Chapter 10 Flowsheet Analysis For Pollution Prevention

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10.1 Introduction

The environmental performance of a process flowsheet depends on both the performance of the individual unit operations that make up the flowsheet and on the level to which the process streams have been networked and integrated. While Chapter 9 describes methods for improving the performance of individual operations, this chapter examines methods for assessing and improving the degree to which the unit operations are integrated.

Specifically, Section 10.2 examines process energy integration and Section 10.3 examines process mass integration. The methods presented in these sections, and the case study presented in Section 10.4, will demonstrate that improved process integration can lead to improvements in overall mass and energy efficiency. Before examining process integration in detail, however, it is useful to review the methods that exist for systematically assessing and improving the environmental performance of process designs. A number of such methods are available. Some are analogous to Hazard and Operability (HAZ-OP) Analyses (e.g., see Crowl and Louvar,1990).

Section 9.7 briefly describes how a HAZ-OP analysis is performed; to summarize, the potential hazard associated with each process stream is evaluated qualitatively (and sometimes quantitatively) by systematically considering possible deviations in the stream. Table 10.1-1 gives the guidewords and examples of deviations used in HAZ-OP analysis. Each guide word is applied to each relevant stream characteristic, the possible causes of the deviation are listed, and the consequences of the deviation are determined. Finally, the action(s) required to prevent the occurrence of the deviation are determined.

Table 10.1-1 Guide words and deviations in HAZ-OP analysis

Guide Word	Example Deviations No flow for an input stream.				
NO or Not					
MORE	Higher flow rate, higher temperature, higher pressure, higher concentrations.				
LESS	Lower flow rate, lower temperature, lower pressure, lower concentrations.				
AS WELL AS	Extra phase present, impurity present.				
PART OF	Change in ratio of components, component missing.				
MORE THAN	Extra phase present, impurity present.				
REVERSE	Pressure change causes a vent to become an INLET.				
OTHER THAN	Conditions that can occur during startup, shutdown, catalyst changes, maintenance.				

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For a single pipeline taking fluid from one storage tank to another, there may be several possible deviations, such as:

- 🕏 no flow
- 🔹 more flow
- 🕏 more pressure
- 🕏 more temperature
- 🔹 less flow
- less temperature
- high concentration of a particular component
- presence of undesirable compounds

Note that each deviation may have more than one possible cause so that this set of deviations would be associated with dozens of possible causes.

Systematic examination of environmental improvements in process flowsheet



a series of systematic questions (DuPont Method)

Hierarchical design methodologies (AMOCO Method)

A similar analysis framework has been employed to identify environmental improvements in process flowsheets (DuPont,1993)

In these case studies, a series of systematic questions are raised concerning each process streams or group of unit processes. Typical questions include:

What changes in operating procedures might reduce waste?

Would changes in raw materials or process chemistry be effective?

Would improvements in process control be effective?

Hierarchical design methodologies (Douglas, 1992)

Other methods for systematically examining environmental improvement opportunities for flowsheets have been developed based on the hierarchical design methodologies developed by Douglas (1992).

The hierarchical levels are shown in Table 10.1-2. The hierarchy is organized so that decisions that affect waste and emission generation at each level limit the decisions in the levels below it.

Table 10.1-2

Levels for hierarchical analysis for pollution prevention

Design Levels

- Level 1. Identify the material to be manufactured
- Level 2. Specify the input/output structure of the flowsheet
- Level 3. Design the recycle structure of the flowsheet
- Level 4. Specify the separation system
 - 4a. General structure: phase splits
 - 4b. Vapor recovery system
 - 4c. Liquid recovery system
 - 4d. Solid recovery system
- Level 5. Process integration
 - 5a. Integrate process heating and cooling demands
 - 5b. Identify process waste recycling and water reuse opportunities

Hierarchical design methodologies (Douglas, 1992)

As an example of the use of hierarchical analysis procedures, consider a case study drawn from the AMOCO/US EPA Pollution Prevention Project at AMOCO's refinery in Yorktown, Virginia (Rossiter and Klee, 1995).

In this example, the flowsheet of a fluidized-bed catalytic cracking unit (FCCU) is evaluated for pollution prevention options. A flowsheet of the unit is shown in Figure 10.1-1.



