It takes a team
INTERPROFESSIONAL PROJECTS PROGRAM

IPRO 346

BP Whiting Refinery Expansion: Developing Lake Michigan Wastewater Cleanup Options

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Final Report

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1.0 Introduction

IPRO346 focuses on familiarizing itself with British Petroleum's (BP) wastewater treatment plant (WTP) for its oil refinery in Whiting, IN. Specifically, this IPRO analyzes the current permits and their stipulations regarding the amount of ammonia and total suspended solids (TSS) in the wastewater being dumped in Lake Michigan. Ultimately, possible methods and designs are devised to reduce the levels of ammonia and TSS remaining in treated wastewater. These designs take the form of a process flow sheet with a computer simulation to model the designs. At the culmination of this IPRO we have several different models for possible upgrades to the Whiting refinery wastewater treatment plant to reduce the levels of ammonia and TSS in the wastewater entering Lake Michigan as well as a cost to implement each solution.

2.0 Background

For the past three years BP has been planning a $3.7billion upgrade to its Whiting refinery to process Canadian heavy crudes. This upgrade will provide several hundred new jobs in the Whiting area and allow the refinery to process 90% Canadian heavy crude instead of mixing it with a minimum of 70% light crude, primarily from the Middle East. Not only will this result in less crude oil coming from politically unstable regions, but it will also allow the plant to increase its gasoline and diesel production by 15%. Unfortunately, the Canadian heavy crude contains a significant amount more nitrogen and sulfur which, with the ever increasing standards for gasoline and diesel, need to be removed. In order to move forward with this project, BP filed for a new permit with the State of Indiana to allow the Whiting refinery to increase the allowed levels of ammonia and TSS in its wastewater to be increased by 50%. This new permit was approved both by the State of Indiana and by the Environmental Protection Agency (EPA) and falls well under the federal maximum for ammonia and TSS waste. However, when the media and public hear of the new permit, there was a public outcry against any increase in the disposal of waste into Lake Michigan. Because of the massive outcry, BP decided that, although it knew of no current technology that could remove ammonia and TSS down to the standards set by the original permit, BP would not implement its design for the Whiting expansion until they could come up with an acceptable design for the wastewater treatment plant which would not increase the amount of ammonia and TSS being dumped into Lake Michigan. If no solution presented itself BP stated that it would scrap the entire project thereby losing nearly all of the $3.7billion budgeted for the expansion.

3.0 Purpose

The overall purpose of this IPRO is to find an alternative design for the wastewater treatment plant that will allow BP to continue with their projected refinery upgrade.
This design will

(1) decrease the emissions of the plant,
(2) remain fiscally reasonable, and
(3) consider and employ a high standard of ethics.

4.0 Research Methodology

In order to solve this problem, the goals of the team are
(1) to gain a better understanding of the problem,
(2) to use this understanding to create several different models, and
(3) to determine the feasibility and economic viability of the models.
To achieve this, the work for the semester has been broken into two Phases.

<u>Phase 1: Research</u>
During this phase, the team will focus on gaining a deeper understanding of the problem and possible solutions. This will be achieved through separating the team into sub teams which will take an in-depth look at various aspects of the problem and then report back to the team through weekly group presentations.

<u>Phase 2: Development</u>
Once several solutions have been established, the sub teams will shift their focus from research to development. This will include developing a process flow sheet for each solution, creating a model to simulate the process, and to determine the feasibility and economic viability of each solution.

5.0 Assignments

The IPRO group split into a new set of sub teams in order to prepare the deliverables. One group gathered information on the current statistics for BP's wastewater. Another group prepared a model of BP's Membrane Model. A third group wrote the final report, and the last group modeled the new options that BP at Whiting has chosen for its improved wastewater treatment.

The team structure (Fig 1.1), Gantt chart (Fig 1.3), and a schedule of specific tasks, their duration, and the associated dates (Fig 1.2) can be seen below.

