DESIGN OF A CAUSTIC INJECTION SYSTEM IN A CRUDE DISTILLATION UNIT

by
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ABSTRACT

ANDREW RUSSELL COPE: Design of a Caustic Injection System in a Crude Distillation Unit
(Under the direction of Dr. Adam Smith)

Caustic Injection is a high-risk chemical process utilized in many refineries across the world to control overhead corrosion in the atmospheric distillation column of the Crude Distillation Unit. This thesis discusses the considerations that need to be accounted for in the design of a caustic injection system, as well as my own work at an internship where I was a member of a design team that worked to design a caustic injection system for a nearby refinery.

TABLE OF CONTENTS

INTRODUCTION

In the summer of 2014 and 2015, I worked as a process-engineering intern at a design firm in Mobile, AL called Hargrove Engineers and Constructors. Over the course of my internship, I worked on various projects for several large chemical and petroleum companies. In the summer of 2015, I spent the majority of my time working on one particular project for a large petroleum refinery. The project was a relatively small project in that it would cost much less than the typical project at the company, but it had to be completed perfectly to avoid any possible incidents. The goal of the project was to design and install a caustic injection system into the crude distillation unit to reduce corrosion in the overhead of the first atmospheric distillation column. The refinery had already performed some preliminary studies and wanted us to model our system off of an already existing system at another refinery the company owned in California. Using this as a guide, I was able to set out and perform the preliminary design of the system.

Corrosion is one of the largest issues facing petroleum refineries today. Millions of dollars are spent every year in attempts to control corrosion and make repairs to pipelines and equipment affected by corrosion. The crude distillation unit (CDU) is one location in every refinery that faces corrosion whenever the plant is in operation. The CDU is the first processing unit crude oil enters in most refineries [1]. A typical CDU takes crude oil from a storage facility and heats it in a series of heat exchangers and a furnace before sending the crude oil to an atmospheric distillation column. The atmospheric distillation column separates the crude oil based on the varying boiling points of the components. Once separated, the different components are refined further in subsequent areas of the plant.

In the preheat stages, prior to the furnace, the crude oil passes through desalters to remove the salts in the crude oil. The desalters are designed to remove the sodium, calcium, and magnesium chlorides (NaCl, $CaCl_2$, $MgCl_2$) in the crude feed [2]. These chlorides are highly corrosive and the desalters, although highly effective, are unable to remove 100% of the salts. The chlorides undergo a hydrolysis reaction at higher temperatures that yield hydrochloric acid that results in the corrosion of process equipment. Even trace amounts of these chlorides results in corrosion in downstream units, primarily in the overhead of the atmospheric distillation column. In order to combat the resulting corrosion, many refineries are turning to injecting dilute sodium hydroxide, often referred to as caustic, downstream of the desalters. However, if not designed and installed properly, a caustic injection system can cause widespread corrosion throughout the downstream equipment and could be catastrophic to the plant. For example, in June of 2012, Motiva was starting up a recent expansion to their existing refinery, where the expansion alone cost roughly $10 billion that would make it the largest refinery in the United States processing up to 600,000 barrels per day [6]. However, the caustic injection system failed to shut down during a low flow period and caused widespread corrosion throughout the refinery that ended up costing Motiva roughly $1 billion [6]. For this reason, many refineries operate without a caustic injection system and take the risk of increased corrosion and thus increased risk for maintenance and expenses.

BACKGROUND

The chlorides present in the incoming crude undergo a hydrolysis reaction when exposed to the high temperatures of the preheat exchangers as well as the furnace and distillation column [3]. The reactions are as follows:

$$CaCl_2 + 2H_2O \leftrightarrow Ca(OH)_2 + 2HCl \quad (1)$$

$$MgCl_2 + 2H_2O \leftrightarrow Mg(OH)_2 + 2HCl \quad (2)$$

$$NaCl_2 + H_2O \leftrightarrow NaOH + HCl \quad (3)$$

It is the hydrochloric acid resulting from these reactions that is the primary corrosive agent in the overhead of the CDU, but each reaction reacts differently at varying temperatures; Reaction 1 shifts strongly toward the products when at temperatures above 250 °C; Reaction 2 shifts towards the products at temperatures above 400 °C; Reaction 3 does not shift towards the products until it reaches above 900 °C [3]. Because fired heaters typically operate between 680 °C and 720 °C, reactions 1 and 2 take place readily and produce the corrosive hydrochloric acid [3]. However, reaction 3 is stable under these conditions and thus shifts towards the reactants. It is this reaction that a caustic injection system seeks to exploit. By injecting dilute caustic downstream of the desalters, the dilute caustic reacts with the hydrochloric acid produced in reactions 1 and 2 to form the more stable sodium chloride produced in the reverse of reaction 3. The resulting sodium chloride is stable at the standard operating temperatures; therefore it is removed from the bottoms of the distillation column resulting in reduced corrosion in the overhead where the vapors of the hydrochloric acid would otherwise rapidly corrode the column.

