

# **Managing Reboiler Steam-side Operation Improves Equipment Reliability and Steam Quality**

**by Loraine A. Huchler, P. E.**

**MarTech Systems, Inc., Lawrenceville, New Jersey USA**

*presented at:*  
**First International Conference on Practical Industrial Water Treatment Technology  
for the New Millennium**

Marriot Houston Westside  
Houston, Texas

January 27 – 29, 1999

**Organized by  
Gulf Publishing and  
HYDROCARBON PROCESSING**

**Published in HYDROCARBON PROCESSING, June 1999  
by Gulf Publishing**

## **Abstract**

Reboilers are perceived as an integral part of the production process but not part of the steam system since they are located far from the main boilers or powerhouse. Consequently, the steam-side operation of reboilers receives minimal attention until a failure occurs. A proactive approach of mechanical optimization and chemical treatment and monitoring is recommended to minimize deposition and corrosion and maximize system reliability and energy efficiency. Mechanical optimization requires an assessment of the reboiler design and operation to ensure proper venting, correct arrangement of steam traps on reboiler supply lines, compatibility of materials of construction, and impact of current system operation (i.e. dry, partially or totally flooded on the steam side). Selecting the correct chemical treatment and monitoring program is a balance between economics, feed considerations, process compatibility and plant preferences. Maintaining the efficiency of the steam-side operation of reboilers is critical to improving the process equipment reliability and maintainability.

## **Introduction**

Centrally located powerhouse boilers produce steam for refining processes and power generation. Operators add chemicals for water treatment and monitor condensate quality at this central location. Water and steam not used in the powerhouse is routed to the refinery for waste heat boilers, reboilers or process requirements.

Reboilers are located far from the powerhouse and, consequently, the steam-side operation of these units receives minimal attention until a failure occurs. One study showed the most common high risk failure events in a fluid catalytic cracking unit (FCCU) were heat exchanger shell or tube leaks or ruptures.<sup>1</sup> Reboilers, like heat exchangers, are equally vulnerable to tube and shell failures. This paper will discuss reboiler design, location and operation within a typical refinery and methods to maximize reliability through proper mechani-

cal operation, monitoring and chemical treatment.

## **Refinery Reboiler Review**

Large quantity distillate products such as gasoline, jet fuel and diesel fuel dictate basic refinery design.<sup>2</sup> Waste streams from each of these products are refined to a variety of finished materials in various process units. Process units that commonly use steam as an indirect heat source in reboilers include:

- Gas plants
  - light ends unit
  - vapor recovery unit
- Alkylation units (HF and Sulfuric)
- Sulfur recovery units
- Aromatics recovery units
  - BTX
  - benzene/cumene
  - UDEX
- Catalytic Reformer

A summary of the reboilers typically found in each process unit is shown in Table 1.

---

<sup>1</sup> Rooney, J., Turner, J., Arendt, J., "Preliminary hazards analysis conducted on FCCU complex," Oil & Gas Journal, August 8, 1988, pages 60-66.

<sup>2</sup> Gary, J., Handwerk, G., Petroleum Refining, Dekker, New York, ©1984.

**Table 1 – Refinery Reboiler Summary**

Process	Reboiler Name/Column	Purpose
Alkylation (Sulfuric)	Depropanizer	Remove and collect propane from alkylate stream
	Deisobutanizer	Produce low vapor pressure alkylate gasoline
Alkylation (HF)	Acid Rerun	Recycle acid stream to remove contaminants
	Depropanizer <sup>3</sup>	Remove and collect propane from alkylate stream
	Acid Stripper	Remove acid from propane stream
	Deisobutanizer	Produce low vapor pressure alkylate gasoline
	Debutanizer	Remove and collect butane from deisobutanizer stream
	Stabilizer	Remove butane and lighter hydrocarbons from reformate stream
Catalytic Reformer	Stripper	Remove aromatics from solvent hydrocarbon stream
	Pre-Extractor	Remove and collect lighter hydrocarbons from reformate charge
Aromatic Recovery	Water Still	Remove water from solvent
	Benzene	Remove and collect benzene from aromatics stream
	Toluene	Remove and collect Toluene from aromatics stream
	Xylene	Remove and collect xylene from aromatics stream
	Stabilizer	Remove butanes and lighter hydrocarbons from gasoline product
	Stripper	Remove very light hydrocarbons such as methane and ethane
Gas Plant	De-ethanizer / Absorber (Stripper)	Produce low vapor pressure alkylate gasoline
	Debutanizer	Stabilize gasoline component
	Rerun (Naphtha Splitter)	Recycle to polish lean oil (solvent) of lighter gasoline fraction
	Depropanizer <sup>4</sup>	Remove and collect propane
	Depentanizer	Remove and collect pentane
	Stabilizer	Remove butane and lighter hydrocarbons from gasoline stream
Sulfur Recovery	Sour Water Stripper <sup>5</sup>	Remove and collect H <sub>2</sub> S and NH <sub>3</sub> from water stream
	Amine Regeneration <sup>6</sup>	Regenerate amine for recycle
Miscellaneous	Vaporizer	Normally found in fuel system to remove butanes
	Splitter	A distillation of two or more hydrocarbon fractions

<sup>3</sup> Reboiler has critical water treatment requirements due to low pressure steam usage.

