Develop Treatment Process For Reuse Of Effluent Water From Waste Water Treatment Plant As Cooling Water Make Up

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This report is submitted as a FYP thesis in partial fulfillment of the requirements for the degree of

(BE in Chemical Engineering)

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School of Chemical & Material Engineering (SCME)

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Certificate

This is to certify that work in this thesis has been carried out by **Mr.Talha Mujeeb, Mr.Maaz Khattak, and Mr.Bilal Murtaza** and completed under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

Our work is dedicated to our school SCME and our beloved Parents

Acknowledgement

First and foremost, we want to thank our Allah Almighty for giving us the will and ability to work on this project and complete it in a proper manner.

We would also like to thank our supervisor Dr Salman Raza Naqvi for always being there for us and guiding us through this project. We would also like to mention the guidance we got from Mr Zeeshan Uddin and Mr Shahzeb from PRL for their continuous support and guidance. We would also like to thank all our teachers here in SCME for teaching us with the best of their abilities and making us able to solve complex problems such as our FYP.

We would also like to thank our Parents for their continuous support guidance and encouragement which came in very handy to complete the project in a successful manner.

Abstract

Cooling water happens to be an important commodity when considering the operation of any manufacturing plant, be it an oil refinery or a fertilizer production plant. The project that was assigned to us by Pakistan Refinery Limited (henceforth referred to as ‘PRL’) was related to their cooling water setup, which currently is supplied by an unreliable source of water from the Karachi Development Authority (KDA). It costs the company 4-5 million PKR per annum, and the supply tends to fluctuate, Furthermore, they are wasting a potential source in the form of effluent water which is dumped into the ocean after treatment till it is up to par with NEQ limits. So we devised a process which would make it feasible for PRL to use its effluent water as cooling tower makeup.

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CHAPTER-I

INTRODUCTION

Develop treatment process for reuse of effluent water from waste water treatment plant as cooling water make up.

1.1 About the Company:

The project has been assigned to us by PRL.

Pakistan Refinery Limited was incorporated in Pakistan as a public limited company in May 1960 and is quoted on the Karachi and Lahore Stock Exchanges. The Refinery is situated on the coastal belt of Karachi, Pakistan. PRL is a hydro skimming refinery designed to process various imported and local crude oil to meet the strategic and domestic fuel requirements of the country. The Refinery has a capacity of processing 47,000 barrels per day of crude oil into a variety of distilled petroleum products such as Furnace Oil, High Speed Diesel, Kerosene oil, Jet fuel and Motor gasoline etc.

The Refinery is operating at two locations. Main processing facility is located at Korangi Creek with supporting crude berthing and storage facility at Keamari. Initially, the design capacity of the Refinery was to process 1 million tons of crude oil annually, which was subsequently expanded to 2.1 million tons per annum.

Pakistan Refinery Limited (PRL)since inception has been the principal manufacturer and supplier of petroleum products to the domestic market and Pakistan defense forces. It continues to serve the energy needs of the country with professional excellence and high degree of commitment. PRL takes pride in the edge it enjoys over its competitors in respect of efficiency, lower operating cost, high quality human resources, reliability and introduction of newer generation technologies.

Our focus is on the Korangi plant.

1.2 Purpose of our study

The purpose of our study was to provide a reliable solution to PRL management regarding their cooling water setup. For this, all the members of our group travelled to Karachi, visited the site, and met with Mr. Abdul Majeed, the production manager of PRL. Our objective was to provide a solution that would allow us to use effluent water as cooling tower makeup.

1.3 Contributions to the Study

Along with the constant support and guidance of our supervisor Dr. Salman Raza Naqvi we had constant support from our contact at PRL, Mr. Zeeshan-ud-Deen and Mr. Shahzeb Hassan. The data regarding all the water specifications and details was provided to the group from PRL in due time. With that articles from science direct and research gate we also brought to good use.

1.4 Organization of the Study

We have progressed with the study keeping in mind the following:

- Literature Review
- Process flow and Description
- Material and Energy balance
- Designing
- Simulation
- Costing

1.5 Reasons for Handing over this project:

- Loss of a potential resource as treated effluent water is flushed into the sea.
- Fluctuating supply from KDA.
- The water from KDA costs the company 300/1000 gallons hence over a period of a year or two a lot of money can be saved.
- Treating effluent would result in an output that goes hand in hand with our requirements.

1.6 Our Goals

- Processing of water to meet required specifications
- Providing a feasible solution to cut down or make the plant completely independent of KDA water supply.

It is not possible for us to completely replace the KDA supply as the flow of effluent would never meet the cooling tower's requirement.

CHAPTER-II

LITERATURE REVIEW

2.1 Cooling Water:

Most of our industrial processes are cooled by water. It is used to regulate the temperature and pressure of systems and fluids by carrying the heat away in cooling water. This results in the heating of the water which must be cooled or refreshed with cold water. The value of the production process depends on if the cooling system can maintain appropriate process pressure and temperature. The system’s specifications depend on the process, the composition of the water and environmental constraints.

Many industrial production processes need cooling water for efficient, proper operation. They all rely on the cooling water system to function. Cooling water systems control system parameters by moving heat from heated process fluids into the cooling water.

2.2 Importance of Treatment and Control

Dependability, productivity, and cost of any industry depend on it’s cooling water system. Monitoring corrosion and various parameters is necessary to provide the best possible Total Cost of Operation. Different treatment methods can be used to ensure that we have the minimum TCO. Monitoring is also a vital aspect of this control. It is used so we can see how well our treatment is working, and how we can tune our parameters to get the best possible cost to benefit ratio.

2.3 Problems associated with cooling water

1. Corrosion

Manufacturing of common metals used in cooling systems, such as mild steel, involves removing oxygen from the natural ore. Cooling water systems are an ideal environment for the reversion of the metal to the original oxide state. This reversion process is called corrosion.

2. Scale

Minerals such as calcium carbonate, calcium phosphate, and magnesium silicate are relatively insoluble in water and can precipitate out of the water to form scale deposits when exposed to conditions commonly found in cooling water systems.

3. Fouling

The deposition of suspended material in heat exchange equipment is called fouling. Foulants can come from external sources such as dust around a cooling tower or internal sources such as by-products of corrosion.

4. Biological contamination

Cooling water systems provide an ideal environment for microbial organisms to grow, multiply, and cause deposit problems in heat exchange equipment. Microbial growth can strongly influence corrosion, fouling, and scale formation, if not controlled properly. Macrofouling can occur in once-through cooling systems or water intakes in lakes and rivers. Various species of clams, mussels, and other marine organisms can attach to the piping, reducing water flow and increasing corrosion.

2.4 Treatment programs

Cooling water treatment program success depends on the following.

- Combination of chemical treatment and autonomous system control programs.
- Employees, including operators, supervisors, engineers, and managers – must understand the value of the cooling water system in relation to production and must be committed to maintain and control the program.
- Monitoring and control must be continuous and must utilize the proper techniques, equipment, and supplies.
- A complete system approach combining these aspects will optimize TCO

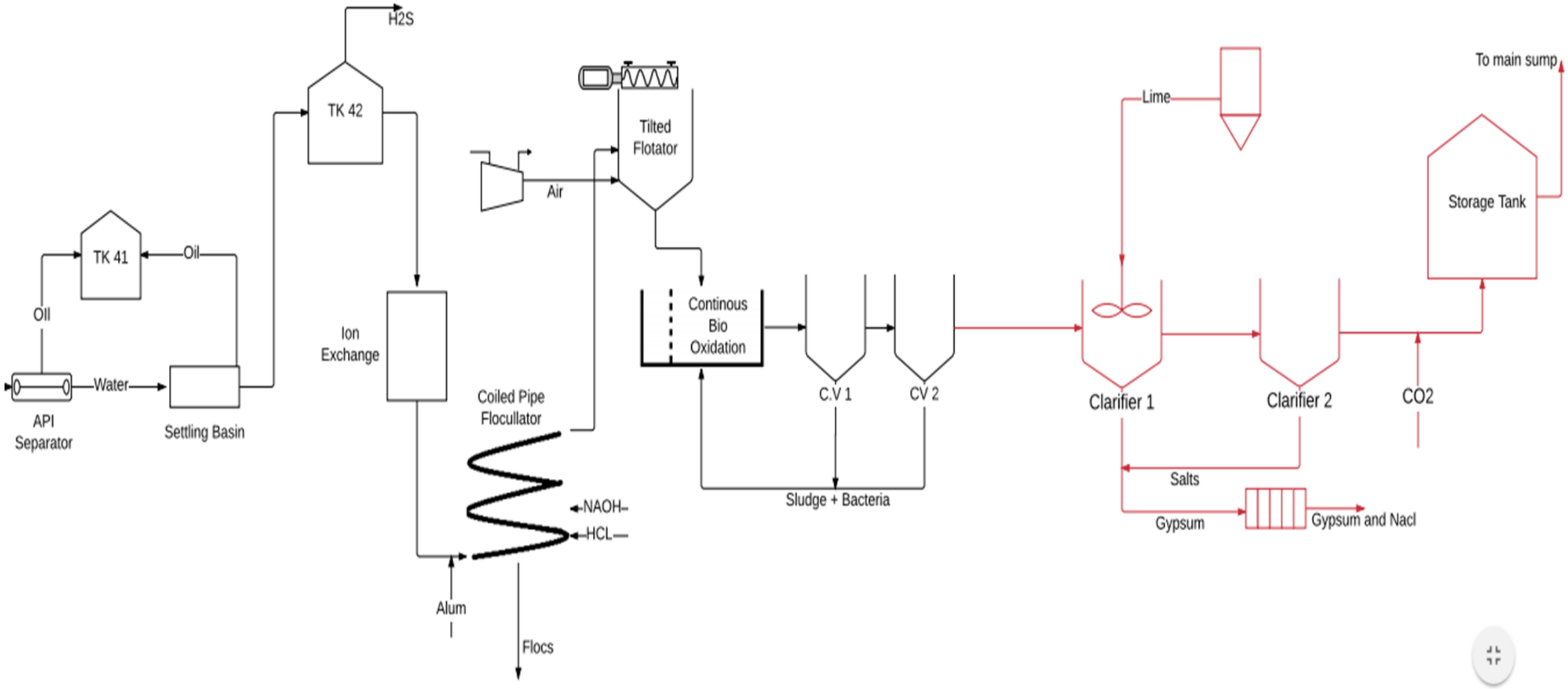
2.7 Treatment of wastewater:

PARAMETER CHECKED	TEST RESULT	PERMISSIBLE LIMIT (NEQS)
Temperature (Degrees Celsius)	26	ΔT of receiving body not to exceed by 3 degrees
pH	7.2	6-9
Total Dissolved Solids (ppm)	1205	3500
Total Suspended Solids (ppm)	17	200
Sulfides (ppm)	0.04	1.0
Sulphates (ppm)	310	600
Oil & Grease (ppm)	8.2	10
Ammonia (ppm)	0.2	40
COD (ppm)	40	150
BOD (ppm)	25	80
Chlorides (ppm)	480	1000
Phenols	0.08	0.1

CHAPTER-III

PROCESS FLOW DIAGRAM AND DESCRIPTION

3.1 THE PROCESS FLOW DIAGRAM:



As it can be seen the process flow is divided into two parts with different color grading the black part signifies the processes that are already incorporated in PRL's system and the part with the red color grade signifies the changes that our group has brought upon in order to make the effluent water usable as cooling water makeup.

3.2 PROCESS DESCRIPTION:

3.2.1 Introduction

The Waste Water Treatment Plant (WWTP) receives all process effluents from the PRL plant together with the potentially polluted crude tank drainage water & boilers blow down, sewage water, water used for neutralization and desalination plant rejected water. Wastewater typically contains hydrocarbons, dissolved chemicals, immiscible solids, ammonia, sulfides, and other compounds. The design capacity of WWTP is 850 m3/day and this plant is capable to produce the effluents with permissible limits required by NEQS.

3.2.2 Pretreatment Operations

Pretreatment involves separating hydrocarbons and solids from wastewater. Interceptor plates, API separators and settling ponds filter out suspended hydrocarbons, oily sludge, and solids using separation by gravity, filtration and skimming. Some oil-in-water emulsions have to be warmed to assist in separating the two. Gravity separation uses the specific gravity variation between water and immiscible oil droplets and allows free oil to be removed from the surface. The pH of acidic water is reduced using soda ash or ammonia or lime. pH is increased of alkaline water by reacting with H_2SO_4, HCL, CO_2-rich flue gas.

3.2.3 Secondary treatment operations

Following pretreatment, immiscible solids are removed using sedimentation or air flotation. Wastewater with low levels of solids may be detected and removed. Secondary treatment processes biologically destroy miscible organic matter using activated sludge, unaerated or aerated lagoons, trickling filter methods, or anaerobic treatments. Materials with high adsorption characteristics are used in fixed-bed filters or added to the wastewater to form slurry, which is removed, by sedimentation or filtration. Additional treatment methods are used to remove oils and chemicals from wastewater. Stripping is used on wastewater containing sulfides and/or ammonia, and solvent extraction is used to remove phenols.

3.2.4 Tertiary treatment operations

Tertiary treatments remove specific pollutants to meet regulatory discharge requirements. These treatments include chlorination, ozonation, ion exchange, reverse osmosis, activated carbon adsorption, etc. Compressed oxygen is diffused into wastewater streams to oxidize certain chemicals or to satisfy regulatory oxygen-content requirements. Wastewater that is to be recycled may require cooling to remove heat and/or oxidation by spraying or air stripping to remove any remaining phenols, nitrates, and ammonia.

3.2.5 Health and safety

A fire hazard exists if free vapors from wastewater containing hydrocarbons are in range of a ignition source during treatment.

3.2.6 Health

Safe work practices and/or appropriate personal protective equipment are needed for exposure to chemicals and waste products during process sampling, inspection, maintenance, and turnaround activities as well as to noise, gases, and heat.

3.2.7 Safety

Waste Water Treatment Plant involves a number of programmable logical controls, which control the start up, shut down, and normal operation of the plant. These controls must be in operative position all the time. By passing these controls could lead to the safety hazards for the plant itself as well as the workers in case of malfunctioning of the equipment's.

3.2.8 Environment

Sulfides are removed from the wastewater before the biological treatment of wastewater. It is done by treating wastewater with HCl. The sulfides are converted into hydrogen sulfide, which can pollute the environment. Care is required to handle this gas. The sludge produced from the unit also needs proper handling and disposal.

3.2.9 Equalization

All refining wastewater streams are presently treated through the existing API separator equipped with CPI packing. The oily process water is pumped from the API to the existing 850 m3 Buffer Tank no 42. This buffer tank is equipped with a pH-measuring unit and a submersible mixer/elector P-11101/J-11101 to obtain a homogeneous quality and to level out peaks in pH, hydrocarbons, sulfide and other constituents. The rather long detention time will see to it that the raw water fluctuations, both in quantity and in quality, are nearly completely leveled out, rendering the downstream waste water processing stable and efficient. The pH of the raw wastewater mixture in the existing 850 m3 buffer tank will be in general between 9 and 11. By keeping the pH of the raw wastewater in the buffer tank at 8.5 by adding a 30% HCI solution the submersible under water ejector (306 m3 air/h @ 13.5 KW) will enhance the stripping out of the formed hydrogen sulphide from the buffer tank. It can be calculated that at a flow rate of 35 m3/h, 24h per day and with a sulphide concentration in the raw waste water of 100 mg/l, the theoretical H2S concentration level in the escaping air will be 12,396 mg/m3 air or 8,167 ppm H2S. For a sulphide concentration of 300 mg/I the hydrogen sulphide concentration in the escaping air from the buffer tank will be 37,188 mg/m3 air or 24,500 ppm (twenty four thousand five hundred). In cases of high sulphide concentration of 600 mg/I in the raw wastewater, the formed hydrogen sulphide gas stream escaping from the buffer tank will be explosive. The homogenized raw water is transferred from the equalization basin to the next stage, the physico-chemical pretreatment, at a constant flow rate of 35 m3/h into the pipe-flocculator R-21101 which is followed by the dissolved air flotation separator S-22101, which serves respectively to de-stabilize and to remove the oily emulsions and colloidal suspensions that are still present in the gravity de-oiled waste water from the preceding API. The flow through the installation is kept constant by means of a flow transmitter and the frequency controlled feed pump P-11201.

3.2.10 Ion Exchange:

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'**.**

Here the ion exchanger works to separate the harder calcium and magnesium ions with the softer sodium ions.

Ion exchange softening, also known as *Sodium Zeolite Softening* is a typical example of how the ion exchange process works to purify the water by removing the hardness level caused by presence of calcium and magnesium. This is normally used in steam boilers and industrial water treatment applications. When the bed gets completely saturated with Ca and Mg ions, it has to be regenerated mainly by increasing the amount of sodium ions. This is done by first performing backwashing to minimize compactness of the bed and to release trapped air pockets. After that, it will be followed by the actual regeneration process using brine solution. Once this is completed, rinsing will be carried out to remove whatever excess brine left in the exchange bed. In modern designs, all these operations are performed using automated programs which can detect the level of saturation and prompt the operators to act accordingly. Overall, depending on the influent characteristics, this will determine the frequency needed to carry out the whole cycle of regeneration.

