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PREDICTION OF AMMONIUM BISULFIDE CORROSION AND VALIDATION WITH REFINERY PLANT EXPERIENCE

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ABSTRACT

Corrosiveness of two separate hydroprocessing units was assessed with a corrosion prediction software tool developed under joint industry sponsorship. The predicted corrosion rates for the piping, using this software tool, were compared with actual field data. The results confirmed the accuracy of the corrosion prediction model incorporated into the software tool, as well as emphasized the need to incorporate both flow modeling and environment variables in the assessment for corrosiveness of alkaline sour water systems. These data and the associated software tool have been successfully used to provide significant economic benefit.

Keywords: refining, reactor effluent air cooler, REAC, sour water, ammonium bisulfide, NH_4HS, hydrogen sulfide, H_2S, hydroprocessing, software, materials selection.

INTRODUCTION

Hydroprocessing units serve several purposes in petroleum refining. Hydrotreating/ hydrodesulfurizing units are used to remove undesirable sulfur and/or nitrogen, while hydrocracking units are used to crack heavier feeds into lower boiling point products. Both of these units use hot, high-pressure hydrogen in the reactor sections of the process. Byproducts of these reactions include ammonia (NH_3) and hydrogen sulfide (H_2S). The product of these two gases can form a salt, ammonium bisulfide (NH_4HS) as the reactor effluent stream cools. Formation of NH_4HS salts can lead to reactor effluent air cooler (REAC) tube plugging, and if wet, can lead to rapid underdeposit corrosion. These salts are readily dissolved in water, and hence these REAC systems are generally water washed ahead of the salt formation point to minimize plugging and underdeposit corrosion. The resulting sour water solutions containing the dissolved NH_4HS salts can be highly corrosive.

In an attempt to manage this corrosiveness, a survey was conducted by NACE Group Committee T-8 (now Specific Technology Group [STG] 34) covering corrosion in the REAC and associated piping in 42 hydrocrackers and hydrotreaters. These results were published in a paper by R. L. Piehl.[1] This paper established general rules of thumb for carbon steel, utilized for many years in these systems. These included limiting tube velocity to less than or equal to 20 ft/s (6.1 m/s) and NH_4HS concentrations to 2% or less. At these levels, corrosion of carbon steel was mild to negligible.

Another corrosion assessment rule of thumb used for material selection in hydroprocessing units has been the K_p factor.[2,3,4] The K_p factor is the product of the mole percent NH_3 and the mole percent H_2S in the dry stream entering the REAC. The higher this value the greater the severity of the NH_4HS corrosion. Values of K_p less than 0.2 resulted in mild corrosion and those exceeding K_p of 0.3 exhibited severe corrosion.

While these rules of thumb served the refining industry well for many years, it was readily evident that there was insufficient corrosion data to fully understand and predict the corrosiveness of NH_4HS solutions. A joint industry program was created to develop a quantitative engineering database and guidelines to predict corrosion in alkaline sour water systems as a function of NH_4HS concentration, velocity (wall shear stress), H_2S partial pressure, and various additional parametric variables. The program was conducted by InterCorr International, Inc.[(1)], in collaboration with Shell Global Solutions (US) Inc., from March 2000 to February 2003. The final report was issued in June 2003 to the 16 refining and engineering companies that jointly sponsored this program.[5]

The results of this effort showed that NH_4HS corrosion was dependent upon a number of factors including NH_4HS concentration, velocity (wall shear stress), H_2S partial pressure, temperature and other secondary variables. The influence of these variables on NH_4HS corrosion has been suitably covered in a separate paper by Horvath, Cayard and Kane.[6]

These data were used as a basis for the development of a more accurate and comprehensive corrosion prediction software tool, including assessment methodologies for control of NH_4HS corrosion of a wide range of materials of construction to help attain safe and reliable operation of process units handling NH_4HS. These data and the associated software tool have been successfully used to provide significant economic benefit.

