

Water Management in Refining Processes



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Background

Water serves many purposes in an oil refinery, including but not limited to cooling high-temperature refining operations, equipment washing, steam generation, unit hydrotests, and fire fightingⁱ. In the process of generating a system modeling water use in a refinery, six units will be explored that use water to absorb contaminants from the crude oil that is processed in the plant. These six processes are caustic treating, distillation, amine sweetening, Merox I sweetening, hydrotreating, and the desalter unit. The contaminants that are removed during the processes are salts, organics, H₂S, and ammonia. Table 1 below lists the maximum inlet and outlet concentrations for the six water-using units.

Process	Contaminant	Cin,max (ppm)	Cout,max (ppm)	Mass Load (kg/h)
(1) Caustic Treating	Salts	300	500	0.18
	Organics	50	500	1.2
	H ₂ S	5000	11000	0.75
	Ammonia	1500	3000	0.1
(2) Distillation	Salts	10	200	3.61
	Organics	1	4000	100
	H ₂ S	0	500	0.25
	Ammonia	0	1000	0.8
(3) Amine Sweetening	Salts	10	1000	0.6
	Organics	1	3500	30
	H ₂ S	0	2000	1.5
	Ammonia	0	3500	1
(4) Merox I Sweetening	Salts	100	400	2
	Organics	200	6000	60
	H ₂ S	50	2000	0.8
	Ammonia	1000	3500	1
(5) Hydrotreating	Salts	85	350	3.8
	Organics	200	1800	45
	H ₂ S	300	6500	1.1
	Ammonia	200	1000	2
(6) Desalter	Salts	1000	9500	120
	Organics	1000	6500	480
	H ₂ S	150	450	1.5
	Ammonia	200	400	0

Table 1. Maximum inlet, outlet concentrations (ppm) for six water-using unitsⁱⁱ

Figure 1 below gives a schematic of a typical refinery. The water-using units are circled in red and the wastewater treatment processes are circled in green.

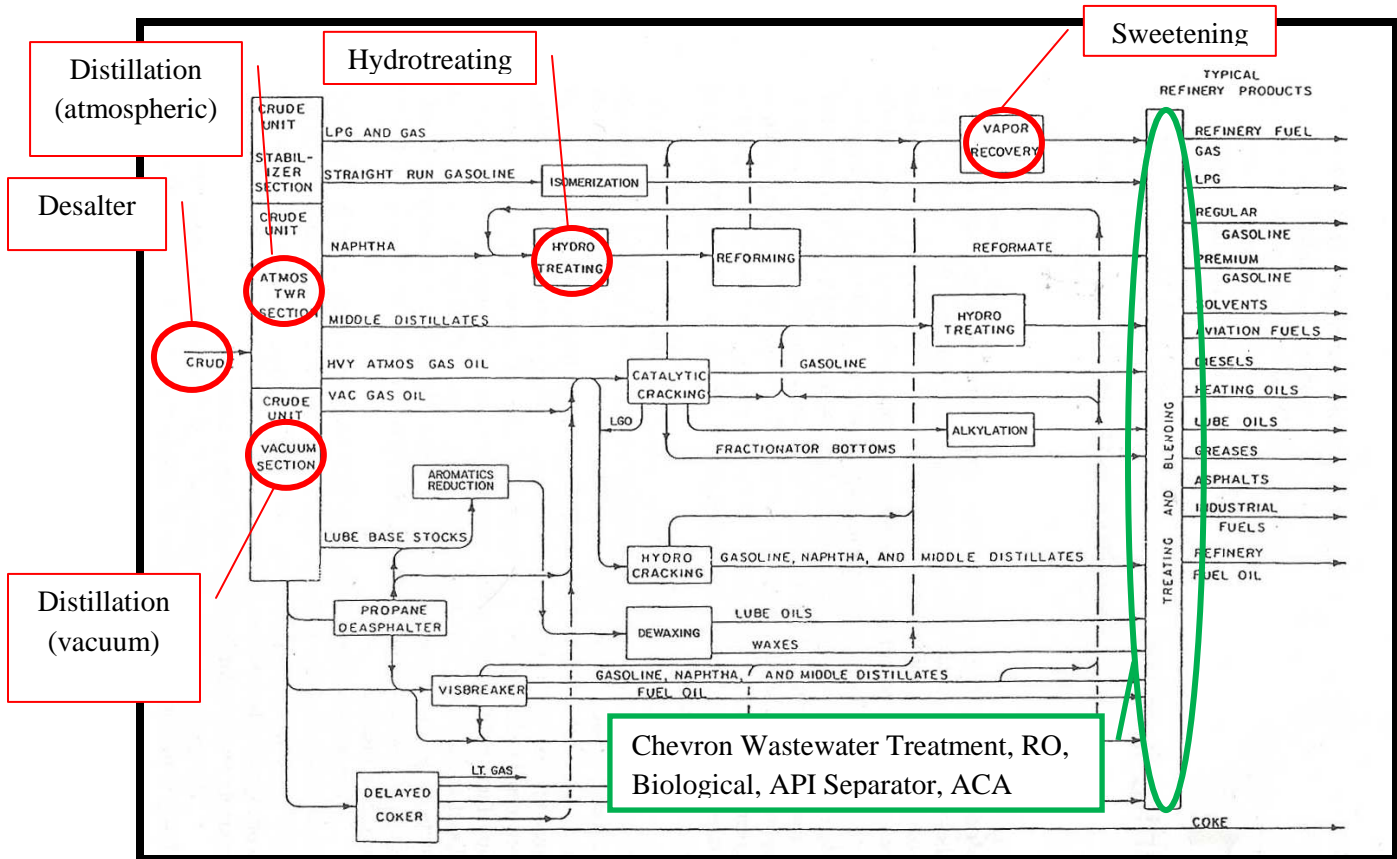


Figure 1. Refinery schematicⁱⁱⁱ

Crude desalting is usually the first step in a petroleum refining process. Crude oil enters into the refining unit from outside storage tanks and contains heavy amounts of contaminants, including water with dissolved or suspended salt crystals. It is heated by heat exchangers in order to increase the viscosity^{iv}. A separate water stream is then introduced to the system and comes into contact with the crude oil, after which the two streams are vigorously mixed over a mixing valve. Water and crude oil are immiscible solvents and since salt has a higher solubility in water, the aforementioned salt particles will partition into the water. A schematic of the desalting process is shown on the following page.

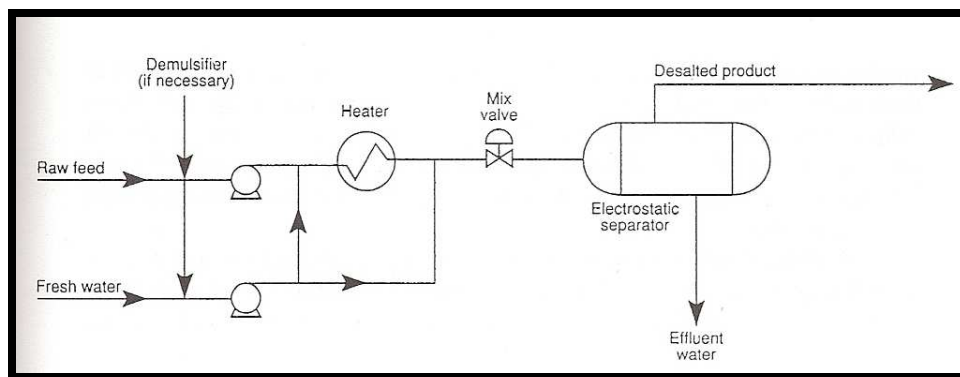


Figure 2. Single-stage electrostatic desalting system^v

There are two types of distillation: atmospheric and vacuum. After the desalting stage, the crude oil is heated in heat exchangers and heated to about 750 degrees Fahrenheit before it enters into an atmospheric distillation unit. Atmospheric distillation separates light end products like natural gas, naphtha, and gas oil from crude oil. The crude is partially vaporized in a fired heater before entering the distillation unit flash zone. Superheated steam is introduced through the column bottom to strip any remaining gas oil from the flash zone liquid. The steam reduces the hydrocarbon partial pressure thereby reducing vaporization temperature. An atmospheric column is shown below:

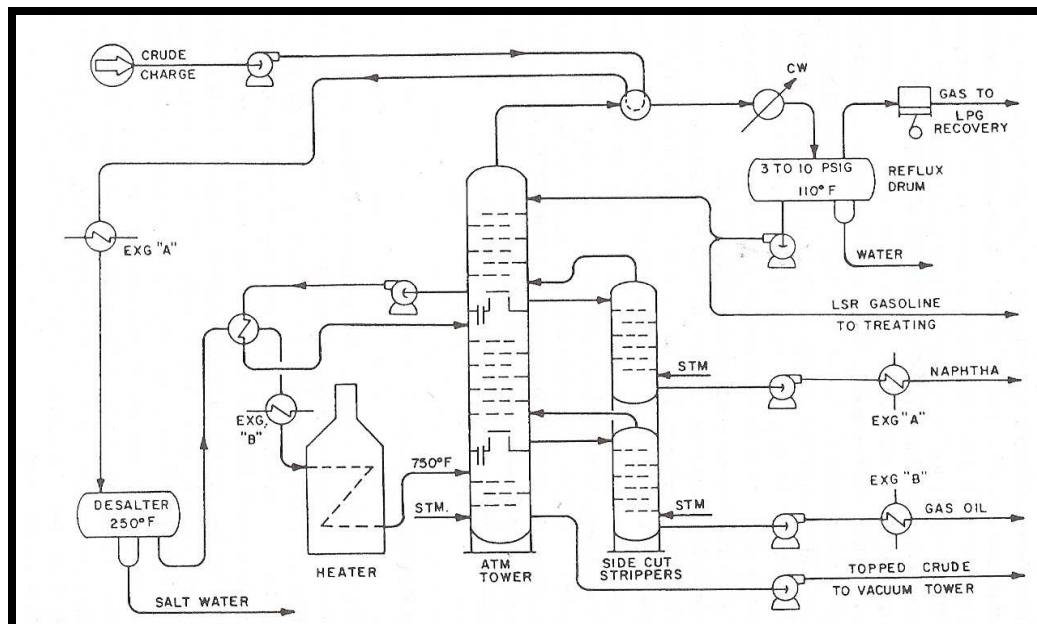


Figure 3. Atmospheric distillation unit^{vi}

Following atmospheric distillation, the heavy bottoms product containing heavier fractions of crude oil is sent to a vacuum distillation tower where distillation under very low pressures (usually 25 to 40 mmHg^{vii}) is carried out. Temperatures required for atmospheric distillation of heavier components would be too high and would result in cracking of hydrocarbons. By lowering the distillation pressure and introducing steam to the system (to improve vaporization), heavier products can be distilled. Prior to entering the distillation column, the topped crude is heated in a furnace to temperatures of about 750-850 degrees Fahrenheit. After distillation, different fractions of heavy components exiting the system pass through pumps and heat exchangers. A vacuum distillation column is shown below:

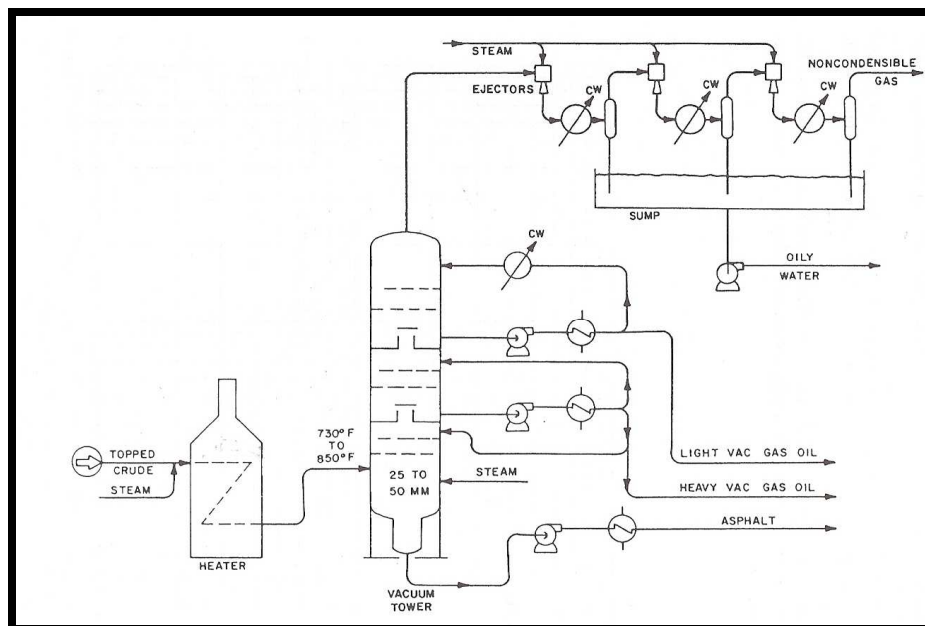


Figure 4. Vacuum distillation unit^{viii}

Caustic treating is a refining process that uses an aqueous solution of NaOH to absorb acid gas compounds, like H₂S, CO₂, and mercaptans, found in natural gas or liquid hydrocarbon streams. Crude oil fractions that exit from the vapor stream in a distillation tower contain sulfur-based compounds, which are odiferous and corrosive. Following distillation, this light crude stream goes through amine treatment, which removes many of the mercaptans and helps to reduce the load that is sent to caustic treatment^{ix}. A caustic solution of normally 15 wt% NaOH and higher is then introduced into an absorption tower where it comes into contact with the

passing stream of light crudes and extracts the contaminants^x. Caustic treating is normally used to clean liquefied natural gas (LNG) and diesel fuels. A diagram of a caustic treatment unit is shown below.

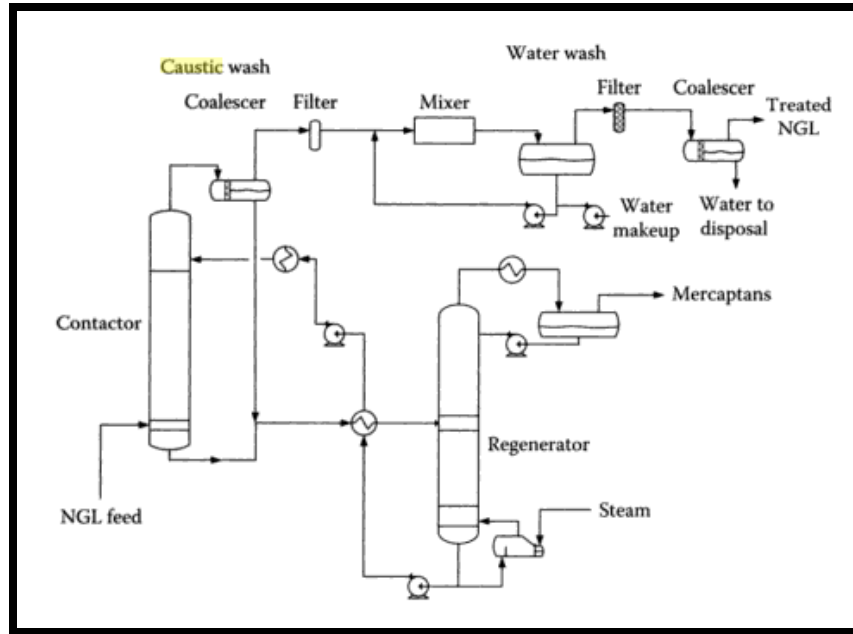


Figure 5. Caustic treating process^{xi}

Amine sweetening is a process whereby aqueous solutions of alkanolamines (such as monoethanolamine or diethanolamine) absorb contaminants like hydrogen sulfide (H₂S), carbon dioxide (CO₂), and mercaptans from a passing stream of natural gas. The absorption process is called sweetening because it eliminates the bitter odor coming from the sour feed making the clean gas smell “sweet”. The acid gas contents are removed through chemical reactions with the amines in the amine solution and come out of the absorber in the rich amine liquid solution. A flash tank is usually installed at the absorber outlet to reduce flash any hydrocarbons that may be in the feed, thereby removing them from the acid gas product^{xii}. A process flow diagram of an amine-sweetening unit is shown in Figure 6.

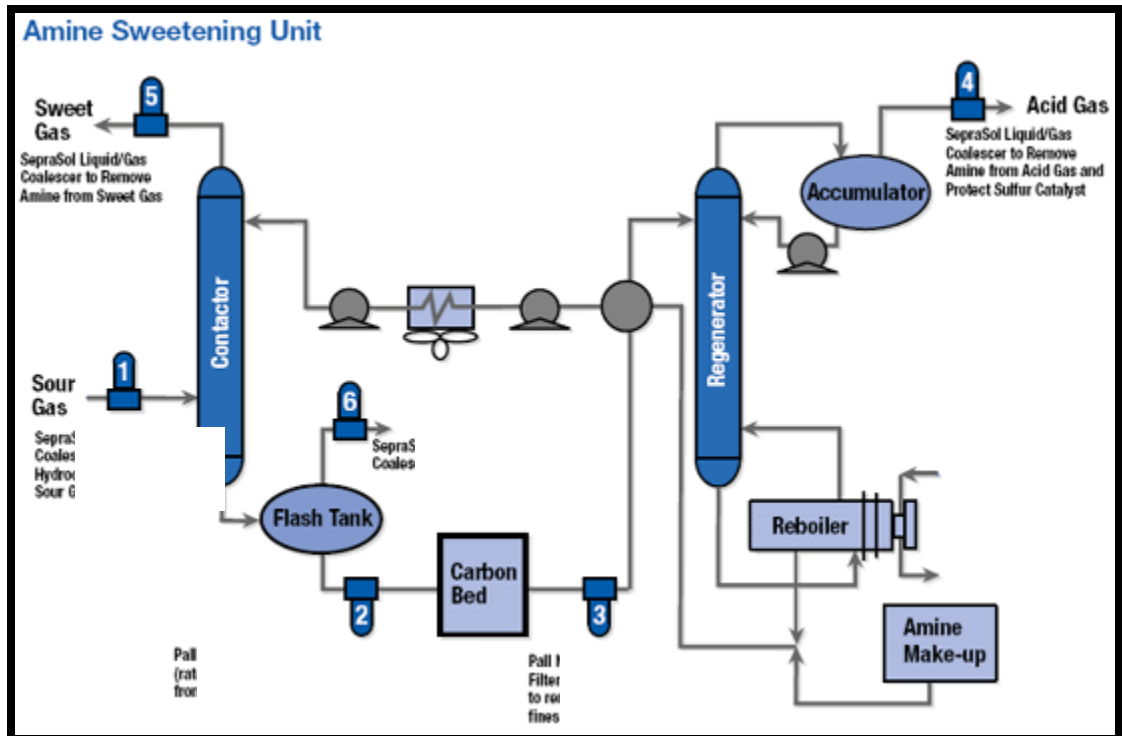


Figure 6. Amine-sweetening unit^{xiii}

Hydrotreating is a process that removes elemental sulfur, nitrogen, oxygen, halides, and trace metals from crude oil in order to improve the quality of its constituents, such as gasoline, diesel fuel, and jet fuels. Hydrotreating is used to convert olefins and unstable diolefins into paraffins by reacting them with hydrogen. A schematic of the hydrotreating process is shown in Figure 7. Hydrogen is mixed with feed liquids and heated in a heating furnace. The heated crudes, at about 700-800°F, are passed through a catalytic reactor where chemical reactions convert organic sulfur and nitrogen compounds to hydrogen sulfide and ammonia. The reactor effluent is cooled in a heating exchanger and condensed hydrocarbons are sent to a stripper, where a desulfurized bottoms product exits.

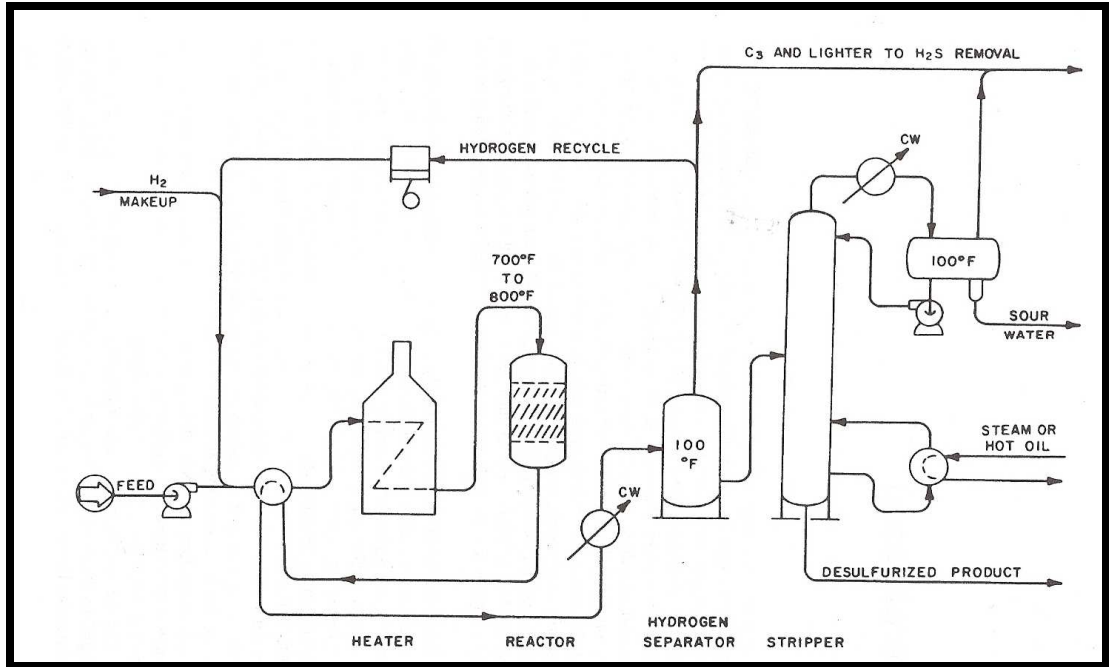


Figure 7. Hydrotreatment unit^{xiv}

API separators separate suspended solids and oil from wastewater streams based on differences in specific gravities between the oil and the wastewater. The differential density is much smaller for oil and wastewater than for suspended solids and wastewater. Thus, the oil globules will rise through the water, suspended solids will sink to the bottom, and the wastewater containing some small amounts of oil particles will exit as the middle layer. After separation, the oil in the top layer is skimmed off and re-processed and the sedimentation from the bottom of the separator is removed using a sludge pump.

The particles settling in an API separator operate on the basis of Stokes Law: the contaminant particles fall through the viscous fluid by their own weight due to a gravitational force. The upward drag of the small particles (which are assumed to be spheres) combine with the buoyancy force balances the gravitational force thereby creating a settling velocity, which is the velocity at which the particles settle. The settling velocity, also termed the terminal velocity, is given by:

$$V_t = \frac{2}{9\mu}(\rho_w - \rho_o)gR^2 \quad \text{Equation 1}$$

where V_t is the settling velocity in cm/s, μ is the fluid viscosity in poise, ρ_w is the density of water at the design temperature in g/cm^3 , ρ_o is the density of oil at the design temperature in g/cm^3 , g is the gravitational constant (981 cm/s^2), and R is the radius of the particle which will be removed in cm. Typically, a particle with a radius no smaller than 0.015 cm, will settle out of the water. A schematic of an API separator is shown below.

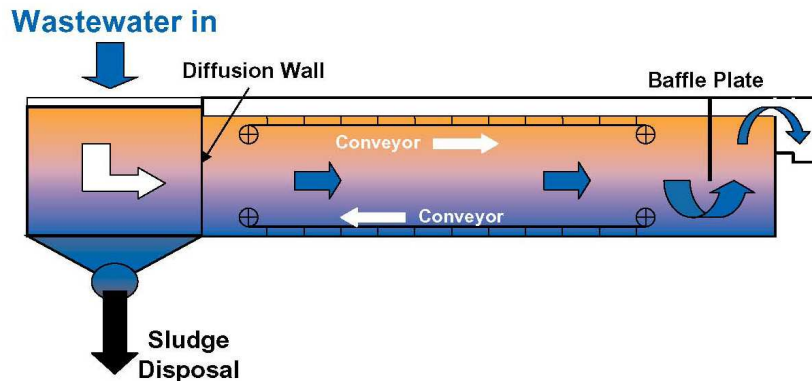


Figure 8. API Separator^{xv}

Reverse osmosis

Theory of reverse osmosis

Reverse osmosis is a process by which dissolved solutes are separated from a solution by a pressure-driven membrane that applies the preferential diffusion for separation. The solution to be separated on one side of the membrane known as the feed is separated by a membrane filled with pure water on the other side. Due to difference in the concentrate between the feed and permeate side instability is created, water then flows from the pure side to the feed to equilibrate the system. The water level in the solution will rise to a point, which is equal to the osmotic pressure, π , of the concentrated solution. When this occurs, the water flux across the membrane to the permeate is equal to that to the feed and equilibrium is reached. At this point of equilibrium, the driving force generated to move the water molecules is then terminated. This process is known as the osmosis process.