3.2.11 Physico-chemical pre-treatment

This is used to remove some free oil, metals, emulsified oil droplets, sulfides, suspended solids, and toxic traces of elements from the raw water. The coagulation is accomplished by means of a pH adjustment to a value that is between 7.0 and 7.3. The value is slightly high for the maximum removal of aluminum, which is deemed acceptable in view of the lesser impact of residual aluminum on the health of activated sludge. The precipitation is assisted by an additional addition of a trivalent metal coagulant, aluminum sulphate upstream of the pH controlled hydrochloric acid injection.

3.2.12 Coiled Pipe Flocculator (CPF)

R-21101 The precipitation processes take place in a plug flow type Coiled Pipe Flocculator (CPF), primary flocculator R-21101, in which all stages of the precipitation process take place sequentially. The addition of the necessary chemicals is arranged sequentially, in a fixed order and at predetermined time intervals. Also the pH is continuously monitored and adjusted to the set point value by means of an in line pH control loop within the confinement of the primary flocculator. The exact process control during the co-precipitation and flocculation reaction allows the application of relatively short reaction times, without running the risk of loss of flocculation potential. The destabilization is done using a flocculator pipe-reactor. For that purpose, a mixture of neutralizing agent; coagulant along with a polymer (3 mg/l) is injected into the pipe-flocculator. pH is kept in the range between 7.0 and 7.3. This causes the destabilization of the emulsion and colloidal particles and leads to their recombination into layer conglomerates that can be removed downstream. Intensive and instantaneous mixing of the pH correcting chemicals, flocculants, and polymer is achieved by the turbulence created in the pipe-flocculator. The dosing rates of coagulant/flocculants are set manually according the feed flow rate, dosing of acid or caustic necessary for pH adjustment is controlled by means of a pH measurement in the CPF. The chemical dosing, including pH control, will be automatically activated once the feeding pump from the buffer-tank has started.

3.2.13 Tilted Plate Flotator (TPF)

In the flotation unit, the oil emulsions and colloidal suspensions are removed. This is caused by the increase of the floating effect of the suspended particles which is because of the attachment of minute air bubbles to the flocculated impurities. The sludge floats rapidly to the liquid surface, where it is completely removed using a pneumatically driven skimmer. Subsequently, the floated sludge is moved by gravity into the sludge collection basin. To dissolve the required air in the water, a part of the treated effluent is recycled and pressurized by means of the recirculation pump P-22101, purposely designed for this duty. At an operation pressure of no less than 5.0 barg a metered volume of compressed air is injected in the suction line of the recycle pump. Due to the high level of turbulence and shearing forces in the pump chamber the water is saturated with air. Just before the water enters the Tilted Plate Flotator unit, the saturated recycle flow is injected into the flocculated oily wastewater into the last section of the pipe flocculator. Due to the sudden pressure loss, the dissolved air isreleased in the form of very small sized air bubbles (30 to 50 microns) that attach themselves to the flocculated and suspended impurities. The clarified effluent is moved under gravity to the next stage, which is the anoxic biologic pre-selector reactor.

3.2.14 Aerobic Biological Treatment

The physically/chemically treated water flows under gravity from the DAF unit directly into the first pre-selector compartment of the biological continuous activated sludge treatment installation. In this flow, if needed FeC13 is injected in a concentration of 5 ppm in order to eliminate the present S2. The Fe3+ will react as intermediary agent for the oxidation S2 to S0 and S042. The biologic wastewater treatment installation is designed to treat 840 m3/day with BOD load of nominal 86 kg/day (peak 107 kg/day) and COD-load of 302 kg/day. The biological system starts with a two stage anoxic pre-selector, in which in the first bio pre-selector the recycle sludge, pumped back from the secondary clarifier is intimately mixed with the raw water under temporarily oxygen pore conditions. The prevailing operating conditions promote according to common experience the growth of microbial species that are capable of rapidly adsorbing and absorbing substrate in a strictly substrate limiting and anoxic environment enabling a quick removal of soluble COD/BOD in the reactors. These species have as a common characteristic that they produce a sufficient amount of extra-cellular polysaccharide to form strong and well compacting flocs during sedimentation. The slower adsorbing species, often of a filamentous nature, tend to hold large volumes of interstitial water show a smaller capability of auto-flocculation and have poorer settling characteristics. Such sludge is rather often associated with sludge bulking problems in conventional, extended aeration activated sludge installations. The aerobic biologic treatment is operated as an extended aeration bioreactor, in which substrate is the limiting factor. The biomass is subjected to a F/M ratio of maximum 0.12 kg BOD/kg MLVSS (~ 0.20 kg COD/kg MLVSS/d) to force it into a maximum biochemical degradation of the organic contaminants. The limiting substrate factor checks at the same time the amounts of sludge growth; under the prevailing operating conditions a growth of no more than 0.3 -0.35 kg MLVSS/kg BOD removed is anticipated under steady state operational conditions. The recycle activated sludge and the incoming physico-chemically pre-treated effluent are intimately mixed and kept homogenized by means of vertical agitators, M-31101 and M-31201, mounted over the two pre-selector reactors. The activated sludge is thus continuously kept in direct contact with the substrate. The amount of recycle (MLVSS) concentration of approximately 3500 mg/l, presuming a settled sludge concentration of 7100 mg/l, a recycle quantity of 100% shall be set.

3.2.15 Bioxpres-selector

The pre-selector consist of 2 separate, concrete tanks (T-31101 and T-31201), each equipped with a mixer device (M-31101 and M-31201), and where in the first one the re-circulated sludge coming from the clarifiers and the DAF treated water are mixed intensively. In the pre-selector a number of important process steps are accomplished.

Pre-selection is a useful tool to avoid sludge bulking. The sludge, being of a luxury type, flourishes only when continuously both food and dissolved oxygen are available to them. As the food is immediately absorbed by the activated sludge itself in the pre-selectors, nothing or at the least not enough is left for the slower growing species. As a result, these species disappear through the process of spontaneous and natural selection. The microbes do not immediately oxidize the waste particles; they primarily hydrolyze them. For that reason the oxygen requirement in the pre-selector basin is fairly low and is only intended for their endogenous respiration. The proper taking-up of oxygen will start in the aeration basin, some 25 minutes after the mixing of the raw water with the recycled activated sludge coming from the clarifiers. The internal configuration of the pre-selector has been designed to minimize hydraulic short-circuiting and back-mixing in the reactors. The second pre-selector flows over under gravity into the extended aeration activated sludge reactor. The hydraulic detention time in the reactor, type oxidation dish, is long, typically in the order of 70 hours, to enable the micro-organisms to completely digest and metabolize the earlier absorbed and adsorbed substrates. A sufficient amount of atmospheric oxygen is provided by means of two submersed ejectoraerators to the activated sludge to support the aerobic digestion and to promote new cell growth. The oxygen supply in the aeration basin of one ejector-aeration device is controlled by means of a dissolved oxygen sensor which is submersed in the mixed liquor and which will control the frequency of the recirculation pump. The control loop maintains the dissolved oxygen level between a preset minimum and maximum value to prevent over-aeration.

3.2.16 Biological oxidation

Organic waste is digested in the biological oxidation basin, where microbes digest the waste that was previously adsorbed in the pre-selectors. A major part of the digestive energy will not be used by the activated sludge: instead, it is released to the environment in the form of heat. The effect is most noticeable during cold periods; the temperature of the basin contents is then well above ambient. The effects are less pronounced during warmer periods as the excess heat is disposed of through evaporation at the water surface. The oxygen the microbes consume during their digestion processes is obtained from the air bubbles that continuously Percolate through the water. The oxygen contained in the air bubbles diffuses through the air bubble water interface layer and reaches the microbes as a solute in water. The microbes are unable to absorb the atmospheric oxygen directly from the air bubble. The amount of oxygen introduced into the mixed liquor (i.e. the mixture of waste water with the recycle flow of activated sludge) is more or less proportional to the amounts of oxidizeable organic contaminants in Waste Water. The air for the activated sludge aeration is supplied by means of two ejectors aeration devices (P-32101/J-32101 and P-32201/J-32201). As already mentioned the re-circulation pump (P-32101) of an ejector device is frequency controlled. Measuring the oxygen concentration in the aeration basin T-32101 will increase/decrease the water flow through the ejector J-32101. The second ejector has a fixed re-circulation flow.

3.2.17 Clarification

The activated sludge is separated by using two (2) parallel operating static settling basins. These are of the Imhof type. The clarification in an Imhof type settler is considered correct since the total flow of effluent to be clarified amounts just 70 m3/h and a sufficient construction height is available to create the necessary steep slope (600) in the bottom structure of the clarifier.

The design overflow rate of each clarifier is never the less a mere 0,5m/h; the surface load is 0.4 kg suspended solids/ m2/h only. An ample margin of safety is thus built into the design. The flow rate to the two clarifiers is balanced by means of a set of clarified effluent discharge weirs in the clarifier outlet compartments. The segregation takes place only by using gravity after the incoming mixed liquor reaches the dormant zones of the settler basin. In first instance, the tranquilizing zone leads to a re-coaglomeration of the activated sludge particles, through their ability to auto-flocculate (one of the important activities of the polysaccharide layer around the microbes' cell wall). The slight density difference between the flocculated activated sludge and the surrounding water is sufficient to have the sludge flocs settled to the lower regions of the settler. Particles that do not readily flocculate for any reason are trapped to a large extent in the activated sludge flocs and filtered out. The clarified water has a high clarity as a result, provided the quantities of non-flocculated particles do not exceed the capture capacity of the activated sludge. The clarified water is discharged directly into the clarified water basin T-34101 and from there to the sewer. The sludge settled in the two clarifiers is permanently pumped out and recycled to the first pre-selector basin. Two, recycle sludge pump (P.33101 and P.33201) are foreseen. The settled activated sludge is nearly in full returned to the first pre-selector reactor T-31101, where it is mixed with the incoming pretreated wastewater. A small sludge side stream from the re-circulation sludge stream, the suspended solids contents that equals the activated sludge growth in the biological oxidation basin, in the order of magnitude of 0.3 times the daily BOD load, is continuously diverted to the sludge thickener T-35101. The rate of the sludge side stream is manually set. This bleed is mandatory to maintain a constant concentration of active biomass in the aeration basin. If left unchecked a too high concentration of biomass may develop in the aeration basin, rendering the digestion unstable and the aeration insufficient. The discharge of settled activated sludge from the sludge thickener is continuous. From the sludge thickener T.36101 the thickener sludge is pumped by means of the sludge pump P35101, into the sludge basin T.41101, where it is mixed with the incoming sludge from the DAF unit. The clarified water in the sludge thickener is discharged by overflow directly into the first pre-selector tank T-31101. Further de-watering of this sludge is performed in a decanter centrifuge. Adding a polymer enhances the dewatering characteristics.

3.2.18 Excess sludge thickening and dewatering station

A treatment residue in the form of a wet sludge is generated due to physic chemical and aerobic biological treatment. A mixture of inorganic and organics, consisting of aluminum hydroxide, together with some recovered organics will make up the physic chemical. The sludge is almost completely organic.

3.2.19 Sludge thickener

The two stages together generate daily approximately 350 kg suspended solids, contained in ca. 10 m3 liquid. Both are collected into the sludge basin T-41101. Only the biological excess sludge is pumped by means of dedicated pump sets P-33101 and P-33201 to a semi-dynamic excess sludge thickener, T-35101. The low surface loading rate of less than 10 kg SS/m2 /day, combined with a solids retention time in excess 5 days will assure to it that a maximum gravity thickening is obtained. The thickener is an Imhof type, with an acutely sloping bottom cone. The lower angle makes a constantly rotating Thickener Bridge unnecessary. The biological excess sludge is sporadically moved; via a pump, out of the thickener bottom and to downstream sludge basin. Both sludge are mixed together with the submersed mixer device .

3.2.20 Sludge dewatering unit

At the sludge mixture, when pumped out with the sludge pump P-45001 from the sludge basin an appropriate measure and variant of flocculants is inserted. The flocculants causes a most possible free water to be ejected out of the floc structure. The resultant suspended solids concentrate has a mechanical strength high enough to endure the pressure exerted onto it in the following stage. The amounts of flocculants needed to accomplish a proper level of mechanical de-watering are kept as low as possibly by accepting a relatively low solids retention rate in the mechanical dewatering device. A higher dosing rate may result in a lesser-suspended solids carry over, but is rather often detrimental to the ultimate de-watering efficiency. The dewatering occurs in a decanter centrifuge. The sludge cake is further compacted by free water ejected by the centrifuge bowl under action of gravity. The aqueous phase is discharged from the centrifuge over an overflow weir assembly at on side of the machine to the API; the cake is pushed out over an "upward" sloping ramp at the opposite side by means of an internal screw running a fraction slower than the bowl. The expelled cake is dumped into a sludge container.

This water, that may contain relatively high concentrations of suspended solids, is bled to the API. It is preferable not returned of the raw water buffer basin, as the solids contained in the centrate are expected to cause an undesirable fouling in that basin.

The decanter centrifuge is in automatically on/off operation, during approximately 10 hours per day.

3.2.21 Chemical solution preparation & dosing system

The industrial wastewater treatment plant requires the following chemical solutions for its steady state operation:

- Aluminum sulphate for coagulation, flocculation and co-precipitation in the physico-chemical pre-treatment station (D.A.F.).
- Hydrochloric acid and sodium hydroxide for pH adjustment in the physicochemical pre-treatment.
- A flocculants polymer for the physico-chemical pre-treatment and for the mechanical excess sludge de-watering and (if found necessary) for the clarification enhancement in the clarifier downstream of the aerobic biologic treatment station.
- Ferric chloride as a catalytic agent for the oxidation of S2, to sulfur and sulphate (optional).
- Phosphoric acid as a phosphor nutrient.

The chemicals used in the physico/chemical pre-treatment installation which cause the precipitation of the contaminants in the effluent are aluminum sulphate, acting as an emulsion breaker and coagulant; sodium hydroxide and hydrochloric acid, required to bring the pH in the for flocculation optimum range and a synthetic, organic poly-electrolyte type flocculants to convert the precipitated contaminants into a separable floc. Ferric chloride is brought to site as a technical grade, 40 – 42% solution having a density of 1.42 kg/dm3 Aluminum sulphate and the flocculants polymer arrive in a dry, granulate form. Before they can be used, they are to be dissolved in water. Permanent line is installed through which liquid caustic is transferred intermittently from caustic intermediate tank 105-FC via 101-J/JA pump to NaOH solution tank. The make up and dosing tanks are sufficiently large to hold at least a 6 days nominal consumption. The liquid forms as hydrochloric acid 35%, Ferric chloride, and sodium hydroxide

25%, apart from the polymer emulsion can be applied as they are; they do not require dilution. The poly-electrolyte (polymer) solutions are prepared automatically and in batch. The relatively low solution strength is typically about 1 gram per liter and also need to be prepared by preference daily. The instability of the dilute solution does not permit a storage time in excess of more than one day; thereafter a progressive loss of chemical efficiency takes place. The decay rate accelerates at rising temperatures. The dry powder, stored in the hopper of the poly-electrolyte solution make up unit, will remain chemically stable for a prolonged period of time, provided the product is kept dry. Further details of the chemical solution make up are given in the Procedure for the Makeup of Chemical Solutions. All dosing pumps are reciprocating types and are except for the hydrochloric acid/sodium hydroxide pump manually controlled. Their capacities are once set by the plant operator in relation to the actual flow and remain constant throughout the plant running. The pumps are of course interlocked with the feed pump to treatment installation, to ensure a homogenous chemical feeding arrangement. The HCl/NaOH dosing pumps are automatically controlled by the pH measured in the CPF flocculator.

3.2.22 Mechanical and piping

It is imperative that the whole wastewater treatment plant has been physically checked and if and where necessary corrected and/or rectified. All liquid lines should have been tested for their absence of leaks, internal obstructions, dirt, and other type of debris into the line. Specifically the HDPE, PVC and other thermoplastic transfer lines must be cleaned thoroughly to remove cuttings and other machining waste left after the cutting and welding of sections. The rather light cuttings travel easily with a flow of water and are likely to cause problems amongst e.g. check valves, dosing pumps etc.

If dirt is found in the pipes, it should be removed first, so that it cannot cause consequential damages etc. Mechanical components such as aerators and pumps are checked for their smooth running and proper alignment with their drivers, once their foundation blocks have been cast and set. A proper alignment and balance re-check will result in a prolonged life expectancy of the equipment and a minimum noise and heat generation. Protective temporarily strainers are placed in pump suction lines (and removed after successful start-up). The sealing/cooling/lubricating oils of the pumps, aerators etc. have to be checked and topped up as per the manufacturers' instructions. The utility supplies must be inspected as well. Compressed air and fresh water lines are blown/flushed out to prevent impurities from entering into control and e.g. chemical solution make-up equipment. Air filters have to be checked. Concerning the chemical dosing, some general advices are given here. Special care should be given to the cleanliness of chemical dosing systems. Tanks, piping, pipe strainers, temporary strainers (where applicable) and other components must be inspected for the presence of fibers, pipe-cutting waste, sealing material fragments. Such impurities will invariably lead to a malfunctioning of the dosing pumps, pressure safety valves, and backpressure valves, injection nozzles and other associated elements. Cleaning all with tap water while there is still no chemical in them is the easiest and the most effective. Special attention must be paid to the correct setting of the dosing equipment and its accessories like back-pressure valves etc. Inaccurate pressure settings may result in too high delivery pressures (with its inherent risk of bodily harm when a chemical dosing line breaks) or in an erratic flow of chemicals to the Coiled Pipe Flocculator. Latter may ultimately result in severe corrosion damage to the TPF basin and its ancillaries.