There are, however, several risks that come with injecting dilute sodium hydroxide. If the caustic is not mixed thoroughly it can become concentrated. If concentrated, caustic is highly corrosive to standard carbon steel used throughout most refineries in both pipes and equipment. It is for this reason that a properly designed caustic injection system contains highly dilute caustic that is thoroughly mixed at high velocity to diminish the risk of any concentrated pockets forming in a pipe or piece of equipment. Furthermore, over treatment with caustic can lead to increased sodium in the heavy products extracted from the bottom of the column [3]. Too much sodium in these heavy products can lead to fouling in downstream units such as visbreakers, cokers, and fluid catalytic cracking units (FCC's) [3]. Lastly, it is virtually impossible to calculate a stoichiometric balance of caustic based upon the quantity of salts found in the crude, so refineries typically run a set amount that will be injected into the crude unless a low flow period arises [4]. It is for this reason that the design to be discussed assumes a set flow rate of caustic solution as specified by the client.

DESIGN

A properly designed caustic injection system is absolutely vital in order to prevent accelerated corrosion in the CDU. Many factors contribute to a correctly designed operating system, including the location of the system. Locating the proper injection point is the first step in designing a caustic injection system. There are three potential locations to inject caustic in a standard crude distillation unit that are shown in Figure 1 below. The first potential location for a caustic injection system, location A, is upstream of the desalter in the crude preparation stage of the CDU. Injection at this location is primarily done to control the acidity of the desalter brine, but if not performed properly can cause emulsions and foaming in the desalter, thus decreasing its effectiveness [3,4]. For this reason, injection at this point is not favored and was not used in my design.

Another potential location for caustic injection is after the desalter, but before the secondary preheat exchangers, location B. Injection at this location is the most common in refineries today because at this location the crude has yet to reach its highest temperatures [3]. Therefore, if an accident were to occur with the caustic injection system, the results would not be as catastrophic. However, case studies have shown that caustic injection at this point often leads to corrosion and fouling in the downstream heat exchangers because while the caustic is injected to reduce corrosion, it has been shown to increase fouling and corrosion in heat exchangers even in dilute quantities. The fouling and corrosion is due to the fact that although the dilute caustic is injected to decrease corrosion, if the caustic does not react it becomes yet another corrosive agent to the carbon steel system, and prior to the secondary heat exchangers, there are less chlorides for the caustic to react with due to the lower temperature of the crude, thus leaving unreacted caustic available for corrosion.

The final possible location to inject caustic is downstream of the secondary preheat exchangers, but upstream of the fired heater, location C. Injection at this point ensures that there is no fouling or corrosion of heat exchangers. However, at this point the crude has reached elevated temperatures that add an increased risk to injecting caustic. At higher temperatures, caustic corrosion happens at a significantly greater rate and for this reason, if the caustic were to become concentrated, rapid corrosion could occur in the crude feed line causing a potentially dangerous and costly rupture of the incoming crude feed to the fired heater. The three locations are detailed below in Figure 1.

