Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems

API RECOMMENDED PRACTICE 932-B
SECOND EDITION, MARCH 2012

ERRATA, JANUARY 2014

AMERICAN PETROLEUM INSTITUTE

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Downstream Segment

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1 Scope

This recommended practice (RP) provides guidance to engineering and plant personnel on equipment and piping design, material selection, fabrication, operation, and inspection practices to manage corrosion and fouling in the wet sections of hydroprocessing reactor effluent systems. The reactor effluent system includes all equipment and piping between the exchanger upstream of the wash water injection point and the cold, low-pressure separator (CLPS). The majority of these systems have an air cooler, however, some systems utilize only shell and tube heat exchangers. Reactor effluent systems are prone to fouling and corrosion by ammonium bisulfide (NH_4HS) and ammonium chloride (NH_4Cl) salts.

An understanding of all variables impacting corrosion and fouling in these systems is necessary to improve the reliability, safety, and environmental impact associated with them. Past attempts to define generic optimum equipment design and acceptable operating variables to minimize fouling and corrosion have had limited success due to the interdependence of the variables. Corrosion can occur at high rates and be extremely localized, making it difficult to inspect for deterioration and to accurately predict remaining life of equipment and piping. Within the refining industry, continuing equipment replacements, unplanned outages, and catastrophic incidents illustrate the current need to better understand the corrosion characteristics and provide guidance on all factors that can impact fouling and corrosion.

This RP is applicable to process streams in which NH_4Cl and NH_4HS salts can form and deposit in equipment and piping or dissolve in water to form aqueous solutions of these salts. Included in this practice are:

- details of deterioration mechanisms;
- methods to assess and monitor the corrosivity of systems;
- details on materials selection, design and fabrication of equipment for new and revamped processes;
- considerations in equipment repairs; and
- details of an inspection plan.

Table 1 lists key issues to REAC system performance and section reference for more detail.

Materials and corrosion specialists should be consulted for additional unit-specific interpretation and application of this document. This is especially important since new proprietary research is underway which challenges several previously held beliefs about NH_4HS corrosion in the reactor effluent system. Each facility needs to establish its own safe operating envelope to assure satisfactory service. This RP helps to identify key variables necessary for monitoring and establishing the operating envelope.

Other equipment downstream of the REAC can also deteriorate from these ammonium salts. These include the recycle gas, sour gas and the H_2S stripper and product fractionator overhead systems. Although these are beyond the scope of this document, plant personnel should be alert to these other locations where ammonium salt fouling and corrosion can occur.

Since the first edition of API 932-B was published in July 2004, findings from a recent joint industry sponsored research program contributed important new data on NH_4HS corrosion relevant to these systems. While not all the data are in the public domain, recent publications have highlighted key data which are incorporated into this current edition of API 932-B.

Table 1—Keys to REAC Systems

Key	Issues	Section
NH_4HS Concentration	Below 2 %, solutions are not highly corrosive to carbon steel. Above 2 %, solutions are increasingly corrosive. Materials of construction, piping configuration, and fluid velocity become important to corrosion.	6.1
Chlorides in Process Stream	Deposition and severe corrosion could result from NH_4Cl. Inject water to remove salts and scrub process gas.	6.6
H_2S Partial Pressure	Higher H_2S partial pressure increases corrosion rate for a given NH_4HS concentration.	6.4
Wash Water	Quantity of water injected to reduce NH_4HS concentration and to allow sufficient free water at injection point.	6.8.2
	Quality of wash water critical to prevent increased corrosion and deposition of inorganic materials.	6.8.1
	Adequate distribution through single or multiple injection points with quills to assure REAC surfaces are washed.	8.5.3.2
Bulk Fluid Velocity	Increasing fluid velocity increases the corrosivity of the process. Velocities should be appropriate for the NH_4HS concentration and material of construction.	6.3
Materials of Construction	Carbon steel performs acceptably under low NH_4HS concentration and velocities. Alloy 825 and duplex stainless steel are appropriate for more severe conditions.	7
REAC Header Box and Tubes	Header box design should promote good flow distribution through tube rows.	8.1.2.1
	U-tubes should be avoided.	8.1.2.2
REAC Inlet and Outlet Piping Design	Piping design should minimize turbulence for NH_4HS solutions.	8.5.2
	Piping configuration should promote balanced flow through all REAC inlets to prevent salt deposition and to distribute wash water.	8.5.3.1
Process Variables and Monitoring	Establish an operating envelope and monitor key process variables to assure they remain within acceptable ranges.	5.3 6.10
Inspection Plan	Inspection plan should address all deterioration mechanisms possible in the equipment and piping system including general and localized corrosion, HIC, SOHIC, and hydrogen blistering.	9

2 Normative References

2.1 Codes and Standards

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API 510, *Pressure Vessel Inspection Code: Maintenance, Inspection, Rating, Repair, and Alteration*

API 570, *Piping Inspection Code: Inspection, Repair, Alteration, and Rerating of In-service Piping Systems*

API Standard 661, *Air-cooled Heat Exchangers for General Refinery Service*

API Publication 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*

API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*

ASME B31.3 [1], *Process Piping*

NACE SP0296 [2], *Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H_2S Environments*

NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*

NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels Used in Wet H_2S Refinery Service*

NACE Publication 34101, *Refinery Injection and Process Mixing Points*

2.2 Other References

The following codes and standards are not referenced directly in this RP. Familiarity with these is recommended because they provide additional information pertaining to this RP. All codes and standards are subject to periodic revision, and the most recent revision available should be used.

API Recommended Practice 572, *Inspection of Pressure Vessels*

API Recommended Practice 574, *Inspection Practices for Piping System Components*

API Recommended Practice 582, *Recommended Practice and Supplementary Welding Guidelines for the Chemical, Oil and Gas Industries*

API Publication 2217A, *Guidelines for Work in Inert Confined Spaces in Petroleum Industry*

ASME *Boiler and Pressure Vessel Code*, Section VIII, “Rules for Construction of Pressure Vessels,”

ASME *Boiler and Pressure Vessel Code*, Section IX, “Qualification Standard for Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators”

NACE TM0177, *Laboratory Testing of Metals for Resistance to Specific Forms of Environmental Cracking in H_2S Environments*

NACE TM0284, *Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking*

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[1] ASME International, 3 Park Avenue, New York, New York 10016-5990. www.asme.org.

[2] NACE International, 1440 South Creek Drive, Houston, Texas 77084-4906. www.nace.org.

3 Terms, Definitions, and Acronyms

3.1 Terms and Definitions

For the purposes of this document, the following definitions apply.

3.1.1
chloride stress corrosion cracking
Cracking of a metal under the combined action of tensile stress and corrosion in the presence of chlorides and an electrolyte (usually water). Austenitic stainless steels are generally considered susceptible to this mode of cracking.

3.1.2
heat exchangers
Shell-and-tube designs, not including air coolers.

3.1.3
hydrogen-induced cracking
HIC
Stepwise internal cracks that connect adjacent hydrogen blisters on different planes in the metal or to the metal surface. No externally applied stress is needed for the formation of HIC. HIC is commonly found in steels with high levels of impurities, especially sulfur.

3.1.4
hydroprocessing unit
For the purposes of this document, "hydroprocessing unit" will be used to indicate all hydrocracking, hydrotreating (also sometimes referred to as desulfurizers or hydrodesulfurizers), and similar units producing ammonia (NH_3) and hydrogen sulfide (H_2S) in reactors. Some unit names are based on licensors' patented processes.

3.1.5
operating envelopes
Unit and equipment process variable ranges where operation in these ranges will not adversely affect the mechanical integrity of the equipment and piping, and defines process monitoring tasks to assure that operating conditions are maintained within the ranges.

3.1.6
polythionic acid stress corrosion cracking
PTA SCC
Cracking of a sensitized austenitic stainless steel or other sensitized austenitic alloys under combined action of tensile stress and corrosion in the presence of polythionic acid that is usually formed from water, oxygen and sulfide scales.

3.1.7
sensitization
A condition of an alloy (usually an austenitic stainless steel or other austenitic alloy) created by the precipitation of constituents (usually carbides) at the grain boundaries producing a chromium depleted zone adjacent to the grain boundary. This precipitation can occur as a result of a heat treatment, whether accidental or intentional such as from high-temperature service, or incidental (as during welding). It often causes the alloy to become susceptible to intergranular corrosion and stress corrosion cracking.

3.1.8
stress-oriented hydrogen-induced cracking
SOHIC
A stacked array of small blisters joined by hydrogen-induced cracking, aligned in the through-thickness direction of the steel as a result of high localized tensile stresses. SOHIC is a special form of HIC that usually occurs in the base metal, adjacent to the heat-affected zone of a weld, where there are high residual stresses from welding. It can also occur at other high stress points, such as the tip of other environmental cracks (e.g. SSC) or geometric anomalies (e.g. at the toe of the weld).

3.1.9
sulfide stress cracking
SSC
Cracking of a metal under the combined action of tensile stress and corrosion in the presence of water and H_2S. Ferritic and martensitic steels above a certain strength level or hardness threshold are considered most susceptible.

3.2 Acronyms

CHPS	cold, high-pressure separator (also referred to as HPLT, high-pressure low temperature separator)
CLPS	cold, low-pressure separator (also referred to as LPLT, low-pressure low temperature separator)
HHPS	hot, high-pressure separator (also referred to as HPHT, high-pressure high-temperature separator)
HLPS	hot, low-pressure separator (also referred to as LPHT, low-pressure high-temperature separator)
PWHT	post-weld heat treatment.
REAC	reactor effluent air cooler.
SCC	stress corrosion cracking.
CML	corrosion monitoring location.

NOTE This was formerly called TML, thickness monitoring location.

4 Background of REAC Corrosion

4.1 History of Reactor Effluent System Corrosion Surveys

Since widespread commercial use of hydroprocessing technology began in the early 1960s, significant equipment and piping failures have resulted from corrosion associated with the NH_3, H_2S and HCl in the reactor effluent stream. R.L. Piehl presented corrosion and failure data at the 1968 API Division of Refining meeting from an internal study of these units conducted by Standard Oil of California.[3] In 1975, NACE published data from a formal survey it conducted of refining corrosion engineers.[4] UOP and Unocal presented data in a NACE paper from a survey conducted in 1996.[5] The last formal survey was conducted for API in 1998 in preparation for this RP. [6] In addition to these surveys, numerous papers were written on individual experiences and research on the subject of REAC corrosion.[7,8,9,10,11]

These surveys had common conclusions:

a) increasing NH_4HS concentration in the aqueous phase increases the corrosion of carbon steel and alloys;

b) increasing fluid velocity increases the corrosion rate. The recommended maximum velocities vary for carbon steels and alloys;

c) wash water injection rate and water distribution are critical to control NH_4HS deposition and aqueous solution concentrations.;

d) wash water quality can influence the corrosivity of the system.;

e) NH_4Cl salt can cause fouling and corrosion in units with chloride present in the reactor effluent stream.

Surveys dealt with flow distribution through air cooler banks, inlet and outlet piping designs, determining and monitoring adequate wash water injection rates, material selection, flow velocities through tubes and piping, etc.

The survey results highlight industry-wide experience with corrosion in the reactor effluent system of hydroprocessing units. From the earliest studies to the most recent, corrosion continues to cause unscheduled unit outages, and in some instances, catastrophic events involving major fires and explosions. Although early studies proposed guidelines for operating, monitoring and inspecting effluent systems, significant corrosion and leaks in these systems are still being reported on a regular basis at industry forums. The continued failures demonstrate the need to reexamine the guidelines and their application in these units.

4.2 Typical Hydroprocessing Units

Hydroprocessing units use hydrogen at elevated temperatures and pressures along with a suitable catalyst to improve the quality of the feedstock. Common to all units is the production of H_2S and NH_3 from the reaction of hydrogen with sulfur and nitrogen present in the hydrocarbon feed.

Hydrotreating processes remove objectionable elements, sulfur, and nitrogen, from the feedstock. The removal of sulfur can be necessary for either processing in downstream units where the sulfur can contaminate the catalyst or for product quality reasons. Feedstocks to the units can vary from light naphtha to heavy vacuum residuum. Generally, the “heavier” feedstocks require the most severe operation (i.e. higher temperature and pressure) and contain higher concentrations of sulfur and nitrogen that produce the highest concentrations of H_2S and NH_3. Several other reactions can also occur, including the conversion of any chlorides in the feed to HCl. The formation of H_2S, NH_3, and HCl are of primary importance to fouling and corrosion in the reactor effluent system. Figure 1 shows a typical process flow diagram.

Hydrocracking is a process whereby low value hydrocarbon feedstocks are cracked or broken down into higher value hydrocarbons. Typically, this takes heavy hydrocarbons and creates lighter hydrocarbons, such as cracking coker distillate to make gasoline. Figure 2 shows a typical process flow diagram.

Hydrocracking and hydrotreating units have similar process characteristics, especially in the front end processing, as illustrated in Figure 1 and Figure 2. The feed is preheated through a series of exchangers and a furnace to temperatures of at least 700 °F (370 °C). Hydrogen is injected into the feed upstream of the reactor. The hydrogen and feedstock enter the reactor where the catalyst promotes the reaction of hydrogen with sulfur and nitrogen to produce H_2S and NH_3. The reactor effluent is a mixture including H_2S, NH_3, hydrogen, hydrocarbons, and possibly HCl and H_2O. Downstream of the reactor, the effluent is cooled through a series of shell-and-tube heat exchangers.

Downstream of the heat exchangers, the effluent is separated into hydrogen-rich vapor, water, and hydrocarbons. Units can have several different design schemes as described more fully in 4.3.

Continuous injection of wash water into the reactor effluent stream is commonly utilized to prevent fouling by NH_4HS and NH_4Cl salts, typically upstream of the REAC or shell and tube heat exchanger. For some hydroprocessing units (primarily low severity naphtha hydrotreaters), good feed quality does not result in salt deposition and therefore the use of wash water is not required. Other units may produce a low volume of salts that may only require intermittent wash water.

In those units utilizing wash water, the water scrubbed effluent is routed into a separator vessel to separate the gas, liquid hydrocarbon, and sour water. The separator sour water at this point contains inorganic salts such as NH_4HS and NH_4Cl. The gas phase is predominantly hydrogen, light hydrocarbons, and H_2S. It is recycled back to the reactor feed section, in some instances, after scrubbing the H_2S from the gas in an amine absorber. The liquid hydrocarbon streams may pass through additional separators or be sent to a H_2S stripper or product fractionator where the hydrocarbon product streams are produced.

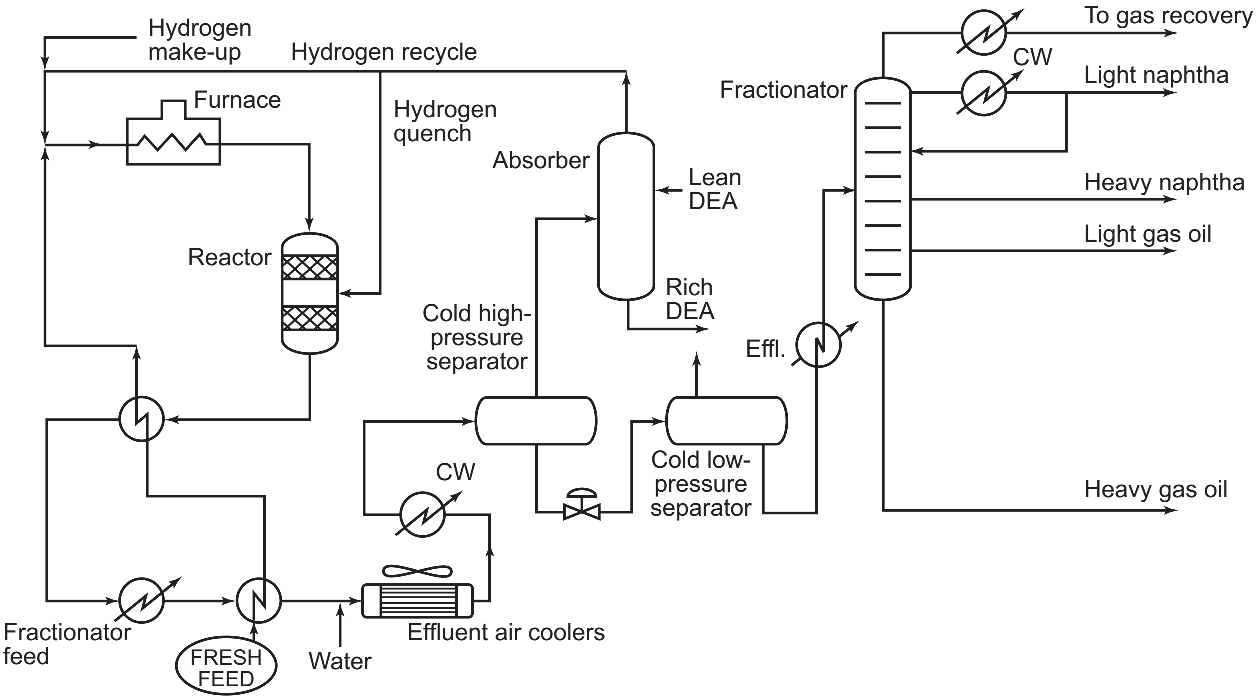


Figure 1—Example Hydrotreating Unit Process Flow Diagram

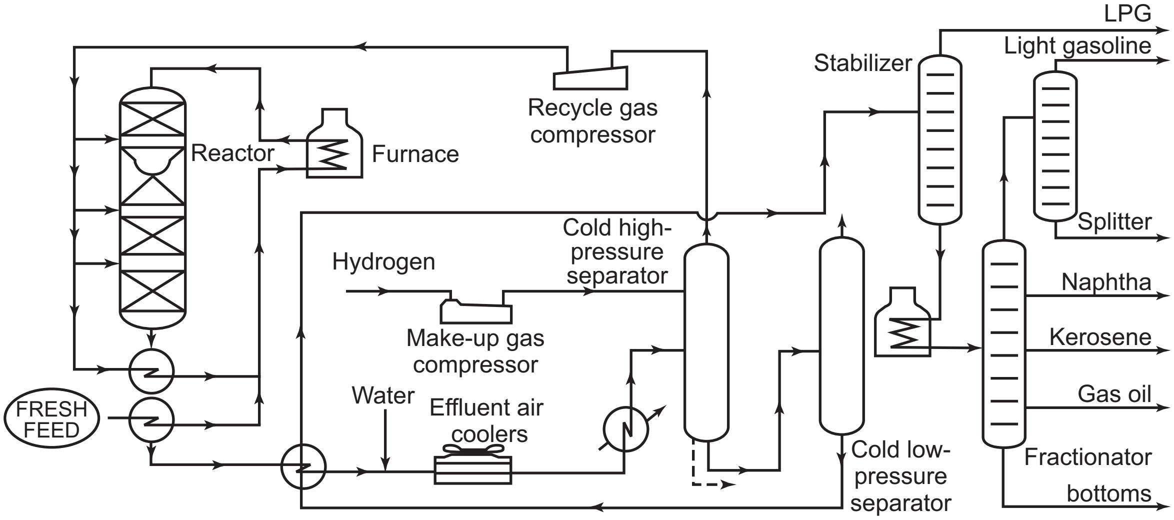


Figure 2—Example Hydrocracking Unit Process Flow Diagram

Makeup hydrogen to the unit can be supplied from either a hydrogen manufacturing unit, like a steam methane reformer, or from a catalytic reformer unit where hydrogen is produced as a byproduct of the reforming reaction. The source and upstream processing of hydrogen can have a significant impact on fouling and corrosion in hydroprocessing units since chlorides can be a contaminant in these hydrogen streams. Catalytic reformer hydrogen can contain HCl. If the hydrogen is not scrubbed of chlorides prior to injecting into the hydroprocessing unit feed stream, it may contain hydrogen chloride. Additional sources of chloride may be organic and inorganic chlorides in the hydrocarbon feed stream. Organic chlorides, such as solvents and cleaners, may not break down in some processing units upstream of the hydrotreater. If organic chlorides are present in the feed stream to the hydrotreater, they will break down in the reactor to form HCl. Inorganic chlorides or salts would likely be stable through the reactor but breakdown of these salts cannot be definitively ruled out.

