ASSOCIATED WASTE REPORT:

DEHYDRATION AND SWEETENING WASTES

January 2000

U.S. Environmental Protection Agency
Office of Solid Waste
Ariel Rios Building
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460

DISCLAIMER

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1.0 INTRODUCTION

1.1 BACKGROUND

In Section 3001(b)(2)(A) of the 1980 Amendments to the Resource Conservation and Recovery Act (RCRA), Congress conditionally exempted several types of solid wastes from regulation as hazardous wastes. Among the categories of wastes exempted were "drilling fluids, produced waters, and other wastes associated with the exploration, development, and production of crude oil or natural gas…" RCRA Section 8002(m) required the Administrator of the U.S. Environmental Protection Agency (EPA) to study these wastes and submit a report to Congress evaluating the status of their management. The Amendments also required the Administrator to determine whether to propose regulations under RCRA Subtitle C if it was determined that the wastes should be regulated as hazardous wastes. In July of 1988, the Agency completed the above-described activities, and reached a determination that regulation under Subtitle C was not warranted and that the wastes could be appropriately controlled through improvements to existing State and Federal regulatory programs (53 FR 25446). Among those exploration and production (E&P) wastes exempted from regulation as hazardous wastes are "gas plant dehydration wastes…" and "gas plant sweetening wastes…"

On March 22, 1993, EPA provided clarification on the scope of the E&P exemption with respect to wastes generated by crude oil reclaimers, service companies, gas plants and feeder pipelines, and natural gas storage fields (58 FR 15284). The FR notice did not change the scope of the E&P exemption; instead it clarified the existing regulatory status of wastes generated from these operations. With respect to gas plants, EPA stated that even though custody of the gas may change between the wellhead and the gas plant, removal of impurities (e.g., water, H_2S, CO_2) from the gas is a necessary part of production. Therefore, wastes that are uniquely associated with the gas production stream and are generated at gas plants, including feeder pipelines, are considered exempt wastes even if a change in custody of the gas has occurred between the wellhead and the gas plant. Also, since removal of sulfur from H_2S is considered treatment of an exempt waste similar to crude oil reclamation, residual waste derived from the H_2S remains exempt. Similarly, EPA stated that operations to store and recover natural gas from underground storage fields and the wastes generated from these operations are similar to those of production operations. Hence, wastes uniquely associated with operations to recover natural gas from underground storage fields are exempt just as if the gas were being produced for the first time.

Currently, EPA is in the process of developing reports on various wastes that are associated with the exploration, development, and production of crude oil or natural gas that are exempt from regulation as hazardous wastes under Subtitle C of RCRA. Initially, EPA has focused on evaluating three groups of associated wastes: crude oil tank bottoms and oily debris, dehydration and sweetening wastes, and completion and workover wastes. The purpose of these papers is to provide a better understanding of the wastes and their management. This report addresses dehydration and sweetening wastes. Section 1.2 below provides an overview of natural gas conditioning activities, followed by a discussion of the scope of wastes to be addressed in this report. Chapter 2 describes dehydration and sweetening processes and the wastes which may result from such operations. Chapter 3 describes waste management practices used for dehydration and sweetening wastes, while Chapter 4 provides an overview of the types of waste minimization and pollution prevention techniques that may be applicable to gas dehydration and sweetening operations. Finally, Chapter 5 presents a brief summary and conclusions.

1.2 OVERVIEW OF NATURAL GAS OPERATIONS

The total annual on-shore production of natural gas in 1994 was 17.1 trillion cubic feet (U.S. DOE, 1995). Once thought of as an inconvenient co-product of oil production, this flammable gas was generally flared (burned) to the atmosphere near the wellhead to eliminate the threat of explosion (Ikoku, 1984). Today natural gas provides roughly 25 percent of all U.S. energy consumption (U.S. DOE, 1996). Table 1-1 shows the annual production of natural gas, by State, for 1994.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 1-1. On-shore Natural Gas Production, by State, 1994

State	Gross Production (MMcf)		
	From Gas Wells	From Oil Wells	All Wells
Alabama	109,855*	9,528	119,383
Alaska	80,839	2,780,760	2,861,599
Arizona	711	48	759
Arkansas	161,967	33,446	195,413
California	102,461	232,526	334,987
Colorado	187,043*	101,379	288,422
Florida	0	8,468	8,468
Illinois^E	323	10	333
Indiana	107	0	107
Kansas	628,900	85,759	714,659
Kentucky	73,081	0	73,081
Louisiana	1,393,543	159,060	1,552,603
Maryland	26	0	26
Michigan	136,989	91,332	228,321
Mississippi	112,205	9,597	121,802
Missouri	8	0	8
Montana	44,350	6,722	51,072
Nebraska	2,093	805	2,898
Nevada	0	16	16

Associated Waste Report:
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Table 1-1. On-shore Natural Gas Production, by State, 1994

State	Gross Production (MMcf)		
	From Gas Wells	From Oil Wells	All Wells
New Mexico	852,051*	200,041	1,052,092
New York	19,937	539	20,476
North Dakota	19,592	43,640	63,232
Ohio	132,151	0	132,151
Oklahoma	1,626,858	308,006	1,934,864
Oregon	4,200	0	4,200
Pennsylvania[E]	148,763	1,465	150,228
South Dakota	1,000	6,264	7,264
Tennessee	0	1,990	1,990
Texas	4,310,086	1,208,892	5,518,978
Utah	304,347	42,672	347,019
Virginia	50,259	0	50,259
West Virginia[E]	182,000	0	182,000
Wyoming	949,343	121,519	1,070,862
Total, U.S.	11,635,088	5,454,484	17,089,572

* Coal bed methane production reported separately and deducted from total.
** Roughly 88% of Alaska production is used for reservoir repressuring, and receives minimal treatment.
[E] Estimated data
Source: U.S. DOE 1995.

While 33 states currently produce natural gas, the top four on-shore producers, Texas, Oklahoma, Alaska, and Louisiana, account for nearly 70 percent of total U.S. on-shore production. The top eight producers, including New Mexico, Wyoming, Kansas, and California, yield roughly 88 percent of total U.S. on-shore production. Table 1-1 shows that nearly seventy percent, or 11.6 trillion cubic feet, of on-shore natural gas production was from the 287,206 producing gas wells in 30 states. However, approximately 30 percent, or 5.45 trillion cubic feet, is produced as associated gas from crude oil wells in 23 states.

Whether produced from gas wells or oil wells, natural gas is a complex mixture of hydrocarbons and impurities. While methane often makes up the majority of natural gas as sold, in the formation the gas may contain widely varying concentrations of hydrocarbons. Typical hydrocarbon constituents include methane, ethane, propane, butane, and heavier hydrocarbons. Table 1-2 lists common hydrocarbons and impurities of natural gas.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 1-2. Typical Constituents of Natural Gas

Constituents	
Hydrocarbons	**Impurities**
Methane	Inert Gases:
Ethane	Nitrogen
Propane	Helium
Butanes (I- and n-)	Argon
Pentanes (I- and n-)	Hydrogen
Cyclopentane	Oxygen
Hexanes and Heavier HCs	Acid Gases:
	Hydrogen Sulfide
	Carbon Dioxide
	Sulfur Compounds:
	Mercaptans
	Sulfides
	Disulfides
	Water:
	Water Vapor
	Free Water
	Metals:
	Arsenic
	Mercury

Sources: Manning, F. and Thompson, R. *Oilfield Processing of Petroleum: Volume One: Natural Gas*. Pennwell Publishing Company, Tulsa OK, 1991.
Block-Bolten, A. and Glowacki, K. 1989 (June). "Natural Gas Separation From Arsenic Compounds." In: *SPE Gas Technology Symposium Proceedings*, Dallas, Texas. June 7-9, 1989. SPE 19078. Society of Petroleum Engineers, Richardson, TX.
Gijselman, P. 1991 (November). "Presence of Mercury in Natural Gas: An Occupational Health Programme." In: *Meeting Our Global Responsibility. The First International Conference on Health, Safety, and Environment* (Volume 1), Sponsored by the Society of Petroleum Engineers. November 11-14, 1991, The Hague, Netherlands. SPE, Richardson, TX.

Nearly all natural gas contains some water vapor. Further, an estimated 25 percent of natural gas produced in the U.S. contains hydrogen sulfide (H_2S) in concentrations above 4 parts per million (ppm) (EPA, 1983). Both nitrogen and carbon dioxide may be present in gas streams at fairly high levels, reducing the heating value of the gas. In rare instances, mercury and arsenic compounds have been found in production streams (Block-Bolten and Glowacki, 1989; Gijselman, 1991).

Impurities in gas production streams can lead to a number of operational and potential human health and safety problems. Free water and water vapor, for instance, promote the formation of gas hydrates (ice-like crystals) which can partially or completely block flowlines, valves, and gauges (Manning and Thompson, 1991). Further, water may condense and freeze in flowlines under certain temperature/pressure conditions. Acid gases, such as H_2S and CO_2, can cause corrosion within flowlines and process vessels (Maddox, 1985). H_2S also can cause severe health risks due to its high toxicity (Manning and Thompson, 1991).

Due to the undesirable properties of these and other impurities, natural gas may require a number of conditioning processes prior to delivery. Delivery specifications in the U.S. generally specify maximum allowable concentrations of water (or maximum dew point temperature), hydrogen sulfide, mercaptans (organic compounds with an -SH end group), carbon dioxide, oxygen, solids, and free water (Manning and Thompson, 1991). Additional requirements cover minimum pressure, maximum temperature, and gross heating value.

Of the conditioning processes required to meet delivery specifications, dehydration is among the most common. Dehydration is the removal of water vapor from production streams. (Removal of gross amounts of free water is referred to as separation, and is beyond the scope of this report.) All natural gas contains some water vapor (API, 1989). However, the extent of dehydration required for any particular gas stream is not solely a function of its water content. Such factors as temperature, pressure, and hydrate formation temperature and pressure together determine the extent of dehydration necessary.

Conditioning for the removal of acid gases, including H_2S and CO_2, is called sweetening. Typical gas delivery specifications for H_2S and CO_2 are 4 ppm and 1-3%, respectively (Manning and Thompson, 1991). The output of the sweetening process may be elemental sulfur, sulfur salts, or acid gas streams. If sufficiently large amounts of sulfur are present in the gas, recovery of elemental sulfur for sale or disposal may be desirable or required in order to meet air emissions standards. Some sulfur recovery methods are inseparable from the sweetening process, and so will be addressed here as well.

Dehydration and sweetening may each be accomplished through a number of distinct methods. Dehydration methods may include liquid and solid desiccant dehydration, and refrigeration dehydration. Likewise, there are as many as 30 distinct methods of sweetening (Maddox, 1985). Among the more commercially significant methods are amine sweetening, iron sponge sweetening, potassium carbonate sweetening, and physical solvent sweetening. Depending on field location and the level of conditioning required, both sweetening and dehydration may be performed in small field facilities (API, 1989). Alternatively, gas may be conditioned at large central plants receiving product from multiple well fields.

1.3 SCOPE OF WASTES COVERED BY REPORT

Due to the wide variability in treatment methods and facilities, it is very difficult to generalize about the volume and characteristics of dehydration and sweetening wastes. As described below, dehydration and sweetening units may generate numerous waste types which may be found at other oil and gas exploration and production sites. For instance, tank bottoms, separator sludges, produced water, produced sand, spent filter media, and other associated wastes may all appear at dehydration and sweetening sites (API, 1989). Given that such wastes generated at gas conditioning sites may exhibit different characteristics from those generated at other E&P sites (due to contact with the specific conditioning materials), it may be useful to consider these among the general category of dehydration and sweetening wastes. However, the most comprehensive review of associated wastes currently available, the API 1985 Production Waste Survey, employs a very narrow definition of sweetening and dehydration wastes which excludes any waste which may fit another associated waste category. In particular, that study defined sweetening and dehydration wastes to include "...primarily waste glycol and amine," and excluded "...solid or sludge-like waste..."

Due to the general lack of data regarding the volume and characteristics of wastes generated at dehydration and sweetening facilities, this report will focus primarily on those sweetening and dehydration wastes explicitly included in EPA's regulatory determination for exploration and production wastes:

- Gas plant dehydration wastes, including glycol-based compounds, glycol filters, filter media, backwash, and molecular sieves; and,
- Gas plant sweetening wastes for sulfur removal, including amine, amine filters, amine filter media, precipitated amine sludge, iron sponge, and hydrogen sulfide scrubber liquid and sludge.

Such wastes are taken to include analogous wastes generated at field and lease facilities in addition to those generated at gas plants. Further, wastes considered will include spent sweeteners other than amine and iron sponge, condensate from dehydration and sweetening facilities, acid gas flaring wastes, and sulfur recovery wastes. Where data permit, other wastes generated at gas conditioning facilities will be described.

1.4 NEW SOURCES OF DATA

EPA's 1987 *Report to Congress on Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* focused largely on produced water and drilling muds and cuttings, providing limited characterization data for dehydration and sweetening wastes. Further, the 1985 API Associated Waste Survey (at the time the most comprehensive study of oil and gas associated wastes) handled dehydration and sweetening wastes as a single category which explicitly excluded non-liquid wastes (e.g., spent filters) and all centralized gas plant wastes. Accordingly, a major goal of this study was to identify and compile any other publicly available sources of dehydration and sweetening waste characterization and generation/management data to provide EPA with a better understanding of the potential risks posed by management of these wastes.

Several important sources of recent information are referred to frequently in this report: the EPA 1992 Sampling Program Results, the Gas Research Institute (GRI) *Topical Report: Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations*, and the "Natural Gas Industry Production Water and Waste Survey Demographics," a summary of a draft report by GRI on a survey of the gas industry. Each of these sources is described briefly below.

EPA undertook a sampling effort in 1992 to characterize a number of associated wastes, including wastes from dehydration and sweetening. During this effort, EPA intended to collect samples of spent glycol, amine, and caustic; amine sludge; molecular sieve; and possibly other wastes. In practice, EPA collected three lean amine (without entrained sulfur) samples (and two duplicate samples), two lean glycol (without entrained water) samples, two glycol still condensate samples, one rich glycol (water-bearing) sample, and one spent (recycled) caustic sample. With the exception of the glycol still condensate and recycled caustic, these samples were actually of process rather than waste fluids so the analytical results of the amine and glycol samples may not be representative of waste amine and waste glycol. In general, samples of sludges, filters, and molecular sieves were not available at the facilities that could be visited. Additionally, in several instances, health and safety considerations (high concentrations of hydrogen sulfide) precluded collection of some samples of rich glycol and rich amine.

Appendix A presents the analytical data for parameters detected in samples collected during EPA's 1992 sampling effort. Results of analyses of specific waste stream samples are discussed in the following chapters of this report. It should be noted that the process fluid sample results are useful in providing additional data on the potential composition of spent solutions.

The GRI *Topical Report: Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations*, (hereafter referred to as the GRI Study) represents the most extensive source of gas industry waste characterization data compiled to date. Released in 1993, the GRI Study focused on wastes from gas conditioning/processing plants, underground storage operations, and mainline compressor stations. Based on an initial survey of 34 facilities nationwide, GRI identified and prioritized 30 gas industry waste streams for sampling and analysis. The study presents results of 63 samples covering 20 waste categories from 23 facilities in 11 States.

The GRI Study includes some waste streams that may be outside the associated waste universe. For instance, mainline compressor stations have not historically been considered E&P sites since they are associated with transportation, not production. Therefore, wastes generated at these compressor stations are not E&P associated wastes. Prior to EPA's March 1993 clarification notice (58 FR 15284), the status of underground storage sites was similarly unclear. In the clarification notice, EPA stated that since operations and the wastes generated at underground storage sites are analogous to those at field production facilities, underground storage sites are part of E&P. It should also be noted that in the clarification notice, EPA defined transportation for natural gas as "beginning after dehydration and sweetening at a gas plant but prior to transport to market." For example, natural gas liquids (NGL) or natural gasoline that has completed the dehydration and sweetening process and is stored prior to transport to market would be considered the beginning point of transportation. Wastes derived from the product at this point, such as tank bottoms, would not be E&P associated wastes.

Additionally, lubrication oils and other materials explicitly excluded from the special waste exemption are among the wastes sampled. GRI did not consider the regulatory status of the wastes in developing its sampling plan; rather, wastes were ranked according to volume generated, expected/presence of constituents of concern, management techniques, availability of analytical data, and uniqueness to the gas industry. Appendix B provides a description of each of the samples presented in the GRI study.

The GRI Study provides general information on the nature of operations for each site sampled such as the site location, quality of inlet gas streams, process flow diagrams and process descriptions, and locations of sampling points. Waste volumes and waste management information are not presented. Additionally, sampling sites explicitly exclude well-head operations. (GRI developed the study in coordination with API; API has performed a similar study for field exploration and production operations.)

"Natural Gas Industry Production Water and Waste Survey Demographics" (referred to hereafter as Koraido 1993) provides *preliminary* results of a GRI survey of the gas industry. Koraido presents national aggregate estimates of the rate of generation of 20 gas industry wastes studied in the survey. As such, these values represent the only known national estimates of gas processing industry waste generation. (Again, it is important to note that these values exclude field operation contributions to the national totals for each waste type. As previously stated, gas processing wastes from field operations are the focus of an API study. The results of the API study were not available as of the date of this report.) No comparable estimates are available elsewhere in the literature. The results of the survey served as the basis for the sampling and analyses conducted for the 1993 GRI study described above.

Additionally, GRI published another study in 1996 titled *Topical Report: Glycol Dehydration Operations, Environmental Regulations, and Waste Stream Survey*. This report focusses primarily on air emissions from glycol dehydration operations, state and federal regulations, and emission controls. Five liquid and solid waste streams were also included in the study. All but one of these, a glycol reclaimer bottom waste, are discussed in the 1993 GRI report mentioned above. Hence, reference to the 1996 report is provided here solely as a source of information on glycol dehydration operations and applicable state and federal regulations.

2.0 DEHYDRATION AND SWEETENING PROCESSES AND WASTES

2.1 DEHYDRATION PROCESSES

As stated previously, dehydration is the removal of water from natural gas. Temperature, pressure, and water content of the production stream together determine the level of dehydration required to meet transportation and/or delivery specifications. Depending on the rate of production and the proximity of a well or well field to a gas plant, some or all of the production stream may be dehydrated in small facilities in the well field. Alternatively, wet gas may travel via field gathering lines directly to a central gas plant for dehydration.

According to *Oil and Gas Journal* (OGJ) survey data, 732 gas processing plants operated in the U.S. at the beginning of 1992 (Anonymous,"Annual Natural Gas Report." Vol. 90, No. 29, *Oil and Gas Journal*, 1992). However, the emphasis of the survey from which this estimate is derived is on the production of natural gas liquids, not on gas conditioning *per se* (True, 1992). Among other energy statistics, the Energy Information Administration (EIA) of the U.S. Department of Energy compiles data on monthly natural gas liquids production (EIA). These data are provided to EIA by gas plant operators on an EIA monthly survey form (EIA-816). According to EIA survey data for May 1996, 701 gas processing plants were in operation at that time (EIA, 1996). As with the OGJ survey, EIA's surveys focus on the production of natural gas liquids rather than gas conditioning. Further, these surveys only cover gas plants, and not small field facilities. Accordingly, the total number of dehydration facilities in operation in the U.S. may be assumed to greatly exceed the number of gas plants reported by OGJ and EIA.

Several attempts have been made to estimate the number of dehydration units operating in the U.S. with results ranging from 20,000 to over 44,000 units (EPA,1996). According to a study conducted for GRI, there were 41,700 ± 8,100 (within 95% confidence limits) units operating in the U. S. in 1993 (GRI, 1996). Of these 41,700 units, it was estimated that 39,600 are glycol dehydration units and the remaining 2,100 are solid desiccant units (GRI, 1996).

A number of distinct dehydration processes have achieved commercial success in the U.S. These may be grouped into three general categories: liquid desiccant processes, solid desiccant processes, and refrigeration processes. Liquid and solid desiccant processes exploit the high affinity for water of some material, the desiccant, to remove water vapor and small amounts of liquid water from the gas stream. Refrigeration processes, on the other hand, rely on the phase behavior of water under changing conditions of temperature and pressure to condense water from the gas stream. Common variations of these processes are described below. All of these are continuous processes.

2.1.1 Liquid Desiccant Processes

In general, liquid desiccant systems require a contactor (or absorber), in which natural gas is exposed to the desiccant, and a desiccant regeneration system, in which water captured by the desiccant is removed for disposal. As the gas stream flows through the contactor, water vapor and entrained droplets of liquid water absorb into the "lean" solution. Over time, the ability of the solution to absorb additional water decreases, as the total water absorption capacity of the desiccant is reached. Without a regeneration system, additional gas flowing through the contactor would pass through the system without giving up any water. Thus, "rich" solution must be regenerated, typically by heating it to boil off the water it contains.

While a number of materials exhibit the capacity to absorb water, only glycols, particularly triethylene glycol (TEG), have achieved significant commercial success as liquid desiccants in the U.S. (Ikoku, 1984). The widespread adoption of glycols for dehydration of gas streams stems both from their high affinity for water as well as the relative ease with which they will give up water during regeneration. Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol, and tetraethylene glycol (TREG) have all been used successfully as dehydration solvents. Currently, TEG is nearly predominantly used, however, due to its

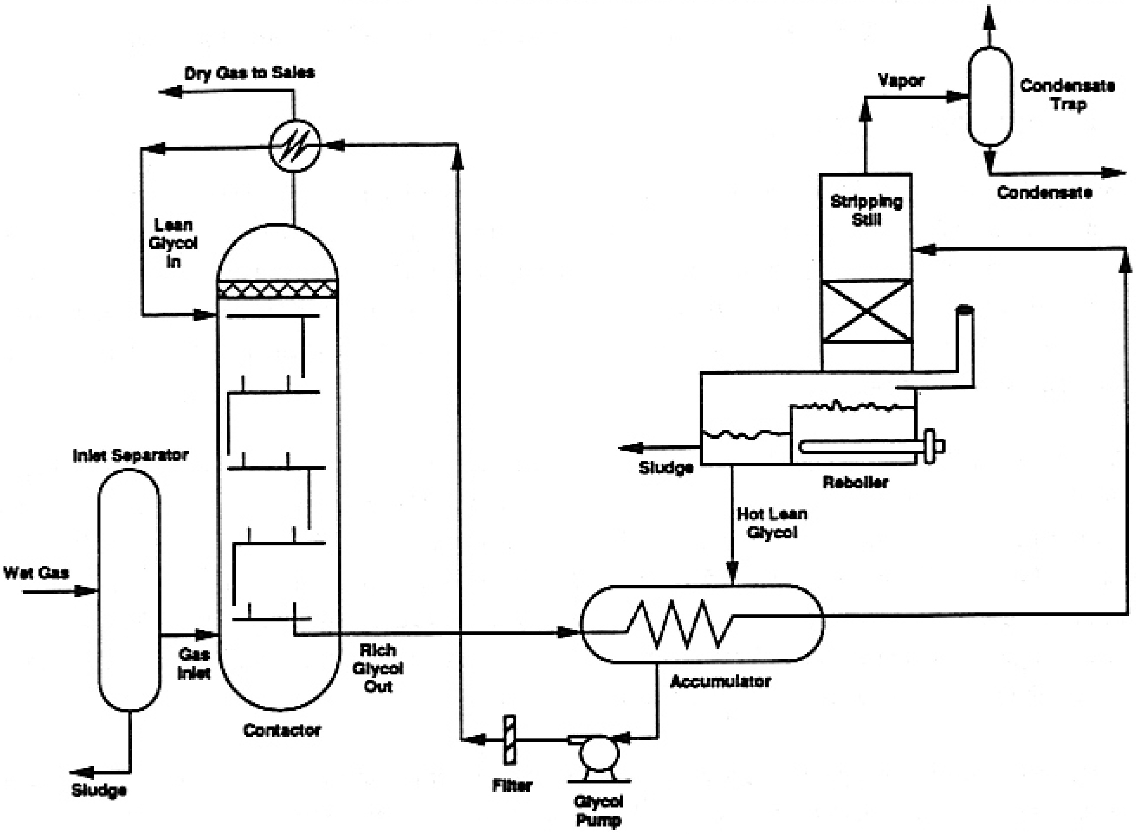

Figure 2-1. Basic Glycol Dehydration Process (After Manning and Thompson, 1991)

higher boiling point (relative to EG and DEG) and high decomposition temperature. These qualities allow a higher temperature in the regenerator without incurring high solvent losses or degradation (Manning and Thompson, 1991).

In 1995, a study was conducted for API which estimated emissions from U.S. TEG units (API, 1995b). With the cooperation of the Gas Processors Association (GPA), a survey was developed and distributed by GPA to natural gas production and processing companies. Data were provided by 29 companies, representing 44% of the nations natural gas supply, for 62 EG units and 844 TEG units of which 43 TEG units are operated offshore. The study indicates that on average, natural gas is dehydrated 1.4 times between the well and the consumer with 74% dehydrated by TEG, 0.6% by DEG, 30% by EG, and 36% using dry bed desiccant.

Figure 2-1 depicts the basic components of a glycol dehydration unit. The design shown is typical of a wellhead unit or small field unit, and requires little maintenance and operator attention. Wellhead gas first enters the inlet separator or scrubber.[1] The inlet separator removes entrained liquids and solids from the gas stream including produced water, hydrocarbons, down-hole additives such as acidizing and fracturing fluids, and sand, scale, and formation fines (API, 1989). Removal of these materials plays an important role in the efficiency of the dehydration unit by reducing contamination of the glycol, foaming difficulties, corrosion, and heat requirements for regeneration (Wieninger, 1991).

From the inlet separator, wet gas enters the contactor. Rising gas flows countercurrent to the glycol, with dried gas exiting from the top of the tower. Lean glycol enters at the top of the tower, while rich, water-bearing glycol leaves from its base. The rich glycol passes through a glycol-glycol heat exchanger and enters the stripping column. Steam rising from the reboiler strips vapor from the glycol as it descends through ceramic packing or stripper trays. Remaining vapor is driven off in the reboiler and in some facilities, is routed through a condensate trap for liquid collection. The hot lean glycol is then returned to the top of the absorber, cooling through the glycol-glycol and glycol-gas heat exchangers, and completing the circuit.

Numerous modifications to the basic system may be employed at larger dehydration facilities, including those at gas plants. For instance, the absorption tower may include an integral scrubber at its base. A mist extractor at the top of the absorber captures entrained glycol from the exiting gas stream, thereby reducing glycol loss due to carryover. Typically, larger units incorporate a number of heat exchangers to increase the overall efficiency of dehydration.