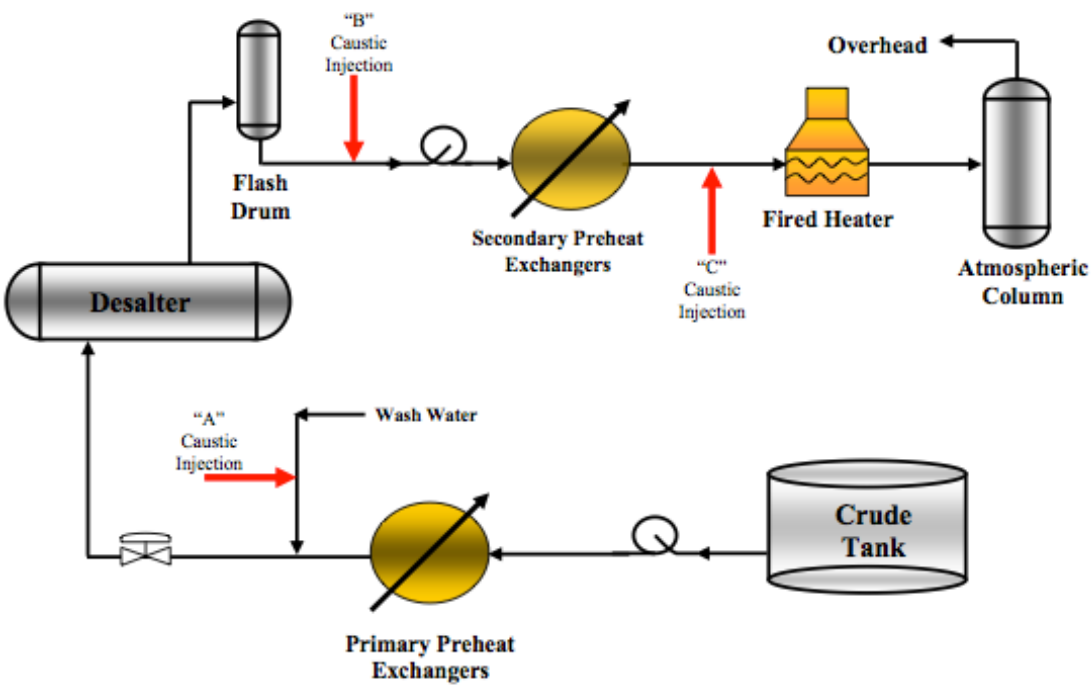

Figure 1: Potential Caustic Injection Locations [3]

Of the three potential caustic injection locations, the focus of the design I worked on was the third location, location C, upstream of the fired heater and downstream of the preheat exchangers. The third location is currently installed in roughly 20% of refineries that run a caustic injection system because the potential risks are more substantial at this location than location B [3]. However, with proper design and installation, the risks associated with this location can be drastically reduced. In fact, one refinery in Saudi Arabia was experiencing considerable fouling and corrosion while injecting caustic upstream of its preheat exchangers [5]. After several years of required maintenance on the exchangers, the refinery redesigned the caustic injection system and moved it downstream of the preheat exchangers [5]. After one year, they had drastically diminished the fouling and corrosion in the exchangers and by doing so they were able to save the refinery $1.8 million annually [5]. For this reason, it has been determined that the optimum location for caustic injection is upstream of the fired heater despite the potential risks and was the location used in my own work during my internship as specified by the client.

The next step in the design process is determining the concentration of the caustic to be injected into the system. Caustic in high concentrations will rapidly corrode carbon steel upon injection into the system, so it is recommended to inject fresh caustic between 1 and 5%, which is caustic that has been diluted with purified water on a mass basis. The exact concentration of caustic will vary based upon the refinery and the type of crude oil being processed. A general rule of thumb is to keep overhead chloride concentrations between 20 – 50 ppm [4]. If the refineries concentrations are considerably high, 5% caustic may be needed, and in turn, if the chloride concentrations are relatively low, 1%

caustic may be used or possibly forgo installing the caustic injection system. For the project that I personally worked on, 3% fresh caustic was used, as it was readily available nearby and could easily be piped to a holding tank before being injected in the system.

One of the most important points in designing a caustic injection system upstream of the fired heater is ensuring that the caustic is well mixed with the incoming crude feed. An insufficiently mixed crude stream can cause rapid corrosion of the carbon steel crude feed line. If the caustic pools at any point along the pipe, the high temperature of the crude will rapidly cause the caustic to corrode the pipe. There are three primary factors that go into ensuring a properly mixed caustic solution. First, the caustic must be injected at a sufficient distance upstream of the fired heater to allow time for thorough mixing. Second, the caustic must be injected with enough velocity to ensure mixing throughout the incoming crude feed [3]. Lastly, a crude slipstream should be used to dilute the caustic further in the crude before injection into the main crude feed line.

The exact distance of the location of the injection point from the fired heater will vary in every refinery. A location should be chosen on the incoming crude feed line that allows easy access for the installation as well as for monitoring purposes. A general rule of thumb for the distance upstream is no less than 50 meters from the fired heater [5]. At this distance, the caustic has sufficient distance to fully mix with the incoming crude line as well as react with any chlorides in the system yielding the desired sodium chloride product that will be removed from the bottom of the column.