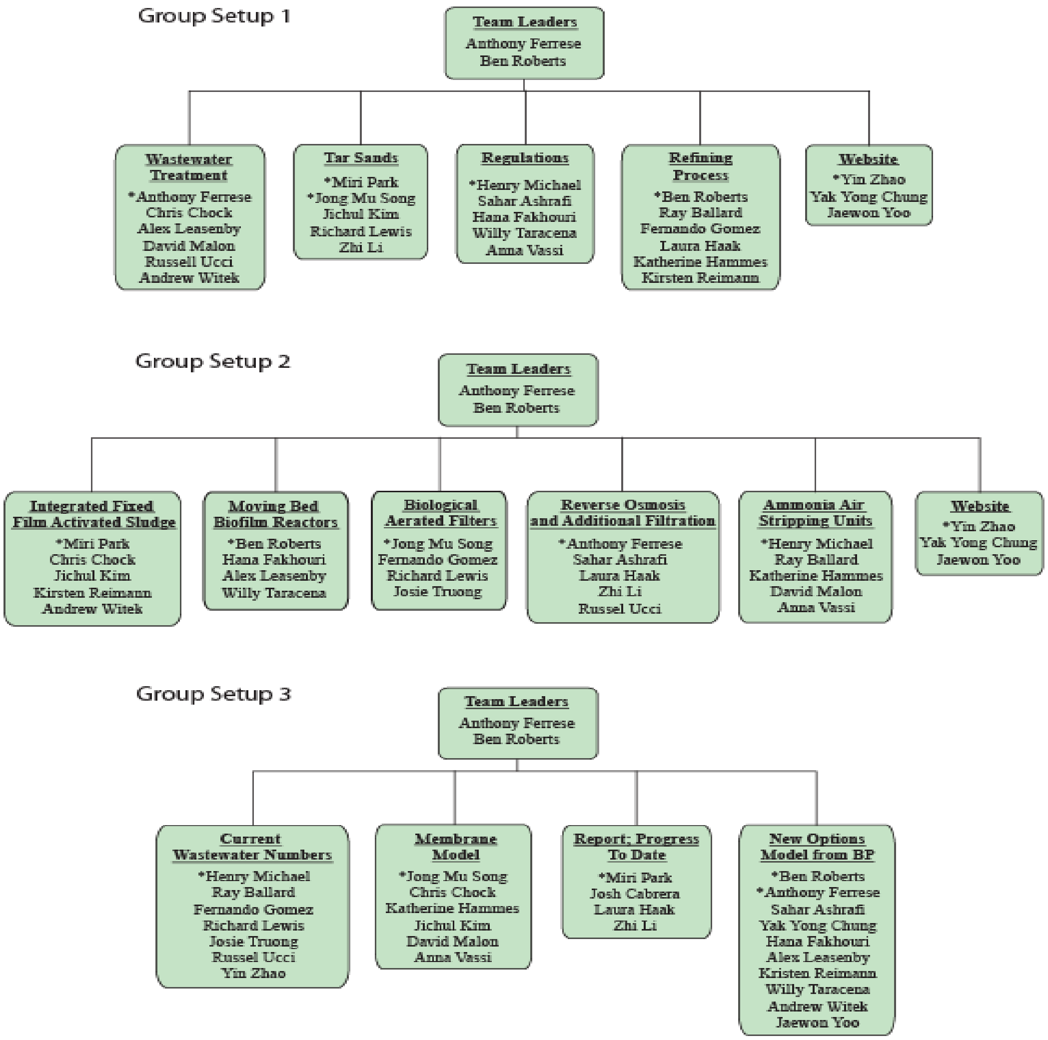

Fig 1.1, Team Structure

Task Name	Duration	Start	End
Refinery Background Research	31 Days	1/29	2/29
Technical Options Research	32 Days	2/29	4/01
Current Wastewater Numbers	17 Days	4/08	4/25
Website	64 Days	1/29	4/08
Meeting Minutes	77 Days	1/29	4/15
Membrane Model	17 Days	4/08	4/25
New Options Model	17 Days	4/08	4/25
Project Plan	10 Days	2/12	2/22
Midterm Oral Presentation	7 Days	2/26	3/04
Code of Ethics report	14 Days	2/22	3/07
Midterm Written Report	11 Days	3/04	3/15
Final Report	24 Days	4/08	5/02
Abstract	17 Days	4/08	4/25
Poster	24 Days	4/08	5/02
Final Presentation	28 Days	4/08	5/06

Fig 1.2, Task Names and Schedules

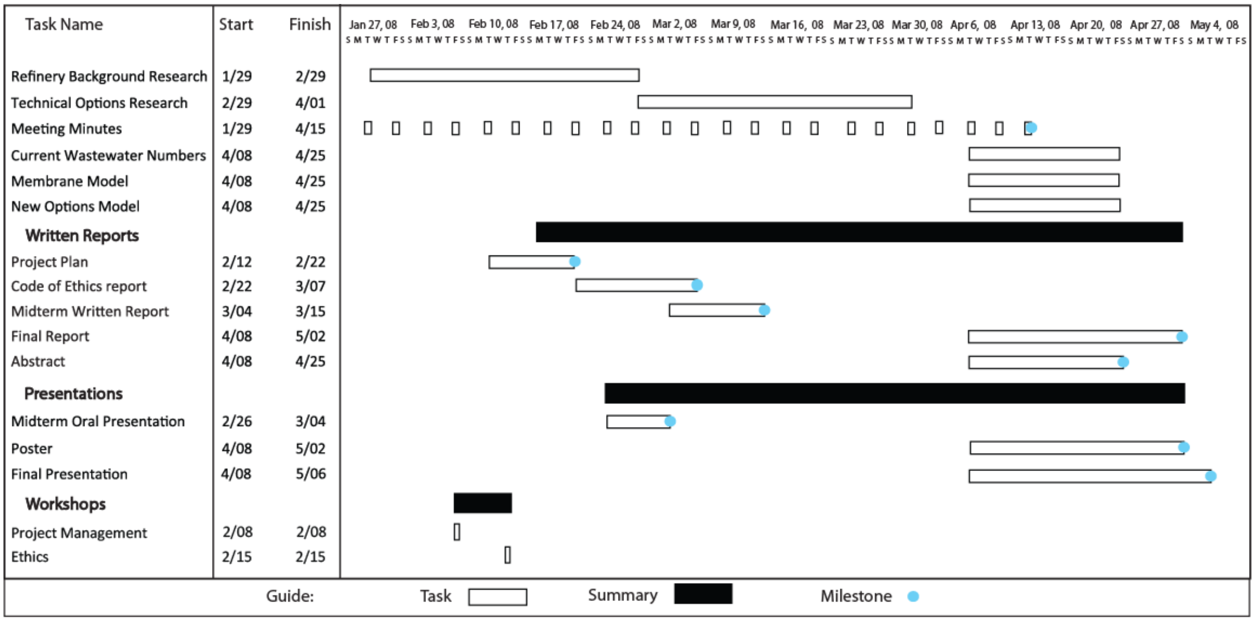

Fig 1.3, Gantt Chart

6.0 Learning Objectives

Teamwork

Team structures were well developed and utilized in IPRO 346. It was necessary for old groups to be dissolved and split into new groups. This recurring process created a more fluid structure which gave the opportunity for more interaction between all team members. It was up to the members to volunteer and assist with the writing of reports and preparation for presentations. For the peer evaluations, all team members evaluated those who they worked with. This allowed them to acknowledge team members who worked hard for the group and appreciate each other's work.

Some problems arose during the meetings of subgroups, where team members would not communicate with team leaders about absence. This problem was overcome through the efforts of team leaders to emphasize to group members the importance of communicating better.

Communication

There were two IPRO meetings scheduled regularly each week for all team members to attend. Further meetings among subgroups were coordinated by the sub-team leaders. However, the crucial research topics for each sub-team were covered during the regular meetings. With sub-group members being delegated tasks in this manner there was frequently no need for additional meetings aside from when a presentation was to be prepared. Email was also a major communication tool for the group. When changes had been made to team structure or new areas were to be researched team leaders would send out emails to inform group members who may have missed the meeting. Also email was useful to check team progress when there were long periods of time in which group members were researching.

Occasionally email was used as the primary means of correspondence amongst team members. When there were problems in getting team members to respond to emails from team leaders it became necessary for the leaders to address the issue during one of the regularly scheduled meetings. This seemed to solve the problem.

Ethical Behavior

Since this IPRO is of a controversial nature and the advisor to the project is an employee of BP, the motives of this group has been called into question. However the IPRO is not sponsored by BP and the advisor gave no advice aside from tips on what would be good areas to look into in order to gain an understanding on wastewater treatment in a refinery. Although this situation may appear to cause bias none of the group members felt influenced by the relationship of the advisor with BP and the advisor did not make his own feelings toward the situation known to the team. Information on BP Whiting was gathered from a wide variety of sources representing different perspectives.

Within the team there was no unethical practice. Team members were at all times respectful of one another and worked towards the teams goal, not their own.

7.0 Obstacles

A main learning component in any IPRO team is working together in an organized fashion. It was apparent from the very beginning this would be a challenge given the size of our IPRO team. IPRO 346 is comprised of 30 members consisting of mostly CHE 296 sophomores. CHE296 students are lower chemical engineering classmen whose main objective is to understand how a team works as a whole. It was apparent from the very beginning this would be a challenge given the size of our IPRO team. IPRO 346 is comprised of 30 members consisting of mostly CHE296 sophomores. CHE296 students are lower chemical engineering classmen whose main objective is to understand how a team works as a whole. After identifying the problem of having too large of a group the seniors decided that in moving forward we would divide the team into subgroups allowing for smaller groups that would allow the team to achieve a higher concentration in completing assigned tasks.

After identifying the problem of having too large of a group the seniors decided that in moving forward we would divide the team into subgroups allowing for smaller groups that would allow the team to achieve a higher concentration in completing assigned tasks. A main learning component in any IPRO team is working together in an organized fashion. As with every IPRO team it is a collection of students with varying skill sets and concentrations. Thus a problem exists in delegating tasks to students that meshes with their abilities. In order to reconcile this with such a large group IPRO 346 had each team member upload a written document outlining their skills and interest so that we may more effectively delegate tasks.