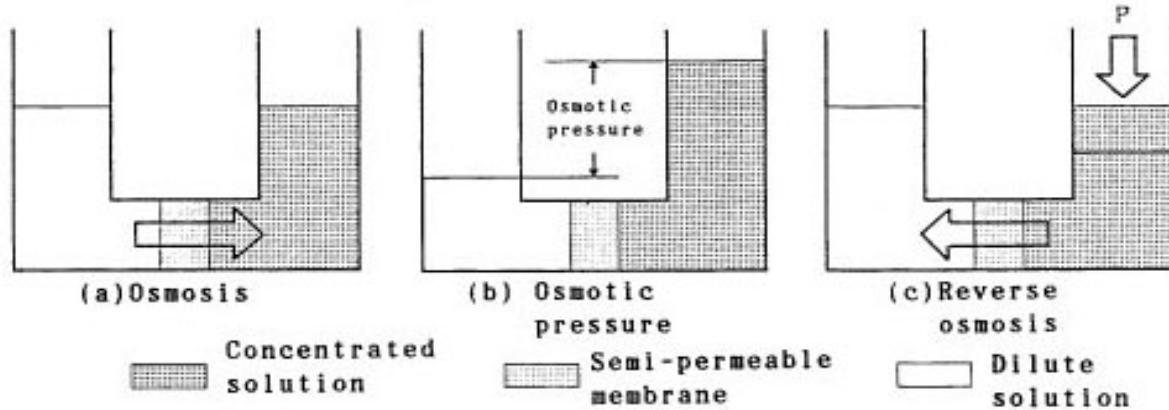


Figure 9. Osmosis and reverse osmosis processes

In reverse osmosis, high pressure is applied at the feed and a differential pressure is created between the permeate and feed sides of the membrane. This results into a pressure change, the system then becomes unstable allowing the flow of water from the feed stream through the membrane to the pure water side (permeate). As water passes through the membrane, the solutes are rejected at the membrane surface increasing the concentration of the feed stream which flows out of the process as a stream called the concentrate. The permeate exits the process at atmospheric pressure, while the concentrate stream leaves the membrane element at high pressure is approximately equal to the feed pressure.

The rate of flow of water molecules in a unit area of the membrane (also known as the water flux) through the membrane is the product of the driving force and the transfer rate as defined by the below equation:

$$J_W = k_w \cdot (\Delta P - \Delta \pi) \quad \text{Equation 2}$$

where: J_W = volumetric flux of water ($L/m^2 \cdot s$)
 k_w = mass transfer coefficient of water flux ($L/m^2 \cdot s \cdot atm$)
 $\Delta P = (P_F - P_P) =$ hydraulic pressure change (atm)
 $\Delta \pi = (\pi_F - \pi_P) =$ change in osmotic pressure in the feed and permeate (atm)

The flow of the solutes (salt) through the membrane is given by the equation below:

$$J_S = k_S \cdot (\Delta C) \quad \text{Equation 3}$$

where: J_S = mass flux of solute ($kg/m^2 \cdot s$)
 k_S = mass transfer coefficient of solute ($L \cdot S/m^2$)

The osmotic pressure of the feed is calculated using van't Hoff law for dilute solutions as in the expression below:

$$\pi = cRT \quad \text{Equation 4}$$

where : c = concentration of solute in feed/permeate (mol/L)

R = gas constant ~ 0.0820578 (L·atm)/(g·mol·K)

T = temperature of solution (K)

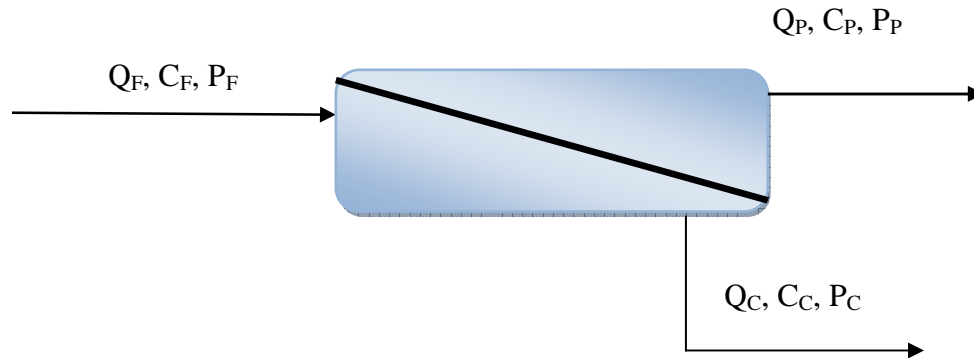
Membrane material

The force directed towards the membrane for the separation of solutes from water based on the physical and chemical properties of the solutes to be removed and the material of the membrane. The resistance to flow through the membrane is inversely related to the thickness which means that for high efficiency, the membrane has to be extremely thin. For a reverse osmosis, the thickness of the membranes ranges from about 0.1 to 2 μm . This extreme size of the material makes the membrane lack structural reliability as a result, membranes usually comprise of several layers with low porosity. The ideal material is one that can produce a high flux without clogging or fouling and is physically durable and chemically inactive. The materials most widely used in reverse osmosis are the cellulosic derivatives and polyamide derivatives (Crittenden).

Process application in wastewater treatment

In wastewater treatment process, reverse osmosis is a technology used for the removal of various inorganic contaminants. However, the main problem with the reverse osmosis technologies in the waste water treatment industry is the disposal of the concentrates and fouling that occurs on the membrane over a period of time as pressure is increased. However, to prevent this from occurring, the wastewater is pretreated by scaling which adjust the PH value, changing the solubility of the precipitates of inorganic contaminants that could be formed during operation (Hendricks).

Mathematical model



A mass balance around the membrane pressure vessel process results to the following equations:

Membrane mass balance

$$Q_F = Q_C + Q_P \quad \text{Equation 5}$$

$$C_F Q_F = C_C \cdot Q_C + C_P \cdot Q_P \quad \text{Equation 6}$$

where:

C_C = concentrate of solute in concentrate water (kg/m^3)

C_P = solute concentrate in permeate water (kg/m^3)

C_F = solute concentrate in feed water (kg/m^3)

Q_P = permeate flow (m^3/s)

Q_F = feed flow (m^3/s)

Q_C = concentrate flow (m^3/s)

The flow rate of water molecules in the permeate is related to the water flux by the equation shown below:

$$Q_P = J_W \times \text{Area of membrane} \quad \text{Equation 7}$$

The flux of the solutes is also related to the flux of water by the equation below:

$$J_S = C_P \cdot J_W \quad \text{Equation 8}$$

The combination of the solute flux in equations 2 and 8, and rearranging the equation, the concentration of salts in the treated water (permeate) C_P , was determined. The final equation that relates the concentration out at the permeate was found to be:

$$C_p = C_F - B \cdot N \quad \text{Equation 9}$$

where N: the number of membranes

B (found using Mathcad):

$$B = \frac{((C_F R T k_w)^2 + 2 C_F R T k_w (3 k_S k_w P_F + k_w P_P) + k_S^2 + 2 k_S k_w (P_F + P_P) + k_w^2 (P_F^2 + 2 P_F P_P + P_P^2))}{R T k_w} \left(\frac{k_S}{2} + \frac{k_w P_F}{2} + \frac{k_w P_P}{2} + \frac{C_F R T k_w}{2} \right)$$

The effect of the design parameters, N, k_w , and k_S , and the feed conditions T and P_F are summarized in the table below:

Increase in variables	Increase/ decrease
Feed temperature, T (K)	increases
Number of membranes, N	decreases
Salt permeability, k_S (L/m ² -atm-s)	increases
Water permeability, k_w (L/m ² -atm-s)	decreases
Feed pressure, P_F (atm)	decreases

Table 2. Effect of feed conditions and design parameter on effluent concentration

From the above table, it can be seen that the operating temperature has to be low in order to obtain a high degree of wastewater purity. Also, the salt permeability which is the ability of the salt to pass through the membrane to the permeate has to be low. As expected, the salt permeability affects the purity of water showing that if the porous membrane used for the process is liable to absorb the salt molecules, then the amount of salt in the permeate will be high. This renders the treatment system inefficient, and therefore the material of the membrane used for the process is highly important. An increase in the number of membranes used, will give a reduction in the contaminants found in the effluent stream as desired. Therefore, a high number of membranes should be used for the treatment process. This is highly recommended because the membrane (whichever type) has the ability to foul if the amount of contaminants in the feed is high and therefore gets attached to the surface.

The table below summarizes the optimum conditions and design parameters to achieve high degree of purity in the wastewater.

Parameters and effects	
Feed temperature, T (K)	Decrease temperature, negligible effect at extreme low temperature
Number of membranes, N	Increase the number used, high degree of purity can be attained
Salt permeability, Ks (L/m²-atm-s)	Choose material with low salt permeability, possibly zero
Water permeability, Kw(L/m²-atm-s)	Choose material with high water permeability
Feed pressure, PF (atm)	Increase the pressure at the feed to allow high degree of diffusion at membrane

Table 3. Feed conditions and design parameters to be considered for process design

Activated Carbon Adsorption

Theory of adsorption

Adsorption is a process by which molecules of substances present in a liquid phase are attached on the surface of a solid matter and removed from the liquid phase. The process involves the molecules in the gas or liquid phase diffuse to the surface of the solid and stay there by chemical bonding or weak intermolecular forces. The solid phase particle which provides the bonding sites is known as the adsorbent and the substance in the adsorbed state is called the adsorbate.

There are two main types of adsorption which are the physisorption and the chemisorption. The physisorption is when the adhesive forces are of physical nature and adsorption is relatively weak and the amount of heat evolved for a mole of gas adsorbed is usually less than 20 kJ (Laidler). For the chemisorption, the adsorbed molecules are bonded to the surface by covalent forces which are stronger than intermolecular forces between the molecules of the adsorbate. In chemisorption which is usually applied in industries, after the surface has been covered with a monolayer of adsorbed molecules, it is said to be saturated and

additional adsorption occurs on the layer that already exists. However, Langmuir emphasized that adsorption formation is of unimolecular layer and once formed adsorption ceases but multilayer can exist for physisorption.

Adsorbent

Adsorbents used in industries are generally synthetic microporous solids: activated carbon, molecular sieve carbon, activated alumina, silica gel, zeolites and bleaching clay. The most important characteristics of adsorbents are pore volume, the pore distribution and the geometry of the particles of the adsorbent. The table below shows the properties of the commonly used activated carbon.

Properties of Activated Carbon				
Property	Activated Carbon			
	Filtrisorb 100	Filtrisorb 200	Filtrisorb 300	Filtrisorb 400
Surface area, BET (m ² /g)	800-900	800-900	950-1050	1000-1200
Apparent density (g/mL)	no data	≥0.48	≥0.48	≥0.44
Wetted density (g/mL)	1.4-1.5	1.4-1.5	1.3-1.4	1.3-1.4
Effective size (mm)	0.8-1.0	0.55-0.75	0.8-1.0	0.55-0.75
Uniformity coefficient	2.1	1.9	2.1	1.9
Abrasion number	75	75	78	75

Table 4. Properties of Activated Carbon

Process description

At equilibrium, the rate of adsorption on the surface of the adsorbent is equal to the rate at which desorption occurs. When this occurs, an increase in the residence time of the adsorbate in the column of adsorbate has no effect. The adsorption process can be described as in the usual chemical reaction as shown below:



where:

C = adsorbent concentration (kg/m³)

C·X = concentration of the sites occupied by adsorbate molecules (kg adsorbate adsorbed/kg adsorbent/m³ solution)

X = adsorbate sites not occupied per unit adsorbent in a unit volume (kg unoccupied adsorbate/kg adsorbent/m³ solution)

At equilibrium, the rate of adsorption and desorption are equal. The equilibrium constant can be then introduced as below.

$$K_{eq} = K = \frac{[C \cdot X]}{[C]^* [X]^*} \quad \text{Equation 11}$$

where: $K_{eq} = K$ = adsorption equilibrium constant
 $[C]^*$ = adsorbate concentrate, C, at equilibrium
(kg adsorbent/m³ solution)

Langmuir Isotherm

Adsorption isotherm relates the amount of substance attached to the surface of the adsorbent to the amount in the solution at a defined temperature. The Langmuir isotherm which is used for the process assumes that the surface of the activated carbon is homogeneous and as mentioned previously adsorption occurs in a single layer.

$$\bar{X} = \frac{X_{max} KC}{KC} \quad \text{Equation 12}$$

where: K = Langmuir equilibrium constant = K_{eq}
 X_{max} = maximum amount of adsorbate in solid phase per adsorbent (kg adsorbate/kg adsorbent)
 C = concentration in solution at equilibrium (kg adsorbate/m³ solution)

It is assumed that the internal (pore) diffusion is rate controlling in the adsorption process. It is also assumed that the geometry of the activated carbon particle is spherical and all the assumptions made for the Langmuir isotherm is also used. Finally, the bed is assumed to be a batch process in a tank of volume, V.

Mathematical model

To design the activated carbon adsorption process, the fixed bed was chosen rather than the slurry adsorption. This is due to the fact that the fixed bed is more efficient and the bed can be regenerated not disposed as in the case of slurry adsorption.

Assuming the process is a plug flow of the wastewater through the bed is at a constant interstitial velocity, there is no axial dispersion and the temperature is constant throughout the

process (isothermal); the mass balance on the solute flowing through a bed length z at differential length Δz is given by the equation:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + \frac{(1-\varepsilon)}{\varepsilon} \cdot \frac{\partial q}{\partial t} = 0 \quad \text{Equation 13}$$

However, when the axial dispersion and transfer of mass from the solute to the activated carbon is not neglected as initially assumed, the equation above is modified to a partial differential which is given below:

$$-D_L \frac{\partial^2 C_b}{\partial z^2} + V \frac{\partial C_b}{\partial z} + C_b \frac{\partial V}{\partial z} + \frac{\partial C_b}{\partial t} + \rho_p \left[\frac{1-\varepsilon}{\varepsilon} \right] \cdot \frac{\partial q_p}{\partial t} = 0 \quad \text{Equation 14}$$

In the above equation, the D_L is known as the term which accounts for the axial dispersion with diffusion to the activated carbon bed, the second term is related to the change in velocity of flow axially. This equation has to be solved numerically, but an analytical solution can be found when the equation is made simple. Klinkenberg approximation was used to determine the solution with certain assumptions which include that the axial dispersion can be ignored, the fluid velocity is constant and the mass transfer model is linear. The Klinkenberg approximation is as below:

$$\frac{C}{C_F} \approx \frac{1}{2} \left[1 + \operatorname{erf} \left(\sqrt{\tau} - \sqrt{\varepsilon} + \frac{1}{8\sqrt{\tau}} + \frac{1}{8\sqrt{\varepsilon}} \right) \right] \quad \text{Equation 15}$$

where: $\varepsilon = \frac{kKz}{u} \left[\frac{1-s}{s} \right]$ Dimensionless distance coordinates

$\tau = k \left[t - \frac{z}{u} \right]$ Dimensionless time coordinate corrected for displacement

Using this formula, the effluent concentration was estimated to be approximately zero based on the residence time in the column.

Chevron waste water treatment

Chevron waste water treatment (WWT) strips hydrogen sulfide and ammonia from sour water generated in petroleum refineries^{xvi}. The two-stage stripping process produces separate purified ammonia and hydrogen sulfide streams, wherein the hydrogen sulfide can be sent to sulfur recovery units, the ammonia can be sold commercially or used again in Selective Catalytic or Selective Non-catalytic Reduction units in the refinery, and the purified wastewater can either be sent to end-of-pipe treatments or reused. A process-flow diagram for a Chevron water treatment plant is shown below.

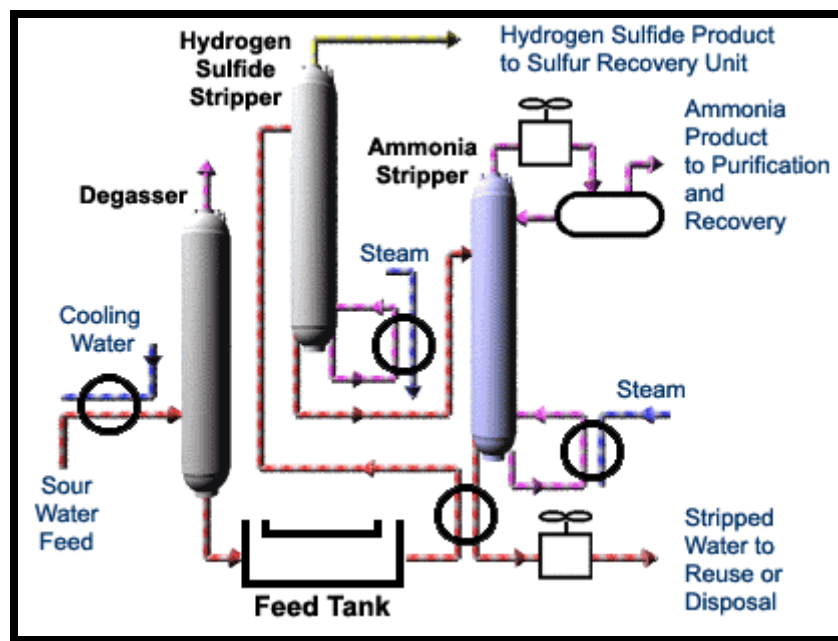


Figure 10. Chevron Wastewater Treatment Plant^{xvii}

Biological treatment

Biological treatment operates on the idea that microorganisms present in wastewater will feed on the carbonaceous organic matter in the wastewater and repopulate in an aquatic aerobic environment. With a sufficient oxygen supply and an organic material food supply, the bugs (bacteria) will consume and metabolize the organic waste and transform it into cell mass, which settles in the bottom of a settling tank.

Most biological treatment plants have two forms of operation: primary and secondary. Primary treatment involves the physical removal of solids and secondary treatment involves the biological removal of dissolved solids^{xviii}. Secondary treatment mainly uses biological treatment processes, whereby the introduction of microorganisms to the system creates solids which precipitate out and are collected in the settling tank. Three common options for secondary treatment include:

- I. Activated sludge
- II. Trickling filters
- III. Lagoons

The treatment that will be modeled in this project is the activated sludge system. The wastewater influent is sent through an aeration tank where air is pumped through the bottom of the tank and rises through the water in the form of bubbles. The purpose for this is two-fold: air provides oxygen to the water and creates turbulent conditions ideal for organic material consumption^{xix}. The wastewater is then sent through what is called a secondary clarifier. The clarifier is a settling tank that separates the used cellular material from the treated wastewater. The cellular material sinks to the bottom of the basin whereby it is either sent back to aeration tank to assist in producing new bacteria or sent as sludge for anaerobic treatment. A schematic of the process is shown on the next page in Figure 11.

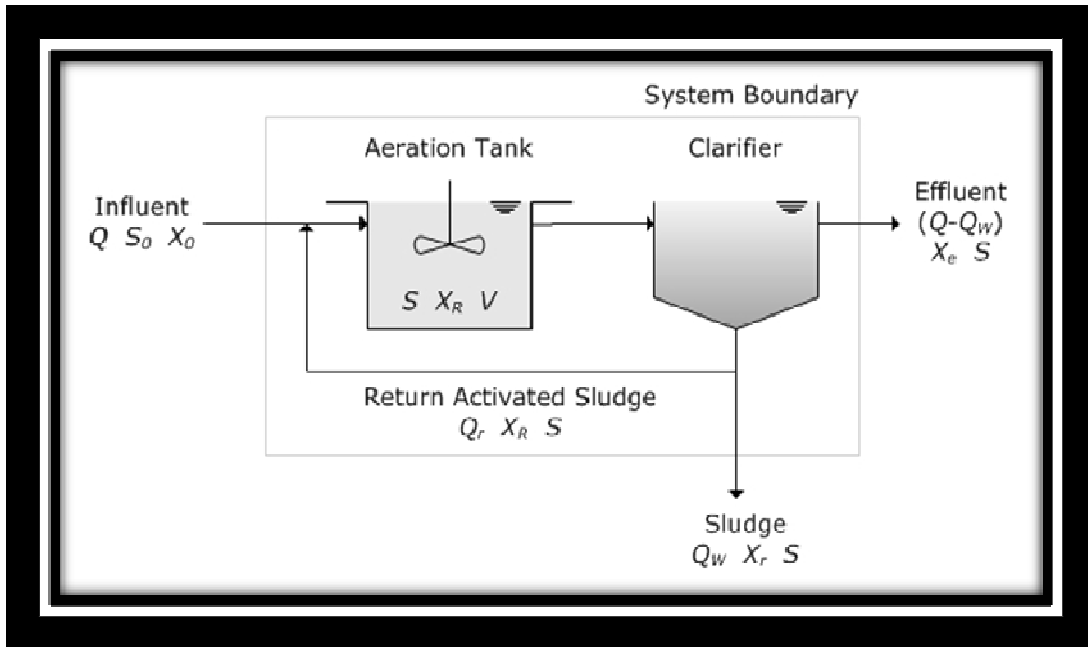


Figure 11. Activated sludge system^{xx}

where:

Q	= flowrate of influent	$[m^3/d]$
Q_w	= waste sludge	$[m^3/d]$
Q_r	= flowrate in return line from clarifier	$[m^3/d]$
V	= volume of aeration tank	$[m^3]$
S_0	= influent soluble substrate concentration (bsCOD)	$[m^3/d]$
S	= effluent soluble substrate concentration (bsCOD)	$[BOD\ g/m^3]$ or $[bsCOD\ g/m^3]$
X_0	= concentration of biomass in influent	$[g\ VSS/m^3]$
X_R	= concentration of biomass in return line from clarifier	$[g\ VSS/m^3]$
X_r	= concentration of biomass in sludge drain	$[g\ VSS/m^3]$
X_e	= concentration of biomass in effluent	$[g\ VSS/m^3]$

Simulation Methods

Several different methods were used in this study to simulate real-life water-using and water treating process units. PRO/II, *Steady*, Mathcad, and Excel were used to generate points by varying inlet system parameters, like temperature, pressure, flowrate, etc. These points were then analyzed to find the nature of correlations between components varied and outlet concentration. The Casestudy function in PRO/II has the capability of varying more than one inlet parameter at once (maximum used in this study was six) and this eased the workload. The Excel files made by the researchers were used mostly for cost analyses purposes.

PRO/II

The primary simulation program used in this study was PRO/II. Its proven accuracy in predicting results from specifications of inlet parameters and its applicability to the processes currently being modeled were the reasons for its use. The H₂S stripper, NH₃ stripper, amine sweetening, and atmospheric columns were modeled in PRO/II as distillation columns. The H₂S differed slightly from the other distillation columns in that it contained only a partial reboiler and not a partial condenser. A snapshot of the crude oil distillation unit is shown in Figure 12.

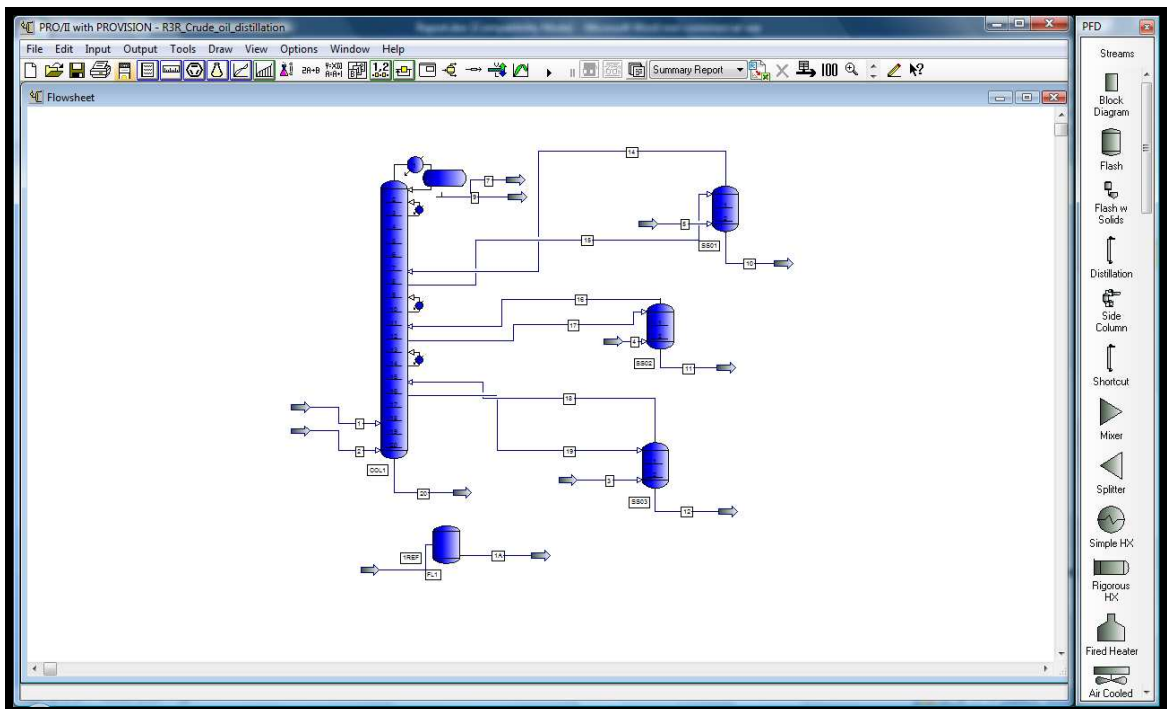


Figure 12. Snapshot of Pro/II crude oil distillation unit

Steady

The simulation program used to model the activated sludge system was a computer program called *Steady*^{xxi}. *Steady* is a steady-state wastewater treatment plant modeling program developed by researchers at the University of Texas that characterizes wastewater in terms of water quality assessment procedures, like BOD₅, TSS, VSS, TKN, and NH₃-N. The model assumes steady-state conditions for influent contaminants to a plant and calculates a plant-wide mass balance and general dimensions of the unit processes involved. *Steady* has the capability of modeling a full activated sludge system, complete with a source stream, aeration tank, clarifier tank with recycle, sludge stream, and a wastewater effluent stream. A snapshot of the file made in this study is shown below.