Sock filters and activated carbon filters may be employed to remove solid and liquid impurities from the glycol (Wieninger, 1991). Impurities in the glycol promote foaming, decrease the efficiency of water

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[1] For field units, associated gas wells, coalbed gas wells, or other wells producing substantial quantities of liquids, a free water knockout and other separators may precede the inlet separator. Such units are beyond the scope of this report.

uptake, and increase the heat energy required to drive off water from the rich glycol. Impurities captured by filters may include hydrocarbons, resins, metallic compounds, compressor lubrication oils, glycol degradation products, and corrosion products (Manning and Thompson, 1991; Simmons, 1991; Wieninger, 1991).

Filters will not remove dissolved salts, however. Eventually, thermal degradation of glycol and accumulation of dissolved salts may warrant reclamation of the glycol (Simmons, 1991). Larger plants may construct semi-continuous glycol reclaimers on site, which distill a portion of the glycol stream. Distillation may remove degradation products, solids, dissolved solids, and other impurities (Simmons, 1991).

Regeneration and reclaiming of glycol can reduce operational difficulties caused by corrosive agents and foaming agents. Additional protection is often accomplished through the injection of anti-foamants and anti-corrosives. For instance, silicone- or alcohol-based anti-foamants may be maintained in the glycol at concentrations of 50 - 100 ppm (Wieninger, 1991). Similarly, borax or triethanolamine (TEA) may be injected into the glycol stream for pH control (Manning and Thompson, 1991).

TEG dehydration systems currently in use span a wide range of operating conditions. TEG systems can accomplish dew point depression of 40 - 150 degrees F. Such systems can achieve dry gas water contents below 0.5 lbs H_2O/million standard cubic feet (MMscf). Further, TEG systems can operate with inlet gas temperatures of 55 - 160 degrees F and pressures from 75 to 2500 psi (Manning and Thompson, 1991).

2.1.2 Solid Desiccant Processes

Solid desiccants, like glycol, exhibit a high affinity for water. Unlike glycol, however, solid desiccants do not *absorb* water; rather, they *adsorb* water on solids surfaces. Accordingly, solid desiccants are manufactured to have very high internal surface areas, maximizing the number of surface sites to which water molecules may bond. Solid desiccant systems are capable of achieving very high dew point depressions, and can achieve high H_2O removal rates even when the inlet concentration of vapor is low. Such systems are almost universally adopted when cryogenic (low temperature) processing standards are required. Most solid desiccant dehydration systems share a number of the design and operational features described below.[2]

Solid desiccant dehydration requires physical contact between the gas stream and the desiccant, as well as some means of regenerating the desiccant once it is saturated with water. Because solids cannot be circulated to a regeneration unit, however, solid desiccants must be regenerated in the contacting tower itself. Accordingly, such systems incorporate two or more towers, such that one may be regenerated while the other(s) continue to operate in the dehydration mode.

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[2] Calcium chloride systems, discussed in the next subsection, exploit a different chemical/physical phenomenon, and are thus exceptions to the general discussion here.

Three basic flow regimes may be incorporated at typical solid desiccant facilities: wet gas regeneration, dry gas regeneration, and extrinsic gas regeneration. Following are descriptions of each process. Figure 2-2 shows the generalized flow diagram for a two-tower system using wet gas regeneration.

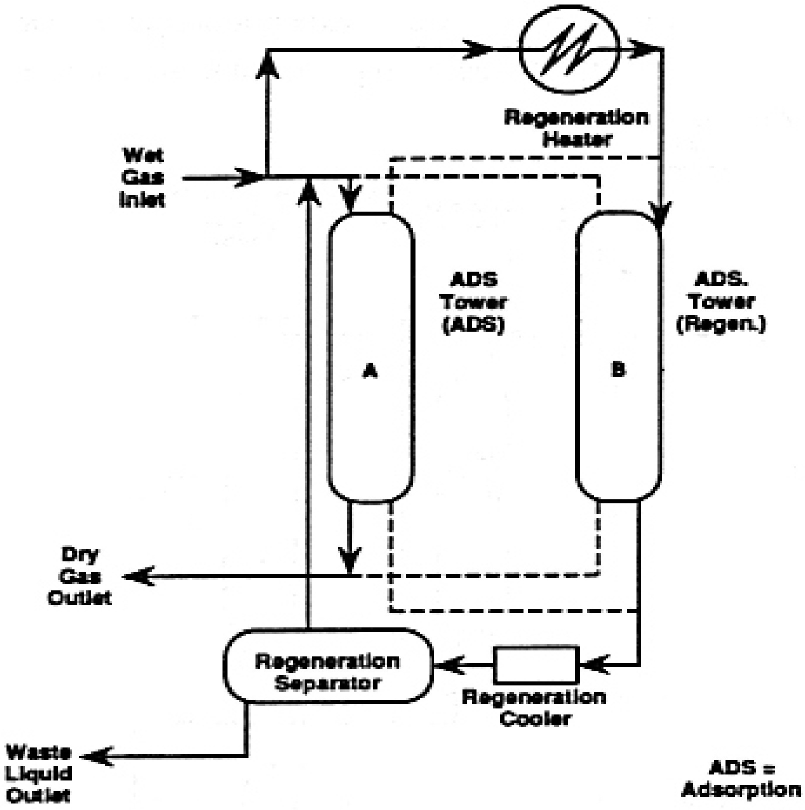

Figure 2-2. Solid Desiccant Dehydration Unit with Wet Gas Regeneration (After Manning and Thompson, 1991)

In this system, wet gas from the inlet separator enters the adsorption tower (tower A) and passes over or through the solid desiccant. As the gas contacts the desiccant, water molecules from the gas are adsorbed on the desiccant. Roughly 90-95 percent of the inlet gas stream is dried in the adsorption tower. The remaining wet gas is diverted to the regeneration heater, which raises the temperature of the gas to 400 - 550 degrees F. The heated gas is then channeled through tower B, where it drives off water from the desiccant surfaces. Gas and steam are first cooled in the regeneration cooler prior to entering the regeneration separator. The condensed water is removed from the separator while the regeneration gas is reintroduced to the inlet stream. After regeneration of tower B the cycle is reversed, with inlet gas flowing to tower B and regeneration gas flowing to tower A (Manning and Thompson, 1991).

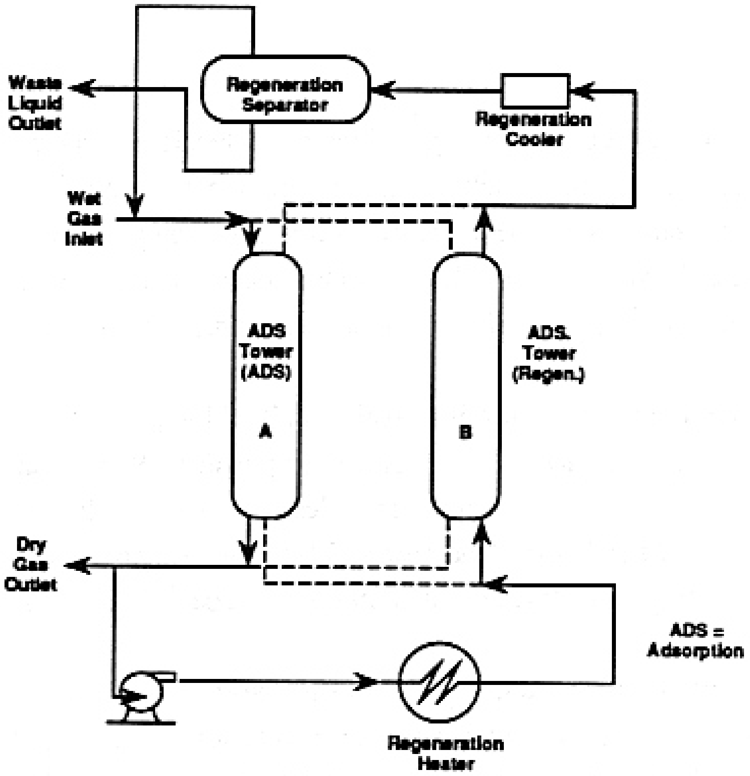

Figure 2-3. Solid Desiccant Dehydration Unit with Dry Gas Regeneration (After Manning and Thompson, 1991)

Figure 2-3 shows a variation of the system, dry gas regeneration. Again, wet gas from the inlet separator enters the adsorption tower (tower A) and passes over or through the solid desiccant which adsorbs water molecules from the gas. A portion of the dried gas exiting the tower is diverted to the regeneration heater and flows counter-current through tower B. The heated gas drives off water and other adsorbed material from the desiccant. After regeneration of tower B the cycle is reversed, with inlet gas flowing to tower B and regeneration gas flowing to tower A.

Finally, Figure 2-4 shows a similar process in which extrinsic gas (e.g., ambient air or other dry gas outside the production circuit) is heated and used for regeneration. As with the wet gas and dry gas regeneration systems, wet gas from the inlet separator enters the adsorption tower (tower A) and passes over or through the solid desiccant. Water molecules from the gas are adsorbed on the desiccant. Extrinsic gas is pulled into a regeneration heater. The heated gas is passed through the regeneration tower (tower B) and drives off water and other impurities from the desiccant. Again, one tower is regenerated while the other is used for gas dehydration.

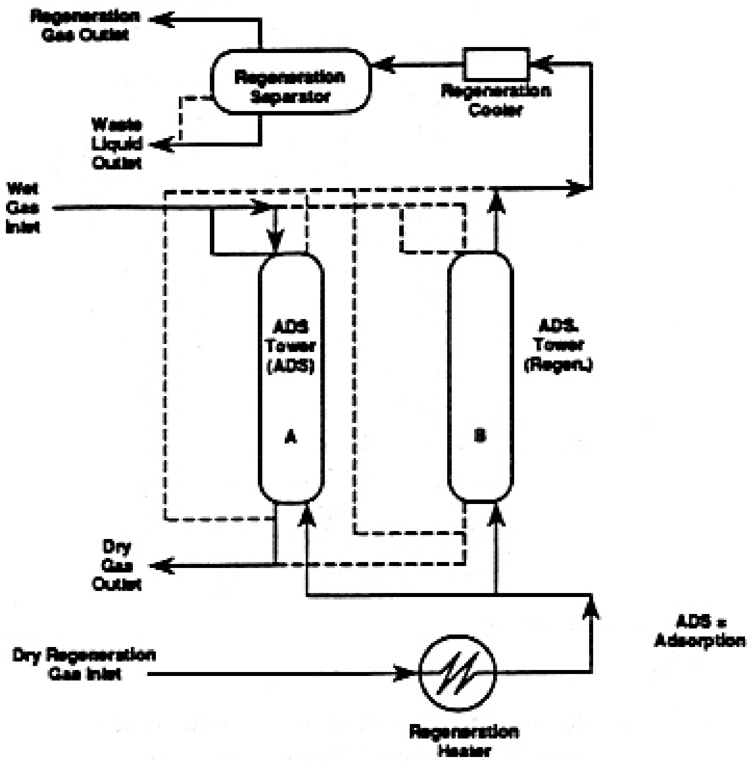

Figure 2-4. Solid Desiccant Dehydration Unit with Extrinsic Gas Regeneration (After Manning and Thompson, 1991)

Solid desiccants commonly used include silica gel, silica-based beads, activated alumina, and molecular sieves. Both silica gel and silica-based beads consist mainly of SiO_2, with small amounts of aluminum oxide (Al_2O_3) and trace amounts of other metal oxides. Activated alumina consists primarily of Al_2O_3 with trace amounts of other metal oxides. Molecular sieves are manufactured from zeolite crystals or metal alumina-silicates, and consist of highly regular crystalline structures with very high internal surface areas.

Solid desiccant systems require very low levels of solid and liquid impurities. Free liquids (e.g., water, hydrocarbons) cause desiccant particles to crack, break, or powder. Solids can block pore spaces and result in sufficient pressure increases to crush the particles. Non-volatile liquids can coat the desiccant particles, reducing efficiency (Manning and Thompson, 1991). Desiccant beds require periodic change out, on the order of once every 6 - 24 months (Maddox, 1985), and spent desiccant must be disposed.

The principal advantage offered by solid desiccants is the ability to produce very dry gas. Molecular sieves, in particular, are the most commonly used desiccants for drying gas to cryogenic processing standards (Manning and Thompson, 1991). Further, molecular sieves can be used for simultaneous sweetening and dehydration of production streams.

2.1.3 Calcium Chloride Dehydration

Calcium Chloride is a special case of solid desiccant dehydration. Calcium chloride exists in its anhydrous form, $CaCl_2$, as well as in several hydrated forms (e.g., $CaCl_2 \bullet H_2O$, $CaCl_2 \bullet 2H_2O$, $CaCl_2 \bullet 4H_2O$, and $CaCl_2 \bullet 6H_2O$). Formation of hydrates from anhydrous calcium chloride is a spontaneous, exothermic reaction such that dried calcium chloride and highly concentrated brine of calcium chloride can strip water from a natural gas stream.

In $CaCl_2$ dehydration units, inlet gas first passes through an inlet separator, often an integral separator since, as mentioned previously, it removes entrained liquids and solids from the gas stream including produced water, hydrocarbons, down-hole additives such as acidizing and fracturing fluids, and sand, scale, and formation fines. Once free of free liquids, the gas flows upward through a series of contactor trays, countercurrent to the movement of $CaCl_2$ brine. The brine strips water vapor from the gas, both through diffusion as well as through the formation of hydrates. From the trays, the gas flows upward into a bed of $CaCl_2$ pellets. Remaining water vapor in the gas absorbs into the pellets and forms saturated brine which moves downward through the trays. Highly concentrated brine discharges from the base of the contactor. Because the desiccant is consumed in the process, no regeneration step is included in the process. Instead, additional $CaCl_2$ pellets must be added to the bed once the remaining height of pellets in the contactor falls below two feet (Manning and Thompson, 1991).

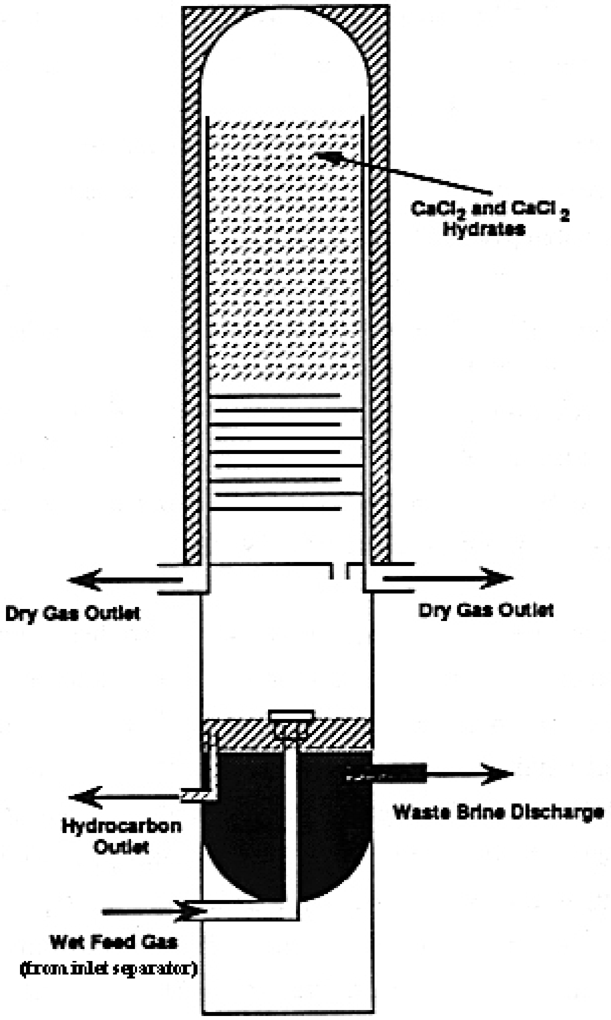

Figure 2-5. Calcium Chloride Dehydration Unit (After Manning and Thompson, 1991)

The number of such units in operation is not known. However, one source indicates that "hundreds" of $CaCl_2$ units may be in operation, particularly in the Rocky Mountains (Manning and Thompson, 1991). The simplicity of the operation and the low maintenance requirements make such units attractive for remote field or lease locations. Further, such facilities have very low power requirements, limited only to heating of the tower during cold periods when brines may freeze and clog flow lines.

2.1.4 Refrigeration Processes

Natural gas loses its ability to contain water in the vapor phase as the temperature decreases at constant pressure. If the temperature of the produced gas stream is unusually high, dehydration by cooling may allow sufficient dew point depression to meet sales requirements (Ikoku, 1984). Low temperature processes may intentionally form and melt hydrates, use hydrate inhibitors, or use mechanical refrigeration to dehydrate gas (Manning and Thompson, 1991).

In the predominately used refrigeration process, hydrates are intentionally allowed to form as the gas stream expands while flowing from wellhead pressure to pipeline pressure. First, the wellhead stream is heated and passed through hydrate melting coils. The gas stream then flows into a heat exchanger where it is cooled to the lowest safe temperature above the hydrate formation temperature at pressure upstream of the choke. The cooled gas stream flows through the choke where it expands from the wellhead pressure to the pipeline pressure. The resulting expansion and cooling in the choke causes some gas and most of the water vapor to liquefy. Hydrates are formed and can be removed at this point by heating the condensate to approximately 65 to 75 degrees F and the water to 80 to 90 degrees F. This enables the hydrates to sink through the condensate layer, float on top of the water layer, and decompose as they flow toward liquid outlets. In addition, vapors may be flashed from the condensate (Manning and Thompson, 1991). While often effective, this type of dehydration method is limited because the product gas remains at the water dew point unless the temperature is raised or the pressure is decreased after the process is completed (Ikoku, 1984).

Sometimes the gas stream cannot be cooled below the hydrate formation temperature in a gas-to-gas exchanger. The resulting temperature is fixed by the available pressure drop from the wellhead to the pipeline. When the traditional expansion and cooling method cannot achieve the desired gas dehydration, additional cooling of the gas is required prior to expanding the gas stream though the choke. Hydrate inhibitors, such as glycol or methanol, are required in this case. First, glycol is sprayed into the gas ahead of the choke. Then the dry cold gas is separated from the glycol and any condensate in a low temperature separator. Liquids leaving the separator are flashed to a lower pressure. The rich glycol is separated from condensate. The rich glycol is regenerated, repressured, filtered, and reinjected. Glycol can be lost from the system by going into solution with liquid hydrocarbons, vaporizing into the exit gas, or decomposing in the regenerator. Methanol injection is a much simpler process than glycol injection because it is often not recovered, so no regeneration equipment is needed. Occasionally, external refrigeration may also be required if the combined cooling of the gas-to-gas exchanger and any expansion is insufficient to provide the desired water and hydrocarbon dew points (Manning and Thompson, 1991).

2.2 DEHYDRATION WASTE GENERATION AND NATURE OF WASTES

Dehydration facilities generate wastes at a number of points in the dehydration cycle. Such wastes[3] may include inlet separator sludge, desiccant reboiler sludge, desiccant filter sludge and spent filter media, spent desiccant, condensate discharge (produced water), and miscellaneous desiccant spills. Some of these wastes are not unique to dehydration facilities. However, where available information permits, all common waste streams will be identified in order to provide a more realistic picture of the waste management activities required at dehydration operations. Typical waste streams are discussed briefly, below. Table 2-1 summarizes various dehydration wastes and the potential constituents they may contain.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-1. Summary Table of Dehydration Wastes Generation

Process	Waste type	Potential Constituents
Glycol dehydration	Glycol filter sludge	Glycol degradation products, corrosion products, hydrocarbons, resins, compressor lubrication oils, fines, pipe scale
	Glycol reclaimer sludge	Glycol degradation products, corrosion products, hydrocarbons, resins, compressor lubrication oils, fines, pipe scale
	Reboiler condensate	Principally water, but may contain dissolved hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylene)
	Spent glycol	Glycol degradation products, corrosion products, hydrocarbons, resins, compressor lubrication oils, fines, pipe scale, sulfur compounds, anti-foamants
Solid desiccant dehydration	Regeneration separator sludge	Powdered desiccant, hydrocarbons, resins, etc.
	Regeneration condensate	Principally water, but may contain dissolved hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylene)
	Spent desiccant	Desiccant, hydrocarbons, lubrication oils, sulfur compounds, resins, etc.
Calcium chloride dehydration	$CaCl_2$ brine	High concentration brine, may contain dissolved hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylene)

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[3] For the purposes of this report, gaseous materials discharged from stripping stills or released from flash tanks are not considered in the discussion of wastes.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-1. Summary Table of Dehydration Wastes Generation

Process	Waste type	Potential Constituents
Refrigeration dehydration	Glycol reboiler sludge	Same as for glycol dehydration.
	Condensate	Same as for glycol dehydration.

2.2.1 Inlet Separator Sludge

Common to all dehydration facilities is the generation of inlet separator or scrubber sludge. Such wastes may include produced water, oily debris, produced sand, pipe scale, emulsions, and downhole additives such as corrosion inhibitors. Note that such wastes are not unique to dehydration facilities and may be found at virtually any oilfield production facility. Such wastes generally are generated upstream of the dehydration process itself and do not include desiccant materials. However, central gas processing facilities receiving the product of multiple leases as well as gas storage facilities may receive gas streams which have been treated by methanol injection and/or glycol injection prior to transport. Available information does not indicate any estimated volume of such wastes specifically generated by dehydration facilities[4].

The GRI Study provides characterization information for a number of inlet separator wastes, including separator wastewater and spent filters. Samples were collected from an underground storage and compression facility (AG-05US-10), and two processing/conditioning plants (AF-01PC-20, AJ-04PC-04). Table 2-2 lists selected analytical results for these samples.

The data indicate that metals concentrations are low for the inlet separator filters sampled; no levels approached TC levels. Volatile organic compounds were rarely detected in any of the samples, with the exception of sample AF-01PC-20, which exceeded RCRA toxicity criteria for benzene at 3,200 ppb (6.4 times the criterion of 500 ppb). Another sample, AG-05US-10, had 180 ppb benzene. The data are insufficient to determine the source of the benzene in the filter samples. Benzene was not observed in the third inlet separator filter sample.

2.2.2 Glycol Reboiler Sludge

Glycol units include glycol reboilers used to regenerate (by distillation) the glycol. Over time, the reboiler may accumulate glycol degradation products, corrosion products, hydrocarbons and coked hydrocarbons, fines, pipe scale, and other materials which settle out from the desiccant stream (Manning and Thompson, 1991). Glycol degradation products and cracked hydrocarbons may result from excessive temperatures in the reboiler. Further, if deposits form on firetube walls in the reboiler, local hot-spots may develop which can increase thermal degradation of the glycol. Glycol degradation products may include lower glycols,

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[4] Note that the API exploration and production waste survey explicitly excludes separator sludges from the dehydration and sweetening waste category.

aldehydes, and acids (Wieninger, 1991). The presence of hydrocarbons results from the high solubility (10 - 20 percent) of aromatic and asphaltic compounds in glycols (Weininger, 1991). Glycol sludges are generally not ignitable (Simmons, 1991), although one source indicates that glycol sludge may have a low flash point, less than 61 degrees C (B.H. Asano Associates, et. al., 1992). Available information does not permit an estimation of the volume of reboiler sludge generated.

Associated Waste Report:
Dehydration and Sweetening Wastes
(U.S. EPA, January 2000)
Table 2-2. Selected TCLP Inorganic and Volatile Organic Constituent Concentrations in Inlet Separator Sludge and Filter Media
(units in ppb except pH)

Analyte			
	AF-01PC-20[1]	AG-05US-10[2]	AJ-04PC-04[3]
pH (s.u.)	NA	NA	NA
RCRA Metals			
Silver	ND	ND	ND
Arsenic	20	40	70
Barium	100	500	900
Cadmium	ND	ND	20
Chromium	ND	30	200
Mercury	ND	70	ND
Lead	ND	ND	200
Selenium	10	ND	ND
Volatile Organic Compounds			
Benzene	3,200	180	NA
Ethylbenzene[4]	NA	NA	NA
Total Xylenes[4]	NA	NA	NA
Toluene[4]	NA	NA	NA
2-Butanone	ND	ND	ND

NA Not analyzed
ND Not detected

[1] Cloth cartridge filter from inlet gas separator.
[2] Cloth-wound, metal core inlet separator filter.
[3] Cloth and paper wrapped, metal core inlet separator filter.
[4] Total constituent data, not TCLP analysis.

Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.2.3 Regeneration Separator Sludge

Solid desiccants, such as silica gel, activated alumina, and molecular sieves, require separation of fluids driven off the regenerated desiccant bed from the regeneration gas. The greatest fraction of the fluids removed from the regeneration gas is water. However, hydrocarbon fractions, powdered desiccant, and resins may also be driven off from the absorber and hence accumulate in the regeneration separator. Such accumulations may also contain BTEX (benzene, toluene, ethylbenzene, and xylene) which can accumulate in the gas stream water (Gosling, et. al., 1991). Available information does not permit an estimation of the volume of regeneration separator sludge generated.

The GRI Study includes characterization data for a sample of spent molecular sieve collected from a drip gas dryer at a gas processing/conditioning facility (sample AI-02PC-31). The spent molecular sieve represents the bottoms or sludge accumulated in the dryer. The sample showed no free liquids. TCLP analyses showed leachate concentrations of all volatiles, semi-volatiles, and metals tested to be below method detection limits. Consequently, data for these samples are not included in any of the tables that follow.

Note that three additional gas conditioning waste samples were collected from this facility (see Sections 2.2.8 and 2.2.4). Spent molecular sieve from the dehydration towers and dehydration water from the molecular sieve regenerator were collected well downstream of initial dehydration and gas-liquid separation units, and amid a train of NGL fractionating units. The two upstream waste samples showed high levels of arsenic (exceeding RCRA toxicity levels) while neither downstream waste sample showed detectable levels of the metal. Although the presence and concentration of arsenic in the production stream is due to characteristics of the producing formation, the data suggests that the location of the process units may influence the level of contaminants contained in the dehydration wastes.

2.2.4 Regeneration Condensate and Reboiler Condensate

In both liquid and solid desiccant systems, the desiccant is regenerated through the addition of heat which boils off water and other volatile fractions. In glycol systems, most of the water escapes from the regeneration still as vapor. Addition of a reflux accumulator (to minimize energy costs) will result in the condensation of some of the removed liquids. In solid desiccant systems, removed liquids are condensed in the regeneration cooler and separated from the regeneration gas in a two-phase separator. In either system, this condensate may contain dissolved hydrocarbons, particularly BTEX (Gosling, et al., 1991, Prosen, et al. 1991).

