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ELECTROLYTE THERMODYNAMIC MODELING FOR CRUDE DISTILLATION UNITS OVERHEAD SYSTEMS

Guilherme Pimentel De Maria da Silva

Dissertação de Mestrado apresentada ao Programa de Pós-graduação em Engenharia Química, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Mestre em Engenharia Química.

Orientadores: Frederico Wanderley Tavares
Rafael de Pelegrini Soares

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Examinada por:

Prof. Frederico Wanderley Tavares, D.Sc.

Prof. Rafael de Pelegrini Soares, D.Sc.

Prof. Frederico de Araujo Kronemberger, D.Sc.

Drª. Elizabeth Ferreira da Fonseca, D.Sc.

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Rafael de Pelegrini Soares

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MODELAGEM TERMODINÂMICA DE ELETRÓLITOS PARA SISTEMAS DE TOPO DE UNIDADES DE DESTILAÇÃO DE PETRÓLEO

Guilherme Pimentel De Maria da Silva

Setembro/2017

Orientadores: Frederico Wanderley Tavares
Rafael de Pelegrini Soares

Programa: Engenharia Química

A presença de ácidos (principalmente ácido clorídrico) nos sistemas de topo de unidades de destilação de petróleo, onde ocorre condensação de água, leva à formação de uma solução com baixo valor de pH, que pode causar corrosão ácida. Para evitar este fenômeno é geralmente adicionado um produto neutralizante (tipicamente amônia ou aminas) e, dependendo da quantidade de ácido clorídrico e/ou neutralizante, pode ocorrer deposição de sais, que são higroscópicos e geram corrosão sob depósito. Existem diversos modelos matemáticos para a previsão de variáveis relacionadas a estes fenômenos corrosivos como ponto de orvalho e pH (indicativos da corrosão ácida) e a temperatura de deposição de sais (indicativo da corrosão sob depósito). Neste trabalho foi feita uma revisão bibliográfica para identificação dos diversos tipos de modelos disponíveis, e modelos rigorosos baseados em termodinâmica de eletrólitos foram identificados como os mais apropriados. Além disso, um simulador comercial foi usado para uma investigação dos impactos causados pelas principais variáveis de processo que influenciam os fenômenos corrosivos. Foram avaliados oito neutralizantes puros (amônia e sete aminas), sendo possível avaliar o desempenho de cada um e suas vantagens e desvantagens; além da avaliação de misturas de neutralizantes, em que foi possível confirmar a redução da tendência de formação de depósitos. Além disso, foram confirmados os efeitos benéficos da redução da concentração de cloretos, do aumento da temperatura de topo da torre e do uso de água de lavagem para minimização dos impactos de corrosão.

Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

ELECTROLYTE THERMODYNAMIC MODELING FOR CRUDE DISTILLATION UNITS OVERHEAD SYSTEMS

Guilherme Pimentel De Maria da Silva

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Advisors: Frederico Wanderley Tavares
Rafael de Pelegrini Soares

Department: Chemical Engineering

Presence of acid compounds (mainly hydrochloric acid) in Crude Distillation Units Overhead Systems, where water condenses, leads to the formation of a low pH aqueous phase that may cause acid corrosion. To avoid that, a neutralizer is usually added to the overhead system (either ammonia or neutralizing amines). However, in case there is an excess of chlorides or neutralizer (or both of them), there may be salt deposition, which leads to under-deposit corrosion. Different mathematical models are available to predict variables related to these corrosion phenomena as dew point temperature and pH (that indicate acid corrosion) and salt deposition temperature (that indicates under-deposit corrosion). A literature review was proceeded here to identify the types of models available, and rigorous electrolyte thermodynamic models were considered most appropriate. Besides, a commercial software was used to investigate the impacts of main process variables that influence corrosion phenomena. Eight pure neutralizers were tested (ammonia and seven amines), and it was possible to describe their performance and identify advantages and disadvantages for each one; and then neutralizer blends, being confirmed that it is possible to reduce salt deposition tendency. Besides neutralizer composition evaluation, chloride concentration reduction, tower top temperature increase and use of wash water were proven beneficial measures to minimize corrosion impacts.

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Chapter 1 - Introduction

Presence of acid compounds (mainly hydrochloric acid) in Crude Distillation Units (CDU) Overhead Systems, where water condenses, leads to the formation of a low pH aqueous phase that may cause acid corrosion. To avoid that, a neutralizer is usually added to the overhead system (either ammonia or neutralizing amines). However, in case there is an excess of chlorides or neutralizer (or both of them), there may be salt deposition, which leads to under-deposit corrosion. Although there are several possible corrosion phenomena in CDUs overhead systems, acid corrosion and under-deposit corrosion are the main ones.

One of the ways to understand and learn how to deal with them is by use of computer-based modeling. Different models are available to predict variables related to these corrosion phenomena as dew point temperature and pH (that indicate acid corrosion) and salt deposition temperature (that indicates under-deposit corrosion).

The main objective of this dissertation is to investigate process variables that influence these corrosion phenomena with an electrolyte model. The results are separated in two main chapters. Specific objectives are included in these two chapters.

First, a literature review was proceeded to identify the types of models available, and rigorous electrolyte thermodynamic models were considered most appropriate. A brief introduction to rigorous electrolyte modeling of CDUs overhead systems is also presented, along with several recommendations. These results are described in Chapter 2.

Then, a commercial software, that contains rigorous electrolyte model, was used to investigate the impacts of main process variables that influence corrosion phenomena: neutralizer composition, chloride concentration, tower top temperature and wash water. Eight pure neutralizers were selected (ammonia and seven amines), and then neutralizer blends, to investigate possible to reduction of salt deposition tendency. Following evaluations include: chloride concentration reduction, tower top temperature increase and use of wash water, to minimize impacts from corrosion phenomena. These results are described in Chapter 3.

General conclusions and suggestions for future work are described in Chapter 4.

Chapter 2 - Electrolyte Thermodynamic Modeling for Crude Distillation Units Overhead Systems

2.1 - Introduction

Recent challenges in the oil and gas industry involving Crude Distillation Units (CDU) overhead systems include an increase in chloride content and a consequent aggravation of corrosion phenomena. A deeper understanding of phenomena involved in overhead systems is required to deal with corrosion impacts.

CDU overhead system corrosion has been widely debated in the literature (BAGDASARIAN *et al.*, 1996; BRADEN *et al.*, 1998; PETERSEN *et al.*, 2001; GIESBRECHT *et al.*, 2002; NACE, 2009). There are several possible corrosion phenomena in overhead systems and different unit configurations and operational conditions lead to different corrosion problems. There are different means to investigate and understand corrosion phenomena that may include historical data investigation, inspection, laboratory analysis and simulation, as suggested by GIESBRECHT *et al.* (2002). While all initiatives are valid, each one provides different results that are usually complementary. Regarding simulation, different models may be used to represent overhead systems conditions, being electrolyte models (also called ionic models) the most appropriate.

Over the past 25 years, different papers have been published with focus on electrolyte modeling (WU, 1994; DUGGAN and RECHTIEN, 1998; VALENZUELA and DEWAN, 1999; LACK, 2005; LORDO, 2006; SUN and FAN, 2010; PATEL *et al.*, 2012; ARMISTEAD *et al.*, 2015; LENCKA *et al.*, 2016). Each author presents different experiences and many suggest different criteria when using electrolyte models to simulate overhead systems. The focus of this work is to gather this information and describe how electrolyte models can be used as a tool to prevent corrosion.

Although focus in this study is on electrolyte modeling for crude distillation unit overhead systems, it is important to mention that this technology can be applied to other process units in refineries such as FCCs (Fluid Catalytic Cracking), DCUs (Delayed Coking Units) and HDTs (Hydrotreaters). In these units there is no need for neutralizer injection, as chloride levels are usually low and ammonia is naturally present in higher amounts. The concern in FCCs and DCUs is the possibility of ammonium chloride deposition (NH_4Cl) and in HDTs, due to high amounts of H_2S and NH_3 and the possible presence of HCl, concerns include both ammonium bisulfide (NH_4HS) and ammonium chloride depositions.

2.2 - Corrosion in Crude Distillation Unit Overhead Systems

Corrosion phenomena are inherent to any Crude Distillation Unit (CDU). Despite its origin, crude oils always have contaminants with negative impacts to the CDU, being the most common: inorganic salts (mainly sodium chloride, magnesium chloride and calcium chloride), sulfur and nitrogen compounds and organic acids (small chain organic acids and naphthenic acids) (NACE, 2009). Types of corrosion phenomena and its consequences depend on hardware configuration, operational conditions and feed quality, so it is unlikely to find two units with the same overhead conditions. Although it is impossible to avoid corrosion completely, it is possible to minimize its negative impacts and control it to acceptable levels.

In Figure 2.1 a schematic representation for a typical configuration of a CDU with focus on equipment related to the overhead system corrosion is shown. Crude oil is first treated with a desalting process to remove inorganic salts and then is heated before distillation. Number of distillations towers vary and depending on unit configuration, a preflash tower may be present before the atmospheric tower and atmospheric tower heaviest fraction may be sent to a vacuum tower. Corrosion phenomena may be present in all three kinds of distillation towers, but atmospheric tower is where chloride concentration is usually higher, and so it is where most corrosion problems appear. Therefore, only an atmospheric tower is presented in the schematic. Side and bottom products from the tower are not represented as focus is on overhead system. Tower top outlet stream (a vapor stream) is sent to the overhead condensers that may be air-coolers or shell and tube heat exchangers. At the end of the condensation process, incondensable gases and both liquid phases (water and hydrocarbon rich) are separated in the overhead accumulator drum (also called overhead drum).

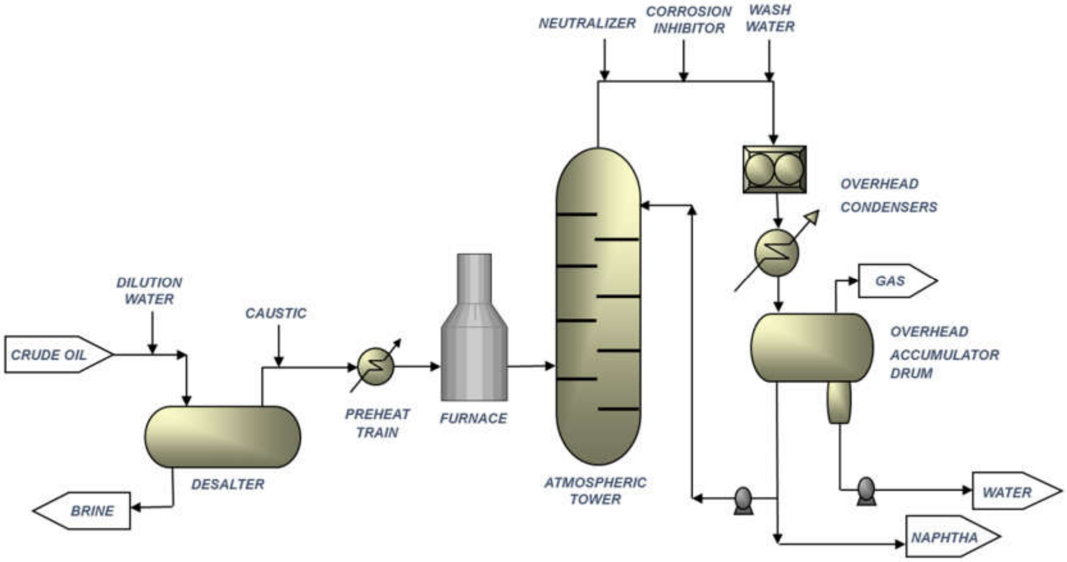

Figure 2.1 - Schematic process configuration of a typical CDU.

Although most CDUs contain desalters to remove salts from crude, some contaminants remain in the desalted oil either because of water solubility in oil or as a result of poor separation. As desalted oil is heated in the atmospheric furnace reaching high temperatures (385 °C), these contaminants are submitted to different reactions. Sulfur and nitrogen compounds may be converted to hydrogen sulfide (H_2S) and ammonia (NH_3). Organic chlorides may be hydrogenated, leading to formation of hydrochloric acid (HCl) and certainly the most common contaminants, which are inorganic salts, are hydrolyzed in the furnace, as shown in the following reactions (NACE, 2009), also leading to the formation of hydrochloric acid (HCl):

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl \qquad \text{Eq.1}$$

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl \qquad \text{Eq.2}$$

$$NaCl + H_2O \rightarrow Na(OH) + HCl \qquad \text{Eq.3}$$

2.2.1 - Acid Corrosion

Hydrochloric acid (HCl) is not corrosive in gas phase and so it moves through the distillation towers with no actual consequence. It causes damage to the unit only in lower temperature zones with the presence of water, which is the case of overhead systems, where tower outlet stream containing hydrocarbons and water condenses partially. Presence of HCl in water condensation originates an aqueous phase with very low pH, reaching values as low as 1.5 (CLARIDA *et al.*, 1997), which causes acid corrosion. Phase diagram for HCl-H_2O binary system shows that even if there is a small amount of

HCl in the vapor, HCl concentration in the liquid can be very significant (SUN and FAN, 2010). Other acid species such as hydrogen sulfide (H_2S), carbon dioxide (CO_2) and organic acids also have an impact, but HCl is usually the main contaminant, being the main factor regarding overhead system corrosion.

2.2.2 - Under-deposit Corrosion

In order to minimize acid corrosion, a neutralizer is usually added in the overhead system. Although NH_3 is naturally present in the overhead system (either as a natural contaminant in the oil or generated via conversion of nitrogen compounds), it is not enough to neutralize all acids (HCl, H_2S, CO_2 and organic acids). Because of its natural presence, ammonia has always been used as a neutralizer. Amines are also used as neutralizing compounds in the overhead system. In both cases, if there is an excess of chlorides, neutralizer, or both of them, there may be salt precipitation. Neutralizer is expected to be present in the aqueous phase to avoid acid corrosion, but salt precipitation (either in solid or liquid phase) must be avoided. Otherwise, under-deposit corrosion may occur. As described by DUGGAN and RECHTIEN (1998), salts formed from weak bases (NH_3 and neutralizing amines) and strong acids (HCl) are weak acids and besides that, these salts are hygroscopic and therefore adsorb water from vapor phase leading to an aqueous solution of a weak acid (even when there is no condensed water). This aqueous phase with a weak acid formed beneath salt deposition is responsible for the so-called under-deposit corrosion.

2.2.3 - Overhead System Corrosion Control

In the overhead accumulator drum, where most part of the water has condensed, pH is usually controlled between 5.5 and 6.5 (DUGGAN and RECHTIEN, 1998; FEARNSIDE and MURPHY, 1998). At this point there are minimum corrosion issues, since pH is already acceptable and any possible salt deposition has already been dissolved. Concerns regarding corrosion lie within the region where condensation starts, with little amount of water that already presents high content of acid or still, the area with high temperature with no water condensed with possible salt deposition. Beginning of condensation is usually described as initial condensation point (ICP) (FEARNSIDE and MURPHY, 1998; DION *et al.*, 2012) or simply water/aqueous dew point. Recent studies show that the presence of electrolytes may influence condensation, as described by SUN and FAN (2010) and ARMISTEAD *et al.* (2015). In the overhead system, the presence of both chloride and neutralizer result in a higher condensation temperature, described as an ionic dew point by ARMISTEAD *et al.* (2015), which is different (and higher) than regular water dew point.

Neutralizer should be able to act in the initial condensation point to avoid low pH and should have a low tendency of salt deposition. There must be a compromise to choose the best neutralizer to attend these needs.

Neutralizer flow rate is often adjusted based on the accumulator water pH (DUGGAN and RECHTIEN, 1998). This may lead to serious corrosion issues since ionic dew point pH may be significantly lower than boot water pH. Nevertheless, it is very difficult and unusual to measure ionic dew point pH (FEARNSIDE and MURPHY, 1998). In spite of that, it is important to be aware of its difference to the accumulator pH. Electrolyte modeling is a useful tool to verify if neutralizer rate guarantees an acceptable ionic dew point pH.

Besides the neutralizer, a corrosion inhibitor (also called film-forming inhibitor or filmer) is usually added to the system, to minimize corrosion effects. The inhibitor may act in different ways (RUE and EDMONDSON, 2001), being formation of a liquid film in the equipment surfaces the main one. The film is supposed to avoid contact between metal and acid solution and possibly avoid the formation of salt deposition. The effectiveness of inhibitors is generally lower for under-deposit corrosion than for acid corrosion (RUE and EDMONDSON, 2001).

In addition to neutralizer and corrosion inhibitor, wash water may be added to the overhead system to control corrosion. Liquid water dissolves the salts (ammonium chloride and amine hydrochlorides are all water soluble) and may be helpful by diluting the acid solution, raising pH in the beginning of condensation. As overhead systems are operated at temperatures between 90 °C and 160 °C, and near atmospheric pressures, most of the wash water injected vaporizes, being necessary to inject a significant amount of water to guarantee saturation and presence of liquid water.

Although neutralizer and inhibitor injections are almost always necessary, it is important to remind that chloride is the main cause of corrosion and so, reducing its concentration should be a priority when facing overhead corrosion issues. This can be achieved by desalter optimization, crude selection or caustic (NaOH) injection. Desalting process must always be optimized to minimize salt content in the unit, so this is always the first option to reduce chloride content. Crude selection (avoiding crudes with higher salt content) is effective but may not be an option due to economic reasons. Caustic injection after the desalter definitely lowers chloride concentration in the overhead system (NaOH either reacts with HCl to form NaCl, or still, NaOH reacts with both $MgCl_2$ and $CaCl_2$ to form NaCl, the most stable salt) (1 / NACE, 2009). The difficulty in using caustic is that it can bring many negative impacts if high amounts are added, such as depositions in pre-heat trains after the desalters, coking acceleration in furnaces (both Distillation and Delayed Coking units), FCC catalyst deactivation by coke formation, caustic corrosion (if a concentrated solution is injected at high temperatures with no proper injection device), among others (RUE and EDMONDSON, 2001).

Finally, there are other corrosion phenomena such as Wet H_2S Cracking and the influence of other species (e.g. oxygen) (NACE, 2009), but acid corrosion (mainly by HCl) and under-deposit corrosion (by salt deposition) are the main phenomena that lead overhead systems equipment to failure.

2.2.4 - Important results from electrolyte models

There are different variables that can be calculated with electrolyte modeling of CDU overhead systems in order to control corrosion, including:

- Salt deposition temperature (also called salting point);
- Dew points (ionic dew point and water dew point);
- pH at dew points;
- Minimum wash water rate;
- Corrosion rates.

These variables may be used as parameters in the evaluation of corrosion phenomena with electrolyte models. Dew points and their pH values are related to acid corrosion and salt deposition temperature is related to under-deposit corrosion. Minimum wash water rate may be used to evaluate if an existing wash water rate is adequate or as a solution for an existing problem in a unit with no wash water. Corrosion rates are usually measured in practice and as simulation output it may be used as a final indicative of corrosion phenomena.

All these variables that may be outputs from electrolyte models may be used in different ways to aid in troubleshooting, unit design and revamping, including:

- Neutralizer selection and/or neutralizer injection rate optimization:

Neutralizer rate or composition may be altered to reach the best compromise between minimum salt deposition and acceptable pH at dew points.

- Operational changes:

Process variables may be altered to minimize corrosion impacts e.g. overhead temperature increase to avoid salt deposition, wash water increase to avoid under-deposit corrosion, and so on.

- Unit configuration changes:

When neutralizer selection and operational changes are not enough to minimize corrosion, unit configuration may have to be altered e.g. heat exchanger redesign, introduction of new injection points of chemical products, metallurgical adaptation and so on.

2.3 - Types of Overhead System Electrolyte Modeling

Crude distillation units overhead systems consist basically of condensation of a vapor stream in heat exchangers and separation of three phases (gas, liquid hydrocarbon and aqueous phase) in a separation drum. A fourth solid phase may be present as a result of salt deposition. Aqueous phase with low pH and presence of solid phase result in acid corrosion and under-deposit corrosion, respectively. All these phenomena are very difficult to describe in a single model and so every model contains simplifying assumptions e.g. only vapor-solid equilibrium modeling to predict salt deposition, only vapor-liquid equilibrium modeling to predict aqueous phase dew point, kinetic modeling to predict corrosion rates and so on. As there is a large number of possible models, different types of overhead system modeling are available and therefore different classifications are proposed.

One major classification refers to the techniques involved in the modeling. According to NACE (2009), these fall into two categories: physical measurement modeling (laboratory and field-testing apparatus) and computer-based modeling. Physical measurement modeling has been described by many authors (FEARNSIDE and MURPHY, 1998; NIU, 1984; LEHRER and EDMONDSON, 1993; LACK, 2015), but despite its importance, it is not the scope of this work, which is focused on computer-based modeling.

There are many possibilities regarding computer-based modeling of overhead systems. As acid corrosion and under-deposit corrosion are the main phenomena involved, modeling options usually include the prediction of solid deposition temperature, dew points (liquid water may dissolve solids), pH, minimum wash water rate and corrosion rates.

A general classification is proposed concerning simplifying assumptions and precision of each approach. The models can be classified into two groups, as described below:

2.3.1 - Simplified Calculations

This group consists of techniques that involve simple calculations that can be easily accomplished by manual calculations (and/or with use of tables, charts or spreadsheets), and include water dew point and solid deposition temperature prediction only.

- Use of Steam Table to Predict Water Dew Point

Steam tables can be used to determine aqueous dew point temperature (NACE, 2009). As steam tables refer to pure water vapor-liquid equilibrium, partial pressure of water in the overhead system must be calculated, assuming that all hydrocarbons and water are in vapor phase (which is true only for the top of the tower and not for the whole overhead system). As temperature decreases, hydrocarbons may condense before water, changing the water partial pressure. As this is not taken into consideration, this method provides unprecise results. It is a fast and simple method that can be used as a preliminary result, but should not be solely considered as a valid result for overhead corrosion evaluation.