4.3 Effluent Separation Designs

Separation of the effluent stream can be accomplished through several different design schemes. Units are typically configured with one to four separators. The process configuration of these separators can differ significantly between units, which uniquely changes the composition of the process streams and, therefore, the location of potential corrosion and fouling. Thus, it is critical to understand the influence of the separation design on the composition of the process streams.

Listed below are brief descriptions of some types of configurations to illustrate their function:

a) *CHPS or CHPS/CLPS System*—The effluent stream is cooled through a series of feed/effluent exchangers and air coolers. Wash water is typically injected upstream of the air coolers. The cold effluent stream, generally 90 °F to 120 °F (32 °C to 49 °C), is separated in a cold, high-pressure separator (CHPS). Sour water is drawn off containing most of the NH_3 from the effluent. The hydrocarbon liquid is drawn off and sent to the fractionation section (see Figure 3). In some units, this high-pressure hydrocarbon liquid and sour water are flashed into a cold, low-pressure separator (CLPS) before routing the liquid hydrocarbon to the fractionation section. See Figure 4.

b) *HHPS/CHPS System*—The effluent stream enters a hot, high-pressure separator (HHPS) after being cooled to 400 °F to 550 °F (204 °C to 288 °C). The HHPS vapor is water washed upstream of the air coolers. Downstream of the air coolers, a CHPS removes the sour water. The HHPS liquid will contain dissolved NH_3, H_2S, and possibly HCl, which can promote corrosion in the downstream fractionator overhead. See Figure 5.

c) *HHPS/CHPS/HLPS/CLPS System*—The effluent stream enters a HHPS after being cooled to 400 °F to 550 °F (204 °C to 288 °C). The HHPS vapor may pass through a shell-and-tube heat exchanger before it is water washed upstream of the air coolers. Downstream of the air coolers, a CHPS removes the sour water. The HHPS liquid passes through a control valve where the pressure is let down. Gases in the liquid flash and are separated in a hot, low-pressure separator (HLPS). The HLPS vapor which contains NH_3, H_2S and possibly HCl, is water washed upstream of the air coolers. A cold, low-pressure separator (CLPS) removes the sour water. The hydrocarbon liquid from the CHPS is often routed into a CLPS. See Figure 6.

4.4 REAC System Corrosion

The reactor effluent system is prone to deposition of NH_4HS and NH_4Cl salts. As the effluent is cooled, NH_4Cl salt can form below its salt deposition temperature and may deposit on cool metal surfaces. Upon further cooling, NH_4HS salt may form below its salt deposition temperature and may deposit on cool metal surfaces. However, in some cases, the NH_4HS deposition temperature is below the water dew point so solid NH_4HS deposition will not be observed. The NH_4Cl deposition temperature is well above that for NH_4HS. The deposition temperatures for these salts can be estimated from the partial pressures of NH_3, H_2S, and HCl in the effluent as detailed in Appendix A.

NH_4HS and NH_4Cl salts can build up to cause a decrease in heat transfer efficiency. If uncorrected, the salt accumulations can restrict flow or completely plug heat exchanger and air cooler tubes, which increases the pressure drop and can promote flow maldistribution.

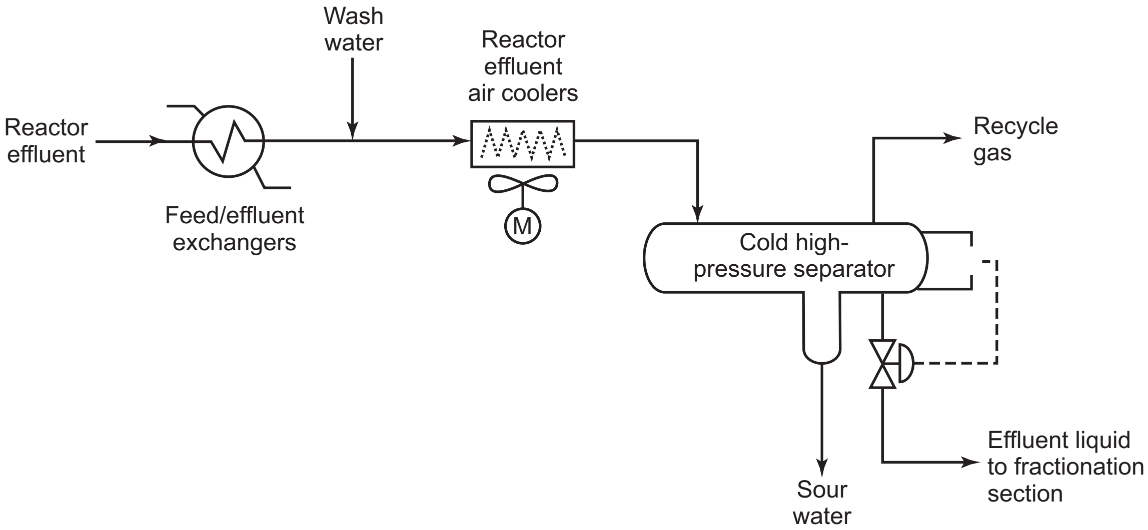


Figure 3—Example Process Scheme with a CHPS

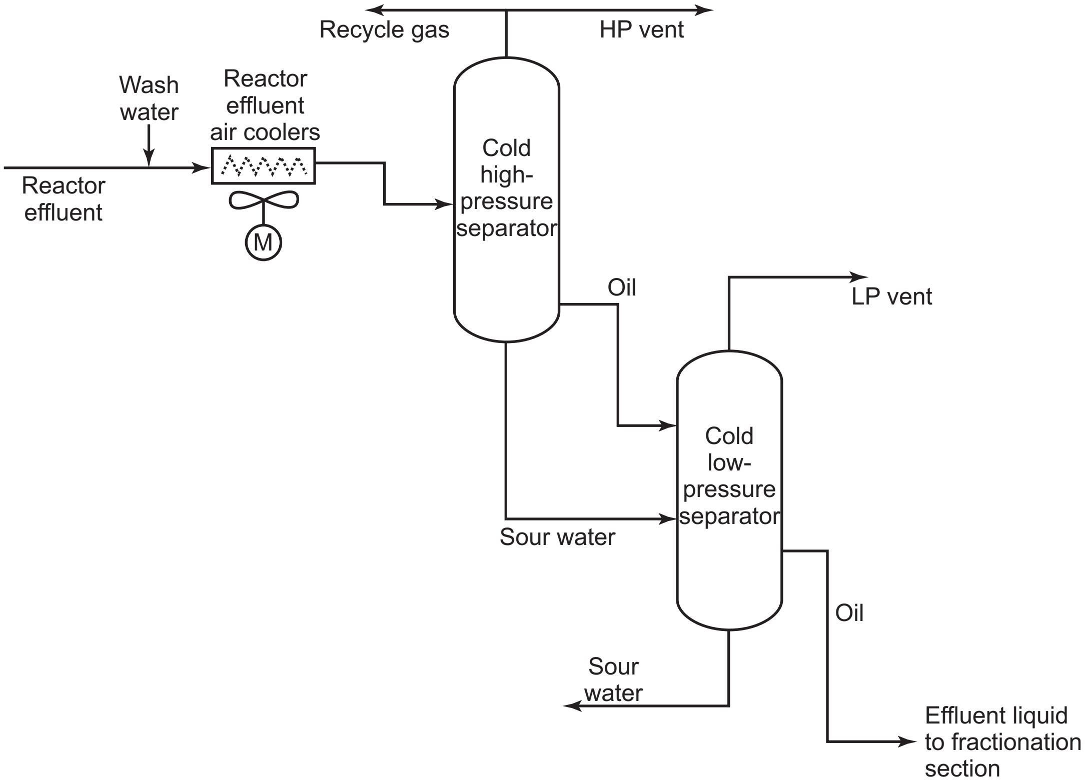


Figure 4—Example Process Scheme with a CHPS and CLPS

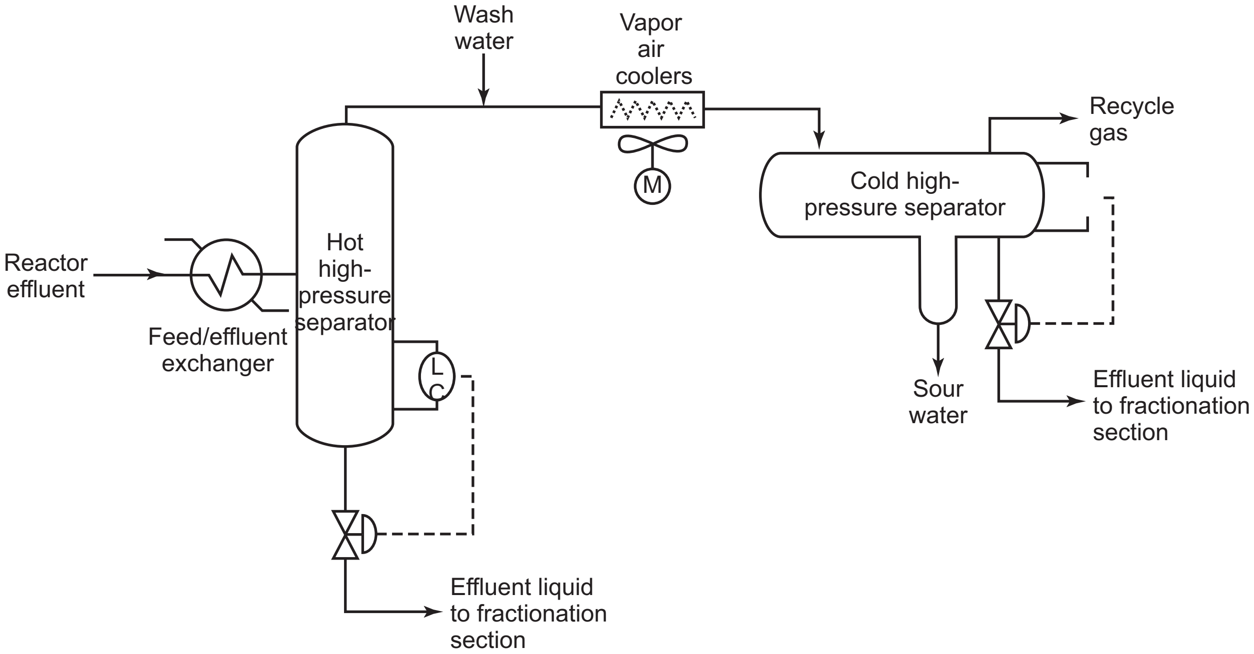


Figure 5—Example Process Scheme with Two Separators, a HHPS and CHPS

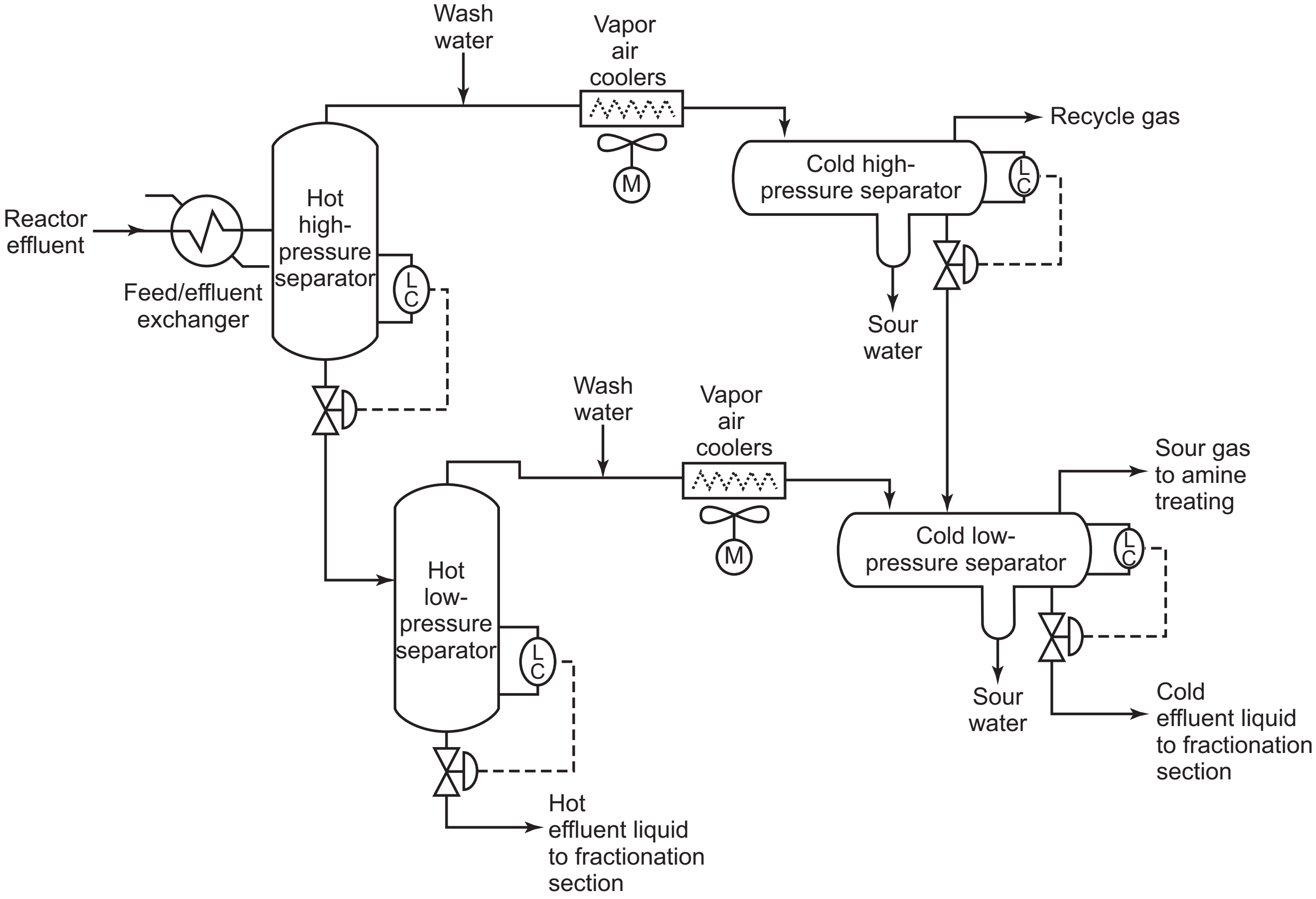


Figure 6—Example Process Scheme with Four Separators

The possible corrosion problems from these salts, both as deposits and aqueous solutions, are:

a) Aqueous NH_4HS forms an alkaline, sour water solution. These solutions can become a significant corrosion concern with increasing concentration, increasing partial pressure of H_2S, and with increasing velocity and turbulence. The predominant mechanism in these instances is erosion-corrosion. However, stagnant, concentrated salt solutions can also be corrosive.

b) Solid NH_4Cl salt can form directly from NH_3 and HCl present in the vapor. Dry NH_4Cl salt at high temperature is not corrosive, but could foul equipment and plug heat exchanger tubes. NH_4Cl salt is hygroscopic (i.e. absorbs moisture from its surrounding environment) and can get wetted due to trace amounts of free water in the reactor effluent stream when below the water dew point. A low pH condition can be created beneath the wet salt producing localized corrosion. Thus, if NH_4Cl salts form upstream of the wash water injection, the salts can be corrosive if sufficient moisture is present in the vapor stream. With concentrated NH_4Cl solutions, the attack can be more general, typical of acid solutions. Downstream of the injection location, if sufficient water is not present to dissolve and dilute the salt deposits, any wet deposits or concentrated salt solutions will be highly corrosive.

c) Wet H_2S solutions can promote cracking, such as SSC, HIC, SOHIC, and hydrogen blistering, in susceptible materials.