EPA and GRI data for selected inorganic and organic constituents of dehydrator regeneration condensate are presented in Table 2-3. Note that as indicated in Table 2-3, some results are qualitative due to matrix interference problems and samples being held beyond the 14 day TCLP sample holding time. Specifically, TCLP organics data are deemed qualitative for benzene and 2-butanone for samples AL-02PC-06, AI-04US-02, and for AI-02PC-03 and its duplicate. Sample AL-02PC-06 experienced matrix interference problems and, therefore, exceeded method detection limits (MDLs) for all the TCLP volatile organics. Sample AI-04US-02 was analyzed outside the TCLP method holding time but did not experience matrix interference problems. Conversely, the duplicate of this sample was not held beyond the method holding time but did experience matrix interference problems for all volatile organics except the two detected analytes, benzene and 2-butanone, and chlorobenzene which was not detected. Both sample AI-02PC-03 and its duplicate were analyzed outside the TCLP method holding time. Sample AX-01PC-02 experienced matrix interference problems for most of the volatile organics. The exceptions were benzene and three analytes that were not detected. For the TCLP metals, data are deemed qualitative for lead for the duplicate of sample AI-04US-02; arsenic for sample AI-02PC-03, and mercury for sample AI-02PC-03 and its duplicate.

During EPA's 1992 sampling program (see Section 2.5), samples of glycol still condensate were collected from two Oklahoma gas plants. GRI collected samples from 6 facilities: an underground storage and compression station in Texas; an underground storage and compression station in Pennsylvania; a gas processing and conditioning plant in Louisiana; a gas processing and conditioning plant in Texas; a gas processing and conditioning plant in New Mexico, and a gas processing and conditioning plant in West Virginia.

All samples displayed moderate pH, ranging from slightly alkaline to slightly acidic. Note that both samples taken from silica bead dehydrators (samples AB-02PC-06 and AI-04US-02 and duplicate) showed a lower pH than samples from either the molecular sieve dehydrator or any of the glycol systems. However, the data are insufficient to determine whether the nature of the desiccant is responsible for this difference.

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-3. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations in Dehydrator Regeneration Condensate (units in μg/L except pH)

Analyte	EPA Sample ID		GRI Sample ID							
	Glycol Processes		Glycol Processes			Solid Bed Processes				
	23643	23649	AG-01US-06	AL-02PC-06	AX-01PC-02	AI-04US-02	AI-04US-02 DUP	AI-02PC-03	AI-02PC-03 DUP	AB-02PC-06
pH (s.u.)	6.52	7.58	8.2	NA	8.6	4.6	4.7	8.1	8.0	5.2
RCRA Metals										
Silver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Arsenic	4.80	ND	ND	ND	ND	ND	ND	6,100[1]	5,800[1]	5
Barium	ND	6.8	30	30	ND	ND	ND	90	200	200
Cadmium	ND	ND	ND	ND	ND	ND	ND	40	30	ND
Chromium	39	ND	ND	ND	100	ND	ND	ND	ND	50
Mercury	ND	54	ND	ND	ND	ND	ND	ND[3]	ND[3]	8
Lead	ND	ND	ND	ND	ND	ND	ND[1]	ND	10	40
Selenium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Volatile Organic Compounds										
Benzene	43,332	1,657	130,000	120,000[4]	32,000	67,000[3]	60,000	ND[3]	ND[3]	2,300
Ethyl-Benzene[2]	15,531	21	NA	NA	NA	ND	ND[5]	640	400	ND
Total Xylenes[2]	246,501	136	NA	NA	NA	12,000	ND[5]	9,800	3,000	940
Toluene[2]	91,192	866	NA	NA	NA	54,000	ND[5]	1,800	1,300	1,700
2-Butanone	ND	ND	1,900	ND[4]	ND	130,000[3]	130,000	5,500[3]	4,800[3]	2,700

ND Not detected NA Not analyzed

[1] QC indicates spike recovery <75%; deemed qualitative results.

[2] Total constituent analysis.

[3] QC indicates sample holding time exceeded; deemed qualitative results.

[4] Method detection limit (MDL) above TCLP requirements due to sample matrix problems.

[5] Matrix interference Problems

Source: EPA 1992 sampling program, GRI Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations.

Metals concentrations were generally low or below detection limit for condensate samples. However, GRI sample AI-02PC-03 and duplicate exhibited RCRA toxicity for arsenic, with extract concentrations equal to 6,100 and 5,800 μg/l, respectively. The GRI sampling report noted that arsenic is indigenous to the producing formation associated with this West Virginia facility. (Note that a sample of spent molecular sieve from the same plant also showed elevated arsenic levels. See Section 2.2.8.)

Dehydrator regeneration condensate samples from seven of eight facilities exceeded the TC level for benzene. Concentrations ranged from 3 to 260 times the RCRA value of 500 μg/l, with benzene below detection in GRI sample AI-02PC-03 and duplicate. Several of the samples also showed high concentrations of ethylbenzene, toluene, and/or xylene. A number of factors may influence the concentration of volatile organic compounds in dehydrator condensate, including the composition of the raw feed stream, the location of the dehydration unit in the plant process train, and the type of desiccant employed.

The two samples showing the highest benzene concentration were collected from dehydrators located at or near the point where gas enters the facility (i.e., little or no prior processing at the plant). Sample AB-02PC-06 showed comparatively low concentrations of benzene and was collected at the end of the process train just prior to the point where the gas enters the sales line . The locations of the EPA samples relative to other process elements were not clear. Sample AI-02PC-03 and duplicate, which showed benzene below detection limits, were also located at the point of entry of gas to the facility. However, none of the other three samples collected at this facility (molecular sieve (mol sieve) from a mol sieve dehydrator, mol sieve from acid gas removal and spent mol sieve from a drip gas dryer) showed detectable levels of benzene, suggesting that benzene is not a major constituent of the raw gas at the plant. Additional data are necessary to confirm the result, but GRI concludes that benzene and associated alkyl benzenes would likely be detected in regeneration condensate irrespective of geographic location and other factors.

Preliminary results of the GRI survey of the natural gas industry suggest that the nationwide generation rate of dehydrator condensate is roughly 1,260,000 lbs/day, with solid bed and glycol systems contributing 74 percent and 26 percent of the total, respectively [Koraido, 1993]. Note, however, that this figure not only includes waters from gas plants but also waters generated by pipeline compressor stations and underground storage facilities. The figure also excludes field-based dehydration units. Given the prevalence of glycol dehydration, the results seem counterintuitive. However, glycol still venting to the atmosphere would tend to decrease the quantity of waste condensate attributed to this category of units.

2.2.5 Glycol Filter Sludge and Spent Filter Media

To minimize foaming, glycol contamination, and flowline fouling problems, glycol dehydration facilities typically include mechanical (sock) and activated carbon filters in the desiccant cycle. Over time, these filters remove from the feed stream glycol degradation products, corrosion products, resins, compressor lubrication oils, fines, pipe scale, and other materials (Manning and Thompson, 1991). Glycol degradation products may include lower glycols, aldehydes, and acids (Wieninger, 1991). The presence of hydrocarbons results from the high solubility (10 - 20 percent) of aromatic and asphaltic compounds in glycols (Weininger, 1991). Glycol sludges are generally not ignitable (Simmons, 1991), although one source indicates that glycol sludge may have a low flash point, less than 61 degrees C (B.H. Asano Associates, et al., 1992).

The GRI study provides analytical results for six glycol filter samples from four facilities, including 2 underground storage and compression stations and two processing/conditioning plants. Four of the samples were sock-type filters while two were charcoal filters; a sock filter sample and a charcoal filter sample were each collected at two of the facilities. Two of the samples (AD-03US-19, AF-02PC-03), both sock filters, were collected from EG units, while all other samples were collected from TEG units. Table 2-4 lists selected analytical results for each sample. GRI indicated that all but two of the samples (AF-02PC-03 and AG-01US-19) had elevated method detection limits (MDLs). However, these were not noted in GRI's TCLP analytical data for any of the detected analytes.

Two of the six samples (AD-03US-19 and AL-02PC-04), each a sock filter, showed elevated RCRA reactive sulfide levels (i.e., above 500 mg H_2S/kg) of 1,490 mg H_2S/kg and 1,280 mg H_2S/kg respectively. One sample (AD-03US-19) was collected from an EG unit and the other (AL-02PC-04) from a TEG unit at plants receiving sweet (<4 ppm H_2S) gas. These levels are substantially higher than the observed levels in either other plant, as well as the levels observed in the charcoal filters. Note that the sulfide concentration of the charcoal filter sample at plant AG-01US was an order of magnitude higher than the concentration seen in the sock filter sample at the same plant. Sweet gas plants are not designed to remove sour gas components. Hence, GRI suggests that the high reactive sulfide levels at the two sweet gas facilities may be the result of a build-up of reactive sulfide levels over time since there are no provisions to remove trace quantities of H_2S in the gas at these plants . It is worth recalling that at sour gas plants dehydration typically occurs after sweetening, such that H_2S levels in gas contacting glycol at such plants may be below the levels observed at sweet gas plants.

Metals levels were generally low or below detection levels in all of the glycol filter samples, although barium was detected in all of the samples (at or below 41 ppm). All but one of the samples exceeded the RCRA TC level for benzene, with extract concentrations ranging between 430 and 38,000 ppb. At the two plants with both sock and charcoal filter samples, benzene levels in the sock filters were significantly higher than the corresponding charcoal filter levels, suggesting a possible relationship between filter type and benzene levels. Additional data are needed to evaluate this result further, the samples from TEG units were significantly higher than two samples from the EG units (AF-02PC-03, AG-01US-19), suggesting a higher affinity of TEG for benzene than EG. Additional data are also required to confirm this.

Currently available information is very limited regarding the quantity of spent filters and filter media generated at gas plants in the U.S. Cartridge-type filters are disposed when the pressure drop across them exceeds a pre-determined value. According to one source, these filters may be changed monthly (ERT, 1988). Sock filters and activated carbon filters may be back-washed prior to changing or recharging. Note that filter sludges and spent filter media are considered as distinct from dehydration wastes in the API associated waste survey. Preliminary results of the GRI gas industry survey suggest that roughly 14,000 lbs of spent dehydration filters are generated daily [Koraido, 1993]. Again, this estimate included underground storage and pipeline compressors as well as gas plants, and does not include field units.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-4. Selected TCLP Inorganic and Volatile Organic Constituent Concentrations in Spent Glycol Filter Media
(units in ppb except pH)

Analyte	GRI Sample ID					
	Sock Filter				Charcoal Filter	
	AD-03US-19	AF-02PC-03	AG-01US-12	AL-02PC-04	AG-01US-19	AL-02PC-05
pH (s.u.)	8.6	NA	NA	NA	NA	NA
Reactive Sulfide	1,490,000	22,000	20,000	1,280,000	320,000	ND
RCRA Metals						
Silver	ND	ND	ND	ND	ND	ND
Arsenic	ND	10	5	ND	ND	ND
Barium	41,000	2,000	500	60	500	1,900
Cadmium	ND	40	20	ND	ND	ND
Chromium	ND	ND	ND	ND	ND	ND
Mercury	ND	5	ND	ND	ND	ND
Lead	ND	ND	ND	ND	ND	ND
Selenium	5	ND	ND	ND	10	9
Volatile Organic Compounds						
Benzene	6,200 [1]	430	38,000 [1]	31,000 [1]	2,600	9,100 [1]
Ethyl-benzene	NA	NA	NA	NA	NA	NA
Total Xylenes	NA	NA	NA	NA	NA	NA
Toluene	NA	NA	NA	NA	NA	NA
2-Butanone	390	ND	ND	ND	ND	ND

[1] Method detection level above TCLP requirements
NA Not analyzed
ND Not detected
Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.2.6 Glycol Reclaimer Sludge

Excessive foaming, corrosion, and firetube fouling may require reclamation of glycol solutions (Simmons, 1991). Still reclaimers generate reclaimer sludge, or still bottom residue. As with other glycol wastes, reclaimer sludge may contain glycol degradation products, corrosion products, resins, compressor lubrication oils, fines, pipe scale, and other materials (Manning and Thompson, 1991). Glycol degradation products may include lower glycols, aldehydes, and acids (Wieninger, 1991). The presence of hydrocarbons results from the high solubility (10 - 20 percent) of aromatic and asphaltic compounds in glycols (Weininger, 1991). Glycol sludges are generally not ignitable (Simmons, 1991), although one source indicates that glycol sludge may have a low flash point, less than 61 degrees C (B.H. Asano Associates, et al., 1992).

The GRI study provides analytical results for three samples of glycol reclaimer sludge from two underground storage and compressor stations and one processing and conditioning plant. Table 2-5 lists selected analytical results for the three samples. Sample AF-03US-15, which exhibited a higher pH than either of the two other samples, was collected from a plant using EG injection. The other plants are TEG units. The EG facility sample also exhibited the highest benzene level, at twice the RCRA TC level for that constituent. Elevated MDLs due to matrix interference problems were experienced for all but one of the undetected volatile organics (2-Butanone) for sample AD-03US-03 and only for one undetected volatile organic (Pyridine) for sample AF-03US-15. While all samples displayed low levels of TCLP metals, generally below detection limits, none experienced elevated MDLs. One sample (AD-03US-03) exhibited RCRA ignitability with a flash point of 113°F in agreement with sources cited above. However, the GRI report states that QC review indicated the possible occurrence of cross-contamination between samples or carry-over of samples in the flashpoint apparatus. Therefore, GRI deemed the ignitability result for this sample to be invalid.

The small number of samples and elevated detection limits due to matrix interference problems prevents any clear indication of the factors most likely to influence the concentrations of constituents of concern in glycol reclaimer sludge. It is worth noting, however, that the operating conditions of the units (not described in the GRI study) could be expected to play an important role in the concentrations of VOCs. Preliminary results of the GRI gas industry survey indicate that the nationwide generation rate of glycol reclaimer wastes is roughly 71 lbs/day [Koraido 1993]. No other estimates are currently available.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-5. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations for Glycol Reclaimer Sludge
(units in μg/L)

Analyte	GRI Sample ID		
	AD-03US-03	AF-03US-15	AJ-04PC-11
	TEG	EG	TEG
pH (s.u.)	7.5	10.76	7.96
Ignitability (°F)	113[1]	>150	>150
RCRA Metals			
Silver	ND	ND	ND
Arsenic	50	ND	ND
Barium	ND	ND	ND
Cadmium	ND	ND	ND
Chromium	ND	ND	ND
Mercury	ND	ND	ND
Lead	ND	ND	ND
Selenium	8	ND	ND
Volatile Organic Compounds			
Benzene	ND[2]	1,000	460
Ethyl-benzene	NA	NA	NA
Total Xylenes	NA	NA	NA
Toluene	NA	NA	NA
2-Butanone	ND	ND	190

NA Not analyzed
ND Not detected
[1] QC review indicates possible cross-contamination or carryover occurred between samples. Therefore, GRI considered the results to be invalid.
[2] Detection limit above TCLP requirements. Data are deemed qualitative.
Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.2.7 Spent Glycol

Over time, glycol in dehydration units loses its capacity to remove water from natural gas efficiently. Deterioration in loading capacity results from contamination (including amine poisoning) and thermal degradation (Manning and Thompson, 1991). Properly operated and maintained, glycol units may operate for 8 to 10 years before change of the glycol is warranted (Manning and Thompson, 1991). However, one source estimates that glycol may be replaced more often, on the order of once every 6-24 months (ERT, 1988).

As with other glycol wastes, spent glycol may contain glycol degradation products, corrosion products, resins, compressor lubrication oils, fines, pipe scale, and other materials (Manning and Thompson, 1991). Glycol degradation products may include lower glycols, aldehydes, and acids (Wieninger, 1991). The presence of hydrocarbons results from the high solubility (10 - 20 percent) of aromatic and asphaltic compounds in glycols (Weininger, 1991). Spent glycol is generally not ignitable (Simmons, 1991).

In 1992, EPA collected samples of lean glycol (i.e., after regeneration and removal of water) from two gas plants (samples 23137 and 12160). These were in-process fluids, not wastes. Metals and general chemistry analytical constituent results were quite variable, with chemical oxygen demand and total organic carbon quite high. Again, very few organic analytes were detected, as shown in Appendix A. Benzene was detected in both samples, at 505 μg/l (23137) and 99,853 μg/l (23160), respective. The benzene concentration in sample 23160 was nearly 200 times the TC level. No other constituent was detected at a concentration that exceeded the TC levels. Toluene was also detected in sample 23160 at 365,570 μg/l.

During EPA's 1992 sampling program, a sample of rich glycol also was collected from a central gas plant. The glycol was not yet spent (i.e., it was to be continued to be distilled and used for dehydration), but the constituents present could be expected to be present when it finally is spent and requires management as a waste--indeed, it is possible that some constituent concentrations would increase as the glycol is repeatedly re-used for dehydration and re-distilled. However, in comments to EPA, GRI noted that accumulation of volatile constituents in spent glycol would be unlikely since volatile constituents are repeatedly driven off during the regeneration cycle. Concentrations of detected organics and TC metals are shown in Table 2-6, as are pH and ignitability results (all results are shown in Appendix A). As can be seen, metals were detected at relatively low concentrations. The concentration of benzene, however, was above the TC level in all five samples, ranging from 1.9 to 163 times the TC level; toluene and xylene levels were also high. Relatively few other organic constituents were detected.

Also shown in Table 2-6 are the results of four samples of spent glycol from the GRI study. The samples were collected from two underground storage and compression facilities, one mainline compressor station that also functions as a gathering system booster station, and one processing/conditioning plant. Sample AI-03ML-01 is a spent DEG, while the remaining samples are spent TEG.

Analytical results indicated that only one waste glycol sample, AX-01PC-01 (from a processing/conditioning plant) showed a moderately alkaline pH, at 10.5 s.u. The remaining samples were roughly neutral. The gas associated with this processing facility is sour, which may affect the glycol pH.

All of the samples contained low to undetectable TCLP metals levels. All samples contained elevated levels of benzene, ranging from 2 to 220 times the RCRA TC level of 500 ppb. The DEG unit showed the lowest

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-6. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations in Glycol Samples
(units in μg/L)

Analyte	EPA Sample	GRI Sample ID			
	23648[1,2]	AD-03US-16	AI-03ML-01	AN-02US-07	AX-01PC-01
		TEG	DEG	TEG	TEG
pH (s.u.)	8.81	6.6	6.2	6.9	10.5
Ignitability (°F)	NA	>150	>150	95	>150
RCRA Metals					
Silver	ND	ND	ND	ND	ND
Arsenic	25.3	ND	10	ND	ND
Barium	ND	ND	300	80	ND
Cadmium	150	ND	ND	ND	ND
Chromium	ND	ND	ND	ND	ND
Mercury	ND	ND	ND	ND	ND
Lead	ND	ND	ND	ND	ND
Selenium	ND	ND	ND	ND	ND
Volatile Organic Compounds					
Benzene	81,581	73,000	970[4]	110,000	6,500[3,5]
Ethyl-benzene	879	NA	NA	NA	NA
Total Xylenes[1]	6,404	NA	NA	NA	NA
Toluene[1]	74,699	NA	NA	NA	NA
2-Butanone	ND	ND	200[3,4]	NA	NA

NA Not analyzed
ND Not detected
[1] All results represent total constituent analysis concentrations, not TCLP.
[2] EPA sample is in-process rich glycol, not spent.
[3] Reported value is below detection limit.
[4] Sample holding time exceeded, therefore, result deemed qualitative.
[5] QC review indicated that 3 of 4 surrogate recoveries were grossly above QC limits, therefore, result deemed qualitative.
Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

benzene concentrations; this facility is a mainline compressor station that also functions as a gathering system booster station. The GRI samples with the highest benzene concentrations were taken from underground storage and compressor stations. The sample with the highest benzene concentration also exhibited RCRA ignitability, with a flash point of 95°F. Note that the TCLP volatile organics data for GRI samples AI-03ML-01 and AX-01PC-01 are deemed qualitative based on GRI's QC review. Given the wide variability of observed benzene concentrations, additional data would be needed to determine the causes of these results. No clear trend with respect to inlet gas composition, location of contactor, or desiccant type is evident.

Preliminary results of the GRI gas industry survey estimate that the nationwide generation rate of spent glycol is roughly 2,100 lbs/day, including gas plants, compressors, and underground storage facilities [Koraido 1993]. Spent glycol is among the wastes covered by the API survey discussed below in Section 3.

2.2.8 Spent Solid Desiccant

As previously stated, solid desiccants may be easily contaminated with liquids and/or solids. Further, excessive contactor pressure or the presence of liquid water may crush or crack silica beads and molecular sieves. Resins, paraffins, and hydrocarbons may coat desiccant particles, reducing their efficiency. Accordingly, such materials must be discarded periodically. The life of solid desiccant material is roughly 6-24 months (Maddox, 1985). As solids, these materials were excluded from the API survey as sweetening and dehydration wastes.

The GRI study provides analytical results for three spent solid desiccant samples, all of which are spent molecular sieve, collected from three facilities. Two facilities are processing/conditioning plants located in the Appalachian region of West Virginia. The third facility is thought to be a processing/conditioning plant in Texas (see Table note). Table 2-7 lists selected results for the samples.

With the exception of arsenic, all of the samples showed TCLP metal and volatile organic constituent concentrations were near or below detection limits. Each West Virginia plant yielded a sample with elevated arsenic levels. Arsenic concentration in sample AJ-03PC-11 is eight times the RCRA TC level for this metal. Arsenic is indigenous to some producing formations in the Appalachian region, likely accounting for these results. Note also that a sample of dehydrator regeneration condensate from facility AI-02PC also yielded a high arsenic level.

Preliminary results of the GRI gas industry survey indicate that the nationwide generation rate of spent solid desiccant is roughly 13,000 lbs/day [Koraido 1993].

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-7. Selected Inorganic and Volatile Organic TCLP Constituent Concentrations for Spent Solid Desiccant (Molecular Sieve)
(units in μg/L)

Analyte	GRI Sample ID			
	AI-02PC-08	AI-02PC-08 DUP	AJ-03PC-11	BB-02PC-06
pH (s.u.)	NA	NA	NA	NA
RCRA Metals				
Silver	ND	ND	ND	ND
Arsenic	1,600	1,200	40,000	ND
Barium	240	300	300	200
Cadmium	ND	ND	60	ND
Chromium	ND	ND	ND	ND
Mercury	ND	ND	ND	ND
Lead	ND	ND	ND	ND
Selenium	ND	ND	ND	ND
Volatile Organic Compounds				
Benzene	8[1]	97[1]	32	47
2-Butanone	ND[1]	21[1]	100	140

NA Not analyzed
ND Not detected

[1] Sample holding time exceeded 14 days; results deemed qualitative.

Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.2.9 Calcium Chloride Brine

Calcium chloride dehydration units generate a continuous stream of concentrated brine as the water vapor in the natural gas dissolves the anhydrous $CaCl_2$ pellets in the absorber. The concentration of the brine is less than saturated, due to the fact that the liquid continues to remove water vapor from the gas in the contactor trays below the solid bed of pellets in the absorber. However, the concentration will generally approach saturation (Manning and Thompson, 1991). The per unit volume of the brine generated is a function of the total water content of the gas. Because no census of such facilities is currently available, it is not now possible to determine the total volume of such materials generated. Additionally, no analytical data are available for calcium chloride dehydration wastes.

2.2.10 Methanol

As discussed earlier, many facilities inject methanol or other desiccants into gas streams to help prevent hydrate formation. While often left in the gas stream, some operators recover methanol before gas leaves the plant. The GRI study provides analytical results for two methanol recovery system filters from an underground storage and compression facility in Iowa (a charcoal filter and a sock filter) and are presented in Table 2-8. The system recovers methanol from water collected in a series of horizontal inlet separators and dehydration units associated with the facility's three formation storage and gathering subsystems. The charcoal filter sampled was used to filter water returned from a reboiler downstream of the methanol/water distillation column. The sock filter sampled was used to filter methanol/water mixture upstream of the distillation column.

Analytical results showed TCLP metal limits and volatile organic concentrations in the filter samples to be generally low or below detection. Arsenic, barium, and cadmium were detected in the sock filter at levels ≤ 0.3 mg/l. Of the TCLP metals, only barium was detected in the charcoal sample (0.1 mg/l). Benzene was detected in the sock filter leachate at 36 times the RCRA TC level but at only 16 mg/l in the charcoal filter leachate. Elevated MDL's were detected for most of the TCLP volatile organics for the sock filter sample. Methanol concentrations in the samples were not determined.

No estimates are available for the quantity of filter wastes generated annually by the industry or the sampled facility. However, the operator used 25,000 gallons of methanol and 600 gallons of unspecified corrosion inhibitor during the winter of 1990-1991 [GRI, 1993].

Associated Waste Report:
Dehydration and Sweetening Wastes
(U.S. EPA, January 2000)
Table 2-8. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations for Methanol Recovery Filters
(units in μg/L)

Analyte	GRI Sample ID	
	AG-03US-26-02	AG-03US-26-03
pH (s.u.)	NA	NA
Ignitability (°F)	NA	NA
RCRA Metals		
Silver	ND	ND
Arsenic	30	ND
Barium	300	100
Cadmium	30	ND
Chromium	ND	ND
Mercury	ND	ND
Lead	ND	ND
Selenium	ND	ND
Volatile Organic Compounds		
Benzene	18,000	16
Ethyl-benzene	NA	NA
Total Xylenes	NA	NA
Toluene	NA	NA
2-Butanone	1,500[1]	8[1]

NA Not analyzed
ND Not detected
[1] Reported value is less than the detection limit. Data are deemed qualitative.
Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.3 SWEETENING PROCESSES

Roughly 25 percent of the natural gas produced in the U.S. requires conditioning for removal of sulfur compounds (EPA, 1983). The concentration of hydrogen sulfide and other sulfur compounds (e.g., mercaptans) in gas streams may range from trace amounts to over 30 molar percent (EPA, 1983). Other acid gases, particularly CO_2, may also be present in natural gas in significant quantities, presenting the potential for hydrate formation, corrosion, and reduction in heat content of the product gas. Due to the wide variability in acid gas content, flow rate, pressure, temperature, and other production parameters, a number of different sweetening methods are currently in use in U.S. natural gas plants and field sweetening units.

In general, natural gas sweetening processes depend on the chemical or physical absorption of acid gases with a sweetening agent. Inlet gas contacts the sweetener in a contact tower and is removed from the gas stream. Sweeteners may be liquid or solid, and may be used in batch processes without regeneration, or may be regenerated continuously until spent. Reaction products may be elemental sulfur, insoluble sulfur salts, or high concentration acid gas streams. Acid gases produced during solvent regeneration may be vented to the atmosphere or incinerated. In many instances, sulfur recovery follows sweetening of the natural gas stream, with the sulfur either sold or disposed.

