

Refinery crude column overhead corrosion control, amine neutralizer electrolyte thermodynamics, thermochemical properties and phase equilibria

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Abstract

Organic neutralizing amines are commonly used to combat corrosion in refinery crude column overhead systems. Yet under-deposit corrosion and active acid corrosion are frequently reported in such refinery process units. Several of these failures can be traced to poor application, or misuse, of organic neutralizing amines. The common cause is usually a lack of understanding of the electrolytic thermodynamics, thermochemical properties and/or phase equilibria of these organic amines. To understand the root cause(s) of these failures, a rigorous, fundamental, thermo-dynamic approach was developed in Shell Oil. Important thermochemical and physical properties were identified and phase equilibria relevant to a typical crude unit overhead were outlined. Custom-developed apparatus and experimental procedures were used to measure the needed data and to validate thermodynamic consistencies. These methodologies and data generation techniques will be described here. The incorporation of these data into the frame work of commercial flowsheeters such as ProVision[®] (electrolytes) and Aspen Plus[®] (with OLI Engine[®]) will also be discussed. The use of commercial flowsheeters is the recommended way to practice our rigorous technology in the field. Complementary forms of output such as Charts, Nomographs, Spreadsheets and Phase Diagrams can also be produced and used by field staff. To successfully apply this technology to refinery crude column overheads in Shell and non-Shell crude towers, we set up a Technology Partnership Program, with a chemical supplier—Baker Petrolite. This relationship has proved to be very successful in the USA and will be outlined. ('ProVision', 'AspenPlus' and 'OLI Engine' are registered trademarks of Simulation Sciences, Aspen Technology and OLI Systems.) © 1999 Elsevier Science B.V. All rights reserved.

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1. Summary

Organic neutralizing (alkyl, alkanol, alkoxy and cyclic ether) amines are commonly used to control corrosion in crude unit overhead systems. Yet under-deposit corrosion and active acid corrosion near the aqueous dew point are frequently reported to occur in such refinery process units. A significant number of the corrosion-related failures in crude unit overhead systems are the result of poor application of organic neutralizing amines. The misapplication usually stems from a lack of understanding of the physical properties and phase equilibrium of these organic amines.

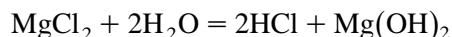
To better address the root cause of these failures, pertinent physical properties and the phase behavior of organic amines and their hydrochloric salts were measured, screened and evaluated. State-of-the-art laboratory equipment and techniques were developed to collect the physical properties and phase equilibrium data needed to predict the behavior of systems involving water, organic (or, inorganic) salts, acid gases and organic amines used for corrosion control. In particular, the thermodynamic state functions (i.e., Gibbs Free Energy, Enthalpy and Entropy changes) and physical properties (e.g., activity coefficients) of dilute amine solutions, and the formation potential of amine hydrochloride salts, were systematically determined.

In the field, the data can be delivered and used in a multitude of ways. The popular forms are Charts, Nomographs, Spreadsheets, Phase Diagrams, etc. The more rigorous approach involves the use of electrolyte process flowsheeters such as Simulation Sciences' PROVISION^{® 1} (electrolytes), or Aspen Technology's Aspen Plus[®] process flowsheeters, to predict salt formation and corrosive conditions in pipes and refinery process units.

In order to apply the rigorously developed technology most effectively to crude column overhead systems, a Technology Partnership arrangement was defined between Shell Oil Products and a chemical supplier—Baker Petrolite. As part of this arrangement, this newly developed basic thermodynamic data and methods were coupled to a customized commercial flowsheeter. Baker Petrolite, a chemical vendor specializing in corrosion inhibitors and neutralizers, now routinely uses this technology to provide Shell (and non-Shell) customers advice on types of additives, neutralizer dosage and injection points in crude column overhead systems.

2. Introduction

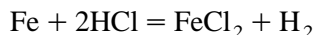
The presence of alkaline-earth (magnesium, calcium, etc.) chloride impurities in the crude oil supplied to refineries introduces hydrochloric acid in the tops of crude columns. In a typical crude column, due to the presence of stripping steam in the column, or water wash in an upstream Desalter Unit, or due to the presence of water in the supplied crude oil, hydrolysis of these alkaline-earth chlorides occurs and releases hydrochloric acid. For example,



While magnesium and calcium chloride salts tend to hydrolyze in the feed heater and bottom section of the crude column, the sodium chloride salt resists hydrolysis and is stable. The HCl vapors

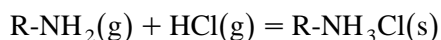
¹ Aspen Plus[®] is a registered trademark of Aspen Technology, and PROVISION[®] is a registered trademark of Simulation Sciences.

are volatile and exit the crude column along with the column overhead vapor. If untreated, the HCl vapor will condense in the vicinity of the aqueous dew point in the crude column overhead system, causing active acid corrosion by the following overall reaction:



Atomic hydrogen can form blisters in the metal wall and iron dissolves in the free water phase produced in the crude column overhead system.