Injection of wash water is typically used to prevent fouling and corrosion of heat exchanger and air cooler tubes. Both NH_4HS and NH_4Cl are highly soluble in water, so properly injected and distributed wash water effectively scrubs the vapor stream and removes any salt deposits. The wash water injection point(s) is usually located upstream of the predicted location where salts will deposit. Corrosion by these aqueous salt solutions can occur if the injection system is not correctly designed and operated and the quality, quantity and distribution of wash water are inadequate.

Section 6 contains detailed discussions of the impact of process variables and wash water on the corrosion mechanisms.

5 Strategies to Promote System Reliability

5.1 General

A well-defined reliability program for the reactor effluent system is critical to maintaining the operability and mechanical integrity of equipment and piping. A program should be specific to individual units as many design and operating characteristics can impact corrosion and fouling. The reliability of equipment and piping in these systems can be sensitive to small changes in process and design conditions thus requiring careful thought in developing reliability programs. A reliability program should define three components:

1) proper material selection and design;

2) operating envelopes;

3) inspection plan.

A reliability program does not necessarily require establishing a “zero corrosion rate” system, but rather establishing operating limits and monitoring and inspection plans to assure that the system responds as expected. This program should allow the operator to manage system reliability and prevent unexpected incidents.

The reliability program is an ongoing process with regular measurements to be reviewed for possible modifications to the program. When inspection data indicate a change, it is necessary to understand the cause of the change so that the operating envelope can be modified or additional process monitoring tasks established as appropriate. The three parts to the reliability program compliment each other for inspection programs alone can not be relied on to provide reliability, especially since the corrosion can be localized.

5.2 Material Selection and Design

The material selection and design of equipment and piping affect their performance in REAC systems. An understanding of how differences in these equipment and piping details change the dependence upon the scope and frequency of inspection and the range of the operating envelope is beneficial to promoting reliability. Section 7 and Section 8 detail these considerations.

For new units, the costs associated with various options for equipment and piping should consider the future recurring costs associated with recommended inspection, process monitoring, ability to maintain operation within an acceptable envelope, and periodic, in-kind renewals. These considerations are resulting in more alloy materials being used today compared to the past.

Existing unit equipment and piping should be reviewed to assess their susceptibility to deterioration and assure that proper operating envelopes are established and inspection plans are in place. This review may identify areas of vulnerability where replacement or upgrading may be appropriate considering the cost of inspection and the constraints imposed by the operating envelope.

5.3 Establishing an Operating Envelope (Integrity Operating Window)

An operating envelope (or integrity operating window, IOW) is the acceptable range for operating variables in the process where the deterioration rate is predictable and tolerable. Establishing and maintaining this envelope helps prevent process conditions from subtly creeping into undesirable ranges where greater deterioration could result. Any consideration for operating outside the envelope invokes the Management of Change (MOC) process.

The envelope can be difficult to establish as several interrelated variables impact the corrosion potential. The effect of each variable and any synergistic effects on corrosion can be complex but needs consideration. In some instances, experience within a particular unit allows a better understanding of corrosion characteristics for that unit and possibly increased flexibility in the envelope. This understanding, however, may not apply to other units.

For new units, the guidance given in this RP is a starting point for developing an operating envelope. For existing units, the current operating variables provide a basis for establishing the envelope. However, they should be compared to the industry guidelines, and those variables operating outside industry guidelines should be reviewed to determine their significance to deterioration. The inspection history and deterioration rate data should be reviewed to identify evidence of deterioration and determine if the system has been properly inspected.

General observations are made on the effect of some operating variables on corrosion however definite conclusions cannot be drawn. These include the process variables given in 6.10 and the design factors listed below:

a) water injection design such as injection quills or spray nozzles, and single versus multiple points;

b) air cooler inlet and outlet piping design—balanced, unbalanced, symmetrical, asymmetrical;

c) air cooler design—multiple inlets, multiple row passes, single inlet, single row passes;

d) use of shell and tube heat exchangers instead of REAC;

e) materials of construction for piping, air coolers, separator, heat exchanger components;

f) piping configuration—short radius versus long radius elbows, tees, etc.;

g) stream velocities and flow regime;

h) feedstock composition—sulfur, nitrogen, and chlorides.

Once an operating envelope is established, operating variables should be maintained within these ranges. All refiners should define actions to be taken if operating outside the range either to correct the process or to implement the MOC procedure to redefine the acceptable range of the operating envelope. Multi-discipline teams, including operations, engineering and inspection, have proven successful in both establishing envelopes and defining appropriate actions if operations change outside the envelope.

Routine monitoring of the process variables is critical to assure that they remain within the envelope. Some variables are easily monitored, like temperature and pressure, while others are much more difficult. However, all process variables defined for the operating envelope should receive appropriate attention and priority.

5.4 Inspection Plans

Periodic inspection is an integral part of the reliability program that should be used to establish whether the rate of deterioration of the equipment and piping is as anticipated. A specific inspection plan should be developed for each unit. A generic plan is not recommended because too many variables influence deterioration. Section 9 provides guidance on typical inspection activities and considerations for developing REAC system inspection plans.

The inspection plan should establish the inspection technique, locations, and inspection intervals for each piece of equipment and piping in the system. Inspection of REAC systems often consists of various techniques in different locations due to the various types of deterioration possible. A multi-disciplined team can often help assure that all of the potential deterioration mechanisms are identified and the most susceptible locations defined. The inspection techniques and scope (extent of inspection) that will effectively detect each particular deterioration mechanism should be utilized. For instance, ultrasonic straight beam testing could detect thin metal but would not detect stress corrosion cracks. Inspection intervals, as a minimum, should meet API 510 and API 570 requirements, which include risk-based inspection concepts. Many units may need frequent inspections, depending on materials, design, process severity, frequency of operational changes, etc.

6 Process Variables Affecting Corrosion

6.1 Ammonium Bisulfide Concentration

The NH_4HS concentration in the sour water is a key variable of the potential corrosivity of an effluent stream. As concentration of NH_4HS increases, the corrosivity of the solution increases. The results of two industry surveys have indicated that an NH_4HS concentration of 2 % is an acceptable upper limit for producing little to no corrosion of carbon steel.[4,5] For many years, the industry has used an upper limit of about 8 % NH_4HS with control of stream velocity to less than 20 ft/s (6.1 m/s) to achieve acceptable carbon steel corrosion control. However, severe corrosion has occurred under certain conditions in some units approaching these levels.

Typically, hydroprocessing units have excess H_2S compared to NH_3, so NH_4HS concentration is “defined” by the feed nitrogen content and unit severity. Controlling NH_4HS concentration by reducing either the nitrogen content of the feed or level of denitrification is often impractical and uneconomical. Other actions to reduce NH_4HS concentration, such as increasing wash water injection rate, are often more appropriate. Before allowing feed nitrogen levels or conversion to increase, the corrosion implications need to be thoroughly reviewed through the MOC process.

The NH_4HS concentration in the sour water should be determined by appropriate process modeling with ionic equilibria considerations or obtained by sampling and testing. Appendix A contains other methods to estimate the NH_4HS concentration.

6.2 Process Conditions at the Water Dew Point

In the reactor effluent system, process simulations and experience suggest that the first condensed water droplets do not contain large concentrations of NH_4HS.[12] This is contrary to many other refinery streams where the first condensed water droplets are often concentrated with corrosives such as condensing streams containing chlorides, where the first water can be highly acidic, with pH’s of 1 to 2. The NH_4HS concentration increases as the effluent stream is further cooled. In a system with wash water injection, the dew point is forced with the injection water. If the effluent stream contains chlorides, then the first water could be somewhat acidic, but it will not be extremely low pH because of buffering.

Corrosion observed upstream of the primary wash water injection is likely due to an acidic or chloride environment. Corrosion either downstream of the air coolers or toward the outlet end of the air cooler is more likely due to NH_4HS.

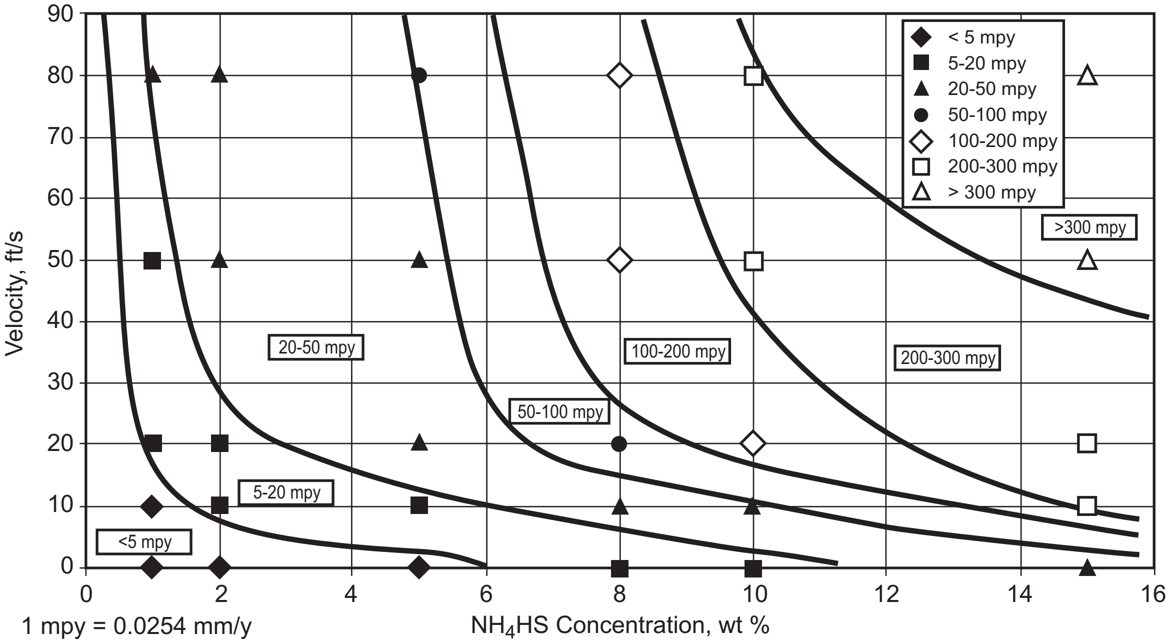
6.3 Fluid Velocities

Bulk fluid velocity is second only to NH_4HS concentration in importance as a key variable in determining aqueous NH_4HS corrosion. For a given NH_4HS concentration, increasing velocity increases the corrosivity.

Many refiners historically limited velocity to a maximum of 20 ft/s (6.1 m/s) (as defined by the bulk, average density flow) for carbon steel systems and 30 ft/s (9.1 m/s) for alloy systems, regardless of NH_4HS concentration, to prevent corrosion. These velocities were based on limited field data. As more data became available, these velocity limits were found to be too conservative in some units and not conservative enough in others. Carbon steel tubes and piping have corroded significantly at 20 ft/s (6.1 m/s), especially at elevated NH_4HS concentrations. Besides velocity, corrosion rates depend upon NH_4HS concentration, flow regime, contaminants (e.g. chlorides, cyanides, etc.), and materials of construction. Hence, it is not appropriate to establish a simple velocity rule set.

Recent research has further defined the velocity and NH_4HS versus corrosion rate with a series of isocorrosion curves for a number of typical alloys of construction in REAC systems. Not all of these data are in the public domain, but the joint industry project work reported by Horvath, et. al.[14] shows the velocity and NH_4HS relationship for corrosion rate in carbon steel as an isocorrosion diagram for NH_4HS concentrations from 1.0 % to 15 % and velocities of 0 ft/sec to 80 ft/sec. This diagram is shown in Figure 7.

[P_{H2S} = 50 psia (340 kPa absolute), Temperature = 130 °F (55 °C)]



1 mpy = 0.0254 mm/y
1 ft/s = 0.3048 m/s

Figure 7—Isocorrosion Curves for Carbon Steel at Various NH_4HS Concentrations and Velocities through Small Orifice (0.15 in.) Coupons

It should be noted, however, that these curves are based on testing done in a flow-through coupon with an 0.15 in. inner diameter. The data are used by calculating the field application shear stress, then determining the velocity required in the 100 % liquid-full, 0.15 in. ID coupon which matches the field shear stress. The velocity is then used in combination with the NH4HS concentration to establish the baseline corrosion rate. The baseline corrosion rate is further adjusted with the H_2S partial pressure, temperature, and hydrocarbon. In summary, the curves shown above only provide a directional guideline, and do not fully incorporate all the data necessary to predict corrosion rate accurately for engineering designs.

Some refiners historically applied a minimum velocity of 10 ft/s (3 m/s) to air cooler tubes to assure sufficient flow to prevent salt deposition and to adequately remove salt deposits. However, strict adherence to this velocity minimum may not be appropriate. Prevention of salt deposits by proper contacting of the injection water with the vapor phase to “scrub” HCl (remove it from the vapor phase and dissolve it in the water) is now believed to be much more critical than maintaining a minimum velocity.

6.4 Hydrogen Sulfide (H_2S) Partial Pressure

The H_2S partial pressure is another key variable of the potential corrosivity of the reactor effluent stream in H_2S-dominated sour water systems [14]. Laboratory studies showed that corrosion rate increases with increases in H_2S partial pressure at given NH_4HS levels. The effect of H_2S becomes even more pronounced at higher NH_4HS concentrations. For carbon steel, the effect is shown in Figure 8.

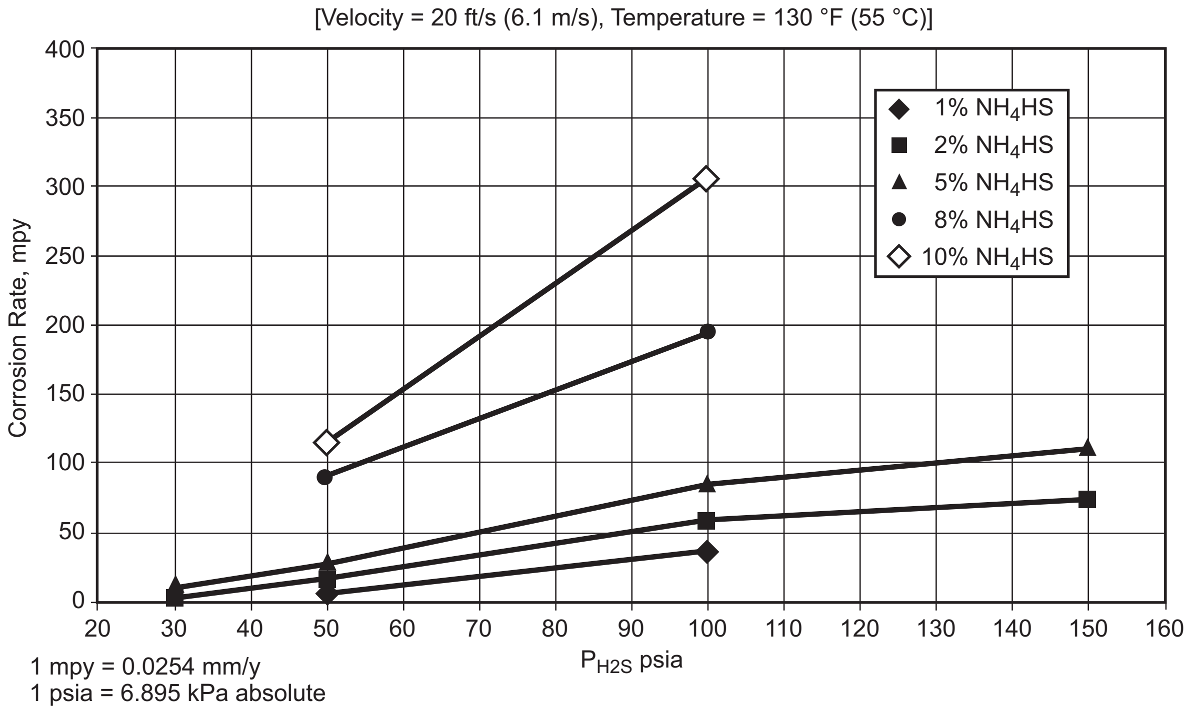


Figure 8—Curves Showing Effect of H_2S Partial Pressure on Corrosion of Carbon Steel

The effect of high H_2S partial pressures causing significant increases of corrosion rate is even prevalent on some high alloys, up to and including stainless alloy 20Cb-3 (UNS N08020), and nickel alloys 825 (N08825), 600, (N06600), and 625 (N06625).

6.5 Flow Regime

Flow regime is another key variable in the corrosivity of a stream, but it has proven difficult to define and operate with an optimum regime in piping or tubing. There are many types of two-phase horizontal flow regimes covered in detail by various references.[8] Since NH_4HS corrosion at times acts fundamentally like erosion-corrosion, flow regimes which strip away and remove the protective sulfide scale are considered detrimental. The regimes considered least harmful are low velocity stratified and annular flows.[8] Most refiners target for an annular flow, especially in air cooler tubes. Flow regimes can be important to wetting and removing salts and also impact liquid distribution through tees in the inlet piping system.

6.6 Chlorides

Chlorides entering the unit in both the hydrocarbon feed stream and the hydrogen stream are converted to HCl in the hydroprocessing reaction. HCl can promote deterioration in the unit through aqueous HCl corrosion, NH_4Cl salt fouling, and corrosion by wet NH_4Cl deposits.