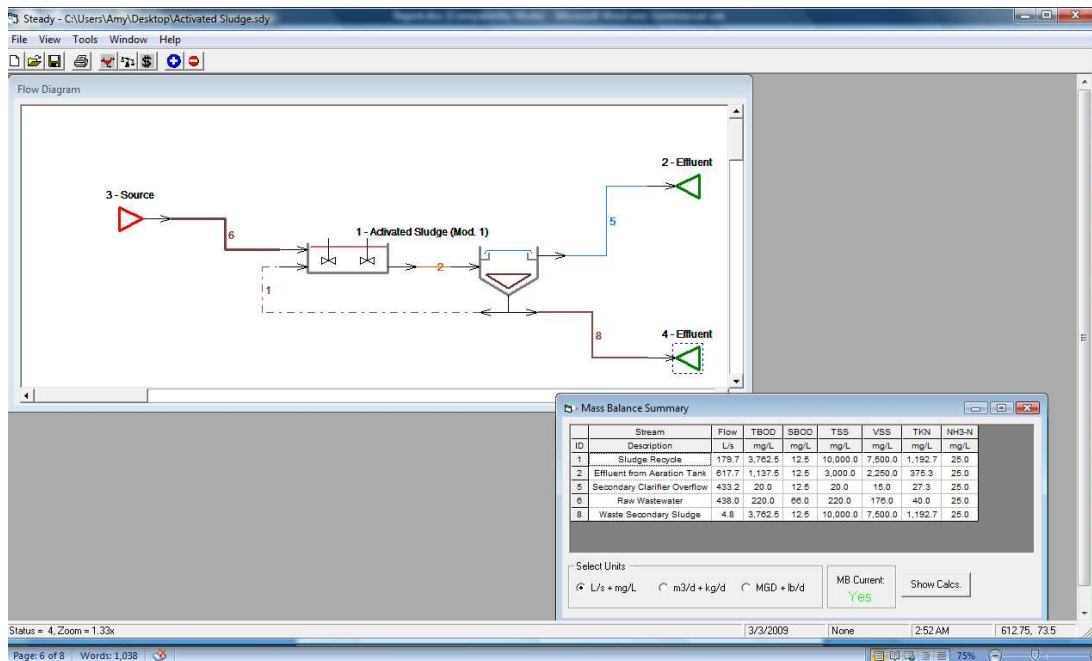


Figure 13. Snapshot of *Steady* file with activated sludge model and mass balance summary

Mathcad

Mathcad was used to generate points for the API separator and the reverse osmosis system. System parameters and inlet stream variables were varied and points were generated to be input to GAMS as tables. A screenshot of the Mathcad file simulating the API separator is shown in Figure 14.

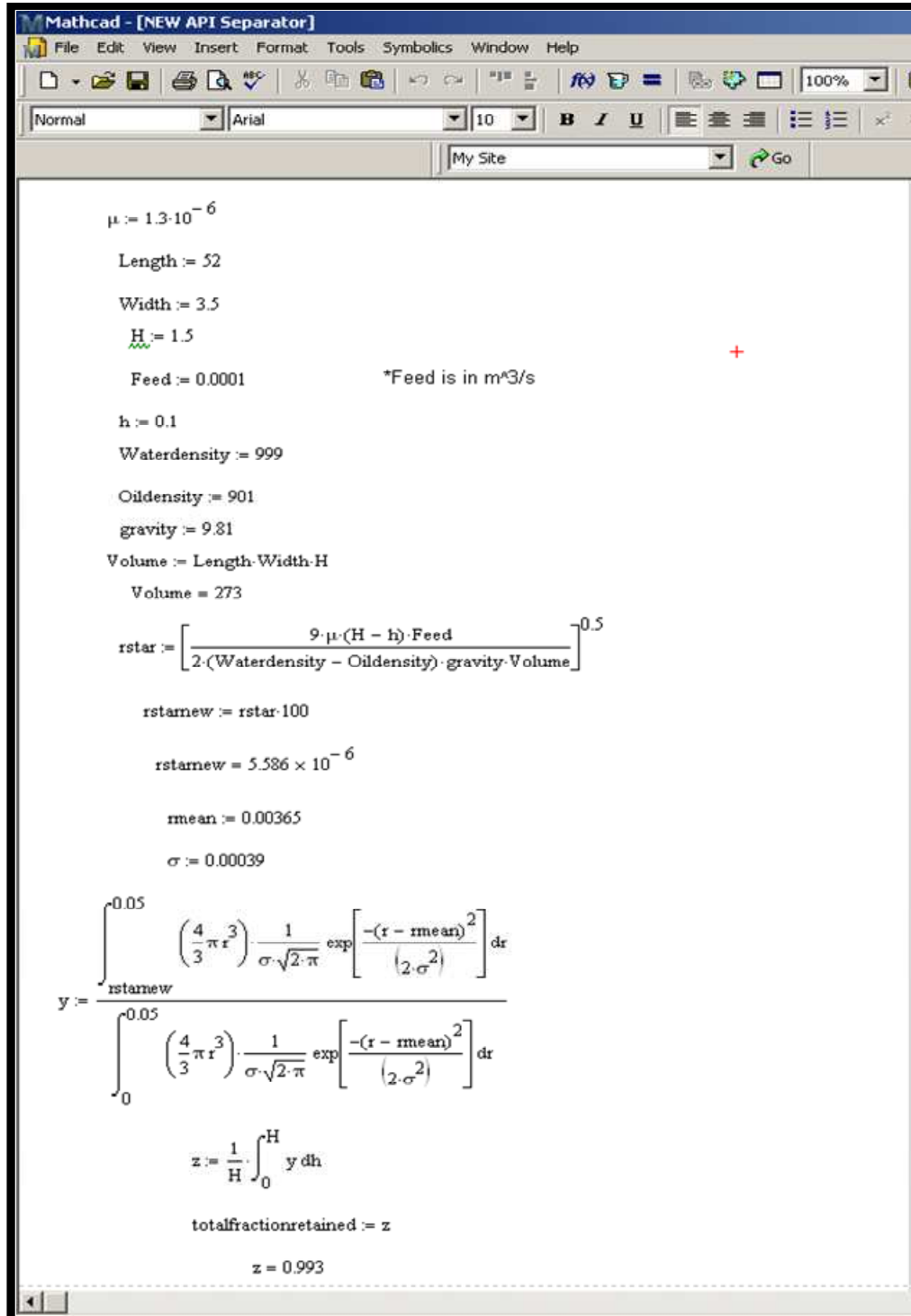


Figure 14. Snapshot of Mathcad file for API separator

Excel

Excel files were made for the API separator and the Chevron Wastewater Treatment plant to model the processes and the cost of the treatment unit. A snapshot is shown in Figure 15.

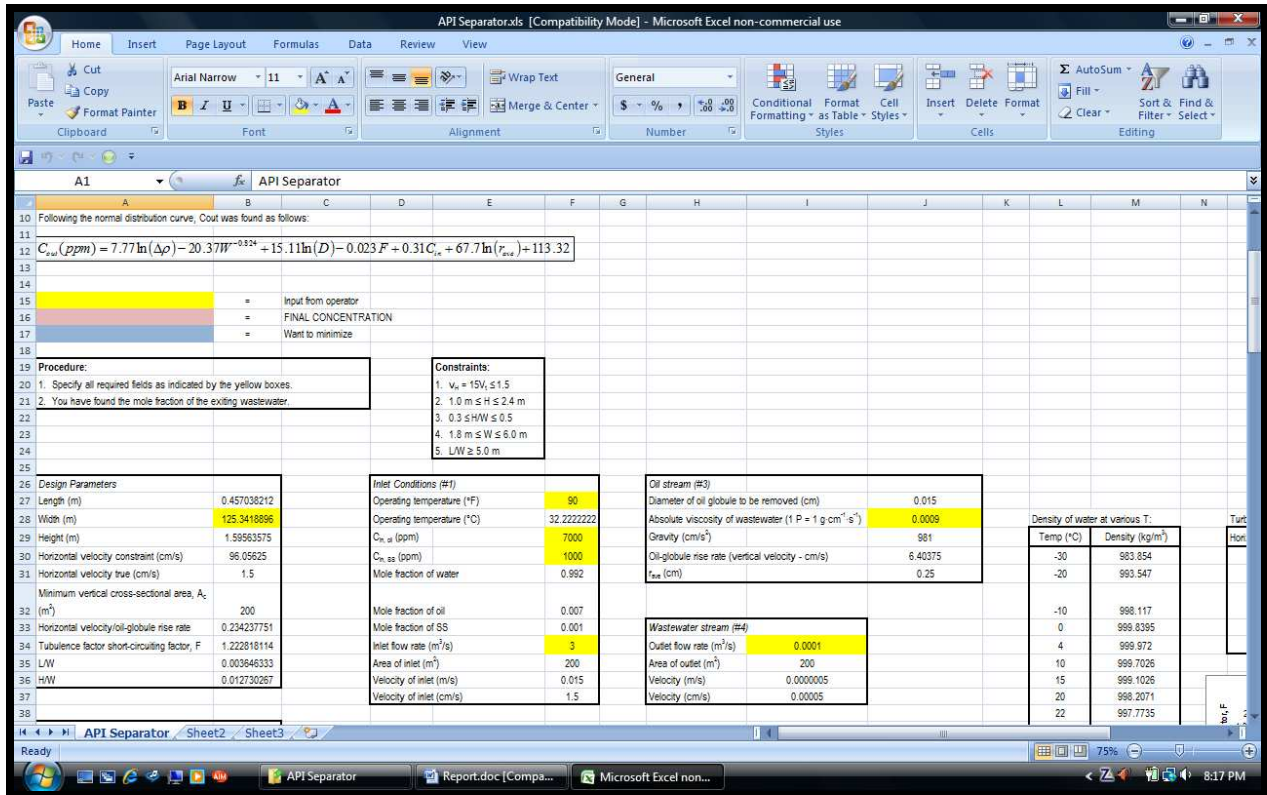


Figure 15. Snapshot of API separator Excel file

Simulations were run in PRO/II, Steady, Mathcad, and Excel, varying any and all parameters that could be varied. Inlet parameters in PRO/II were varied based on the model being used and they include, but are not limited to, column efficiency, number of trays, inlet temperature, inlet concentration, pressure, reboil and/or reflux ratio, and feed flowrate. A case study was performed for each simulation in PRO/II and results were exported to Microsoft Excel. Graphs plotting outlet concentration (dependent variable) vs. each inlet parameter (independent variable) were then generated to find the relationship between the two variables. Whatever shape the points in the graph appeared to take was the basis of determination of which type of regression (linear or non-linear) would be performed. So, for instance, if the graph appeared to follow a straight line, a linear regression was performed. If the graph had some

curvature to it, a non-linear regression (including exponential fit, power law, or logarithmic) was performed. The regression which produced the highest coefficient of determination, R^2 , was kept and regarded as the best fitting line. The graph with the highest coefficient of determination was kept because it represented the smallest difference between the actual and predicted values for that curve. All R^2 and regressions were performed in and by Excel algorithms.

After graphs were generated in Excel, a model was guessed that represented an outlet contaminant concentration as a function of all of the aforementioned inlet variables. This model was essentially based on adding together all of the best fit equations of the component curves that were found to have an effect on effluent concentration. For instance, if C_{out} were found to depend on pressure in the form $C_{out} = a \cdot \ln(P)^b$ as determined by non-linear regression in Excel and temperature in the form $C_{out} = c \cdot T + d$ as determined by linear regression in Excel, then the resulting model would be $C_{out} = a \cdot \ln(P)^b + (c \cdot T + d)$. Parameters a-d were guessed to have the same values as each component curve did in Excel. All data points and the guessed model were entered into Polymath and Polymath was left to perform a final non-linear regression.

It's worth mentioning that although it's probable that these parameter effects are not additive and probably have some co-dependence on each other, it will not matter in obtaining an end result. There is not one right answer in the final model. For any equation guessed as a model, Polymath takes the non-linearities into account if one uses non-linear data point regression. As long as the numbers converge and the simulation program used to generate the data points is accurate, the predicted model will be accurate as well. All results obtained in this study converged under the maximum number of iterations.

Results

Two types of models were generated in this study: outlet concentration models and equipment cost models. The outlet concentration models describe the outlet contaminant concentration being investigated in units of parts per million (ppm) as a function of inlet parameters such as feedrate (ton/hr), pressure (psia), temperature ($^{\circ}$ F), number of trays (N), tray efficiency (η), etc. These types of models were made for the API separator, H_2S stripper, NH_3 stripper, biological treatment (activated sludge), activated carbon adsorption treatment, reverse

osmosis, and the atmospheric distillation column. The equipment cost models were made for the API separator, Chevron Wastewater Treatment plant, activated sludge, and the reverse osmosis units. They describe process machinery cost in terms of dimensional parameters (length, width, height), number of trays, reboil ratio, etc. Results are shown in the proceeding sections.

Outlet Concentration models

I. API separator

The API separator was modeled under the assumption that all of the particles coming into the separator follow a normal distribution, also called a Gaussian distribution. All particles ranged in size from miniscule to some maximum measured size and the majority of particles lay somewhere near the average mean particle size. Outliers exist (i.e. particles very large or very small), but they are present in small quantities and of course, no particles are seen beneath the $z = 0$ line on the Gaussian curve. Particles cannot have a negative radius. As the contaminant particle enters the separator, it has a horizontal velocity v_x as well as a vertical settling velocity v_y . The time for a particle to reach the other end of the API Separator (t_L), that is to travel its length L is determined by:

$$t_L = \frac{L}{v_x} \quad \text{Equation 16}$$

But v_x is given by the flowrate F divided by the cross sectional area A given by the product of width and height, that is $A = W \cdot H$. Therefore

$$t_L (s) = \frac{L}{F / \{H \cdot W\}} = \frac{L \cdot H \cdot W}{F} = \frac{V}{F} \quad \text{Equation 17}$$

where V is the volume of the API separator. At the same time, the time that a particle that is at height h at the beginning of the separator will reach the top is:

$$t_h (s) = \frac{(H - h)}{v_y} \quad \text{Equation 18}$$

The settling velocity of a particle with radius r is given by Stokes Law seen previously in Equation 1:

$$v_y = \frac{2}{9\mu} (\rho_w - \rho_o) g r^2 \quad \text{Equation 19}$$

Thus:

$$t_h = \frac{9\mu(H-h)}{2(\rho_w - \rho_o)gr^2} \quad \text{Equation 20}$$

If we now equate $t_h = t_L$, we will obtain the radius of the particle that will exactly reach the top, if started at height h .

$$t_h = \frac{9\mu(H-h)}{2(\rho_w - \rho_o)gr^2} = \frac{V}{F} = t_L \quad \text{Equation 21}$$

The radius is then given by:

$$\hat{r} = \sqrt{\frac{9\mu(H-h)F}{2(\rho_w - \rho_o)gV}} \quad \text{Equation 22}$$

This equation for \hat{r} was assigned as the critical radius, above which, all particles separate and will be removed from the wastewater (and stay in the API separator). Below which, particles are carried with the wastewater effluent stream (particles smaller than \hat{r} will stay in the exiting water). Finally, assuming a Gaussian distribution of particle sizes, we find that the fraction of particles y_h that started at height h that are retained is:

$$y_h = \frac{\int_{\hat{r}}^{\infty} \left(\frac{4}{3} \pi r^3 \right) e^{-\frac{(r-\hat{r}_s)^2}{\sigma^r}} dr}{\int_0^{\infty} \left(\frac{4}{3} \pi r^3 \right) e^{-\frac{(r-\hat{r}_s)^2}{\sigma^r}} dr} \quad \text{Equation 23}$$

Being a normal density function, finding the mass of contaminant at any given time involves a simple multiplication of the density (g/cm^3) and the volume (cm^3). Now, the particles are uniformly distributed in height. Then, the total fraction of contaminants removed is:

$$z = \int_0^H y_h \cdot \frac{1}{H} dh \quad \text{Equation 24}$$

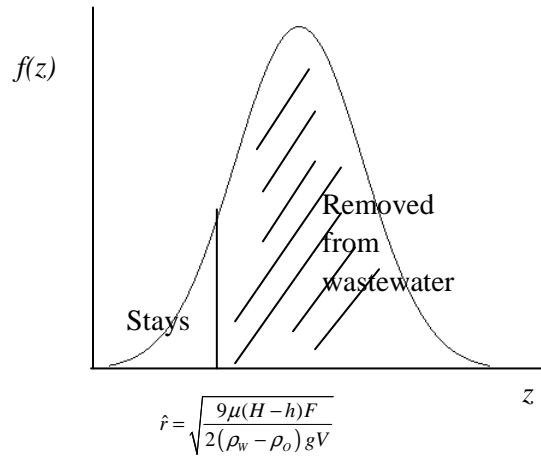
Therefore,

$$z = \frac{1}{H} \int_0^H \left\{ \frac{\int_{\hat{r}}^{\infty} \frac{9\mu(H-h)F}{2(\rho_w - \rho_o)gV} \left(\frac{4}{3} \pi r^3 \right) e^{-\frac{(r-\hat{r}_s)^2}{\sigma^r}} dr}{\int_0^{\infty} \left(\frac{4}{3} \pi r^3 \right) e^{-\frac{(r-\hat{r}_s)^2}{\sigma^r}} dr} \right\} dh \quad \text{Equation 25}$$

The outlet concentration of organics is then given by:

$$c_{out}^{Org} = (1 - z)c_{in}^{Org} \quad \text{Equation 26}$$

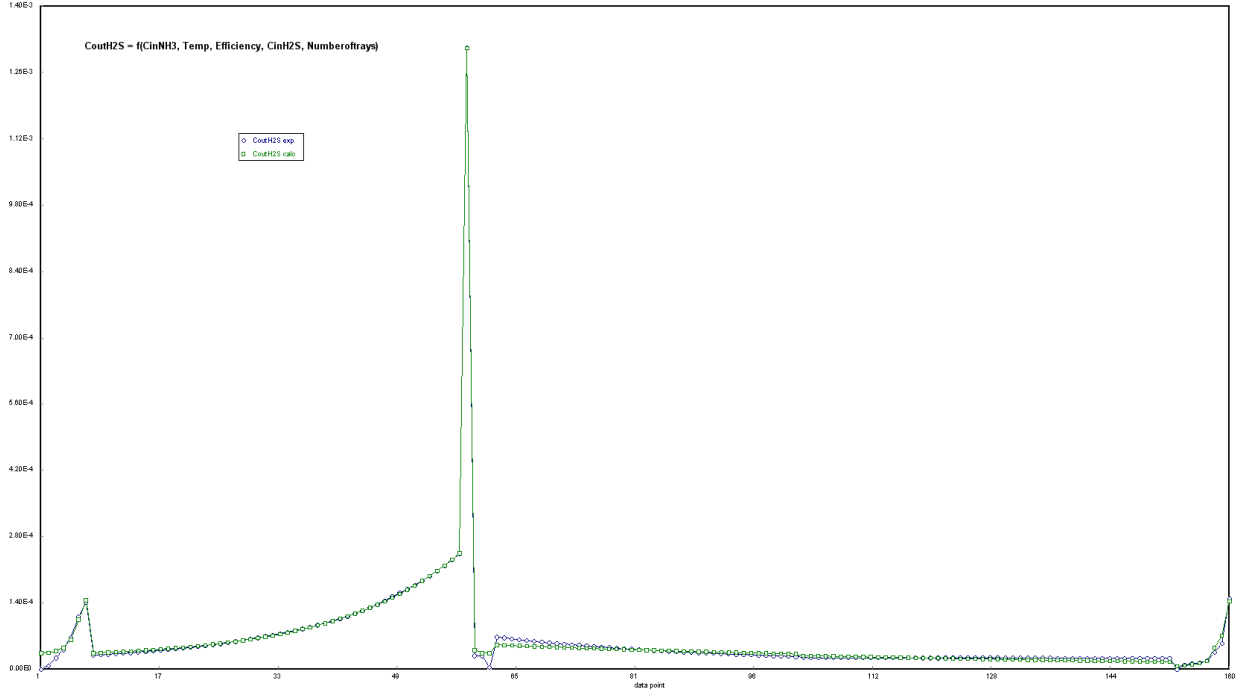
We conclude that $c_{out}^{Org} = c_{out}^{Org}(c_{in}^{Org}, V, H)$. In doing this we are assuming that the distribution of particles is known (it is Gaussian with known mean and std. dev). In addition, an underlying assumption exists that temperature does not significantly affect the densities of water and the organic phase. A pictorial representation of the normal density function is seen below.



The area that is shaded is the percentage of the contaminants (oil or suspended solids) removed from the influent wastewater. All particle sizes are represented in the normal distribution, thus the area under the Gaussian curve is 1, where 1 represents the entire range of contaminants sizes from 0 to r_{max} . The table generated from simulating the numerical integration in Mathcad is seen in Appendix I.

II. Chevron Wastewater Treatment

As stated before, the Chevron Wastewater Treatment consists of a hydrogen sulfide stripper followed by an ammonia stripper. The H_2S , with a partial reboiler, strips H_2S from the influent wastewater leaving mostly H_2S and a negligible amount of ammonia in the vapor stream. The wastewater then enters into an ammonia stripper, containing a partial reboiler and a partial condenser, where ammonia is stripped from the wastewater. The curve for the hydrogen sulfide stripper is shown below.



From points 1-11, the mole fraction of hydrogen sulfide coming into the stripper was varied. From points 12-21, the number of trays was varied. From points 22-55, tray efficiency was varied from 0.56 through 0.89. From points 56-177, the case study function was used in Pro/II where the feedrate was varied by increments of 1 kg/hr and the result was the outlet concentration of H₂S. From points 178 on, the inlet temperature was varied. It's important to mention that reboiler duty and inlet pressure were run as parameters in the case study in Pro/II, but the outlet concentration of H₂S was found to not be affected by it. A model was guessed and the result of non-linear regression in Polymath is as follows:

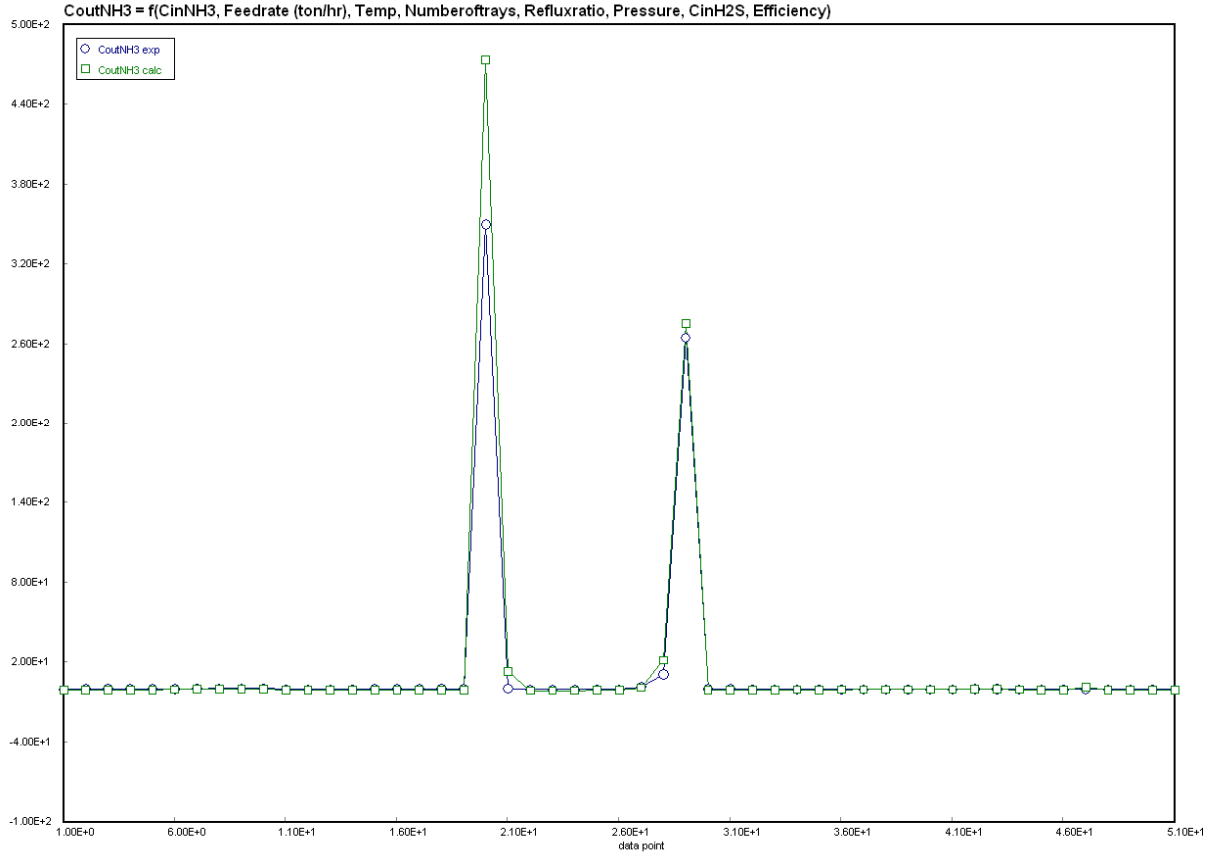
$$C_{out,H_2S} (ppm) = 0.0024e^{0.079C_{in,NH_3}} - e^{-0.039T} - 0.014\eta^{-0.138} + (1.011 \times 10^{-4}) \cdot C_{in,H_2S}^2 - 0.0012 \cdot C_{in,H_2S} + 21,700(\text{Numberoftrays})^{-7.077} + 0.0158$$

Equation 27

The Polymath report for H₂S is seen in Appendix I.