Fig. 10.1-1 Process flow diagram of a fluidized-bed catalytic cracking unit

Level 1: identify the material to be manufactured

Note that Level 1 in this table applies only to processes that are being designed, not to existing processes.

Level 2: input-output structure

In Level 2 of the hierarchy listed in Table 10.1-2, the following pollution prevention strategies were generated:

- Improve quality of the feed to eliminate or reduce the need for the vapor line washing system shown in the upper right- hand corner of Figure 10.1-1.
- 2) Reduce steam consumption in the reactor so that there is less condensate to remove from the distillation system.
- 3) Within the catalyst regeneration system, the loss of fines (upper left hand corner of Figure 10.1-1) is partly a function of the air input rate. A reduction in air flow (e.g. by using oxygen enrichment) is a possible means of reducing the discharge of fines.

Level 3: review of the recycle structure

- 1) The reactor uses 26,000 lb/hr of steam. This is provided from the utility steam system. If this could be replaced with steam generated from process water, the liquid effluent from the unit would be reduced. Volatile hydrocarbons contained in the recycled steam would be returned directly to the process. Catalyst regeneration consumes more than 11,000 lb/hr of steam. It may be possible to satisfy this duty with "dirty steam" as well, since the hydrocarbon content would be incinerated with the coke in the regenerator.
- 2) Used wash water is collected at several points and then purged from the process. If it could be recovered and recycled instead, or if recycled water from other sources could be used for washing in place of fresh water, fresh water usage and wastewater generation could both be reduced by about 10,500 lb/hr.

Level 4 : separation systems

Three options were identified for separation systems (level 4):

- 1) Replace heating done by direct contacting with steam by heating with reboilers.
- 2) Place additional oil-water separators downstream of existing condensate collection points and recover hydrocarbons.
- 3) Improve gas-solid separation downstream of the regenerator to eliminate loss of catalyst fines. This might simply require better cyclone and/or ductwork design, or electrostatic precipitation.

Level 5 : Process integration

These first four levels of the design hierarchy lead us to the types of process improvements described in Chapter 9— improvements in the reactor and improvements in the separation system.

As Table 10.2-1 notes, the next step in the design process is to identify opportunities for process integration. This is the main topic of this chapter and the next several sections describe methods for process *energy integration* and methods for identifying *process waste recycling and reuse opportunities*.

10.2 Process Energy Integration

- Process streams frequently need to be heated to achieve the correct conditions for a desired reaction or to achieve separation of materials
 - ~ Heating is generally done in furnaces, or by steam generated in a boiler
 - ~ Heating a process stream requires combustion of fuels, adding expense and environmental impacts to a process
- Process streams also frequently need to be cooled
 - ~ Cooling is done with cooling water and cooling towers are used to keep cooling water temperature, but operating these cooling waters consumes energy and causes the loss of water through evaporation, adding expenses and environmental impacts
- Process heat(energy) integration is to use heat from streams that need to be cooled for heating streams that need their temperature raised.

10.2 Process Energy Integration

HEN (heat exchanger network)

Process heat integration is generally done using an analysis by **HEN** synthesis. All of the heating and cooling requirements for a process are systematically examined to determine the extent to which

streams that need to have their temperature raised can be heated by the streams that need to be cooled.

Heating a process stream requires combustion of fuels, adding expense and environmental impacts to a process

10.2 Process Energy Integration

Simple Example of HEN synthesis

A heat balance diagram (**Fig. 10.2-1**) for a stream that needs to be heated from 50 to 200C and a stream that need to be cooled from 200 to 30 C.

- ~ Both streams have heat capacity of 1 kJ/(kg C)
- ~ Stream needs to be cooled has a flow rate of 1 kg/s
- ~ Stream needs to be heated has a flow rate of 2 kg/s
- ~ Heating and cooling utilities could be applied to the two streams separately



Fig. 10.2-1 Heat balance diagram for a hot process stream and a cold process stream

Example of HEN synthesis

- The requirements for heating and cooling utilities are less if heat exchanger between the two streams occurs (Fig. 10.2-2).
- There are 2 thermodynamic constraints to heat transfer
- 1. Heat absorbed by the cold stream (the stream that needs to be heated) is equal to the quantity of heat lost by the hot stream (the stream that needs to be cooled).
- 2. Heat flows from higher T streams to lower T streams.