3.2.23 pH control

The pH-correction of the wastewater is particularly important during the initial period of plant start up, in both cases of high and of low pH-values. The incoming wastewater from tank T-11101 has an alkaline character (average pH = 8.5). Correction for the flocculation pH takes place in the coiled pipe flocculator R-21101. HCI is automatically injected by P-51102 and controlled via 211Q/TO1. The activated sludge can only start developing itself properly when the raw water pH is in the range of 6.0 - 9.0. pH-values beyond these limits inhibit the growth of the microbial populations. The pH-control circuitry needs to be set accordingly, so that at all times a proper pH wastewater is fed to the biologic oxidation basins. The requirements for a pH-control become less severe once the microbiologic population has started growing.

Especially higher pH-values are well tolerated, as the microbes are capable of auto neutralization through the mechanism of the CO2 – HCO3 equilibrium. A mature biologic system that is consistently charged with high pH-levels can in this way accept pH-values above 10 -10.5, provided a sufficient amount of carbon dioxide is generated through the digestion of organics The amount of high pH tolerance is established during a normal plant operation, by gradually reducing the acid dosing to the high pH raw effluent. The tolerance of a microbiologic system for low pH values is distinctly less than that for high pH-levels, unless the acids are organic in nature and are biodegradable. A maximum degree of stability in the neutralized raw water pH is of a major importance. Widely fluctuating pH-values are more detrimental than the pH-extremes by themselves. The more stable the pH; the better will be the overall treatment result. As a guideline, a mixed liquor pH in the range of 6.8 to 8.5 should be targeted for the biologic oxidation basin T-32101.

3.2.24 Nutrient control

The process effluent emanating from the refinery plant does probably not contain sufficient concentrations of phosphorus (P) to satisfy the requirements of the activated sludge population. To compensate for this lack, H3PO4 is injected into the wastewater. Injection ratio BOD: N: P = 100:2:0.2 (min.) The amounts of H3PO4 are not critical, even during the startup period. Nevertheless, it is advised to be slightly generous in the initial stages of an activated sludge generation. The slightly elevated N and P levels prevent a nutrient shortage in the accelerated growth cycle of the bacteria. The amounts of urea and H3PO4 can be reduced upon maturation of the activated sludge.

The water leaves the bio oxidation clarifiers with high levels of sulphates and chlorides and here we add our CESR process.

3.3 CESR theory (wateronline.com):

Many industrial wastewaters, particularly those associated with mining and mineral processing, contain high concentrations of sulfate. These concentrations typically exceed the secondary drinking water standard of 250 mg/L and may be subject to discharge limits between 250 and 2000 mg/L.

The Cost Effective Sulfate Removal (CESR) process was developed to address the shortcomings of other technologies used for sulfate removal. The advantages of the CESR process are:

- Low concentrations of sulfate in treated water,
- Additional removal of metals and other parameters,
- No liquid waste, and
- A minimal volume of hazardous solid waste.

CHAPTER-IV

MATERIAL AND ENERGY BALANCE

To understand our process we first need to go through the material and energy balance respectively.

4.1 Material Balance

Composition of treated effluent water:

pH = 7.2

Flow rate = 720 m^3 / day = 720000 kg/day

Component	Mass per unit of water ppm	Flow rate Kg/day
TDS	1205	867.6
TSS	17	12.24
H_2S	0.04	0.0288
Oil and grease	8.2	5.904
Ammonia	0.2	0.144
COD	40	28.8
BOD	25	18
Cl^-	480	345.6
Phenols	0.08	0.0576
Sodium Sulfate	310	223.2

Table 1 Composition of effluent water

4.1.1 Material balance on Clarifier 1

Chemical reaction occurring:

$Na_2SO_4 + Ca(OH)_2 + 2H_2O \Rightarrow CaSO_4.2H_2O + 2NaOH$ (1)

We know that 1.8 lb gypsum is formed from 1 lb of sulfate

Molecular weight of Sodium Sulfate is 142 g/mole

Hence we find the molar flow rate of Sodium sulfate as 1.57183 kmol/day.

From the equation we know that Calcium hydroxide reacts with the sodium sulfate in a 1:1 ratio, so:-

Moles of $Ca(OH)_2$ needed are 1.57183 kmol/day, which translates to 116.3155 kg/day of lime.

90% conversion occurring

Na_2SO_4	+	$Ca(OH)_2$	+	$2H_2O$	=>	$CaSO_4.2H_2O$	+	2NaOH
1.57183		1.57183				1.4146		2.83

Unreacted reactants

Na_2SO_4 = 0.157183 kmol/day = 22.32kg/day

$Ca(OH)_2$ = 0.157183 kmol/day = 11.63kg/day

Gypsum formed

0.172*1.4146*1000 = 243.31kg/day

Component	Flow rate Kg/day
TDS	867.6
TSS	12.24
H_2S	0.0288
Oil and grease	5.904
Ammonia	0.144
COD	28.8
BOD	18
Cl^-	345.6
Phenols	0.0576
Sodium Sulfate	22.32
$Ca(OH)_2$	11.63
NaOH	113.168

Table 2 Composition after Clarifier 1

Overall material balance on clarifier 1:

720000 + 116.315 - 243.3 = 719873.005

4.1.2 Material balance on Clarifier 2

Chemical reaction occurring:

$NaOH + HCl \Rightarrow NaCl + H_2O$ (2)

Converting mass flows to molar flows, we can use simple stoichiometry to calculate the amount of product formed.

80% conversion occurring

$NaOH$	+	HCl	=>	$NaCl$	+	H_2O
0.56584		0.56584		2.26336		2.26336

Unreacted reactants

NaOH = 22.6336 kg/day

HCl = 9.4685-2.26336 = 7.20514*36.5 = 263kg/day

NaCl formed

2.26336*58.5 = 132.4kg/day

Water formed

40.74 kg/day

Component	Flow rate Kg/day
TDS	867.6
TSS	12.24
H_2S	0.0288
Oil and grease	5.904
Ammonia	0.144
COD	28.8
BOD	18
Cl^-	263
Phenols	0.0576
Sodium Sulfate	22.32
$Ca(OH)_2$	11.63
NaOH	22.6336

Table 3 Composition after Clarifier 2

CO2 required

2 lb : 1000 g is the ratio needed, so accordingly

0.907185 mol :1000 g = x mol: 190135.4

Converting x to kg/day, we have 172.5 kg of CO2/day which goes to the storage tank.

Overall balance on Clarifier 2:

719873.005 – 132.4 = 719740.605

719740.605 + 172.5 = 719913.039

4.2 Energy balance

The temperature at which the energy balance would be performed on both clarifiers is 25C.

Component	Heat of formation kJ/mol
Calcium Hydroxide	-985.2
NaOH	-425.609
Sodium sulfate	-1387.1
Hydrated Gypsum	-2022.63

Table 4 Heat of Formation for Reaction 1

Δ H of reaction: Products – Reactants
((-2022.63) + (-425.609)) – (1387.1-985.2)

=-2448.239 – 2372.3

=-7594kJ/mol

E_{in} + accumulation = E_{out}

-2372.3-75.94=2448.239

E_{out} = 2448.239 kJ/mol

Component	Flow rate Kgmoles/day	Specific heat C_p kJ/mol.K	m C_p J/day.K
$Ca(OH)_2$	0.157183	87.5	13.75
NaOH	2.83	59.66	168.8378
Na_2SO_4	0.157183	128.2	20.15
H_2O	40000	75.8	3032000
Ammonia	0.0085	35.06	0.0298
Hydrated Gypsum	14146	223.48	316
HCl	9.4685	33.4	316.2479
			3032835.011

Table 5 Energy balance table for Clarifier 1

4.2.1 Energy balance on clarifier 1

$\Delta H = (-75.94*1000)*(14146+2.83)$

$\Delta H = -322334.924$ Kj/mol

$mC_p = 3032835.016$ J/dayK

$\Delta H = mC_p * \Delta T$

$\Delta T = -0.1063C$

$-0.1063 = x-25$

$T_2 = 25.1063$ C

4.2.2 Energy balance on clarifier 2

$NaOH + HCl \Rightarrow NaCl + H_2O$

Component	Heat of formation kJ/mol
HCl	-92.3
NaOH	-425.609
NaCl	-411.153
H_2O	-285.9

Table 6 Heats of Reaction for reaction 2

ΔH of reaction = -411.153 – 285.9 – (-425.609 – 923)

= -179.144 * (452*1000) KJ/MOL

ΔT = - 810916.62/3031887.879=0.2674 °C

T2 =25.2674 °C

“This material and energy balance explains the process as in how does our setup reduces the concentrations of sulfates and chlorides to allowable levels for the water to be used as cooling tower makeup water.”

CHAPTER-V

DESIGN

5.1 Kinetics models:

Mori and Minegishi kinetic model:

$$\boxed{[1 - (1-\alpha)^{1/3}] = kt^N}$$

Generalized Nucleation and growth kinetic model:

$$\boxed{-\ln(1-\alpha) = kt^N}$$

A = Fractional degree of reaction

K= Rate constant

t= time

n= 0.5 for diffusion control

n= 1 for surface area control

Kinetic Model	**K**	**N**	**α**	**x**
	1/day			
Mori and Minegishi	3.56*10^-2	0.47	0.014	0.985
Generalized nucleation and growth	9.78* 10^-2	0.53	0.010	0.989

5.2 Reactor Design (CSTR):

5.2.1 Volume calculation:

Volume = volumetric flow rate x residence time (1)

= mass flow rate x residence time x density

=720,000 kg/day x (1/24hrs) x 1 hr x m3/1000kg

Volume = 30 m^3

85% volume is used, hence actual volume = 30 x 0.85

Volume = 25.5 m_3

5.2.2 Calculation of diameter and height:

$\text{Volume} = \frac{\pi D2}{4}$ (2)

For CSTR;

Diameter: Height = 1 : 2

30 = (3.14 x D2 x 2D)/4

D= $\sqrt[3]{\frac{4 \text{ x } 30}{3.14 \text{ x } 2}}$

Diameter = 2.67

H = 2x Diameter

Height = 2 x 2.67

H= 5.34m

Impeller Diameter = 0.4 x tank diameter (3)

=0.4 x 2.67

=1.04m

Impeller opening = impeller Diameter (4)

=1.04m

Impeller height above vessel floor = E = Impeller Diameter (5)

=1.04m

Length of impeller blade = Impeller Diameter x .025 (6)

= 1.04 x 0.25

= 0.26m

Number of impeller = 3

Number of impeller blades = 6

Tip Velocity = 3 to 6 m/sec.

Tip Velocity = 5m/s (7)

Tip velocity = π x D x N

5 = 3.142 x N x 1.04 x (1/60)

N = 5/ (π x 1.04 x 0.017)

N = 90RPM

5.2.3 Baffles design:

4 Flat Baffles in 90^o centre.

Width of baffle = 0.8 x tank diameter (8)

= 0.8 x 2.67

=2.136m.

5.2.4 Power requirement:

Power = Power Number x density x N3 x Impeller Diameter (9)

For radial impellers ;

Power Number = 6

Power = 6 x 1000 x (31/60)3 x 1.04

=860W

=0.86KW.

5.2.5 Power requirement:

Power = Power Number x density x N3 x Impeller Diameter

For radial impellers ;

Power Number = 6

Power = 6 x 1000 x (31/60)3 x 3.084

=2551.2W

=2.5KW.

5.2.6 Clarifier design:

Volumetric Flowrate = mass flow rate / Density (10)

Flowrate = 719873 Kg/hr x m3/1000

=719.87m3/day

OverFlow Rate = Flow / surface area (11)

Solid loading rate = 1.2 kg /m3 .hr

Amount of NaCl formed = 132.4 kg/day

Detention time= 3hours = 180 minutes

Tank volume = detention time x Flow rate (12)

=3hrs x 719.87 (m3/day) x (1day/24hrs)

=90m3

Length : width = 1 : 2

Solid loading rate = soli8ds applied / area (13)

Surface area = 132.4kg/day x $\frac{\mathrm{m2}}{1.2\mathrm{kg}}$ x (1 day/24hr)

Surface area = 4.6m2

Length : width

1:2

Area = Length x width (14)

W= area / Length

Width = $(4.6/2)^{0.5}$

W=1.52m.

Length = 2 xW

=2 x 1.52

=3.04

Wier Length= 4 x Width

4 x 1.52

=6.08m

Wier Overflow Rate =total Flow/ length of wier (15)

= (719.87 m^3/day) / 6.08m

=118.4 m3/m.day

CHAPTER-VI

SIMULATION

6.1 Simulation vs. Scale Model

We realized during the economic analysis of our project that the budget of our work was something that required us to approach every single detail with as much certainty as was humanly possible. The reasons we decided on a virtual simulation of our project were as following.

- Virtual systems are exponentially cheaper than attempting to create a scale model of the project.
- Virtual systems provide us with much more freedom to tinker and innovate, without forcing us into a set path once we begin as is the case with physical projects.
- The amount of instrumental and intricate data that is available to us via virtual simulation is an order of magnitude more than what can be achieved through measurements of physical parameters.

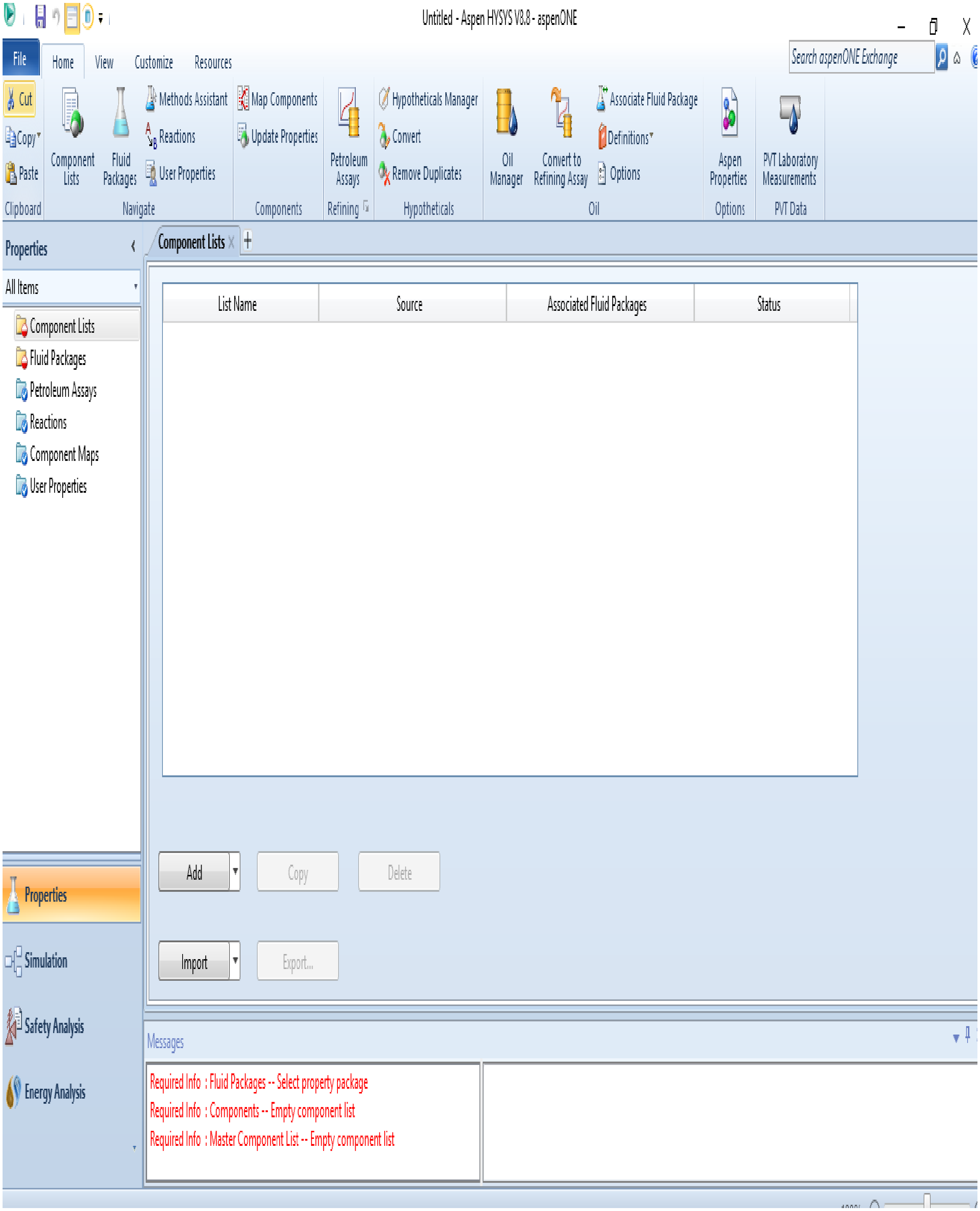
These were the reasons we decided to proceed with using a virtual simulation.

6.1.1 Choosing the software package

The next step was to decide on a software package to simulate our software. The most obvious choice was Aspen software package due to the fact that it was easily available and present in our computer laboratories. But still we performed a short feasibility study to ensure we were using the most suitable choice for our needs. Aspen won over other software like Ariane and Apros but we made the decision to go with Aspen due to the following reasons:

- Aspen Plus provides the widest array of tools to construct and optimize process models including best-in-class physical properties, ability to handle solid, liquid, and gas processes, advanced electrolytes and equation oriented (E/O) modeling mode.
- It is continually upgraded to improve performance and add new functionality.
- It is easily available through university channels.