- Salt Deposition Temperature Calculations

Phase diagrams based on thermodynamic equilibrium can be used to predict salt deposition temperature. Hydrochloric acid and the neutralizer added (ammonia for example), both in the vapor phase, react and may deposit according to the following reaction:

$$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g) \qquad \text{Eq.4}$$

At a defined temperature, salt deposition initiates when the concentrations of HCl and NH_3 reach a certain limit. Therefore, depending on the amount of HCl and NH_3 a solid phase may be present in the system, which leads to under-deposit corrosion, as described before. For a given amount of acid and base, it is possible to predict minimum temperature at which a solid phase is present. The phase diagram for NH_4Cl is presented in Figure 2.2.

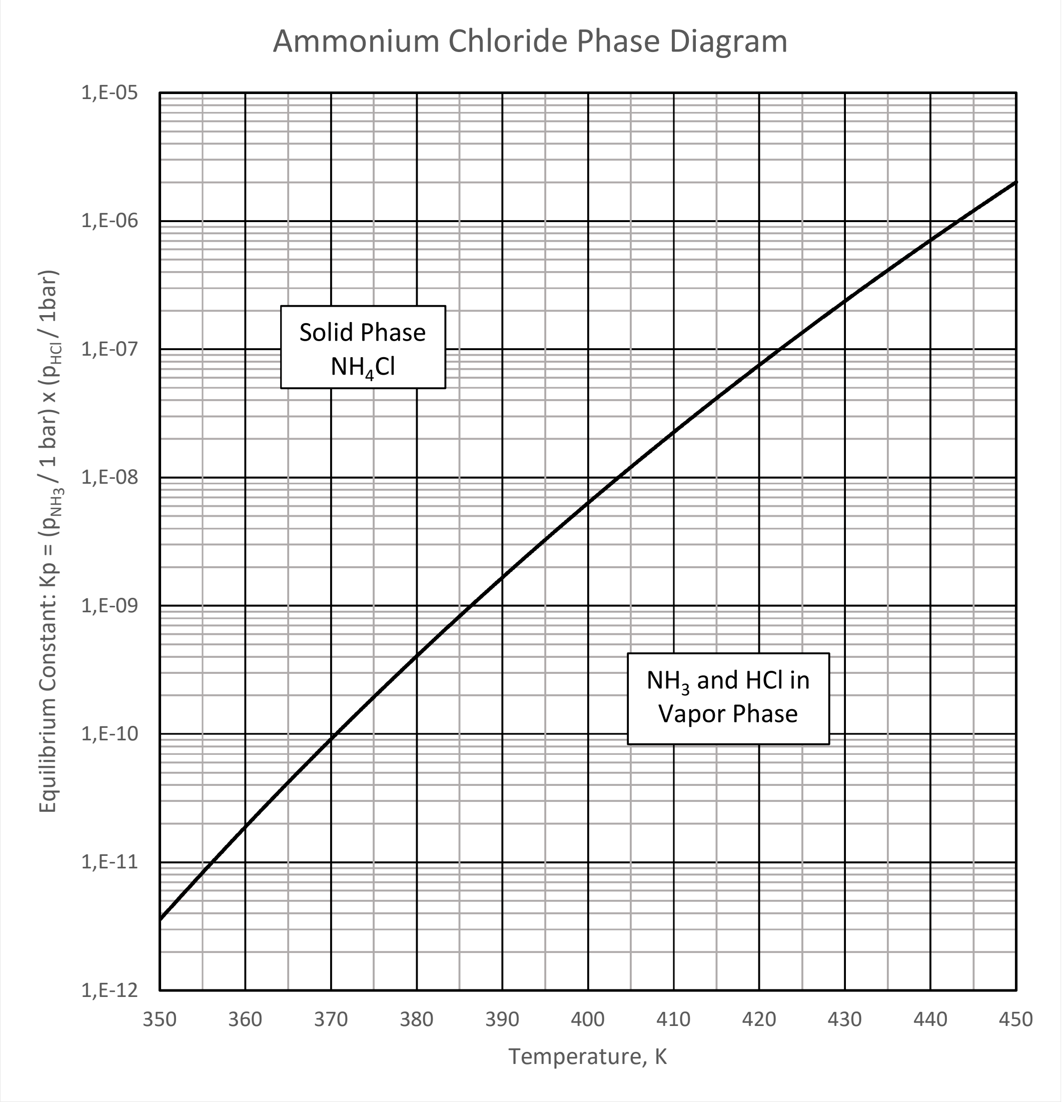

Figure 2.2: Phase Diagram for NH_4Cl (1).

(1) Constructed from OLI (2) database.

(2) OLI is a registered trademark of OLI Systems, Inc. URL: http://www.olisystems.com.

Again, it must be assumed that all hydrocarbons and water are in vapor phase and no liquid phase forms before the salt, possibly leading to an incorrect prediction. Other assumptions are made, namely: no interactions between the species are considered; and pressure is fairly low (near atmospheric pressure), so ideal gas approximation may be considered valid. Thermodynamic equilibrium is taken into consideration with no aspects regarding kinetics or flow regimes. With these assumptions, the reaction in Eq. 4 can be represented by an equilibrium constant as a function of partial pressures:

$$Kp_{NH_4Cl} = (p_{NH3} / 1bar) * (p_{HCl} / 1bar) \qquad \text{Eq.5}$$

API (2012) and WU (1994) describe the calculation procedure and the data need for the estimation of both ammonium chloride (NH_4Cl) and ammonium bisulfide (NH_4HS) equilibrium constants. Ammonium bisulfide deposition occurs when high amounts of H_2S are involved, which is unlikely to happen in CDUs (but is very usual in Hydrotreating units). Other authors also present these data for NH_4Cl (NACE, 2009; FEARNSIDE and MURPHY, 1998; LEHRER and EDMONDSON, 1993; GUTZEIT, 2006).

As reported by VALENZUELA and DEWAN (1999), there is limited data for ammonium chloride phase diagrams and very few data for amine hydrochlorides. LEHRER and EDMONDSON (1993) and LENCKA *et al.* (2016) provide data for some amines and amine hydrochlorides. Nevertheless, LENCKA *et al.* (2016) observed that the vapor pressures of Lehrer and Edmondson (1993) for ammonium chloride are lower than the generally accepted data.

2.3.2 - Rigorous Calculations

This group consists of techniques that involve simulators due to the complexity of calculations.

- Use of Process Simulators to Predict Water Dew Point

Typical steady-state commercial process simulators can be used to more precisely estimate water dew point. Material and heat balances are calculated along the overhead system providing more precision, especially to the hydrocarbon phase, which is characterized by pseudocomponents. Both hydrocarbon and water condensation are predicted with no need to assume that all species are in vapor phase, as described in simplified methods. Thus, when a hydrocarbon-rich phase appears before the aqueous phase (which is usually the case) the actual water molar fraction in the vapor phase is considered in the water dew point calculation.

Besides predicting water dew point, process simulators can be used to estimate an important parameter to the overhead system corrosion control: wash water rate. As mentioned before, it is necessary to inject a significant amount of water to guarantee saturation and the presence of liquid water. After the calculation of water dew point it is easy to evaluate wash water injection. GIESBRECHT *et al.* (2002) describe the calculation procedure and criteria usually adopted to estimate wash water rate. First, the minimum wash water rate is calculated by an iterative process in which water is added to the tower outlet stream until it reaches saturation (water dew point). Then an excess of 25%-50% is added to guarantee that liquid water will be available. McLAUGHLIN and WU (1997) describe an alternative procedure that starts with the calculation of solids deposited and the wash water added must ensure solids dissolution (resulting in an aqueous phase with no more than 2% mole of ion concentration).

- Electrolyte Modeling

Most traditional process simulators do not implement the electrolyte models needed to predict the behavior of electrolytes in water, including chloride, ammonia and amines. In order to predict condensation (both hydrocarbon and water), pH (the most important parameter to evaluate acid corrosion) and solid deposition, the following phenomena should be included in electrolyte modeling:

- Vapor-Liquid equilibrium of the species involved: Hydrocarbons, Water, HCl, CO_2, H_2S, NH_3 and amines (and possibly other weak acids, such as small chain organic acids). With its prediction it is possible to determine hydrocarbon dew point, water dew point (and consequently wash water rate) and, with all the components concentrations in liquid water, pH.

- Liquid-Liquid equilibrium of the species involved: Hydrocarbons, Water, HCl, CO_2, H_2S, NH_3 and amines (and possibly other weak acids, such as small chain organic acids). As both hydrocarbons and water condense, a liquid-liquid equilibrium model should be added to represent the system.

- Solid-Vapor and Solid-Liquid equilibrium of the species involved: ammonium chloride and amine hydrochlorides. With its prediction it is possible to determine salt deposition temperature (in case salts deposit from the vapor phase) and salt dissolution (when liquid water is present).

As condensation is the primary concern in overhead systems, it is obvious that vapor-liquid equilibrium is a priority for any electrolyte model. As salt deposition is feasible, solid-vapor equilibrium is as important as such and should also be a priority. Nonetheless, SUN and FAN (2010) point out that in spite of NH_3, HCl and NH_4Cl small solubilities in hydrocarbon, hydrocarbon relatively larger volumes may have an impact in the total mass balance, depicting the need for liquid-liquid equilibrium.

These phenomena are usually modeled based on thermodynamics, with no consideration with aspects regarding kinetics or flow regimes. NACE (2009) presents a list of several authors who propose different approaches. Some propose models that include only vapor-liquid equilibrium while others propose vapor liquid equilibrium combined with liquid-liquid equilibrium and/or solid-liquid equilibrium. To the best of our knowledge, only one model proposed (WANG *et al.*, 2002; WANG *et al.*, 2004; WANG *et al.*, 2006) includes all four equilibria (vapor-liquid, liquid-liquid, solid-liquid and solid-vapor). This model (MSE – Mixed Solvent Electrolyte) was recently extended with application to amines and amine hydrochlorides (LENCKA *et al.*, 2016).

According to NACE (2009), electrolyte modeling can be classified into two groups: “strict equilibrium thermodynamic models” and “combined thermochemical-eletrochemical models”. The first one consists of models based only on thermodynamic equilibrium, as described above. The second one consists of models that, besides electrolyte thermodynamics, also include kinetic models to predict corrosion rates.

LORDO (2006) classifies electrolyte models in two categories: detailed use and general use. The first one consists of models that “require extensive data collection and samples that are not routinely available”, therefore taking a long time for development (weeks to months). These are usually used for troubleshooting or for evaluation of long-term strategic operational changes. The second one consists of models that “accept readily available data” and are usually used for routine monitoring and trending or still, short-term adjustments.

2.4 - Electrolyte Modeling

Although there are different possibilities to overhead system electrolyte modeling, focus in this work will be on thermodynamic-based (equilibrium) models, described as “strict equilibrium thermodynamic models” by NACE (2009), considering all the possible phase equilibria (vapor-liquid, liquid-liquid, solid-liquid and solid-vapor) as described by LENCKA *et al.* (2016).

LENCKA *et al.* (2016) present a complete description of the model including different reactions (amine hydrolysis, dissociation of dissolved acid gases and both solid-vapor and solid-liquid equilibria). What differs MSE from other models is the way chemical potentials are calculated. Chemical potential of species *i* in liquid phase is calculated with:

$$\mu_i^L = \mu_i^{L,0,x}(T,P) + RT \ln x_i \gamma_i^{x,*}(T,P,x) \qquad \text{Eq.6}$$

where:

μ_i^L is the standard-state chemical potential expressed on the mole fraction basis;

xi is the mole fraction;

$\gamma^{x,*}$ is the unsymmetrically normalized mole fraction-based activity coefficient of species i;

The mole fraction-based standard-state chemical potential is related to the more frequently used molality-based standard-state chemical potential:

$$\mu_i^{L,0,x}(T,P) = \mu_i^{L,0,m}(T,P) + RT \ln \frac{1000}{M_{H_2O}} \qquad \text{Eq.7}$$

where:

M_{H2O} is the water molar mass.

The molality-based standard-state chemical potential is calculated as a function of temperature and pressure from the Helgeson-Kirkham-Flowers (HKF) equation of state. According to LENCKA *et al.* (2016), thermodynamic properties are accurately reproduced by the HKF model (and, hence, the equilibrium constants for reactions between them) up to 1000 °C and 5 kbar. For water, the standard-state chemical potential is defined as that of pure water and is calculated from the Haar-Gallagher-Kell equation of state.

Activity coefficients in Eq. 6 are obtained from an expression for the excess Gibbs energy, that in this case is represented as a sum of three contributions:

$$G^{ex} = G_{LR}^{ex} + G_{II}^{ex} + G_{SR}^{ex} \qquad \text{Eq.8}$$

where:

G^{ex}_{LR} is the contribution of long-range electrostatic interactions;

G^{ex}_{II} represents ionic (ion-ion and ion-molecule) interactions;

G^{ex}_{SR} accounts for a short-range contribution resulting from intermolecular interactions.

Long-range interactions are calculated from the Debye-Hückel theory; ionic interactions are calculated from an ionic strength-dependent, symmetrical virial-type expression and short-range interactions are calculated from an UNIQUAC equation, as described by LENCKA *et al.* (2016)

When creating a simulation model, the first step consists of defining the tower outlet stream i.e. the vapor stream that leaves the tower. In some cases, this stream is already available in a process simulation (e.g. from a previous study on the operating conditions, usually with no information about HCl and neutralizer), but in most cases this stream must be modeled from data available in the refinery. To compute the tower outlet stream with refinery data it is necessary no gather information on the three streams that exit the accumulator drum. In Figure 2.3, a schematic representation for a typical process configuration of an overhead system is shown, comprehending these streams.

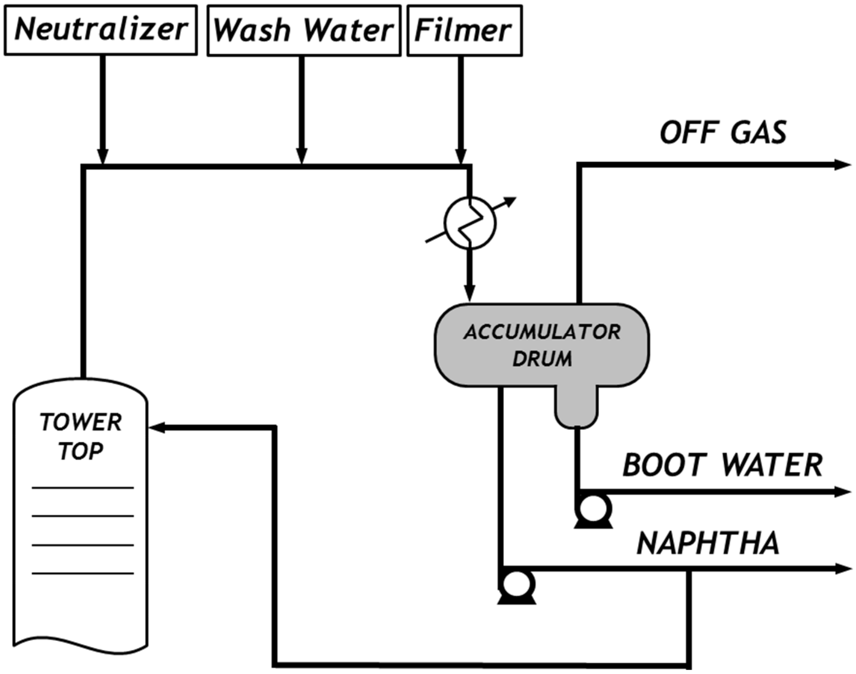

Figure 2.3: Schematic process configuration of a typical overhead system.

The combination of the three exiting streams from the accumulator (Off Gas, Boot Water and Naphtha) result in the combination of the tower outlet stream and the streams injected in the overhead pipeline. As composition and flowrate of these injections are usually known, it is possible to compute the tower outlet stream by mass balance. Filmers are usually not taken into account in electrolyte modeling as the phenomenon involved (liquid film formation) is not usually modeled under equilibrium assumptions.

The tower outlet stream combined with the neutralizer and possibly, wash water, is cooled down until the accumulator drum temperature. To represent this cooling process with a thermodynamic model it is necessary to calculate phase equilibria at different temperatures (from the tower top temperature to the accumulator drum temperature). This is a simplifying assumption, because in the real system a multiphase flow with high velocities is cooled down and equilibrium is not necessarily reached in each temperature. Nevertheless, this approach is conservative and according to BRADEN *et al.* (1998), “deposition is almost never as severe as predicted”.

2.4.1 – Input Data

Input Data needed for the simulation are described below. The information needed may vary according to the already available data, but considering the case where the tower outlet stream must be created using the three accumulator outlets, one must consider:

- Operational conditions in the overhead system:
    - Temperature and pressure in the tower top
    - Temperature and pressure in the accumulator drum
- Flowrates and compositions of the three exiting streams from the accumulator:

Boot water - routine analysis in the refinery usually include pH, chloride, ammonia and iron content. Chloride and ammonia (both always present in the system) are essential to the model and pH is very important to confront calculated data with the experimental value. However, these may not be enough for a rigorous model. Other species as amines and weak acids, including small chain organic acids (such as formic, acetic, propionic and butyric acids), CO_2 and H_2S are usually present. Even when ammonia is used as a neutralizer, amines may be present (these are called tramp amines and wil be discussed in section 4). When refinery routine analysis are not enough, a detailed investigation on the boot water sample must be carried to detect these species. In order to confront calculated data with experimental data, electroconductivity and density may be measured, besides pH.

Naphtha – it is important to detach that the hydrocarbon flowrate used in the model must be the total flowrate that leaves the drum and that is usually the sum of both naphtha product and naphtha reflux (as presented in Fig. 3). A distillation curve (D86 or TBP) and density are necessary to represent the hydrocarbon stream in the model. If a process simulation is available, naphtha representation in light hydrocarbons and hypothetical components (also called pseudocomponents) is enough.

Gas – although not a routine analysis, a gas chromatography of the gas stream is needed for the model. As for the naphtha, if a process simulation is available, gas stream representation with pure components and hypothetical components is enough.

- Flowrates and compositions of the streams injected in the overhead pipeline:

Neutralizer – in many cases flow measurement of neutralizer is not available (because usually small alternative pumps are used and their flow measurement is not easy) and so, as an alternative, weekly or monthly consumption may be used as a mean value. It is essential to know the composition of the neutralizer to represent the overhead system with an electrolyte model.

Wash water – in most cases boot water is used as the source of wash water (it is close to the overhead system and there is no risk of other contaminants entering the system). In these cases, composition is already known from boot water analysis. In other cases, water samples must be taken and the same analysis used to the boot water must be provided.

It is important to mention that when analyzing boot water samples, both neutralizer and wash water are included in the boot water. With the knowledge of both neutralizer and wash water streams, a mass balance may be needed in case of evaluation of other neutralizers or changes in wash water (flowrate or composition). If a tower outlet stream is available from a previous study, than it is necessary to compute all ionic species analyzed in the boot water as molecular compounds in this vapor stream, with a simple mass balance. BRADEN *et al.* (1998) provide further information on which data are required for the simulations, including measurement techniques and methods for each variable and RECHTIEN and DUGGAN (2006) provide details on amine measurement in refinery water samples. LORDO (2006) provides further details on samples collection and storage.

2.4.2 – Recommendations

As mentioned before, different papers have been published with focus on electrolyte modeling. Besides modeling results and case studies, some authors have given recommendations and proposed criteria for the overhead system simulation. These are not rules that must be strictly followed, but suggestions that reflect others' experience and therefore it is interesting to be aware of them.

LORDO (2006) presents guidelines and describes limitations of overhead system electrolyte modeling. One of the most important recommendations is to understand the model mechanics and ionic interaction portion of the model. The model should be chosen according to the objectives and it is essential to know the model to understand its limitations and to properly interpret the results.

When collecting data on the boot water composition it is easy to notice that contaminant levels usually vary substantially, so it is important to extract at least three samples for detailed analysis or, in case of already available data from the refinery, gather information from a long time period. With so much information and variations it may be difficult to decide what composition should be used in the simulation. DUGGAN and RECHTIEN (1998) recommend creating a "base case" model of the system to represent typical operating conditions. Based on this, various perturbations such as neutralizer substitution or variations on contaminants concentrations can be evaluated.

Once the data on composition and flowrates of the streams are consolidated, the model can be effectively constructed. LACK (2005) proposes three criteria to confirm a valid simulation of an overhead system:

1 – Overhead stream must be at its hydrocarbon dew point at the tower top operational conditions. As the overhead stream is the vapor that leaves the first tray, it is in equilibrium with liquid hydrocarbon and is therefore saturated.

Mass balance from the simulation shall agree with measured values:

2 – Total naphtha API and rate as well as off gas rate in the simulation must be in good agreement with measured data.

3 – Composition and pH of boot water in the simulation must be in good agreement with measured data.

BRADEN *et al.* (1998) recommend that the first check is to confirm that calculated pH is within 0.5 units of experimental pH. If not, there must be either an error with the analysis or it means that not all of the species that impact pH have been measured. If the difference remains even after re-sampling and/or re-analysis, then a further investigation must be pursued, such as speciation of less common acids.

If the focus is choice of neutralizer or if neutralizer substitution is a possible solution in a corrosion control program, then the neutralizer flowrate is an essential variable in the model. According to FEARNSIDE and MURPHY (1998), minimum neutralizer rate is the stoichiometric rate required to neutralize the hydrochloric acid, but the actual neutralizer rate should be 1.05 to 1.20 the stoichiometric rate.

After the simulations are calculated and the results are obtained, extra care must be taken within its interpretations. First of all, as it happens with any simulation model, it is important to remind that the model itself has an intrinsic error and that input data are gathered from laboratory analysis that also include errors implied. Besides that, there are all the assumptions discussed before, that imply in a lack of accuracy.