Fig. 10.2-2 Heating and cooling requirements before heat integration

Pinch Diagram: The way to graphically depicts the streams to be heated and cooled in a flowsheet

- 1. This diagram can be used to determine the extent to which heat transfer is possible and also to determine which hot streams should be paid with cold streams.
- 2. Heat transferred to and from the streams is on the yaxis in a pinch diagram and temperature is on the x-axis.
- **3.** Hot streams are represented as lines and slope downward and to the left, while cold streams are represented by lines that slope upwards and to the right.

- 4. The hot and cold streams in Fig. 10.2-1 are depicted in the pinch diagram of Fig. 10.2-3.
 - The cold stream (that needs to be heated) begins at 50°C, it ends at 200°C and at enthalpy 300 kW higher that it started
 - The hot stream (that needs to be cooled) begins at 200°C and ends at 30°C, and an enthalpy 170 kW lower than it started.
- 5. Both hot and cold stream lines are free to move vertically. However, heat transfer between the streams can take place only in regions where the hot stream lies to the right of the cold stream



Fig. 10.2-3

Hot stream and cold stream load line diagram for HEN synthesis

- 6. Maximum theoretical heat transfer between the streams occurs when the two streams touch but do not across (This point called the *thermal pinch*).
- 7. The region where the hot stream lies to the right of the cold stream becomes smaller and the amount of heat transferred between the streams decreases.
- 8. The utility requirements for heating and cooling the streams to the target temperatures increase.

- 9. In contrast, the heat exchanger for transferring heat from the hot stream to the cold stream gets smaller as the lines move apart. Thus, there is an optimum temperature driving force where total annualized costs are minimized.
- 10. Of the optimum temperature difference is 10°C, then the pinch diagram (Fig. 10.2-3) shows the optimum heat transfer between the two streams to be 240 kJ –100 kJ = 140 kJ.

- 11. The diagram also shows that, under these conditions, the cold stream is heated from 50 to 120°C and the hot stream is cooled from 200 to 60°C.
- 12. Comparison of *Fig. 10.2-4* with *Fig. 10.2-2* shows that heat integration results in a substantial decrease in the utilities needed to heat and cool the two streams to their target temperatures.



Fig. 10.2-4

Heating and cooling requirements after heat integration

Remarks on Pinch Technology.....

Exchange of energy between process streams that need to be heated and to be cooled (process energy integration) can reduce overall energy demand for a process

10.3 Process Mass Integration

Just as heat integration is the use of heat that would otherwise be wasted, mass integration is the use of materials that would otherwise be wasted.

Three tools for mass integration

- 1. Source-sink mapping (most visual and intuitive one)
- 2. Strategy for determining optimum mixing, segregation,& recycle
- 3. Mass exchange network synthesis, which is the mass integration analogue for heat exchange network synthesis

10.3.1 Source-Sink Mapping

Source-sink mapping is used to determine whether waste streams can be used as feedstocks.

1st step : identify the source and sink of material for which integration is desired

Ex. If water integration is desired

- the wastewater streams ("source") are identified
- the process that are required water ("sink") must also be identified
- the flow rates of source and sink also must be known
- contaminants in source and that pose a potential problem for the sinks must be identified

10.3.1 Source-Sink Mapping

2nd step

✤ Once all these parameters are known, the source-sink diagram can be drawn

✤ If only one contaminant is a concern, the diagram is 2-dimensional, with source and sink flow rates plotted on the y-axis and contaminant concentration plotted on the x-axis.

*Each sink is represented by an area corresponding to its upper and lower limits of tolerance for flow rate and contamination, and each source is represented by a point.