<sup>4</sup> Reboiler has critical water treatment requirements due to low pressure steam usage.

<sup>5</sup> Low corrosion potential due to internally generated low pressure steam.

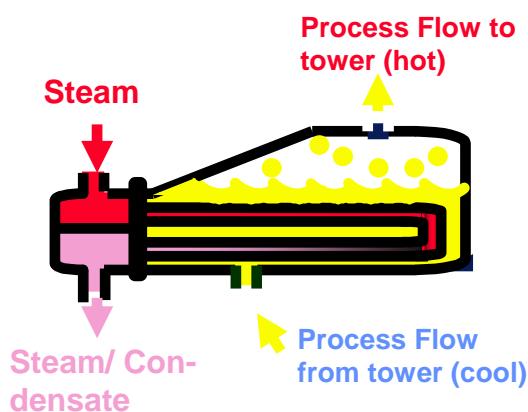
<sup>6</sup> Low corrosion potential due to internally generated low pressure steam.

## **Types of Reboilers**

Reboilers are essentially shell and tube heat exchangers with process fluid on one side and steam or a mixture of steam and condensate on the other side. Three of the most common reboiler designs are kettle, forced recirculation and thermosiphon.

### **Kettle Reboilers**

Kettle reboilers, also known as pool boilers, are often used for light hydrocarbons (propane, butane). These reboilers handle process flow fluctuations and high heat fluxes better than other reboiler designs, but kettle reboilers have a greater tendency to foul on the process side (Figure 1).



**Figure 1 - Kettle Reboiler**

A liquid condensate level must be maintained at or near the top tube row by means of a weir or a level controller.

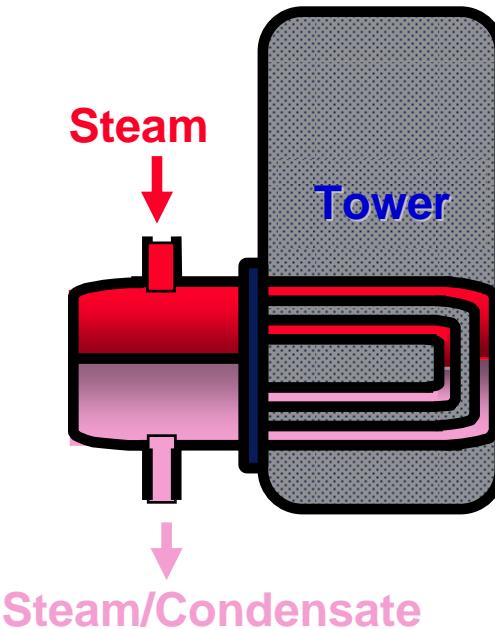
Typically, the tube bundle has baffles to allow liquid movement and reduce the potential for vapor blanketing.

In kettle reboilers there has to be adequate head-space to permit the separation of the aqueous liquid phase from the vapor phase. Demisters can be used to minimize the entrainment of liquid in the outlet flow. These reboilers do

not operate at high pressures because they must have adequate liquid/vapor separation.

### **Internal or “Stab-In” Reboilers**

A variation of a kettle reboiler is an internal or “stab-in” tube bundle that is inserted directly into the column (Figure 2).

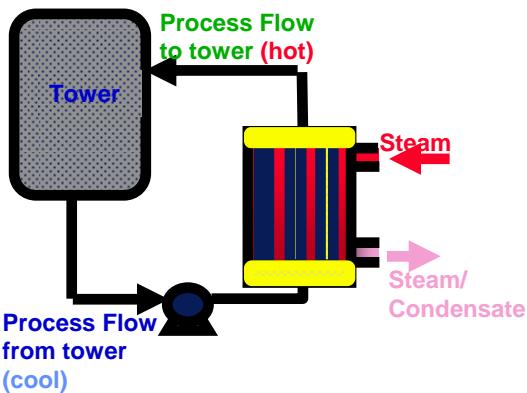


**Figure 2 - Stab-in Reboiler**

The operating characteristics of a stab-in reboiler are almost identical to a kettle boiler with the exception that the units have lower heat fluxes due to the size restriction to fit the column and have a lower process-side fouling tendency. The capital cost of a stab-in unit is lower than the capital cost for kettle reboilers, but maintenance is more difficult.

### **Forced Recirculation Reboilers**

Figure 3 shows a forced recirculation reboiler. This unit uses a pump to move process liquid through the reboiler.

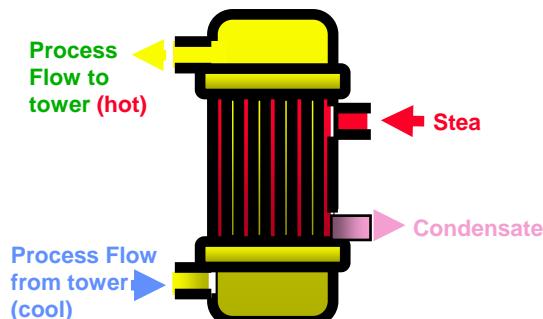


**Figure 3 - Forced Recirculation Reboiler**

Forced recirculation boilers have two mechanisms of heat transfer: sensible heat transfer followed by nucleate boiling. Process flow is typically on the tube side of a standard exchanger in the vertical position. At low process flowrates, these units are prone to fouling.