A 1982 API Gas Plant Survey identified 278 gas streams conditioned for acid gas removal out of a total survey population of 731 gas streams (EPA, 1983). Many of the gas streams underwent "field sweetening" prior to gas plant processing. Survey data indicate the type of field and plant sweetening methods employed, inlet and product acid gas concentrations, and acid gas disposal methods, as well as the type of sulfur recovery employed and total sulfur production, if any, for most of the gas streams in the survey[5].

These data fall short of permitting an estimation of the number of sweetening facilities in operation, however. First, the population survey represents roughly 72 percent of the marketed production of natural gas for 1982. Even assuming that the occurrence of acid gases in the remaining 28 percent of the gas produced is roughly equivalent to the value determined for the survey population (roughly 25 percent), it is not now possible to estimate the number of distinct *gas streams* which account for that production. Second, while the survey notes the number of gas streams which underwent sweetening at field facilities, it is silent with regard to the number of *facilities* that performed such sweetening.

A 1991 survey of the natural gas processing industry conducted for GRI identified 617 U.S. gas sweetening plants (GRI, 1995). Of these, 394 or 64 percent use chemical solvents and process 34,259 million cubic feet per day (MMscfd) of a total of 47,387 MMscfd for all sweetening plants. Over 92% of the plants

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[5] A number of survey respondents indicated inlet gas acid gas concentrations above pipeline specifications but did not specify the sweetening methods used.

using chemical solvents were using some variety of amine. Further, 105 gas processing plants were also recovering sulfur of which at least 60 percent use the Claus process or a variant of the Claus process; e.g., Selectox.

Table 2-9 indicates that, of the gas streams identified in the GRI survey, amine sweetening was by far the most commonly used method. The predominant amines used include monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA). Sulfinol (mixed amine solution), and other solvents were also used to a far less extent. Together, amine sweetening processes were used for 73 percent of the gas streams and 82 percent of the total throughput identified in the survey. Fifteen gas streams in the survey underwent iron sponge sweetening, accounting for less than three percent of the total throughput. The data also included 105 sulfur recovery plants, of which at least 60 percent employed some variation of the Claus process to produce sulfur from acid gases.

It is worth noting that the remaining gas production unaccounted for in the survey may have been from numerous small-quantity producers, many of which may have utilized small field or lease sweetening units. For instance, the survey indicates that 15 gas streams in the survey underwent sweetening by the iron sponge process. Other sources indicate that iron sponge is widely used, however, with "thousands" of units in service in the U.S. (Harrel and Manning, 1986; Thompson, R.E., 1992; ERT, 1988). Harrel and Manning also report that Chemsweet and Sulfacheck systems each number around 100 (see below for description) (Harrel and Manning, 1986).

The following discussion briefly explains the major sweetening processes currently in use. Table 2-10 also provides some details on processes. Batch processes (those without regeneration of reactants) are discussed first, then continuous processes. Finally, sulfur recovery operations are briefly described.

2.3.1 Iron Sponge Process

One of the oldest methods for removing sulfur compounds from gas streams, the iron sponge process, is based on the reaction of ferric oxide (Fe_2O_3) and hydrogen sulfide (H_2S) to form iron sulfide (Fe_2S_3) (Harrel and Manning,1986). Typically, the "sponge" consists of wood chips or other light-weight, porous media, impregnated with hydrated Fe_2O_3. The wood chips fill the absorber through which scrubbed inlet gas flows. As H_2S reacts with the Fe_2O_3, Fe_2S_3 accumulates on the surface of the sponge, while sweetened gas exits from the top of the vessel. Figures 2-6 and 2-7 show typical iron sponge systems. Figure 2-6 depicts a flow diagram for a non regenerating single absorber system. Because the absorbent is discarded once spent, iron sponge systems may also be configured with two absorbers so that one may be recharged while the other continues to condition the gas stream (Figure 2-7). The absorbent is regenerated until it is no longer effective. The spent absorbent is disposed of and replaced with new absorbent. Because of additional costs and potential operational problems, regenerating iron sponge systems are not common.

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)

Table 2-9. Distribution of Gas Plants by Sweetening Process, Sulfur Recovery Process and Throughput from 1991 GRI Gas Plant Survey

Process	Number of Gas Plants	Total U.S. Capacity[a] (MMscf/day)	Percent of Total U.S. Capacity
Sweetening			
Chemical Solvents:			
Monoethanolamine (MEA)	116	8,105	17
Diethanolamine (DEA)	189	15,946	34
Methyldiethanolamine (MDEA)	30	2,721	6
Diglycolamine (DGA)	36	3,661	8
Benfield	7	579	1
Other	16	3,247	7
Subtotal	394	34,259	72
Physical Solvents:			
Sulfinol (DIPA)	57	4,580	10
Selexol	5	1,020	2
Other	4	105	0
Subtotal	66	5,705	12
Non-amine Sweetening:			
Molecular Sieves	[b]	3,711	8
Direct Conversion:		1,626	3
Iron Sponge	15	[b]	0
LO-CAT	13	[b]	0
Sulferox	7	[b]	0
Sulfatreat	3	[b]	0
Sulfacheck	2	[b]	0
Stretford	1	[b]	0
Membranes	[b]	175	0
Extractive Distillation	[b]	538	1
Unknown	[b]	1,121	2
Subtotal	157	7,423	16
Total Sweetening Plants/ Capacity	617	47,387	100

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)

Table 2-9. Distribution of Gas Plants by Sweetening Process, Sulfur Recovery Process and Throughput from 1991 GRI Gas Plant Survey

Process	**Number of Gas Plants**	**Total U.S. Capacity[a] (MMscf/day)**	**Percent of Total U.S. Capacity**
Sulfur Recovery			
Thermal/Catalytic:			
Claus	58	5,415	77
Selectox	5	450	6
Other/Unknown	21	421	6
Liquid Redox:			
LO-CAT	13	336	5
Sulferox	7	417	6
Stretford	1	8	0
Total Sulfur Plants/ Capacity	105	7,047	100

[a] Capacity in terms of volume of raw gas to sweetening unit.

[b] Not available

Source: GRI 1995

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-10. Sweetening Processes Summary Table

Process	Process Type	Active Agents/Additives	Regeneration	Comments
MEA	Continuous/chemical absorption	MEA (10-20%) Corrosion inhibitors Anti-foamants	Steam stripping/reboiler Distillation reclaimer	Corrosive, high potential for thermal degradation. May be used for NGL sweetening.
DEA	Continuous/chemical absorption	DEA (10-20%) Corrosion inhibitors Anti-foamants	Steam stripping/reboiler	Corrosive. May be used for NGL sweetening.
DGA	Continuous/chemical absorption	DGA (40-70%) Corrosion inhibitors Anti-foamants	Steam stripping/reboiler Distillation reclaimer	Corrosive, high potential for thermal degradation. May be used for NGL sweetening.
MDEA	Continuous/chemical absorption	MDEA (30-50%) Corrosion inhibitors Anti-foamants	Steam stripping/reboiler	Corrosive. May be used for NGL sweetening.
Sulfinol	Continuous/chemical and physical absorption	MDEA or DIPA, and Sulfolane as physical solvent Corrosion inhibitors Anti-foamants	Steam stripping/reboiler	Significant absorption of hydrocarbons
Potassium carbonate	Continuous/chemical absorption	K_2CO_3 Metal borates (Catacarb process) Vanadium oxide (Benfield process)	Steam stripping/reboiler	
Iron sponge	Batch/chemical reaction	Fe_2O_3 Caustic soda	Partial revivification through addition of oxygen	Low acid gas concentrations, low throughput. Sulfur produced but unrecovered.
Chemsweet	Batch/chemical reaction	ZnO $ZnAc_2$	None. (ZnO replenishes the $ZnAc_2$ in absorber, but sweetening ceases when all ZnO is consumed.)	

(continued)

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-10. Sweetening Processes Summary
(continued)

Process	**Process Type**	**Active Agents/Additives**	**Regeneration**	Comments
Sulfa-Check	Batch/chemical reaction	$NaNO_2$ Buffer	None.	Sulfur produced but unrecovered. May result in by-production of nitrogen oxides.
Selexol	Continuous/physical absorption	Dimethyl ethers of polyethylene glycols	Low pressure flash, stripping with flash gas, or steam stripping, depending on system configuration and amount of hydrocarbon and H_2S in solvent.	
Stretford	Continuous/liquid redox	Sodium carbonate Anthraquinone disulfonic acid (ADA) Sodium vanadate Sodium citrate or sodium thiocyanate	Continuous reoxidation of catalysts through addition of oxygen.	Sulfur produced, may be recovered for sale. Product sulfur may be contaminated with vanadium. Side reactions produce thiosulfates and sulfates. May entail high solution changeout rates.
Molecular sieve (Gas/NGL)	Continuous(with multiple contactors)/adsorption	Silicates Alumina Zeolytes	Hot gas regeneration, with regeneration gas separation.	Very high removal rates for water and H_2S.
Caustic Wash (NGLs)	Continuous/chemical reaction	NaOH Various additives (see text)	Optional. Reboiler/steam stripping.	

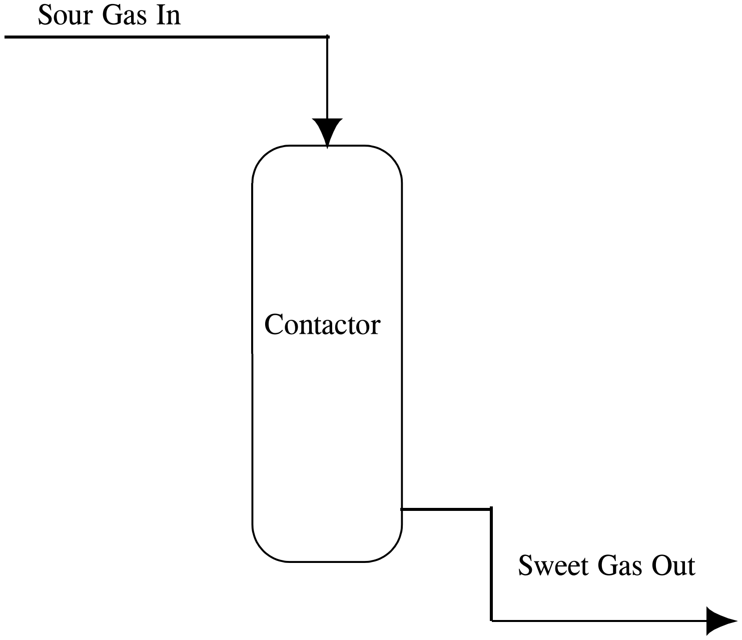

Figure 2-6. Iron Sponge Sweetening Unit with Single Absorber (Non Regenerating)

Iron sulfide reacts readily with oxygen to form Fe_2O_3 and elemental sulfur. Addition of air to the absorber provides the possibility of regenerating the iron sponge as sweetening occurs. However, elemental sulfur will eventually accumulate sufficiently to cover the sponge surfaces until no further sweetening can occur. More importantly, the reaction of Fe_2S_3 to form sulfur is exothermic, such that with excessive air input the sponge may combust. Accordingly, regeneration is often not employed with iron sponge systems (Harrel and Manning, 1986).

Iron sponge systems are regarded as easily operated and very cost effective, particularly for gas streams with low to very low concentrations of H_2S, and/or low volume production rates (Manning and Thompson, 1991). According to one source, there are "thousands" of such systems in use throughout the U.S. (Harrel and Manning, 1986).

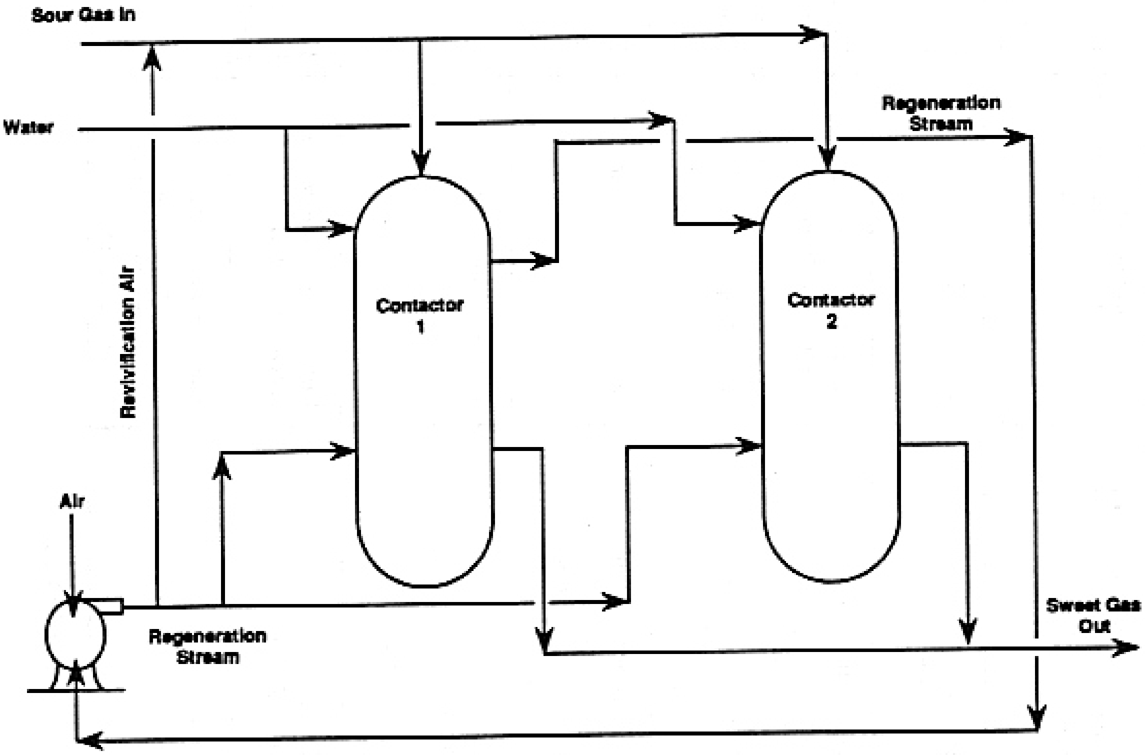

Figure 2-7. Iron Sponge Sweetening Unit with Two Absorbers (Regenerating) (After Manning and Thompson, 1991)

2.3.2 Chemsweet Process

Like iron sponge systems, Chemsweet systems are batch processes in which sour gas is fed through the contactor until no further sweetening occurs, at which point the spent sweetener is discarded. Chemsweet, manufactured by NATCO, is a mixture of zinc oxide, zinc acetate, and a dispersant to maintain a suspension of reactants (Manning and Thompson, 1991). Inlet gas is bubbled through the absorber where H_2S reacts with the zinc acetate, forming zinc sulfide and acetic acid. The zinc oxide replenishes the acetate and the reaction continues until all of the zinc exists as zinc sulfide. Normal bed life is 30 to 90 days (Harrel and Manning, 1986).

Chemsweet is typically used for low acid gas production streams and low production rates. The system is insensitive to high CO_2 concentrations. According to one source, there are roughly 100 of these units in operation throughout the U.S (Harrel and Manning, 1986).

2.3.3 Sulfacheck Process

Sulfacheck, manufactured by NL Treating Chemicals, is a buffered aqueous solution of sodium nitrite ($NaNO_2$), with pH maintained above 8 (Manning and Thompson, 1991). Sulfacheck systems are simple batch absorbers through which scrubbed inlet gas is bubbled. Sodium nitrite reacts with H_2S in the gas, forming caustic soda, ammonia, and elemental sulfur. Sweetening proceeds until available nitrite is consumed. Typically utilized for low flow rate and low acid gas concentration production streams, the process does not generate sufficient sulfur to warrant sulfur recovery (Manning and Harrel, 1986). Because it is a batch process, two absorbers are required for continuous operation; otherwise, production must be interrupted during recharge of the absorber. Normal bed life is 30 to 90 days (Harrel and Manning, 1986)

Use of Sulfacheck may be limited in some areas due to the potential for high by-product generation of nitrogen oxides (NO and NO_2) in excess of 300 ppm, as well as ammonia (NH_3) (Schaak and Chan, 1989). Nitrogen oxides and ammonia leave the absorber as impurities in the sales gas stream and may exceed contract specifications. According to one source, there are roughly 100 of these units in operation throughout the U.S (Harrel and Manning, 1986).

2.3.4 Amines

Sweetening amines are a family of organic molecules which react readily with acid gases. The use of amines to sweeten gas streams has been practiced for over fifty years, and amines today remain the most widely used sweetening agents in the U.S. natural gas processing industry (EPA, 1983; Manning and Thompson, 1991). The amines of greatest commercial significance are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA). These solvents may be used alone or in specialty mixtures with corrosion inhibitors, buffers, anti-foamants, and promoters (Manning and Thompson 1991). Currently available information indicates DEA is the most commonly used sweetening solvent (Manning and Thompson, 1991; GRI, 1995).

Figure 2-8 shows the general flow diagram for amine sweetening units. Inlet gas is scrubbed for removal of free liquids and solids prior to entering the absorber. As the gas flows through the absorber, acid gases react with the amines and remain in solution as the sweetened gas exits through the top of the tower. Lean amine is supplied at the top of the tower and flows countercurrent to the rich amine outlet at the base of the absorber. Because amines absorb some hydrocarbons along with the acid gases, rich solvent enters a flash tank, allowing hydrocarbons to escape. The rich amine is then filtered and injected into the regeneration still. Heat drives off the acid gases, producing a high concentration acid gas stream which is flared, incinerated, or sent to a sulfur recovery circuit.

Amine circuits generally include filters for the rich and lean streams. The filters remove accumulations of condensed and cracked hydrocarbons, amine degradation products, organic acids, corrosion products, and other materials (Manning and Thompson, 1991). Additionally, primary amines (e.g., MEA, DGA) require reclaimers for additional regeneration (Manning and Thompson, 1991; Simmons, 1991). The amine reclaimer continuously distills a portion of the amine (typically 1-3 percent) in the presence of a strong base (caustic soda or soda ash). The reclaimer is necessary to remove salts formed with the amines as well as iron sulfide, amine degradation products, and heavier hydrocarbons (Manning and Thompson, 1991).

Manning estimates that there are currently over 700 amine units in operation in the U.S. While many of these are DEA units, other amines are still in use.

2.3.5 Selexol Process

The Selexol process has been used for bulk removal of CO_2 as well as simultaneous removal of H_2S and CO_2 (Manning and Thompson, 1991). Selexol is a physical solvent of dimethyl ethers of polyethylene glycols (DMPEGs), which absorb acid gases, heavier hydrocarbons, and aromatic compounds (Maddox, 1985). Figure 2-9 shows the basic flow diagram for the process.

Inlet gas flows countercurrent through the absorber, where acid gases and some hydrocarbons are absorbed. Sweetened gas leaves the top of the absorber while rich Selexol is conveyed to a separator or surge tank. The separator allows removal of methane and lighter hydrocarbons absorbed in the solvent. The rich solution then passes through a series of flash tanks of decreasing pressure in which all of the acid gasses are flashed and removed to a vent (or flare, depending on the H_2S content). Depending on the methane content of the rich stream, gases from the high pressure flash tank may be recycled to the absorber or utilized as fuel gas (Maddox, 1985). The last flash tanks may be atmospheric and vacuum flashes capable of driving off nearly all of the absorbed gases. Available information does not indicate the number of Selexol units in operation.

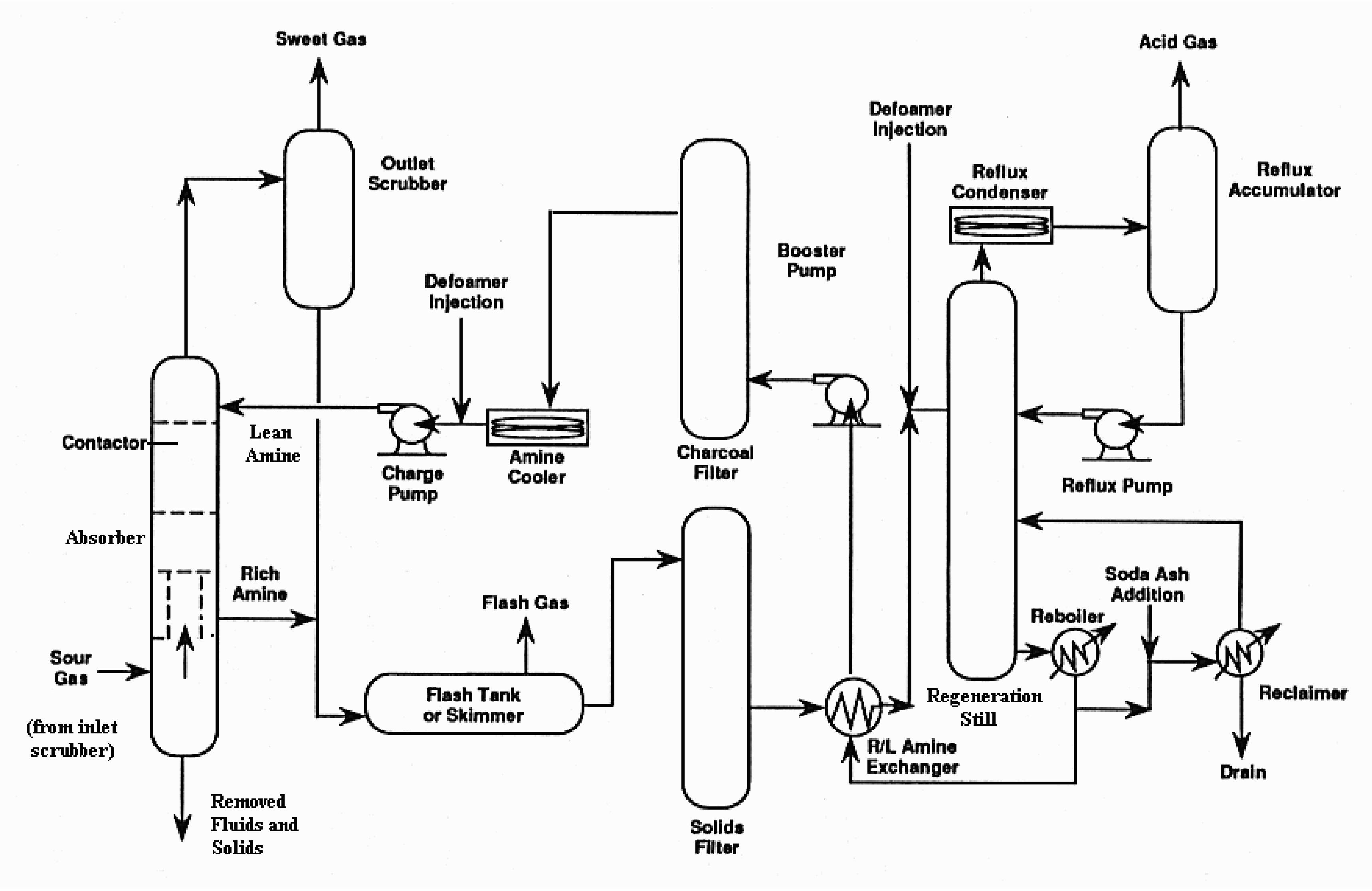

Figure 2-8. Basic Amine Sweetening Process (After Manning and Thompson, 1991)

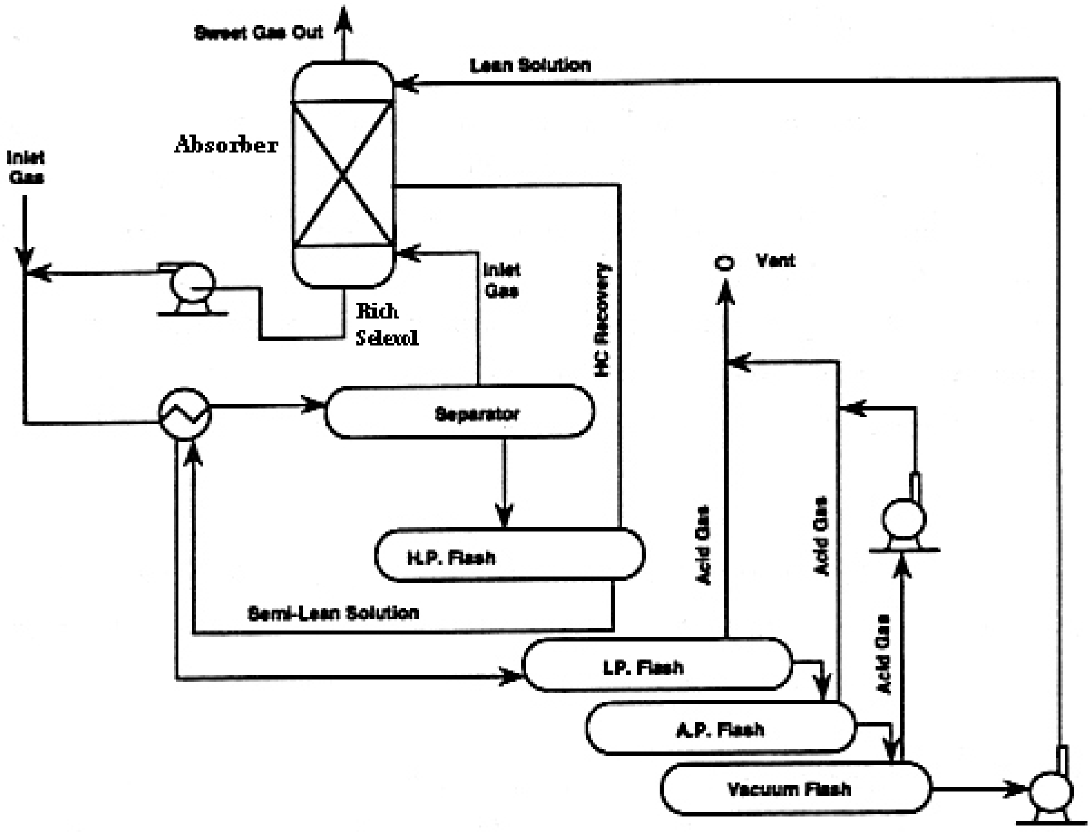

Figure 2-9. Basic Selexol Process (After Manning and Thompson, 1991)

2.3.6 Potassium Carbonate Sweetening

In hot potassium carbonate (K_2CO_3) processes, sour gas flows countercurrent through an absorber containing K_2CO_3 heated to 220 to 400 degrees F (Manning and Thompson, 1991). Carbon dioxide and H_2S react with the potassium to form bicarbonate and bisulfide salts in solution. The solution is easily regenerated in a stripping still, yielding a high concentration acid gas waste stream. In the Catacarb process, alkali metal borates are added to the solvent to improve the rate of reaction (Manning and Thompson, 1991). Similarly, the Benfield process uses vanadium oxide as a catalyst (Maddox, 1985). Corrosion inhibitors may include arsenic and vanadium salts, as well as dichromates (dichromates are not used in the presence of carbon dioxide) and filming amines (Maddox, 1985). Available information does not indicate the number of potassium carbonate sweetening units in operation.