10.3.1 Source-Sink Mapping

Example

- Consider the sources and sinks in Table 10.3-1
- The material for which integration is sought (assume as water)
- ✤ is available at the flow rate specified
- Contaminant of concern is X
- Fig. 10.3-1 shows a source-sink diagram for the streams described in the table

Table 10.3-1

Example stream data for source-sink diagram

Sinks					Sources		
	flow rate, kg/s		concentration of X, ppm				concentration
Label	max	min	max	min	Label	flow rate, kg/s	of X, ppm
1	4.8	4.0	5	0	A	3.0	7
2	2.5	2.1	1	0	В	5.0	15
					С	1.0	4


Fig. 10.3-1 Source-sink diagram for the streams of Table 10.3-1

• In Fig. 10.3-1,

- Sources A, B and C are shown as points (because the flow rate and contaminant concentrations are point values), while sinks 1 and 2 are shown as shaded areas (because the flow rate needed and acceptable contaminant concentrations are ranges of values)
- Stream C can be used to partially satisfy the water demand for stream 1, since stream C's contaminant concentration falls within the range allowed for stream 1
- 3. No other direct reuse opportunities are available; however, stream A has a concentration that is not too far above the maximum allowable contaminant concentration for stream 1.

• In Fig. 10.3-1,

Question:

Would it be possible to blend streams A and C and satisfy the contaminant constraint for stream 1 ?

Source streams whose concentration of contaminants is too far for feeding to any sink (such as A) can be combined with lowconcentration sources (such as C) to lower the concentration. A point representing a combination of sources A and C is depicted

The flow rate of the combined streams is simply the sum of flow rates of the individual streams, and the concentration of X in the combined stream is the weighted average of the concentration in streams A and C,

$$\frac{3.0\frac{\text{kg}}{\text{s}} \times 7\text{ppm} + 1.0\frac{\text{kg}}{\text{s}} \times 4\text{ppm}}{3.0\frac{\text{kg}}{\text{s}} + 1.0\frac{\text{kg}}{\text{s}}} = 6.25 \text{ ppm}$$



The combined stream A+C has a flow rate within the acceptable range for sink 1, but its contaminant concentration X is too high to allow the combined stream to be used directly in sink 1.

To lower X to within acceptable limits, uncontaminated material (fresh water with 0 concentration of X) must be used in addition to sources A and C. The uncontaminated material that can be added to the stream to lower the X is 0.8 kg/s, because more than that will create a stream with a large flow rate than the upper bound allowed by sink 1.

$$\frac{3.0\frac{\text{kg}}{\text{s}} \times 7\text{ppm} + 1.0\frac{\text{kg}}{\text{s}} \times 4\text{ppm} + 0.8\frac{\text{kg}}{\text{s}} \times 0\text{ppm}}{3.0\frac{\text{kg}}{\text{s}} + 1.0\frac{\text{kg}}{\text{s}} + 0.8\frac{\text{kg}}{\text{s}}} = 5.2 \text{ ppm}$$

This is still higher than the limit allowed by sink 1. To lower the concentration further without exceeding the limit on flow rate, only a portion of source A can be used.

For example, if 2.8 kg/s of source A, all of source C, and 1.0 kg/s of uncontaminated material were combined, the resulting stream could be fed to sink 1. This is shown graphically in Fig. 10.3-2



Fig. 10.3-2 Source-sink diagram for Table 10.3-1, with sources and fresh feed combined to coordinate with a sink

Example 10.3-1 Source-Sink Mapping for Acrylonitrile Production

A simplified flowsheet for the production of acrylonitrile





Figure 10.3-4 Source-sink diagram for acrylonitrile process (AN = acrylonitrile).



Figure 10.3-5 Mass balance diagram for scrubber in acrylonitrile process (AN = acrylonitrile).



Figure 10.3-6 Mass balance diagram for decanter in acrylonitrile process (AN = acrylonitrile).



Figure 10.3-7 Mass balance diagram for the distillation column in the acrylonitrile process (AN = acrylonitrile).





Output Characteristic	Before Wastewater Reuse	After Wastewater Reuse
Fresh water feed required	71 kg/s	21 kg/s
Acrylonitrile in product stream	31 kg/s	4.4 kg/s
Flow rate to treatment	13.1 kg/s	7.7 kg/s
Mass fraction acrylonitrile in stream sent to treatment	0.092	0.078
Concentration of ammonia in stream sent to treatment	20 ppm	35 ppm
Concentration of ammonia in product stream	1 ppm	2 ppm

Table 10.3-2 Outputs from the Production of Acrylonitrile Before and After Wastewater Reuse.