Organic amines are added to the column overhead system to raise the pH at the aqueous dew point and all points downstream of the aqueous dew point. It is practically impossible to measure the pH of the first water droplet produced. Hence the traditional practice in industry has been to overdose the neutralizer amine added to the crude column overhead. For amine hydrochloride salts having limited miscibility in water at the tube skin temperatures in the overhead exchanger bundles, this excess may cause solid amine salt to drop out by the following reaction:



This reaction may occur above or below the aqueous dew point.

If the temperature at which the above reaction occurs is higher than the melting point of the salt, then we make no distinction between the aqueous dew point and the salt formation temperature: molten salts are never dry, as long as there is even a very small amount of water in the overhead vapors. In the flowsheet, when molten salts are formed, there is some subcooling before an independent free water phase can coexist. The wet salts, either solid or molten, are known to be very aggressive in corrosion.

To provide an effective corrosion control program, adequate pH levels must be maintained throughout the crude column overhead system while avoiding the deposition of corrosive amine hydrochloride salts. The open literature provides limited phase diagrams for ammonia and ammonium chloride deposition. Very little (if any) data are available for organic amines. The effort within Shell Oil Products has focused on generation of the thermochemical properties and phase equilibrium data for neutralizer amines and amine hydrochloride salts.

3. Corrosion control in crude column overheads

The use of filming inhibitors and/or neutralizer amines to control corrosion in refinery crude column overhead systems is a common refinery practice. Traditionally, ammonia has been used for this service for many years. In the last two decades, the use of organic neutralizing amines has become increasingly popular. Typically, the neutralizer amine is added to the overhead vapor (or, sometimes to the reflux returning to the column) in very small dosage(s). Often a single injection point is used to introduce the chemical into the overhead system. Overhead systems with multiple trains of condensers and reflux drums require a more elaborate, multipoint injection system.

The design of a crude column overhead system corrosion control program must address the following items:

1. Single (or, Multiple) Drums
2. The pH at the Aqueous Dew point and pH in Drums
3. Other Slop/Tramp Feeds to the Crude Column

4. Rate of Neutralizer Injection
5. Temperatures at Injection Point, Bulk Process and Skin Temperatures
6. Amine Hydrochloride Salt Formation
7. Hydrocarbon Fluid Flow
8. Injection System Design
9. Compatibility of Neutralizer and Filming Inhibitor

All of the above items are important for the successful use of neutralizers in crude column overhead systems. The practice is to pick a suitable neutralizer chemical that will raise the aqueous dew point pH sufficiently while preventing amine hydrochloride salt formation above the aqueous dew point. This will allow the minimization of acid corrosion in the vicinity of the aqueous dew point and under-deposit salt corrosion above the aqueous dew point.

4. Thermodynamic framework

Phase and chemical equilibria calculations are done in commercial flowsheeters by specialized subroutines accessing databanks containing data and parameters for a variety of species. The information stored in these banks should be comprehensive enough to allow reliable prediction of phase and chemical equilibria involving a variety of species in a broad range of temperature, pressure and composition. Given all these requirements, the amount of raw data needed to be stored can become too large to be practical. However, thermodynamics provides us with a framework that ensures self-consistent results, minimizes experimental effort, reduces the amount of information to be stored, and provides reliable ways of extrapolating and interpolating experimental data.

Classical thermodynamics establishes the phase equilibrium criteria as the equality of partial molar Gibbs Free Energy, G , of every chemical species in every phase. For reactive systems, the requirement is that the stoichiometric sum of the partial molar Gibbs Free Energy of the reactants and products should be zero for every chemical reaction occurring in the system. Consequently, our capacity to predict phase and chemical equilibrium is determined, to a large extent, by our ability to compute the partial molar Gibbs Free Energy of every species, in every phase, in the target system. Thermodynamic path calculations (e.g., gas to liquid, liquid to aqueous, aqueous to crystal) are performed to obtain the Gibbs Free Energy in each phase. Mathematical details of thermodynamic path calculations are omitted to keep the length of this paper manageable.