#### **Thermosiphon Reboiler**

Thermosiphon reboilers (Figure 4) operate using natural circulation with process flow on the shell side in horizontal units and process flow on the tube or shell side in vertical units.



**Figure 4 - Thermosiphon (Vertical Type)**

These reboilers do not require a pump for recirculation and are the least likely to foul in service due to relatively high process flow velocities. Like forced recirculation reboilers, thermosiphon reboilers have sensible heat transfer followed by nucleate boiling.

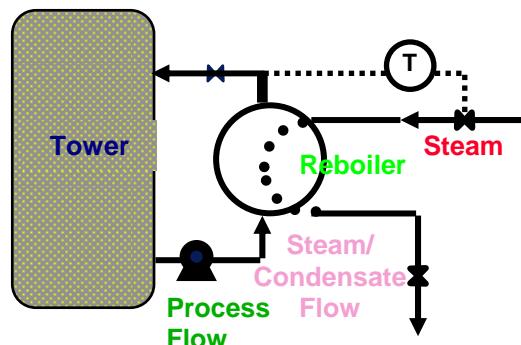
#### **Steam-side Operation**

Reboilers are specially designed steam heat exchangers that transfer heat to the process by circulating some of the process fluid through the reboiler and back to the column.

#### **Reboiler Steam Control Strategies**

A temperature control system accurately controls the steam flow and hence the heat transfer rate.

The most common temperature control system consists of a flow/pressure control valve on the steam inlet to the reboiler tied to the process outlet temperature as shown in Figure 5.



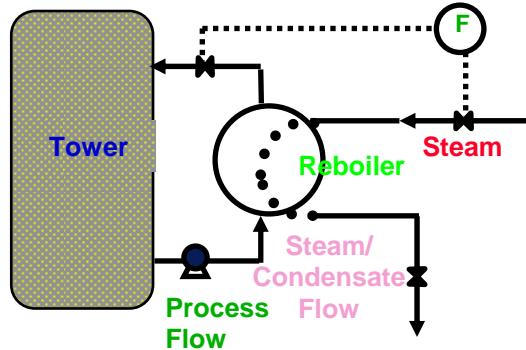
**Figure 5 - Reboiler Temperature Control System**

Process temperature fluctuations are controlled by modulation of the steam flow control valve.

Variations in process fluid flow require more complex process control algorithms that use process flowrate or a

combination of process temperature and flowrate to actuate the steam control valve. Figure 6 shows how the process flow control valve would operate based on a process variable signal.

If the process flow increases beyond the reboiler design, liquid condensate will accumulate, a condition known as “flooding.” Accumulation of condensate in reboilers increases the risk of corrosion. Chemical treatment of steam to reduce the condensate corrosion potential is discussed in the Chemical Treatment and Monitoring Section.

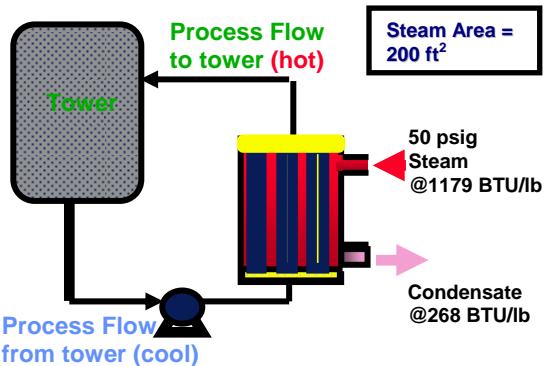


**Figure 6 - Reboiler Flow Control System**

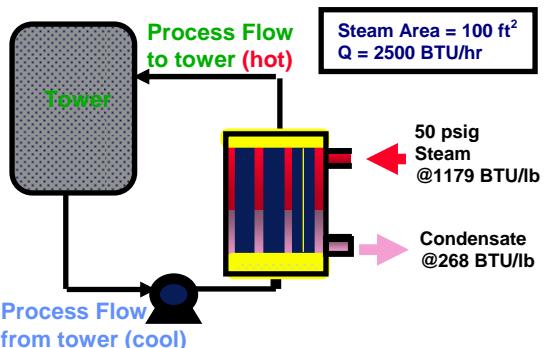
#### ***Impact of Changing Process Demands***

The demands of the process flowrate and heat exchange requirements control the steam-side operation of the reboiler. Refineries frequently modify their processes in response to market requirements, changing the process flowrates and the heat exchange requirements. Consequently, reboilers may be operated very differently from the original design conditions shown in Figure 7. For example, when flooding occurs, (Figure 8), the heat transfer rate declines from 5000 BTU/hour to 2500

BTU/hour when the surface area exposed to steam is reduced by 50%.



**Figure 7 - Reboiler Operating at Design Conditions**



**Figure 8 - Reboiler Operating Above Design Conditions**

To avoid flooding a reboiler under conditions of increased process flow the plant might consider using the flow control shown in Figure 6. Reboiler control issues are unique and each system should be analyzed accordingly.

Reboilers are designed to operate with no liquid condensate level. Unintentional condensate flooding of reboilers results in a greater risk of corrosion since corrosion processes occur in the liquid phase. Uncontrolled corrosion can lead to reboiler failure and unplanned shutdown. Plant personnel

rarely track changes in the steam-side operation of reboilers, resulting in many reboilers operating with reduced energy efficiency and reduced reliability.