10.3.2 Optimizing Strategies for Segregation, Mixing and Recycle of Streams

- As the processes to be analyzed become more complex and the number of sources and sinks increase, mathematical optimization techniques, coupled with process simulation packages, are generally employed to identify opportunities for recycle, segregation, and mixing of streams.
- The linear and nonlinear mathematical programming techniques employed in these optimizations.

(Example 10.3-2: Source-sink matching for chloroethane)

3. Mass Exchange Network Synthesis

(One of the more rigorous flowsheeting tools for mass integration is MEN, Mass Exchange Network)

- MEN synthesis is analogous to HEN for mass efficiency
- Unlike source-sink mapping and optimization, MEN does not achieve mass integration through re-routing of process streams. (MENs involve direct exchange of mass between streams)
- MEN synthesis can be used for any countercurrent, direct-contact mass transfer operation (absorption, desorption, or leaching)
- Mass transfer is limited by mass balance constraints and equilibrium constraints
 - 1) total mass transferred by the rich stream (the stream from which a material is to be removed) must be equal to that received by the lean stream (the stream receiving the material)
 - 2) mass transfer is possible only if a positive driving force exists for all rich stream/lean stream matches

3. Mass Exchange Network Synthesis

(One of the more rigorous flowsheeting tools for mass integration is MEN, Mass Exchange Network)

Phenol is a pollutant in water effluent, but it can be a valuable additive. MEN can be used to transfer phenol to the streams where its presence is desirable, thus preventing phenol pollution in refinery wastewaters. Phenol has a positive value in some streams and cannot be referred to as a pollutant, the compound whose transfer is desired will be identified as the "solute".

A mass balance on the solute to be transferred from stream i to stream j results in the equation (Fig. 10.3-13)

$$R_{i}(y_{i}^{in} - y_{i}^{out}) = L_{j}(x_{j}^{out} - x_{j}^{in})$$

where \mathbf{R}_i is the flow rate of rich stream i, \mathbf{L}_j is the flow rate of lean stream j, y_i is the mass fraction of the solute in rich stream, and x is that of in lean stream j



Fig. 10.3-13 Mass balance diagram for MEN synthesis

(Illustration of MEN synthesis (Phenol in a petroleum refinery)

- Rich streams are streams in which the solute concentration is higher than desired
- The flow rates of the streams are assumed to be constant
- Equilibrium between a rich and a lean stream can be represented by

$$y_i = m_j x_j^* + b_j$$

where $\mathbf{x_i}^*$ is the mass fraction of the solute in stream j that is in equilibrium with the y_i and m and b are constants that may be obtained from experimental data

- The positive driving force constraint for mass transfer is satisfied when $x_i > x_i^*$
- The tools of MEN are composition interval diagram(CID) that depicts the rich and lean streams (**Table 10.3-5** and **Fig. 10.3-14**)

Table 10.3-5 Stream data for two rich streams and one lean stream

Rich Stream				Lean Stream			
Stream	Flow Rate, kg/s	y ⁱⁿ	y ^{out}	Stream	Flow Rate, kg/s	x ⁱⁿ	x ^{out}
R ₁	5	0.10	0.03	L	15	0.00	0.05
R_2	10	0.07	0.03			×	



Fig. 10.3-14 Composition Interval Diagram (CID) for the streams of Table 10.3-5

10.4 Case Study of a Process Flowsheet

The process flowsheet for a generic crude oil processing unit at a petroleum refinery is described, along with pollution prevention techniques that were developed for the unit.

These pollution prevention techniques demonstrate the usefulness of both qualitative and quantitative flowsheeting tools and illustrate the complexity and integration found in processes in the chemical processing and refining industries.

In this case study, proposed pollution prevention techniques, including both heat and mass integration, result in substantial environmental improvements at a cost savings.

The schematic crude unit is shown in *Fig. 10.4-1*



Fig. 10.4-1 A simplified schematic of the petroleum refining crude unit

It consist of a desalter (which removes salt and other contaminants from crude oil), an atmospheric distillation tower, and a vacuum distillation column.