For units containing high chlorides, aqueous HCl corrosion can be aggressive. One location prone to corrosion is at the initial water condensation point, most often the wash water injection point. The HCl in the effluent vapor has a great affinity to dissolve in water, even at elevated temperatures. Ammonia present in the reactor effluent stream will be absorbed into the aqueous condensate, but to a much lesser extent because NH_3 is not very readily absorbed at higher temperature. Therefore, the first water to condense may have a lower pH than the fully condensed aqueous phase in the downstream separator, and in fact may be somewhat acidic. Corrosion can occur in other areas downstream of the wash water injection point in systems that do not have good contacting and scrubbing of the vapor phase with the wash water.

Solid NH_4Cl salt can form directly from the NH_3 and HCl present in the reactor effluent stream, depending on their concentrations and temperatures. These salts usually deposit at temperatures above the water condensation point up to 400 °F (204 °C) or higher. Deposition is most likely in reactor effluent heat exchangers (upstream of the water injection), at the inlet end of the REAC, and in the top section and overhead system of the fractionator. Salt deposition has also occurred in hot high-pressure separators when operating at too low a temperature and in cool dead legs such as relief valve inlets, control valve bypass lines, instrumentation connections, and intermittently used process piping connections. Dry NH_4Cl salts are not corrosive but can create significant fouling problems. “Dry” is defined as salt in equilibrium with a vapor phase with less than 10 % relative humidity. However, the salts are hygroscopic, and tend to absorb moisture from the process stream. Wet NH_4Cl salts can be very corrosive because the salt is acidic.

The control of fouling and corrosion associated with NH_4Cl usually focuses on eliminating or at least minimizing the deposition of the salt by:

a) determining the source of chlorides and attempting to lower their concentration or eliminate them from unit feed (hydrocarbon and hydrogen) streams;

b) maintaining the temperature above the salt deposition temperature; or

c) adding wash water.

Knowing the salt deposition temperature, and monitoring of chlorides to determine any changes, is essential.

Direct measurements of the concentration of chlorides in the unit feed streams (both hydrocarbon and hydrogen) are preferred, but this is sometimes difficult, especially for the hydrocarbon feed stream. Chlorides in the hydrogen can be more easily measured, but may vary considerably with time if the source is a catalytic reformer. Typically, units send the hydrogen through an adsorbent-filled drum to scrub chlorides, but may have chloride breakthrough when the adsorbent is spent.

A commonly used approach to estimate the level of chlorides entering with the hydrocarbon feed is to measure the concentration of chlorides in the cold separator sour water and the wash water. The difference between the two would be coming from the feed streams, either hydrogen or hydrocarbon. Determining the contribution of chlorides from the hydrogen allows an estimation of chlorides coming in with the hydrocarbon feed. This knowledge allows steps to be taken to minimize the chloride levels and trace them back to the source. High chloride levels in the hydrocarbon feed stream have occurred as a result of poor desalting in the crude unit, presence of organic chlorides not removed by desalting, and processing of contaminated slops and purchased feeds.

Some chlorides may be present in the wash water, but these should not pose a problem if sufficient water is being injected to maintain an aqueous phase (i.e. NH_4HS solution) after injection. The effect of chlorides dissolved in NH_4HS solutions was studied by Scherer, et. al.[8] In their laboratory testing of 4.5 % to 10 % NH_4HS solutions with additions up to 1000 ppm chloride, they found that increases in chloride content of the NH_4HS solution did not magnify either the average corrosion rate or the pitting of carbon steel. Conversely, they found that stainless steels and certain nickel-based alloys were sensitive to pitting and stress corrosion cracking with chlorides present in the NH_4HS solutions.

This lack of appreciable increase in corrosion due to chlorides was also validated in the joint industry project reported by Horvath, et. al.[14] Their paper reported no appreciable increase of general corrosion rate for up to 1000 ppm chlorides in NH_4HS solutions of 1.0 % to 15 %.

6.7 Other Process Variables

A number of other process variables that could influence the corrosivity of the process fluid include temperature, cyanide concentration, H_2S concentration (used to calculate H_2S partial pressure), and oil/water ratio.

Scherrer, et.al. studied the effect of temperature on corrosion by NH_4HS solutions.[10] In their laboratory testing of 4.5 % to 10 % NH_4HS solutions, the temperature of NH_4HS solutions did not significantly affect corrosion from 176 °F to 212 °F (80 °C to 100 °C).

The role of cyanides in REAC corrosion is uncertain because cyanides have rarely been reported in measurable quantities in the reactor effluent stream. Piehl reported a correlation of increased corrosion with plants responding "yes" to cyanides in the NACE survey.[4] However, few data were provided. Experience with aqueous NH_4HS solutions in other processes shows that cyanides will increase the corrosivity of the solution. Hydrogen blistering, HIC, and SOHIC have been reported in carbon steel exposed to these solutions.

Determining the concentration of cyanide in REAC separator water has always been difficult. Tens of thousands of ppm H_2S in these solutions interfere with the measurement of a few ppm of cyanide. In recent years, improved test methods have been developed to address the H_2S interference however the user is cautioned to investigate and validate the test techniques.

6.8 Wash Water

Wash water should be injected, if required, in sufficient quantity to lower the dissolved NH_4HS and NH_4Cl salt concentration to the desired level and effectively scrub HCl from the vapor phase into the water phase. The quality of water is important so as not to contribute to the corrosion potential.

6.8.1 Water Quality

The primary water sources are stripped sour water, steam condensate, and boiler feedwater. Some refiners also utilize recycled sour water streams, though this is generally not as effective. Stripped sour waters containing cyanides should be avoided. Table 2 lists a summary of commonly used quality parameters for the combined wash water injected into the process.

Oxygen content is a critical variable of the wash water depending on the process water pH. The presence of oxygen increases the potential corrosion due to chloride pitting at and just downstream of the water injection point. Oxygen

Table 2—Quality Parameters of Injected Wash Water

Parameter	Maximum	Desirable Target
Oxygen (ppbw)	50	15
pH	9.5	7.0 to 9.0
Total Hardness (ppmw as Ca hardness)	2	< 1
Dissolved Iron (ppmw)	1	0.1
Chlorides (ppmw)	100 [a]	5
H_2S (ppmw)	—	< 1000 [b]
NH_3 (ppmw)	—	< 1000 [b]
Free Cyanide (ppm)	—	0
Total Suspended Solids (ppm)	0.2	Nil

[a] While chloride levels up to 1000 ppm in NH_4HS solutions have shown no apparent increase in carbon steel corrosion, chlorides should be kept to 100 ppm or less due to the potential for stress corrosion cracking of any 300-series stainless steel in the downstream sections of the hydroprocessing unit.

[b] Target and maximum concentrations are system-specific as H_2S and NH_3 are additive to the process stream concentrations.

also increases corrosion due to sulfides, especially at the lower concentrations of bisulfide (lower pH) present at the water injection point. Oxygen is a strong oxidizer and will react with the bisulfide ion to form elemental sulfur. At certain lower pH and temperature conditions, the elemental sulfur is stable and will cause fouling and corrosion in this wet sour system. However, at pH conditions above about 8, the elemental sulfur will subsequently react with NH_4HS in the sour water to form ammonium polysulfide, which can act as a corrosion inhibitor further downstream in this wet sour system.

The oxygen content of steam condensate or boiler feedwater should be reviewed. Steam condensate may be aerated depending upon where and how it is being stored. If the condensate is coming directly from a flash drum, the oxygen levels will be low compared to an unblanketed, cold condensate tank. Boiler feedwater should be drawn downstream of the deaerator. Stripped sour water, however, is generally oxygen-free.

Iron levels should be low because iron in the water will form insoluble iron sulfide and could deposit in the tubes and equipment. For instance, 50 gpm (11.3 m^3/h) of wash water containing only 1 ppm of iron will form over 300 lbs (14 kg) of iron sulfide in a year.

It should be noted that the parameters of Table 2 were developed with respect to carbon and low alloy steel REAC piping and exchanger circuits. These parameters may arguably be somewhat conservative for REAC circuits where the entire circuit is built from corrosion-resistant high alloys, but care must be taken to ensure that the circuit in question is indeed all high alloy.

Suspended solids should be kept to a minimum as well. Particulates can plug the spray nozzle or quill depending upon the design, regardless of alloy.

In addition to the primary water source, some locations may have an alternate source of water for use when the primary source is unavailable. The quality of these alternate sources should be reviewed especially if they are needed for extended periods.

6.8.2 Water Quantity

The quantity of water to be injected is dictated by two criteria:

a) producing an acceptable NH_4HS concentration in the separator water, and

b) allowing sufficient free water to exist at the injection point (i.e. an aqueous phase exists downstream of injection point).

Appendix A details sample calculations to estimate the appropriate amount of wash water.

To ensure sufficient free water, the rule-of-thumb is to have at least 25 % remaining after the injection point. Some users only target 20 % excess water. Whichever criterion is used, it might need to be adjusted based upon user experience. For instance, depending upon the inlet piping design, even 25 % may be insufficient to obtain enough free water flow to all piping branches.

Some refiners have limited capacity to handle additional sour water. At these locations, recycling a sour water stream is possible provided the overall water quality is maintained within its operating envelope.

6.8.3 Intermittent Wash Water Injection

Wash water may only be injected intermittently on some units rather than continuously. Intermittent wash water injection may be acceptable for less severe services where only periodic removal of salts is necessary. Continuous injection is usually required on units with high operating severity where salt deposition would limit unit operations through fouling and corrosion.

Intermittent wash water injection can have potential benefits but also other risks. Potential benefits from an intermittent injection include minimizing the amount of sour water produced and avoiding the need for a continuous water supply. However, there is greater potential for increased corrosion and errors in injection due to the on-off nature of the injection versus continuous injection systems. Salts must be completely washed away to prevent severe corrosion that could occur from merely wetting them. This is especially true upstream of the water dew point where salts would normally be dry and non-corrosive.

Each unit should develop a wash water injection procedure specifying quantity, duration and testing. Testing should confirm that the injection completely removes the chlorides from the process equipment and piping. This is often accomplished by showing that the chloride levels in the wash water are equal to those in the separator water through direct measurements or by conductivity. After injection, the wash water system should be effectively isolated from the process to prevent water leaking in.

Section 8.4 and Section 8.5.3.2 provide additional considerations on equipment and wash water designs.

6.8.4 Loss of Continuous Wash Water

Contingency plans should be developed for loss of the wash water injection and documented in the operating practices for the unit. Items to consider in developing contingency plans include predicting how much salt buildup occurs over a length of time, and defining potential corrosion. The amount of salt buildup is conservatively estimated by using the mass flow rate of NH_3 produced and assuming it will form NH_4HS in the air cooler tubes. In reality, this will overestimate the salt buildup since some of the NH_3 is soluble in the hydrocarbon and some salt may pass through the air cooler without depositing. Corrosion mechanisms, typically controlled with wash water injection, can occur during wash water outages. If the reactor effluent system contains chlorides, the first condensed water droplets can be highly acidic. Contingency plans could vary considerably between units due to operating differences.

The contingency plans may include a timeline for prompting actions. For instance, it may be necessary to decrease the severity of operation and minimize the denitrification of the feed or cut feed rates. This will lower the NH_3 concentrations in the effluent and resulting salt produced.

6.9 Corrosion Inhibitors

The use of corrosion inhibitors in the effluent system has been limited and has had mixed results. Some refiners have used filming amine-type inhibitors and others have used ammonium or sodium polysulfide injection. The injection of polysulfide requires different controls than an amine-type inhibitor. The user is cautioned to review polysulfide injection requirements prior to implementation. It is known that use of certain polysulfides require tight control on water quality, particularly oxygen content and pH. For example, a good practice is to limit wash water to a maximum of 15 ppb oxygen with a pH of 8 to 10 when using ammonium polysulfide (APS). Various refining companies have their own internal guidelines for use of corrosion inhibitors such as ammonium polysulfide and sodium polysulfide, therefore, the reader is encouraged to consult with specialists in this technology for additional guidance.

Performance of the amine inhibitors has been difficult to assess. Since the NH_4HS corrosion can be a form of erosion-corrosion, only the filming amines that are persistent enough to resist the turbulence associated with the locations of highest corrosion potential should be used. Performance can also vary with flow regime. These amines partition to the liquid phases and generally provide no protection in vapor areas that are downstream of a separator.

6.10 Air Cooler Fan Operations

The operation of air cooler fans can significantly impact the salting tendency in the tubes. The process temperature is often controlled with a single outlet thermocouple which is a composite of several banks of air coolers. When individual fans are turned on and off to achieve the temperature target, an imbalance can result between banks which influences the amount of cooling in one bank and can change the flow characteristics and liquid distribution. The additional cooling in some tubes can lead to isolated salt deposits in some locations while not in others, which can further change flow characteristics.

6.11 Process Monitoring

Process monitoring is critical to ensure that the key process variables are maintained within ranges defined in operating envelopes (refer to 5.3). Typical process variables that should be monitored regularly include:

a) feed sulfur levels;

b) feed nitrogen levels;

c) denitrification percent;

d) sulfur conversion;

e) H_2S concentration in the cold separator vapor phase;

f) operating temperature and pressure at air cooler inlet and outlet;

g) wash water rate;

h) NH_4HS concentration in the cold separator water;

i) pH of the cold separator water;

j) chloride and cyanide levels in the cold separator water;

k) wash water pH, chloride levels, iron and oxygen in the cold separator water.

Additional process monitoring to proactively indicate and prevent potential corrosion problems requires a combination of sampling and calculations. Calculated variables include velocities throughout the piping and tubing, flow regimes, H_2S partial pressure, etc.

Table 3 presents guidelines for monitoring key process variables. The frequency for monitoring these variables varies and should be adjusted for the particular operating characteristics of the unit. An example might be a routinely changing feedstock could require more frequent monitoring of the NH_4HS concentration in the separator water. Furthermore, dramatic changes in variables such as nitrogen content of the feed might require more frequent monitoring of variables like NH_3 and CN^-.

Table 3—Guidelines for Monitoring Process Variables

Process Variable Related to Corrosion	Sample Location	Example Frequency
Sulfur levels	Feed	Daily to weekly
Sulfur conversion	Feed/Product	Daily to weekly
Nitrogen levels	Feed	Daily to weekly
Nitrogen conversion	Feed/Product	Daily to weekly
Chlorides	Feed	Depends on history and concern level
Operating temperatures and pressures	Various	Continuous/shift
NH_3 and H_2S	Separator Water	Weekly to monthly
Concentration of Cl^-	Separator Water	Weekly to monthly
Concentration of CN^-	Separator Water	Quarterly to as needed
pH	Separator Water	Weekly to monthly
Wash water rate	Wash Water Injection (Flow Meter)	Continuous to daily
Water quality e.g. pH, O_2, Fe, TSS, hardness	Wash Water	Monthly to quarterly

Sampling of the sour water from the cold high pressure separator is often difficult to perform and requires addressing safety and environmental concerns. This location is at high pressure, but closed samples can be obtained using a sample cylinder designed for the operating pressure. Sampling is sometimes performed downstream in a lower pressure separator or degassing drum. H_2S, hydrogen and light ends can evolve from the water as a result of the pressure drop, but only insignificant amounts of NH_3 evolve from these cold samples. In obtaining the water sample, oxygen ingress should be avoided and the sample should be capped immediately. Inconsistency on these steps can dramatically alter the results and make it difficult to trend results.

7 Materials of Construction

7.1 General

Materials of construction and mechanical design of equipment and piping have a profound impact on the corrosion experienced in a plant. The performance of various materials of construction is often governed by the mechanical design (e.g. by promoting balanced flows and appropriate limiting velocities for a given set of operating conditions). For new installations, alloy materials are more often employed for high severity units to allow greater flexibility in the mechanical design and operation. For existing installations changing to more severe conditions, operators have attempted to push the existing materials to higher limits. In cases where carbon steel failed or was predicted to have deterioration problems, it was upgraded to alloy materials.

7.2 Material Selection Criteria

Materials currently in use in REAC systems include carbon steel, Type 400 series stainless steels, Type 300 series stainless steels, duplex stainless steel alloys 3RE60 and 2205, Alloy 800, Alloy 825 and Alloy C-276. Alloy 400 has also been used in some units. Table 4 shows the composition of alloys referred to in this section. The selection of a material and its performance in service vary depending upon operating conditions and fabrication practices. None of these materials are entirely immune to corrosion in these services although some deterioration mechanisms are easier to manage with some alloys than others. Each material will be discussed as to its considerations for use in these services.

Note that this discussion focuses on resistance to NH_4HS corrosion and not on resistance to wet NH_4Cl salts. Potential high alloy upgrades that could be considered are Alloy C-276, Alloy 625 and a super duplex stainless steel Alloy 2507. However, deterioration from NH_4Cl is best prevented through process controls discussed in 6.6 as opposed to material upgrades. Some refiners have used Alloy C-276 where NH_4Cl is a concern in cold dead legs such as small instrument connections.

7.2.1 Carbon Steel

Carbon steel is a standard material of construction in the cooler portions of the effluent system for piping and pressure vessels, and for air coolers under low severity NH_4HS conditions. The areas suitable for carbon steel use generally too cool for sulfidic corrosion or high-temperature hydrogen attack of carbon steel. However, carbon steel has the least resistance to corrosion by NH_4HS and is susceptible to hydrogen blistering, HIC, SOHIC and SSC. It would also suffer extremely high corrosion rates under wet NH_4Cl deposits (as would most alloys). Carbon steel plate for this service is sometimes specified to be “low sulfur” and possibly “inclusion-shaped controlled” to enhance the resistance to HIC and SOHIC.