SOFTWARE TOOL

A software tool called Predict®-SW[(2)] was developed as part of the joint industry program to incorporate the program data, industry experience and streamline the calculation of corrosion rates with incorporation of the shear stress acting on the tube/pipe wall associated with the process stream. This software tool provides a data screen for input of the environment, application and process stream variables. This information is then used to estimate the corrosion rate on the 14 materials evaluated in the joint industry program using the following sequence:

- Calculate effective wall shear stress from process flow conditions
- Convert the field wall shear stress into an equivalent laboratory flow loop velocity

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[(1)] Currently Honeywell Process Solutions

[(2)] Predict is a registered trademark and Predict-SW is a software product of InterCorr International, Inc. (currently Honeywell Process Solutions)

- Use the laboratory flow loop velocity and the NH_4HS concentration to predict corrosion rates for all 14 materials from their respective isocorrosion diagrams (i.e., baseline conditions)
- Correct corrosion rates at baseline conditions for the effect of H_2S partial pressure, temperature, hydrocarbon content, and chemical treatment

The software tool input screen is shown in Figure 1. The environment section provides input for the total pressure, H_2S content, temperature, NH_4HS concentration, oil (hydrocarbon) type, chemical type and dosage. The choices for oil type include user defined, light and heavy. If user defined is selected, the user must enter values for the density and viscosity of the hydrocarbon in the liquid hydrocarbon properties section at the bottom right portion of the input screen. If light or heavy is selected, density and viscosity are calculated from respective hydrocarbons used in the joint industry program as a function of the temperature and entered into the liquid hydrocarbon properties section. The choices for chemical treatment type are: ammonium polysulfide, imidazoline, or none.

The application section includes input for tube/pipe inside diameter (ID), corrosion allowance, design life and pipe roughness. Choices for pipe roughness include new, lightly corroded and heavily corroded, corresponding to roughness values of 0.0015, 0.01 and 0.04 inches (0.038, 0.25, and 1.0 mm), respectively. A custom roughness dialogue box is provided if the user desires to incorporate a custom roughness value. It is important to point out that increased surface roughness, either inherent from the manufacturing process or via process corrosion, will increase the effective wall shear stress at equivalent flow velocities.

The process stream conditions section includes the piping configuration and type of flow. Configurations include straight, 3-D bend, 90° elbow and weld protrusion. These configurations are used to amplify the effective wall shear stress determined in the flow modeling, which assumed a straight configuration. These amplification factors, derived from the literature,[7,8] are provided in Table 1. This section further allows the user to input a custom shear stress and flow regime.

The final required inputs are the process stream flow rates and properties. Vapor, sour water and liquid hydrocarbon properties are required. All three phases require input of flow rate. The other required properties include the specific gravity and viscosity of the vapor, and densities and viscosities of the sour water and liquid hydrocarbon.

Upon calculation, the software tool completes the sequences as previously detailed above. The importance of understanding the mechanical forces produced by flowing media in plant systems, where multiphase environments and various flow regimes are involved <u>cannot</u> be overemphasized — the use of velocity alone as an indication of severity is insufficient. Figure 2 shows a correlation of velocity and wall shear stress for two pipe sizes. As shown, a velocity of 28 ft/s (8.5 m/s) produces a wall shear stress of 100 Pa for a 2-inch NPS (60-mm nominal OD), schedule 40 pipe. To attain an equivalent wall shear stress in a 12-inch NPS (324-mm nominal OD), schedule 40 pipe requires a velocity of 37 ft/s (11 m/s). While these correlations discussed above apply to 100% liquid flow, differences are also present in multiphase flow conditions. The flow modeling embedded in the software tool incorporates accurate mapping of different flow regimes and characterization of corresponding hydrodynamic parameters for multiphase flowing systems. The software tool utilizes widely known flow maps from Taitel-Dukler and Mendhane et. al. and provides the end user the ability to assess pressure drops, liquid hold up, dimensionless factors and wall shear stress for both vertical and horizontal, single-phase and multiphase fluid systems.[9-21]

The software tool results screen shown in Figure 3 displays the corrosion rates for 14 materials ranging from carbon steel to alloy C-276 (UNS N10276). Adjacent to the corrosion rate value calculated for each material is a box colored either green or red. A green box (indicated by light gray shading in the example given in Figure 3) indicates the material's corrosion rate was deemed acceptable based on the user inputs for corrosion allowance and design life. A red box (indicated by the dark gray shading in this example) indicates the corrosion rate exceeds a rate allowable for the corrosion allowance and design life provided. In addition to the corrosion rate results, the results screen displays the flow regime, calculated wall shear stress, superficial liquid and gas velocities and equivalent laboratory flow velocity (100% sour water). A comments section is also provided to document the user assumptions, scenarios, etc. Input and results can be saved as a consultation and printed.

