

General Operating Manual

MEROX[®] PROCESS UNIT CAUSTIC EXTRACTION

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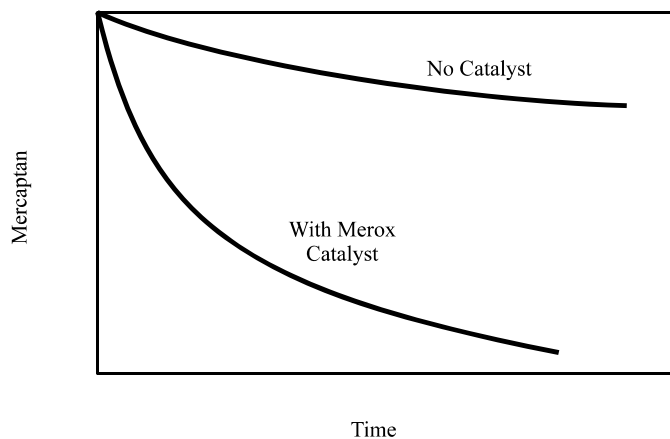
I. INTRODUCTION

A. MEROX PROCESS OVERVIEW

The UOP Merox Process is an efficient and economical catalytic process developed for the chemical treatment of petroleum distillates for **removal** of sulfur present as mercaptans (Merox Extraction) or **conversion** of mercaptan sulfur to a less objectionable form (Merox Sweetening). The name "Merox" is an acronym derived from MERcaptan OXidation. The process relies on a special catalyst to accelerate the oxidation of mercaptans to disulfides at economical product rundown temperature. The Saturate LPG Unit is an extraction process.

The Merox process is based on the ability of a catalyst composed of iron group metal chelates in an alkaline environment to promote the oxidation of mercaptans to disulfides using air as the source of oxygen. This technique without a catalyst has long been known but was generally impractical. It was not until UOP introduced Merox catalyst in 1958 that the great economic advantage of regeneration of caustic by use of atmospheric oxygen was fully realized (see Figure I-1).

Figure I-1
***Oxidation of Mercaptans
with Air and Caustic***



MRX-Sec. 6-14
MRX-R00-12

The reaction proceeds at an economically practical rate at normal temperatures for refinery rundown streams. For light stocks, operating pressure is controlled slightly above the bubble point to assure liquid phase operation; for heavier stocks, operating pressure is normally set to keep air dissolved in the reaction section. Downstream pressure requirements are easily taken care of by use of appropriate size product pumps.

Merox treatment can, in general, be utilized in the following ways:

1. Odor improvement on all stocks. (Extraction and Sweetening or both when Extraction cannot remove all of the mercaptans.)
2. Meet product specifications requiring a negative Doctor Test. (Sweetening)
3. Reduce sulfur content of LPG products to meet specifications. (Extraction)
4. Reduce sulfur content of FCC, coker or visbreaker C₃/C₄ olefins resulting in decreased acid consumption in alkylation operations using these materials as feedstocks and meeting the requirement of low sulfur for sensitive catalyst used in various chemical synthesis processes. (Extraction)
5. Improve susceptibility of gasoline stocks to oxidation inhibitors added to prevent gum formation during storage. (Sweetening and Extraction)
6. Improve lead susceptibility of light gasolines. (Extraction)

Depending on the application and the results desired, the Merox Process is applicable to the treatment of stocks boiling to 343°C (650°F) endpoint or higher.

B. MEROX ADVANTAGES

Relative to other treating processes, the Merox Process has the following advantages:

1. **Low operating cost and investment requirement.** The non-corrosive environment in which the process operates requires no alloys or other special materials, thus minimizing investment. The initial investment in many applications can be very low based on the conversion of existing equipment for use in Merox Treating processes and minimal plot area requirement. Low utility and chemical usage result in low operating costs.
2. **Ease of operation.** Merox Process Units are simple to operate; the air injection rate is the only direct adjustment necessary to accommodate wide variations in feed rate or mercaptan content. Operating labor requirements are minimal.
3. **Proven reliability.** The Merox process has been widely accepted by the petroleum industry; over 1500 units of various kinds (extraction, liquid, and fixed bed sweetening) have been placed in operation.
4. **Minimal chemical disposal requirements.**
5. **Proven ability to produce specification products.** There is no damage of product deterioration due to side reactions or addition of undesirable materials to the treated product.

C. HISTORY OF THE UOP MEROX PROCESS

The 1500th UOP Merox Unit started initial operations on October 19, 1993, thirty-five years after the first Merox Unit was put on stream on October 20, 1958.

The remarkable popularity of the UOP Merox process around the world is unrivaled by any other petroleum refining process and very few oil refineries are in operation without one or more Merox Units to treat the products. The popularity of the UOP Merox Process can be traced to its economical operation, ease of control, and ability to chemically treat mercaptans in a manner unique to Merox.

The basic Merox patents were issued to UOP researchers W. K. T. Gleim, et al. in the late 1950's and early 1960's. The manager of the UOP Treating Department, Kenneth M. Brown, saw the myriad advantages for the Merox catalyzed mercaptan oxidation over the other available processes and set out to convince UOP management to commercialize the process. At this point in time, the major treating processes in commercial use were:

Caustic Extraction/Steam Regeneration – for LPG and light gasolines

Caustic Scrubbing/Inhibitor Sweetening – for FCC and light thermal gasolines

Copper Chloride Sweetening – for low mercaptan feedstocks

Doctor Sweetening – for high mercaptan feedstocks

Having spent 20 years trying to develop procedures to understand and overcome the shortcomings of these processes, Ken Brown could scarcely contain his enthusiasm for the new catalytic process. Ken Brown is credited with developing and molding the research work into a viable, economical, commercial refinery process which we today call "Merox".

During the 1960's, UOP continued to improve the Merox process and its application to the treatment of LPG (extraction), FCC and light gasolines (liquid-liquid sweetening), and kerosene and jet fuels (fixed bed sweetening). In the early 1970's, changes in FCC Unit operations led to the development of the Minalk version of the fixed bed sweetening process. The first extraction unit treating a mercaptan rich gaseous methane stream was put in service in 1976. In the same year, two, relatively new, easy-to-use Merox catalyst were commercialized and an entirely new catalyst for sweetening kerosene feedstocks was created.

In 2001, customers were given the option of using the Extractor Plus™ design. The new design combines the functions of the caustic prewash, extractor, caustic knockout and sand filter vessels into one column. The use of a multifunctional column reduces unit plot area and results in a reduction of the initial investment cost for the unit. Other features of the new design are: continuous caustic prewash circulation, automated plant air control, caustic heater and oxidizer outlet temperature control, continuous Merox reagent injection, and improved handling of the spent gas stream.

Over the years, the UOP Merox process has revolutionized the refining industry in the chemical treatment of petroleum products. It is UOP's constant aim to improve and simplify the Merox process and to educate our licensees in its application. There was a time when treating was an art, not a science, practiced in the far corners of the refineries by people long suspected of possessing magical rather than technical skills. Today there exists a sound logical understanding of chemical treating which needs only to be put into practice.

The distribution of operating Merox Units by type is approximately:

Extraction	32%
Extraction + Sweetening	12%
Other Sweetening	42%
Minalk Fixed Bed Sweetening	14%

The following table (Table I-1) illustrates the applications for treating the various streams via the Merox process.

Table I-1
Applications of the Merox Process

<u>Typical Hydrocarbon Streams</u>	<u>Applicable Merox Treatment</u>
Gas, Natural Gas, Fuel Gas	A
LPG (C ₂ , C ₃ , C ₄)	A
Pentanes	A,B,C,E
Light Straight-Run Naphtha	A,B,C,E
Light Thermally Cracked Naphtha	A,D
FBR Straight-Run Naphtha	D,E
FBR FCC Cracked Naphtha	B,C,E
Heavy FCC Cracked Naphtha	C,E
Heavy SR Naphtha	D
Aviation Turbine Fuel	D,F
Kerosine	D,F
Distillate Fuel (to 350°C EP)	D

Key to Treatment Methods

- A Mercaptan Removal (Extraction)
- B Liquid-Liquid Mercaptan Conversion (Sweetening)
- C Minimum Alkali (Minalk) Fixed-Bed Mercaptan Conversion (Sweetening)
- D Fixed-Bed Mercaptan Conversion (Sweetening)
- E Caustic-Free Fixed Bed Mercaptan Conversion for Gasoline (Sweetening)
- F Caustic-Free Fixed Bed Mercaptan Conversion for Kerosine (Sweetening)

FBR = Full Boiling Range

D. GENERAL TREATING TERMS

azeotrope	a mixture of substances that behaves as a single substance in that the vapor produced by partial evaporation has the same composition as the liquid.
antioxidant	chemical additive to inhibit oxidation reaction
barrel	42 U.S. gallons measured at 60°F
BPD	barrels per day (also BSD)
caustic	sodium hydroxide solution
C/H	caustic/hydrocarbon volume ratio
delta P (dP)	differential pressure
delta T (dT)	differential temperature
disulfide	class of sulfur compounds characterized by a sulfur-to-sulfur bond and relatively low volatility represented by the general formula RSSR
EP	endpoint (ASTM distillation)
extraction	removal of mercaptan sulfur from hydrocarbon
Extractor Plus™	current design configuration of the extraction version of the Merox process. A caustic prewash section for H ₂ S removal, a mercaptan extraction section, and a coalescing section to remove entrained caustic are integrated into one column.
GC or GLC	gas chromatography
gph	U.S. gallons per hour
gpm	U.S. gallons per minute
gum	polymerized hydrocarbon
hydroperoxide	compound responsible for propagation of gum forming chain reaction (-OOH)
IBP	initial boiling point (ASTM distillation)

inhibitor	compounds responsible for delaying or terminating a chemical reaction
LHSV	liquid hourly space velocity
mercaptan	common name given to class of compounds having thiol functional groups represented by the general formula RSH
Merox [®] Process	a UOP licensed process that uses a metal based catalyst to oxidize mercaptan sulfur to disulfide oil.
naphthenic acid	organic (carboxylic) acid
Nm ³	normal cubic meter (1 atm. 0°C)
std. m ³	standard cubic meter (1 atm. 15°C)
organo-metallic	complex compound characterized by weak carbon to metal bonds
ppm	parts per million
PW	prewash
re-entry sulfur	entrained disulfide sulfur in regenerated caustic that enters and dissolves into the exiting hydrocarbon product from an extractor
RX	reactor
SCFH	standard cubic feet per hour (1 atm. 60°F)
sweetening	conversion of mercaptan to disulfide without desulfurization
stability	quality of a fuel to remain unchanged for long periods of time in storage
thiol	sulfur-to-hydrogen bond
thiophenol	common name given to aryl mercaptans; also the compound C ₆ H ₅ SH
vol., vol%	volume, volume percent
wt., wt%	weight, weight percent

CHEMICAL ABBREVIATIONS AND SYMBOLS

A•	inhibitor free radical
C	carbon
C ₁	hydrocarbon with 1 carbon atom (e.g., methane)
C ₂	hydrocarbon with 2 carbon atoms (e.g., ethane)
C _n	hydrocarbon with n carbon atoms
CaCO ₃	calcium carbonate
CO ₂	carbon dioxide
H	hydrogen
H ₂ S	hydrogen sulfide
Na	sodium
NaHS	sodium bisulfide
Na ₂ CO ₃	sodium carbonate
NaOH	sodium hydroxide (caustic)
Na ₂ S	sodium sulfide
NaSR	sodium mercaptide
Na ₂ S ₂ O ₃	sodium thiosulfate
O	oxygen
O ₂	diatomic oxygen (normal form in gaseous state)
R-	alkyl group side chain
R•	alkyl free radical
RSH	mercaptan
RSSR	disulfide
S	sulfur
S°	elemental sulfur
-SH	thiol (mercapto functional group)



unsaturated cyclic hydrocarbon compound



saturated cyclic hydrocarbon compound

[]

solution concentration (moles/liter)

English-Metric Conversions and Abbreviations

	<u>English Unit</u>	<u>Abbrev.</u>	<u>Multiplied By</u>	<u>Metric Unit</u>	<u>Abbrev.</u>
length	inch	in	25.4		mm
	foot	ft	304.8		mm
area	square foot	ft ²	0.09290	square meter	m ²
volume	cubic foot	ft ³	0.02832	cubic meter	m ³
	standard cubic feet of gas*	SCF	0.02826	standard cubic meters of gas	std m ³
	gallon	gal	0.003785	cubic meter	m ³
	barrel	bbl	.1590	cubic meter	m ³
temperature	degrees Fahrenheit	°F	°C = 5/9(°F-32)	degrees Celcius	°C
pressure	pound per square inch	psi	6.895	kiloPascal	kPa
	inch of mercury at 32°F	in Hg	0.1333	kiloPascal	kPa
	inch of water at 4°C	in H ₂ O	0.2491	kiloPascal	kPa
	pound per square inch	psi	0.07030	kilograms per square centimeter	kg/cm ²
mass	pound mass	lb or lbm	0.4536	kilogram	kg
energy	British Thermal Unit	Btu	1.055	kiloJoule	kJ
power	horsepower	hp	0.746	kilowatt	kW
	British Thermal Units per hour	Btu/hr	0.2931	watt	W

*UOP calculates standard cubic feet of gas at 60° F and 14.696 psia. UOP proposes to calculate standard cubic meters of gas at 15° C and 101.325 kPa.

II. PROCESS PRINCIPLES

Low molecular weight mercaptans are soluble in caustic soda solution. Therefore, when treating LPG, the Merox process can be used to extract mercaptans, thus reducing the sulfur content of the treated product. In the extraction unit, sulfur reduction is directly related to the extractable mercaptan content of the fresh charge.

The LPG Merox process utilizes liquid-liquid contacting to extract the mercaptans from the hydrocarbon with a strong aqueous alkali solvent. The mercaptan-rich solvent, which also contains the dispersed Merox catalyst, is sent to a regeneration section where air is injected and the mercaptans are oxidized to disulfides. The disulfides are subsequently separated from the solvent by coalescing, gravity settling, and withdrawal; the regenerated lean solvent is recycled back to the extractor. Thus, the process consists of two primary steps; mercaptan extraction and caustic regeneration; the latter being a combination of mercaptan oxidation and disulfide oil separation.

The remainder of this section discusses the reaction chemistry involved in the LPG Extraction process.

A. CHEMISTRY OF THE MEROX PROCESS

To fully understand the Merox process and how it can be applied to such a broad range of treating problems, it is necessary to review the basic chemical reaction of the process and how it is applied in a variety of ways.

1. Merox Reactions

The name "Merox" originates from the function of the process itself; namely the conversion of *mercaptans* by *oxidation*.

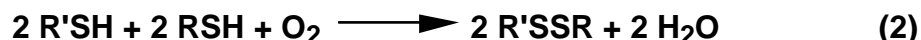
MERcaptan
OXidation

The word "mercaptan" is a descriptive name applied nearly 200 years ago to organic compounds with a sulfhydryl functional group (-SH) and derived from the Latin *mercurium captans*, due to their mercury seizing properties. Today's literature, however, assigns the word "thiol" for this functional group. In the common system used by the petroleum industry, mercaptans are named after their analogous alcohol counterparts. Thus, CH₃SH, by the common system, is methyl mercaptan just as one would name an alcohol having the formula CH₃OH methyl alcohol; the strict formal name is "methanethiol". Likewise, n-butyl mercaptan becomes 1-butanethiol, t-butyl mercaptan becomes 2-methyl-2-propanethiol. The aryl mercaptans are commonly called thiophenols, while in the formal system as used by Chemical Abstracts, these compounds are benzenethiol, toluenethiol, etc. This publication uses the common mercaptan terminology as practiced in the petroleum industry.

The Merox process in all of its applications is based on the ability of an organo-metallic catalyst to accelerate the oxidation of mercaptans to disulfides at near ambient temperatures and pressures. The overall reaction can be written:



R is a hydrocarbon chain that may be straight, branched, or cyclic. These chains may be saturated or unsaturated. In most petroleum fractions, there will be a mixture of mercaptans to the extent that the R chain might have 1, 2, 3,... 10 or more carbon atoms in the chain. When this reaction occurs, two different mercaptans might enter the reaction. This is indicated by showing R and R' in the reaction. The reaction is then written:



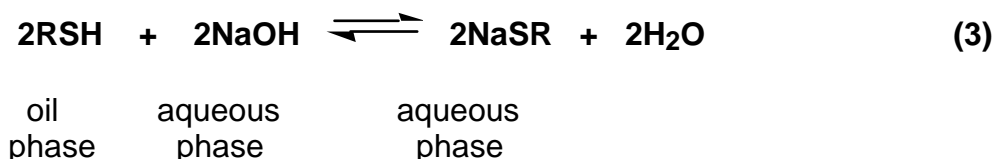
This reaction occurs spontaneously, but at a very slow rate, whenever any sour mercaptan bearing distillate is exposed to atmospheric oxygen.

Extraction can be applied to both gaseous and liquid hydrocarbon streams. The degree of completeness of mercaptan extraction depends upon the solubility of a mercaptan in the alkaline solution. That, in turn, depends primarily upon the following:

- a. molecular weight of mercaptan
- b. degree of branching of mercaptan molecule
- c. caustic soda concentration
- d. temperature of the system

As the molecular weight of the mercaptan increases, solubility in the alkaline solution decreases, and as chain branching increases, solubility decreases.

The following equation illustrates the mechanism of mercaptan extraction:



The ability of the Merox process to completely regenerate caustic depends on the following equation:



Of course, nothing can be done to control the amount of mercaptans present as this is a function of the crude source and/or the upstream process unit. The molecular weights of the mercaptan compounds are indirectly controlled by upstream fractionation.

For mercaptans having the same molecular weight, primary mercaptans are most completely extracted, secondary mercaptans are less completely extracted, and tertiary mercaptans are the least completely extracted. This, too, is a function of the feedstock.



primary mercaptan secondary mercaptan tertiary mercaptan

Because of these factors, mercaptan extraction is used mainly for low boiling range petroleum fractions such as fuel gas, C₃ and/or C₄ streams, and light gasolines, all of which contain relatively low molecular weight mercaptans. Mercaptan extraction is ideal where reduction in total sulfur content is also needed or desired.

III. PROCESS VARIABLES

The purpose of this section is to discuss the major Merox process variables and their effect on performance. Specific emphasis will be placed on identifying the optimum operating conditions. Feedstock quality is covered separately at the end of this section since Merox operators generally have little control over the feedstock.

The following represent the five primary process variables. Each will be discussed as an independent with all others held constant.

C atalyst
O xygen
A lkalinity
C ontact
H eat

A. CATALYST CONCENTRATION

The extractive Merox process requires the use of UOP Merox Reagent WS. It is supplied as a dark blue water solution packaged in 3.8 liter (1 U.S. gallon) sealed polyethylene bottles. Each bottle contains one kilogram (2.2 pounds) of water-soluble active ingredient. Alternatively, Merox WS can be supplied in 55 U.S.-gallon drums and 330 U.S.-gallon IBC containers.

Catalyst concentration is a direct operating variable in the extraction process. For initial makeup, or whenever fresh caustic is added to replenish the system, a catalyst concentration of approximately 200 ppm in the caustic is recommended. This roughly corresponds to 2 pounds of UOP Merox Reagent WS active ingredient per 1000 U.S. gallons of caustic inventory (0.24 kilograms per 1000 liters). A regular schedule of catalyst addition must be followed to maintain this catalyst activity level. As an initial recommendation, catalyst should be added at a rate of 1 pound per

10,000-25,000 barrels of hydrocarbon feed (1 kilogram per 3,500 to 9,200 cubic meters). Plant performance will indicate if this catalyst addition rate is sufficient.

Note: A formal, analytical method to determine active catalyst concentration in the Merox caustic does not exist.

B. OXYGEN INJECTION

Oxygen is supplied to the caustic regeneration section of the Merox Unit in the form of compressed atmospheric air. The stoichiometric, or theoretical, amount of oxygen necessary is 0.25 kg per kg of mercaptan sulfur (or 0.25 pounds oxygen per pound of mercaptan sulfur). At standard conditions of temperature and pressure, one cubic meter of atmospheric air contains about 0.28 kg of oxygen (one cubic foot of air contains about 0.018 pounds of oxygen). Therefore, about 0.88 std m³ of air is needed for each kg of mercaptan sulfur to be oxidized (14.2 SCF air per pound of mercaptan sulfur). It is necessary to have at least a slight excess of oxygen present but it is always recommended to keep the excess to a minimum. The amount of excess air injection necessary is highly dependent upon the individual feedstock, but normally ranges between 1.2 to 2.0 times the theoretical requirement. Thus, a good initial injection rate at 2.0 times theoretical may be calculated from the formula below:

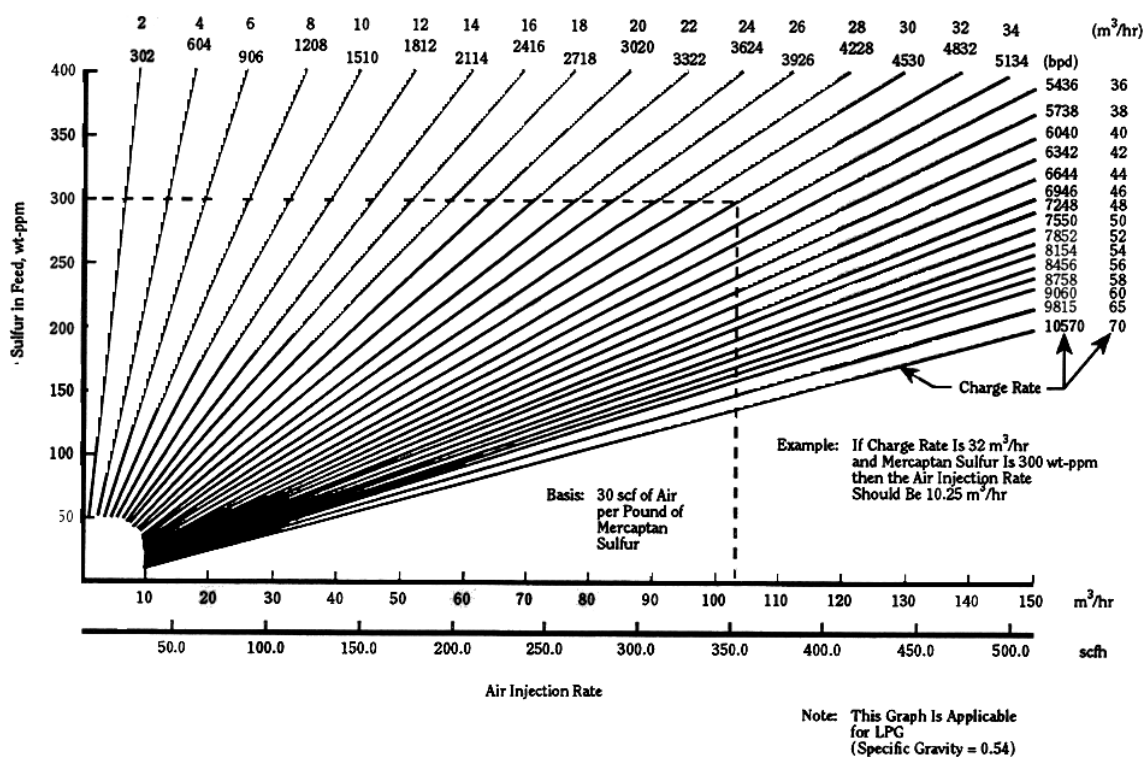
$$(\text{Air}) = 2.0 (K) (\text{Feed rate}) (\text{S.G.}) (\text{RSH}) / (10,000)$$

where:

	English	Metric
Air = Air injection rate	SCFH	std m ³ /hr
K = Constant	2.07	8.81
Feed rate = Feed flow rate	BSD	m ³ /hr
S.G. = Specific gravity @	60°F	15°C
RSH = Mercaptan sulfur	wppm	wppm

A graph of this formula, as shown in the following figure, is helpful in maintaining the proper air injection rate as the feedrate and mercaptan level varies.

Figure III-1
Air Injection Rate



For extraction Merox Units, the air is mixed with the caustic flowing to the oxidizer. All other variables being equal, an increase in air injection results in a more rapid and complete caustic regeneration. Thus, the regenerated caustic returning to the extractor would contain a relatively lower sodium mercaptides content and possess a greater capacity to extract mercaptan. However, increasing air injection decreases residence time in the oxidizer. Unless an unusually large excess of air is used, this has little effect.

While a low mercaptan concentration is desirable, the caustic should never be completely regenerated for the following reasons:

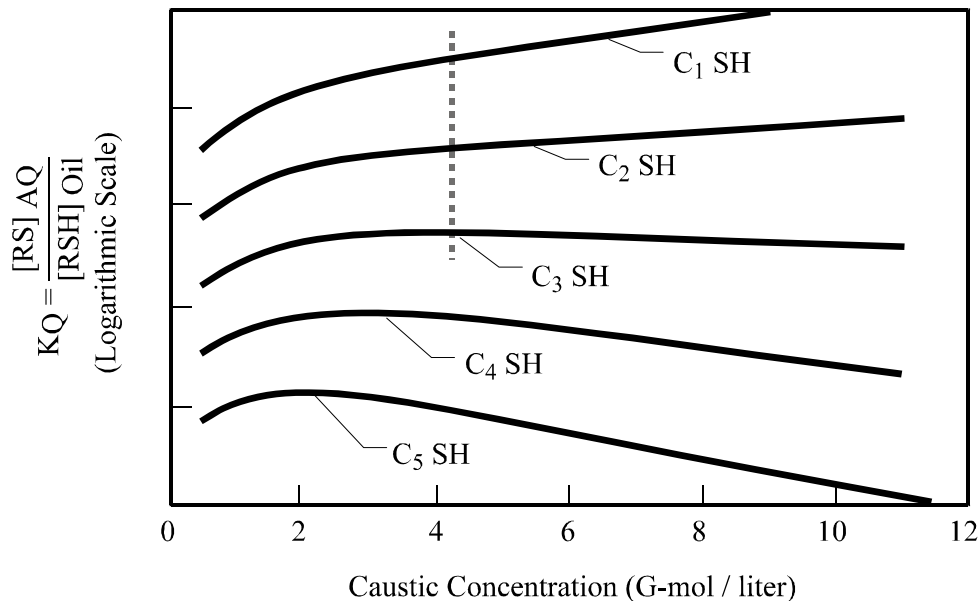
- a. Oxygen can dissolve in the caustic and cause sweetening to occur in the extractor.
- b. The excess spent air will have a higher oxygen concentration that may result in increased corrosion and potential hazards.
- c. Maintaining a small amount of mercaptide in the circulating caustic ensures better catalyst dispersibility in the aqueous caustic.

C. ALKALINITY

Alkalinity is provided by aqueous sodium hydroxide, or caustic, solution. In both of the liquid-liquid versions of the Merox process (extraction and sweetening), caustic is the solvent provided for mercaptan extraction and also the medium in which catalyst is dispersed. In addition, it provides the alkaline environment necessary for the mercaptan oxidation reaction to proceed in all versions of the Merox process.

For mercaptan extraction processing LPG hydrocarbon, caustic concentrations close to 20° Baume (14.4 wt% or 4.15 g/mol/liter) work well for mercaptans dissolution. For low molecular weight mercaptan molecules (methyl and ethyl mercaptan), increasing caustic strength increases extraction. As higher molecular weight mercaptan molecules are encountered, increasing caustic strength decreases extraction as shown in Figure III-2. An upper limit of 25° Baume (19 wt%) is the maximum practical concentration. Above this strength, competition from the hydroxide ions already in solution hinders any increase in mercaptan solubility. Also, at these strengths emulsification problems begin to occur.