From Figure 10 on page 19, it is clear that the liquid stream that exits from the bottom of the hydrogen sulfide stripper is the entering stream ammonia stripper. Thus, the outlet concentration of the H₂S stripper is the inlet concentration of the NH₃ stripper. The component

H₂S was the contaminant that was modeled in this study. The non-linear regression graph is shown below.



In this case, case study function was used rather than single-handedly generating points, which is tedious. A step size of 100 variations was specified and run in PRO/II. Inlet parameters were specified to be overall column tray efficiency, feedrate (ton/hr), inlet pressure (psia), reflux ratio (by changes of 0.5), and inlet temperature (degrees Fahrenheit) was varied. The result was outlet concentration of H₂S and given in units of ppmw.

$$C_{out,NH_3} (ppm) = 0.00068F^2 - 0.0065F - 0.057C_{in,NH_3} + 1546e^{-0.697N} + 0.00008069e^{0.025T} + 0.0613RFR - 4436000P^{-2.941} - 0.527\eta^2 - 0.752\eta + 7.105C_{in,H_2S}^{0.47} + 0.238$$

Equation 28

An inequality exists that must be able to find optimal column diameter based on flowrate. From Seader and Henley's *Separation Process Principles*^{xxii}:

$$D_T = \left[\frac{4VM_V}{fU_f \pi (1 - A_d / A) \rho_V} \right] \quad \text{Equation 29}$$

where: V = molar vapor flow rate

M_V = molecular weight of the vapor

f = the fraction of flooding, typically taken as 0.80

$$U_f = \text{flooding velocity} = \left(\frac{4d_p g}{3C_D} \right)^{1/2} \cdot \left(\frac{\rho_L - \rho_V}{\rho_V} \right)^{1/2}$$

ρ_V = density of the vapor, ρ_L = density of the liquid

d_p = particle diameter, g = gravity, C_D = drag coefficient

$$\frac{A_d}{A} = \begin{cases} 0.1, & F_{LV} \leq 0.1 \\ 0.1 + \frac{(F_{LV} - 0.1)}{9}, & 0.1 \leq F_{LV} \leq 1.0 \\ 0.2, & F_{LV} \geq 1.0 \end{cases}$$

$$F_{LV} = \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \quad \text{Equation 30}$$

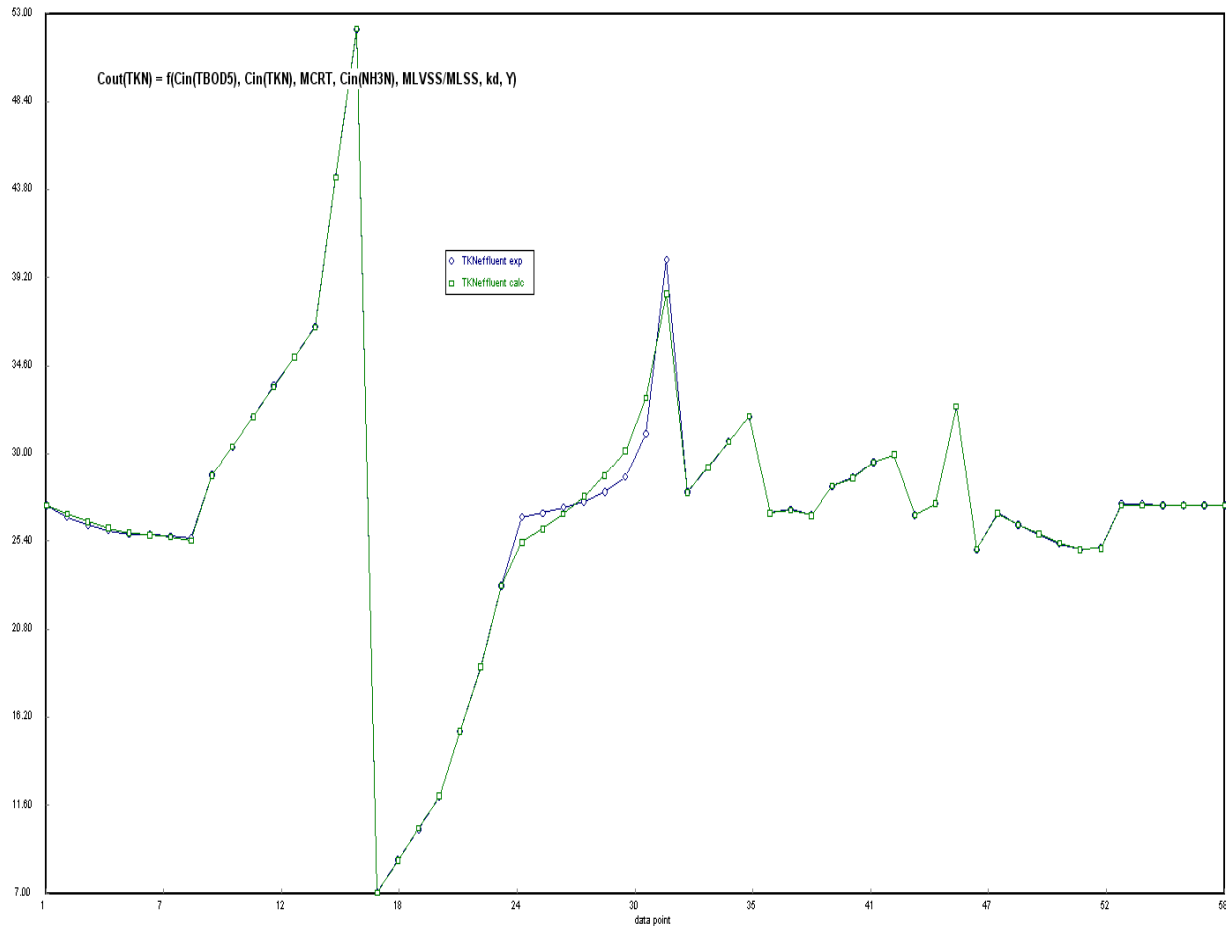
So, the procedure for determining this inequality is to first calculate F_{LV} (abscissa ratio) and then choose one of three options:

Case	Inequality that must be satisfied	Result
1	$F_{LV} = \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \leq 0.1$	$D_T = \left[\frac{4VM_V}{0.80 \cdot [4d_p g / (3C_D)]^{1/2} \cdot [(\rho_L - \rho_V) / \rho_V]^{1/2} \cdot \pi \cdot 0.90 \cdot \rho_V} \right]$
2	$0.1 \leq F_{LV} = \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \leq 1.0$	$D_T = \left[\frac{4VM_V}{0.80 \cdot [4d_p g / (3C_D)]^{1/2} \cdot [(\rho_L - \rho_V) / \rho_V]^{1/2} \cdot \pi \cdot \left[8 - \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \right] / 9 \cdot \rho_V} \right]$
3	$F_{LV} = \left(\frac{LM_L}{VM_V} \right) \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \geq 1.0$	$D_T = \left[\frac{4VM_V}{0.80 \cdot [4d_p g / (3C_D)]^{1/2} \cdot [(\rho_L - \rho_V) / \rho_V]^{1/2} \cdot \pi \cdot 0.80 \cdot \rho_V} \right]$

Table 5. Total column diameter as a function of liquid and vapor flowrates

III. Biological Treatment (Activated Sludge)

The most commonly used biological treatment is the activated sludge process^{xxiii}, where microorganisms present in wastewater feed on the organic constituents thereby purifying the water. Since activated sludge is the most common process, it was the one modeled. As mentioned before, the program *Steady* developed by professors at the University of Texas was used to simulate an activated sludge process. The activated sludge simulation required outlet concentrations of TBOD₅ (mg/L) and SBOD (mg/L) to be specified, and since no nitrification was occurring in the process, the only outlet concentration that varied was the outlet concentration of the TKN (mg/L). This was the contaminant that was modeled. Results from the non-linear regression are shown below.



From points 1-8, inlet concentration of TBOD₅ (mg/L) was varied. From points 9-16, inlet concentration of TKN (mg/L) was varied. From points 17-23, inlet concentration of NH₃—N (mg/L) was varied. From points 24-31, the Y value, which is the biomass yield, was varied.

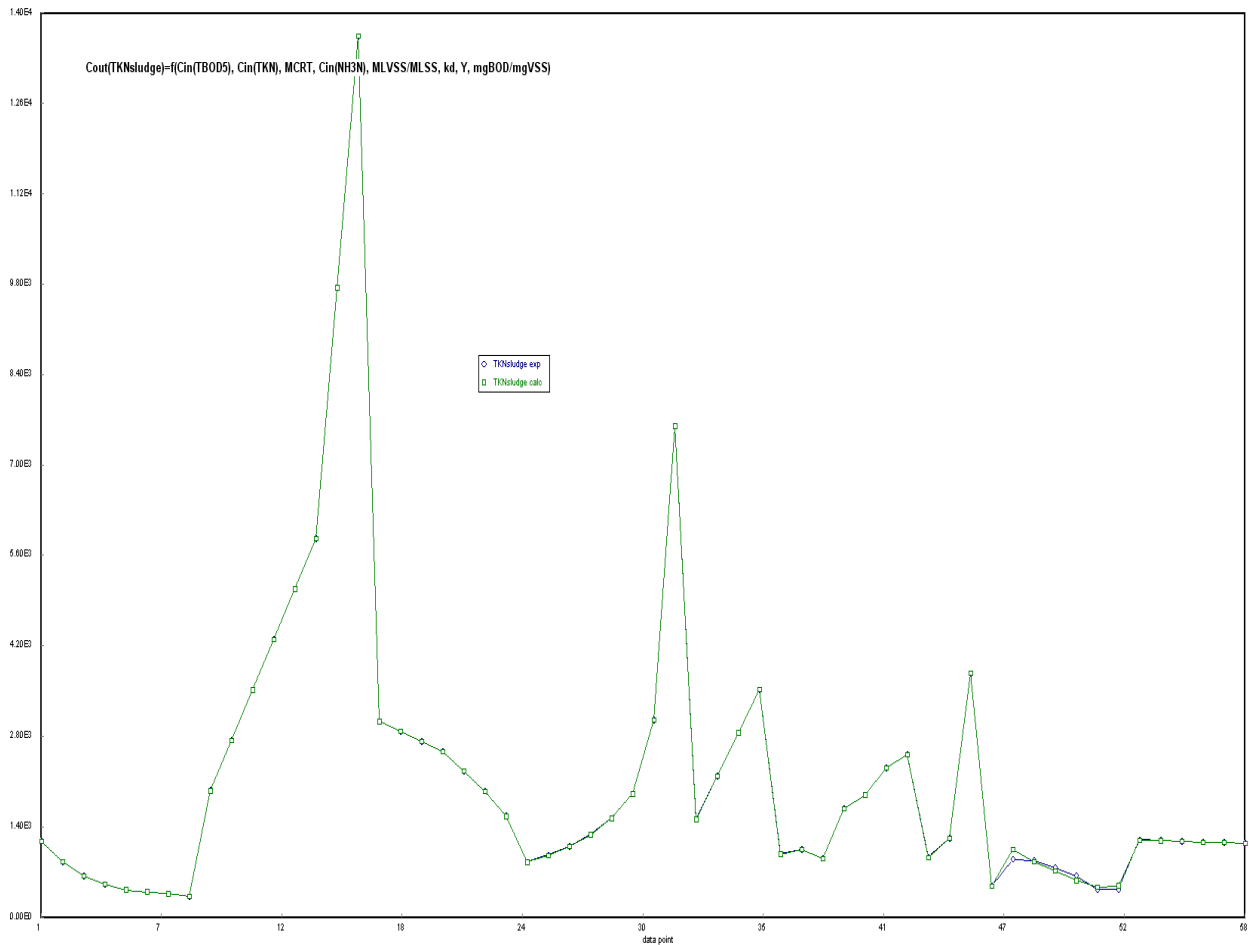
Biomass yield is the grams of biomass produced per gram of substrate utilized [g VSS/g COD used]. From points 32-38, k_d was varied and k_d is the endogenous decay coefficient [g VSS/g VSS·d]. From points 39-45, the mean cell residence time (MCRT), the amount of time a contaminant stays in the process, was varied. From points 46-52, the ratio of mixed liquor volatile suspended solids to mixed liquor suspended solids was varied. The final result is given below:

$$C_{TKN, effluent} (ppmw) = -135C_{in, TBOD5}^{0.01} + 0.16C_{in, TKN} + 0.84C_{in, NH_3-N} - 2287Y^{0.0026} + 13.4k_d + 0.08MCRT - 12.25e^{-0.27\left(\frac{MLVSS}{MLSS}\right)} + 2436$$

Equation 31

The sludge that exits from the secondary clarifier is rich in the microorganisms used to eat the contaminants. This stream was also modeled to aid the pre-treatment process for this stream.

Regression graph results are shown below:



Parameters were varied in the same manner as for the effluent wastewater stream, however, an extra parameter was found to make a difference in outlet TKN concentration; [mgBOD/mg VSS]. The outlet TKN concentration in the exiting sludge is:

$$C_{TKN, sludge} (ppmw) = 3.436 \times 10^5 C_{in, TKN}^{-1.057} + 77.9 C_{in, TKN} - 77 C_{in, NH_3-N} + 762.5 Y^{-0.998} + 6684.5 k_d + 41.8 MCRT - 99.8 e^{1021.6 \left(\frac{MLVSS}{MLSS} \right)} - 75.9 \frac{mgBOD}{mgVSS} - 3663.7$$

Equation 32

The Polymath report can be seen in Appendix I for the activated sludge process.

IV. Desalter

Finding the outlet H₂S concentration in water was the first task in modeling the desalter. In order to accomplish this, a contaminant mass balance was performed for H₂S:

$$F_{oil} x_{H_2S, in}^{Oil} + F_{Water} x_{H_2S, in}^{Water} = F_{oil} x_{H_2S, out}^{Oil} + F_{Water} x_{H_2S, out}^{Water} \quad \text{Equation 33}$$

A partition coefficient was then applied because water and crude oil are vigorously mixed prior to entering the desalter and so a two-phase mixture exists of water (aqueous) and oil (organic). H₂S partitions between these two phases and exits with the water. The partition coefficient is a function *solely* of temperature and is defined as the differential solubility of H₂S in water and oil:

$$K(T) = \frac{x_{H_2S}^{Water}}{x_{H_2S}^{Oil}} \quad \text{Equation 34}$$

A schematic is shown below for process flow of a desalter. However, PRO/II was NOT used in the derivation of the desalter equation. The diagram in Figure 16 is used for aesthetic and description purposes only.

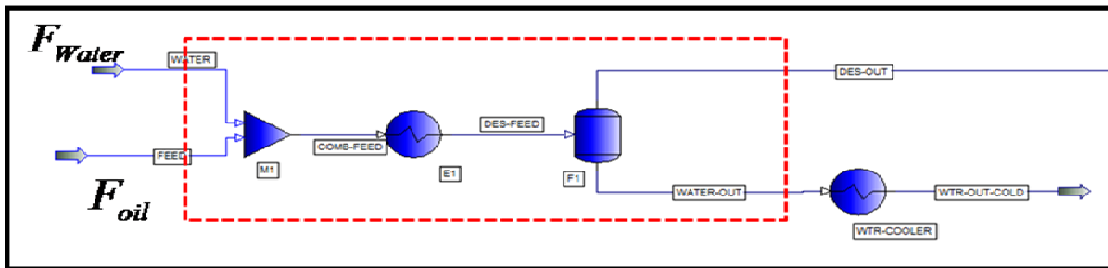


Figure 16. PRO/II file for desalter

Rearranging Equation 16 to solve for $x_{H_2S, out}$ and combining with Equation 17:

$$x_{H_2S, out} = \frac{F_{Oil} x_{H_2S, in}^{Oil} + F_{Water} x_{H_2S, in}^{Water}}{F_{Water} + \frac{F_{Oil}}{K(T)}} \quad \text{Equation 35}$$

From <http://www.atsdr.cdc.gov/toxprofiles/tp114-c4.pdf>, the solubility of H₂S in water at various temperatures is:

at	10	°C	5.3	g/L
at	20	°C	4.1	g/L
at	30	°C	3.2	g/L

Also, the solubility of H₂S in oil at various temperatures is:

at	20	°C	6	g/L
at	100	°C	3	g/L

Plots of these solubilities as a function of temperature is seen as:

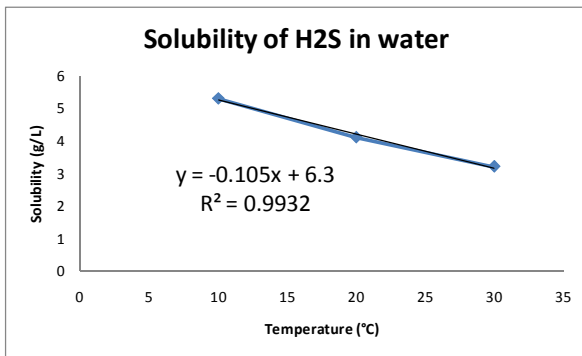


Figure 17. Solubility of H₂S in water

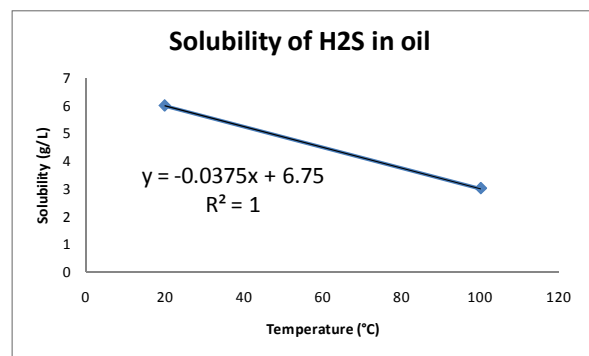


Figure 18. Solubility of H₂S in oil

The solubilities of H₂S in water and oil are then:

$$K(T) = \frac{x_{H_2S}^{Water}}{x_{H_2S}^{Oil}} = \frac{-0.105T + 6.3}{-0.0375T + 6.75} \quad \text{Equation 36}$$

Finally,

$$x_{H_2S, out} = \frac{F_{Oil} x_{H_2S, in}^{Oil} + F_{Water} x_{H_2S, in}^{Water}}{F_{Water} + F_{Oil} \left(\frac{-0.0375T + 6.75}{-0.105T + 6.3} \right)} \quad \text{Equation 37}$$

Finding the outlet salt concentration in water from the desalter was the second task in modeling the desalter. A paper written by Gary W. Sams and Kenneth W. Warren titled *New Methods of Application of Electrostatic Fields* prepared for presentation at AIChE Spring National Meeting was referenced. In a desalter, a suspended water droplet between a pair of electrodes is acted on by five forces:

1. Gravity
2. Drag
3. Electrophoretic
4. Di-electrophoretic
5. Dipole

The following diagram shows the five forces at work in a desalter:

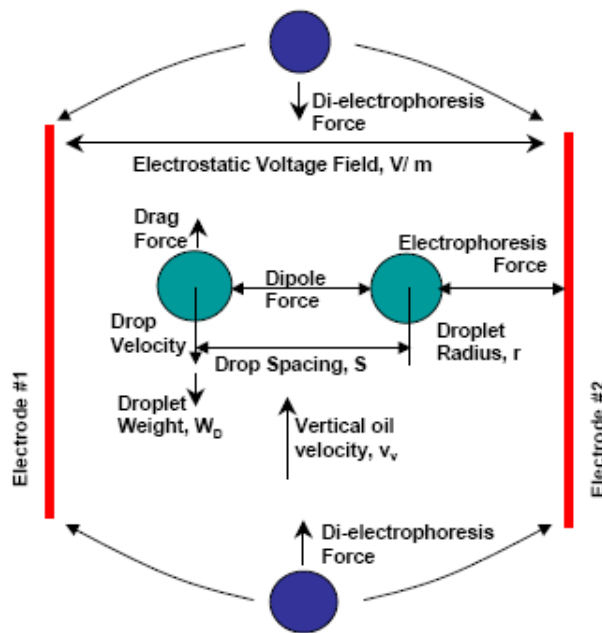


Figure 19. Forces acting on a water droplet inside of a desalter

Gravity and drag forces are taken into account when using Stokes Law (see Equation 1) and in order to maximize desalting process performance, electrostatic forces must enhance coalescence to droplet sizes larger than Stokes diameter.

Dipole forces are established due to the alignment of polar water molecules in the droplet and are given by the equation:

$$F_{dipole} = \frac{6KE^2r^6}{s^4} \quad \text{Equation 38}$$

Electrophoretic forces are attractive and repulsive forces between charged droplets and electrodes and are given by the equation:

$$F_e = C\pi^3\mu\epsilon_C r^2 E^2 e^{\left(\frac{-\sigma_C t}{\epsilon_C}\right)} \quad \text{Equation 39}$$

Finally, di-electrophoretic forces are attractive forces established in a non-uniform field (all particles exhibit di-electrophoretic activity in the presence of electric fields).

$$F_{diel} = 2\pi r^3 \epsilon_C \left(\frac{\epsilon_D^* - \epsilon_C^*}{\epsilon_D^* + 2\epsilon_C^*} \right) \nabla E^2 \quad \text{Equation 40}$$

In order to find the minimum particle size, a force balance was performed for the x and y components of the force acting on a suspended particle in the desalter. Because each particle would be falling at a constant velocity, the sum of the forces were set equal to 0 as acceleration would be 0.