In order to obtain sufficient velocity and mixing of the crude, a crude slipstream is suggested as detailed in Figure 2. The slipstream should contain 1% of the flow of the

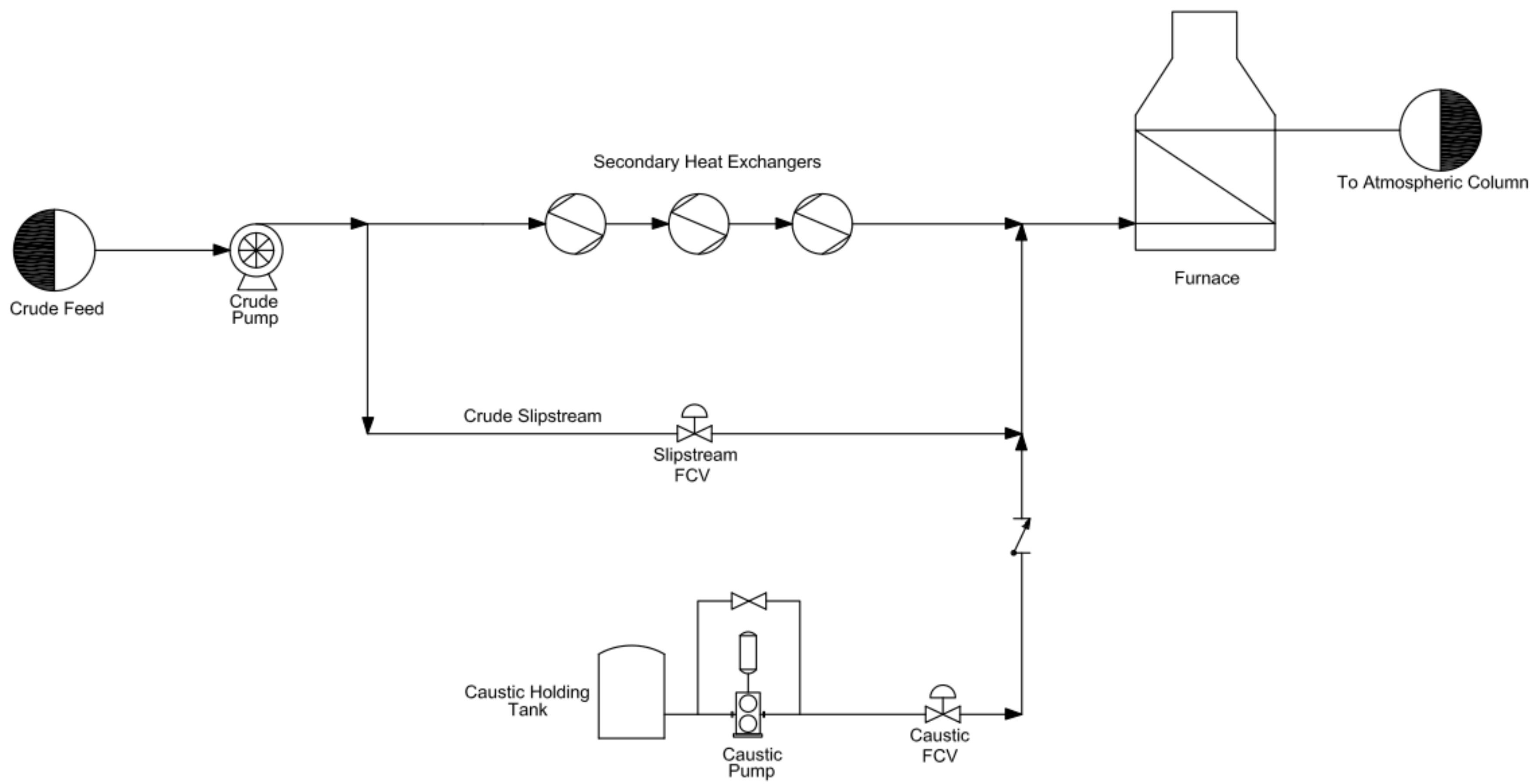

Figure 2: Caustic Injection System with Slipstream

main crude feed line at maximum operating conditions. The crude slipstream will first mix with the incoming caustic in a mixing tee before it is then injected into the main crude feed line through the injection quill. The slipstream can be pulled from multiple locations, but the ideal location, and the one used in my design, is to tie-in into the main crude feed line upstream of the preheat exchangers. By pulling off the slipstream at this point, the slipstream will have sufficient pressure to mix with the main crude feed line after the heat exchangers. One drawback from the use of a slipstream at this location is a very slight increase in the duty on the furnace. The 1% of the flow that is bypassing the heat exchangers will be at a cooler temperature than the main crude feed line, but by bypassing with such a small fraction of the total flow the increased duty on the fired heater can be assumed to be negligible. The slipstream should have a control valve that maintains the flowrate at 1% of the maximum flowrate through the main crude feed line, thus for the system I designed it was to be maintained at a flowrate of 1,850 bbls/day. The pressure drop across the control valve will be substantial, as it will drop the pressure to the same pressure of the main crude feed line at the injection point.