Crude oil and water are the primary feed materials and several output streams are produced including crude tower overhead (fuel gas and unstabilized gasoline), a light naphtha fraction, a kerosene fraction, a heavy distillate fuel fraction, an atmospheric gas oil (heavy) fraction, light vacuum gas oil, heavy vacuum gas oil and vacuum residue.

The streams from the crude unit are sent to many other processing units, many of which are reactors (fluidized-bed catalytic crackers, hydroprocessors, and cokers) to convert large hydrocarbon molecules into more saleable products. Other reactors create compounds with a high octane rating, or combine small hydrocarbon compounds to create large ones. Still other downstream processing units are used to purify and blend the refinery processing streams. Finished refinery products include gasoline, jet fuel, diesel fuel, fuel oil, waxes, asphalt, and petrochemical feedstocks.

Desalter

It removes salt in the crude that would cause corrosion of the process equipment. It also remove metals and suspended solids that would foul catalysts in downstream processing units.

In the first step of the desalting process, the crude oil is mixed with partially treated wastewater recycled from the refinery. Next, the oil is heated using a series of heat exchangers (1-5) in preparation for desalting.

In the desalter, which has two stages, hot oil and hot recycled water create a dispersed mixture of oil and water. The water extracts additional salts from the oil, and the salt-rich water (brine) is separated from the oil using an electric field.



Fig. 10.4-2

The desalter and crude oil preheaters for the hypothetical petroleum refining crude unit. Heat exchangers are numbered for cross-reference with **Fig. 10.4-3 and 10.4-4**

The desalted crude is then sent to another series of heat exchangers (6-10) for heating to 427°F, then, sent to atmospheric pressure distillation process unit (Fig. 10.4-3) and fuel-fired heaters supply energy to the tower.

In the vacuum distillation unit (Fig. 10.4-4), the bottoms from the atmospheric distillation unit are further fractionated into vacuum tower overhead, light vacuum gas oil, heavy vacuum gas oil, and vacuum tower bottoms. The energy for the tower is provided by a fuel-fired heater.

The overhead stream is contacted with steam, then cooled and sent to a overhead drum where oil and water phases are separated. The water stream from overhead drum is sent to the refinery sour water stripper, which is a wastewater treatment process that recovers ammonia and H_2S .

From this simplified process that the crude unit is a complex process and generates a variety of gaseous, liquid and solid waste. (Table 10.4-1)



Fig. 10.4-3

The atmospheric distillation tower for the hypothetical petroleum refining crude unit. Heat exchangers are numbered for cross-reference with Fig. 10.4-2



Fig. 10.4-4

The vacuum distillation tower for the hypothetical petroleum refining crude unit. Heat exchangers are numbered for cross-reference with Fig. 10.4-2

Table 10.4-1Major waste and emission streams from a petroleum refining crude unit

Type of Emission or Waste	Origin	Constituents
Stack air emissions	combustion of fossil fuels in boilers (for steam generation) and heaters (for heating the feed to the two distillation columns)	volatile organic compounds, carbon monoxide, particulate matter, sulfur dioxide, and nitrogen oxides
Fugitive air emissions	small leaks through packing on valves, pump seals, compressor seals, flanges, etc.; emissions from sewers; emissions from sampling operations; process fluid leaks into cooling water	volatile organic compounds whose composition depends on crude oil composition, but would include benzene, toluene, ethylbenzene, xylene, and cyclohexane
Cooling tower blowdown	cooling tower cools cooling water via evaporation; water evaporates more readily than the salts in the water; blowdown stream is necessary to prevent salts from getting too concentrated	salts
Condensate from steam drains		crude oil and other chemicals
Water plant sludge	sludge from purifying boiler and cooling tower water	salts
Oily wastewater	desalter wash water, sample drains, instrument drains, vessel drains	solids, phenols, chemical oxygen demand, ammonia, sulfides, crude oil components, heavy metals
Oily wastewater treatment sludges	treatment of oily wastewater generates a stream of slop oil, emulsified oil and water, and oily sludge	solids, crude oil components, heavy metals