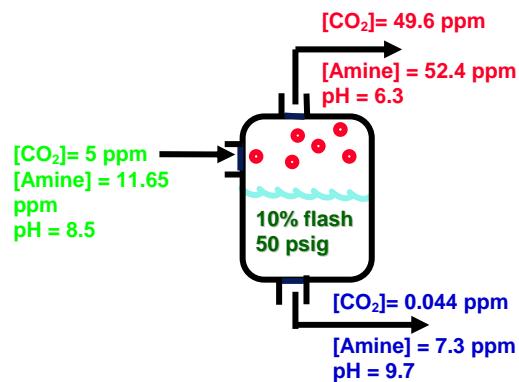
### **Impact of Steam Pressure Reduction Strategies**

The steam pressure in reboilers depends on the process temperature and heat exchange requirements. The steam pressure is typically less than 300 psig and often less than 100 psig. The pressure of the steam supplied from the utility boilers or from waste heat boilers is usually reduced using either a flash tank or a pressure-reducing valve (PRV). The method of steam pressure reduction will influence the corrosion potential of the steam.

The concentration of the more volatile contaminants and treatment chemicals in the flash tank will be higher in the flashed steam than in the inlet steam and bottoms or liquid phase. Thus, the flashed steam will have a high concentration of carbon dioxide and typically a low pH. When the steam condenses, the condensate will have a very high corrosion potential.

Figure 9 shows how a flash tank concentrates some common contaminants and treatment chemicals. The carbon dioxide concentration is over one thousand times as high in the vapor phase (49.6 ppm) as the liquid phase (0.044 ppm). The pH of the vapor or steam phase is 6.3 and the pH of the liquid phase is 9.7.

Any equipment that receives steam from this flash tank is vulnerable to corrosion when the steam condenses, since corrosion occurs in the liquid phase, not the vapor phase.



**Figure 9 - Flash Tank**

If the steam pressure is reduced using “let-down” stations (pressure reducing valves (PRV)), then the concentration of contaminants and treatment chemicals in the high pressure and the reduced-pressure steam is the same. The corrosion potential of the condensate is unchanged by the pressure reduction process.

Treatment of the steam to minimize corrosion is recommended as described in the “Chemical Treatment and Monitoring” section.

### **Reboiler Optimization**

Optimizing reboiler operation requires attention to both mechanical operation and steam side operations and chemical water treatment and monitoring program.

#### **Mechanical Operation<sup>7</sup>**

There are several mechanical operational issues that will limit the heat transfer efficiency of a reboiler, including vapor lock, flooding, and poor heat transfer. The solutions for these problems

<sup>7</sup> G. C. Shah, “Heat Transfer, Troubleshooting Reboiler Systems,” Chemical Engineering Process, July 1979, pages 53-58.

include proper venting, installation and maintenance of steam traps, selecting the correct metallurgy, properly sizing the steam inlet control valve and selecting the correct process control algorithm.

### **Venting**

The operational efficiency of some reboilers is improved with the addition of vents. Venting non-condensable gases such as carbon dioxide ( $\text{CO}_2$ ), ammonia ( $\text{NH}_3$ ) and air from the reboiler will improve the heat transfer efficiency. In the case of  $\text{CO}_2$ , venting also reduces the risk of corrosion if liquid condensate accumulates in the reboiler. The energy improvements can be dramatic: as little as 0.05% by volume of air can reduce the heat transfer rate by 50%. Air and carbon dioxide concentrations are not normally high enough to cause severe heat transfer problems except during start-up. Process leaks can cause high concentrations of vapors, creating a condition known as vapor lock during normal service. Vapor lock causes a significant reduction in heat transfer efficiency.

Vents should be located at or near the top of the tubesheets in vertically-oriented reboilers and downstream of the discharge pass in horizontally-oriented reboilers. Vents should be located in the vapor space as close to the liquid level as possible in both vertical and horizontal reboilers that operate with a liquid level. The maximum venting rate is between 0.2% and 0.5% of the inlet flow. For safety or energy conservation, some plants have installed traps on these vent lines. Vent traps tend to limit the venting rate and are not recommended. If live vents are not acceptable, consider condensing the vent

stream and routing it to the sewer. An example of the impact of air vent traps on a system is shown in Table 2.<sup>8</sup>

**Table 2 - Effect of Vent Air Traps on Condensate Quality**

	<b>With</b>	<b>Without</b>
	<b>Air Vent Trap</b>	<b>Air Vent Trap</b>
<b>pH</b>	5.72	6.45
<b>Fe</b>	0.44 ppm	0.22 ppm
<b>CO<sub>2</sub></b>	30 ppm	<10 ppm
<b>Vent Rate</b>	5 ml/min	200 ml/min

Vents are particularly important during system start-up to purge non-condensable gases that may have accumulated during downtime. Some reboilers have a balance line that equalizes the pressure across the reboiler during start-up or shutdown. The balance line may result in vapor lock by recycling non-condensable gases from the bottom to the top of the reboiler. Plants often install a vent on the balance line that is opened only during start-up or shutdown to prevent vapor lock.