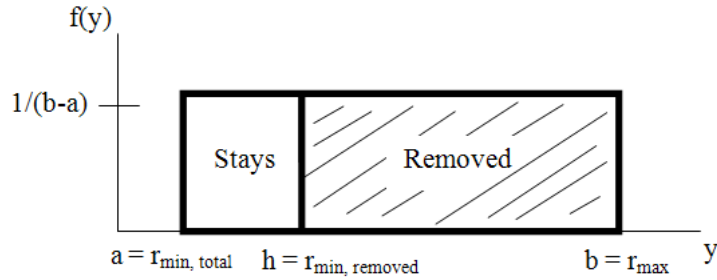
$$\sum F_x = F_{dipole} + F_e + F_{diel} = \frac{6KE^2r^6}{s^4} + C\pi^3\mu\epsilon_C r^2 E^2 e^{\left(\frac{-\sigma_C t}{\epsilon_C}\right)} + 2\pi r^3 \epsilon_C \left(\frac{\epsilon_D^* - \epsilon_C^*}{\epsilon_D^* + 2\epsilon_C^*} \right) \nabla E^2 = 0$$

Equation 41

where the minimum particle size removed in the desalter is represented in the rearrangement of Stokes Law as seen in Equation 13:

$$\hat{r} = \sqrt{\frac{9\mu(H-h)F}{2(\rho_w - \rho_o)gV}} \quad \text{Equation 42}$$

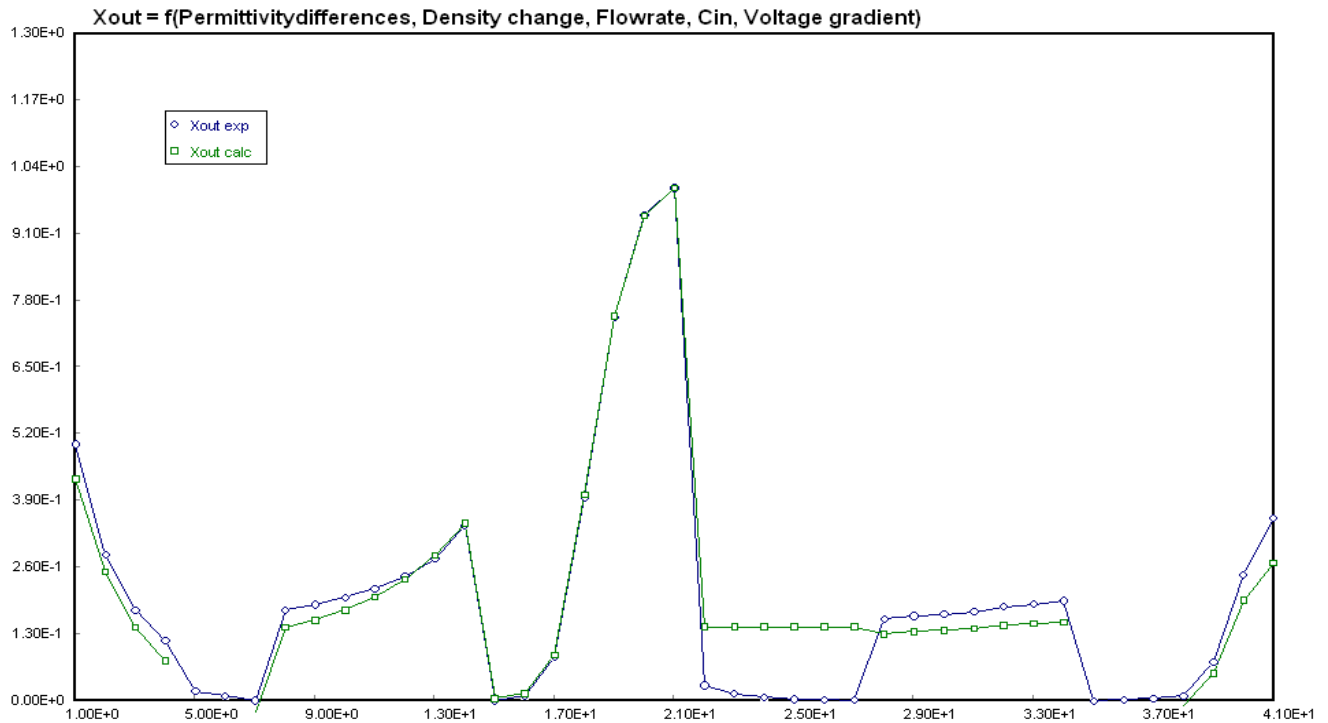
The water particles entering the desalter were assumed to be uniformly distributed throughout the crude oil. Thus, the particles follow a uniform probability distribution:



Thus, the mass fraction of contaminants removed from the wastewater is:

$$y = \frac{\int_a^h \left[\left(\frac{4}{3} \pi r^3 \right) \cdot \frac{1}{H} \right] dr}{\int_0^\infty \left[\left(\frac{4}{3} \pi r^3 \right) \cdot \frac{1}{H} \right] dr} \quad \text{Equation 43}$$

System properties such as voltage, electric field gradient, C_{in} , density change, flowrate, etc. were varied and the mass fraction of contaminants remaining in the desalter was measured. The results from a non-linear regression are shown below:



From points 1-7, permittivity differences in the group of $\epsilon_C \left(\frac{\epsilon_D^* - \epsilon_C^*}{\epsilon_D^* + 2\epsilon_C^*} \right)$ (Farad/meter) were varied. From points 8-14, the $\frac{\Delta\rho}{F}$ (g·hr/cm³·ton) was varied. From points 15-21, inlet concentration of organics (C_{in}) (mg/L) was varied. From points 22-27, voltage (V) was varied. From points 28-34, the exponential of conductivity divided by continuous phase permittivity $e^{\left(\frac{-\sigma_C t}{\epsilon_C}\right)}$ was varied. From points 35-41, the voltage field gradient, ΔE, in Volts, was varied. The final resulting equation is shown below:

$$X_{out} = 0.035e^{(5.40 \times 10^{-6})\epsilon_C \left(\frac{\epsilon_D^* - \epsilon_C^*}{\epsilon_D^* + 2\epsilon_C^*}\right)} + (5.77 \times 10^{-5})e^{4.77 \frac{\Delta\rho}{F}} + (1.85 \times 10^{-23})C_{in}^{1.03 \times 10^{-4}} + 2.99V^{0.0013} + (3.69 \times 10^{-4})e^{\left(\frac{-\sigma_C t}{\epsilon_C}\right)} + (5.04 \times 10^8)\Delta E^{8.26 \times 10^{-4}} + 0.00023$$

Equation 44

V. Crude oil distillation column

The crude oil distillation column modeling was completed using a Casestudy, built-in distillation column made from the creators of PRO/II as seen in Figure 20 below. The stream circled in red is the wastewater stream. Inlet stream variables and system properties were varied. The different types and amount of organics present in the wastewater stream were various (i.e. ethane, pentane, propane, n-butane, etc.), thus the total amount of organics leaving in the wastewater was found by subtracting sum of all organics from unity.

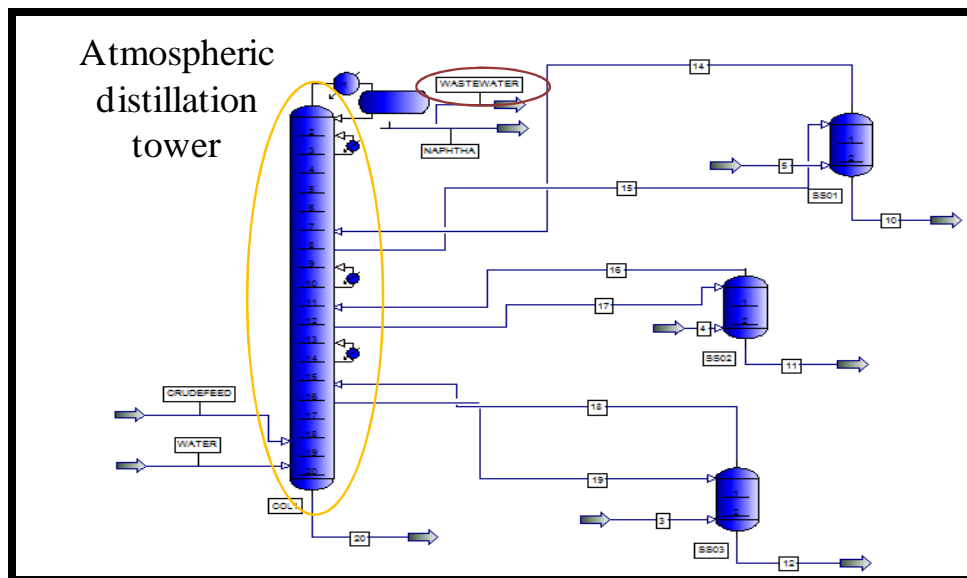
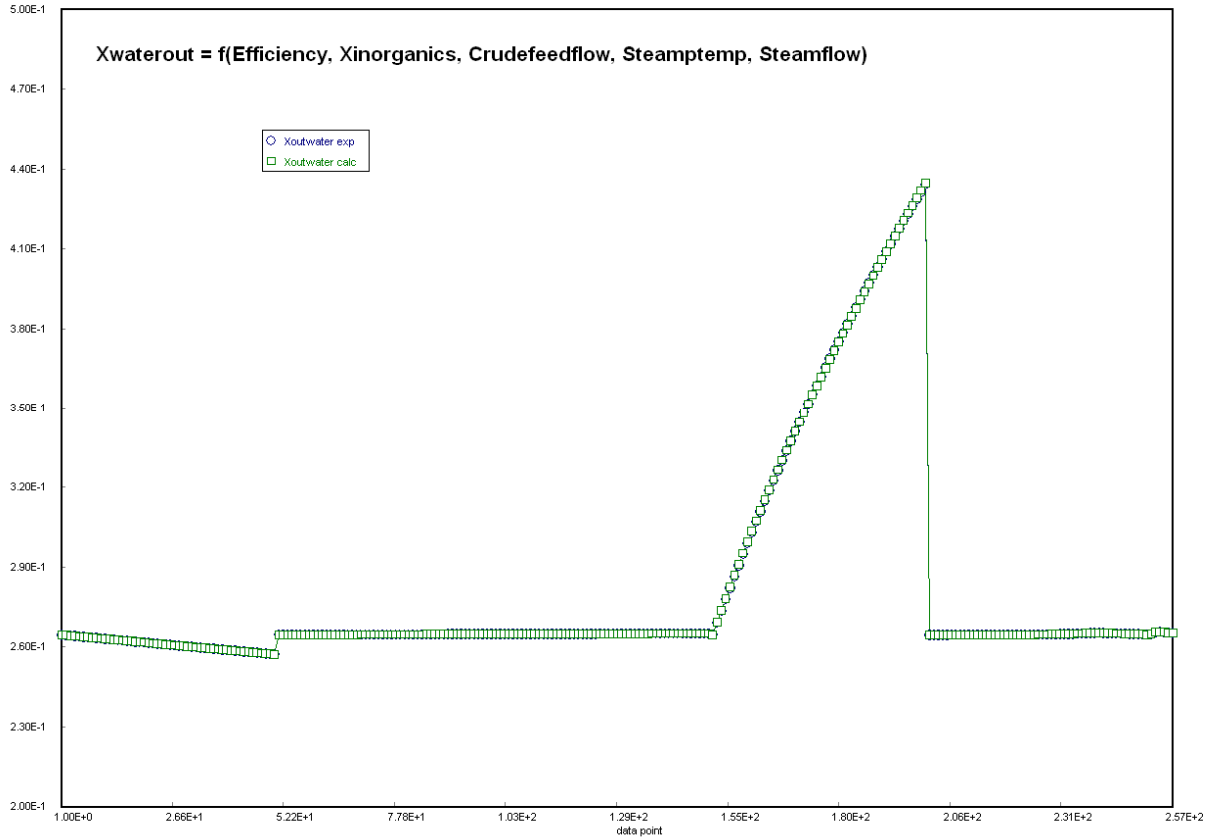


Figure 20. Crude oil distillation column

The non-linear regression is shown below:



From points 1-50, crude feedrate, F_{crude} (ton/hr), was varied. From points 51-150, steam temperature, T ($^{\circ}\text{F}$), was varied. From points 151-200, steam flowrate, F_{steam} (ton/hr), was varied. From points 201-250, efficiency (η) was varied. From points 251-257, the mass fraction of organics in ($X_{\text{in, organics}}$) was varied. The resulting equation is shown below:

$$x_{\text{out,old}} = 0.113 \cdot \eta^6 - 0.606 \cdot \eta^5 + 1.298 \cdot \eta^4 - 1.419 \cdot \eta^3 + 0.834 \cdot \eta^2 - 0.250 \cdot \eta - (3 \times 10^{-5}) F_{\text{crude}} + (2.202 \times 10^{-7}) T + (1.88 \times 10^{-4}) F_{\text{steam}}^{0.557} + 0.014 \cdot x_{\text{in}}^4 - 0.135 \cdot x_{\text{in}}^3 + 0.472 \cdot x_{\text{in}}^2 - 0.719 \cdot x_{\text{in}} + 0.686$$

Equation 45

Comparison of concentration models with simulation results

As is obvious from descriptions of how the equations were developed, the models are linear in the sense that they were made by varying only one parameter at a time (for instance, pressure was varied for 10 points, temperature for 10 points, flowrate for 10 points, etc.) Effects between parameters were not considered (like how temperature would realistically change with pressure) and this was hypothesized to introduce differences between real, simulated results and those predicted from the theoretical, developed equations. To check for differences, inlet stream parameters and system properties were randomly varied and 15 points were generated using the simulation program and these results were compared to those predicted from the theoretical equations. A correction equation was then applied to any model with a percent error of greater than 5%, as this would be a difference of ~1-2 ppm (an acceptable difference).

$$\% \text{ error} = \frac{|Actual \text{ result} - theoretical \text{ result}|}{Theoretical \text{ result}} \times 100\% \quad \text{Equation 46}$$

An example of a table generated is shown in Tables 6-7 below for the activated sludge system. The % error was found to be at most ~3%.

From Simulation (Steady)								
	Cin.TBOD ₅ (mg/L)	Cin.TKN (mg/L)	Cin. NH ₃ -N (mg/L)	Y (mg VSS/mg SBOD ₅)	k _n (d ⁻¹)	MCRT (d)	MLVSS/MLSS	Cout.TKN (ppm)
Run 1	220	40	25	0.65	0.05	8	0.75	27.3
Run 2	220	85	50	0.65	0.05	8	0.75	55.4
Run 3	400	70	40	0.65	0.05	8	0.75	43
Run 4	200	70	40	0.4	0.1	5	0.75	49
Run 5	300	65	30	0.6	0.2	7	0.6	36.8
Run 6	110	30	12	0.3	0.09	3	0.55	20.8
Run 7	275	50	45	0.8	0.3	4	0.55	45.6
Run 8	275	50	25	0.65	0.15	8	0.4	29.2
Run 9	220	45	35	0.7	0.15	8	0.7	37.1
Run 10	200	70	50	0.65	0.3	10	0.3	54
Run 11	350	85	30	0.5	0.05	5	0.75	39.1
Run 12	325	85	25	0.8	0.25	8	0.8	36.5
Run 13	220	100	25	0.55	0.08	6	0.5	37.8
Run 14	300	35	30	0.65	0.05	7	0.5	30.4
Run 15	285	55	20	0.6	0.07	5	0.75	25.9

Table 6. Simulated results from *Steady* by randomly varying variables that affect outlet concentration

From Equation								
	Cin.TBOD ₅ (mg/L)	Cin.TKN (mg/L)	Cin. NH ₃ -N (mg/L)	Y (mg VSS/mg SBOD ₅)	k _n (d ⁻¹)	MCRT (d)	MLVSS/MLSS	Cout.TKN (ppm)
Run 1	220	40	25	0.65	0.05	8	0.75	27.78433656
Run 2	220	85	50	0.65	0.05	8	0.75	55.98433656
Run 3	400	70	40	0.65	0.05	8	0.75	44.32997909
Run 4	200	70	40	0.4	0.1	5	0.75	48.6319467
Run 5	300	65	30	0.6	0.2	7	0.6	37.53360999
Run 6	110	30	12	0.3	0.09	3	0.55	20.41721864
Run 7	275	50	45	0.8	0.3	4	0.55	47.10733691
Run 8	275	50	25	0.65	0.15	8	0.4	29.41451499
Run 9	220	45	35	0.7	0.15	8	0.7	37.74815131
Run 10	200	70	50	0.65	0.3	10	0.3	55.93760778
Run 11	350	85	30	0.5	0.05	5	0.75	39.83904217
Run 12	325	85	25	0.8	0.25	8	0.8	36.00782756
Run 13	220	100	25	0.55	0.08	6	0.5	37.91973565
Run 14	300	35	30	0.65	0.05	7	0.5	29.96312713
Run 15	285	55	20	0.6	0.07	5	0.75	26.11839694

Table 7. Predicted results from *Steady* by randomly varying variables that affect outlet concentration

The corresponding % error between each simulated and theoretical result is shown in Table 8. The greatest % error is highlighted in yellow.

Cout, TKN (ppm) SIMULATION	Cout, TKN (ppm) THEORETICAL	% Error
27.3	27.78433656	1.774126584
55.4	55.98433656	1.054759129
43	44.32997909	3.092974631
49	48.6319467	0.75112918
36.8	37.53360999	1.99350542
20.8	20.41721864	1.840294983
45.6	47.10733691	3.30556339
29.2	29.41451499	0.734640393
37.1	37.74815131	1.747038569
54	55.93760778	3.58816255
39.1	39.83904217	1.890133416
36.5	36.00782756	1.348417653
37.8	37.91973565	0.316760976
30.4	29.96312713	1.437081801
25.9	26.11839694	0.843231418

Table 8. % error between simulation and theoretical results

The maximum % error was 3.59 %. As this is under 5%, the equation was regarded as acceptable in predicting outlet concentrations. This same procedure was followed for the other equations developed through a simulation program (Mathcad, PRO/II). The results are shown below:

<u>Water-using unit</u>	<u>Error</u>
H ₂ S Stripper	± 38%
NH ₃ Stripper	± 31%
Crude oil distillation	± 5%
Biological Treatment	± 3%

Table 9. % Error for water-using units between simulated and theoretical equations

The crude oil distillation and biological treatment produced acceptable ranges for error, while the H₂S stripper and the NH₃ stripper produced errors on the magnitude of ~30-40%. Thus, a correction equation was developed to account for these differences and to try to equate the

equation result with the simulated result. As the H₂S stripper always produced concentrations less than the maximum outlet concentration of the Chevron Wastewater Treatment plant (5 ppm), no correction equation was made. The ammonia stripper results are shown in Figure 21. The correction equation is found to be $y = 0.9392x + 4.1579$, where “x” is the result predicted from the equation and “y” is the result found from the simulation program. The coefficient of determination was found to be $R^2 = 0.6289$. It’s clear that an applied linear regression did not provide the best fit between simulated and predicted results. If any differences exist between actual data from a refinery and predicted results, neglecting effects between stream variables whilst developing models for the regeneration processes could be the source of error.

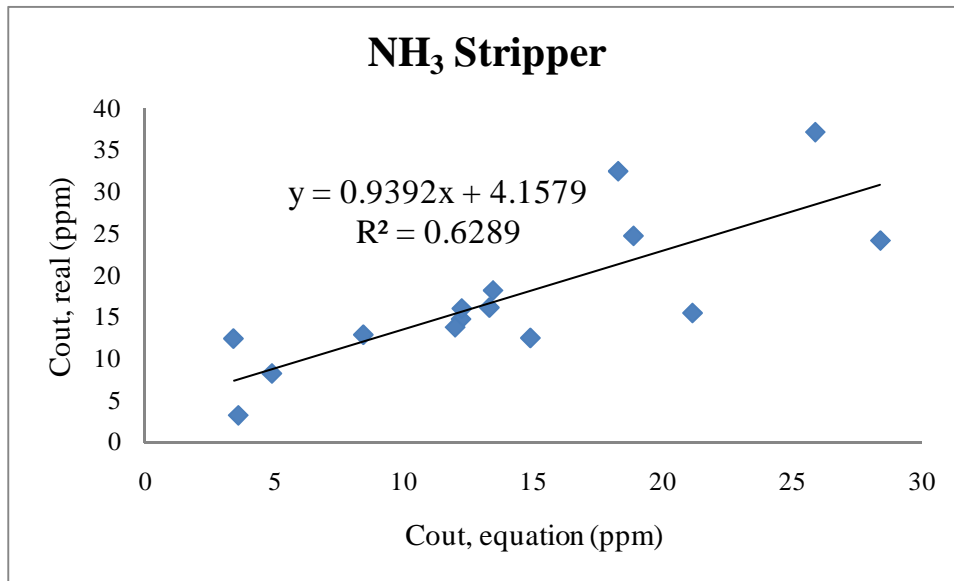


Figure 21. Correction equation for NH₃ Stripper

Equipment Cost models

I. API separator

The majority of the costs that go into purchasing an API separator are the costs of the material being used. Therefore, equipment cost will be a function primarily of the separator volume. All that needs to be done are simple multiplications involving properties of the material chosen to build the reactor. Stainless steel will be chosen as the API separator material because it is durable and resistant to corrosion^{xxiv}. The final equation is based off of density, volume, and price of steel. A full derivation is shown in Appendix II.

$$Cost = 6539.05 \cdot V(m^3) \quad \text{Equation 47}$$

II. Chevron Wastewater Treatment

Equipment costs for a Chevron Wastewater Treatment (CWWT) plant are dependent on the number of trays, feedrate, vertical height of the columns, reboil ratio, materials cost, and density difference between the passing streams. Since the CWWT plant consists of two stripping columns, the equipment cost for one will be dependent on the same parameters as the other. Basically, the diameter of the column was first solved for in terms of feedrate and the Souders and Brown factor, which is a function of the density difference between passing streams. Standard tray spacing for large-diameter columns are generally either 0.46 or 0.61 m^{xxv}. 0.61 meter tray spacing was chosen in this study. The final result of equipment cost for a CWWT is shown in Equation 27. A full derivation of the CWWT plant equipment costs is shown in Appendix II.

$$Equipment\ Cost = 7423H + (674.4N) \cdot e^{\frac{1.12\sqrt{F}}{-0.071\Delta\rho^{1/4} \ln(RBR \cdot \Delta\rho^{1/2}) + 0.195\Delta\rho^{1/4}}} + 42193$$

Equation 48

III. Biological Treatment (Activated Sludge)

As mentioned before, an activated sludge system is the most common biological treatment type. The system consists of an aeration tank where air is bubbled through the tank wastewater followed by a settling tank where cellular material is removed by gravitational

settling. The aeration tank was modeled as an ideal CSTR. The turbulent conditions created by the high flow rate air stream establish a perfect mixing environment. Equipment cost for the secondary clarifier (settling tank) was found to be dependent on reactor size (m^3), inlet flow rate (ton/hr), and inlet concentration (ppm). A full derivation is shown in Appendix II.

$$\text{Equipment Cost}(\$) = 183 \cdot V(m^3) = \frac{646.48 \cdot F \cdot (100 - C_{in,org})}{[0.1 \cdot (C_{in,org} - 100) + 0.001]} + 866,019 \cdot F \quad \text{Equation 49}$$

$$\text{where } V \geq \frac{70.65 \cdot F \cdot (100 - C_{in,org})}{(C_{in,org} - 100) + 0.01} + 9464 \cdot F \quad \text{Equation 50}$$

IV. Reverse Osmosis

The cost of the reverse osmosis was computed based on the most significant equipment costs associated with the plant in the industry. These are the cost of the membrane replacement, which has to be done frequently to avoid fouling and reduce efficiency and the pump cost. The equation governing this cost was found to be:

$$\text{Equipment Cost} \left(\frac{\$}{yr} \right) = 180 \cdot A \cdot N + 8053.25 \cdot \left(\frac{\Delta P \cdot F}{\eta} \right) \quad \text{Equation 51}$$

where A: area per membrane

N: number of membrane used

F: flow rate to the process

V. Activated Carbon Adsorption

As a result of the adsorption being a fixed bed, the basic cost of the process was the cost of regeneration of the bed after saturation. This cost of the fixed bed adsorber depends on the capacity of the bed based on the feed concentration of the wastewater and given the equation:

$$\text{Equipment cost}(\$) = \$7200 C_F Q \quad \text{Equation 52}$$

Mathematical Programming Results

General Algebraic Modeling System (GAMS)

The GAMS mathematical modeling program was used to optimize the placement and size of the water streams in an oil refinery setting. Using the mixed integer program (MIP) and the relaxed mixed integer program (rMIP) to solve the linear portions of the model as well as the mixed integer non-linear program (MINLP) to solve the non-linear portions, we were able to employ the CPLEX and DICOPT solvers to optimize the water regeneration system.

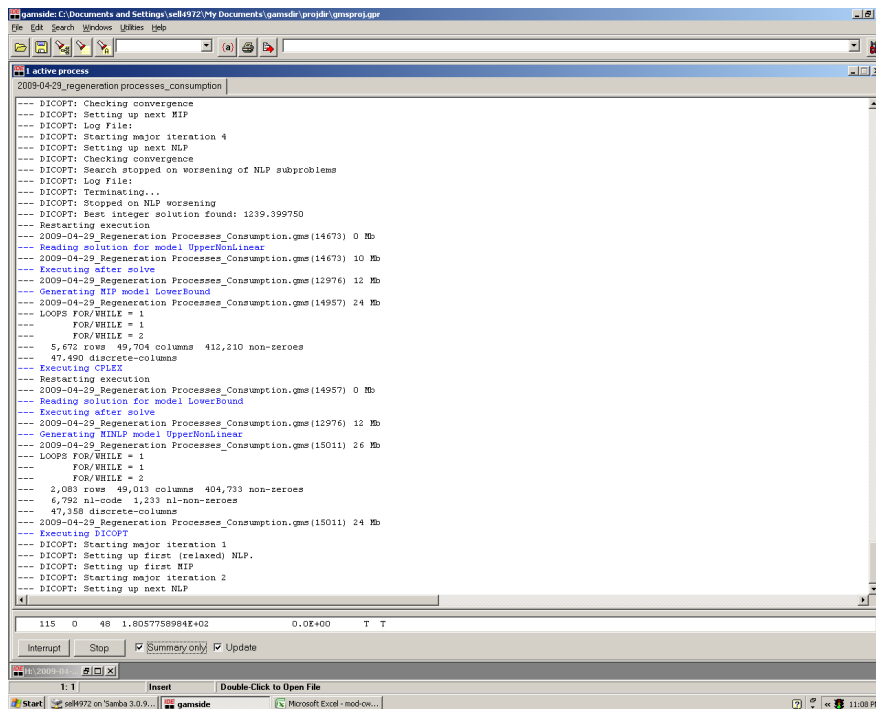


Figure 22. GAMS Program Screenshot

We optimized the system of equations based on two different objective functions, cost and consumption:

- $Cost = Annual\ Operation\ Cost + Annual\ Fixed\ Cost$
- $Consumption = Freshwater\ to\ water-using\ units + Freshwater\ to\ regeneration\ units$

With these two objective functions, we set the output to give the lowest total annualized cost or the lowest annual amount of freshwater consumed.

Past models of water regeneration processes made assumptions for the outlet concentrations coming out of the water-using units and the regeneration processes. Assumptions such as a fixed outlet concentration or a fixed unit efficiency caused previous models to provide

less than ideal results. With the modeled outlet concentrations mentioned in the first part of this report, we are able to find more realistic results spanning a wider range of operating conditions. With these more realistic results, a more confident conclusion can be reached on the economic and environmental impact of utilizing the regeneration process model.