PLANT APPLICATIONS

Hydrotreater A

Corrosion was encountered in the recycle gas piping off the top of the cold, high-pressure separator (CHPS) leading to the amine contactor. A simplified hydrotreating process flow diagram is shown in Figure 4. This line was carbon steel carrying saturated vapor at a temperature of 130°F (55°C). A corrosion rate of 68 mpy (1.7 mm/y) was measured on a 90° elbow with an ID of 9 inches (230 mm). The line was not insulated, and as a result experienced a high level of condensation in the winter months. The line was estimated to contain a solution of 8 to 10 wt% NH_4HS, with a velocity of 32 ft/s (9.8 m/s). Flow rates consisted of 120 MMSCFD (3,400,000 m^3/d) of vapor, 11.1 bpd (1,765 L/d) of sour water and no liquid hydrocarbon. The H_2S partial pressure was 100 psia (690 kPa absolute).

The software tool was used to predict the corrosion rates based on the environment, piping configuration and process stream conditions. The flow regime was determined to be churn flow with a corresponding wall shear stress of 10 Pa. The predicted corrosion rate for carbon steel was 65 mpy (1.7 mm/y). As indicated previously, the corrosion rates would be expected to undergo seasonal variance. In the winter, the line was considered more corrosive due to the higher level of condensation, whereas in the summer months, this line may have been relatively non-corrosive. Based on this scenario, the predicted corrosion rate was in good agreement with the actual field measurements.

This line was replaced with carbon steel, weld overlayed with alloy 825 (UNS N08825). The software tool predicted a corrosion rate of 2 mpy (0.05 mm/y) for alloy 825. The new line was not insulated and has not experienced any problems since installation in 2002.

Hydrotreater B

Using the general rules of thumb for severity of NH_4HS corrosion, there was a serious concern for corrosion in this hydrotreater unit. The affected equipment consisted of carbon steel inlet and outlet piping to the REAC and the associated eight carbon steel air-fin exchangers. Both the inlet and outlet piping were balanced. A schematic of the outlet piping is shown in Figure 5. The process stream consisted of a solution of 8 wt% NH_4HS at 130°F (55°C) with an H_2S partial pressure of 27 psia (190 kPa absolute). Flow rates consisted of approximately 360 MMSCFD (10,200,000 m^3/d) of vapor, 6,000 bpd (954,000 L/d) of sour water and 10,000 bpd (1,590,000 L/d) of liquid hydrocarbon. Based on feedstock variations, bulk velocities approaching 80 ft/s (24 m/s) on the inlet piping were calculated. Outlet piping velocities approached 30 ft/s (9.1 m/s).

K_p factors were calculated and approached 0.25. This suggested moderate corrosion would be expected based on the existing industry K_p guidelines. Velocities approaching 80 ft/s (24 m/s), as well as an NH_4HS concentration of 8 wt%, suggested the likelihood for severe corrosion. No significant corrosion loss was detected by extensive inspection, but there was still concern that the potentially localized corrosion may have been missed. Hence, plans were made to replace the piping with carbon steel, weld overlayed with alloy 825, and upgrade the air-fin exchangers with alloy 2205 at a cost approaching US$10 million.

The software tool was subsequently used to predict the corrosion rates based on the environment, piping configuration and process stream conditions. Wall shear stress values were a maximum of 25 Pa. The predicted corrosion rates for carbon steel varied with the configuration and type of flow in the various sections of the piping system, with a maximum of 4.3 mpy (0.11 mm/y). Based on the predicted corrosion rates, plans for upgrades were dropped with significant economic benefit. Continued inspection of this carbon steel piping to date has revealed an average of 5 to 7 mpy (0.13 to 0.18 mm/y). The low corrosion rates are the result of low wall shear stress in combination with a low H_2S partial pressure.

Subsequent to the joint industry program, the software tool has continued to evolve to include additional software functionality, user conveniences and a further refined corrosion model at low H_2S partial pressures. These changes have further improved corrosion rate prediction under certain conditions while also aiding utilization of the software for evaluation of process conditions, process parameter sensitivity studies, multipoint analyses and interface with commonly used process modeling programs.