Figure III-2
Equilibrium Distribution



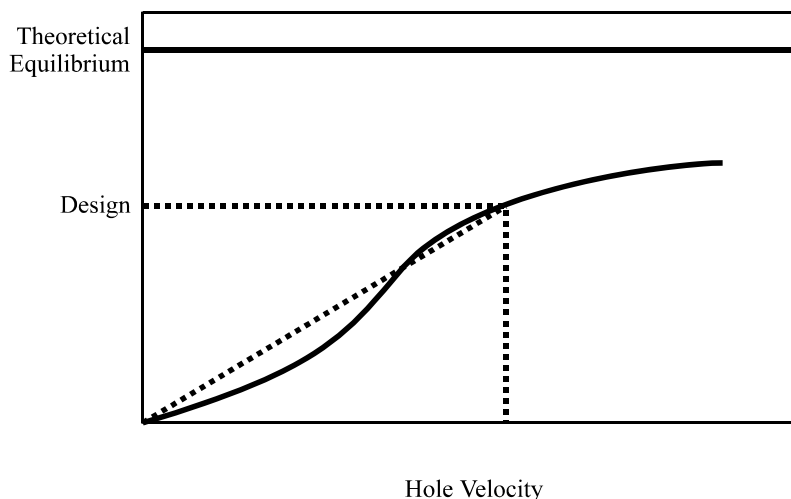
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D. CONTACT

Contact may be defined as mixing intimacy of the reactants and is accomplished by one of several means. Contact can be characterized by duration of mixing time, volumetric ratio of reactants, or differential pressure that implies degree of dispersion. With a fixed flow restriction, the differential pressure is directly related to the linear velocity so that velocity is often taken to be the process variable.

For extraction units, hydrocarbon tray hole velocity is one of the variables with which contact is characterized. The optimum hole velocity (Figure III-3) is designed for each unit based upon the intended design throughput. As hole velocity decreases, extraction efficiency decreases. However, the lower extraction efficiencies at turndown rates are compensated by higher caustic to hydrocarbon ratios obtained by maintaining constant the net caustic rates to the top of the extractors.

Figure III-3
UOP Merox Extraction Tray
Overall Efficiency



MRX-Sec. 6-22
MRX-R00-17

The other important contact variable for extraction is the volume of caustic circulated relative to the volume of hydrocarbon throughput. This is referred to as the caustic to hydrocarbon ratio (C/H). As this ratio is increased, contact is increased and the extraction potential is increased. Increased extraction occurs as a result of a favorable shift in the complex equilibrium conditions discussed earlier.

In order to increase the C/H ratio at constant hydrocarbon feed rate, the caustic circulation rate must be increased. Any entrained disulfide oil remaining in the regenerated caustic as it enters the top of the extractor is essentially completely extracted by the exiting hydrocarbon stream. Sulfur in the Merox product as a result of this effect is referred to as re-entry sulfur (Figure III-4). At a constant feed rate, re-entry sulfur increases in the treated hydrocarbon in direct proportion to the caustic circulation rate increase. The re-entry sulfur in the product may be calculated as follows:

Figure III-4
Re-Entry Sulfur

$$S_r = S_c(C/H)(G_c/G_h)$$

Where

S_r Re-entry sulfur in the product (wt-ppm)

S_c Disulfide sulfur in the regenerated caustic (wt-ppm)

C = Caustic volumetric flow rate

H = Hydrocarbon volumetric flow rate

G_c = Specific gravity of the regenerated caustic

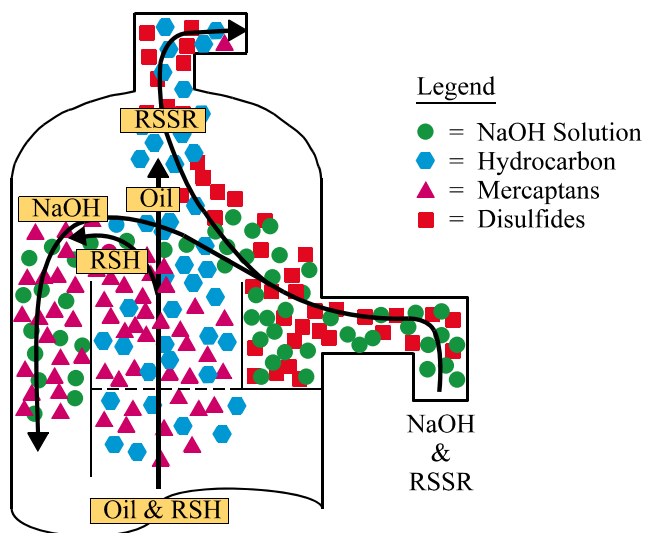
G_h = Specific gravity of the hydrocarbon

With C & H expressed in the same volume units

MRX-Sec. 6-27

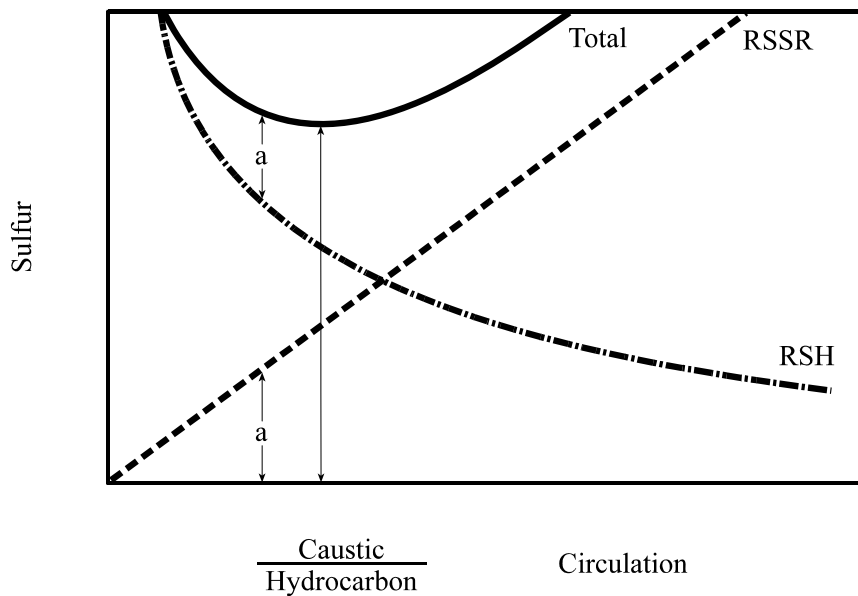
Since increasing the caustic to hydrocarbon ratio increases re-entry sulfur proportionally and decreases mercaptan sulfur exponentially, there exists a single optimum ratio where total mercaptan sulfur plus re-entry sulfur is minimized, typically, but not necessarily, in the 1-3% range for LPG-type streams (see Figures III-5 and III-6). Above the optimum C/H ratio, increased re-entry sulfur can be excessive; below it, mercaptan sulfur extraction may be inadequate.

Figure III-5
Re-Entry Sulfur



MRX-Sec. 6-26
MRX-R00-19

Figure III-6
Optimum Caustic



MRX-R00-20

E. HEAT (TEMPERATURE)

Mercaptan extraction is favored by lower temperature. The lowest practical hydrocarbon feed temperature for extraction is about 90°F (32°C). Below this temperature, caustic entrainment, or caustic haze, may become a problem. Above 110°F (43°C) mercaptan extraction will be lower and may cause excessive temperatures in the regeneration section. Liquid-liquid extraction Merox Units operate best within a temperature range of 90 to 100°F (32°-38°C).

The Merox caustic regeneration reaction is favored by higher temperature. Thus, in Merox Extraction Units a small heater or exchanger is provided to heat the rich caustic before it enters the oxidizer. Although the oxidizer temperature should always be kept as low as possible, the caustic temperature at the oxidizer inlet will normally be 100-110°F (38°-43°C).

The oxidizer temperature should always be run at as low a temperature as possible while still maintaining the desired degree of mercaptan regeneration. This avoids over-oxidation reactions that can lead to acid generation and cause caustic neutralization and corrosion of the disulfide separator and related equipment and piping. Operation above 120°F (49°C) must be avoided to minimize corrosion of carbon steel.

Some Merox units are designed to extract very high levels of mercaptans (multi-1,000 wppm levels). In such cases, a high exothermic reaction across the Oxidizer is expected due to the high quantity of mercaptides in the circulating caustic. To minimize the delta T across the Oxidizer, a slipstream of lean caustic may be recycled back to the inlet of the Caustic Heater via a spillback line from the Caustic Circulation pump. This stream dilutes the concentration of mercaptides by increasing the total volume of caustic and thus reduces the exotherm across the Oxidizer. At times, the steam supplied to the caustic heater is discontinued to avoid high temperatures across the Oxidizer, assuming proper caustic regeneration can be maintained.

IV. PROCESS FLOW AND CONTROL

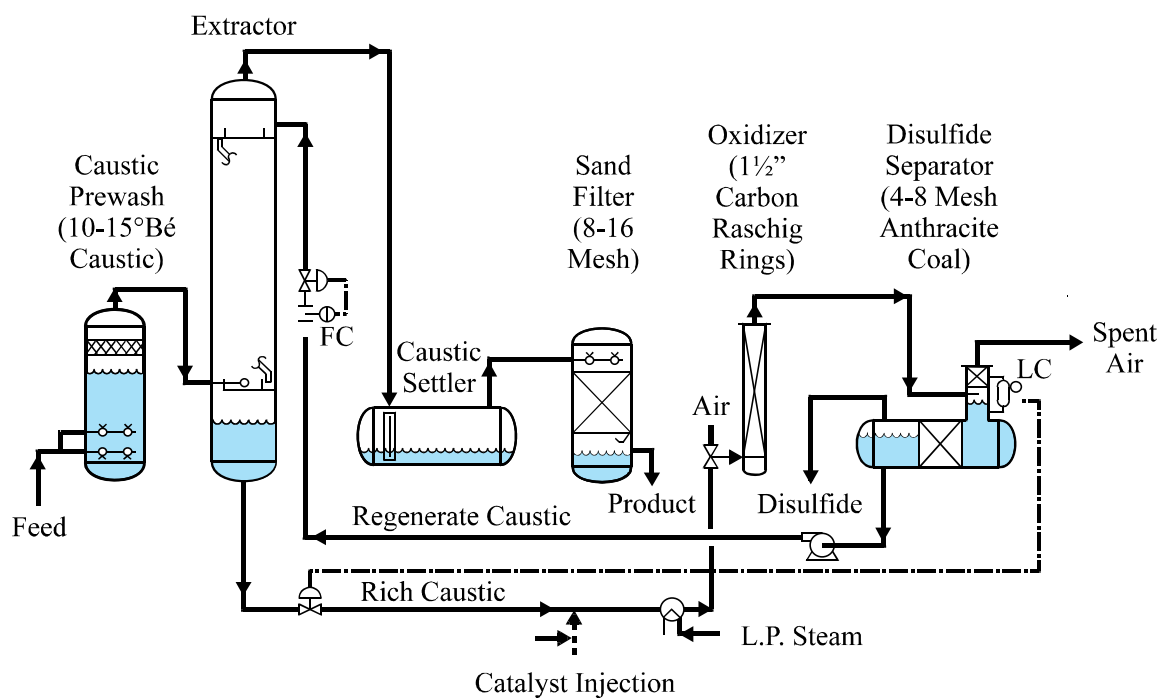
A. PROCESS FLOW

There are two versions of Merox extraction units: the conventional type with a traditional Extractor, and a newer type known as Extractor Plus™. The conventional type includes a caustic prewash, extractor, caustic settler, and sand filter as stand-alone vessels, while the Extraction Plus type has the vessels stacked as part of one column. The sand filter is replaced with a Coalex pad located at the top of the column after a disengaging zone.

In both cases, fresh feed is scrubbed with caustic to remove H₂S in either the Caustic Prewash, or the prewash section of the Extraction Plus column. Subsequently, H₂S-free feed flows to the extractor or the extraction section of the Extraction Plus column in which mercaptans are countercurrently extracted using caustic. Following extraction, the hydrocarbon stream is sent to a downstream caustic settler and/or sand filter, or it passes through the Coalex pad to remove any entrained caustic before it leaves the unit.

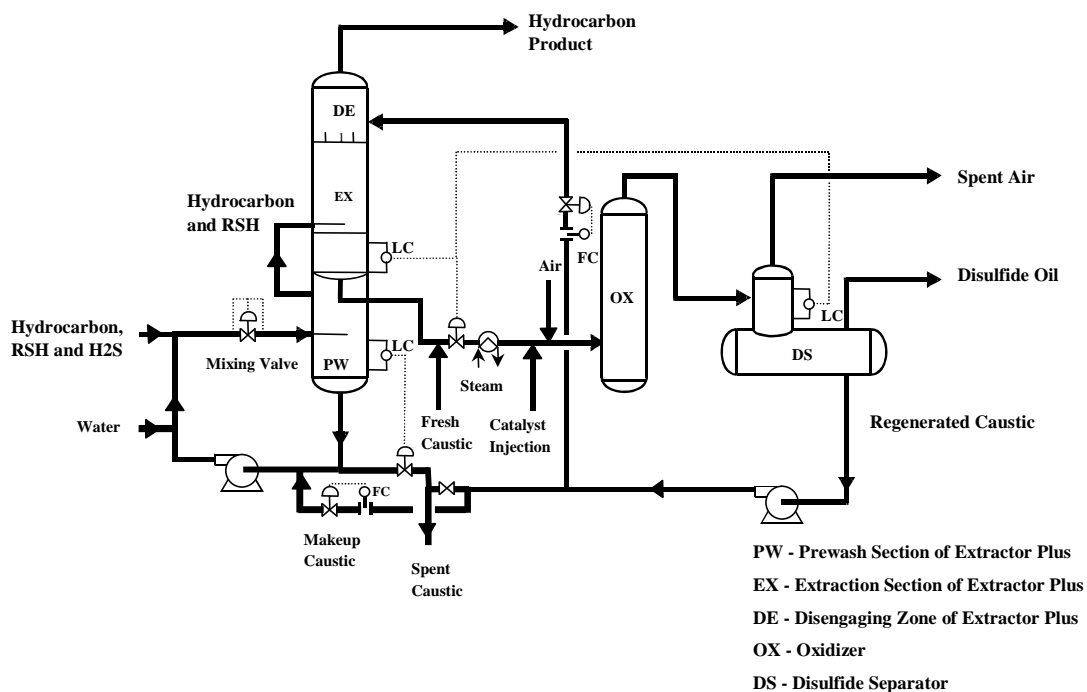
Mercaptan-rich caustic solution from the bottom of the extractor flows to the regeneration section. Here, the stream is heated and air is injected before the combined stream flows to the Oxidizer where the mercaptans in the caustic are oxidized and converted to disulfide oils. From the Oxidizer, the caustic, disulfide oil, and spent air proceed to the Disulfide Separator. Spent air is vented, usually to a fired heater within the refinery; disulfide oil is withdrawn and sent to disposal or another process unit as part of the combined feed to a hydrotreater or FCC Unit); regenerated (lean) caustic is circulated back to the Extractor or Extractor Plus™ column. Merox WS catalyst is added periodically to enable mercaptan conversion to disulfide oils in the regeneration section of the unit.

Figure IV-1
UOP Merox Process
Typical Extraction Unit



MRX-R00-24

Figure IV-2
UOP Merox Process
Extraction Plus™ Unit



MRX-R00-01

1. Pretreatment

Hydrocarbon feed with objectionable levels of H_2S flows to the Caustic Prewash. In the traditional configuration, this is a separate vessel upstream of the Extractor and is typically operated batch-wise.

With Extractor PlusTM, the prewash is the bottom section of the column where H_2S is removed from the stream by a continuously circulating caustic stream. The caustic from the bottom of the caustic prewash section is pumped into the incoming feed, contacted across a static mixer, and circulated back to the caustic prewash section where hydrocarbon and caustic separate.

The continuous caustic circulation provides better mixing of the hydrocarbon and caustic resulting in better H_2S removal. Streams containing less than 100 wppm of H_2S can be treated in this section. Feeds with much higher levels of H_2S require amine treating upstream of the prewash.

2. Extraction Section

Mercaptan rich feedstocks are mixed countercurrently with caustic solution in a trayed tower. The circulating caustic solution contains dispersed Merox catalyst, but the catalyst has no effect on mercaptan extraction. During mixing, mercaptans transfer from the hydrocarbon feed to the caustic solution. In a perfect or theoretical stage of contact, dynamic equilibrium would be reached. At conditions of dynamic equilibrium, there is no further net transfer of mercaptans from the hydrocarbon to the caustic; that is, the rate of mercaptan transfer from the hydrocarbon to the caustic equals the rate of mercaptan transfer from the caustic back into the hydrocarbon. In any real or actual stage of contact, true or complete equilibrium is not reached. The closer the approach to true equilibrium, the more efficient is the stage of contact.

The trays specified are high efficiency jet decks, which permit the use of low caustic rates. Because the caustic rates are low, the physical size of the caustic

regeneration section is relatively small. The extractor is simply a liquid-liquid countercurrent contactor. Untreated hydrocarbon enters near the bottom of the contactor, and regenerated caustic is pumped into the top of it. Due to their gravity differences, hydrocarbon will flow upward while the caustic will flow downward. The contactor is designed so that intimate contact between the two liquids occurs. This is necessary to ensure maximum mercaptan transfer from the hydrocarbon by the caustic.

The concept of the countercurrent principle is that as the hydrocarbon flows upward stage by stage, it is in contact with leaner and leaner caustic. Therefore, the "cleanest" hydrocarbon will be in contact with the leanest caustic at the last stage of contact (top tray). Conversely, at the first stage of contact (bottom tray), the mercaptan-rich hydrocarbon is in contact with the richest caustic. This arrangement results in an equilibrium favorable to the least possible amount of mercaptan in the hydrocarbon leaving the top of the extractor.

3. Regeneration Section

The mercaptan-rich caustic solution containing dispersed Merox WS Reagent catalyst is withdrawn from the bottom of the Extractor or the extraction section of the Extractor Plus™ column and sent to the regeneration section of the unit. The mercaptan-rich caustic is heated slightly and injected with a controlled amount of air in the Oxidizer. The resulting catalytic reaction converts the aqueous soluble mercaptides to oil soluble disulfide oils that are relatively insoluble in the caustic solution. The mixed phase of air, caustic and disulfide oil then flows to the Disulfide Separator where they are separated.

The first separation occurs between vapor and liquid. This allows the oxygen depleted spent air to be sent to disposal. The vented air has a foul odor due to the presence of disulfide vapors. There may also be a small amount of unreacted mercaptans and/or residual hydrocarbon. In normal operation, the spent air mixture flows through a Vent Tank and two detonation arrestors to a fired heater or incinerator. During normal operation, the oxygen content of the spent air is too low to support combustion. Spent air lines are hydraulically designed so that the velocity

through them is high enough to minimize the possibility of spent air flame backflash. However, due to the possible presence of hydrocarbons, detonation arrestors must be properly installed and kept in good working condition to arrest backflow should a backflash occur. Older units have a diluent fuel gas line connected to the spent air line to reduce the O₂ concentration below safety limits.

A second separation is then effected between the regenerated caustic and the disulfide oil in the main body of the Disulfide Separator. This portion of the vessel has a coalescing zone followed by a gravity settling zone. Upon separation, the disulfide oil is periodically (or continuously) withdrawn to disposal as an upper oil phase. The lower regenerated caustic phase, freed of substantially all but a slight amount of entrained disulfide, is recirculated to the Extractor to complete the caustic loop.

B. CONTROL PHILOSOPHY

The arrangement of level controls is such that flow surges in the unit, which would upset the normal caustic hold-up in the plant, will be absorbed by fluctuation of caustic level in the Extractor. It is advisable to hold such a level in the Extractor during normal operation so that maximum caustic surge space is available, consistent with surges in hydrocarbon flow normally encountered. The extractor is the only part of the plant that can be seriously affected by surges in hydrocarbon flow. There is usually no problem with surging flow on units charged with a pump. In many cases the unit will be charged directly from a fractionating column in which case fluctuations in fractionator instrumental control can cause surges in the Merox unit extractor. Fractionator controls should be adjusted to give smooth control.

Pressure within the Merox unit is controlled at two locations. The pressure of the hydrocarbon section is maintained using a back pressure controller located on the treated product effluent line. The pressure is set high enough to prevent hydrocarbon vaporization and create pressure drop needed for caustic flow to the regeneration section. Vaporizing hydrocarbons in the unit may cause caustic

entrainment and pump cavitation. The pressure in the regeneration section is set to allow disposal of the spent air stream and usage of plant air.

In the case of Extractor Plus™, caustic is transferred from the regeneration section to the prewash section as needed to maintain prewash caustic concentration and achieve a better overall caustic utilization. A level controller, located on the prewash section of the Extractor Plus™ column, is used to control caustic being removed from the system through a control valve. As the controller set point is decreased, a control valve will open to lower the caustic level in the caustic prewash section. The spent caustic is typically first degassed and then sent to safe disposal systems. Regeneration caustic can be added to the prewash section using a flow controller valve located on the caustic transfer line from the caustic circulation pumps. After caustic is transferred, it may be diluted to the desired concentration by injecting water into the system through the water injection pumps. Fresh caustic must be added to the regeneration section to make up caustic levels in the extraction section.

Rich caustic flow from the extractor to the oxidizer is cascaded off of the level controller on the air-liquid interface of the Disulfide Separator stack. The bottom of the extractor acts as a reservoir for the contents of the circulating caustic. It can also be controlled using a level controller on the extractor. This is the case when two or more extractors share the same caustic regeneration section.

The caustic heater outlet and oxidizer outlet temperatures may be controlled using a low signal selector to select the temperature control location. Caustic flow to the regeneration section is heated to 105°-110°F (40.5°-43°C). Both controllers will cause the steam flow to the caustic heater to either increase or decrease to provide required heat input.

A regeneration caustic circulation pump spill back controller may be designed to meet pump minimum flow requirements or lower the circulating caustic delta temperature across the oxidizer.

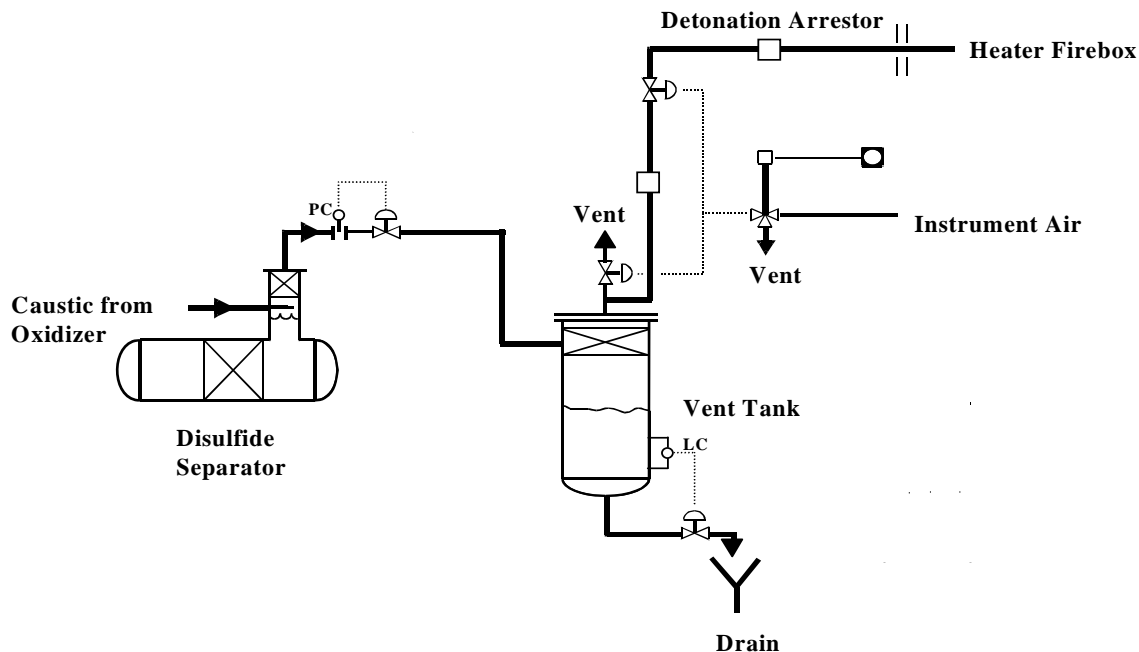
In most flow schemes, the optimum caustic-hydrocarbon ratio that produces the minimum total sulfur in the product is determined and a control valve on the lean caustic to the extractor is used to maintain the desired flow of caustic.

Plant air flow is controlled using a flow controller on the plant air inlet. The controller uses measurements from an oxygen analyzer located on the disulfide separator stack spent air outlet to maintain the required plant air flow. When the oxygen concentration of the spent air is outside the typical 9-12 wt% range, a control valve will open or close more to manipulate the fresh air rate to the regeneration section.

During normal operations, spent air from the top of the disulfide separator stack, is routed to a vent gas tank and then to a heater. In case of an emergency, spent air from the vent tank can be diverted to atmosphere by closing a valve on the spent air flow to the heater and opening a valve on the vent tank vent line to atmosphere.

The following diagram illustrates our current vent gas control scheme.

Figure IV-3
Typical Vent Gas Control Scheme



MRX-R00-02

The Merox reagent, Merox WS, must be regularly added to the regeneration caustic to enable the conversion of mercaptides to disulfide oil. In the batch system, bottles of Merox WS solution are poured into the Catalyst Addition Pot and then pressured into the regeneration section with air.

With a small proportioning pump, Merox WS may also be injected during programmed time intervals, providing excellent catalyst distribution into the circulating caustic inventory.

V. PROCESS EQUIPMENT

The extraction Merox process will be discussed vessel by vessel along with any important pieces of equipment. A description of internals is provided as well as the key features on each vessel. The traditional Extraction and Extraction PlusTM differ only on the hydrocarbon streams; the regeneration sections of the two are identical. Traditional Extraction uses separate vessels for the H₂S scrubbing (Caustic Prewash), mercaptan removal (Extractor), bulk caustic removal (Caustic Knock Out Drum), and caustic coalescing (Sand Filter). Extraction PlusTM combines these functions into one tower.

A. PRETREATMENT

Virtually all extraction unit feedstreams need pretreatment before entering the Merox Unit proper. The purpose of pretreatment is to remove acidic impurities such as H₂S and/or CO₂. The type and quantity of impurities or contaminants in the feedstock will determine which pretreatment equipment is required.

1. Amine Treating Unit

An amine unit is generally provided on feedstocks containing relatively high concentrations of acid gases (H₂S and CO₂). An aqueous solution of an amine, usually an ethanolamine, is utilized in a countercurrent contact to extract the acid gases. This unit is typically provided upstream of extractive type Merox Units that are treating natural gas, fuel gas, propane, butane, or combined LPG. An amine unit will remove acid gases to an equilibrium level dependent on amine regeneration; however, this level is not low enough to send amine treated feed directly to a Merox Unit. Further pretreatment in the form of a caustic prewash is required to remove the last traces of acid gases present. The design and operation of the amine unit equipment is outside of the scope of this manual.

2. Amine Water Wash

The water wash is a horizontal vessel that may be installed to remove soluble and/or entrained amine from the hydrocarbon downstream of the amine absorber (upstream of the Extraction Merox Unit). The water wash may be either continuous or batch operated. For either type of water wash, a level of water is maintained in the vessel and used for re-contacting with the incoming hydrocarbon stream. The mixture of water and hydrocarbon is passed through a mixing valve or static mixer just upstream of the vessel to allow for intimate contacting. The water is allowed to settle in the water wash vessel and then recycled back to the inlet for further contacting. Note: During normal operations, the amine concentration in the circulating water should be monitored. For batch water wash, once the spent water amine concentration reaches 1-3 vol-%, or whatever concentration is required to prevent amine breakthrough, the spent water should be replaced with fresh water. For continuous water wash, the fresh water injection rate should be adjusted to obtain the desired concentration of amine in the spent water.