The flowrate of the dilute caustic to be mixed will vary from refinery to refinery depending on the type of crude being processed. A detailed study should be performed on the incoming crude to determine the exact quantity as it depends on the efficiency of the desalters as well as the type of crude being processed [4]. For example, if the desalters were not very efficient, and the incoming crude contained high levels of chloride, the desired flowrate of caustic would need to be increased to combat those higher levels of chlorides. For the project during my internship, the company had already performed a study, and chose to follow their guidelines that opted for injecting 1 ppm of dilute caustic to every thousand barrels of crude per day of the maximum flowrate in the main crude feed. For example, in the design I was responsible for, the maximum flowrate expected in the system was 185,000 barrels per day. For this system, that would mean 185 ppm per day, which came out to 34.28 bbls/day of dilute caustic or 1 gpm. This flowrate would be a set flowrate that would not change under standard times of decreased production. However, if the flowrate were to drop to two thirds of the design flowrate, or 125,000 bbls/day, a low flow controller should close the control valve on the caustic line in order to ensure that caustic is not pumped into the system without high volumes of crude passing through the process [3]. If the low flow controller were to fail and caustic were to be pumped into the system without high volumetric crude flowrate, the effects would be catastrophic with widespread corrosion across the refinery from the resulting pockets of concentrated caustic in the carbon steel system.

The caustic to be injected will have to overcome the high pressure of the slipstream and the main crude feed line. However, because the flowrate of the caustic stream will be very low, a standard centrifugal pump will not suffice because at low flow rates centrifugal pumps tend to become less efficient. Furthermore, centrifugal pumps are designed to operate over a range of flowrates, but a positive displacement pump typically operates at one flowrate and can attain much higher pressures. For this reason, a small positive displacement pump was specified in my internship as the caustic injection system required one set flowrate that would not be varied, but simply shutdown under low flow situations. The pump should be installed with a recycle line and a downstream pulsation dampener. The recycle line will have a gate valve that should remain closed unless issues were to arise with the system in which case the control valve on the caustic injection feed line would be closed and the recycle line would be opened in order to allow the pump to continue operation until standard operation can be resumed. The pulsation dampener will act to ensure a steady pressure in the caustic line that will eliminate all fluctuations due to the mechanics of the positive displacement pump. Downstream of the pulsation dampener, a one-way valve should be installed prior to the mixing quill, so as to prevent any backflow in the dilute caustic line due to upsets in the pressure of the main crude feed line.

The injection quill where the crude/caustic is injected was the final detail to be worked out in the design process. The injection quill ensures the caustic and crude slipstream mix thoroughly and are then injected into the crude feed so as to achieve maximum mixing. The quill should inject the crude/caustic mix in the center of the main crude feed line so as to ensure thorough mixing throughout the profile of the flow [3]. The quill needs to inject the crude/caustic at a velocity at least 2 times the velocity of the main crude feed line [3]. In order to achieve this, the quill should have a small orifice facing downstream to achieve maximum velocity. For the design I was working on, the main crude velocity was 11 ft/s and the client specified the injection velocity to be 30 ft/s. From the flowrates I calculated, I was able to determine that in order to achieve the velocity of 30 ft/s the orifice needed to be 0.859" in diameter. The quill itself would be constructed onsite by our client, and we simply had to specify the exact size of the orifice. The exact layout of the injection quill can be seen in Figure 3.

