dose x Dose	1	5.16	3.91	0.006
Residual error	7			pH x pH	1	1.75	1.33	0.227
LOF	3	61.61	0.001	Dose x pH	1	-4.67	-2.69	0.031
Pure Error	4							

The larger the value of the T value and the smaller the value of P, indicates a greater significant of the corresponding term. As stated by Bezerra et al, (2008), 'a model will be well fitted to the experimental data if it presents a significant regression and a non-significant lack of fit (LOF)'. The LOF test indicates the variation in the data around the fitted model, if the data does not fit the model sufficiently the LOF will be significant. The low probability of the p-value indicates that the models were highly sufficient. The high F-values and the low p-values indicate that the model is statistically significant and the developed equations can be used to adequately describe the response. Although some terms of the model may seem insignificant, they are still considered as it is a hierarchical model (Baskan & Pala 2010).

Table 5.5 – ANOVA Response Residual Aluminium

Residual Aluminium								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Aluminium</b>				Constant	1	0.893	4.26	0.004
				Dose	1	-0.065	-0.28	0.791
Regression	5	7.84	0.009	pH	1	0.946	4.03	0.005
Residual error	7			Dose x Dose	1	0.328	0.92	0.386
LOF	3	30.62	0.003	pH x pH	1	1.603	4.51	0.003
Pure Error	4			Dose x pH	1	0.726	1.55	0.165

The data in Tables 5.4 and 5.5 shows that all models are significant with a confidence level greater than 95%, as shown by the low p-value for the regression of less than 0.05. These p-values show that the quadratic and linear effects of does and pH are highly significant. As identified in literature these two factors are the main governing factors of the coagulation process. As can be seen in Tables 5.4 and 5.5 the variable with the largest effect on turbidity removal was pH with a value of 0.010, pH<sup>2</sup> shows the least significant effect for turbidity removal with a value of 0.227 but shows a great effect for residual aluminium with a value of 0.003. Residual turbidity and residual aluminium both show a reliance on pH which is to be expected.

Graphical representations of the regression equations generated by Minitab are depicted in Figures 5.5 and 5.6. These two figures include surface and contour plots for residual turbidity and residual aluminium. These two figures are based on the effects of two factors being dosage and pH. These plots provide a visual method to interpret and analyse the relationships between dosage and pH. As can be seen in Figure 5.5 the optimum contour falls within the boundaries of optimal pH range as identified by James, EK & Johannes, H, (2011). The optimum contour is the point of maximum turbidity removal or minimum residual turbidity.

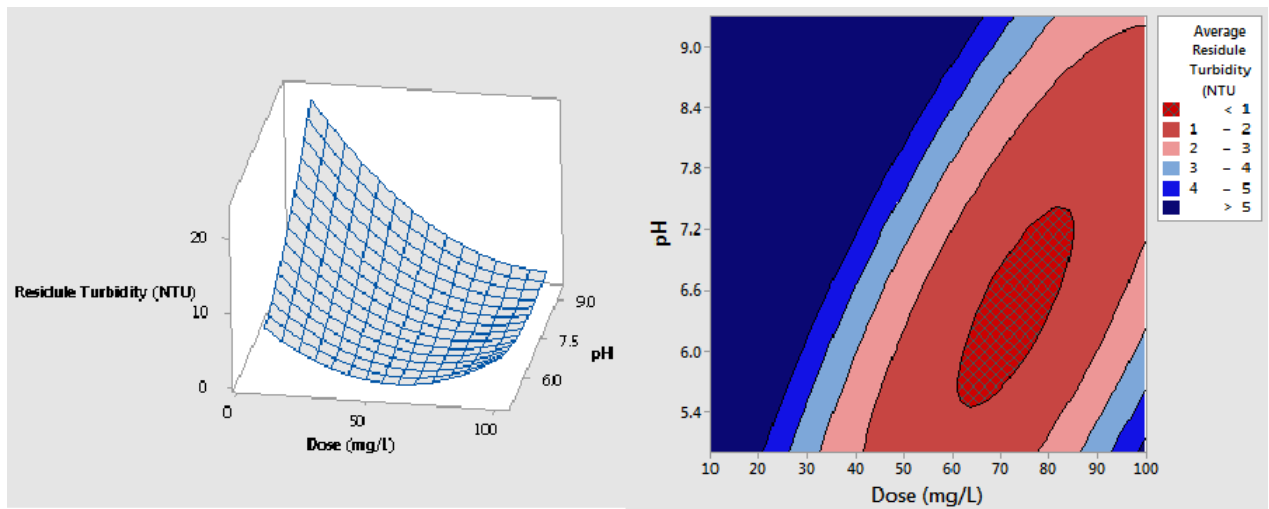


Figure 5.5– Surface and Contour Plots for Residual Turbidity

Figure 5.6 identifies the amount of residual aluminium for each dosage of coagulant at a specified pH. As can be seen the optimal contour falls within the design parameters of the experiment. This optimal point is the region where residual aluminium is at its minimum, in other words the ideal situation is to have little to no aluminium remaining in the water after testing. Figure 5.6 does not take into account turbidity removal. The optimal value of pH, residual turbidity, and residual aluminium is indicated by Figure 5.7.

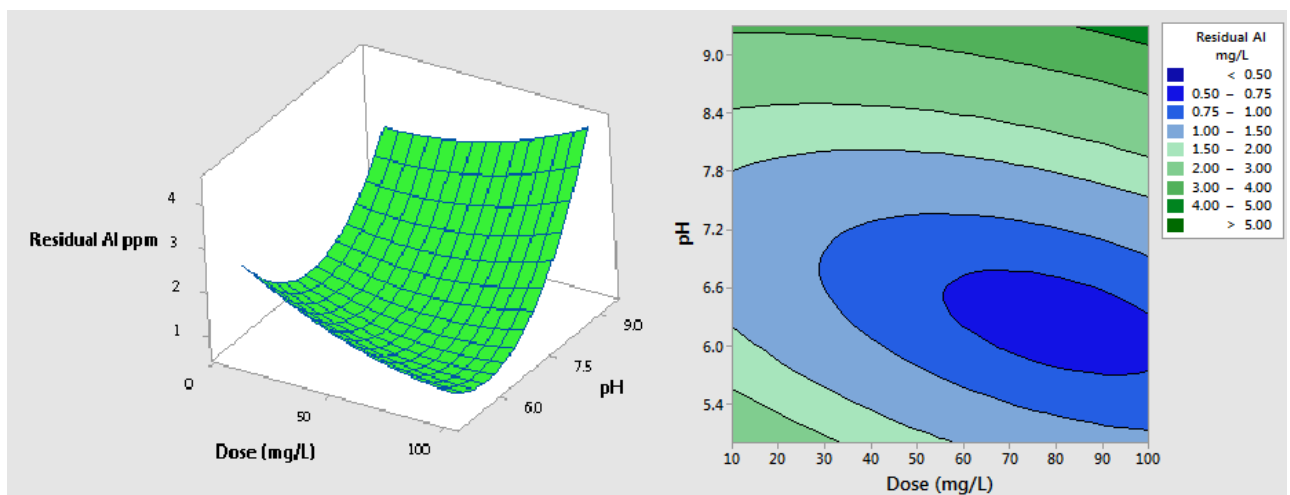


Figure 5.6 – Surface and Contour Plots for Residual Aluminium

Figure 5.7 is an overlaid contour plot of the regression equations developed by Minitab for residual Turbidity and Residual Aluminium. The plot illustrated below shows the area of

optimum turbidity removal providing the least amount of residual aluminium. This point is between dosages of 55 mg/L and 87 mg/L in the pH range of 5.7 to 6.7 respectively. The point of absolute optimum with in the overlaid contours is discussed in Section 5.6.

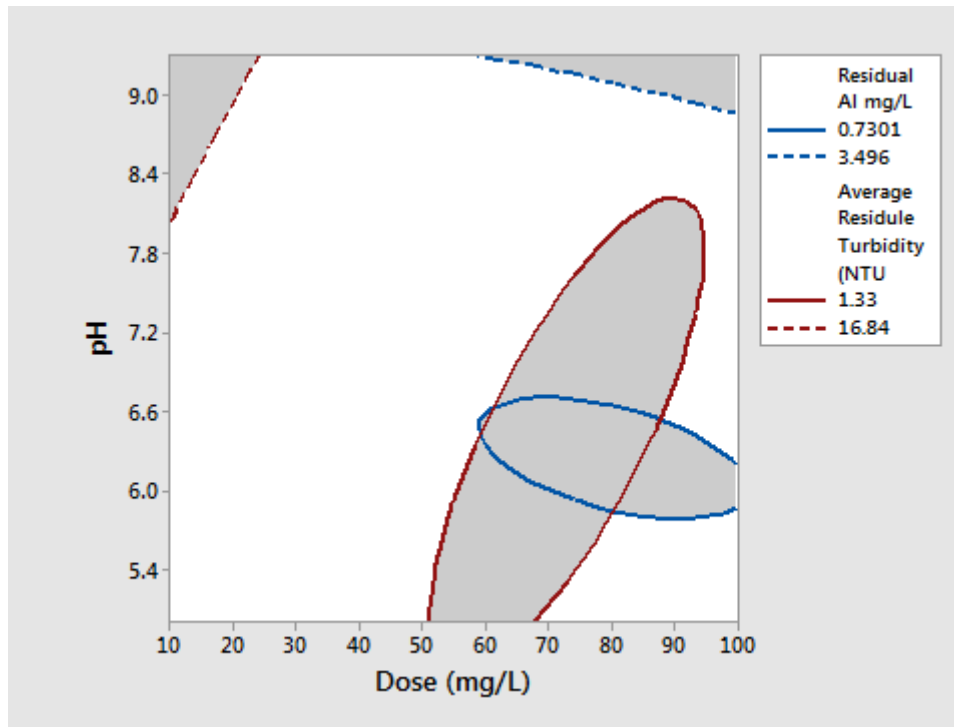


Figure 5.7 – Overlaid Contour Plot of Residual Turbidity and Residual Aluminium

## 5.6 The optimum Value

Residual turbidity and residual aluminium are two separate responses, their optimal as discussed in Section 5.5 falls in two separate areas. Due to this fact a compromise between the two is desirable to reach a singular point of optimum for both cases. Figure 5.7 indicates the optimum region accounts for values of residual turbidity and residual aluminium of 1.33 NTU and 0.7301 mg/L respectively. The optimum level of each factor of dosage and pH for each case has been obtained by the derivative of the fitted equations 3 and 4. The optimum conditions are a set of  $X_1$  (dosage) and  $X_2$  (pH) terms, where the derivative becomes zero as indicated in Figure 5.8.



$$\frac{\partial Y}{\partial X_1} = \frac{\partial Y}{\partial X_2} = \frac{\partial Y}{\partial X_3} = \dots = 0$$

Figure 5.8 – Partial Derivative for Fitted Equations

Mathematical modelling software Matlab has been used to solve the equation for each case. This method has provided the precise point of optimum, while only considering one variable at a time. Table 5.6 represents the point of optimum for each response; residual turbidity and residual aluminium. Also provided in Table 5.6 are the eigenvalues for each equation, these values are the results of a canonical analysis. Canonical analysis is used to investigate the overall shape of the curvature and to determine the stationary point, either maximal, minimal, or the saddle point.

Table 5.6 – Point of Optimum

Response	$\lambda_1$ & $\lambda_2$	Dosage (mg/L)	pH
Residual Turbidity (NTU)	-0.0036, 0.3841	73.1144	6.4305
Residual Aluminium mg/L	-0.0000, 0.3470	80.6549	6.2357
<b>Optimal Point</b>		76.8847	6.3331

A positive eigenvalue indicates the shape is an upwards curvature, a negative eigenvalue indicates the shape is a downward curvature. For each response the eigenvalues are negative and positive, this indicates that the stationary points are a single point of minimum response.