### **Steam Traps<sup>9</sup>**

Steam traps drain the condensate from the reboiler, preventing flooding. Flooding severely reduces the heat transfer efficiency since the submerged surface transfers only sensible heat, while the tube surfaces in contact with steam transfer both the latent heat of vaporization and the sensible heat.

<sup>8</sup> Unpublished Course Notes, "Advanced Boiler Training," Betz Water Management Group, circa 1990.

<sup>9</sup> Radle, J., "Select the Right Steam Trap," Chemical Engineering Progress, January, 1992, pp. 30-47.

The correct location of steam traps is on the reboiler steam outlet line. Properly-sized equipment is critical since undersized traps, drain lines and discharge lines will result in condensate collecting in the reboiler vessel, i.e. "flooding." Greatly oversized traps may cause water hammer problems when the pressure differential between the trap and the condensate return line is large. The most commonly used trap designs include the inverted bucket (IB) and the float and thermostatic (F & T). Inverted bucket traps should not be insulated to allow steam to condense at the inlet and prime the trap. Float and thermostatic traps are unsuited for high pressure systems. A surge chamber can be installed upstream of an F&T trap to reduce hydraulic hammer. Additional information on steam traps is provided in Reference 1

Reboilers should have dedicated traps. When there is one condensate collection vessel or "pot" serving several reboilers on the same column, the plant should provide separate condensate drain lines from each reboiler to the pot. Reboiler flooding can occur when condensate drain lines are connected to a common drain line.

### ***Materials of Construction***

The selection of materials of construction for reboilers is similar to the methodology used for standard heat exchangers. Mild steel alloys have excellent heat transfer efficiency and good service life. Copper alloys are typically not used due to process compatibility concerns. Occasionally the plant will replace mild steel tube bundles with stainless steel tube bundles reduce the failures due to corrosion. The heat transfer efficiency of the stainless steel

alloy is significantly lower than mild steel alloys, and the overall energy balance for the column will be affected. The replacement of the mild steel tube bundle with stainless steel will significantly limit production when reboilers are operating at maximum throughput.

### ***Properly Sized Inlet Steam Control Valves***

Steam control valves may be incorrectly sized due to operational changes in the column from changing production requirements. An oversized steam control valve can limit the process efficiency if the pressure in the reboiler is significantly lower than the pressure in the steam supply line. Thermodynamically, the control valve is an adiabatic system, i.e. the pressure will decline across the control valve without a change in temperature. When the pressure drops and the temperature remains the same, the steam becomes superheated. Because superheated steam is much less efficient in transferring heat than saturated steam, the reboiler heat transfer rates will decline.

If the process flows are dynamic, large changes in heat transfer requirements may result in the steam control valve being both under and over-sized, depending on the operating conditions. In these systems, a more complex set of control valves must be installed as described in Reference 2.

### ***Chemical Treatment and Monitoring***

The objective of chemical treatment for reboilers is to minimize the corrosion processes in the condensate, reduce the quantity of iron returned to the boilers, reduce the risk of equipment failure and unplanned shutdown, thereby increasing system reliability. Condensate

is returned to the central powerhouse from each process unit through an extensive condensate-return piping system. Since corrosion occurs only in the presence of liquid, not vapor, efforts to measure and control corrosion focus on chemical treatment of the condensate.

### **Contaminants**

The primary sources of reboiler corrosion are acidic contaminants in the condensate such as carbon dioxide, acidic process intrusions or dissolved oxygen.

Carbon dioxide is present in condensate in systems that use softened water make-up in the boilers. The softening process removes the hardness ions but does not remove the naturally occurring alkalinity. In the boiler, the heat breaks down the alkalinity to form carbon dioxide, a gas, which will leave the boiler with the steam. In the condensate, carbon dioxide will dissolve in water to form carbonic acid, a corrosive species. A higher feedwater alkalinity will result in a higher condensate carbon dioxide concentration.

Dissolved oxygen is rarely present in condensate systems, except during system start-up, intermittent operation or when air is being educted through malfunctioning condensate transfer pump seals.

Acidic process fluids can leak into the steam or condensate, resulting in deposition of the process materials as well as corrosion. Plants usually do not treat to control deposition until there is a large process leak or a failure occurs. Process leaks and contaminated steam will cause deposits and reduce the heat transfer efficiency of the reboiler.

Chemical treatment is evaluated on an individual basis when there is a process

leak. Unless the reboiler operation compromises the production process, the reboiler remains in service. The reboiler will be cleaned and repaired during the next scheduled outage.

The condensate system has a large surface area of steel pipe that is exposed to a corrosive environment. Even at low corrosion rates, a large quantity of iron is returned to the powerhouse boilers. As shown in Table 3, for a medium-sized system operating in conformance to the ASME guidelines, 1051 pounds per year of iron corrodes from the condensate system and is deposited into the boiler.

**Table 3 - Feedwater Iron Calculations**

Boiler Operating Pressure	150 psig
Utility Steam Production	600,000 pph
Maximum Boiler Feedwater [Iron] <sup>10</sup>	100 ppb
Percent of Condensate Return	50%
Maximum Condensate [Iron]	200 ppb
Quantity of Iron moved from Condensate System to Boiler	1051 pounds/year

Iron in the boilers will cause deposits on high heat transfer surfaces, increasing the risk of a tube failure and reducing the boiler's reliability and availability.

