Neutralization of Spent Caustic from LPG Plant at Preem AB Göteborg

Master of Science Thesis in Chemical and Biological Engineering

WAQAR AHMAD

DEPARTMENT OF CHEMICAL AND BIOLOGICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, November 2010

Neutralization of Spent caustic from LPG Plant at Preem AB Göteborg
Waqar Ahmad

Examiner: Börje Gevert
Supervisor: Carina Åman (Process Engineer Preem AB Göteborg)

Chalmers University of Technology
Department of Chemical and Biological Engineering
Göteborg
Sweden

Abstract

Handling of spent caustic at refinery sites mostly creates problems during the treatment in biological water treatment plants due to higher chemical oxygen demand (COD) and pH. Different methods are available for neutralization of this spent caustic after which this effluent can be released to biological water purification plants. The main objective of this research is to find a suitable method to get rid of spent caustic (NaOH solution) that is produced in the LPG plant at Preem AB Göteborg. The company is using 10% caustic soda to wash hydrogen sulphide from propane and butane product streams. Currently, the spent caustic is used for crude overhead corrosion control after propane and butane washing. The injection of spent caustic is causing problems of improper corrosion control in the crude overhead system and higher amount of sodium in the residue. These problems need to be avoided by selecting a new method for treatment of spent caustic or by improvements in the process. Results from this work shows that use of spent caustic for corrosion control is not the problem (i.e. incidents of off specs sodium and chlorides in residue and crude overhead respectively). The problems of higher sodium in the residue and higher chloride in overhead can be avoided by improving the caustic dilution and injection system and procedure used at plant. Although different methods for neutralization are discussed briefly but it is considered better to improve the existing system, without installing a new neutralization system for treatment of spent caustic.

Acknowledgements

My sincere thanks to my university supervisor and examiner, Börje Gevert, who has supported me throughout my thesis work and provided me the opportunity to work independently in my own way.

Special thanks to my industrial supervisor, Carina Åman, who helped me throughout the period of this research. Without her help and encouragement this work seems to be impossible. I could not desire more helpful and friendlier supervisor.

My heartiest thanks to Preem AB Göteborg for providing resources, facilities and financial means.

My gratitude is for my loving parents and my siblings for keeping me motivated during this period of research work. It is all due to prayers of my family, friends and relatives.

At the end, my regards to all the people that are connected to me and supported me directly or indirectly during the course of this thesis project.

Waqar Ahmad

Table of Contents

Chapter: 1 Introduction

A petroleum refinery is an industrial process plant that refines crude oil to different useful petroleum products. It is basically a series of different physical and chemical processes that aim to change the physical and chemical properties of crude oil to make useful products like petrol, diesel, liquefied petroleum gas (LPG) fuel oil and lubricating oil etc. Due to desired quality of products and environmental regulations different treatment methods are used to get the required specifications. Hydrogen sulphide (H_2S) is removed from the products as it is a very poisonous and toxic gas with rotten egg smell and cannot be left to the environment. In the petroleum industry it is common practice to use caustic solution for treatment of lighter hydrocarbons to remove H_2S [1]. Similarly the LPG stream is treated with caustic solution to remove mercaptans and traces of H_2S but before that amine scrubbing of this stream is done to remove mercaptans (the sulphur containing organic compounds) and H_2S. The strength of the caustic solution decreases with the passage of time and before a certain limit of concentration the solution is replaced with a fresh solution with higher concentration. Spent caustic solution cannot be easily neutralized in most of biological waste water treatment plants due to very high chemical oxygen demand (COD). Different other solutions and treatment methods are used and suggested for the neutralization of this spent caustic.

1.1 Background

This thesis opportunity was basically published by the Swedish oil refinery named Preem AB Göteborg. Preem AB is the biggest oil refining company within Sweden with refining capacity of totally 18 million tons of crude oil per year. [2] It has two refining sites, one in Göteborg with capacity of 6 million tons per year and the other in Lysekil with 12 million tons per year. The purpose of this research was to find a better solution for neutralization of the spent caustic produced after the treatment of propane and butane in the LPG plant at Göteborg.

The crude oil feed contains inorganic salts. The major contents of these salts are sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). When the crude oil is preheated up to 120°C about 20-50% of $MgCl_2$ and 10-20% of $CaCl_2$ start to hydrolyze to hydrochloric acid (HCl).[3]

$$MgCl_2 + 2H_2O \xleftrightarrow{heat} 2HCl + Mg(OH)_2$$

$$CaCl_2 + 2H_2O \xleftrightarrow{heat} 2HCl + Ca(OH)_2$$

NaCl does not hydrolyze as it is more temperature stable compared to $MgCl_2$ and $CaCl_2$. The formation of the HCl causes corrosion in the overhead system of the crude distillation tower and caustic solution is injected to neutralize the HCl formed.

At Preem AB Göteborg, 10% caustic solution is used for propane and butane washing. Later the spent caustic solution is injected to the crude feed for the corrosion control in the overhead system. Experts from refinery think that injection of the spent caustic solution creates problems in controlling the sodium content in one of the products. Another cost effective solution of treating the spent caustic should be suggested. The objective was to find a suitable processing technique for neutralization of the spent caustic so that it could be released to the biological water treatment plant without adverse consequences.

Nowadays most of the refineries in the world neutralize spent caustic solution separately in a special manner instead of injecting it into the crude oil. It is also recommended in manuals from UOP [19] and other literature to not use the spent caustic for corrosion control in the overhead product as it may possibly cause different problems.

1.2 Challenges

Due to higher content of sodium in the spent caustic it is difficult to optimize the injection rate to the crude feed. Increasing the injection rate may give lower chloride content in the overhead system but with trade-off of higher sodium content in the residue. Residue is used as feed material to Crackers and Cokers in other refineries. The catalyst in these crackers is sensitive to sodium or metals in general. This is why we like to keep the sodium content in the residue low, max 8 ppm. Similarly lowering injection rate will give lower residue sodium but will result in higher chloride content in the overhead system (poor corrosion control downstream).

If the residue goes off-spec in terms of sodium then the customer will not accept this shipment as Preem AB does not process residue within the refinery in Göteborg. So the off-spec residue is diluted with heavy gas oil to achieve the lower concentration of sodium which cost too much to the company. The company has faced number of similar accidents in the recent years. That is why the company wants to solve this problem to avoid more loss of money. When the sodium concentration increases in the residue, the caustic injection rate is lowered to avoid off-spec problem but this result in poor corrosion control. Due to poor corrosion control in downstream equipment, it needs to be changed out after every four or eight years at the time of shutdown because of corrosion.

1.3 Aims and Objectives

The aim of this thesis is to get the knowledge about processes of the refinery related to caustic injection and utilization of fresh and spent caustic and to understand the cause of higher sodium and chloride content in the residue and overhead product respectively. After getting better understanding of process and problem, possibility of optimising the existing plant by only operational changes needs to be investigated. If optimisation is not possible then a suitable solution for neutralization of spent caustic by surveying the available equipments in the market was to be found so that spent caustic could be released to biological water treatment plant without any adverse consequences. The technique is to be developed by laboratory testing so that performance of various technologies can be evaluated. After selecting the technology a cost estimation and suggestion for the placing of the new equipment was to be done. Optimisation of the existing plant would be the most cost effective solution to the problem.

1.4 Research Methodology

This section will explain the methodology that has been used for this Master thesis study and also the changes in the planning to achieve the desired results.

At the start of this thesis the main emphasis was to develop a new process and its cost estimation. Later it was seen that the problem cause was not due to spent caustic but lot of other operational activities. A better solution was achievable by some changes and optimisation in the caustic injection system. Sometimes there were different upsets kept on happening in the operation and it was not easy to conclude a specific result with surety but suitable assumptions were taken to get the results. After the conclusion that spent caustic is not the problem the emphasis was changed to investigate the other problems which resulted in upsets. Research methodology used for this study can be explained in the following steps,

- Get the understanding of the whole system
- Data collection from process for consultant from Shell Global Solutions
- Meeting with Consultant
- Literature research for suggestions from consultant

- Analysis of previous plant results available
- Follow ups on different parameters
- Finding possible solution for optimisation
- Review of possible treatment methods for spent caustic

Before meeting with the consultant spent caustic was considered as a major cause of upsets but according to him it was not. So, other possibilities were considered and follow ups were done on the plant which showed that spent caustic was not the problem. Due to this confirmation emphasis was diverted to optimise the plant instead of finding a method to neutralize the spent caustic.

1.5 Introduction to Concerned Process Plants

There are three process plants related to the problem with spent caustic. The brief introduction about description of flow and operations is given in this section.

1.5.1 LPG Plant

The LPG plant is designed on the basis of feed processed in CDU plants described in 1.5.2 CDU Plant. The LPG plant takes its feed from the DHT hydrotreaters and from the former stabiliser overhead which combines in the feed surge drum 6C-15. The feed surge drum provides feed stock to the Deethaniser 6C-1. The Deethaniser is a fractionating column that separates feed to ethane with lighter hydrocarbons in the overhead and the bottom product containing propane and butane. It is provided with a thermosyphon reboiler 6E-3 to provide the desired temperature for continuous process. The overhead product from the deethaniser is condensed in the overhead condenser 6E-2, and collected in the overhead accumulator 6C-2. Glycol is injected to the overhead stream in 6E-2 to avoid water entrainment. Ethane gas leaves at the top, settled glycol with water leaves from the bottom of 6C-2 and condensed overhead liquid is returned to the deethaniser. The glycol stream, containing water is sent for recovery, recirculation and reinjection. Ethane gas is released to the refinery gas header and also used to control the pressure in 6C-2 vessel. The bottom product from the deethaniser provides feed to the propane-butane splitter 6C-3 which is designed to split feed into two fractions of propane overhead and butane bottoms.

The propane butane splitter is provided with a thermosyphon reboiler 6E-4 to maintain the desired temperature for distillation. The overhead product passes through a fan condenser and is collected in the overhead accumulator 6C-4. Part of the overhead is sent back to the top of 6C-3 splitter and remaining is sent for further treatment. This stream is cooled in the cooler 6E-9, before treatment with MDEA (Methyl di-ethanol amine) to remove H_2S gas. Treatment with MDEA is done in the propane extractor 7C-1 where the feed enters from the bottom and leaves from the top. From the top of 7C-1 the propane is fed further to 7C-2 (propane/MDEA separator) where traces of amines are separated from the propane. Caustic washing of the propane stream is done in the propane washing 6C-5 vessel to remove the remaining traces of H_2S gas which will be described in detail further in this chapter. After caustic washing the propane stream is passed through a salt filter 6C-6 to remove the moisture content and further enters a drier section. The drier section contains two vessels 6C-7A and 6C-7B with desiccant, one functioning at a time. The propane stream enters to the top of one of these driers and passes through an alumina desiccant and leaves the bottom as a dry product which is further directed to storage. The bottom product from the propane butane splitter is sent to the butane washing vessel 6C-8 similar to the propane washing but before that it is cooled down in the heat exchanger 6E-1 and air cooler 6E-6. The aim of the butane wash is to remove traces of H_2S and odour from butane. After the butane wash this butane stream is sent to storage tanks.

Table 1.1 Equipment Functions w.r.t. Tag Names for LPG 6

Equipment tag name	Function
C-1	Deethanizer column
C-3	Propane/Butane splitter
C-37	Chloride trap
C-15	Feed surge drum
C-2	Deethanizer overhead accumulator
C-9	Compressor knock out pot
C-13	Refrigeration Drum
C-26	Vent gas vessel
C-4	Splitter overhead accumulator
C-8	Butane caustic wash tank
C-5	Propane caustic wash tank
C-6	Propane salt filter
C-20	Glycol regenerator
C-7A, C-7B	Propane driers
C-38,39	Butane driers
7C-1	Propane extractor
7C-2	MDEA separator
C-22,C-23	Condensate surge pots
G-5	Deeth feed booster pump
G-1	Reflux pump
G-8	Glycol injection pump
G-2	Splitter reflux pump
G-9	Splitter overhead product pump
G-3,G-4	Caustic pumps
7G-4	Amine sump pump
E-19	Feed cooler
E-2	Deethanizer overhead condenser
E-8A,B	Refrigeration condenser
E-14	Glycol condenser coil
E-15	Glycol surge tank cooling coil
E-13	Glycol reboiler coil
E-4	Splitter reboiler
E-5A,B,C,D	Overhead condenser
E-6	Butane cooler
E-9	Propane cooler
E-10	Regasser heater
E-7	Re-activation heater
K-1	Propane compressor
T-1	Coalescer Filter

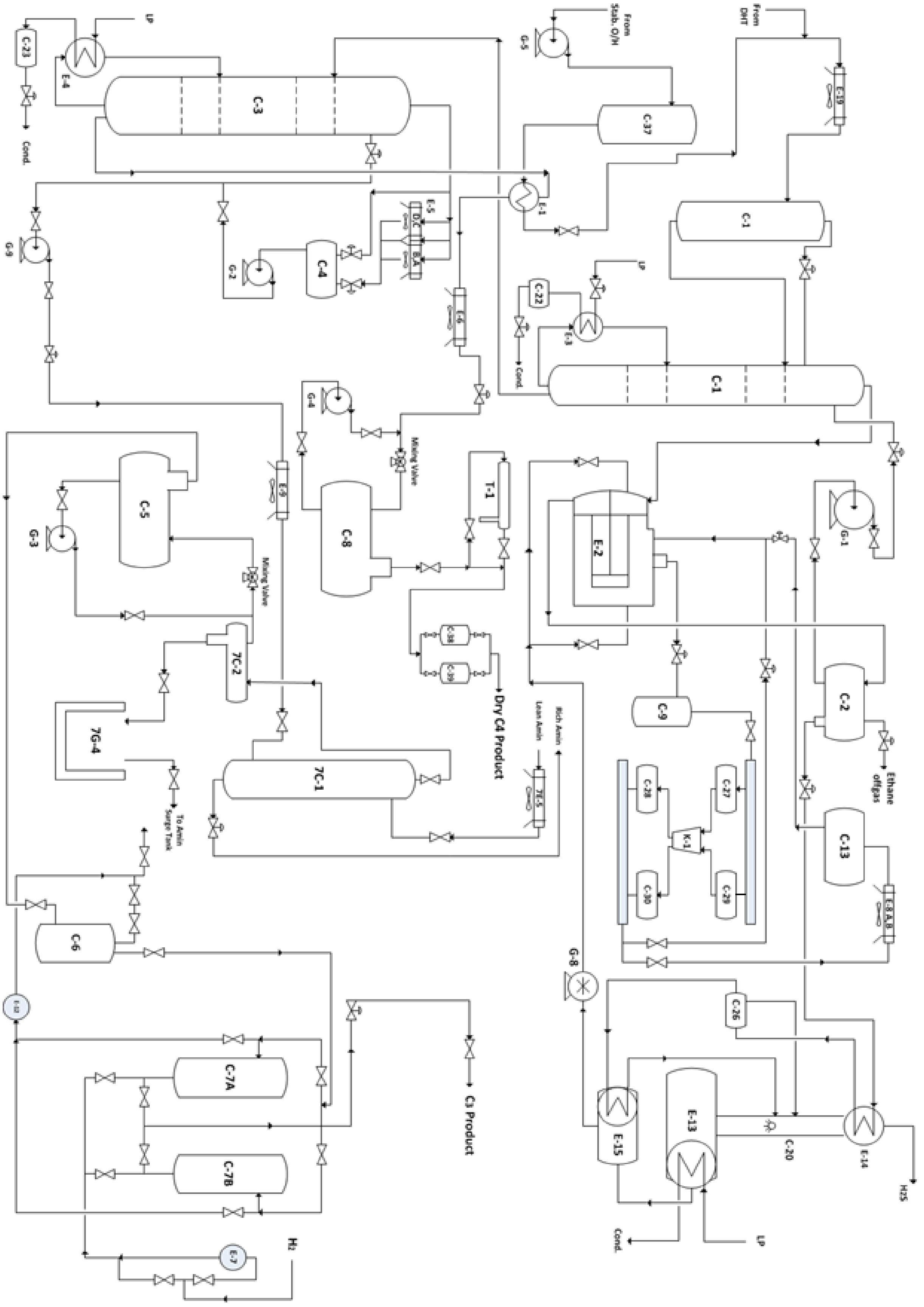

Figure 1.1 Flow Diagram for LPG 6 plant

1.5.2 CDU Plant

There are two identical crude distillation units (CDU) at the refinery each with 65,000 barrels per day of design feed capacity. In this section, only one of the units will be described. Each crude distillation unit includes one crude distillation column, one desalter, one feed heater, light and heavy gas oil strippers, and light and heavy gas oil vacuum driers. Necessary piping, exchangers, and coolers join above main process equipments. Each crude unit is designed to separate the crude oil in the overhead product, light gas oil (LLGO and HLGO), and heavy gas oil (HGO) and bottom residue.

The crude oil is pumped to the crude distillation units from storage tanks and passes through heat exchangers with a purpose of preheating before entering the desalter. There are three injection connections on the crude oil feed line upstream the preheaters, one is for the demulsifying chemical from pumps 22G-8,9,10, second is the desalter water injection line coming from the overhead water accumulator and the third is for 10% fresh caustic injection from caustic solution storage vessel C-12 that is never used. Demulsifying chemical is provided by a vendor company and is used for separation of water from oil emulsion in the desalter. Water addition is for desalting purpose while 10% caustic solution is not used these days. 10% caustic solution is used when the chloride content of the overhead water becomes greater than 80 ppm.