Pollution Prevention Strategies in Crude Oil Processing Unit

- 1. Reboil with hot oil rather than steam to avoid oil/water contacting operations. Two additional side strippers must be added to the tower when this is done because the product specifications cannot be met with the existing side strippers when hot oil is used instead of steam for reboiling.
- 2. Add a liquid ring vacuum pump to the vacuum tower in order to reduce the pressure in the vacuum tower, which results in lower allowable operating temperatures, which in turn results in reduced cracking and fouling of the furnace tubes in the furnace, so that production of sour water is reduced

SOUR WATER STRIPPER

Refineries that process crudes containing sulfur will liberate the sulfur in various unit operations as hydrogen sulfide. Gas that contain hydrogen sulfide is called sour gas, and water that contains sulfide is called sour water. Reuse or disposal of sour water requires removing the sulfides from the water in a process called stripping.



FIGURE 1. Sour Water Stripper

The stripping process (Figure 1) uses a gas stream to force both the hydrogen sulfide (H_2S) and ammonia (NH_3) out of solution and into the gas phase for further treatment in a sulfur recovery unit (SRU), such as a Claus unit. Although air stripping can be used, steam stripping (which liberates more H_2S due to higher temperatures) is typically required in refinery sour water treatment to meet specifications for the stripped water. The process operation is complicated by the added presence of other chemicals, such as ammonia, phenol, and cyanide. The stripped water is typically used as process water in other parts of the refinery, or may be disposed if heavily contaminated.

Pollution Prevention Strategies in Crude Oil Processing Unit

3. Replace burners with new generation low-NO_X burners and retrofit for flue-gas re-circulation in order to reduce NO_X emissions







low-NO_X burners

a liquid ring vacuum pump

Pollution Prevention Strategies in Crude Oil Processing Unit

- 4. Reduce fugitive emissions by implementing a stringent inspection and maintenance program for piping components, using leakless valves when replacing small valves wherever it is economical to do so, using graphite or Teflon packing and seals when repairing valves, specifying double seals when replacing pumps, installing rupture disks on pressure relief valves and venting them to a flare, modifying the compressor, blind-flanging all the vents and drains, eliminating flanges where possible, and making all the sampling systems closed-loop.
- 5. Segregate mildly-contaminated wastewater and treat it so that it can be reused.



rupture disks

Pollution Prevention Techniques in Crude Oil Processing Unit

In addition to the above strategies, pinch analysis to reduce external energy requirements showed that air emissions could be reduced substantially by increasing the surface area of the existing preheaters by 8% by adding three additional preheaters.

The capital cost of these 3 preheaters was estimated to be \$2,268,000, while the annual savings in fuel costs were estimated to be \$1,692,000, Therefore, the additional heat exchangers were projected to have a payback period of one and a third years.

Table 10.4-2 shows estimated wastes and emissions for the hypothetical crude processing unit with and without the pollution prevention measure.

- \clubsuit the measure were projected to decrease emissions of NO_x by 60 %
- VOC emissions to air were projected to decrease by 93 %
- The quantity of oil and grease in wastewater was nearly halved
- The total suspended solids in wastewater were decreased by 32 %
- Sulfides in wastewater were decreased by 19 %
- Production of hazardous solid waste was decreased by over 90 %
- A non hazardous waste stream was generated
Table 10.4-2Estimates of crude unit emissions and waste generation beforeand after pollution prevention alternatives are implemented

Emission or Waste	Without Additional Pollution Prevention Measures	With Additional Pollution Prevention Measures
Air emissions, tons/yr		
Nitrogen oxides	420	170
Carbon monoxide	180	170
Volatile organic compounds	180	12
Suspended particulate matter	23	21
Sulfur dioxide	3.3	3.0
Wastewater		
Oil and grease, gal/day	230	120
Fotal suspended solids, lb/day	11,000	7,500
Biological oxygen demand, lb/day	1,200	
Chemical oxygen demand, lb/day	4,600	4,600
Ammonia	570	570
Sulfides	160	130
Phenol	200	200
Hazardous waste, tons/day	6.3	0.5
Nonhazardous wastes, tons/day	none (mixed with hazardous)	3.7



- Even the simplest chemical processes generally consist of a number of process units whose characteristics can influence overall waste generation.
- It was shown that pollution prevention can sometimes be achieved by examining the mass and energy integration of process units.