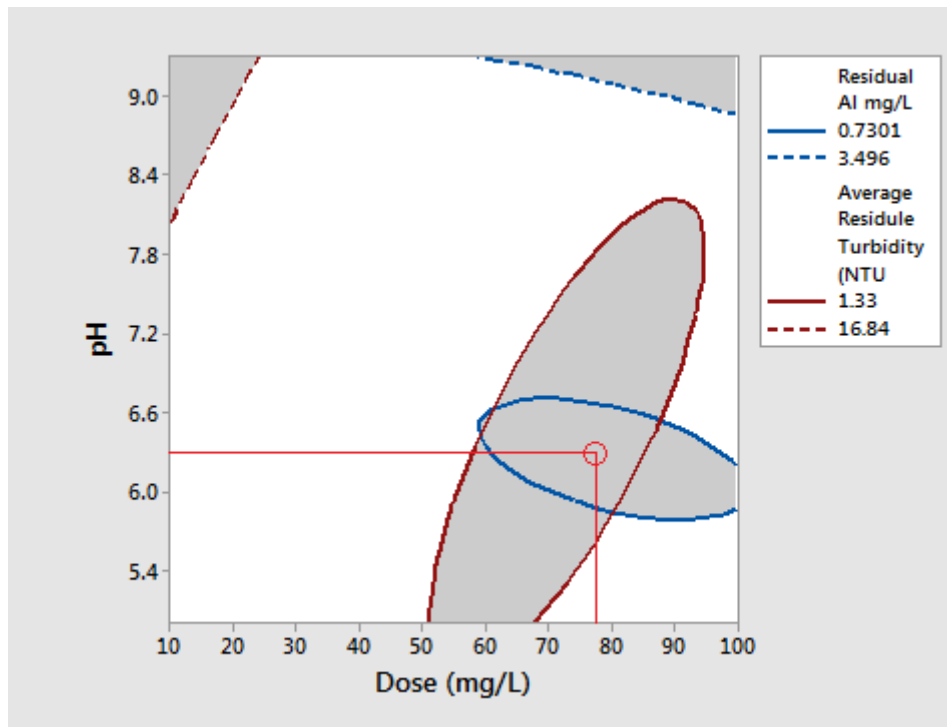


Figure 5.9 – Point of Optimal Residual Turbidity & Residual Aluminium

The model predicted an optimum, as shown in Figure 5.9, a dosage of 76.8847 mg/L of Aluminium Sulphate at a pH of 6.331. At the optimal dosage and pH, the amount of residual turbidity is 0.915 NTU, and the amount of residual aluminium is 0.682 mg/L. The dosage and pH result in a 99.46 % removal of turbidity. To confirm the results an additional two experiments were conducted at the optimal point to ensure the credibility of the results. As can be seen in Table 5.7, the residual turbidity and residual aluminium results obtained from the additional testing are very close to the estimated values mentioned in Table 5.6. The results of additional testing account for a relative error of 7.2%, these results imply that the RSM approach was appropriate for optimisation of the conditions of the coagulation process.

Table 5.7 – Optimal Conformational testing

	Coagulation Condition			
	Dose	pH	Residual Turbidity (NTU)	Residual Aluminium (mg/L)
Experimental Value	76.88	6.33	0.915	0.682
Predicted Value	76.88	6.33	0.9801	0.709
Error (%)			7.2	4.1

## Chapter 6 – Ferric Chloride as a Coagulant

Chapter 6 includes all results and discussion for the experiments undertaken at a set level of turbidity of 150 NTU ( $\pm 20$  NTU). The experiments analysed and discussed in Chapter 7 have utilised ferric chloride as the primary and sole coagulant. As identified in literature ferric based coagulants are used commonly and sea-water desalination. Sanghyun, J, et al, (2011)

### 6.1 Preliminary Experiments

Preliminary experiments have been conducted to form the basis for optimisation. Dosages from 10 mg/L to 100 mg/L have been trialled to first and foremost identify ferric chloride's suitability for PFW, and then identify the most effective range of dosage for refinement. As can be seen in Table 6.1 ferric chloride has been proven effective for pre-treatment of PFW, initial testing has resulted in an overall turbidity reduction of 95.94%. Ferric chloride has a minimal buffering effect on water pH as keen be seen by the slightly reducing pH level in Table 6.1, no additional pH reduction was undertaken for these experiments. As identified in Chapter 2, ferric chloride's optimal working pH range is 5.5 – 8.5 (Gebbie, P, 2006). This would indicate pH reduction is necessary to ensure an optimum dose that will results in small to no heavy metal residual.

Table 6.1 - Initial Ferric Chloride Results

Jar	Dosage (mg/L)	Turbidity (NTU)	pH
Initial	0	170	9.50
1	10	13.5	9.50
2	20	10.8	9.50
3	40	9.3	9.50
4	60	8.4	9.30
5	80	8.4	9.30
6	100	6.9	9.30

As can be seen in the below Figure 6.1, the turbidity is continually declining and has not reached a saddle point. This has indicated that the optimum dosage falls outside of the graphs range. Due to this fact optimisation has focused on a dosage range between 60 and 150 mg/L.

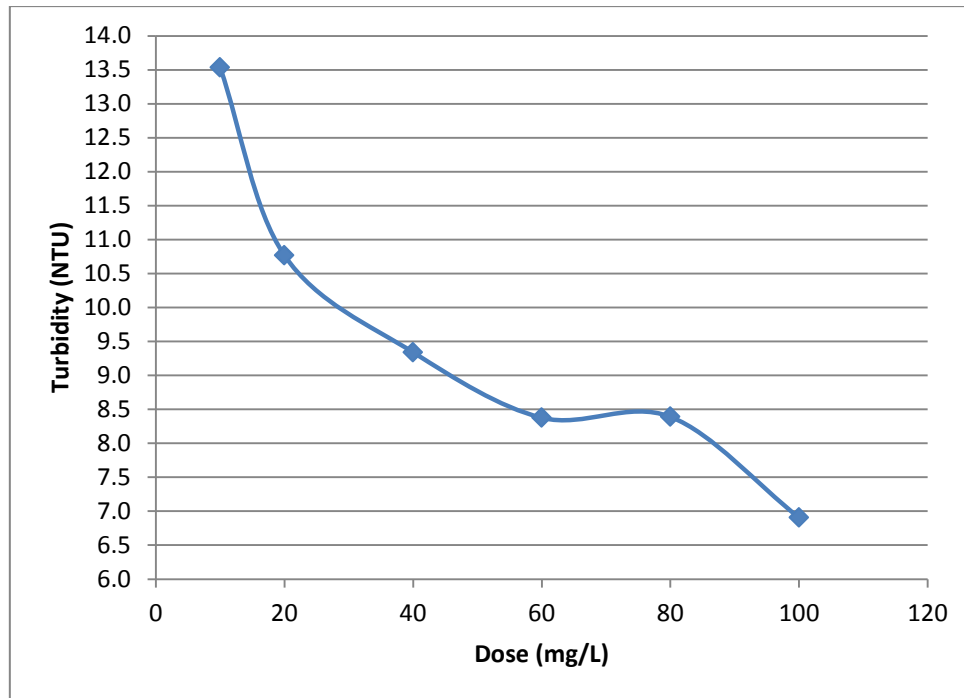


Figure 6.1 - Dosage vs. Turbidity Ferric Chloride

## 6.2 Results and Discussion of preliminary experiment

Initial testing has resulted in satisfactory results and confirms the literature identifying ferric chloride as a suitable coagulant for high pH, and high alkalinity water. Ferric chloride has accounted for a 95.94% reduction in turbidity with no pH reduction. This testing has formed the basis for refinement with a dosage range outside of the plotted region in Figure 6.1. The pH will be set between the range of 5 and 9.3, and dosages in the range of 60 to 150 mg/L. The experiment will be optimised for the required dosage providing the best turbidity removal with minimal heavy metal residual.

### 6.3 Optimisation Experiments

Table 6.2 identifies thirteen observed responses; these responses have been used to compute the model using response surface methodology and the least square method. The required dosage and pH levels have been generated in Minitab. From the generated data, 13 jar tests have been conducted following the same testing procedures identified in Section 5.3 of the report. The interpretation of the results achieved from optimisation will reflect the optimum dosage at the optimum pH that will result in a minimal ferrous residual. This will be achieved by the analysis of an overlaid contour plot. All conducted testing has been replicated a second time to ensure the reliability of results achieved, these results are tabulated in Table 6.2 below.

Table 6.2 – Ferric Chloride Optimisation

	Coded Variable	Real Variables		Experimental Results				
	X <sub>1</sub>	Dose (mg/L)	pH	Residual Turbidity (NTU)	Predicted Residual Turbidity (NTU)	% Turbidity Removal (NTU)	Residual Iron (mg/L)	Predicted Residual Iron (mg/L)
<b>1</b>	0	105.0	7.2	1.77	1.67	98.78	0.4277	0.2825
<b>2</b>	0	105.0	7.2	1.58	1.67	98.91	0.2530	0.2825
<b>3</b>	1	136.8	8.7	2.42	2.36	98.33	0.8022	0.6821
<b>4</b>	1	73.2	5.6	1.41	1.47	99.03	0.4901	0.5977
<b>5</b>	-1	105.0	9.3	3.34	3.34	97.70	0.8396	0.8614
<b>6</b>	0	105.0	7.2	1.59	1.67	98.90	0.2030	0.2825
<b>7</b>	1	136.8	5.6	1.36	1.30	99.07	0.4308	0.3327
<b>8</b>	1	73.2	8.7	3.23	3.29	97.77	0.4717	0.5570
<b>9</b>	0	105.0	7.2	1.80	1.67	98.76	0.2748	0.2825
<b>10</b>	0	105.0	7.2	1.63	1.67	98.88	0.2538	0.2825
<b>11</b>	-1	105.0	5.0	1.30	1.30	99.10	0.6524	0.6431
<b>12</b>	-1	150.0	7.2	1.42	1.50	99.02	0.1313	0.2830
<b>13</b>	-1	60.0	7.2	2.35	2.27	98.38	0.5213	0.3820

The two responses being residual turbidity and residual aluminium have been correlated with the two initial factors (Dosage and pH). This correlation has enabled the computation of quadratic regression models represented in Equations 6.1 & 6.2 depicted below. The  $R^2$  and  $R^2_{ADJ}$  values are also included with the equations.

**Residual Turbidity (NTU) =**

$$4.55 - 0.0022 * Dose - 1.121 * pH + 0.000103 * Dose^2 + 0.1404 * pH^2 - 0.00393 * Dose * pH \quad (6.1)$$

$$(R^2=98.82\%, R^2_{ADJ}=97.98\%)$$

**Residual Iron (mg/L) =**

$$7.02 - 0.0207 * Dose - 1.614 * pH + 0.000025 * Dose^2 + 0.1016 * pH^2 + 0.00202 * Dose * pH \quad (6.2)$$

$$(R^2=80.64\%, R^2_{ADJ}=66.82\%)$$

The quadratic regression Equations 6.1 and 6.2 have been used to predict values for residual turbidity and residual iron depicted in Table 6.2. These values have formed the basis for the validation of the mathematical models.

## 6.4 Validation of the Model

As previously mentioned in Section 5.4 the validation of the model is of the utmost importance. It is necessary to check the fitted model to ensure it provides an adequate approximation of the actual system, (Trinh & Kahn 2010). As can be seen below the graphical and numerical models have been used for this process. The graphical models depicted in Figures 6.2 and 6.3 characterises the nature of the residuals in model and ensures there is no pattern to the model. It is clear from analysis of these graphs that there is no pattern to the model, implying that the residuals are randomly distributed.

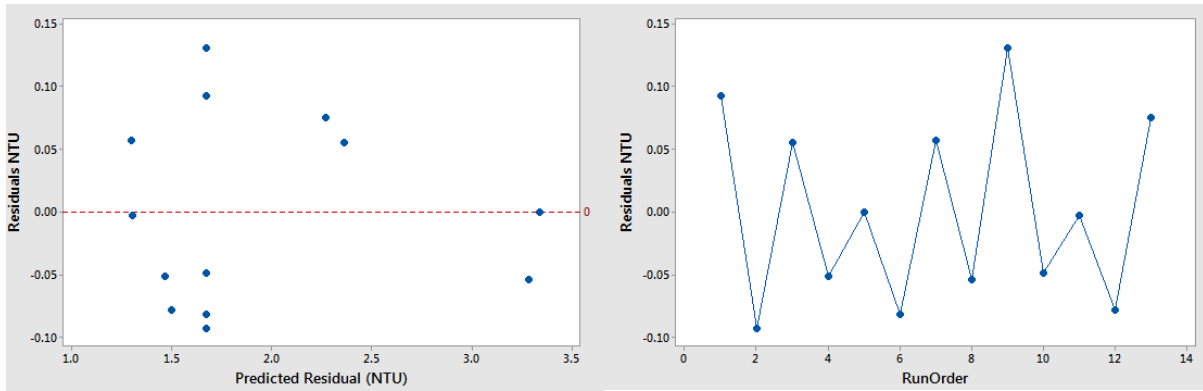


Figure 6.2 – Residual vs. Predicted Residual (NTU) & Normal Probability

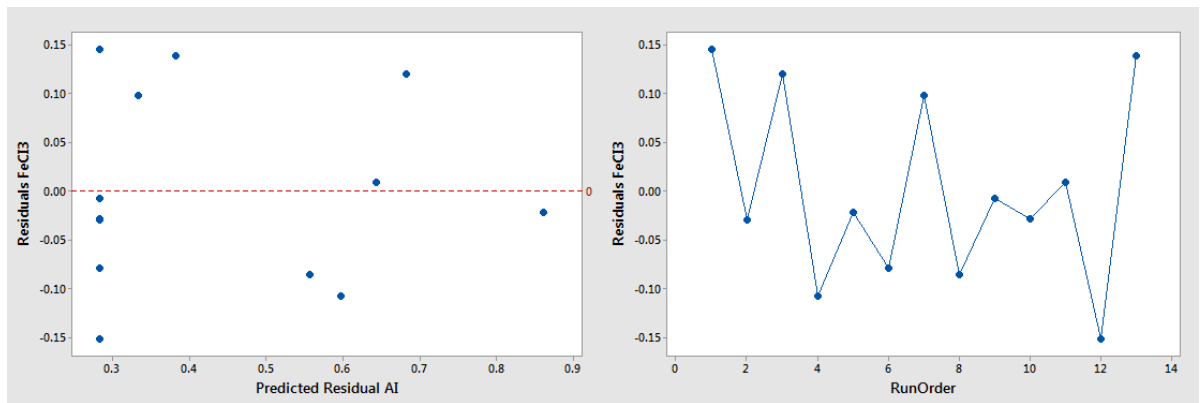


Figure 6.3 – Residual vs. Residual AI & Normal Probability

As can be seen in in Figure 6.4 the residuals have been plotted against a theoretical normal distribution. These residuals fall in a straight line, this indicates a normal distribution and the assumption of normality for this model has been satisfied.