CONCLUSIONS

Based on the findings presented herein, the following conclusions were made:

1. A user-friendly software tool was developed that successfully incorporated quantitative data obtained in a joint industry program, and combined these data with flow modeling calculations on plant piping configurations to predict the corrosion rates of 14 materials studied over a wide range of NH_4HS concentration, H_2S partial pressure, temperature, hydrocarbon content and chemical treatment.
2. This program demonstrated the importance of understanding the mechanical forces in plant systems where multiphase environments and various flow regimes are involved. It further highlights the point that velocity is not the key parameter, but rather the shear stress acting on the tube/pipe wall.
3. The software tool was used to predict the corrosion rate observed in a recycle gas line off the top of a CHPS, and was in good agreement with the measured corrosion rates. The results were further utilized to select a replacement metallurgy expected to yield a suitable design life.
4. Old rules of thumb were used to assess the severity of NH_4HS corrosion in a carbon steel REAC system of a hydrotreater. Based on these rules, corrosion was expected to be severe and alloy upgrades were planned. The software tool was used and revealed that the old rules were conservative and the decision was made to continue the use of carbon steel at significant economic benefit. The existing carbon steel piping system continues to provide safe and reliable service with minimal corrosion.

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TABLE 1
SHEAR STRESS AMPLIFICATION FACTORS
FOR VARIOUS PIPING CONFIGURATIONS

Configuration	Shear Stress Amplification Factor
Straight	1
3-D Bend	1.5
90° Elbow	2.6
Weld Protrusion (5 mm)	3.5