2.3.7 Liquid Redox (Reduction-Oxidation) Processes

A number of sweetening processes rely on the direct conversion of H_2S to elemental sulfur in an alkaline solution. Called liquid redox processes, these processes utilize metal complexes (vanadium or iron) which convert H_2S to sulfur and are subsequently reoxidized with oxygen in the reaction vessel. Such processes include the Stretford process, the Sulferrox process, and the Lo-Cat process. The Stretford process utilizes vanadium in a continuous regenerative process producing elemental sulfur froth which may be separated for recovery. Lo-Cat and Sulferrox processes utilize iron chelation to promote direct conversion, and generate sulfur/solution slurries which may be separated for sulfur recovery. The Stretford process is discussed below.

Stretford solution is an aqueous solution of sodium carbonate, with anthraquinone disulfonic acid (ADA) serving as an oxygen carrier and sodium vanadate ($NaVO_3$) serving as a catalyst (Delaney and Schraam, 1991, Maddox 1985). In the process, H_2S absorbs into the basic solution and reacts with the soluble vanadium salt, forming sulfur (Maddox, 1985). The reduced vanadium is oxidized by the ADA, which is subsequently reoxidized by oxygen added to the solution. Sulfur produced by the reaction forms a froth in the oxidation vessel and is removed to the skim tank. From the skim tank the sulfur may be treated in a number of ways for sulfur recovery. Figure 2-10 shows the basic flow diagram for the Stretford process.

During sulfur recovery, Stretford solution is separated from the sulfur via filtration or centrifugation and returned to the oxidation vessel. The sulfur may be dried to form sulfur cake. Alternatively, heating the divided sulfur particles yields molten sulfur.

Stretford operations may be hindered by undesirable side reactions. In particular, soluble thiosulfate salts ($S_2O_3^{2-}$) and sulfates may form (Leppin, et. al., 1991). At high sodium thiosulfate concentrations, ADA and vanadium may precipitate out of solution (Trofe and DeBerry, 1991). Salting out of reactants may require partial or complete blowdown or change out of solution. As a result, some facilities may add sodium citrate or sodium thiocyanate to reduce thiosulfate formation (Trofe and DeBerry, 1991). Additionally, biocidal agents may be employed in the solution (Eisele, 1991).

Stretford operations have been utilized in a number of industries. Available information does not provide an estimate of the total number of Stretford units in operation as natural gas sweetening units.

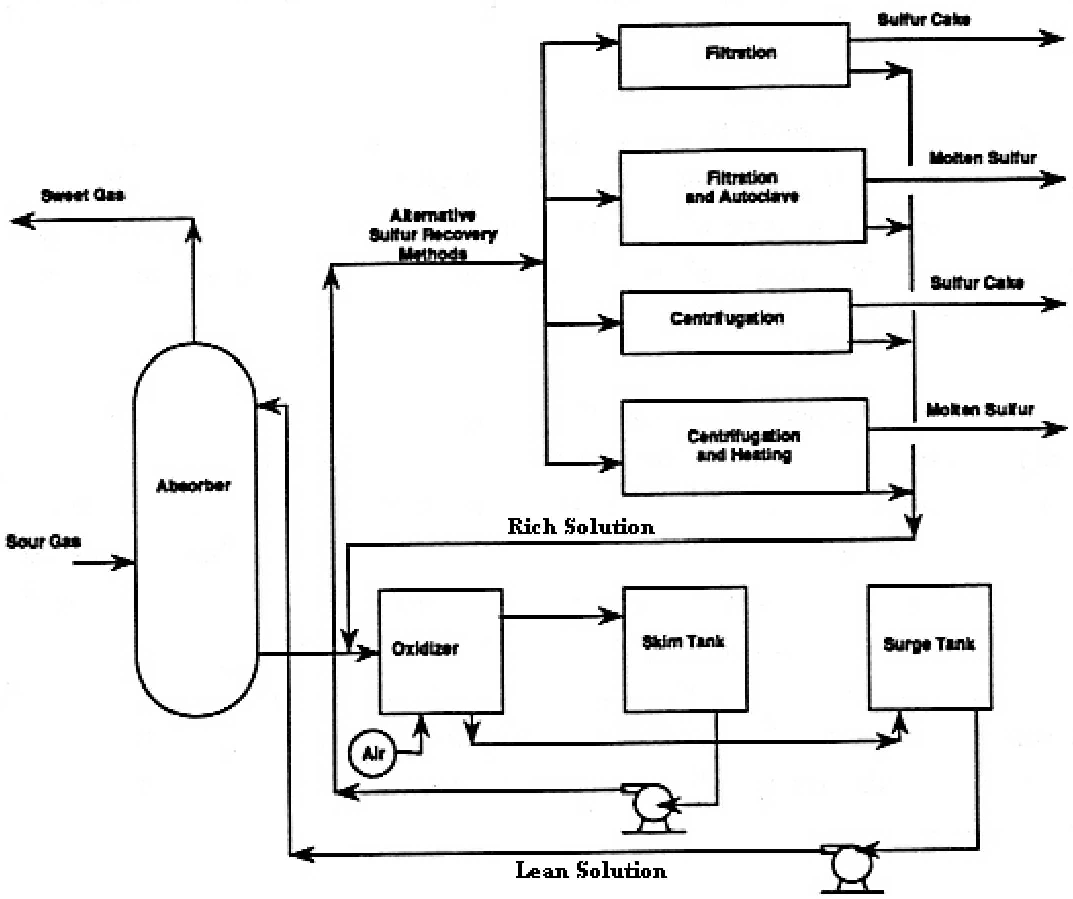

Figure 2-10. Basic Stretford Process (After Manning and Thompson, 1991)

2.3.8 Caustic Wash Sweetening of Natural Gas Liquids

Natural gas liquids (NGLs), like gas, may contain sulfur compounds. Sulfur species which may be present in NGLs include hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide, and mercaptans (Maddox, 1985). COS tends to concentrate in propane often requiring treatment (Markovs, 1990).

A number of processes exist to sweeten NGLs. These include the caustic wash process (with or without regeneration of spent caustic), amine sweetening, and use of molecular sieves. NGL sweetening processes are briefly described below.

Sodium hydroxide (NaOH) is frequently used to remove sulfur compounds from NGLs (API, 1989a). Caustic wash systems may be very simple, with inlet hydrocarbons mixed with a dilute caustic solution prior to entering a phase separator. Typically, caustic solution containing Na_2S and dissolved hydrocarbons is discarded, with sweetened hydrocarbons requiring dehydration prior to sales (Maddox, 1985). Alternatively, the rich caustic may be regenerated using a reboiler and stripper. Steam from the reboiler strips sulfur compounds from the rich caustic. Steam leaving the still is condensed, with sulfur compounds removed from the condensate. Water and regenerated caustic are then recycled back to the contactor (Maddox, 1985).

A number of substances may be added to caustic solutions to increase the solubility of sulfur compounds. Table 2-11 lists substances which have been used for this purpose. Available information does not indicate the extent to which these substances are used in operating natural gas sweetening facilities not associated with refineries. Further, available data does not indicate the number of caustic wash facilities in use throughout the U.S.

During EPA's 1992 sampling program (see Section 2.5), a sample of recycled caustic was collected from a sour gas plant in Texas. In this plant, caustic was regenerated and re-used; the sample was taken after the regeneration step (how many times it had been regenerated previously was not determined) before subsequent re-use for sweetening. Thus, the sampled material was not a waste; however, the constituents present could be expected to be present when it finally becomes spent and requires management as a waste--indeed, it is likely that at least some constituent concentrations would increase as the caustic is repeatedly re-used and regenerated. Concentrations of selected constituents are shown in Table 2-12 (all results are shown in Appendix A). As can be seen, metals were detected at relatively low concentrations. As would be expected, sodium and sulfur concentrations and pH were all very high. No organic compounds were detected.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-11. Substances that Increase Solubility of Sulfur Compounds in Caustic

- Acid oil
- Alcohols
- Aliphatic or alicyclic dicarboxylic acids
- Alkyl glycerol
- Alkylol amines
- Alkyl phenols
- Alkyl phenols and isobutyric acid
- Amines, cresylates and naphthenates
- Aminoalkylamines or alkanolamines
- Aminobutylene glycol
- Aromatic monocarboxylic acids
- Butylene glycol
- Butyric or propanoic acid
- Carboxy ethers
- Chloroacetic acid
- Chlorophenol, chlorocresol or chlorohydroquinone
- Compounds containing amino and hydroxy radicals and oxygen or sulfur
- Clutaric acid
- Copal and cresol
- Cumic acid
- Diamine alcohols
- Ethylene glycol
- Ethylene glycol and naphthenic acids
- Ethyl thioglycolic acid
- Glycols and naphthenic acids
- Hydroxy butyric acid
- Hydroxy valeric acid
- Isobutyric acid
- Methyl cellosolve, naphthenic acids and cresols
- Methyl alcohol
- Monomethyl glyceryl ether
- Morpholine
- Naphthenic acids and phenols
- Nitroparaffins
- Oxidation products of petroleum and cresols
- Polyether acids
- Polyhydroxy biphenyls
- Polyphenols
- Propylene glycol
- Rosin
- Rosin and cresols
- Shellac
- Substituted amino acids
- Tannic acid
- Tannic acid and oxygen
- Tar acids
- Thioacids of phosphorus
- Thiocresols
- Thioethers
- Triethylene glycol
- Trimethyl ammonium hydroxide
- Yacca Gum

Source: Maddox 1985

Associated Waste Report:
Dehydration and Sweetening Wastes
(U.S. EPA, January 2000)
TABLE 2-12. Concentrations of Selected Constituents in Caustic Sample

Analyte	µg/L
pH (s.u.)	13.12
Arsenic	ND
Barium	27.2
Cadmium	ND
Chromium	ND
Lead	ND
Magnesium	ND
Mercury	ND
Selenium	ND
Silver	ND
Sulfur	627,000

NA Not analyzed
ND Not detected

2.3.9 Amine Sweetening of Natural Gas Liquids

Several amines, including MEA, DEA, and DGA (the Malaprop process), have been used to remove sulfur compounds from natural gas liquids (Maddox, 1985). Such systems rely on the same reactions as gas sweetening systems, but require liquid/liquid contactor vessels versus the typical gas/liquid absorbers. Sulfur compounds react with the amine in the contactor and enter the amine phase of the treatment stream. Different specific gravities allow separation of the sweetened hydrocarbon from the rich amine. The hydrocarbon leaves the contactor and is filtered prior to entering the sales line. Rich amine is regenerated in the same manner as in gas sweetening facilities (see above). Available information does not permit estimation of the number of such facilities in operation.

2.3.10 Molecular Sieve Sweetening of NGLs

Sweetening of NGLs with molecular sieves is accomplished in the same manner as sweetening of sour gases. Hydrocarbons flow through the contactor, where both water and sulfur compounds are adsorbed by the zeolite crystals. For regeneration, liquids are drained from the contactor and heated regeneration gas is cycled through the bed, driving off water and adsorbed sulfur compounds. For more details, see the discussion of dehydration using molecular sieves above.

2.3.11 Sulfur Recovery

Iron sponge, Chemsweet, and other batch sweetening processes produce elemental sulfur or sulfur salt slurries which are disposed in solid form. Due to the small volume of sulfur and the often high difficulty in converting it to a marketable product, sulfur recovery is not practiced with these systems. Liquid redox systems, such as the Stretford and Lo-Cat processes, generate elemental sulfur through direct conversion of hydrogen sulfide. These systems produce sulfur of variable quality which may be sold or disposed depending on the quantities produced as well as the quality of the product and available markets.

For most continuous gas processes, sweetening results in the production of an acid gas stream. The acid gas may be vented, flared, or incinerated. However, in many instances the gas generated contains sufficient H_2S concentration to warrant conversion to elemental sulfur. By far the most frequently used sulfur recovery method is the Claus process (with several variations) (Anonymous,"Annual Natural Gas Report." Vol. 90, No. 29, *Oil and Gas Journal*, 1992). This section briefly explains the Claus process for sulfur recovery, which is illustrated in Figure 2-11.

In the Claus process, sulfur in the acid gas is oxidized with air over a bauxite or iron ore catalyst to form elemental sulfur (Maddox, 1985). Several variations of the basic process exist, with the choice of system in part determined by the concentration of sulfur in the feed stream (EPA, 1983). Typically, the process involves burning one-third of the H_2S to form SO_2, and then reacting the SO_2 with the remainder of the feed to form elemental sulfur. Depending on the process used, Claus sulfur recovery may reach up to 97 percent of the sulfur in the feed stream. The sulfur is produced as molten sulfur at roughly 300 degrees F, and may be marketed in molten form or cooled and sold as a solid.

2.4 SWEETENING WASTE GENERATION AND NATURE OF WASTES

Like dehydration facilities, sweetening units may generate a wide variety of wastes, some of which are not unique to gas conditioning operations. Among the wastes generated at such facilities are those that were explicitly listed in EPA's regulatory determination for oil and gas exploration and production wastes: amine, amine filters, amine filter media, backwash, precipitated amine sludge, iron sponge, and hydrogen sulfide scrubber liquid and sludge. Other wastes which may be generated at sweetening plants include: amine reclaimer sludge, spent sweeteners other than amine and iron sponge (e.g., K_2CO_3, and molecular sieves), and regeneration condensate. Additionally, flare pit sludge and wastes from sulfur recovery may be generated at sweetening facilities.

One survey of dehydration and sweetening wastes, the API survey, does not distinguish between the two categories (with the exception of spent iron sponge, which is handled as a distinct category of wastes). Waste volume data from the API survey will be presented along with waste management data in Section 3.1 of this report. GRI has also developed national estimates of several sweetening wastes, and these are presented in the following section.

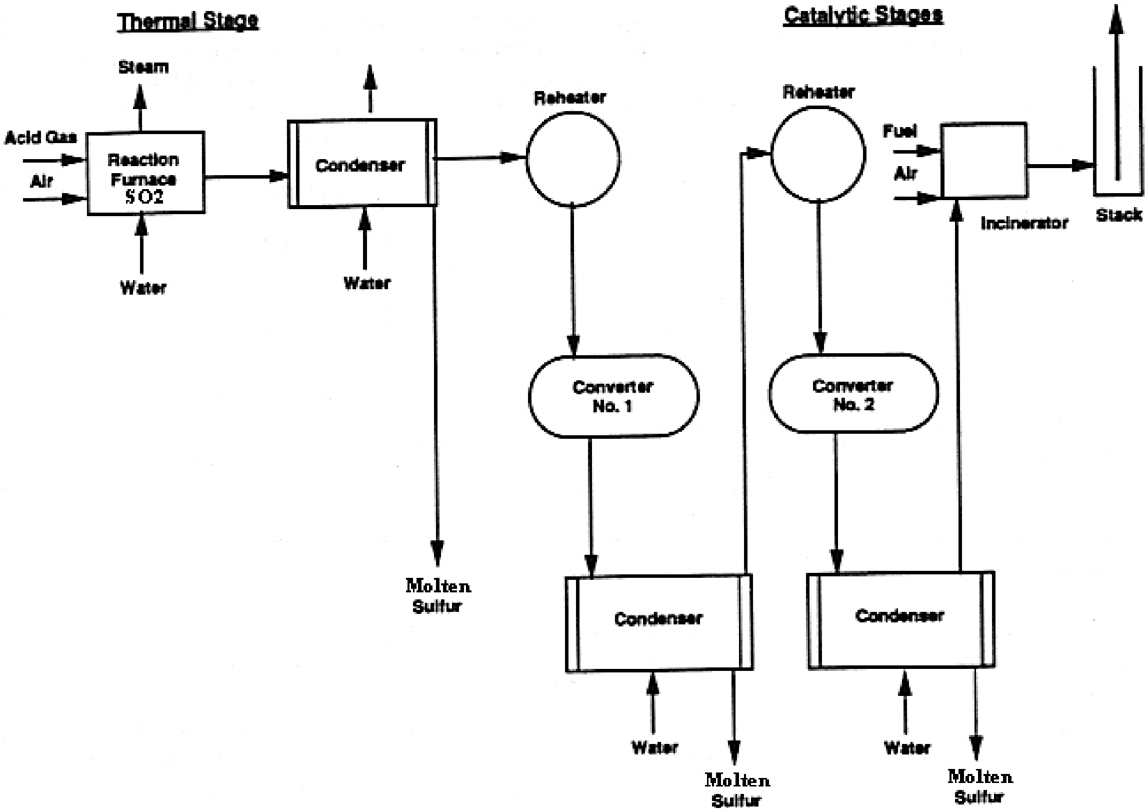

Figure 2-11. Claus 2-Stage Sulfur Recovery Process (After EPA, 1983)

2.4.1 Spent Iron Sponge

Iron sponge sweetening is a batch process in which all of the sweetener is eventually consumed. Reaction of the Fe_2O_3 and H_2S yields Fe_2S_3. Spent iron sponge consists principally of wood chips coated with elemental sulfur and Fe_2S_3. Note that iron sponge is sometimes described as both reactive and pyrophoric (Manning and Thompson, 1991, Harrel and Manning, 1986; Maddox, 1985; Schaak and Chan, 1989). On the other hand, analysis of a single sample of spent iron sponge presented in the 1988 API report indicated that the waste sample tested was not pyrophoric (see waste characteristics, ERT, 1988). In either case, the ability of the ferric sulfide to react with atmospheric oxygen forming sulfur and liberating heat is transitory, ceasing when all ferric sulfide has been oxidized to elemental sulfur. The rate of reaction, and hence the ignitability of iron sponge, is partially controlled by water. Thus, hydrated iron sponge will display a lower tendency to autocombust than dried sponge (Schaak and Chan, 1989). Typically, iron sponge is fully wetted in the absorber before being removed for disposal. Spent iron sponge is covered by the API survey, and is discussed further in Section 3.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-13. Sweetening Process Waste Summary

Process	Waste Type	Nature of Wastes
Amines (MEA, DEA, DGA, MDEA, DIPA)	Amine Filter Sludge	Inorganic: Pb, Vn, Cd, Hg, Ar may be present. Cyanide, thiocyanates may be present Organic: Amines and cyclic amines Aliphatics Aromatics Organic acids
	Amine Reclaimer Sludge	
	Spent Amine	
Mixed Amine Solutions (e.g., Sulfinol)	Filter Sludge	No information available. May be similar to amine process wastes.
	Reclaimer Sludge	
	Spent Solvent	
Potassium Carbonate	Filter Sludge	No information available.
	Spent Solvent	
Selexol	Filter Sludge	No information available.
	Spent Sweetener	
Molecular Sieve	Regenerator Sludge	Principally water, but may contain dissolved hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and toluene).
	Regenerator Condensate	
	Spent Molecular Sieve	Molecular sieve, hydrocarbons. lubrication oils, sulfur compounds.
Iron Sponge	Spent Iron Sponge	Consists of iron oxide, elemental sulfur, and wood chips. May be pyrophoric.
Chemsweet	Spent Solvent	Aqueous slurry of zinc sulfide in water, acetic acid, with dissolved hydrogen sulfide. Acidic.
Sulfacheck	Spent Solvent	Two phase mixture of sulfur, sodium and ammonium salts, in water and sodium hydroxide. Basic.
Stretford Process	Spent Solution	Hydrocarbons, sulfur, organics, thiosulfates, thiocyanates, vanadium salts.
	Scrap Sulfur	Sulfur with impurities, including thiocyanates, vanadium salts.

2.4.2 Spent Chemsweet Solution

Because the Chemsweet process is a batch process with no regeneration, no filtration, and no evolution of condensate or other side streams, the primary sweetening waste stream generated by such facilities is spent solution. Spent Chemsweet solution is a two-phase mixture, with zinc sulfide as the solid phase and water with dissolved hydrogen sulfide and acetic acid as the liquid phase, with dispersant material also present (Harrel and Manning, 1986). Spent solution is acidic, but available information does not indicate the range of pH that such wastes may exhibit or other waste characteristics. Available information does not permit an estimation of the total volume of spent Chemsweet solution generated.

2.4.3 Spent Sulfacheck Solution

Because the Sulfacheck process is a batch process with no regeneration, no filtration, and no evolution of condensate or other side streams, the primary sweetening waste stream generated by such facilities is spent solution. Solution replacement is required once every 60-90 days (Schaak and Chan, 1989). Spent Sulfacheck solution is a two-phase mixture, with fine sulfur particles and sodium and ammonium salts as the solid phase, and water with dissolved hydrogen sulfide, sodium hydroxide, and ammonium hydroxide as the liquid phase, with dispersant material also present (Harrel and Manning, 1986; Schaak and Chan, 1989). Because caustic soda is generated in the reaction, the pH of the solution may reach 12.5 (Manning and Thompson, 1991). However, CO_2 present in the feed reacts with sodium hydroxide, neutralizing the spent solution to some extent. Available information does not include waste characteristics. Available information does not permit an estimation of the total volume of spent Sulfacheck solution generated annually.

2.4.4 Spent Potassium Carbonate Solution

Available information does not indicate the nature of spent potassium carbonate solution, nor the volume of such wastes generated throughout the U.S.

2.4.5 Spent Selexol Solution

Available information does not indicate the nature of spent Selexol solution, nor the volume of such wastes generated throughout the U.S.

2.4.6 Amine Filter Sludge and Filter Media

As stated previously, amine filters remove accumulations of condensed and cracked hydrocarbons, amine degradation products, organic acids, and other materials. Backwashing of filters and replacement of filter charges results in the generation of filter sludges and used filter media. Such wastes will include those materials previously removed from the amine stream. Note, however, that the composition of such wastes may change substantially depending on how they are managed and the nature of other wastes with which they may come into contact (Boyle, 1990).

A number of studies have been performed in Canada to characterize amine filter, sludge, and reclaimer bottom wastes generated at sour gas plants in that country. Another study by GRI examined wastes from amine-based sweetening and Claus sulfur recovery processes (GRI, 1995) and also includes data presented by Boyle and others. Results obtained from those studies may provide an indication of the potential characteristics of amine plant wastes in the U.S. It is important to note, however, that the characteristics of filter sludge, filter media, and other amine wastes can vary substantially with the quality of the feed gas, the type of amine used, and other operating conditions of the unit generating them (Boyle, 1990).

Table 2-14 presents data on the inorganic constituents found in amine filters and amine sludges[6] from unspecified sources. The data indicate the potential for high heavy metals concentrations in amine filters and sludges. In particular, lead, vanadium, cadmium, mercury, and arsenic are shown at very elevated levels. Additionally, cyanide and thiocyanate are shown at very high concentrations. Note, however, that these results are generally much higher than other values reported by Boyle and others. Table 2-15 shows inorganic constituents found in DEA filter sludges at three Canadian gas plants. Comparing the data from the two tables shows reasonable agreement between reported values for chromium, copper, and zinc, but large disparities for other constituents. (Boyle provides no explanation of the wide disparity between the values reported by various sources).

The data in Table 2-14 also indicate the variability in waste constituents due to differences in operating practices. Boyle reports that Plant B operators added sodium hydroxide to amine solution to control corrosion difficulties, while Plant C operators did not. These differences are partially reflected in the difference in pH for the two plants, as well as in the different concentrations of copper and nickel detected. No explanation was provided for the large differences in nitrogen levels.

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[6] Data reported by Wootherspoon and Associates, et. al., 1989, 1990, as cited in Boyle, 1990. Boyle states that sources of wastes, sampling methods and analytical methods were not reported in original data, and so urges caution in interpreting the results. Note also that these results show metals concentrations much greater than other sampling results reported by Boyle.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-14. Inorganic Constituents in Amine Filters and Sludges

Parameter	Concentration in Amine Wastes[*] (ppm)	
	Amine Filters[**]	Amine Sludges[**]
Cyanide	50 - 250	up to 200
Thiocyanate	600 - 2000	NR
Arsenic	NR	0.01 - 15
Cadmium	NR	1 - 950
Copper	10 - 30	NR
Chromium	NR	1 - 67
Lead	100 - 400	0.5 - 1000
Mercury	NR	0.01 - 3.5
Nickel	25 - 50	0.2 - 35
Vanadium	400 - 500	NR
Zinc	75 - 150	NR

NR = Not Reported
[*] Data from Wootherspoon and Associates, et. al., 1989, 1990, as cited in Boyle, 1990.
[**] Type of amine and amine sludge (e.g., filter v. reclaimer, etc.) not specified.

A number of studies have examined the presence of organic compounds in amine sweetening plant wastes. Previous discussion has indicated that sources of organics in amine wastes include the amines, amine degradation products, and the hydrocarbon feed. The presence of organics in amines and amine wastes may vary substantially with hydrocarbon feed (due to differences in gas composition), the type of amine used (due to the variability of amines with respect to solubility of hydrocarbons), and operating conditions of the facility (e.g., temperature and maintenance of reboiler and/or reclaimer) (DuPart, et al., 1991). An additional factor concerning organics in amine filter media and sludges is the type of filter employed: mechanical filters will not remove organics, while carbon filters will. Diatomaceous earth filters, which may be used in amine plants, may not remove substantial quantities of organics (Maddox, 1985).