Water from light gas oil (LGO) and heavy gas oil (HGO) strippers are injected upstream the desalter before the mixing valve to facilitate the desalting operation. A large amount of the water comes from C-6 (CDU O/H vessel) which in turn comes from condensed stripping steam. The desalter function is to reduce the salt content and other impurities (BS&W, Basic sediment and water) from the crude feed and is discussed in details in section 1.6.3 in this chapter. The brine solution is separated in the desalter and is used for preheating of the wash water for desalting. 3% caustic solution is injected to the crude feed downstream to the desalter from the caustic solution vessel C-22 to control the chloride content of the overhead product. The spent caustic from LPG unit comes to C-22 for dilution and is then injected to the crude feed. Chloride contents in the product cause corrosion in downstream equipments. The caustic injection system is explained in detail in this chapter (section 1.6.4).

Most preheating of the crude is done in the preheat exchanger train downstream to the desalter. The incoming crude is heated up with different effluent products before it arrive to the fired heater. In the fired heater fuel oil or fuel gas is combusted to provide convective and radiant heat to the crude to make it partially vaporized. This partially vaporized feed is fed to the crude distillation column C-1, to separate it into different fractions. The residue is removed from the bottom and excess heat is recovered from it. The residue is not processed further in Preem AB and is sold to other customers. The intermediate products from the crude column C-1 are sent to light and heavy gas oil strippers for further purification of the products. The overhead product from the column passes through the heat exchanger train to cool down. Water is separated from the overhead product in the overhead accumulator as a result of phase separation. This water is used as desalting water and the overhead product is sent to the DHT plant for further processing.

Table1.2 Equipment Functions w.r.t Tag Names for CDU 1, 2

Equipment tags	Function
C-5	Crude desalter
C-6	Atmospheric tower overhead accumulator
C-22	3% caustic vessel
C-12	10% caustic vessel (not working)
C-1	Crude atmospheric tower
C-15	HGO stripper
C-17	LGO stripper
C-37	LLGO stripper
C-16	HGO drying drum
C-18	LGO drying drum

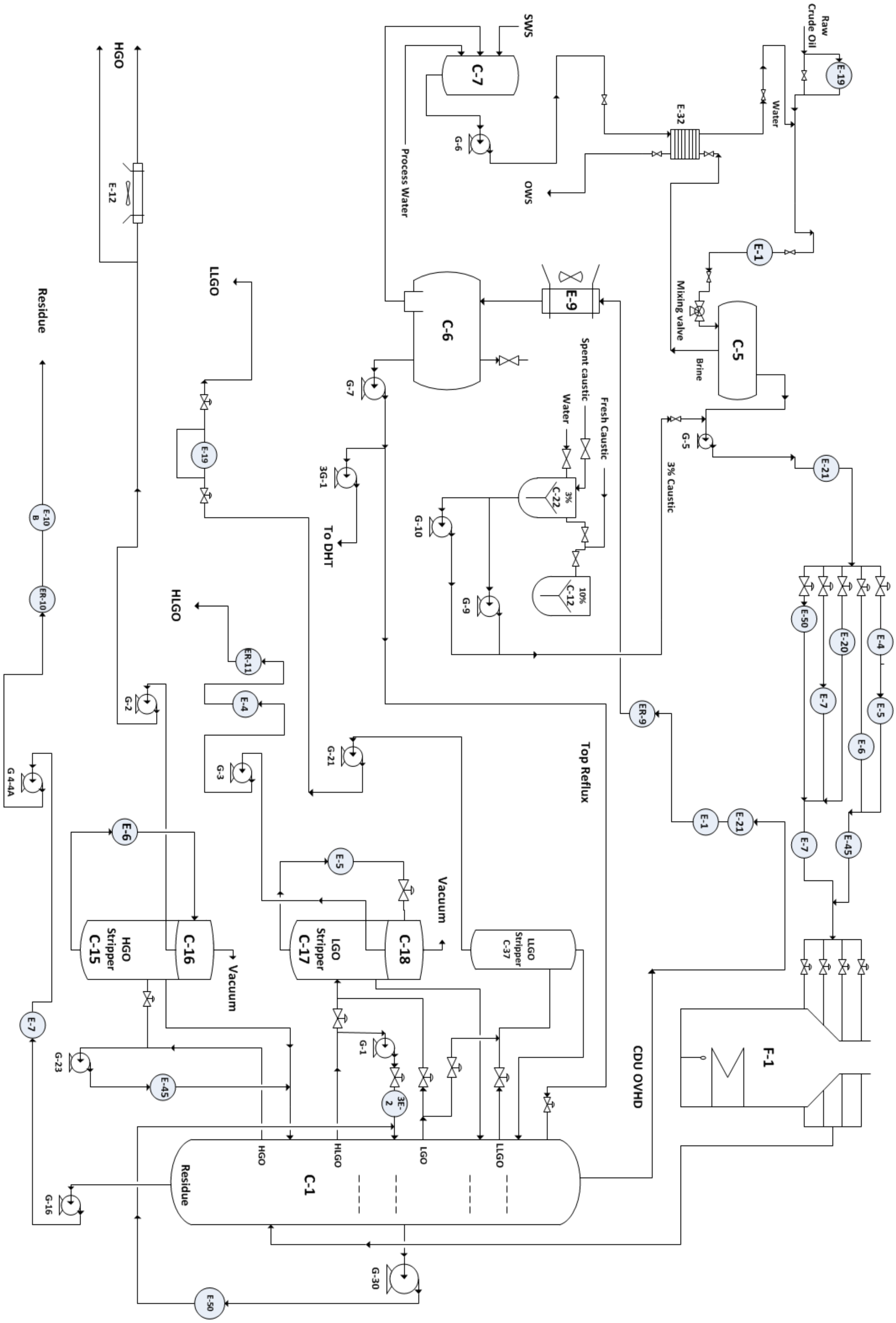

Figure 1.2 Flow Diagram for CDU 1, 2

1.5.3 DHT Plant

The DHT plant is fed with the CDU overhead product. There are two identical DHT plants. The process taking place in this plant is not much related to research and is not described in detail. The feed stream is preheated in a series of heat exchangers and corrosion is recorded on the shell side of exchanger 3/4E-1F and 3/4E-1A that can be seen in the flow diagram. The shell sides of these exchangers are changed after every four years and the tubes sides are changed after every eight years at time of shut down due to corrosion. The corrosion is due to ammonia and chloride content in the water entrained from the overhead vessel 1/2 C-6 at the CDUs. These specified exchangers and cooler can be seen in the flow diagram of this DHT plant.

Table 1.3 Equipment Functions w.r.t Tag Name for DHT 3

Equipment tag	Function
C-13	Recycle compressor knock out drum
C-2	High pressure separator
C-1	Reactor
C-12	Disgaging drum
C-14	Debutanizer overhead accumulator
C-4	Debutanizer column
C-3	Low pressure separator
C-14	Debutanizer overhead knock out drum
G-1	Hydrotreater feed pump
G-4	Debutanizer overhead product pump
G-3	Reflux pump
K-1	Recycle gas compressor
K-2	Debutanizer overhead gas compressor
E-1A-K	Feed/effluent exchanger
E-4	Reactor effluent air cooler
E-13	Overhead condenser
E-2	Reboiler of debutanizer
E-5	Debutanizer feed/bottoms exchanger
F-1	Feed heater

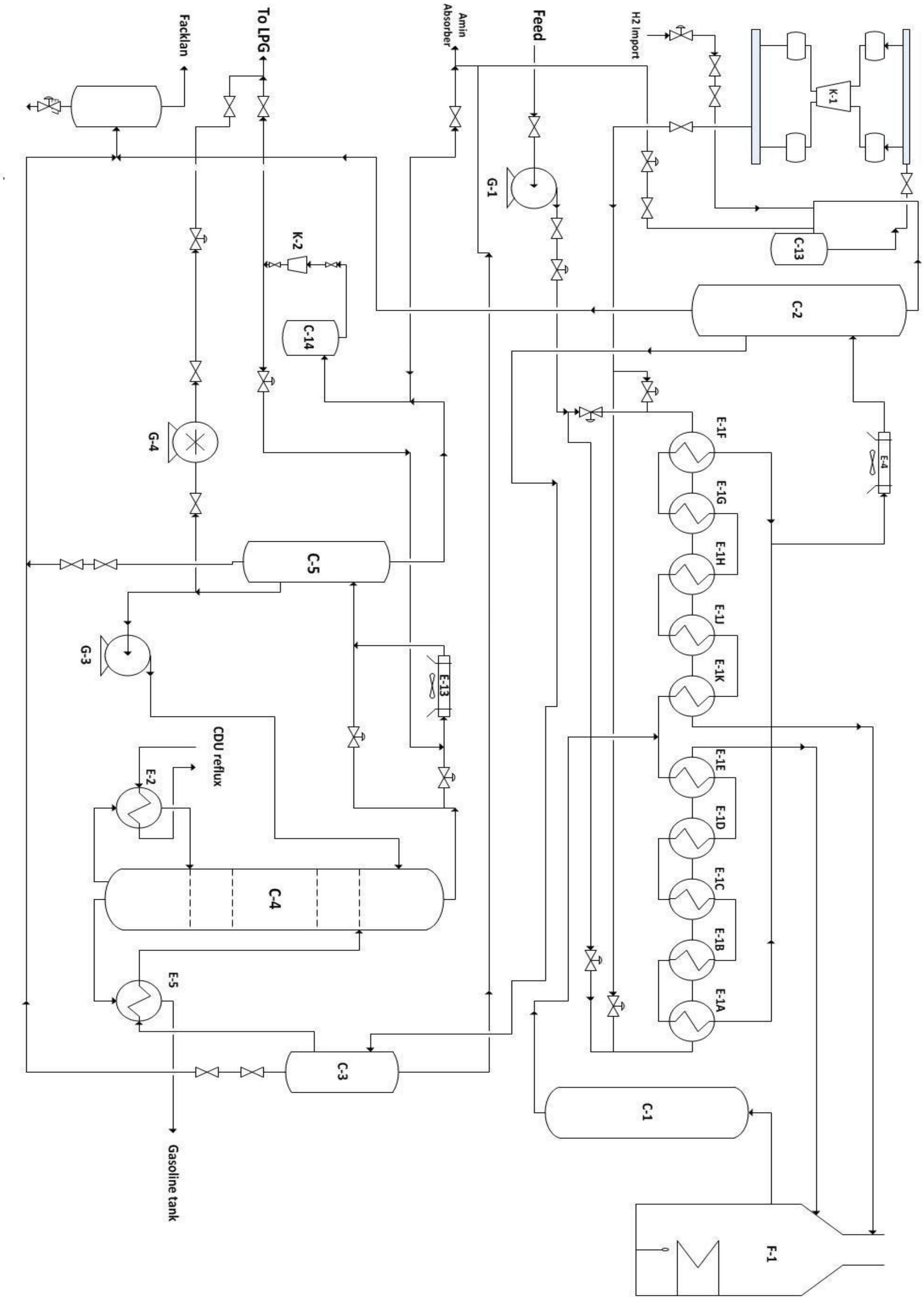

Figure 1.3 Flow Diagram for DHT 3

1.6 Details of Important Processes

This section will cover the detailed description of important processes that are directly related to this research.

1.6.1 Propane Treatment

Propane treatment is a part of the LPG plant described before in the section 1.5.1. The propane stream from the propane-butane splitter is firstly treated with MDEA (methyl di-ethanol amine) to remove major amount of H_2S in the propane extractor 7C-1. Lean 37-45% amine which is a solution of MDEA enters from the top of the vessel while the propane stream is introduced from the bottom. H_2S in the propane stream is absorbed by the lean amine forming a solution removed from the bottom. The purified propane stream with small entrained droplets of amine solution leaves the top of 7C-1 and goes to the MDEA separator 7C-2 where traces of MDEA left in the propane separates out from the propane stream due to action of gravity and leaves from the bottom.

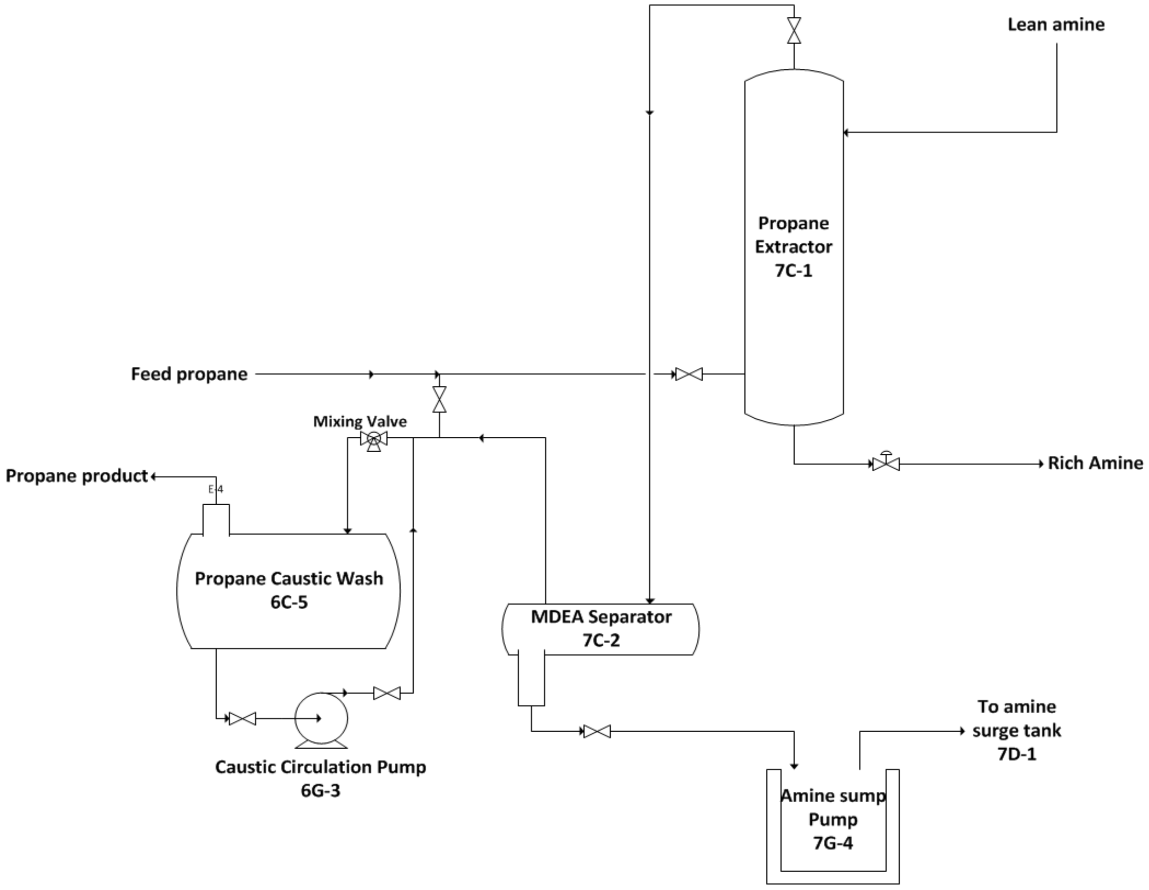

Figure 1.4 Propane Treatment at LPG 6

After the amine treatment the propane is washed with 10% caustic in the caustic washing drum 6C-5 which is a horizontal cylindrical pressure vessel with 1.25 meter in diameter and 5.5 meter long between the tangents of dished heads. This vessel is provided with flanged nozzle connections for inlet, vent, drain and safety relief valves, propane liquid top outlet, caustic bottom outlet and level gauge. The caustic leaving the bottom is circulated by a motor driven centrifugal pump 6G-3 to the inlet of the caustic wash drum 6C-5 where a mixing valve is installed for good mixing of caustic solution and propane. The propane product, free from H_2S, leaves from the top of vessel 6C-5.

1.6.2 Butane Treatment

The butane washing is done in a similar vessel as the propane caustic wash drum 6C-5. Amine treatment of the butane stream is not required so only caustic wash of the butane stream is done in the caustic wash tank 6C-8 to remove typical smell. It is a horizontal pressure vessel with diameter of 1.85 meter and length of 6.1 meter between the tangents of dished heads. The caustic wash drum 6C-8 is provided with flanged nozzle connections for inlet, drain, vent and safety valves, butane top outlet, caustic bottom outlet, and level gauge.

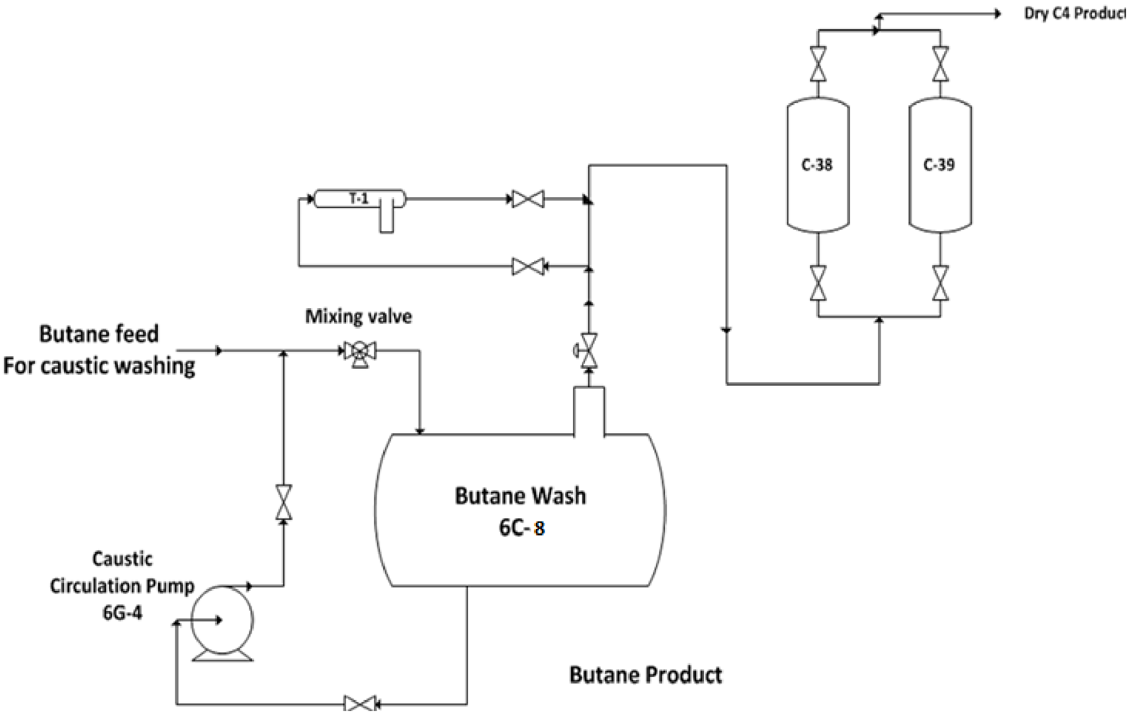

Figure 1.5 Butane Treatment at LPG 6

A coalescer 6T-1 is installed after the 6C-8 vessel to prevent the caustic/water entrainment with the product butane. A centrifugal motor driven pump 6G-4 is provided for the circulation of caustic to the inlet of 6C-8 from the bottom. At the inlet of the washing tank a mixing valve is installed for good mixing of 6C-8 butane and caustic solution. The butane free from the odour leaves from the top of vessel 6C-8.