- Our group has undergone a semester of training in the use of the package under the teaching of Doctor IftikharSalarzai.



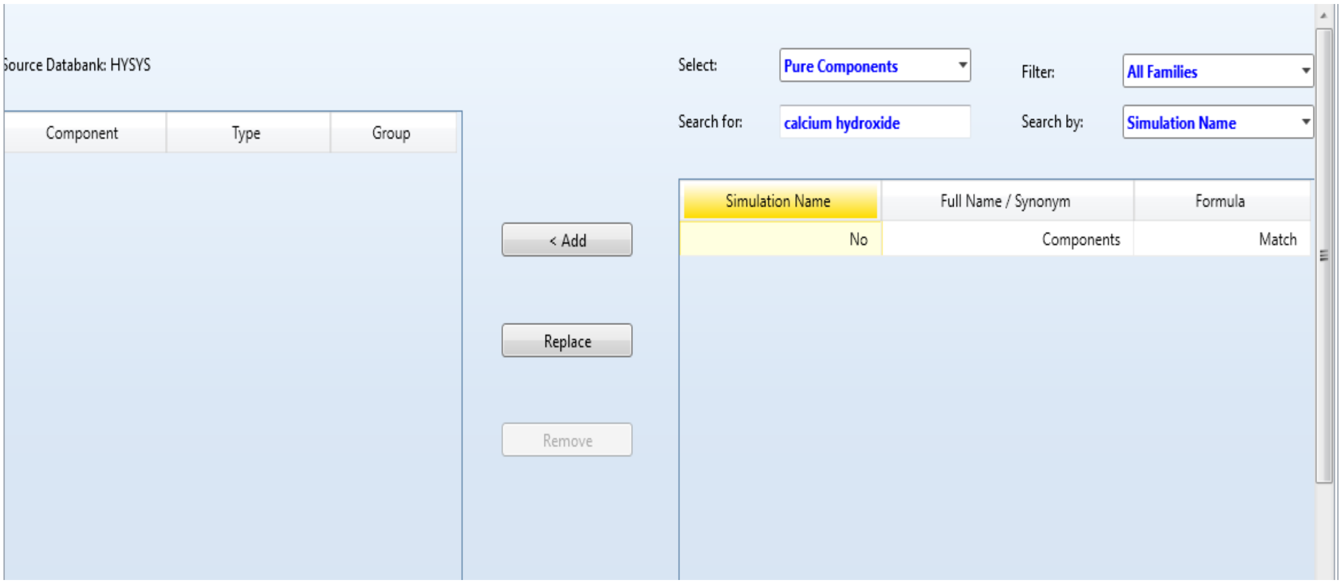
Required Info : Fluid Packages -- Select property package
Required Info : Components -- Empty component list
Required Info : Master Component List -- Empty component list

Picture 1 Properties Environment for HYSYS

6.2 Simulating in Aspen HYSYS

6.2.1 Adding components

Now armed with our software we decided to begin simulating our process. We first decided to use Aspen HYSYS software for the simulation but immediately ran into our first problem. The components we required namely Calcium Hydroxide and hydrated gypsum were not available in the regular HYSYS component list.


Source Databank: HYSYS

Select: Pure Components

Filter: All Families

Search for: calcium hydroxide

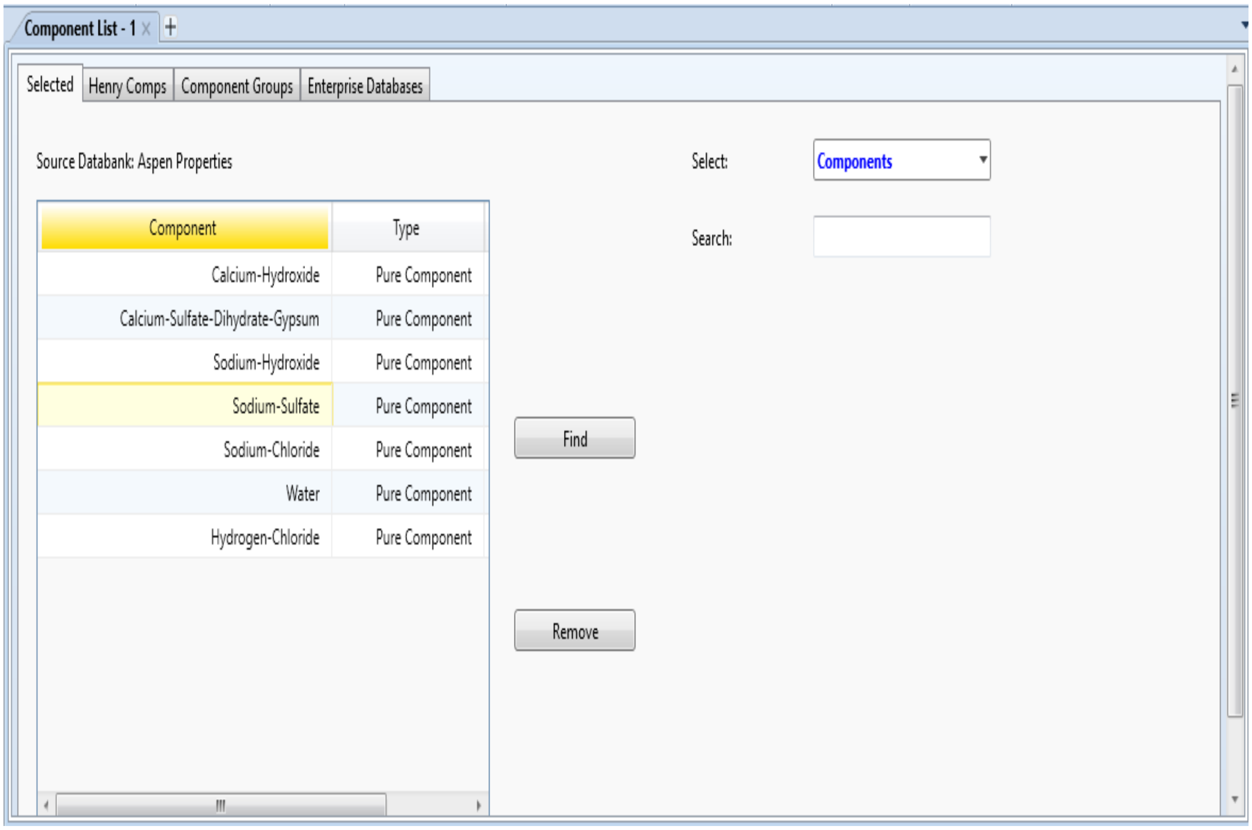
Search by: Simulation Name

Component	Type	Group

Simulation Name	Full Name / Synonym	Formula
No	Components	Match

Picture 2 Component Addition in HYSYS

Thus we decided to use the Aspen Properties database instead which contained all the components we required.



Source Databank: Aspen Properties

Select: Components

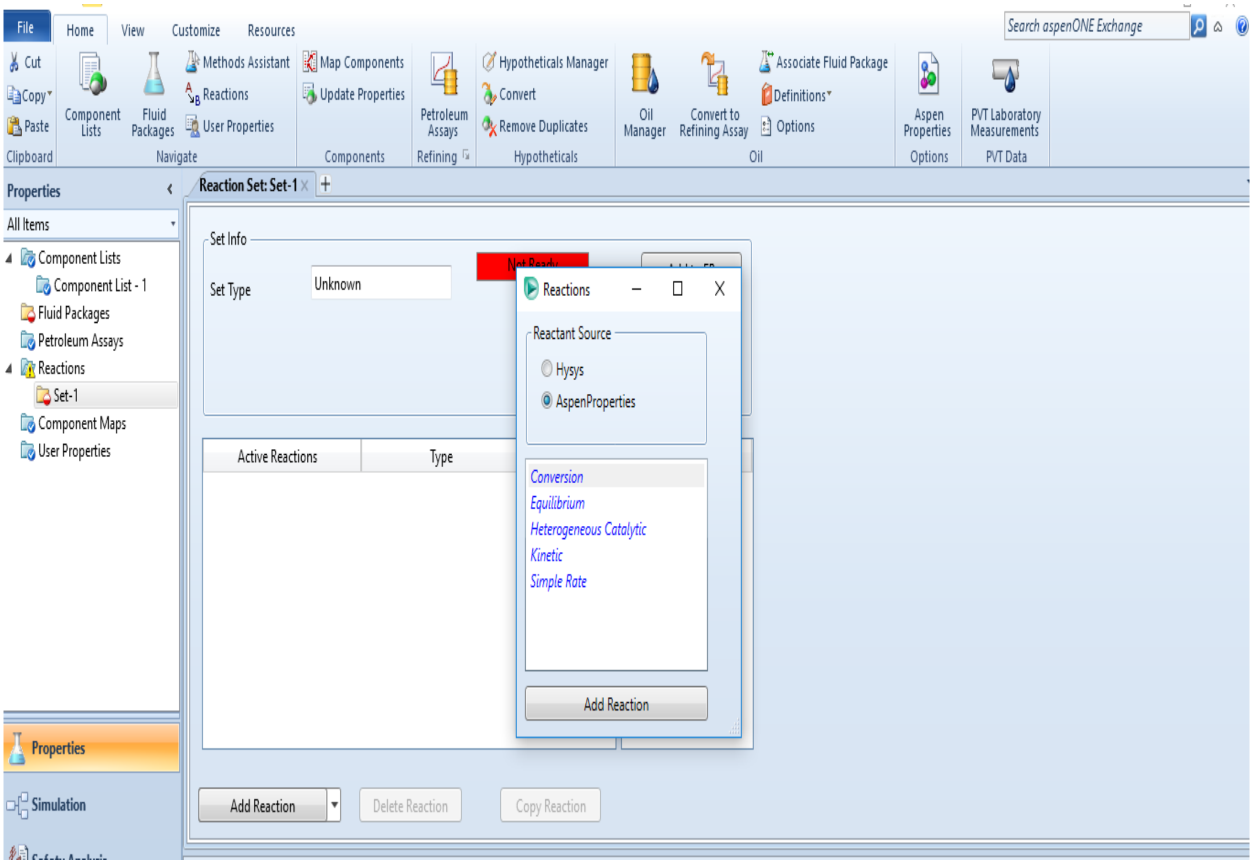
Search:

Component	Type
Calcium-Hydroxide	Pure Component
Calcium-Sulfate-Dihydrate-Gypsum	Pure Component
Sodium-Hydroxide	Pure Component
Sodium-Sulfate	Pure Component
Sodium-Chloride	Pure Component
Water	Pure Component
Hydrogen-Chloride	Pure Component

Picture 3 Components Added for HYSYS

6.2.2 Choosing reaction set

After this we moved on to the reaction tab, where we were careful to use the Aspen properties option for the reaction set. Then we chose the conversion reaction type.

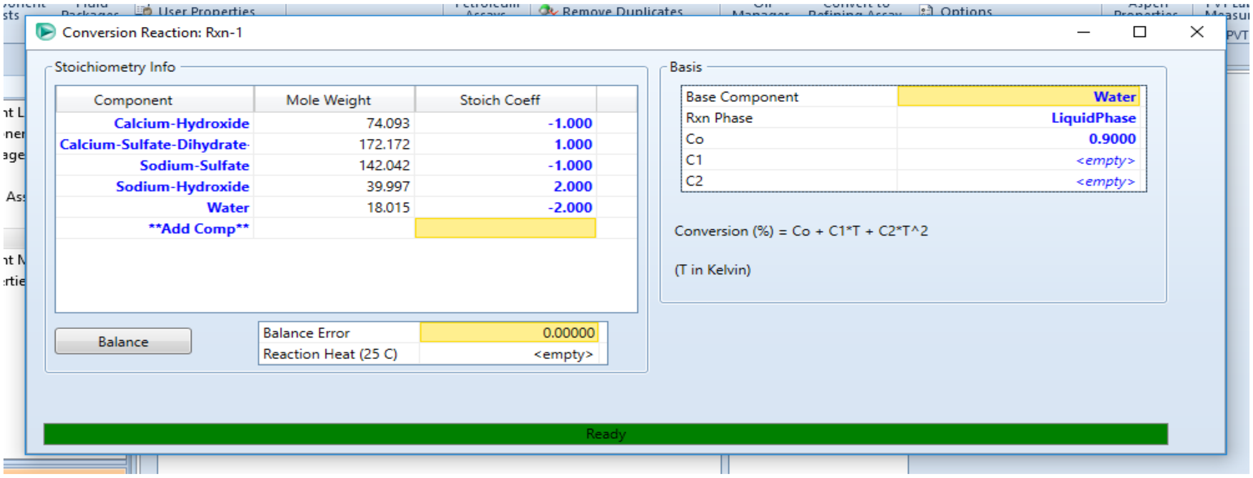


Set Type: Unknown

Reactant Source
○ Hysys
● AspenProperties

Picture 4 Choosing the Reaction type

We then specified the reaction parameters for the first reaction that will occur namely: **$Na_2SO_4 + Ca(OH)_2 + 2H_2O => CaSO_4.2H_2O + 2NaOH$ (1)**


Conversion Reaction: Rxn-1

Stoichiometry Info

Component	Mole Weight	Stoich Coeff
Calcium-Hydroxide	74.093	-1.000
Calcium-Sulfate-Dihydrate	172.172	1.000
Sodium-Sulfate	142.042	-1.000
Sodium-Hydroxide	39.997	2.000
Water	18.015	-2.000
Add Comp		

Balance Error	0.00000
Reaction Heat (25 C)	<empty>

Basis

Base Component	Water
Rxn Phase	LiquidPhase
Co	0.9000
C1	<empty>
C2	<empty>

Conversion (%) = Co + C1*T + C2*T^2

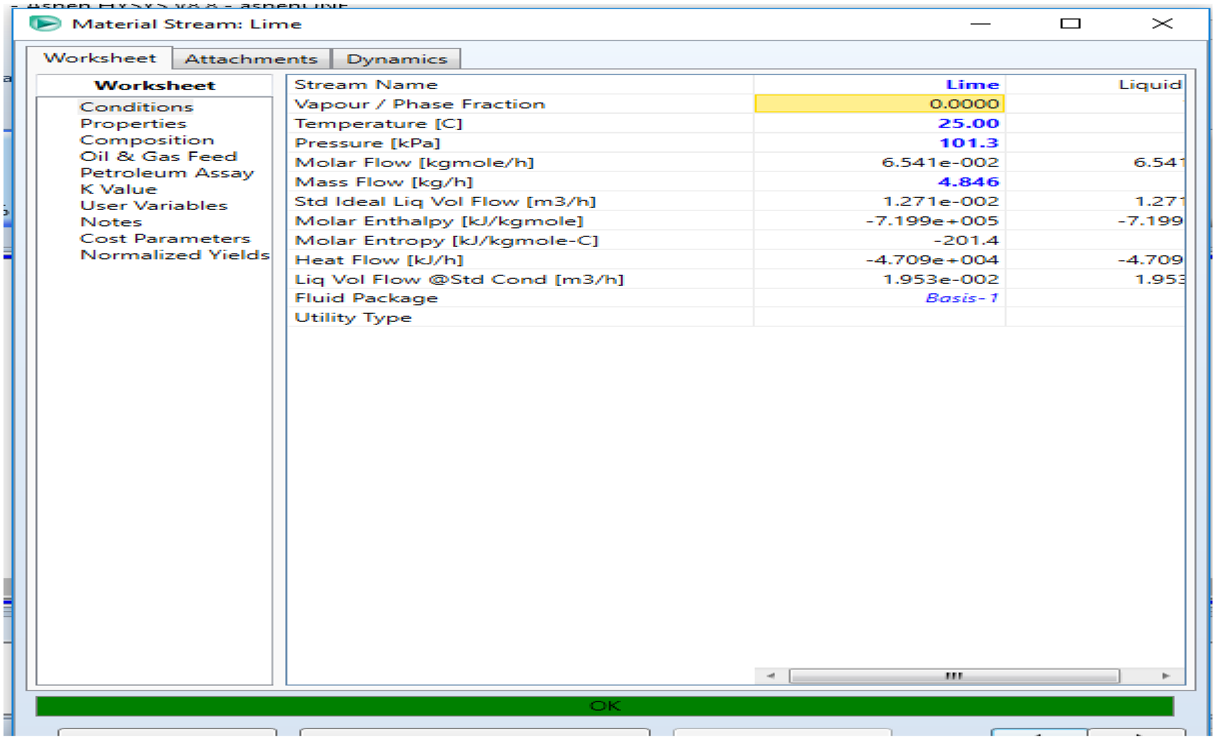
(T in Kelvin)

Picture 5 Setting the Reaction parameters

6.2.3 Choosing fluid package

We then added it to the fluid package NRTL. Finally our properties were complete, so we moved on to the simulation environment.

Here we first defined the lime stream that will be added to the effluent water stream.