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-15. Inorganic Constituents in DEA Filter Sludges

Parameter	Concentration in DEA Filter Sludge (ppm)		
	Plant A*	Plant B** Range (n=3)	Plant C*** Range (n=3)
pH (s.u.)	10.6	10.5-10.6	4.5-4.6
Arsenic	0.71	<0.05	<0.05
Barium	6.3	217-265	273-284
Cadmium	0.38	2	2
Chromium	12	105-118	89-90
Copper	8.0	13-22	280-310
Lead	4.3	2	<2
Mercury	0.06	<0.005	<0.005
Molybdenum	1.5	<0.2	<0.2
Nickel	4.8	49-52	160-180
Nitrogen	160	16,300-24,800	450-700
Selenium	<0.4	<0.3	<0.3
Silver	NA	<0.5	<0.5
Vanadium	6.7	78-86	36-46
Zinc	11	42-45	37-39

* Data from Monenco Consultants, Ltd., 1987, as cited in Boyle, 1990. Source of waste not known

** Data from Boyle, 1990.

*** Data from Boyle, 1990.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-16. Organic Constituents of DEA Filter Sludges

Compound	**Concentration in DEA Filter Sludge[*] (ppm)**	
	Plant B	**Plant C**
MEA	NA	7,100
DEA	480	57,000
TEA	NR	6,800
H_2N-CH_2-R	532	NR
N,N'-bis(2-hydroxyethyl)piperazine	NR	7,800
N-(2-hydroxyethyl)piperazine	NR	6,000
N,N'-bis(2-hydroxyethyl)imidazolidone	NR	2,700
N,N,N'-tris(2-hydroyethyl)ethyldiamine	NR	2,500
Unknown, N-containing (MW 277-392)	NR	36,800
Unknown, not N-containing	26,620	13,100
Unknown, difficult to interpret	7,300	NR
Total	34,932.00	139,800.00

NA = Not Analyzed
NR = Not Reported
[*] Source: Boyle, 1990.

Table 2-16 lists organics detected in two DEA filter sludges. The data show substantial differences in the total concentrations of organic compounds present in the filter sludges of the two plants sampled. Further, the filters demonstrate markedly differing abilities to remove DEA, the amine used in the plants. Boyle notes that the Plant B filter tested was a diatomaceous earth filter, while the Plant C filter was a diatomaceous earth and cellulose fiber filter. The sludges showed between 1.3 and 2.7 percent organic material not containing nitrogen, while Plant C showed 3.7 percent N-containing organics and 14 percent organics in total. It is worth noting that Boyle described the smell of the Plant C filter sludge as smelling strongly of gasoline, suggesting it may have contained volatile organic compounds.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-17. Selected Inorganic and Volatile Organic Constituent TCLP Data for Spent Amine Filter Media
(units in ppb except pH)

Analyte	GRI Sample ID				
	AF-01PC-03*	BB-02-PC-01*	AF-01PC-04	BB-02PL-O2	AW-01PC-09
	Sock	Sock	Carbon	Carbon	Paper
pH (s.u.)	NA	NA	NA	NA	NA
RCRA Metals					
Silver	ND	ND	ND	ND	ND
Arsenic	ND	ND	ND	ND	ND
Barium	90	30	60	40	ND
Cadmium	ND	ND	ND	ND	ND
Chromium	100	ND	40	ND	ND
Mercury	ND	ND	ND	ND	ND
Lead	ND	ND	ND	ND	ND
Selenium	ND	10	ND	ND	ND
Volatile Organic Compounds					
Benzene	ND	11[1]	ND	550	ND
2-Butanone	ND	ND	ND	ND	ND

ND Not detected

*AF-01PC is an MDEA sweetening system; BB-02PC is a DEA sweetening system; AW-01PC is a DGA sweetening system.

[1] Reported result below detection limit.

Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations." and
GRI. "Amine-Based Gas Sweetening and Claus Sulfur Recovery Process Chemistry and Waste Stream Survey."

While silent with respect to filter sludges, the GRI study provides analytical results for five spent amine filter media samples. The samples were collected from three facilities. The samples cover a range of 3 States, amine types (DEA, MDEA, DGA), and feed gas compositions (from lean to rich). Results of the samples are listed in Table 2-17. Matrix interference problems were experienced for two TCLP semi-volatile organics that were not detected in sample AF-01PC-03. No other QA/QC problems were reported by GRI for any of the other analytes for this sample including those in Table 2-17.

TCLP volatile organics generally were not detected in the filter samples. Only two samples, the sock filter and the carbon filter samples from a single plant, showed detectable levels of benzene. Note that sample

BB-02PC-02 exceeded the RCRA TC level for benzene by 10 percent. Unlike the results reported for the Canadian samples, the GRI samples contained very low levels of TCLP metals. Barium was detected in four samples at two plants (≤ 90 ppb), and chromium was detected in both samples from a single plant (≤ 100 ppb). Differences may have been at least partially the result of the GRI samples being leachates, but this is not certain. The limited data do not allow a comparison between samples according to amine type, feed gas type, or geographic location.

Preliminary results of the GRI gas industry survey indicate that the nationwide generation of used filters from sweetening operations is roughly 82,000 lbs/day [Koraido, 1993]. While this figure includes contributions from both underground storage and compression operations it is expected that the majority of sweetening-related wastes would be generated at conditioning/processing plants. However, it is less obvious what the contribution of field/lease sweetening units would be to the total quantity.

2.4.7 Amine Filter Backwash

Amine filter backwash is generated by the flushing of filter beds. Carbon filters, sock filters, and diatomaceous earth filters as discussed above may require periodic backwashing to remove accumulated debris and the accompanying increase in pressure drop across the filter. Backwashing is typically accomplished with amine solution, although other materials may be used. Note that not all plants/facilities generate filter backwash, as not all plants use filters for which this practice is required/appropriate. Available information does not describe the nature of filter backwash from amine filters. However, amine filter backwash may similar constituents as the filter sludge/spent filter media discussed above, though perhaps with lower concentrations(Boyle, 1990). For example, they may contain various amounts of amine solution, which is discussed below under Spent Amine. Available information does not permit an estimation of the volume of amine filter backwash generated throughout the U.S.

2.4.8 Amine Reclaimer Sludge

As stated previously, amines, particularly primary amines (e.g., MEA, DGA), require reclaiming to maintain solution quality. Reclamation is necessary to remove iron sulfide, amine degradation products, heavier hydrocarbons, and other accumulated materials (Manning and Thompson, 1991). Over time, amines may accumulate concentrations of heat-stable salts (HSS) which are not removed by filtration or in regeneration stills. Such salts may include chlorides; nitrates and nitrites from corrosion inhibitors; sulfates and thiosulfates formed from oxidation of sulfur species; formates, oxalates, and acetates, formed from oxygen degradation and thermal degradation; thiocyanates; and phosphates (DuPart, et. al., 1991). Reclaimer sludges may contain any of the above materials. Generally, amine reclaimer sludges are not flammable, corrosive, or reactive, but may be toxic (particularly due to the potential for detectable levels of benzene) (Simmons, 1991).

Data on the inorganic and organic characteristics of amine reclaimer bottoms have been collected at a number of Canadian sour gas plants. These data may be instructive of the potential characteristics of amine reclaimer sludges in the U.S. It is again noted, however, that the nature of wastes generated at gas plants depends on many operational factors, such that the data presented may not be applicable to all operations in the U.S.

Table 2-18 presents inorganic constituent data reported for a number of Canadian sweetening facilities using MEA solutions. Compared with the filter sludge data above, the reclaimer sludges exhibit very low levels of metals, with the exception of chromium and molybdenum in the Plant D sludge. Note also the high levels of nitrogen present in all three plants' sludges. Plant F data include the single value detected for ammonia (8,500 ppm). Not shown in the table were reported values of dissolved sodium and sulfate concentrations for Plant D and Plant E. These values were, for sodium, 10,500 and 13,630 ppm, respectively, and, for sulfate, 3,020 and 5,830 ppm, respectively. These values confirm the above general discussion that reclaimer bottoms may contain high levels of heat stable salts. Anion concentrations were not provided.

Amine reclaimer bottoms may contain high concentrations of organic material. Sources of organics, as discussed above, include the gas feed stream, the amine solution, and amine degradation products. Non-volatile organics may remain in reclaimer sludges. Table 2-19 lists some organic constituents and their concentrations as observed for DEA reclaimer bottoms at a Canadian sour gas plant. These data show the reclaimer sludge to contain nearly 28 percent amine compounds. Both TEA and oxazolidone (OX), may be carcinogenic (Boyle, 1990). The data also show a number of organic acids at high concentrations, as suggested above.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-18. Inorganic Constituents of MEA Reclaimer Bottoms

Parameter	**Concentration in MEA Reclaimer Bottoms (ppm)**		
	Plant F*	**Plant D** Range (n=3)**	**Plant E*** Range (n=3)**
pH (s.u.)	12.6	10.9 - 11	11.5 - 11.7
Ammonia	8,500	N/A	N/A
Arsenic	0.33	<0.5	<0.5
Barium	<0.5	<0.1	<0.1
Cadmium	<0.05	0.2 - 0.6	<0.1
Chromium	1.4	150 - 164	0.1 - 0.2
Copper	<0.1	0.1 - 0.3	<0.1
Lead	<0.5	0.4	<0.4
Mercury	0.015	<0.05	<0.05
Molybdenum	0.3	15.2 - 18.0	0.7 - 0.9
Nickel	<0.1	31 - 34	0.1 - 0.2
Nitrogen	56,000	12,800 - 16,000	42,400 - 43,400
Selenium	<0.02	<2	<2
Silver	N/A	<0.01	<0.01
Vanadium	<0.05	<0.1	<0.1
Zinc	2.7	5.2 - 5.9	1.4 - 1.5

N/A = Not Available

[*] Data from Monenco Consultants, Ltd., 1987, as cited in Boyle, 1990. Source of waste not known

[**] Data from Boyle, 1990.

[***] Data from Boyle, 1990.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-19. Amines and Organic Acids in DEA Reclaimer Sludge

Compound	**Percent**
DEA	16.4
TEA	3.0
Hydroxyethylimidazolidone (HEI)	3.2
Aminoethylethanolamine	0.4
Oxazolidone (OX)	1.0
Diethanol piperazine	3.4
Ethylene Glycol	0.2
TOTAL	27.60
Compound	**Concentration (ppm)**
Formic Acid	56,000
Acetic Acid	44,000
Proprionic Acid	5,000
Oxalates	13,000

Source: Canterra Energy, Ltd., 1988, as cited in Boyle, 1990.

Table 2-20 shows additional data on the concentration of organic compounds in amine reclaimer bottoms. These data are for two of the MEA plants discussed above. Both reclaimer bottoms showed high levels of total organics. However, constituents present in the two wastes did not overlap, with the exception of N(hydroxyethyl)-1,2-ethylenediamine (Boyle, 1990). Each plant's reclaimer bottoms contained high concentrations of amines, with the Plant E waste showing 82,000 ppm MEA. No MEA was detected at Plant D. Note that both sludges were reported to smell strongly of gasoline, suggesting the presence of volatile organic compounds though the full range of compounds tested for was not provided (Boyle, 1990).

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-20. Organic Constituents of MEA Reclaimer Bottoms

Compound	**Concentration in MEA Reclaimer Bottoms (ppm)**	
	Plant D[*]	**Plant E**[*]
MEA	NR	82,000
DEA	6,000	NR
MDEA	NR	5,700
Unknown ethanolamines	12,700	NR
N(2-hydroxethyl)piperazine	57,000	NR
N(hydroxyethyl)imidazolidone	NR	34,000
$HN(C_2H_4OH)-CH_2R$ (MW 361, 389, 424)[**]	14,300	NR
N(hydroxyethyl)N'-methyl imidazolidone	NR	17,000
H_2NCH_2R (MW 389, 405)[**]	7,300	NR
2-hydroxyethyl-methylamine	2,800	NR
2-(2-aminoethoxy)ethanol	NR	12,000
Polycyclic, N-containing	2,500	NR
Glycine	NR	6,300
N,N'-bis(hydroxyethyl)-1,2-ethylenediamine	1,900	NR
N(hydroxyethyl)-1,2-ethylenediamine	1,800	NR
N(2-hydroxyethyl)-1,2-ethylenediamine	NR	4,700
2-ethylhydroxy-3-propylhydroxyamine	NR	4,400
Unknown, N-containing	29,600	22,000
Unknown, not N-containing	7,200	8,700
Total	143,100.00	196,800.00

NR = Not Reported
[*] Source: Boyle, 1990.
[**] MW = molecular weight of compound(s)

Finally, Table 2-21 presents a list of other organic materials identified in amine reclaimer bottoms[7]. Most of the substances on this list were not detected in the sludges discussed above. However, the list is intended to suggest other constituents which may be present in reclaimer bottoms. Note that phenol and ethylbenzene appear on the list.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-21. Other Organic Constituents of Amine Reclaimer Bottoms

Phenol	Pentathiepane
Methyl phenol	Ethenythio octane
Dimethyl phenol	Tetrahydro 1,1-dioxide thiopene
Ethyl phenol	2-(2-phenoxy ethoxy)ethanol
Ethylbenzene	Benzoic acid
Dimethyl benzene	Quinoxaline
Aliphatic acids (C2-C7)	Monoethanolamine
Tetradecanoic acid, ester	NN'-bis(hydroxyethyl)ethylenediamine
Hexadecanoic acid, ester	N-(2-hydroxyethyl)ethylenediamine
Cyclic thioethers	1-(2-hydroxyethyl)imidazolidone

Source: Monenco Consultants, Ltd., 1987, and Erickson, 1985, as cited in Boyle, 1990.

The above data indicate that amine reclaimer bottoms may contain a number of constituents of concern. Metals concentrations appear lower in reclaimer bottoms than in other amine wastes. Among organic constituents of concern are amines, phenol, and ethylbenzene. Additionally, cyanide, thiocyanates, oxylates, and formic acid have been reported to be present in reclaimer bottoms. Data also indicate that the inorganic and organic constituents and concentrations found in reclaimer bottoms are highly variable.

Available information does not permit an estimation of the volume of amine reclaimer bottoms generated throughout the U.S.

2.4.9 Spent Amine

Previous sections have indicated that accumulations of contaminants and thermal degradation can eventually decrease the performance of amines as gas sweetening agents. Once below a certain level of performance, degraded amines must be changed or replenished. Generally, an entire stock of amine in a system will not be replace except, perhaps, if extensive maintenance of a system is required. Instead, make-up amine will be added to the system as needed, in some cases after removing some of the 'spent' amine. Spent amines may contain many of the materials discussed above, though concentrations may vary. For instance, spent amine may contain high concentrations of heat-stable salts (HSS) which are not removed by filtration or in regeneration stills. Such salts may include chlorides; nitrates and nitrites from corrosion inhibitors;

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[7] Data from Monenco Consultants, Ltd., 1987, and Erickson, 1985, as cited in Boyle, 1990. Sources of wastes, number of samples, and analytical procedures were not identified.

sulphates and thiosulfates formed from oxidation of sulfur species; formates, oxalates, and acetates, formed from oxygen degradation and thermal degradation; thiocyanates; and phosphates (DuPart, et. al., 1991). Table 2-22 presents a partial list of amine degradation compounds detected in amine solutions.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-22. Amine Degradation Compounds Found in Amine Solutions

bis(hydroxyehtylaminoethyl)ether	N-(hydroxyethyl)ethylenimine
bis(hydroxyethyl)ethylenediamine	3-(2-hydroxyethyl)oxazolidinone
N,N'-bis(hydroxyethyl)imidazolidone	N,N'-bis(2-hydroxyethyl)piperazine
N,N-bis(hydroxyethyl)piperazine	methyldiethanolamine
N,N-bis(hydroxyethyl)glycine	oxazolidinone
N,N-bis(hydroxyethyl)urea	triethanolamine
2-diethylaminoethanol	N,N,N,N,-tetra(hydroxyethyl)ethylenediamine
N-(2-hydroxyethyl)ethylenediamine	N,N,N-tris(ethylenediamine)
1-(2-hydroxyethyl)imidazolidone	

Source: Mather and Hrudey, 1985, as cited in Boyle, 1985.

In 1992, EPA collected five samples (including duplicates) of lean amine from three sour gas plants (samples 23138, 23159, 23646, and duplicates 23162 and 23647). The fluids sampled were not wastes but were in-process lean amines. As might be expected, the pH of lean amine samples was relatively high, ranging from 8.797 s.u. (23138) to 11.24 s.u. (23159). Biochemical and chemical oxygen demand also were high (The laboratory reported that samples 23159 and its duplicate 23162 contained substances toxic to the seed used in the biochemical oxygen demand analyses. Therefore, there are no biochemical oxygen demand results for these samples). Very few volatile and semi-volatile organics were detected in the samples, all at levels below TC levels. Metals concentrations were also uneven across the samples. Sulfur, as expected, was detected in all samples, but was widely variable, ranging from 21,500 (23159) to 963,000 μg/l (23138); the latter was surprisingly high for "lean" glycol. All results are presented in Appendix A.

The GRI study presents analytical results for two samples of spent amines collected as reflux accumulator carryover at two separate conditioning plants. Sample AB-02PC-12 was collected from a DEA unit while sample AB-03PC-17 was collected from a MEA unit. Both facilities are in New Mexico. Table 2-23 lists selected results for each of the samples.

Results of analysis of each sample are very similar. Each waste stream showed a near-neutral pH, with all TCLP metals below detection limits except for barium ($\leq$ 30 ppb) in sample AB-02PC-12. Both samples exhibited RCRA ignitability, with flash points of 125 and 138°F however, these results are deemed invalid since GRI's QC review indicated probable carry-over between sample or standards. Both showed moderately elevated levels of reactive sulfide at 103 and 234 ppm although these concentrations are well below the RCRA level of 500 ppm. Each sample exceeded the RCRA TC level for benzene at 560 (sample AB-02PC-12) and 2,500 ppb (sample AB-03PC-17) however, the later result is deemed qualitative

Associated Waste Report:
Dehydration and Sweetening Wastes
(U.S. EPA, January 2000)
Table 2-23. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations for Spent Amines
(units in μg/L)

Analyte	GRI Sample ID	
	AB-02PC-12	AB-03PC-17
	DEA	MEA
pH (s.u.)	6.9	6.5
Ignitability	125[1]	138[1]
Reactivity	103,001	234,100
RCRA Metals		
Silver	ND	ND
Arsenic	ND	ND
Barium	30	20
Cadmium	ND	ND
Chromium	ND	ND
Mercury	ND	ND
Lead	ND	ND
Selenium	ND	ND
Volatile Organic Compounds		
Benzene	560	2,500[2]
2-Butanone	ND	ND

ND Not detected

[1] QC indicates probable carryover between samples or standards therefore, results are deemed invalid.

[2] Sample holding time exceeded. Results are deemed qualitative.

Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

since the TCLP method holding time was exceeded for this sample. Note that while the four-fold difference between the DEA and MEA benzene levels could suggest that MEA has a greater affinity for benzene, additional data are necessary to confirm the result.

Preliminary results of the GRI gas industry survey indicate that the nationwide generation rate for spent amines is roughly 2,200 lbs/day [Koraido 1993]. The majority of these wastes may be attributable to gas plants. No other estimates of the volume of spent amines generated per year are currently available.

2.4.10 Wastes from the Stretford Process

Due to the accumulation of contaminants, Stretford solution is periodically replaced with fresh solution. Spent Stretford solution will contain a variety of impurities. For instance, one source reports this spent solution may contain the following: 1-1.5 percent organics, ADA salt, hydrocarbons, and biocides; sodium ammonium vanadate, typically at 1 percent; elemental sulfur at 1-5 percent; sodium thiosulfate salts up to 25 percent; and potentially sodium thiocyanate salts (Eisele, 1991). Additionally, waste sulfur may be generated from the Stretford process. Vanadium salts may remain in produced sulfur due to imperfect cleaning processes (Leppin, et. al., 1991). If concentrations of these impurities are sufficiently high, the sulfur will not be saleable, and thus require disposal as solid waste. According to Eisele (1991), spent Stretford solution rarely exhibits hazardous characteristics. Available information does not indicate the volume of such wastes generated throughout the U.S.

2.4.11 NGL Conditioning/Processing Wastes

As described above, molecular sieve beds may be used for dehydrating and/or sweetening natural gas liquids. Further, NGL fractionating may be performed using lean oil as the contacting medium, which oil must be regenerated in a still in a fashion similar to glycol stripping. These processes will give rise to wastes similar to those previously discussed. The GRI study provides analytical results for four NGL processing wastes: condensate from a lean oil stripping still; water from a three-phase separator; spent molecular sieve from a drip gasoline dryer; and spent filter media from a lean oil adsorption unit. Table 2-24 lists selected results for these samples.

Sample AB-03PC-12 is condensate from a lean oil stripping still. Results show that TCLP metals and volatiles were below detection limits for all parameters except mercury and chromium (1 μg/L and 50 μg/L, respectively). No TCLP volatile organics were detected although these results are deemed qualitative as noted in the table. It may be stated that many of the volatile and semi-volatile organic compounds are more soluble in adsorption oil than in water, possibly accounting for the low observed concentration of those parameters in the condensed stream. The reason for the high pH of the sample (11.2 s.u.) is not known.

Sample AF-03US-02 is water from a three phase separator that is discharged into an evaporation pond. The separator collects water and hydrocarbons from wellhead separators, gas plant drips, and scrubbers. Barium was the only TCLP metal detected (100 μg/L); however, this result is not deemed reliable since the TCLP barium result is higher than the total barium result for this sample. Benzene was detected at 4,200 ppb. Although GRI points out that elevated MDLs were experienced for this sample, GRI's report indicates that this only occurred for one of the undetected TCLP volatile organics. Finally, the pH of the water was found to be neutral (7.01 s.u.).

Sample AI-02PC-31 was collected well downstream of the point of entry of gas to the facility. The sample is a molecular sieve from a drip gasoline dehydrator . The sample contained no detected concentrations of TCLP metals, TCLP volatiles, or TCLP semi-volatiles. Note that no arsenic was detected in the sample, despite the high concentration of this metal in regeneration condensate and spent molecular sieve from up-stream units in the same plant (see §§ 2.2.3, 2.2.4, and 2.2.8). The data may reflect the tendency of metals to remain in the water phase preferentially, relative to the NGL phase. Further data would be needed to confirm this result.

Sample AJ-03PC-12 is a used sock filter from a lean oil adsorption unit. The sample was coated with charcoal fines. The filter is used for particulate removal from the NGL stream as it passes from the molecular sieve dehydrator and chillers into the lean oil contacting tower. Sample results showed the filter to contain generally low concentrations of TCLP volatiles and semi-volatiles, with benzene detected at 300 ppb (below the TC level). Metals concentrations, except for arsenic, were similar to those observed in the other NGL wastes: generally low concentrations, with barium observed at 200 ppb and chromium at 40 ppb. Arsenic was elevated in the sample, measuring 7 times the RCRA TC level. This result is consistent with the finding of elevated arsenic in the spent molecular sieve sample from this facility as well as other media sampled at a second facility operating in the same geographical area. A wide range of wastes may be lumped under the heading NGL recovery wastes, with the above serving as but a few examples. Preliminary results of the GRI gas industry survey indicate that roughly 13,000 lbs/day of NGL recovery wastes are generated nationwide.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, July 1999)
Table 2-24. Selected Inorganic and Volatile Organic TCLP Leachate Constituent Concentrations in Various NGL Recovery Wastes
(units in ppb except pH)

Analyte	GRI Sample ID			
	AB-03PC-12	AF-03US-02	AI-02PC-31	AJ-03PC-12
	Condensed striping steam from lean oil stripping	Water phase from 3-phase separator	Spent mol sieve from drip gasoline dryer	Used sock filter from lean oil adsorption unit
pH (s.u.)	11.2	7.01	NA	NA
RCRA Metals				
Silver	ND	ND	ND	ND
Arsenic	ND	ND	ND	3,600
Barium	ND	100[3]	ND	200
Cadmium	ND	ND	ND	ND
Chromium	50	ND	ND	40
Mercury	1	ND	ND	ND
Lead	ND	ND	ND	ND
Selenium	ND	ND	ND	ND
Volatile Organic Compounds				
Benzene	ND[1]	4200	ND[1]	300
2-Butanone	ND[1]	ND	ND[1]	94[2]

NA = Not Analyzed
ND = Not detected

[1] Sample holding time exceeded 14 days; results deemed qualitative.
[2] Reported result below detection limit.
[3] TCLP barium greater than total barium; results deemed qualitative.
[*] Results below detection limit.

Source: GRI. "Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations."

2.4.12 Sulfur Recovery Wastes

Currently available information is limited with regard to wastes from Claus plant operations, the most prevalent type of sulfur recovery units in the U.S. The GRI study provides analytical results for one sample of spent alumina catalysts from a Claus unit. The solid sample, which contained no free liquids, contained no TCLP volatile or semi-volatile organic compounds above detection levels. Barium, chromium, lead, and selenium were detected in the sample extract at 40, 600, 40, and 25 ppb, respectively (all below the TC levels). Analysis for miscellaneous amines and mercaptans showed that the sample extract contained 40 ppm of butyl mercaptan. Given the operating conditions of Claus units it is not surprising that no organics were detected in the sample. The origin of the metals in the sample cannot be determined from a single point. Additional information is required to determine the representativeness of this sample.

2.4.13 Other Dehydration and Sweetening Waste Considerations

In very rare instances, mercury and arsenic may be present in natural gas (Block-Bolten and Glowecki, 1989; Gijselman, 1991). The presence of these materials may present severe human health and safety risks. Mercury may concentrate in sludges, filters, glycol reboilers, produced water, and piping and equipment (Gijselman, 1991). Arsenic compounds tend to reside in the waters associated with gas production, but may also form a powdery substance on the interior of piping and equipment (Block-Bolten and Glowecki, 1991). The frequency of occurrence and concentrations of arsenic and mercury compounds in dehydration and sweetening units wastes have not been quantified, although several of the waste analyses reported above included arsenic at levels of concern.

According to one publication, naturally occurring radioactive materials (NORM) can be expected at nearly every petroleum facility (Gray, 1991). The author also suggests that some facilities can be contaminated to a point where maintenance and other personnel may be exposed to hazardous concentrations. Hazardous concentrations were not defined in the publications so it is assumed the author is referring to NORM levels above regulatory levels as being hazardous. NORM regulations do not exist currently at the Federal level[8] however, regulations are being developed at the State level. For example, Louisiana adopted regulations

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[8] Since there currently are no federal regulations or environmental standards for NORM, radioactivity is not a hazardous waste characteristic. However, in 1978, EPA proposed RCRA hazardous waste rules and a companion RCRA Advance Notice of Proposed Rulemaking (ANPR) (43 Fed. Reg. 58946; December 18, 1978) which did address radioactive wastes in response to concerns about certain radioactive mining wastes that were proposed for classification among "special wastes" as high volume, low hazard wastes. The ANPR proposed that radioactivity be included on the list of hazardous characteristics and described a solid waste (other than source, special nuclear, or by-product material as defined by the Atomic Energy Act of 1954) as a hazardous waste if a representative sample exhibited Ra^{226} concentrations in excess of 5 picoCuries per gram (pCi/g) for solid wastes or 50 picoCuries per liter (pCi/L) of Ra^{226} and Ra^{228} combined for liquid wastes, or a total Ra^{226} concentration equal to or exceeding 10 microCuries (µCi) for any discrete source. In 1980, Congress amended RCRA to temporarily exempt certain wastes, including radioactive wastes, from hazardous waste regulations under RCRA Subtitle C. Hence, EPA deferred development of regulations for radioactive wastes until Congress to further action. Furthermore, EPA believed that radioactive wastes could be effectively regulated at the state level so Federal regulations would not be necessary.

in 1989 (LAC 30.XV.1404) which set regulatory levels for NORM concentrations at 5 pCi/g for radium-226 or radium-228 above background levels. As many as one-third of domestic oil and gas wells may produce some radium-contaminated scale. The geological location of the oil reserve and the type of production operation strongly influence the prevalence of NORM accumulations. NORM concentrations change over time, and the trend is for the relative quantity of NORM to increase as the production field ages and resources are depleted (EPA, 1991a).