3. Caustic Prewash

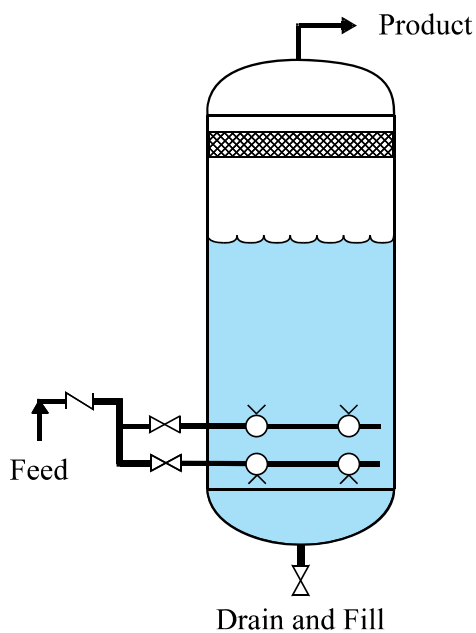
A single batch-type caustic prewash is typically used when removing moderate levels of hydrogen sulfide, H_2S , (up to ca. 100 wt. ppm). At times, higher levels of H_2S may be present in the feedstock even though an amine treating unit cannot be justified. In that case, two batch-type caustic prewashes may be employed in series and manifolded such that either prewash can be placed first in line. The two-stage prewash will allow greater utilization of caustic without risking H_2S breakthrough to the Merox Unit.

The simple batch-type caustic prewash consists of a single vertical vessel. Hydrocarbon enters the bottom of the vessel and jets through a distributor with holes oriented downward. The distributor hole area and orientation is designed to provide adequate mixing and should be checked for conformance to specification. The number and size of the distributor holes will vary with the application. The vessel is normally operated half full of

dilute caustic and caustic is replaced batch-wise. Occasionally, for higher H_2S loadings, continuous caustic injection and withdrawal of spent caustic on automatic level control is specified, such as when the Caustic Prewash is part of the Extractor Plus™ vessel. A full diameter stainless steel wire mesh blanket is provided in the upper section of the vessel below the hydrocarbon outlet to coalesce and remove most of the entrained caustic. The mesh blanket should be adequately secured to its support with tiedown wires. Periodic inspections should be conducted to evaluate mesh blanket integrity. The batch prewash is normally supplied with two inlet distributors, one near the bottom and the second several feet above. Normal operation utilizes the bottom distributor. The top distributor, with holes oriented upward, is used only when it is necessary to changeout caustic. This upward hole orientation distributor allows a calm caustic phase essentially free of undissolved hydrocarbon to be withdrawn from the bottom of the vessel.

NOTE: Sulfidic caustic carryover from the prewash into the extractor is not acceptable. The prewash caustic level may need to be lowered to avoid spent caustic carryover into the extractor.

Figure V-1
Caustic Prewash



MRX-R00-21

B. POST TREATMENT

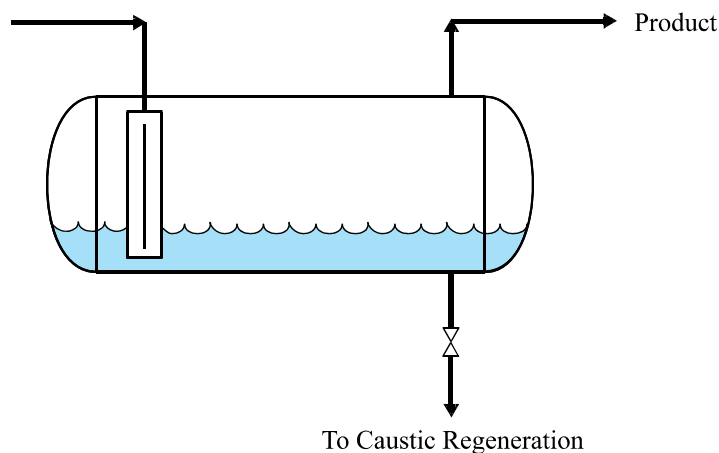
Most Merox units will have some type of treatment equipment after the extractor to remove impurities and/or contaminants such as COS, amine, caustic, etc. The ultimate product destination, use, and specifications will determine the type of post treatment required. The following post treatment equipment is often included with the various types of Merox Units.

1. Caustic Knock Out Drum

The Caustic Knock Out Drum, also known as an Emergency Knock Out Drum, is a horizontal vessel designed to permit gravity separation of aqueous caustic solution from the hydrocarbon product. An inlet distributor is provided to avoid excess inlet turbulence and promote an even flow distribution through the vessel. It usually consists of a single pipe arranged vertically through nearly the full width of the vessel diameter with one full-length slot facing the nearest head of the vessel.

Generally, the intent of this vessel is to catch all of the caustic from the trays in case of flooding, therefore its installation is considered optional. Hence, this vessel may not be available on all Extraction Merox Units.

Figure V-2
Caustic Knock Out Drum



MRX-R00-22

2. Sand Filter

When the Merox treated product goes to any downstream processing (fractionation, drying, etc.), a sand filter is usually provided to coalesce any entrained caustic solution. Prolonged settling will accomplish the same purpose. A coalescer is therefore a means of reducing settler size. A sand filter may be desirable even if the product simply goes to storage. Hydrocarbon product from a properly maintained sand filter will usually be visibly clear (gasoline products) and contain less than 1 wt. ppm sodium.

The sand bed consists of a specified depth of 8-16 mesh quartz or silica sand. The sand bed is supported on a special Johnson Screen proprietary design steel grid. Hydrocarbon enters at the top of the vessel, through a slotted distributor, passes downward through the sand bed, through the support grid, and turns before exiting from the side of the vessel, below the sand support grid. The hydrocarbon outlet is protected by a special chordal baffle permitting the coalesced aqueous phase to run down the walls and collect at the bottom of the vessel. Care should be taken that the sand is of the same size and grading as specified so that excessive pressure drop does not develop.

A Sand Filter may not be present if an Extractor Plus™ vessel is installed.

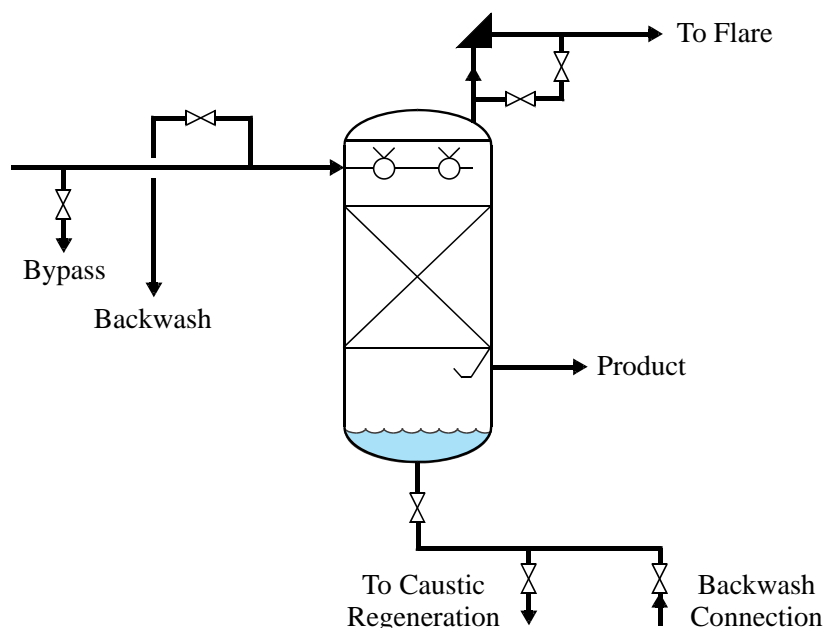
Make sure the sand support is correctly installed. Check for levelness and for sealing strips over the section joints. Make certain that the nylon rope packing around the perimeter of the support grid is properly installed.

The first 2 inches (50 mm) of sand should be loaded by hand via the side manway, leveled, and allowed to sit for about one hour. This will confirm proper support grid installation and absence of any leaks.

Prior to loading the sand, temporarily cover the inlet distributor with plastic film or cloth to prevent the sand from seeping into the distributor slot. The sand is preferably loaded with a sock to prevent any cone effect and

classification from developing. The sock loading method also reduces the amount of dust generated if the sand is dry.

Figure V-3
Sand Filter
8-16 Mesh Quartz Silica Sand



MRX-R00-23

C. LIQUID-LIQUID EXTRACTION UNIT

1a. Extractor

The extractor is a vertical vessel consisting of a series of specially designed perforated trays (Figure V-4 and V-5). Each tray consists of a caustic inlet reservoir with the inlet weir separating this reservoir from the central mixing region. The center section is the mixing region of each tray and contains perforations to allow the upflowing hydrocarbon to contact the cross-flowing caustic. The caustic mixes with the hydrocarbon, disengages as it is carried upward and overflows the outlet weir, collecting in the caustic outlet

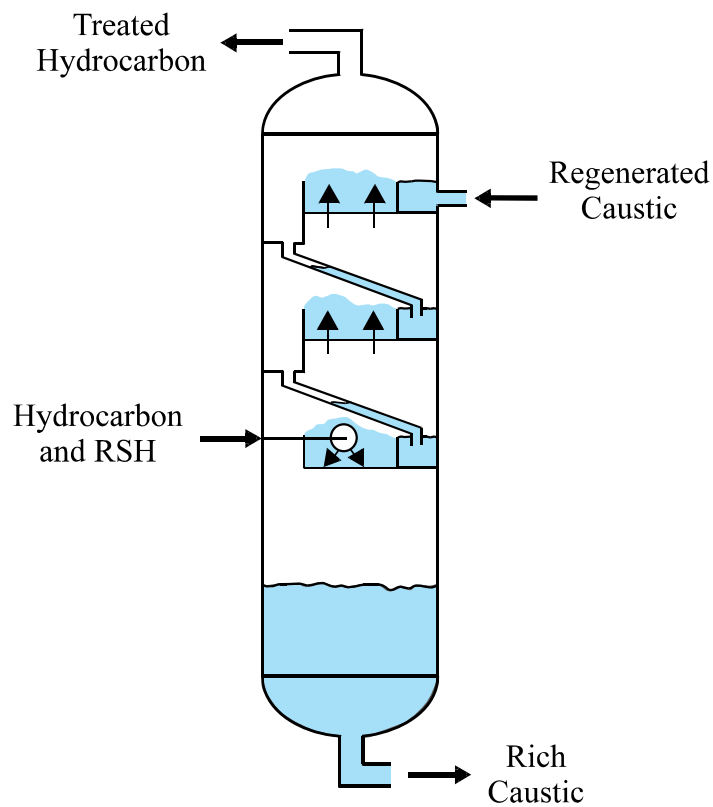
reservoir. A downcomer pipe transfers the caustic to the next tray inlet reservoir by gravity flow.

Since the caustic flow rate is often low relative to the hydrocarbon flow as allowed by the high velocity and high efficiency trays, it is very important that both inlet and outlet weirs are level. Also, no caustic leakage can be tolerated at any point in the tray. The trays should be entirely sealed except for manways; these are sealed with neoprene rubber gaskets. The initial checkout should include a water leak test. For this test the downcomer pipes are plugged and filled with water to the top of the outlet weir. If the inlet weirs have holes accessing the mixing region for drainage purposes, these should be plugged and the inlet reservoirs leak tested as well. Both reservoirs should not leak. Even the tiniest leak will reduce extraction efficiency and capacity by upsetting the tray hydraulics. When the caustic flow rate is less than 2 or 3 gpm (0.5 or 0.7 m³/hr), the inlet weir drainage hole should be omitted or welded shut.

The feed tray contains no holes in the mixing section but instead contains an inlet distributor designed with holes oriented downward to allow a good mixing between hydrocarbon and caustic solutions (Figure V-6). The size and number of holes should be verified. The end must be capped.

The bottom of the extractor column serves as a caustic surge reservoir for the entire system. Generally, it is fitted with a level glass and level indicator with a low level alarm.

Figure V-4
Extractor



MRX-R00-25

Figure V-5
Extractor Tray

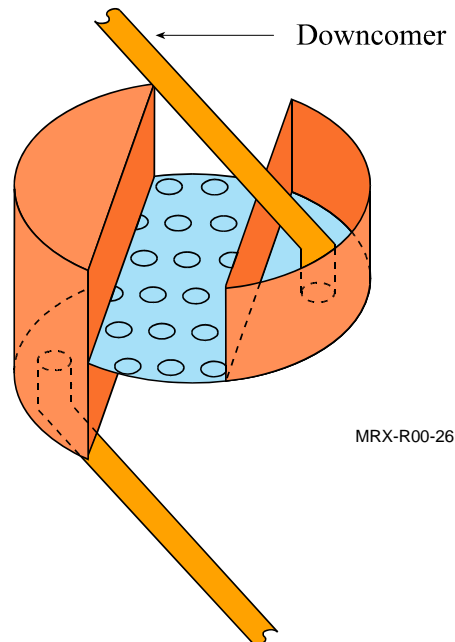
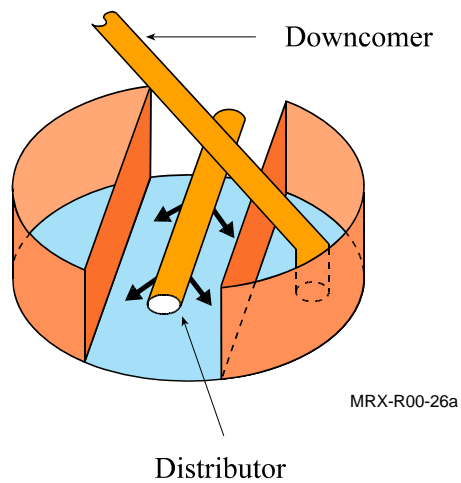


Figure V-6
Feed Tray



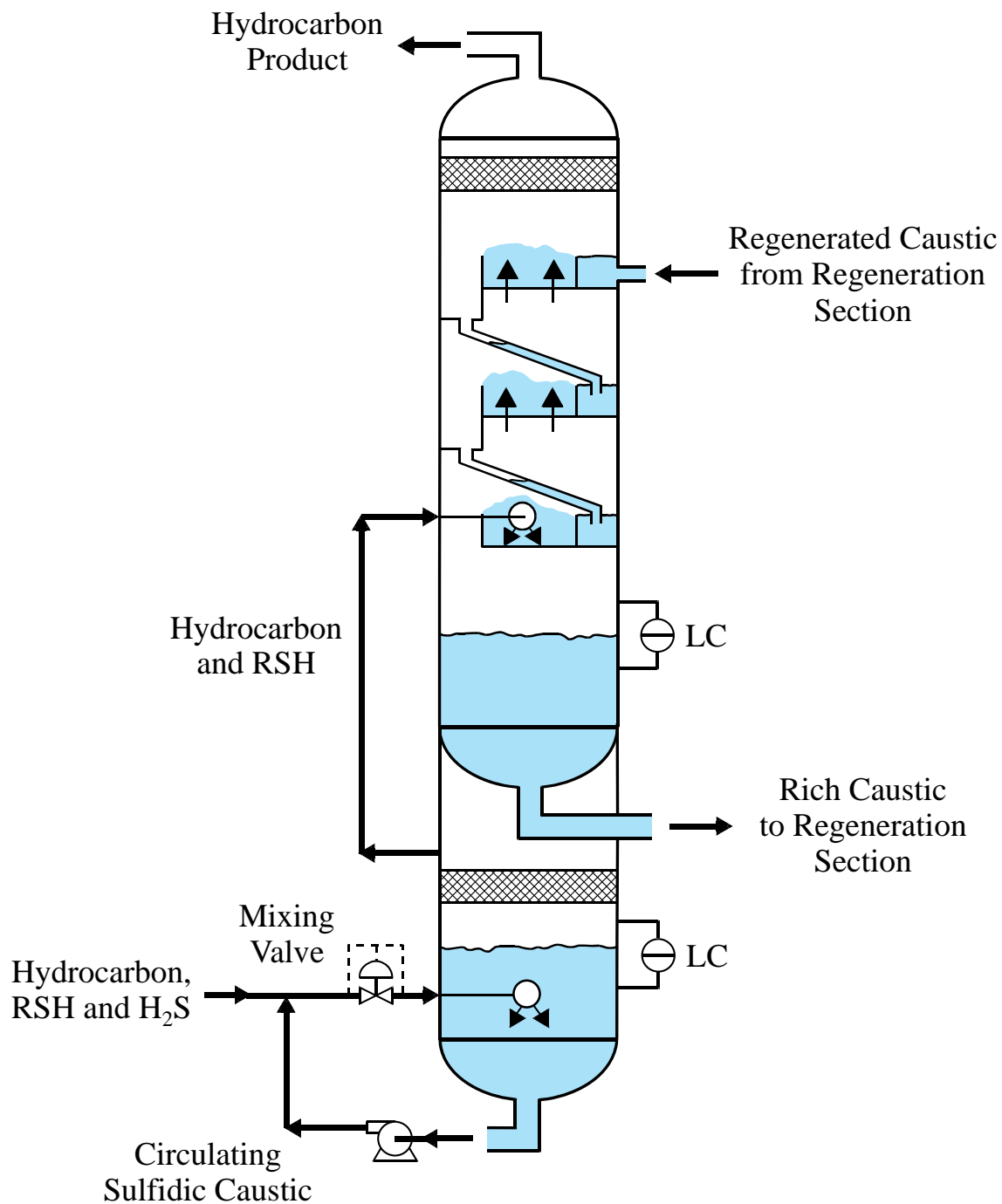
1b. Extractor Plus™

The Extractor Plus™ is a combination column that generally contains a pretreatment, an extraction and a post-treatment section. Hence, the Extractor Plus™ vessel serves three purposes: H₂S removal, mercaptan extraction and entrained caustic removal.

The details of this vessel are as previously described for the Caustic Prewash, Extractor, Caustic Knock Out Drum and Sand Filter. The Caustic Prewash section, if provided, is located in the lower portion of the vessel. This is a continuous rather than batch caustic prewash. The hydrocarbon stream is mixed with circulating sulfidic caustic via a mixing valve or static mixer before entering the bottom of the Extractor Plus™ Column. Typically, regenerated caustic is continuously added/transferred via a control valve to the discharge of the circulating sulfidic caustic pumps. Fresh water may also be added at this point to dilute the lean caustic below 15° Baume. Water addition may be avoided only if the hydrocarbon feed temperature is high enough (>95°F or >35°C) and if the percent spent of the circulating caustic is controlled at 50% maximum to avoid precipitation of the sodium sulfides. After the mixing valve or static mixer, hydrocarbon enters the bottom of the vessel through a distributor, is washed completely of H₂S and passes through a wire, stainless steel mesh blanket before exiting the top of this section of the vessel.

The hydrocarbon then enters the extraction section of the vessel located above the prewash. The hydrocarbon passes upflow through the perforated sections of the trays, being counter-currently washed with caustic and allowing the mercaptans to be extracted. (See “Extractor” vessel previously described for more details.) Finally, the hydrocarbon passes through a Coalex Coalescer to remove any entrained caustic from the hydrocarbon.

Figure 7
Extractor Plus™



MRX-R01-025

2. Oxidizer

The oxidizer is a vertical vessel designed as a mixer to contact rich caustic from the bottom of the extractor, containing Merox catalyst and sodium mercaptides, with air for regeneration. This vessel contains a mixed vapor/liquid phase, and is packed with 1½ inch (38 mm) diameter carbon Raschig rings. Carbon is used because it is inert to the strong caustic and severe oxidizing environment. The loading should be done with the vessel filled with water to avoid breakage of the rings. The vessel should be completely full of rings, flush with the top manway. Otherwise ring attrition will occur as a result of the abrasive contact caused by subtle shifting action.

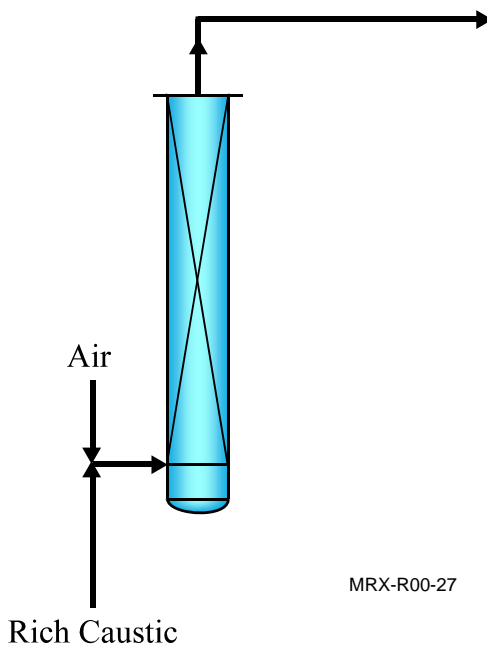
An inlet distributor is provided consisting of a perforated pipe enclosed by a slotted sleeve. The slot in the sleeve points downward while the holes in the pipe are oriented upward. This arrangement is designed to provide maximum mixing. Should the inner pipe ever plug or require modification, it can be removed without having to unload the Raschig rings.

Any outlet connections should be protected by a bar grating, which usually consists of one or two ¼ inch (6 mm) bars welded across the nozzle to prevent any Raschig rings migration.

The vessel drain is protected by a broken ring trap consisting of a slotted pipe to exclude ring fragments.

Oxidizer

(1½" Carbon Raschig Rings)



MRX-R00-27

Figure V-8

3. Disulfide Separator

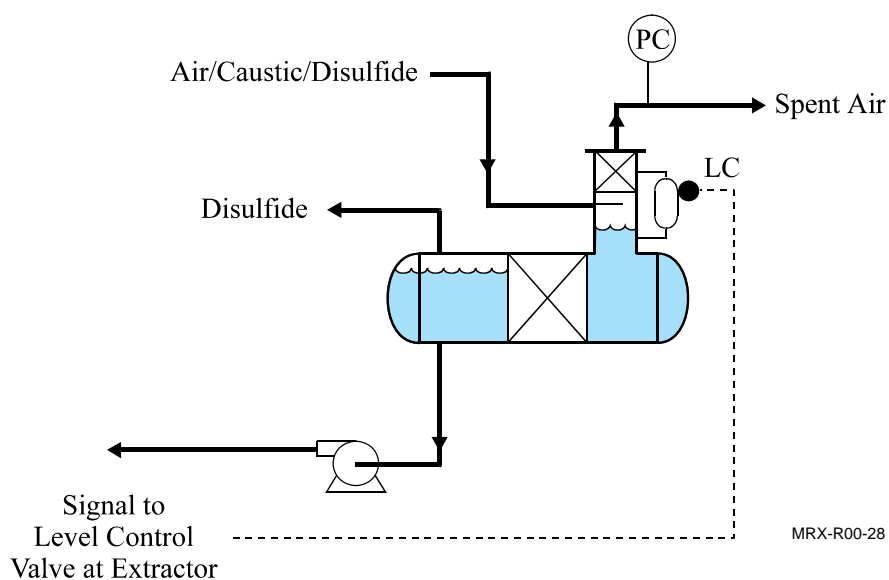
The disulfide separator is a horizontal settler vessel with a small air disengaging stack at the inlet end. The inlet distributor enters at the midpoint of this stack. It is slotted top and bottom to aid both disengaging and distribution.

The excess air flows upward into a packed bed. This packing consists of 1 inch (25 mm) diameter carbon steel Raschig rings or 1.5 inch (38 mm) diameter carbon Raschig rings. The carbon steel (not carbon) rings are susceptible to corrosion, especially during periods of sustained operation at high oxygen contents and high temperatures in the vent gas. These carbon steel rings should be inspected regularly at each unit turnaround.

The liquid passes downward into the main vessel or horizontal section of the separator. It encounters a second packed zone, 4 feet (1200 mm) in length. This zone is packed with 4 x 8 mesh anthracite coal which acts as a coalescer to aid in the separation of disulfide oil from the regenerated caustic. The coal retaining screens are 9 x 9 mesh with 0.063 inch (1.6 mm) diameter wire supported by standard deck-type grating. It is important that the annular space between these screens and the vessel wall, along with any space between screen sections, be carefully sealed with nylon rope to prevent coal leakage.

Both packed zones should be loaded with the vessel full of water, especially the coal bed. The water aids in achieving a random orientation of particles and thus results in a tighter packing arrangement. This is particularly important for the coal loading to avoid later attrition resulting from abrasion if the coal is not tightly loaded, as discussed earlier with the carbon rings in the oxidizer. Again, both packed zones should be filled as completely as possible with no void spaces.

Figure V-9
Disulfide Separator
(4–8 Mesh Anthracite Coal)



4. Vent Tank

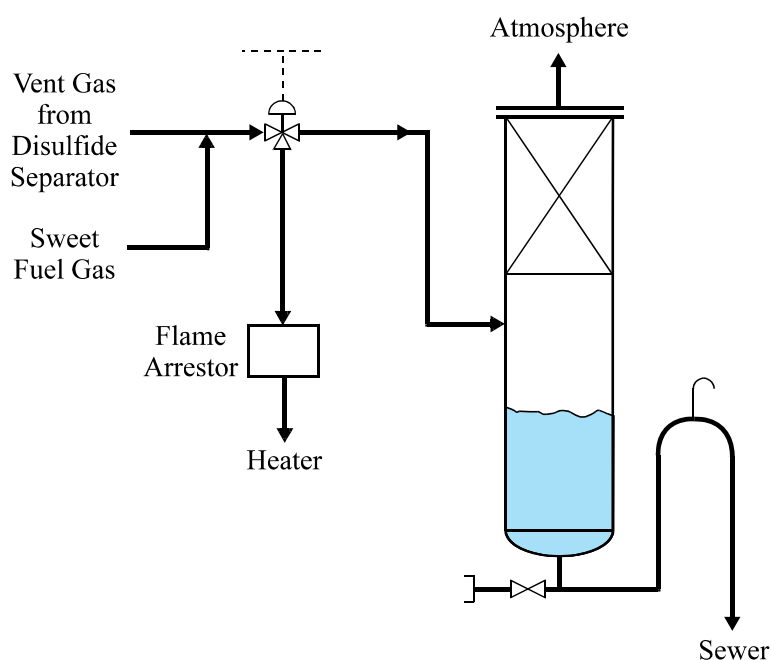
A small vertical atmospheric vent tank is provided to separate any liquid carryover from the vent gas exiting the disulfide separator during startup or periods of unsteady operation. Liquid carryover is not normally expected to occur. Because of odor and safety concerns and regulations, the preferred disposal of vent gas is to incineration rather than to the atmosphere.

A packed zone is provided to coalesce any liquid and provide a safety function as a flame arrester. The packing consists of 1 inch (25 mm) diameter carbon steel Raschig rings or 1.5 inch (38 mm) diameter carbon Raschig rings which are subject to the same loading and maintenance as detailed for the Disulfide Separator stack.

The bottom drain is open to the sewer but sealed by means of a hydraulic overflow seal. Thus for startup, the vent pot must initially be filled with water to provide a seal.

For recent designs, the Vent Tank is normally in service (rather than bypassed) as shown in Figure IV-3 of the Process Flow and Control section of this manual.