Weld procedures and techniques should be chosen so as to produce welds and heat-affected zones within a hardness limit to resist SSC as recommended by NACE RP0472. Additionally, specifying PWHT of equipment made from plate is commonly done to improve resistance to SSC and SOHIC. Refer to NACE Publication 8X194 and NACE RP0472, for additional details. Piping thicknesses often found in the higher pressure REAC systems require PWHT due to the ASME code requirements. Some users specify PWHT of the piping regardless of thickness to improve resistance to cracking in this wet H_2S service.

7.2.2 Duplex Stainless Steels

Duplex stainless steels are often successfully used in these systems because they offer advantages of both the ferritic and austenitic stainless steel families. They are often cost effective due to their higher strength and reduced alloy element content compared to other higher alloys. However, since this material consists of dual phase microstructure, heat-treating, fabrication and welding techniques need to be carefully reviewed and monitored to assure that the balanced microstructure is not compromised.[13] In the past, Alloy 3RE60 was successfully used, but it had inferior corrosion resistance and toughness at the welds and is no longer available. The most commonly used grade today is Alloy 2205.

Duplex stainless steels have failed by hydrogen embrittlement cracking in these services, but these problems were attributed to improper fabrication. Specific considerations to minimize the possibility of deterioration are to specify a minimum of 0.14 % N content and a water quench. This helps avoid intermetallic precipitates. Weld procedures should be developed to assure ferrite content in the 35 % to 65 % range (measured by ferrite scope). Higher ferrite content can lead to hydrogen-related cracking and reduced corrosion resistance. There have been a few failures in duplex stainless steel header box welds and duplex stainless tube-to-tubesheet welds the designer or user need to be aware of. Additional guidance on materials and fabrication practices to achieve good corrosion resistance in duplex stainless steels are given in API 938-C.

Super duplex stainless steels such as Alloy 2507 are predicted to perform better than Alloy 2205, and hence are promising for resisting severe environments.

Table 4—Referenced Material Compositions

ALLOY/ UNS NUMBER	C	Si	Mn	Fe	Cr	Ni	Mo	Cu	N	Al	Ti	Nb
Carbon Steel	0.3	0.1 min	0.29 – 1.06	Bal								
Type 410 S41000	0.15	1.0	1.0	Bal	11.5 – 13.5	0.75						
Type 430 S43000	0.12	1.0	1.0	Bal	16.0 – 18.0	0.60						
Type 304L S30403	0.03	0.75	2.0	Bal	18.0 – 20.0	8.0 – 10.5						
Type 321 S32100	0.08	1.0	2.0	Bal	17.0 – 19.0	9.0 – 12.0			0.10		5(C+N) – 0.7 max	
Type 347 S34700	0.08	1.0	2.0	Bal	17.0 – 19.0	9.0 – 12.0						10XC, – 1.0 max
3RE60 S31500	0.030	1.4 – 2.0	1.5 – 2.0	Bal	18.0 – 19.0	4.25 – 5.25	2.5 – 3.0					
Alloy 2205 S31803	0.030	1.0	2.0	Bal	21.0 – 23.0	4.50 – 6.50	2.50 – 3.5		0.08 – 0.20			
Alloy 2205 S32205	0.030	1.0	2.0	Bal	22.0 – 23.0	4.50 – 6.50	3.0 – 3.5		0.14 – 0.20			
Alloy 2507 S32750	0.030	0.8	1.2	Bal	24.0 – 26.0	6.0 – 8.0	3.0 – 5.0		0.24 – 0.32			
Alloy 800 N08800	0.10	1.0	1.5	Bal	19.0 – 23.0	30.0 – 35.0		0.75		0.15 – 0.60	0.15 – 0.60	
Alloy 825 N08825	0.03	0.5	1.0	30	19.5 – 23.5	38.0 – 46.0	2.5 – 3.5	1.5 – 3.0		0.2	0.6 – 1.2	
Alloy 400 N04400	0.3	0.5	2.0	2.5		63 min		28.0 – 34.0				
Alloy C-276 N10276	0.01	0.08	1.0	4.0 – 7.0	14.5 – 16.5	Bal	15.0 – 17.0					
Alloy 625 N06625	0.1	0.5	0.5	0 – 5.0	20.0 – 23.0	58 min	8.0 – 10.0					3.15 – 4.15

NOTE Single values refer to maximum content.

7.2.3 Alloy 825

Alloy 825 is widely used for its resistance to NH_4HS, PTA SCC, and chloride SCC. Alloy 825 contains lower carbon and increased titanium to minimize the potential for sensitization to prevent deterioration from PTA SCC and intergranular corrosion. In addition, the molybdenum content in the alloy improves its passivity and thus pitting and corrosion resistance. Alloy 825 is also highly resistant to chloride stress corrosion cracking by virtue of its nickel content.

For Alloy 825, a high nickel filler metal is commonly used which exceeds the properties of Alloy 825 and has superior corrosion resistance.

7.2.4 Other Alloys

7.2.4.1 Type 400 Series Stainless Steels

The Type 400 series stainless steels have limited use in REAC service and their use is no longer recommended. One major refining company has successfully used Type 410 (12 Cr) stainless steel for over 30 years in REAC service with NH_4HS concentrations up to 5 %, because of its improved resistance to NH_4HS corrosion in this concentration range, as compared to carbon steel. However, pitting has been experienced in a few applications as a result of chlorides, especially at low velocities. Type 430 (17 Cr) stainless steel has also been used. However, Piehl noted that tube life had been unsatisfactory in every case where it was used for hydrocracker REACs.[4] Alvarez and Robertson reported Type 430 stainless steel HDS REAC tubes failed within one year due to severe localized pitting under scale and sludge present in the tubes.[7] The majority of the corrosion pitting was found in tubes with low flow.

7.2.4.2 Type 300 Series Stainless Steels

The Type 300 series stainless steels should be avoided in REAC service due to chloride SCC concerns above 140 °F (60 °C). The alloys have improved resistance to NH_4HS corrosion and have been used for air coolers in older plants with relatively low REAC inlet temperatures. One common application is as cladding or weld overlay in the separator. When selecting a Type 300 series stainless steel, an “L” grade is commonly used to avoid sensitization from welding.

7.2.4.3 Alloy 800

Alloy 800 was a standard material in the past due to its resistance to NH_4HS and chloride SCC. However, several failures attributed to PTA SCC decreased its use in favor of Alloy 825. Depending upon the carbon content of the alloy, Alloy 800 can become sensitized (e.g. during welding) and susceptible to PTA SCC. Several failures were reported with Alloy 800 when carbon contents were at or above 0.06 %. For some older units, Alloy 800 LC (low carbon) was specified with a maximum carbon content of 0.05 % and fine grain; however, this material is no longer available. In a few cases, Alloy 800 tubes also suffered chloride-pitting damage attributed to improper lay up procedures during extended downtime.

7.2.4.4 Alloy 400

Alloy 400 has provided years of successful service in a few locations reporting its use. However, there are concerns about the use of this nickel-copper alloy in elevated pH, high NH_3 content REAC systems. Piehl reported that Alloy 400 was resistant in REAC systems containing up to 2 % to 3 % NH_4HS. [4] Scherrer, et.al., measured corrosion rates of 32 to 37 mpy (0.8 to 0.9 mm/y) for Alloy 400 exposed to 4.5 % to 5 % NH_4HS at velocities of 11 to 21 ft/s (3.4 to 6.4 m/s).[10]

7.2.4.5 Alloy C-276 and Alloy 625

Alloy C-276 and Alloy 625 perform very well under severe conditions in the few process units using them. Alloy 625 has been used successfully for cladding and weld overlay in cold separators and REAC piping.

7.2.4.6 Relative Ranking of Alloys in Aqueous NH_4HS Service

Horvath, et. al.[13] studied 14 different alloys in their program in solutions of 1 to 30 weight percent ammonium bisulfide with 50 psia hydrogen sulfide at 130 °F. Data from these tests can be shown to show relative ranking of these alloys in order to assist in materials selection. The data are plotted as a relative corrosion resistance ranking versus NH_4HS in H_2S-dominated alkaline sour waters as shown in Figure 9. The reader is cautioned that for actual operating systems, these rankings are relative and are approximates, in terms of corrosion rates and ratios of corrosion rates.

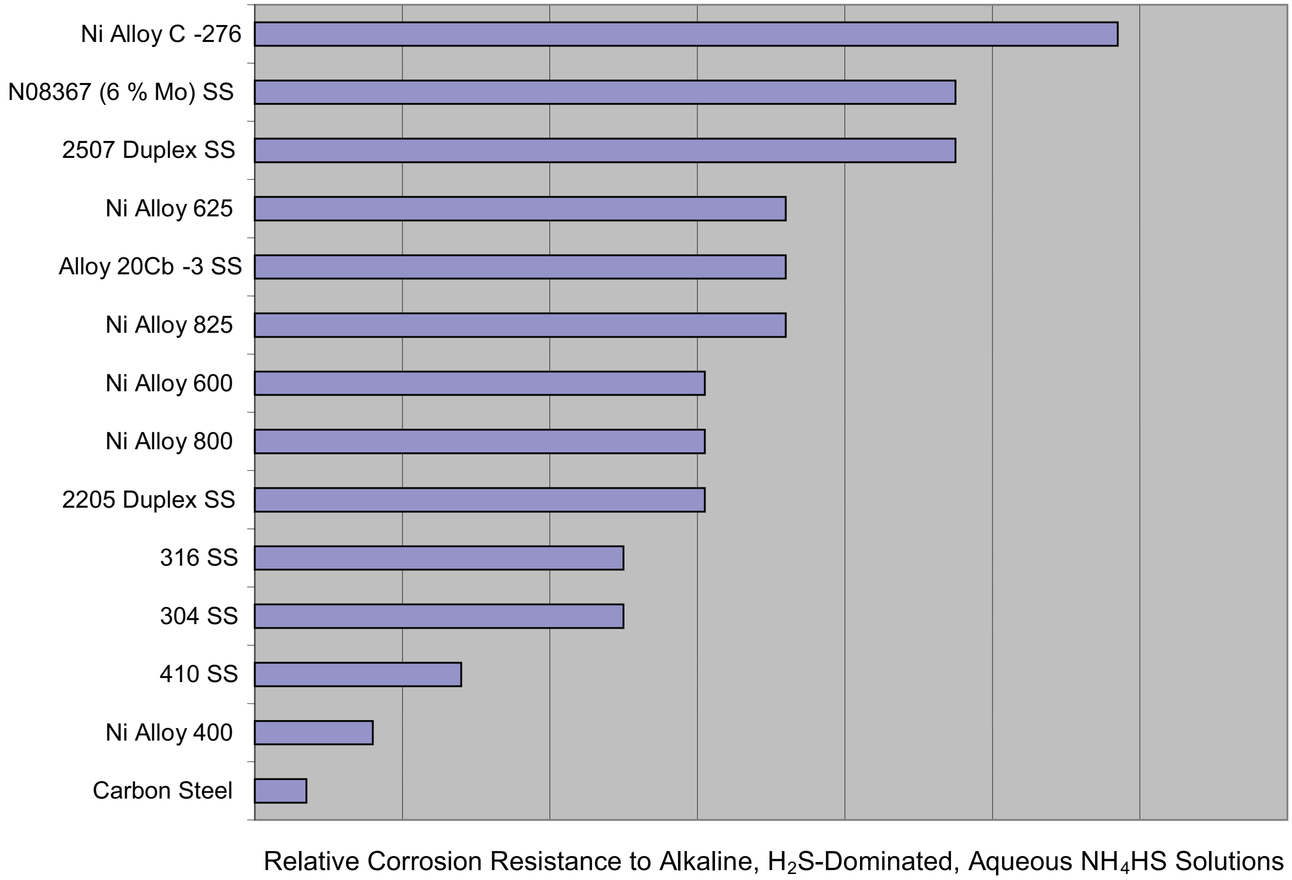


Figure 9—Relative Alloy Performance in Aqueous NH_4HS Service

8 Equipment Specific Design Considerations

8.1 Fin Fan Air Coolers

8.1.1 Materials of Construction

Material selection for the REAC considers the application, operating experience, and laboratory data. Carbon steel has performed acceptably in most low severity units. In moderate to severe units, carbon steel has mixed performance usually related to design issues or unit operating variables. Alloy materials are often used for new installations in moderate and severe units and for upgrading present materials where performance has been unsatisfactory.

REAC header boxes should be the same alloy material as the tubes for new installations. For upgrades, the header boxes are usually replaced with an alloy matching the tubes; however, in some low to moderate corrosion systems, tubes have been upgraded while the existing carbon steel header boxes have been reused.

8.1.2 Design and Fabrication Considerations

8.1.2.1 Header Boxes

REAC header boxes typically have multiple inlet and outlet nozzles to better assure adequate flow distribution through the bank. Header boxes designed with only one row of tubes per pass or one row of tubes for the first pass can be used to minimize flow maldistribution within a pass. In “problem” systems, users have observed greater corrosion in upper rows of tubes when there are multiple tube rows per pass and attributed it to flow maldistribution and partitioning between tube rows in multiphase liquid and gas services. For these reasons, single tube row passes or a single tube row inlet pass should be considered. This is especially critical in units where NH_4Cl deposition is likely to occur in the hot first pass of coolers due to inadequate contacting of a HCl-containing vapor stream with wash water, but less so in units with either low chlorides or acceptable contacting.

Header box design prevents double-sided welds from being used for many joints. Single-sided welded joints can be prone to lack of fusion defects and require specialized inspection techniques such as ultrasonic shearwave.

Carbon steel header boxes are subject to PWHT in accordance with API 661. This heat treatment occurs prior to tube installation and any associated tube-to-tubesheet welding.

8.1.2.2 Tubes

U-tube designs should not be used with carbon steel tubes due to the risk of erosion-corrosion of the bends. Failures have been reported with the use of carbon steel U-tubes.[4] However, U-tubes have been used by some refiners in alloy air coolers. In many new designs, U-tubes are avoided because they are difficult to clean if they become fouled with heavy polynuclear aromatics and the U-bend areas are difficult to inspect.

8.1.2.3 Tube Ferrules

Austenitic stainless steel tube ferrules have occasionally been used at the inlet and outlet ends of carbon steel tubes. The ferrule provides a corrosion resistant liner in the regions prone to localized corrosion from flow turbulence. Ferrules are about 10 in. (250 mm) in length, which is usually long enough to extend beyond the location of increased corrosion and turbulence. The ferrule is designed to fit tightly into the tube and is installed by light rolling or by shrink fitting.

A minimum 4:1 taper is recommended at the end of the ferrule to prevent localized turbulence that have caused localized corrosion of the carbon steel tube.

8.1.2.4 Tube-to-Tubesheet Joint

The tube-to-tubesheet joint has three design options including rolled, rolled and seal welded, and strength welded. The rolled joint is satisfactory for mechanical strength under most operating conditions. However, tube expansion should be limited when rolling duplex stainless steel. Excessive expansion produces high hardness from work hardening and reduces corrosion resistance. Some users specify a maximum of 2 % expansion, mainly for positioning before strength welding. The austenitic stainless steels work harden as well. Special close tolerance hole dimensions for the tubesheet should be specified by the user to avoid difficulties during tube rolling.

Rolled and seal welded or strength welded tube-to-tubesheet joints are typically specified by some users in high-pressure applications or where additional assurance against a joint leak is believed necessary. The difference between the two is that the tube roll provides the mechanical strength in the rolled and seal welded, whereas the weld provides the strength (a roll is not necessary although a light roll may be performed to facilitate assembly) in the strength welded design. Welds in duplex stainless steel require special attention (ferrite/austenite ratio) to assure that the corrosion resistance is not compromised, especially in strength welds where any corrosion or cracking can lead to failure.

8.1.2.4.1 PWHT of Cr-Mo Alloy Steel Tube-to-Tubesheet Joints

Normally, REAC header boxes and tubes are built from carbon steel, or other corrosion-resistant alloys such as duplex stainless, nickel alloy 825 or higher. These materials are chosen dependent on operating parameters such as temperature, NH_4HS content, and H_2S partial pressure [H_2SPP]. Generally, REACs operate at temperatures well below the API 941 Nelson Curve for high temperature hydrogen attack (HTHA), but may see temperatures that exceed the Nelson Curves during upsets and these temperature excursions would only be for very brief periods of time.

In limited cases, designers and/or users have specified 1 $^1/_4$ Cr – $^1/_2$ Mo alloy steel to mitigate risk of incurring HTHA damage during upset conditions when the combination of temperature and partial pressure of hydrogen puts operating conditions above the Nelson Curve for carbon steel for these short excursions. Since it is sometimes impractical to PWHT tube-to-tubesheet welds, the user should consider the risk of wet sulfide stress cracking (SSC) of the non-PWHT'd material. The highest area of concern for SSC is in the heat affected zone of the tube-to-tubesheet strength or seal welds.

Since PWHT of tube-to-tubesheet welds in an air cooler header box is difficult, the designer and/or user is encouraged to look at alternate approaches to mitigate both HTHA for these short excursions and avoid high hardness in the HAZs of the tube to tubesheet strength or seal welds. NACE MR0103 gives recommended hardness limits for steels in wet H_2S service*.*

8.2 Shell-and-Tube Trim Coolers

The design and materials of construction of these exchangers is often a compromise between several competing considerations including the following.

a) *Cooling Water*—The cooling water side and its corrosivity are important design considerations because, unlike most conventional cooling water exchangers, these exchangers in high-pressure units may have cooling water on the shell side.

b) *Effluent on Tubeside or Shellside*—Effluent location and NH_4HS concentration are important considerations as they impact material selection and type of bundle. As the NH_4HS concentration increases, regions of high velocity or turbulence pose a corrosion problem. Regions of stagnant or very low flow can be prone to fouling and underdeposit corrosion.

c) *Operating Pressure*—For high-pressure units with effluent on the tube side, the use of flanged joints are often minimized to remove potential leak locations. Integral channel and tubesheet designs are often used for high-pressure exchangers and are generally more economical.

d) *U-tubes*—Trim coolers often use U-tube bundle designs. Alloy tubes should be considered for NH_4HS services subject to erosion-corrosion.

e) *Wash Water Distribution*—The main cooler occasionally uses shell-and-tube exchanger design and therefore can require wash water. Distribution of wash water can be difficult but should be considered in the design.

f) *Inspection Limitation*—The use of alloy tubes minimizes the need for and expense associated with inspection of this complex and massive type of assembly.