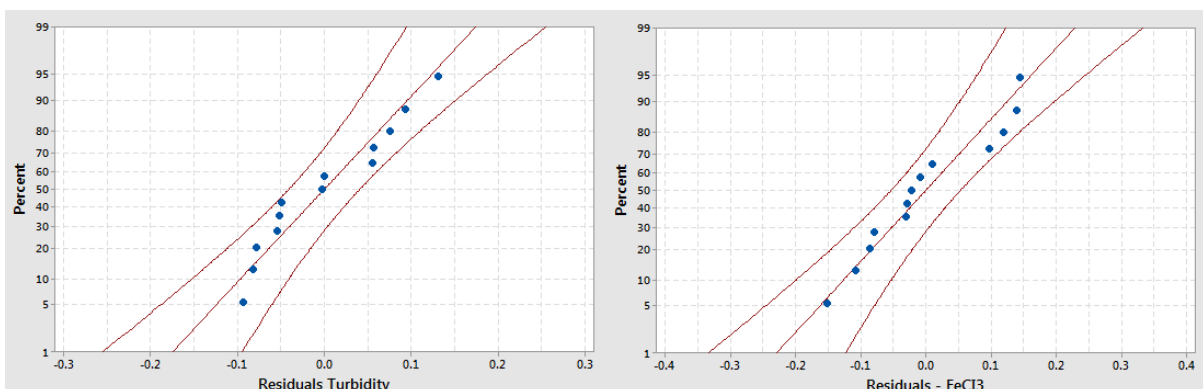


Figure 6.4 – Normal Distribution of Residual Turbidity and Residual AI

The models have been checked using the numerical method coefficient of determination. The coefficients of determination have been calculated using Equations 5.4 and 5.5 in Section 5.4. Table 6.3 depicted below shows the values for  $R^2$  &  $R^2_{ADJ}$  for the surface response model developed in Minitab.

**Table 6.3 - Coefficient of Determination Values**

	$R^2$	$R^2_{ADJ}$
<b>Residual Turbidity</b>	98.82%	97.98%
<b>Residual Iron</b>	80.64%	66.82%

The  $R^2$  value for residual turbidity is of a very high percentage with the  $R^2_{ADJ}$  showing only a marginal difference, this indicates a very high satisfactory adjustment of the quadratic model when comparing to the experimental values. Residual iron's  $R^2$  value is low compared to that of residual turbidity; however residual iron's  $R^2$  value is in a close enough proximity to satisfy the requirements. Furthermore, the  $R^2_{ADJ}$  value falls within a close enough proximity to be deemed satisfactory. These values indicate a satisfactory adjustment of the quadratic model. The regression models closely represent the residual turbidity and residual iron values to a satisfactory level.

## 6.5 Optimisation Analysis

Graphical Analysis of the acquired data has been undertaken using ANOVA. Tables 5.4 and 5.5 depict the ANOVA as calculated by Minitab. Table 5.4 corresponds to residual turbidity, while Table 5.5 corresponds to residual iron. As indicated in section 6.4 the  $R^2$  value for residual iron is 80.64% this means that the model cannot account for almost 20% of the variation. The low  $R^2_{ADJ}$  is compensated by the p-value of the model regression of less than 0.05, as depicted in Table 5.5. The table indicates a p-value of 0.019 for the model regressions (significant), and 0.588 for the LOC (insignificant). These values clearly indicate the significance of the model correlation between the variables and the process response (Baskan & Pala 2010). The p-value of residual turbidity is well below 0.05, this confirms a high accuracy fit.



Table 6.4 - ANOVA Response of Residual Turbidity

Residual Turbidity								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Turbidity</b>				Constant	1	1.6737	38.09	0.000
				Dose	1	-0.3871	-7.88	0.000
				pH	1	1.0195	20.75	0.000
Regression	5	117.28	0.000	Dose x Dose	1	0.2088	2.80	0.026
Residual error	7			pH x pH	1	0.6488	8.71	0.000
LOF	3	0.73	0.588	Dose x pH	1	-0.3800	-3.87	0.006
Pure Error	4							

Tables 5.4 illustrates that all variables have a significant effect on turbidity removal in equation 8. Table 5.5 indicates that the terms with the least effect on residual iron is Dose and Dose<sup>2</sup> with a p value of 0.465 and 0.622 respectively. The p values of the models show that the linear and quadratic effects of dose and pH are significant, more so for residual turbidity. It can be concluded that both dosage and pH factors are significant in explaining the relationship with the regression model.

Table 6.5 – ANOVA Response of Residual Iron

Residual Iron								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Iron</b>				Constant	1	0.2825	4.93	0.002
				Dose	1	-0.0495	-0.77	0.465
				pH	1	0.1091	1.70	0.132
Regression	5	5.83	0.019	Dose x Dose	1	0.0501	0.51	0.622
Residual error	7			pH x pH	1	0.4698	4.83	0.002
LOF	3	3.93	0.110	Dose x pH	1	0.195	1.52	0.172
Pure Error	4							

Minitab software has been used for graphical representation of the of the developed regression equations. The generated graphical representations are depicted in Figures 6.5 and 6.6. These figures are 3d surface plots and contour plots for residual turbidity and residual iron based on two factors dosage and ph. As can be seen in Figure 6.5, the contour of minimal residual turbidity falls between dosage 60 to 170 mg/L in the pH range of 4.3 to 7.0. This contour is the optimal point for minimum residual turbidity or maximum turbidity removal.

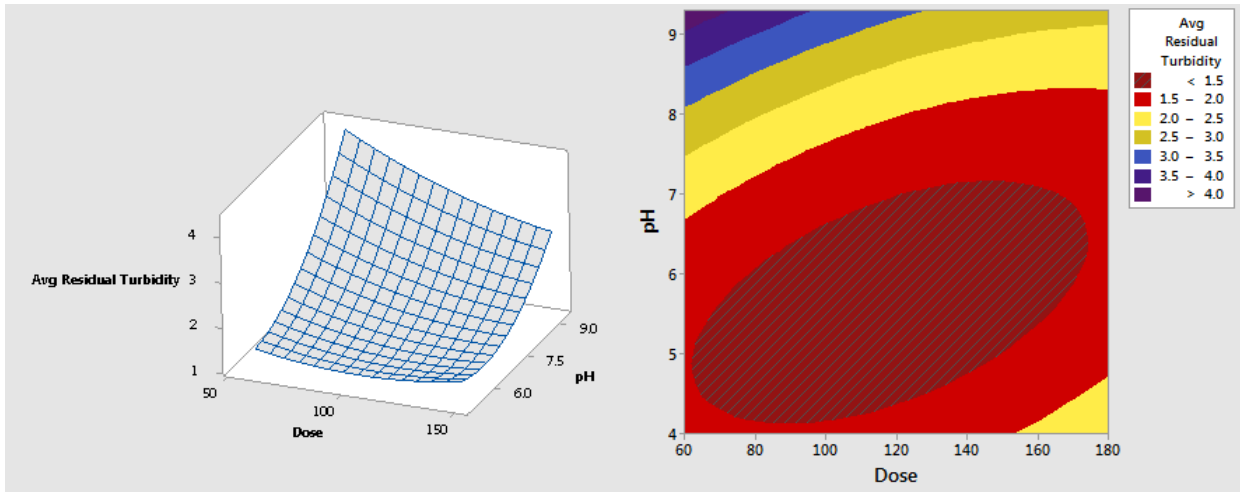


Figure 6.5 – Surface and Contour plots for Residual Turbidity

Figure 6.6 identifies the contour of minimal residual iron. As can be seen in the figure the contour falls within a dosage of 120 to 190 mg/L of coagulant at a pH range of 5.5 to 7.0. Figure 6.6 does not take into account turbidity removal and only focuses on the residual iron of the water after testing. The optimal point of dosage and pH that provides the most efficient turbidity removal that result in minimal residual iron is depicted in Figure 6.7.

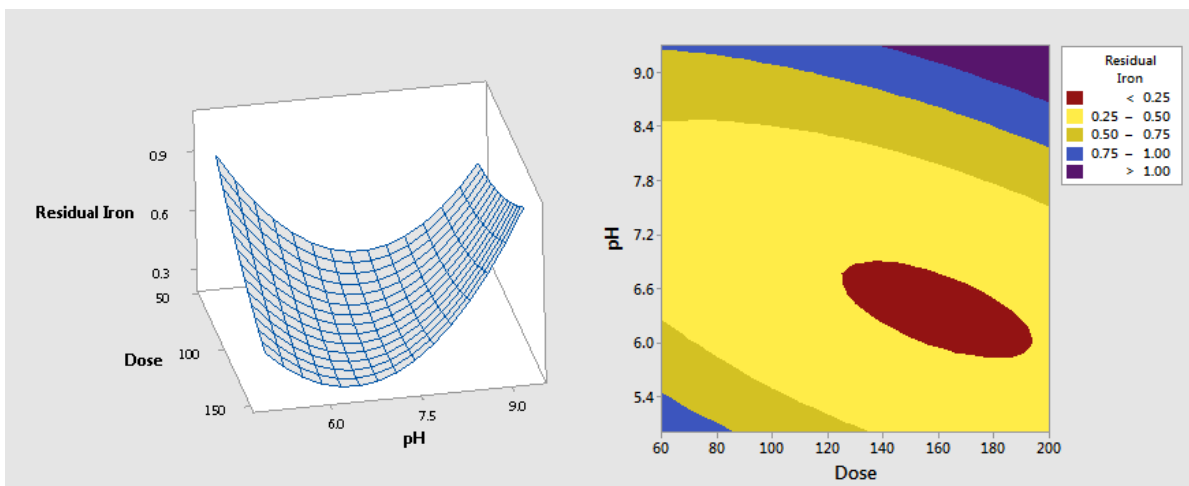


Figure 6.6 – Surface and Contour Plots for Residual Iron

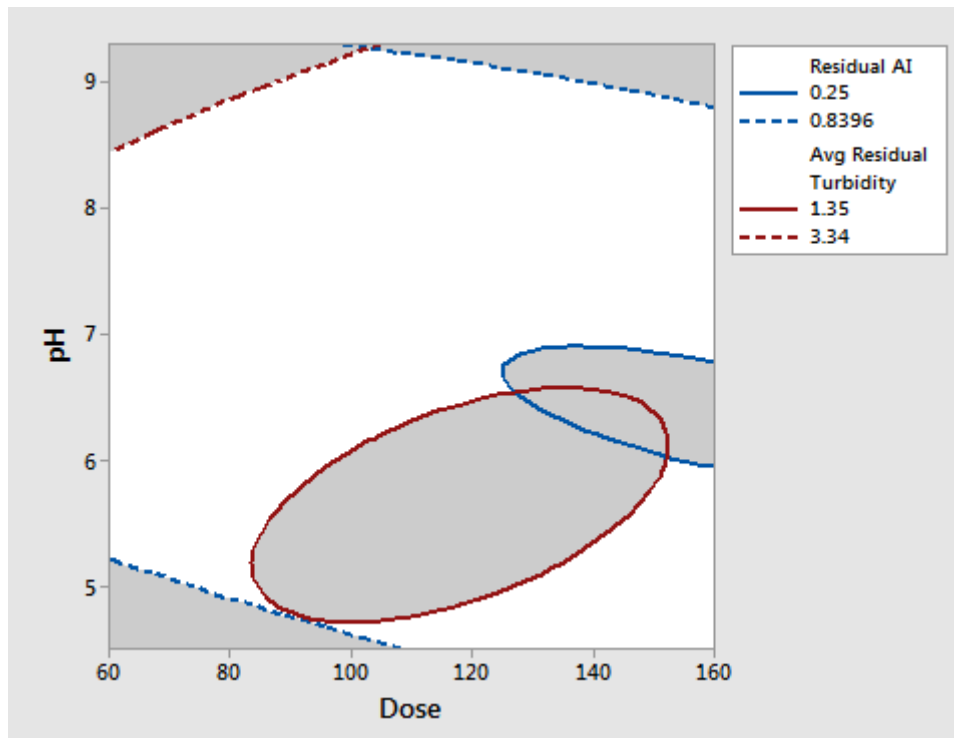


Figure 6.7 – Overlaid Contour Plot of Residual Turbidity and Residual Iron

Figure 6.7 is a depiction of overlaid contour plots of the regression equations developed by Minitab. This figure utilises the regression equations for residual turbidity and residual iron. The plot depicted above illustrates the region of overlapped contours; this region is the point of minimal residual turbidity and minimal residual iron. As shown again the region is between coagulant dosages 125 mg/L and 150 mg/L at a pH level between 6 and 6.5. The point of absolute optimum is discussed below in Section 6.6.

## 6.6 The optimum Value

To reach a singular point of optimum a compromise between the two separate responses, residual turbidity and residual iron, has to be reached. As indicated by Figure 5.7, the optimum region accounts for values of residual turbidity and residual iron of 1.35 NTU and 0.8396 mg/L. To obtain the optimum point for each factor of each response, the derivative of Equations 6.1 and 6.2 has to be obtained. This has been undertaken using Matlab, with the coding supplied in Appendix 4.