<sup>10</sup> "Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers," prepared by the Feedwater Quality Task Group of the industrial Subcommittee of the ASME Research and Technology Committee on Water and Steam in Thermal Power Systems, The American Society of Mechanical Engineers (ASME), New York, NY, 1994, p. 22.

Thus, control of corrosion in the condensate system has a direct impact on the reliability of the steam generating system.

### ***Chemical Treatment Options***

Depending on the contaminants in the system, there are three technologies that can be used individually or in combination to control corrosion. Application of these three technologies results in five chemical treatment programs.<sup>11</sup>

1. Filming amines
2. Filming amines with neutralizing amines
3. Neutralizing amines
4. Passivating agents
5. Neutralizing amines with passivating agents.

#### ***1. Filming amines***

Filming amines are long chain hydrocarbons that have one hydrophobic end and one hydrophilic end. Filming amines form a “film” on the tube surface, creating a physical barrier on the tube surface that prevents the corrosion agents from reaching the steel tube surface. The integrity of this chemical film is strongly dependent on the pH of the aqueous phase. The most common filming amine is octadecylamine, for which the condensate pH must be maintained between 6.5 and 7.6 to prevent solubilization of the amine and subsequent removal of the protective chemical treatment on the tube surfaces. The newer, proprietary materials such as tal-

low-based or soya-based amines, tolerate a wider system pH (6.5 to 9.5).

When filming amines are fed into the boiler feedwater, only a small proportion volatilizes into the steam phase and is available in the steam. The majority of the filming amine chemical remains in the liquid phase and leaves with the blowdown stream. The most effective locations to feed these products are the steam header at the powerhouse or the steam supply line at the reboiler. Filming amines must be fed continuously at a constant concentration, not in proportion to the contaminant concentration. For systems with high contaminant concentrations, this feed strategy results in a lower cost treatment program than programs such as neutralizing amines that are fed in direct proportion to the contaminants.

Overfeed of filming amines or a high condensate pH can have disastrous consequences. When the system pH exceeds the maximum control pH, the film is rapidly removed from the tube surfaces, a process known as “stripping.” This causes “gunking” wherein large quantities of filming amine are transported with the condensate flow, plugging steam traps, valves, and other equipment. Ultimately these insoluble materials return to the boiler with the feedwater and mix with the calcium, magnesium, and iron in the boiler to form rather harmless, sticky, deposits known as “gunk balls.” Overfeed of filming amines can result in similar problems with insoluble materials trapped in the system.

---

<sup>11</sup> L. A. Huchler, “Select the Best Boiler-Water Chemical Treatment Program,” Chemical Engineering Progress, August 1998, pp. 45 – 50.

## **2. Filming amines with neutralizing amines**

Often filming amines are used in combination with neutralizing amines to elevate the pH to the desired control range. These programs are similar to the filming amine programs that require system pH controlled to a narrow range and good feedrate control. Filmer/neutralizer programs are ideal for complex systems such as refineries. The neutralizing amine will concentrate in the vapor phase of a flash tank while almost all of the filming amine will remain in the liquid phase.

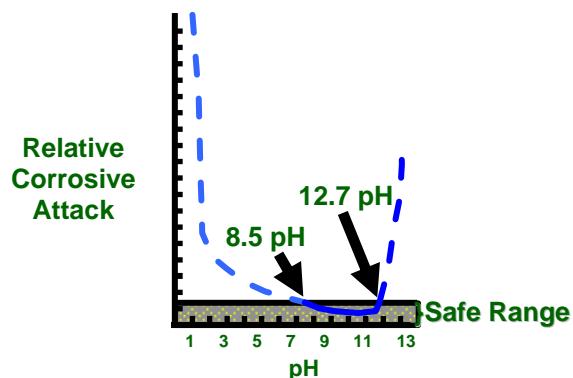
Filmer/neutralizer programs are more expensive than filming amines alone, but cheaper than a neutralizing amine program. Because they form a chemical barrier that is impenetrable to dissolved oxygen, passivating agents are not necessary and are not used in combination with filming amine treatment programs.

## **3. Neutralizing amines**

Neutralizing amines are the most widely applied corrosion control treatment chemicals in steam condensate systems. There are several advantages, including ease of feeding, simple control methods and compatibility with many other boiler treatment chemicals.

A chemical reaction or neutralization reaction occurs between neutralizing amines and the acidic species in the condensate. All of the acidic contaminants will be neutralized when the concentration of neutralizing amine stoichiometrically matches the concentration of acidic contaminants. At this neutralizing amine concentration, the pH of the condensate will be 7. Higher concentrations of neutralizing amine will

result in condensate pH above 7. As shown in Figure 11, the corrosion rate of iron in an aqueous system is lowest between a pH of 8.5 and 12.7.



**Figure 11 - Minimum Iron Corrosion Rate**

Because it would be uneconomical and chemically impossible to control the condensate pH to 12.7, the control range for neutralizing amine treatment programs is at a pH between 8.8 and 9.2.

Because neutralizing amines are fed stoichiometrically or in direct proportion to the concentration of acidic contaminants, the chemical feedrate and costs increase as the concentration of contaminants increases. For example, a system with high carbonate alkalinity in the feedwater will have a high concentration of carbon dioxide and require a high concentration of neutralizing amines.