Figure V-10
Vent Tank

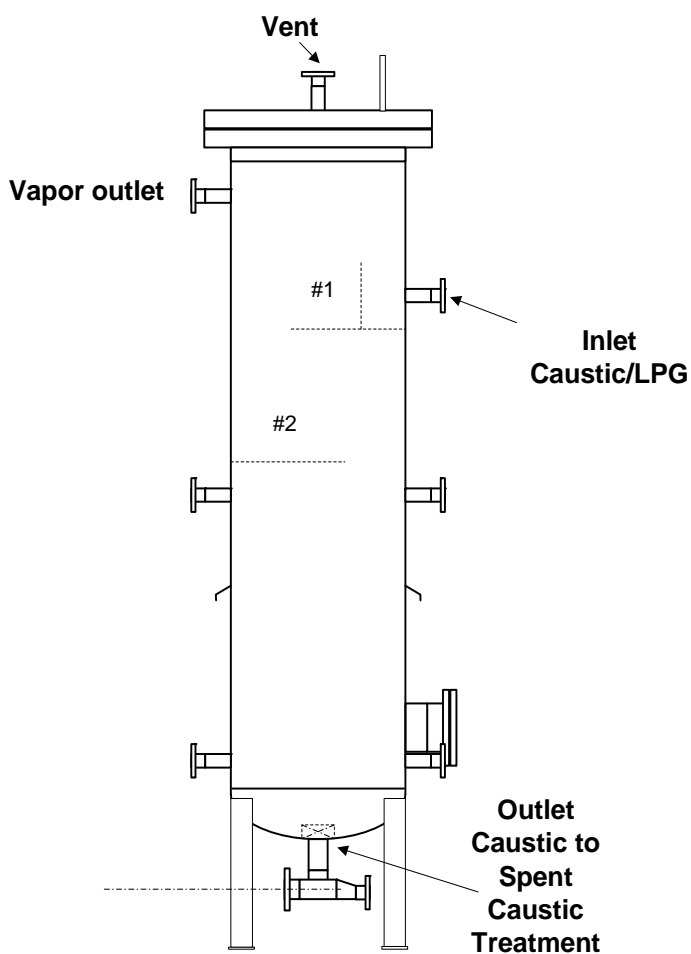


MRX-R00-29

5. Spent Caustic Degassing Drum

The Spent Caustic Degassing Drum is a vertical vessel in which spent caustic enters near the top of the vessel and falls downward over one weir and down two, non-perforated trays. The caustic collects in the bottom of the vessel, until the level reaches a high alarm, typically 90%, in which the Spent Caustic Pump is automatically activated to direct the caustic to spent caustic treating facilities. The pump will automatically shutoff when the level reaches a low alarm, typically 10%.

Figure V-11
Spent Caustic Degassing Drum

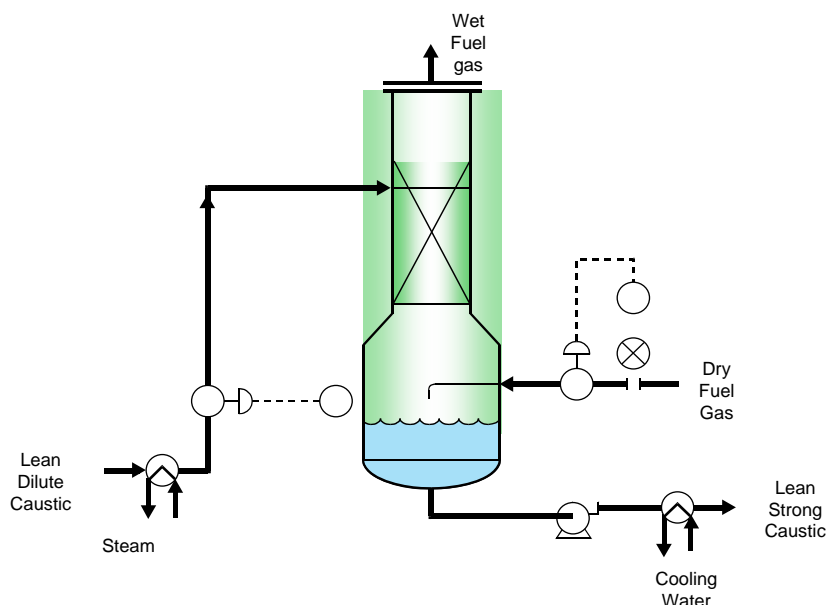


This vessel allows any entrained LPG in the spent caustic to disengage from the caustic before the caustic is sent to spent caustic treating facilities. All sources of spent caustic are directed to this vessel, the major contributors coming from the Caustic Prewash and the Extractor, but also usually includes caustic from level glass, level transmitter and control valve assembly drain lines. While the caustic is collected in the bottom of the vessel, any LPG released from the caustic is directed to the flare header system through a line that is free-draining back to the Spent Caustic Degassing Drum and through an isolation valve that is locked open.

6. Water Balance Column

A Water Balance Column is used to strip water from lean caustic that experiences a severe dilution effect due to a very high mercaptan level in the feed. This is accomplished by scrubbing the lean, diluted, caustic with dry fuel gas. With the dilution effect eliminated, spending of the caustic is due solely to carbon dioxide present in the air and any contaminant H_2S that may be present, therefore drastically reducing the caustic make-up quantities.

Figure V-12
Water Balance Column



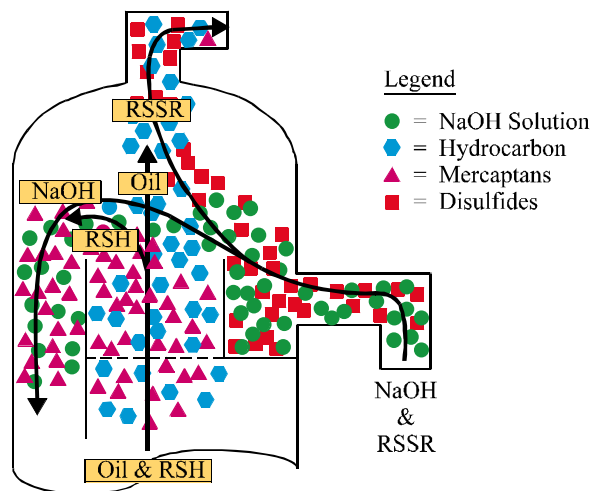
The operation of the vessel is such that the lean, diluted caustic is heated to approximately 60°C (140°F), and then enters the upper portion of the Water Balance Column via a packed section of stainless steel Raschig Rings. Dry fuel gas enters the column in the lower portion of the vessel, and counter-currently contacts the diluted caustic in the packed section. The high surface area of the rashig rings allows the water to be stripped from the caustic and carried out with the fuel gas. The strong, lean caustic collects in the bottom of the vessel and is then pumped out through a cooler in which the caustic is cooled to approximately 43°C (110°F) and eventually directed back to the Extractor. The wet fuel gas can still be effectively used to dilute the Disulfide Separator offgas.

The level control in the column is cascaded to the caustic flow controller into the vessel.

7. Wash Oil System

A Wash Oil system is an optional system used to remove entrained disulfide oil from the regenerated caustic in an Extraction Merox Process Unit. Otherwise, this entrained disulfide oil will return with the regenerated caustic back to the extractor. This can be seen from the graphic below:

Figure V-13
Re-Entry Sulfur



The disulfide oil will return to the hydrocarbon, increasing the amount of total sulfur in the Merox treated product. This disulfide oil sulfur is known as re-entry sulfur, when it returns to the hydrocarbon in the Extractor. Removing disulfide oil from the regenerated caustic will decrease the re-entry sulfur and consequently the total sulfur level in the hydrocarbon product.

A Wash Oil system improves the separation of the disulfide from caustic by increasing the specific gravity differential between the two fluids. The wash oil step is most typical in Gasoline Merox Units that use lower concentration of caustic, such as 10°Baumé and in all Extraction Merox Units that need minimal sulfur in the Merox treated product.

The Wash Oil system reduces the re-entry (disulfide) sulfur content of a Merox extracted product. By lowering the re-entry sulfur, the product total sulfur is lowered. This is accomplished by contacting the circulating caustic with a sweet, low vapor pressure hydrocarbon stream. This washing step decreases the amount of disulfide returned to the extraction section by: 1) Scavenging or extracting entrained droplets of insoluble disulfide formed in the caustic during the regeneration process; and 2) Reducing the specific gravity of the immiscible disulfide oil enhancing separation from the regenerated caustic. The relationship between disulfide oil in the regenerated caustic and re-entry sulfur is summarized as:

Re-Entry Sulfur

$$S_r = S_c(C/H)(G_c/G_h)$$

Where

- S_r Re-entry sulfur in the product (wt-ppm)**
- S_c Disulfide sulfur in the regenerated caustic (wt-ppm)**
- C = Caustic volumetric flow rate**
- H = Hydrocarbon volumetric flow rate**
- G_c = Specific gravity of the regenerated caustic**
- G_h = Specific gravity of the hydrocarbon**

With C & H expressed in the same volume units

As stated above, a Wash Oil system is designed for use when the LPG product total sulfur specification is particularly low or the unit C/H ratio is particularly high.

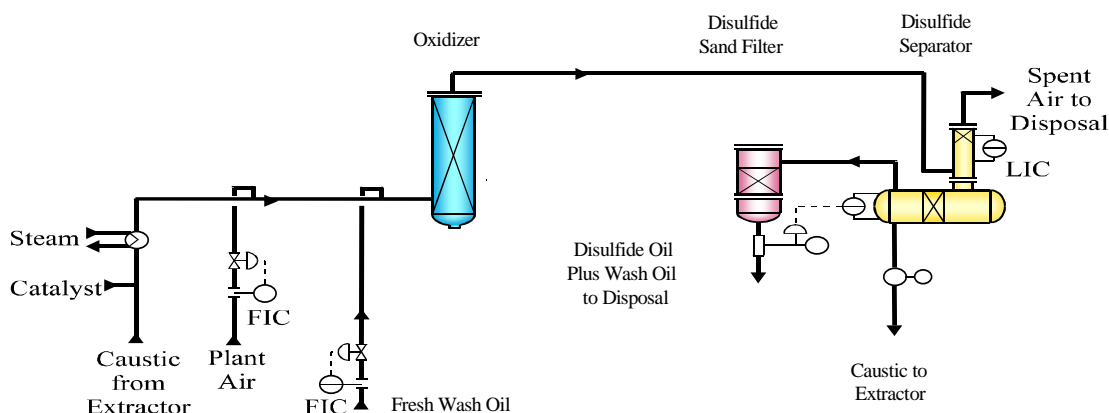
There are four variations of the Wash Oil system. Two are called simple systems; in these systems, the wash oil is mixed with the bulk of the disulfide oil phase. The other two are called complex; in these systems, the wash oil is not mixed with the bulk of the disulfide oil phase. Both simple and complex systems have the option of being single or two-stage wash oil systems.

In many cases, lean naphtha is available for use in a simple Wash Oil system. When the refiner either does not have low vapor pressure material available for washing the circulating caustic or wishes to keep the wash oil stream separate from the bulk of the disulfide oil phase, a complex Wash Oil system is utilized.

a. Simple, Single-Stage Wash Oil System

The most common Wash Oil system, a simple single stage wash, consists of fresh wash oil injection into the rich caustic stream entering the oxidizer. Entrained disulfides are extracted or dissolved in the hydrocarbon as they are formed in the oxidizer. The three-phase mixture of regenerated caustic, spent air, and disulfide oil/wash oil solution enters the disulfide separator where the two liquid phases are separated from the spent air. The caustic and disulfide/wash oil flow down the stack and through the packed coalescing section into the settling section of the separator. The lighter hydrocarbon phase containing disulfides and spent wash oil floats to the top of the vessel and is decanted. The lean caustic flows out from the bottom of the vessel to the suction of the caustic circulation pump.

Figure V-14
Simple One Stage Wash Oil System



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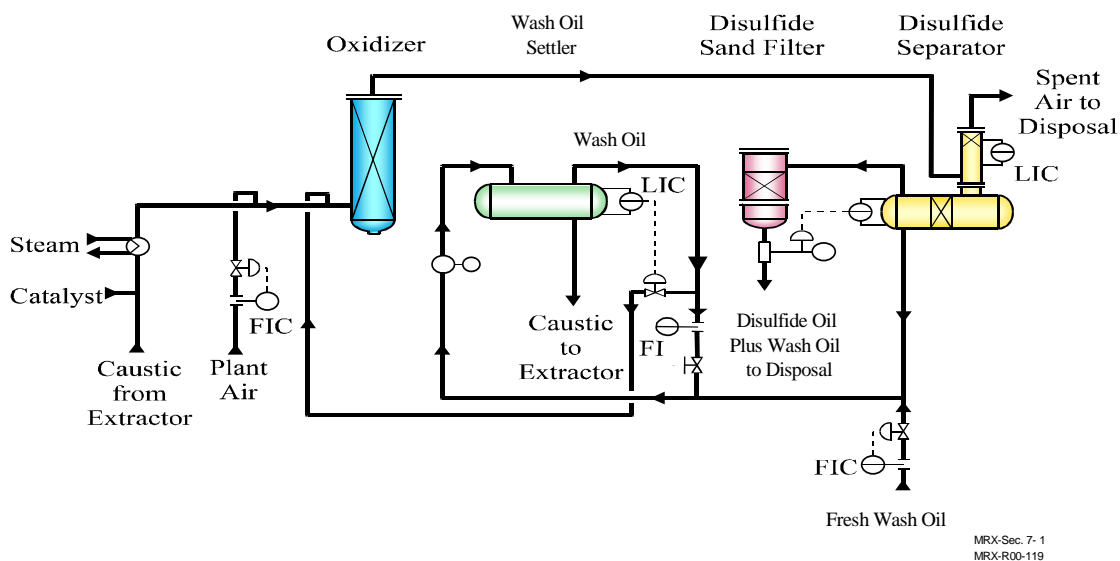
b. Simple, Two-Stage Wash Oil Process Flow

The flow and control scheme for a two-stage system is shown in the attached process flow diagram, Figure V-15. Fresh wash oil is directed into the lean caustic leaving the disulfide separator. Recycle wash oil from the top of the wash oil settler is also routed to the pump suction. The combined lean caustic and wash oil are pumped from the disulfide separator to the wash oil settler through a mixing valve. Lean caustic from the bottom of the settler returns to the extraction section. Wash oil leaves the top of the settler and is split into two streams - one goes to the oxidizer to provide the first stage of washing and the second, a recycle stream, goes to the suction of the circulating pump. The second stream serves as the second stage of washing with the circulating wash oil combining with the fresh wash oil in the pump suction line. Wash oil flow to the oxidizer operates on level or interface control on the wash oil settler. Once a level is established in the settler and the control valve is operating, the flow to the oxidizer is effectively equal to that of the fresh wash oil entering the system. The internal recycle is adjusted by means of a globe valve on the recycle stream. Recycle may be from one

to three times that of fresh wash oil makeup, with normal operation using three times.

Spent wash oil removal in a two-stage system will be equal to the makeup wash oil rate plus disulfide oil generated in the mercaptan oxidation reaction. The spent wash oil is decanted by the disulfide/spent wash oil pump, if needed, operating on interface control on the body of the disulfide separator.

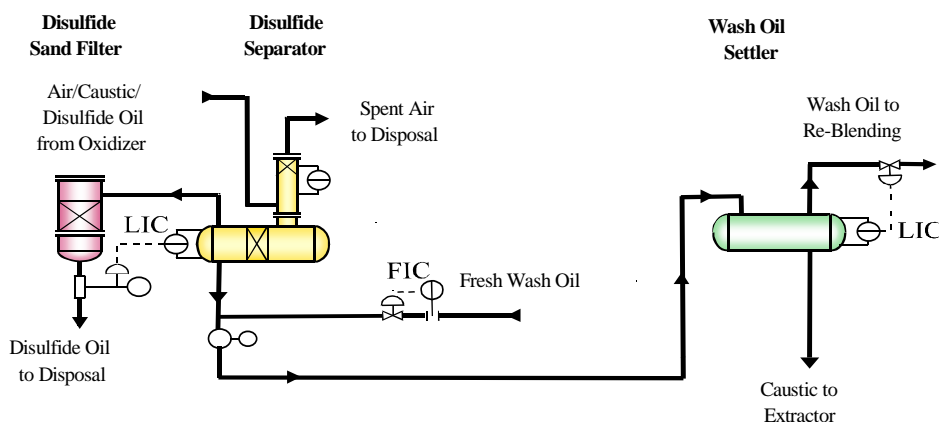
Figure V-15
Simple Two-Stage Wash Oil System



c. Complex, Single-Stage Wash Oil Process Flow

A complex single stage wash consists of fresh wash oil injection into the lean caustic exiting the disulfide separator, upstream the caustic circulation pump. Entrained disulfide is extracted and/or dissolved in the wash oil. The two-phase mixture of regenerated caustic and entrained disulfide oil/wash oil enters a wash oil settler where the lighter hydrocarbon material containing disulfides floats to the top of the vessel and is decanted. The lean caustic flows out of the bottom of the vessel and is directed back to the extractor.

Figure V-16
Complex One Stage Wash Oil System



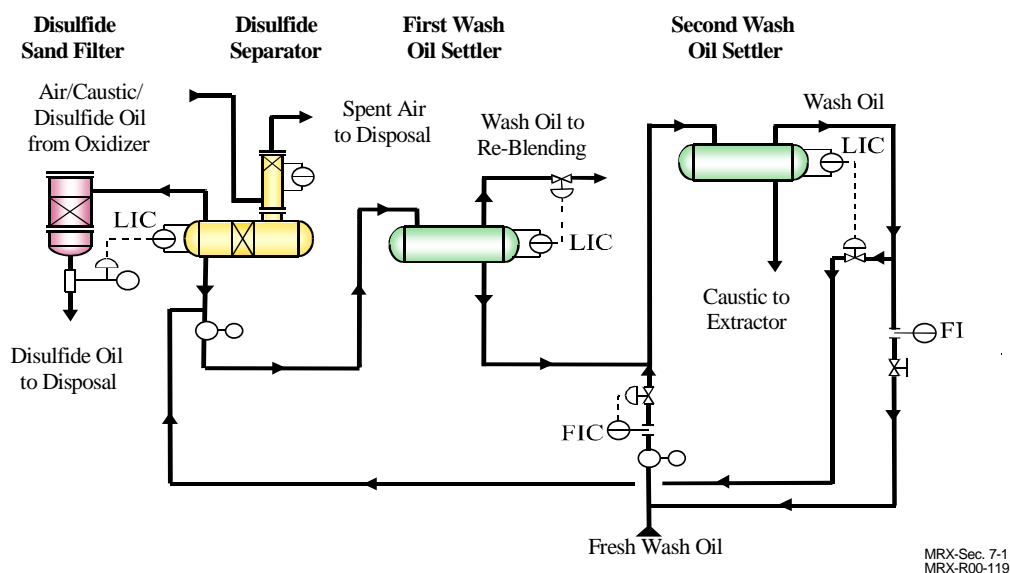
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ii. Complex, Two-Stage Wash Oil Process Flow

Fresh wash oil, in combination with a recycle wash oil stream, is pumped into the lean caustic leaving the first wash oil settler. This is considered the second stage of washing. The combined lean caustic and wash oil are combined through a mixing valve to the second wash oil settler. Lean caustic from the second wash oil settler returns to the extraction section. Wash oil

leaves the top of the second wash oil settler and is split into two streams. The majority of the wash oil is recycled back to the suction of the fresh oil pump located at the inlet of the second wash oil settler. The remaining portion of wash oil is added to the lean caustic from the disulfide separator at the circulation pump suction for the first stage of washing. The lean caustic and wash oil are directed to the first wash oil settler. Wash oil leaves the top of the first wash oil settler at the rate as the fresh wash oil addition. Lean caustic leaves the bottom of the first wash oil settler to be washed a second time.

Figure V-17
Complex Two-Stage Wash Oil System



8. Disulfide Oil Sand Filter

The Disulfide Oil Sand Filter is a small, vertical vessel designed to coalesce any entrained caustic from the disulfide oil before the disulfide oil is directed to downstream processing.

The sand bed consists of a specified depth of 8-16 mesh quartz or silica sand. The sand is supported on a special Johnson Screen proprietary design steel grid with 0.025 inch (0.6 mm) openings. Disulfide oil enters at the top of the vessel, through a slotted distributor, passes downward through the sand bed, through the support grid and makes a 135° turn before exiting from the side of the vessel, below the sand support grid. The hydrocarbon outlet is protected by a special chordal baffle permitting the coalesced aqueous phase to run down the walls and collect at the bottom of the vessel. Care should be taken that the sand is of the same size and grading as specified so that there is efficient coalescence and to avoid excessive pressure drops.

The Disulfide Oil Sand Filter is liquid full during normal mode of operations. Once a disulfide oil level has been established in the Disulfide Separator, the Sand Filter inlet and equalization lines should be continuously opened, thus allowing the Disulfide Separator and Sand Filter to be one system, at one pressure, and completely liquid full to the height of the liquid stack level. The regeneration section pressure is usually sufficient enough to direct the disulfide or disulfide/wash oil mixture directly to rundown. Alternatively, a disulfide oil pump may be used to facilitate disulfide oil removal from the Sand Filter to downstream processing facilities. The disulfide oil pump may be operated continuously or batchwise.

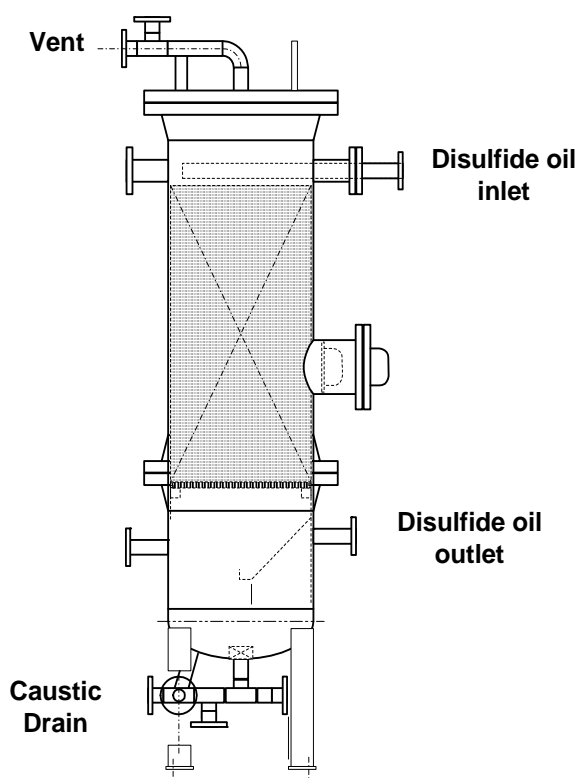
When removing disulfide oil batchwise, any coalesced caustic that has been collected in the Sand Filter should be drained prior to removing disulfide oil. The caustic/disulfide oil interface is usually visible in the level indicator. In addition, when removing disulfide oil from the system, the levels in the Disulfide Separator must be monitored carefully as the stack level has a tendency to decrease rapidly, usually much faster than the main body.

During the commissioning of the unit, make sure that the sand support is correctly installed. Check for levelness and for sealing strips over the section joints. Ensure that the nylon rope packing around the perimeter of the support grid is properly installed.

The first 2 inches (50 mm) of sand should be loaded by hand, leveled and allowed to sit for about one hour. This will confirm proper support grid installation and absence of any unobserved leaks.

Temporarily cover the inlet distributor with plastic film or cloth to prevent the sand from seeping into the distributor slot. The sand is preferably loaded with a sock to prevent any cone effect and classification from developing. The sock loading method also reduces the amount of dust generated if the sand is dry.

Figure V-18
Disulfide Oil Sand Filter
(8-16 Mesh Quartz or Silica Sand)



9. Oxygen Analyzer

Process considerations require that the oxygen level of the off-gas be monitored either continuously or intermittently to ensure sufficient oxygen quantities are being consumed, which directly indicates the quality of the regeneration of the circulating caustic within the system. An oxygen analyzer is installed on the Disulfide Separator off-gas line for continuous monitoring of the oxygen level. If the oxygen content is less than 9 volume percent, then the air injection is too low and therefore insufficient mercaptan oxidation is present. If the oxygen content is greater than 12 vol-%, then either too much air is being injected or not enough oxygen is being consumed, which would require either more catalyst or higher temperature to promote a greater degree of regeneration.

10. Special Check Valve

The Special Check valve prevents a backflow of either caustic or hydrocarbon to the source of air, whether the source is a dedicated compressor or plant air system. It is installed directly on the air line just upstream of the injection point into the mercaptan-rich caustic stream.

The features of this check valve include its low cracking requirement (2-4 psig; 0.14-0.28 kg/cm²) and positive spring loaded closing action. Although no check valve is 100% fail safe, these valves have proven themselves quite reliable over the years

The valve must be installed in a vertical position, and it is recommended to use stainless steel tubing on its inlet side to prevent potential extended pipe threads either hindering the operation of or damaging the valve internals.

VI. COMMISSIONING

The following section will discuss the various aspects associated with the commissioning of the Caustic Extraction Unit. This section contains information about the precommissioning and initial startup of the unit. The precommissioning procedures ensure that the unit is safe, operable, and constructed as specified by thorough inspection and testing.

A. PRECOMMISSIONING

As the construction of the unit nears completion, a large amount of work must begin to prepare it for startup. These precommissioning activities have three main purposes:

1. To ensure, by thorough inspection and testing, that the unit is safe, operable, and constructed as specified;
2. To prepare equipment for operation by flushing, running in, etc. and
3. To acquaint the operators with the unit.

The importance of these activities cannot be overemphasized. No matter how well a unit is designed, if the equipment is not as specified, not properly brought on stream, or not understood by the operators, it will not perform as expected.

All of the following typical activities are required to properly precommission any Extraction Merox unit. However, the exact order of presentation need not be strictly followed. Depending on the progress of construction, certain procedures may be required earlier or later than suggested here. A thorough knowledge of the entire precommissioning operation will allow the plant personnel to schedule activities in the most time-saving and labor efficient way. These are the necessary precommissioning activities:

1. Vessel Inspection
2. Inspection of other Major Equipment
3. Piping and Instrument Check
4. Hydrostatic Testing
5. Line Flushing
6. Run-in of Pumps and Drivers
7. Servicing and Calibration of Instruments
8. Commissioning of Plant Services
9. Availability Check of Chemicals, Catalysts, and Other Materials
10. Plant Pressure Test
11. Air-Freeing
12. Commissioning of Additional Plant Services

The material in this section gives general guidelines for preparing a unit for startup. Some sections need to be expanded to give specific instructions, but this can best be done by personnel on site.

1. Vessel Inspection

Inspection of all vessels should be made at an early stage of construction. The actual installation should be compared to the vessel drawings in the Project Specifications. Particular attention should be given to the following details:

- a. Vessel temperature, pressure, and vacuum rating.
- b. Vessel wall thickness and metallurgy.
- c. Vessel elevation and support.
- d. Vessel cladding: thickness and metallurgy.
- e. Distributors: type, levelness, orientation, size, number, and size of openings.
- f. Nozzles: location and size.
- g. Vortex breakers, baffles, wear plates.
- h. Demisters and coalescing screens: thickness, materials, support.
- i. Thermowells: location and length.
- j. Level instruments: type, length, location of nozzles.
- k. Insulation.
- l. Fireproofing.
- m. Cleanliness.

CAUTION: Before entering a vessel, the refinery's safety precautions should be observed. These usually include the following:

- sampling the vessel for toxic vapors and oxygen concentration,
- wearing a safety harness, and
- having an attendant outside the vessel.

AN UNATTENDED VESSEL SHOULD NEVER BE ENTERED.