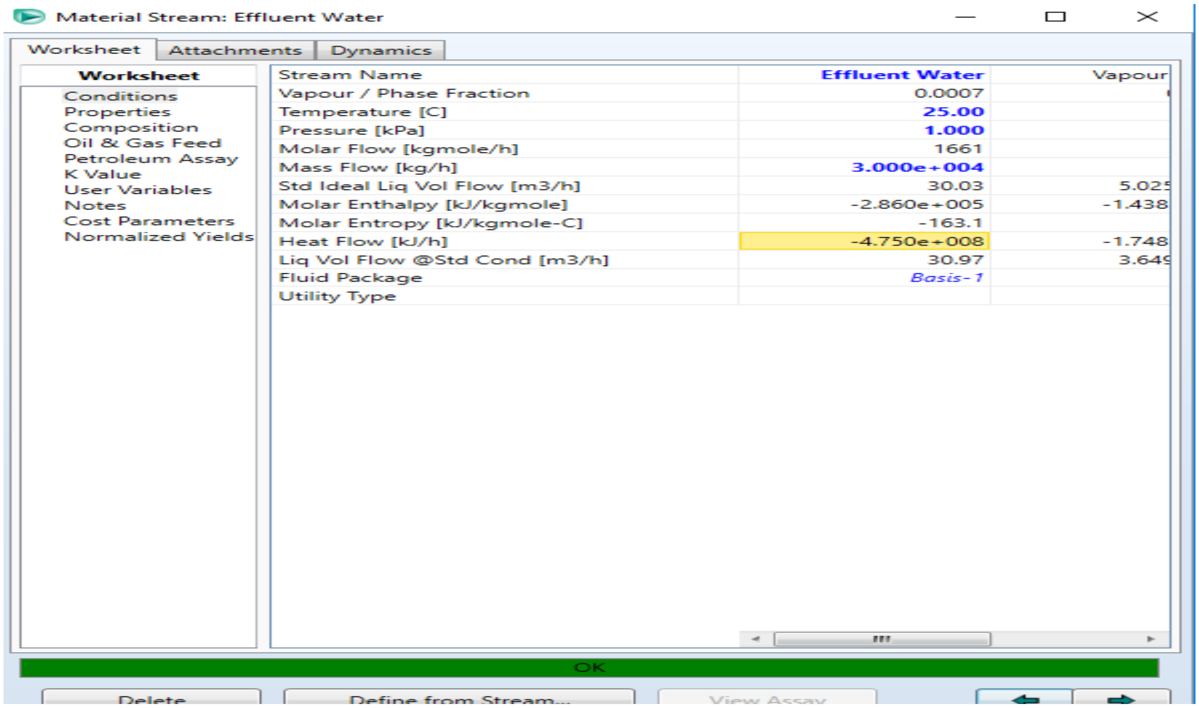

Material Stream: Lime

Stream Name	Lime	Liquid
Vapour / Phase Fraction	0.0000	
Temperature [C]	25.00	
Pressure [kPa]	101.3	
Molar Flow [kgmole/h]	6.541e-002	6.541
Mass Flow [kg/h]	4.846	
Std Ideal Liq Vol Flow [m3/h]	1.271e-002	1.271
Molar Enthalpy [kJ/kgmole]	-7.199e+005	-7.199
Molar Entropy [kJ/kgmole-C]	-201.4	
Heat Flow [kJ/h]	-4.709e+004	-4.709
Liq Vol Flow @Std Cond [m3/h]	1.953e-002	1.953
Fluid Package	Basis-1	
Utility Type		

Picture 6 Defining the lime stream

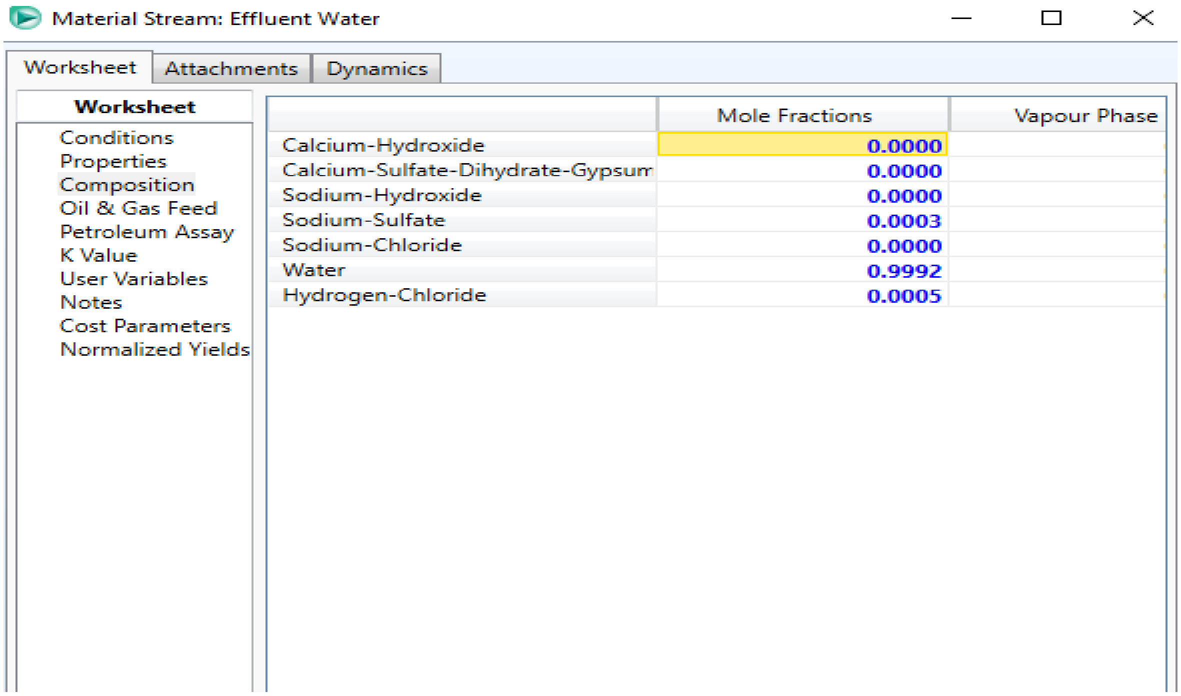
6.2.4 Defining the fluid streams

After this we defined the effluent water stream that we had to purify and make fit for use as cooling tower makeup. The only components we had that exceeded the NEQ for cooling water were sodium sulphate and hydro chloric acid.



Stream Name	Effluent Water	Vapour
Vapour / Phase Fraction	0.0007	
Temperature [C]	25.00	
Pressure [kPa]	1.000	
Molar Flow [kgmole/h]	1661	
Mass Flow [kg/h]	3.000e+004	
Std Ideal Liq Vol Flow [m3/h]	30.03	5.02
Molar Enthalpy [kJ/kgmole]	-2.860e+005	-1.438
Molar Entropy [kJ/kgmole-C]	-163.1	
Heat Flow [kJ/h]	-4.750e+008	-1.748
Liq Vol Flow @Std Cond [m3/h]	30.97	3.64
Fluid Package	*Basis-1*	
Utility Type		

Picture 7 Defining effluent stream parameters



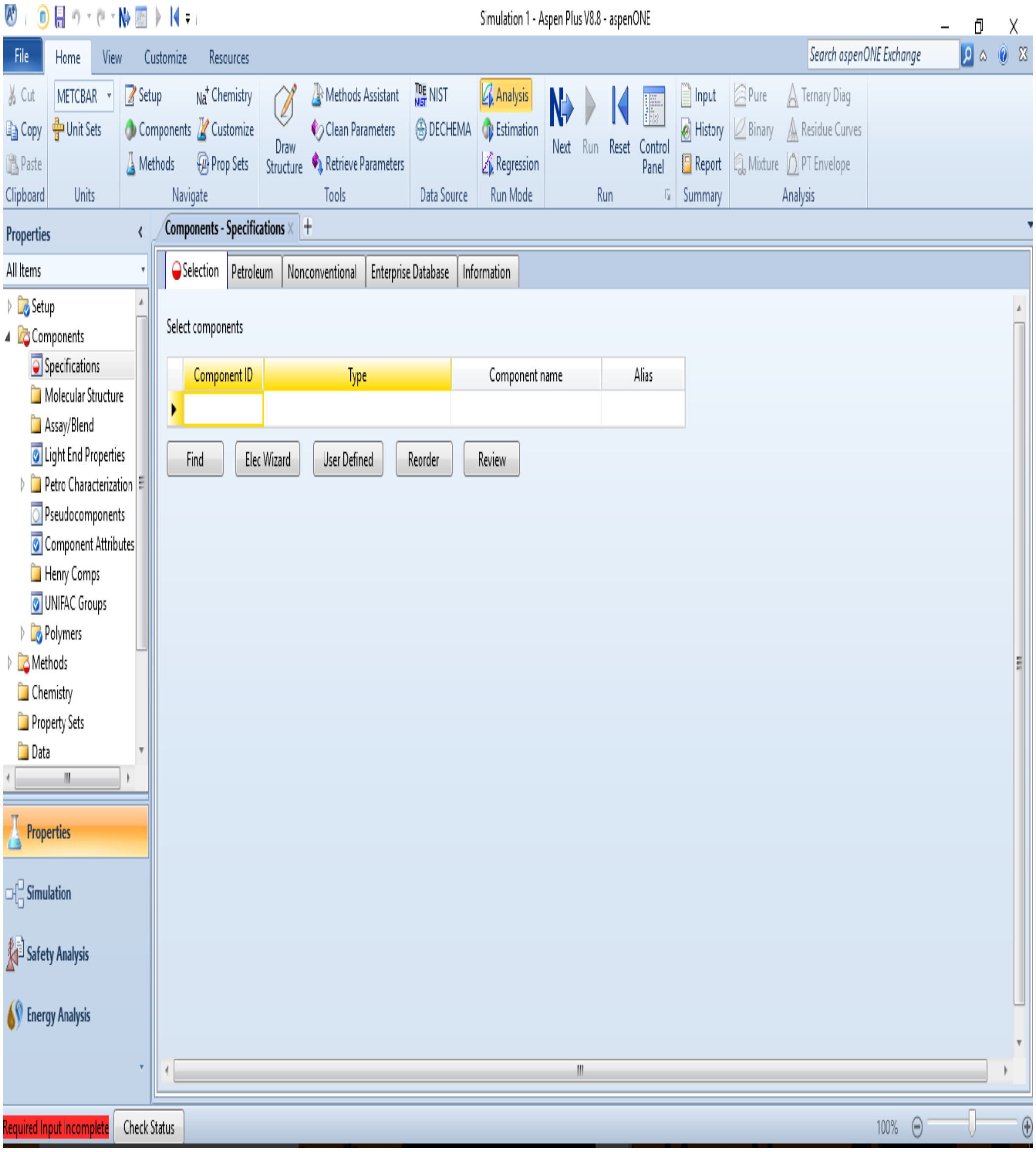
	Mole Fractions	Vapour Phase
Calcium-Hydroxide	0.0000	
Calcium-Sulfate-Dihydrate-Gypsum	0.0000	
Sodium-Hydroxide	0.0000	
Sodium-Sulfate	0.0003	
Sodium-Chloride	0.0000	
Water	0.9992	
Hydrogen-Chloride	0.0005	

Picture 8 Inputting composition for Effluent stream

However this is when we ran into the first major hurdle in our simulation. The fact was that all the reactor operations in Aspen HYSYS, be they Continuous Stirred Tank Reactors, conversion reactors, Equilibrium reactors all were hard coded to **always** give 2 output streams of **vapour and liquid only.** Whereas in our case we needed to have only liquid streams exiting the vessels. Consequently, a new approach was called for.

6.3 Simulating on Aspen PLUS

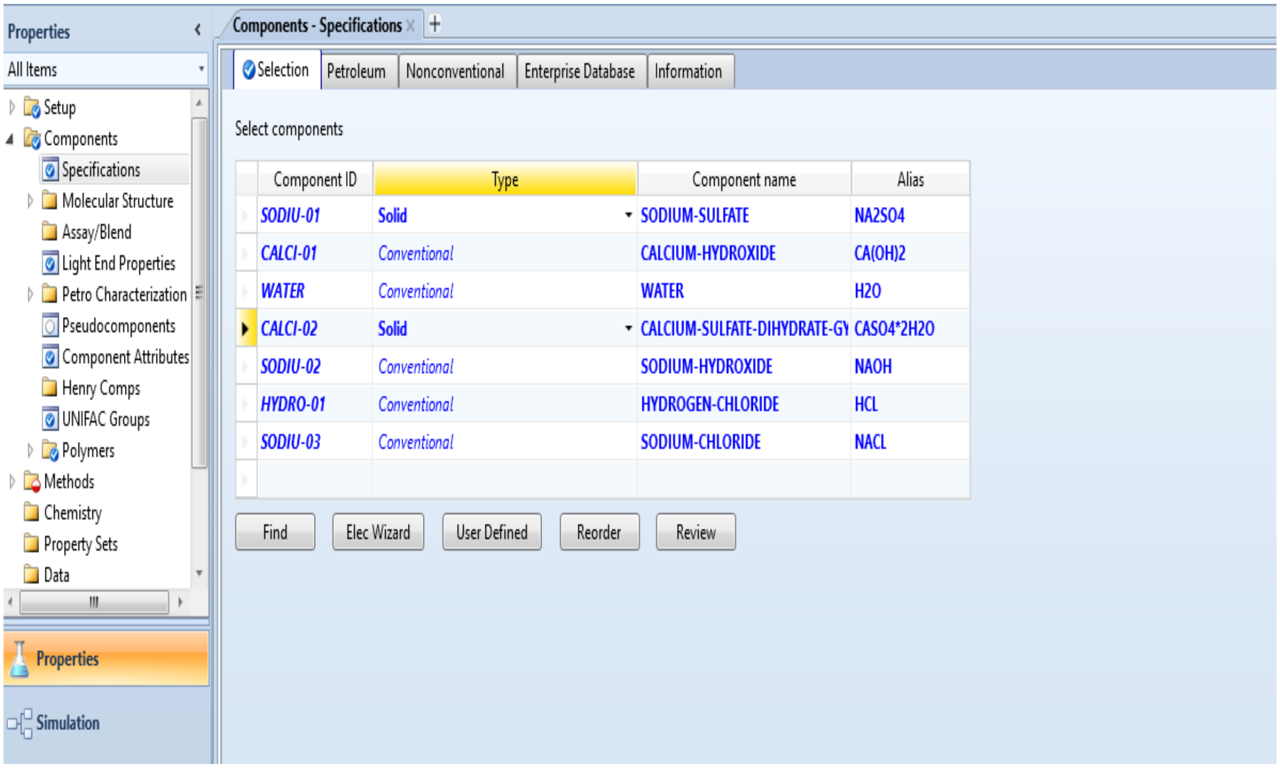
Aspen Plus is the premier chemical process simulation software used for the designing, operation, and optimization of safe, profitable manufacturing facilities. We decided to use Aspen PLUS because it offered us multitudes more freedom than Aspen HYSYS, allowing us to build reaction vessels to our needs and specifications, and to alter stream characteristics as we see fit. This software was sufficiently different from Aspen HYSYS that we required a few days to get acquainted with it.



Picture 9 PLUS component addition environment

6.3.1 Adding components

The first step as always, was to add the components to the system. In Aspen PLUS we faced no difficulty in acquiring the components that we required.



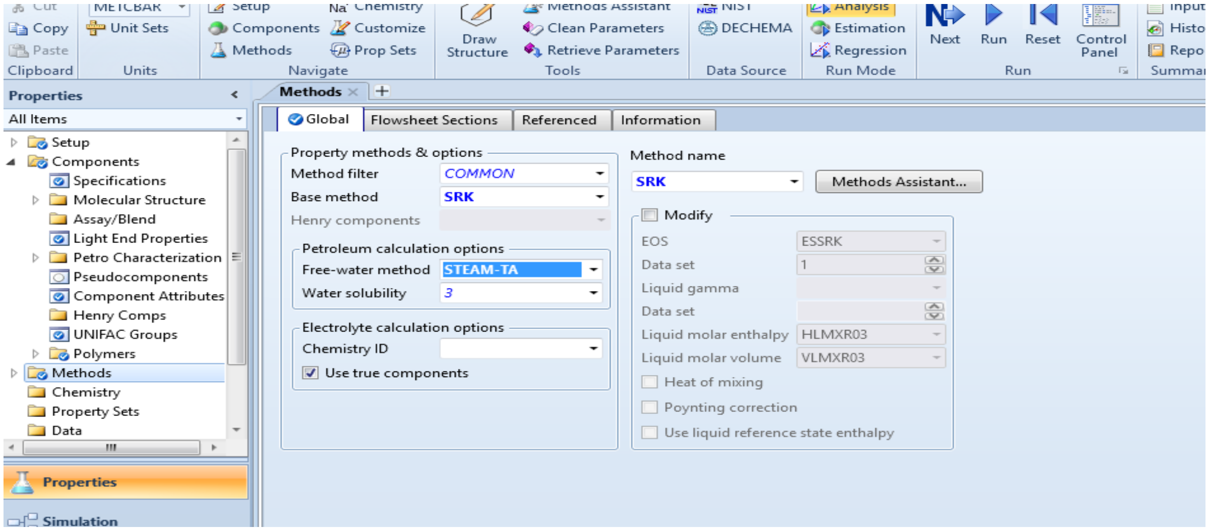
Component ID	Type	Component name	Alias
SODIU-01	Solid	SODIUM-SULFATE	NA2SO4
CALCI-01	Conventional	CALCIUM-HYDROXIDE	CA(OH)2
WATER	Conventional	WATER	H2O
CALCI-02	Solid	CALCIUM-SULFATE-DIHYDRATE-GY	CASO4*2H2O
SODIU-02	Conventional	SODIUM-HYDROXIDE	NAOH
HYDRO-01	Conventional	HYDROGEN-CHLORIDE	HCL
SODIU-03	Conventional	SODIUM-CHLORIDE	NACL

Picture 10 Components added to Aspen PLUS

Another feature that should be immediately visible is how we were able to specify what form the components were in, another upgrade over Aspen HYSYS. Resultantly, we gave the lime we were to use and the resulting gypsum a *solid* type.