Many different neutralizing amine chemicals are commercially available. The most widely used materials are cyclohexylamine, morpholine and diethylaminoethanol amine (DEAE). These amines are used singly or in combination to take advantage of each

chemical's physical and regulatory properties such as volatility, neutralizing capacity, distribution ratio, process compatibility or approval for use in regulated environments such as food plants or steam humidification applications.

Neutralizing amines may be fed with other steam system chemicals (except oxygen scavengers) and can usually be fed into the feedwater circuit with minimal chemical losses through the boiler blowdown. With the exception of regulated systems, the only consequences of overfeed is additional cost. For regulated systems, the consequences of overfeed are non-compliance and possible health effects in non-ventilated spaces.

#### **4. Passivating Agents**

In systems where dissolved oxygen is a contaminant, oxygen scavengers are added to reduce corrosion and protect or passivate the metal surfaces. These oxygen scavengers are known as passivating agents because the chemical reaction between the scavenger and the dissolved oxygen is an electrochemical reduction reaction similar to the reduction reaction of iron oxide with dissolved oxygen to form magnetite.<sup>12</sup> In most systems, passivating agents will reduce the iron concentration in the condensate.

#### **5. Neutralizing Amines with Passivators**

Frequently passivating agents are blended with neutralizing amines in fully formulated products. The feedrate is controlled by system pH, similar to a neutralizing amine program.

#### **Chemical Feed Issues**

All of the condensate treatment chemicals are fed continuously, using conventional chemical feed equipment. However, there are two chemical feed issues that merit special attention: process compatibility of treatment chemicals and satellite chemical feed strategies.

Because steam is often injected directly into the process stream, the compatibility of the treatment chemicals with the catalysts and the various processes is important. In refineries, there are no common incompatibilities between the treatment chemicals with the catalysts and processes. In other petrochemical processes, there are some known incompatibilities with amines such as latex manufacturing or certain catalysts. The plant should conduct a laboratory study prior to the use of condensate treatment in previously untreated systems, unless a case history from a similar system is available. Each process compatibility issue must be evaluated individually.

Typically, the refinery will add corrosion control chemicals at the powerhouse. At each process unit, the steam will be mixed with steam generated locally by waste heat boilers and reboilers, diluting the corrosion control chemicals. Consequently, there may be an inadequate concentration of corrosion control chemicals in units that are located the furthest from the powerhouse or in low pressure reboilers. Often additional chemical feed is needed at the unit, a procedure known as "satellite feed." The reduction in the iron concentration and condensate corrosion rates in refineries using satellite feed of chemicals has been modeled us-

<sup>12</sup> Huchler, L., "Passivation: The Known and the Unknown," NACE Corrosion '94.

ing a complex computer based program as well as empirically determined.<sup>13, 14</sup>

### **Corrosion Monitoring<sup>15</sup>**

The most direct method of measuring the corrosion rate by installing corrosion coupons in the critical reboilers is rarely used in reboiler steam systems. Unlike the other methods discussed herein, corrosion coupons provide a direct measurement of the corrosion rate in a system, and should be used in critical locations or for confirmation of findings from other analytical methods.

As an alternative, some plants evaluate the corrosion rate indirectly by measuring the concentration of iron in the condensate from a specific reboiler. To accurately measure the concentration of insoluble iron in condensate, the sample must be cooled and constantly flowing at 1000 ml/min. This method can be difficult since most plants do not have condensate sample points downstream of each reboiler. When there is a cooled condensate sample available at a specific reboiler, the pH can be routinely measured. The simplest process contamination monitor is condensate conductivity.

There are no published guidelines for reboiler condensate quality, however, control limits have been derived from the ASME guidelines. An example of the maximum condensate iron concen-

tration as derived from the maximum feedwater iron concentration is shown in Table 4.

**Table 4 - Determination of Maximum Condensate Iron Concentration**

Boiler Operating Pressure	150 psig
Maximum Boiler Feedwater [Iron]*	100 ppb
Percent of Condensate Return	50%
Maximum Condensate [Iron]	200 ppb

The feedwater is comprised of two sources of water: condensate and make-up. The make-up water is assumed to have no iron contaminant concentrations. The condensate equals fifty percent of the feedwater, and therefore will be diluted by a factor of two. Therefore, prior to dilution by make-up water, the condensate can have twice as much iron as the maximum feedwater concentration, or 200 ppb.

Although the ASME guidelines are used in this example, the maximum concentration of iron will vary based on boiler operating pressure, boiler design, historical experience, plant monitoring accuracy and control conformance and the boiler manufacturer's recommendations.

### **pH Monitoring**

The most common method for monitoring corrosion is to routinely monitor the pH of the combined condensate returning from all of the units. Unfortunately, the corrosion potential of individual reboilers cannot be evaluated from this single, composite pH measurement. To accurately measure pH, the plant must

<sup>13</sup> Beardwood, E.S., "Operational Steam Condensate Corrosion Control of Reboilers & Reheaters," 1997 International Water Conference, IWC-97-25.

<sup>14</sup> Reggiani, G., "Predict and Optimize Boiler Cycle pH Control Using Advanced Computer Simulation," 1997 International Water Conference, IWC-97-26.