2. Inspection of Other Major Equipment

When inspecting the following equipment, special attention should be given to the associated items:

- a. **Heat Exchangers:** metallurgies, tubes, grounding wires, expansion provisions; manufacturer's ratings for temperature, pressure, and pressure drop; nozzles, flanges.

Shell and Tube: elevation, insulation, tubesheets, baffles, channel covers, differential pressure rating.

- b. **Pumps:** metallurgy, suction and discharge block valves, suction strainer, discharge pressure gauge, check valves, lubrication and cooling systems, piping expansion provisions, drains, steam tracing and insulation of pump and associated lines; vendors ratings for head, capacity, temperature, and pressure.

Centrifugal: NPSH and speed rating, balancing line, warmup lines, seal flush, bearings.

Positive Displacement: discharge relief valve, pulsation dampeners, packing, speed and stroke rating.

3. Piping and Instrument Check

The unit should be checked to ensure that it conforms to the UOP piping and instrument diagram. In addition to verification of the correct process flow, the inspection should include the following:

- a. Line sizes and metallurgy
- b. Flanges and gaskets
- c. Bolting
- d. Drains and vents
- e. Relief valve settings
- f. Piping supports and expansion provisions
- g. Equipment accessibility
- h. Utility lines
- i. Tie-ins with other units/storage
- j. General safety requirements

4. Hydrostatic Testing

After all fabrication has been completed the unit vessels and piping should be pressure tested hydraulically. Hydrostatic tests are made on new or repaired equipment to prove the strength of materials and welds. This test is made by completely filling the equipment with water (typically) and increasing the pressure. Normally a positive displacement pump will be used to raise the pressure. This test is normally performed by construction personnel and it should not be confused with other less severe tests generally carried out before a startup to check the tightness of connections.

- a. Vessels that have met hydrotesting requirements in the fabricators shop may be isolated from the hydrotest if desired and if allowed by applicable codes. Before hydrotesting any vessel it should be confirmed that the vessel is designed and supported such that it can safely be filled with water. If not, the applicable code should be consulted for testing requirements.

- b. Care should be taken not to exceed the pressure rating of any vessels or equipment when preparing a hydrotest circuit. Internals, such as displacers, level ball floats, or other instruments not designed for the test pressure must be removed. All relief valves (PSV's) should be removed, blinded, or gagged during the hydrotest. Since all relief valves must be bench tested and set before final installation, it may be desirable to perform the testing at this time.
- c. Vents must be provided at all high points of vessels and piping in the hydrotest circuit(s) to purge possible air pockets while filling.
- d. All internal valves within a test circuit should be confirmed open.
- e. Usually the hydrostatic pressure test is carried out at 1.5 times the design pressure, but the proper test pressure must be confirmed for each vessel or piping circuit in question.
- f. Care should be taken that the temperature is not too low, causing the metal to become brittle. The vessel/piping and water temperature should always be above 15.5°C (60°F) to eliminate the possibility of cold-fracturing the metal.
- g. Note that a water filled system requires venting when being drained in order to avoid pulling a vacuum and possibly collapsing equipment.

5. Line Flushing

All piping must be thoroughly cleaned of debris and scale. This may be done after hydrostatic testing, before the test water is drained. Generally, liquid lines are flushed with water and thoroughly drained. Gas lines may be either water flushed or air blown, but water should be blown from gas lines if water flushed. Gas lines to compressors must be free of water.

The following items are suggested as a guide for line flushing:

- a. Where practical, clean water should be supplied to the vessels, and contiguous lines should be flushed away from the vessel. Never flush into equipment.
- b. No matter what the flushing medium – steam, air, or water – maximum volume and velocity should be used for thorough cleaning.
- c. Remove orifice plates before flushing.
- d. Control valves should be removed.
- e. Instrument lines should be closed off or disconnected. The instrument air header should be thoroughly blown with clean, dry air.
- f. Relief valves should be blinded if they have been returned to service following hydrostatic testing.
- g. Regulate the flushing medium at its source. As examples, water from a vessel should be regulated at the vessel; and steam, at the valve in the supply to the line being blown.
- h. Where possible, flush downward or horizontally.
- i. Always flush through a piece of equipment's bypass to an open end before flushing through the equipment.
- j. Disconnect lines at exchangers and flush to the openings.
- k. Flush through all vents and drains.

l. At pumps:

- 1) Disconnect suction and discharge piping and flush lines.
- 2) Install temporary screens in pump suction strainers.
- 3) Reconnect lines for circulating water.
- 4) See further discussion under "Run-in of Pumps and Drivers."

m. Flush or blow:

- 1) The main header, from source to end, then
- 2) Each lateral header, from the main to end, and
- 3) Each branch line, from the lateral header to end.

n. For steam systems, flush well through dirt leg drains and steam trap bypasses before placing the traps in service.

Upon completion of line flushing of any system, carefully check that all temporary breaks are re-connected, control valves are replaced, and pump alignments are normal. Also, verify that all free water has been drained.

6. Run-in of Pumps and Drivers

Proper installation and operation of pumps and drivers is essential for trouble-free performance. The pumps and drivers should receive careful handling during initial run-in. The initial run-in of pumps is generally done by circulating water through the new equipment. Temporary strainers are installed in the suction line of the pumps, conveniently located for removal and cleaning. The screens also should be positioned so that dirt particles will not gravitate to inaccessible places when flow is stopped. During run-in of pumps, the strainers may cause some restriction of flow. As debris collects in the strainers, flow to the pumps will fall off. When this happens to a centrifugal pump, it will be necessary to throttle the pump discharge by partially closing the discharge valve. This will prevent the pump from cavitating, which can cause damage to the pump. However, also avoid restricting the pump discharge to the extent that it causes internal slippage and excessive heat generation.

In starting a turbine driven centrifugal pump, the rotation should be brought up to speed as rapidly as possible. Normal operating speeds are usually attained rapidly and automatically with motor-driven pumps, assuming proper motor starting.

The development of discharge pressure is essential to flush and lubricate the wearing rings. After initially starting the pump, close the discharge valve for a short time. Subsequently, it is always advisable, where practical, to close the pump discharge valve immediately prior to shutting down a centrifugal pump. However, discharge valves on operating positive displacement pumps should never be closed. These pumps can over pressure themselves and downstream lines and equipment. The following items are suggested for checking prior to run-in:

- a. The manufacturer's operating instructions for any specific precautions that should be observed.
- b. Completion of overall installation.
- c. Alignment of pump and driver for cold operation. No undue strain by the piping on the pump or driver is allowable.
- d. Cooling fluid piping and seal or gland oil piping:
 - 1) Conventionally packed pumps in hot service are generally furnished with gland oil. Verify that this installation is correct and complete.
 - 2) For pumps with mechanical seals, verify that all of the components of the flushing system (such as strainers, separators, restriction orifices, and coolers) have been correctly installed and are clean. Loss of flush or dirty flush may cause the failure of seals.
- e. Packing or seals are installed.
- f. Bearings and shafts have been cleaned prior to final lubrication.

- g. Pump and driver are lubricated according to lubrication instructions.
- h. Rotation of electric motor drivers uncoupled from the pump. Run-in uncoupled for a minimum of four hours, verifying good motor operation.

During run-in, many pumps are delivering a higher density liquid (water) than the normal process fluid, but the pumps drivers are sized for the normal pumping fluid. Consequently, there is potential for the overload of many electric motors. To avoid overloading the motor of a centrifugal pump, the flow must be limited by throttling the pump discharge valve. When doing so, if possible, check the amperage usage against design. The following procedure is suggested for pump run-in:

- a. Rotate pump and driver by hand, verifying that they roll freely.
- b. Check that run-in water circulation is lined up.
- c. Open suction valves fully, venting air from piping and pumps, completely filling with liquid.
- d. Establish flow of cooling fluid, where required.
- e. Check that lubrication is satisfactory.
- f. Make sure electric power is available from the switch gear to the starter of the electric motor driver.
- g. Barely open the discharge valve on the centrifugal pump.
- h. Start the pump; if the pressure does not build immediately, stop and resolve problem.
- i. When the discharge pressure has increased satisfactorily after starting, gradually open the discharge valve to obtain the desired flow rate.

- j. In the event of unusual noise, vibration, overheating, or other abnormal conditions, shut the pump down immediately. Correct the cause before resuming use of the pump. Continue to check for abnormal conditions as these may occur after prolonged operation.
- k. Check shaft sealing; mechanical seals should show no leakage. Conventionally packed stuffing boxes must always be permitted to leak slightly to provide some lubrication and to prevent overheating. Stuffing box gland nuts are generally only finger tight. A leaking mechanical seal will show some leakage on startup. However, after the pump is started and stopped a few times, the leakage may stop.
- l. Operate the pump, directing flows through all suction and discharge piping circuits.
- m. Inspect and clean screens as required.
- n. Recheck and realign if required, after any disturbance of piping, such as required for suction screen inspection if pipe flanges have to be parted for screen removal.
- o. When shutting down, close the discharge valve first, maintaining discharge pressure while the pump rolls to a stop. This will protect against the pump rolling backwards should the discharge check valve leak, and gives the wearing rings a quick flush.
- p. After all lines available to a pump have had suitable flushing, the temporary screen may be removed, but only after it has shown free of debris on two successive examinations. The permanent strainers may then be installed where required.

7. Servicing and Calibration of Instruments

Preparation of the plant instrumentation for startup and operation should include the following inspections and tests:

- a. Visual inspection of instruments to verify compliance with specifications.
- b. Visual inspection of instrument installation to verify compliance and installation specifications in the instrument instruction manual.
- c. Pressure testing of instrument piping.
- d. Testing and calibration of instruments.
- e. Testing of instrument air signal lines.
- f. Testing of thermocouple wiring.
- g. Loop checking.
- h. Testing of safety relief valves, if not done during hydrostatic testing.
- i. Final preparation.

In inspecting instruments for compliance with specification, attention should be given to instrument range, pressure rating, connections, materials of construction, size, electrical characteristics, and special features. Special attention should be paid to notes in the specification. Orifice plates should be inspected as soon as possible so they will be ready for installation when line flushing is complete; inspection should include size, materials of construction, location of weep hole, if any, counterbore, overall condition, measurement of orifice bore, and verification of information stamped on tab.

Inspection of installations should include attention to location of transmitters with respect to the connection point; to piping for proper drainage, and for proper valves and gaskets; to transmitters and control valves to insure that they are not installed backwards; and to special treatments such as winterizing for proper coverage and insulation. Orifice installations should be checked as soon as possible to ensure that straight run requirements are met, so that required piping changes can be completed before startup.

Instrument piping should be inspected visually for completeness and condition of welds and connections, and tested by pressuring with instrument air and brushing joints with soap solution. During hydrostatic testing of the plant, control valves should be isolated from the test system and adjacent drain valves should be opened to relieve any pressure. Control valve assemblies may be included in the hydrostatic test, provided that it is understood by all personnel that any leaks at control valve stem packings will be corrected by a qualified instrument technician. It is generally safer to exclude the control valve assemblies from the hydrostatic test.

Testing and calibration of instruments should include calibration of transmitters (in place, if possible), control board equipment, and local controllers. Control valves and positioners should be adjusted. Temperature transmitters should be checked for proper thermocouple burnout protection. Meter factor tags and valve position indication on controller output indicators should be installed at this time, and control actions should be set. ("Tuning")

Instrument air signal lines should be checked for leakage, kinked tubing, and for connections to the proper port of shutdown solenoid valves and controllers. Thermocouple wiring should be inspected for proper polarity at the thermocouple head. Point by point verification of the switch identification at the temperature indicator in the control room can be accomplished by selecting a point to be checked and opening the circuit at the thermocouple head. With proper identification, the corresponding temperature indicator will drive upscale or otherwise indicate an open circuit. Loop checking involves checking inputs and outputs to ensure that piping and wiring has been properly installed. A signal should be simulated at the transmitter, and the control board instrument should be watched

for response. The controller output should be adjusted manually, and the control valve watched for response. Proper response of control valves to air failure should be verified. All safety relief valves should be bench tested and set, if this was not done previously during the hydrostatic testing.

Final preparation includes checking instrument piping to verify that valves are in the proper position, making preliminary control mode adjustments, filling seal pots and seal legs, and making sure that instrument air and electrical power are supplied to all instruments. It may also be necessary to have the steam tracing operable at this time.

Commissioning of instruments will be carried out as the plant comes on stream. Differential pressure instrument piping must be drained to eliminate accumulated dirt and water, and the instrument zero must be adjusted to obtain a correct zero reading on the indicator scale on the control board. Controllers must be tuned, interface level transmitters must be zero checked. Scale, weld slag, and trash must be removed from sticking control valves, and other malfunctions must be corrected.

8. Commissioning of Plant Service

For ease of operation, the plant's utility systems should be placed into service as soon as possible. Lines should be flushed and leak tested. Steam lines should be warmed up slowly to prevent damage from water hammer. All steam traps and control valves are to be placed into service and tested. The following list of systems should be commissioned:

- a. Plant water and treated water systems. These systems should already have been commissioned prior to the line flushing procedure.
- b. All electrical and light systems, including emergency power backups.
- c. All plant and instrument air systems.
- d. Nitrogen system.

- e. Steam and condensate systems, excluding steam tracing for the moment.
- f. All drains and effluent systems.
- g. All storage tanks must be thoroughly flushed, leak tested, dried, and perhaps air-freed if the tank is in hydrocarbon service. Those tanks that have been air-freed should be left under slight positive nitrogen pressure. All lines to and from tankage must be flushed, blown dry with nitrogen, and pressure tested.

The steam tracing, plant cooling water, and flare systems will be commissioned after the plant pressure test has been completed.

9. Availability Check of Chemicals and Other Materials

A check of chemicals, catalysts, and other materials should be made to assure no delays due to shortages. All necessary laboratory equipment and reagents should be obtained.

10. Plant Pressure Test

The purpose of the plant pressure test is to check the piping and equipment for tightness of flanges, connections, and fittings. These tests should not be confused with the hydrostatic tests made during construction. Generally plant air or nitrogen is used for this test.

The basic procedure consists of pressuring the vessels and lines in the appropriate circuit to either their maximum operating pressure or 3.5 kg/cm² (50 psig), whichever is less, and then conducting the pressure test. The test pressure should be held for a minimum of one hour, while every flange and joint in the system is closely examined for leaks. Stubborn flange leaks may often be stopped by simply unbolting and rebolting the flanges. Screwed connections may require Teflon tape.

11. Air Freeing

Before admitting hydrocarbons into any process lines or vessels, safe refinery practice requires that the unit be freed of air. The air may be displaced with water, steam, or inert gas, such as nitrogen.

If steam is used, precautions should be taken to avoid the following potential problems or hazards:

- a. Collapse due to Vacuum: Some of the vessels may not be designed for vacuum. This equipment must not be allowed to stand blocked in with steam since the condensation of the steam will develop a vacuum. Thus, the vessel must be vented during steaming and then immediately followed up with an inert fuel gas or nitrogen purge at the conclusion of the steamout.
- b. Flange and Gasket Leaks: Thermal expansion and stress during warmup of equipment along with dirty flange faces can cause small leaks at flanges and gasketed joints. These must be corrected at this time.
- c. Water Hammering: Care must be taken to prevent “water hammering” when steam purging the unit. Severe equipment damage can result from water hammering.

The following steps briefly outline air freeing by steam purging:

- a. Block in the cooling water to all coolers and condensers. Shut down fans on Fin-Fan coolers and condensers.
- b. Open high point vents and low point drains on the vessels to be steam purged.
- c. Start introducing steam into the low points of the all vessels. It may be necessary to make up additional steam connections to properly purge some piping which may be “dead-ended.”

- d. Thoroughly purge all equipment and associated piping of air. The progress of the steam purge can be followed by marking up a P&I diagram to indicate the lines purged. Verify that sufficient drains are open to drain the condensate that will collect in low spots in the unit.
- e. When the steam purging is completed, start to close all the vents and drains. Immediately start to introduce fuel gas or nitrogen into all vessels and then cut back the steam flow until it is stopped. Regulate the fuel gas or nitrogen flow and the reduction of steam so that a vacuum due to condensing steam is not created in any vessel or that the refinery fuel gas system pressure is not appreciably reduced. Pressure the unit up to approximately 0.7 kg/cm² (10 psig) with fuel gas or nitrogen.
- f. Drain any residual condensate from the unit.

12. Commissioning of Additional Plant Services

At this time the following plant services should be put into operation:

- a. Plant cooling water system.
- b. Plant steam tracing.
- c. Plant flare header.

The plant cooling water system should be flushed, drained, and leak tested. When flushing, the cooling water lines should be disconnected at exchangers and the exchanger flanges blinded.

The flare system should be flushed and drained. Also, the flare header must be purged of oxygen down to an acceptable level, generally less than 1.0%.

The steam tracing system should be flushed with steam to verify free flow of steam. All steam tracing and condensate return lines should be checked to ensure that the steam and condensate are free flowing. After commissioning, the tracing should be checked to verify that it is hot.

B. INITIAL STARTUP

This subsection presents general procedures for startup of an Extraction Merox Unit. Almost every unit will require some specific adaptations or modifications of these procedures. These steps do not represent complete startup instructions. Rather, they represent an operations philosophy which, by judicious application, may be evolved into specific instructions for a particular unit.

1. General Preparations

- a. All safety equipment required for hydrocarbon addition to the unit must be on site and operable. Check that:
 - 1) All portable fire equipment is in place.
 - 2) The fire hydrant system is in service.
 - 3) Miscellaneous safety equipment is available.
 - 4) The area is reasonably free from obstructions.
 - 5) Necessary warning signs are posted.
 - 6) All relief valve test gags are removed.
 - 7) Adequate lighting is available for night operations (night time review).
- b. Make sure that all blinds have been removed including those below pressure relief valves. The unit blind list should always be current.
- c. Air freeing of the unit is completed.
- d. Make sure that all instruments are ready for operation.

- e. Close all vents, drains, and sample connections.
- f. Make sure that all valves are open to level glasses and pressure gauges.

2. LPG Extraction Merox Unit Startup Procedure

The following steps are required to commission the LPG Extraction Merox Unit.

- a. Isolate the extractor from the regeneration section by closing the line at the bottom of the extractor.
- b. Open the disulfide separator vent gas line at the pressure control at the top of the stack on the disulfide separator.
- c. Begin filling the regeneration section with 20° Baume caustic. Pump caustic from storage into the oxidizer via the caustic filling line, venting air from vessels as needed. (Note: It is not necessary to air-free the regeneration section.)
- d. When the oxidizer is full, begin filling the disulfide separator until a level of caustic appears in the gauge glass on the horizontal section.
- e. Inventory the atmospheric vent tank with water (to the level of the hydraulic overflow seal). In cold weather, ensure that the heat tracing on the tank and the overflow pipe is in service.
- f. Pump sufficient 10° Baume caustic to the prewash until the specified caustic level is reached.
- g. Line up caustic flow from the disulfide separator through one of the caustic circulation pumps and begin transferring caustic to the extractor at design flow rate.

- h. As the caustic level in the disulfide separator decreases, bring in sufficient additional 20° Baume caustic from storage to maintain a caustic level in the gauge glass on the top side of the disulfide separator.
- i. With the flow of caustic going to the extractor, eventually a level will start to build in the bottom surge reservoir of the extractor.
- j. As soon as a working level of caustic appears in the bottom of the extractor, slowly crack open the bypass around the level control valve (activated by the level control on the stack of the disulfide separator) and regulate the flow manually to maintain a constant level in the bottom of the extractor.
- k. Activate the air system and start **minimal** flow of air to the oxidizer. This flow of air is only required to maintain pressure on the regeneration section. Once hydrocarbon is introduced, the air flow should be increased to a rate of approximately 30 SCF/lb RSH sulfur (1.8 std. m³/kg RSH sulfur). (The extraction section will need to be pressure up with nitrogen to establish a sufficient pressure differential that will allow the caustic to flow from the Extractor to the Disulfide Separator. Also, the nitrogen pressure will minimize the hydrocarbon flashing across the extractor.)
- l. Activate the pressure control on the excess air from the stack on the disulfide separator to maintain operating pressure on the separator. Route the excess air to the atmospheric vent tank initially, until steady operation is achieved.
- m. Activate the level control on the stack of the disulfide separator and when the caustic level in the stack is visible in the gauge glass, close the level control valve bypass and open the level control valve at the bottom of the extractor.
- n. When the caustic level in the bottom of the extractor starts to rise, stop the flow of caustic going to the regeneration section. Record the amount of caustic pumped into the system for future reference.

- o. At this time the Merox WS catalyst should be added to the caustic going to the regeneration section. The procedure for Merox WS catalyst addition can be found in section XIII Special Procedures.
- p. Start steam to the caustic heater and bring the temperature of the caustic from the heater to 100-110°F (38-43°C).
- q. Inventory the amine water wash, if provided, with water until a water level of about 25% of the vessel volume is visible in the gauge glass(es). In cold weather, ensure that the heat tracing on the tank and the overflow pipe is in service. Start the water wash recirculation pumps. Note: During normal operations, the amine concentration in the recirculated water should be monitored. For batch water wash, once the spent water amine concentration reaches 1-3 vol%, or whatever concentration is required to prevent amine breakthrough, the spent water should be replaced with fresh water. For continuous water wash, the fresh water injection rate should be adjusted to obtain the desired concentration of amine in the spent water.
- r. Pump sufficient amine to the amine absorber until a level of amine appears in the gauge glass. Begin the recirculation pumps.
- s. Slowly admit hydrocarbon to the amine absorber, amine water wash, prewash, extractor, and settler. Vent inert gas or drain water as necessary to relieve pressure. (Note: This operation may be conducted concurrently with caustic filling of the regeneration section.)
- t. When these vessels are full of hydrocarbon, begin increasing pressure to the recommended operating pressure held by the back pressure controller.
- u. Slowly increase hydrocarbon flow to design flow rate.
- v. The Merox Unit is now on stream and should require only minor adjustments to make specification product.

- w. When stable operation is achieved, the vent gas may be routed to incineration. The quantity of fuel gas added should be equal to or greater than the total air flow rate for dilution of excess oxygen (refer to Figure V-10 of this manual). Note: For newly designed units, no fuel gas is added (refer to the Typical Vent Gas Control Scheme Figure IV-3 of this manual).

2. Wash Oil Introduction and Disulfide Oil System Commissioning

This step is the last step in the series of commissioning activities to be completed, prior to or after hydrocarbon introduction. The Caustic Prewash vessel should already be inventoried, the regeneration section should be inventoried with caustic and circulation established, the Merox WS catalyst initial inventory should already be added to the system and circulated, and the Amine Absorber, if present, should be inventoried with amine and circulation established.

Before introducing wash oil into the system the wash oil should be sampled to confirm the sulfur contents are within specifications. The wash oil should have <5 wppm mercaptan (RSH), <1 wppm H₂S and an acid number of <0.002 mg KOH/g

The following steps detail the commissioning activities for a Two-Stage Wash Oil Wash. For a One-Stage Wash Oil System, simply follow the above paragraph and then start wash oil flow, through the flow controller to the Oxidizer. Then follow steps m) through s).

- a. Verify that the globe valve on the Disulfide Oil Sand Filter drain line is closed.
- b. Close the gate valve on the hydrocarbon pumpout line.
- c. Close the gate valve on the backwash drain.
- d. Open the gate valve on the Disulfide Oil Sand Filter Outlet line.
- e. Open the isolation valves on the suction and discharge lines of one of the Disulfide Oil pumps. The other pump should stay isolated.

- f. Open the two gate valves on the disulfide outlet line at battery limits.
- g. Close the globe valve on the wash oil recycle line (through the flow transmitter) to the Caustic Circulation pumps.
- h. Close the Wash Oil Settler level controller to 0% in manual until wash oil circulation is ready to be commissioned.
- i. If there are fresh wash oil pumps, prepare to commission them by opening the gate valves on the suction and discharge lines of one of the pumps. The other pump should remain isolated.
- j. After the wash oil has been sampled and deemed suitable, start a **minimal** flow of wash oil to the Wash Oil Settler via the Caustic Circulation pump.
- k. Commission the Wash Oil Settler level controller to a set point of 50%. Watch the level carefully and be prepared to stop the fresh wash oil flow if any problems with the level controller arise.
- l. When the level controller is commissioned, the wash oil will be directed to the Oxidizer and then to the Disulfide Separator, where an interface level will begin to form.
- m. When the interface level of caustic and wash oil in the Disulfide Separator main body level falls to 20%, open the gate valve on the Disulfide Oil Sand Filter inlet line to direct the wash oil from the Separator to the Disulfide Sand Filter.
- n. The gate valve on the vent/equalization line should also be opened.
- o. When opening the Disulfide Oil Sand Filter inlet line, the wash oil will be sent from the Disulfide Separator to the Disulfide Sand Filter, causing the caustic/wash oil interface to increase. If the interface level increases to 80% while liquid filling the Disulfide Oil Sand Filter, temporarily close the gate

valve on the Disulfide Oil Sand Filter inlet line until the interface level falls below 80%. **Do not allow the interface level to increase beyond 80%, thus increasing the risk of sending caustic to the Disulfide Oil Sand Filter and thereby to rundown!**

- p. The Disulfide Oil Sand Filter will become liquid full with wash oil and should be maintained liquid full at all times during normal operations.
- q. After inventorying the Disulfide Oil Sand Filter, the wash oil inventory in the Disulfide Separator will increase with further addition of wash oil. Because wash oil/disulfide oil is decanted off the top of the Disulfide Separator, an increased level of wash oil will make the interface level decrease. When the caustic/wash oil interface level reaches 20%, make sure the Disulfide Oil Pump autostarts. When the caustic/wash oil interface increases to 80%, make sure the pump auto-stops. **There should always be an interface level visible in the Disulfide Separator main body level glass!** Do not allow the interface level to increase higher than 80%.
- r. Before the wash oil is pumped from the Disulfide Sand Filter via the Disulfide Oil pump, confirm that there is no caustic in the Disulfide Sand Filter by opening the globe valve to the drain to confirm the Disulfide Sand Filter is liquid full with wash oil.
- s. When the interface level in the Disulfide Separator falls to 20%, make sure that the pump auto-starts. Do not allow the interface level falls below 20%, thus significantly increasing the possibility of sending disulfide oil to the Wash Oil Settler and then to the Extractor.
- t. When the Wash Oil Settler level controller has stabilized and is functioning properly, **slowly** increase the wash oil flow at the Wash Oil Pump to the design rate.
- u. Confirm the fresh wash oil flow with the calibrated level glass on the Wash Oil Drum, if available.

- v. When the fresh wash oil flow is at design flow rate, slowly crack open the globe valve on the wash oil recycle line to the Caustic Circulation Pumps. **Slowly** increase the wash oil recycle flow to the design rate, as indicated on the local flow indicator.
- w. Once hydrocarbon is introduced and mercaptan is converted to disulfide oil and extracted, this wash oil flow will progressively have a greater and greater content of disulfide oil until equilibrium is achieved.

VII. NORMAL STARTUP

The procedure used for starting up the Caustic Extraction Merox unit after any shutdown is identical to the procedure used for initial startup. The Initial Startup procedure given in Section VI (Commissioning) of this manual should be followed for restarting the Caustic Extraction unit.

VIII. NORMAL OPERATIONS

This section will discuss various aspects associated with the normal operation of the LPG Extraction Merox Unit, including operation guidelines, performance evaluation, and unit optimization. A table listing the recommended operating ranges of the various variables is included at the end of this section (Table VIII-1). The proper operation of a liquid-liquid extraction Merox unit depends almost entirely upon two factors: caustic solution quality control and optimization of the extractor operating parameters. The suggested analytical schedule for the Caustic Extraction unit is shown in section IX of the manual.