Table 6.6 – Point of Optimum

Response	$\lambda_1$ & $\lambda_2$	Dosage (mg/L)	pH
Residual Turbidity (NTU)	-0.0000, 0.1405	118.4741	5.6503
Residual Aluminium mg/L	-0.0000, 0.1405	155.5985	6.3961
Optimal Point		140.0000	6.3500

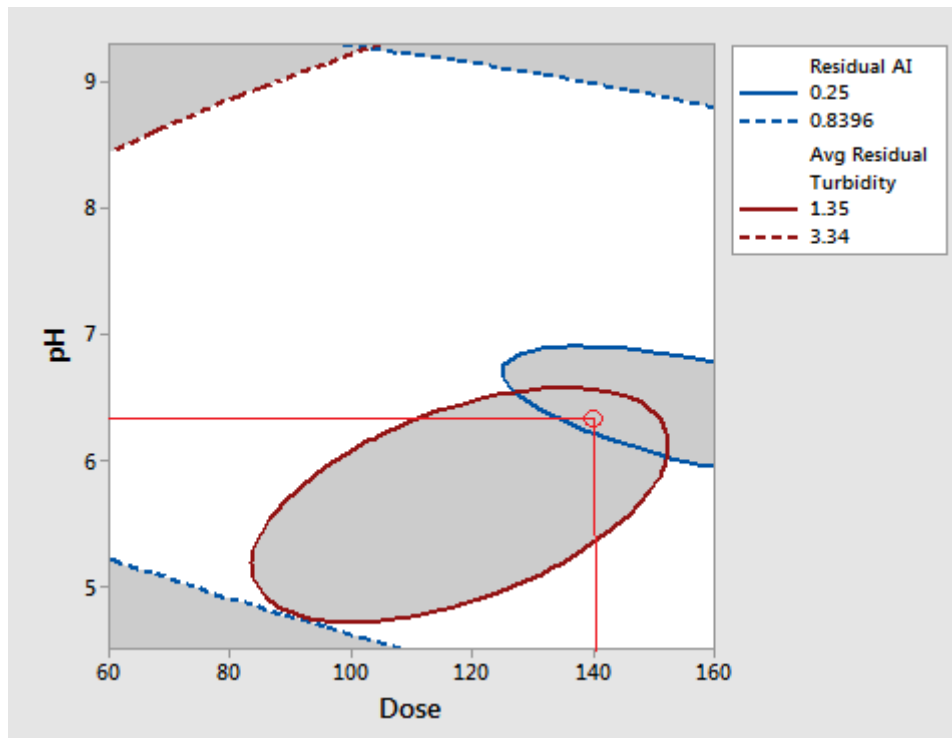


Figure 6.8 – Point of Optimal Residual Turbidity & Residual Iron

The model predicted an optimum as show in Figure 6.8, this optimum accounted for a coagulant dosage of 140 mg/L at a pH of 6.35. At the optimal dosage and pH, the residual turbidity is 1.309 NTU, with residual iron of 0.2729 mg/L. The optimal range of dosage and pH accounted for a turbidity removal of 99.01%. To confirm the results an additional two experiments have been conducted to ensure the reliability of the predicted results. Depicted in Table 6.7, the residual turbidity and the residual iron results obtained from initial testing are within a satisfactory margin of the predicted results. The additional testing results accounted for a relative error of below 10%. The results tabulated below imply that the RSM approach was appropriate for optimisation of the factors for the coagulation process.

**Table 6.7 – Optimal Conformation Testing Results**

	<b>Coagulation Condition</b>			
	<b>Dose</b>	<b>pH</b>	<b>Residual Turbidity (NTU)</b>	<b>Residual Iron (mg/L)</b>
<b>Experimental Value</b>	140.00	6.35	1.438	0.2729
<b>Predicted Value</b>	140.00	6.35	1.309	0.2556
<b>Error (%)</b>			9.85%	6.79%

## Chapter 7 – Ferric Sulphate as a Coagulant

Chapter 7 includes the results and discussion for all experiments carried out at a set level of turbidity of 150 NTU ( $\pm 20$  NTU). The coagulant discussed in this chapter utilises the coagulant Ferric Sulphate at a concentration of 10 mg/L, this coagulant is the primary and sole coagulant. Ferric Sulphate has been trialled as a coagulant in sea water desalination (Sanghyun, J, et al, 2011), due to this fact Ferric Sulphate has been trialled as a coagulant for produced formation water.

### 7.1 Preliminary Experiments

Initial testing has identified the suitability and provided an indication of the optimal effective range of dosage for optimisation. As shown in Table 7.1 the turbidity response of the coagulant has started to decrease in effectiveness after a dosage of 60 mg/L, this may indicate the saddle point. pH reduction has not been undertaken in these trials, the coagulant has a slight reduction effect on pH.

Table 7.1 - Initial Ferric Sulphate Results

Jar	Dosage (mg/L)	Turbidity (NTU)	pH
Initial	0	170	9.50
1	10	12.4	9.40
2	20	8.9	9.40
3	40	7.6	9.40
4	60	5.0	9.40
5	80	6.2	9.35
6	100	6.1	9.30

Ferric Sulphate like other iron salts has a working envelope in the range of pH of 5.5 to 8.5 (Gebbie, P, 2006). The dosage range of initial testing has been conducted in the ranges of 10 to 100 mg/L. Table 7.1 indicates that the optimum range for refinement will be between 60 and 140 mg/L. Refinement testing has been conducted with the aid of pH reduction to allow

the coagulant to work in its optimal pH range. The pH range for refinement testing has been undertaken between pH levels of 5.0 and 9.3.

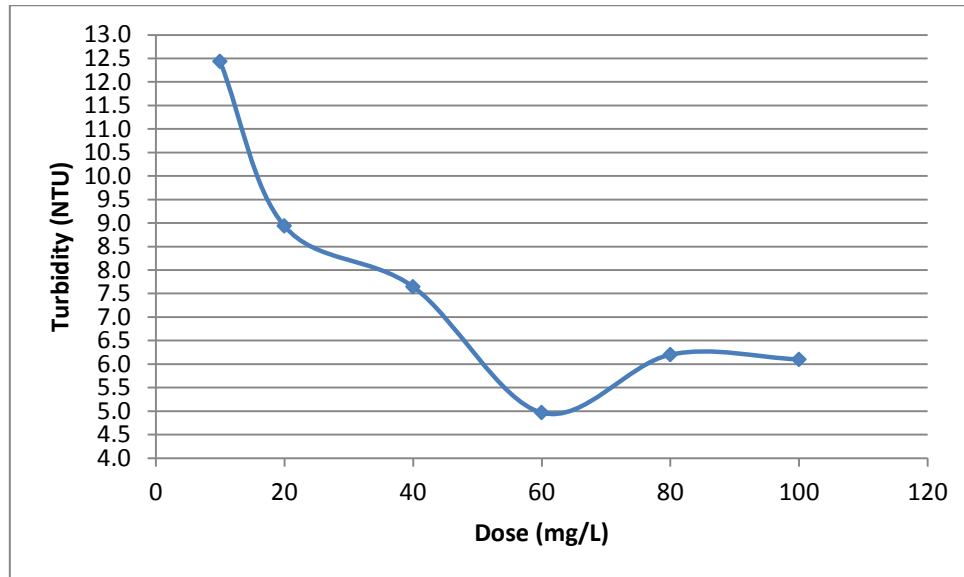


Figure 7.1 - Dosage vs. Turbidity Ferric Sulphate

## 7.2 Results and Discussion of preliminary experiment

As identified by Figure 7.1 Ferric Sulphate dosed outside of its optimal pH range still is a satisfactory coagulant of produced formation water. As shown in Table 2.4 Ferric Sulphate is not as and effective coagulant as Aluminium Sulphate and Ferric Chloride (Altaher, H, 2012). Despite this fact Ferric Sulphate will still be optimised for comparative purposes. The initial testing detailed in Section 7.1 has formed the basis for refinement testing. Dosages and pH will range from 60 to 140 mg/L and 5.0 and 9.3 respectively.

## 7.3 Optimisation Experiments

Optimisation experiments have been conducted with the aid of thirteen observed responses; these responses have been used to compute the model using the least square method. The thirteen responses have formed the parameters for thirteen jar tests using the same methods identified in Section 5.3. Each experiment undertaken has been replicated to ensure the reliability of the results. All results from refinement testing are tabulated below in Table 7.2.

**Table 7.2 – Ferric Sulphate Optimisation**

	Coded Variable	Real Variables		Experimental Results				
	X <sub>1</sub>	Dose (mg/L)	pH	Residual Turbidity (NTU)	Predicted Residual Turbidity (NTU)	% Turbidity Removal (NTU)	Residual Iron (mg/L)	Predicted Residual Iron (mg/L)
<b>1</b>	0	105.0	7.2	4.62	3.32	97.11	0.1562	0.2069
<b>2</b>	0	105.0	7.2	3.05	3.32	98.09	0.2717	0.2069
<b>3</b>	1	136.8	8.7	3.49	3.44	97.82	0.1531	0.1386
<b>4</b>	1	73.2	5.6	1.46	1.57	99.09	0.4433	0.3455
<b>5</b>	-1	105.0	9.3	4.90	4.88	96.94	0.0813	0.1115
<b>6</b>	0	105.0	7.2	2.19	3.32	98.63	0.3903	0.2069
<b>7</b>	1	136.8	5.6	1.77	1.74	98.90	0.5120	0.4607
<b>8</b>	1	73.2	8.7	5.09	5.18	96.82	0.1344	0.0733
<b>9</b>	0	105.0	7.2	3.37	3.32	97.89	0.0096	0.2069
<b>10</b>	0	105.0	7.2	3.40	3.32	97.88	0.2070	0.2069
<b>11</b>	-1	105.0	5.0	1.18	1.13	99.26	0.4496	0.5318
<b>12</b>	-1	150.0	7.2	2.34	2.40	98.54	0.2280	0.2513
<b>13</b>	-1	60.0	7.2	3.64	3.51	97.72	0.0345	0.1236

Equations 7.1 and 7.2 are quadratic regression equations generated by Minitab. These equations are the results of correlation between two initial factors, namely dosage and pH. Depicted below each equation are the  $R^2$  and  $R^2_{ADJ}$  values. These coefficients of determination indicate how much of the variability of the observed data is accounted for by the model (Trinh & Kang, 2010).



### Residual Turbidity (NTU) =

$$-14.50 + 0.0960 * Dose + 2.89 * pH - 0.000181 * Dose^2 + 0.069 * pH^2 - 0.00983 * Dose * pH \quad (7.1)$$

$$(R^2=84.28\%, R^2_{ADJ}=73.05\%)$$

### Residual Iron (mg/L) =

$$1.72 + 0.0053 * Dose - 0.425 * pH - 0.000010 * Dose^2 + 0.0248 * pH^2 - 0.00026 * Dose * pH \quad (7.2)$$

$$(R^2=66.19\%, R^2_{ADJ}=42.04\%)$$

The quadratic regression models depicted above have been used to predict the values of residual turbidity and residual iron depicted in Table 7.2. These values have formed the basis for the validation of the mathematical model.

## 7.4 Validation of the Model

To ensure an adequate approximation to the actual model it is necessary to check the fitted model. This is to ensure the reliability and validation of the model. The primary tool used to confirm or discredit the validation of the model has been graphical and numerical approaches. Figures 7.2 and 7.3 characterise the nature of the residuals in the models. The residuals have been defined by Equation 5.4 and 5.5 in section 5.4.