IPRO 346 is working a highly controversial topic, especially considering the proximity to that of the source of the problem, BP-Whiting, IN Refinery. With topics of this notoriety everyone, including members of IPRO 346, have their own opinion. Having said that students have become increasingly passionate about their views, some students believe BP is acting responsible with regards to increased effluent levels into Lake Michigan, while others feel BP is acting irresponsible and should be a leader in reducing pollution. Thus a bias exists in the group on both sides and it is important as members of this project to know all the facts and understand both sides. In order to resolve this issue, students were asked to read many factual articles that were as unbiased as possible in order to understand the facts. This allowed students to grasp the problem in a more objective view. Although students of IPRO 346 will always have their own opinions we felt it was important to overcome the bias in keeping an objective view of the problem.

8.0 Results

A. **First Research Groups; Refining, Tar sands, Regulatory, Current Regulation, Refining**
IPRO346 researched on backgrounds of wastewater treatment. We divided teams of five which are refining, tar sands, regulatory, current regulation, and refining groups to educate ourselves on the background knowledge.

Refining

There are a few refining units that were examined one of them was an amine gas treater. The process is also known as acid gas removal and gas sweetening. It removes sour gases such as hydrogen sulfide and mercaptans from the liquid hydrocarbons during the gas treating process. Amines used in removing hydrogen sulfide and mercaptans include: Monoethanolamine, Diethanolamine, Methyldiethanolamine, Diisopropylamine, and Diglycoamine. In the absorber unit of the treater an amine solution is used to absorb the sour gases and produces a sweetened gas stream. This amine solution then flows through the regenerator to produce "lean" amine that is recycled for reuse. he stripped gas from the regenerator is concentrated with the sour gasses, primarily composed of hydrogen sulfide. This gas stream then undergoes a Claus process which converts the hydrogen sulfide to elemental sulfur. Amine treatment is also used in the process of removing excess carbon dioxide during the steam reforming process of hydrocarbons to produce hydrogen to be used for industrial synthesis of ammonia.
Another unit was a cooling tower. These remove heat by circulating cooling water. Heat transferred to the water causes it to evaporate. The tower dissipates the evaporated water into the atmosphere. There are several different configurations: Cross-flow: Air flow is perpendicular to water flow and as air enters the tower through one vertical face it flows past the water flow. Moist, heated air flows out the top of the tower and the cooled water collects in the hot water basin. Counter-flow: air flow enters the tower in an open area below the fill media and is drawn up through the tower. As the hot water enters the tower it is sprayed out and flows downward through the fill, heating and evaporating into the upward flowing air. Another unit is wastewater.
Waste water treating systems consist of API separators, dissolved air flotation units, etc. to meet wastewater disposal standards. An API separator is a device that separates the oil and suspended solids from the waste water by taking advantage of the different specific gravities of the substances. Dissolved air flotation is a process that clarifies the wastewater by removing suspended solids and oil by first dissolving air into the water under pressure and releasing the air at atmospheric pressure into a flotation tank. This released air forms bubbles which adhere to the suspended matter and brings it to the surface to be removed by a skimming device. Activated sludge is a process in which pure oxygen is bubbled through the wastewater along with organisms to develop a biological floc which reduced organic content in the wastewater. This mixture is then discharged into settling tanks where the sludge produced in the process will settle and be separated to be reused.
An additional unit is steam reforming. Steam reforming, also known as steam methane reforming, is a method of producing hydrogen from hydrocarbons. This hydrogen is to be used in the hydro cracking process. At high temperatures while in the presence of a metal based catalyst, such as nickel, steam reacts with methane yielding carbon monoxide and hydrogen.
The last unit looked at was the Hydro cracker. The Hydro cracker uses hydrogen to upgrade large, complex organic molecules and hydrocarbons which are found in the sulfur and nitrogen hetero-atoms into simpler molecules by breaking the carbon-carbon bonds. The process

produces saturated hydrocarbons. Variations in conditions such as temperature, pressure, and catalyst activity result in different types of hydrocarbons ranging from ethane, LPG to heavier hydrocarbons which are primarily composed of isoparaffins.

Tar Sands

Tar sands are deposits of bitumen, which is a heavy, black, and viscous crude oil. It must be rigorously treated to convert it into an upgraded crude oil before it can be used by refineries to produce gasoline and diesel fuels. Bitumen is also substantially heavier than other crude oils, which poses a problem for transportation and refining of the oil for use. This type of crude oil can be found in three places in Canada, where BP is looking to get the bitumen. There are three places in Alberta being looked at - the Athabasca, Peace River and Cold Lake regions - and this region covers a total of nearly 140,200 square kilometers. Bitumen is described as a mixture of organic liquids that is highly viscous, black, sticky, and entirely soluble in carbon disulfide. It is composed primarily of highly condensed polycyclic aromatic hydrocarbons. Naturally occurring or crude bitumen shows up in the form of a sticky, tar-like form of petroleum which is so thick and heavy that it must be heated or diluted before it will flow. Most types of bitumen contain sulfur and several heavy metals such as nickel, vanadium, lead, chromium, mercury and also arsenic, selenium, and other toxic elements.

Extraction Method 1: Cyclic Steam Stimulation Process (CSS)

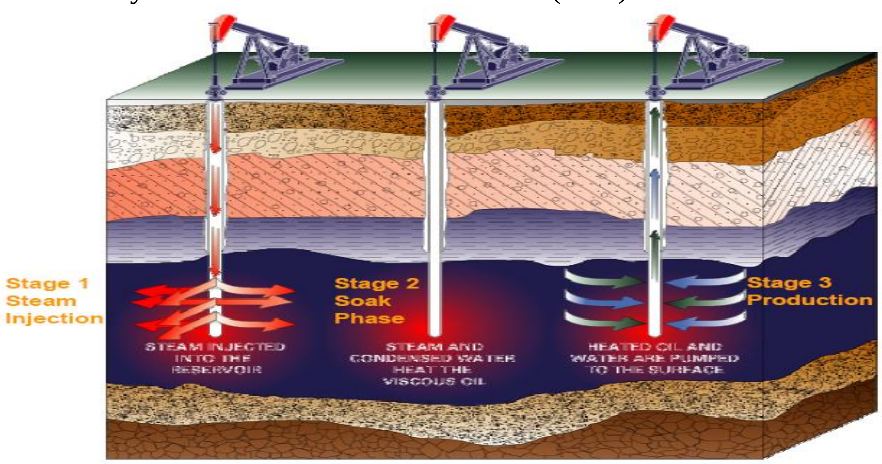

Fig 2.1, 3-Step Model of CSS[1]

Cyclic Steam Stimulation Process is one way to extract tar sand from the ground that has been researched. The Cyclic Steam Stimulation Process consists of 3 stages: injection, soaking and production. The process can be quite effective, especially in the first few cycles.
It is typically only able to retrieve approximately 20% of the Original Oil in Place (OOIP). It is quite common for wells to be produced in the cyclic steam manner for a few cycles before being put on a steam flooding regime with other wells. The well is first injected with steam and then the steam and condensed water heat the oil. The last phase is the pumping of the heated oil and water back to the surface for refining.