Results

The GAMS model that was created provided over 400,000 non-zero terms with over 1,200 non-linear, non-zero terms. The model took anywhere from one to five hours to run for each simulation and read and processed over 17,000 lines of code. The output of the model provided stream by stream data linking the freshwater source, water-using units, regeneration processes, and water disposal sites all together. An example of the output data is shown in the appendix. The program was run with only the regeneration processes containing outlet concentration models. The water-using units will be added to the program at a later date. With the model standing as it is now though, the process flow diagram of the refinery’s water using units changed from a traditional flow like this:

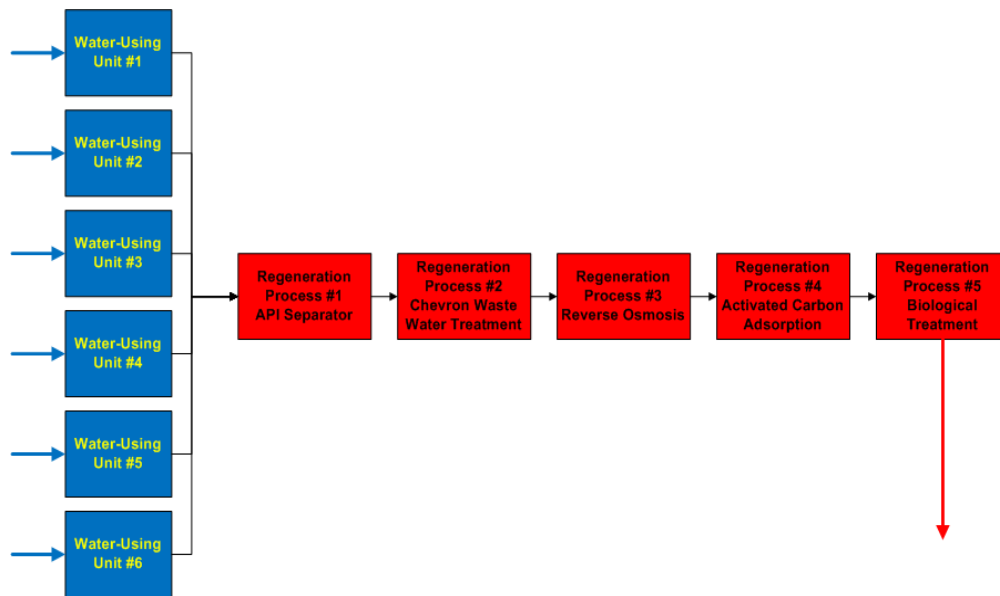


Figure 23. Traditional Water Regeneration

to a new output where streams can flow back and forth from regeneration processes to water-using units and back in the most efficient manner. An example of this new output is shown below:

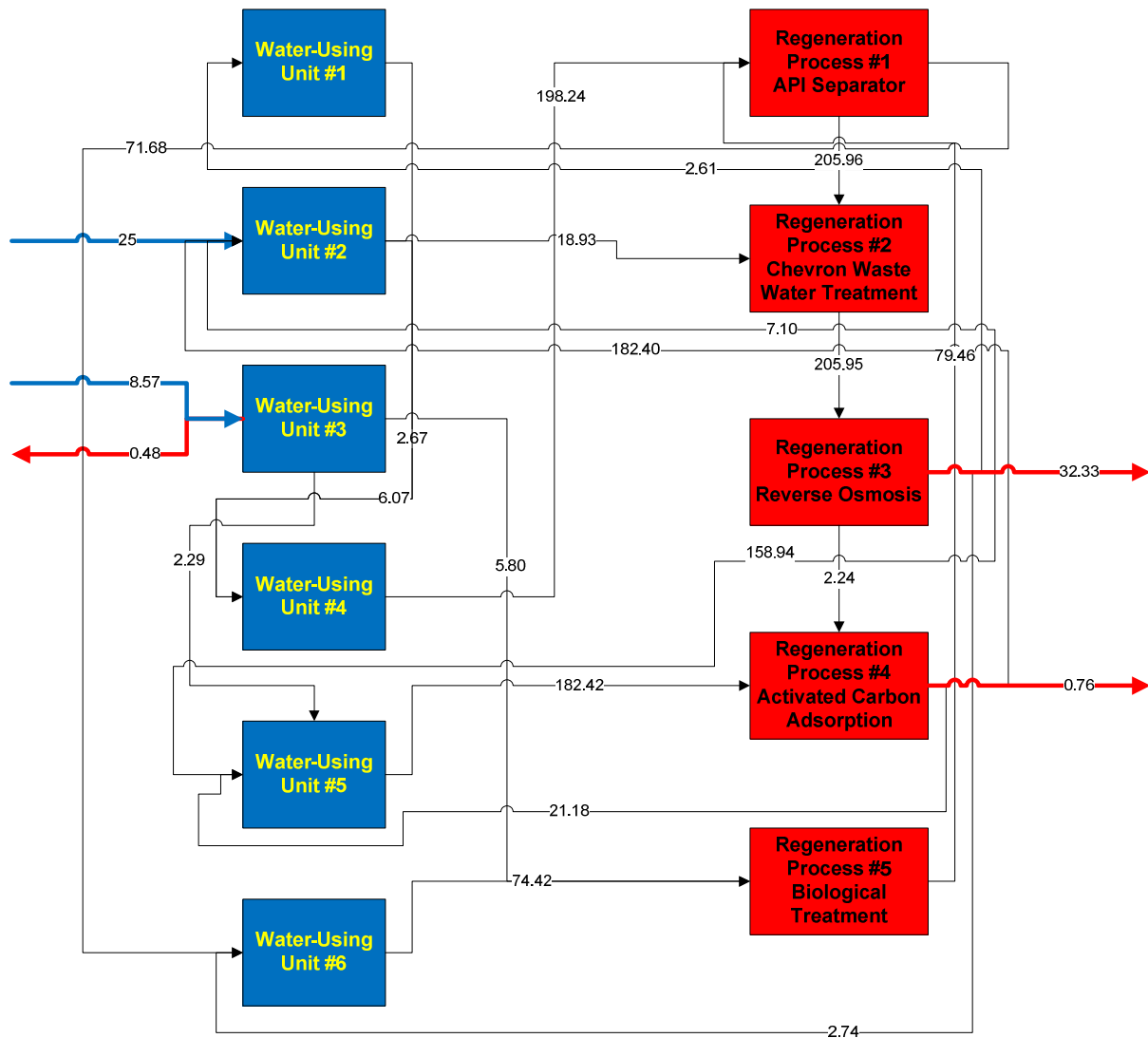


Figure 24. Optimized Water Regeneration

with this schematic, the following contaminant concentrations were cleaned using the regeneration processes:

Contaminant Stream Concentration Reduction (ppm)			
Salts	Organics	H ₂ S	Ammonia
621.18	7153.77	27.23	18.61

By including the modeled outlet concentrations of the regeneration processes into our mathematical model, we provided more realistic results to conclude an expected cost of \$950,000 (instead of \$1,220,000 as seen with the fixed outlet concentration model) and a water consumption of 31 tons/hour (instead of 33 tons/hour). We obtained these results by setting

constraints of 250 tons/hour as the maximum stream flow rate and a contaminant outlet limit of 20, 50, 5, and 30 ppm for salts, organics, H₂S, and ammonia respectively. These model results might differ minimally between fixed outlet concentrations and modeled outlet concentrations, but the improved reliability and confidence provides a more usable program for any user who might find it useful. Further tables indicating water stream placement (i.e. flow rate to and from water-using and regeneration processes in ton/hr) are seen in Appendix III.

Conclusions

This study focused on deriving original correlations for predicting wastewater contaminant levels from water treatment and a few water-using units in petroleum refineries. While there is no exact model that exists to find contaminant levels, non-linear regression can be used to approximate a highly accurate answer (with determination coefficients in the range of ~0.99). However, since developed models were found by varying one parameter at a time, non-linear models (i.e. accounting for how pressure might be related to temperature simultaneously) of the outlet concentration of contaminants provide a more accurate model to represent refinery waste water generation. Of course, all of the procedures aforementioned are performed based on the assumption that the simulation method used is highly accurate. For the sake of this study, which uses programs like PRO/II and Mathcad to generate points for a guessed model, it will be assumed that errors are at a minimum within the system. Other simulation programs like Aspen's HYSYS could be used to check the accuracy of PRO/II runs, if made available to the student. Also, comparing actual data from a petroleum refinery with theoretical model results would ensure that the guessed models in this study are at least close to predicted values, if not entirely incorrect. Once again though, availability is the dilemma at hand, as the information needed to compare could be closely guarded and perhaps laden with legal consequences. As government regulations are becoming increasingly strict in laws regarding treated wastewater, it is, in effect, becoming important to develop more accurate models. Accurate predictions of treated water streams and obeying the government standards set for these contaminant levels not only guarantees a trouble-free work environment, but also promotes a safe and healthy living environment. A final conclusion is that equipment costs of the water regeneration processes are a function of inlet concentrations and flow rates, as well as design parameters.

Recommendations

The crux of wastewater management lies in the optimization of wastewater and freshwater streams. Thus, as optimization models increase in accuracy, the accuracy of corresponding stream placement and flowrates increase. Recommendations for future work in the continuing water management problem include:

- Modeling of the vacuum distillation column, hydrotreatment unit, and Merox I sweetening unit
- More accurate modeling of operating costs for the regeneration processes
- Implement all newly-found models in GAMS file (mathematical model)
- Expand the scope of the project to include other industrial cases where water is used to treat contaminants, e.g. a tricresyl phosphate process or a paper mill process
- Derive an economic plan for refinery wastewater system (including costs of piping, costs of process units, location and prices of pumps, salaries, etc.)
- Investigate water treatment and water-using units for countries other than the U.S., like Canada or Mexico
 - Find out if the water treatment and water-using units are similar to those used in the U.S.
 - What are the permitted drinking water contaminant levels in that country? Are they similar to the U.S.? If so, are large oil companies abiding by these laws?
 - Are industries really following government guidelines? Is the government even setting a guideline? If not, could this be the reason why so many oil companies are willing to export their business to countries outside of the U.S. so they don't have to adhere to strict water laws? What kind of money could be saved if water treatment processes were used at a bare minimum?

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Polymath results for activated sludge:

POLYMATH Results

No Title 03-02-2009

Nonlinear regression (L-M)

Model: TKNeffluent =

$$a*(TBOD5^b)+c*TKN+e*NH3N+g*(Y^i)+j*kd+m*MCRT+(o*MLVSSoMLSS*MLVSSoMLSS)+(p*MLVSSoMLSS)+d$$

<u>Variable</u>	<u>Ini guess</u>	<u>Value</u>	<u>95% confidence</u>
a	35	20.033392	0.2483401
b	-0.04	-0.1381159	0.0022601
c	0.16	0.0055365	0.0021003
e	0.843	0.4414261	0.0049
g	26	15.213166	0.1693005
i	-0.11	0.8397723	0.0251757
j	13.4	-69.166537	1.3530784
m	0.083	-0.4107851	0.0080561
o	25	7.3439867	0.2195136
p	0.123	-13.176989	0.1637615
d	1300	1290.1729	0.1163555

Nonlinear regression settings

Max # iterations = 300

Precision

R^2 = -3.233E+04

R^2adj = -3.921E+04

Rmsd = 167.96354

Variance = 2.019E+06

General

Sample size = 58

Model vars = 11

Indep vars = 7

Iterations = 22

Polymath report for sludge in activated sludge:

POLYMATH Results

No Title 02-25-2009

Nonlinear regression (L-M)

Model: TKNsludge =

$$a*(TBOD5^b)+c*TKN+e*NH3N+g*(Y^i)+j*kd+m*MCRT+(o*MLVSStoMLSS*MLVSStoMLSS)+(p*MLVSStoMLSS)+(q*mgBODtomgVSS)+d$$

<u>Variable</u>	<u>Ini guess</u>	<u>Value</u>	<u>95% confidence</u>
a	2.447E+05	3.436E+05	6.195E+05
b	-0.989	-1.0566498	0.3699678
c	77.9	77.885427	0.2837419
e	-77	-77.035544	1.3641259
g	780	762.48543	74.635933
i	-0.99	-0.998504	0.03776
j	6673	6684.5207	127.00663
m	42	41.789081	0.7679007
o	-1798	-99.853572	307.24985
p	1829	1021.5736	253.5563
q	-83.4	-75.891695	97.216543
d	4598	-3663.6664	255.4147

Nonlinear regression settings

Max # iterations = 300

Precision

R^2 = 0.9998816

R^2adj = 0.9998533

Rmsd = 3.3082243

Variance = 800.36492

General

Sample size = 58

Model vars = 12

Indep vars = 8

Iterations = 27

Polymath report for Amine Sweetening

POLYMATH Results

03-08-2009

Nonlinear regression (L-M)

Model: steam = (a*(Regcondenpress^(-1)))+(b*Feedtemp)+c)

<u>Variable</u>	<u>Ini guess</u>	<u>Value</u>	<u>95% confidence</u>
a	1.705	0.0232341	8.851E-04
b	1.0E-08	-2.967E-05	7.559E-06
c	0.125	0.006946	0.0040712

Nonlinear regression settings

Max # iterations = 64

Precision

R^2 = 0.9887651

R^2adj = 0.9885335

Rmsd = 3.421E-04

Variance = 1.206E-05

General

Sample size = 100

Model vars = 3

Indep vars = 2

Iterations = 5

Polymath results for H₂S Stripper:

POLYMATH Results

No Title 04-20-2009

Nonlinear regression (L-M)

Model: CoutH2S =

$$a*\exp(b*CinNH3)+c*\exp(d*Temp)+e*(Efficiency^f)+g*(CinH2S^2)+(h*CinH2S)+i*(Numberoftrays^j)+k$$

<u>Variable</u>	<u>Ini guess</u>	<u>Value</u>	<u>95% confidence</u>
a	2.0E-06	0.0023514	6.18E-04
b	0.7648	0.0792118	0.0565716
c	3.0E-06	-1.0002578	0.3104719
d	0.0142	-0.0385425	0.0020614
e	3.0E-05	-0.0143649	7.966E-04
f	-0.908	-0.137697	0.1722801
g	1.0E-06	0.0112059	2.959E-05
h	-2.0E-06	0.0012207	1.618E-04
i	5244	2.17E+04	24.371227
j	-7.377	-7.0772926	0.0010207
k	9.0E-06	0.015824	8.152E-05

Nonlinear regression settings

Max # iterations = 300

Precision

R² = 0.9994561

R²adj = 0.9994201

Rmsd = 0.0013088

Variance = 2.977E-04

General

Sample size = 162

Model vars = 11

Indep vars = 5

Iterations = 71

Polymath results for NH₃ Stripper:

POLYMATH Report
Nonlinear Regression (L-M)

No Title
28-Apr-2009

Model: CoutNH3 =

$$a*(Feedrate^2)+b*Feedrate+c*CinNH3+d*\exp(NumberOftrays*e)+f*\exp(g*Temp)+h*RFR+i*(Pressure^j)+k*(Efficiency^2)+l*Efficiency+m*(CinH2S^n)+o$$

Variable	Initial guess	Value	95% confidence
a	0.0006	0.0006762	3.554E-06
b	0.0106	-0.0064736	9.96E-05
c	0.0306	-0.056633	0.0006159
d	9106.6	1.546E+04	0.4341984
e	-0.824	-0.6966562	5.606E-06
f	7.0E-05	8.069E-05	3.885E-09
g	0.0247	0.0250764	8.003E-08
h	0.0069	0.0612676	0.0005577
i	4.481E+04	-4.436E+06	2.257E+04
j	-2.572	-2.940971	0.0009171
k	0.1883	-0.5269187	0.0029861
l	-0.3277	-0.7517399	0.0023763
m	0.041	7.1049645	7.0639645
n	-0.065	0.470095	0.535095
o	0.322	0.237672	0.0018679

Nonlinear regression settings

Max # iterations = 300

Precision

R ²	0.9148893
R ² adj	0.8817907
Rmsd	2.460408
Variance	437.3733

General

Sample size	51
Model vars	15
Indep vars	8
Iterations	18

Source data points and calculated data points

	Feedrate	CinNH3	Numberoftrays	Temp	RFR	Pressure	Efficiency	CinH2S	CoutNH3	CoutNH3 calc	Delta CoutNH3
1	5	3	15	250	3	250	0.8	5	0.00642	-0.6054326	0.6118526
2	10	3	15	250	3	250	0.8	5	0.0752	-0.5870836	0.6622836
3	15	3	15	250	3	250	0.8	5	0.0924	-0.5349234	0.6273234
4	20	3	15	250	3	250	0.8	5	0.124	-0.448952	0.572952
5	25	3	15	250	3	250	0.8	5	0.187	-0.3291694	0.5161694
6	30	3	15	250	3	250	0.8	5	0.277	-0.1755756	0.4525756
7	35	3	15	250	3	250	0.8	5	0.406	0.0118294	0.3941706
8	40	3	15	250	3	250	0.8	5	0.597	0.2330456	0.3639544
9	42	3	15	250	3	250	0.8	5	0.697	0.3309992	0.3660008
10	43	3	15	250	3	250	0.8	5	0.755	0.3820047	0.3729953
11	15	0.3	15	250	3	250	0.8	5	0.00541	-0.3820144	0.3874244
12	15	0.75	15	250	3	250	0.8	5	0.0153	-0.4074992	0.4227992
13	15	1	15	250	3	250	0.8	5	0.0219	-0.4216575	0.4435575
14	15	1.5	15	250	3	250	0.8	5	0.0334	-0.449974	0.483374
15	15	2	15	250	3	250	0.8	5	0.0461	-0.4782904	0.5243904
16	15	2.5	15	250	3	250	0.8	5	0.061	-0.5066069	0.5676069
17	15	4	15	250	3	250	0.8	5	0.108	-0.5915564	0.6995564
18	15	5	15	250	3	250	0.8	5	0.143	-0.6481894	0.7911894
19	15	6	15	250	3	250	0.8	5	0.18	-0.7048223	0.8848223
20	15	3	5	250	3	250	0.8	5	350	473.8129	-123.8129
21	15	3	10	250	3	250	0.8	5	0.424	13.5967	-13.1727
22	15	3	20	250	3	250	0.8	5	0.00483	-0.9688562	0.9736862
23	15	3	25	250	3	250	0.8	5	0.00000242	-0.9821808	0.9821832
24	15	3	30	250	3	250	0.8	5	0.00000022	-0.9825899	0.9825901
25	15	3	15	200	3	250	0.8	5	0.0236	-0.5653663	0.5889663
26	15	3	15	300	3	250	0.8	5	0.0273	-0.4282608	0.4555608
27	15	3	15	400	3	250	0.8	5	1.8	1.254832	0.5451683
28	15	3	15	500	3	250	0.8	5	11.2	21.9163	-10.7163
29	15	3	15	600	3	250	0.8	5	265	275.5544	-10.55436
30	15	3	15	250	2	250	0.8	5	0.0658	-0.596191	0.661991
31	15	3	15	250	4	250	0.8	5	0.0503	-0.4736559	0.5239559
32	15	3	15	250	5	250	0.8	5	0.0399	-0.4123883	0.4522883
33	15	3	15	250	7	250	0.8	5	0.0283	-0.2898532	0.3181532
34	15	3	15	250	8	250	0.8	5	0.025	-0.2285856	0.2535856
35	15	3	15	250	3	300	0.8	5	0.0354	-0.3716959	0.4070959
36	15	3	15	250	3	400	0.8	5	0.00475	-0.2403553	0.2451053
37	15	3	15	250	3	500	0.8	5	0.00332	-0.1928509	0.1961709

38	15	3	15	250	3	600	0.8	5	0.00338	-0.1715953	0.1749753
39	15	3	15	250	3	700	0.8	5	0.00251	-0.1606753	0.1631853
40	15	3	15	250	3	750	0.8	5	0.00217	-0.1571789	0.1593489
41	15	3	15	250	3	800	0.8	5	0.00165	-0.154492	0.156142
42	15	3	15	250	3	250	0.4	5	0.0658	0.0186935	0.0471065
43	15	3	15	250	3	250	0.5	5	0.0503	-0.1039031	0.1542031
44	15	3	15	250	3	250	0.6	5	0.0399	-0.2370382	0.2769382
45	15	3	15	250	3	250	0.7	5	0.0283	-0.3807116	0.4090116
46	15	3	15	250	3	250	0.9	5	0.025	-0.6996736	0.7246736
47	15	3	15	250	3	250	0.8	0.5	0.0448	1.791348	-1.746548
48	15	3	15	250	3	250	0.8	1	0.0391	-0.4300377	0.4691377
49	15	3	15	250	3	250	0.8	2	0.0388	-0.5302663	0.5690663
50	15	3	15	250	3	250	0.8	6	0.0357	-0.5349673	0.5706673
51	15	3	15	250	3	250	0.8	10	0.0365	-0.5349987	0.5714987

Polymath results for crude oil distillation column:

POLYMATH Report
Nonlinear Regression (L-M)

No Title
20-Apr-2009

Model: $X_{outwater} = a \cdot Efficiency^6 - b \cdot Efficiency^5 + c \cdot Efficiency^4 - d \cdot Efficiency^3 + e \cdot Efficiency^2 - f \cdot Efficiency - g \cdot Crudefeed + h \cdot Steamtemp + i \cdot Steamflow^j + k + l \cdot (X_{inorganics}^4) + m \cdot (X_{inorganics}^3) + n \cdot (X_{inorganics}^2) + o \cdot X_{inorganics}$

Variable	Initial guess	Value	95% confidence
a	0.1236	0.1129874	0.1295418
b	0.6655	0.6058456	0.684952
c	1.4344	1.297872	1.466419
d	1.5817	1.418556	1.622575
e	0.9411	0.8338002	0.9757995
f	0.2865	0.2497371	0.3015229
g	3.0E-05	2.992E-05	4.024E-07
h	1.0E-07	2.202E-07	3.411E-08
i	0.0174	0.0055334	0.0001881
j	0.4295	0.5565462	0.003919
k	1.7	0.7096117	0.3139925
l	0.0149	0.0143246	0.0101507
m	-0.1402	-0.1353119	0.0970516
n	0.488	0.4716159	0.3442684
o	-0.7433	-0.7189798	0.5370286

Nonlinear regression settings

Max # iterations = 300

Precision

R ²	0.999988
R ² adj	0.9999873
Rmsd	9.227E-06
Variance	2.324E-08

General

Sample size	257
Model vars	15
Indep vars	5
Iterations	26

Source data points and calculated data points

	Efficiency	Crudefeed	Steamtemp	Steamflow	Xinorganics	Xoutwater	Xoutwater calc	Delta Xoutwater
1	0.4	6548.3	600	555	3	0.26486	0.2648542	5.751E-06
2	0.4	6553.3	600	555	3	0.26471	0.2647047	5.346E-06
3	0.4	6558.3	600	555	3	0.26456	0.2645551	4.942E-06
4	0.4	6563.3	600	555	3	0.26441	0.2644055	4.537E-06
5	0.4	6568.3	600	555	3	0.26425	0.2642559	-5.868E-06
6	0.4	6573.3	600	555	3	0.2641	0.2641063	-6.273E-06
7	0.4	6578.3	600	555	3	0.26395	0.2639567	-6.678E-06
8	0.4	6583.3	600	555	3	0.2638	0.2638071	-7.083E-06
9	0.4	6588.3	600	555	3	0.26365	0.2636575	-7.487E-06
10	0.4	6593.3	600	555	3	0.26349	0.2635079	-1.789E-05
11	0.4	6598.3	600	555	3	0.26334	0.2633583	-1.83E-05
12	0.4	6603.3	600	555	3	0.26319	0.2632087	-1.87E-05
13	0.4	6608.3	600	555	3	0.26304	0.2630591	-1.911E-05
14	0.4	6613.3	600	555	3	0.26289	0.2629095	-1.951E-05
15	0.4	6618.3	600	555	3	0.26274	0.2627599	-1.992E-05
16	0.4	6623.3	600	555	3	0.26259	0.2626103	-2.032E-05
17	0.4	6628.3	600	555	3	0.26244	0.2624607	-2.073E-05
18	0.4	6633.3	600	555	3	0.26229	0.2623111	-2.113E-05
19	0.4	6638.3	600	555	3	0.26214	0.2621615	-2.154E-05
20	0.4	6643.3	600	555	3	0.26199	0.2620119	-2.194E-05
21	0.4	6648.3	600	555	3	0.26184	0.2618623	-2.235E-05
22	0.4	6653.3	600	555	3	0.26169	0.2617128	-2.275E-05
23	0.4	6658.3	600	555	3	0.26154	0.2615632	-2.316E-05
24	0.4	6663.3	600	555	3	0.26139	0.2614136	-2.356E-05
25	0.4	6668.3	600	555	3	0.26124	0.261264	-2.396E-05
26	0.4	6673.3	600	555	3	0.26109	0.2611144	-2.437E-05
27	0.4	6678.3	600	555	3	0.26094	0.2609648	-2.477E-05
28	0.4	6683.3	600	555	3	0.26079	0.2608152	-2.518E-05
29	0.4	6688.3	600	555	3	0.26065	0.2606656	-1.558E-05
30	0.4	6693.3	600	555	3	0.2605	0.260516	-1.599E-05
31	0.4	6698.3	600	555	3	0.26035	0.2603664	-1.639E-05
32	0.4	6703.3	600	555	3	0.2602	0.2602168	-1.68E-05