A. AMINE ABSORBER

Before any hydrocarbon stream can be sent to a Merox Extractor column (downstream of the Prewash Caustic), H_2S must be removed to less than 1 wppm. This will prevent premature spending of the Merox circulating caustic. Feedstocks containing more than 100 wppm H_2S are normally amine treated to reduce the H_2S level to 50 ppm or less before the Caustic Prewash.

B. AMINE WATER WASH

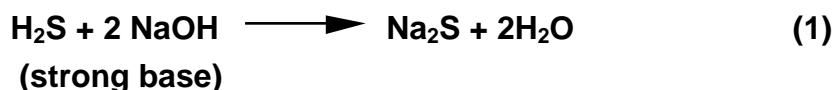
The methyldiethanolamine (MDEA) and other amines such as DGA and DIPA used in amine absorbers are soluble in LPG to some extent. Since any nitrogen is detrimental to downstream catalytic units and since amine cause emulsions when contacting caustic, an Amine Water Wash is provided between the absorber and the caustic prewash to remove any MDEA from the LPG stream. The Wash Water is monitored for amine content during operation. When the MDEA and other amines concentration reaches 1-3 wt%, the water batch is changed out, sending the amine rich water back to the amine unit where MDEA is recovered. Continuous Amine Water washes are also available.

C. PREWASH CAUSTIC SOLUTION

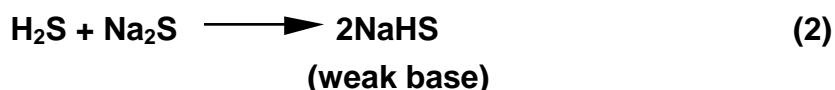
An additional caustic prewashing step is necessary to completely remove the remaining H_2S before the extractor to minimize the contamination of the circulating Merox caustic. Contamination of the circulating caustic with sulfide can prevent the mercaptan-rich caustic from being regenerated sufficiently, causing insufficient mercaptans oxidation, and ultimately poor mercaptans extraction efficiency. Thus, the only reasons for replacing circulating caustic should be excessive spending due to accumulation of Na_2CO_3 (as a result of CO_2 in the air) and/or excessive dilution as a result of water make (water of reaction).

1. Percent Spent

As hydrocarbon flows through the caustic prewash vessel, H_2S reacts with the caustic solution as follows:



This reaction will proceed as long as free NaOH is available. Additionally, the sodium sulfide (Na_2S) produced will continue to neutralize H_2S as follows:



Note: Na_2S will titrate as 50% strong base and 50% weak base.

It is very important to regularly monitor the condition of the prewash caustic solution. The use of a simple double titration method (see Section IX, Analytical, UOP-209) allows this to be done quite easily. The first phase of the titration is a measure of the strong base (pH 7). The second phase is a measure of the total base or total alkalinity (pH 3). This titration does not include the neutral salts of strong acids, such as NaCl , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_4 , etc.

Percent spent is defined as follows:

$$\% \text{ Spent} = \frac{(\text{Total Base} - \text{Strong Base})}{\text{Total Base}} \times 100 \quad (3)$$

Thus, as the caustic solution neutralizes H_2S , the strong base alkalinity (NaOH) depletes and the amount of weak base alkalinity ($\text{Na}_2\text{S} + \text{NaHS}$) increases. By definition of the analysis, when there is no free NaOH , the solution is 50% spent. When there is no free Na_2S , the solution is 100% spent. It is recommended that the solution not be allowed to be spent greater than 50% (70% max) to ensure that H_2S does not breakthrough to the Merox extractor. A quick field test, not as accurate as UOP-209, to determine the percent spent can be done at the unit by operations if so equipped. This field test can be found in Section IX (Analytical): Prewash Caustic Field Test.

2. Caustic Strength

Dilute caustic solutions are necessary to prevent the precipitation of sodium sulfide (Na_2S) crystals in the prewash vessel. Economic considerations usually limit the practical range of H_2S removal by this method to hydrocarbon streams containing not more than 100 wppm H_2S . The optimum caustic strength for the prewash vessel is 6-7 wt% as NaOH (approximately 10° Baume). Table VIII-2 & 3 attached at the end of this section provides the correlation of Baume to weight percent NaOH . In some cases the proper concentration of caustic will have to be prepared using a higher strength caustic. A sample calculation to prepare caustic solution blends is provided in Table VIII-4.

The following table lists the typical properties of spent caustic derived from neutralizing H₂S from LPG streams:

Prewash Caustic
(Sulfidic)

Appearance	Yellow to Dark Brown
Percent Spent	50 (70 max)
Total Alkalinity	5-10 wt% as NaOH
Total Sulfur	3-4 wt%
Na ₂ S	3-4 wt%
NaHS	3-4 wt%

D. MEROX CIRCULATING CAUSTIC

Obtaining maximum mercaptan extraction requires keeping good circulating caustic quality as shown:

Extraction Caustic
(LPG, LSR)

Appearance	Olive Green to Blue
Percent Spent	10-20
Total Alkalinity	12-19 wt% as NaOH
Strong Alkalinity	10-12 wt% as NaOH
Total Sulfur	<1 wt% as Na ₂ S ₂ O ₃ , Na ₂ SO ₃ and Na ₂ SO ₄
Mercaptide Sulfur	30-120 wppm
Sulfide Sulfur	0 wppm
Disulfide Sulfur	10-200 wppm
Na ₂ CO ₃	1-5 wt%
Merox Catalyst	50-500 wppm
Lead Acetate Paper	Not discolored

The discussion of the topics below will help optimizing the operation and overall performance of the Merox unit.

1. Caustic Strength

As discussed earlier, the ability to extract mercaptans depends upon the caustic concentration or specifically, the concentration of unneutralized (free) sodium hydroxide. For optimal mercaptan extraction, circulating caustic with total alkalinity of 12-19 wt% is recommended; for clean/fresh caustic solution, the corresponding solution gravity is 17-25° Bé or 1.13-1.21 SG. Operation at lower caustic concentrations may reduce extraction efficiency. The minimum caustic concentration required will vary somewhat from unit to unit, but is always at least 12 wt% as total alkalinity. Since the mercaptan oxidation reaction produces water, the circulating caustic will dilute over time and lower the concentration of free sodium hydroxide and consequently require replacement of a portion of the caustic with fresh, strong caustic. Spent caustic is normally withdrawn from the regenerated (not mercaptan rich) caustic stream, which contains only a small amount of mercaptide and disulfide sulfur. This regenerated caustic is often transferred in the caustic prewash for further utilization.

2. % Spent

The circulating caustic is also limited to 20% spent max, since the ability to extract mercaptans depends upon the concentration of unneutralized (free) NaOH in the caustic solution. Percent spent is determined using UOP Method 209 (Section IX, Analytical). This test will indicate the accumulation of non-mercaptan acidic compounds such as hydrogen sulfide, carbon dioxide (from the regeneration air), and other non-regenerable acidic materials. These sodium salts lower the concentration of free sodium hydroxide and thus the ability of the caustic to extract mercaptans. When the circulating caustic is the range of 10%-20% spent, a portion of the caustic is withdrawn from the unit and replaced with fresh, strong caustic (>25° Bé).

3. Caustic Gravity

Caustic gravity measured using an hydrometer should be checked daily. Accumulation of neutral salts or sediments will tend to increase the solution gravity. Operation with dirty, high gravity caustic is one cause of caustic carryover in the hydrocarbons leaving the extractor.

Using the total alkalinity lab result, the predicted caustic gravity for clean caustic solution can be found from a caustic table (see Table VIII-3). This should be compared with the measured (hydrometer) caustic gravity. The difference in these gravities is an indication of the presence of non-basic sodium salts such as thiosulfates and sulfates. The gravities difference should be no more than 2° Bé. Periodically, and as determined by experience, some caustic must be purged from the system and replaced with fresh caustic to prevent excessive accumulation of non-titratable salts: thiosulfates and sulfates.

Large changes in gravity may also be caused by the dilution effect due to water make. Also, dry feedstocks, such as butane may increase the gravity of the caustic solutions. Therefore, caustic gravity adjustments should be made when deemed necessary by either adding water or strong caustic to minimize:

- a. dilution effect,
- b. de-hydration effect,
- c. neutralization effect, and/or
- d. accumulation of strong salts.

4. Mercaptide Concentration

The regenerated caustic should be checked daily for mercaptides and sulfides. Sufficient air should be used to maintain the mercaptide sulfur in the regenerated caustic between 0.003 to 0.012 wt% (30 to 120 wppm). Maintaining a small amount of mercaptans ensures better catalyst dispersibility in caustic. Thus, any tendency for catalyst to settle at the disulfide-caustic interface in the disulfide separator is reduced. However, this is not a real problem when UOP Merox Reagent WS is used. More importantly, the presence of mercaptide indicates that no oxygen is present in

the regenerated caustic and therefore, oxygen cannot be introduced to the top of the extractor. Oxygen in the extractor is not desirable because it could potentially caused undesirable mercaptans sweetening, and safety concerns when it accumulates in the downstream fractionators.

5. Catalyst Concentration

The catalyst makeup rate is routine, based on performance, and the makeup rate is changed if required. Catalyst is always added when fresh caustic is added. Frequent analyses of the caustic solution will establish the frequency of caustic solution maintenance. The catalyst addition procedure can be found in Section XIII, Special Procedures.

E. REGENERATED CAUSTIC FROM DISULFIDE SEPARATOR

Make a visual check to see that the caustic is free of entrained disulfide, and it is not muddy and murky; presence of sulfides can be checked using lead acetate paper. To maintain good quality of the Merox circulating caustic, the prewash caustic may be replaced on a faster cycle due to the increased caustic transfer from the regeneration.

The regenerated caustic from the disulfide separator should be analyzed for extractable sulfur (disulfides) as required, using UOP 393 to check the disulfide oil separation efficiency. It can be assumed that all of the extractable sulfur in the caustic will re-enter the hydrocarbon stream at the top of the extractor unless the unit is equipped with a wash oil system to further reduce the level of such disulfides.

NOTE: Using lead acetate paper, check both the lean and rich caustic for presence of sulfides. The lead acetate paper must be clear.

F. SAND FILTER

if scale or rust has accumulated on top of the sand, backwashing may be used to relieve plugging and restore good performance. When ~ 2 psi (14 kPa) pressure drop develops, the sand filter should be water backwashed. Back flushing procedures are included in Section XIII, Special Procedures.

Caustic carried into the sand filter slowly etches the sand and may in time reduce its effectiveness as a coalescer. If this is suspected and good performance cannot be restored despite back flushing, the sand should be changed out.

G. OPTIMIZATION

The operating parameters not under direct control in the Merox unit operators are hydrocarbon flow rate, hydrocarbon quality, and hydrocarbon temperature. The Merox operator should alert the operators in the other areas so that corrective actions can be taken. The operating parameters under direct control in the Merox operator are caustic/hydrocarbon ratio (C/H), caustic regeneration temperature, catalyst makeup, caustic concentration, and air injection rate.

1. Air Injection

The primary operating variable for Merox Unit control is the air injection. The required air rate is based on mercaptans sulfur loading, therefore it will change for large changes in hydrocarbon feed rate or feed mercaptan content. Figure III-1 in the Process Variables section shows the air injection chart that can be developed for each unit. The Shake Test (Section X, Troubleshooting) and the air injection chart will aid operations in determining the necessary adjustments to be made to the unit. Confirmation of the proper air rate is given by caustic mercaptide analysis (30 to 120 wt-ppm NaSR-S) or by performing the Shake Test. When the mercaptide content is within this range, and the air injection is 200% theory, the vent gas oxygen content should be 9 to 12 vol%. Higher oxygen content should be avoided.

Note: The spent air concentration of oxygen must not exceed 12 vol% to avoid high corrosion rates in the Disulfide Separator vapor phase.

2. Caustic/Hydrocarbon Ratio (C/H)

The caustic circulation rates should be kept as constant as possible regardless what the hydrocarbon feedrates are. Optimization of extraction efficiency is achieved by determining the optimum caustic/hydrocarbon flow ratio at design capacities. Insufficient caustic flow will result in insufficient dissolution of mercaptans in the circulating caustic and therefore, excessive mercaptans in the product. Excessive caustic flow will result in excessive transfer of disulfide oil to the product. The optimal product sulfur reduction is achieved when the C/H ratio is sufficiently low to minimize the re-entry sulfur and sufficiently high to extract most of the mercaptans. This can be seen by referring to Figure III-6 of the Process Variables section. To determine the optimum C/H ratio, plant operation should be correlated against minimum product mercaptan sulfur plus re-entry sulfur analyses. UOP Method 393 is used to analyze for disulfide oil content in the regenerated caustic and UOP Method 163 (for gasoline) and UOP Method 212 (for LPG) to analyze for mercaptan sulfur in the hydrocarbon.

3. Hydrocarbon Flow Rate

Operation at low hydrocarbon flow rates (relative to the design case) will result in poorer contact that will reduce mercaptan extraction efficiency. This will require a higher C/H ratio for compensation, but will result in higher re-entry sulfur. It is impossible to maintain the same design mercaptan sulfur plus re-entry sulfur content at lower-than-design feed rates. As discussed above, the optimum C/H ratio for minimum mercaptan plus re-entry sulfur must be determined by plant operation. In addition, every effort should be made to adjust the instrumentation controlling the extractor feed rate to give the steadiest flow rate possible. Feed rate fluctuations will result in difficulty in sustaining optimum performance and cause potential caustic carryover from the top of the extractor.

4. Hydrocarbon Temperature

As discussed previously, higher temperatures lead to decreased solubility of mercaptans in caustic. Although the mercaptans extractability during the design is typically based on 100°F (38°C), the RSH extraction will be more than adequate when operating the unit between 90° → 110° F (38° → 43° C). Lower temperatures result in increased extraction efficiency. However, operating the unit below 90° F (38° C) may trigger emulsions and therefore, potential caustic carryover.

5. Oxidizer Temperature

A small heater is provided to heat the caustic to about 100°-110°F (38° – 43°C). The oxidizer should be run at as low a temperature as possible while still maintaining a desired degree of regeneration. Rarely the oxidizer should be allowed to reach a maximum outlet temperature of 120°F (49°C).

6. Feed Composition

A sudden increase in the product mercaptan content under otherwise stable, well controlled conditions may result from a change in feedstock composition, which introduces higher boiling mercaptans. This can be remedied by changes in the upstream equipment operation. If the feedstock cannot be altered and heavier mercaptans are present, a new and higher optimum C/H ratio must be determined by plant operational adjustment to minimize the product mercaptan sulfur plus re-entry sulfur.

TABLE VIII-1

EXTRACTION MEROX UNIT: TYPICAL OPERATING GUIDELINES

STREAM COMPONENT		RECOMMENDED GUIDELINES		
Prewash Caustic		TARGET	MINIMUM	MAXIMUM
Gravity, ° Baumé		10	8	15
Total Alkalinity, wt%		7	5	10
Percent Spent, %		< 50	0	70
Regenerated Merox Caustic				
Gravity, ° Baumé		20	17	25
Sulfide, wppm		0	0	0
Mercaptide, wppm		60	30	120
Disulfide, wppm		<200	10	200
Thiosulfate, wt%		0	0	1
Total Alkalinity, wt%		14	12	19
Percent Spent, %		<10	0	20
Shake Test*, seconds		60	30	120
Merox WS Catalyst Dosage, wppm		200		
Lead Acetate Paper		Not Discolored (Black or Brown indicates presence of sulfides)		
Rich Regenerated Merox Caustic				
Sulfide (Lead Acetate Paper)		Not Discolored (Black or Brown indicates presence of sulfides)		
Disulfide Separator Vent Gas				
O ₂ (before fuel gas)		10.5	9	12
O ₂ (after fuel gas)		0	0	5
Other Typical Operating Targets:				
Hydrocarbon Feed Temperature, °F		100 (38)	90 (32)	110 (43)
Oxidizer Inlet Caustic Temperature, °F		105 (40.5)	100 (38)	110 (43)
Oxidizer Outlet Caustic Temperature, °F		110 (43)	105 (40.5)	120* (49)
Caustic Circulation Rate (LPG), vol-%		2	1	3
Caustic Circulation Rate (Gasoline), vol-%		15	10	20
Merox WS Catalyst Addition Rate		1 lb/10,000-25,000 barrels (1 kg/3,500-9,000 m ³)		
Air Injection Rate		30 SCF/lb RSH-S (1.75 Nm ³ /kg RSH-S)		

*Shake Test must be successfully obtained at the lowest oxidizer outlet temperature possible; in most cases 105° F = 40.5° C is more than adequate.

Table VIII-2
COMPOSITION OF SODIUM HYDROXIDE SOLUTIONS

°Bé At 59°F or 20°C	59°F		20°C		°Bé At 59°F or 20°C	59°F		20°C	
	Lb per Bbl of Solution NaOH H ₂ O		Kg per Cu Meter of Solution NaOH H ₂ O			Lb per Bbl of Solution NaOH H ₂ O		Kg per Cu Meter of Solution NaOH H ₂ O	
1	2.10	349.5	8	999	26	84.00	342.5	243	975
2	3.78	351.5	14	1000	27	88.60	340.5	257	972
3	6.71	350.5	21	1000	28	93.65	339.5	271	968
4	9.24	350.0	28	1000	29	98.30	338.5	286	964
5	11.32	351.0	35	1001	30	103.8	337.5	300	961
6	13.85	351.5	42	1001	31	109.2	336.0	316	956
7	16.38	351.0	50	1001	32	114.7	334.5	332	951
8	18.90	351.0	58	1000	33	120.6	333.0	349	946
9	21.85	351.0	66	1000	34	126.3	331.0	366	940
10	24.35	351.5	74	1000	35	133.1	327.5	384	934
11	27.28	352.5	82	1000	36	139.8	326.0	403	927
12	30.65	351.0	91	999	37	145.8	324.5	423	920
13	34.00	350.0	100	998	38	154.2	320.0	443	912
14	37.35	350.0	109	998	39	161.2	316.5	464	904
15	39.90	350.5	119	996	40	169.0	314.5	486	895
16	43.25	350.0	128	996	41	176.4	311.5	509	885
17	47.45	349.0	138	995	42	185.0	306.5	532	876
18	50.80	348.5	149	993	43	194.2	303.0	557	865
19	54.15	348.5	159	992	44	203.0	299.0	582	854
20	58.40	348.0	170	990	45	212.0	295.5	609	841
21	61.70	347.5	182	987	46	216.5	296.0	638	827
22	65.95	345.5	193	986	47	232.5	293.5	668	812
23	70.10	345.0	205	984	48	242.5	281.0	699	796
24	74.80	344.5	217	981	49	253.5	275.0	732	778
25	78.90	344.5	230	978	50	266.5	267.0	767	759

See adjoining column for example of blending calculations.

TABLE VIII-3

Degrees Baume'	Density (15°C)	Wt% NaOH	G-Mole NaOH per liter	Grams NaOH per liter	Pounds NaOH per U.S. Gallon
1	1.007	0.60	0.15	6.04	0.050
2	1.014	1.22	0.31	12.35	0.103
3	1.021	1.86	0.47	18.97	0.158
4	1.028	2.50	0.64	25.68	0.214
5	1.036	3.15	0.82	32.61	0.272
6	1.043	3.81	0.99	39.70	0.331
7	1.051	4.50	1.18	47.25	0.394
8	1.058	5.18	1.37	54.75	0.456
9	1.066	5.88	1.57	62.62	0.522
10	1.074	6.60	1.77	70.20	0.590
11	1.082	7.31	1.98	79.02	0.659
12	1.090	8.05	2.19	87.67	0.731
13	1.098	8.79	2.41	96.43	0.804
14	1.107	9.54	2.64	105.51	0.880
15	1.115	10.30	2.87	114.74	0.957
16	1.124	11.09	3.11	124.54	1.038
17	1.133	11.88	3.36	134.48	1.121
18	1.142	12.69	3.62	144.79	1.207
19	1.151	13.51	3.88	155.36	1.295
20	1.160	14.33	4.15	166.08	1.385
21	1.169	15.17	4.43	177.17	1.477
22	1.179	16.02	4.72	188.70	1.573
23	1.189	16.89	5.02	200.64	1.673
24	1.198	17.78	5.32	212.81	1.774
25	1.208	18.68	5.64	225.45	1.880
26	1.218	19.61	5.97	238.63	1.989
27	1.229	20.55	6.31	252.33	2.104
28	1.239	21.50	6.65	266.15	2.219
29	1.250	22.47	7.02	280.62	2.340
30	1.261	23.46	7.39	295.57	2.464

TABLE VIII-4
USE OF TABLE
“COMPOSITION OF SODIUM HYDROXIDE SOLUTIONS”
TO CALCULATE COMPONENTS FOR CAUSTIC BLENDS

PROBLEM: Prepare a 10 barrel blend of 20° Bé caustic from 5 barrels of 10° Bé caustic and X barrels of 50° Bé caustic.

SOLUTION: 20° Bé solution 10 barrels required
 NaOH required $10 \times 58.40 = 584 \text{ Lb}$
 Water required $10 \times 348.0 = 3480 \text{ Lb}$

10° Bé solution 5 barrels available
 NaOH available $5 \times 24.35 = 122 \text{ Lb}$
 NaOH available $5 \times 351.5 = 1760 \text{ Lb}$

NaOH req. by diff. $584 - 122 = 462 \text{ Lb}$
 Water req. by diff. $3480 - 1760 = 1720 \text{ Lb}$

50° Bé

Required $\frac{462}{266.5} = 1.73 \text{ Bbl}$

Water included w/50° Bé $= 1.73 \times 267 \text{ 463 Lb}$

Extra water required by diff.
 $1720 - 463 = 1257 \text{ Lb}$

$\frac{1257}{350} = 3.6 \text{ Bbl}$

Summary for 10 Bbl of 20° Bé Blend

Water	3.6 Bbl
10° Bé caustic	5.0 Bbl
50° Bé caustic	1.7 Bbl

IX. ANALYTICAL

The ultimate objective of petroleum refining is to produce product hydrocarbon streams that meet all specifications required for their ultimate end use. To accomplish this objective, it becomes necessary to characterize the important physical and chemical properties of the various refinery streams utilizing specific laboratory analytical testing procedures. Thus, satisfactory refinery operation depends largely upon proper analytical procedures for quality control. An analytical quality control program requires five steps as outlined.

A. PROCEDURE

1. Sampling

The initial objective must be to obtain a characteristic sample of the particular product stream. Depending upon the properties of the product in question, specialized techniques may be necessary to obtain a proper sample. UOP Method 516 outlines the general techniques recommended for obtaining an air free sample, an important consideration in control of chemical treating process units.

The sample point itself should be located where no unusual conditions exist. This normally requires a sample point location in a vertical run of pipe or from the side of a horizontal run of pipe.

The refinery operation should be steady and free from fluctuations.

The sample point should be well purged to eliminate aged material, water, dirt, etc., and to assure withdrawal of a sample representative of the material flowing in the pipe. The sample container must be adequate for the analysis to be obtained. The above by no means is intended to be a comprehensive discussion of sampling; we refer those who are intrigued by this subject to the excellent publications of organizations such as API, NPRA, and ASTM. Rather, we want to introduce the

refinery operations staff to some of the basic considerations needed to obtain the best sample possible.

2. Sample Preservation

Once a proper sample has been obtained, it must, if possible, be preserved intact until it can be analyzed. This requires the prevention of any physical or chemical changes in the sample. Changes, particularly chemical, can occur as a result of many factors. Some of the most perplexing changes have later been traced to influences of the sampling equipment and container. Often a sample may be inherently unstable, requiring immediate analysis. Others can be stabilized by the addition of a passivating compound or preservative. Some specific conditions to be avoided are as follows:

- Do not use plastic containers
- Never use copper or copper alloys including tubing, valves and fittings
- Avoid exposure to light by using amber glass sample bottles
- Avoid exposure to heat
- Minimize exposure to air by using N₂ purged containers

3. Analysis

Follow the analytical method PRECISELY. Each method represents the end result of many hours of study, testing, and experience. The methods often note appropriate precautions indicating potential problems to be avoided.

Laboratory apparatus and equipment must be properly calibrated and rechecked frequently.

4. Error

There are two terms with which one may qualify an analytical result – precision and accuracy.

Precision refers to the dispersion, or spread, of results. One must consider both repeatability (duplicate results by the same analyst) and reproducibility (duplicate results by different analysts) of results in order to determine the permissible tolerance in each specification. A high degree of precision usually requires minimizing the random experimental error during development of the method.

Accuracy refers to the deviation between a reported analytical result and the true value. It is accuracy that can be the most damaging since it is normally the result of systematic error. If any of the above procedures have been compromised, the effect is always seen in the accuracy of the value reported.

5. Significance

The significance or interpretation of the result obtained is the final step in any analytical procedure. Misinterpretation of the result would render the whole procedure useless. Therefore this step is the most important. Often several analyses measuring different properties may be related to a common characteristic (physical or chemical). Proper analytical procedure should lead to supporting rather than conflicting conclusions. In attaching appropriate significance to the analysis, one must consider and relate all of the previous steps of the analytical procedure to the operation of the process unit. A firm understanding of the process and its capabilities is essential. From a thorough application of these five steps, the necessary changes in operation may be implemented in order to reach the ultimate objective of meeting the necessary product specification.

B. SCHEDULES/METHODS

Suggested analytical schedules follow for typical Merox Units. These represent a minimum recommendation for an adequate quality control program.

PREWASH CAUSTIC FIELD TEST

PROCEDURE

When the prewash caustic is rapidly or erratically spent, its condition should be carefully monitored. If laboratory turnaround time allows the caustic to become overspent and H₂S breakthrough to occur, it is suggested that the plant operators be trained to run the % spent on the prewash caustic. Here is a simple and easy method, while not rigorously accurate, that gives a good indication of the condition of the prewash caustic:

1. Take about 10 ml of caustic into a 250 ml flask (volume not critical).
2. Dilute with about 100 ml of distilled water.
3. Add several drops of phenothalein indicator and observe that the solution turns pink.
4. Add 1.0 M HCl while stirring the solution in the flask. Continue adding until the solution becomes clear. Record the amount added in ml (this is X).
5. Add several drops of methyl orange indicator and observe that the solution now turns orange.
6. Add more acid while mixing the flask until the solution turns red. Record the amount added in ml (this is Y).
7. The percent spent can be determined with the following formula:

$$\text{Percent Spent} = 100 * Y / (X + Y)$$

PREWASH CAUSTIC: Should be less than 50% (70% max) Spent for H₂S service to avoid breakthrough, less than 50% spent if both H₂S and CO₂ are present (Fuel Gas Merox units).

CIRCULATING CAUSTIC: Should be less than 10% Spent.