One of the most important results is the salt deposition temperature (or salting point). Once this temperature is known, it is necessary to compare it with the temperatures of the overhead system. Temperatures important to the system include the tower top temperature and the inlet and outlet temperatures of the condenser(s). DUGGAN and RECHTIEN (1998) suggest that the difference of the system temperature and the salting point, named Salt ∆T, is the parameter that should be used for salt deposition evaluation. A positive Salt ∆T indicates that salt will not deposit and on the contrary, a negative salt ∆T indicates salt deposition. When Salt ∆T equals zero it is an indicative of a point of incipient salt deposition. As amine hydrochloride and ammonium chloride salts are soluble in water, there is no need to calculate Salt ∆T at temperatures below the water dew point, as detached by DUGGAN and RECHTIEN (1998). NACE (2009) states that the difference between the tower top temperature (tower outlet stream temperature) and the salting point is usually greater than 14 °C (25 °F) and that salting point is normally suggested to be 14 °C (25 °F) lower than water dew point. These criteria may be difficult to be respected depending on chloride content and type of neutralizer. ARMISTEAD *et al.* (2015) mention that the minimum difference between the tower top temperature and the ionic dew point should be 14 °C (25 °F).

Another important result is pH profile along condensation, being initial condensation point the most critical as a low pH in the dew point is an indicative of probable acid corrosion. DUGGAN and RECHTIEN (1998) indicate that 4.0 is a minimum value for systems with carbon steel and use of filmers. According to LEHRER and

EDMONDSON (1993), pH at initial condensation point must be raised to above 4.5 and, preferably, 5.0.

LORDO (2006) points out that depending on the model supplier, initial water dew point definitions do differ. While an academic definition of the first water drop as a very small amount of water may be used, a higher percentage of condensed water may be more representative. BRADEN *et al.* (1998) suggest that a minimum percentage of 5% water is appropriate and that for this value, pH must be approximately 5.0 or greater.

Although pH at dew point is most critical, it is unfortunately difficult to measure it as a routine in the refinery (FEARNSIDE and MURPHY, 1998). Therefore, in most units, pH is controlled with samples from the accumulator drum, where most water is condensed and pH has been raised, being controlled usually between 5.5 and 6.5 (DUGGAN and RECHTIEN, 1998; FEARNSIDE and MURPHY, 1998).

With the development of electrolyte modeling, its use has been extended to real-time applications in the refineries. As contaminant levels in the accumulator drum may vary significantly, it may be necessary to run the model online in order to act in time to minimize corrosion impacts. LACK (2008) describes an overhead corrosion control program called TOPGUARD that includes monitoring key parameters on a daily basis using an ionic model and field data and SARPONG (2011) presents a case study with this technology. SUN and FAN (2010) have implemented an integrated system consisting of a corrosion model along with ionic equilibrium and thermodynamic packages that receives real-time process data.

2.4.3 – Software Available

Electrolyte modeling software are available through some chemical suppliers that along with chemical products also provide technical assistance with this technology, or as commercial software.

BRADEN *et al.* (1998) present theoretical considerations regarding overhead system corrosion control, including the development of a program called PATHFINDERTM. This program is comprised of three parts: novel chemistry (to deal with amine blends), software package (to calculate all the parameters of interest, such as pH profile, salt deposition potential and neutralizer rates, among others) and a suite of on-line monitoring hardware. Different case studies are also presented.

DUGGAN and RECHTIEN (1998) present the basis for ionic modeling when describing the technology called Ionic Equilibria Modeling (IEM), including case studies with this model. This model is the result of a technological partnership between Baker Hughes and Shell Oil. The theory and assumptions adopted in this model are presented by VALENZUELA and DEWAN (1999). ARMISTEAD *et al.* (2015) point out that Shell Oil developed an ionic model for salt formation in conjunction with OLI Systems in the mid-1990s. Different papers were published with reference to this technology. LACK (2005) evaluates amine behavior in Crude Units with focus on liquid-liquid equilibrium in order to investigate amines recycle. GIESBRECHT and DUGGAN (2007) describe a case study in which washing water was proved ineffective. DUGGAN *et al.* (2009) describe a case study of a single unit in which three corrosion phenomena were observed: ammonium chloride deposition, hydrogen sulfide attack on copper and velocity-accelerated corrosion.

PAYNE (2012) describes the concerns regarding overhead system corrosion and presents an ionic equilibrium model called LoSalt, proprietary of GE Water & Process Technologies.

OLI Systems is a company that provides commercial software with focus on electrolyte models and has recently developed an amine hydrochloride databank in a joint industry project (JIP) that provides predictions to the overhead system. Different papers were published with reference to this technology. As mentioned earlier, LENCKA *et al.* (2016) present an extension of the Mixed Solvent Model (MSE) to simulate the behavior of amines in the overhead system, calculating simultaneously solid-vapor, solid-liquid, and vapor-liquid equilibria, liquid-phase chemical equilibria, and caloric properties. SUN and FAN (2010) studied the effects of environment factors on the behavior of an NH_3-HCl-NH_4Cl-H_2O system. PATEL *et al.* (2012) evaluate the effects of basic species (as salt deposition and ionic dew point), including tramp amines. ARMISTEAD *et al.* (2015) illustrate the difference between water dew point, ionic dew point and salt point and present case studies in which electrolyte modeling was used as an important tool.

2.5 - Case Study

A CDU presented evidence of salt deposition as overhead condensers needed constant cleaning and maintenance services. To evaluate the possibility of salt deposition, information was gathered from the refinery routine analysis and simulations were carried.

Input data for two case studies are listed in Table 2.1. As discussed in section 3, operational conditions (pressure and temperature) in the tower top and in the accumulator drum, as well as accumulator drum outlet streams (boot water and naphtha) are presented. There are no data available for the off gas stream, because of the lack of routine analysis. This stream may be neglected tough, as its rate is extremely low because of the presence of a pre flash tower (where most of the light components are removed from the crude). The difference between cases 1 and 2 lies in the contaminant levels in the boot water. Case 1 represents the highest contaminant levels and case 2, the lowest. These are two extreme conditions and most of the time unit operates in intermediary conditions.

Table 2.1: Input data for two case studies.

Tower Overhead			**Naphtha**	
Temperature (°C)	115		Naphtha Product (std m3/d)	804.54
Pressure (abs) (kgf/cm^2)	1.27		Naphtha Reflux (std m3/d)	2705.73
Acumulator Drum			Distillation (D86) (°C)	
Temperature (°C)	60		0% vol	38.8
Pressure (abs) (kgf/cm^2)	1.18		5% vol	61.8
			10% vol	69.3
Boot water			20% vol	80.8
Boot water (m3/d)	203.20		30% vol	91
Case 1			50% vol	107.9
Chloride (mg/L)	**100**		70% vol	124.1
Ammonia (mg/L)	**70**		80% vol	133.2
Case 2			90% vol	144.5
Chloride (mg/L)	**40**		95% vol	154.1
Ammonia (mg/L)	**28**		100% vol	168.2

As chloride concentration ranges from 40 mg/L to 100 mg/L, ammonia (used as a neutralizer in this unit) also varies, ranging from 28 mg/L to 70 mg/L. The amount of ammonia may seem a little high at first. If only hydrochloric acid and ammonia were present in the system and an equimolar relation could be enough for neutralization, a molar ratio of 1 (1 mol NH_3/ 1 mol HCl) would be represented by a mass ratio of 0.47 (17.03/36.46). Even considering an excess of 20% on the neutralizer, as suggested by FEARNSIDE and MURPHY (1998), mass ratio could be 0.56. The actual mass ratio is 0.70 (28/40 or 70/100) and this larger amount of ammonia is needed because of presence of weak acids in the system.

Both cases were simulated using both simplified and rigorous methods. The simplified methods include salt deposition temperature and dew points predictions. Salt deposition temperature was estimated using data proposed by WU (1994) and dew points were estimated using Steam Tables. The same predictions were made with a rigorous electrolyte model, using commercial software OLI Studio (version 9.3.2). The objective is to compare results and discuss the differences between these two approaches.

The first step in using a simplified method for salt deposition prediction includes partial pressures calculations. There are different ways to calculate naphtha molar mass and therefore its molar flow (which is needed to calculate molar compositions). To avoid another variable in the comparison between simplified and rigorous methods, molar rates and therefore partial pressures calculated with the rigorous model were used as inputs for simplified methods. Results are presented in Table 2.2 and water and hydrocarbon condensing curves as a function of temperature from the electrolyte model are presented in Figures 2.4 and 2.5.

Condensing curves as a function of temperature from overhead systems shall be interpreted from right to left, the process sequence, as high temperatures represent tower top temperature and lower temperatures represent the accumulator drum. Presence of two liquid phases is represented with Liquid-1 as the aqueous phase and Liquid-2 the hydrocarbon-rich phase. In both cases there is no vapor phase at 60 °C, what is expected from input data (no off-gas data was used). On the other hand, there is a small liquid hydrocarbon phase at the tower top temperature (115 °C). If off-gas data was used, this would probably not have happened and at 115 °C there would only be a vapor phase, as expected.

Table 2.2: Results for the case studies.

Simplified Methods	**Case 1**	**Case 2**
Salt Deposition Temperature (°C)	109.8	97.7
Water Dew Point Temperature (°C)	105.9	105.9
Rigorous Method		
Salt Deposition Temperature (°C)	109.2	99.0
Ionic Dew Point Temperature (°C)	92.4	92.9
Water Dew Point Temperature (°C)	83.6	84.1

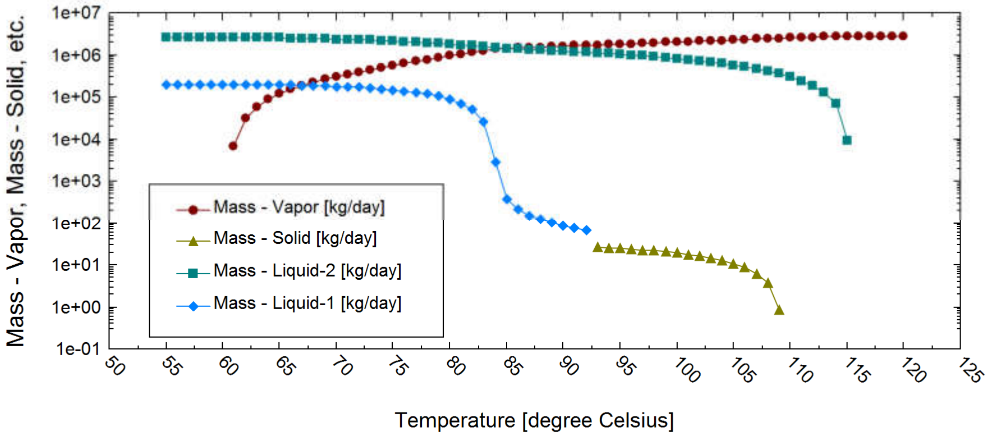

Figure 2.4: Rigorous electrolyte model results for case 1 - 100 mg/L Chlorides and 70 mg/L Ammonia.

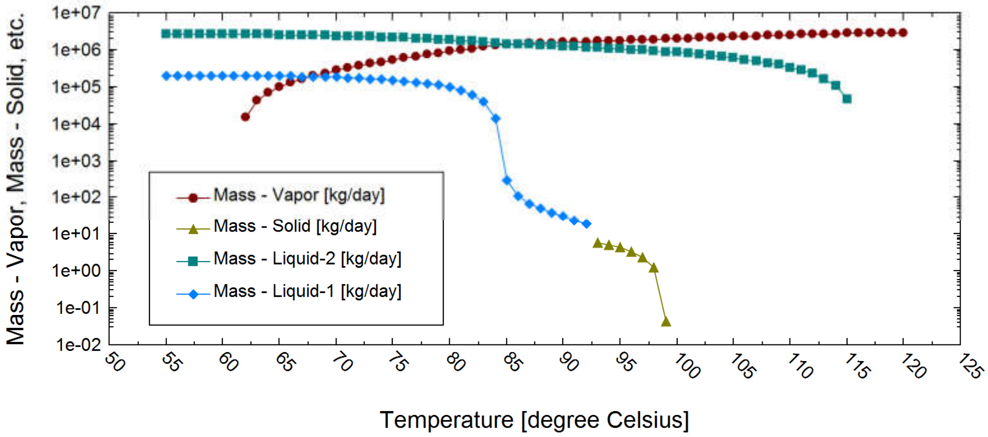

Figure 2.5: Rigorous electrolyte model results for case 2 - 40 mg/L Chlorides and 28 mg/L Ammonia.

There are two main comparisons that may be analyzed with these results: impact of contaminant levels and differences between methods. Impact of contaminant levels can be seen comparing cases 1 and 2 outputs with simplified methods. Solid deposition temperature is 109.8 °C in case 1 and 97.7 °C in case 2. With higher concentrations of chlorides and ammonia in case 1, a higher solid deposition temperature was already expected. Salt deposition temperatures show good agreement between simplified and rigorous methods, as the latest provides results of 109.2 °C and 99.0 °C for cases 1 and 2, respectively (differences lower than 1.5 °C). The first conclusion is that both methods are very similar for salt (NH_4Cl) deposition temperature prediction. It is important to detach that partial pressures were calculated using a rigorous simulator and so, depending on how these are predicted when using only simplified methods, poorer results can be expected.

The main issue lies on dew points calculations. As with simplified methods, water dew point is predicted with steam tables, and the result is the same for both cases, as the only input data are tower top pressure and water molar fraction. With a rigorous electrolyte model two distinct dew points are observed, as previously discussed in section 1: an ionic dew point and a water dew point. Ionic dew point is a result of the presence of electrolytes in the system and therefore can only be observed in a rigorous model. The ionic dew point and water dew point for case 1 are 92.4 °C and 83.6 °C, respectively, and for case 2, 92.9 °C and 84.1 °C. The little differences (0.5 °C) between cases 1 and 2 is a result of contaminant levels, showing that they do influence water condensation. In comparison with the simplified method either ionic or water dew point are extremely lower.

The problem in the differences between simplified and rigorous methods for water dew point prediction is the possible lead for erroneous conclusions. If this unit were evaluated only with simplified methods, the conclusions would be that with higher contaminants (case 1), salt deposition temperature is very close to the tower top temperature (115 °C) and what is worse, higher than water dew point and so dry salts deposition is a possible problem. For lower contaminant levels (case 2), salt deposition is approximately 17 °C lower than the tower top temperature and now with water dew point (105.9 °C) higher than salt deposition temperature (97.7 °C), any salts deposited will be rapidly dissolved. The conclusion is that operation with 40 mg/L chlorides and 28 mg/L ammonia is safe.

On the other hand, if this unit were evaluated with the rigorous method, the conclusions for the case with higher contaminants (case 1) would be the same, but not for the second one. For lower contaminant levels (case 2), salt deposition is 16 °C lower than the tower top temperature, but both ionic dew point and water dew point are still lower than salt deposition temperature, and so salts deposited are not dissolved by water. The conclusion is that operation with 40 mg/L chlorides and 28 mg/L ammonia may still be unsafe.

This case study shows that although simplified methods provide quick results, caution must be taken. Ammonium chloride deposition temperature is predicted by both methods with little difference. When it comes to other neutralizers tough, few data on amine hydrochlorides in the literature lead to the need for an electrolyte model. As for the water dew point, it was shown that steam tables do not provide precise results. NACE

(2009) and LORDO (2006) present examples of calculations comparison between steam tables and rigorous methods (dew point calculations with process simulators, as discussed before). In the example by NACE (2009) the difference is approximately 8°C and in the example by LORDO (2006), approximately 20 °C, confirming that predictions with steam tables are not recommended.

2.6 - Neutralizers

Ammonia has always been used as a neutralizer in overhead systems to avoid acid corrosion (NIU, 1984; LEHRER and EDMONDSON, 1993; FEARNSIDE and MURPHY, 1998; BRADEN *et al.*, 1998; Lack *et al.*, 2008), either in gas phase or in a solution. It is difficult to control flowrate when using gaseous ammonia, so a solution is preferred. Either way, ammonia presents a few disadvantages as a neutralizer: its high vapor-liquid equilibrium constant hinders it from neutralizing hydrochloric acid in the initial condensation point (allowing a low pH at dew point that may lead to acid corrosion) and it presents a considerable potential for salt deposition (ammonium chloride) above the dew point.

Amines have also been used as neutralizers for many years (NIU, 1984; LEHRER and EDMONDSON, 1993; BRADEN *et al.*, 1998; FEARNSIDE and MURPHY, 1998; PETERSEN AND LORDO, 2004; Lack *et al.*, 2008). Amines used as neutralizers usually present lower vapor-liquid equilibrium constants and lower boiling points, which favor acid neutralization in the initial condensation point. Salt deposition potential varies among the different amines used. To minimize deposition, a blend of amines can be used, because in ideal conditions, each amine will react separately with hydrochloric acid and each amine will have a low tendency for salt deposition (BRADEN *et al.*, 1998; FEARNSIDE and MURPHY, 1998; Lack *et al.*, 2008).

PETERSEN and LORDO (2004) discuss the most important physical and chemical properties of common neutralizers (ammonia and amines). Some of them are presented below:

- Boiling Point – as hydrochloric acid and other acids are present in vapor phase before water condensation, it is best that the neutralizer (usually in liquid phase outside the tower) evaporates after its injection, so that it reaches all acids before condensation. A neutralizer that remains in liquid phase may not encounter with acids, acting only to raise pH in the accumulator, but not preventing corrosion in the whole overhead system (pipeline and condensers). A quill or spray nozzle may be used to accelerate vaporization, as smaller droplets require less time to evaporate. According to FEARNSIDE and MURPHY (1998), neutralizers' boiling points should range between 93 °C (200 °F) and 149 °C (300 °F) and they must be thermally stable up to at least 204 °C (400 °F).

- Vapor-Liquid Equilibrium (VLE) Constant – vapor-liquid equilibrium constant of a substance is the ratio of concentrations in vapor phase and in liquid phase and it varies with temperature and with aqueous phase pH. During condensation in the overhead system, each substance will be distributed in both phases (vapor and aqueous) according to this constant. As hydrochloric acid presents a low VLE constant, the neutralizer should present a low constant as well, in order to neutralize it in aqueous phase, avoiding acid corrosion.

- Base Strength (ionization constant) – Strong acids and bases dissociate completely in water, while weak acids and bases dissociate partially. Although hydrochloric acid is a strong acid, weak acids (CO_2, H_2S and organic acids) are usually present in the system and lead to a buffered solution (it takes large amounts of acid or base to change pH), therefore the ionization constant of the neutralizer (that varies among the common neutralizers) plays an important role in the system.

- Salt deposition potential – each neutralizer (ammonia or amine) presents a different tendency to salt deposition and there are different ways to compare this tendency. PETERSEN and LORDO (2004) present a graphical comparison based on the product of partial pressures (as described in section 2), that can be plotted against temperature. It is shown that trimethylamine (TMA) and dimethylisopropanolamine (DMIPA) present lower tendencies, while ethylenediamine (EDA) and monoethanolamine (MEA) present higher tendencies for salt deposition. LEHRER and EDMONDSON (1993) propose a precipitation potential that is the ratio of the average vapor pressure of ammonium chloride and the vapor pressure of an amine hydrochloride. These averages are calculated in the range of 107 °C (225 °F) to 149 °C (300 °F) and the result is a deposition potential relative to ammonium chloride. Morpholine (MORPH), monoethanolamine (MEA) and ethylenediamine (EDA) present precipitation potentials, respectively, 2.5, 13 and 140 times higher than ammonia, which agrees with the information from PETERSEN and LORDO (2004). The comparison of various amines and their precipitation potential by LEHRER and EDMONDSON (1993) show that amines with lower ionizations constants (the focus of the patent) present lower precipitation potentials.

- Salt Melting Point – ammonium chloride and amine hydrochlorides are all soluble in water, so once there is an aqueous phase, all solids are dissolved. There must be a concern in areas with no aqueous phase (high temperatures, above water dew point). As these salts are hygroscopic and water propitiates under-deposit corrosion, these salts are corrosive. Although salts in solid phase bring operational issues (increase in pressure drop, lower heat transfer in case of deposition inside condensers, increase in filters maintenance, and so on) it has been observed (RUE and EDMONDSON, 2001; RECHTIEN and DUGGAN, 2006) that molten salts are more aggressive, leading to higher corrosion rates in case of deposition.

PAYNE (2012) states that the neutralizer is selected based on three primary factors: base strength, vapor-liquid equilibrium constant and salt deposition potential. According to PETERSEN and LORDO (2004), the ideal neutralizer should have a relatively low boiling point, a large ionization constant, a low VLE constant and a low salt deposition tendency. On the other hand, CLARIDA *et al.* (1997) propose the use of neutralizers with low base strength to minimize salt deposition, presenting successful case studies.

2.6.1 – Neutralizing Amines

A non-exhaustive list of amines commonly used in refineries is presented below (FEARNSIDE and MURPHY, 1998; LENCKA *et al.*, 2016):

- Primary alkyl amines: methylamine (MA), ethylamine (EA), propylamine (PA), butylamine (BA), cyclohexylamine (CHA), etc.
- Secondary alkyl amines: dimethylamine (DiMA), diethylamine (DiEA), ethylenediamine (EDA)
- Tertiary alkyl amines: trimethylamine (TMA)
- Alkoxy amines: 3-methoxypropylamine (MOPA)
- Cyclic ether amines: morpholine (MORPH), N-methylmorpholine (MMORPH), N-ethylmorpholine (EMORPH), etc.
- Alkanolamines: (mono)ethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), dimethylethanolamine (DMEA), dimethylisopropanolamine (DMIPA), diglycolamine (DGA), etc.

Many authors propose the use of different neutralizers that include single amines or multi-amine blends:

NIU (1984) mention that already used neutralizers include ammonia, morpholine (MORPH), cyclohexylamine (CHA), diethylaminoethanol, monoethanolamine (MEA) and ethylenediamine (EDA), among others, and proposes neutralizers composed of DMEA and/or DMIPA that raise pH in the initial condensation point with a relatively low tendency for salt deposition. DMIPA selectively neutralizes hydrochloric acid instead of hydrogen sulfide and therefore should not be used alone, but in conjunction with DMEA.