The material selection for the tubes should consider the NH_4HS concentration, tube velocity, type of bundle and corrosivity of the cooling water. Carbon steel is used in less severe services. Duplex stainless steels and Alloy 825 are considered in higher NH_4HS concentrations and velocities. They also provide good resistance to most cooling water corrosion although higher alloys would be necessary for salt water cooling applications.

8.3 Cold High-Pressure Separator (CHPS)

The separator design should consider the concentration of NH_4HS and be sized to adequately separate the water. Carbon steel or alloy clad or weld overlaid steel are typical materials of construction. There is increased use of austenitic stainless steel or Alloy 825 clad (or equivalent alloy weld overlay) shells to prevent HIC and SOHIC concerns and eliminate future WFMT inspection costs. In some units, carbon steel experienced significant hydrogen blistering, HIC and SOHIC damage. The worst damage was in streams with NH_4HS concentrations exceeding 8 % to 10 % and high H_2S partial pressures. HIC-resistant steels may not perform well enough under these aggressive conditions. Alloy cladding or weld overlay allows the carbon steel base metal to be a common grade without special requirements for HIC resistance. Alloy cladding or weld overlay should be considered for elevated NH_4HS

concentrations where there is a significant concern for HIC and SOHIC. Units designing for elevated NH_4HS concentrations by alloying upstream equipment (e.g. REAC) and piping, should also use an alloy clad or weld overlaid separator.

The separator design (vessel orientation, sizing, nozzles, internals and instrumentation) should minimize liquid water entrainment in the overhead vapor stream and in the hydrocarbon liquid draw. Water carryover in the hydrocarbon draw can result in sour water corrosion downstream such as in higher velocity areas like control valve stations, at mixing points, and in the fractionation tower and overhead systems.

Sour water carryover into the overhead vapor stream or into the hydrocarbon liquid draw results in H_2O, NH_3, H_2S, and Cl contaminants going to downstream locations where NH_4HS corrosion and underdeposit NH_4Cl corrosion can then occur.

Several reports of localized corrosion in downstream gas piping systems from the separator were attributed to NH_4HS corrosion from water carryover (or perhaps condensation of a portion of the water vapor present in the overhead gas). With proper separator and internals design, liquid water entrainment in the CHPS overhead gas can be minimized. Heat tracing of the overhead line is an additional measure to minimize the presence of a liquid water phase, but steam tracing can actually aggravate ammonium salt corrosion at the steam tracing contact points. Standoffs or proprietary designed steam tracing which prevent contact with the piping should be considered. In addition, other operators have installed trayed water washes within the CHPS vessel itself to remove additional NH_3 from the separator overhead, thereby preventing NH_4HS corrosion in the downstream piping.

8.4 Heat Exchanger or Air Cooler Upstream of REAC

Although most reactor effluent systems have a shell-and-tube heat exchanger upstream of the REAC, a limited number of units have another air cooler upstream of the REAC.

The chloride levels in the process and the possible use of intermittent wash water upstream often govern the material selection for these exchangers. These exchangers are particularly susceptible to NH_4Cl deposition and corrosion since they operate in the deposition temperature range. The process design of these exchangers should assure that the temperature of the cooled effluent stream remains sufficiently above the water dew point conditions during normal operation when intermittent upstream wash water injection is not being conducted.

Often, wash water is intermittently injected upstream of this equipment to remove NH_4Cl salts. Exchangers requiring the use of wash water should be designed to assure that adequate wash water is present and properly distributed following the guidelines given in 6.7. The design should also consider the NH_4HS corrosion accompanying any wash water and velocities should be properly reviewed to assure that corrosion is not aggravated. For infrequent wash water injection, significant rates of NH_4HS corrosion may be acceptable for the short duration of the wash. For frequent or long-duration water wash injection, there can be a significant concern.

Exchangers operating above about 450 °F (230 °C) may be susceptible to high-temperature hydrogen attack. API 941 should be reviewed to select an appropriate material with resistance to high-temperature hydrogen attack.

Material selection for these exchangers thus depends upon several factors. The common materials for the effluent process side are carbon and Cr-Mo steels. High alloy materials might be necessary for resistance to NH_4HS corrosion; however, even these materials would not provide full resistance to wet NH_4Cl corrosion. Nickel alloys such as Alloy 625 and Alloy C-276 should be considered if corrosion is suspected due to high chlorides.

8.5 Piping & Valves

8.5.1 Materials of Construction

The material selection for piping components should be based upon the location within the system and potential deterioration mechanisms. Material for high temperature piping systems operating above about 450 °F (230 °C) should be in accordance with API 941. Typically, the material selection for piping systems is predominantly governed by NH_4HS corrosion. However, due consideration should be given to the presence of chlorides that could lead to HCl or wet NH_4Cl corrosion, such as at wash water injection points or in cool process dead legs.

The most common materials for piping systems are carbon steel and Alloy 825. Austenitic stainless steel is not considered for this application due to the potential for chloride SCC. However, there have been successful applications of austenitic stainless steels downstream of air coolers where the temperatures are below 140 °F (60 °C) and there is sufficient water to keep chlorides diluted.

Duplex stainless steels have also been used successfully in practice. In the recent joint industry project reported by Horvath, et. al. [14], duplex stainless alloy 2205 had better performance than carbon steel, ferritic stainless steel, and 300-series austenitic stainless steels. Therefore, duplex stainless steels could be considered for moderate NH_4HS conditions. This work also showed that the more highly alloyed 2507 duplex stainless steel had lower corrosion rates than nickel alloy 625. Since the ferrite to austenite balance of duplex stainless steels is key to their good performance, welding and other fabrication techniques need to be reviewed carefully. In addition duplex stainless steels can be subject to chloride stress corrosion cracking and sulfide stress cracking under certain circumstances. API 938-C discusses welding, fabrication, and applications of duplex stainless steel, and the reader is advised to review that document.

Alloy 825 and Alloy 625 clad (or weld overlaid) carbon steel are used in a few units instead of solid alloy due to cost and the greater availability of clad piping today. In high-pressure systems, clad piping may offer a cost savings over solid alloy due to the wall thickness required for pressure containment.

Material selection for valves is also governed by NH_4HS corrosion. However, it is important to recognize that valve internals may be subject to significant turbulence especially around the seats. Even though the valve seats may be an alloy, the body can suffer severe metal loss either undermining the seats or penetrating through the body. Thus alloy valve bodies and seats should be considered when NH_4HS corrosion is a concern. Pressure letdown valves with a significant drop in pressure and resulting turbulence generally have alloy valve bodies (e.g. Alloy 825 or Type 316 stainless steel) and cobalt-alloy trim. This is typical for pressure letdown valves in the water and liquid hydrocarbon lines off the CHPS. Alloy piping is also often used for a distance of ten pipe diameters downstream of the letdown valve or at least past the first change of direction.

For valve trim, austenitic 300-series stainless steel is commonly selected over ferritic and martensitic 400-series stainless steels, due to the greater sulfide stress cracking concerns of the 400-series stainless alloys.

8.5.2 Piping Design and Fabrication Issues

Piping system design should address velocity and turbulence of the multiphase streams and flow distribution into and out of air coolers. The velocity limits for the particular material selected should be established and adhered to. In designing the piping layout and sizing, consideration for how the unit will be operated is necessary. For instance, if bypass piping is to be installed around exchangers, the size should be selected considering the velocity through the bypass when in use.

Carbon steel piping in these systems is often fabricated with practices to reduce localized turbulence. This can include specifying a welding process such as GTAW to produce a root pass flush with the inside surface and using NDE acceptance criteria that do not allow any excessive penetration. In large diameter systems, the root pass can be ground flush if necessary.

ASME B31.3 requires heat treatment of carbon steel piping above $^3/_4$ in. (18 mm) wall thickness. However, some users specify heat treatment for this piping regardless of the Code requirements. PWHT helps assure that the material will better resist SSC and SOHIC (although on piping welded from one side, there have been very few cases of SSC or SOHIC in these services on non-heat treated piping). In addition, the stress reduction accompanying PWHT is beneficial in improving the tolerance of the steel to defects when considering brittle fracture and fitness-for-service concepts. There have been incidents of hydrogen blistering in piping indicating a severe hydrogen-charging environment. These are often related to high NH_4HS concentrations.

Valves should be selected considering the turbulence associated with the particular valve type, valve operation, and material of construction. Particular attention should be given to pressure letdown valves, like the sour water letdown valve off the CHPS. The valve, reducers upstream and downstream of the valve, and corresponding piping immediately downstream can be severely attacked.

8.5.3 Piping Configurations

8.5.3.1 REAC Inlet and Outlet Piping

Balanced flow through the air cooler banks and inlet and outlet piping is important to reduce the potential for localized corrosion and fouling of the piping and air cooler tubes. Corrosion is dependent upon the materials of construction and the process fluid characteristics. However, fouling is independent of material of construction. An unbalanced flow can create high flow rates in some banks and low flow rates in others, and variations in the water distribution. These influence the type, amount and location of corrosion and fouling.

Distribution of the process flow through multi-bank air coolers is highly dependent upon the piping configuration. Piping configurations that increase pressure drop through a particular air cooler bank can cause maldistribution of the process flow. Use of a balanced inlet and outlet piping configuration is the most common approach to help assure proper distribution to each bank of the REAC.

Figure 10 shows an example of balanced and unbalanced flow designs for REAC inlet piping configurations. For balanced flow, each split in the REAC inlet piping downstream of the wash water injection should be divided into two identical branches to achieve equal distribution of vapor, liquid hydrocarbon, and water. Thus, the total number of REAC inlet nozzles will equal 2^n where the exponent “n” is the number of splits to achieve the equal distribution. In addition, the details of the inlet piping geometry should be specified so as to resolve any liquid phase flow bias due to centrifugal force. The distance of the straight run piping before the tee typically affects whether the liquid splits evenly at the tee. In lieu of this approach, proprietary inlet piping designs incorporating specially designed piping components have been used successfully to achieve balanced flow and uniform water distribution. These may be more difficult to design, but are usually cost-effective for REAC systems with a large number of air cooler banks.

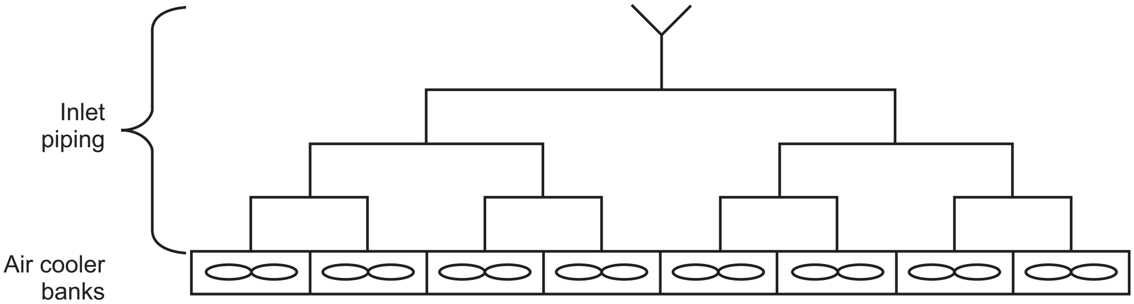
The design of the REAC outlet piping to the separator should be balanced although this may be less critical than the REAC inlet piping. At this stage of the process, the liquids have already condensed and corrosion will be dependent upon fluid velocity, NH_4HS concentration and material of construction. The piping configurations should minimize changes in direction and incorporate long-radius elbows to control turbulence.

Balanced flow may be the intent of the design, but when the system is in service, the flow can be influenced by operational factors. Particular air cooler banks can be operated differently which promotes greater fouling or increased cooling in one than another. This is especially true when the fans are operated unevenly. These actions can increase the pressure drop, and therefore, unbalance the flow. Attention to operational factors is still important even for those systems with a balanced flow design.

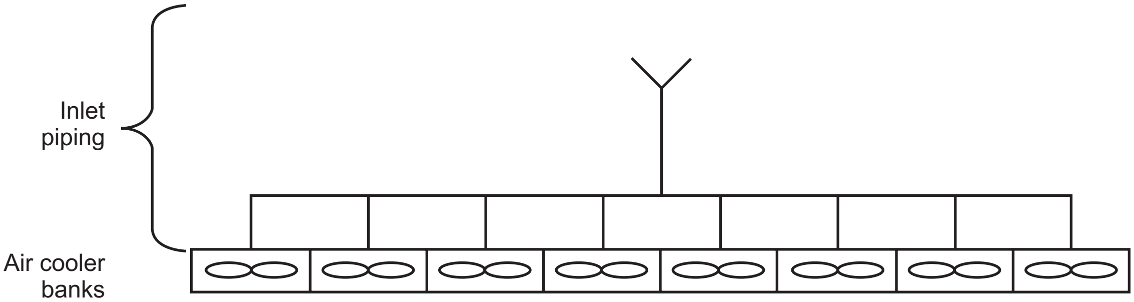
Additionally, bypass piping and compressor spillback line tie-ins should be configured to avoid creating dead legs and holding liquid while not in use. They should be configured to be self-draining (e.g. branch connections are at twelve o’clock on horizontal lines).

8.5.3.2 Wash Water Injection Systems

Wash water injection systems are configured with either a single or multiple injection points. The decision to use a single or multiple points often depends upon the configuration of the inlet piping.



Symmetrical, Balanced



Unbalanced

Figure 10—Illustration of a Balanced and Unbalanced Inlet Piping Configuration

For existing unbalanced, non-symmetrical systems, multiple injection points can better assure that water is being distributed into each of the inlet streams. Injection points tend to be on the inlet line to each inlet nozzle (an air cooler may have multiple inlets). However, the reliability can be poor and small branches are more prone to plugging with multiple injection points. Contacting time for removal of chlorides from the vapor phase is also limited, whereas the single injection point is usually much further upstream and allows greater contact time.

For balanced, symmetrical systems, a single injection point can be used since the water will be distributed somewhat equally through the system and the water will have more contacting time with the vapor phase. However, some users also choose a multiple injection system for balanced systems. Another option is a combined single and multiple point injection system.

Other factors should be considered in designing a single versus multiple injection wash water system. Water flow rates to each injection point should be sufficient so that at least 25 % liquid water remains after injection. For an unbalanced system, it can be difficult to assess the process flow through each inlet leg and therefore harder to determine the amount of water needed at each injection point. Material of construction of the piping and air coolers could also influence the selection since alloy materials are generally more forgiving of poor water distribution when considering NH_4HS corrosion.

The design of a multiple water injection system is often more complex than a single point. The challenge with multiple points is assuring that at each injection there is the proper amount of water being injected. This design often entails orifice plates or small manual valves and flow meters on each water injection line to obtain and measure water distribution. Manual systems present an ongoing challenge for operators to maintain the desired water flow to each injector. Automated control systems should be considered with multiple point injection systems to provide the most uniform water distribution.

Injection quills or spray nozzles should be used for the water injection into the process stream. The design should assure that good contact with the process vapor stream is achieved and that direct impingement upon the pipe wall is avoided. Current practices now tend to prefer use of co-current spray nozzles, rather than counter-current nozzles. This is because there have been a few failures reported which were believed to be due to impingement on the one side of the piping due to counter-current nozzle flow. Spray nozzles are generally preferred over injection quills due to superior water droplet dispersion and mixing. Some refiners have successfully used in-line static mixers in conjunction with spray nozzles or injection quills to further facilitate good mixing of water with process fluid. For additional information on injection quill designs and considerations, refer to NACE Publication 34101.

Intermittent wash water injection systems should have a positive shutoff of the water when not in use. A small amount of water leaking in can produce high corrosion rates. Positive shutoff is often achieved by double block and bleed valves. If the wash water is used rarely, installation of a blind is recommended.

8.5.3.3 Dead Legs, Pipe Supports

Dead legs in these piping systems should be avoided. Dead legs upstream of the REAC are prone to salt deposition and corrosion (especially due to wet NH_4Cl salt) as they tend to be cooler than the primary line. Intermittent water wash injection connections should be considered as dead legs in design and inspection.

Pipe support designs and placement should consider the need for inspection of piping components prone to corrosion. For instance, “dummy legs” on elbows make inspection of a corrosion-prone component more difficult. Therefore, “dummy legs” are not recommended on carbon steel piping within the scope of this document. Some designs do not allow “dummy leg” supports for any piping regardless of material of construction.

9 Inspection of the REAC System

9.1 General

The inspection strategy for the reactor effluent system is to monitor, assess, and maintain the integrity of equipment and piping in the system. This is accomplished through identifying the potential deterioration mechanisms, detecting the deterioration, monitoring the deterioration rate, and taking action when needed to alter the deterioration rate or to make repairs. The varied deterioration mechanisms possible in the effluent system make a thorough inspection plan a necessity. Inspection plans should address each possible deterioration mechanism by detailing the location to examine, appropriate NDE technique(s) and inspection interval. As a minimum, inspection plans should conform to API 510 and API 570 requirements including the provisions of risk-based inspection. Inspection of pressure vessels for wet H_2S cracking should be performed in accordance with NACE RP0296.