1.6.3 Desalter Operation

Crude desalting is a very important process in the refining plant for corrosion control. It removes inorganic salts from the crude. These inorganic salts undergoes hydrolysis at higher temperature $\geq 120^{o}$C to form HCl which causes corrosion in the downstream process equipment. The desalting process is part of the crude distillation unit (CDU) plant described earlier in this chapter.

Each desalter is designed to provide a residence time of 20 minutes in normal operation for design feed capacity of crude oil feed to CDU. The design temperature for the desalter is in the range of 116-138^{o}C. The design pressure for the desalter is 10.68 barg and the operating pressure is 9 barg which is maintained by the upstream pressure control valve. The desalter inside diameter is 4.26 meter with 10.2 meters length between the tangent lines of dished heads. The desalter is provided with two electrical grids to create a potential difference that increases the coalescence of water. There are also two Agar probes present to monitor the oil water interface. Water addition to crude oil is considered as 5% of crude oil feed.

The feed (crude oil and water) to the desalter first passes through a mixing valve installed at the inlet before the desalter to be thoroughly mixed. Demulsifying chemicals and water for desalting are already being added to the crude feed. The Desalting water consists of recovered water from the crude overhead accumulator1C-6, the vacuum drier condensate drum 1C-19 and make up water from the utility section. The desalter water and crude oil feed passes through a mixing valve and a well-mixed stream enters the desalter. During the residence time smaller droplets of water present in the oil containing salt, combines under the action of the electric field and an emulsion layer is formed. The brine is collected at the bottom of the desalter. The brine leaves from the desalter effluent level control valve while the crude with lesser salt content and water leaves from the top.

1.6.4 Caustic Dilution and Injection System

Caustic dilution and injection to the crude feed is done at the CDU plants described earlier in this chapter. There are two caustic storage tanks C-22 and C-12 installed but only one (C-22) is used. There is a C-22 vessel on each CDU plant. There is a level indicator on the side of the vessel. Both fresh and spent caustic solution is diluted in this vessel.

In case of fresh caustic solution about 12.5% caustic solution is injected from the main storage to C-22 and the increase in level is noted. Water is injected from the top to dilute the caustic to 3%. After the addition of water, the mixer in the vessel is started to make the solution homogeneous. Similar is the case when diluting with spent caustic. Spent caustic solution is lined from the propane or the butane wash systems at the LPG plant when the caustic needs to be replaced with fresh caustic in washing vessels of propane and butane.

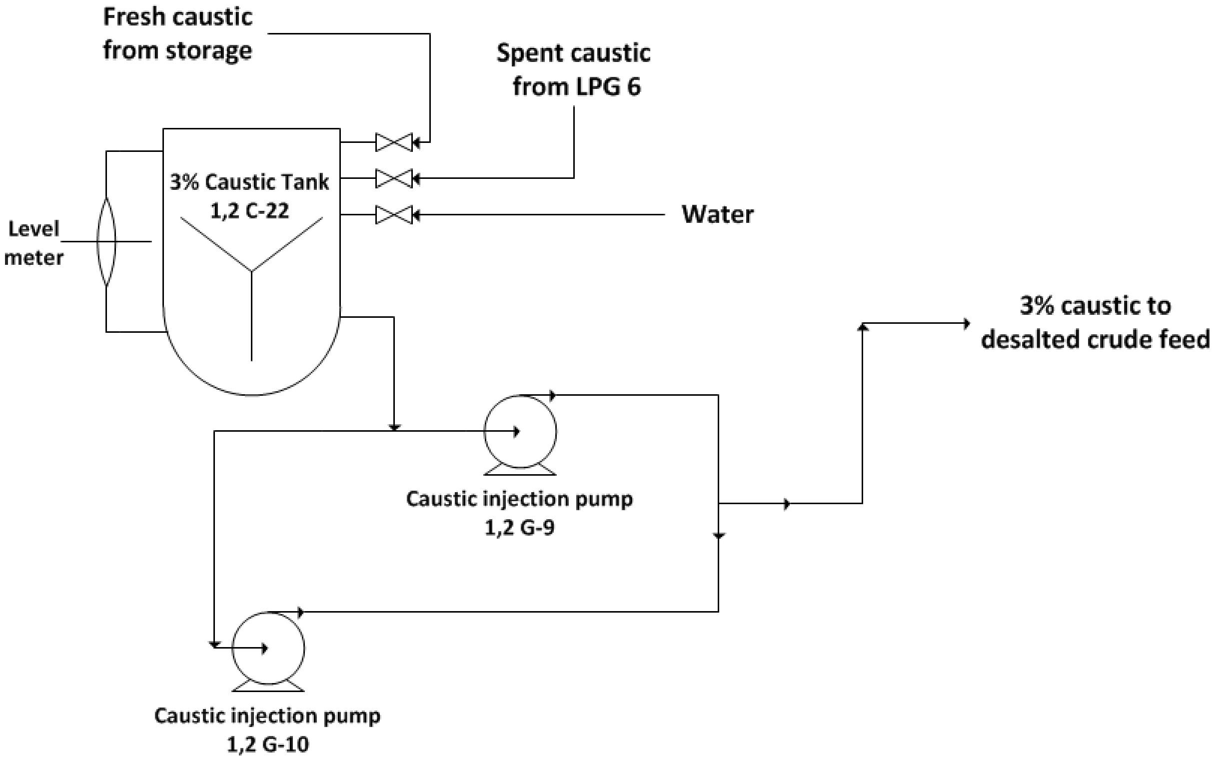

Figure 1.6 Caustic Injection System at CDU 1, 2

Spent caustic from either propane or butane washing is lined to one or both 1/2 C-22 vessels on both CDUs up to certain levels. After addition of spent caustic the same procedure is repeated for dilution as in the case of fresh caustic solution. During all the addition and dilution procedures there is continuous removal of caustic solution from the bottom of C-22. After C-22 fill up, level keeps on decreasing day by day due to continuous injection of caustic solution into crude feed for corrosion control. When the level in C-22 reaches a certain lower level, the vessel is filled up again with either fresh or spent caustic.

1.7 Structure of Report

This thesis report is structured to give a complete understanding of the whole related refining plant and problems of the spent caustic injection system. Later in the report investigation of the problem along with possible solutions for better handling of the spent caustic are described. Results from research, conclusions and possible recommendations for the improvement in the system are described at the end part.

Report comprises of seven chapters which are,

1. **Introduction.** Brief background, objective of this thesis, research methodology used, process plant description and structure of the report are given in this chapter.
2. **Literature Review.** Desalting operation, caustic injection systems, and handling of spent caustic is described in terms of literature perspective.
3. **Investigation of Problem Cause.** How different follow ups, data collection, recent accidents investigations, and sample tests were done is described in this part.
4. **Neutralizing of Spent Caustic.** Best recommended practices from other companies and neutralization methods for spent caustic described in literature are given in this chapter.
5. **Results and Discussions.** Results obtained from this thesis work are reported along with explanation of results and obtained conclusions from discussion are described.
6. **Recommendations.** Different new actions (installations and practices) to improve the system that are recommended to avoid problems that are described.

Chapter: 2 Literature Review

This thesis project was initiated with plant manuals reading and literature research of important operations to get the complete understanding of the process and process units. The main purpose was to get the knowledge about the remote parameters, their effects on the process and limitations.

2.1 Desalting Operation

Crude oil feed to refineries contains water soluble salts such as sodium chloride, calcium chloride, magnesium chloride, sulphates etc along with insoluble salts, solids and water. There may be up to 5 % of water present in the crude oil feed having soluble salts dissolved in it. Water present in feed is in the form of emulsions and this emulsified crude oil is treated in a special kind of operation to remove the water, salts and suspended solids before further processing.[4] This kind of operation is known as desalting. Desalting of crude oil is done in several steps in series depending on the crude oil feed quality requirement for further processing. Removal of salts from the crude is important as the salts at higher temperature cause hydrolysis and form HCl that causes corrosion in the downstream equipment and at lower level of pH chlorides results in more rapid corrosion.

Demulsifying chemicals are added to emulsify the crude oil in the desalting process. The feed stream is well mixed and some residence time is given in a vessel called the desalter. A high voltage electric field is applied to the crude/water emulsion between two plates using alternating current in the desalter. The voltage may range from 300 to 30,000 volts. The high voltage affects the interface of emulsion droplets of water present in the crude and causes them to coalesce. This coalescence of water droplets further helps in phase separation of the water and salts from the crude oil hydrocarbons. [5] Water due to higher value of density is collected at the bottom of the desalter leaving crude oil, with smaller amount of water and salts, at the top. The temperature normally used in desalters range from 95 to 150^{o}C. There are lots of parameters that are considered important for kinetics of demulsification which favours desalting operation. Demulsification depends upon operating condition (voltage, temperature, degree of mixing, distance between two plates etc.) and emulsion properties (density, viscosity, water drop size etc.). [6]

2.2 Caustic Injection Systems

Injection of either spent or fresh diluted caustic solution to crude oil downstream to the desalter is considered as an effective way to control the HCl formation in the downstream preheaters and crude overhead. The caustic solution reacts with HCl to form a stable salt NaCl. The NaCl formation reduces the total amount of free HCl produced, resulting in reduced corrosion in the downstream equipments. Although the injection of caustic solution has benefit of controlling HCl there is also a risk of fouling in preheaters, caustic stress corrosion and catalytic deactivation in downstream equipments. [3] To avoid this kind of problems of corrosion and fouling guidelines are provided in literature and plant manuals. It is considered better to use fresh caustic instead of spent caustic with a concentration of 2 to 3 weight percent of caustic in water as spent caustic may have variable amounts of free NaOH available in it to neutralize HCl. Due to variable amount of NaOH present it is very difficult to control the proper injection amount.

To avoid the cons of caustic injection and get the efficient process, injected solution should be properly mixed with the crude oil. To get this better mixing caustic solution should be injected trough the Monel quill into the pipe to one third of pipe diameter upstream to crude oil booster pump after the desalter. It is not recommended by experts to inject caustic solution upstream to desalter because in this case emulsions may form due to higher pH of water present and also possibility of ammonia driven into the crude. Another drawback of adding spent caustic upstream the desalter is that the NaOH added will be removed with the brine at the bottom of the desalter and no NaOH will remain available for HCl neutralization at the time of hydrolysis. Caustic solution should not be injected to crude oil over temperature 150^{o}C. If systems do not contain desalter units then the caustic solution should be injected at about desalter outlet temperature i.e. 135^{o}C. It is also recommended to inject caustic solution to crude oil upstream to pumps, control valves and preheaters etc. as early as possible (minimum 2 meters).

2.3 Handling of Spent Caustic

Spent caustic produced in industries is handled in many traditional ways. Spent caustic may be of many types depending upon the industry producing it. Spent caustic is produced at refinery plants, chemical manufacturing plants, LPG plant, Natural gas plant and geothermal energy plants etc. The most common and most dangerous compound in all spent caustics is the hydrogen sulphide which is highly toxic and odorous. [7] There are many traditional and advanced methods used in the industry to get rid of the spent caustic. Some of these are listed below,

- Deep well injections
- Dilution and then treatment at waste water treatment plant
- Incineration
- Oxidation methods like wet air oxidation, catalytic oxidation etc
- Export to pulp and paper mills

About the spent caustic produced at oil refineries it is also possible to reuse some kinds of spent caustic. Usually at oil refining plant there are three types of spent caustics produced i.e. sulphide, naphthenic and phenolic spent caustics. If sulphide and naphthenic spent caustics are produced at the refinery then their reuse is recommended by experts for crude oil neutralization. For using this spent caustic as crude oil neutralization there should be a wash water system present to avoid the accumulation of these compounds in the overhead system.

The benefit of using the spent caustic for neutralizing crude oil is that the amount of spent caustic produced at the plant will be decreased resulting in less spent caustic to get rid of. The negative effect of using this spent caustic is that the concentration of sodium is not constant and proper injection amount is difficult to control. So, some experts advice to never use spent caustic for neutralization purposes as it may cause higher concentration of sodium in the products and improper control of chloride content in the overhead.

Chapter: 3 Investigation of Problem Cause

The study started by consulting Shell Global Solutions who sent Jelle Bouma to Preem AB for a two days site visit. Jelle Bouma has experience in desalting operations and caustic injection systems for corrosion control in overhead from crude distillation column. The main purpose of the visit was to get a better understanding of the process and the operations taking place and to suggest a suitable solution to solve the problem.

3.1 Data Collection from Plant

Data collection from the plant relevant to the problem was requested by the consultant before his visit to the refinery so he could get to know about the important process conditions and plant geometry. The questionnaires about the crude overhead system, the sour water stripper, the desalter and a desalter test run were provided by the consultant to be answered. Provided questionnaires were answered as much as possible with the help of plant engineers, lab results, plant flow and control data. Some flow diagrams and P&Ids were also provided to understand the flow schemes.

A test run for the desalter was performed on CDU 1 to answer the desalter test run questionnaire. The test run was done at the day of crude feed change and six different samples were collected. Samples to be collected were,

1. Crude feed to desalter (after 4 hours of crude change)
2. Desalted crude (after 4 hours of crude change)
3. Total desalter wash water (after 1 hour of taking samples 1. and 2.)
4. Total desalter effluent water (after 1 hour of taking samples 1. and 2.)
5. Water from the CDU overhead accumulator (after 1 hour of taking samples 1. and 2.)
6. Overhead hydrocarbon product from the atmospheric tower (after 1 hour of taking samples 1. and 2.)

The collected samples were analysed in the laboratory to get the requested information about the different streams.

3.2 Consultant Site Visit

Jelle Bouma came to Preem AB for a two days site visit on 22nd of June 2010. During the two days he had meetings with plant engineers and officials to get the detailed knowledge about the plant. Important parts of the plant like the desalter operation and the caustic injection system were reviewed and the procedure of caustic dilution in 1/2C-22 was also monitored. At the end of the 2nd day the results and recommendations for improvements in the plant were presented.

3.2.1 Purpose of Site Visit

The main purpose of the site visit was to review

- The desalter operation, geometry and performance
- The caustic injection system and procedure of caustic dilution
- Performance indicators related to corrosion control

A clear picture of the desalter operation, the caustic injection system, the overheads corrosion control and recommendations for improvements were promised to be given at the end of the site visit.

3.2.2 Recommendations

After a detailed review of the desalter and caustic injection system, recommendations were given at the end of the site visit to improve the system performance in order to get better corrosion control and to decrease sodium content in the residue.

The test run performed on the desalter at CDU 1 showed 80% efficiency of the desalter, which is less compared to normal which should be more than 90%. Results from the test run are shown in appendix A-1, 2. There is only one mixing valve installed upstream of the desalter, having a pressure drop of 0.4 bars. It is recommended to install a static mixer together with the mixing valve giving a total pressure drop of 0,5-0,7 bar. The total pressure drop across the mixing valve and static mixer should have its optimum value between 0.5-0.7 bars. Higher pressure drop will decrease the efficiency of the desalting operation. There is not a large difference between the optimum and running pressure drop so the current performance is considered OK.

It is fine to use spent or fresh caustic for the crude overhead neutralization. The caustic is injected in small amount and it is much diluted.

At Preem AB Göteborg the caustic is injected directly to the desalted crude. It is recommended that the diluted caustic should be premixed with a slipstream of the desalted crude, typically 1 wt% of crude, before it is added to the desalted crude line to achieve better mixing. The premixing of caustic with desalted crude will help increase the injected volume and enhance mixing. There is also advantage of limiting the contact of caustic with the feed pipelines.

Wash water addition to the crude feed for desalting operation is recorded to be only 4vol% while the recommended amount is 5-7vol%. More wash water should be added to the crude to improve the desalter efficiency.

There is no mud wash system installed in the desalters. Accumulation of dirt particles at the bottom of the desalter will gradually occur with the course of time. Under deposit corrosion may be observed under this accumulated dirt which could result in decrease in efficiency of the desalter operation. The installation of a mud wash system in the desalters was recommended by Jelle Bouma.

It was recommended to change the chloride specification in the overhead water from currently 3 ppm to 5-10 ppm. To achieve the low chloride specification of 3 ppm more caustic has to be injected and as a result there will be an increased risk of the sodium in the residue becoming off spec.

To avoid the corrosion on the shell side in the preheat train in the DHT due to entrained water containing ammonia and chloride a coalescer should be installed before the DHT feed pump.

It is important to monitor the level of the emulsion layer because a higher layer will result in shut down of electricity between the electrodes and carry-over of emulsion to the crude tower as a result. This carry-over will give rise to fouling in downstream equipment and corrosion control will be affected.

3.2.3 Investigations of Recommendations

The recommendations from the site visit were a very good starting point for this research. It was really helpful in understanding the whole process and what actions affect the process. Detailed investigation of the recommendations about improving the performance of the desalter operation was considered to be investigated.