LEHRER and EDMONDSON (1993) mention that amines such as morpholine (MORPH) and methoxypropilamine (MOPA) have been used successfully in corrosion control. Highly basic amines (pKa>8) such as ethylenediamine (EDA) and monoethanolamine (MEA) have also been used, but they increase potential to salt deposition. To avoid this, they propose the use amines with pKa between 5 and 8, which include pyridines, quinolines, picolines and morphline derivatives (methylmorpholine - MMORPH and ethylmorpholine - EMORPH), among others. As an alternative, they propose a blend with a minor amount of highly basic amine with a low pKa amine. These blends minimize salt deposition issues and grant a buffering ability to improve pH control in the desired range.

LEHRER and EDMONDSON (1994) propose the use of tertiary amines with the formula R-NR'-R'', where R, R' and R'' are independently C1 to C6 straight branched or cyclic alkyl radicals or C2 to C6 alkoxyalkyl or C3 to C6 hydroxyalkyl radicals, with a low molecular weight per amine functionality. Examples include trimethylamine, triethylamine, N,N-dimethyl-N-(methoxypropyl) amine, N,N-dimethyl-N-(methoxyisopropyl) amine, among others. These amines are described to avoid acid corrosion while not allowing salt deposition. Examples of real refinery cases are presented with comparison of salting point of different amines. A decreasing order in salting point is observed in both examples: EDA > MEA > MOPA > DMEA > DMIPA > TMA, showing that the only tertiary amine (TMA) presents the lowest salting point.

According to FEARNSIDE and MURPHY (1998), suitable neutralization amines include morpholine (MORPH), methoxypropilamine (MOPA), ethylenediamine (EDA), monoethanolamine (MEA) and dimethylethanolamine (DMEA). A key element of this invention is the formulation of a blend to include a sufficient number of different amines to avoid inducing deposition of salts upstream of water dew point temperature.

According to LACK *et al.* (2008), morpholine (MORPH) and methoxypropilamine (MOPA) have been used successfully to control corrosion and highly basic amines as ethylenediamine (EDA), monoethanolamine (MEA) and hexamethylenediamine have also been used, but these usually result in salt deposition. The focus of this invention is also the use of single amines and/or formulation of amine blends to avoid salt deposition. Single amines include tert-butylamine, ethyldimethylamine or isopropyldimethylamine, while blends must consist of at least two from: dimethylethanolamine (DMEA), n-butylamine (BA), sec-butylamine, tert-butylamine, diethylamine, diethylethanolamine, dimethylamine, dimethylbutylamine, dimethylisopropanolamine, ethylamine (EA), ethyldimethylamine, n-ethylmorpholine (EMORPH), isopropylamine, isopropyldimethylamine, methylamine (MA), morpholine (MORPH), n-propylamine, trimethylamine (TMA).

LACK (2015) proposes the use of highly basic amines (pKa between 10.5 to about 12) because these form relatively weak salts in comparison with ammonia or other amines naturally present in the overhead system (tramp amines). While using these highly basic amines, the salts formed will not be as corrosive as those formed by ammonia and/or tramp amines. As chloride concentration is currently increasing, salt deposition may be unavoidable, so a choice for less corrosive salts is pointed as a solution. The highly basic amines presented by LACK (2015) include: dimethylamine, diethylamine, dipropylamine, diisopropylamine, di-n-butylamine, diisobutylamine, di-sec-butylamine, di-tert-butylamine, pyrrolidine, piperidine, and combinations thereof.

Although it would be of most interest, unfortunately there is not a single neutralizer (or still, a single blend) that is suitable for all situations (BRADEN *et al.*, 1998; PETERSEN and LORDO, 2004). The choice of neutralizer is affected by factors such as chloride concentration, overhead temperature and wash water availability, among others. As there are many variables involved, neutralizer should be chosen with the support of an electrolyte modeling tool (LACK, 2005).

2.6.2 – Tramp Amines / Amine Recycle

As discussed before, ammonia is naturally present in the overhead system and if an amine or an amine blend is used as a neutralizer on the overhead system, these will be obviously present in the system. Even so, it is usual to find other amines in the system. PAYNE (2012) defines tramp amines as any amines present in the system that were not intentionally added as a neutralizer. And though not desired and usually in low levels, they can have a considerable impact in the overhead system, especially in salt deposition. Even levels as low as 5 ppm may have a significant impact on salt point (PAYNE, 2012).

When focusing inside the crude unit battery limits, the sources of tramp amines include desalter wash water, cold wet reflux, slop oil and the crude (LACK, 2005; PAYNE, 2012) and when focusing outside the crude unit, the main sources are steam neutralizers, alkanolamine units, sour water strippers and H_2S scavengers (PAYNE, 2012).

Desalter wash water is the most common source. Overhead systems' boot waters are usually sent to sour water strippers (where ammonia is stripped but not most amines) before returning to the CDU or may be used directly as a desalter wash water. In either case, amines can cycle-up in the unit raising salt deposition potential. Slop oils may contain different amines, especially in refineries where slops receive material with gas scrubbing amines (with high potential for salt deposition) as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) (LACK, 2005). According to RECHTIEN and DUGGAN (2006) these gas scrubbing amines (especially MDEA) can undergo decomposition resulting in different amines such as triethanolamine (TEA), trimethylamine (TMA) and diethanolamine (DEA). Crudes may contain different amines, being the most common source the case of H_2S scavengers' by-products. Crudes with high H_2S content are usually treated with chemical additives named H_2S scavengers and its most traditional type is triazine; a nitrogen-based compound that reacts with H_2S and releases either monoethnolamine (MEA) or methylamine (MA) (GARCIA and LORDO, 2007).

When present in the system, these amines are partitioned between water and hydrocarbon liquid phases. Thus, a possible amine recycle may happen both in the desalter and in the overhead accumulator. In case of desalters, amines that should remain in the brine and leave the CDU may migrate to the oil phase and be carried to the distillation towers. In case of accumulators, amines that should remain in the boot water may migrate to the naphtha stream and if this naphtha is used as a cold reflux (which is the case of most CDUs), these amines may return to first trays in the tower. In both cases the result is an increase in risk of salt deposition.

It has been observed that pH plays an important role in amine partitioning. LACK (2005) presents a methodology to predict amine partitioning in both scenarios using electrolyte-based simulation. The effects of amines nature and structure and operational conditions on the partitioning are explored. Main observation is that an increase in aqueous phase pH leads to a higher oil partitioning of the amine. Therefore, a slightly acid pH may avoid amine oil partitioning, preventing amines into the desalted oil (from the brine) and preventing amine reflux to the tower top trays (from the overhead accumulator). PAYNE (2012) points out that amine partitioning to the hydrocarbon phase increases substantially if aqueous phase pH is higher than 5.5 and Garcia and LORDO (2007) present data on amine partitioning in a pH range of 6 to 8, confirming it.

Tramp amines and amine recycle should always be considered. Not only in the evaluation of the corrosion control program and troubleshooting but also in the choice of neutralizer. LACK (2005), for example, suggests that if the boot water is used as the desalter wash water, this must be taken into consideration in the choice of neutralizer. The presence of tramp amines may contribute to salt deposition, as reported by PATEL *et al.* (2012) that present a case study in which only 5 ppm MDEA and 3 ppm DEA increase salting point and therefore potentially increasing corrosion issues. SARPONG (2011) presents a case study of a unit where MEA is used as neutralizer. After evaluation with ionic model MEA-HCl salt deposition was confirmed and MEA was substituted for another neutralizer. Even after the switch to a new neutralizer, MEA was still present in the overhead (as a tramp amine). As the most probable source was the crude oil, brine water pH was reduced from the range of 7.5 to 8.5 to the range of 5.5 to 6.0 with the addition of a chemical product, to avoid MEA partitioning to the oil phase. There are cases where tramp amines levels are so high that are enough to neutralize all the acids in the overhead system resulting in no actual need for neutralizer injection, as reported by RECHTIEN and DUGGAN (2006). These cases reaffirm the need for attention to tramp amines.

In order to investigate the presence of tramp amines, there is no other option than collecting and analyzing unit samples. To minimize sampling effort in this investigation, focus should be on a few streams. The recommended water samples are: desalter wash water, brine, boot water, overhead wash water (if another source rather than the boot water is used) and the neutralizer. And the recommended hydrocarbon-rich samples are: crude oil, desalted oil and overhead reflux stream (stream used to control tower top temperature).

Although amine impacts are becoming more frequent, the detection of these species is not a common analysis in most refineries. Amine speciation in water samples is simpler than in hydrocarbon-rich samples and is usually done by Ion Cromatography (RECHTIEN and DUGGAN, 2006). ARMISTEAD *et al.* (2015) describe an investigation case in a refinery where amines where detected in an aqueous extract of a pumparound sample, indicating it is also possible to measure amines in liquid hydrocarbon. GARCIA and LORDO (2007) indicate a method consisting of an aqueous extraction followed by gas chromatography to detect MA or MEA in water and crude oil samples.

2.7 - Conclusions

Recent challenges in the oil and gas industry involve crude distillation unit overhead systems corrosion issues. Electrolyte modeling is a useful tool to aid in troubleshooting, unit design and revamping, providing information for selection and injection rate optimization of neutralizers, operational changes and unit configuration changes (either process configuration or metallurgical adaptation), among others.

Different computer-based models and their simplifying assumptions have been presented. A classification concerned by complexity is proposed and consists of: simplified calculations, including water dew point calculation with steam tables and solid deposition temperature prediction based on phase diagrams; and rigorous calculations, including water dew point calculation with commercial process simulators and electrolyte models (with different approaches for phase equilibria) to predict dew points, pH profile along condensation, solid deposition temperature and wash water rate, among others.

A case study with comparison between simplified calculations and a rigorous electrolyte model is presented, in which it is clear that simplified calculations, though quick and simple to use, may provide misleading results. Ammonium chloride deposition temperature is predicted by both methods with little difference. When it comes to other neutralizers tough, lack of data on amine hydrochlorides in the literature leads to the need for an electrolyte model. As for the water dew point, it was shown that steam tables do not provide precise results. This reassures the indication of rigorous electrolyte modeling for overhead system corrosion evaluation in most cases.

One of the most important applications of electrolyte modeling is the performance evaluation of different neutralizers. Ammonia, neutralizing amines or a blend of different neutralizers may be used to achieve optimal conditions to avoid corrosion. Most important properties include boiling point, vapor-liquid equilibrium constant, base strength, salt deposition potential and salt melting point.

Although a considerable effort has already been done in electrolyte modeling, there is still room for more development. Thermodynamic-based models already provide substantial results for the users, and still further development (new neutralizing amines or new blends for example) should be considered. One aspect that still needs a considerable effort for new development is prediction of corrosion rates, which requires kinetic-based models. In terms of application, it is already possible to evaluate corrosion phenomena in the overhead system, but recent events in refineries involve solids deposition inside crude distillation towers (in the first top trays or still in lower fractionation sections) and this is a challenge that can be explored with electrolyte modeling.

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Chapter 3 - Use of Electrolyte Modeling to Minimize Corrosion Impacts in Crude Distillation Units Overhead Systems

3.1 - Introduction

Crude Distillation Unit (CDU) overhead systems corrosion phenomena are inherent to the process and therefore it is necessary to learn how to deal with them, minimizing their negative impacts. Among different contaminants present in crude oils, inorganic salts (mainly sodium chloride, magnesium chloride and calcium chloride) are responsible for most corrosion problems in overhead systems. Although crude oils are treated with desalting systems, desalted crude oils still contain a minor amount of these salts, that hydrolyze under atmospheric furnace conditions (~385 °C) leading to formation of hydrochloric acid (HCl) (NACE, 2009).

Although not corrosive in gas phase (with no impacts to furnaces or distillation towers), HCl causes damage in lower temperature zones with presence of water (the case of overhead systems, where hydrocarbons and water from the distillation towers condense partially). Presence of HCl in water condensation leads to a low pH aqueous phase that causes acid corrosion. To avoid that, a neutralizer is usually added to the overhead system (either ammonia or neutralizing amines). However, in case there is an excess of chlorides or neutralizer (or both of them), there may be salt deposition, which leads to under-deposit corrosion.

Presence of chlorides in the overhead system is the main reason for acid corrosion and under-deposit corrosion. In the past years there has been an increase in chloride content of different crude oils, urging the need for a deeper understanding of corrosion phenomena. There has already been a wide debate in the literature about these phenomena (BAGDASARIAN *et al.*, 1996; BRADEN *et al.*, 1998; PETERSEN *et al.*, 2001; GIESBRECHT *et al.*, 2002; NACE, 2009). One of the ways to understand and learn how to deal with them is by use of computer-based modeling.

In the past 25 years, many advances were accomplished in overhead system modeling to minimize corrosion effects (WU, 1994; DUGGAN and RECHTIEN, 1998; VALENZUELA and DEWAN, 1999; LACK, 2005; LORDO, 2006; SUN and FAN, 2010; PATEL *et al.*, 2012; ARMISTEAD *et al.*, 2015; LENCKA *et al.*, 2016). While different models can be used to simulate CDUs overhead systems, rigorous electrolyte models (or ionic models) have proven to be the most appropriate (as described in Chapter 2).

Even with so many different papers and discussions on CDU electrolyte modeling, most of them consist of modeling description or case studies. Besides, many information about neutralizers and influence of operational conditions are described, but only few results are presented. The objective of this work is to show the use of an electrolyte model and investigate the influence of different process variables that influence corrosion phenomena, including:

- Neutralizer composition;
- Chloride concentration;
- Tower top temperature;
- Wash water rate.

3.2 - Software Verification

As described before (in Chapter 2), chemical suppliers usually provide technical assistance with electrolyte modeling along with chemical products. To the best of our knowledge, only one company provides commercial software including all four equilibria (vapor-liquid, liquid-liquid, solid-liquid and solid-vapor) for the species involved in overhead systems: hydrocarbons, water, HCl, CO_2, H_2S, NH_3, neutralizing amines and other weak acids, such as small chain organic acids. Different software with these capabilities are provided by OLI Systems, a company specialized in electrolyte thermodynamics. An amine hydrochloride databank has been developed in a joint industry project (JIP) with focus in overhead systems simulation to improve the model already developed by OLI Systems. Different papers were published with reference to this technology (SUN and FAN, 2010; PATEL *et al.*, 2012; ARMISTEAD *et al.*, 2015; LENCKA *et al.*, 2016). In this work, software OLI Studio (version 9.3.2) was used for all simulations.

It is important to stress that this is a strictly thermodynamic-based model, with assumption of equilibrium between species, with no aspects regarding kinetics or flow regimes. Model outputs include prediction of which phases (vapor, solid and/or liquid) are present and how species are distributed between these phases. It is possible then to obtain important parameters as: salt deposition temperature (also called salting point), dew points (ionic dew point and water dew point), pH at dew points and minimum wash water rate. Therefore, predictions of vapor-liquid equilibrium (directly related to acid corrosion) and vapor-solid equilibrium (directly related to under-deposit corrosion) are extremely important to the model.

Before using the electrolyte model with real CDUs overhead systems conditions, a verification was followed to ensure that the software was capable of handling these predictions: first, vapor-liquid equilibrium (VLE), and then, vapor-solid equilibrium (VSE). Ideally, experimental data with conditions of CDU overhead systems should be used e.g. an experiment with hydrocarbons, water, HCl and a neutralizer, but these are very hard to find. Instead, more simple systems were chosen.

3.2.1 – Vapor-Liquid Equilibrium (VLE)

At first, there was a search for ternary systems like H_2O-HCl-NH_3, but even for this case, HCl and NH_3 concentrations available were higher than those in overhead systems. As both electrolytes are present in boot water up to hundreds of mg/L, their concentrations should be approximately 0.01% wt for the system to be representative. With such low concentrations, only binary systems data were found (NH_3-H_2O and HCl-H_2O). There are only few data for neutralizing amines and so only NH_3 was used for this verification. Two references were used for each binary system.

3.2.1.1 – VLE for the NH_3-H_2O System

CLIFFORD and HUNTER (1933) present experimental data for total pressure and both liquid and vapor compositions (NH_3 concentration) for wide ranges of temperatures (60 °C to 150 °C) and concentrations (0% to 100% wt NH_3 in vapor phase). As only low concentrations were interesting for this work, a subset of these data were selected, as presented in Table 3.1, along with results from simulations in Oli Studio and the differences between both. As results in OLI Studio were conveniently expressed in molar fractions, original data for NH_3 in vapor phase presented in mass fraction (% wt) was converted to ease comparison.

Table 3.1: VLE verification of NH_3-H_2O system with data by CLIFFORD and HUNTER (1933).

Original Data				Converted Data	OLI Studio Results			Differences	
T (°C)	NH3 in L (% wt)	NH3 in V (% wt)	P (atm)	Y NH3 (mol/mol)	T (°C)	P (atm)	Y NH3 (mol/mol)	P	Y NH3 (mol/mol)
60	0.96	17.2	0.240	0.180	60	0.227	0.140	-6%	-22%
60	1.97	28.8	0.286	0.300	60	0.262	0.265	-8%	-12%
80	0.96	14.3	0.546	0.150	80	0.528	0.122	-3%	-19%
80	1.97	28.2	0.634	0.294	80	0.598	0.234	-6%	-20%
90	0.50	6.90	0.742	0.073	90	0.734	0.061	-1%	-16%
90	0.96	13.12	0.797	0.138	90	0.774	0.114	-3%	-17%
100	0.50	6.14	1.064	0.065	100	1.056	0.057	-1%	-12%
100	1.47	18.0	1.205	0.188	100	1.174	0.160	-3%	-15%

CLIFFORD and HUNTER (1933) (Extracted from Table 1)

Deviations for pressure range between 1% and 8% and were considered acceptable. For NH_3 concentration, deviations range between 12% and 22%. While experimental error is not presented for these specific data with low NH_3 content, it is expected that experiments with such low content present a considerable experimental error, as reported by PERRY *et al.* (1999), that present errors between 15% and 20% for HCl-H_2O data for temperatures as high as 110 °C and concentration of HCl as low as 6%. So, these results were also considered acceptable.

POLAK and LU (1975) present experimental data for temperature and both liquid and vapor compositions (NH_3 concentration) for two different pressures (14.69 psia and 65 psia) with concentrations ranges of approximately 0% to 40% wt NH_3 in vapor phase. As only atmospheric pressure (14.69 psia) was interesting for this work, a subset of these data were selected, as presented in Table 3.2, along with results from simulations in Oli Studio and the differences between both.

Table 3.2: VLE verification of NH_3-H_2O system with data by POLAK and LU (1975).

Original Data				OLI Studio Results		Differences	
NH3 in L (% wt)	NH3 in V (% wt)	T (°C)	Y NH3 (mol/mol)	T (°C)	Y NH3 (mol/mol)	T	Y NH3 (mol/mol)
0.097	1.280	99.65	0.0135	99.69	0.0113	0.04%	-17%
0.146	1.937	99.46	0.0205	99.55	0.0170	0.09%	-17%
0.276	3.739	98.94	0.0395	99.15	0.0320	0.21%	-19%
0.308	4.129	98.80	0.0436	99.05	0.0357	0.25%	-18%
0.368	5.188	98.08	0.0547	98.87	0.0426	0.80%	-22%
0.482	6.499	98.08	0.0685	98.51	0.0557	0.44%	-19%
0.634	8.284	97.51	0.0872	98.04	0.0729	0.55%	-16%
0.665	9.120	96.90	0.0960	97.95	0.0764	1.08%	-20%
1.199	15.80	94.84	0.1656	96.28	0.1353	1.52%	-18%
1.445	18.80	93.90	0.1967	95.50	0.1615	1.71%	-18%
1.950	24.02	92.00	0.2506	93.90	0.2136	2.07%	-15%
2.343	28.10	90.73	0.2925	92.65	0.2525	2.12%	-14%

POLAK and LU (1975) (Extracted from Table I)

Deviations for temperature range between 0.04% and 2.12% and were considered good results. For NH_3 concentration, deviations range between 14% and 22%, as in the first evaluation, which was considered acceptable.

3.2.1.2 – VLE for the HCl-H_2O System

FRITZ and FUGET (1956) present data for total pressure and HCl partial pressure for temperatures between 0 °C and 50 °C. From this temperature range, only higher temperatures (close to accumulator drum conditions) were considered interesting for this work. Again, a subset of these data were selected, as presented in Table 3.3, along with results from simulations in Oli Studio and the differences between both.

Table 3.3: VLE verification of HCl-H_2O system with data by FRITZ and FUGET (1956).

Original Data				Converted Data		OLI Studio Results				Differences	
T (°C)	HCl in L (% wt)	P_{HCl} (mmHg)	P (mmHg)	P_{HCl} (atm)	P (atm)	T (°C)	P (atm)	Y HCl (mol/mol)	P_{HCl} (atm)	P	P_{HCl}
40	0.0364	1.32E-07	55.324	1.74E-10	0.073	40	0.073	2.39E-09	1.74E-10	0.07%	0.15%
40	0.1820	2.79E-06	55.23	3.67E-09	0.073	40	0.073	5.01E-08	3.64E-09	0.10%	-0.80%
40	0.3633	1.01E-05	55.13	1.33E-08	0.073	40	0.073	1.83E-07	1.33E-08	0.11%	-0.08%
40	0.724	3.72E-05	54.94	4.89E-08	0.072	40	0.072	6.77E-07	4.90E-08	0.12%	0.14%
40	1.790	2.20E-04	54.35	2.89E-07	0.072	40	0.072	4.19E-06	3.00E-07	0.12%	3.74%
50	0.0364	3.35E-07	92.51	4.41E-10	0.122	50	0.122	3.58E-09	4.36E-10	0.09%	-1.17%
50	0.1820	7.00E-06	92.44	9.21E-09	0.122	50	0.122	7.47E-08	9.08E-09	0.03%	-1.38%
50	0.3633	2.52E-05	92.18	3.32E-08	0.121	50	0.121	2.72E-07	3.30E-08	0.14%	-0.37%
50	0.724	9.37E-05	91.88	1.23E-07	0.121	50	0.121	1.00E-06	1.22E-07	0.13%	-1.38%
50	1.790	5.41E-04	90.94	7.12E-07	0.120	50	0.120	6.19E-06	7.41E-07	0.08%	4.06%

FRITZ and FUGET (1956)

Deviations for pressure range between 0.03% and 0.14% and were considered very good results, as experimental error was estimated as 2%. For HCl partial pressures, deviations range between 0.08% and 4.06% and were considered also very good results.