33	0.4	6708.3	600	555	3	0.26005	0.2600672	-1.72E-05
34	0.4	6713.3	600	555	3	0.25991	0.2599176	-7.608E-06
35	0.4	6718.3	600	555	3	0.25976	0.259768	-8.013E-06
36	0.4	6723.3	600	555	3	0.25961	0.2596184	-8.418E-06
37	0.4	6728.3	600	555	3	0.25946	0.2594688	-8.823E-06
38	0.4	6733.3	600	555	3	0.25932	0.2593192	7.725E-07
39	0.4	6738.3	600	555	3	0.25917	0.2591696	3.677E-07
40	0.4	6743.3	600	555	3	0.25902	0.25902	-3.716E-08
41	0.4	6748.3	600	555	3	0.25888	0.2588704	9.558E-06
42	0.4	6753.3	600	555	3	0.25873	0.2587208	9.153E-06
43	0.4	6758.3	600	555	3	0.25859	0.2585713	1.875E-05
44	0.4	6763.3	600	555	3	0.25844	0.2584217	1.834E-05
45	0.4	6768.3	600	555	3	0.25829	0.2582721	1.794E-05
46	0.4	6773.3	600	555	3	0.25815	0.2581225	2.753E-05
47	0.4	6778.3	600	555	3	0.258	0.2579729	2.713E-05
48	0.4	6783.3	600	555	3	0.25786	0.2578233	3.672E-05
49	0.4	6788.3	600	555	3	0.25771	0.2576737	3.632E-05
50	0.4	6793.3	600	555	3	0.25757	0.2575241	4.591E-05
51	0.4	6548.3	600	555	3	0.26498	0.2648542	0.0001258
52	0.4	6548.3	625	555	3	0.26498	0.2648598	0.0001202
53	0.4	6548.3	650	555	3	0.26498	0.2648653	0.0001147
54	0.4	6548.3	675	555	3	0.26499	0.2648708	0.0001192
55	0.4	6548.3	700	555	3	0.26499	0.2648763	0.0001137
56	0.4	6548.3	725	555	3	0.26499	0.2648818	0.0001082
57	0.4	6548.3	750	555	3	0.265	0.2648873	0.0001127
58	0.4	6548.3	775	555	3	0.265	0.2648928	0.0001072
59	0.4	6548.3	800	555	3	0.265	0.2648983	0.0001017
60	0.4	6548.3	825	555	3	0.26501	0.2649038	0.0001062
61	0.4	6548.3	850	555	3	0.26501	0.2649093	0.0001007
62	0.4	6548.3	875	555	3	0.26501	0.2649148	9.519E-05
63	0.4	6548.3	900	555	3	0.26502	0.2649203	9.968E-05
64	0.4	6548.3	925	555	3	0.26502	0.2649258	9.418E-05
65	0.4	6548.3	950	555	3	0.26503	0.2649313	9.867E-05
66	0.4	6548.3	975	555	3	0.26503	0.2649368	9.316E-05
67	0.4	6548.3	1000	555	3	0.26503	0.2649423	8.766E-05

68	0.4	6548.3	1025	555	3	0.26504	0.2649478	9.215E-05
69	0.4	6548.3	1050	555	3	0.26504	0.2649534	8.665E-05
70	0.4	6548.3	1075	555	3	0.26504	0.2649589	8.114E-05
71	0.4	6548.3	1100	555	3	0.26505	0.2649644	8.564E-05
72	0.4	6548.3	1125	555	3	0.26505	0.2649699	8.013E-05
73	0.4	6548.3	1150	555	3	0.26505	0.2649754	7.462E-05
74	0.4	6548.3	1175	555	3	0.26506	0.2649809	7.912E-05
75	0.4	6548.3	1200	555	3	0.26506	0.2649864	7.361E-05
76	0.4	6548.3	1225	555	3	0.26506	0.2649919	6.811E-05
77	0.4	6548.3	1250	555	3	0.26507	0.2649974	7.26E-05
78	0.4	6548.3	1275	555	3	0.26507	0.2650029	6.71E-05
79	0.4	6548.3	1300	555	3	0.26508	0.2650084	7.159E-05
80	0.4	6548.3	1325	555	3	0.26508	0.2650139	6.608E-05
81	0.4	6548.3	1350	555	3	0.26508	0.2650194	6.058E-05
82	0.4	6548.3	1375	555	3	0.26509	0.2650249	6.507E-05
83	0.4	6548.3	1400	555	3	0.26509	0.2650304	5.957E-05
84	0.4	6548.3	1425	555	3	0.26509	0.2650359	5.406E-05
85	0.4	6548.3	1450	555	3	0.2651	0.2650414	5.856E-05
86	0.4	6548.3	1475	555	3	0.2651	0.265047	5.305E-05
87	0.4	6548.3	1500	555	3	0.26511	0.2650525	5.754E-05
88	0.4	6548.3	1525	555	3	0.26511	0.265058	5.204E-05
89	0.4	6548.3	1550	555	3	0.26511	0.2650635	4.653E-05
90	0.4	6548.3	1575	555	3	0.26512	0.265069	5.103E-05
91	0.4	6548.3	1600	555	3	0.26512	0.2650745	4.552E-05
92	0.4	6548.3	1625	555	3	0.26512	0.26508	4.001E-05
93	0.4	6548.3	1650	555	3	0.26513	0.2650855	4.451E-05
94	0.4	6548.3	1675	555	3	0.26513	0.265091	3.9E-05
95	0.4	6548.3	1700	555	3	0.26513	0.2650965	3.35E-05
96	0.4	6548.3	1725	555	3	0.26514	0.265102	3.799E-05
97	0.4	6548.3	1750	555	3	0.26514	0.2651075	3.249E-05
98	0.4	6548.3	1775	555	3	0.26514	0.265113	2.698E-05
99	0.4	6548.3	1800	555	3	0.26515	0.2651185	3.147E-05
100	0.4	6548.3	1825	555	3	0.26515	0.265124	2.597E-05
101	0.4	6548.3	1850	555	3	0.26516	0.2651295	3.046E-05
102	0.4	6548.3	1875	555	3	0.26516	0.265135	2.496E-05

103	0.4	6548.3	1900	555	3	0.26516	0.2651405	1.945E-05
104	0.4	6548.3	1925	555	3	0.26517	0.2651461	2.395E-05
105	0.4	6548.3	1950	555	3	0.26517	0.2651516	1.844E-05
106	0.4	6548.3	1975	555	3	0.26517	0.2651571	1.293E-05
107	0.4	6548.3	2000	555	3	0.26518	0.2651626	1.743E-05
108	0.4	6548.3	2025	555	3	0.26518	0.2651681	1.192E-05
109	0.4	6548.3	2050	555	3	0.26519	0.2651736	1.642E-05
110	0.4	6548.3	2075	555	3	0.26519	0.2651791	1.091E-05
111	0.4	6548.3	2100	555	3	0.26519	0.2651846	5.405E-06
112	0.4	6548.3	2125	555	3	0.2652	0.2651901	9.899E-06
113	0.4	6548.3	2150	555	3	0.2652	0.2651956	4.394E-06
114	0.4	6548.3	2175	555	3	0.26521	0.2652011	8.888E-06
115	0.4	6548.3	2200	555	3	0.26521	0.2652066	3.382E-06
116	0.4	6548.3	2225	555	3	0.26521	0.2652121	-2.124E-06
117	0.4	6548.3	2250	555	3	0.26522	0.2652176	2.371E-06
118	0.4	6548.3	2275	555	3	0.26522	0.2652231	-3.135E-06
119	0.4	6548.3	2300	555	3	0.26523	0.2652286	1.359E-06
120	0.4	6548.3	2325	555	3	0.26523	0.2652341	-4.147E-06
121	0.4	6548.3	2350	555	3	0.26523	0.2652397	-9.652E-06
122	0.4	6548.3	2375	555	3	0.26524	0.2652452	-5.158E-06
123	0.4	6548.3	2400	555	3	0.26524	0.2652507	-1.066E-05
124	0.4	6548.3	2425	555	3	0.26524	0.2652562	-1.617E-05
125	0.4	6548.3	2450	555	3	0.26525	0.2652617	-1.168E-05
126	0.4	6548.3	2475	555	3	0.26525	0.2652672	-1.718E-05
127	0.4	6548.3	2500	555	3	0.26526	0.2652727	-1.269E-05
128	0.4	6548.3	2525	555	3	0.26526	0.2652782	-1.819E-05
129	0.4	6548.3	2550	555	3	0.26526	0.2652837	-2.37E-05
130	0.4	6548.3	2575	555	3	0.26527	0.2652892	-1.92E-05
131	0.4	6548.3	2600	555	3	0.26527	0.2652947	-2.471E-05
132	0.4	6548.3	2625	555	3	0.26527	0.2653002	-3.022E-05
133	0.4	6548.3	2650	555	3	0.26528	0.2653057	-2.572E-05
134	0.4	6548.3	2675	555	3	0.26528	0.2653112	-3.123E-05
135	0.4	6548.3	2700	555	3	0.26529	0.2653167	-2.673E-05
136	0.4	6548.3	2725	555	3	0.26529	0.2653222	-3.224E-05
137	0.4	6548.3	2750	555	3	0.26529	0.2653277	-3.774E-05

138	0.4	6548.3	2775	555	3	0.2653	0.2653333	-3.325E-05
139	0.4	6548.3	2800	555	3	0.2653	0.2653388	-3.876E-05
140	0.4	6548.3	2825	555	3	0.26531	0.2653443	-3.426E-05
141	0.4	6548.3	2850	555	3	0.26531	0.2653498	-3.977E-05
142	0.4	6548.3	2875	555	3	0.26531	0.2653553	-4.527E-05
143	0.4	6548.3	2900	555	3	0.26532	0.2653608	-4.078E-05
144	0.4	6548.3	2925	555	3	0.26532	0.2653663	-4.629E-05
145	0.4	6548.3	2950	555	3	0.26533	0.2653718	-4.179E-05
146	0.4	6548.3	2975	555	3	0.26533	0.2653773	-4.73E-05
147	0.4	6548.3	3000	555	3	0.26533	0.2653828	-5.28E-05
148	0.4	6548.3	3025	555	3	0.26534	0.2653883	-4.831E-05
149	0.4	6548.3	3050	555	3	0.26534	0.2653938	-5.381E-05
150	0.4	6548.3	3075	555	3	0.26534	0.2653993	-5.932E-05
151	0.4	6548.3	600	555.09	3	0.26498	0.2648711	0.0001089
152	0.4	6548.3	600	580.09	3	0.26943	0.2694967	-6.668E-05
153	0.4	6548.3	600	605.09	3	0.27384	0.2740347	-0.0001947
154	0.4	6548.3	600	630.09	3	0.27819	0.2784903	-0.0003003
155	0.4	6548.3	600	655.09	3	0.28249	0.2828682	-0.0003782
156	0.4	6548.3	600	680.09	3	0.28674	0.2871725	-0.0004325
157	0.4	6548.3	600	705.09	3	0.29094	0.2914073	-0.0004673
158	0.4	6548.3	600	730.09	3	0.29509	0.295576	-0.000486
159	0.4	6548.3	600	755.09	3	0.2992	0.2996818	-0.0004818
160	0.4	6548.3	600	780.09	3	0.30325	0.3037278	-0.0004778
161	0.4	6548.3	600	805.09	3	0.30726	0.3077167	-0.0004567
162	0.4	6548.3	600	830.09	3	0.31123	0.311651	-0.000421
163	0.4	6548.3	600	855.09	3	0.31515	0.3155331	-0.0003831
164	0.4	6548.3	600	880.09	3	0.31902	0.3193652	-0.0003452
165	0.4	6548.3	600	905.09	3	0.32285	0.3231494	-0.0002994
166	0.4	6548.3	600	930.09	3	0.32664	0.3268874	-0.0002474
167	0.4	6548.3	600	955.09	3	0.33039	0.3305812	-0.0001912
168	0.4	6548.3	600	980.09	3	0.33409	0.3342323	-0.0001423
169	0.4	6548.3	600	1005.1	3	0.33776	0.3378437	-8.375E-05
170	0.4	6548.3	600	1030.1	3	0.34138	0.3414142	-3.417E-05
171	0.4	6548.3	600	1055.1	3	0.34497	0.3449464	2.364E-05
172	0.4	6548.3	600	1080.1	3	0.34851	0.3484416	6.836E-05

173	0.4	6548.3	600	1105.1	3	0.35202	0.3519012	0.0001188
174	0.4	6548.3	600	1130.1	3	0.35549	0.3553263	0.0001637
175	0.4	6548.3	600	1155.1	3	0.35893	0.3587179	0.0002121
176	0.4	6548.3	600	1180.1	3	0.36232	0.3620771	0.0002429
177	0.4	6548.3	600	1205.1	3	0.36569	0.3654048	0.0002852
178	0.4	6548.3	600	1230.1	3	0.36901	0.3687022	0.0003078
179	0.4	6548.3	600	1255.1	3	0.3723	0.3719699	0.0003301
180	0.4	6548.3	600	1280.1	3	0.37556	0.3752089	0.0003511
181	0.4	6548.3	600	1305.1	3	0.37878	0.3784199	0.0003601
182	0.4	6548.3	600	1330.1	3	0.38198	0.3816038	0.0003762
183	0.4	6548.3	600	1355.1	3	0.38513	0.3847613	0.0003687
184	0.4	6548.3	600	1380.1	3	0.38826	0.387893	0.000367
185	0.4	6548.3	600	1405.1	3	0.39136	0.3909997	0.0003603
186	0.4	6548.3	600	1430.1	3	0.39442	0.3940819	0.0003381
187	0.4	6548.3	600	1455.1	3	0.39745	0.3971404	0.0003096
188	0.4	6548.3	600	1480.1	3	0.40045	0.4001756	0.0002744
189	0.4	6548.3	600	1505.1	3	0.40343	0.4031882	0.0002418
190	0.4	6548.3	600	1530.1	3	0.40637	0.4061787	0.0001913
191	0.4	6548.3	600	1555.1	3	0.40928	0.4091476	0.0001324
192	0.4	6548.3	600	1580.1	3	0.41217	0.4120954	7.461E-05
193	0.4	6548.3	600	1605.1	3	0.41503	0.4150226	7.423E-06
194	0.4	6548.3	600	1630.1	3	0.41786	0.4179296	-6.961E-05
195	0.4	6548.3	600	1655.1	3	0.42066	0.4208169	-0.0001569
196	0.4	6548.3	600	1680.1	3	0.42344	0.423685	-0.000245
197	0.4	6548.3	600	1705.1	3	0.42619	0.4265342	-0.0003442
198	0.4	6548.3	600	1730.1	3	0.42891	0.4293649	-0.0004549
199	0.4	6548.3	600	1755.1	3	0.43161	0.4321776	-0.0005676
200	0.4	6548.3	600	1780.1	3	0.43428	0.4349725	-0.0006925
201	0.4	6548.3	600	555	3	0.26486	0.2648542	5.751E-06
202	0.42	6548.3	600	555	3	0.26487	0.2648271	4.287E-05
203	0.44	6548.3	600	555	3	0.26487	0.2648193	5.072E-05
204	0.46	6548.3	600	555	3	0.26487	0.2648246	4.538E-05
205	0.48	6548.3	600	555	3	0.26487	0.2648382	3.185E-05
206	0.5	6548.3	600	555	3	0.26488	0.2648559	2.407E-05
207	0.52	6548.3	600	555	3	0.26488	0.2648749	5.108E-06

208	0.54	6548.3	600	555	3	0.26488	0.2648928	-1.277E-05
209	0.56	6548.3	600	555	3	0.26488	0.264908	-2.799E-05
210	0.58	6548.3	600	555	3	0.26488	0.2649196	-3.958E-05
211	0.6	6548.3	600	555	3	0.26489	0.2649271	-3.71E-05
212	0.62	6548.3	600	555	3	0.26489	0.2649305	-4.05E-05
213	0.64	6548.3	600	555	3	0.26489	0.2649301	-4.011E-05
214	0.66	6548.3	600	555	3	0.26489	0.2649265	-3.651E-05
215	0.68	6548.3	600	555	3	0.26489	0.2649205	-3.052E-05
216	0.7	6548.3	600	555	3	0.26489	0.2649131	-2.306E-05
217	0.72	6548.3	600	555	3	0.2649	0.2649052	-5.167E-06
218	0.74	6548.3	600	555	3	0.26491	0.2648979	1.211E-05
219	0.76	6548.3	600	555	3	0.26492	0.2648923	2.773E-05
220	0.78	6548.3	600	555	3	0.26493	0.2648893	4.071E-05
221	0.8	6548.3	600	555	3	0.26493	0.2648898	4.017E-05
222	0.82	6548.3	600	555	3	0.26494	0.2648946	4.535E-05
223	0.84	6548.3	600	555	3	0.26495	0.2649043	4.567E-05
224	0.86	6548.3	600	555	3	0.26495	0.2649193	3.068E-05
225	0.88	6548.3	600	555	3	0.26496	0.2649398	2.018E-05
226	0.9	6548.3	600	555	3	0.26496	0.2649659	-5.857E-06
227	0.92	6548.3	600	555	3	0.26497	0.2649972	-2.725E-05
228	0.94	6548.3	600	555	3	0.26501	0.2650336	-2.358E-05
229	0.96	6548.3	600	555	3	0.26506	0.2650742	-1.425E-05
230	0.98	6548.3	600	555	3	0.2651	0.2651184	-1.844E-05
231	1	6548.3	600	555	3	0.26513	0.2651651	-3.515E-05
232	1.02	6548.3	600	555	3	0.26516	0.2652132	-5.322E-05
233	1.04	6548.3	600	555	3	0.26519	0.2652614	-7.136E-05
234	1.06	6548.3	600	555	3	0.26522	0.2653082	-8.816E-05
235	1.08	6548.3	600	555	3	0.26529	0.2653521	-6.212E-05
236	1.1	6548.3	600	555	3	0.26538	0.2653917	-1.175E-05
237	1.12	6548.3	600	555	3	0.26546	0.2654255	3.448E-05
238	1.14	6548.3	600	555	3	0.26552	0.265452	6.799E-05
239	1.16	6548.3	600	555	3	0.26558	0.2654699	0.0001101
240	1.18	6548.3	600	555	3	0.26563	0.265478	0.000152
241	1.2	6548.3	600	555	3	0.26556	0.2654755	8.446E-05
242	1.22	6548.3	600	555	3	0.26546	0.2654619	-1.857E-06

243	1.24	6548.3	600	555	3	0.26539	0.2654368	-4.68E-05
244	1.26	6548.3	600	555	3	0.26534	0.2654007	-6.069E-05
245	1.28	6548.3	600	555	3	0.2653	0.2653544	-5.439E-05
246	1.3	6548.3	600	555	3	0.26525	0.2652995	-4.945E-05
247	1.32	6548.3	600	555	3	0.2652	0.2652382	-3.817E-05
248	1.34	6548.3	600	555	3	0.26516	0.2651737	-1.369E-05
249	1.36	6548.3	600	555	3	0.26513	0.2651101	1.985E-05
250	1.38	6548.3	600	555	3	0.2651	0.2650528	4.724E-05
251	0.7	6548.3	600	555	3	0.265	0.2649131	8.694E-05
252	0.7	6548.3	600	555	2.73	0.2651	0.2650876	1.241E-05
253	0.7	6548.3	600	555	2.54	0.2657	0.2657772	-7.72E-05
254	0.7	6548.3	600	555	2.45	0.2661	0.2660144	8.563E-05
255	0.7	6548.3	600	555	2.1	0.2658	0.2658702	-7.024E-05
256	0.7	6548.3	600	555	2	0.2657	0.2656414	5.861E-05
257	0.7	6548.3	600	555	1.82	0.2655	0.2655088	-8.754E-06

CWWT table example:

Flowrates	Efficiencies	Reflux Ratio	Number of Trays	Inlet H2S	Inlet NH3 (mass %)	Inlet H2S (mass %)	Inlet NH3	0.05	0.1	0.15	0.2	0.25	0.3	0.345
10	30	1	1	5	100	0.01	49.11209	49.10954	49.10677	49.10386	49.10102	49.09818	49.09534	49.09250
10	30	1	1	5	1000	0.01	50.02542	50.02287	50.02011	50.01735	50.01459	50.01183	50.00907	50.00631
10	30	1	1	5	1000	0.1	50.69793	50.69537	50.69281	50.69025	50.68769	50.68513	50.68257	50.68001
10	30	1	1	5	3000	0.3	52.31912	52.31656	52.31400	52.31144	52.30888	52.30632	52.30376	52.29920
10	30	1	1	5	5000	0.5	53.40993	53.40737	53.40481	53.40225	53.39969	53.39713	53.39457	53.39201
10	30	1	1	5	7000	0.7	54.28554	54.28298	54.28042	54.27786	54.27530	54.27274	54.27018	54.26762
10	30	1	1	5	9000	0.9	55.03606	55.03350	55.03094	55.02838	55.02582	55.02326	55.02070	55.01814
10	30	1	1	5	10900	1.05	55.70666	55.70410	55.70154	55.69898	55.69642	55.69386	55.69130	55.68874
10	30	1	1	10	100	0.01	3.344057	3.341502	3.338947	3.336392	3.333837	3.331282	3.328727	3.326172
10	30	1	1	10	500	0.05	4.263002	4.260447	4.257892	4.255337	4.252782	4.250227	4.247672	4.245117
10	30	1	1	10	1000	0.1	4.929892	4.927337	4.924782	4.922227	4.919672	4.917117	4.914562	4.912007
10	30	1	1	10	3000	0.3	6.551082	6.548527	6.545972	6.543417	6.540862	6.538307	6.535752	6.533197
10	30	1	1	10	5000	0.5	7.641891	7.639336	7.636781	7.634226	7.631671	7.629116	7.626561	7.624006
10	30	1	1	10	7000	0.7	8.517499	8.514944	8.512389	8.509834	8.507279	8.504724	8.502169	8.499614
10	30	1	1	10	9000	0.9	9.268028	9.265473	9.262918	9.260363	9.257808	9.255253	9.252698	9.250143
10	30	1	1	10	10900	1.09	9.902622	9.900067	9.897512	9.894957	9.892402	9.889847	9.887292	9.884737
10	30	1	1	15	100	0.01	1.941095	1.938540	1.935985	1.933430	1.930875	1.928320	1.925765	1.923210
10	30	1	1	15	500	0.05	2.86004	2.857484	2.854929	2.852374	2.849819	2.847264	2.844709	2.842154
10	30	1	1	15	1000	0.1	3.52693	3.524375	3.521820	3.519265	3.516710	3.514155	3.511600	3.509045
10	30	1	1	15	3000	0.3	5.14812	5.145564	5.143009	5.140454	5.137899	5.135344	5.132789	5.130234
10	30	1	1	15	5000	0.5	6.238929	6.236374	6.233819	6.231264	6.228709	6.226154	6.223599	6.221044
10	30	1	1	15	7000	0.7	7.145327	7.142772	7.140217	7.137662	7.135107	7.132552	7.130000	7.127445
10	30	1	1	15	9000	0.9	7.865065	7.862510	7.859955	7.857400	7.854845	7.852290	7.849735	7.847180
10	30	1	1	15	10900	1.09	8.49966	8.497104	8.494549	8.491994	8.489439	8.486884	8.484329	8.481774
10	30	1	1	20	100	0.01	1.898089	1.895534	1.892979	1.890424	1.887869	1.885314	1.882759	1.880204
10	30	1	1	20	500	0.05	2.817034	2.814478	2.811923	2.809368	2.806813	2.804258	2.801703	2.799148
10	30	1	1	20	1000	0.1	3.483924	3.481368	3.478813	3.476258	3.473703	3.471148	3.468593	3.466038
10	30	1	1	20	3000	0.3	5.105114	5.102558	5.099999	5.097444	5.094889	5.092334	5.089779	5.087224
10	30	1	1	20	5000	0.5	6.25922	6.256664	6.254109	6.251554	6.248999	6.246444	6.243889	6.241334
10	30	1	1	20	7000	0.7	7.071523	7.068967	7.066412	7.063857	7.061302	7.058747	7.056192	7.053637
10	30	1	1	20	9000	0.9	7.822059	7.819504	7.816949	7.814394	7.811839	7.809284	7.806729	7.804174
10	30	1	1	20	10900	1.09	8.416654	8.414098	8.411543	8.408988	8.406433	8.403878	8.401323	8.398768
10	30	1	1	25	100	0.01	1.89767	1.895115	1.892560	1.890005	1.887450	1.884895	1.882340	1.879785
10	30	1	1	25	500	0.05	2.815715	2.813160	2.810605	2.808050	2.805495	2.802940	2.800385	2.797830
10	30	1	1	25	1000	0.1	3.482606	3.480051	3.477496	3.474941	3.472386	3.469831	3.467276	3.464721
10	30	1	1	25	3000	0.3	5.103796	5.101241	5.098686	5.096131	5.093576	5.091021	5.088466	5.085911
10	30	1	1	25	5000	0.5	6.194605	6.192049	6.189494	6.186939	6.184384	6.181829	6.179274	6.176719
10	30	1	1	25	7000	0.7	7.067021	7.064466	7.061911	7.059356	7.056801	7.054246	7.051691	7.049136
10	30	1	1	25	9000	0.9	7.820741	7.818185	7.815630	7.813075	7.810520	7.807965	7.805410	7.802855
10	30	1	1	25	10900	1.09	8.455335	8.452778	8.450223	8.447668	8.445113	8.442558	8.440003	8.437448
10	30	1	1	30	100	0.01	1.898089	1.895534	1.892979	1.890424	1.887869	1.885314	1.882759	1.880204
10	30	1	1	30	500	0.05	2.817034	2.814478	2.811923	2.809368	2.806813	2.804258	2.801703	2.799148
10	30	1	1	30	1000	0.1	3.483924	3.481368	3.478813	3.476258	3.473703	3.471148	3.468593	3.466038
10	30	1	1	30	3000	0.3	5.105114	5.102558	5.099999	5.097444	5.094889	5.092334	5.089779	5.087224
10	30	1	1	30	5000	0.5	6.25922	6.256664	6.254109	6.251554	6.248999	6.246444	6.243889	6.241334
10	30	1	1	30	7000	0.7	7.071523	7.068967	7.066412	7.063857	7.061302	7.058747	7.056192	7.053637
10	30	1	1	30	9000	0.9	7.822059	7.819504	7.816949	7.814394	7.811839	7.809284	7.806729	7.804174
10	30	1	1	30	10900	1.09	8.416654	8.414098	8.411543	8.408988	8.406433	8.403878	8.401323	8.398768
10	30	1	1	35	100	0.01	1.89767	1.895115	1.892560	1.890005	1.887450	1.884895	1.882340	1.879785
10	30	1	1	35	500	0.05	2.815715	2.813160	2.810605	2.808050	2.805495	2.802940	2.800385	2.797830
10	30	1	1	35	1000	0.1	3.482606	3.480051	3.477496	3.474941	3.472386	3.469831	3.467276	3.464721
10	30	1	1	35	3000	0.3	5.103796	5.101241	5.098686	5.096131	5.093576	5.091021	5.088466	5.085911
10	30	1	1	35	5000	0.5	6.194605	6.192049	6.189494	6.186939	6.184384	6.181829	6.179274	6.176719
10	30	1	1	35	7000	0.7	7.067021	7.064466	7.061911	7.059356	7.056801	7.054246	7.051691	7.049136
10	30	1	1	35	9000	0.9	7.820741	7.818185	7.815630	7.813075	7.810520	7.807965	7.805410	7.802855
10	30	1	1	35	10900	1.09	8.455335	8.452778	8.450223	8.447668	8.445113	8.442558	8.440003	8.437448
10	30	1	1	40	100	0.01	1.898089	1.895534	1.892979	1.890424	1.887869	1.885314	1.882759	1.880204
10	30	1	1	40	500	0.05	2.817034	2.814478	2.811923	2.809368	2.806813	2.804258	2.801703	2.799148
10	30	1	1	40	1000	0.1	3.483924	3.481368	3.478813	3.476258	3.473703	3.471148	3.468593	3.466038
10	30	1	1	40	3000	0.3	5.105114	5.102558	5.099999	5.097444	5.094889	5.092334	5.089779	5.087224
10	30	1	1	40	5000	0.5	6.25922	6.256664	6.254109	6.251554	6.248999	6.246444	6.243889	6.241334
10	30	1	1	40	7000	0.7	7.071523	7.068967	7.066412	7.063857	7.061302	7.058747	7.056192	7.053637
10	30	1	1	40	9000	0.9	7.822059	7.819504	7.816949	7.814394	7.811839	7.809284	7.806729	7.804174
10	30	1	1	40	10900	1.09	8.416654	8.414098	8.411543	8.408988	8.406433	8.403878	8.401323	8.398768
10	30	1	1	45	100	0.01	1.89767	1.895115	1.892560	1.890005	1.887450	1.884895	1.882340	1.879785
10	30	1	1	45	500	0.05	2.815715	2.813160	2.810605	2.808050	2.805495	2.802940	2.800385	2.797830
10	30	1	1	45	1000	0.1	3.482606	3.480051	3.477496	3.474941	3.472386	3.469831	3.467276	3.464721
10	30	1	1	45	3000	0.3	5.103796	5.101241	5.098686	5.096131	5.093576	5.091021	5.088466	5.085911
10	30	1	1	45	5000	0.5	6.194605	6.192049	6.189494	6.186939	6.184384	6.181829	6.179274	6.176719