Inspection plans will typically involve tasks performed on-stream and other tasks performed during maintenance turnarounds. On-stream inspection provides a periodic means of monitoring deterioration and provides data to assess the operating process envelope. It also provides data to better plan activities during scheduled maintenance outages. Inspection during maintenance turnarounds provides the opportunity to internally inspect equipment for localized deterioration. The periodic internal inspection of equipment is especially important in effluent systems due to the known localized corrosion potential of these processes. Internal inspections also provide a check that the on-stream inspection locations are in the optimum locations and are representative of the deterioration in the system.

Each effluent system is unique in terms of process conditions, material of construction, design, and configuration. The inspection details provided in this RP are for general guidance and should be changed to reflect to the particulars of each system.

9.2 Reactor Effluent Air Coolers

The inspection plan for air coolers is highly dependent upon the material of construction of the header boxes and tubes. Carbon steel air coolers generally require more comprehensive inspection than alloy air coolers due to the lower resistance of carbon steel to NH_4HS corrosion and its susceptibility to wet H_2S cracking mechanisms.

In general, the refining operator should review each hydroprocessing unit separately to identify potential problem areas. Items discussed in previous sections of this RP, such as water wash quality, symmetric and balanced flow, injection point locations, etc., should all be evaluated to assess whether or not they are optimal. If not, then more frequent inspection, and more-robust inspection techniques may be necessary.

Although outside the focus of this document, the air cooler mechanical components, like fans and louvers, should be inspected and maintained to assure their operability. This is important to maintain a balanced flow through the banks.

9.2.1 Header Boxes

Straight beam ultrasonic testing (UT) with scanning capability is one recommended technique to identify localized corrosion. Automated ultrasonic testing (AUT), close-grid manual UT, or B-scanning UT (with its longer encoded scan) can be effective on header boxes. Particular attention should be given to turbulent areas of the header box like at the inlet and outlet nozzles, and the tubesheets in the area near the nozzles. Borescope video inspection may be used to inspect header boxes for localized corrosion and tube inlet corrosion. Expected dead spots and crevice type areas also need to be inspected closely. Figure 11 shows a cross section of an internal surface of a REAC outlet nozzle that failed because of NH_4HS corrosion. This figure shows the failure at the point where a leak occurred. The corrosion left a gouged appearance, attributed to the high turbulence in this region.

Carbon steel header boxes should be inspected for wet H_2S cracking and localized corrosion from NH_4HS. Inspection is difficult and often limited due to the lack of internal access and to their geometry. Most often, header box welds are ultrasonic shearwave tested for sulfide stress cracking (SSC). Since the weld geometry is not ideal, review of the inspection procedure and testing of the technician with mock-ups is recommended. For welds that were not ultrasonic shearwave tested during fabrication, the NDE technician may need to perform extra validation to separate in-service flaws from indications due to fabrication defects. More advanced ultrasonic inspection techniques, might be necessary to differentiate between stress corrosion cracks and fabrication defects and to size any indications. For new header boxes, it is recommended to perform crack inspection before putting the unit into service in order to provide a “baseline” for comparison to future in-service inspections.

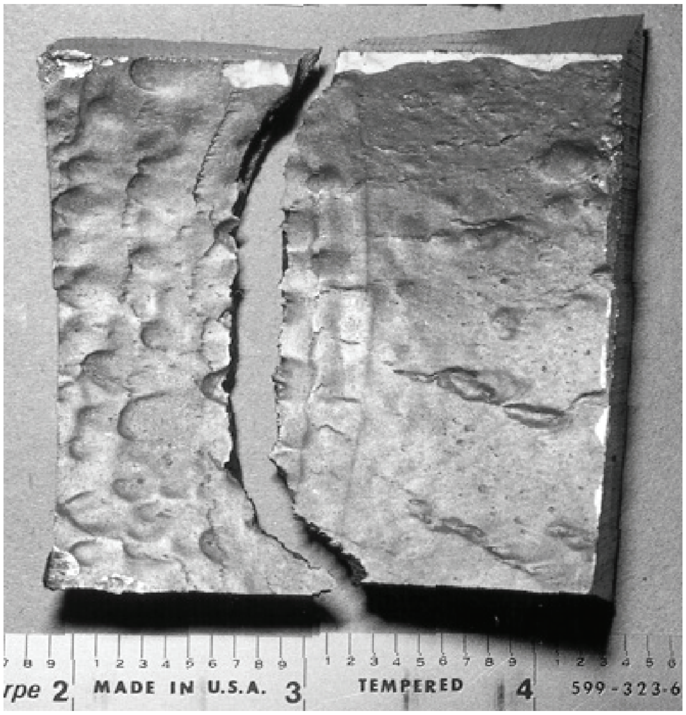


Figure 11—Cross Section of Internal Surface of Failed REAC Outlet Nozzle

9.2.2 Air Cooler Tubes

Tubes should be inspected to assess their condition at their inlets, outlets and along the full lengths. Using a boroscope or fiberoptic device can provide a visual examination along the length of the tube. However, it may not be effective in identifying pitting if the tubes are not adequately cleaned of internal deposits and scale. Also, general tube thinning is difficult to identify visually.

IRIS (internal rotary inspection system), an ultrasonic technique, is commonly used to measure tube wall thickness. IRIS can also identify pitting within certain detection limits, but not cracking. For IRIS to provide quality results, the internal surface of the tubes must be very clean and slow pulling speeds need to be maintained especially when looking for isolated pitting. In some cases, this can require grit blasting. One limitation of IRIS is the loss of the first 4 in. to 5 in. of reading at the tube inlet. This can be remedied by inserting the probe from the opposite end of the tube, running it all the way to the original end in question. A quicker technique is to use an adaptor (a small piece of tube) fitted on the tube end inside the header box to allow inspection without the data loss.

Remote field eddy current (RFEC) and magnetic flux leakage (MFL) can be used to assess ferromagnetic tubes. RFEC and MFL are faster but less accurate than IRIS. RFEC and MFL techniques are less effective at the tube inlet and outlet where the tube is located in the tube sheet. RFEC can be difficult on finned air cooler tubes. The fins interfere with electromagnetic fields and can lead to erroneous interpretation of the RFEC data. Some refiners use RFEC or MFL as an initial screening technique and follow it up with IRIS to confirm the RFEC or MFL results. As with any inspection technique, RFEC, MFL and IRIS should be proved up with mock-ups and sample tubes to confirm the adequacy and calibration of the instruments, the procedures and the competence of the technicians.

Near-field Testing (NFT) and Externally Referenced Remote Field Testing (XRFT) are newer and have proven more effective than RFEC for inspection of finned tubes. The Near Field Technique is specifically suited for aluminum finned air coolers and works under the same principles as the External Reference Field Technique (XRFT). NFT is faster, has less attenuation loss in finned tubes, and requires less tube ID surface cleaning than IRIS. Refiners and inspection companies have reported that up to 400 tubes can be inspected in one work shift using NFT. However, NFT does not quantify tube wall losses as well as IRIS, therefore, it is a good practice to use IRIS to more-accurately quantify the most-suspect areas found by an NFT examination technique.

XRFT is a variation of RFT where an external reference to create a balanced system reduces the effects of unwanted noise such as from aluminum fins. It was originally developed for detection of inlet and outlet erosion-corrosion. It is limited mainly to detection of internal wall loss and external wall loss over 75 % through-wall. Limitations on small volume defects are similar to RFT.

Profile radiography can also assess the corrosion of the tubes. However, this is often limited to the top and bottom rows and adjacent to the tubesheets where there is the best access. In addition, a portion of the external fins may need to be stripped away in the area to be inspected.

Inspection of tube ends can be an important indicator of NH_4HS corrosion. Tube ends should be visually inspected through the tubesheet. Caliper measurements of tube ends historically has been performed to establish a corrosion rate and determine timing for tube plugging. However, the user is cautioned not to assume the condition of the tube ends reflects the condition of the tube elsewhere. Another corrosion indicator is to visually or ultrasonically inspect the back end of the tube plugs especially in the area of the inlet and outlet nozzles.

Alloy tubes may require less inspection due to the more limited deterioration mechanisms possible. Eddy current testing of the tubes is beneficial for the identification of stress corrosion cracking, pits, and fatigue cracks. The NDE technician should understand the potential defects in the tubes so that sample tubes can be made for calibration and testing.

While the unit is on-stream, the use of infrared thermography can be useful in identifying unbalanced flow, two-phase flow, and tube plugging.

9.3 Piping

Piping inspection plans vary depending upon the material of construction, piping design and configuration. Inspection techniques focus on identifying wall thickness loss, hydrogen blistering of carbon steel and stress corrosion cracking of susceptible materials. These piping systems can be more easily inspected on-stream for they are not typically insulated and operate at relative colder temperatures.

Typical inspection techniques for these systems include ultrasonic straight beam, electromagnetic acoustic transducers (EMAT) and profile radiography for wall thickness loss. Straight beam ultrasonic testing is the most common approach to identify wall thinning. Ultrasonic scanning, such as an A-, B- or C-scan, is preferred over obtaining spot thickness readings due to the potential localized nature of corrosion. EMAT, which sends and receives Lamb waves in the pipe circumferential direction, can be used as a rapid screening tool to detect localized corrosion. Profile radiography is an alternative to ultrasonic scanning although follow-up ultrasonic testing is likely necessary to better quantify wall losses. Real-time radiography can be used as a screening tool to inspect any insulated piping for localized corrosion.

Ultrasonic scanning is useful to detect and map hydrogen blisters (typically found in the most severe services). If blisters are found, ultrasonic shearwave testing of the blister edges should be performed to assess the presence of any HIC (step-wise cracking). The NDE technician performing this testing should be experienced and qualified in identifying and detecting these defects. The owner/user should require performance demonstration testing to feel confident in the technician’s ability. When inspecting for hydrogen blisters and HIC, a multi-channel AUT system that has the capabilities to overlay the shear wave results onto the L-wave results can provide detailed analysis.

Carbon steel piping should be inspected in the locations of highest turbulence and on representative straight sections. Particular locations include changes in direction associated with the inlet and outlet piping, reducers, pressure letdown valve bodies, and piping downstream of pressure letdown valves. Figure 12 shows a carbon steel piping elbow that was located just downstream of the weld with severe localized erosion-corrosion. The cause was ammonium bisulfide containing liquid condensate in a high velocity vapor line leaving the CHPS in a hydrotreater unit.

Wall thickness measurements on the piping define the corrosion rate and allow a comparison between various piping branches. Differing corrosion rates can indicate an unbalanced flow. Inspection of only a percentage of the piping branches to or from the air cooler nozzles is not recommended since each piping branch can have a unique environment and corrosion rate. Elbows should be scanned on the outside radius, neutral axis, inside radius and immediately downstream. Corrosion can be found in these locations depending upon orientation and the amount of liquid in the process.

Figure 12—Erosion-Corrosion of Carbon Steel Piping Elbow

Additionally, localized corrosion can occur on the straight sections, depending upon several factors such as the liquid flow regime, and has appeared as a spiral pattern down the line. Sections of straight piping lengths should be scanned to identify any potential thickness losses.

The wash water injection point is a common location for localized corrosion. The piping should be ultrasonically inspected for thickness with a close-grid pattern starting upstream of the injection point and moving downstream. Any impingement areas resulting from the presence and type of injection quill also should be ultrasonic scanned. Radiographic inspection of the quill is often beneficial to assess its integrity and assure the water is injected into the pipe properly. Refer to API 570 for additional guidance on inspection of injection points.

Alloy piping may be monitored with a limited number of CMLs strategically placed at the highest turbulence areas, since thinning is less expected. However, depending upon the alloy and its fabrication, it may be susceptible to stress corrosion cracking from chlorides or polythionic acid. Ultrasonic shearwave of representative welds for cracking should be considered in these cases.

9.4 Pressure Vessels—Separators, Heat Exchanger Shells

Carbon steel pressure vessels exposed to the effluent stream should be inspected for wet H_2S cracking mechanisms in accordance with NACE RP0296. A typical inspection technique is WFMT (wet fluorescent magnetic particle testing) of welds. The surface should be cleaned to a near-white metal finish. Surface preparation is usually achieved by abrasive grit blasting, and sometimes followed up with flapper wheel polishing to increase detection sensitivity. ACFM (alternating current field measurement) has also been used successfully to detect wet H_2S cracking, although it is not as sensitive as WFMT. Internal visual inspection and ultrasonic straight beam testing can complement each other when inspecting for hydrogen blisters. Detection and assessment of HIC and SOHIC will require ultrasonic shearwave inspection.

Automated ultrasonic testing, using straight-beam, angle-beam, or time-of-flight diffraction, is preferred to better identify and size crack indications and to allow meaningful assessment of crack growth. A multi-channel AUT pulse-echo system capable of overlaying shear wave results onto the L-wave results can define cracking and blistering. Acoustic emission may also be used to detect cracking in the through-wall direction.

Shells and all major components should be inspected with ultrasonic straight beam testing to measure wall thickness and establish a corrosion rate. Additional CMLs should be added if appropriate from inspection results or internal visual inspection results.

Refer to 9.2.2 for inspection of the heat exchanger tubes.

10 Limitations and Recent Improvements in the Industry Knowledge Base

10.1 Experience

The guidance provided in the first edition of this document is based predominantly upon findings drawn from operating experiences of plant personnel, and design engineers. Since the early 1960s, corrosion and deterioration experiences have been documented. Guidance and “empirical formulas” developed from these experiences have produced mixed results as failures continue to occur.

Limitations associated with using operational experiences for the reactor effluent system are the quality and consistency of the reported data. As the interaction of numerous process variables influence the deterioration, a complete understanding of these experiences is difficult to compile. Process stream compositions and operating variables are difficult to characterize since they are not constant. Thus, “empirical formulas” derived from experiences with reactor effluent systems provide direction to address particular situations but should not be used to precisely predict performance.

10.2 Recent Joint Industry Research

A joint industry project initiated in 1998 obtained more precise and quantitative understanding of the role of various process conditions on the NH_4HS corrosion of carbon steel and many alloys typically used in REAC systems. Significant work was completed using controlled laboratory experiments to study REAC process, alloys, and corrosion variables independently. In addition, process simulation software was developed to further review the interaction of chemical species in the process stream. Since the project was privately funded, not all of the information is in the public domain, but some of the key findings have been published and are incorporated into Section 1 through Section 9 in this edition of API 932-B. A summary of the findings is presented in the next section.

A summary of the joint industry project findings are as follows:

1) For H_2S dominated, alkaline, sour water systems, three discrete NH_4HS corrosion regimes were indicated for carbon steel:

    a) At low NH_4HS concentrations (2 wt % or less), low corrosion rates were observed at low velocity. Corrosion rates increased only marginally with increased velocity.

    b) At intermediate NH_4HS concentrations (2 to 8 wt %), low to moderate corrosion rates were observed at low velocity. Corrosion rates increased markedly with increased velocity.

    c) At high NH_4HS concentrations (greater than 8 wt %), moderate to high corrosion rates were observed at low velocity. Corrosion rates increased markedly with increased velocity.

2) H_2S partial pressure has a significant effect on the corrosion of carbon steel and all the alloys tested. The corrosion rates of carbon steel and several of the alloys at P_{H2S} = 100 psia to 150 psia (690 kPa to 1,000 kPa absolute) were significantly higher than their respective corrosion rates at P_{H2S} = 50 psia (340 kPa absolute).

3) H_2S partial pressure proved to be a major variable that must be considered when assessing the potential for NH_4HS corrosion in alkaline sour environments. Previously, refiners had focused on two variables, NH_4HS concentration and velocity. The recent research demonstrated this approach to be inadequate, and that H_2S content must be considered as the third key variable controlling corrosion.

4) Test results do not support the continued use of the 20 ft/s (6.1 m/s) velocity limit for controlling NH_4HS corrosion of carbon steel. That limit is too conservative at low NH_4HS concentrations and low H_2S partial pressures, and too liberal at high NH_4HS concentrations and high H2S partial pressures. Furthermore, it does not adequately account for differences resulting from multiphase flow regimes present in most REAC systems. Wall shear stress was found to be a much better scaling parameter than velocity for correlating corrosion performance of materials.

5) Although used with historic success, duplex stainless alloy 2205, and nickel alloy 825 still can corrode at intermediate and high NH_4HS concentrations, especially at high velocities and high H_2S partial pressures.

6) Duplex stainless alloy 2507 and nickel alloy N08367 were shown to be more corrosion resistant than duplex stainless alloy 2205 and many other nickel alloys. Nickel alloy C-276 was also shown to have the highest resistance of all the alloys tested in the laboratory program.

7) The corrosion rates of carbon steel and all alloys evaluated in this program increased with increasing temperature. The effect of temperature on the corrosion rate of carbon steel was greatest at low NH_4HS concentrations, and diminished as the NH_4HS concentration increased. Temperature appears to have less effect on corrosion than NH_4HS concentration, velocity (wall shear stress), and H_2S partial pressure.

8) The presence of hydrocarbon mixed with sour water resulted in reduced corrosion rates when compared to 100 vol % sour water. Substantial protection was achieved for carbon steel at hydrocarbon contents greater

than 25 vol %. Substantial protection was achieved for the higher alloys tested at lower hydrocarbon contents.

9) Addition of 50 ppm to 500 ppm volume ammonium polysulfide (APS) successfully reduced the NH_4HS corrosion rate of carbon steel by 75 % to 90 %. At low velocity (wall shear stress), APS formed a more stable protective film on the metal surface that led to greater protection. At higher velocities (wall shear stress), this film became less stable, resulting in reduced protection.

10) Addition of 100 ppm to 500 ppm volume imidazoline reduced the NH_4HS corrosion rate of carbon steel by 35 % to 95 %, but it showed a high degree of variability. The successful results with imidazoline relied on sufficient mixing to ensure contact of the imidazoline with the metal surface. Thus, the potential reduction of corrosion when using imidazoline may not be realized with certain flow regimes, particularly stratified or laminar flow.