The desalting operation is highly dependent on temperature. Temperature between 95-150^{o}C is often used to get a good settling rate for the brine. [5] At Preem AB the operational temperature for the desalter is about 115^{o}C. The desalters at CDU 1 and CDU 2 are designed to operate at 116-150^{o}C but the desalters are operating at the lower limit of the design temperature which means that the residence time needs to be increased to get good settling of the brine. On the other hand the plant is running at overcapacity so the residence time is less than ideal and higher temperature is required for increased flow rates [5]. For higher flow rates higher operating temperatures are required to achieve better separation by gravitation. Later it was acknowledged that the desalter temperature has been lowered to achieve better heat efficiency in the preheat train on the CDU. To obtain a higher desalting temperature, higher running cost will be required.

Wash water flow rate is 4vol% while it was recommended to be 5-8vol% of the crude charge. [5] The source of the wash water is more than 50% from the city line and the remaining is from the CDU overhead. Analysis of the water from the city shows a high amount of sodium which means that contents of sodium in the residue can be the result of diluting the caustic with the city water. Analysis of city water supplied to refinery is shown in appendix B-1.

Analysis have shown that water content entrained from the crude overhead vessel to the DHT feed may be up to 3000 wt ppm of water containing chlorides and ammonium. The presence of ammonium and chloride in the DHT feed is contributing to corrosion at the shell side of the heat exchangers in the preheat train. The purpose of 1/2C-6 is to separate the water from the hydrocarbons. Due to small capacity of separator, sometimes entrained water goes to the DHT but this is not always the case Tests were done in 2006 for consideration of installing a coalescer before the DHT feed pump to reduce the water content to 100ppm. A coalescer hasn't been installed yet.

The chloride specification in the overhead water is considered to be much low at the refinery i.e. target is 3 ppm. This means that higher amounts of caustic needs to be injected to achieve this low specification which will result in higher amount of sodium in the residue. In common practice the chloride content in the overhead water should be less than 25ppm to avoid corrosion [3]. Shell Global Solutions recommends chloride content between 5 – 10 ppm.

3.3 Analysis of Previous Plant Data

It has been found that the injection of sulphide caustic to the crude, produced at the LPG plant, is not the cause of the problem of high chloride content in the overhead water and high sodium content in the residue. It is recommended to reuse the spent caustic for crude neutralization both by consultant and literature if it is done in a controlled way. The target specification is not allowed to exceed 8 ppm. In 1965 when the system was built nobody cared about sodium specs in the residue, but today it is important especially for Preem AB Goteborg to be able to sell of the residue to other plants. These plants can upgrade the residue and there comes the importance of the spec for Na in residue. If it is not possible to hold the target of Na in residue, the refinery has to dilute the residue with HGO to a high cost if there is no tank available for storage until it can be diluted with residue with less amount of Na. The other possibility is to be extra careful with processing the rest of the residue to be able to dilute the off spec residue.

CDU1 Year 2010:

Previous data from plant is available about the amount of chlorides in the overhead and sodium in the residue. Daily reporting about the levels of 1/2C-22 is also available, from which it could be seen at which date filling up of caustic in the vessel is done. Unfortunately there was no information available about indication if filled caustic was fresh or spent. All results on sodium content in the residue from year 2010 (to date analysis was done) are plotted in figure 3.1. Dates on which caustic filling in 1/2C-22 happened are also marked with vertical red lines.

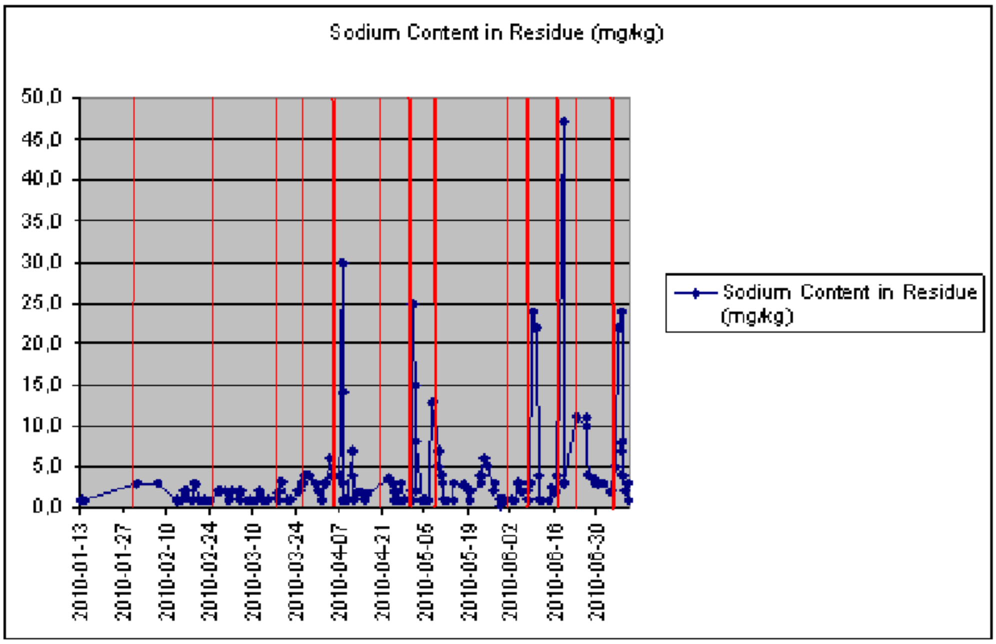

Figure 3.1 Sodium Content (mg/kg) in Residue at CDU 1 (2010)

Bold face vertical lines in red are showing the dates when caustic filling was done and at the same time or some period after the sodium content in the residue was off spec. Delay in off spec from the date of filling may be due to delay in analysis and reporting from the lab. When the six bold lines were spotted on chloride trends, it could be seen that at the dates with bold lines there was only one date when there was a problem with the chloride content. On this particular date of off spec it can be said that to control the higher chloride content in the overhead, the caustic injection was increased which resulted in higher amount of sodium in the residue.

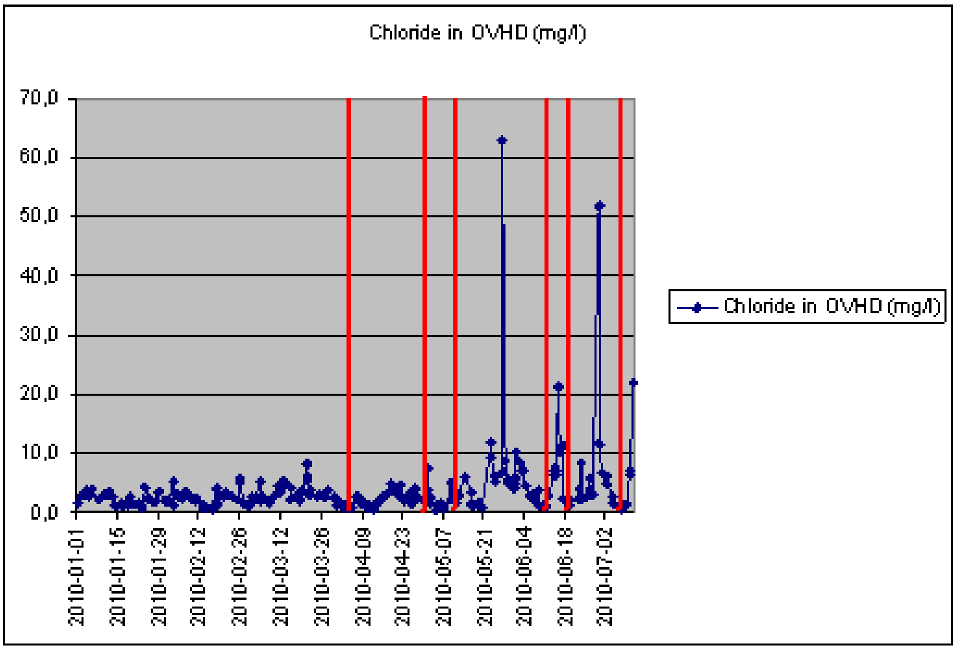

Figure 3.2 Chloride Content (mg/l) in Overhead Water at CDU1 (2010)

It is noted from figures 3.1 and 3.2 that after a while, one or two days with off spec on sodium, problems with off spec in chloride also occurs. This may happen because the caustic injection rate was decreased to avoid the effects of high sodium content in the residue resulting in an increase in chloride content in the overhead.

CDU1Year 2009:

The same kind of analysis was also done for year 2009. The y-axis of the graph in figure 3.3 shows the amount of sodium content while the vertical lines in red shows the dates at which the vessel 1C-22 was filled up. Five bold lines show when the residue went off spec after the vessel had been filled up. From the 15th of August to the 8th of October 2009 no data were available from the filling of the vessel 1C-22 although some off spec of sodium in the residue had been recorded during this time.

These dates with sodium off spec are then indicated on the trends of chloride content in the overhead in the same year. In October 2009, it was recorded that both off spec of sodium in the residue and off spec of chloride in the overhead happened at the time of filling up. It can be concluded from comparison when chloride content is normal even then sodium content goes off spec at the time of C-22 fill up. This shows that caustic injection was not increased at that time to control the chloride content but off spec in sodium happened due to improper dilution system at the time of C-22 fill up.

Trends for sodium and chloride for year 2009 are shown in figure 3.3 and 3.4 respectively.

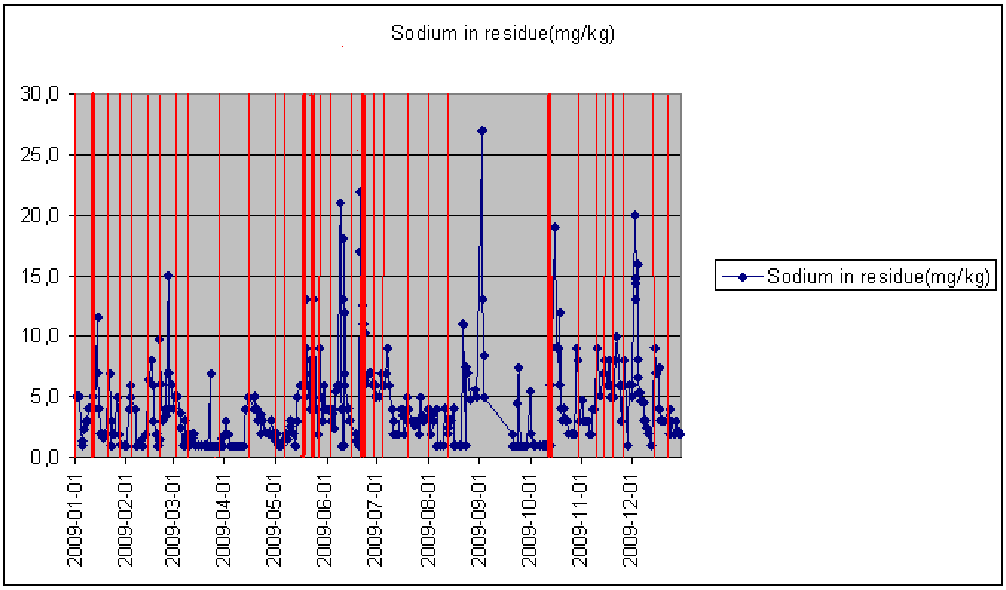

Figure 3.3 Sodium content (mg/kg) in Residue at CDU1 (2009)

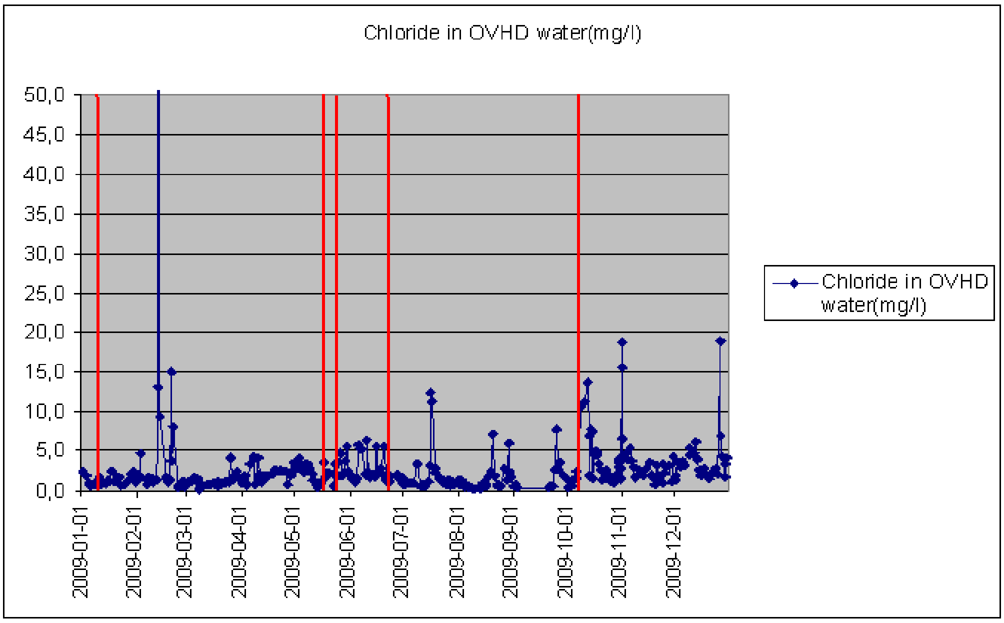

Figure 3.4 Chloride Content (mg/l) in Overhead Water at CDU1(2009)

CDU2 Year 2010:

The analyses of CDU2 showed fewer problems in terms of off spec of sodium in the residue and chloride in the overhead. Trends of sodium in residue and chloride in the overhead for year 2010 are shown in figure 3.5 and figure 3.6 respectively. The vertical lines in red are showing the time of filling up vessel 2C-22. Four occasions are recorded when the sodium content in the residue was higher than usual although the residue did not get off spec at these times.

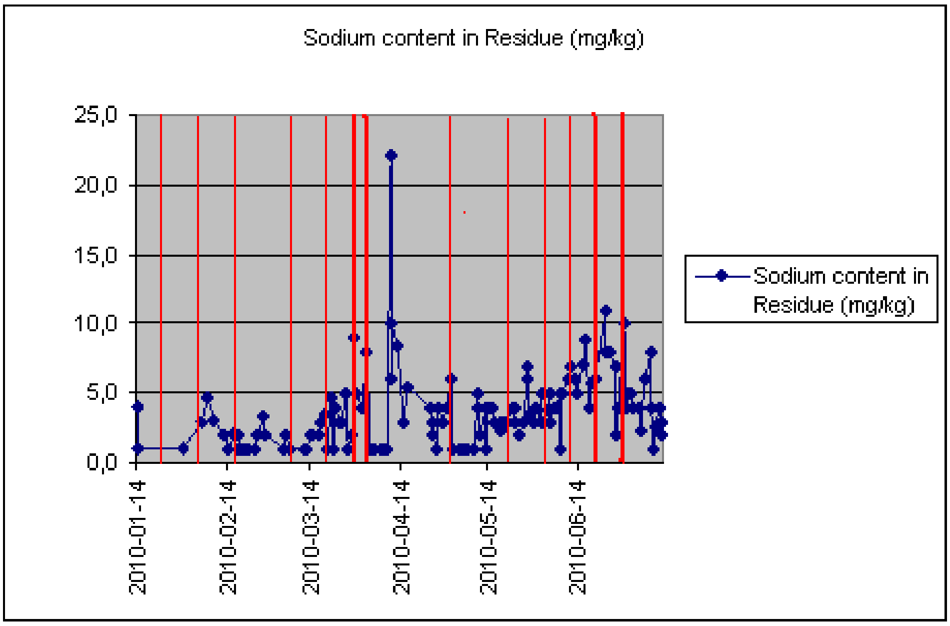

Figure 3.5 Sodium Content (mg/kg) in Residue at CDU2 (2010)

After indicating these dates on chloride trends it can be seen that the chloride content increases at these particular times. It is assumed that the level in 2C-22 is low; the caustic strength in the vessel is not strong enough to neutralize the crude. If the caustic is not well mixed in the vessel at the time of dilution, then the concentrated caustic solution with higher density will settle at the bottom leaving a caustic solution with less strength or simply water at the top. The caustic injection line is connected at the bottom of the C-22 vessels. As the level in the vessels decreases with time, less concentrated solution remains on top and the strength of the caustic is left insufficient for controlling chloride content in the overhead.

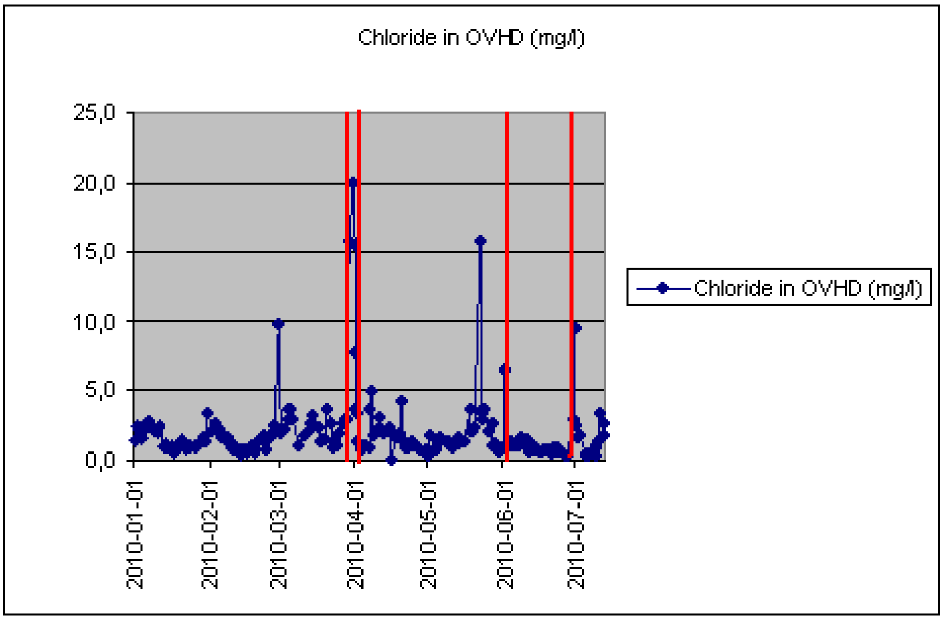

Figure 3.6 Chloride Content (mg/l) in Overhead Water at CDU2 (2009)

CDU2 Year 2009:

The trends for year 2009 are similar to year 2010 i.e. not many occasions with off spec in sodium and chloride contents occurred. Some dates are marked at which the sodium content is greater than at normal operation at the time of 2C-22 fill up. Some times to decrease the chloride content in the overhead system the caustic injection rate is decreased which after wards resulted in higher chloride content in the overhead.