6.3.2 Choosing method/fluid package type

Next we specified the method or the fluid package that would be used. The SRK package suited our process the best so we used that.



Property methods & options
Method filter: COMMON
Base method: SRK
Henry components:

Petroleum calculation options
Free-water method: STEAM-TA
Water solubility: 3

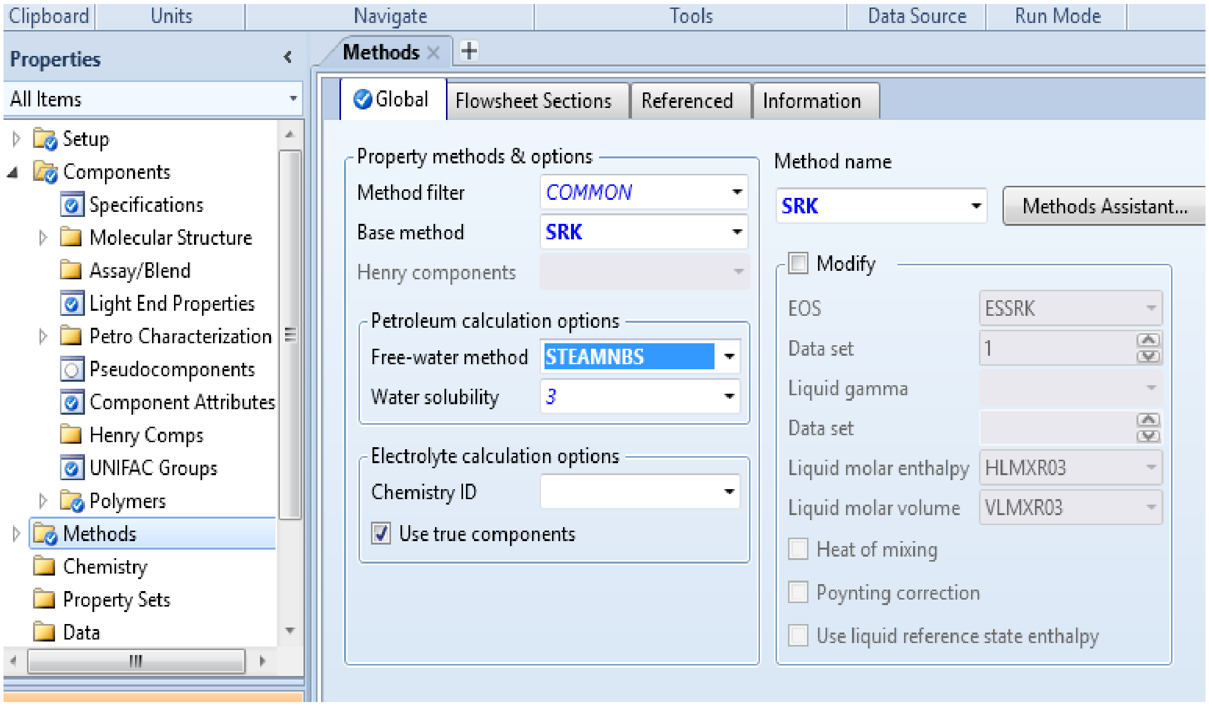
Electrolyte calculation options
Chemistry ID:
☑ Use true components

Method name: SRK

☐ Modify
EOS: ESSRK
Data set: 1
Liquid gamma:
Data set:
Liquid molar enthalpy: HLMXR03
Liquid molar volume: VLMXR03
☐ Heat of mixing
☐ Poynting correction
☐ Use liquid reference state enthalpy

Picture 11 Specifying the fluid package

Before we proceeded further, we also decided to specify a water type of STEAMNBS.



Property methods & options
Method filter: COMMON
Base method: SRK
Henry components:

Petroleum calculation options
Free-water method: STEAMNBS
Water solubility: 3

Electrolyte calculation options
Chemistry ID:
☑ Use true components

Method name: SRK

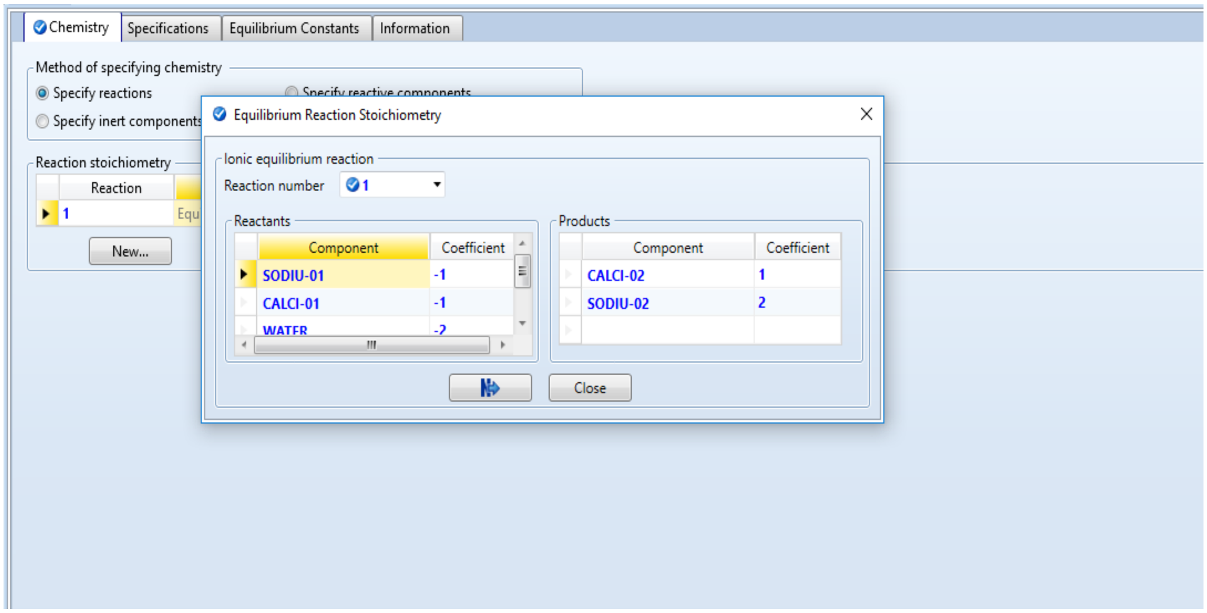
☐ Modify
EOS: ESSRK
Data set: 1
Liquid gamma:
Data set:
Liquid molar enthalpy: HLMXR03
Liquid molar volume: VLMXR03
☐ Heat of mixing
☐ Poynting correction
☐ Use liquid reference state enthalpy

Picture 12

6.3.3 Choosing and specifying the reactions

We then decided to add the reactions that would be occurring during our process. The first reaction that would occur was

$Na_2SO_4 + Ca(OH)_2 + 2H_2O \Rightarrow CaSO_4.2H_2O + 2NaOH$



Method of specifying chemistry

● Specify reactions ○ Specify reactive components

○ Specify inert components

Ionic equilibrium reaction

Reaction number 1

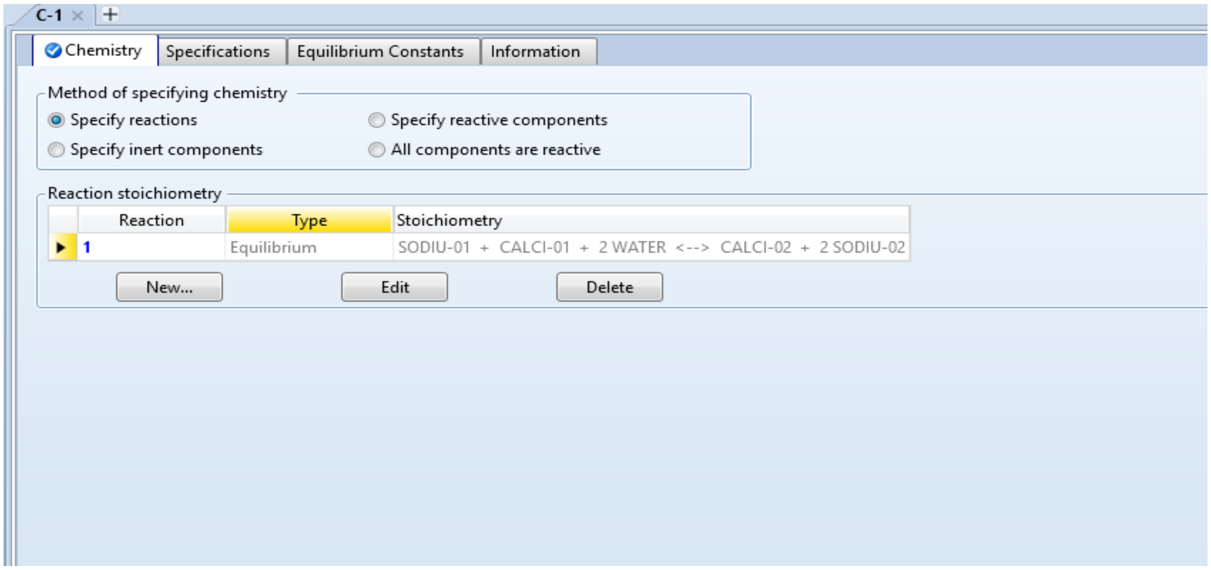
Reactants

Component	Coefficient
SODIU-01	-1
CALCI-01	-1
WATER	-2

Products

Component	Coefficient
CALCI-02	1
SODIU-02	2

Picture 13 Calibrating the reactions



Method of specifying chemistry

● Specify reactions ○ Specify reactive components

○ Specify inert components ○ All components are reactive

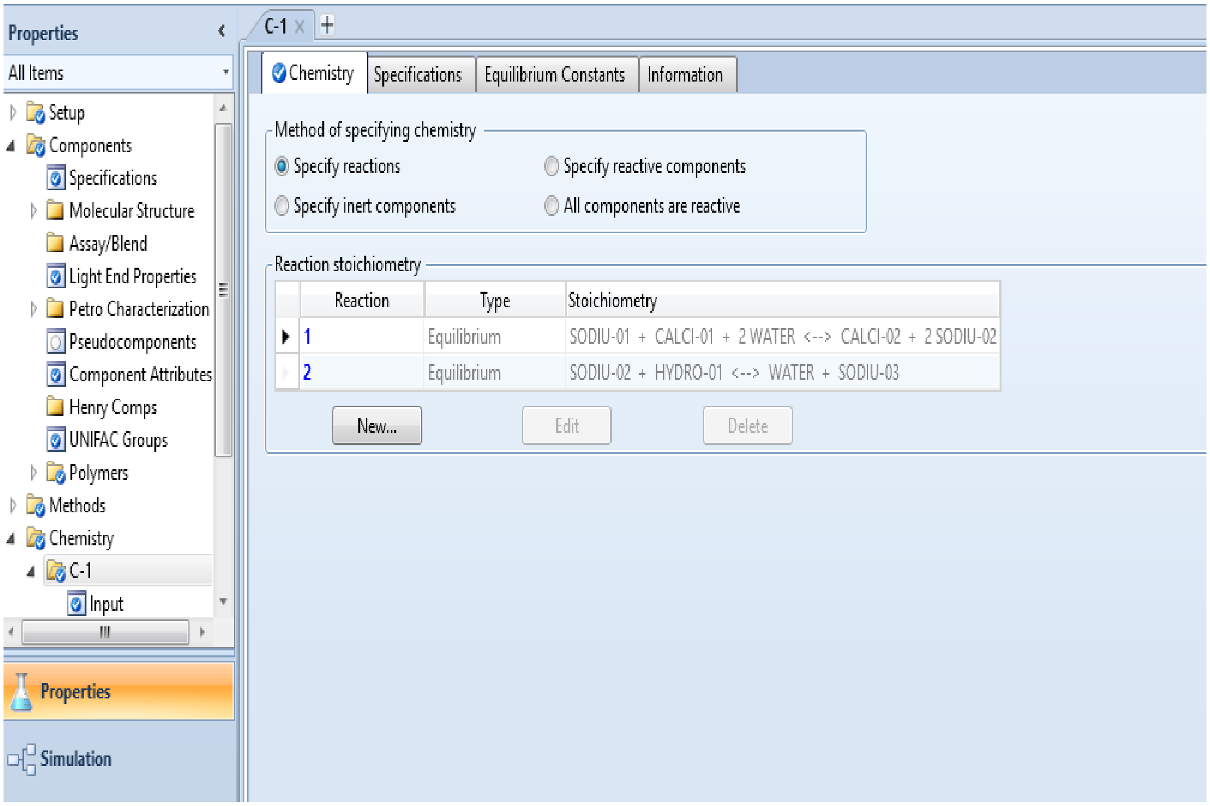
Reaction stoichiometry

Reaction	Type	Stoichiometry
1	Equilibrium	SODIU-01 + CALCI-01 + 2 WATER <--> CALCI-02 + 2 SODIU-02

Picture 14 Reactions Calibrated

The next reaction we added was for the removal of chlorides from the water stream. The resulting chemical reaction took the form of:

$NaOH + HCl \Rightarrow NaCl + H_2O$ (2)



Method of specifying chemistry

● Specify reactions ○ Specify reactive components

○ Specify inert components ○ All components are reactive

Reaction stoichiometry

Reaction	Type	Stoichiometry
1	Equilibrium	SODIU-01 + CALCI-01 + 2 WATER <--> CALCI-02 + 2 SODIU-02
2	Equilibrium	SODIU-02 + HYDRO-01 <--> WATER + SODIU-03

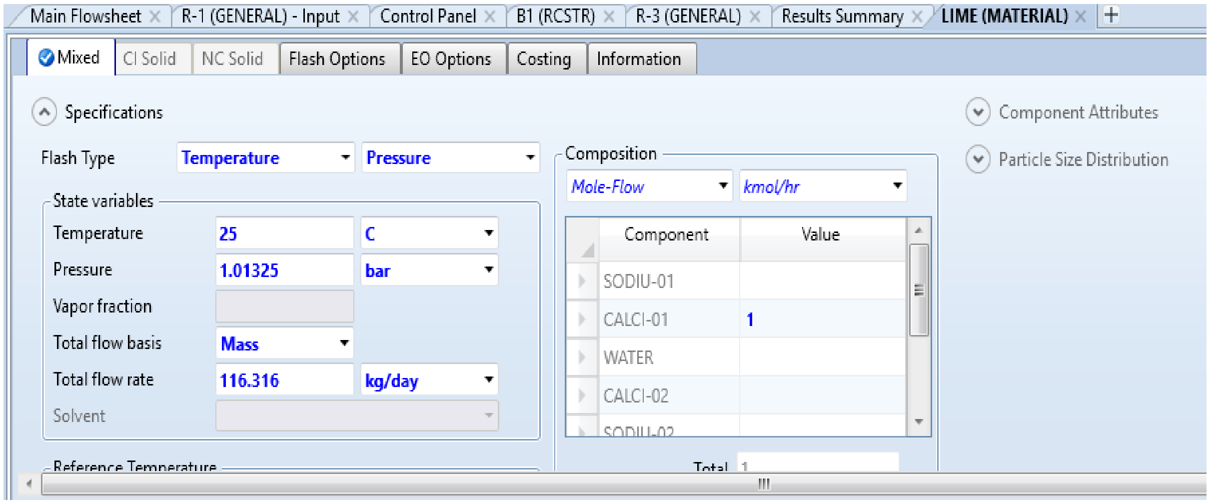
Picture 15 Reaction 2 Calibrated

Thus the required reactions were specified.

6.3.4 The Simulation environment

The next step was to actually build the simulation in the simulation environment.

The first step was defining the lime stream.