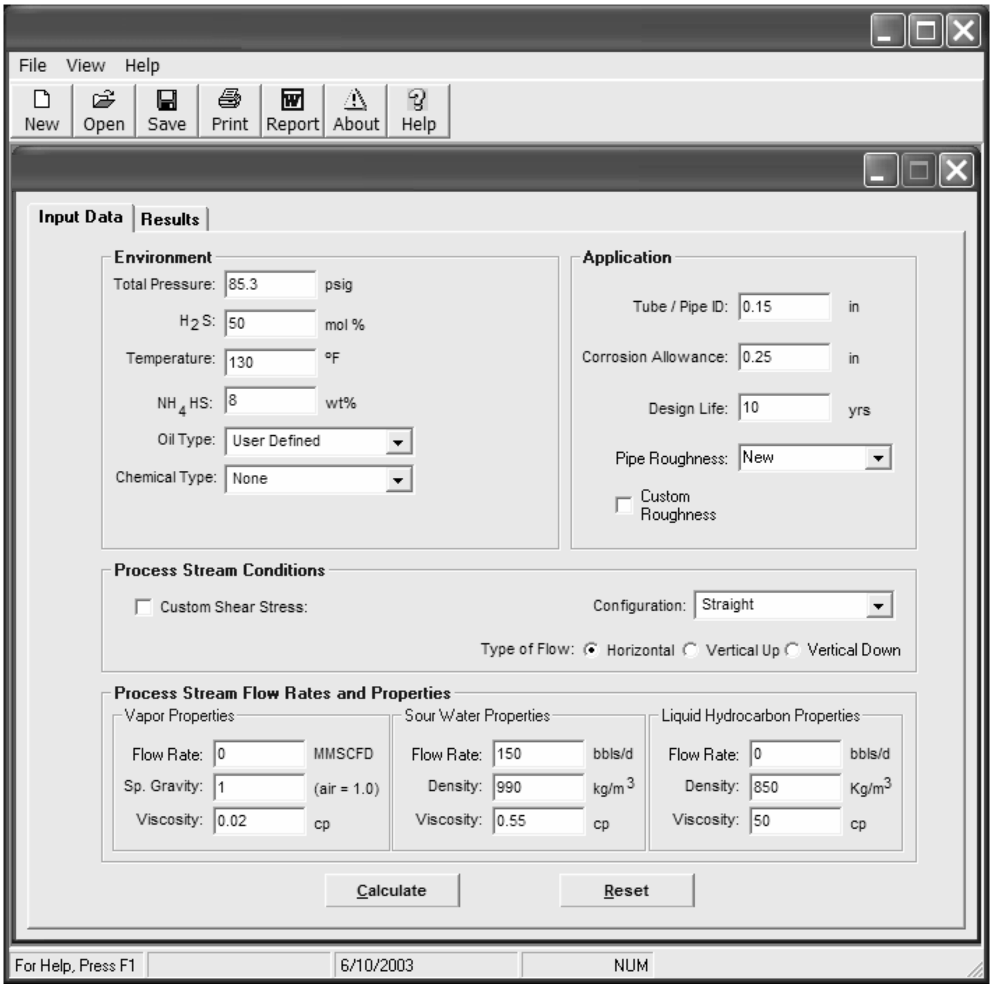

FIGURE 1 – Corrosion prediction software tool input screen.

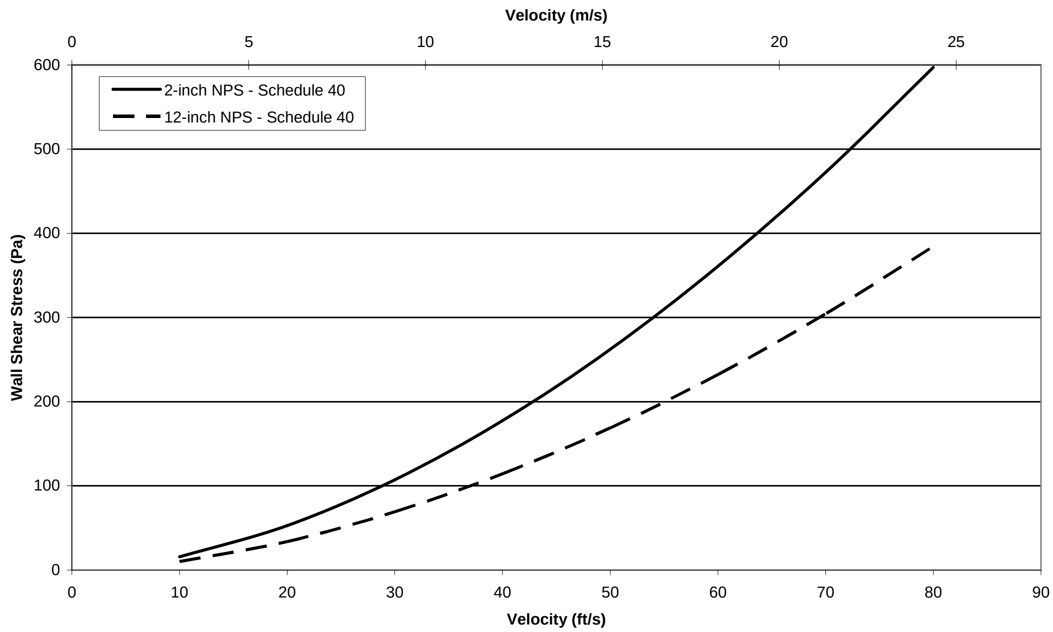

FIGURE 2 – Wall shear stress vs. velocity correlation. [100% liquid flow; 8 wt% NH_4HS; 130°F (55°C); 50 psia (340 kPa absolute) H_2S; straight pipe section.]