Results for year 2009 are shown in figure 3.7 and figure 3.8.

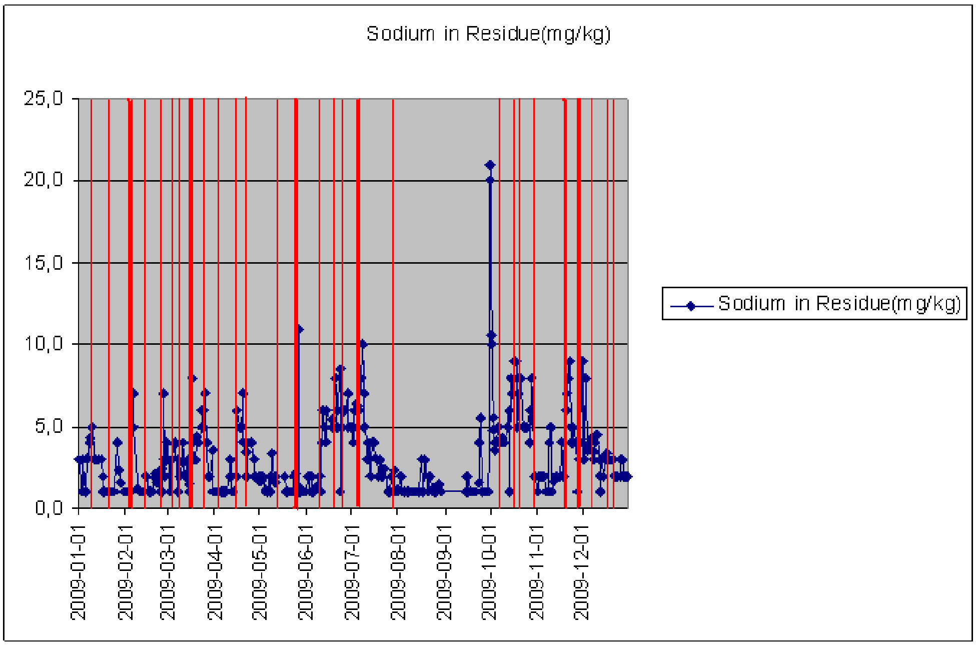

Figure 3.7 Sodium Content (mg/kg) in Residue at CDU2 (2009)

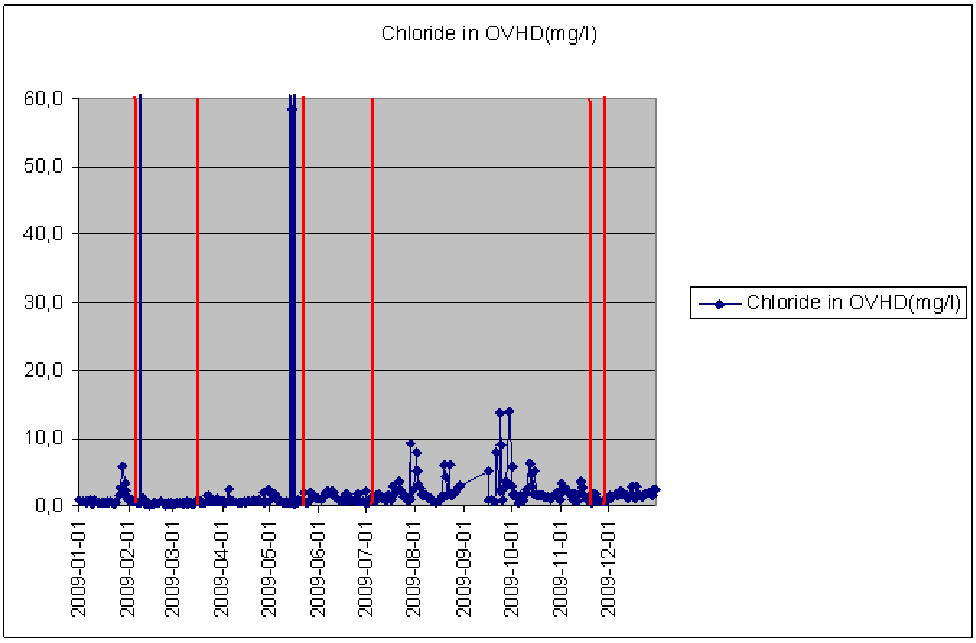

Figure 3.8 Chloride Content (mg/l) in Overhead Water at CDU2 (2009)

3.4 Follow Up on Caustic Injection System

To investigate if there are any problems due to the caustic injection, it was decided to get the information about how the injection system is operated. For this purpose details about the caustic injection system were collected from plant manuals, engineers and operators at the plant. After getting the complete understanding of the operation some follow ups were done on the caustic injection system. This is described in detail in this section.

3.4.1 Caustic Filling in C-22 Vessels

Vessel C-22 is either filled with fresh or spent caustic, when the level in the vessel is near to minimum, 25 cm from the bottom. A level gauge is present on the side of the vessel to read the level. At the time of filling, caustic is injected to the vessel from the top and the increase in level is noted. Water is added to increase the level 2-3 times the origin minimum level. During the filling of the vessel the mixer in the vessel is turned on to get a well-mixed solution. The whole procedure of filling is done manually and takes about 30-50 minutes depending on how much the overall level is increased. Follow ups on filling with fresh and spent caustic were done on different dates and results obtained are described below.

2C-22 Filling with Fresh Caustic (16th July, 2010):

On 16th of July the vessel 2C-22 was filled with fresh caustic. The caustic with the strength 10-12.5 wt. % (as told by engineer on duty) was lined from the storage vessel to 2C-22 to increase level through 20 cm. After the addition of caustic, water was added to increase the level through 60 cm. Operators were doubtful about the performance of the level meter. When the mixer in the vessel was turned on it didn't work so the resulting diluted solution was not made homogeneous. Exact strength of fresh caustic added from storage was also not known. The resulting solution from the added water (one part of 12.5% caustic solution and three parts of water) should have a concentration of 3.4% which is mixed with the rest of the caustic at the bottom of the vessel. As the strength of the caustic at the bottom in the vessel was not known, the new concentration could not be calculated unless a sample was not analysed in the lab.

1C-22 Filling with Fresh Caustic (28th of July, 2010):

The filling of the vessel 1C-22 with fresh caustic was monitored on the 28th of July. The initial level recorded on the level meter was 26 cm from the bottom. 10 wt. % of fresh caustic (as told by engineer on duty) was added to increase the level to 97cm. Diluting water was added to increase the level from 97cm to 220cm. The addition of water was 1.73 times that of caustic and the resulting solution should have the strength of 3.9%. There was some caustic at the bottom in the vessel with unknown concentration. A sample of caustic taken at the end of filling was analysed in the lab to get the new caustic strength. The sample was 4 wt. % in terms of caustic. The strength of fresh caustic was not known for sure as it was told to be 10 wt. % in comparison to 12.5 wt. % from previous follow-up on the 16th of July.

2C-22 Filling with Fresh Caustic (28 July, 2010):

Vessel 2C-22 was also filled up with fresh caustic of 10 wt. % on the same date as the 1C-22 was filled up. Increase in level due to 10 wt. % fresh caustic and diluting water was 68cm and 152cm respectively. Actually the diluting water was to be added only 1.7 times that of caustic but when addition of water was to be stopped there was a mistake done by the operator. The valve controlling the water flow rate, that should be closed, was rotated in the opposite direction and the level in the vessel went up to 250cm instead of stopping at 220cm. The resulting strength of this added caustic and water should be 2.9 wt. % after mixing. The caustic strength of the solution at the end of filling was analysed in the lab to 7 wt. %. This high strength of caustic is considered very strange as water was added more than usual but still higher strength of caustic was analysed.

1C-22 Filling with Spent Caustic from LPG C-3 Washing (14th of September, 2010)

After the experience from previous follow ups on caustic filling, a detailed follow up was planned on filling up the 1C-22 with spent caustic from the propane C-3 wash. Three samples were requested for the follow up,

1) Caustic content of already present caustic solution at the bottom of 1C-22
2) Caustic content of LPG C-3 wash that is to be filled to 1C-22 (spent caustic)
3) Caustic content of solution after filling up

Very useful results were obtained from the analysis of these three samples. The strength of the caustic already present in 1C-22 was analysed to 1.0 g/100 ml or 1 wt. % in terms of caustic. This low strength of caustic was maybe due to density difference between caustic solutions of different concentrations produced due to insufficient mixing. More concentrated caustic with higher density left the vessel earlier as injection line to crude goes from the bottom of the vessel leaving behind caustic with lower density.

The strength of spent caustic from the LPG C-3 wash was 4.8 wt. % which was further diluted with water at the time of filling.

The initial level of the vessel 1C-22 was 58 cm from the bottom which was then increased to 99 cm with the help of spent caustic from LPG C-3 wash. Water was added to increase the level from 99cm to 200cm. The resulting caustic content of the solution should be 1.4 wt. % which was mixed with already present 1 wt. % solution in the vessel. Final solution should be about 1.0-1.4 wt. %, but final solution analysed by the lab was 2.7 wt. %. These results show that there must be either problem with the level meter or improper mixing or both.

Some notes were taken from the plant engineer during the filling up of spent caustic,

- From the coalescer 6T-1 water containing unknown concentration of caustic is drained with a pump to the vessels C-22 which causes increase in level of C-22.
- Caustic forms crystals in the level meter due to which the level meter get stuck and do not show the exact level.
- Level in the level meter is not easy to read.
- It is difficult to dilute 10% caustic to exactly 3%.
- Caustic cause corrosion in the system which causes the pumps to get stuck because of corrosion particles e.g. Injection rates of caustic are thus affected. Once during this summer the suction filter of one pump was clogged.
- Some kind of sonar measurement for the level is considered to be better than the level gauge.

3.4.2 Change in Level with Pump Speed

As the level gauges connected to vessels C-22 are reported problematic right from the start some follow ups were done on daily level reporting. Rate of level decrease can be judged by the caustic injection rates. Change in caustic injection rate can be seen from the frequencies of the caustic injection pumps G-9 and G-10 that were available through Aspen Process Explorer. A follow up was done from 15th of July to 20th of July. The level reported was compared to the pump frequencies and changes in sodium in the residue. After comparing the pump frequency with the decrease in level, it was seen that the decrease in level for a period of 24 hours was different from one day to another while the pump frequency obtained from Aspen Process Explorer was unchanged. Also the sodium in the residue wasn't in accordance with the decrease in level. Changes in level in 2C-22 and sodium content in the residue are listed in table 3.1 on different dates. Pump 2G-10 frequency is also given in figure

3.8. Pump 2G-10 was running at the same frequency during 14 – 20th of July but on the 20th of July the sodium content increased in spite of large decrease in level of 2C-22 and at that time the caustic came from the bottom of vessel 2C-22 to be injected into the crude downstream to desalter. There may be problem with the level gauge as discussed previously.

Table 3.1 Follow up on 2C-22 during 15-20 July, 2010.

Date	Level height in 2C-22 (cm)	Change in level height (cm)	Sodium content in residue(mg/kg)
14-07-2010	87		-
15-07-2010	73	-14	3.0
16-07-2010	60	-13	3.0
17-07-2010	180	+120	4.0
18-07-2010	172	-8	4.0
19-07-2010	163	-9	2.0
20-10-2010	130	-33	5.0

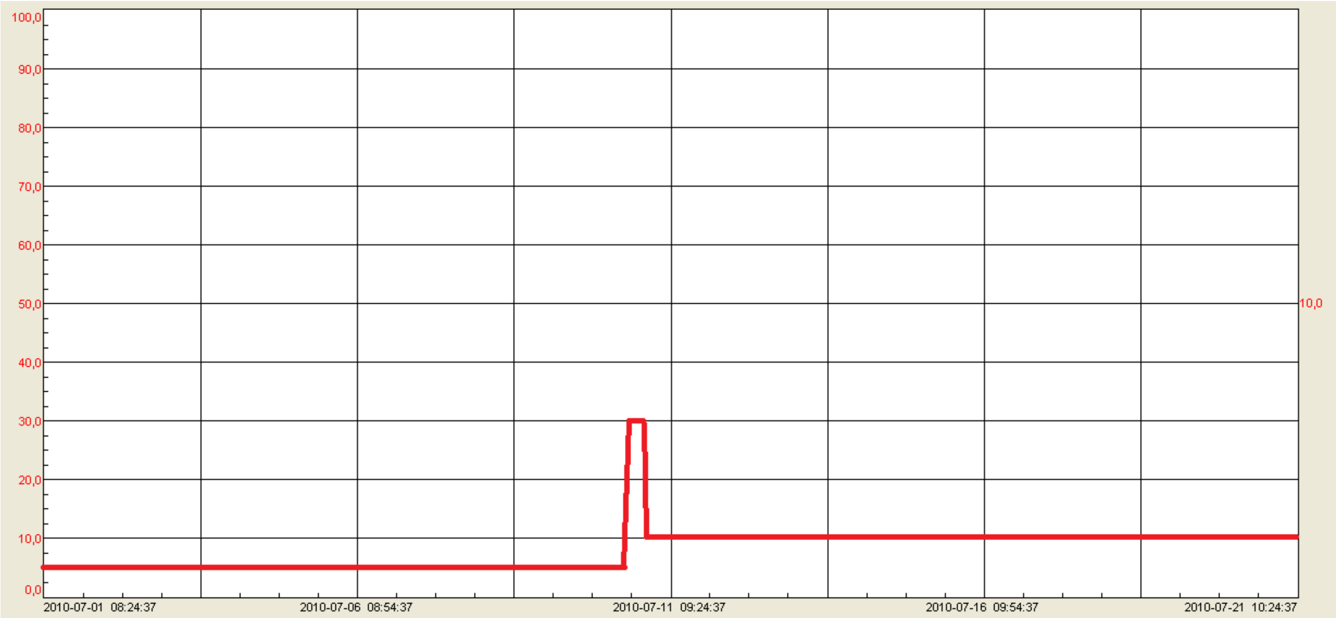

Figure 3.9 Pump (2G-10) Frequency from 1-21 July 2010

In figure 3.9 the percentage of the total frequency is given on the Y-axis while the X-axis is showing the dates in the month July. By comparison of the change in level in table 3.1 with the pump frequency during the 14-20th of July it is seen that the decrease in level per day varies from 13 cm to 33 cm while the frequency remains the same. The filling of vessel 2C-22 happened on the 16th of July which is why the level increased from 60 to 180 cm between 16th and 17th of July. The result for sodium content on the 19th of July is quite strange as the caustic injection was increased as seen from the decrease in level on the 19th of July. These results aren't reliable because the residue sample is analysed after a period of one day. A follow up on the injection pumps and levels of C-22 vessels was done later by recording the changes personally. The injection rate of caustic to crude is controlled by the pump frequency and stroke lengths. Usually stroke lengths remains constant and only frequency is changed to vary the injection rate. The pumps are overdesigned so half of the total stroke length is used. It is recommended by the pumps manufacturer to operate the pump at full stroke length and only change frequency to vary the flow rate. At the time the follow up was done, the injection pumps at CDU1 and CDU2 were operating at stroke lengths 7 mm and 10 mm, respectively.

Follow up on caustic injection system was done on the 22-27th of July by recording different parameters personally at plant site and getting results from the lab about sodium content in the residue and chloride content in the overhead water. The results are reported in table 3.2 and 3.3 for CDU1 and CDU2 respectively,

Table 3.2 Follow up CDU 1 22-27 July, 2010.

Date	Time	Level in 1C-22 (cm)	Change in level height (cm)	Pump in Use	Stroke Length (mm)	Sodium in Residue (mg/Kg)	Chloride in OVHD (mg/l)
22-07-2010	14:15	103		1G-10	7	1	5.6
23-07-2010	09:20	101	-2	1G-10	7	1	4.8
23-07-2010	14:00	100.5	-0,5	1G-10	7	1	4.8
26-07-2010	10:00	85.5	-15	1G-9	7	1	-
26-07-2010	14:00	81.5	-4	1G-9	7	1	-
27-07-2010	12:00	57	-24,5	1G-9	7	2	3.5
27-07-2010	14:00	54	-3	1G-9	7	2	3.5

Table 3.3 Follow up CDU2 22-27 July, 2010.

Date	Time	Level in 2C-22 (cm)	Change in level height (cm)	Pump in Use	Stroke Length (mm)	Sodium in Residue (mg/Kg)	Chloride in OVHD (mg/l)
22-07-2010	14:15	114		2G-10	10	2	1
23-07-2010	09:20	104	-10	2G-10	10	3	1
23-07-2010	14:00	101	-3	2G-10	10	3	1
26-07-2010	10:00	66	-35	2G-10	10	3	1.2
26-07-2010	14:00	61	-5	2G-10	10	3	1.2
27-07-2010	12:00	53	-8	2G-10	10	2	-
27-07-2010	14:00	51.5	-1,5	2G-10	10	2	-

In the above tables, dashed lines in the columns of chloride and sodium contents are those days on which these samples were not analysed or reported. Important aspects of the caustic injection system that were spotted during this follow up are listed below,

- It is difficult to see the exact value in the level gauge
- Caustic causes corrosion and fouling in the system. The suction filter of 1G-10 was clogged on 24th of July and the caustic injection almost stopped. The decreased flow rate due to a clogged suction filter caused higher chloride content in the overhead. The resulted higher chloride cannot be seen here because it was during weekend and readings in the table were taken during week days. Chloride content in the overhead water was 10.4 ppm on 24th of July as analysed by the lab.