Flash Type: Temperature, Pressure

State variables

Temperature: 25 C

Pressure: 1.01325 bar

Vapor fraction:

Total flow basis: Mass

Total flow rate: 116.316 kg/day

Solvent:

Reference Temperature

Composition: Mole-Flow, kmol/hr

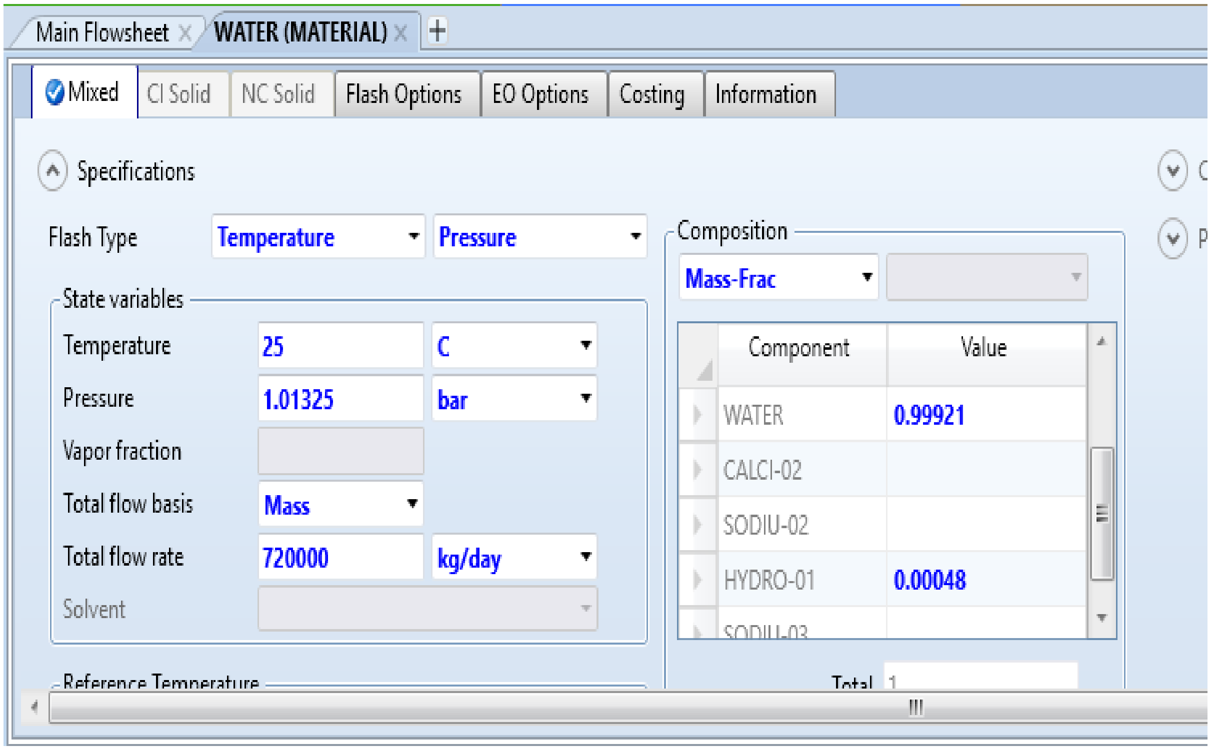
Component	Value
SODIU-01	
CALCI-01	1
WATER	
CALCI-02	
SODIU-02	

Total: 1

Picture 16 Defining the lime stream

We added the temperature, and pressure the stream would be operating under and the flow rate was calculated during our material balance.

After this, the stream for the effluent water was defined, with the assumption that it would be operating under atmospheric conditions and at 25 Celsius.



Flash Type: Temperature, Pressure

State variables

Temperature: 25 C

Pressure: 1.01325 bar

Vapor fraction:

Total flow basis: Mass

Total flow rate: 720000 kg/day

Solvent:

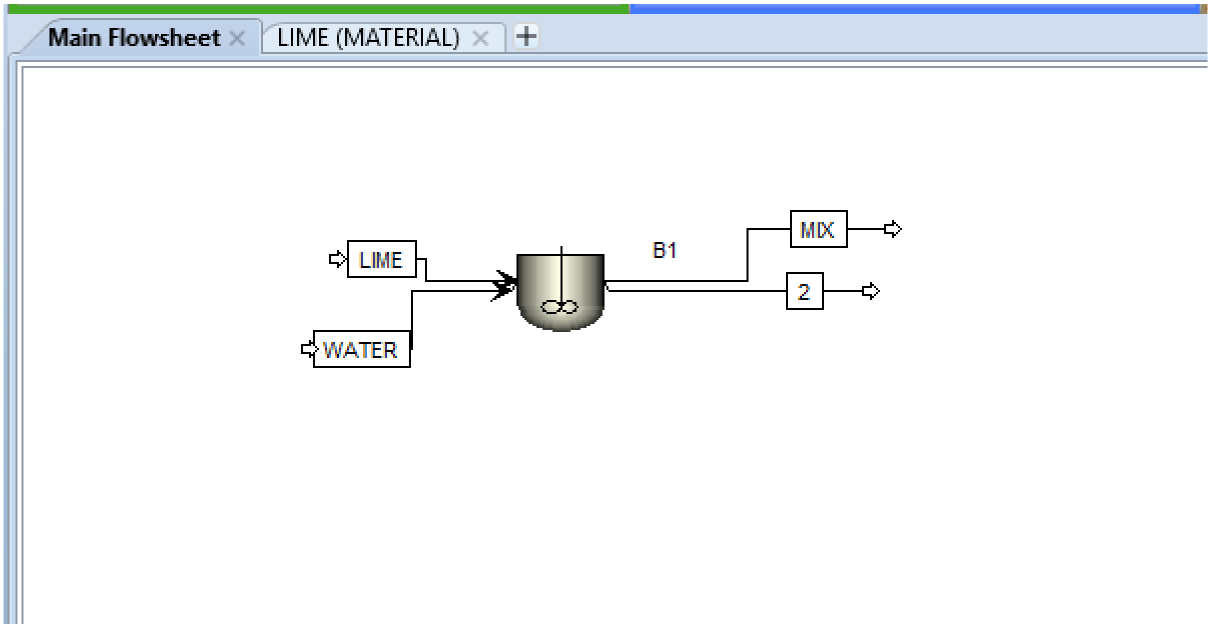
Composition: Mass-Frac

Component	Value
WATER	0.99921
CALCI-02	
SODIU-02	
HYDRO-01	0.00048
SODIU-03	

Total: 1

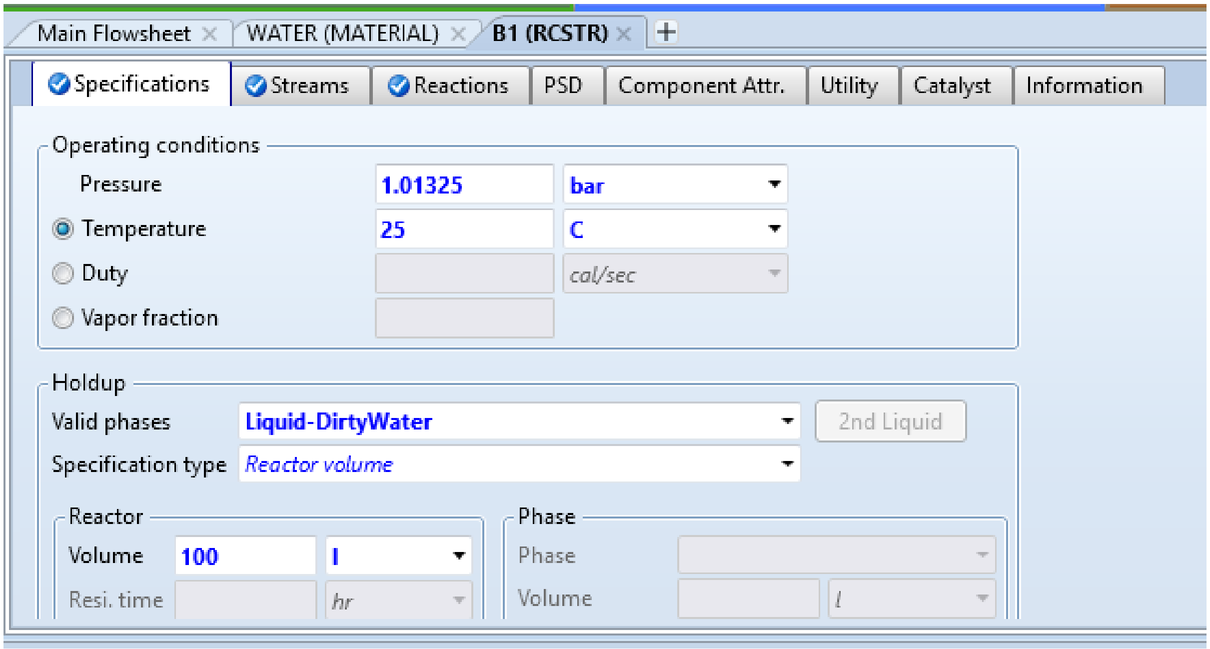
Picture 17 Effluent Water stream defined

Next, we decided to add the first reaction vessel and connect the two streams to it along with two output streams.



Picture 18 Adding the first reaction vessel

Further, we then decided to calibrate and specify the conditions for the reaction vessel.



Operating conditions

Pressure 1.01325 bar

● Temperature 25 C

○ Duty cal/sec

○ Vapor fraction

Holdup

Valid phases Liquid-DirtyWater

Specification type *Reactor volume*

Reactor

Volume 100 l

Resi. time *hr*

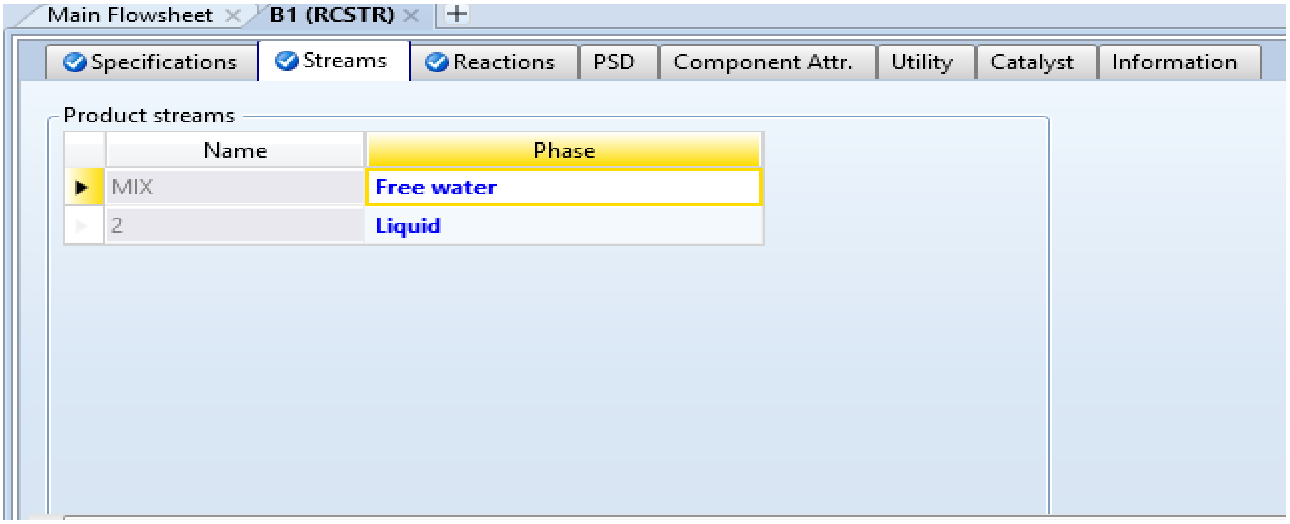
Phase

Phase

Volume *l*

Picture 19 Reaction vessel conditions

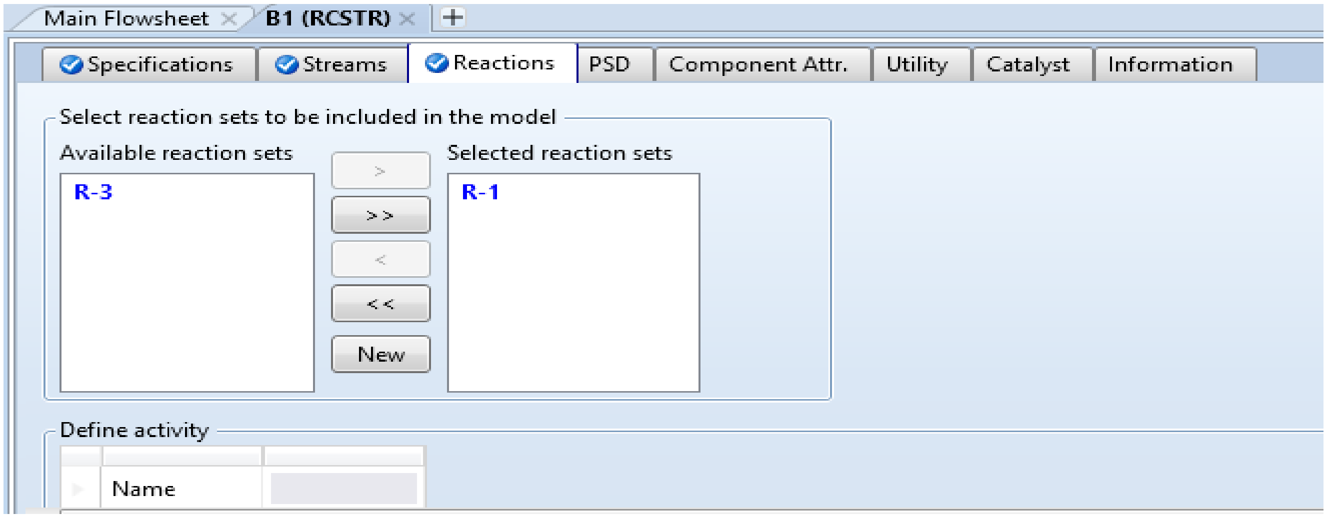
The conditions were assumed to be under temperature of 25 Celsius and at atmospheric pressure, and the reactor volume taken as 100 liters. The two phases were further specified as liquid-dirtywater



Product streams

Name	Phase
MIX	Free water
2	Liquid

Picture 20 Phases specified



Select reaction sets to be included in the model

Available reaction sets	Selected reaction sets
R-3	R-1

Define activity

Name

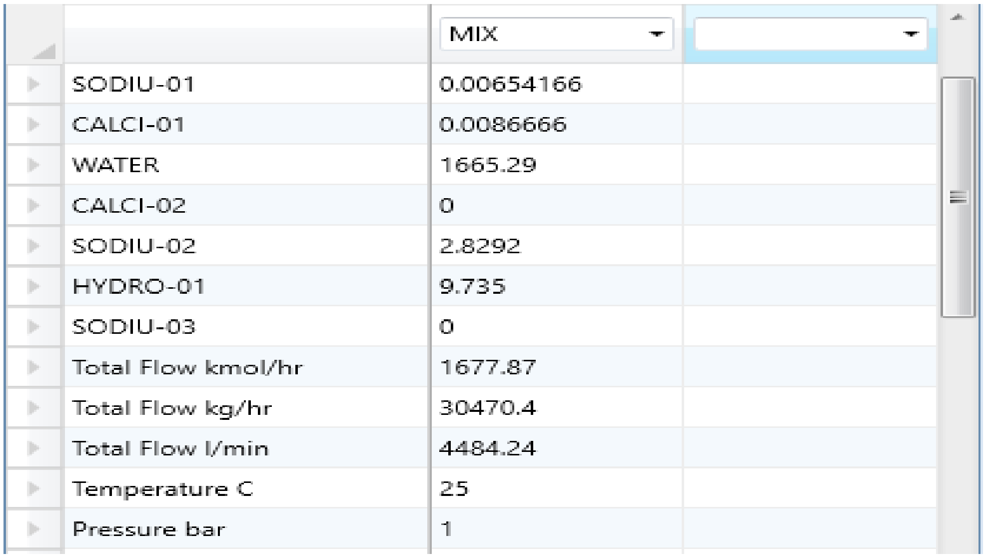
Picture 21 Reaction sets specified

The reaction R1 is the first reaction we mentioned, namely

$$\mathbf{Na_2SO_4 + Ca(OH)_2 + 2H_2O => CaSO_4.2H_2O + 2NaOH}$$

The resulting stream specifications were as follows.