Extraction Method 2: Steam assisted gravity drainage (SAGD)

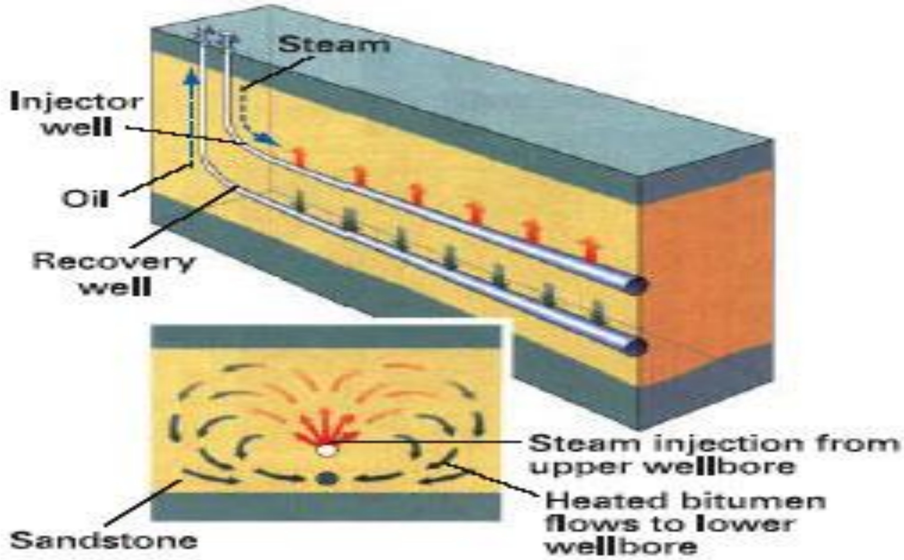

Fig 2.2, Visual Summary of SAGD[2]

Steam assisted gravity drainage is another way of extracting the tar sands. This process is an enhanced oil recovery technology for heavy crude oil and bitumen. Two parallel horizontal oil wells are drilled in the formation of the system. The upper well injects steam and the lower one collects the water that results from the condensation of the injected steam and the crude oil or bitumen. The injected steam heats the crude oil or bitumen and lowers its viscosity which allows it to flow down into the lower wellbore. The large density contrast between steam on one side and water / hot heavy crude oil on the other side ensures that steam is not produced at the lower production well.

Regulatory

Due to the concern about TSS (total suspended solids) production, regulatory requirements are being designed to limit the amount of this byproduct that can be released into Lake Michigan. This is an issue for BP, since the Whiting refinery is trying to use crude oil from Canada, which will produce more TSS, but public outcry has made them decide to try to design a new way to use the Canadian oil and still have the same amount of TSS permitted by the regulations already in effect. This change would require changes in design of the plant in order to lessen the amount of TSS. The current regulations, as well as predicted future ones, were studied in order to determine the limits on the amount of TSS which could be emitted. This amount affects how much of a change in BP’s refinery would be needed.

Current Regulations

Concerns regarding TSS emissions are becoming the subject of many more media discussions then ever before. The subject is strongly making its way into the main stream and is gaining the attention of investors and chemical companies. Since the proposed TSS emission increases are going into Lake Michigan, public opinion has not been favorable, even though the emissions would still be below the federal limit. This has caused BP to consider finding a way to keep emissions the same, yet use Canadian crude oil, which is heavier and more viscous. BP has already addressed problems concerning ammonia emissions, so the focus of the regulations is on

TSS. There are certain water quality standards that BP has to meet with the new system. There are three tiers to be considered. Tier 1 maintains and protects existing uses and water quality conditions necessary to support such uses, tier 2 maintain and protect “high quality” waters -- water bodies where existing conditions are better than necessary to support CWA § 101(a)(2) "fishable/swimmable" uses, and tier 3 maintain and protect water quality in Outstanding State Resource Waters (OSRW). The current and proposed TSS effluent limitations for the BP Whiting refinery are shown in the table below;

TSS Effluent Limits

	Monthly Average	Daily Maximum
Existing	3,646 lbs/day	5,694 lbs/day
Proposed	4,925 lbs/day	7,723 lbs/day

The EPA has also been pushing to eliminate mixing zones that include bio-accumulative chemicals, such as mercury. The BP permit does not allow a mixing zone for mercury. The mixing zone authorized in the BP permit applies to TTS and ammonia, and federal and state law authorizes mixing zones for these parameters. IDEM is proposing to allow a discharge induced mixing zone through a diffuser in Lake Michigan which produces a mixing volume of lake water that is 37.1 times greater than the discharge volume of 21.4 million gallons per day from Outfall 001. The alternate mixing zone will encompass a 182 feet radius from the diffuser. BP has three years to install the diffuser to create an alternate mixing zone. The reporting of limits must begin as soon as possible, but no later than 3 months after the effective date of the permit.

<u>Wastewater</u>

A typical waste water treating system consists of API separators, dissolved air flotation units, and activated sludge to meet wastewater disposal standards. An API separator is a device that separates the oil and suspended solids from the waste water by taking advantage of the different specific gravities of the substances. The dissolved air flotation unit uses a process that clarifies the wastewater by removing suspended solids and oil by first dissolving air into the water under pressure and releasing the air at atmospheric pressure into a flotation tank. This released air forms bubbles which adhere to the suspended matter and brings it to the surface to be removed by a skimming device. The activated sludge is a process in which pure oxygen is bubbled through the wastewater along with organisms to develop a biological flock which reduced organic content in the wastewater. This mixture is then discharged into settling tanks where the sludge produced in the process will settle and be separated to be reused.

B. <u>Second Research Groups; BAFs, IFAS, MBBR, Ammonia Stripping Unit, Leopold Elimi-NITE Denitrification System, Corrugated Plate Interceptors</u>

Second Research Groups were divided into 6 sub-groups so that we can learn about the technologies that remove Total Suspended Solid(TSS) and Ammonia. The technical options are Biological Aerated Filters(BAFs), Integrated Fixed-film Activated Sludge(IFAS), Mixed Bed Biofilm Reactors(MBBR), Ammonia Stripping Unit, Leopold Elimi-NITE Denitrification System, and Corrugated Plate Interceptors. We evaluated each technologies and make one choice that we are going to model.