Appendix II

Derivation of API separator equipment cost

$$\text{Cost} = f(\text{Volume})$$

$$\text{Cost} = \text{Weight}(\text{tons}) \cdot \text{Cost of steel} \left(\frac{\$}{\text{ton}} \right) = \text{Mass}(\text{kg}) \cdot \frac{0.001 \text{ ton}}{1 \text{ kg}} \cdot \text{Cost of steel} \left(\frac{\$}{\text{ton}} \right)$$

$$\text{Cost} = \text{Density} \left(\frac{\text{kg}}{\text{m}^3} \right) \cdot V(\text{m}^3) \cdot \frac{0.001 \text{ ton}}{1 \text{ kg}} \cdot \text{Cost of steel} \left(\frac{\$}{\text{ton}} \right)$$

$$\text{Cost} = 7850 \frac{\text{kg}}{\text{m}^3} \cdot V(\text{m}^3) \cdot \frac{0.001 \text{ ton}}{1 \text{ kg}} \cdot \frac{\$833}{\text{ton}}$$

$$\text{Cost} = 6539.05 \cdot V$$

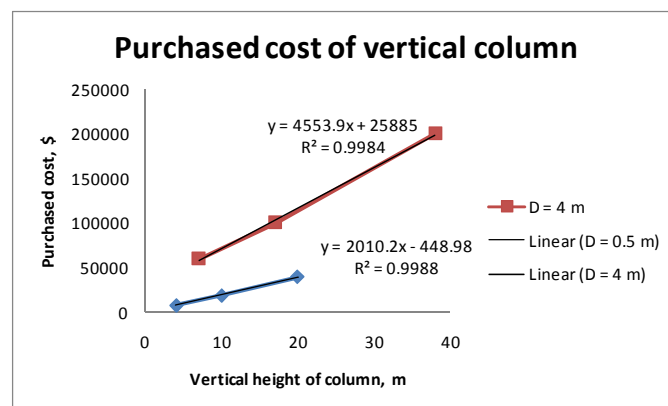
Derivation of Chevron Wastewater Treatment plant cost:

$$D = \left(\frac{4A_c}{\pi} \right)^{1/2} = \left(\frac{4A_n}{0.85\pi} \right)^{1/2} = \left(\frac{4F}{0.85\pi V_n} \right)^{1/2} = \left(\frac{4F}{0.85\pi \cdot 0.8V_{nf}} \right)^{1/2} = \left(\frac{1.87F}{V_{nf}} \right)^{1/2} = \left(\frac{(20)^{0.2} (1.87)F}{C_{sb}(\sigma)^{0.2} (\Delta\rho)^{1/2}} \right)^{1/2}$$

Assume the downcomer occupies 15 percent of the cross-sectional area of the column ($A_n = 0.85A_c$) and $A_n = (F/V_n)$. Assume 80 percent flooding ($V_n = 0.8V_{nf}$).

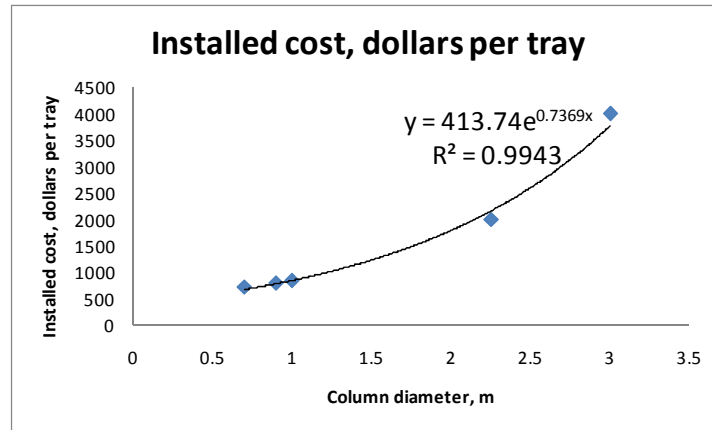
$$D = \left(\frac{3.40F}{C_{sb}(\sigma)^{0.2} (\Delta\rho)^{1/2}} \right)^{1/2}$$

Standard tray spacings for large-diameter columns are generally either 0.46 or 0.61 m.



Points taken from Figure 15-11 on page 783 in PT&W *Plant Design and Economics for Chemical Engineers*. Thus, equation is of the form:

$$\text{Purchased cost (\$)} = a * \text{Vertical Height of column (meters)} + b$$



Points taken from Figure 15-13 on page 794 in PT&W *Plant Design and Economics for Chemical Engineers*. This equation is valid for a sieve tray made of stainless steel. The non-linear regression equation is of the form:

$$\text{Installed cost (\$/tray)} = a * \exp[b * \text{Column Diameter (meters)}]$$

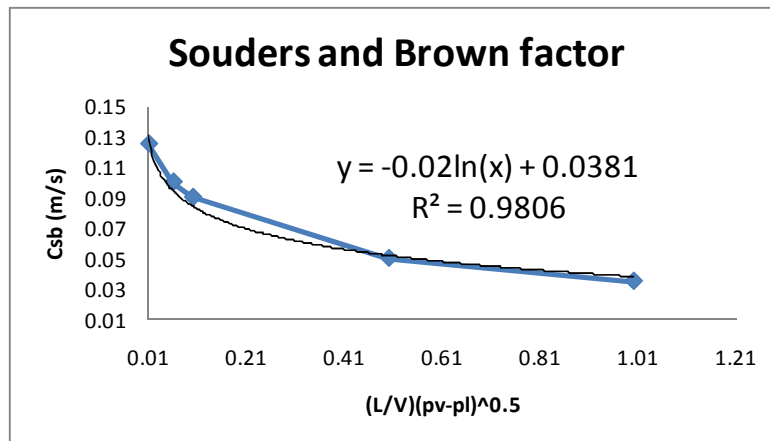
Thus,

$$\text{Total cost} = \text{Purchased cost (\$)} + \text{Installed cost (\$/tray)} * \text{Number of trays (tray)}$$

$$\text{Total cost} = 1.63 \cdot (4553.9H + 25885) + 1.63 \cdot (\text{Installed cost} \cdot N)$$

$$\text{Total cost} = 1.63 \cdot (4553.9H + 25885) + 1.63 \cdot N \cdot (413.74e^{0.7639D})$$

Now, it's necessary to find D in terms of feedrate and other parameters. Using Figure 15-5 on page 778 of PT&W *Plant Design and Economics for Chemical Engineers*:



This figure was used for a standard tray spacing of 0.61 meters. The non-linear regression equation is of the form:

$$\text{Souders and Brown factor} = a * \ln[\text{RBR} * (\Delta\rho)^{0.5}] + b$$

Thus,

$$D = \left(\frac{3.40F}{10^{0.2}(-0.02 \ln(\text{RBR} \cdot (\Delta\rho)^{0.5}) + 0.0381) \cdot (\Delta\rho)^{1/2}} \right)$$

Note that a surface tension of 10 was used; H₂S surface tension values range from 11.3 to 8.7 dyne/cm. Check reference folder for details.

Rearranging terms:

$$D = 1.46 \left(\frac{F}{(-0.02 \ln(\text{RBR} \cdot (\Delta\rho)^{0.5}) + 0.0381) \cdot (\Delta\rho)^{1/2}} \right)$$

$$\text{Total cost} = 7423H + 42193 + 674.4N \left[e^{1.12 \left(\frac{F}{(-0.02 \ln(\text{RBR} \sqrt{\Delta\rho}) + 0.0381) \sqrt{\Delta\rho}} \right)^{1/2}} \right]$$

$$\text{Total cost} = 7423H + 674.4N \left[e^{\frac{1.12F^{1/2}}{(-0.02 \ln(\text{RBR} \sqrt{\Delta\rho}) \sqrt{\Delta\rho} + 0.0381 \sqrt{\Delta\rho})^{1/2}}} \right] + 42193$$

$$\text{Total cost} = 7423H + 674.4N \left[e^{\frac{1.12F^{1/2}}{-0.14 \Delta\rho^{1/4} \cdot \frac{1}{2} \ln(\text{RBR} \sqrt{\Delta\rho}) + 0.195 \Delta\rho^{1/4}}} \right] + 42193$$

Final equation:

$$\text{Total equipment cost} = 7423H + 674.4N \left[e^{\frac{1.12\sqrt{F}}{-0.071 \Delta\rho^{1/4} \cdot \ln(\text{RBR} \sqrt{\Delta\rho}) + 0.195 \Delta\rho^{1/4}}} \right] + 42193$$

Derivation of Activated Sludge process:

From Wikipedia.com: Atmospheric air or pure oxygen is bubbled through primary treated sewage (or industrial wastewater) combined with organisms to develop a biological floc which reduces the organic content of the sewage. Thus, we're measuring outlet organic content.

What's going on inside of an activated sludge system is the wastewater flows first through an aeration tank where oxygen is bubbled through to create turbulent conditions. Then, the wastewater is sent to a secondary clarifier where particles settle naturally to the bottom (bacteria consume carbonaceous matter in the aeration tank and then settle by weight in the calm conditions of the secondary clarifier). Assume ideal CSTR for the aeration tank. Why? Perfect mixing because oxygen is being pumped through the aeration tank at very high speeds. It's like a stirrer stirring the mixture.

$$V = \frac{F_{AO} X}{-r_{A,exit}} \quad \text{where A is organics}$$

$$Cost(\$) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 m^3} \cdot V(m^3) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 m^3} \cdot \frac{F_{AO} \left(\frac{C_{out,org} - C_{in,org}}{C_{in,org}} \right)}{-r_{A,exit}}$$

\$70/yd is the price of concrete. A former wastewater plant operator told me that concrete was widely used to build activated sludge systems.

$$Cost(\$) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 m^3} \cdot \frac{F_{AO} \left(\frac{C_{out,org} - C_{in,org}}{C_{in,org}} \right)}{-r_{A,exit}} = \frac{91.5 \cdot (C_{A0} \cdot v_o) \left(\frac{C_{out,org} - C_{in,org}}{C_{in,org}} \right)}{-r_{A,exit}}$$

Using the Monod equation for biological reactions:

$$-r_A = \frac{k C_S C_C}{K_M + C_S}$$

where k is the maximum utilization rate for the substrate per unit mass of bacteria

K_M is the half velocity coefficient for the substrate

C_S is the $C_{in, organics}$

$$C_C = 0.1(C_{S0} - C_S) + 0.001$$

Look on page 75 of the Kinetics reaction book for reference.

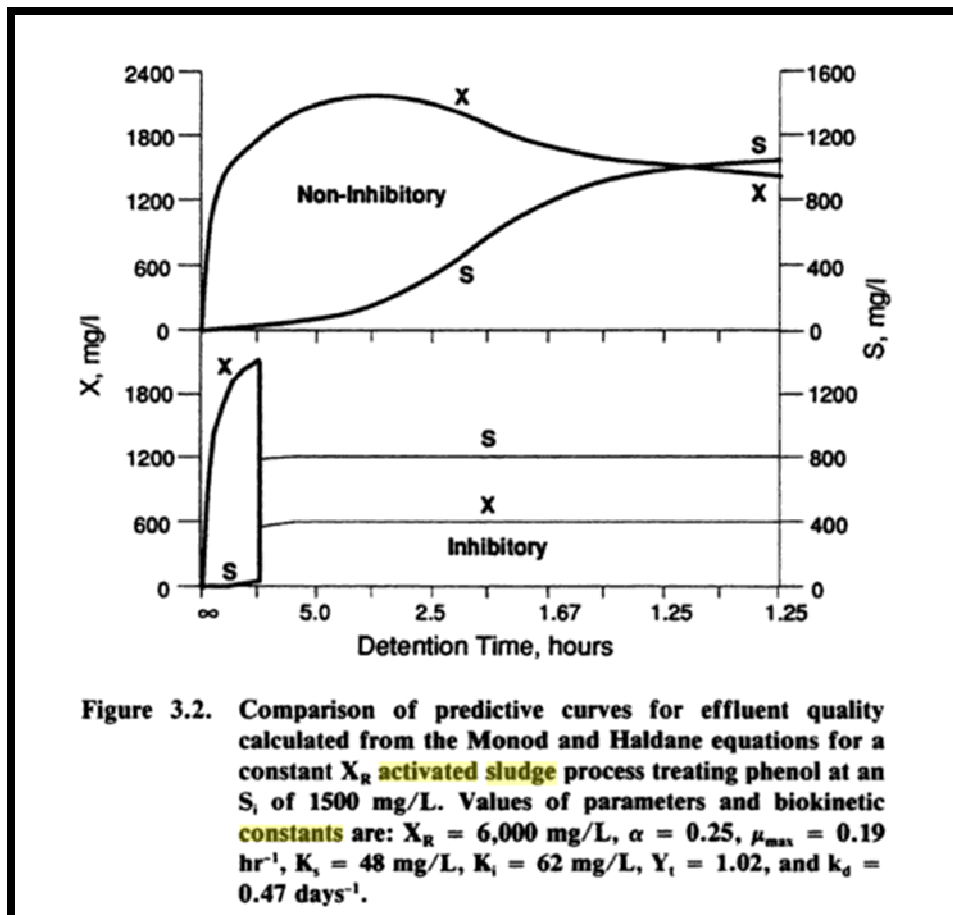
Thus,

$$Cost(\$) = \frac{91.5 \cdot (v_o)(C_{out,org} - C_{in,org})}{k \cdot C_{out,org} [0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]} = \frac{91.5 \cdot \left(\frac{F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton}}{1 \frac{kg}{m^3}} \right) (C_{out,org} - C_{in,org})}{k \cdot C_{out,org} [0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]} = \frac{91.5 \cdot \left(\frac{F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton}}{1 \frac{kg}{m^3}} \right) (C_{out,org} - C_{in,org})}{K_M + C_{out,org}}$$

because volumetric flowrate is flowrate divided by density.

I found a paper online that gave a “k” and “K_M” value for phenol. Phenol is an organic. Source is down below. k = 0.19/hr, K_M = 48 ppm (mg/L).

From the book: *Design and Operation of Activated Sludge Processes Using Respirometry* by Alan F. Rozich, Anthony F. Gaudy; CRC Press, 1992, page 46.



Finally:

$$Cost(\$) = \frac{91.5 \cdot \left(907 \cdot F \frac{m^3}{hr} \right) (C_{out,org} - C_{in,org}) \cdot (48 + C_{out,org})}{0.19 \cdot C_{out,org} [0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001] \cdot \frac{1000 \text{ mg}}{g}}$$

$$Cost(\$) = \frac{436.81 \cdot F \cdot (C_{out,org} - C_{in,org}) \cdot (48 + C_{out,org})}{C_{out,org} [0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]}$$

where F is in ton/hr and $C_{out,org}$ and $C_{in,org}$ are in ppm.

That was the cost of the first part of the biological treatment (the aeration tank). There is a second part: the secondary clarifier. Particles settle naturally (by gravity). Conditions are calm and no reaction is occurring so neither a CSTR or a batch reactor can be used.

Reactor tank is emptied once a day. Source: wastewater plant operator. Assume 24 hr time period.

$$Volume \text{ needed } (m^3) = Efficiency \cdot F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton} \cdot 24 \text{ hr} \cdot \frac{m^3}{kg} = \frac{C_{in,org}}{C_{out,org}} \cdot F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton} \cdot 24 \text{ hr} \cdot \frac{m^3}{kg}$$

But, $C_{in,org} = C_{out,org}$, aeration tank. $C_{out,max} = 230 \text{ ppm}$ from the slide show (I have a reference). Let's specify a maximum outlet concentration to give a maximum amount of volume that we need.

We'll use concrete as a tank material.

$$Cost(\$) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 \text{ m}^3} \cdot V(m^3) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 \text{ m}^3} \cdot \frac{C_{in,org}}{230 \text{ ppm}} \cdot F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton} \cdot 24 \text{ hr} \cdot \frac{m^3}{kg}$$

Even though there is a recycle that enters into the clarifier, we'll assume it is zero for now.

Finally,

$$Cost(\$) = \frac{\$70}{yd^3} \cdot \frac{yd^3}{0.765 \text{ m}^3} \cdot \frac{C_{in,org}}{230 \text{ ppm}} \cdot F \left(\frac{ton}{hr} \right) \cdot \frac{907 \text{ kg}}{ton} \cdot 24 \text{ hr} \cdot \frac{m^3}{kg}$$

$$Cost(\$) = 8660.19 \cdot Cin,org \cdot F \left(\frac{ton}{hr} \right)$$

$$Cin,org = \frac{Cost(\$)}{8660.19 \cdot F \left(\frac{ton}{hr} \right)}$$

$$Total\ Cost(\$) = Cost1 + Cost2 = \frac{436.81 \cdot F \cdot (Cout,org, Aera - Cin,org) \cdot (48 + Cout,org, Aera)}{Cout,org, Aera[0.1 \cdot (Cin,org - Cout,org, Aera) + 0.001]} + 8660.19 \cdot Cin,org, Clarifier \cdot F \left(\frac{ton}{hr} \right)$$

Assume $Cout,org, Aera = Cin,org, Clar = 100$ ppm.

$$Total\ Cost(\$) = Cost1 + Cost2 = \frac{436.81 \cdot F \cdot (100 - Cin,org) \cdot (48 + 100)}{100[0.1 \cdot (Cin,org - 100) + 0.001]} + 8660.19 \cdot 100 \cdot F \left(\frac{ton}{hr} \right)$$

Finally,

$$Total\ Cost(\$) = 183 \cdot V(m^3) = \frac{646.48 \cdot F \cdot (100 - Cin,org)}{[0.1 \cdot (Cin,org - 100) + 0.001]} + 866,019 \cdot F$$

To find constraint for volume needed for the activated sludge, it is clear that any volume predicted by the equation given below is the minimum volume needed for removing specified contaminant level. Any volume larger is acceptable and is capable of removing more organics:

$$V_{\text{aeration tank}} \geq \frac{F_{AO} X}{-r_{A,exit}} \quad \text{where A is organics}$$

$$V_{\text{secondary clarifier}} \geq \frac{Cin,org}{230\ ppm} \cdot F \left(\frac{ton}{hr} \right) \cdot \frac{907\ kg}{ton} \cdot 24\ hr \cdot \frac{m^3}{kg} \geq 94.64 \cdot Cin,org \cdot F$$

Of course, the volume needed is the addition of $V_{\text{aeration tank}} + V_{\text{secondary clarifier}}$.

$$Total\ volume = V_{\text{aeration tank}} + V_{\text{secondary clarifier}} \geq \frac{F_{AO} X}{-r_{A,exit}} + 94.64 \cdot Cin,org \cdot F$$

$$Total\ volume \geq \frac{\left(907 \cdot F \frac{m^3}{hr} \right) (Cout,org - Cin,org) \cdot (48 + Cout,org)}{0.19 \cdot Cout,org [0.1 \cdot (Cin,org - Cout,org) + 0.001] \cdot \frac{1000\ mg}{g}} + 94.64 \cdot Cin,org \cdot F$$

$$Total\ volume \geq \frac{\left(4.77 \cdot F \frac{m^3}{hr}\right)(C_{out,org} - C_{in,org}) \cdot (48 + C_{out,org})}{C_{out,org}[0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]} + 94.64 \cdot C_{in,org} \cdot F$$

Assume $C_{out,org}, A_{era} = C_{in,org}, C_{lar} = 100$ ppm.

$$Total\ volume \geq \frac{\left(4.77 \cdot F \frac{m^3}{hr}\right)(100 - C_{in,org}) \cdot (48 + 100)}{100[0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]} + 94.64 \cdot 100 \cdot F$$

$$Total\ volume \geq \frac{\left(7.065 \cdot F \frac{m^3}{hr}\right)(100 - C_{in,org})}{[0.1 \cdot (C_{in,org} - C_{out,org}) + 0.001]} + 9464 \cdot F$$

Finally,

$$V \geq \frac{70.65 \cdot F \cdot (100 - C_{in,org})}{(C_{in,org} - 100) + 0.01} + 9464 \cdot F$$

Appendix III

Tabulated data for water stream placement:

Freshwater to Units		
	2	3
FW	25.00	8.57

Units to Units		
	4	5
1	2.67	0.00
2	6.07	0.00
3	0.00	2.29

Units to Sink	
	1
3	0.48

Units to Regeneration			
	API	ACA	AS
2	0.00	18.93	0.00
3	0.00	0.00	5.80
4	198.24	0.00	0.00
5	0.00	182.42	0.00
6	0.00	0.00	74.42

Regeneration to Units				
	1	2	5	6
API	0.06	0.00	0.00	71.68
RO	2.61	7.10	158.94	2.74
ACA	0.00	182.40	21.18	0.00

Regeneration to Regeneration				
	API	CWW	RO	ACA
API	0.00	205.96	0.00	0.00
CWW	0.00	0.00	205.95	0.00
RO	0.00	0.00	0.00	2.24
AS	79.46	0.00	0.00	0.00

Regeneration to Sink	
	1
RO	32.33
AS	0.76

Contaminant Concentration Out of Units				
	Salts	Organics	H2S	Ammonia
1	101.09	500.00	286.85	67.91
2	144.40	4000.00	10.00	32.00
3	70.00	3500.00	175.00	116.67
4	66.64	502.67	20.97	46.90
5	45.48	342.84	14.17	43.47
6	2230.79	6500.00	51.38	47.93

Contaminant Concentration Into Regeneration				
	Salts	Organics	H2S	Ammonia
API	641.18	376.01	32.23	48.61
CWW	641.18	50.00	32.23	48.61
RO	641.18	50.00	5.00	30.00
ACA	54.40	679.69	13.68	42.26
AS	2074.55	6283.08	60.32	52.90

Contaminant Concentration Out of Regeneration				
	Salts	Organics	H2S	Ammonia
API	641.18	50.00	32.23	48.61
CWW	641.18	50.00	5.00	30.00
RO	20.00	50.00	5.00	30.00
ACA	54.40	75.00	13.68	42.26
AS	2074.55	60.00	60.32	52.90

Endnotes

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