SAKO *et al.* (1985) present vapor pressure data for different binary and ternary systems, including HCl-H_2O. Total pressure was measured for different HCl concentrations at temperatures between approximately 50 °C and 115 °C. From this data, only the lowest HCl concentration was considered interesting for this work. Data were selected, as presented in Table 3.4, along with results from simulations in Oli Studio and the differences between both. Deviations for pressure range between 3.3% and 5.2% and were considered good results.

Table 3.4: VLE verification of $HCl-H_2O$ system with data by SAKO *et al.* (1985).

Original Data			Converted Data		OLI Results	Difference
T (K)	P (kPa)	C_{HCl} (mol/kg)	T (°C)	P (atm)	P (atm)	P
323.4	12.06	1.262	50.3	0.119	0.113	-5.2%
333.0	18.93		59.9	0.187	0.179	-4.2%
344.5	31.55		71.4	0.311	0.299	-4.0%
354.1	46.87		81.0	0.463	0.446	-3.6%
364.6	70.50		91.5	0.696	0.671	-3.5%
372.0	92.62		98.9	0.914	0.882	-3.5%
376.9	110.23		103.8	1.0879	1.0497	-3.5%
383.6	138.47		110.5	1.3666	1.3208	-3.3%
387.5	157.57		114.4	1.5551	1.5036	-3.3%

SAKO et al. (1985)
(Extracted from Table I)

For all vapor-liquid evaluations, results were considered acceptable. Pressures and temperatures were predicted with low deviations. While HCl partial pressures was predicted with very low deviations, NH_3 concentration predictions present higher deviations, but still acceptable values.

3.2.2 – Vapor-Solid Equilibrium (VSE)

As for the VLE cases, there are only few data for neutralizing amines hydrochlorides and so only ammonium chloride was used for this verification. Although there are different data for ammonium chloride data, previous studies show that data by WU (1994) that was already mentioned by so many authors, can be used as a reference. WU (1994) presents equations for prediction of ammonium chloride equilibrium temperature based on HCl and NH_3 partial pressures.

A case base was defined for the comparison, with pressure equal to 1 bar (absolute) and water flowrate of 10000 kg/h (as if it were boot water from the accumulator drum). Different concentrations for HCl and NH_3 in boot water were tested, ranging from 10 mg/L up to 300 mg/L. For each case, both HCl and NH_3 were considered with equal values, just for simplification. With concentrations, water flowrate and total pressure, partial pressures were calculated and equations provided by WU (1994) were used for equilibrium temperature calculation. Same conditions were then used in OLI Studio for estimation of temperatures were solid phase is present. Results are presented in Table 3.5. Deviations range between 1.0% and 2.1% and were considered very good results.

Table 3.5: VSE verification of NH_4Cl with data by WU (1994).

HCl concentration (mg/L)	10	25	50	75	100	125	150	200	250	300
NH_3 concentration (mg/L)	10	25	50	75	100	125	150	200	250	300
T (WU, 1994) (°C)	95.3	107.3	116.9	122.8	127.1	130.5	133.3	137.9	141.5	144.5
T (OLI Studio) (°C)	93.3	105.5	115.2	121.2	125.5	128.9	131.8	136.4	140.0	143.0
Deviation (%)	-2.1	-1.7	-1.5	-1.3	-1.3	-1.2	-1.1	-1.1	-1.1	-1.0

For both VLE and VSE evaluations, OLI Studio was proven to produce results compatible with experimental observation and was therefore used to investigate CDUs overhead systems in the following investigation.

3.3 - Investigation of Process Variables Influence on Overhead System Corrosion

A real average crude distillation unit with 10.500 m3/d (approximately 66000 bbl/d) feed was used as a base case for this study. The unit contains a two-stage desalting system and a typical atmospheric tower with a single overhead accumulator drum. Tower top temperature and accumulator drum are, respectively, 100 °C (212 °F) and 45 °C (113 °F), chloride concentration is typically around 100 mg/L and ammonia is used as a neutralizer. Unit data necessary for the electrolyte model were available from a previous study with a typical process simulator and are listed in Table 3.6. Pseudocomponents properties are listed in the appendix.

Table 3.6: Input data for the base case.

Operational Conditions			**Compositions (mole %)**	**Naphtha**	**Off-Gas**
			Methane	4.212E-04	4.187E-02
Tower Top			Ethane	4.614E-03	1.117E-01
Temperature (°C)	100		Propene	5.324E-03	4.873E-02
Pressure (abs) (bar)	1.95		Propane	3.318E-02	2.617E-01
			i-Butane	1.643E-02	5.375E-02
Acumulator Drum			n-Butane	3.971E-02	9.704E-02
Temperature (°C)	45		i-Pentane	5.067E-02	5.274E-02
Pressure (abs) (bar)	1.7		n-Pentane	1.531E-01	1.255E-01
			H2O	1.581E-03	5.646E-02
Accumulator Drum Outlet Streams			Hypo40*	1.364E-02	1.046E-02
			Hypo50*	3.237E-02	2.026E-02
Naphtha			Hypo60*	7.255E-02	3.243E-02
Naphtha Product Rate (std m3/h)	39.81		Hypo70*	9.118E-02	2.981E-02
Naphtha Reflux Rate (std m3/h)	224.53		Hypo80*	8.535E-02	2.050E-02
Total Naphtha Rate (std m3/h)	264.34		Hypo90*	7.587E-02	1.261E-02
			Hypo100*	7.668E-02	9.047E-03
Off-Gas			Hypo110*	8.414E-02	7.161E-03
Off-Gas Rate (std m3/h)	5.71		Hypo120*	8.323E-02	5.057E-03
			Hypo130*	5.973E-02	2.553E-03
Boot water			Hypo140*	1.792E-02	5.419E-04
Boot Water Rate (m3/h)	11.10		Hypo150*	2.073E-03	4.207E-05
			Hypo160*	2.186E-04	3.086E-06
Boot Water Composition			Hypo170*	2.412E-05	2.376E-07
Chloride (mg/L)	100		Hypo180*	2.024E-06	1.303E-08
H_2S (mg/L)	20		Hypo190*	2.001E-07	8.721E-10
CO_2 (mg/L)	20		Hypo200*	1.650E-08	0.000E+00
Acetic Acid (mg/L)	20		Hypo210*	1.362E-09	0.000E+00

The investigation is comprised of four different process variables that may influence overhead system corrosion:

- Neutralizer composition – Neutralizer selection is essential to control corrosion and changing neutralizer composition is an easy measure as it does not involve operational changes and usually does not require additional investments (cost usually depends only on neutralizer composition).

In this work, different neutralizers, including ammonia (the actual neutralizer), amines and blends were evaluated.

- Chloride concentration – Chloride concentration should always be as low as possible and its reduction may be achieved by desalter optimization, crude selection or caustic (NaOH) injection. Although desalter optimization may not include costs, crude selection and caustic injection usually have negative economic impacts.

An alternative concentration of 50 mg/L (a 50% reduction from the original value) was considered.

- Tower top temperature – Tower top temperature is an important aspect as it is directly related to salt deposition temperature. Increasing this temperature is a common solution, but is usually cost-prohibitive as lower overhead temperatures lead to higher production of distillates.

An alternative temperature of 130 °C (266 °F) was evaluated.

- Wash water rate – Wash water rate is always an option to avoid salt deposition and to minimize acid corrosion. If the unit is not designed with this facility, costs involved in this solution are usually high as they may involve additional piping, spray nozzle (highly recommended) and new pumping systems.

Wash water (that is not actually available at the unit) was evaluated, including two different flowrates.

As many process variables are involved, a methodology is proposed for the investigation, regarding the following steps:

1 – Definition of a base case with no neutralizer;

2 – Neutralizer composition – Evaluation of different neutralizer compositions using base case. Operational conditions include: boot water chloride concentration of 100 mg/L, tower top temperature of 100 °C and no wash water;

Three neutralizer compositions were chosen from Step 2 and then used in following evaluations:

3 – Chloride concentration – Evaluation of chloride reduction from 100 mg/L to 50 mg/L;

4 – Tower top temperature – Evaluation of overhead temperature increase from 100 °C to 130 °C;

5 – Wash water rate – Evaluation of two different wash water flowrates.

3.3.1 – Base case with no neutralizer

A model was created with input data from Table 3.6 and water and hydrocarbon condensing curves as a function of temperature (mass flows profiles) are presented in Figure 3.1. As temperatures range from 45 °C to 100 °C, profiles are plotted from 40 °C to 105 °C. Condensing curves from overhead systems shall be interpreted from right to left, following process sequence, as high temperatures indicate tower top conditions and lower temperatures indicate accumulator drum conditions. Each phase mass flow (vapor, liquid or solid) is represented with its own profile as a function of temperature, with aqueous phase represented as Liquid-1 and hydrocarbon-rich phase as Liquid-2. Aqueous phase pH is also presented.

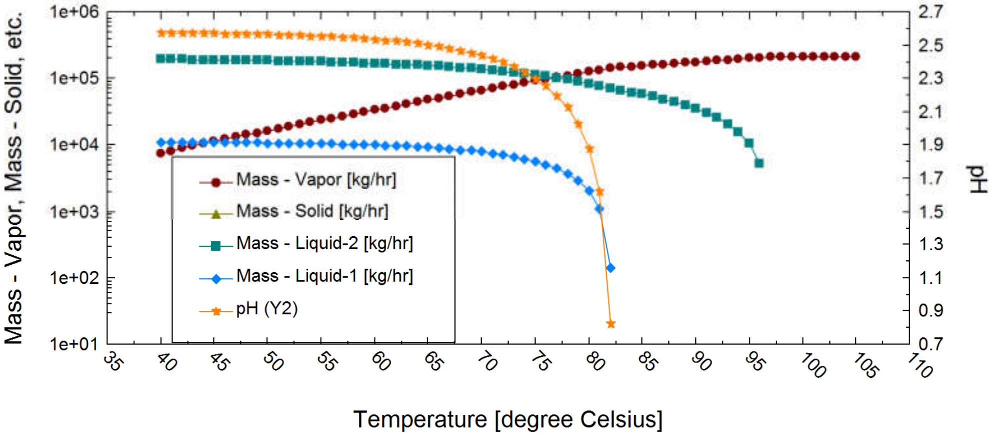

Figure 3.1: Base Case with no Neutralizer – Overhead Temperature 100 °C – 100 mg/L Chlorides.

Presence of solid phase is impossible for this first case because of absence of neutralizer. All species are in vapor phase at tower top temperature (100 °C) and hydrocarbons condensation begins at 96.9 °C and water at 82.4 °C. pH values range from 0.32 at water dew point temperature (82.4 °C) to 2.57 at accumulator drum temperature (45 °C). Profiles in Figure 3.1 are plotted with an interval of 1 °C so that it is easier to visualize results and this is why dew points for hydrocarbon and water appear to be 96 °C and 82 °C. For more precise results a detailed temperature survey (with a 0.1 °C interval) may be done in the region of interest.

Besides hydrocarbons and water, only acids are present in this first case, which explains such low pH values. Hydrochloric acid is the main contaminant with 100 mg/L and other weak species that are usually present in overhead systems were added to the model. When these weak acids are not taken into consideration, pH is extremely sensible to temperatures variations (especially when neutralizers are present). As weak acids do not dissociate completely in aqueous phases, their presence propitiate a buffering condition that reduces pH variations. In this study, hydrogen sulfide (H_2S), carbon dioxide (CO_2) and acetic acid were considered. These acids are not commonly measured in routine analysis and using a single value for the three of them was an option to reduce the number of variables in the investigation. The amounts of weak acids are the same in all cases and each one represents 20% of the chloride mass of this base case (100 mg/L HCl in boot water). Each weak acid amount is inputted as 20 mg/L in boot water (as in Table 3.6), but these are then distributed between vapor and liquid phases, and final concentration in boot water varies depending on accumulator drum operational conditions and pH.

Beginning of condensation is the most critical region as pH values are usually low with probable acid corrosion. FEARNSIDE and MURPHY (1998) and DION *et al.* (2012) describe it as initial condensation point (ICP) and many authors have proposed different criteria for pH values. DUGGAN and RECHTIEN (1998) indicate that 4.0 is a minimum value (considering systems with carbon steel and use of filmer) and LEHRER and EDMONDSON (1993) suggest 4.5 and, preferably, 5.0. As dew point may be defined with a liquid phase amount as small as calculation precision permits, a higher percentage of condensed water may be more representative as suggested by LORDO (2006) and BRADEN *et al.* (1998). BRADEN *et al.* (1998) suggest that a minimum percentage of 5% water condensed is an adequate criterion and that pH at this point must be equal or greater than 5.0.

In this base case 5% of boot water flowrate is condensed at 81.5 °C (which is very close to the water dew point - 82.4 °C) and pH at this temperature is 1.37. These reference values will be used in the following evaluations. Water dew point is considered as the temperature where 5% of boot water flowrate has already condensed with a minimum pH of 5.0.

3.3.2 – Influence of Neutralizer Composition

Many different neutralizers can be used in CDUs overhead systems. Ammonia (NH_3) has always been used in overhead systems (NIU, 1984; LEHRER and EDMONDSON, 1993; FEARNSIDE and MURPHY, 1998; BRADEN *et al.*, 1998; LACK *et al.*, 2008). A common sense in literature is that it presents a few disadvantages as a neutralizer: difficulty to neutralize hydrochloric acid in the initial condensation point and potential for salt deposition (ammonium chloride) above water dew point.

Besides NH_3, neutralizing amines have also been used as neutralizers for many years (NIU, 1984; LEHRER and EDMONDSON, 1993; FEARNSIDE and MURPHY, 1998; BRADEN *et al.*, 1998; PETERSEN AND LORDO, 2004; LACK *et al.*, 2008). Amines are usually described with a higher neutralization capacity in the initial condensation when comparing to NH_3, while salt deposition potential varies. If salt deposition is a real concern, a blend of amines can be used. Amines will ideally react separately with hydrochloric acid and each amine will present a low tendency for salt deposition (FEARNSIDE and MURPHY, 1998; BRADEN *et al.*, 1998; LACK *et al.*, 2008).

To investigate their influence on overhead system corrosion, different neutralizer compositions were tested. The model with no neutralizer was the base for all neutralizers evaluations. As different neutralizers have different neutralizing potentials (LEHRER and EDMONDSON, 1993; PETERSEN AND LORDO, 2004), using the same amount of neutralizer would not be a fair comparison. Methodology used was based on what is done in practice in real crude distillation units, where neutralizer is added to the overhead system and pH value is controlled in the accumulator drum, usually between 5.5 and 6.5 (DUGGAN and RECHTIEN, 1998; FEARNSIDE and MURPHY, 1998).

To compare different neutralizers, each one was added in a certain amount to reach pH equal to 6.0 (approximately) in the accumulator drum. As pH varies significantly with the amount of neutralizer, values between 5.9 and 6.1 were considered valid. According to FEARNSIDE and MURPHY (1998), minimum neutralizer rate is the stoichiometric rate required to neutralize the hydrochloric acid, but the actual neutralizer rate should be 1.05 to 1.20 the stoichiometric rate. Using this suggestion, first value adopted for neutralizer rate was a stoichiometric rate (equimolar) to hydrochloric acid and then this rate was altered in an iterative process until pH 6.0 was reached.

Results from the simulations consist basically of dew points with their pH values as references to acid corrosion and salt deposition temperature (salting point) as reference to under-deposit corrosion. As discussed before, initial condensation pH is most critical. In this work, suggestion by BRADEN *et al.* (1998) that pH for 5% condensed water must be higher than 5.0 is followed.

As for salting point, different criteria are proposed. DUGGAN and RECHTIEN (1998) suggest that a salting point higher than system temperature indicates salt deposition. NACE (2009) indicates that tower top temperature is usually 14 °C (25 °F) higher than salting point and that salting point is normally suggested to be 14 °C (25 °F) lower than water dew point. ARMISTEAD *et al.* (2015) mention that ionic dew point should be at least 14 °C (25 °F) lower than tower top temperature. All these criteria were observed in the following evaluations.

3.3.2.1 – Neutralizers evaluated

As mentioned before, NH_3 has always been used as a neutralizer and was therefore the first choice for a neutralizer evaluation. There are several amines proposed in the literature and also different amine-blends. The choice of amines was based on the most common neutralizing amines and blends compositions were based on results of pure neutralizers evaluations.

Ethylenediamine (EDA), Monoethanolamine (MEA), Methoxypropilamine (MOPA), Dimethylethanolamine (DMEA) and Morpholine (MORPH) are usually mentioned as common neutralizers (NIU, 1984; LEHRER and EDMONDSON, 1993; FEARNSIDE and MURPHY, 1998; LACK *et al.*, 2008) and were therefore selected for the evaluation. EDA and MEA are mentioned as amines with high potential for salt deposition (LEHRER and EDMONDSON, 1993; LACK *et al.*, 2008), and so this was expected to be seen with this evaluation.

Methylamine (MA) and trimethylamine (TMA) were also selected for different reasons. MA is a by-product of H_2S scavengers (as MEA) (GARCIA and LORDO, 2007) and it is commonly present as a tramp amine in overhead systems. TMA is supposed to have one of the lowest salt deposition potentials (LEHRER AND EDMONDSON, 1994; PETERSEN AND LORDO, 2004).

Based on this, the following neutralizers were chosen for the evaluation: ammonia (NH_3), ethylenediamine (EDA), monoethanolamine (MEA), methoxypropilamine (MOPA), dimethylethanolamine (DMEA), morpholine (MORPH), methylamine (MA) and trimethylamine (TMA).

Ammonia (NH_3)

Results for ammonia evaluation are presented in Table 3.7 and in Figure 3.2, including all steps from the iterative process until pH 6.0 was reached. At first, a stoichiometric molar flow was simulated (Neutralizer/HCl ratio equal to 1.0). At high temperatures, all species are in vapor phase, as expected, but a solid phase (ammonium chloride) is present below 106 °C. This indicates that salt deposition temperature (salting point) in this case is 106 °C. As tower top temperature is 100 °C, it does not mean that there will be salt deposition inside the tower. The composition in the model contains all the ammonia injected as neutralizer, what happens usually in the overhead line before condensers. This result shows that as soon as ammonia is injected and encounters vapor stream at 100 °C, solid ammonium chloride may deposit. Presence of salt leads to an ionic dew point at 89 °C with a pH value of 2.25, which is extremely low. As discussed before, concerns about acid corrosion are evaluated here with a higher percentage of water (5% of boot water flow rate), and this point is considered as water dew point. Water dew point for this case is 81.6 °C (practically the same as the base case) and pH at this temperature is 3.31, still lower than 5.0. Although these results indicate probability of acid and under-deposit corrosion, it is most important to note that accumulator drum pH (4.35) is below the control range, and therefore this is not a probable situation in a refinery.

Ammonia flow rate was then altered to reach pH 6.0 in boot water (45 °C). A first increase of 10% is presented, where pH was 5.82, and then lower increments were simulated with 11% and 12% excess ammonia, where pH values are, respectively, 6.04 and 6.29. The case with 11% excess ammonia was considered the final result for evaluation of ammonia as a single neutralizer.

Table 3.7: Results for Ammonia Evaluation.

Neutralizer	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH_3	1	106	89	2.25	3.31	4.35
	1.10	107	89	2.35	4.33	5.82
	1.11	**107**	**89**	**2.36**	**4.37**	**6.04**
	1.12	107	89	2.37	4.41	6.29

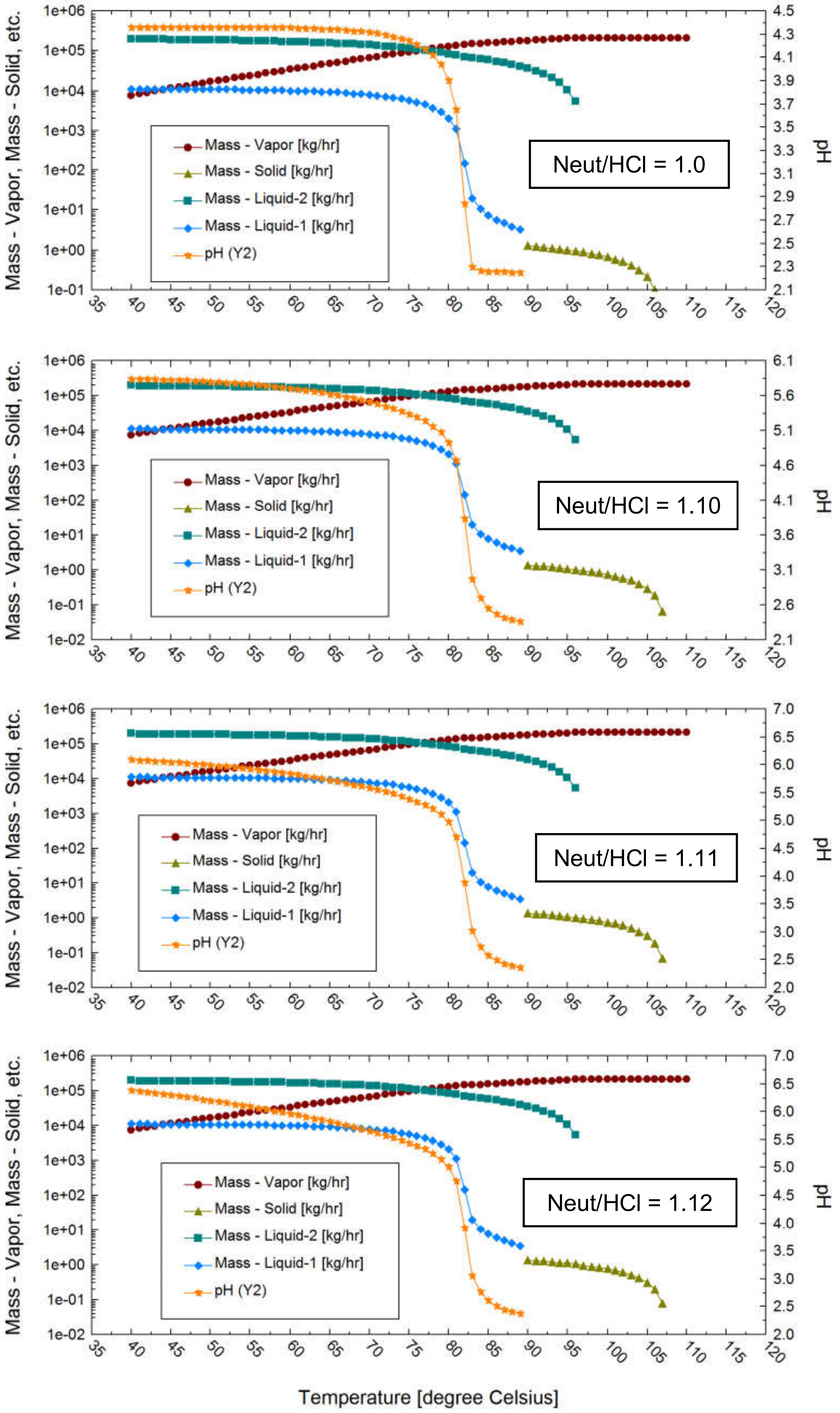

Figure 3.2: Neutralizer: NH_3 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

In comparison to the first stoichiometric case, a higher amount of ammonia was expected to increase salting point and pH values, and this was confirmed. The case with 11% excess ammonia represents a likely situation to be found in the refinery, where ammonia is used as neutralizer. Salting point is 107 °C and therefore higher than tower top temperature (100 °C), indicating probable salt deposition. Solid phase deposition rate is highest at 90 °C and after that, aqueous phase is sufficient to dissolve ammonium chloride. Presence of salt leads to the existence of an ionic dew point at 89 °C, at which pH is 2.36. Difference between tower top temperature and ionic dew point is 11 °C, lower than the 14 °C recommended by ARMISTEAD *et al.* (2015). Water dew point is 81.6 °C and pH at this temperature is 4.37, still lower than 5.0. These results imply that, considering the criteria chosen, ammonia is not a proper choice as a single neutralizer for this case.