<u>BAFs (Biological Aerated Filters)</u>

i) BAFs; The Biological Aerated Filter is used in aeration, filtration, interception and backwash with the contact oxidation process. The biological film formed on the medium surface when wastewater flew into tank. At the same time, air flew into tank from aerating pipe. The wastewater can be cleaned by organics degradation under the metabolism of microorganism. Solid substance and biological sludge can be intercepted by filtrate medium. The backwashing starts when pressure loss over a set value. BAF has characteristics of being a small size and its cost is low. Also it has strong capability of resisting sudden load change and low temperature tolerance so that it is easy to form biological film.

ii) BIOSTYR; The BIOSTYR system is an up-flow submerged fixed-film filter that biologically treats carbonaceous and nitrogenous wastes (CBOD, NH4-N, NO3-N) and removes insoluble pollutants (TSS) through the filtering mechanism of the process. BIOSTYR prevents the nozzles from clogging and provides easy access for nozzle maintenance or replacement. The counter-current backwashing sequence ensures efficient removal of accumulated solids. And the backwash water is supplied from a common reservoir above the filter cells, eliminating the costs associated with backwash pumping. Used backwash water is not exposed to the atmosphere, so the potential for odor problems is dramatically reduced. For the BIOSTYR System Cost, the calculations are based on annual average flow and loads; and 30 of 40 cells will be in filtration. The present worth costs were calculated for a life cycle of 20 years and with an interest rate of 7%. - The cost of electricity was assumed to be 0.0812 $/KWhr. - The present worth factor was estimated to be 12.8.

Operating Factor	Run Time (hr/yr)	Energy (KWhr/yr)	Annual Cost ($)	Present Worth Cost ($)
Process Air Blowers	4745	18400000	1494080	19124224
Backwash Air Scour Blowers	730	1700000	138040	1766912
Feed Pumping	8760	14300000	1161160	14862848

Fig 3.1, Energy Requirements and Costs Incurred[3]

From The table in Fig 3.1, we can see that the total Annual Operating Cost is $ 2793280, while the total Present Worth Cost is $ 35753984

Item	Cost ($)
BIOSTYR System Cost	35753984 + or - 20%

Fig 3.2, Summary of BIOSTYR system cost

Integrated Fixed Film/Activated Sludge Systems (IFAS)

IFAS definition; IFAS systems add the benefits of Fixed Film systems into the suspended growth Activated Sludge process. Activated Sludge has process flexibility and provides a high degree of treatment. Fixed Film processes are inherently stable and resistant to organic and hydraulic shock loadings. Placing Fixed Film media into Activated Sludge basins combines the advantages of both of these systems. The additional biomass provided by placing Fixed Film media directly into the suspended growth reactor does not increase clarifier solids loading (a factor that often limits the treatment capacity of existing Activated Sludge systems).
IFAS technology addresses the need for increasing Activated Sludge plant capacity, with little or no added tankage, because of the additional fixed biomass. The fixed biomass also contributes to the ability of the process to respond to organic or hydraulic shock loads and to recover from

upsets. There are several types of media used to fix the biomass in the Activated Sludge basin. They include “Dispersed Media” entrapped in the aeration basin, and “Fixed Media,” such as structured sheet media or knitted fabric media that is placed in the aeration basin.

IFAS Applications; IFAS technology has been incorporated into both municipal and industrial wastewater facilities (new and upgrade) in many variations of suspended growth systems. When included in new plant design, reduced tank volumes result. In retrofit applications, increased treatment capacity may be realized, along with the other benefits of fixed film type processes.

APPLICATIONS OF IFAS SYSTEMS	
PROCESS	DESIGN CONSIDERATIONS
New Plant Construction	• Design tank and aeration system geometry to incorporate fixed or dispersed media • Add equipment for dispersed media reactor, if selected.
Existing Plant Retrofits	• Add pre-fabricated fixed modules to aeration tanks. • Evaluate aeration for increased BOD removal and biomass respiration. • Add equipment for dispersed media reactor, if selected.
Nitrification/ Denitrification Conversions	• Add biomass to increase Solids Retention Time (SRT) to value needed for nitrification and convert to appropriate BNR process. • Add modules to provide more biomass without additional tankage.

Fig 4.1, Applications of IFAS Systems[4]

Mixed Bed Biofilm Reactor (MBBR)

A mixed bed biofilm reactor is a relatively new technology that helps remove ammonia out of an industrial wastewater process. The MBBR application uses plastic media, known as biocarriers, to transport large communities of microorganisms in a stream of the applicable wastewater. These biocarriers are specifically designed to have a high surface area allowing for maximum contact between the microorganisms and the wastewater stream thus removing a higher amount of ammonia.

As these biocarriers flow within the wastewater stream they are spontaneously hit with air bubbles due to an aeration grid allowing for suspension and appropriate mixing. In the reactor these biocarriers take up approximately, depending on the type of MBBR, 30%-67% of the reactor volume. The biocarriers range in length from 31 to 50mm and from 31 to 60mm in diameter.

MBBR is a promising technology due to the footprint of the unit and the potential effectiveness in removing ammonia from a wastewater stream. Estimates have been said to be in the range of 85-95% removal of ammonia.

MBBR faces hurdles in potential environments due to its dependence on temperature (41F-86F) and its vulnerability to pH as well as an need of nutrients to be effective. The MBBR process is ideal for stream concentrations of 8g/L-10g/L ammonia that could pose a problem in some industrial applications.

Ammonia Air Stripping Unit

Ammonia Air Stripping units remove up to 99% of ammonia from a liquid stream containing ammonia, water, and volatile organic liquids by exposing the liquid stream to air in a large packed distillation column. The liquid inlet is distributed equally with a spray nozzle over a packing membrane of large surface area in the tower. An air blower is located below the packing and sprays air up through the tower. As the liquid stream trickles through the packing material, the air stream removes the volatile chemicals and ammonia from the stream in a gaseous form that leaves the top of the column. Once the water trickles to the bottom, it exits as clean water in the outlet stream. Thus, clean water is produced, and ammonia is removed from the stream. While very successful at removing ammonia from the stream, several problems result from the aforementioned system. For the stripping unit to work in its described form, the liquid inlet may not contain any compounds except water, ammonia, and volatile chemicals that can be removed easily with the air. Also, once ammonia is removed from the liquid, it is still in gaseous form and must not be disposed into the atmosphere. Therefore, two techniques for containing ammonia in a solid, clean form include: 1) combine it with other compounds to create a fertilizer, and 2) use thermal destruction, outputting only Nitrogen into the atmosphere. Both have extremely high initial costs and maintenance costs, and so the large financial cost for a company planning to remove ammonia from its output stream still exists.

If such a stream (containing only ammonia and water) exists, then the latter techniques for containing ammonia should be used for clean outputs to result, regardless of high costs. However, after discussion with Beyond Petroleum (BP), it appears that a stream of these parameters does not exist. Instead, BP is planning to use a similar stripping unit that removes both sulfur and ammonia, referred to as a sour water stripping unit, which is a much more efficient unit for removing pollutants. The unit is the most expensive upgrade they plan on building, with estimates ranging from 70 to 72 million dollars. While this is a very costly upgrade, it will remove a high percentage of ammonia and sulfur from the stream.