SUGGESTED ANALYTICAL SCHEDULE

LPG MEROX UNIT

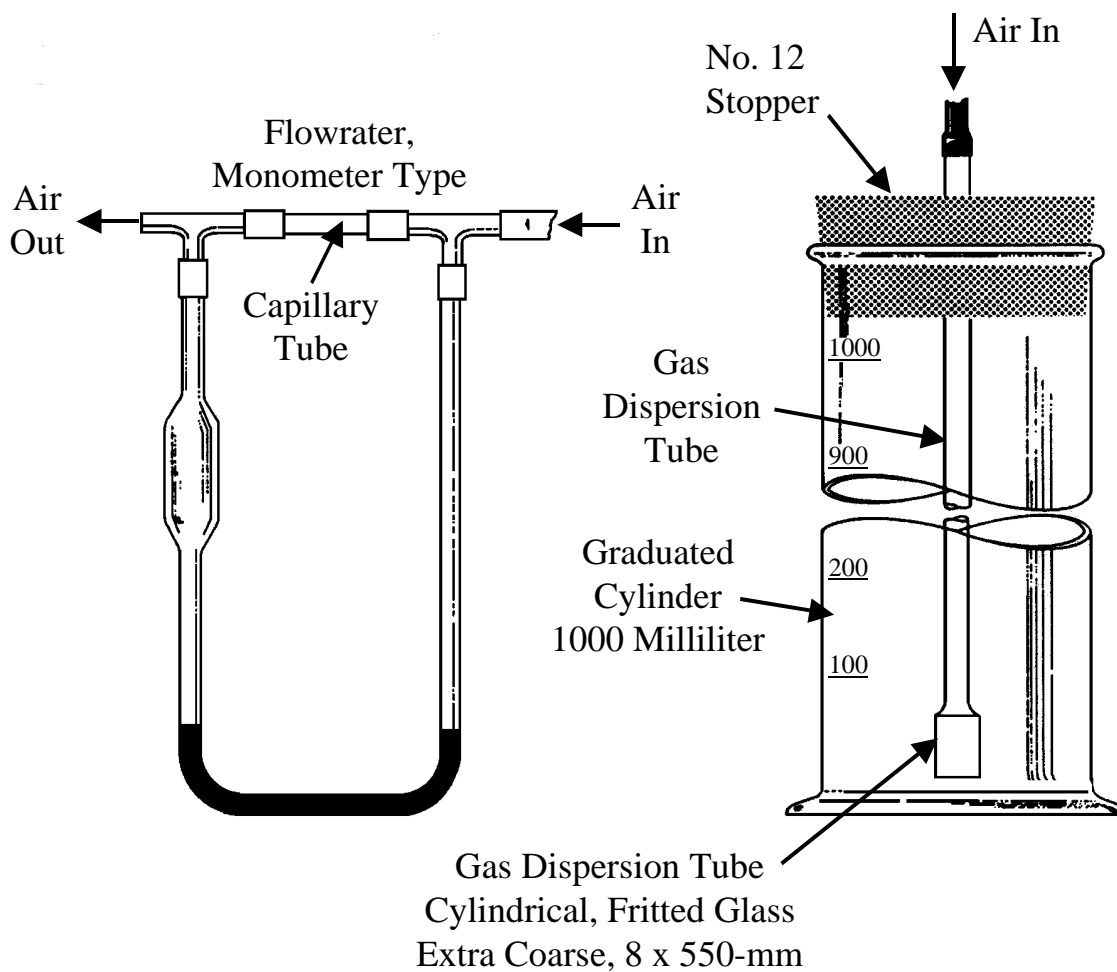
Stream/Component	Method	Frequency
1. LPG Feed to Prewash		
Composition	UOP 539	Daily
H ₂ S, RSH, COS	UOP 212	Daily
Total Sulfur	UOP 923 or ASTM D 6667	Daily
2. LPG Feed to Extractor		
H ₂ S*	ASTM D 2420	Daily
H ₂ S, RSH, COS	UOP 212	Daily
Total Sulfur	UOP 923 or ASTM D 6667	Daily
3. LPG Product to Storage		
RSH, COS	UOP 212	Daily
Total Sulfur	UOP 923	Daily
4. Prewash Caustic		
Gravity	ASTM D 1429 (Hydrometer)	Daily
Total Alkalinity	UOP 209	Daily
Percent Spent	UOP 209	Daily
5. Lean/Rich Merox Caustic		
Sulfide	Pb Ac Paper	1/Shift
6. Regenerated Merox Caustic		
Gravity	ASTM D 1429 (Hydrometer)	Daily
Sulfide	UOP 209	Daily
Mercaptide	UOP 209	Daily
Disulfide	UOP 393	As Req'd
Thiosulfate	UOP 953	As Req'd
Total Alkalinity	UOP 209	Daily
Percent Spent	UOP 209	Daily
Shake Test*	See Op. Instructions	1/Shift
7. Disulfide Separator Vent Gas		
O ₂ (before fuel gas)	Orsat or UOP-539	Daily
O ₂ (after fuel gas)	Orsat or UOP-539	Daily

Stream/Component	Method	Frequency
8. Regenerated Amine to Absorber		
Free MEA or DEA	UOP 825, 824	Daily
Apparent H ₂ S	UOP 827	Daily
Thiosulfate	UOP 818	As Req'd
Total Amine	UOP 828	Daily
CO ₂	UOP 826 or 829	As Req'd
Foam Test	See next page	As Req'd
9. Rich Amine from Absorber		
Apparent H ₂ S	UOP 827	Daily
10. Spent Water from Amine Water Wash		
Total Amine	UOP 828	Daily

*Done by operators at the unit.

Foam Test – Determination of Foaming in Aqueous Amine Solutions

1. **Scope:** This test is intended for the determination of the foaming characteristics of aqueous amine solutions.
2. **Principle:** Air is bubbled through the sample at a definite rate for five minutes, and the foam height and stability are measured.
3. **Apparatus:**
 - (a) Stop watch, calibrated in seconds
 - (b) Foaming apparatus - 1000 ml graduated cylinder, glass dispersion tube – cylindrical, fritted glass extra coarse, 8 x 550 mm, manometer/capillary tube flow rater.
4. **Procedure:**
 - (a) Pour 200 ml. of sample into the 1,000-ml. cylinder. Connect the air delivery tubes and introduce oil-free air at four liters per minute.
 - (b) Allow the bubbling to continue for five minutes, stop the air flow and start the stopwatch. Immediately record the height of the foam (cf. 5) and also the time in seconds for foam to break completely after the air supply is shut off.
5. **Note:** Foam height, in milliliters, is the difference between the height of the foam and the initial height of the liquid (200 ml.).
6. **Comments:**
 - (a) This method can be used to evaluate the effects of antifoam agents on a sample. Care should be exercised in cleaning the equipment since a very small amount of antifoam agent may affect the test.
 - (b) Foaming is sometimes caused by materials that can be removed by activated carbon treatment. The effect of activated carbon filtration can be evaluated by running foam tests on treated and untreated samples. The sample is treated by mixing with enough carbon (12-20 mesh) to completely remove the contaminant, and filtering the mixture through Whatman No. 41 filter paper.

Figure IX-1**Foaming Apparatus**

X. TROUBLESHOOTING

The following section contains some guidelines that are helpful in troubleshooting the Caustic Extraction unit.

A. EXTRACTION

Extraction efficiency may be affected by the following:

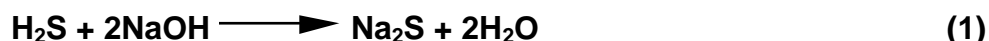
1. Insufficient caustic flow rate – indicated by excessive product mercaptan.
2. Excessive caustic flow rate – indicated by excessive product disulfide.
3. Excessive caustic neutralization or dilution (see Section VIII Normal Operations).
4. Low hydrocarbon flow rate (relative to design flow rate).
5. Insufficient mercaptan solubility (higher boiling feedstock).
6. Excessive hydrocarbon feed temperature (reduced extraction efficiency).
7. Accumulation of non-regenerable acidic materials. In time, regardless of the care used in prewashing, there will be some spending of the caustic due to carbon dioxide present in the air injected into the Oxidizer.

B. REGENERATION

Insufficient mercaptans oxidation may be attributed to:

1. Insufficient Air – The vented gas from the Disulfide Separator stack should be analyzed to ensure that the O₂ ranges between 9 → 12 vol%. Another method to check for sufficient air injection is the Shake Test.
2. Low Oxidizer Temperature – The Oxidizer inlet temperature should not be below 100° F (38° C).
3. Insufficient Catalyst – If a regular catalyst addition is not followed, the catalyst concentration in the circulating caustic may drop too low to promote adequate oxidation of mercaptides. The Shake Test may be used to ascertain if catalyst is sufficient or not.
4. Presence of Sulfide – The sulfides in the circulating caustic should be zero.

H₂S Breakthrough to Extractor – If hydrogen sulfide is present in the feed to a Merox Unit, it will react with caustic to form sodium sulfide.



Sodium sulfide, derived from H₂S breakthrough of sulfidic caustic carryover from the Caustic Prewash, can then be expected to oxidize according to the following reactions to form sodium thiosulfate and sodium sulfate:



This formation of sodium sulfate or sodium thiosulfate is most common in Merox Extraction units because feedstocks that are most amenable to mercaptan

extraction are also the most likely to contain H_2S . Sodium sulfides present in Merox regeneration section pose the following problems:

- (a) Caustic is consumed irreversibly. When sodium thiosulfate is produced, each mole of H_2S sulfur consumes one mole of sodium hydroxide. This is equivalent to 1.25 wppm NaOH consumed for each wppm of H_2S sulfur.
- (b) Oxygen requirements increase substantially. The stoichiometric or theoretical oxygen requirement for sodium sulfide oxidation is four times that of sodium mercaptide oxidation when sodium thiosulfate is produced, and eight times that of sodium mercaptide oxidation when sodium sulfate is produced. Thus, air injection capability can very quickly become the limiting factor in caustic regeneration.
- (c) The presence of sulfide suppresses mercaptide oxidation. It is necessary to essentially completely oxidize the sulfides before good mercaptide oxidation can be attained.
- (d) The oxidation kinetics are significantly slower for sulfide than for mercaptide. The mercaptan oxidation may be inadequate since a large amount of sulfides may not be oxidized completely on the first pass through the Oxidizer.

Sodium sulfate or thiosulfate, thus produced, remains in the aqueous phase. These are neutral salts that deplete alkalinity needed for mercaptan extraction and increase the salting out effect. If these salts are left to accumulate, their solubility limits could be exceeded leading to crystalline precipitation and possible plugging.

The presence of sulfides in the regenerated caustic may interfere with the potentiometric determination of mercaptan sulfur. (See Section IX, Analytical UOP 209).

Sulfide contamination is easily detected by testing the rich caustic with lead acetate paper or solution. The sulfides present in the circulating caustic must be addressed promptly by checking the operation and performance of the prewash. Increasing the catalyst concentration, oxidizer temperature, and air rate may be used to speed up the elimination of sulfide interference.

If sulfide contamination has been severe, for reasons discussed above, some or the entire caustic inventory may require replacement.

C. OTHER TOOLS TO CHECK THE CAUSTIC REGENERATION SECTION

1. Shake Test

The "shake test" is a simple method that can be used at the unit by the operators to estimate the effectiveness of Merox caustic regeneration.

Procedure:

Half fill a small, clear glass bottle with regenerated Merox caustic solution taken after the disulfide separator. The color of the solution should be dull green or greenish blue. Stopper the bottle and shake vigorously. The color of the solution should change to a bright green or deep blue within two minutes of shaking.

If more than two minutes of shaking are required to make the color change, either insufficient air is being injected to the oxidizer, the oxidizer temperature is too low, or there is insufficient catalyst in the caustic. If less than 30 seconds of shaking is required to make the color change, either excessive air is being injected, the oxidizer temperature is too high, or there is an excessive amount of catalyst in the caustic. A deep blue solution when the sample is taken indicates that there are no mercaptides remaining in the regenerated caustic. In this case, dissolved oxygen could be carried back to the extractor, allowing disulfide formation in the extractor as mentioned before.

NOTE: This test may be impractical when the caustic is heavily discolored, muddy, murky, and contains a high concentration of thiosulfates as a result of sulfides contamination.

2. Disulfide Separator Vent Gas

The oxygen content of the vent gas can be helpful when troubleshooting unit performance. Oxygen content below 9% would indicate inadequate air injection, excessive oxidizer temperature, or presence of sulfide. Oxygen content above 12% indicates excessive air injection, inadequate oxidizer temperature, or inadequate catalyst concentration in the Merox caustic.

D. DISULFIDE SEPARATION

If the disulfide oil separation is poor, there will be re-entry of disulfides into the hydrocarbon. If this is suspected, the regenerated Merox solution from the disulfide separator should be checked for disulfide oil content, using UOP Method 393.

E. EMULSIFICATION AND CAUSTIC ENTRAINMENT

Merox catalyst in caustic solution does not increase the tendency of caustic solutions to emulsify with hydrocarbons, but strong salts do. Scale and dirt will be almost completely dislodged by Merox caustic. Finely divided suspended material can stabilize emulsions. It may be necessary to discard the first batch of caustic during the startup if caustic picks up a big load of scale and dirt from used equipment. Part of this scale and dirt may be iron sulfide.

XI. NORMAL SHUTDOWN

The following section contains information on the necessary procedures involved in a normal shutdown.

- a. Stop air injection to the regeneration section by closing at least one positive shutoff valve. Close the vertical valve on the air injection line downstream of the special check valve.
- b. Divert hydrocarbon flow to off-specification storage facilities.
- c. Open the Merox unit bypass if provided, and block in the unit inlet and outlet valves.
- d. Close the Extraction Section back pressure controller to maintain pressure on the system.
- e. Close the lean caustic to extractor flow controller. Also close the extractor level controller. Shut off the caustic circulation pump.
- f. Stop lean amine circulation by closing the lean amine to amine absorber flow controller. Also close the Amine Absorber level controller. If present, the lean amine pump should also be stopped.
- g. Divert disulfide separator offgas to vent tank. The vent tank should have a water level to provide an odor seal. If applicable, stop the fuel gas dilution flow by closing the flow controller. The fuel gas should not be resumed until the offgas is redirected back to the heater.
- h. Close the regeneration section back pressure control valve to maintain pressure on the regeneration section.

- i. If applicable, stop the wash oil addition to the system.
- j. If the wash oil system is two-stage, close the wash oil setter level controller. The globe valve on the wash oil recycle line should also be closed until wash oil circulation is resumed.
- k. Ensure that valve on disulfide oil line from the Disulfide Separator to the Disulfide Sand Filter is closed.
- l. Block in the steam to the rich Caustic Heater.
- m. If the shutdown is only temporary, try to maintain operating pressure on the unit. For a longer term shutdown, follow normal refinery safety procedures for venting, draining, disposing of hydrocarbon/caustic and blinding.

XII. EMERGENCY PROCEDURES

The emergency procedures for shutdown of the Caustic Extraction Merox Unit are identical to those of the normal shutdown procedure found in Section XI.

XIII. SPECIAL PROCEDURES

This section covers the procedures that are unique to the operation of the Caustic Extraction Merox Unit.

1. Merox WS Catalyst Addition

Merox WS is a form of Merox catalyst used in extractive units for caustic regeneration and in liquid-liquid sweetening units. Merox WS is supplied as a dark blue water solution packaged in 3.8 liter (1 gallon) sealed polyethylene bottles. Each bottle contains one kilogram (2.2 lb) of water-soluble active ingredient.

Merox WS requires no additional handling or mixing prior to use. It is recommended that the bottles of reagents be well shaken before dispensing to avoid settling and ensure proper addition to the process. It is also recommended that personnel handling Merox WS wear protective clothing such as that worn when handling caustic soda solutions, i.e., rubber gloves, apron, and eye protection.

It is important that the catalyst be added to the rich caustic entering the oxidizer. Carbon Raschig rings, as well as dirt and scale, tend to adsorb catalyst and remove it from solution. Any tendency to remove catalyst will result in deposition of catalyst on the Raschig rings where it will be effective in performing its function. Catalyst should only be added after caustic circulation has been established.

- a. Verify that the $\frac{3}{4}$ " gate and globe valves on the catalyst outlet line are closed.
- b. Isolate the 1" gate and globe valves on the air inlet line to the Catalyst Addition Pot.
- c. Verify that the Catalyst Addition Pot is depressured (PSV bypass is open).
- d. Open the ball valve at the top of the Catalyst Addition Pot.

- e. Proper protective equipment should be worn during this step since the catalyst is an irritant and will stain the skin and take several days to wear off. Thoroughly shake a bottle of Merox WS. Add 3 bottles maximum per batch. Transfer the contents of the bottle(s) to the Catalyst Addition Pot by pouring the contents into the funnel. The Merox WS bottle(s) should be rinsed several times with water and the rinsings also poured into the Catalyst Addition Pot.
- f. Close the ball valve beneath the addition funnel.
- g. Close PSV bypass.
- h. Slowly begin a small air flow to the Catalyst Addition Pot. This is done by opening gate valve completely and **slowly** introducing air via the globe valve.
- i. Slowly increase the air flow so the Catalyst Addition Pot pressure begins to build. **This pressure must remain greater than the regeneration back pressure at the oxidizer inlet or mixer inlet to allow catalyst transfer into the system.**
- j. Stop air addition to the Catalyst Addition Pot by closing the 1" globe valve. Once catalyst addition is started, the air flow will have to be slowly restarted to maintain the Catalyst Addition Pot at the required pressure.
- k. Inform the control board operator that catalyst addition will begin and that the regeneration pressure should be watched carefully as this pressure is expected to increase.
- l. Open the $\frac{3}{4}$ " gate valve on the catalyst outlet line. The flow of catalyst solution to the system can be controlled by slowly opening the $\frac{3}{4}$ " globe valve on the catalyst outlet line. Catalyst transfer can be seen through the sight glass. Add the contents of the Catalyst Addition Pot slowly to ensure the catalyst is well distributed throughout the system.

- m. The Catalyst Addition Pot is empty when the Pot pressure falls quickly. Other ways to tell that the catalyst addition is complete is when catalyst solution flow is no longer seen in the sight glass and air will be heard (i.e. a hissing sound) going into the system. Also, the regeneration section pressure will increase rapidly. **(Watch this pressure carefully! The operators should be familiar with the set pressure of the Disulfide Separator PSV.)** When one of these events happens, close the ¾" gate and globe valves on the outlet line of the Catalyst Addition Pot and stop the air flow.
- n. Slowly open the 1" gate valve on the PSV bypass line to fully depressure the pot.
- o. For the initial catalyst fill, valid when discarding spent caustic and replenishing, continue to add bottles of Merox WS until the concentration of Merox WS active ingredient constitutes at least 200 wppm in the circulating caustic. For operating units, add 1 lb active ingredient for every 10,000 BBLs of hydrocarbon treated. When fresh caustic is added, add enough catalyst to equal 200 wppm in the amount of caustic (or water) added.

NOTE: It is best to make several small additions of catalyst, pressuring the solution in slowly so as to get a better distribution of the catalyst throughout the caustic in the plant. A single large addition of catalyst may saturate one portion of the circulating caustic while other portions are deficient. Furthermore, during normal operations, addition of catalyst should be made on as frequent a basis as is practical. For instance, it is better to add smaller amounts on a daily basis than a larger amount weekly.

2. Sand Filter Backwashing

As contaminants or impurities collect in the sand bed, it will lose its coalescing efficiency and the differential pressure across the sand filter will gradually increase. Initially the differential pressure across the filter will be negligible (near indiscernible). When a differential pressure is apparent, as indicated by a difference of >14 kPa (>2 psi), the sand filter should be taken out of service for backwashing.

Failure to do so will result in continued differential pressure buildup and will lead to mechanical failure of the sand support screen and inefficient coalescing of hydrocarbon impurities. Backwashing should be conducted as follows:

- a. Open the hydrocarbon line bypassing flow around the sand filter vessel and block in the Sand Filter.
- b. Pump out or drain the remaining hydrocarbon from the vessel. Displace the hydrocarbon with steam or inert gas while taking the necessary precautions to ensure that the vessel is maintained under a slight positive pressure at all times. In the case of LPG, depressure the sand filter to the flare and displace the residual vapors with water.
- c. Open the backwash line provided at the sand filter inlet line, removing the blind, if provided.
- d. Connect a temporary water supply to the connection provided at the vessel drain.
- e. Begin filling with water.
- f. When the vessel is full of water, flush at a vigorous water flow rate, upflow taking care that no sand is floated out the inlet.
- g. The backwashing may be considered complete when the effluent is essentially clear and free of suspended matter.
- h. Put Sand Filter back into service, using safe refinery practices.

3. Leak Test Instructions

These instructions are for leak testing the inlet and outlet weirs (downcomers included) on the Merox Extractor and Amine Absorber columns. It is recommended that the leak testing be conducted initially on the lowest tray and then on each subsequent upper tray. All tray manways need to be removed for the leak test.

- a. Check the level on the weir top edge. The edge should be level. Repair or adjust the level as necessary as per the specified tolerance.
- b. Tightly plug the downcomer with the blind plate and neoprene gasketing.
- c. Plug the inlet weir weep hole if one exists with a plug, cloth, plastic or other suitable material.
- d. Starting with the bottom trays, carefully fill the inlet and outlet weirs to approximately $\frac{1}{4}$ " from the top of the weir plate with water. This can most conveniently be done with a long hose with an on/off valve on the end. Try to minimize the spillage outside of the weir pans to avoid the amount of drying required.
- e. Very thoroughly dry all areas of the tray and vessel shell underneath the outlet and inlet weir pans using cloths or an air hose. This will allow any leaks present to be very easily identified.
- f. Check **all** weld points:
 - On the downcomer,
 - Where the downcomer connects with the outlet weir bottom pan,
 - Along all edges of the inlet and outlet weirs, both above and below the tray (weir sides, weir pan bottom, edges immediately above and below the tray).

- g. **Note that no leaks, dripping, seeping or sweating is allowed!** Mark any of these defects for repair with a crayon or chalk.
- h. Unplug the downcomer and the weir weep hole to drain all the water.
- i. Repair any and all leaks found as marked per UOP recommendations. Repeat from Step 4 upon the completion of the repairs until no leaks, dripping, seeping or sweating are evident.
- j. Remove the downcomer blind plates.
- k. Ensure that the trays are clean of all debris and/or dirt before proceeding with closing of the tray manways. (Note: When installing the tray manways, verify that the tray manways are correctly installed so as the specified equilateral pitch is maintained across the manway and tray.) A one-piece neoprene gasket should be used for the tray manways.

4. Prewash Caustic Changeout Instructions Using Fresh Caustic

Before beginning caustic preparations, confirm that the condensate or demineralized water and caustic are below 60°C (140°F) and that the steam tracing on these lines are on only if necessary to prevent freezing. Caustic embrittlement begins at 65°C (150°F) and will cause excessive corrosion if allowed above this temperature for an extended amount of time.

- a. Take a sample of the caustic in the Caustic Prewash Vessel via the provided Sample Station. If the caustic is between 50-70% spent or if H₂S breakthrough is occurring, then a caustic changeout is necessary.
- b. Verify that the globe valve on the caustic filling line is closed. The gate and globe valves on this line to the Extractor should also be closed.
- c. Verify that the gate and globe valves on the caustic transfer line are closed.

- d. Confirm that the Spent Caustic Degassing Drum level glass and level transmitter are ready for servicing.
- e. Prepare to operate one of the Spent Caustic Pumps by opening the isolation valves to one of the pumps. Verify that the automatic on/off switch is ready for servicing. This switch should turn the pump on at a high level (i.e. 80%) in the Spent Caustic Degassing Drum and should turn the pump off at a low level (i.e. 20%).
- f. Make sure the Spent Caustic Disposal System is ready to receive caustic.
- g. Make sure the 2" gate valve on the Spent Caustic Degassing Drum outlet line to the open drain is closed.
- h. Slowly open the gate valve to the top inlet distributor and close the bottom, gate valve. This switches the direction of the flow to minimize entrained LPG exiting with the caustic.
- i. Open the gate valve at the bottom of the Caustic Prewash.
- j. Begin to send caustic to the Spent Caustic Degassing Drum by slowly opening the gate and globe valves on the waste transfer line.
- k. Watch the level in the Caustic Prewash carefully. When the Caustic Prewash level has decreased to approximately **30%** of the vessel, or **300 mm (1 foot) above the top inlet distributor**, close the gate and globe valves on the waste caustic transfer line. Do not drain the level below the top inlet distributor to avoid losing the contact between hydrocarbons and caustic, which would result in H₂S carry over to the Extractor, especially when very high levels of H₂S are present in the feed. Control the flow by taking ½ of the pressure drop across the globe valve and the rest across the restriction orifice.

- l. Prepare to add caustic to the Caustic Prewash vessel by opening the gate valve on the caustic inlet line. Make sure the Water Break Tank is isolated at the outlet before opening this valve!
- m. Open the globe valve on the caustic filling line to the Caustic Prewash.
- n. Start the Water/Caustic Addition Pump (if provided) and begin transferring caustic to the Caustic Prewash Vessel. Fill caustic to below 50% of the vessel. Watch this addition carefully to avoid filling the Caustic Prewash too quickly and/or too high and risk causing caustic to carryover into the Extractor.
- o. Ultimately, the *total* aqueous solution height in the Caustic Prewash should be **at** 50% of the vessel. However, if the caustic supply concentration is greater than 10 wt% (15° Bé), caustic should be added to **below** 50% to allow for the volume of water which will be added to reduce the combined caustic strength in the Caustic Prewash to 5-10 wt% (8-15° Bé). If the fresh caustic concentration is within 5-10 wt%, additional water will not be necessary and the caustic can be added to 50% of the vessel.
- p. When the level is below 50% of the Caustic Prewash vessel, stop the Water/Caustic Addition Pump and close the gate valve on the caustic inlet line.
- q. If the caustic supply concentration is greater than 10 wt% (15° Bé), water will have to be added to dilute the caustic. Prepare to add water to the Caustic Prewash by lining up the water to the Water/Caustic Addition Pump.
- r. Start the Water/Caustic Addition Pump and begin transferring water to the Caustic Prewash Vessel. Add water up to 50% of the vessel. (This level should be marked on the level glass.) Watch this addition carefully, so as not to add too much water and dilute the caustic or risk having caustic carryover into the Extractor due to a high caustic level.

- s. When the level is **at** 50% of the Caustic Prewash vessel, stop the Water/Caustic Addition Pump and close the gate valve on the outlet line from the Water Break Tank.
- t. Close the globe valve on the caustic filling line.
- u. Close the filling/draining gate valve at the bottom of the Caustic Prewash.
- v. Slowly open the gate valve on the lower inlet distributor. Close the gate valve on the upper inlet distributor.
- w. The LPG flow through the lower inlet distributor will help to further mix the caustic solution. Wait 2 hours and sample the prewash caustic for total alkalinity. The target caustic concentration is 5-10 wt% (8-15° Bé). If the total alkalinity is greater than 10 wt%, add more water. If more water is needed, it will be necessary to drain some of the prewash caustic before adding more to avoid overfilling. Do not operate the Caustic Prewash vessel with a level greater than 50% to avoid the risk of having caustic carryover into the Extractor.

5. Prewash Caustic Changeout Instructions Using Regenerated Caustic

In order to utilize the caustic in the unit to its fullest extent, the regenerated caustic, which is typically less than 10% spent, can be transferred and used in the Caustic Prewash when changeout of the prewash caustic is necessary. This prewash caustic can then be further used until the caustic is 50% spent (70% maximum). Note that the prewash caustic should not be changed out until the percent spent is 50-70%. If other considerations require that the regeneration caustic be changed out, remove only enough caustic from the Caustic Prewash to accommodate the quantity of caustic that will be removed from the Extractor and regeneration section, without having to add fresh caustic to the Caustic Prewash. This will minimize the overall caustic consumption.

While similar to the Prewash Caustic Changeout Instructions Using Fresh Caustic, deviations do exist that should be noted. These include 1) The required dilution of the caustic prewash due to the higher regeneration caustic concentration, 2) Preparation and careful monitoring of the regeneration section during the transfer, 3) Addition of fresh caustic to the regeneration section to make-up caustic loss to the prewash, 4) Addition of Merox WS catalyst to adequately concentrate the fresh caustic added to the circulating caustic. The procedures that follow outline this method. **Please note:** Due to the sulfidic nature of the prewash caustic, the prewash caustic *cannot* be used in the regeneration section!