These results do not mean that solid deposition and acid corrosion are actual problems in this refinery. While analyzing electrolyte model results it is necessary to remember that there are several simplifying assumptions in electrolyte modeling, including thermodynamic equilibrium, and in real systems a multiphase flow with high velocities is cooled down and equilibrium is not necessarily reached in each temperature. According to BRADEN *et al.* (1998), deposition is almost never as severe as predicted. Nevertheless, the objective of this work is not a case study of the actual unit, but rather an investigation of variables important to the overhead systems.

Neutralizing Amines

As ammonia was the first neutralizer evaluated, all profiles for each step were presented. For all other neutralizers, a table with all steps is presented, but only final profiles are shown. All results from iterative processes to reach pH equal to 6.0 in accumulator drum are presented in Table 3.8, in which ammonia results are included for comparative reasons. Each amine evaluation is discussed separately below.

Table 3.8: Results for Ammonia and Neutralizing Amines Evaluations.

Neutralizer	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH_3	1	106	89	2.25	3.31	4.35
	1.10	107	89	2.35	4.33	5.82
	1.11	**107**	**89**	**2.36**	**4.37**	**6.04**
	1.12	107	89	2.37	4.41	6.29
EDA	1	181	109	5.64	6.76	7.24
	0.80	180	107	5.58	6.2	6.61
	0.7	180	105	5.42	5.92	6.27
	0.65	**179**	**103**	**5.46**	**5.75**	**6.06**
	0.6	179	101	5.4	5.53	5.76
MEA	1	140	140	3.43	4.19	4.36
	1.05	140	140	3.44	5.86	5.06
	1.10	141	141	3.45	6.23	5.87
	1.105	**141**	**141**	**3.45**	**6.26**	**6.00**
	1.11	141	141	3.45	6.29	6.17
	1.125	141	141	3.45	6.36	6.77
	1.15	141	141	3.46	6.47	7.30
MOPA	1	123	123	3.16	3.99	4.36
	1.10	123	123	3.18	5.70	5.88
	1.105	**123**	**123**	**3.19**	**5.72**	**6.01**
	1.11	123	123	3.19	5.74	6.18
	1.125	124	124	3.19	5.80	6.82
	1.15	124	124	3.19	5.88	7.36
DMEA	1	117	117	3.37	3.92	4.35
	1.05	117	117	3.38	5.25	5.06
	1.10	118	118	3.39	5.55	5.82
	1.11	**118**	**118**	**3.39**	**5.59**	**6.05**
	1.125	118	118	3.39	5.65	6.42
MORPH	1	121	97	3.36	3.70	4.35
	1.10	122	97	3.44	5.11	5.73
	1.11	122	97	3.45	5.15	5.89
	1.12	**122**	**97**	**3.46**	**5.19**	**6.05**
	1.125	122	97	3.47	5.20	6.13
MA	1	114	108	2.93	3.92	4.36
	1.10	115	108	2.97	5.55	5.89
	1.105	**115**	**108**	**2.97**	**5.57**	**6.05**
TMA	1	100	100	2.37	3.32	4.35
	1.10	100	100	2.39	4.35	5.75
	1.11	100	100	2.40	4.39	5.92
	1.115	**100**	**100**	**2.40**	**4.41**	**6.01**
	1.12	100	100	2.40	4.42	6.10

Ethylenediamine (EDA)

Results for EDA evaluation are presented in Table 3.8 and in Figure 3.3. At first, a stoichiometric molar flow was simulated and as EDA is a diamine (each molecule reacts with two HCl molecules), a reduction in neutralizer flow rate was needed. Molar ratio of 0.65 was considered an optimal result with boot water pH of 6.06. A solid phase is already present at high temperatures, what indicates that salting point is higher than 110 °C. Another temperature survey indicates that solid deposition starts at 179 °C, confirming the high tendency of salt deposition for EDA (LEHRER AND EDMONDSON, 1993; LACK *et al.*, 2008; PETERSEN AND LORDO, 2004).

On the other hand, both water dew point pH and ionic dew point pH are higher than 5.0, indicating that EDA is really excellent for dew point neutralization and avoiding acid corrosion. pH profile is totally different from what was seen with ammonia. When aqueous phase and solid phase are both present, pH lowers with temperature decrease, and after salts are dissolved, pH rises in two different patterns, before and after water dew point. Significant pH variation with temperatures between 40 °C and 80 °C means that 0.65 may not be a precise result for the molar ratio, but the conclusion of high tendency for salt deposition is valid for all steps.

Presence of salt leads to an ionic dew point higher than tower top temperature (100 °C), indicating probable salt deposition. Salt amount is so high that even the presence of aqueous phase (below ionic dew point) is not enough to dissolve all the salts. These results also imply that EDA is not a proper choice as a single neutralizer for this case.

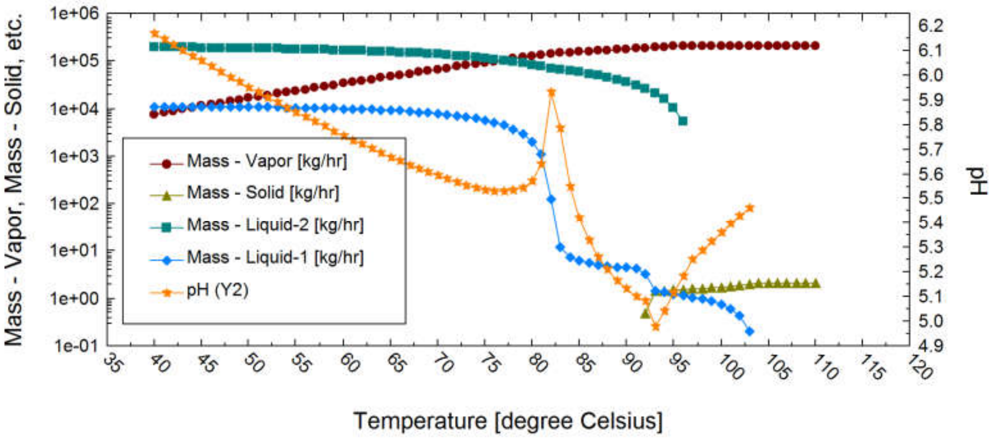

Figure 3.3: Neutralizer: EDA – Neutralizer/HCl molar ratio of 0.65 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

Monoethanolamine (MEA)

Results for MEA evaluation are presented in Table 3.8 and in Figure 3.4. Preliminary results showed that besides vapor phase, a liquid phase as also present at 110 °C, and a further investigation (temperatures higher than 110 °C) indicated begin of aqueous phase at 141 °C, composed mostly (>97% wt) of MEA and Chloride. This indicates that MEA hydrochloride is not dissolved, but rather in its liquid form (in other words, a molten salt). To confirm this, another investigation followed, based on a procedure suggested by ARMISTEAD *et al.* (2015). Another case was run with the number of water, hydrocarbons and weak acids mols substituted by an inert (Nitrogen in this case). In this new case, presented in Figure 3.5, amine hydrochloride salt behavior can be visualized despite condensation (water or hydrocarbon). Salting point in this case is 140 °C (slightly different from the complete case with all species) and MEA hydrochloride melting point is 90.5°C and therefore it appears as a liquid phase in the complete case with all species. Even so, it confirms the high tendency of salt deposition for MEA (LEHRER AND EDMONDSON, 1993; LACK *et al.*, 2008; PETERSEN AND LORDO, 2004). On the other hand, although ionic dew point pH (3.45) is below 4.0, water dew point pH (6.26) is much higher than 5.0, indicating that MEA may also be a good option to avoid acid corrosion.

As for EDA, presence of salt leads to an ionic dew point higher than tower top temperature (100 °C), also indicating probable salt deposition, showing that MEA is also not a proper choice as a single neutralizer for this case.

It is important to detach that evaluation with an inert is a good way to visualize physical state of the salt and its behavior without condensation, but salting point may be different from the complete case. In this case, salting point from the inert evaluation was 140 °C and actual ionic dew point in the complete case (with all species) was 141 °C. As ionic dew point is present by the presence of salt, it may also be considered as the salting point (especially for cases where no solid phase is present before ionic dew point).

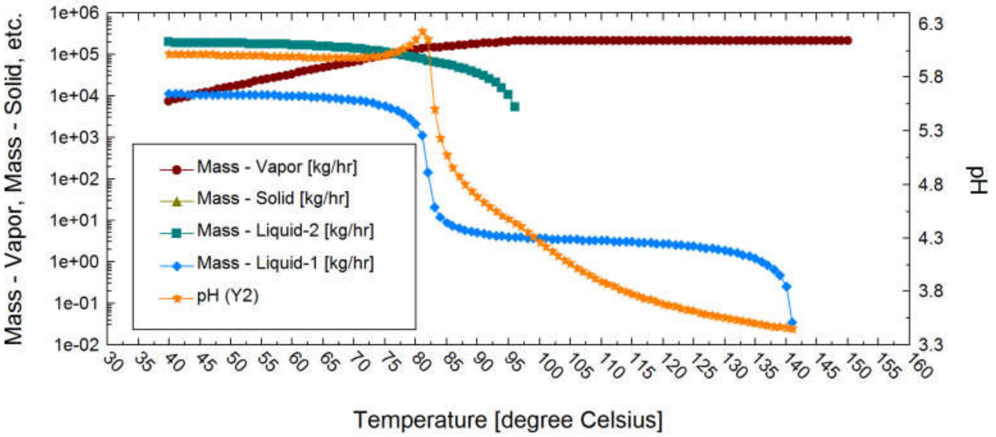

Figure 3.4: Neutralizer: MEA – Neutralizer/HCl molar ratio of 1.105 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

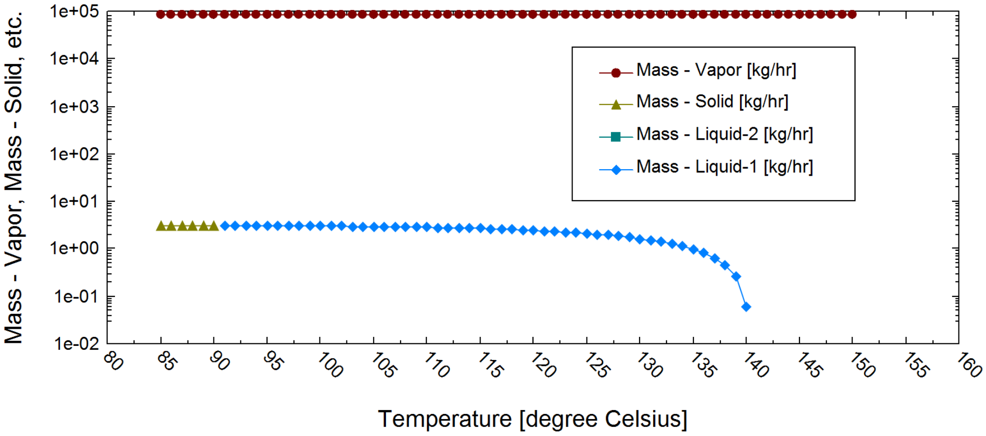

Figure 3.5: MEA Hydrochloride behavior in the presence of an inert.

Methoxypropilamine (MOPA)

Results for MOPA evaluation are presented in Table 3.8 and in Figure 3.6. Profiles are similar to MEA evaluation, including a liquid phase at high temperatures (higher than 110 °C), leading to a further investigation with an inert (Figure 3.7). An aqueous phase appears at 123 °C, composed mostly (>93% wt) of MOPA and Chloride, indicating that MOPA hydrochloride is also a molten salt with melting point of 101.3 °C. As for MEA, although ionic dew point pH (3.19) is below 4.0, water dew point pH (5.72) is much higher than 5.0, indicating that MOPA may also be a good option to avoid acid corrosion.

As for EDA and MEA, presence of salt leads to an ionic dew point higher than tower top temperature (100 °C), indicating probable salt deposition, showing that MOPA is also not a proper choice as a single neutralizer for this case.

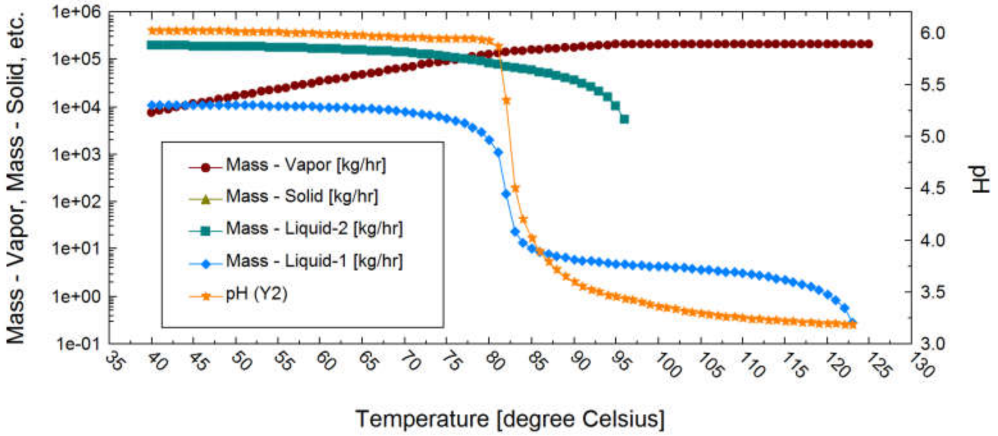

Figure 3.6: Neutralizer: MOPA – Neutralizer/HCl molar ratio of 1.105 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

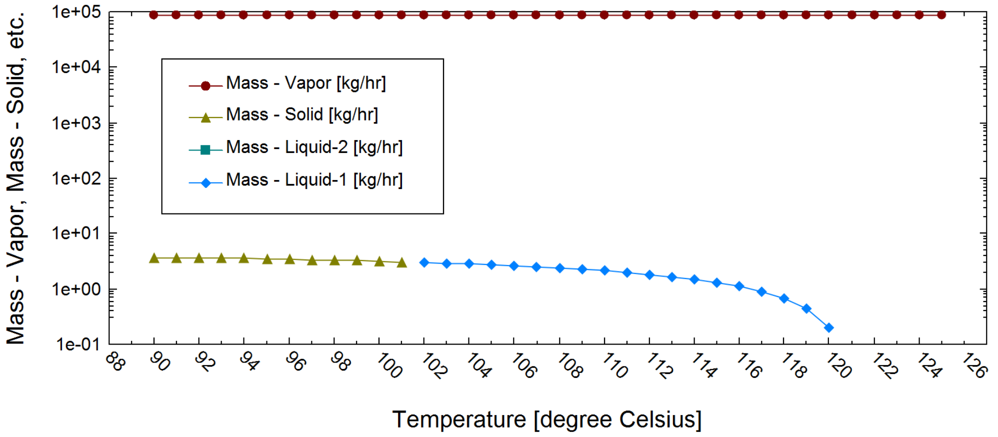

Figure 3.7: MOPA Hydrochloride behavior in the presence of an inert.

Dimethylethanolamine (DMEA)

Results for DMEA evaluation are presented in Table 3.8 and in Figure 3.8. Profiles are similar to cases with MEA and MOPA. An aqueous phase appears at 118 °C, composed mostly (>87% wt) of DMEA and Chloride, indicating that DMEA hydrochloride is also a molten salt. An investigation of this salt behavior is presented in Figure 3.9 and for all the temperature range between 40 °C and 115 °C DMEA hydrochloride is a molten salt, which means that its melting point is lower than 40 °C and therefore is not a concern regarding deposits for overhead systems (accumulator drum temperatures are rarely lower than 40°C). As for MEA and MOPA, although ionic dew point pH (3.39) is below 4.0, water dew point pH (5.52) is higher than 5.0, indicating that DMEA may also be a good option to avoid acid corrosion.

As for EDA, MEA and MOPA, presence of salt leads to an ionic dew point higher than tower top temperature (100 °C), indicating probable salt deposition, indicating that DMEA is also not a proper choice as a single neutralizer for this case.

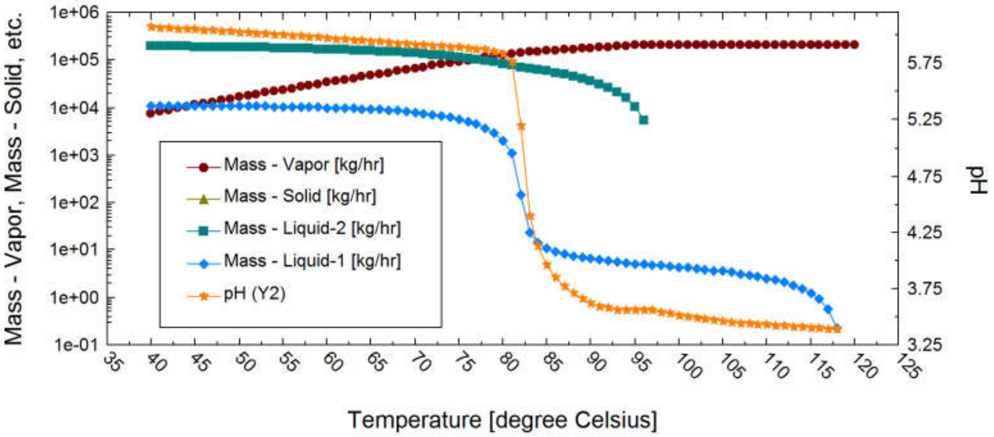

Figure 3.8: Neutralizer: DMEA – Neutralizer/HCl molar ratio of 1.11 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

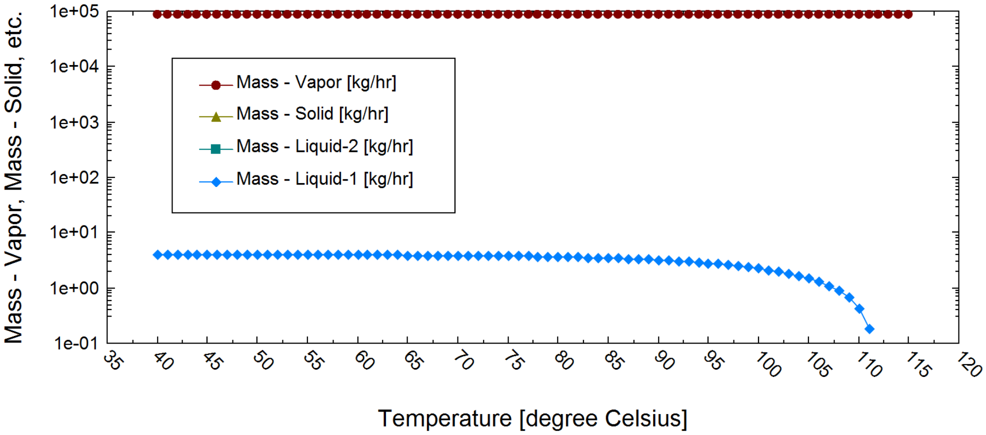

Figure 3.9: DMEA Hydrochloride behavior in the presence of an inert.

Morpholine (MORPH)

Results for MORPH evaluation are presented in Table 3.8 and in Figure 3.10. Profiles are similar to NH_3. All species are in vapor phase at high temperatures and solid phase (morpholine hydrochloride) is present below 122 °C, the salting point (much higher than tower top temperature). Ionic dew point temperature is 97 °C (only 3 °C below tower top temperature) and although pH (3.46) is below 4.0, water dew point pH (5.19) is higher than 5.0, indicating that MORPH may also be a good option to avoid acid corrosion.

As for NH_3, ionic dew point is lower than tower top temperature (100 °C), although not as low as recommended by ARMISTEAD *et al.* (2015). But still, salting point indicates probable salt deposition, showing that MORPH is also not a proper choice as a single neutralizer for this case.