Leopold Elimi-NITE Denitrification System

The elimi-NITE system was originally looked as part of the technical options that were mentioned in the Tetra-Tech report as a way to remove the ammonia (or nitrogen compounds) from the wastewater stream. In its basic form it is simply a porous media gravity filter where gravity is used to force the water through a porous substrate. Most commonly this substrate is differing sizes and densities of gravel, but in the elimi-NITE system it is a mono-media . Normally gravity filters are used to filter out suspended solids, but the elimi-NITE system combines the filtering capability with microbial growth to efficiently remove nitrogen based compounds as well. For this to work, a carbon source (food for the microbes) must be added to the filter influent to allow an organic substrate for the denitrifying microbial culture to grow. These microbes then feed off of the nitrogen (such as ammonia) that is in the feed stream and converts it to nitrogen gas. The bubbles of nitrogen gas are trapped in the porous media under the downward pressure of the flow until a backwash cycle is completed.

One of the drawbacks to any type of gravity filter is that when it removes the suspended solids (and in the case of elimi-NITE, traps nitrogen gas) it is entrained in the filter media until a backwashing cycle is completed. During this cycle, the flow in the filter is reversed and the waste that is trapped in the filter media is pushed out the entrance and is collected thereby cleaning the filter and keeping it from becoming plugged. For the elimi-NITE system, the nitrogen gas that is trapped in the filter is released into the atmosphere. During this 'backwash' cycle, the unit is out of service and the wastewater flow must be diverted to other units until the backwash cycle is completed. Therefore, one of the prime components to look at before selecting a gravity filter is how often and for how long a backwash cycle is needed. Ultimately this system was discarded as a viable technical option when, after talking with people in charge of the waste water facility at BP, it was discovered that gravity filters of a similar nature were already being used in the process.

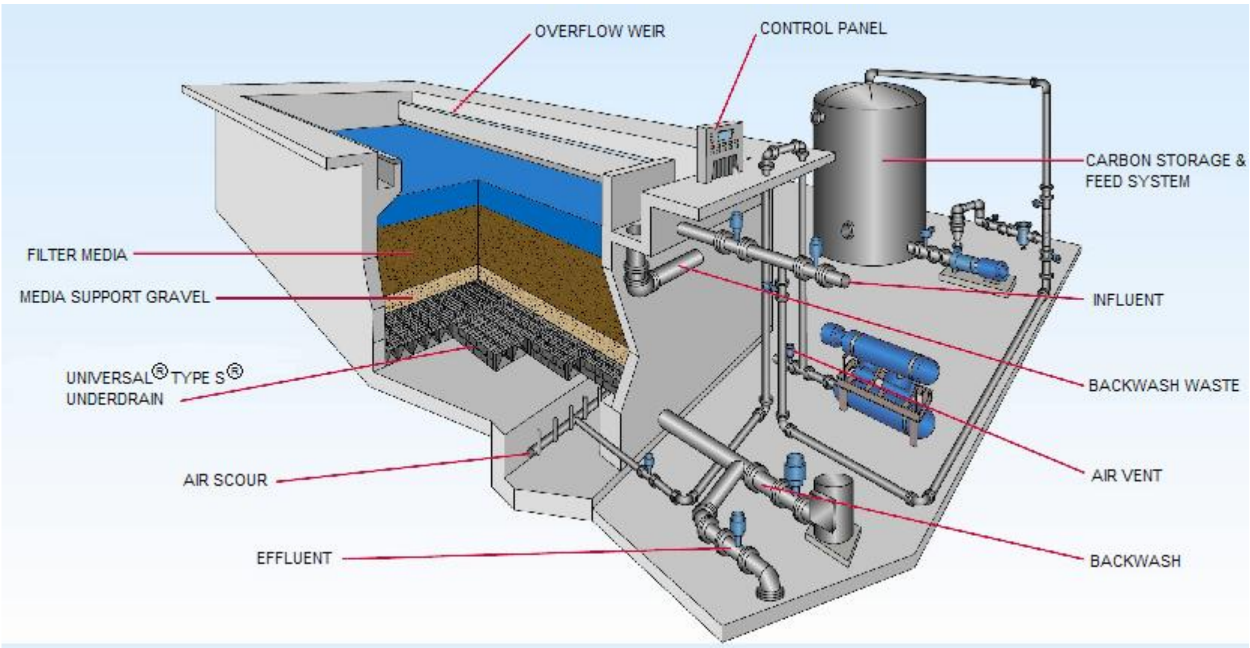

Fig 4.2, Typical Leopold Elimi-NITE System[5]

Corrugated Plate Interceptors

Corrugated Plate Interceptors are pretreatment devices that are involved in wastewater treatment plants. CPI devices are tilted plates that allow the filtering of sludge and other suspended solids to be removed from wastewater treatment of crude oil. Most effectively, these plates can remove waste approximately 25 microns in size. They are also able to be retrofitted into existing filter tanks although this is somewhat difficult due to the variation of angles the plates may be placed at. When dealing with heavy Canadian crude oils, however, CPI proves to be inefficient because of its inability to effectively viscous material contained in the wastewater. When using CPI with heavy Canadian crude oils the filter needs cleaning more often and is prone to generating solid waste lodged in between the two plates used for filtering. The overall design of the CPI is not suitable for heavy Canadian crude oils. The filters will have to be maintained with greater diligence and replaced more often resulting in higher maintenance costs for BP.

C. Third Research Groups; Wastewater progress, Membrane modeling

The third research groups were formed to study in detail with our suggestion on membrane model for the removal of TSS and ammonia for BP. Research on Waste water progress was done to understand current BP's wastewater treatment methods through the investigation of the layout f the treatment plant. Our suggestion comes with membrane model. We examined how it will reduce TSS and ammonia by retrofitting membrane model in the current BP system.

Wastewater progress

There are ten distinct units in the current BP wastewater system. The first unit is simply the wastewater inlet. Wastewater from the refinery enters the wastewater treatment plant with 3,500 mg/L of TSS and 2,112 mg/L of ammonia. The plant processes 22 million gallons per day (MGD) of wastewater. However, each unit in the plant is designed to handle 10 to 40 MGD. The first step in treatment is to remove the largest suspended solids, by means of bar screens and the grit chamber. A bar screen filter comprises a number of bars arranged in closely spaced parallel relation so as to define slots through which liquid flows. A scraper element is disposed above the bar screen and has a set of free floating knife blades projecting downwardly through the slots between the sand bars. BP uses a bar screen 108 feet in diameter. The solid debris caught by the screen is raked through a cycle that is mounted on a support frame in front of the screen, and then moved to the bottom of the screen where they are removed through a discharge channel. The wastewater also passes through the grit chamber, which is enabled to remove debris, including floating solids. The chamber is 18 feet in diameter and 16.6 feet in height. Together, the bar screens and grit chamber act as one unit, bringing TSS levels down to 2,625 mg/L.