<sup>15</sup> Chen, T., Batton, C., Cicero, D., Port, R., "Condensate Corrosion in Steam Generating Systems," NACE Corrosion '98, Paper 718.

install sample coolers on each condensate return streams.

### **Millipore Method**

There are several test methods used to monitor iron: Millipore, colormetric/spectrophotometric, atomic absorption, turbidimeter, particle counter, particle monitor. The Millipore method is a semi-quantitative method developed by the Babcock and Wilcox Company. This method is easily done in the wet lab at the process unit. It consists of passing one liter of sample through a 0.45 micron membrane filter. The color and intensity of the filter is visually compared to a standard chart that correlates iron concentration with the filter appearance.

### **Colormetric/Spectrophotometric**

The colormetric/spectrophotometric methods use a chemical digestion to solubilize particulate iron followed by a reaction that forms a soluble metal ion complex. That metal ion complex has a strong absorbance in a specific wavelength that is correlated to the iron concentration. This method is easily completed in the process unit wet lab and has been adapted as an on-line analyzer. Like all on-line analyzers, this analyzer requires a sample conditioning panel and a maintenance support to routinely calibrate, refill the reagents, and maintain the equipment in working order.<sup>16</sup>

### **Atomic Absorption**

Atomic absorption uses a precise wavelength to evaluate soluble concentrations. This method is typically con-

ducted off-site at an analytical laboratory. The advantage of this method is that iron and other contaminants can be easily measured. In most refineries atomic absorption is used as an occasional measurement of condensate contaminants.

### **Turbidimeter**

A turbidimeter uses visible light reflected from surface of a sample to evaluate the insoluble particulates, including iron. This analyzer does not measure soluble iron concentrations and is not useful in tracking the corrosion rate. Turbidimeters are on-line analyzers installed in the condensate system to monitor condensate quality during start-up, but they are not typically used in reboiler condensate.

### **Particle Counters and Particle Monitors**

Particle counters and particle monitors are two very different analyzers that use light to measure insoluble particulates. Particle counters are typically laboratory instruments that measure particle quantity as a function of their size. Particle monitors are installed on-line in the condensate system and provides a particle index. This particle index is not a measure of the number of particles, but rather a relative measurement of the concentration of insoluble particulates. Like the turbidimeter, particle counters and particle monitors are very useful to track condensate quality during start-up but they are not typically used for reboiler condensate.

### **Chemical Treatment Monitoring**

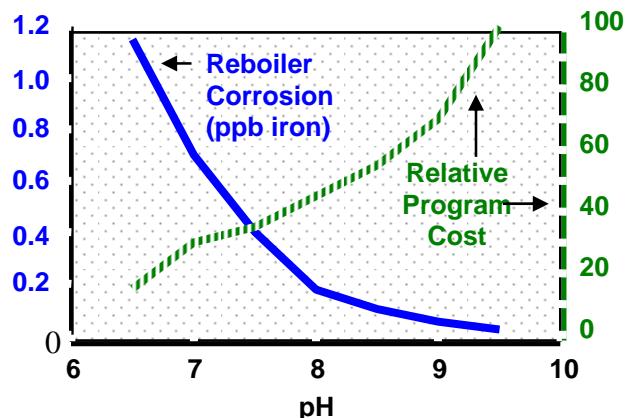
The success of a corrosion control program is typically described by measuring the cost of the chemical treatment ver-

<sup>16</sup> Huchler, L., Herbert, W., "Keys to On-line Monitoring in Steam Generating Systems," 1998 International Water Conference, IWC-98-19.

sus the corrosion rate. First, the reboilers that have the most severe service are identified as “critical reboilers.” Typically these reboilers are units that receive the lowest pressure steam or are located far from the powerhouse.

Second, the optimal condensate chemical treatment rate must be identified. As the condensate chemical concentration is increased, the treatment cost increases and the corrosion rate decreases. The most cost-effective chemical treatment cost is at the intersection of the two curves. The costs shown in Figure 12 are relative costs. To evaluate a specific system, the actual costs and corrosion rates would need to be evaluated at a variety of chemical feedrates.

Chemical treatment monitoring is often combined with corrosion monitoring, since corrosion control is the primary objective of most chemical treatment programs. To monitor the correct application of the chemical treatment program, the plant should routinely measure the pH and conductivity of the critical reboiler condensate streams.



**Figure 12 - Cost/Benefit of Neutralizing Amine Treatment**

## Summary

Reboilers are found throughout refineries and are critical to reliable plant operation. Regardless of the reboiler design, the equipment requires proper mechanical and chemical treatment to maximize reliability and performance and minimize outages. The dynamic nature of the petrochemical markets and the uniqueness of each process require individual system audits to evaluate proper mechanical operation and chemical treatment and monitoring.

There are several key monitoring tools that can be used to evaluate the risk of corrosion and deposition problems in reboilers. Consistent monitoring and corrective action will prevent failures, reduce operating costs, significantly improve system reliability and extend system life.

## References

1. Radle, J., “Select the Right Steam Trap,” Chemical Engineering Progress, January, 1992.
2. Beardwood, E.S., “Operational Steam Condensate Corrosion Control of Reboilers & Reheaters,” 1997 International Water Conference, IWC-97-25.