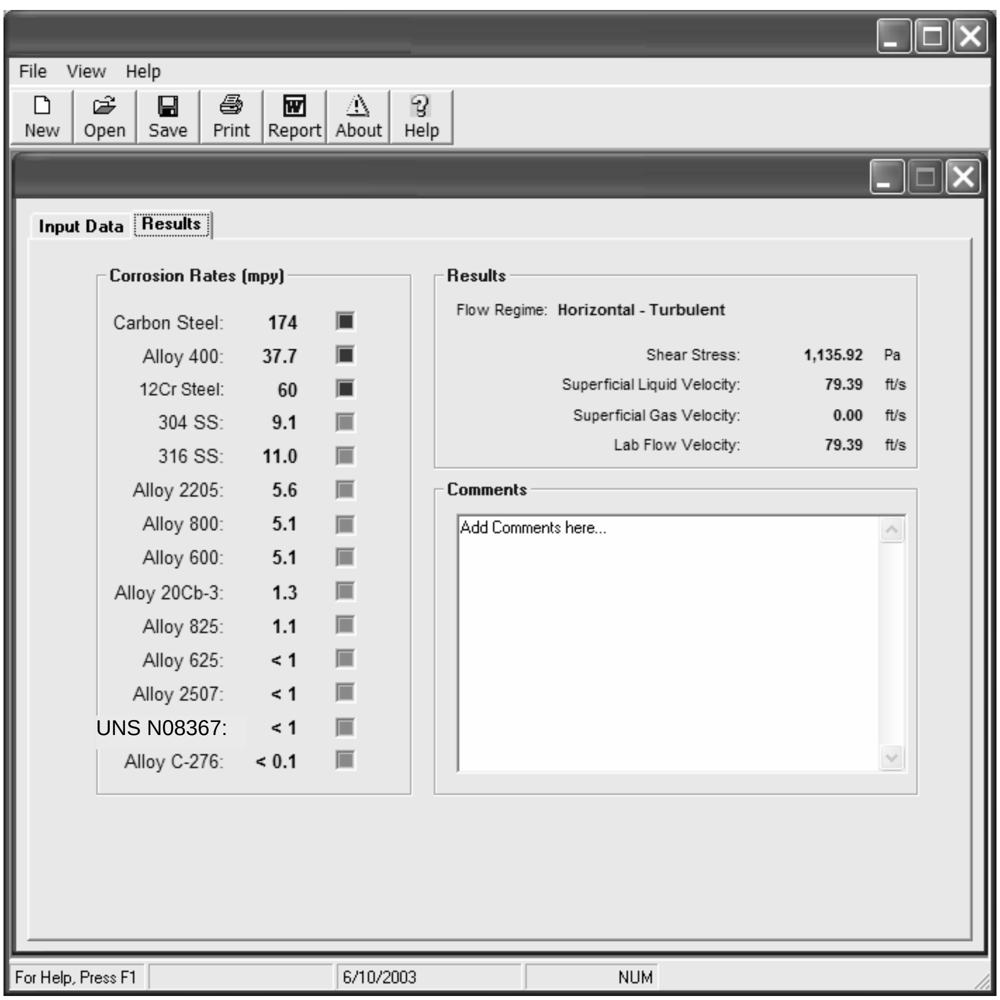

FIGURE 3 – Corrosion prediction software tool results screen.