- It is difficult to control the sodium and chloride contents due to late results from the lab.
- There was no information available about the flow rate of caustic. The caustic injection rate can be increased or decreased first when the lab results of sodium and chloride are available from the lab. If there is an off spec situation the operation will not have any knowledge about it before they get the lab results which means, at the worst, those actions may be delayed with one day.

3.4.3 Pump Calibration

The flow meters on the caustic injection line were not working. The only information available on how much caustic was injected to the crude for neutralization was the decrease of level in the vessels 1/2C-22. The flow rate of caustic depends on both stroke length and frequency of the injection pumps. The caustic injection pumps were therefore calibrated to get an idea about the flow rate. There are four identical injection pumps with two pumps in operation i.e. one at each CDU with one spare pump. The calibration of one pump was enough to get the flow rate from different combinations of stroke length and frequencies.

Calibration of pump 1G-9 was done and similar behaviour is applicable for the remaining three pumps. The water line was connected upstream to the pump and the pump was set to operate at stroke length 15mm. The stroke length is adjustable on site by screw adjustment. For a constant stroke length of 15mm the time was noted to get the volume of 5 litres for a definite frequency. From the volume collected during the specific time period the flow rate could be calculated. The time to inject 5 litres of water into a bucket at different frequencies was taken for the stroke length 15mm. Similar procedure was repeated for stroke lengths of 4mm, 7mm and 10mm. The results from the calibration are shown in table 3.4.

Table 3.4 Pump Calibration 1G-9

Frequency (% of total)	***Flow rates in l/h at stroke length 4mm***	***Flow rates in l/h at stroke length 7mm***	***Flow rates in l/h at stroke length 10mm***	***Flow rates in l/h at stroke length 15mm***
10	7.61	14.57	20.93	29.51
30	20.18	36.00	52.33	82.95
60	43.37	85.31	139.53	209.30
90	80.00	200.00	300.00	418.60

A graph is plotted between frequency and flow rate at different stroke lengths. From the graph, interpolation can be done to get the value of flow rate for any desired value of stroke length and frequency. SL is representative of stroke length in the graph and its value is in millimetre.

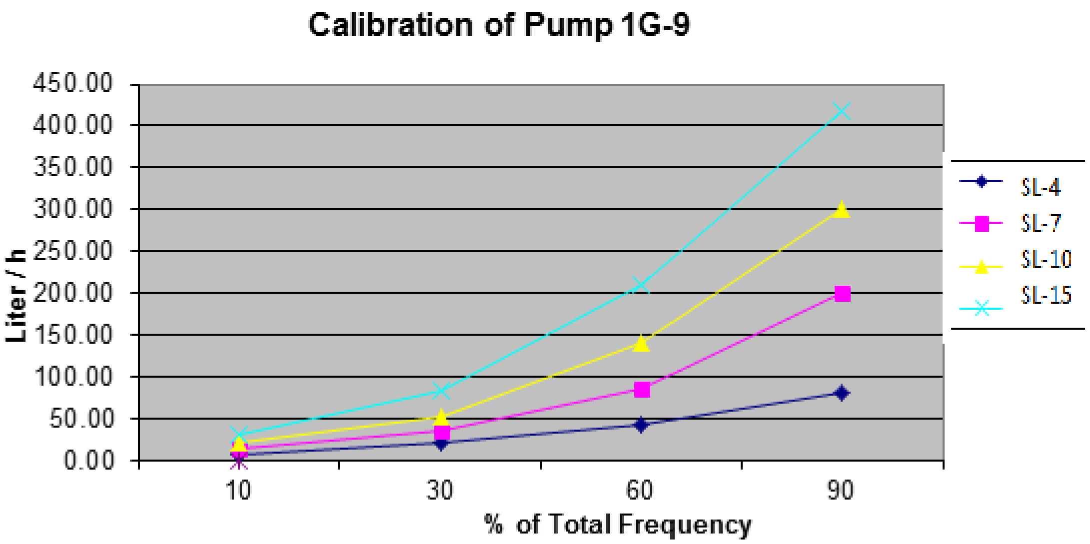

Figure 3.10 Pump Calibration 1G-9

Recommendations are available from Shell Global Solutions about calculation of the caustic required for neutralization of crude. The caustic injection rate varies with the change in feed flow rate. An adjustment is made to connect the flow control of caustic injection to the feed flow control. The caustic injection to the crude should be varied automatically when change in feed crude flow rate takes place. It was also recommended by the process engineer at the plant to operate the injection pumps at lower stroke lengths and higher frequencies to get the required flow rates.

3.5 Sampling Procedure

Sampling for analysis of sodium content in the residue and chloride content in the overhead water was done every 24 hours. It is decided from the analysis that either caustic injection rate should be increased, decreased or remain unchanged. Sometime the results from the lab are delayed which makes it difficult to judge the current performance. Sometimes off specs may happen during these delays when samples are not analysed in time. In these cases sampling results may cause too much loss of money due to off spec problem. It is also very difficult to maintain exact caustic injection rate required for crude neutralization without availability of results from the lab.

3.6 Investigation of Recent Accidents

Investigation of recent accidents has been done that happened between the 1st of June and the 14th of July. Most of the accidents happened in CDU1 as expected as CDU1 is considered more problematic than CDU2. Problem is due to poor desalting operation in CDU1 as one electrostatic grid in desalter is not working and repairing was recommended by Jelle Bouma from Shell Global Solutions. Off spec of sodium in the residue happened three times during this time period for which the analysis is done. Every time off spec happened, the vessel 1C-22 had been freshly filled the day before. It is not always the case that off spec happens due to caustic injection. There are other factors that may cause off spec of sodium in the residue. Trends of sodium content in the residue and chloride content in the overhead are shown for the one and half month of June-July 2010. Vertical lines in the figures shows the date on which caustic filling in 1C-22 vessel was done.

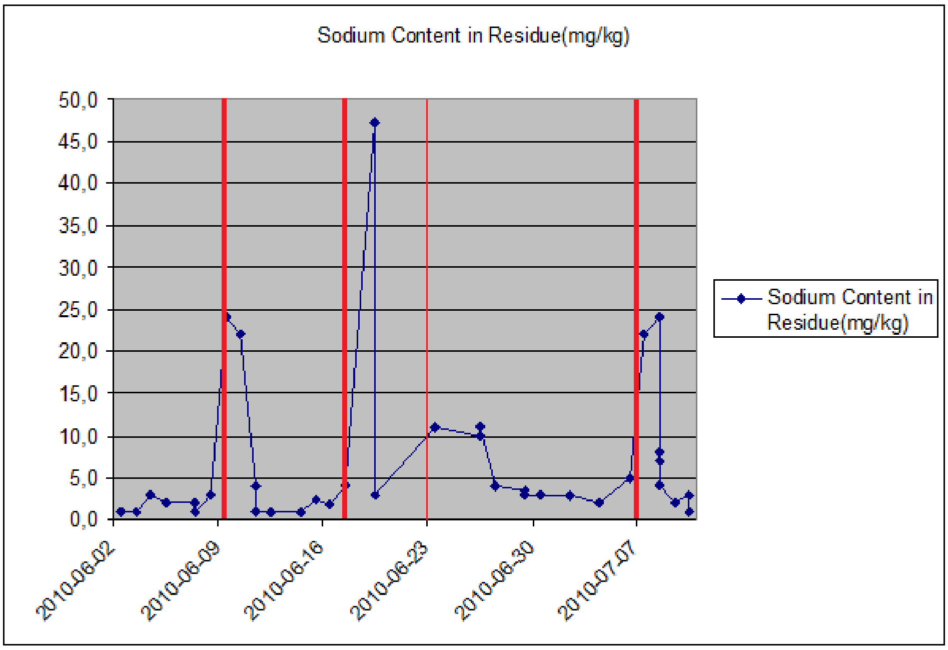

Figure 3.11 Sodium Content (mg/kg) in Residue at CDU1 June-July (2010)

The filling of caustic was done four times in this period of time as shown by four vertical lines, three bold lines are showing the time when the residue got off spec on sodium (>20 mg/kg) and caustic filling in 1C-22 was done in the same day. On the 23rd of July vessel 1C-22 was filled with spent caustic but no off spec in terms of sodium in residue was noticed. On the 17th of June the crude feed flow rate was decreased from 9950 m^3/d to about 7500 m^3/d with the same caustic injection rate. Reduced feed flow rate also resulted in reduced residue flow rate. The reduced residue flow rate may also be due to off spec of sodium in the residue, as same the caustic injection rate for smaller flow rate of crude resulted in higher concentration of sodium. During filling of caustic on the 7th of July operators were unable to dilute caustic to 3% and the concentration at the end of the caustic filling was 8.5%. The problem was due to the level meter because when the vessel was filled up with caustic the level suddenly increased unexpectedly from a very low to a high value. After the increase in level there was no space left to add more water for dilution.

The four vertical lines of caustic filling are also drawn for the same period of time on chloride trends in figure 3.12. The chloride content in the overhead water was greater than 3 mg/l several times in the trends. The greatest off spec i.e. 52 mg/l, is seen for the duration of spent caustic injection to the crude during the 24th of June to the 8th of July. The spent caustic may not be strong enough to neutralize HCl formed and resulted in higher chloride content in the overhead water.

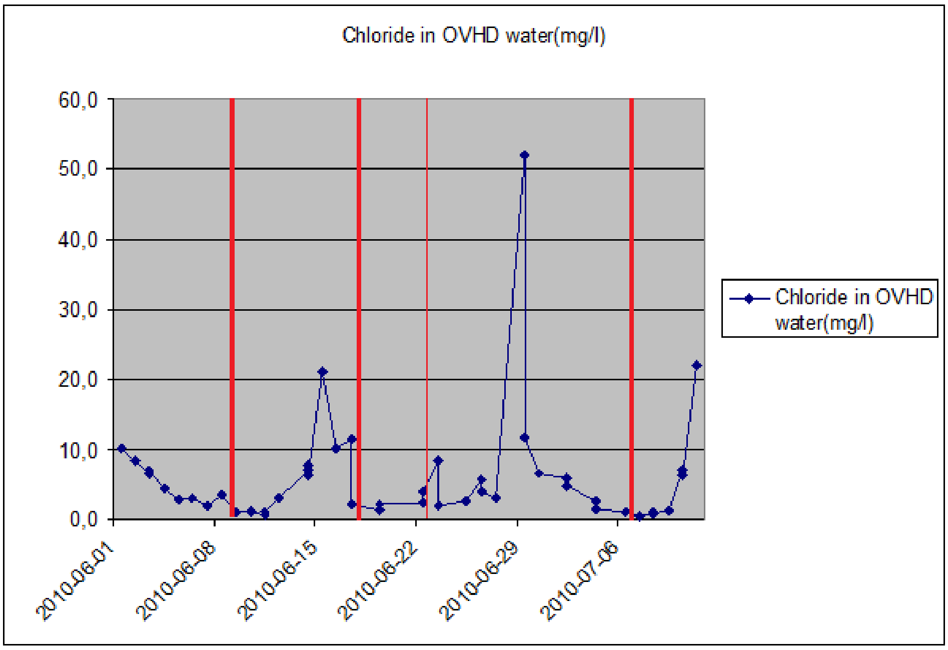

Figure 3.12 Chloride Content (mg/l) in Overhead Water at CDU1 June-July (2010)

It is noted by engineers that after the change of crude feed, the caustic injection rate is increased but it was not possible to control chloride content even if no off spec in terms of sodium in residue is seen due to this higher injection rate. It is quite possible that this caustic is sometimes not concentrated enough to control chloride content as it was seen during the caustic filling of the 15th of September 2010 that resulted in the caustic strength of maybe between 1-2 % in actual. Sometimes the caustic strength of sample from vessel C-22 analysed in the lab is not representative for the actual strength. The problem may be improper mixing and as a result, the solution in the vessel is not fully homogeneous.

3.7 Problematic Crudes

The crude feed to the refinery is a mixture of crude oils from different locations. Certain crudes with high amount of naphthenic acids can cause high chloride contents in the crude overhead. The naphthenic acids give the crude oil buffering capacity which makes it difficult to neutralize with caustic. Crude oils with high buffering capacity will be easier to process if they are mixed with crude oils that are easy to neutralize with caustic.

3.8 Process Water for Desalting

The process water used for desalting purpose is provided by Alelyckans Water Purification Plant. The sodium content in this water may range from 13-26 mg/l with an average of 20 mg/l (see Appendix B-1). The amount of sodium in the process water will of course contribute to the higher sodium content in the residue as the same water is used for dilution of caustic solution in the C-22 vessels. Every step to improve the system counts so change of this water line with higher sodium content with water of lower sodium content may also help in avoiding off spec of sodium in the residue.

During filling of caustic on the16th of July, 2010 water was added to increase the level through 60cm. Total volume of water added was 1999.7 litres (Diameter of 1/2C-22 vessel are 2060mm). If the average amount of sodium is coming with this water i.e. 20 mg/l then additional sodium added from the water will be 0.04 kg. Mostly water added during filling up causes 100cm increase in height. This amount of water will take 0.066 kg of sodium into the system.

3.9 Tests for Off Spec Sodium Content

The use of spent caustic for neutralization of crude was considered the main cause of off spec on sodium in the residue and ineffective control of chloride content in the overhead water. To conclude that spent caustic is not problematic some tests for sodium content were done for both fresh and spent caustic injection. As spent caustic is supposed to contain more sodium content as compared to fresh caustic a material balance was done to see how much additional sodium comes with caustic injection for both fresh and spent caustic. The alkalinity for both butane and propane wash was tested to make sure that that the strength of caustic is good enough to be used for corrosion control. Actual alkalinity of was tested from which caustic strength can be calculated. The results of these tests and method of calculating caustic strength from alkalinity is given in appendix C-1. There is no problem to use spent caustic from C3 and C4 washing since caustic is diluted from 10 to 3 wt. %. Although, C4 wash is changed earlier because there is a coalescer after the C4 wash. There is no pre-filter installed before the coalescer so the coalescer can be blocked with particles. To avoid this blockage for longest possible, the caustic is changed out earlier than necessary. Caustic leaves the coalescer after the C4-wash as well and is normally recycled back to the vessel 2C-22.

There is a limit value in the waste water plant for phenol to be max 1 mg/l. Both samples contained phenol so we cannot drain the caustic to the waste water without any treatment. The same can be said for the COD and TOC values. Earlier there was a limit value on COD of 100 mg/l. It has been changed and nowadays there is a limit value on TOC which is max 20 mg/l. So, the spent caustic must be treated in some way if we would like to let it out in the waste water.

Tests were done on CDU1 as it is more problematic in terms of off spec because of the electrostatic grid problem in the desalter. Results from both tests were then compared to get the result (injection of spent caustic is not a reason for higher sodium content in the residue).

3.9.1 Fresh Caustic

Two samples were taken for one single result. One sample was taken from the crude after the desalter but before the caustic injection and the other was taken from the residue. A material balance for sodium is done to see how much additional sodium is coming in residue due to caustic injection. Samples that are analysed are taken at three different occasions,

1. After the filling of caustic in C-22
2. When the sodium content in the residue is greater than 10 mg/kg
3. When the sodium content in the residue is smaller than 10 mg/kg

The assumptions made for the material balance calculations are,

- Average Density of feed = 837 kg/m^3
- Average density of residue = 945 kg/m^3
- Crude feed flow rate is taken as flow rate of feed after the desalter
- Sodium content in crude after the desalter was < 1 mg/kg but that value has been set to 1 mg/kg to simplify the calculations.

The analysis of the samples with dates and results of material balance are presented in table 3.5 below,

Table 3.5 Analysis of Sodium Content at CDU1 for Fresh Caustic

Date	Feed flow rate (m^3/day)	Residue flow rate (m^3/day)	Sodium in residue (mg/kg)	Sodium in feed per day (kg)	Sodium in reside per day (kg)	Difference in sodium amount (kg/day)
28-07-2010	7068	1521	32	5.9	45.99	40.08
14-08-2010	7949	1799	14	6.65	23.80	17.15
30-07-2010	7043	1724	8	5.89	13.03	7.14

The difference in sodium amount in the feed and residue is due to sodium coming with the caustic injection. If flow rates and caustic strength of the solution injected to crude is known then this sodium content can be compared with the sodium content of the caustic solution coming as caustic. This comparison will tell how much additional sodium is coming from other sources than caustic.

3.9.2 Spent Caustic

A similar analysis is done at the time when spent caustic was injected. The same sampling procedure was used as described in chapter 3.9.1. Results from the analysis are presented in table 3.6.

Table 3.6 Analysis of Sodium Content at CDU1 for Spent Caustic

Date	Feed flow rate (m^3/day)	Residue flow rate (m^3/day)	Sodium in residue (mg/kg)	Sodium in feed per day (kg)	Sodium in residue per day (kg)	Difference in sodium amount (kg/day)
14-09-2010	9628	2456	3	8.05	6.96	-1.09
19-09-2010	9400	2365	19	7.87	42.46	34.59
24-09-2010	9702	2317	2	4.38	4.38	-3.74

The negative results in the column “Difference in sodium amount” may have appeared due to assumptions taken or maybe due to samples analysed by the lab that were not representative. The overall increase of sodium in the residue due to injection of spent caustic is comparable to the increase of sodium when using fresh caustic. So, it can be concluded that the injection of spent caustic is Ok if it is done in a controlled way. Off spec on sodium in the residue also happens during the injection of fresh caustic. Although it is very difficult to conclude anything for sure from this kind of analysis as there are other parameters and assumptions that may affect the results.