The cleaner wastewater now enters the API separators. These separators are designed, according to standards set by the American Petroleum Institute (API), to separate oil, water and solids, based on the difference in their specific gravities. Three layers form within the separators. The top layer is oil, being much less dense than water and suspended solids. A portion of the suspended solids settle to form the sediment layer on the bottom, while the remaining water forms the middle layer. Each layer is treated differently. As before, the solids in the sediment are removed from the system. The top layer of oil is skimmed and sent to the surge tank, where a more thorough oil-water separation occurs. The remaining wastewater is sent to the equalization tank. At this point in time, TSS levels in the wastewater have been reduced by 90% from 2,625 to 262.5 mg/L.

The surge tank receives an oil-water mixture from the API separators. BP's storm surge tank is 200 feet in diameter and 40 feet tall. The oil and water in the mixture are thoroughly separated inside the surge tank, with the oil being re-processed and the water joining the effluent from the API separators.

Water from the API separators gets sent to the equalization tank, which has the same size as the surge tank. It takes about 10 million gallons, and the retention time of the fluid ranges from 6-12 hours. The equalization tank lowers the TSS levels from 263 mg/L to 197 mg/L. The waste products from this unit are sent to an incinerator. The equalization tank also stabilizes the pH of the wastewater, reducing the range from pH6-pH10 to a narrower range of pH6-pH8. However, ammonia levels are not changed in the equalization tank.

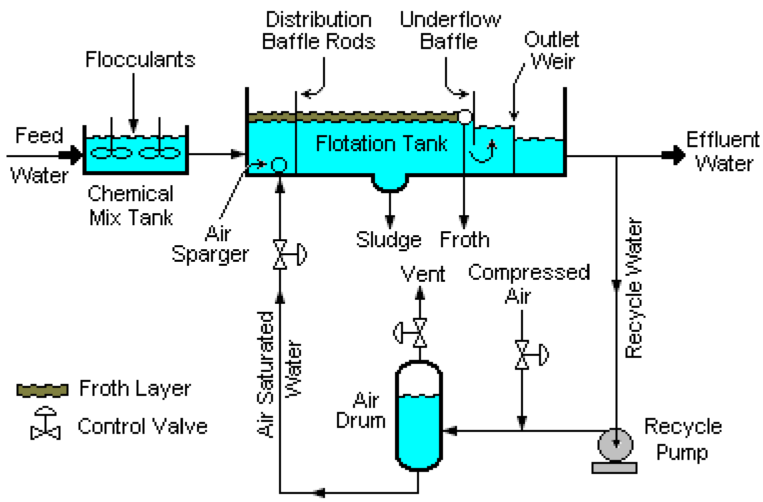

Fig 5.1, Flowchart of DAF Unit in Wastewater Treatment[6]

Water exiting the equalization tank is subjected to the Dissolved Air Flotation (DAF) process, shown in Fig 5.1, which removes suspended solids and oil. The water is first doped with a coagulant such as ferric chloride or aluminum sulfate to flocculate the suspended matter. What happens is that the suspended matter will form clumps, making them easier to remove. A portion of clarified effluent is pumped into pressure vessel where compressed air is introduced. By dissolving air in the wastewater under pressure and then releasing the air at a reduced pressure, bubbles are formed in the water, which stick to the suspended matter, causing the suspended matter to float to the surface of the water, forming a froth which is skimmed off.

The next step involves the aeration unit. Wastewater from the DAF unit enters the two aeration tanks in the BP treatment system which is connected in series, each with a capacity to hold 5.7 million gallons of wastewater. They contain microorganisms which process the ammonia contained in the wastewater, lowering the concentration of ammonia from 15 mg/L to 0.5 mg/L. Like the other units in the system, the tanks are designed for flow rates of 10-40 MGD, but unlike other units which operate at 22 MGD, the aeration tanks operate at 32 MGD. The extra 10 MGD comes from a recycle stream coming from the secondary clarifiers, which are the units after the aeration tanks. Because of this recycling, the wastewater enters the aeration tanks with TSS levels of 2,500 mg/L but exit at higher concentrations of 3,000 mg/L. The stream in this process has a retention time of approximately six hours.

As previously mentioned, the secondary clarifiers are the next unit into which the wastewater flows. Upon entering the secondary clarifiers, matter that is present in the solid phase within the wastewater is separated from matter in the liquid phase. As a result, the 3000mg/L concentration of TSS in the wastewater is reduced to about 30 mg/L after passing through the secondary clarifiers. It is then directed into the tertiary clarifiers.

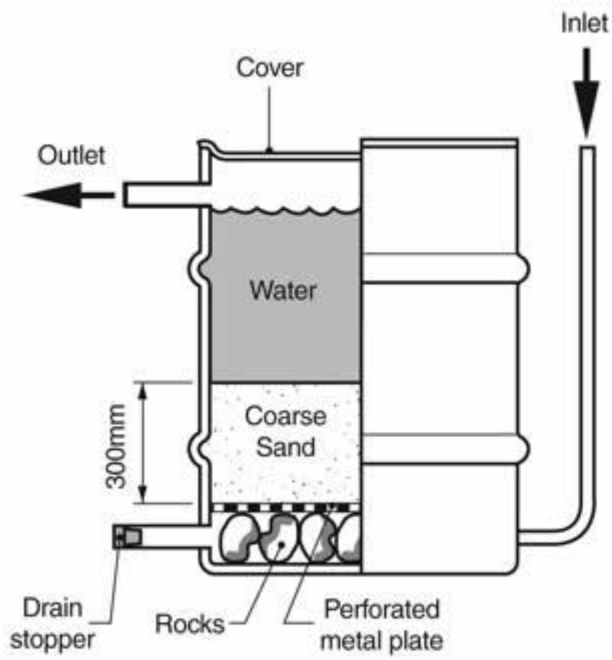

Fig 5.2, Tertiary clarifiers using rapid gravity filtration[7]

Tertiary clarifiers are the final step with regards to clearing the water of TSS and other unwanted substances. It removes small solids like sand, and even dissolved gases like nitrogen. The mechanism employed is known as gravity sand filtration, or rapid gravity filtration. The feed wastewater is first doped with flocculation chemicals like salts of aluminum or iron. The water now flows through relatively coarse sand and other granular media under gravity. Pumped pressure may also be used. The flocculated materials become trapped in the sand matrix, and are thus removed from the water. With continued usage, the flocculated material tends to block the sand filters, necessitating the frequent backwashing of said filters. This is done by reversing the direction of flow of the wastewater and adding compressed air to fluidize the filter bed. Compared to slow sand filters, rapid gravity filters are able to handle higher flow rates while taking up less space, making them much more efficient. The BP plant employs eight tertiary filters working simultaneously in parallel to clear the TSS remaining in the feed from the secondary filters. These clarifiers can process a total of 4.8 million gallons of water at any one time. Most of any impurities that escaped the primary and secondary filtration units are removed in this unit.

In the final step in the treatment process, the highly purified water is sent to the treated effluent diffuser, which disperses the water coming from the tertiary filters into the Outfalls and Great Lakes. The water is so clean that, even at 22 million gallons a day, the total ammonia and TSS released into the environment daily are only 1,030 and 3,646 pounds respectively.