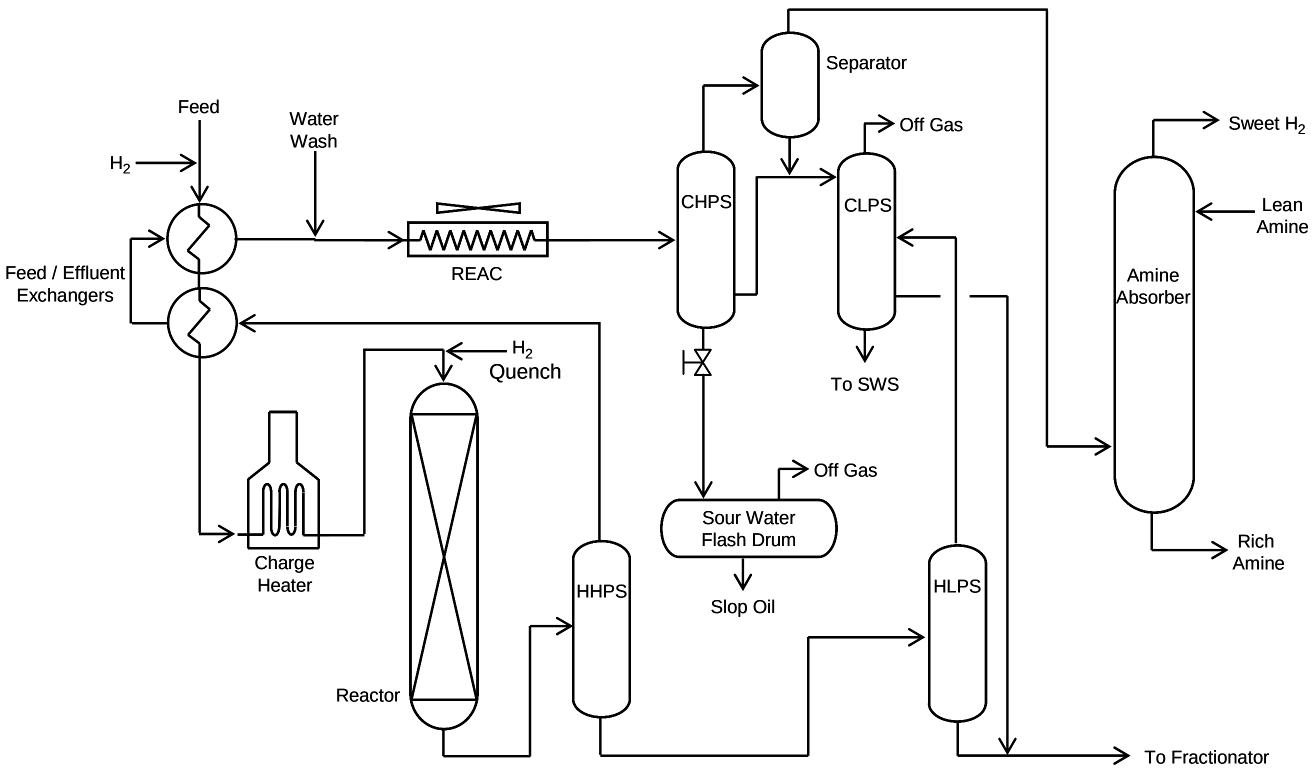

FIGURE 4 – Hydrotreating process flow diagram.

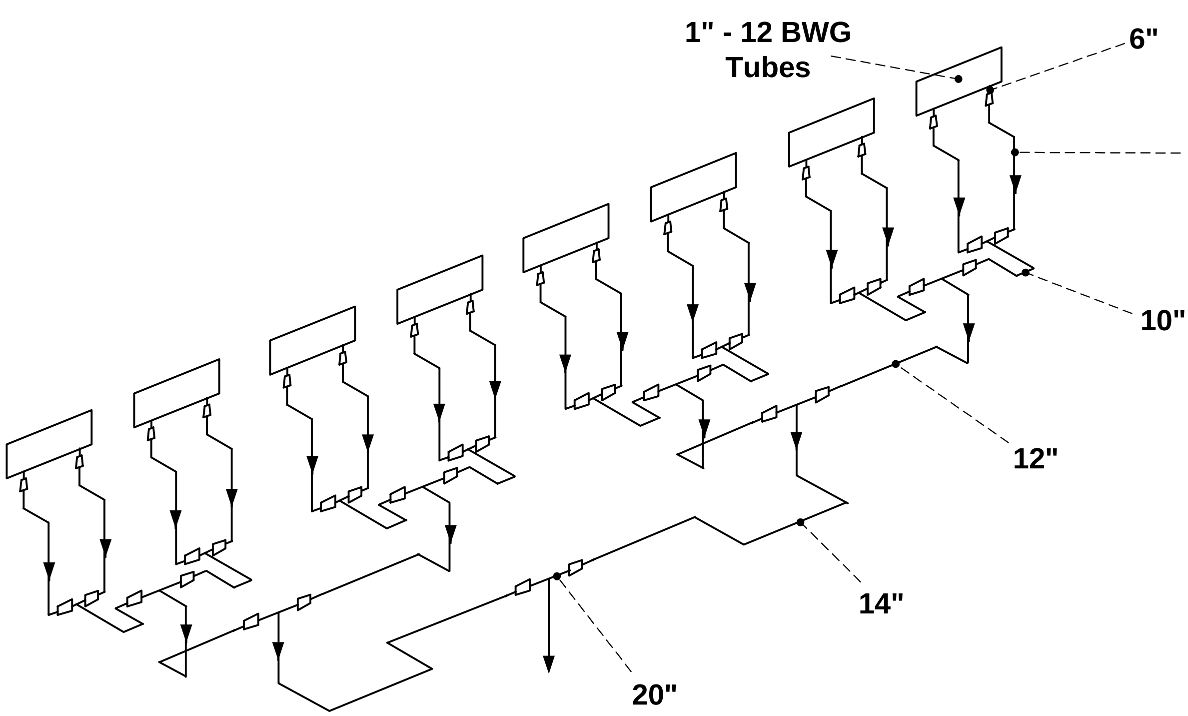

FIGURE 5 – Balanced REAC piping circuit modeled in Hydrotreater B.

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