5. Reduction to practice

The reduction to practice from a fundamental approach to tangible results that can be used in the refinery, is best done using customized commercial flowsheeters. This allows the practicing engineer to retain the rigor of the methodology while obtaining simulation results quickly and easily. For everyday use, several traditional forms of complementary output can be produced that allow field staff to examine tentative cases without having to run the commercial flowsheeters.

5.1. Charts

Charts are usually defined to depict various operating condition changes in the field (e.g., partial pressures of hydrocarbons and water within an overhead tube bundle).

5.2. Nomographs

The traditional method of pH control in crude column overhead systems is to monitor the boot water pH in the refinery and adjust the neutralizer dosage based on field measurements in the accumulator boot. This approach suffers from a critical shortcoming. The pH at the aqueous dew point is only implicitly related to the accumulator boot water pH. We have found that the accumulator boot water pH can often be in an acceptable range of 5.5 to 6.0 while the aqueous dew point pH is unacceptably low (i.e., less than 4.0 for carbon steel). From our rigorous model work, we can determine the optimum dosage for achieving an acceptable pH across the entire overhead system. Specifically, the minimum amount of neutralizer needed to achieve an acceptable aqueous dew point pH can be determined as a function of both chloride and ammonia content in the boot water.

5.3. Spreadsheets

With the advent of Microsoft Excel^{® 2} and Lotus-123[®] spreadsheets, process engineers have become very versatile in observing trends and analyzing data by changing one variable at a time and studying the impact of that change. Two forms of spreadsheets are easily produced from our rigorous approach. The first form of spreadsheet is designed for thermodynamic consistency checking of thermochemical properties. As different thermodynamic pathways are measured in the laboratory and their data collated, they are entered into the spreadsheet. Individual thermodynamic pathways can be numerically added to see if there is data closure. It also serves as a convenient vehicle to transmit data to other developers who build thermodynamic data banks and customize flowsheeters for more rigorous use.

The second spreadsheet is oriented more for the practicing engineer doing ‘what if’ amine hydrochloride salt formation studies. By entering process conditions at a given point in the overhead system, the engineer can then compare salting tendencies for various amine hydrochlorides and determine which is best suited for the application. A new variable, ‘Salt Delta T ’, is defined for this purpose. If this variable is positive, there is no salting tendency; a value of zero is the incipient salt formation point; a negative value flags salt formation. In practice, a fuzzy boundary around zero is used to delineate the incipient salt point.

5.4. Phase diagrams

The Phase Diagram for Ammonium Chloride Salt serves as an example of another form of output which a refinery chemist might find useful.

5.5. Computer programs

Several computer programs such as (ESP, CSP, ProVision(e) Hysim(e), Aspen Plus) are commercially available from commercial flowsheeter vendors. The choice of computer program is governed by the end-user’s preference for a given tool and his familiarity and dexterity in using the same.

² Excel[®] is a registered trademark of Microsoft, and Lotus-123[®] is registered trademark of Lotus.

6. Conclusions and future work

Traditional methods used to control corrosion in refinery crude column overhead systems are inadequate. Depending solely on boot water pH and analyses of a few ions in solution are a potential trap for the practicing engineers. Acceptable pH readings in the boot water can provide a false sense of security, while the overhead system has active acid corrosion at the aqueous dew point.

Neutralizer organic amines are often misapplied in the refinery due to a lack of understanding of the physical properties, thermochemical behavior and phase equilibria of amines and their hydrochloride salts. Excess dosage of these neutralizers causes under-deposit corrosion above the aqueous dew point and is frequently the cause of failure in overhead systems.

It is almost impossible to measure the pH of the first water droplet at the aqueous dew point. It happens to be the most aggressive point for acid corrosion. A rigorous thermodynamic model, such as our work, can bridge this gap.

There is a severe paucity of data for organic amines and their hydrochloric acid salts. We have successfully developed the Thermodynamic Framework and needed experimental data to rigorously model crude column overhead units via customized commercial flowsheeters. Alternate forms of output such as Charts, Nomographs and Spreadsheets can be used to conduct screening studies.

The developed fundamental methodology is thermodynamically consistent, rigorous and allows interpolation/extrapolation over a wide range of crude column tops conditions. Besides studying the use of neutralizer chemicals, it can also be used to investigate water washing of tube bundles as an alternate corrosion mitigation solution. Various water sources (once-through water feeds, or recycle water feeds) can be simulated to determine the most optimum configuration for a particular refinery.

The development of a Technology Partnership between Shell Oil Products and a chemical supplier such as Baker Petrolite, allows us to make the most optimum and timely use of our rigorous Thermodynamic Framework for Shell (and non-Shell) crude column overhead systems. (This technology has been successfully applied to over 30 refinery crude unit tops in North America.)