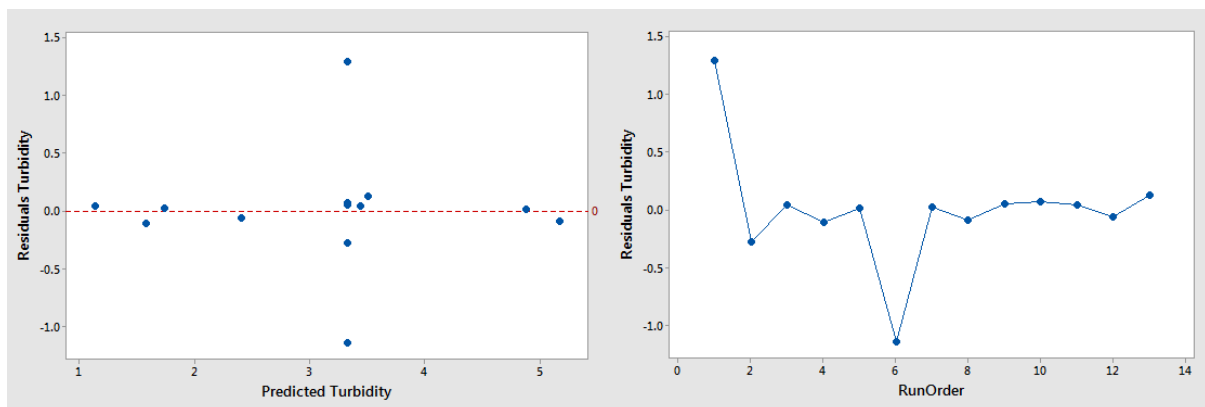
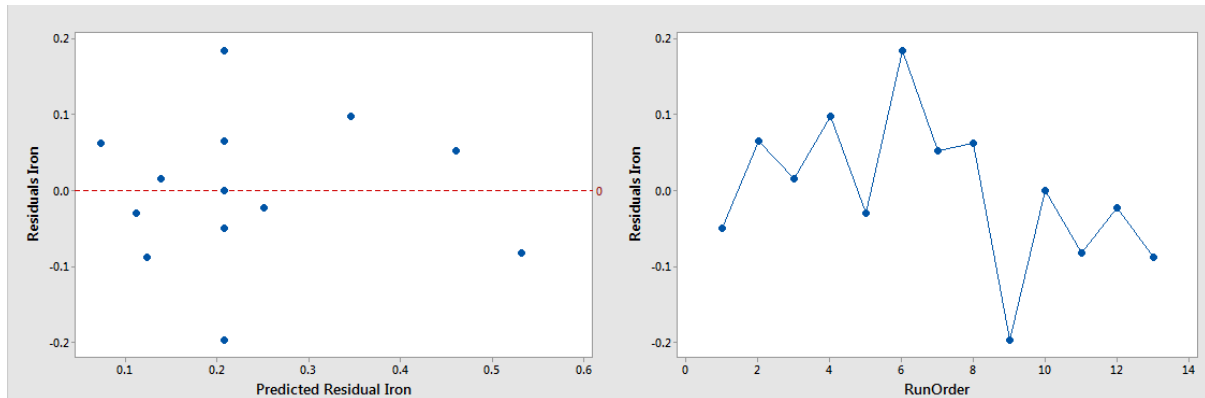


Figure 7.2 – Residual vs. Predicted Turbidity & Normal Probability

Figures 7.2 and 7.3 are plots of residuals used to examine the functional part of the model. And residuals plotted against run order. These plots have been used to examine the sufficiency of the model and to ensure no obvious patterns are present in the model. From examination of Figures 7.2 and 7.3 it is obvious there is no pattern, implying that the residuals are randomly distributed.



**Figure 7.3 - Residual vs. Predicted Residual Iron & Normal Probability**

Figure 7.4 is the theoretical normal distribution plotted against the residuals of the models. As identified by Trinh & Kang (2010), the points should fall in an approximate straight line, deviation from this line would indicate a deviated from normal distribution. As can be seen in Figure 7.4 the first plot identifies a non-ideal normal distribution, this indicates a deviation from normal distribution. Interpretation of Figures 7.3 and 7.4 indicate that a satisfactory level of normality of the model has identified albeit not ideal for the normal distribution for residual turbidity.

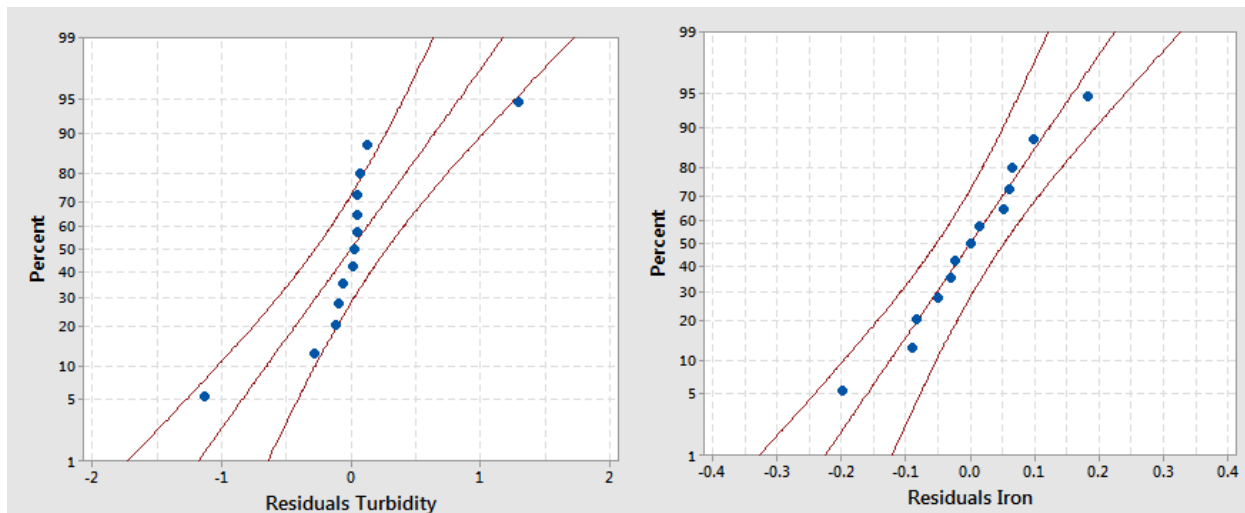


Figure 7.4 – Normal Distribution for Residual Turbidity and Residual Iron

As identified by Minitab the coefficients of determination listed in Table 7.3 have been used as a numerical method for checking of the model. The  $R^2$  value for residual turbidity is close to 90% and the  $R^2_{ADJ}$  value falls close within a close margin of the  $R^2$  value. This would indicate a satisfactory adjustment of the quadratic model when compared with the experimental values. The residual iron  $R^2$  is low in comparison to residual turbidity, and the  $R^2_{ADJ}$  value shows a significant difference between the  $R^2$  value for residual iron. This indicates a non-ideal adjustment between the quadratic regression model and the experimental values. The regression model satisfactory represents the turbidity value, but is non-ideal for the residual iron values.

Table 7.3 - Coefficient of Determination Values

	$R^2$	$R^2_{ADJ}$
<b>Residual Turbidity</b>	84.28%	73.05%
<b>Residual Iron</b>	66.19%	42.04%

## 7.5 Optimisation Analysis

The ANOVA calculated by Minitab is displayed in Tables 7.4 and 7.5. ANOVA has been used for graphical analysis of the gained data. The data correlated in Table 7.4 corresponds to residual turbidity with Table 7.5 corresponding to residual iron.

Table 7.4– ANOVA Response Residual Turbidity

Residual Turbidity								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Turbidity</b>				Constant	1	3.324	11.19	0.000
				Dose	1	-0.554	-1.67	0.139
Regression	5	7.50	0.010	pH	1	1.876	5.65	0.001
Residual error	7			Dose x Dose	1	-0.367	-0.73	0.490
LOF	3	0.02	0.995	pH x pH	1	-0.317	-0.63	0.549
Pure Error	4			Dose x pH	1	-0.951	-1.43	0.196

Table 7.4 indicates that dose<sup>2</sup> and pH<sup>2</sup> are the factors which have the least effect on turbidity removal in the quadratic regression model. The factor with the greatest influence in Equation 7.1 is pH followed by dose. As shown in Table 7.5 dose<sup>2</sup> and dose x pH are the factors identified that effect Equation 7.2 the least. pH is again the main influencing factor for the model representing residual iron. The p-values for both models are significant indicating that the quadratic linear effects of dose and pH are also significant. Although the terms that affect the models the least may be considered insignificant, they are still considered as both models are hierarchical (Baskan & Pala 2010).

Table 7.5 – ANOVA Response Residual Iron

Residual Iron								
Model	d.f	F-value	p-value	Parameter	d.f	Coefficient	T value	P
<b>Residual Iron</b>				Constant	1	0.2070	3.66	0.008
				Dose	1	0.0638	1.01	0.346
Regression	5	2.74	0.111	pH	1	-0.2101	-3.33	0.013
Residual error	7			Dose x Dose	1	-0.0195	-0.20	0.844
LOF	3	0.03228	0.679	pH x pH	1	0.1147	1.20	0.270
Pure Error	4			Dose x pH	1	-0.025	-0.20	0.849

Surface and contour plots have been generated using the regression equations provided by Minitab. These Figures 7.5 and 7.6, provide a graphical representation of residual turbidity and residual iron for factors of dosage and pH. Figure 7.5 does not identify an optimal contour for minimal residual turbidity this can be attributed to the non-ideal circumstances discussed in Section 7.4.

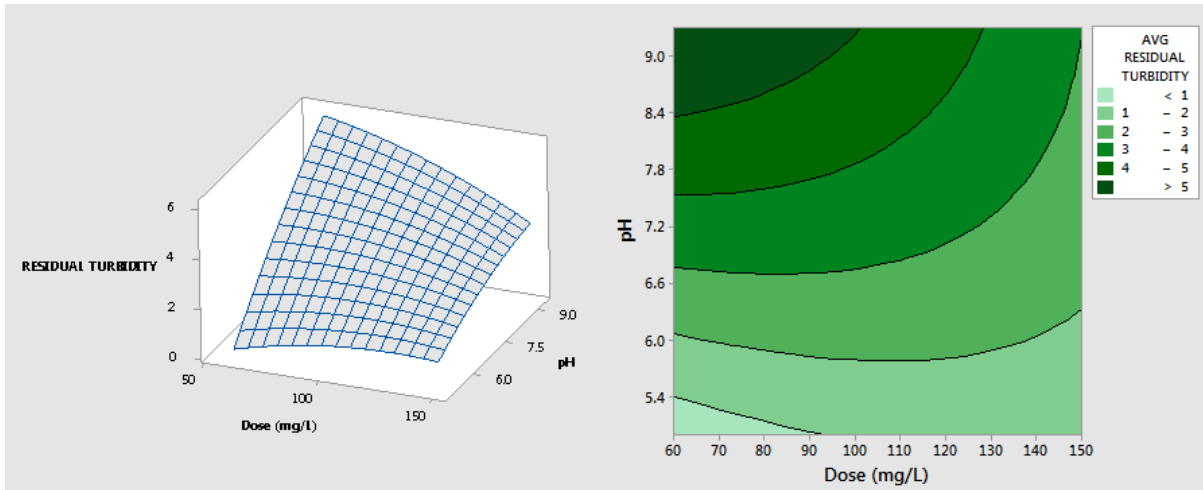


Figure 7.5 – Surface and Contour Plots for Residual Turbidity

Figure 7.6 identifies a contour of minimal residual iron, this contour fall in the pH range of 7.4 to 9.3 and the dosage range of 60 to 95 mg/L. The identified minimal contour is far from ideal, this non-ideal contour can be attributed to the low  $R^2$  and the difference between the  $R^2_{ADJ}$  values. The surface and contour plots generated for residual iron do not take into account residual turbidity.

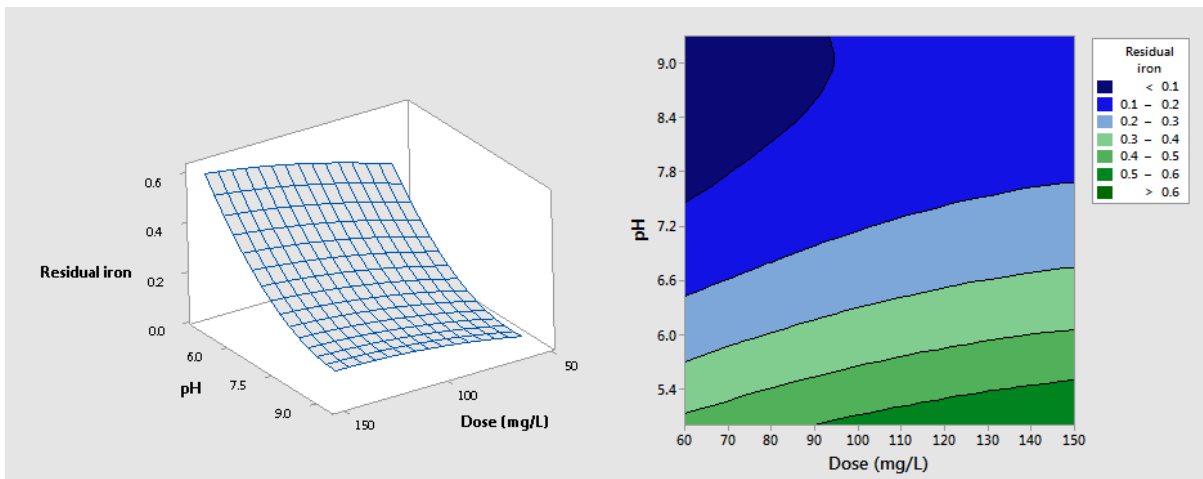


Figure 7.6 – Surface and Contour Plots for residual Iron

The residual turbidity and residual iron are two individual responses, and as can be seen in Figures 7.5 and 7.6 their optimisation has been achieved under different optimal conditions. To define a point of optimum a compromise between the two responses was required. Figure 7.7 is graphical representation of an overlaid contour plot of both responses. To

achieve the region of optimum identified by the white unshaded area, residual turbidity and residual iron had to be compromised from their minimal values of <1 NTU and <0.1 mg/L to 2.5 NTU and 0.3 mg/L respectively. The point of absolute optimum is discussed in Section 7.6.