3.10 Problem in Caustic Injection Pumps

According to the notes taken from engineers from plant, the caustic pumps may be running but not give any actual flow due to fouling in the check valves inside the pump. A couple of years ago flow meters were installed but they do not work due to pulsating flow / pressure drop in the flow meters. Since the pumps have linear characteristics, stroke lengths and pump frequency are used to calculate the flow. To know if there really a flow, a manual level reading on C-22 is performed on a daily basis (the calibration pot is not in use due to fouling) but this leads to a slow response on chlorides in the overhead sodium in the residue. An improvement would be to have a flow indication installed, but since the flow is pulsating this may not be feasible. But relatively cheap flow meters from ProMinent, specifically designed for chemical dosing are available. Maximum flow is 30 liters/h which in most cases would work but not at all times when higher flows of caustic is needed. To get a controlled caustic injection, following suggestions are given by engineers at Preem AB,

- Try to resolve problems with the purchased flow meters
- Clean up / refresh existing caustic system including calibration pots
- Consider upgrading the filters before the caustic pumps into finer mesh and periodic cleaning of filters
- Invest in new flow meters (Dulcoflow from Prominent)
- Install flow indication and trust the pump characteristics (about as expensive as the Dulco-flowmeters)

Chapter: 4 Neutralization of Spent Caustic

There are different ways of handling spent caustic, some of which are discussed in the section of the literature review. This section will explain the recommended practice from experiences of other companies and some other methods for neutralization of spent caustic. Neutralization of spent caustic means processing of spent caustic in such a way that it can be released to the biological water purification plant without adverse consequences. There are different systems available on the market for spent caustic neutralization. Some of which are used by other refineries to get rid of the refinery spent caustic.

4.1 Recommended Best Practices

It is clearly described in the UOP Manual to never use spent caustic for crude neutralization as it contains higher amount of sodium and has less capacity to neutralize the overhead water [19]. Due to these properties of spent caustic it is very difficult to control chloride content in the overhead and higher amount of sodium may end up in the residue.

Sulphidic spent caustic is produced at the LPG plant. According to data provided, it is fine to use sulphidic spent caustic for neutralization but there should be a wash water system (that takes water from crude distillation overhead) for the overhead to avoid accumulation of compounds present in the caustic.

The consultant from Shell Global Solutions recommended using spent caustic for control of chloride content in the overhead. According to him the spent caustic is much diluted and will not cause adverse consequences to the system.

Spent caustic injection to crude to overcome corrosion in the overhead is considered a good solution for waste reduction in refineries. [1]

Although sulphidic spent caustic usage for corrosion control is considered a good way for reduction of waste and is recommend by many experts, most companies do not reuse their spent caustic. Reuse of spent caustic for corrosion control can only be done in a very controlled way. It is much difficult to provide proper injection rates due to variable contents of caustic and higher amount of sodium. Neutralization of produced spent caustic is done in a separate plant usually through oxidation in most of the refineries.

4.2 Other Companies´ Experiences

In this section experience of some refineries about handling their spent caustic is discussed. Most of the companies neutralize their spent caustic through oxidation but some of them get rid of the spent caustic in a profitable way which is described below,

The Shell Puget Sound Refinery in the United States cut off their waste disposal costs by providing their spent caustic to the pulp and paper mill industry in the northwest. Previously this spent caustic was transported to a waste facility about 2000 miles away from the plant site in Texas. The spent caustic is used in the pulp and paper mill’s Kraft process in green liquor. This new practice helped both industries to cut their costs about $ 400,000 per year [8].

Zimpro® Wet Air Oxidation is used by Repsol YPF’s La Pampilla since 2005. It is the largest oil refining site in Peru. The refinery produces spent caustic from treatment of gasoline, kerosene and LPG. The spent caustic is then treated on site through wet air oxidation which will give no odour in the off gas. A case study of the system showed that wet air oxidation of this spent caustic is very effective as it reduces mercaptans and sulfides to very low levels. TOC and COD are also reduced and pH of the neutralized products is 8-10. The treated spent caustic is then discharged to the sea without any adverse consequences. [9]

A case study from a refinery in Brazil named Refinaria de Petroleos de Manguinhos, S.A. (RPDM) also showed that wet air oxidation is an effective technique to neutralize all types of spent caustic on site. The refinery was previously doing off-site disposal of refinery spent caustic. As the refinery is situated in a polluted area, wet air oxidation was considered to be best for the plant and was installed in 1995. Even after 5 years of operation the system was able to reduce the COD up to 80%. There was no problem with odour. The caustic was neutralized on site instead of being transported to an off-site treatment. On site disposal of spent caustic reduced the environmental risks of transportation and handling etc. [10]

Formosa Petrochemical Company has been using Zimpro® Wet Air Oxidation for their ethylene plant spent caustic and refinery spent caustic since 1994. The system helps to get rid of the disposal of spent caustic and odour. The system is supplied by the US Filter Corporation, a Siemens company which provides waste water treatment systems and services to customers all over the world. More than 20 wet air oxidation systems have been installed by US Filter Corporation in the recent years. [11]

Wet Air Oxidation is considered to be a reliable technique for disposal of spent caustic if it cannot be supplied to the pulp and paper mill industry. There are other technologies available for the handling of spent caustic like PRETREAT Technology, ozonation, catalytic oxidation, chemical reagent oxidation etc. but most of them are not developed on industrial scale.

4.3 Methods of Neutralization

In this section the Wet Air Oxidation of spent caustic is discussed in detail along with brief introduction to some other process of neutralization.

4.3.1 Wet Air Oxidation

The Wet Air Oxidation (WAO) or hydrothermal treatment is a high temperature process for oxidation of materials that are suspended or dissolved in water with oxygen. The wet air oxidation technique for treatment of spent caustic liquor was first patented by Sweden in 1911. WAO was commercialized almost 60 years ago. Up to 2002 there were more than 200 full scale wet air oxidation systems in operation used for different applications. Application for industrial water treatment plants was commercialized in 1970 for the first time. [12]

Spent caustic has high chemical oxygen demand (COD). This is not accepted in biological water purification plant. Wet air oxidation system oxidizes sulphides and mercaptans to reduce COD of spent caustic. After treatment with WAO the effluent has a lower COD and can then be treated in the biological purification plant. In a typical WAO system, the feed is pumped to the system at a higher pressure (about 28 barg). The feed stream is mixed with compressed air and pre-heated with outgoing effluent from reactor in a heat exchanger. The feed stream can also be heated directly with steam to increase the temperature before it enters the reactor. The hot fluid stream is then held in a reactor for one hour residence time at 200^{o}C without any catalyst. The reactions takes place in the liquid phase and the oxygen must be transferred to the liquid phase from the gas phase to carry out the reaction. Excess air is supplied to achieve good conversion. Sulphide compounds oxidize partially to form thiosulphate, further oxidation gives sodium sulphate. The organic compounds present in the spent caustic are only partially oxidized. The total organic carbon is not affected much, but its nature is changed which results in lower COD and lower fouling rates. The process also improves bio-treatability of the organic compounds [13]. A simplified process flow diagram of the WAO is shown in figure 4.1.

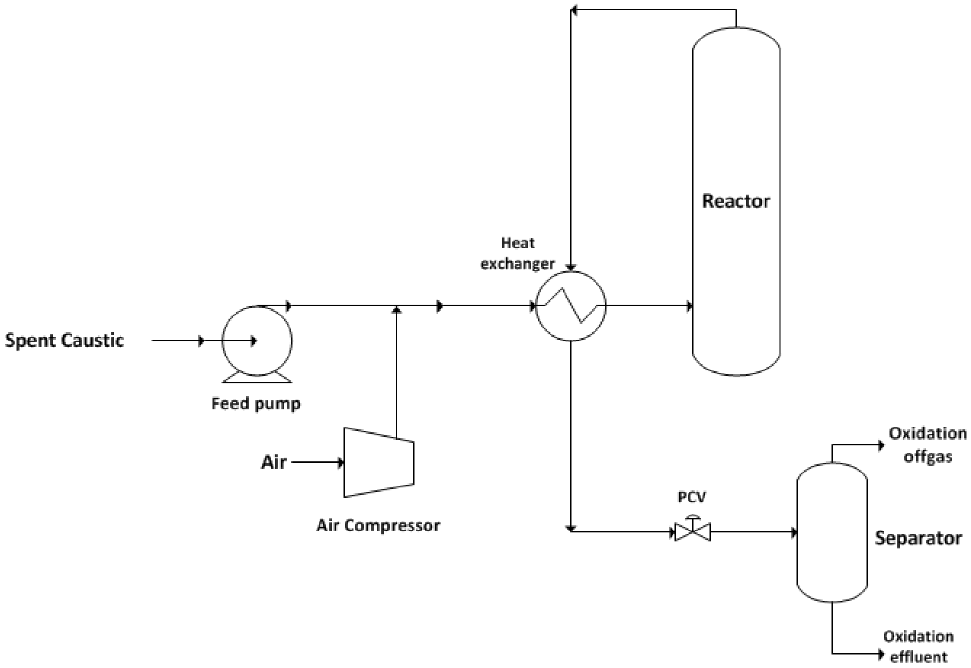

Figure 4.1 Flow Diagram for the WAO System

4.3.2 Chemical Reagent Oxidation

Chemical reagent oxidation of sulphidic spent caustic is done to make it environmentally acceptable. In this process, spent caustic is mixed with water-immiscible solvent (like pyrolysis gasoline) for extraction of polymerized hydrocarbons to avoid fouling in downstream equipments. The residence time is supplied to the mixture to get phase separation and thereafter the solvent phase is removed from the aqueous phase. The aqueous phase is then treated with air for oxidation in a process like WAO to reduce COD [14].

4.3.3 Catalytic Oxidation

In the process called catalytic oxidation, spent caustic is fed to an oxidizer with steam, air and carbondioxid. The oxidizer is a reactor with catalyst in the form of a fixed bed. The reaction takes place under mild conditions over the catalyst particles. After the reaction in the oxidizer excess air is separated from the aqueous stream. Sodium sulphides and bisulphides in the spent caustic are converted to sodium thiosulphates. Due to mild conditions only a small amount of sodium sulphate is formed. The treated solution has less COD, BOD and pH and can therefore be charged to the biological treatment plant without any harm. [15]

4.3.4 Pretreatment Technology

A pretreated spent caustic technology provides caustic free of all kinds of organics which can be further used for its sulphidic alkali content. In this process the spent caustic is treated with hydrogenated gasoline in a liquid-liquid extractor. The treatment with gasoline is followed by steam stripping. Pretreat also improves the efficiency of oxidation processes if this caustic is treated further with WAO etc. [16].

4.3.5 Biological Treatment

A new process for biological treatment of spent caustic has been developed. Oxidation of sulphidic caustic is done in an aerobic reactor containing sulphide oxidizing bacteria. The sulphides present in the spent caustic are converted partially to sulphate and elemental sulphur. Sulphides and mercaptans in spent caustic are biologically treated with a bacterium called Methylophanga Sulphidovorans. The conversion to elemental sulphur and sulphates is obtained by controlling the redox potential of the bacterial medium. [17]

4.3.6 Treatment with Regeneration

In this process spent caustic is oxidized with an air/ozone mixture at ambient temperature. The mixture contains 99% air and 1% ozone. The residence time in the reactor is 5 hours. After the oxidation in the reactor the solution is treated with ultraviolet radiation and passed through a micro- and nanofilter in series. The filtrate from the nanofilter is regenerated with caustic solution which is recycled back to the caustic solution tank. [18]

Chapter: 5 Conclusions and Discussions

In this section all the results and conclusions obtained from thesis work are reported.

5.1 Results

1. The injection of spent caustic instead of fresh caustic for crude neutralization is not the cause of residue and overhead water off specs.
2. Higher sodium content in the residue is often the result of filling up of the caustic vessels 1/2C-22 with incorrect concentration.
3. The chloride content in the overhead water goes off spec (>3ppm) after one or two days of caustic fill up in the 1/2C-22 vessel.
4. Higher chloride content in the overhead water happens mostly during the injection of spent caustic.
5. Late reporting from the lab can also cause off spec problems.
6. Maximum allowable chloride (1-3ppm) content in the overhead is less than recommended 5-10 ppm.
7. The average sodium content in the process water used for desalting purpose is very high (20 mg/l).
8. Sudden reductions in crude feed flow rates also results in higher sodium content in the residue.
9. The procedure of the dilution of caustic in the 1/2C-22 vessels to obtain 3% caustic is not good enough.
10. The level gauges on the 1/2C-22 vessels are sometimes not representative for the actual level.
11. The caustic injection pumps are overdesigned and operation at lower flow rates causes problems.
12. The nature of the caustic makes the system dirty which results in clogging of the injection pumps and level gauge. Also the piping of the caustic system is old and corroded leading to a lot of particles which blocks check valves in the caustic pumps.
13. The mixing of 3% caustic with desalted crude at the point of injection is not optimal but the booster pump should mix the caustic with the desalted crude relatively good.
14. The operating temperature of the desalter is less than required for an optimized operation.
15. The amount of water added to the crude feed for desalting is less than recommended.
16. The water content in the DHT feed causes corrosion in the heat exchangers in the DHT plant.
17. Improper mixing of caustic to the crude can result in high chloride content in the overhead even if the salt content in the crude is low.

5.2 Discussions and Conclusions

In this section all results reported in previous sections are discussed one by one in detail.

The use of sulphidic spent caustic for crude overhead corrosion control is recommended by consultant from Shell Global Solutions. From the beginning it was believed that injection with spent caustic to the crude would give higher sodium content in the residue and that the strength of the spent caustic would be weaker. It is clarified from analysis that problem with higher sodium content in the residue also arises when using fresh caustic. Analysis for off spec of sodium content showed that differences in sodium content of injected caustic and residue are comparable for both fresh and spent caustic. It is considered safe to use spent caustic for the crude overhead corrosion control as it is much diluted.

As the vessels 1/2C-22 are filled up with fresh or spent caustic, the concentrated caustic is first added to the vessel and then water is added for dilution. If the mixing of caustic is not good enough, different layers of caustic in the vessel with different concentration of caustic may form due to density differences. Concentrated caustic is denser than caustic of lower strength and will settle to the bottom. The caustic injection is done from the bottom of the 1/2C-22 vessel. In the beginning of injecting caustic from a new solution the caustic can be more concentrated than in the end before new caustic needs to be blended again. This will result in higher sodium content in the residue directly after a fresh solution of caustic has been blended in the C-22 vessel.

Higher chloride contents were recorded in the overheads about one or two days after the vessels 1/2C-22 had been freshly filled up. When the caustic injection is decreased to reduce the sodium content in the residue, no sample was taken to confirm that the adjustments made on the system were right. Lab samples on the system are normally taken only one time per day. Sometimes the injection rate is decreased so much that it isn’t sufficient to control chloride content in the overhead water.

Spent caustic has less strength than that of fresh caustic but it is diluted in the same way as fresh caustic. The dilution procedure makes spent caustic more diluted (<3%) than required which is sometimes not enough to control chlorides in the overhead water.

It is difficult to adjust the caustic injection rate on the basis of the lab results. Samples are only taken once in 24 hours and it is difficult to judge about the new adjustment before the samples have been analyzed. If wrong adjustments are made it comes to knowledge first after 24 hours.

For corrosion control in the overhead, the maximum allowable chloride amount is about 20-25 ppm in recommended practices. Shell Global Solutions recommends between 5 – 10 ppm. The limit used at Preemraff Göteborg for chloride in the overhead water is 3 ppm.

To maintain this lower chloride content in the overhead water more caustic needs to be injected. Higher injection rate of caustic means more sodium into the system and more chances of off spec of sodium in the residue.

A big amount of process water is added to the crude for desalting purpose. The sodium content in the process water is high which means that more sodium is introduced to the system. The use of this process water for desalting the crude feed increases the risk of high sodium contents in the residue.

When the feed flow rate to the plant is changed the caustic injection rate has to be changed as well. If the crude feed flow rate is decreased and the caustic injection rate remains the same, the same amount of sodium will end up in lower amount of residue which will increase the concentration of the sodium in the residue.

The initial strength of the caustic solution (spent or fresh) is sometimes unknown before dilution. To get an exact 3% solution during the filling up of the caustic vessel is almost impossible if the initial strength is not known. For dilution of caustic the level gauge on the vessel is trusted, but the level gauge is actually not considered trust worthy and easy to read.

The level gauge on the 1/2C-22 vessels mostly do not give representative readings of the actual level in the vessel. Crystals of caustic cause the level gauge to clog and behave improperly.

There is a calibration pot 1/2C-11 with a graduated measuring glass connected to it. If there is doubt about having a flow of caustic into the crude this graduated measuring glass on C-11 should be used to control the flow rate. Due to fouling in C-11 the graduated measuring glass stops function after some time and needs to be cleaned very often. The cleaning is difficult to do because of the nature of the corrosive content in the pot. The operators have stopped using this possibility to control the flow rate.

The caustic injection pumps 1/2G-9/10 are designed to operate at maximum stroke lengths. Only the frequency (RPM) should be changed to control the injection rate. Small flow rates of caustic are required so pumps are operated at almost half of the total stroke lengths because they are overdesigned.

The caustic forms crystals that may cause clogging of the level gauge on the 1/2C-22 vessels and the suction filters of the injection pumps. The caustic system is old and contains a lot of rust particles that can block the pump. It happens relatively often that the pumps stop working due to fouling. The operators clean the filters themselves, normally once every third month. Once a year a work order is written to let the maintenance personal clean the filter.