Membrane Processes for wastewater treatment

Our research into Membrane Bioreactor’s (MBR’s) encompassed four main methods; Biofiltration, Ultrafiltration, Nanofiltration, and Reverse Osmosis. Areas such as particulate removal efficiencies, flux conditions, and general operating conditions were compared in an attempt to arrive at the most applicable process to be applied to BP Whiting’s Refinery Expansion.

All four MBR methods had characteristics common among them. These include; actual unit reductions leading to smaller footprints, easy modification with possible automation, insignificant/nonexistent chemical usage with no secondary chemical byproducts, less sludge production, and water reuse. Also, these MBR methods were found to have some limits such as; low membrane lifetime, membrane fouling, varied selectivity in particulates(in select processes), as well as high capital and operating costs.

The four main methods of filtration are primarily characterized by the filter pore size, which correlates to what types of pollutants can be filtered. In order of largest to smallest in terms of pore size; Microfiltration, Ultrafiltration, Nanofiltration, and Reverse Osmosis. Reverse Osmosis was found to be the most effective at capturing the greatest amount of pollutants, with the only by-product being the discharged water. The units pore size of around 0.0005 microns allows it to capture all of the following particles; mono/multivalent ions, viruses, bacteria, and in the refinery's case, suspended solids. It also has an added benefit of possibly being able to reverse the flow of the water membrane for maintenance, and possible reuse of the filtering membrane.

It is recommended that MBR's be further investigated, especially concerning the maintenance, and possible fouling issues involved. Overall, MBR's constitute an important possible future application if further research is done in this field. Important future research must be made into operating conditions, and measurement accuracies. The application of MBR's in wastewater treatment has been demonstrated to be highly possible; yet more work remains for MBR's to become a viable source of filtration for BP Whiting's wastewater treatment facility.

9.0 Recommendations

Sour Water Stripper

Sour water strippers are used to take streams with high hydrogen sulfide and ammonia levels and clean them up before they are sent into the over all waste water treatment units.

To remove the hydrogen sulfide and ammonia the unit passes hot steam through the down coming sour water. The ammonia and hydrogen sulfide enter the gas phase and exit out of the top of the unit. The water that continues to the bottom of the unit is sent to a reboiler and turned into the rising steam while a slip stream of stripped water is sent to the over all waste water treatment units. pH effects the stripping efficiency. At a high pH hydrogen sulfide forms its ions HS^- and S^{-2}. Stripping cannot remove dissolved ions which makes lower pH better for the removal of hydrogen sulfide. Ammonia on the other hand is easier to strip from sour water at a higher pH. At a lower pH ammonia becomes its ion and cannot be stripped. In order to strip both ammonia and hydrogen sulfide a pH between 7 and 8 is used for operation.

Brine Treatment

The Brine treatment unit operation is a gas flotation unit as part of the pre-treatment process of crude oil. Normally, the effluent from a desalter unit travels into a brine treatment unit for further purification of heavy crude oils. If the oil is not desalted, corrosion to other refining equipment will result. Brine treatment is the process of removing inorganic cations from a crude oil stream. Brine solution is made by softening water and precipitating out the divalent and trivalent cations. In the treatment unit, crude oil and approximately 12% volume brine wash is combined with a simultaneous pressure drop to create emulsions that transfer corrosive cations from the oil to the wash water. When this occurs, inorganic cations are transferred from the crude oil to the wash water. The emulsions must then be broken to create two layers: the aqueous brine layer and the crude oil layer. The aqueous and crude layers are then separated so the aqueous layer is softened to be used as brine once again and the crude layer is repeatedly treated with a brine solution to remove more of the inorganic cations.

Cost Evaluation

	Inlet/Feed				
Unit Operation	TSS, mg/L	Flow, MGD	NH_3-N, mg/L	pH	Temp.(^oF)
Refinery Process water	15,000	22	300	6 to 10	70 to 120
Brine Treatment Unit	15,000	22	300	6 to 10	70 to 120
Sour Stripper	300	22	300	6 to 10	70 to 120
Bar Screen & Grit Chamber	15,000	22	300	6 to 10	70 to 120
API Separators	11,250	22	300	6 to 10	70 to 120
Surge Tank	Only used during upset event				
Equalization Unit	1,125	22	300	6 to 10	70 to 120
Dissolved Air Flotation	844	22	300	6 to 8	70 to 120
Aeration Tanks	47,025	32	206	6 to 8	70 to 120
Secondary Clarifiers	58,781	32	10.3	6.5 to 7.5	60 to 105
Tertiary Filters	588	22	10.3	6.5 to 7.5	60 to 105
Treated Effluent to Lake					

Note: All values are estimates for steady state conditions.

Outlet/Effluent					
TSS, mg/L	Flow, MGD	NH_3-N, mg/L	pH	Temp.(^oF)	
300	22	300	6 to 10	70 to 120	
300	22	30	6 to 10	70 to 120	
11250	22	300	6 to 10	70 to 120	Bar Screen & Grit Chamber
1125	22	300	6 to 10	70 to 120	API Separators
Only used during upset event					Surge Tank
844	22	300	6 to 8	70 to 120	Equalization Unit
84	22	300	6 to 8	70 to 120	Dissolved Air Flotation
58781	32	10.3	6.5 to 7.5	60 to 105	Aeration Tanks
588	22	10.3	6.5 to 7.5	60 to 105	Secondary Clarifiers
196	22	10.3	6.5 to 7.5	60 to 105	Tertiary Filters
35994	22	1,894	6 to 8	70 to 90	Treated Effluent to Lake
lbs/day		lbs/day			

TSS (lb/day) =	36000	± 20%
NH_3 (lb/day) =	1900	± 20%

10.0 References

1. Canadian Environmental Assesment Agency Website <http://www.acee-ceaa.gc.ca/015/001/017/images/Figure-4_e.jpg>

2. Attanasi, E. D., Meyer, R. F. “Heavy Oil and Natural Bitumen – Strategic Petroleum Resources” U.S. Geological Survey Fact Sheet 70-03 (2003) <http://pubs.usgs.gov/fs/fs070-03/fs070-03.html>

3. Bartholomew, R. “The BIOFOR® Biological Aerated Filtration System: An Innovative Wastewater Treatment Process.” Pennsylvania Dept. of Environmental Protection Website. 20 Sep. 2007. <http://www.dep.state.pa.us/dep/deputate/watermgt/wsm/WSM_TAO/InnovTech/ProjReviews/BioFor.htm>

4. Brentwood Industries Website <http://www.brentwoodindustries.com/water/ifas_main.html>

5. Water Online Top 10 Water Treatments <http://images.vertmarkets.com/CRLive/files/Images/72F11FAA-C3EA-44C1-86BE-

4C250AF393D4/elimi-nite.jpg>

6. Wikipedia (Article on DAF)
<http://en.wikipedia.org/wiki/Dissolved_air_flotation>

7. Doulton Website
<http://doultonusa.com/doulton_water_filters/593SIMUP.jpg>

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