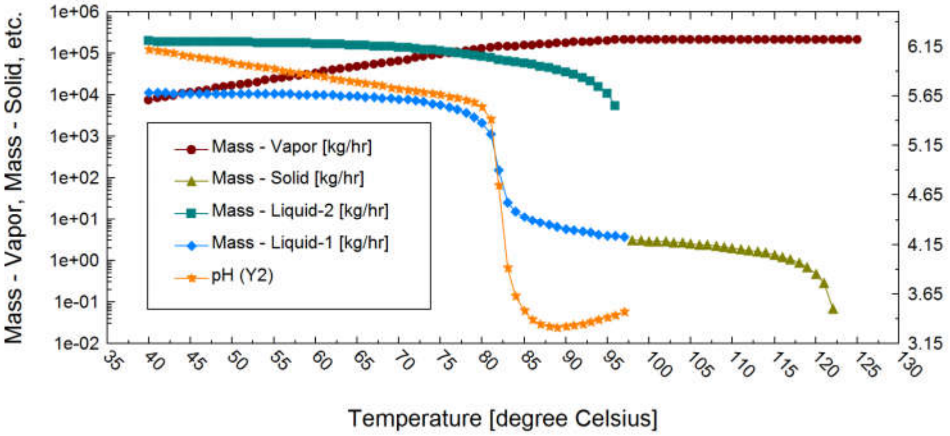

Figure 3.10: Neutralizer: MORPH – Neutralizer/HCl molar ratio of 1.12 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

Methylamine (MA)

Results for MA evaluation are presented in Table 3.8 and in Figure 3.11. Profiles are similar to NH_3 and MORPH, but in this case salting point is 115 °C. Ionic dew point temperature is 108 °C (higher than tower top temperature) and although pH (2.97) is below 4.0, water dew point pH (5.57) is higher than 5.0, indicating that MA may also be a good option to avoid acid corrosion. Even so, salting point also indicates probable salt deposition, showing that MA is also not a proper choice as a single neutralizer for this case.

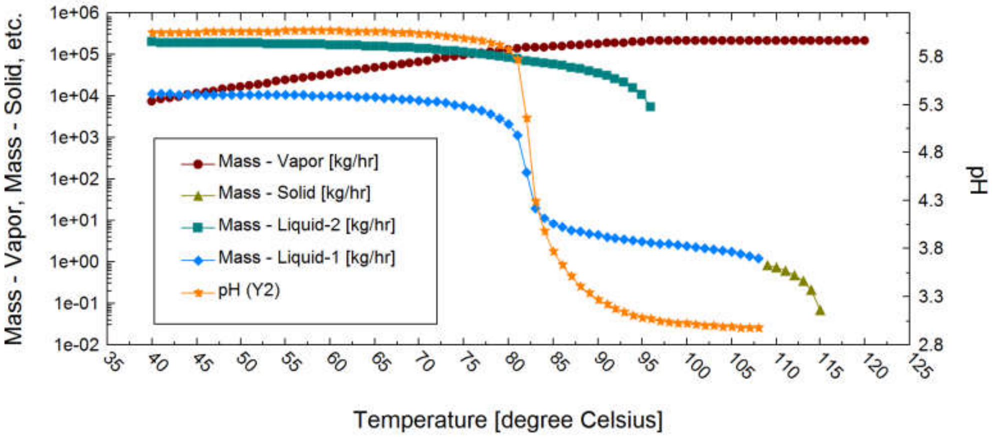

Figure 3.11: Neutralizer: MA – Neutralizer/HCl molar ratio of 1.105 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

Trimethylamine (TMA)

Results for TMA evaluation are presented in Table 3.8 and in Figure 3.12. Profiles are similar to those of MEA, MOPA and DMEA, but with a much lower ionic dew point. To investigate if TMA also forms a molten salt, a case with an inert (nitrogen) as simulated, with result presented in Figure 3.13, in which is shown that TMA hydrochloride is solid for temperatures related to overhead systems. An aqueous phase appears at 100 °C, composed mostly (>69% wt) of TMA and Chloride, indicating that this is the actual ionic dew point and, as discussed earlier, the salting point.

Ionic dew point temperature is 100 °C (same as tower top temperature) and while ionic dew point pH (2.40) is below 4.0, water dew point pH (4.42) is lower than 5.0, indicating that while TMA provides better results regarding to salt deposition, it may not be a good option to avoid acid corrosion.

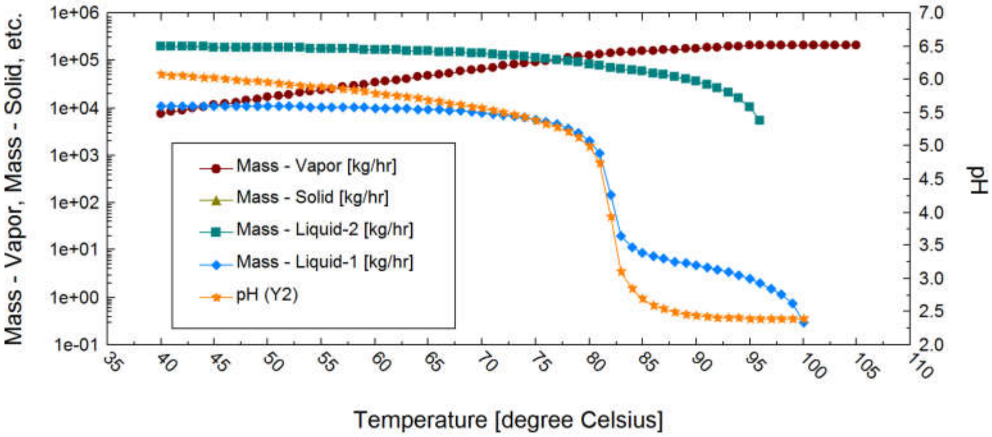

Figure 3.12: Neutralizer: TMA – Neutralizer/HCl molar ratio of 1.115 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

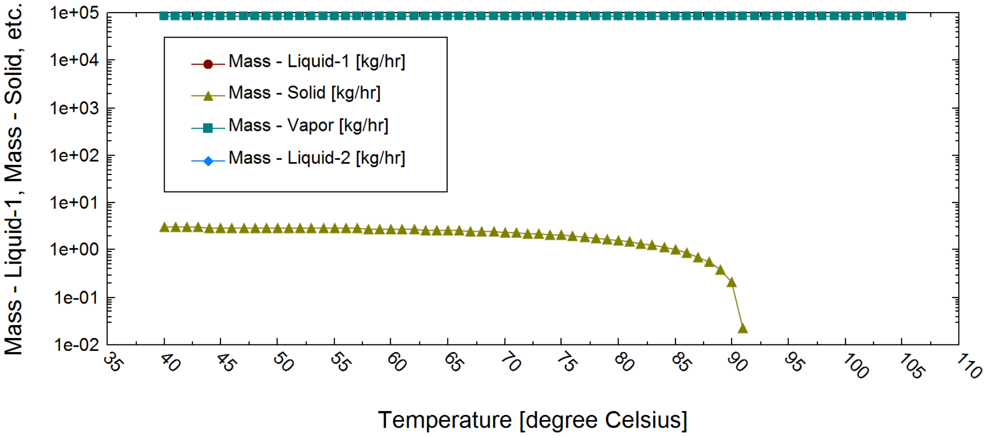

Figure 3.13: TMA Hydrochloride behavior in the presence of an inert.

A comparison with all pure neutralizers evaluated is presented in Table 3.9. These are the same results presented in Table 3.8, but now only with final results.

Table 3.9: Results for pure neutralizers.

Neutralizer	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH3	1.11	107	89	2.36	4.37	6.04
EDA	0.65	179	103	5.46	5.75	6.06
MEA	1.105	141	141	3.45	6.26	6.00
MOPA	1.105	123	123	3.19	5.72	6.01
DMEA	1.11	118	118	3.39	5.59	6.05
MORPH	1.12	122	97	3.46	5.19	6.05
MA	1.105	115	108	2.97	5.57	6.05
TMA	1.115	100	100	2.40	4.41	6.01

With exception of EDA (a diamine), all neutralizers flow rates excesses in relation to their stoichiometric rate range from 10.5% to 12%, in agreement with FEARNSIDE and MURPHY (1998), that mention an excess of 5% to 20%. Dew to the relatively high chloride content (100 mg/L), salting points are higher than tower top temperature (except for TMA, with a salting point equal to the tower top temperature) and salting points are equal or higher than ionic dew points, indicating severe conditions for under-deposit corrosion. Values of pH at water dew point are higher than 5.0 for most cases, except for NH_3 and TMA (that present lowest salt deposition tendencies).

As expected, EDA and MEA present highest salting points (LEHRER AND EDMONDSON, 1993; LACK *et al.*, 2008; PETERSEN AND LORDO, 2004) and TMA presents the lowest one (LEHRER AND EDMONDSON, 1994; PETERSEN AND LORDO, 2004). For cases when solid deposits before ionic dew point (NH_3, EDA, MORPH and MA), salting point and ionic dew point have distinct values. No neutralizer presents results that respect all recommendations: difference from tower overhead to salting point of 14 °C and/or difference of tower overhead to ionic dew point of 14 °C and at the same time, pH at water dew point higher than 5.0. From these results arose the need for investigation of neutralizer blends.

Neutralizer Blends

Results for pure neutralizers evaluations were used to select different blends. To reduce the number of cases evaluated, only three neutralizer compositions were selected for the following evaluations.

EDA and MEA, that present highest salt deposition potentials, were not considered for this evaluation. Although TMA presents the lowest salt deposition potential, it was not considered for the blends, because TMA is a gas at standard conditions (PETERSEN AND LORDO, 2004) and this creates difficulties in handling. Although NH_3 is also gas at standard conditions, it was used in blends as it is the most traditional neutralizer and also costs less than most amines, which is an important advantage. As MORPH and MA both present solid salt deposition, MA was chosen because of its relative lower salting point. MOPA and DMEA were chosen for this evaluation as they present molten salts. Although it has been observed (RUE and EDMONDSON, 2001; RECHTIEN and DUGGAN, 2006) that molten salts present higher corrosion rates, negative impacts of solid deposition (such as maintenance costs and loss of performance) may lead to the preference to molten salts.

Pure neutralizers chosen for blends evaluation are therefore NH_3, MA, DMEA and MOPA. NH_3 and MA present lower salt deposition potentials, but salt in solid phase, while DMEA and MOPA present higher deposition tendencies, but molten salts. In order to try to benefit from both, NH_3 and MA were not used simultaneously in the same blend and the same criterion was used with DMEA and MOPA. Blends with three or more amines are possible, but costs tend to increase, so only two amines were evaluated in each blend. DMEA presents a lower salting point than MOPA and was therefore preferred as a first choice for blends with MA and NH_3. In order to reduce the number of possible evaluation cases, MOPA was tested with NH_3 only.

Even with only two amines, many different compositions are possible and based on the fact that extremely low levels are not practical and based on preliminary tests, it was decided that blends with molar ratios of 50%/50% and 30%/70% would be tested.

Blends proposed are therefore MA/DMEA, NH_3/DMEA, and NH_3/MOPA, each one with three different compositions: 50%/50%, 30%/70% and 70%/30%. All results for each blend are presented in Table 3.10, including their respective pure neutralizers results for comparison. Each blend evaluation is discussed separately below.

Table 3.10: Results for neutralizer blends.

Neutralizer	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
MA	1.105	115	108	2.97	5.57	6.05
NH_3	1.11	107	89	2.36	4.37	6.04
DMEA	1.11	118	118	3.39	5.59	6.05
MOPA	1.105	123	123	3.19	5.72	6.01
30% MA - 70% DMEA	1.105	117	117	3.32	5.57	5.96
50% MA - 50% DMEA	1.105	117	117	3.27	5.57	5.98
70% MA - 30% DMEA	1.105	116	116	3.20	5.57	6.00
30% NH_3 - 70% DMEA	1.11	116	116	3.31	4.91	6.05
50% NH_3 - 50% DMEA	1.11	114	114	3.23	4.68	6.04
70% NH_3 - 30% DMEA	1.11	111*	111	3.11	4.53	6.04
30% NH_3 - 70% MOPA	1.11	120	120	3.11	4.94	6.13
50% NH_3 - 50% MOPA	1.11	119	119	3.04	4.70	6.10
70% NH_3 - 30% MOPA	1.11	115*	115	2.92	4.53	6.07

*Ammonium Chloride solid phase simultaneously with an aqueous phase

Blend 1: MA and DMEA

All profiles are very similar to that of pure DMEA (Figure 3.8). There is no solid phase deposited, even in the case with 70% MA and 30% DMEA. This indicates that presence of DMEA avoids solid deposition. A lower amount of DMEA with the same amount of chloride result in a lower salting point (in comparison to pure DMEA). MA hydrochloride, which deposited as a solid phase in the case with MA as a pure neutralizer, is now dissolved because of the high temperature ionic dew point caused by DMEA hydrochloride.

All results indicate that blends lead to intermediary results in comparison to the respective pure neutralizers. pH at water dew point is higher than 5.0, but salting point is still higher than tower top temperature.

These cases show that blending neutralizers really reduce salting point (FEARNSIDE and MURPHY, 1998; BRADEN *et al.*, 1998; LACK *et al.*, 2008). Nevertheless, in this case all MA/DMEA blends tested do not result in ideal conditions to avoid corrosion.

Blend 2: NH_3 and DMEA

Results are similar to the first blend: all profiles are very similar to that of pure DMEA (Figure 3.8). The difference is that with a high NH_3 percentage (case with 70% NH_3) a solid phase is present even with an aqueous phase, indicating that this aqueous phase is not enough to dissolve the total amount of ammonium chloride, as shown in Figure 3.14. Solid phase is present from 101 °C to 93 °C. This shows that NH_3 content in the blend should be lower than 70%.

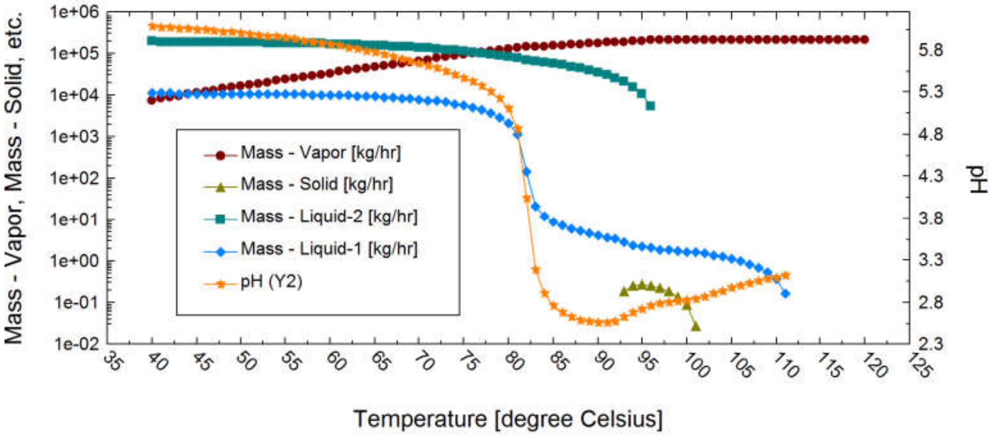

Figure 3.14: Neutralizer: 70% NH_3 - 30% DMEA – Neutralizer/HCl molar ratio of 1.11 – Overhead Temperature 100 °C – 100 mg/L Chlorides.

As NH_3 presents a lower salting point than MA (comparing cases of pure neutralizers), blends of NH_3/DMEA also present lower salting points than those of MA/DMEA. On the other hand, pH at water dew point is lower than 5.0 for all NH_3/DMEA cases. It is important to note that salting point decrease is relatively small (1 °C when comparing pure DMEA to the 30%/70% blend) and pH decrease is substantial (5.59 to 4.91). Again, no NH_3/DMEA blends tested result in ideal conditions to avoid corrosion.

Blend 3: NH_3 and MOPA

A third blend was tested to confirm the tendencies presented before. All profiles are very similar to those of pure MOPA (Figure 3.6) and pure DMEA (Figure 3.8). Yet again, with a high NH_3 percentage (70%) a solid phase is present even with an aqueous phase (in this case from 100 °C to 93 °C). This shows that even with MOPA, NH_3 content in the blend should be lower than 70%.

As pure MOPA results in a salting point higher than pure DMEA, all cases with NH_3/MOPA present higher salting points than those of NH_3/DMEA. pH values at ionic dew point are even lower in blends with MOPA and at water dew points values are very similar.

As in cases with DMEA, MOPA avoids solid deposition (at least for cases with NH_3 percentage lower than 70%), but salting points are still higher than tower top temperature and pH values at water dew point are lower than 5.0. Again, salting point decrease is relatively small (3 °C when comparing pure MOPA to the 30%/70% blend) and pH decrease is substantial (5.72 to 4.94) These indicate, again, that all NH_3/MOPA blends tested do not result in ideal conditions to avoid corrosion.

Evaluation of neutralizer blends confirmed literature information about salting point reduction, which is an extremely important result. Besides, electrolyte modeling was confirmed as a tool to investigate different blend compositions. In this study, no blend was considered appropriate to avoid corrosion phenomena (at least not with the criteria adopted). This leads to need for evaluation of other variables that consist of: chloride concentration reduction, tower top temperature increase and addition of wash water.

Based on the results of neutralizer evaluations, NH_3, DMEA and the 50% NH_3/ 50% DMEA blend were chosen for the following evaluations. NH_3 was chosen not only because it is traditionally used in overhead systems, but also by its relative low salting point (lower than all amines, except for TMA). All amines were capable of raising pH above 5.0 at water dew point, except TMA. EDA and MEA present highest pH values, at expense of presenting highest salting points. MORPH and MA present solid salts as MOPA and DMEA present molten salts, with DMEA hydrochloride salting point lower than that of MOPA hydrochloride. Therefore, DMEA was chosen as a pure amine for the following evaluations. A blend of NH_3 and DMEA seemed an appropriate choice for comparison with both pure neutralizers in the following evaluations.

3.3.3 – Influence of Chloride Concentration

To evaluate the influence of chloride concentration, all other variables were kept the same as the base case. Chloride concentration was changed from 100 mg/L to 50 mg/L in the boot water. As a first evaluation, base case with no neutralizer was run again with new chloride concentration. Profiles are very similar to base case (Figure 3.1) but with higher pH values: pH at water dew point (5% condensed water) is 1.56 instead of 1.37 and pH at accumulator drum, 2.86 instead of 2.57. Higher pH values were already expected but there is still a need for neutralizer injection. After that, cases with the three neutralizers chosen were run (NH_3, DMEA and a blend of 50% NH_3/50% DMEA, as described before). All results (including original cases with 100 mg/L HCl, for comparison) are presented in Table 3.11.

Table 3.11: Results for chloride concentration reduction.

Neutralizer	Chloride Concentration (mg/L)	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH_3	100	1.11	107	89	2.36	4.37	6.04
DMEA	100	1.11	118	118	3.39	5.59	6.05
50% NH_3 - 50% DMEA	100	1.11	114	114	3.23	4.68	6.04
NH_3	50	1.215	98	89	2.36	4.62	6.04
DMEA	50	1.215	110	110	3.42	5.79	6.05
50% NH_3 - 50% DMEA	50	1.215	107	107	3.27	4.96	6.05

As in cases for neutralizers evaluations, an iterative process was needed for each case, until pH 6.0 was reached in the boot water (at 45 °C). As a first initial guess, neutralizer/HCl molar ratio of 1.11 (final value for original cases) was tested. As described before, all other variables but chloride concentration were kept the same, including weak acids amounts. This means that in cases with lower chloride content, weak acids amounts are relatively higher and as neutralizers react with all acids, a higher excess (higher molar ratio) is necessary. Final molar ratio is 1.215 for all cases.

Profiles are very similar to the original cases, with differences only in the parameters values. Salting points (that are proportional to chloride and neutralizers partial pressures) are lower and pH values are higher, as expected. Again, NH_3/DMEA blend provides intermediary results from pure neutralizers, as observed before.

Even with lower chloride content, solid ammonium chloride may deposit when NH_3 is used as a neutralizer. Salting point (98 °C) is now lower than tower top temperature (100 °C), but difference is lower than 14 °C. Besides, pH value at water dew point is still lower than 5.0. With DMEA as a pure neutralizer, there is no solid phase (as DMEA hydrochloride is a molten salt), but salting point (110 °C) is still higher than tower top temperature. As the original case, pH at water dew point is higher 5.0. Again, NH_3/DMEA is an interesting solution as salting point is lower than the case with pure DMEA and pH at water dew point is close to 5.0.

From chloride concentration reduction evaluations, it can be seen that this is really an effective measure to reduce corrosion impacts. For this study, still no ideal conditions are reached.

3.3.4 – Influence of Tower Top Temperature

To evaluate the influence of tower top temperature, a few variables needed to be recalculated. There may be different procedures to increase this temperature, depending on the tower configuration. In this case, configuration consists of a traditional atmospheric tower with a single overhead drum and reflux naphtha to control tower top temperature. Previous study with process simulator was revisited to create a case with higher tower top temperature. Reflux flowrate was reduced until tower top temperature increased from 100 °C to 130 °C. Reflux flow rate is now 169.65 m3/h (instead of 224.53 m3/h) and tough product naphtha is now higher (62.86 m3/h instead of 39.81 m3/h), total naphtha flowrate is lower (232.51 m3/h instead of 264.34 m3/h). Not only flowrates but also naphtha composition has changed. With a higher temperature, heavier compounds are now present, resulting in a heavier naphtha. Off-gas follows the same tendency: lower flowrate and heavier compounds. Boot water remains practically the same (11.13 m3/h instead of 11.10 m3/h). New input data for this case are presented in Table 3.12.

Table 3.12: Input data for cases with higher tower top temperature.