Annex A
(normative)

Process Calculations and Estimates

The NH_4HS concentration in the water can be obtained by sampling and testing or determined by appropriate process modeling with ionic equilibria considerations. Other methods can approximate the NH_4HS concentration in the separator water. Generally, new units use estimated values from feed nitrogen and denitrification. For existing units, estimates can also be made but verification with sampling is recommended since estimates can be misleading. Calculations in this section are from "Design of Hydroprocessing Effluent Water Wash Systems" by James Turner.[12]

A.1 NH_4HS and NH_4Cl Deposition Temperatures

To use the chart in Figure A.1 (from reference 12) for NH_4HS deposition, the engineer should calculate the mass action term for the NH_4HS salt, which is the product of the partial pressure of NH_3 and the partial pressure of H_2S in the reactor effluent, or:

$$Kp = [\mathrm{NH}_3 pp] \times [\mathrm{H_2S}\ pp]$$

The partial pressure of each component, i, can be calculated by taking the moles of the component in the vapor phase divided by the total moles in the vapor phase multiplied by the absolute pressure (P) in the process.

$$\mathrm{P}p i = (\mathrm{n}i \text{ vapor phase}) / (\mathrm{n}total \text{ vapor phase}) \times \mathrm{P}$$

Where ni, is the mole fraction (in the vapor) of the ith component.

The same procedure can be used to estimate the NH_4Cl deposition temperature from Figure A.2.

The net NH_3 yield can be calculated from the nitrogen level in the feed and the percent denitrification. If a licensor or catalyst vendor is involved, they will normally supply the reactor net yields.

If the unit is operating with a reactor effluent water wash, the NH_3 content in the reactor effluent is basically the same as the amount of NH_3 produced in the reactor. This is because essentially all of the NH_3 is absorbed in the water and hydrocarbon liquid phases in the separator(s), and removed from the reactor loop. However, if no wash water is present, the NH_3 content will be considerably higher, because NH_3 will be recycled back to the reactor with the recycle gas.

A.2 NH_4HS Concentration in the Separator Water

The following formula can be used to estimate the wt % NH_4HS in the CHPS water for all cases where there is no HHPS and the net reactor H_2S yield is greater than the net NH_3 yield:

$$\text{Wt\% NH}_4\text{HS in solution} = \frac{(\mathrm{MW\ NH_4HS}) \times Wf \times Fn \times CN \times 100}{(\mathrm{MW\ N}) \times WWr \times 100 \times 100}$$

$$\text{which simplifies to} = 0.0364 \times Wf \times Fn \times Cn / WWr$$

where

Wf is the mass flow rate of unit feed;

Fn is the wt% Nitrogen in the unit feed;

Cn is the % Denitrification in the reactor (net nitrogen conversion);

WWr is the mass flow rate of wash water injection;

MW NH_4HS is the Molecular weight of NH_4HS = 51;

MW N is the molecular weight of nitrogen = 14.

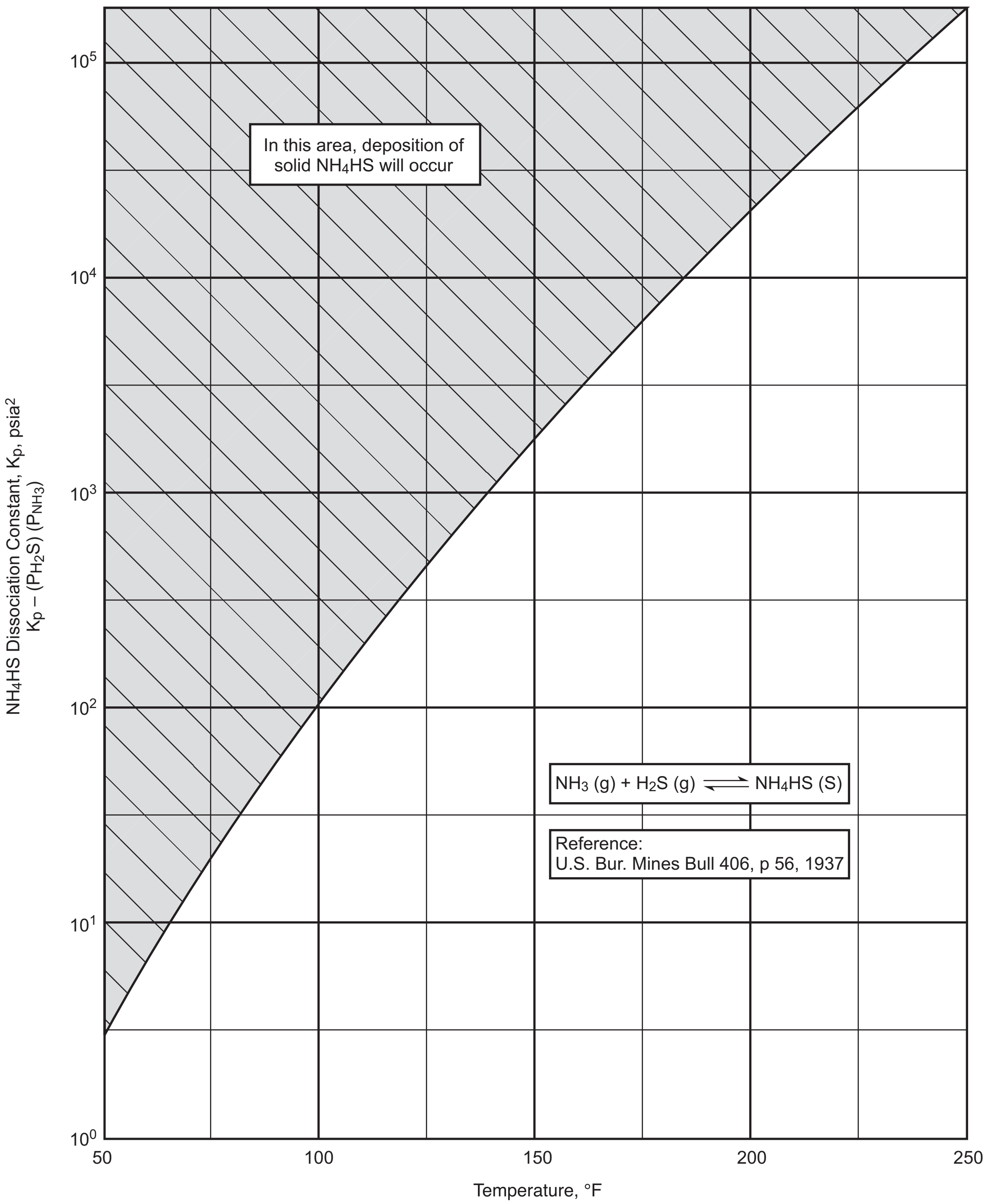


Figure A.1—Estimating NH_4HS Deposition Temperature from Process Stream Composition

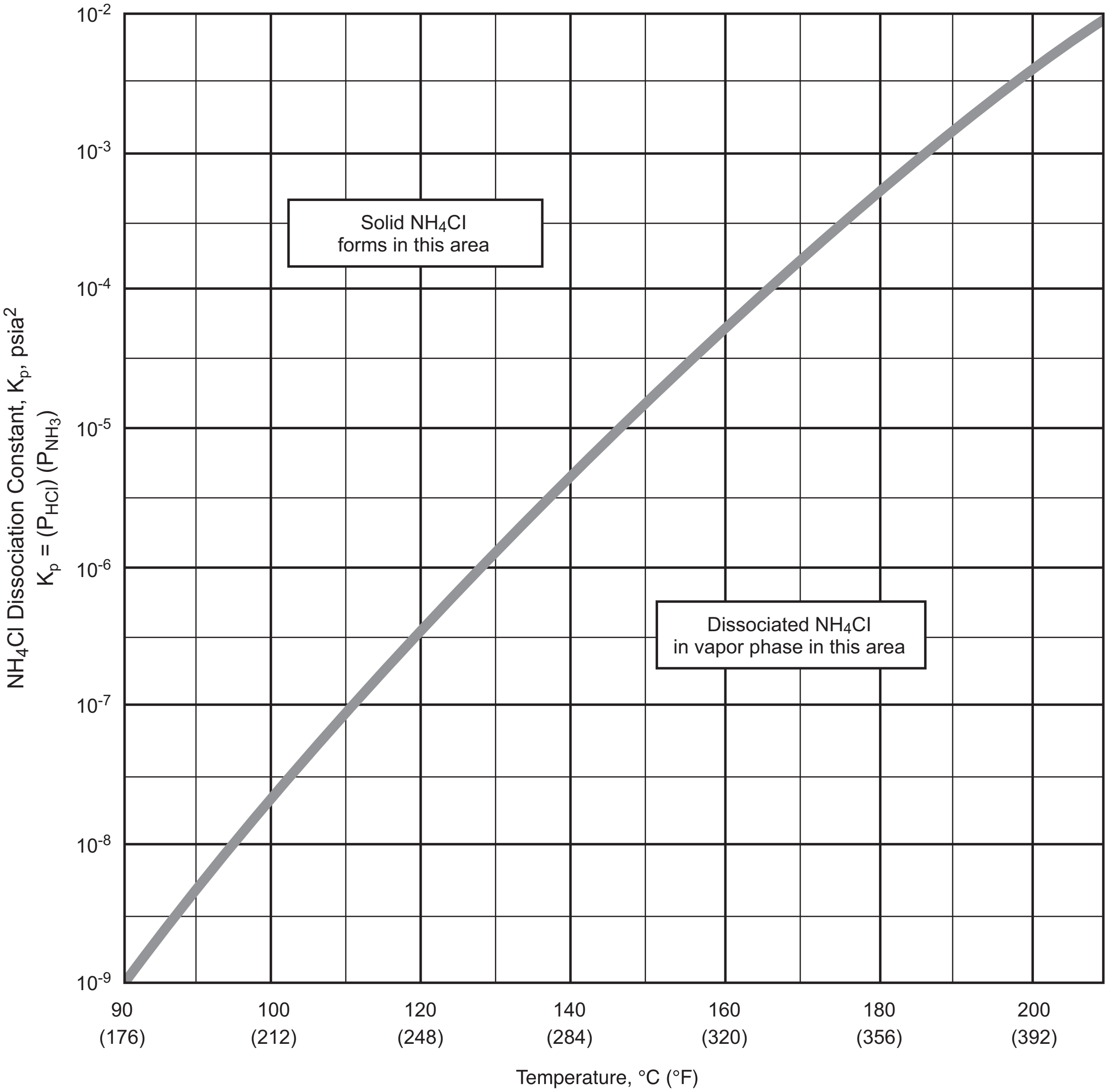


Figure A.2—Estimating NH_4Cl Deposition Temperature from Process Stream Composition

This calculation assumes that all of the NH_3 is absorbed as NH_4HS in the water at the CHPS conditions. This should be a reasonable assumption, as plant data and simulation results indicate that typically 99% + of the NH_3 will be dissolved in the water after cooling. The calculation also assumes all of the available water has been condensed (this is a reasonable assumption although a small amount of water remains in the vapor and hydrocarbon phases).

This formula can be rearranged to calculate the wash water rate required to provide a given NH_4HS concentration.

A.2.1 NH_4HS Concentration

The NH_3 and H_2S concentrations in the process stream determine the amount of NH_4HS formed. The NH_4HS content in mol/h can be estimated from the difference between the hourly mass flow of nitrogen in the feed and the hourly mass flow of nitrogen in the product divided by the molecular weight of 14 Another common approach is to take the hourly mass flow of nitrogen in the feed, multiply it by the nitrogen conversion in the reactor, and divide by the molecular weight. This assumes that there is excess H_2S, which is true for most units.

The concentration of bisulfide in the condensed water can be estimated from the following relationships:

If wt% $H_2S < 2 \times$ wt% NH_3,
then wt% NH4HS = $1.5 \times$ wt% H_2S

If wt% $H_2S > 2 \times$ wt% NH_3,
then wt% $NH_4HS = 3 \times$ wt% NH_3 (most common case)

These relationships are easily derived from the fact that NH_4HS is created by equal number of NH_3 and H_2S moles. Therefore, the amount of NH_4HS that can form is limited by the least molar concentration of either component.

A.2.2 Amount of Water Required To Saturate Vapor Phase

The flash calculation to determine how much water is required to saturate the vapor phase is normally done by a process simulator. However, the required rate can be calculated by hand using the following procedure. Note that this calculation is only an estimate, and may differ by up to 5 % from the value calculated by simulations.

a) Estimate the equilibrium injection temperature. The temperature will typically be 30 °F to 100 °F (17 °C to 55 °C) less than the process temperature before injection if there is not a hot separator present, but may be 200 °F (110 °C) or more less than the process temperature if a hot separator is present.

b) Using steam tables, determine the saturation pressure at the above temperature.

c) Estimate the molar flow rate of hydrogen/hydrocarbon in the vapor phase at the injection point. (This is normally very close to the vapor flow rate from the cold high pressure separator.)

d) Use the following formula to estimate the number of moles of water required to saturate the vapor at the given conditions:

$$\text{Wash water molar flow} = Fc \times \text{vapor molar flow HC} \times \frac{P_{\text{sat sm}}/P_{\text{system}}}{(1 - P_{\text{sat sm}}/P_{\text{system}})}$$

where

vapor molar flow HC is the molar flow of H_2 and hydrocarbon in the vapor phase at injection point;

$P_{\text{sat stm}}$ is the absolute pressure of saturated steam at process injection temperature;

P_{system} is the absolute pressure of process at injection point;

Fc is defined in Table A.1. Interpolate Fc values for other operating pressures.

This calculation will yield an estimate of the required water rate to saturate the vapor phase at the injection point. To estimate how much water would be required to provide 25 % excess (25 % of the wash water remaining aqueous), simply multiply the water rate calculated from the above formula by 1.25.

Table A.1—*FC* Value

Operating Pressure		
psig	**(kPa)**	***Fc***
500	(3450)	1.1
1000	(6900)	1.2
1500	(10300)	1.3
2000	(13800)	1.4

Bibliography

The following publications are referenced by number in this RP.

[3] R.L. Piehl, "How to Cope with Corrosion in Hydrocracker Effluent Coolers," *Oil & Gas Journal*, July 8, 1968.

[4] R.L. Piehl, "Survey of Corrosion in Hydrocracker Air Coolers," *Materials Performance*, Vol 15 (1), 1976, pp 15 – 20.

[5] A. Singh, C. Harvey and R.L. Piehl, "Corrosion of Reactor Effluent Air Coolers," NACE International CORROSION/97, 1997, Paper No. 490.

[6] American Petroleum Institute Publication 932-A, *A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems*, September 2002.

[7] A.M. Alvarez and C.A. Robertson, "Materials and Design Considerations in High Pressure HDS Effluent Coolers," *Materials Performance*, Vol 12 (5), May 1973, pp 16 – 21.

[8] Ehmke, E., "Corrosion Correlations with Ammonia and Hydrogen Sulfide in Air Coolers," *Materials Performance*, July 1975, p. 20.

[9] D.G. Damin and J.D. McCoy, "Prevention of Corrosion in Hydrodesulfurizer Air Coolers and Condensers," *Materials Performance*, December 1978, p. 23.

[10] C. Scherrer, M. Durrieu, and G. Jarno, "Distillate and Resid Hydroprocessing: Coping with High Concentrations of Ammonium Bisulfide in the Process Water," *Materials Performance*, Vol 19 (11), November 1980, pp 25 – 31.

[11] C.A. Shargay, A.J. Bagdasarian, J.W. Coombs, and W.K. Jenkins, "Corrosion in Hydroprocessing Unit," presented at NACE International, *Corrosion in the Oil Refining Industry*, Houston, TX, September 1996.

[12] J. Turner, "Design of Hydroprocessing Effluent Water Wash Systems," NACE Corrosion/98 Conference, Houston, TX, March 1998, Paper 98593.

[13] A.K. Singh, E.L. Bereczky, and A.J. Bagdasarian; "Duplex Stainless Steel in Refinery Hydroprocessing Units Success and Failure Stories," TWI Duplex Stainless Steels 94, Paper #16, Glasgow, Scotland, 13 – 16 November 1994.

[14] R.J. Horvath, M.S. Cayard, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions," NACE International, Corrosion 2006, Paper No. 06576.

[15] M.S. Cayard, W.G. Giesbrecht, R.J. Horvath, R.D. Kane, and V.V. Lagad, "Prediction of Ammonium Bisulfide Corrosion and Validation with Refinery Plant Experience," NACE International, Corrosion 2006, Paper No. 06577.

The following selected publications provide additional information pertaining to this RP.

Y. Wu, "Calculations Estimate Process Stream Depositions," *Oil & Gas Journal*, January 3, 1994.

C.A. Shargay and K.R. Lewis, "Cost Comparison of Materials Options for Hydroprocessing Effluent Equipment and Piping," presented at NACE International CORROSION/96, 1996, Paper No. 600.

C.A. Shargay, G.E. Jacob, and M.D. Price, “Ammonium Salt Corrosion in Hydrotreating Unit Stripper Column Overhead Systems,” NACE Corrosion/99, Paper 99392, San Antonio, TX, April 1999.

C. Harvey and A. Singh, “Mitigate Failures for Reactor Effluent Air Coolers,” *Hydrocarbon Processing*, October 1999, p. 59 – 72.

C.A. Shargay, J. Turner, B. Messer, “Design Considerations to Minimize Ammonium Chloride Corrosion in Hydrotreater REAC’s,” NACE Corrosion/01 Conference, Houston, TX, March 2001.

A.C. Gysbers and J.J. Danis, “Creating Materials Envelope Statements for Petroleum Refining Operating Units,” NACE Corrosion/98 Conference, Houston, TX, March 1998, Paper 98589.

J. H. Gary and G.E. Handwerk, *Petroleum Refining*, Marcel Dekker, New York, 1975.

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