API conducted a survey of NORM occurrence in oil production and gas processing equipment to identify the geographic areas and specific equipment exhibiting the highest NORM levels (EPA ,1991a). Data were collected in 20 States primarily at sites suspected of exhibiting NORM concentrations. The API survey showed a wide variation in NORM levels depending on the geographic location of the equipment. The geographic areas with the highest equipment readings were northern Texas and the Gulf Coast from southern Louisiana and Mississippi to the Florida panhandle. Very low levels of NORM were observed in California, Utah, Wyoming, Colorado, and northern Kansas (EPA, 1991a).

In a separate thirteen-State survey, up to 90 percent of production wells in Mississippi were reported to have NORM, compared to none or a few in Colorado, South Dakota, and Wyoming (McArthur, 1988; cited in EPA, 1991a). Ten percent of Mississippi wells were estimated to have scale with elevated radium concentrations (cited in EPA, 1991a). For example, in 1986 barium sulfate scale was found in production tubing during a workover of a well in Mississippi at levels of 6,000 pCi/g of radium-226 and 1,000 pCi/g of thorium-232 co-precipitated in the scale matrix (EPA, 1991a).

Produced with fluids from the reservoir, NORM has been observed to accumulate in sludges, scale, piping and equipment, particularly in reflux accumulators (API, 1989b; EPA, 1991). API found that the highest concentrations of NORM were found in wellhead piping and in production piping near the wellhead and the largest volumes of scale were found in water lines associated with separators, heater treaters, and gas dehydration units (EPA, 1991). A statistical evaluation of the external radiation exposure level data from the API survey indicated that approximately 64 percent of the gas producing equipment and 54 percent of the oil producing equipment surveyed showed NORM radioactivity at or near background levels (EPA, 1991). Radiation exposure levels associated with NORM in gas processing equipment are presented in Table 2-25.

Due to their slight solubility, radium and radium daughters may remain in solution or may precipitate in piping and equipment of dehydration and sweetening units. Radioactive sludges may be contaminated with several thousand pCi/gram of the long-lived radon decay products (*e.g.*, lead-210, bismuth-210, and polonium-210). These heavy metal decay products may attach to dust particles and aerosols to become part of the sludge (Gray, 1991). The frequency of occurrence and concentration (activity) of NORM in dehydration and sweetening units wastes have not been quantified (EPA, 1991).

Whereas NORM contamination of oil production facilities is commonly associated with radium, natural gas production and processing facilities are more prevalently contaminated with radon and radon decay products. Natural gas liquids (NGL) facilities are especially subject to NORM contamination. Gasoline and NGL facilities would be among the most highly contaminated areas in a gas producing/processing system (Gray, 1991).

NORM radionuclides may accumulate in gas plant equipment from radon (Rn-222) gas decay. The radon gas originates in underground formations and becomes dissolved in the organic petroleum fractions in the gas plant. Once in the plant equipment, the gas is partitioned into the propane and ethane fractions by solubilities. The radon daughters are freed and accumulate invisibly on the interior surfaces of the equipment.

The boiling (or condensing) point for radon is intermediate between the boiling points of ethane and propane. Upon subsequent processing, radon tends to further accumulate in the propylene distillation stream. Radon tends to be recovered more completely in gas processing plants achieving high ethane recovery (Gray, 1991).

Radon, with a half-life of 3.8 days, does not pose a waste disposal problem for radon-contaminated equipment. However, this is not the case with lead-210, a radon decay product with a 22-year half-life, which contaminates the surface of some gas plant processing equipment. Because lead-210 decays primarily by beta emission, it consequently does not pose a radon or gamma emission component (EPA, 1991).

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 2-25. Summary of Radiation Exposure Levels Associated with NORM in Gas Processing Equipment (Source: API, 1989; as cited in EPA, 1991a)

Equipment	Number of Observations	Number of Observations Above Background	Difference Above Background (µR/hr)				
			Minimum	25th Percentile	Median	75th Percentile	Maximum
COMPRESSORS (including associated equipment)	648	119	0.3	1.00	2.0	3.0	490
DEHYDRATORS	244	72	0.3	1.35	3.0	6.7	530
SWEETENERS	234	30	0.2	1.00	3.4	19.0	220
INLET SCRUBBERS	593	156	0.1	1.00	5.0	19.0	700
METERS	101	32	0.3	1.15	5.5	51.0	700
CRYOGENIC UNITS	50	20	1.0	2.00	6.0	22.0	3,000
OTHER TANKS	423	140	0.2	2.00	6.0	30.0	380
OTHER PROCESSING EQUIPMENT	430	165	0.3	2.90	7.0	23.0	990
FRAC TOWERS	272	123	0.2	1.50	9.5	33.0	400
PROPANE REFRIGERATION SYSTEM EQUIPMENT	143	56	0.1	2.00	16.0	69.0	590
BOTTOMS PUMPS	40	30	0.5	3.00	17.0	45.0	220
PROPANE TANKS	124	90	0.5	7.30	25.0	66.0	680
OTHER PUMPS	232	114	0.4	6.80	28.0	96.0	1,400
PROPANE PUMPS	71	53	0.1	9.50	31.0	98.0	1,100
PRODUCT LINES	146	82	0.1	14.00	35.0	110.0	1,080
ALL PUMPS	3	2	3.0	3.00	38.0	73.0	73
REFLUX PUMPS	110	95	0.2	16.00	76.0	290.0	3,000
BACKGROUND				5.0	7.0	9.0	

3.0 TYPICAL WASTE MANAGEMENT METHODS

3.1 THE API SURVEY

In 1987, EPA released its *Report to Congress on Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* (RTC). The report included the Agency's findings regarding the generation, volume, characteristics, management, and State regulation of E&P wastes. The RTC relied heavily on the *API 1985 Production Waste Survey* results in discussions of the volumes of large volume wastes (e.g., produced water and drilling fluids) and the cost estimations for alternative regulatory scenarios. The RTC did not present extensive information on estimated volumes generated of low-volume associated wastes. The API Survey remains the most comprehensive study of associated wastes performed to date. Given the attention afforded to the API Survey in the RTC, as well as the general shortage of data regarding the volume of low-volume associated wastes, this section will present a summary of the survey data and discuss its usefulness in determining the waste volumes generated and prevailing management practices for dehydration and sweetening wastes. Other and more recent sources of information exist on dehydration and sweetening wastes and the methods used for their management and disposal (e.g., Fillo and Evans, 1995); however, since these sources provide little new information, they are not discussed.

Part II of the API Survey presents data on estimated volumes and disposal practices for a number of associated waste groupings. The data are compiled from survey responses voluntarily submitted by 158 American Petroleum Institute and Independent Petroleum Producers Association member/operators representing 53 percent of U.S. on-shore crude oil production (API, 1988). Survey respondents provided estimates of the volumes of 12 associated waste groups generated by their operations for each state in which they operated in 1985. Volume estimates were reported according to the waste management practice employed (e.g., 4 barrels of spent iron sponge disposed by on-site burial, etc.).

A number of the associated waste categories covered in the survey are common to crude oil production and gas conditioning operations alike. For instance, "tank bottoms, separator sludges, or pig trap wastes" may be generated at virtually any exploration and production facility. Accordingly, the fraction of such wastes attributable specifically to gas sweetening and dehydration facilities cannot be determined. However, two of the waste categories covered in the survey relate uniquely to dehydration and sweetening facilities, namely, "spent iron sponge" and "dehydration and sweetening unit wastes, including glycol and amine waste, but excluding iron sponge." According to survey instructions, "dehydration and sweetening unit wastes..." include "...primarily waste glycol and amine." The category excludes "solid or sludge-like waste..."

Several aspects of the survey severely limit the usefulness of the data for estimating the volume of dehydration and sweetening wastes generated throughout the U.S. Among these are:

- The survey explicitly excludes gas plant wastes from consideration. Roughly 75 percent of U.S. marketed gas production undergoes some degree of processing in natural gas plants, such that these facilities may generate a sizeable fraction of all sweetening and dehydration wastes (U.S. DOE, 1990).

- The survey extrapolates total State volumes of wastes on the basis of the percentage of total state crude oil production represented by the respondents. The data do not indicate the percentage of total state gas production represented by the respondents.
- While "dehydration and sweetening wastes" includes spent glycol and spent amine, it does not include regenerator/reboiler condensate, spent filter media and filter sludge, reclaimer bottoms, or other wastes generated at gas conditioning sites[9].
- Reported values of "dehydration and sweetening wastes" provide no indication of the amounts attributable to each type of operation, respectively.

Due to the above limitations, the relationship of the reported values to the total volume of dehydration and sweetening wastes generated is blurred. For instance, because the survey does not indicate the volume of on-shore gas production represented by the respondents, it cannot be determined if the extrapolation factors (based on crude oil production) overstate or understate total state waste generation. Since gas plants are excluded, the estimates can at best estimate field facility waste generation. As discussed earlier, the majority of solid waste generated at iron sponge facilities is probably the spent sponge itself. Thus the survey values may be reasonable estimates of the sweetening unit wastes generated by respondents. Again, however, with no indication of the total gas production represented by the respondents, it is impossible to relate these values to State aggregate volumes generated. Accordingly, the API Survey estimates for "dehydration and sweetening wastes" and "spent iron sponge" cannot be considered reliable estimates of the total volume of dehydration and sweetening wastes generated throughout the U.S.

Such shortcomings notwithstanding, the API results may be instructive regarding the management of dehydration and sweetening wastes generated at field or lease units. As previously stated, respondents provided the volume of dehydration and sweetening wastes they managed in each of a number of treatment/disposal methods. The factors influencing decisions on management options are manifold, including State and local regulations, climatic and geological conditions, waste characteristics, proximity to central treatment/disposal facilities, and so on (RTC). Because the population of gas producers responding to the survey was not identified, it is not possible to determine whether such factors affecting respondents might differ from those affecting non-respondents. It is, therefore, assumed that the relative distribution of wastes managed by identified options in the survey applies to all gas dehydration and

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[9] Other gas conditioning site wastes may be reported under other associated waste categories descriptive of the process from which they are generated. Again, however, the volume attributable to gas conditioning sites is subsumed in the total for all E&P sites, and cannot be determined.

sweetening wastes[10] by state, with the exception of gas plant wastes. Therefore, in the following sections API Survey results regarding the percentage of wastes managed by particular methods will be indicated.

It is important to note that because the API estimates were derived independently for each State and for the U.S. as a whole, they cannot be summed across methods. For example, API estimated that, for the U.S. as a whole, 406,000 barrels of dehydration and sweetening wastes (excluding iron sponge) were injected; however, if injection totals for the 10 States for which API derived independent estimates are added, the total comes to 16,512 barrels, only 4.1 percent of the national total (see Table 3-1).

The waste management methods covered by the survey include recycle/reuse, roadspreading, landspreading, injection (not iron sponge), incineration, on-site pits and on-site burial (iron sponge only), off-site disposal, and other. Recycle/reuse is intended to cover any storage for reuse or returning of spent materials to service companies or vendors. Roadspreading was defined in the survey to mean application of wastes to road surfaces for dust suppression. Landspreading is the application of waste materials to soils through which biodegradation of materials in the waste may occur. Incineration refers to the combustion of materials for disposal. The survey does not indicate if the wastes incinerated are burned alone or in conjunction with other materials.

"Injection" refers to the injection of materials into the producing formation or other formation for enhanced oil recovery (EOR) or disposal. Injection of E&P related materials is regulated under the Underground Injection Control (UIC) Program established by the Safe Drinking Water Act. UIC wells are classified under five categories (Class I-V). Wells which inject fluids for E&P waste disposal, enhanced recovery, and hydrocarbon storage are classified as Class II wells and include the following subcategories:

- 2A - annular disposal wells,
- 2D - produced fluid disposal wells,
- 2H - hydrocarbon storage wells,
- 2R - enhanced recovery wells, and
- 2X - other Class II wells.

Oilfield operations may involve the use of pits for temporary storage of materials. Such pits may be lined to mitigate potential migration of constituents of pit contents. Pit solids may be disposed in place, after dewatering, by backfilling the pit with soil. On-site burial refers to the disposal of wastes by covering them with soil.

Off-site disposal includes the use of commercial treatment, reclamation, and disposal facilities for waste management. Such services may include landspreading/landtreatment, oil/solvent reclamation, incineration,

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[10] "All wastes" here means spent glycol and amine, and does not include such wastes as were not intended to be covered in the API Survey. Management practices for other wastes will be described as available information permits.

landfilling, and underground injection. The survey does not break down off-site disposal into distinct treatment and disposal methods.

Table 3-1 lists the percentage of dehydration and sweetening wastes by management/disposal practice and State as reported in the API Survey. It is again emphasized that these wastes include primarily spent glycol and amine from field facilities, and exclude gas plant wastes and spent iron sponge. The data suggest that most liquid dehydration and sweetening wastes generated by field/lease facilities are disposed via on-site injection[11]. Operators in Alaska and Kansas reported that 100 percent of generated glycols and amines were disposed by this method. Respondents from New Mexico and Oklahoma reported that roughly 50 percent of these wastes were injected on-site for each state.

Off-site disposal (by various methods, not specified but likely to be mostly injection) appears as the next most prevalent practice for disposal of liquid conditioning wastes from field/lease facilities. Florida, California, and Texas operators reported that the amount of dehydration and sweetening wastes disposed off-site is roughly 100 percent, 95 percent, and 83 percent, respectively. It is worth noting that California regulations require spent glycol to be managed as hazardous, with spent amines also likely to require such management if it exhibits a hazardous characteristic.

An estimated one percent of liquid conditioning wastes may be incinerated according to the survey. The survey does not reveal in which states this disposal method may be practiced. Landspreading and other on-site disposal methods together account for most of the remaining wastes disposed, as reported in the Survey. Much of the landspreading is attributable to respondents in Texas. Further, Oklahoma respondents reported that 18.5 percent of these wastes are disposed on-site, including by on-site burial.

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[11] Off-site injection is included in "Off-site/commercial".

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)

Table 3-1. Waste Management Practices Used for Dehydration and Sweetening Wastes (Excluding Iron Sponge), 1985 [A]

State	Waste Generation		Volume Generated (bbl) and Percentage Disposed, by Method of Disposal														
	Number of Barrels Generated	Percentage of U.S. Total	Recycled/Reused[B]		Roadspread		Landspread		Injection		Incineration		Off-site[C]		Other	
			Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%
Alaska	1,497	0.3	0	0.0	0	0.0	0	0.0	1,497	100.0	0	0.0	0	0.0	0	0.0
California	5,314	1.2	0	0.0	0	0.0	0	0.0	272	5.1	0	0.0	5,043	94.9	0	0.0
Florida	239	0.1	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	239	100.0	0	0.0
Kansas	5,206	1.1	0	0.0	0	0.0	0	0.0	5,206	100.0	0	0.0	0	0.0	0	0.0
Louisiana	10,659	2.3	73	0.7	26	0.2	0	0.0	793	7.4	5,289	49.6	4,311	40.4	166[D]	1.6
Michigan	981	0.2	0	0.0	0	0.0	0	0.0	378	38.5	0	0.0	0	0.0	603	61.5
New Mexico	188	0.0	18	9.6	0	0.0	0	0.0	91	48.4	0	0.0	76	40.4	3	1.6
Oklahoma	6,993	1.5	312	4.5	0	0.0	19	0.3	3,795	54.3	0	0.0	1,572	22.5	1,294	18.5
Texas	46,764	10.2	133	0.3	107	0.2	1,848	4.0	4,480	9.6	0	0.0	39,060	83.5	1,136[E]	2.4
Wyoming	3,056	0.7	0	0.0	0	0.0	151	4.9	0	0.0	0	0.0	2,358	77.2	548[F]	17.9
Total U.S. **(See Note G)**	459,538	100.0	0	0.0	0	0.0	2,000	0.4	406,000	88.4	5,000	1.1	44,000	9.6	1,000	0.2

NOTES:

A In conducting the survey, API used the following definition of dehydration and sweetening unit wastes: "primarily waste glycol and amine. Used iron sponge is accounted for in its separate category. Solid or sludge-like waste such as iron sulfide obtained when units are cleaned out would be accounted for in the tank bottoms and separator sludge category."

B As defined by API: "storage for reuse" or "returned to service company."

C Off-site commercial facility, including off-site injection.

D API reports 34 of these barrels were buried on-site and the remainder managed by unspecified other methods.

E API reports 83 of these barrels were placed in evaporation/onsite pits, 416 barrels were buried on-site, and the remainder managed by unspecified other methods.

F API reports 137 of these barrels were placed in evaporation/onsite pits, 46 barrels were buried on-site, and the remainder managed by unspecified other methods.

G Total U.S. includes AZ, IN, KY, MO, NV, NY, OH, PA, SD, TN, and VA. Totals for these States cannot be calculated, individually or collectively, since the values for each reported State and for the total U.S. are independent statistical estimates made by API and are therefore not additive across States. Total U.S. also includes AL, AK, CO, IL, MS, MT, NE, ND, VT, and WV, for which API reported total volumes but not volumes managed by specific methods. Since States' and U.S. totals were calculated independently, totals are additive across rows (i.e., by State) but not columns (i.e., by method). Thus, the National total for a specific method may equal zero even though State's totals for the same management method are positive.

SOURCE: American Petroleum Institute. 1988 (June). *API 1985 Production Waste Survey. Part II - Associated and Other Wastes Statistical Analysis and Survey Results* . Final Report. Data on quantities of dehydration and sweetening wastes taken from source. Percentages are calculated.

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 3-2. Waste Management Practices Used for Spent Iron Sponge, 1985 [A]

State	Waste Generation		Volume Generated (bbl) and Percentage Disposed, by Method of Disposal													
	Number of Barrels Generated	Percentage of U.S. Total	Recycled/Reused[B]		Roadspread		Landspread		Pits[C]		On-site burial		Off-site[D]		Other	
			Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%	Bbls	%
Alaska	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
California	1,018	1.9	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	1,018	100.0	0	0.0
Florida	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Kansas	4,809	8.9	0	0.0	0	0.0	0	0.0	327	6.8	327	6.8	4,155	86.4	0	0.0
Louisiana	7	0.0	0	0.0	0	0.0	0	0.0	0	0.0	7	100.0	0	0.0	0	0.0
Michigan	8,406	15.5	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	8,406	100.0	0	0.0
New Mexico	48	0.1	0	0.0	0	0.0	0	0.0	0	0.0	48	100.0	0	0.0	0	0.0
Oklahoma	3,975	7.3	183	4.6	0	0.0	0	0.0	0	0.0	1,223	30.8	1,753	44.1	815	20.5
Texas	16,530	30.5	0	0.0	28	0.2	85	0.5	7	0.0	16,084	97.3	157	1.0	169	1.0
Wyoming	24	0.0	0	0.0	0	0.0	0	0.0	0	0.0	24	100.0	0	0.0	0	0.0
Total U.S. **(See Note E)**	54,150	100.0	0	0.0	0	0.0	0	0.0	9,000	16.6	29,000	53.6	16,000	29.5	0	0.0

NOTES:

A In conducting the survey, API used the following definition of spent iron sponge wastes: "Obtained from iron sponge sweetening units. It does not include iron sulfide collected in production vessels or pig traps as a corrosion byproduct but only spent iron sponge collected from sour gas treatment units."

B As defined by API: not clear (questionnaire not clear on what responses were included in this category.

C As defined by API: "evaporation pits" or other "on-site pits"

D Off-site commercial facility, including off-site injection.

E Total U.S. includes AZ, IN, KY, MO, NV, NY, OH, PA, SD, TN, and VA. Totals for these States cannot be calculated, individually or collectively, since the values for each reported State and for the total U.S. are independent statistical estimates made by API and are therefore not additive across States. Total U.S. also includes AL, AK, CO, IL, MS, MT, NE, ND, VT, and WV, for which API reported total volumes but not volumes managed by specific methods. Since States' and U.S. totals were calculated independently, totals are additive across rows (i.e., by State) but not columns (i.e., by method). Thus, the National total for a specific method may equal zero even though State's totals for the same management method are positive.

SOURCE: American Petroleum Institute. 1988 (June). *API 1985 Production Waste Survey. Part II - Associated and Other Wastes Statistical Analysis and Survey Results* . Final Report. Data on quantities of spent iron sponge wastes taken from source. Percentages are calculated.

Table 3-2 lists the percentage of spent iron sponge by management/disposal practice and State as reported in the API Survey. The data suggest that roughly half of the spent iron sponge generated from field/lease sweetening operations was managed through on-site burial. Texas, Louisiana, New Mexico, and Wyoming reported utilization of this technique at or near 100 percent of generation. Off-site commercial facilities received 30 percent of field/lease generated iron sponge. Again, a number of States show high utilization for this method, with California and Michigan at 100 percent of generation, and Kansas at 86 percent of generation. On-site pits account for 16 percent of spent iron sponge disposal, though the States reporting this practice are not indicated in the survey.[12]

Several sources have described recommended disposal practices for iron sponge (Harrel and Manning, 1986, API 1989a, Schaak and Chan 1989). Methods described include pit disposal and surface burial. In general, the disposal practice includes soaking the sponge in the contactor with water prior to removal. The sponge is then placed in an on-site pit or disposal pit and kept wet for a period of roughly 10 days, while the remaining iron sulfide is oxidized to elemental sulfur. When no further heat is evolved from the material (e.g., no more reaction with atmospheric oxygen occurs), the waste is buried with 10 inches of soil. The general use of these practices is suggested by the results of the API Survey.

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[12] Note that respondents in Utah indicated a high generation rate for iron sponge, relative to other States. The API 1985 Production Waste Survey: Final Analysis and Survey Results (October, 1987), shows that 100 percent of these wastes were disposed via on-site pits. However, the later Part II report did not provide a breakdown by management method for Utah.

3.2 MANAGEMENT OF OTHER DEHYDRATION AND SWEETENING WASTES

As stated previously, the API survey specifically excluded gas plant wastes from its scope. Additionally, many of the wastes generated at gas dehydration and sweetening facilities, while perhaps covered, are subsumed in the data for other waste categories along with other E&P wastes. This section discusses available information on dehydration and sweetening wastes not explicitly addressed by the API Survey. In general, however, little detailed information was found regarding the management of dehydration and sweetening wastes.

3.2.1 Spent Solid Desiccant/Molecular Sieve

Generally, spent solid desiccants are considered to be non-hazardous solid wastes (API, 1989a). According to the API survey, such materials are typically disposed by burial on-site, or sent to off-site commercial facilities for disposal (API, 1989a).

3.2.2 Regenerator/Reboiler Condensate

Water vapor removed from gas production streams is typically driven off from the desiccant using heat, either in a liquid desiccant reboiler, or by passing regeneration gas over solid desiccant beds. In either system, water vapor may be recondensed in reflux accumulators of regeneration separators, producing a liquid waste. Mostly water, the waste stream may contain dissolved hydrocarbons. Historically, this condensate stream may have been discharged to the surface, often in unlined pits (Gosling, et al., 1991, API 1989a). However, due to the presence of hydrocarbons, management methods now practiced include injection (with other produced waters or fluids) and storage/evaporation in lined pits (Gosling, et al., 1991, API 1989a).

3.2.3 Spent Chemsweet and Sulfacheck Solutions

As discussed above in Section 2, spent batch sweetening solutions such as Chemsweet and Sulfacheck consist primarily of water with sulfur and other salts. According to Harrel and Manning (1986), separation of the liquid and solid fractions permits burial of the residual salts on-site, provided they do not exhibit hazardous characteristics. Because the water may contain dissolved hydrogen sulfide, it must be "degassed" away from humans and animals (Harrel and Manning, 1986). The remaining liquid may then be added to other waste waters for disposal.

3.2.4 Spent Stretford Liquor

Limited information has been found on the universe of Stretford Process operators and the methods used for management of spent solution which they generate. However, one recent article provides a breakdown of the management methods used by Stretford facilities spanning a number of industries, including natural gas processing (Eisele, 1991). According to the article, while spent Stretford solution will rarely test hazardous under Federal regulations, it will generally be treated as hazardous in California. As a result, many California operators dispose of their spent Stretford solutions by transporting them to the E.I. DuPont de Nemours & Co. Chambers Works Wastewater Treatment Facility in Deepwater, New Jersey. As shown in Table 3-3, alternative methods include discharge to Publicly Owned Treatment Works (POTWs), landfilling, on-site wastewater treatment, injection, evaporation, and "no purge," suggesting that these operators do not change out their solution. Another method, discussed below under Pollution Prevention, involves the on-site treatment of Stretford solution for regeneration and removal of contaminants (Becker and Losier, 1991).

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 3-3. Management Practices for Spent Stretford Solution

Management Practice/Facility	**Number of Operators Using Practice**	**Treatment (Yes/No)**
Off-Site		
DuPont Chambers Works Facility, NJ	12	Yes
Crimet (Vanadium Recovery), LA	2	No
Global (Desalting Process)	3	(Recycle)
Landfill	1	No
POTW	1	No
On-Site		
On-site Wastewater Treatment	2	Yes
Evaporation in Pond	2	No
Reinjection into Gas Formation	2	No
No Purge	8	

Source: Eisele, 1991.

In comments regarding this report, GRI offered the following observations from their survey of the natural gas industry:

- Spent filter media (including separator, dehydration, and acid gas removal filters) are managed predominantly through either disposal in a landfill or recycling/reuse.

- Dehydration, sweetening, pipeline cleaning, and NGL recovery waters are managed through a combination of underground injection, surface water disposal (i.e., through an NPDES permit or to a POTW with proper treatment), and/or surface impoundments (i.e., evaporation from lined pits).

- Solid wastes (e.g., spent dehydration desiccants, Claus catalyst) are managed predominantly by either landfill disposal or roadspreading, where permitted.

- Spent liquid dehydration and sweetening solutions (i.e., glycols and amines) are managed almost exclusively by recycling/reuse. Reclamation of these solutions is essential given the high cost of their replacement.