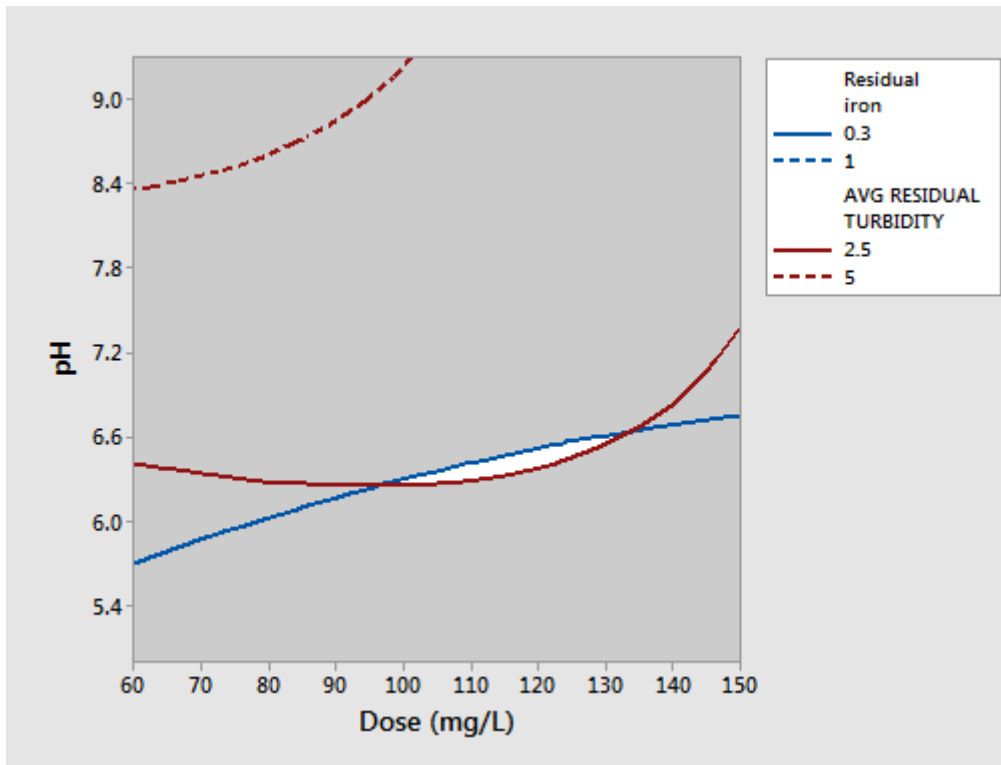


Figure 7.7 – Overlaid Contour Plot of Residual Turbidity and Residual Iron

## 7.6 The optimum Value

A compromise between the two separate responses, residual turbidity and residual iron, has to be reached to reach the singular optimum point. Figure 7.7 indicates the region of this optimum which accounts for values of residual turbidity and residual iron of 2.5 NTU and 0.3 mg/L. To obtain the optimum values of dosage and pH for each region the derivative of Equation 7.2 has been computed. Due to the non-ideal regression equation (Equation 7.1) the derivative was not computed as un-realistic results were obtained. Mathematical modelling software Matlab has been used for this task.

Table 7.6 – Point of Optimum

Response	$\lambda_1$ & $\lambda_2$	Dosage (mg/L)	pH
Residual Turbidity (NTU)	N/a	N/a	N/a
Residual Aluminium mg/L	-0.0000, 0.0248	143.81	9.32
Optimal Point		115.00	6.45

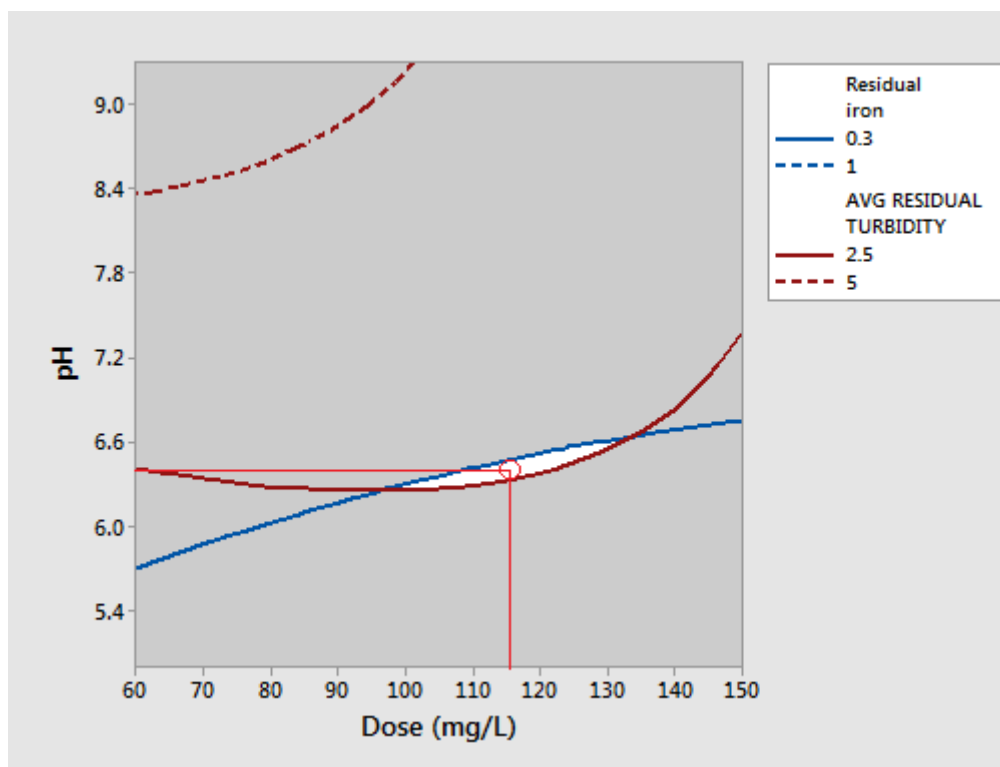


Figure 7.8 – Point of Optimal Residual Turbidity & Residual Iron

Interpretation of Table 7.6 reveals that a noticeable compromise is needed to ensure the point of optimum falls within the region identified in Figure 7.7. The point of optimum identified in Figure 7.8 is at dosage and pH, 115 mg/L and 6.4 respectively. This dosage and pH range accounts for a residual turbidity of  $\approx$  2.5 NTU and 0.34 mg/L of residual iron. The optimal value was tested twice to ensure the credibility and reproducibility. As can be seen in Table 7.7 the Residual Turbidity resulted in an error of 19.0% this can be accounted for by the non-ideal residual turbidity equation. Further testing and refinement is required to amend the erroneous equation.

Table 7.7 - Optimal Conformational testing

	Coagulation Condition			
	Dose	pH	Residual Turbidity (NTU)	Residual Iron (mg/L)
<b>Experimental Value</b>	145.00	6.35	3.19	0.36
<b>Predicted Value</b>	145.00	6.35	2.50	0.34
<b>Error (%)</b>			19.0%	6.0%



## Chapter 8 – Conclusion and Recommendations

### 8.1 Conclusion

The focus of this research was to identify and optimise a suitable coagulant for pre-treatment of Coal Seam Gas produced formation water. The research aimed to identify a coagulant capable of reducing turbidity to a minimum whilst resulting in little to no residual heavy metals. Ferric Chloride and Ferric Sulphate were identified from their wide spread use in sea water desalination. Sea water desalination shares a close water characteristic comparison with produced formation water. Ferric Chloride and Ferric Sulphate have been tested and optimised, in regard to their efficiency in removing turbidity while providing minimal residual iron. Their performance has been compared with the conventional coagulant Aluminium Sulphate, commonly used in raw water treatment plants. Aluminium Sulphate was selected due to its wide spread use, and proven capabilities as a coagulant.

The main goal of this research was to identify a suitable coagulant that possessed the capabilities of being an effective pre-treatment method for Coal Seam Gas produced formation water. Jar testing has been utilised as the most effective platform for testing and has formed the basis for all testing. The dosed water has been tested for residual aluminium and residual iron. The focus of optimisation is minimal residual turbidity resulting in minimal heavy metal residual. Statistical analysis software Minitab was used to formulate the experimental designs, and the models required for optimisation analysis, based on two factors being dosage and pH. Thirteen observed responses were generated requiring thirteen experiments for each coagulant. Statistical and graphical methods of validation have been employed to analysis the goodness of fit of the model. Aluminium Sulphate, Ferric Chloride, and Ferric Sulphate have all been tested and optimised, indicating their optimal dosage and pH. Aluminium Sulphate and Ferric Chloride showed a satisfactory fit with the generated model. Ferric Sulphate failed to satisfy the fitting criteria for residual turbidity, however was satisfactory for residual iron. The generated residual turbidity model for Ferric sulphate was not used due to its failure to fit. Each experiment has been replicated, and three samples of each measurement were taken to ensure reliability of the results. To ensure the optimum fell with the experiments design parameters many experiments were conducted and repeated. After confirmation of the models validity, optimisation analysis was undertaken. To find the optimum condition for each response two methods were utilised. The first method required calculation of the derivatives of the regression equations and solving for each response separately. This method had the ability of finding the optimum response of residual turbidity and residual aluminium separately, but did not give an indication to the optimal with the two combined. For this reason the second approach proved to be the most satisfactory, being an overlaid contour plot of each response. Overlaid contour plots are considered more realistic as they take into

account both responses, graphically representing an optimal contoured region. The point of optimum predicted from analysis of both methods, has been validated from experiments at the optimum parameters. The results from this testing has been compared with the predicted results with an absolute error between 1 and 10% respectively.

The optimal conditions and the results achieved at the optimal conditions are tabulated in Table 8.1. The optimal results were gained from testing of produced formation water at a set turbidity of 150 NTU for all coagulants. Aluminium sulphate as a coagulant has performed similarly with comparable results identified in literature. At optimal conditions Aluminium Sulphate accounts for a residual turbidity of 0.915 NTU at a pH of 6.33 this resulted in a turbidity removal of 99.4%. The residual aluminium present in the water from optimal testing is 0.682 mg/L, when compared to the aluminium content of Aluminium sulphate (11.5 mg/L), it is evident that the majority of aluminium has settled with the flocs. Regarding Ferric Chloride, the turbidity removal % and pH results are within a close margin to Aluminium Sulphate. The foremost differences between the two coagulants are dosage and residual. At the optimum Ferric Chloride requires almost twice the dosage to achieve similar results in residual turbidity, however residual iron only accounts for 0.273 mg/L. Ferric Sulphate was proven to be not as effective as the two before mentioned coagulants. Although not as effective, Ferric Sulphate still resulted in a residual turbidity of 3.190 NTU at the same dosage and pH of Ferric Chloride. The optimal achieved by Ferric Sulphate resulted in a turbidity removal percentage of 97%, with residual iron of 0.340 mg/L present in the test water. The results achieved by Ferric Sulphate are slightly higher then was achieved in sea water desalination identified in literature. It is evident by the results depicted in Table 8.1 that ferric salts, although requiring twice the dosage, results in substantially less heavy metal residual then that of Aluminium Sulphate while still being comparably effective as a coagulant.

**Table 8.1 – Optimal Achieved Results for all Experiments Conducted**

<b>Optimal Achieved Results</b>						
<b>Coagulant Type</b>	<b>Dosage, mg/L</b>	<b>pH</b>	<b>Residual Turbidity, NTU</b>	<b>Residual Aluminium, mg/L</b>	<b>Residual Iron, mg/L</b>	<b>Turbidity Removal, %</b>
Aluminium Sulphate	76.88	6.33	0.915	0.682	--	99.4
Ferric Chloride	140.00	6.35	1.438	--	0.273	99.1
Ferric Sulphate	140.00	6.35	3.190	--	0.340	97

## **8.2 Recommendations for Further Work**

Research has only been conducted in regards to the use of coagulants as the sole and primary coagulant. Further research is suggested, having arisen throughout the course of this dissertation:

- Investigate the effectiveness of flocculent aids in conjunction with, and as a standalone pre-treatment process.
- Consider other variables that affect the coagulation process, such as alkalinity and temperature.
- Study the effects of coagulants of low turbidity produced formation water .
- Trial the effectiveness of identified coagulants with water produced during the drilling process, containing higher levels of suspended solids, and high carbon content.

## References

Abousnina, R, Nghiem, L, Bundchuh, J, 2014, 'Comparison between oily and coal seam gas produced water with respect to quantity, characteristics and treatment technologies: a review', *Desalination and Water Treatment*, pp. 1-16.

Accepta advance Environmental Technologies, 2014, Reverse Osmosis (RO) Process Water Treatment, view 4 June 2014, < <http://www.accepta.com>>

Altaher, H, 2012, 'The use of chitosan as a coagulant in the pre-treatment of turbid sea water', *Journal of Hazardous Materials*, Department of Chemical Engineering Technology Yanbu Industrial College, Yanbu Al-Sinaivah, Saudi Arabia.

Amir, T, Ismail, N, Alkarkhi, AFM & Teng, TT 2009, 'Optimization of coagulation process for landfill leachate pre-treatment using response surface methodology (RSM)', *Journal of Sustainable Development*, vol. 2, no. 2, pp. 159–167.

Aravinthan, V, 2014, ENV4203 Public Health Engineering, University of Southern Queensland, Toowoomba.

Australian pacific LNG 2014, CSG to LNG production, viewed 15 May 2014, <http://www.aplng.com.au/>

Baskan, BA & Pala, A 2010, 'A statistical experiment design approach for arsenic removal by coagulation process using aluminium sulfate', *Desalination*, vol. 254, no. 1–3, pp. 42–48.

Bezerra, M, Santelli, R, Oliveiraa, E, Villar, L, Escaleraa, L 2008, 'Response surface methodology (RSM) as a tool for optimization in analytical chemistry', *Talanta*, vol. 76, no. 5, pp. 965–977.