Operational Conditions			**Compositions (mole %)**	**Naphtha**	**Off-Gas**
			Methane	6.731E-04	6.862E-02
Tower Top			Ethane	6.249E-03	1.550E-01
Temperature (°C)	130		Propene	5.903E-03	5.507E-02
Pressure (abs) (bar)	1.95		Propane	3.553E-02	2.861E-01
			i-Butane	1.459E-02	4.853E-02
Acumulator Drum			n-Butane	3.352E-02	8.316E-02
Temperature (°C)	45		i-Pentane	3.841E-02	4.031E-02
Pressure (abs) (bar)	1.7		n-Pentane	1.138E-01	9.400E-02
			H2O	1.582E-03	5.648E-02
Accumulator Drum Outlet Streams			Hypo40*	1.008E-02	7.811E-03
			Hypo50*	2.361E-02	1.486E-02
Naphtha			Hypo60*	5.208E-02	2.328E-02
Naphtha Product Rate (std m3/h)	62.86		Hypo70*	6.480E-02	2.108E-02
Naphtha Reflux Rate (std m3/h)	169.65		Hypo80*	6.028E-02	1.441E-02
Total Naphtha Rate (std m3/h)	232.51		Hypo90*	5.341E-02	8.815E-03
			Hypo100*	5.424E-02	6.345E-03
Off-Gas			Hypo110*	6.057E-02	5.103E-03
Off-Gas Rate (std m3/h)	3.11		Hypo120*	6.442E-02	3.868E-03
			Hypo130*	6.696E-02	2.824E-03
Boot water			Hypo140*	6.663E-02	1.985E-03
Boot Water Rate (m3/h)	11.13		Hypo150*	6.034E-02	1.204E-03
			Hypo160*	5.199E-02	7.208E-04
Boot Water Composition			Hypo170*	4.087E-02	3.948E-04
Chloride (mg/L)	100		Hypo180*	1.609E-02	1.015E-04
H_2S (mg/L)	20		Hypo190*	3.001E-03	1.280E-05
CO_2 (mg/L)	20		Hypo200*	3.555E-04	1.009E-06
Acetic Acid (mg/L)	20		Hypo210*	4.146E-05	7.905E-08
			Hypo220*	6.496E-06	0.000E+00
			Hypo230*	9.399E-07	0.000E+00
			Hypo240*	1.242E-07	0.000E+00

Again, a first evaluation with no neutralizer was run with new input data. Profiles are very similar to base case (Figure 3.1) but dew points are now higher. Hydrocarbon-rich phase condensation begins at 124.2 °C instead of 96.9 °C and water at 88.9 °C instead of 82.4 °C. pH profile is practically the same (pH at water dew point is 1.38 instead of 1.37 and pH at accumulator drum is also 2.57). After that, cases with NH_3, DMEA and the blend (50% NH_3/50% DMEA) were run and results (including original cases with tower top temperature of 100 °C, for comparison) are presented in Table 3.13.

Table 3.13: Input data for cases with higher tower top temperature.

Neutralizer	Tower Ovhd Temp. (°C)	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH_3	100	1.11	107	89	2.36	4.37	6.04
DMEA	100	1.11	118	118	3.39	5.59	6.05
50% NH_3 - 50% DMEA	100	1.11	114	114	3.23	4.68	6.04
NH_3	130	1.11	111	97	2.33	4.27	6.01
DMEA	130	1.11	121	121	3.36	5.43	6.02
50% NH_3 - 50% DMEA	130	1.11	117	117	3.18	4.58	6.02

With no changes in boot water flowrate and composition, there was no need for change in neutralizer/HCl molar ratios. Profiles are very similar to the original cases, with differences only in the parameters values. Salting points are a little higher. This happens because with a higher hydrocarbon dew point there is a slight increase in both chloride and neutralizers partial pressures. pH values are very similar but slightly lower, probably because of the change in water dew point. Once more, NH_3/DMEA blend provides intermediary results from pure neutralizers, as observed before.

Even tough with higher values, now all salting points are lower than tower top temperature (130 °C). With NH_3 as neutralizer, salting point is now 19 °C lower than tower top temperature, but still a solid phase is present before water dew point. With DMEA and the blend, differences are, respectively, 9 °C and 13 °C, and in both cases, molten salts are present, avoiding the presence of a solid phase. pH higher than 5.0 at water dew point is achieved only with DMEA.

From tower top temperature increase evaluations, it can be seen that this is really an effective measure to reduce corrosion impacts. For this study, NH_3 is not a proper choice because of solid phase before water dew point, and tough both DMEA and blend do not satisfy all criteria proposed, conditions are much better than in original cases.

3.3.5 – Influence of Wash Water

To evaluate the influence of wash water, all other variables were kept the same as the base case. Wash water stream definition depends on two important aspects: composition and flowrate. Composition of wash water depends on its source. In this study, wash water composition was assumed to be the same as boot water composition, for two reasons. First, use of boot water as a source of wash water is very common in practice: source is near the injection point and there is no risk of bringing other contaminants to the overhead system. Besides that, defining another composition would result in the inclusion of another variable to study. A schematic of a typical overhead system with wash water from boot water is presented in Figure 3.15.

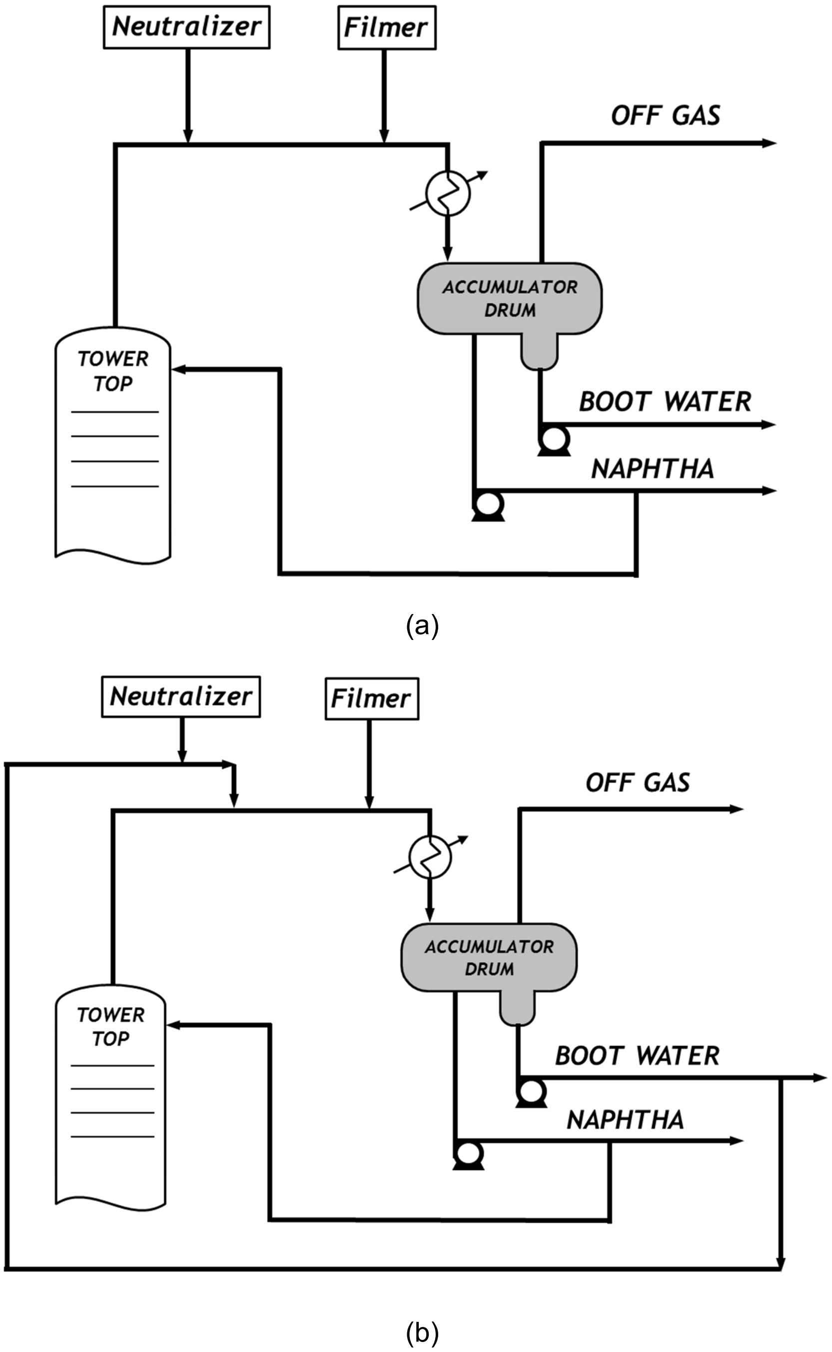

Figure 3.15: Comparison between a typical overhead system with no wash water (a) and a system with water from boot water (b).

Wash water is injected with a main purpose to dissolve any salt deposited, as ammonium chloride and amine hydrochlorides are all water soluble. Besides that, wash water may be helpful to raise pH in the beginning of condensation, by diluting the acid solution. For both objectives, water must be present in liquid phase. However, operational conditions usually favor water vaporization (temperatures range from 90 °C and 160 °C and pressure is close to atmospheric values). Wash water flowrate must be therefore calculated to guarantee saturation and presence of liquid water. Flowrate calculation procedure and criteria usually adopted are described by GIESBRECHT *et al.* (2002). First, water is added to the tower outlet stream in an iterative process until it reaches saturation (water dew point). Then, an excess of 25%-50% is added to guarantee that liquid water will be available.

In this case, it was assumed that neutralizer is injected simultaneously with wash water (what is also a common practice), to simplify calculations. Boot water from the base case was created as a reference stream and was added to the tower outlet stream. A fraction of boot water is used as wash water, and so the process may be repeated with different flowrates until saturation, or, as presented in Figure 3.16, a survey with different flowrates from 0% to 100% boot water flowrate. It can be seen that with 55% of boot water flowrate used as wash water, an aqueous phase is present. As for the profiles, in Figure 3.16 a survey with an interval of 0.05 is presented so that it is easier to visualize results. A detailed survey confirmed that 55% is the minimum wash water rate. In order to confirm this result, the previous study with process simulator was revisited to calculate minimum wash water rate with this procedure and the same value was obtained.

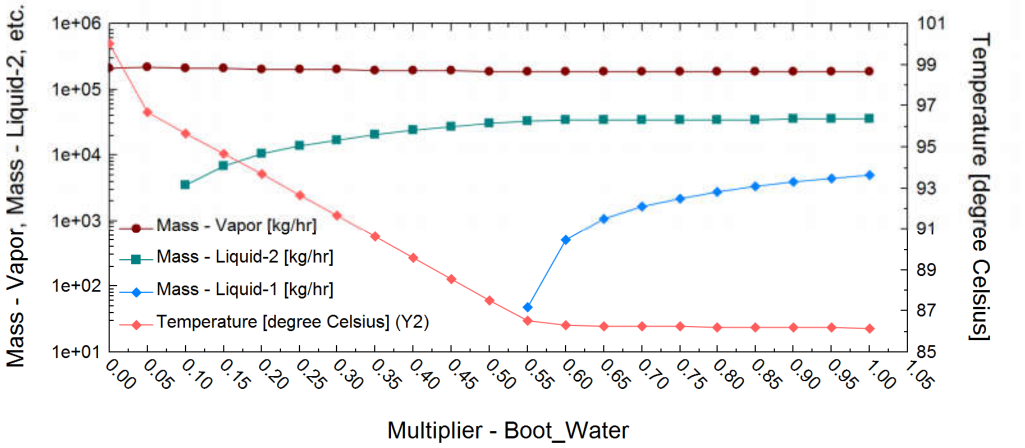

Figure 3.16: Wash water flowrate survey.

Boot water flowrate is 10919.1 kg/h and so minimum wash water rate is 6005.5 kg/h. As proposed by GIESBRECHT *et al.* (2002), an excess was added to guarantee liquid water. Evaluation was proceeded with two different wash water rates: 25% and 50% excess. An excess of 25% in minimum wash water rate leads to 7506.9 kg/h and in the case of 50% excess, 9008.3 kg/h. It is important to note that in the base case, with no wash water, water dew point was 82.4 °C and as wash water is added to the tower outlet stream, temperature is reduced from 100 °C to approximately 86 °C (86.3 °C in the case with 25% excess and 86.2 °C in the case with 50% excess). As in other evaluations, cases with NH_3, DMEA and the blend (50% NH_3/50% DMEA) were run and results (including original cases with no wash water, for comparison) are presented in Table 3.14.

Table 3.14: Results for wash water injection.

Neutralizer	Wash Water Rate (kg/h)	Molar Ratio Neut./HCl	Salting Point (°C)	iDP (°C)	pH@iDP	pH@wDP	pH@45 °C
NH_3	0	1.11	107	89	2.36	4.37	6.04
DMEA	0	1.11	118	118	3.39	5.59	6.05
50% NH_3 - 50% DMEA	0	1.11	114	114	3.23	4.68	6.04
NH_3	7506.9	1.11	-	-	-	4.51	6.04
DMEA	7506.9	1.11	-	-	-	5.84	6.05
50% NH_3 - 50% DMEA	7506.9	1.11	-	-	-	4.82	6.04
NH_3	9008.3	1.11	-	-	-	4.79	6.04
DMEA	9008.3	1.11	-	-	-	5.91	6.05
50% NH_3 - 50% DMEA	9008.3	1.11	-	-	-	5.06	6.04

As in evaluation cases of tower top temperature increase, there was no need for change in neutralizer/HCl molar ratios. However, profiles are very different to the original cases, as presented in Figure 3.17 for NH_3 (case with 25% excess wash water). In the original case with no wash water (Figure 3.2), ammonium chloride is present as a solid phase, a consequent ionic dew point at 89 °C (pH 2.36) and 5% water condensed at 81.6 °C (pH 4.37). With wash water, although profiles presented seem very similar, all species are at vapor phase at 100 °C (tower top temperature) and as soon as wash water is injected, temperature drops to 86.3 °C (wash water stream is at accumulator drum conditions – 45 °C – and a fraction of wash water vaporizes, reducing system temperature). Real results in Fig. 3.17 are represented on the left side of the red line (86 °C), below which all possible ammonium chloride is dissolved and at the same time, more than 5% water is already condensed. This way, salting point and ionic dew point are no longer identified. Although wash water is able to dissolve ammonium chloride, pH at initial condensation is still below 5.0, but now much closer to this value. Even with a higher amount of wash water (50% excess), pH is still below 5.0 with NH_3. It can be seen that a higher amount of wash water is benefic tough, as pH rises from 4.51 to 4.79.

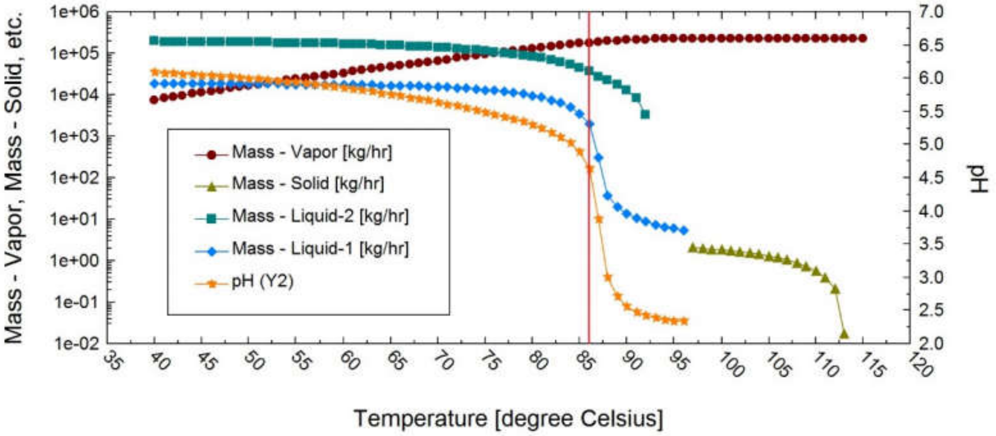

Figure 3.17: Neutralizer: NH_3 – Neutralizer/HCl molar ratio of 1.11 – Overhead Temperature 100 °C – 100 mg/L Chlorides – 25% Excess Wash Water (7506.9 kg/h).

Although only the first case for NH_3 is presented (Figure 3.17), all cases present similar profiles. In the original case of DMEA evaluation with no wash water (Figure 3.8), pH was already elevated at water dew point, bus salting point was higher than tower top temperature. With wash water, salt deposition is no longer an issue when using DMEA. A lower amount of wash water is enough when using DMEA as a neutralizer. Once again, NH_3/DMEA blend provides intermediary results from pure neutralizers, as observed before. It is important to note that as NH_3 is present, a higher amount of wash water is needed to raise pH above 5.0.

From wash water evaluations, it can be seen that this is also a really effective measure to reduce corrosion impacts by avoiding salt deposition and raising pH profiles. For this study, NH_3 is close to be chosen as proper neutralizer as no solid phase is present and pH is close to 5.0. DMEA is a proper choice, even with lower was water rate, with all criteria respected. NH_3/DMEA blend is a proper choice with a higher wash water rate, with no solid phase and high pH at initial condensation point.

These results show that ammonia can be used a neutralizer when an effective wash water is available, as mentioned by BRADEN *et al.* (1998). Besides, it can also be used in neutralizing blends with other amines to improve neutralization in the initial condensation point. Though not a scope of this study, neutralizers present different costs, being amines costs usually much higher than that of ammonia. In this case, addition of NH_3 and DMEA reduce neutralizers costs when compared to pure DMEA.

3.4 - Conclusions

An electrolyte model was used to investigate the impacts of different process variables that influence corrosion phenomena in CDUs overhead systems. The model selected is based on rigorous electrolyte thermodynamics, with assumption of phase equilibria (with no aspects regarding kinetics or flow regimes) and outputs include prediction of which phases (vapor, solid and/or liquid) are present and how species are distributed between these phases. Important parameters can be obtained with the model, including: salt deposition temperature (also called salting point), dew points (ionic dew point and water dew point), pH at dew points and minimum wash water rate.

As a commercial software was used (OLI Studio, by OLI Systems, Inc.), a verification of the model was proceeded. Vapor-liquid equilibrium (VLE) and vapor-solid equilibrium (VSE) were considered most important to indicate acid corrosion and under-deposit corrosion and were therefore chosen for this first step. Because of lack of complex multicomponent systems and amine hydrochlorides data, simple binary systems (NH_3-H_2O and HCl-H_2O) were used for VLE evaluation and ammonium chloride, for VSE. When compared with experimental data for these systems, OLI Studio was proven to produce results compatible with experimental observation.

Eight different neutralizers have been investigated in this work, including: ammonia (NH_3), ethylenediamine (EDA), monoethanolamine (MEA), methoxypropilamine (MOPA), dimethylethanolamine (DMEA), morpholine (MORPH), methylamine (MA) and trimethylamine (TMA). As mentioned in the literature, NH_3 was proven to be inadequate to neutralize HCl in the initial condensation point, but it presents a lower salt deposition tendency than most amines (except for TMA). EDA and MEA present highest salt deposition tendency and TMA, the lowest one. Most pure neutralizers were proven to be adequate to avoid acid corrosion, except for NH_3 and TMA (that present lowest salt deposition tendencies).

Based on the results from the eight pure neutralizers evaluations, four of them were chosen to compose nine different neutralizer blends and results confirmed literature information about salt deposition tendency reduction, which is an extremely important result. Besides, electrolyte modeling was confirmed as a tool to investigate different blend compositions.

It was shown that chloride concentration reduction, tower top temperature increase and addition (or increase) of wash water are benefic to overhead systems corrosion control. Lower chloride concentration leads to higher pH profiles (reducing acid corrosion impacts); higher tower top temperatures reduce the risk of salt deposition and wash water (if properly dimensioned) dissolves salts and raises pH by diluting the aqueous phase.

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Appendix

Pseudocomponents Properties:

	Boiling Temp. (°C)	Molecular Weight	Specific Gravity
Hypo40*	38	72.195	0.6588
Hypo50*	45	75.527	0.7070
Hypo60*	55	80.308	0.6838
Hypo70*	65	84.342	0.6914
Hypo80*	75	88.729	0.7141
Hypo90*	85	92.709	0.7451
Hypo100*	95	98.184	0.7495
Hypo110*	105	103.476	0.7535
Hypo120*	115	108.165	0.7569
Hypo130*	125	113.674	0.7616
Hypo140*	135	118.992	0.7659
Hypo150*	145	124.663	0.7740
Hypo160*	155	131.403	0.7838
Hypo170*	165	133.685	0.7927
Hypo180*	175	142.204	0.8011
Hypo190*	185	145.484	0.8086
Hypo200*	195	152.939	0.8168
Hypo210*	205	158.465	0.8255
Hypo220*	215	161.176	0.8331
Hypo230*	225	172.984	0.8401
Hypo240*	235	179.966	0.8463

Chapter 4

General Conclusions

In the first part of this work, a literature review was proceed and different types of CDUs overhead systems modeling are presented. A new classification is proposed for these models, dividing them as simplified and rigorous methods. Rigorous electrolyte models were considered most appropriate to simulate overhead systems conditions. A brief introduction to rigorous electrolyte modeling of CDUs overhead systems was also presented, including several recommendations from many different authors.

In the second part, a commercial software was used to investigate the impacts of main process variables that influence corrosion phenomena. Eight pure neutralizers were tested (ammonia and seven amines), and it was possible to describe their performance and identify advantages and disadvantages for each one. Neutralizer blends were also tested, and it was confirmed that they may help reduce salt deposition tendency. Besides neutralizer composition evaluation, chloride concentration reduction, tower top temperature increase and use of wash water were proven beneficial measures to minimize corrosion impacts.

Suggestions for Future Work

For future work, we recommend the following analysis:

- Evaluation of other neutralizing amines. Seven neutralizing amines evaluated in this work were the ones considered the most common and/or more interesting from literature. Twenty amines are available in OLI Systems software though, and so there may be other interesting neutralizing amines;
- Evaluation of weak acids behavior. Hydrogen sulfide (H_2S), carbon dioxide (CO_2) and acetic acid were considered in this work with a single concentration value. These species are present in aqueous, hydrocarbon-rich and gas phases, and then, they should be computed in the model. Here, these compounds were considered but not deeply investigated. Other species (including other small chain organic acids) may also be evaluated.