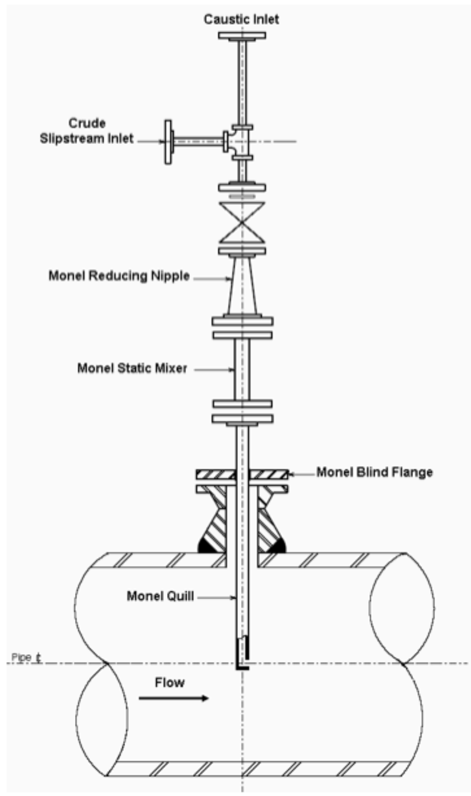

Figure 3: Caustic Injection Quill [3]

Once we had an idea of exactly what we needed to accomplish, I set out to model the software to ensure it would operate properly. Perhaps the most beneficial skill I gained during my internship was learning the use of multiple modeling softwares. In order to model the caustic injection system, I used AFT Fathom, a powerful fluid dynamics modeling software. In order to determine the appropriate line sizes, I went into the software and first built the existing system from scratch. My model started at the pump feeding the secondary preheat exchangers. In order to do this, I went through all of the P&ID's from the refinery to determine the line sizes, and I went through several weeks of operating data for the plant to determine the pressures in the system as well as the pressure drop through each heat exchanger. From my research, and collaboration with the client, it was determined the system I was modeling was a 16" carbon steel main crude feed line operating at pressures well above 400 psi. Once all of the flowrates, pressures, pump curve, and line sizes were determined, I began to build my model of the existing system by inputting a crude assay specified by the client and all of the existing equipment. Once the existing model had been created, it was sent to the client to ensure its accuracy before further modeling could take place. Upon approval from the client, I set about modeling the new caustic injection system. I was able to insert a slipstream by placing a tee on the main crude feed line before the heat exchangers. The pressure at this point was just above 600 psi. I was able to place a control valve on the line to regulate the flow at 1,850 bbls/day. Next, I began to input various line sizes to determine the proper line size. In order to do this, I would input a line size and the program would output the pressure drop per 100 feet of pipe. The goal was to have the highest possible velocity while maintaining a pressure drop that was still reasonable. After trying multiple sizes and discussing the pressure drop with the lead engineer, it was determined that the optimum pipe size for the crude slipstream would be 2” schedule 80 pipe. Schedule 80 was to be used because of the high pressures the system would be under and schedule 80 has thicker walls and, therefore, is stronger than Schedule 40 pipe. With this pipe size, the velocity in the pipe would be 5.9 ft/sec, which is sufficient velocity to mix with the dilute caustic stream. The slipstream was then reconnected to the main crude feed line in the model downstream of the heat exchangers where the pressure was now 420 psi.

Lastly, the dilute caustic line was inserted into the Fathom model. It was modeled with a positive displacement pump that would be capable of overcoming the 420 psi required at the injection quill. After multiple trials with varying pipe sizes, similar to those performed on the slipstream, it was determined the optimum pipe size for the dilute caustic line would be ¾” Schedule 80 pipe. With a flowrate of 1 gpm, ¾” Schedule 80 pipe yielded a velocity of 0.75 ft/s. The dilute caustic stream was then connected to the crude slipstream at the injection quill. Modeling of the injection quill was complex in that we needed to model all of the fittings and pipe sizes down to the orifice, as the quill would experience the largest pressure drop. In order to do this, very small portions of the pipe (less than 6”) were placed in the model to show the expansions, contractions, and the flow orifice in the injection quill. Figure 3 shows the exact layout of the injection quill that was modeled.

Once everything had been modeled for the maximum flowrate of 185,000 bbls/day, the model was duplicated and modeled at the minimum flowrate of 125,000 bbls/day to ensure the system would operate properly at both maximum and minimum flowrates. After both models were completed, the design was sent to the client for approval once more. The model was approved and the design then moved into the next phase, for the modification of P&ID’s and material selection. Unfortunately, my time at my internship ended before we were able to move on to the next phase of the project, but the system was installed the following year at the next planned shutdown of the CDU.

CONCLUSION

By pursuing and attaining an internship and working on this and several other projects, I learned invaluable information I would not have learned in the classroom. Prior to my internship, my knowledge of the oil refining process was very limited as well as my knowledge of the overall design process. Now, I understand the intricate level of detail required to design equipment and processes that incorporate everything I have learned in college. I was able to work with design software that I would be unable to see at any university or institution, thus giving me an advantage over most undergraduates as we move forward after graduation.

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