Bina, B, Mehdinejad, MH, Nikaeen, M & Attar, HM 2009, 'Effectiveness of chitosan as natural coagulant aid in treating turbid waters', *Iranian Journal of Environmental Health Science and Engineering.*, vol. 6, no. 4, pp. 247–252.

Chesters, SP, Darton, EG & Silvia Gallego, FD, 2009, 'the safe use of cationic flocculants with reverse osmosis membranes', *Desalination and Water Treatment*, vol 6, pp.144-151.

Davey, A, Howick R, Armbruster, R, 2012, 'Treatment of Coal Seam Gas Methane Water in Talinga, Dalby, and Moranbah', *Water in Mining*, Vol 39, no 3, pp. 73-75.

Driscoll, CT & Letterman, RD 1995, 'Factors regulating residual aluminium concentration in treated waters', *Environmetrics*, vol. 6, no. 3, pp. 287–309.

Eaton, A, Clesceri, L, Rice, E, Greenberg, A, 2005, *Standard Methods for the examination of water & waste water*, 21<sup>st</sup> edn, American Public Health Association, Washington DC, USA

Edzwald, J & Tobiason, J 1999, 'Enhanced Coagulation', *Water Science and Technology*, vol. 40, no. 9, pp. 63–70.

Gebbie, P, 2006, 'An operators guide to water treatment coagulants', Queensland water industry workshop, University Central Queensland, Rockhampton, Australia.

Hamawand, I, Yusaf, T, Hamawand, S, 2013, 'Coal Seam Gas and Associated Water: a review paper', *Renewable and Sustainable Energy Reviews* 22, pp. 550-560.

James, EK & Johannes, H, 2011, 'Seawater pre-treatment for reverse osmosis: Chemistry, contaminants and coagulation', University of Massachusetts, MA, USA, University of Johannesburg, Johannesburg, South Africa.

Khai, EL & Tjoon, TT, 2011, 'Flocculation activity of novel ferric chloride-polyacrylamide (FeCl<sub>3</sub>-PAM) hybrid polymer', School of Industrial Technology, University Sains, Malaysia.

Ladewig, B & Asquith, B, 2012, *Desalination Concentrate Management*, Springer, United Kingdom.

Lenntech Water Treatment Solutions 2014, *Particles, Scaling and Biofouling-membrane technology*, viewed 10 April 2014, < <http://www.lenntech.com/particles-scaling-biofouling.htm>>.

Montgomery, D, Wiley, J & Sone 2001, *Design and Analysis of Experiments*, New York.

Nghiem, L, Ren, T, Aziz, N, Porter, I, 2011, 'Treatment of coal seam gas produced water for beneficial use in Australia: A review of best practices', *Desalination and water treatment* 32, pp. 316 – 323.

Sanghyun, J, Firoozeh, N, Tien, V, Saravanamuthu, V & Tuan, AT, 2011, 'Pre-treatment for seawater desalination by flocculation: Performance of modified poly-ferric silicate(PFSi- δ) and ferric chloride as flocculants', University of Technology, Sydney, Australia.

Standard Methods for the Examination of Water and Wastewater (SMEWW) 2006, viewed 10 October 2013, < <http://standardmethods.org/>>.

Standard Methods for the Examination of Water and Wastewater 1998, 19th Edition, American Public Health Association.

The Free Dictionary, Farlex, 2014, 'Coagulation', viewed 4 May 2013, <http://www.thefreedictionary.com/coagulation> COAGULANT

Water Treatment Solutions, Lentech, 2014, 'Reverse Osmosis Desalination Costs Analysis', viewed 15 May 2014, <<http://www.lenntech.com/processes/desalination/energy/general/desalination-costs.htm>>.

Water/Wastewater Distance Learning, 2011, Lesson 4 coagulants and flocculants, viewed 1 June 2014, <http://water.me.vccs.edu/>

Yogeshkumar, N, Stul, S, Adhikrao, V, 2013, 'Chitosan and its Applications: A Review of Literature', *International Journal of Research in Pharmaceutical and Biomedical Sciences*, Vol. 4, pp.312 – 331.

Zeroday, 2001, process water and wastewater treatment products, viewed 4 April 2014, <<http://www.zerodayllc.com/>>

# Appendix A: Project Specifications

**University of Southern Queensland**

**Faculty of Engineering and Surveying**

For: Byron Manthey

Topic: Investigation into suitable coagulant for use of pre-treatment of Coal Seam Gas (CSG) waste water

Supervisor: Vasantha Aravinthan

Enrolment: ENG4111-S1, 2014  
ENG4112-S2, 2014

Project Aim: This Project aims to identify a suitable coagulant for use of pre-treatment of coal seam gas waste water, and optimise the process of coagulation/flocculation for CSG waste water pre-treatment

## **Programme:**

1. Conduct and extensive literature review on coagulation and flocculation processes applicable to water treatment
2. Collect data on reported coal seam gas waste water/basin and compare them to identify the differences. Research on any reported pre-treatment of CSG using coagulants and critically identify gaps.
3. Collect and Analyse the CSG water characteristics such as pH, turbidity, total organic carbon and other as required. Select suitable coagulants and or flocculent aids needed for the removal of turbidity from CSG water based on the identified characteristics.
4. Conduct preliminary jar tests to determine the range of dose of coagulants and other parameters such as pH, rapid mixing, slow mixing, time and rate that need optimisation.
5. Apply the statistical technique Design of Experiments (DoE) to setup computational aid to find out the minimum runs needed to optimise the identified variables in 4.
6. Design in lab 'bench test' for testing of different flocculants in the treatment of coal seam gas waste water and test the flocculants for suitability as found in 3 and 4.
7. Analyse the experimental data received for optimum parameters that can maximise the turbidity removal by deriving systematic mathematical models that adequately describe and predict the experimental phenomena using surface response methodology available in Mini tab software.

8. Identify the suitable coagulant by; critically evaluating the performance of the different coagulants, their effect on the environment-and their optimum range in the pre-treatment of CSG water using the results from 6 and 7.
9. Submit an academic dissertation on the research.

*If time permits*

10. Testing of treated water for total dissolved solids remaining.
11. Analyse the coagulation of the solids and treat if required with coagulation aids.

## **Appendix B: Risk Management**

### **Introduction**

A consequential side effect as part of the testing involved with this project involves conducting risk assessment. This process involves identifying all associated risks and safeguards and documenting the process. Risks are encountered throughout this project in all manners from minimal to extreme. As a result of this it is important to identify, classify and raise awareness of all involved risks and establish a level of continuing responsibility.

### **Risk Identification**

The primary risks associated with this project can be classified as sample preparation, sample testing, housekeeping, and project sustainability. Each before mentioned category can be further refined into additional risk.

The risks associated with sample preparation involve the use of acids, manual handling and safe disposal of hazardous materials. Sample testing poses the greatest risk, as the testing machine used to analyse residual metals in the sample uses explosive gases and a flame. The operator is subjected to exhaust gases from the process, noise, and potential for eye irritation. Each of these hazards can potentially cause operator harm, with the injuries possibly ranging from asphyxiation, skin and eye irritation, and operator death. General risks associated with housekeeping involve areas such as wet floors from spills, untidy work area, trip hazards and incorrectly labelled chemicals and equipment.

Project sustainability is the risk associated with the environment and the future users of this project. Risk to the environment may relate to improper disposal of chemicals, hazardous materials such as the test water and improper use of testing equipment. The sustainability of resources used is also important and should be considered. Future direct users of this project are not expected to be exposed to any risks.

### **Risk Evaluation**

The risks mentioned above generally fall into the low risk category, and represent a low level of risk to any person involved. The risks associated with sample preparation can be characterised as being low risk with the associated use of materials relatively harmless if



handled and used correctly, if safe handling is not adhered to the potential for harm is much greater and the likelihood of occurrence increases.

The highest likelihood for injury may be encountered throughout the sample testing stage. The risk associated with the testing equipment can be categorised as minor to moderate, with the possibility for irreversible injury to the operator if the machinery is improperly used is present. The injuries may be due to exposure to heat, flammable gasses or explosion all of which will cause significant serious injury. The probabilities of these mention incidents occurring are minimal if all machine instructions are correctly followed.

The associated risk due to housekeeping is unlikely as, the laboratories are frequently cleaned and kept in a tidy clutter free condition. Spills are cleaned when they occur and signage is placed alerting others of a wet floor while it dries. Benches are also cleaned after use to remove any possibility of spilt chemicals.

Environmental risk is low as the majority of materials used for testing are of natural occurrence. The small amounts of toxic substances used throughout the project are minimal so will pose a significant environmental impact. The laboratories are provided with suitable disposal containers to ensure chemicals are not disposed of incorrectly.

## **Risk Control**

The risks that operators are exposed too during the project are controlled utilising the following risk action plan;

- 1 Do I understand the task I am about to conduct?
- 2 Have I completed the required training to successfully and safely complete the task?
- 3 What hazards may be associated with performing the task?
- 4 What controls can I implement to reduce the risk associated with performing the task?

Once these questions have been answered to a satisfactory level, the operator is able to safely perform the required task. All tasks were explained in detail by my supervisor and the laboratory supervisor before performing the task. Training was provided in the form of a demonstration and safety inductions regarding all aspects of the project, such as material handling, machine operation, and the location of fire escapes and meeting points.

Before the start of any task an informal job safety assessment (JSA) was conducted to aid in the identification of any risk. Controls where then used to minimise any occurrence of risks with the current task. These controls consisted of wearing appropriate personal protective equipment (PPE); lab coat, glasses and gloves.

## Appendix C: Results of testing

### Test equipment details:

<b>Test machine:</b>	Turbidity meter
<b>Model Number:</b>	SN 10/24315
<b>Calibration date:</b>	08/08/2014

<b>Test machine:</b>	VITLAB Continuous Rs
<b>Model Number:</b>	n/a
<b>Calibration date:</b>	14/09/2014

<b>Test machine:</b>	HANNA Instruments pH & conductivity meter
<b>Model Number:</b>	9017
<b>Calibration date:</b>	26/02/2014

<b>Test machine:</b>	Shimadzu Atomic Absorption Spectrometer
<b>Model Number:</b>	AA-7000
<b>Calibration date:</b>	17/06/2014

<b>Test machine:</b>	Stuart gang stirring apparatus
<b>Model Number:</b>	N678
<b>Calibration date:</b>	n/a

Table C.1 - Alum Initial Test 1

Alum - 10g/L Int NTU 155 Test 1										
Jar	Dose (ml)	pH	Acid Required (ml)	Turbidity (NTU)			AVG (NTU)	pH	Conductivity (mS)	Turbidity Removal %
1	1	7.2	3.25	9.57	9.76	10.1	<b>9.81</b>	7.17	10.82	<b>93.67</b>
2	2.32	5.6	12	3.09	2.75	2.79	<b>2.88</b>	5.4	10.68	<b>98.14</b>
3	2.32	8.7	1.39	15.8	15.9	15.8	<b>15.83</b>	8.58	10.62	<b>89.78</b>
4	5.5	5	13.5	2.44	2.62	2.77	<b>2.61</b>	4.99	10.58	<b>98.32</b>
5	5.5	7.2	3.25	2.11	2.13	2.11	<b>2.12</b>	7.13	10.69	<b>98.63</b>
6	5.5	9.3	0.75	4.36	4.36	4.33	<b>4.35</b>	8.61	10.71	<b>97.19</b>
7	8.68	5.6	12	1.17	1.15	1.11	<b>1.14</b>	5.4	10.49	<b>99.26</b>
8	8.68	8.7	1.39	1.97	1.99	2.02	<b>1.99</b>	8.35	10.59	<b>98.71</b>
9	10	7.2	3.25	1.19	1.25	1.21	<b>1.22</b>	7.14	10.45	<b>99.22</b>
10	5.5	7.2	3.25	1.92	1.98	2.06	<b>1.99</b>	7.04	10.46	<b>98.72</b>
11	5.5	7.2	3.25	2.5	2.7	2.83	<b>2.68</b>	7.21	10.7	<b>98.27</b>
12	5.5	7.2	3.25	3.11	3.07	3.13	<b>3.10</b>	7.07	10.42	<b>98.00</b>

Table C.2 – Alum Initial Test 2

<b>Alum Test - 2</b>											
<b>Jar</b>	<b>Dose (ml)</b>	<b>pH</b>	<b>Acid Required (ml)</b>	<b>Turbidity (NTU)</b>			<b>AVG (NTU)</b>	<b>pH</b>	<b>Conductivity (mS)</b>	<b>Turbidity Removal %</b>	<b>Residual Al ppm</b>
<b>1</b>	1	7.2	3.25	14.4	15.9	15.7	<b>15.33</b>	7.17	10.82	<b>90.11</b>	1.0133
<b>2</b>	2.32	5.6	12	7.17	6.89	6.95	<b>7.00</b>	5.4	10.68	<b>95.48</b>	1.6505
<b>3</b>	2.32	8.7	1.39	16.9	18.1	18.6	<b>17.87</b>	8.58	10.62	<b>88.47</b>	2.7481
<b>4</b>	5.5	5	13.5	2.35	2.34	2.35	<b>2.35</b>	4.99	10.58	<b>98.49</b>	1.5444
<b>5</b>	5.5	7.2	3.25	3.5	3.15	3.13	<b>3.26</b>	7.13	10.69	<b>97.90</b>	0.8363
<b>6</b>	5.5	9.3	0.75	13.2	12.9	13.2	<b>13.10</b>	8.61	10.71	<b>91.55</b>	4.9431
<b>7</b>	8.68	5.6	12	1.49	1.62	1.62	<b>1.58</b>	5.4	10.49	<b>98.98</b>	0.9425
<b>8</b>	8.68	8.7	1.39	5.93	5.53	5.56	<b>5.67</b>	8.35	10.59	<b>96.34</b>	3.4916
<b>9</b>	10	7.2	3.25	1.42	1.44	1.53	<b>1.46</b>	7.14	10.45	<b>99.06</b>	0.7301
<b>10</b>	5.5	7.2	3.25	2.11	2.27	2.39	<b>2.26</b>	7.04	10.46	<b>98.54</b>	1.1196
<b>11</b>	5.5	7.2	3.25	2.3	2.4	2.48	<b>2.39</b>	7.21	10.7	<b>98.46</b>	0.8363
<b>12</b>	5.5	7.2	3.25	2.26	2.39	2.49	<b>2.38</b>	7.07	10.42	<b>98.46</b>	0.8363