Before beginning caustic preparations, confirm that the condensate or demineralized water and caustic are below 60°C (140°F) and that the steam tracing on these lines are on only if necessary to prevent freezing. Caustic embrittlement begins at approximately 65°C (150°F) and will cause excessive corrosion if allowed above this temperature for an extended amount of time.

- a. Take a sample of the caustic in the Caustic Prewash Vessel via the provided Sample Station. If the caustic is between 50-70% spent or if H₂S breakthrough is occurring, then a caustic changeout is necessary.
- b. Verify that the globe valve on the caustic filling line is closed. The gate and globe valves on this line to the Extractor should also be closed.
- c. Verify that the gate and globe valves on the caustic transfer line are closed.
- d. Confirm that the Spent Caustic Degassing Drum level glass and level transmitter are ready for servicing.
- e. Prepare to operate one of the Spent Caustic Pumps by opening the isolation valves to one of the pumps. Verify that the automatic on/off switch is ready for servicing. This switch should turn the pump on at a high level (i.e. 80%) in the Spent Caustic Degassing Drum and should turn the pump off at a low level (i.e. 20%).

- f. Make sure the Spent Caustic Disposal System is ready to receive caustic.
- g. Make sure the 2" gate valve on the Spent Caustic Degassing Drum outlet line to the open drain is closed.
- h. Slowly open the gate valve to the top inlet distributor and close the bottom, gate valve. This switches the direction of the flow to minimize entrained LPG exiting with the caustic.
- i. Open the gate valve at the bottom of the Caustic Prewash.
- j. Begin to send caustic to the Spent Caustic Degassing Drum by slowly opening the gate and globe valves on the waste caustic transfer line.
- k. Watch the level in the Caustic Prewash carefully. When the Caustic Prewash level has decreased to approximately **30%** of the vessel, or **300 mm (1 foot) above the top inlet distributor**, close the gate and globe valves on the waste caustic transfer line to isolate the Caustic Degassing Drum. Do not drain the level below the top inlet distributor to avoid losing the contact between hydrocarbons and caustic, which would result in H₂S carry over to the Extractor, especially when very high levels of H₂S are present in the feed. Control the flow by taking ½ of the pressure drop across the globe valve and the rest across the restriction orifice.
- l. Open the gate valve on the caustic transfer line to the Caustic Prewash.
- m. Prepare to transfer lean caustic from the Caustic Circulation Pumps by opening the gate valve on the caustic transfer line from the Circulation Pumps.
- n. Slowly open the globe valve on the caustic transfer line and slowly begin transferring lean caustic from the Regeneration Section to the Caustic Prewash. NOTE: To avoid decreasing the lean caustic flow to the top of the Extractor, it may be necessary to either start the spare Caustic Circulation

Pump or to close the minimum flow spillback, if present. **The extractor level should be watched very carefully during this step!** When the Extractor level reaches 20%, caustic transfer to the Caustic Prewash should be stopped and the globe valve on the caustic transfer line from the Caustic Circulation Pumps closed. Also close the gate valve on the caustic transfer line. (Confirm that a level of 20% will not interfere with the Low Level Shut Off Valve on the Extractor outlet line.)

- o. While transferring caustic from the Regeneration Section into the Caustic Prewash, the Caustic Prewash level should also be monitored. Caustic should be filled to below 50% of the height of the Caustic Prewash vessel, however the Extractor level will more likely reach 20% before the Caustic Prewash level reaches below 50%. Watch the caustic transfer carefully to avoid filling the Caustic Prewash too quickly and/or too high and risk causing caustic to carryover into the Extractor.
- p. Ultimately, the *total* aqueous solution height in the Caustic Prewash should be **at** 50% of the vessel. However, caustic should be added to **below** 50% to allow for the volume of water which will be added to reduce the combined caustic strength in the Caustic Prewash to 5-10 wt% (8-15° Bé).
- q. If the Extractor level reaches 20% before the Caustic Prewash level reaches 50%, as expected, fresh caustic will need to be added to top off the prewash caustic level.
- r. Prepare to add fresh caustic to the Caustic Prewash vessel by opening the gate valve on the fresh caustic inlet line. Make sure the Water Break Tank is isolated at the outlet before opening this valve!
- s. Start the Water/Caustic Addition Pump (if provided) and begin transferring caustic to the Caustic Prewash Vessel. Fill caustic to below 50% of the vessel. Watch this addition carefully to avoid filling the Caustic Prewash too quickly and/or too high and risk causing caustic to carryover into the Extractor.

- t. When the appropriate level is reached in the Caustic Prewash vessel, stop the Water/Caustic Addition Pump and close the gate valve on the fresh caustic inlet line.
- u. Since the regeneration caustic and fresh caustic supply concentrations are usually greater than 10 wt% (15° Bé), water may have to be added to dilute the caustic. Prepare to add water to the Caustic Prewash by lining up the water to the Water/Caustic Addition Pump.
- v. Start the Water/Caustic Addition Pump and begin transferring water to the Caustic Prewash Vessel. Add water up to 50% of the vessel. (This level should be marked on the level glass.) Watch this addition carefully, so as not to add too much water and dilute the caustic or risk having caustic carryover into the Extractor due to a high caustic level.
- w. When the level is at 50% of the Caustic Prewash vessel, stop the Water/Caustic Addition Pump and close the gate valve on the outlet line from the Water Break Tank.
- x. Close the globe valve on the caustic filling line.
- y. Close the filling/draining gate valve at the bottom of the Caustic Prewash.
- z. Slowly open the gate valve on the lower inlet distributor. Close the gate valve on the upper inlet distributor.

The LPG flow through the lower inlet distributor will help to further mix the caustic solution. Wait 2 hours and sample the prewash caustic for total alkalinity. The target caustic concentration is 5-10 wt% (8-15° Bé). If the total alkalinity is greater than 10 wt%, add more water. If more water is needed, it will be necessary to drain some of the prewash caustic before adding more to avoid overfilling. Do not operate the Caustic Prewash vessel with a level greater than 50% of the height of the vessel to avoid the risk of having caustic carryover into the Extractor.

The Extractor level will need to be replenished with fresh caustic. This can be accomplished by the following procedures:

- a. Open the gate valve completely and crack open the globe valve on the caustic filling line to the Extractor.
- b. Prepare to add fresh caustic to the Extractor by opening the gate valve on the fresh caustic inlet line. Make sure the Water Break Tank is isolated at the outlet before opening this valve!
- c. Start the Water/Caustic Addition Pump (if provided) and **slowly** begin transferring fresh caustic to the Extractor. Fill caustic to 50% of the surge volume, as seen on the level glass. Watch this addition carefully to avoid filling the Extractor too quickly and/or too high and risk causing caustic to carryover. The addition rate can be controlled using the globe valve on the caustic transfer line. **Note: If the addition rate is much above 10 vol% above the hydrocarbon rate, the tray seal may be broken and massive caustic carryover will occur.**
- d. Depending on the strength of the regeneration caustic, the strength of the fresh caustic supply and the quantity of caustic added, water may have to be added to dilute the regeneration caustic. (Note that if water will have to be added, the caustic should be filled accordingly so the total aqueous solution height is approximately 50%.) Prepare to add water to the Extractor by lining up the water to the Water/Caustic Addition Pump.
- e. Open the gate and globe valves on the caustic filling line at the Extractor.
- f. Start the Water/Caustic Addition Pump and begin transferring water to the Extractor. Add water up to 50% of the surge volume. (This level should be marked on the level glass.) Watch this addition carefully, so as not to add too much water too quickly and dilute the caustic or risk having caustic carryover.

- g. When the level is at 50% of the Extractor surge volume, stop the Water/Caustic Addition Pump and close the gate valve on the outlet line from the Water Break Tank.
- h. Close the globe and gate valves on the caustic filling line at the Extractor.
- i. Finally, Merox Reagent WS catalyst should be added to the system to concentrate the estimated fresh caustic/water addition to the targeted 200 wppm, which is equivalent to 2 pounds (or 0.24 kilograms) of Merox WS per 1000 gallons of fresh caustic solution.

The ideal, targeted Extractor level is 50%. While maintaining an Extractor level of 80% would allow for the maximum amount of caustic to be removed/changed out from the regeneration system, refiners with high mercaptan levels in the feed should be cautious of maintaining this high of a level! High mercaptan levels in the feed will form water upon contact with the caustic and will dilute the regeneration caustic, quickly increasing the Extractor level to potentially above the sight glass. This would require the removal of caustic from the regeneration section so the Extractor level can be properly monitored. Further, this Extractor surge level will drastically change with large hydrocarbon flowrate changes. Based on experience, refiners should determine the optimum Extractor level that best accommodates the dilution effect of the particular unit and the stability (or instability) of the hydrocarbon flowrate.

6. Sand Filter Loading Instructions

Prior to starting the loading the Sand Filter, confirm that a sufficient amount of **8-16 mesh** quartz silica sand is available for loading.

- a. Verify that the vessel is completely blinded and isolated.
- b. Verify that the line leading to and from the level glass are closed.
- c. After the Sand Filter is mechanically complete, open the top manway.
- d. Verify that the Sand Filter is clean inside and that no garbage is on the grid.

- e. Tightly cover the distributor slot with a plastic tarp or other suitable material to prevent sand from entering the distributor.
- f. Begin adding sand from the side manway. Add enough sand to cover the support by 2 to 4 inches. Confirm that the sand has not leaked through.
- g. Once the support has been determined to be stable, perform a final closure on the side manway and continue loading sand from the top manway. Level the sand once the sand nears the top and measure the distance from the middle of the distributor to the top of the bed.
- h. Fill the sand until the level top of the bed is **450 mm (18")** below the *center* of the distributor, or as specified in the vessel drawing of the Schedule A. Make sure the bed is leveled well.
- i. When the loading is completed, uncover the distributor and close the top manway with the proper gasket installed.
- j. Note the quantity of sand loaded for future reference and complete the loading diagram.

7. Sand Filter Unloading Precautions

When a reduction in the pressure drop across the sand filter cannot be achieved via a backwash, or when the frequency of backwashing becomes impractical, then the sand in the Sand Filter will have to be replaced. Prior to removing the sand from the vessel, safety considerations recommend that a backwash be performed to remove any caustic and/or residual hydrocarbon from the sand before handling. After sufficiently backwashing the sand, the side and top manways can be opened for manual and/or pneumatic removal of the sand.

8. Oxidizer Loading Instructions

Prior to starting loading the Oxidizer, confirm that a sufficient amount of **40 mm (1½") Diameter Carbon Raschig Rings** are available for loading.

- a. Verify that the Oxidizer is completely blinded and isolated, except for the drain.
- b. Verify that a final closure has been performed on the 8" blankoff on the Oxidizer.
- c. Install a blind at the gate valve on the pumpout line from the Oxidizer to the Caustic Circulation Pumps.
- d. Verify that the gate valve on the Oxidizer bottoms line to the open drain is closed.
- e. After the Oxidizer is mechanically complete, open the top manway (or top head).
- f. Verify that the Oxidizer is clean inside and that no garbage was left in the vessel or drain. Check the nozzle weld bars.
- g. Fill the Oxidizer with clean water (meets Merox water quality standards) until the level is just below the neck of the manway.
- h. Carefully begin adding the Raschig Rings through the manway, minimizing the amount of rings that are broken, and maintaining a water level just below the neck of the manway.
- i. Fill the Oxidizer with Raschig Rings to a level flush with the flange, making sure the entire vessel is filled and avoiding a coning effect.

- j. When the loading is completed, drain the water. After all the water is removed, the level may fall and more rings may need to be added to maintain the level flush with the flange.
- k. Fill the bed again and then rinse the bed of fines.
- l. When finished draining the vessel of water, close the manway. Verify that the 2" utility connection on the Oxidizer outlet is closed.

9. Oxidizer Unloading Precautions

When the refiner wishes to open the Oxidizer for maintenance and/or inspection purposes, care must be taken to remove any hazardous chemicals and or hydrocarbons prior to opening the vessel. UOP recommends that the vessel and internals be very thoroughly rinsed with water to flush out the caustic (most simply indicated by a reduction in pH of the waste water). Only after full safety procedures have been followed, should the side and top manways be opened for removal of the raschig rings.

10. Disulfide Separator Loading Instructions

Prior to starting the loading of the Disulfide Separator, confirm that a sufficient amount of screened **4-8 Mesh Anthracite Coal** and **40 mm (1½") Diameter Carbon Raschig Rings** are available for loading. The coal may need to be screened at site if it contains lots of fines.

- a. Verify that the following vessel blinds are installed:
 - Vessel Inlet Line Flange.
 - At the gate valve on the Oxidizer pumpout line to the Caustic Circulation Pumps.
 - Stack outlet equalization line to/from the Disulfide Sand Filter.
 - Main Body disulfide outlet/level glass line at the top of the vessel.
 - Main Body level glass, lower nozzle connection to vessel.

- b. Verify that the lines leading to and from the Separator Stack level glass and level transmitter are closed. Isolate the main body level glass.
- c. Verify that the isolation valves around the flow control valve for the caustic inlet to the Extractor are closed.
- d. Close the two gate valves on the Caustic Circulation Pumps discharge minimum flow line to the Disulfide Separator.
- e. Confirm that the 2" gate valve from the Disulfide Separator to the open drain is closed.
- f. Verify that the Circulating Caustic Sampling Station is closed.
- g. Confirm that the Caustic Circulation Pumps are valve isolated at the suction and discharge.
- h. After the Disulfide Separator is mechanically complete, open the top and side manways.
- i. Verify that the Disulfide Separator is clean inside and that no garbage was left in the vessel. Inspect internal screens.
- j. Perform a final closure with the proper gasket on the side manway.
- k. Confirm that a final closure with the proper gasket has been performed on the 6" unloading blankoff on the bottom of the coalescing zone.
- l. Fill the Separator with clean water until the level is approximately 200-300 mm (8-12 in) below the neck of the manway.
- m. Carefully begin adding the coal through the manway, maintaining a water level just below the neck of the manway. Drain water as necessary to keep a level just below the neck of the manway.

- n. Special attention should be given to getting an even bed of coal to the top. It is critical that the area in the upper corners are also filled with coal. This can be done using a clean, long wooden plank to push the coal in the corners. No void areas should be present anywhere in the coalescing zone. Be careful: If you push too hard, you may rupture that support screen.
- o. To account for settling, fill the neck of the manway completely, flush with the flange.
- p. When the loading is completed, drain the water through the drain at the separator bottoms outlet line. Make sure any lines that were inadvertently filled with water are also drained. After all the water is removed, the level may fall and more coal may need to be added. For vessels with a diameter larger than 5 feet, refill the main body portion of the vessel with water again and drain quickly. If level of coal slumps again, add more coal.
- q. Perform a final closure on the manway with the proper gasket.
- r. Open the manway at the top of the Separator Stack. Make sure that the packing support is in place. Check the nozzle weld bars.
- s. Fill the stack with Raschig Rings as high as possible without interfering with the closure of the manway.
- t. Perform a final closure on the manway with the proper gasket.

11. Disulfide Separator Unloading Precautions

When the refiner wishes to open the Disulfide Separator for maintenance and/or inspection purposes, care must be taken to remove any hazardous chemicals and or hydrocarbons prior to opening the vessel. UOP recommends that the vessel and internals be very thoroughly rinsed with water to flush out the caustic (most simply indicated by a reduction in pH of the waste water). Only after full safety procedures

have been followed, should the side and top manways be opened for removal of the anthracite coal and raschig rings.

12. Vent Tank Loading Instructions

Prior to starting the loading of the Vent Tank, confirm that a sufficient amount of **25 mm (1") diameter Carbon Steel Raschig Rings** is available for loading.

- a. Verify that the following vessel blinds are installed:
 - Vessel Inlet Line Flange
 - Vessel Drain Line Flange
- b. Verify that the lines leading to and from the level glass are closed.
- c. After the Vent Tank is mechanically complete, open the top manway. Check the nozzle weld bars.
- d. Verify that the Vent Tank is clean inside and that no garbage is on the support grid.
- e. Make sure that the packing support is in place.
- f. Fill the Vent Tank Drum with Raschig Rings as high as possible without interfering with the closure of the manway.
- g. Level the Raschig Rings and close the top manway.
- h. Note the quantity of raschig rings loaded for future reference and complete the loading diagram.

13. Disulfide Sand Filter Loading Instructions

Prior to starting the loading the Disulfide Sand Filter, confirm that a sufficient amount of quartz silica **8-16 mesh** sand is available for loading.

- a. Verify that the following vessel blinds are installed:
 - Vessel Inlet Line Flange
 - Vessel Outlet Line Flange
 - Vessel Drain Line Flange
 - Vessel Outlet to Top of Disulfide Separator
- b. Verify that the lines leading to and from the level glass are closed.
- c. After the Disulfide Sand Filter is mechanically complete, open the top manway.
- d. Verify that the Disulfide Sand Filter is clean inside and that no garbage is on the grid.
- e. Tightly cover the distributor slot with a plastic tarp or other suitable material to prevent sand from entering the distributor.
- f. Begin adding sand. Add enough sand to cover the support by 2 to 4 inches. Confirm that the sand has not leaked through.
- g. Once the support has been determined to be stable, perform a final closure on the side manway and continue loading sand from the top manway. Level the sand once the sand nears the top and measure the distance from the middle of the distributor to the top of the bed.
- h. Fill the sand until the level top of the bed is approximately **70 mm (3")** below the *center* of the distributor, or as specified in the vessel drawing of the Schedule A. Make sure the bed is leveled.

- i. When the loading is completed, uncover the distributor and close the top manway with the proper gasket installed.
- j. Note the quantity of sand loaded for future reference and complete the loading diagram.

XIV. SAFETY

All of the ordinary rules of safety in refinery operation apply to the operation of the Merox process. Safe petroleum refinery practices are thoroughly discussed in voluminous safety literature published by the American Petroleum Institute, National Safety Council, Manufacturing Chemists' Association, National Fire Protection Association, and other such organizations.

All employees and persons responsible for operation of the Merox process should be experienced in petroleum refinery operating techniques and should be familiar with applicable safety practices. All necessary precautions should be taken to avoid accidents. Employees should be instructed as to the use of steam snuffing lines, shutting off air supply and other means of extinguishing combustion. The licensee should ascertain for himself that the unit meets his own safe practices code.

A. INTERNAL FIRE

The presence of air and hydrocarbons in Merox Process equipment, particularly the disulfide separator and the excess air vent line, is not considered to be any more hazardous than other situations in refineries in which air and hydrocarbon vapors exist, such as: in copper sweetening units, vapor space in storage tanks (including fuel tank on vehicles), venting of air during filling of equipment with hydrocarbon, etc.

As previously discussed, precautionary devices to prevent destructive combustion in the disulfide separator have been built into the unit, and it is believed that all necessary precautions have been taken to avoid accidents. However, employees should be given instructions as to use of steam snuffing lines, shutting off air supply, and other means of extinguishing combustion inside the equipment should ignition take place. The Licensee should ascertain for himself that the unit meets his own safe practices code.

B. CHEMICALS

1. Caustic Soda

Refer to the appropriate safety bulletin published by the National Safety Council or the Manufacturing Chemists' Association.

Caustic solution, commonly called lye, and technically known as sodium hydroxide (NaOH) is used so widely in petroleum refining that its potential hazards are often carelessly overlooked. The Merox process does not employ hot caustic solutions and therefore is potentially less dangerous than other types of treating units.

Goggles or face shields should be worn at all times in the processing area.

Painful injury and possibly blindness can result if caustic reaches the eyes. A bubbler fountain should be provided for the purpose of washing the eyes if an accident should occur. Boric acid solution should be available for first aid, after washing the injured eye with copious quantities of water. All eye injury cases, however slight, should be referred to a physician.

Workmen should be impressed with the fact that caustic does not give immediate warning of its presence on the skin by burning or irritation as in the case of many other chemicals. A severe burn can result from caustic before the individual realizes its presence on the skin. However, the presence of caustic on the skin before a burning sensation develops can be recognized by its slippery, soapy feeling or by its testing with a 1% solution of phenolphthalein which will turn pink when applied to contaminated areas. A physician should be consulted in the case of a severe skin burn. Some refiners keep a tub of diluted vinegar handy to neutralize caustic on tools, rubber gloves, etc., after washing in water.

Workmen should be instructed to wear, in addition to face shields or goggles, rubber gloves and rubber aprons when performing any work which exposes them to caustic. Depending upon conditions, it may be advisable to wear protective rubber footwear, as caustic is destructive to leather. Incidentally, cotton material is more

resistant to caustic than wool and therefore is preferable for clothing although it should not be considered as a protective material.

When caustic has come in contact with the skin, the area should be immediately flushed with water for several minutes, and depending upon the severity of the exposure, this can be followed by a two percent acetic acid (vinegar) wash to neutralize any traces of caustic. Facilities for quick action water-washing should be available. A treadle operated safety shower equipped with a quick opening valve should be installed in the area. In cold seasons provisions should, of course, be made to supply the shower with warm water.

2. Catalyst/Reagents

Merox catalysts and reagents have been used by the petroleum industry for over 25 years without any known adverse human health hazards. However, as with most industrial chemicals, inhalation and ingestion are to be avoided. Eye injury and skin irritation may occur if contacted areas are not immediately and thoroughly washed.

Please refer to the Merox Reagents and Catalysts Material Safety Data Sheets in the Appendix for information regarding safety and handling.

3. H₂S

Hydrogen sulfide is an extremely toxic and dangerous gas. It has been responsible for fatalities among refinery workers and must be treated with respect at all times. While this is not meant to be a course in refinery safety, it is important to emphasize a few of the reasons why H₂S is so insidious:

- While H₂S has a very obnoxious odor, this odor is not a good indication of dangerous concentrations because the olfactory sense is easily fatigued, and it is possible that after a short exposure the H₂S will no longer be detectable by odor.

- H_2S acts to paralyze the nerves controlling involuntary muscle activity. Thus, a single inhalation of a high concentration can cause death from asphyxiation due to paralysis of the muscles controlling breathing.

4. Disulfide

Disulfides are high boiling oily organic liquids having a specific gravity from 0.95 to 1.06, depending on the molecular weight. They have an obnoxious odor resembling onions. There is very little data available on their dangerous properties. They may cause skin irritation and therefore should not be allowed to contact the skin. It is unlikely that any would be taken internally because of the obnoxious odor. They are insoluble in water but may be washed off the skin with warm water and a good detergent. In no case should a worker continue to wear clothing that has become wetted with disulfide. While it is believed that disulfides are not particularly dangerous, prudence dictates that they be treated with the same precaution as carbon disulfide. Human contact and breathing of vapors should be avoided.

XV. EQUIPMENT EVALUATION

During a scheduled shutdown of the unit, there are several vessels and/or pieces of equipment of which the integrity should be inspected and proven to be according to specifications. The following is a list of recommended inspections to be completed, not including specific standard refinery practices.

These suggestions for unit inspection and maintenance assume complete unit shutdown, isolation and preparations for vessel openings and inspection. This includes feed flow shutdown, unit and vessel isolation, hydrocarbon, caustic and amine drainage, and isolated and blinded pressure safety valves.

A. AMINE ABSORBER

If a trayed Amine Absorber is present in the unit, all of the trays in the Amine Absorber (including both the inlet and outlet weirs) should be releak-tested and confirmed to be leak tight. Any and all leaks found should be eliminated via seal welding and confirmed to have been eliminated with another leak test. Please note that this may require the vessel to be re-post weld heat treated. Failure to eliminate any leaks will reduce the efficiency of the absorber, encourage excessive amounts of hydrogen sulfide to be directed to the Merox Unit, which will cause numerous problems, primarily amine carry over and a significantly increased caustic consumption.

B. CAUSTIC PREWASH

The mesh blanket in the Caustic Prewash should be inspected and confirmed to be in good condition and well secured. There should not be any gaps in the mesh blanket that would allow any entrained sulfidic caustic to be carried out with the hydrocarbon and into the Extractor, thus lowering the quality of the circulating caustic.

C. EXTRACTOR

All of the trays in the Extractor (including both the inlet and outlet weirs) should be re-leak tested and confirmed to be liquid tight. Any and all leaks found should be eliminated via seal welding and confirmed to have been eliminated with another leak test. Please note that this may require the vessel to be re-post weld heat treated. Failure to eliminate any leaks will reduce the efficiency of the Extractor, causing increased sulfur levels in the product and possibly failure to meet product specifications, in addition to massive caustic carryover.

D. DISULFIDE SEPARATOR

If time allows, the Disulfide Separator should be completely emptied of anthracite coal so the support mesh can be inspected to ensure no holes have developed that would allow migration of the coal. Please note that excessive handling of the anthracite coal will require the coal to be screened for fines removal. If time does not allow for coal removal, then at the minimum, the top of the coal bed should be checked to ensure that no slumpage has occurred, adding coal to the lip of the loading manway, if required. If coal slumpage has occurred and is not quickly rectified by adding more coal, disulfide oil will not coalesce out of the caustic, but will remain in the lean caustic that is directed back to the extractor. This ultimately will cause high total sulfur content in the product. This is a very important step in the inspection process, and is especially critical for very large (i.e. main body greater than 8 feet in diameter) disulfide separators and indicates how well the initial loading of the coal was performed.

The packing in the stack should also be inspected to be in good condition. This is a very corrosive environment, which could corrode the packing and require replacement. Replacement packing should always be available during the inspection.

E. SAND FILTER

If time allows the Sand Filter should be completely emptied of sand so the support grid can be inspected to be in good condition, capable of supporting the sand while preventing sand migration. If time does not allow for sand removal, it is recommended that the sand at least be backwashed. This will clean the bed of any contaminants or impurities that have accumulated in the bed and may cause an increased pressure drop. Completing a backwash during the schedule shutdown will minimize the potential for necessitating a backwash during normal operations. The top of the sand bed should also be inspected, the top 3 or 4 inches removed if heavily contaminated and topped off, if necessary.

F. OXIDIZER

The carbon rings in the Oxidizer should be inspected and topped off, if necessary. Please note that if the raschig rings are to be removed from the Oxidizer, they will have to be done carefully to avoid breakage. Otherwise they will have to be replaced. The weld bars on the top manway and the broken ring trap at the bottom of the vessel should also be verified to be in good condition.

G. DISULFIDE SAND FILTER

If time allows, the Disulfide Sand Filter should be completely emptied of sand so the support grid can be inspected to be in good condition, capable of supporting the sand while preventing sand migration. If time does not allow for sand removal, it is recommended that the sand at least be backwashed. This will clean the bed of any contaminants or impurities that have accumulated in the bed and may cause an increased pressure drop. Completing a backwash during the schedule shutdown will minimize the potential for necessitating a backwash during normal operations. The top of the sand bed should also be inspected, the top 3 or 4 inches removed if heavily contaminated and topped off, if necessary.

H. SPECIAL CHECK VALVE

The special check valve should be removed for cleaning and inspection to ensure that the check valve is in good working condition. This will prevent contamination of the air injection line with caustic during a low air flow and/or pressure situation. In addition, the filters upstream the air control valve should be pulled and cleaned.

I. FLAME / DETANATION ARRESTOR

The flame or detonation arrestor(s) on the spent air line should be removed for cleaning and inspection to ensure that it is good, working condition.

J. PUMPS

All pump strainers, especially the Caustic Circulation Pump strainer, should be pulled and cleaned.

K. LINE AND VESSEL FLUSHING

During the extended shutdown, all vessels and lines should be very thoroughly flushed. Stagnant, non-flowing caustic has a tendency to dry out and salt up, which will plug lines (especially smaller instrument lines), coat and possibly damage pump seals, and possibly plug holes in distributors and trays.