The caustic is injected to the desalted crude directly into the main stream. For proper neutralization of the crude, mixing of caustic solution with desalted crude is very important. If the caustic is injected directly into the crude, as it is done at Preemraff Göteborg, there is a possibility that caustic cannot reach all the HCl formed. The untreated HCl will result in higher chloride content in the overhead.

The temperature of the desalter is very important for controlling the chloride content in the overhead. The amount of salt present in the crude corresponds to the amount of HCl formed from the salt via hydrolysis at high temperature. To get high efficiency of the desalter (higher amount of salt removal) a high desalter temperature is desired.

Water added to the crude for desalting operation is less than recommended from Shell Global Solutions for better efficiency. High amount of water added will increase the salt removal efficiency which will provide better corrosion control in the overhead.

Most of the chlorides end up in the water phase. At high throughput the water is entrained to the DHT. It is recommended that the DHT feed should be free of water as it contains chlorides that cause corrosion in downstream equipments.

Although analysis of salts in the desalted crude does not indicate increased amounts of salts, the chloride concentration in the CDU overhead may be very high. This might be due to samples taken that aren’t representative or that the analysis method is not good enough. However, often when high chlorides are detected in the CDU overhead something is wrong in the desalter. It can be due to too low temperature or strong emulsion layer in the desalter. Another thing noticed is that when the caustic dosage was increased several hundred per cent the sodium content in the residue was still acceptable. The only reasons that can be considered are,

- The caustic sample is very week in terms of sodium content.
- The sample analysed for sodium content in the residue is not representative of the whole residue.
- The analysis method for sodium content is not right and some other analysis method should be considered.

Chapter: 6 Recommendations

In this section some recommendations are given for improvement on the system for better control of sodium and chloride contents in residue and overhead respectively.

6.1 The Caustic Dilution System

1. The caustic strength of fresh and spent caustic should be analysed before dilution in vessel 1/2C-22. After knowing the initial concentration of the caustic, the water quantity to be added can be calculated to get the required strength of caustic to be injected.
2. As the level gauge does not work properly due to caustic crystals, there should be some other kind of level indicator in the caustic vessels 1/2C-22. The better option for this may be some kind of radiation or sonar level meter.
3. For dilution, system flow meters can also be installed and used for dilution instead of trusting level meters. Flow meters can measure exact amounts of water and caustic added to be mixed.
4. During follow up on caustic injection it is noted that when vessel is full with diluted caustic, the caustic injected has higher concentrations as compared to when the vessel is closer to minimum level. The problem occurs due to improper mixing of water and caustic at the time of dilution. Caustic with high concentration rests at the bottom of the vessel and leaves the vessel before the less concentrated caustic at the top, as the injection line takes caustic from the bottom. This results in higher sodium content in the residue directly after the operators have prepared C-22 with new caustic On the contrary, the control of chlorides in the overhead will not be sufficient as the level approaches to minimum due to lower caustic strength. To get the better control, a new level and blending system is suggested as proposed in figure 7.1.

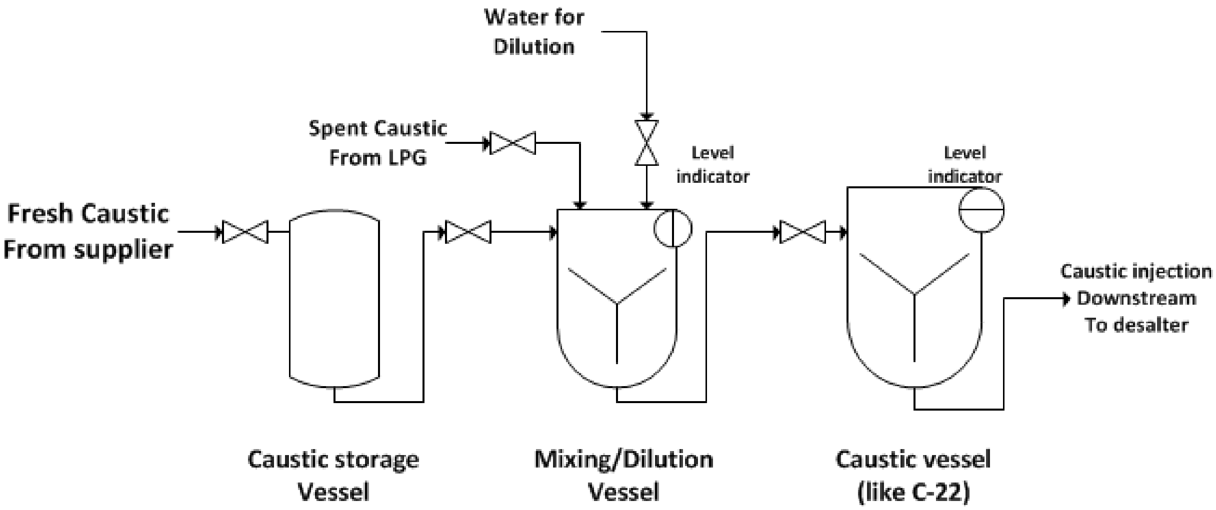

Figure 7.1 Suggested Caustic Dilution System

The caustic storage vessel is the vessel where fresh caustic is stored. The mixing/dilution vessel is the vessel where the caustic is diluted to 3%. The caustic vessel on the right hand side is a vessel just like C-22 from which caustic is taken for injection to the desalted crude. The level indicator in this vessel should be set in such a way that when the level decreases in the caustic vessel it should give a signal for the filling valve to open. In this way, the level in the caustic vessel can be maintained to a certain point. Mixing in the caustic vessel should be done from time to time to maintain homogeneous caustic solution.

6.2 Caustic Injection

For better mixing of caustic with the desalted crude, the caustic should be mixed with a slip stream, which then is added to the crude. The slip stream could be 1wt% of the main crude feed stream. Figure 7.2 shows how the mixing should be done with the slip stream.

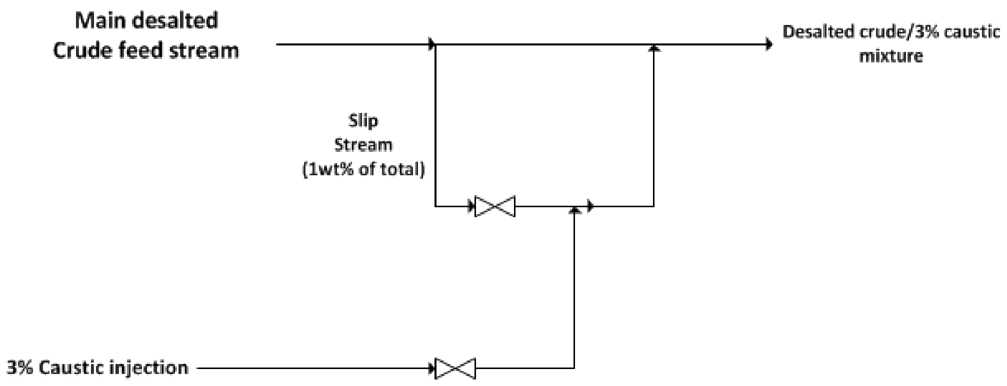

Figure 7.2 Mixing of Caustic with Slip Stream

6.3 Desalter Improvements

This section will explain what can be done to improve the performance of the desalter.

1. The amount of wash water added to the desalter could be increased to get the better efficiency.
2. Mixing of the crude feed with wash water can be improved by installing a static mixer along with a mixing valve giving an increased pressure drop around this adjustment. The better the mixing the better the desalter efficiency.
3. A mud wash system can also be installed in the desalter. Accumulation of mud can affect the performance of the desalter. Along with the mud wash system, an internal wash water recycle is also a good way to increase performance as it will promote better mixing of water and crude.

References

[1] . **D.A. Dando, D.E. Martin**., *A Guide for Reduction and Disposal of Waste from Oil Refineries and Marketing Installation:* CONCAWE Brussels November, 2003.

[2] . http://preem.se/templates/page____15.aspx [Cited 22-11-2010]

[3] . **Ara Bagdasarian, Jim Feather, Bob Hull, Ray Stephenson, Russell Strong.,** *Crude Unit Corrosion and Corrosion Control*: Water and gas processing technologies. 2006.

[4] . **William K. Stephenson, Joe Scott Walker Bordan W. Krupay, Sheraldean A. Wolesy-Iverson**, *Desalting Adjunct Chemistry:* September 19, 2009.

[5] . **Erik Fetter Pruneda Enrique Rivero Borrell Escobedo y Francisco Javier Garfias Vázquez***., *Optimum Temperature in the Electrostatic Desalting of Maya Crude:* Journal of Mexican chemical Society. March 15, 2005.

[6] . **Byoung –Yun Kim, Jun Hyuk Moon, Tae Hyun Sung, Seung/Man Yang, Jong Duk Kim.,** *Demulsification of Water in Crude Oil Emulsions by a Continuous Electrostatic Dehydrator*: Separation scince and technology, 2002.

[7] . **Jelle Bouma,** Preem GTB Spent Caustic and Desalter Review: Shell Global Solutions, June 23, 2010.

[8] . A document from US business council for sustainable development, *Examples of By-Product Synergy*: [ohiobps.org/documents/BPS_Examples.pdf][Cited 22-11-2010]

[9] . **Clay Maugans, Felix Huaman.,** *Disposal of Spent Caustic at the Repsol YPF Refinery in La Pampilla, Peru:* Environmental Conference Austin 24-25 September, 2007.

[10] . **Tania Mara S. Carlos, Clayton B. Maugans**., *Wet Air Oxidation of Refinery Spent Caustic: A Refinery Case Study:* NPRA conference Texas, September 2000.

[11] . *http://www.solidwaste.com/article.mvc/Formosa-Petrochemical-Relies-On-USFilter-Agai-0001?VNETCOOKIE=NO* [Cited 10-08-2010]

[12] . **Clyton B.Maugans, Claude Ellis.,** *Wet Air Oxidation: A Review of Commercial Sub-critical Hydrothermal Treatment:* US filter's Zimpro products USA, May 2002.

[13] . **C. Maugans, M Howdshell, S. De Haan**, A special report on *Update: Spent Caustic Treatment*: Hydrocarbon processing, April 2010.

[14] . **Robert L. DeRoeck, Allan R. Huntely**, *Spent Caustic Treatment:* Stone and Webster Engineering England, Sept 14, 1993.

[15] . An advertisement on *UOP Sulfide Oxidation Process for Treating Spent Caustic*: UOP Des Plaines U.S.A.

[16] . **Joseph M. Gondolfe and Sabah A. Kurukchi**., *Spent Caustic Treatment: The Merits of PRETREAT™ Technology:* Shaw Stone and Webster incorporated.

[17] . **Albert Joseph Janssen, Gatze Lattinga, Jan Bontsema, Gerrit Van Straten, Johannes Gijsbrecht Kuenen, Joyln Martha Maria De Zwart**, *Biological Treatment of Spent Caustics:* April, 2000.

[18] . **Stephen Z. Masoomian.,** *Apparatus for Treating and Regenerating Spent Caustic:* Nov 29, 1994.

[19] . **Nile D. Coble**, *Corrosion and Fouling Control*: UOP, Des Plaines, Illinois, U.S.A., 1992.

Appendix

A-1

Analysis Data for test run

Refinery Location:	**Preemraff Göteborg**				
Testrun date:	14/6 2010 1) and 2) sampled at 11 o'clock, 3), 4), 5) and 6) sampled between 12:30 -12:55.				

Sample	**Location**	**Property**	**Units**	**Preferred Method**	**Comments**	**Result**
(1)	Crude feed to desalter	Cl- content	mg/kg	(1)		15 mg/kg
		Na content	mg/kg	Atomic absorption/ICP		5 mg/kg
		total water	g/100g	Karl Fisher ASTM D-4928		573 mg/kg
(2)	Desalted crude	Cl- content	mg/l	(1)		3 mg/kg
		Na content	mg/kg	Atomic absorption/ICP		<1 mg/kg
		total water	w/w%	Karl Fisher ASTM D-4928		0,21%m/m
(3)	Total desalter wash water	pH				7.2
		H2S* content	mg/kg	ASTM D-4658		139 mg/l
		NH3** content	mg/kg	ASTM D 1426 method B		2,1 mg/l
		Cl- content	mg/kg	ASTM D-512		4 mg/kg
(4)	Total desalter effluent water, brine	pH				6.8
		H2S* content	mg/kg	ASTM D-4658	missed to order analysis	-
		NH3** content	mg/kg	ASTM D 1426 method B		3 mg/l
		Cl- content	mg/kg	ASTM D-512		153 mg/l
		oil content	mg/l	ASTM D3921	sampled 16/6 2010	>200 mg/l, not visible, grey
(5)	Water from CDU overhead accumulator boot	pH	-			6.7
		H2S* content	mg/l	ASTM D-4658		2 mg/l
		NH3** content	mg/l	ASTM D 1426 method B		2,2 mg/l
		Cl- content	mg/l	ASTM D-512		7 mg/l
		Fe content in water	mg/kg	NACE monitoring practice RP 0192-92		0,194 mg/l
(6)	Overhead hydrocarbon product from atmospheric tower	IBP	°C	ASTM D86		28.5
		T5%v	°C	ASTM D86		41.9
		T10%v	°C	ASTM D86		57
		T20%v	°C	ASTM D86		77
		T30%v	°C	ASTM D86		90.7
		T40%v	°C	ASTM D86		101.4
		T50%v	°C	ASTM D86		110.6
		T60%v	°C	ASTM D86		120.6
		T70%v	°C	ASTM D86		132.1
		T80%v	°C	ASTM D86		145.4
		T90%v	°C	ASTM D86		161.1
		T95%v	°C	ASTM D86		172.7
		FBP	°C	ASTM D86		192.8
		d15/4	kg/m^3		SG at 15 ^{o}C	729.9

A-2

Results of Desalter Review from Jelle Bouma

	Preem AB	**Shell Recommended /Best practice**
Desalting efficiency	80%	>90%
Grid rate low velocity	14m/h	10m/h
Mixing valve pressure drop	0.4 bar	0.5-0.7 bar
Mixing device	Mixing valve	Mixing valve+ static mixer
Desalter temperature	115°C	125-150°C
Emulsion thickness	1 triline	1 triline
Level measurement	2 AGAR probes	≥ 2 AGAR probes
Caustic injection type	Fresh/spent	Fresh/spent
Caustic injection location	Downstream desalter	Downstream desalter
Caustic injection how?	Directly in desalted crude	Premixed with desalted crude split stream
Water in desalted crude	0.2%wt	0.3%wt
Wash water flow rate	4% on crude	5% on crude
Wash water location	25% in upstream Hex 75% before mixing valve	25% in upstream Hex 75% before mixing valve
Effluent water pH	6.8	6-8
Effluent water oil content	200 ppm	< 300 ppm
Chemical Vendor reports	None	≥ 1x per week

B-1
Analysis of Water Supply from City

The water used at Preemraff GOR is coming from Alelyckans Water Purification Plant.
Source: based on analysis of water from Alelyckan between Jan-Apr 2009.

	Unit	Min-Max	Average
Temperature	^oC	0,6 – 11,3	1,6
Conductivity	mS/m	17,9 – 21,1	19,1
pH		7,7 – 8,1	7,9
Permanganate KMnO4		Not tested	
COD-Mn	mg/l	<1 – 1,5	1,2
Colour, Pt	mg/l Pt	<5	<5
Turbidity	FNU	<0,05	<0,05
Alkalinity, HCO3	mmol/l	0,76 – 1,0	0,91
Iron, Fe	mg/l	<0,01	<0,01
Aluminium, Al	mg/l	0,012 – 0,073	0,017
Sodium, Na	mg/l	13 – 26	20
Manganese, Mn	mg/l	0,002 – 0,004	0,003
Calcium, Ca	mg/l	7,0 – 22	19
Phosphor, P	ug/l	<5	<5
Chlorides, Cl	mg/l	7 – 11	9
Magnesium, Mg	mg/l	1,5 – 1,7	1,6
Sulphur, S		Not tested	
Sulphate, SO4	mg/l	26 – 29	28
Fluoride, F	mg/l	<0,1	<0,1
Silica, SiO2		Not tested	
Oxygen saturation		Not tested	
Corrosion rate		Not tested	

C-1

Analysis of C3 Wash

Date of sampling: August 23, 2010.
Date of Reporting: August 31, 2010.

Test	Method	Unit	Result
Total alkalinity	ASTM E291		
Alkalinity as sodium oxide		Mass%	10.52
Alkalinity as potassium oxide		Mass%	15.99
Total organic carbon (TOC)	NEN_N 1484	mg/L	92000
Chemical oxygen demand (COD)		mg/L	260900
Phenol Content		mg/kg	6.5
Hydrogen sulphide and mercaptan sulphur	SMS 304		
Hydrogen sulphide as S		mg/kg	13930
Mercaptan, as S		mg/kg	8810

Analysis of C4 Wash

Date of sampling: June 21, 2010.
Date of Reporting: July 06, 2010.

Test	Method	Unit	Result
Total alkalinity	ASTM E291		
Alkalinity as sodium oxide		Mass%	7.13
Alkalinity as potassium oxide		Mass%	10.84
Total organic carbon (TOC)	NEN_N 1484	mg/L	150000
Chemical oxygen demand (COD)		mg/L	510700
Phenol Content		mg/kg	4.6
Hydrogen sulphide and mercaptan sulphur	SMS 304		
Hydrogen sulphide as S		mg/kg	100
Mercaptan, as S		mg/kg	570

The strength of the spent caustic can be calculated from alkalinity in sodium oxide. According to ASTM E291 the sodium hydroxide is calculated with the formula,
%mass = 1.2907 x %Na_2O.

The strength of the C3 wash was calculated to be 13.57 wt. % compared to the analysed caustic strength to be 7.8 g/100 ml. The strength in the C4 wash was calculated to be 9.2 wt. % compared to the caustic strength analysed 10.2 g/100 ml.
The strength with respect to Na_2O is OK for both spent caustic (from C-3 and C-4 wash).