**Table C.3 - Ferric Sulphate Initial test 1**

Ferric Sulphate 10g/L int NTU 160										
Jar	Dose (mg/L)	pH	Acid Required (ml)	Turbidity (NTU)			AVG NTU	pH	Conductivity	% turbidity removal
1	10.5	7.2	3.25	4.23	4.2	4.48	4.30	7.1	10.89	97.31
2	10.5	7.2	3.25	3.15	2.86	2.92	2.98	7.11	10.87	98.14
3	13.7	8.7	1.39	3.25	3.6	3.7	3.52	8.17	10.86	97.80
4	7.3	5.6	12	1.48	1.46	1.46	1.47	5.59	10.91	99.08
5	10.5	9.3	0.75	4.86	5	4.92	4.93	8.66	10.91	96.92
6	10.5	7.2	3.25	2.17	2.24	2.16	2.19	7.18	10.94	98.63
7	13.7	5.6	12	1.77	1.79	1.8	1.79	5.44	10.91	98.88
8	7.3	8.7	1.39	4.83	4.99	5.48	5.10	8.32	10.84	96.81
9	10.5	7.2	3.25	3.26	3.46	3.38	3.37	7.05	10.84	97.90
10	6.0	7.2	3.25	3.64	3.63	3.7	3.66	7.09	10.9	97.71
11	10.5	5.0	13.5	1.14	1.16	1.26	1.19	5.07	10.91	99.26
12	15.0	7.2	3.25	2.41	2.25	2.35	2.34	7.23	10.74	98.54

Table C.4 Ferric Sulphate Initial Test 2

Ferric Sulphate 10g/L Test 2											
Jar	Dose (mg/L)	pH	Acid Required (ml)	Turbidity (NTU)			AVG NTU	pH	Conductivity	% turbidity removal	Residual Iron
1	10.5	7.2	3.25	5.1	4.71	4.98	4.93	7.16	10.9	96.92	0.1562
2	10.5	7.2	3.25	3.12	3.25	3.55	3.12	7.11	10.87	98.05	0.2717
3	13.7	8.7	1.39	3.23	3.52	3.62	3.46	8.17	10.86	97.84	0.1531
4	7.3	5.6	12	1.47	1.44	1.46	1.46	5.59	10.91	99.09	0.4433
5	10.5	9.3	0.75	4.88	4.88	4.87	4.88	8.66	10.91	96.95	0.0813
6	10.5	7.2	3.25	2.17	2.24	2.15	2.19	7.18	10.94	98.63	0.3903
7	13.7	5.6	12	1.77	1.79	1.67	1.74	5.44	10.91	98.91	0.512
8	7.3	8.7	1.39	4.88	4.98	5.35	5.07	8.32	10.84	96.83	0.1344
9	10.5	7.2	3.25	3.33	3.44	3.37	3.38	7.05	10.84	97.89	0.0096
10	6.0	7.2	3.25	3.55	3.65	3.66	3.62	7.09	10.9	97.74	0.0345
11	10.5	5.0	13.5	1.17	1.11	1.23	1.17	5.07	10.91	99.27	0.4496
12	15.0	7.2	3.25	2.48	2.22	2.33	2.34	7.23	10.74	98.54	0.228

Table C.5 - Ferric Chloride Initial Test 1

Ferric Chloride 10g/L Int NTU 145										
Jar	Dose (mg/L)	pH	Acid Required (ml)	Turbidity (NTU)			AVG NTU	pH	Conductivity	% turbidity removal
1	10.5	7.2	3.25	1.33	1.33	1.36	1.34	7.13	10.89	99.08
2	10.5	7.2	3.25	1.24	1.18	1.24	1.22	7.09	10.72	99.16
3	13.7	8.7	1.39	1.71	1.58	1.6	1.63	8.13	10.52	98.88
4	7.3	5.6	12	1.16	1.17	1.18	1.17	5.32	10.79	99.19
5	10.5	9.3	0.75	1.92	1.94	1.92	1.93	8.53	10.83	98.67
6	10.5	7.2	3.25	1.28	1.26	1.33	1.29	7.05	10.86	99.11
7	13.7	5.6	12	1.51	1.42	1.41	1.45	5.42	10.67	99.00
8	7.3	8.7	1.39	1.72	1.86	1.93	1.84	8.49	10.8	98.73
9	10.5	7.2	3.25	1.39	1.46	1.46	1.44	7.01	10.84	99.01
10	6.0	7.2	3.25	1.77	1.87	1.75	1.80	7.13	10.84	98.76
11	10.5	5.0	13.5	1.15	1.14	1.15	1.15	4.99	10.83	99.21
12	15.0	7.2	3.25	1.16	1.22	1.2	1.19	7.12	10.8	99.18

Table C.6 - Ferric Chloride Initial Test 2

Ferric Chloride 10g/L Int NTU 145											
Jar	Dose (mg/L)	pH	Acid Required (ml)	Turbidity (NTU)			AVG NTU	pH	Conductivity	% turbidity removal	Residual Iron
1	10.5	7.2	3.25	2.25	2.17	2.16	2.19	7.13	10.89	98.49	0.4277
2	10.5	7.2	3.25	1.94	1.95	1.93	1.94	7.09	10.72	98.66	0.253
3	13.7	8.7	1.39	3.09	3.3	3.21	3.20	8.13	10.52	97.79	0.8022
4	7.3	5.6	12	1.65	1.68	1.64	1.66	5.32	10.79	98.86	0.4901
5	10.5	9.3	0.75	4.81	4.67	4.79	4.76	8.53	10.83	96.72	0.8396
6	10.5	7.2	3.25	1.82	1.82	2.04	1.89	7.05	10.86	98.69	0.203
7	13.7	5.6	12	1.35	1.21	1.23	1.26	5.42	10.67	99.13	0.4308
8	7.3	8.7	1.39	4.72	4.71	4.46	4.63	8.49	10.8	96.81	0.4714
9	10.5	7.2	3.25	2.07	2.27	2.18	2.17	7.01	10.84	98.50	0.2748
10	6.0	7.2	3.25	2.93	2.85	2.9	2.89	7.13	10.84	98.00	0.5213
11	10.5	5.0	13.5	1.45	1.52	1.39	1.45	4.99	10.83	99.00	0.6524
12	15.0	7.2	3.25	1.61	1.72	1.59	1.64	7.12	10.8	98.87	0.1313



Table C.6 - Minitab - Alum

Dose (mg/L)	pH	Residual Turbidity (NTU)	Residual Al mg/L	Predicted Residual Turbidity	Predicted Residual Al (mg/L)	Residuals - Turbidity	Residuals Al	% Predicted Turbidity Removal
55.0	7.2	2.09	1.1196	0.77821	0.89300	-0.43100	0.226600	98.51
55.0	5.0	2.40	1.5444	1.37570	1.55030	1.18225	-0.005904	99.28
55.0	7.2	2.25	0.8363	0.77821	0.89300	-0.27100	-0.056700	98.51
23.2	8.7	16.84	2.7481	1.37570	2.20994	2.30826	0.538163	91.40
55.0	7.2	2.88	0.8363	0.77821	0.89300	0.35900	-0.056700	98.51
86.8	8.7	3.82	3.4916	1.37570	2.84446	2.07088	0.647140	98.97
10.0	7.2	12.45	1.0133	1.37570	1.28585	-0.96077	-0.272555	92.06
86.8	5.6	1.38	0.9425	1.37570	0.78144	-0.72243	0.161062	98.76
55.0	7.2	2.72	0.8363	0.77821	0.89300	0.20400	-0.056700	98.51
55.0	7.2	2.66	0.8365	0.77821	0.89300	0.13900	-0.056500	98.51
23.2	5.6	5.04	1.6506	1.37570	1.59851	-0.48505	0.052085	96.73
100.0	7.2	1.33	0.7301	1.37570	1.15677	-0.62506	-0.426670	98.85
55.0	9.3	4.56	2.7481	1.37570	3.44142	-2.76808	-0.693321	95.66

Table C.7 - Minitab Ferric Chloride

Dose (mg/L)	pH	Residual Turbidity (NTU)	Residual Iron mg/L	Predicted Residual Turbidity	Predicted Residual Al (mg/L)	Residuals - Turbidity	Residuals Iron	% Predicted Turbidity Removal
105.0	7.2	1.77	0.4277	1.67	0.2825	0.09300	0.145240	98.76
105.0	7.2	1.58	0.2530	1.67	0.2825	-0.09367	-0.029460	98.58
136.8	8.7	2.42	0.8022	2.36	0.6821	0.05527	0.120113	98.67
73.2	5.6	1.41	0.4901	1.47	0.5977	-0.05194	-0.107638	90.04
105.0	9.3	3.34	0.8396	3.34	0.8614	-0.00037	-0.021787	98.30
105.0	7.2	1.59	0.2030	1.67	0.2825	-0.08200	-0.079460	97.74
136.8	5.6	1.36	0.4308	1.30	0.3327	0.05711	0.098123	92.63
73.2	8.7	3.23	0.4714	3.29	0.5570	-0.05378	-0.085648	99.19
105.0	7.2	1.80	0.2748	1.67	0.2825	0.13133	-0.007660	98.39
105.0	7.2	1.63	0.2538	1.67	0.2825	-0.04867	-0.028660	98.43
105.0	5.0	1.30	0.6524	1.30	0.6431	-0.00297	0.009312	97.01
150.0	7.2	1.42	0.1313	1.50	0.2830	-0.07878	-0.151732	99.22
60.0	7.2	2.35	0.5213	2.27	0.3820	0.07544	0.139257	97.30

Table C.8 - Minitab Ferric Sulphate

Dose (mg/L)	pH	Residual Turbidity (NTU)	Residual Iron mg/L	Predicted Residual Turbidity	Predicted Residual Al (mg/L)	Residuals - Turbidity	Residuals Iron	% Predicted Turbidity Removal
105.0	7.2	4.62	0.1562	3.32	0.2069	1.29233	-0.050750	97.11
105.0	7.2	3.05	0.2717	3.32	0.2069	-0.27600	0.064750	98.09
136.8	8.7	3.49	0.1531	3.44	0.1386	0.04515	0.014526	97.82
73.2	5.6	1.46	0.4433	1.57	0.3455	-0.11057	0.097824	99.09
105.0	9.3	4.90	0.0813	4.88	0.1115	0.01867	-0.030199	96.94
105.0	7.2	2.19	0.3903	3.32	0.2069	-1.13600	0.183350	98.63
136.8	5.6	1.77	0.5120	1.74	0.4607	0.02530	0.051262	98.90
73.2	8.7	5.09	0.1344	5.18	0.0733	-0.09072	0.061088	96.82
105.0	7.2	3.37	0.0096	3.32	0.2069	0.04900	-0.197350	97.89
105.0	7.2	3.40	0.2070	3.32	0.2069	0.07067	0.000000	97.88
105.0	5.0	1.18	0.4496	1.13	0.5318	0.04675	-0.082151	99.26
150.0	7.2	2.34	0.2280	2.40	0.2513	-0.06337	-0.023250	98.54
60.0	7.2	3.64	0.0345	3.51	0.1236	0.12878	-0.089100	97.72

## Appendix D: Example Matlab Code

```
% Byron Manthey
% Ferric Chloride
% Turbidity (NTU)=
%(4.55-0.0022*Dose-1.121*pH+0.000103*Dose^2+0.1404*pH^2-0.00393*Dose*pH)
clc
clear
% optimum dose and pH
%
B= [0.000103,-0.00393/2;-0.00393/2,0.1404];
%
b= [-0.0022;-1.121];
%
y =-0.5*inv(B)*b

%%
% eigenvalues for above equations
A = [0.000103,-0.00393;-0.00393,0.1404];
eig = eig(A)

% Byron Manthey
% Ferric Chloride
% Residual Iron=
%(7.02-0.0207*Dose-1.614*pH+0.000025*Dose^2+0.1016*pH^2+0.00202*Dose*pH)
clc
clear
% optimum dose and pH
%
B= [0.000025,0.00202/2;0.00202/2,0.1016];
%
b= [-0.0207;-1.614];
%
y =-0.5*inv(B)*b

%%
%eigenvalues for above equations
A = [0.000103,-0.00393;-0.00393,0.1404];
eig = eig(A)
```