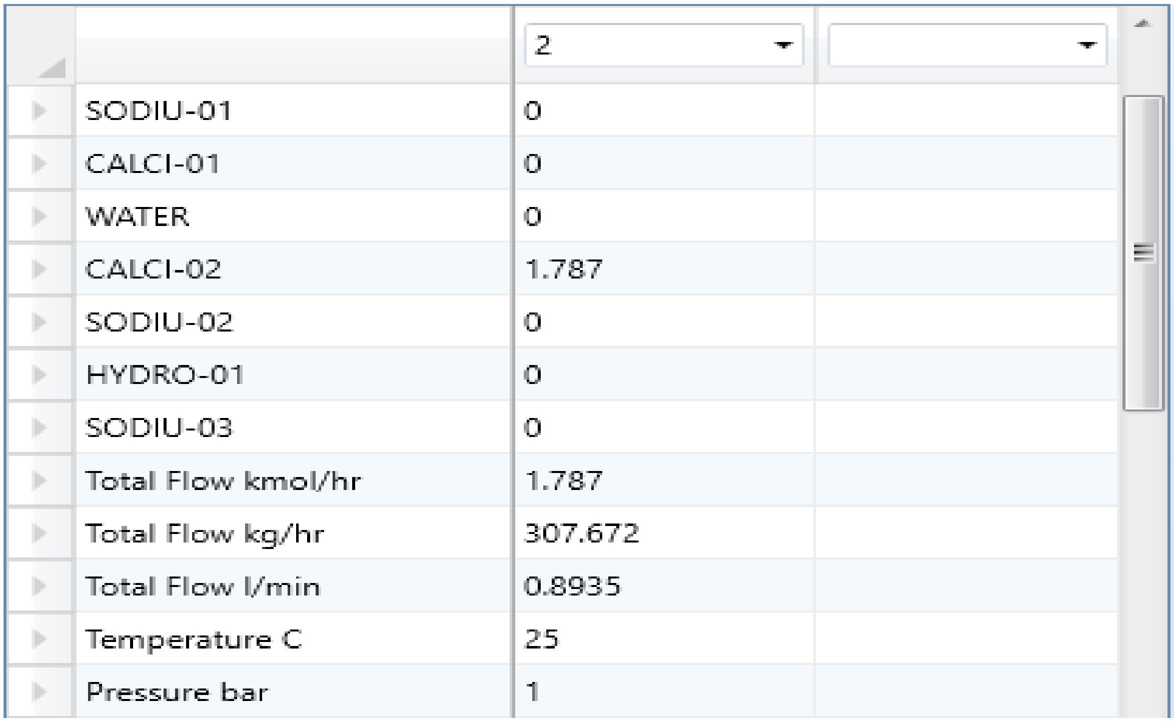
Stream MIX:



	MIX	
SODIU-01	0.00654166	
CALCI-01	0.0086666	
WATER	1665.29	
CALCI-02	0	
SODIU-02	2.8292	
HYDRO-01	9.735	
SODIU-03	0	
Total Flow kmol/hr	1677.87	
Total Flow kg/hr	30470.4	
Total Flow l/min	4484.24	
Temperature C	25	
Pressure bar	1	

Picture 22 MIX composition

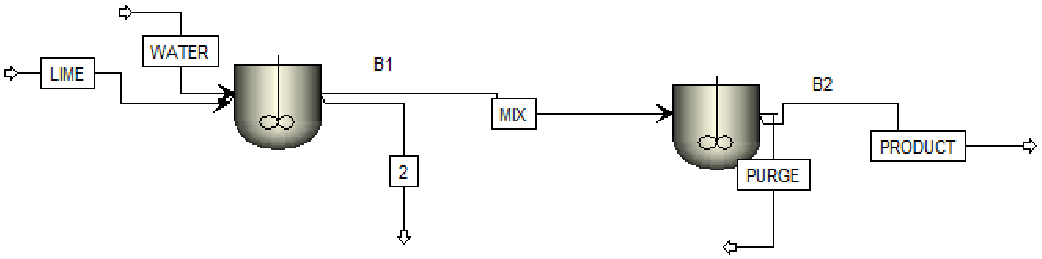
Stream 2:



	2	
SODIU-01	0	
CALCI-01	0	
WATER	0	
CALCI-02	1.787	
SODIU-02	0	
HYDRO-01	0	
SODIU-03	0	
Total Flow kmol/hr	1.787	
Total Flow kg/hr	307.672	
Total Flow l/min	0.8935	
Temperature C	25	
Pressure bar	1	

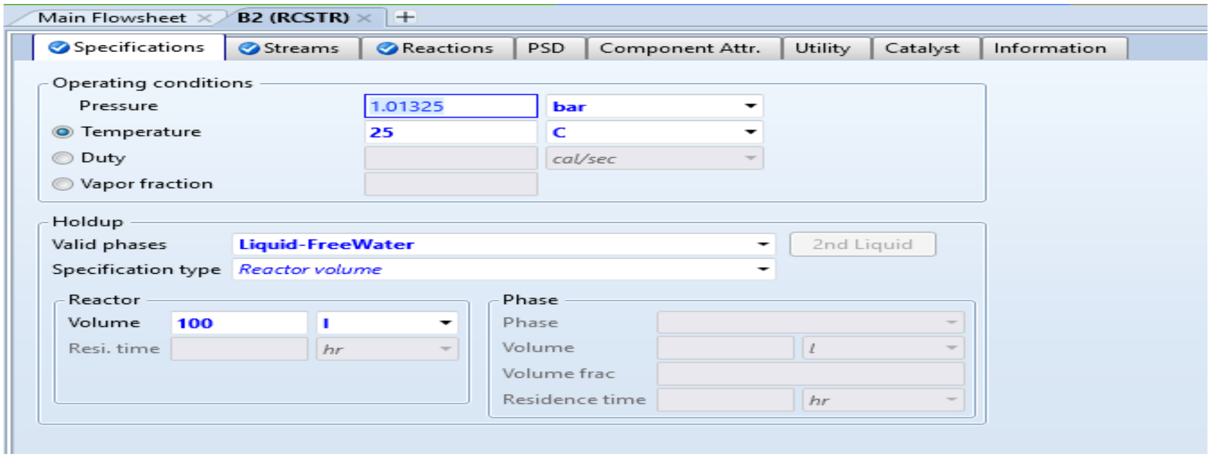
Picture 23 Stream 2 Composition

The next step was adding another reactor and then added the MIX stream to it along with two output streams. The resulting sim was as follows.



Picture 24 Reactor 2 added

Next we specified the reactor 2 conditions.



Operating conditions
Pressure 1.01325 bar
● Temperature 25 C
○ Duty cal/sec
○ Vapor fraction

Holdup
Valid phases Liquid-FreeWater
Specification type Reactor volume

Reactor
Volume 100 l
Resi. time hr

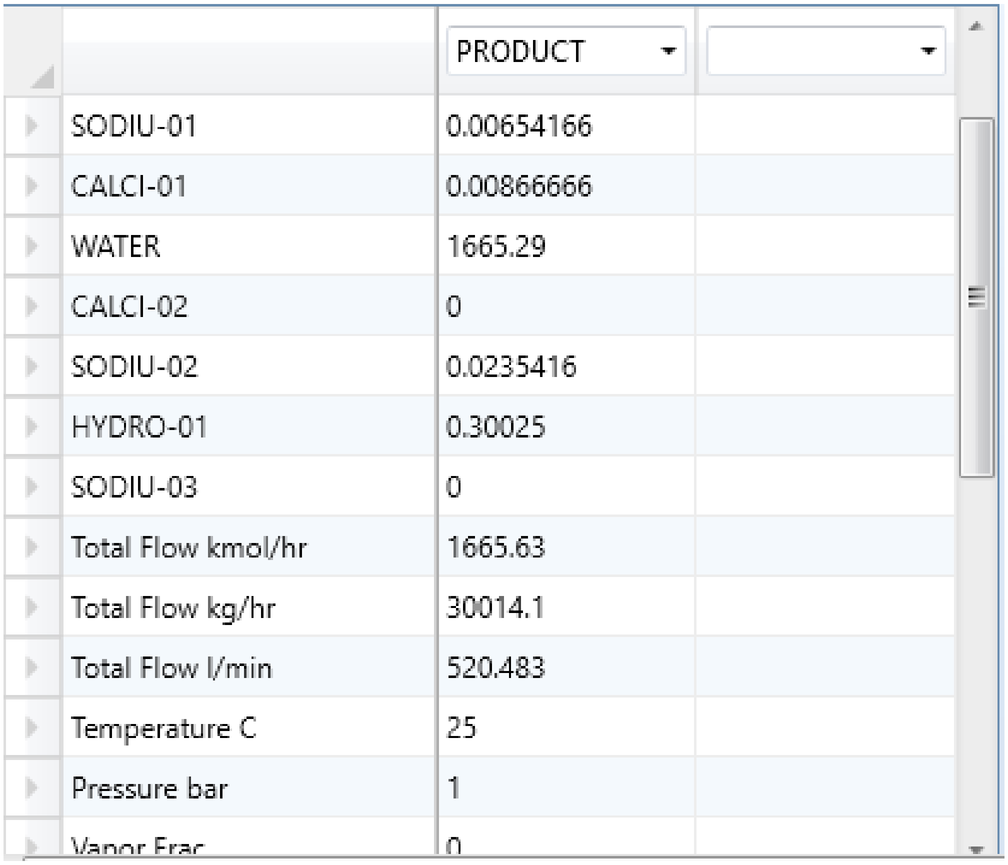
Phase
Phase
Volume l
Volume frac
Residence time hr

Picture 25 Reactor 2 conditions

Again we assumed conditions of 25 Celsius and 1 atm pressure with a reactor volume of 100 liters. We also showed that one stream will be basically almost completely free water.

The resulting stream specifications were as follows.

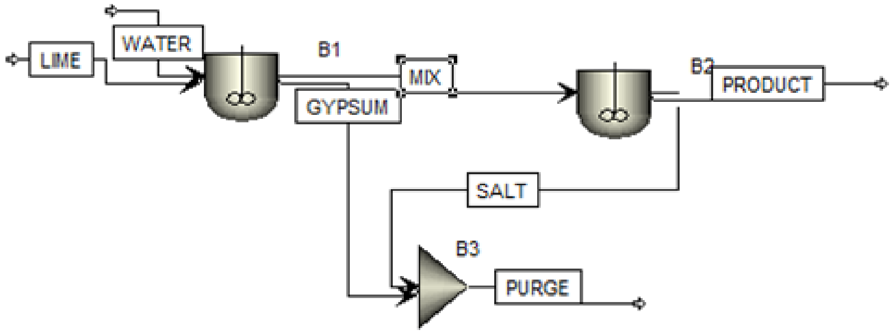
Stream PRODUCT:



	PRODUCT	
SODIU-01	0.00654166	
CALCI-01	0.00866666	
WATER	1665.29	
CALCI-02	0	
SODIU-02	0.0235416	
HYDRO-01	0.30025	
SODIU-03	0	
Total Flow kmol/hr	1665.63	
Total Flow kg/hr	30014.1	
Total Flow l/min	520.483	
Temperature C	25	
Pressure bar	1	
Vapor Frac	0	

Picture 26 Stream PRODUCT composition

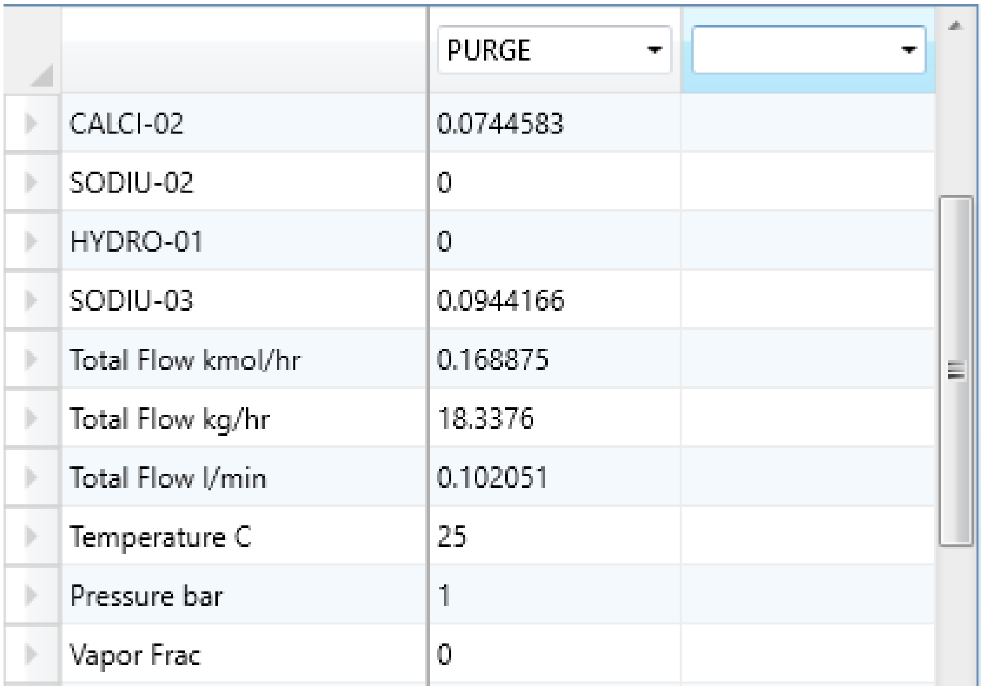
After this we added a splitter and sent both stream 1 and stream 2 to it. The output was stream 4.



Picture 27 Splitter added

The purge stream specifications are as follows.

Stream PURGE:



	PURGE
CALCI-02	0.0744583
SODIU-02	0
HYDRO-01	0
SODIU-03	0.0944166
Total Flow kmol/hr	0.168875
Total Flow kg/hr	18.3376
Total Flow l/min	0.102051
Temperature C	25
Pressure bar	1
Vapor Frac	0

Picture 278 Stream PURGE composition

CHAPTER-VII

HAZOP ANALYSIS:

We distributed the HAZOP analysis into two portions:

1. Analysis of the already existing water treatment plant
2. Analysis of the new process suggested by our team.

For the analysis of the already existing plant, we had a great deal of help from our industrial correspondence who provided us with the information needed and the access to User Manuals from the plant so we could understand the risks associated to the process and the trouble shooting procedures.

For the process we proposed, a detailed study of all the parameters were made so as to really understand the process and to come with possible mishaps and their respective remedies.

7.1 Analysis on the existing water treatment plant:

Main Process Step	**Item code**	**Trouble**	**Probable cause**	**Remedy**
Equalization	T-11101, P-11101/J-11101	Insufficient mixing, pH not 8.5	Mixer clogged, Off-set pH electrode, No HCL injected	Lift mixer & clean
Physico-chemical Pre-treatment				
pH adjustment & flocculation	R-21101, S-22101	pH not between 7.0-7.3, Insufficient or no floc	Off-set pH electrode, No HCL/NaOH injected, No Alum injected, pH to low, No flocculants injected	Calibrate/check pH QIT21101, Check HCL storage & dosing, Check Alum storage & dosing, Calibrate/replace electrode, Check flocculants storage & dosing
Flotation	S-22101	Floc carried over in effluent	See above, Plate pack clogged, To high feed flow	Clean plate pack, Adjust flow, Check flow setting/control
sludge discharge		Sludge to sticky	Quality waste water, Dosing P.E to high	Rise water level in S-22101, Reduce dosing rate of P.E

Rise water level in S-22101, Reduce dosing rate of P.E				
Pre-selection	T-31101, T-31201	Mixed liquor grey/black sludge has a bad smell	Insufficient aeration, Excess raw water load, Toxic discharge	Check aerator P-32101/32201, Check sources of raw water & shut illegal discharge into the system, check disposal routines of toxic liquid waste
Aeration	T-32101	Mixed liquor grey/black, sludge has bad smell, BOD/COD removal low	Insufficient aeration, Excess raw water load, Toxic discharge, MLSS in oxidation basin too low, Toxic or biological contaminants in waste water	Check aerator P-32101/32201, Check sources of raw water & shut illegal discharge into the system, check disposal routines of toxic liquid waste, Increase recycle sludge rate & check F/M ratio, Check disposal routines of toxic liquid wastes
Secondary X clarifier	T-33101, T-33201	Clarified water is turbid, Floating	Activated sludge not yet fully	Activated sludge not yet fully

		sludge in clarifier basin	mature, Toxic discharge, Too low MLSS in biological oxidation basin, Periodic excessive raw water loads, Denitrification insufficient in T-32101	mature, Toxic discharge, Too low MLSS in biological oxidation basin, Periodic excessive raw water loads, Denitrification insufficient in T-32101

Table 7 HAZOP analysis

CHAPTER-VII

COSTING

The method we used for calculating the associated costs was the one that was taught to us in our Plant Design course and the details of this method were taken from the book Coulson and Richardson's Chemical Engineering Volume 6 (Coulson).

8.1 Equipment Costs:

Continuous Stirred Tank Reactor Cost:

$C=CS^n$ (1)

$=31000 \times (30^{0.45})$

=$143240/-

Settling Tank (vessel) Cost:

According to literature, for the column range, Horizontal tank must be used.

$C=CS^n$

$=2900 \times 90^{0.6}$

=$43146

Purchased Cost of Equipment = 43146 + 143420 (2)

= $186,566

8.2 Plant Capital Expenditure(PCE)

f1	Equipment Erection	0.45
f2	Piping	0.45
f3	Instrumentation	0.15
f4	Electrical	0.1
f5	Building,process	0.1
f6	Utilities	0.45
f7	Storages	0.2
f8	Site development	0.05
f9	Ancillary buildings	0.2

Physical Plant Cost (PPC) = PCE (1+0.45 +0.45+0.15+0.1+0.1+0.45+0.2+0.05+0.2) (3)

PPC= 186566 x 3.15
PPC =$587683

8.3 Indirect Capital Cost

f10	Design and Engineering	0.25
f11	Contractor's fee	0.05
f12	Contingency	0.1

Fixed Capital = PPC x (0.25 + 0.05 +0.1) (4)

=587683 x 0.40

= $235073

Working Capital = 5% of Fixed Capital (5)

=0.05 x 235073

=$11753.66

Total investment = Fixed Capital + Working Capital (6)

=11753.66 + 235073

= **$246826**

8.4 Raw materials cost:

Lime used per day = 116.3155kg

Cost per metric ton = $110

Cost of lime per day = (110 x 116.3155) / 1000 (7)

= $ 12.79 / day

= 12.79 x 365

=**$4668.35**

Direct Production Costs:

Maintenance costs (5% of fixed Capital)	$ 1,100
Operating Labour	$ 700.00
Supervision	$ 59.05
Plants Overhead (50% of operating labour)	$ 350.00
Laboratory	$ 118.09
Capital Charges (10% of fixed Capital)	$ 2,361.88
Insurance	$ -
Local Taxes	$ -
Royalties	$ -

Total cost of production = 4668 + 1100 + 700+ 59+350 +118 + 2361 (8)

= **$ 9356**/-

CONCLUSION

Calculations and Simulations suggest that using the Cost Effective sulfate removal process is a feasible alternative with minimum complexities and very acceptable and affordable power requirements. When we compare it to the already existing solution of buying water from an external source, this process serves as a better alternative as it's cost can be recovered in a few years and also that it provides a sustainable long term solution. The total cost of investment would take around 4 years to be returned but what we are doing here is that we are providing PRL with a solution in which the company is not wasting its potential resources and secondly we are trying to minimize the use of KDA which is costly as well as makes the company dependent on an external source. Hence the CESR technology is the way forward it makes water usable as cooling water makeup and would provide a huge plus to the plant.

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