3.3 POTENTIAL ENVIRONMENTAL EFFECTS

Very little information has been located on actual or potential environmental impacts of natural gas dehydration and sweetening waste management in the U.S. However, the following subsections provide some information on waste management methods identified as being used for sweetening and dehydration wastes in the API survey. Also included are brief discussions of the use of the methods in various States, as reported in Tables 3-1 and 3-2 from the API survey. It is important to note that this data is based on States' allowable waste management practices at the time of the API survey. Permissible waste management practices and the percentage of waste disposed by method may be different due to changes in States' regulatory programs or companies' operating practices. Finally, potential environmental impacts are described that could result if E&P wastes are not managed properly using appropriate methods such as those discussed below .

3.3.1 Roadspreading

Various oilfield wastes may be applied to roads, if permitted by State regulations, as dust suppressants, surface deicers, or simply for disposal. API recommends a pH range from 6 to 9 for roadspread wastes (API, 1995).

Nationally, API estimated that no field/lease-generated dehydration and sweetening wastes were roadspread in 1985; two States, however, did show roadspread wastes. The apparent discrepancy is an artifact of the statistical estimations of State and national totals, which were independent. Two States accounted for all of the roadspread fluids: Louisiana and Texas, in each of which 0.2 percent of the State's fluids were reported to be roadspread. Texas was also the only State for which operators reported roadspreading spent iron sponge, 0.2 percent of the State total. The API survey did not distinguish between roadspreading on private (i.e., on-lease) and public roads.

The primary environmental concern for roadspreading would be surface run-off from storm water and snowmelt as well as from the application of excess volumes. Run-off that leaves the roadway could carry whatever constituents from roadspread materials that were on the road's surface. These could contaminate soils and sediments and could affect vegetation directly or could be accumulated in plants, then affect animals consuming the plants as forage. In addition, volatilization of organics could present a localized problem, as could dust that carried metal or organic constituents. NORM could also be a localized concern where very high radioactivity levels occur or where wastes were roadspread over a period of time. No incidents were identified where roadspread dehydration and sweetening wastes were responsible for environmental damages.

3.3.2 Landspreading

The term "landspreading" encompasses a number of overlapping practices. These include land treatment (by volatilization or biodegradation of organics), land application (for evaporation, infiltration, or simple dilution), landfarming (for biodegradation and/or soil enrichment), and landfilling. API recommends that free oil be removed from landspread wastes and that wastes be spread evenly and disked into the soil (API, 1989a). API also recommends that soil pH be maintained between 6 and 9, soil conductivity be less than 4 mmho/cm, and the oil and grease content be less than 1% in the final soil-waste mixture. API has also developed general guidance values for 10 of 12 metals it considers to be of potential environmental concern (API, 1995a). API's recommended guidance values for maximum soils concentration of metals are shown in Table 3-4 along with those from Louisiana State Wide Order 29-B and the Canadian Interim Soil Remediation Criteria for Agriculture as published by API (API, 1995a). The extent to which operators who landspread dehydration and sweetening wastes follow these recommendations is not known, although many States regulate various forms of landspreading .

In 1985, API estimated that only 0.4 percent of dehydration and sweetening wastes were disposed/managed by landspreading (off-lease but noncommercial landspreading would presumably be included under landspreading, but commercial landspreading would be captured under off-site commercial facilities). Of States for which API provided data, Texas accounted for nearly all of the dehydration and sweetening wastes reported as being landspread (4.0 percent of the State total). Texas was the only State for which landspreading of iron sponge was reported, with 0.5 percent of that State's iron sponge disposed by this method.

Available information does not describe the extent to which gas plant (as opposed to field unit) dehydration and sweetening wastes are disposed by landspreading/land treatment. Boyle (1990) discusses the potential of landspreading as a treatment method for amine sludges. Results of lab-scale testing indicate that soil microflora may degrade organic compounds, while immobilization of constituents toxic to fish and wildlife may also occur. The author noted that sodium concentrations were of particular concern in considering landspreading for management of amine sludges (Boyle, 1990).

Environmental concerns from landspreading would involve all media: soils, surface water and groundwater, and air. Metals, organics, and particularly salts could contaminate soils if fluids contain excess concentrations of any constituent or if excess materials are applied. Excess salts can effectively sterilize soils for years, and some metals and organics can be incorporated into plant tissue, thereby presenting a risk to animals or humans who consume them. Precipitation-induced run-off or excess volumes of applied materials can contaminate sediments and surface waters with salts, metals, and/or organic contaminants, and constituents could leach into groundwater as well. Finally, volatilization of organics could present a localized problem, as could dust that carried metals or organic constituents. NORM could also be a localized concern if very high radioactivity levels occur or if large volumes of wastes containing NORM are landspread over a period of time. No incidents were identified where landspread dehydration and sweetening wastes were responsible for environmental damages.

Associated Waste Report:
Dehydration and Sweetening Wastes (U.S. EPA, January 2000)
Table 3-4. API, Louisiana 29-B, and Canadian
Maximum Soil Concentration Values for Metals

Element	API Guidance	Louisiana 29-B	Canadian Agriculture
Arsenic	41	10	20
Barium	180,000	20,000 40,000 100,000	750
Boron	2 mg/L	--	2 mg/L
Cadmium	26	10	3
Chromium	1500	500	750
Copper	750	--	150
Lead	300	500	375
Mercury	17	10	0.8
Molybdenum	--	--	5
Nickel	210	--	150
Selenium	--	10	2
Zinc	1400	500	600

All concentrations in mg/kg unless otherwise specified.
Source: API 1995a

3.3.3 On-site Pits

Nearly 17 percent of spent iron sponge generated in the U.S. from field/lease facilities was managed in on-site pits in 1985 (and very small volumes of other dehydration and sweetening wastes, as indicated in the notes for Table 3-1). Nearly all of the pit-managed iron sponge wastes were generated in States for which no breakdown of wastes by management practice was provided. Accordingly, very little can be said regarding the types of pits used or prevailing regulations affecting such management.

Available data do not indicate the management practices used for gas plant-generated dehydration and sweetening wastes. Such wastes include condensate, which may be stored in pits, either alone or mixed with other oilfield wastes. In many field/lease situations, various production pits may be used to store or dispose of produced fluids. Production pits are typically excavated below-grade and may be surrounded by raised berms or dikes. Depending on environmental conditions and regulatory requirements, production pits may be lined with clay or synthetic liners. In some areas, the excavation may be near or below the water table, in which case API (1989a) recommends the use of liners. Liquids may be periodically removed from the pit, oil to go to reclaimers or the production line, water (brine, not fresh water) to be injected, roadspread, landspread, or otherwise managed.

The oldest and most common method of closing pits is by dewatering and backfilling. The water is evaporated or otherwise removed (and managed as noted above) and the residue covered with material from either the pit wall or surrounding soil, and compacted. Remaining free liquids may be absorbed with dirt or straw before being covered with soil. Where dewatering is not practical, pit contents can be transported off-site or solidified in place; after removing as much water as possible, cement, fly ash, kiln dust, and polymers may be used to solidify pit contents. Solidification can immobilize, at least for a time, various constituents in the wastes. The solidified material then may be buried, left as it is, or used for landfill cover or road material. If the surface of backfilled pits is not carefully graded and revegetated or otherwise protected, over time the cover could erode and lead to uncontrolled releases.

The potential for environmental harm from on-site pits is in part a function of the wastes disposed in the pits. Risks stem from the potential for surface and subsurface migration of waste constituents and potential emissions of volatile organic compounds or other hazardous air pollutants.

3.3.4 On-site Burial

According to API, over 50 percent of spent iron sponge generated at field/lease sweetening facilities was managed by on-site burial in 1985 (small quantities of other dehydration wastes were also buried on-site, as indicated in the notes for Table 3-1). Texas operators accounted for the majority of iron sponge disposed by this method.

On-site burial should pose direct risks neither to surface waters (so long as the material remains buried and salts or other contaminants do not migrate to the surface) nor to air. Depending on the site, the material buried, and the constituents involved, leachate contamination of groundwater could be of concern. Indirectly, surface water could be affected in such cases if there is groundwater recharge of surface waters. If free liquids are actually buried, clearly the risk of leaching would be increased. Since the non-fluid wastes would be the same as discussed previously, so too would the constituents of concern in those wastes: metals, organic constituents such as benzene, salts, and NORM. If the surface is not carefully graded and revegetated or otherwise protected, materials overlying buried wastes could erode and lead to uncontrolled releases. No incidents were identified where dehydration and sweetening wastes buried on-site were responsible for environmental damages.

3.3.5 Off-site Commercial Facilities

Nationally, nearly 30 percent of spent iron sponge was reported by API to have been managed at off-site commercial facilities. This percentage was in part inflated by the exclusive use of this practice by operators in California and Michigan, as well as the large amounts so managed in Kansas and Oklahoma. For dehydration and sweetening wastes excluding iron sponge the fraction was lower (roughly 10 percent). Note, however, that Texas operators reported having sent nearly 84 percent of these wastes to off-site facilities. Specific management methods used for wastes at such facilities can include all of the methods described above as well as underground injection, described below.

Whether injected or managed by other methods, the potential environmental impacts from off-site commercial management of dehydration and sweetening wastes should be similar to those managed on-site or noncommercially. One possible difference between off-site commercial management of wastes and on-site management would be the wider variety of wastes likely to be managed in various units at commercial facilities. The wider variety of wastes could include a wider variety of constituents of concern, possibly in more concentrated forms.

API (1989a) counsels caution in using off-site facilities due to the joint and several liability provisions of CERCLA and similar State statutes. API recommends periodic inspections of commercial facilities by States and/or operators to verify compliance and identify areas of environmental concern. Finally, API suggests that operators track off-site waste shipments, even where this is not required.

3.3.6 Underground Injection

All indications are that the vast majority of liquid sweetening and dehydration wastes are injected into the subsurface along with produced water and other fluids. Most wells used for injection of oil and gas wastes are classified as Class II wells under the Underground Injection Control (UIC) program. Some States, however, may require certain wastes to be injected in Class I wells (e.g., California, when wastes are classified as hazardous wastes under State regulations (IOGCC, May 1993)). API (1989a) has recommended that injection be used for disposal of all exempt exploration and production wastes where practical. API regards underground injection as the safest and most practical means for disposing of dehydration and sweetening wastes.

While available information on the management of gas plant wastes has been limited, Boyle (1990) notes that Canadian operators dispose of most gas plant fluid wastes via injection. Such wastes include spent amines, amine filter backwash, and amine sludges (with dilution).

The potential environmental impacts from underground injection would be largely confined to groundwater, except insofar as surface management (in tanks or pits) prior to injection presented risks to soils, surface water, or air. Leaks from improper injection well casing or corroded casing could allow fluids to escape the injection well before reaching the receiving formation and possibly contaminate fresh water aquifers.

In addition, the presence of abandoned wells in the same formation in which injection occurs may provide a conduit for injected fluids to reach overlying aquifers or even the surface.

4.0 WASTE MINIMIZATION AND POLLUTION PREVENTION

The title of the 1976 amendments to the Solid Waste Disposal Act, the "Resource Conservation and Recovery Act," focused attention on what was and is the ultimate purpose of RCRA: the prevention of pollution by conserving and recovering resources. The various programs administered by EPA under the Clean Air Act; the Federal Water Pollution Control Act; the Toxic Substances Control Act; the Federal Insecticide, Fungicide, and Rodenticide Act; the Safe Drinking Water Act; and other statutes all have that goal, and have made substantial progress toward its achievement by requiring specific pollution control technologies, placing limits on releases to the environment, and/or monitoring and reporting on toxic materials used or released. In response, those who are subject to the programs often meet requirements by changing industrial processes or feedstocks, by reducing or eliminating the volume of releases, and/or by installing treatment technologies. In the 1984 amendments to RCRA, Congress declared it to be national policy that the generation of hazardous waste was to be reduced or eliminated. Finally, in the Pollution Prevention Act of 1990, Congress formally established a national policy of "pollution prevention."

Having long complemented its traditional permit programs, which require treatment or otherwise limit releases, with active encouragement of what has become to be known as "pollution prevention," EPA in May of 1992 responded to the 1990 Act with a formal "Statement of Definition" that placed "pollution prevention" first in a hierarchy of approaches to be used by EPA in its environmental management activities (EPA, 1992). In decreasing order of preference, the hierarchy includes:

- *Pollution prevention*: source reduction and other practices, such as in-process recycling, that reduce or eliminate the creation of pollutants through increased efficiency and/or conservation of resources. It includes reducing the amount of hazardous substances, pollutants, or contaminants entering any waste stream or being released prior to recycling, treatment, or disposal; or reduces risks associated with releases.

  Source reduction is any practice which (i) reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and (ii) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants. This includes equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of raw materials, and improvements in housekeeping, maintenance, training, or inventory control.

- *Recycling*: specifically, out-of-process recycling, since in-process recycling is included in pollution prevention above. This would include environmentally sound beneficial reuse of "waste" materials as well as energy recovery.

- *Treatment* prior to disposal or release: this would not include contained disposal.

- *Disposal or release*.

A number of waste- and/or pollution-limiting developments have gained acceptance in the gas conditioning industry which increase both the efficiency and environmental performance of such operations. Such developments achieve reductions in the volume of wastes generated, the toxicity of the wastes, or decrease the total amount of resources consumed through recycling or reuse, or some combination of these. Note that many techniques may fit equally well into any of these categories. Some of the significant waste minimization and pollution prevention techniques applicable to gas conditioning are presented in this section.

It is worth noting that waste minimization, whether through source reduction or recycling, can be an attractive objective to gas conditioning operators because it can lower waste treatment and disposal costs and reduce the potential for future liability resulting from waste mismanagement. At the same time, however, it may require the use of more expensive or less suitable materials or require changes in processes or operations. Due to the wide variability in production and treatment parameters, not all waste minimization techniques are appropriate for all operators, but must be weighed against the trade-offs that each presents.

Volume Reduction

Perhaps the most basic technique to reduce volumes of waste fluids that are managed in pits or other land units, such as sumps, is to divert run-off, equipment wash water, and other such liquids from the pit. If allowed to enter the pit, the water becomes a waste that must be managed.

When fluids with environmental contaminants are added to a pit (or other unit) with more benign wastes, the entire contents can become contaminated and either require more expensive management methods (Spell, et al., 1990) or cause more environmental problems. Central Gulf Coast case studies evaluated a "Pit Management System," in contrast to the more conventional reserve pit or a closed system. In summary, a managed pit system may consist of several pits or bermed cells surrounded by a raised berm or levee. The system allows individual waste streams to be segregated and managed according to their special characteristics (drilling wastes were the paper's topic, but the concept of waste segregation could apply equally to dehydration and sweetening wastes managed in pits or other units). By preventing certain wastes from contaminating other wastes, significant cost savings were achieved in the case studies examined. (Spell, et al., 1990)

Process changes may also lead to reductions in the volume of wastes generated. Efficient filtration of amines, glycols, or other solvents is often critical to reducing degradation of the solvents, foaming difficulties, and carryover (See Section 2). Reduction of contaminants through filtration serves to extend the life of the process solvent, thereby reducing the rate of disposal. Other volume reduction methods that have proven successful in field trials include the recovery of gas conditioning fluids from conditioning fluid sludges; dewatering of gas conditioning fluid sludges and recycling of the recovered water back into gas conditioning processes; reducing the volume of used filters by using longer life, reusable, and back washable filters (Benoit and Schuh, 1993); and reducing the volume of waste water from cooling towers by using more efficient scale inhibitors (Railroad Commission of Texas, 1994).

Another process change which can reduce the volume of waste generated is the use of concurrent extractors in caustic and amine NGL sweetening units (Baker and Isom, 1991). Such systems utilize the increased effective surface area contact achievable by simultaneously injecting the solvent-hydrocarbon two-phase stream through a mixing valve or other matrix where reaction between the solvent and the acid gases occurs. A two-phase separator allows removal of product from the rich solution. In typical countercurrent contactors, the richest product (i.e., highest acid gas concentration) is in contact with the richest solvent, decreasing the rate of reaction between acid gases and solvent (Baker and Isom, 1991). However, in concurrent extractors, the richest product is in contact with the leanest solvent, maximizing removal. Such systems can achieve high acid gas removal rates with less than 25 percent of the solvent required for comparable countercurrent contactors (Baker and Isom, 1991).

The potential benefits of concurrent contactors include reduced capital costs (from smaller equipment size requirements), reduced operating costs (from reduced pump loads and regeneration heat loads due to lower solvent volumes), and reduced spent solvent generation, due to smaller total amounts of solvent in the system (Baker and Isom, 1991).

Sulfur recovery is perhaps the best example of pollution prevention currently practiced in the gas industry. As discussed above, sulfur recovery by the Claus process and other techniques produces elemental sulfur from the hydrogen sulfide present in the production stream. The Claus process reduces the discharge of acid gases to the atmosphere. Liquid redox processes remove sulfur via direct conversion, but such processes can be made to produce saleable product sulfur. In 1991, natural gas sulfur recovery from gas plants totaled roughly three million metric tons (Anonymous,"Annual Natural Gas Report." Vol. 90, No. 29, *Oil and Gas Journal*, 1992).

Additional pollution prevention also is achievable. Many Claus plants, particularly plants with very high acid gas concentrations, install tail gas scrubbers to increase the total sulfur recovered from the gas stream (Maddox, 1985). Tail gas scrubbers process the flue gasses from the primary Claus systems. Use of tail gas scrubbers can increase sulfur recovery to over 99 percent of the sulfur in the feed gas (EPA, 1983; Maddox, 1985).

Toxicity Reduction

The replacement of formaldehyde-based sweetening solvents with less hazardous materials is another example of toxicity reduction currently practiced in gas conditioning operations. Formaldehyde-based solvents typically consist of mixtures of formaldehyde, methanol, water, and various additives (Schaak and Chan, 1989). Marketed under trade names Scavinox, Di-Chem, Magnatreat, and others, these solutions may result in strong, objectionable odors in product streams as a result of by-product formation of mercaptans. Further, formaldehyde is considered to be a carcinogen in the U.S. For these reasons, use of formaldehyde in sweetening operations has been limited in the U.S. (Manning and Thompson, 1991).

Recycling/Reuse

The use of amine and glycol reclaimers in gas conditioning operations may be considered waste minimization through recycling/reuse. Amines, particularly primary amines, are very susceptible to degradation, both thermal and chemical. These solutions can be reclaimed through distillation in reclaimers. Such practices reduce amine losses and operating difficulties, and accordingly, the amount of waste generated by the unit. Similarly, glycol reclaimers can regenerate degraded and contaminated glycol, thus avoiding the need to dispose of the treated solvent.

Stretford solution may also be amenable to reclamation. Becker and Losier (1991) describe the development of a process to remove thiosulfate salts from contaminated Stretford solution. The claimed advantages of this treatment include the reduction in solution pumping energy costs and increased useful life of the solution. Additionally, the operation allows reclamation of vanadium, which may then be returned to the solution (Becker and Losier, 1991).

Regeneration of caustic wash also qualifies as recycling/reuse. While not unlike regeneration in glycol and amine systems, regeneration in caustic wash systems has often not been practiced due to the low cost of chemicals and the high capital cost of the reboiler/still/separator unit. However, increasing disposal costs and reduction in product loss have combined to make regeneration more attractive (Maddox, 1985).

As mentioned above in the section on volume reduction, recovered water from dewatering gas conditioning fluids sludges can be recycled as make-up water in reboilers, wash water, and other utility waters. Additionally, wash water accounts for a significant volume of waste water at gas plants. Opportunities exist to recover and reuse large quantities of wash water (Benoit and Schuh, 1993).

In comments on this report, GRI points out that the natural gas industry has been and continues to utilize waste minimization and pollution prevention practices to manage wastes more effectively. GRI specifically emphasizes the following practices:

- Source reduction including filter changeout based on performance (e.g., pressure drop, suspended particulate), gas conditioning fluid changeout based on quality, and optimization of dehydration and sweetening unit performance.

- Recycling/reuse of filters, spent gas conditioning fluids, dehydration and natural gas liquids recovery waters, and glycol reclamation wastes.

5.0 SUMMARY AND CONCLUSIONS

The purpose of this report has been to provide a profile of the generation, characteristics, and management of dehydration and sweetening wastes. Along with other wastes associated with the exploration, development, and production of crude oil and natural gas, gas plant (and field unit) dehydration and sweetening wastes are exempted from regulation as hazardous waste under RCRA Subtitle C. Since completion of the *Report to Congress on Management of Wastes from Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy,* and the subsequent regulatory determination for these wastes, comparatively little information has been published on the generation and management of dehydration and sweetening wastes.

5.1 DEHYDRATION PROCESSES AND WASTES

In the recent past, there were a total of 732 gas processing plants in operation in the U.S. An unknown but large number of small field/lease units also exist. While no census of gas conditioning units throughout the U.S. has been found, available information sources indicate that over 40,000 dehydration units are in operation. These same sources generally agree that triethylene glycol (TEG) is by far the most widely used desiccant material in natural gas dehydration operations. The apparent appeal of this over other glycols is explained by the high loading capacity, high thermal degradation temperature, and relatively low regeneration heating requirements of TEG.

Typical TEG systems operate continuously, removing water from inlet gas, and regenerating the solvent through the addition of heat. Regeneration results in the continuous generation of condensate which may contain dissolved hydrocarbons. Available waste characterization data indicate, although inconclusively, that regeneration condensate typically contains high concentrations of benzene, and may exhibit the characteristic of toxicity for this volatile organic compound. It is worth noting that the only information found regarding damages from gas plant wastes involved natural gas condensate.[13]

Trace impurities in the gas stream, carry-over of free liquids from inlet separators, corrosion products, glycol degradation products, and other impurities eventually reduce the water-holding capacity of TEG to the point where it must be reclaimed or disposed. Accordingly, among the wastes of glycol dehydration are spent glycol and glycol reclaimer sludge, intermittently generated. Filtration of in-stream glycol extends the life of the solvent, but also results in generation of solid/semi-solid wastes, filter sludge and filter media. While these materials generally would not exhibit hazardous characteristics, they may contain high levels of total organics, including glycols, aldehydes, BTEX, and organic acids. GRI recently

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[13] Wastes associated with gas development on the Kenai Peninsula of Alaska were illegally disposed from 1970 to 1985 in a gravel pit. An investigation by the Alaska Department of Environmental Conservation (ADEC) revealed that the pit contained barrels of unidentified wastes, drilling muds, gas condensate, gas condensate contaminated peat, abandoned equipment, and soil contaminated with diesel oil and chemicals. According to ADEC laboratory reports from 1986 and earlier, there was "demonstrated contamination of adjacent water wells with organic compounds related to gas condensate."

conducted a survey of natural gas operations and waste streams that provides comprehensive new information on gas dehydration wastes and waste constituents (GRI, 1993). Available information indicate that injection of all fluid dehydration wastes is the norm. This includes reboiler condensate, spent glycol, and diluted sludges.

A number of other dehydration processes have been identified and described in this report. Such systems may be viewed as specialty processes, typically utilized when location, production scale, production stream characteristics, and/or delivery specifications combine to warrant alternative methodologies. For instance, solid desiccants were shown to be universally used when very low water contents are required, such as for cryogenic gas processing. The number of such facilities is not known, but is believed to be small relative to glycol units.

Calcium chloride units also present a special case. These units require little maintenance and operator attention beyond the periodic refilling of the calcium chloride pellet bed. According to available information, they are frequently used in remote locations, such as the Rocky Mountains. While no information was found on the volumes involved, calcium chloride dehydrators produce a continuous discharge of concentrated brine. While the methods used to manage this discharge are not documented, it is possible that evaporation/percolation pits are used.

5.2 SWEETENING PROCESSES AND WASTES

Information collected by API (1982) indicates that roughly 278 sour gas plants were in operation in the U.S. at the time of the survey. More recently, GRI estimated that 617 sour gas plants are operating in the U.S. (GRI, 1995). Again, however, the data are silent with regard to the number of field/lease units (e.g., iron sponge units) currently existing. Several sources place the number of iron sponge units in the "thousands," with additional "hundreds" of other batch sweetening units such as Chemsweet and Sulfacheck systems adding to the total.

By far the most used sweetening agents in gas plants are alkanolamines. In particular, monoethanolamine (MEA) and diethanolamine (DEA) appear to dominate the large-scale end of the industry. Other amines (MDEA, DGA, Sulfinol) find applications in situations where selectivity for acid gases or other factors make these more attractive than MEA and DEA. One source numbers amine units in operation at around seven hundred, suggesting that numerically most of these are not centralized gas plant scale dehydration facilities.

Like glycol plants, amine units operate continuously, producing sweet gas and rich (sour) solvent. Solvent regeneration requires the input of heat, yielding an acid gas stream typically of high concentration. Historically vented or flared to the atmosphere, acid gases are often fed to a sulfur recovery plant for production of elemental sulfur.

Accumulation of impurities such as thermal degradation products, free liquid carryover from inlet separators, corrosion products, scale, and hydrocarbons reduce the sulfide holding capacity of the amines. Contaminated amines must be disposed or reclaimed, though only the primary amines (MEA, DGA) are highly amenable to distillation reclaiming. Accordingly, amine sweetening results in the intermittent generation of spent amines and amine reclaimer sludges. Further, amine systems always generate filter sludges and spent filter media.

The environmental characteristics of amine sweetening wastes have received comparatively little attention relative to glycol dehydration wastes. Available information indicate that spent amine and spent amine filters may occasionally exhibit one or more hazardous characteristics - toxicity (principally for benzene), reactivity (for reactive sulfide), and/or corrosivity. Data collected from Canadian sour gas plants suggest amine sweetening wastes may contain high metals concentrations as well. Preliminary results of the GRI survey of the gas industry indicate that sweetening wastes are generated in smaller quantities than dehydration wastes.

Iron sponge was found to be the most widely used of all the batch sweetening processes. These units range in size from small to moderately large, though they are most often used when production rate and/or hydrogen sulfide concentrations are low. The principal by-product of iron sponge systems is spent iron sponge, typically wood shavings with elemental sulfur and residual ferric oxide on the surface. While there’s a potential for it to auto-combust, spent iron sponge is typically managed as a non-hazardous waste, most often buried on-site or sent to a commercial facility.

Emerging liquid redox processes, such as the Stretford process, apparently provide an alternative to the capital-intensive Claus sulfur recovery process for moderately sour gas producers. Such facilities produce elemental sulfur, potentially of sales quality, and can achieve very good sulfur reductions. These systems may present environmental challenges for the operator, however, due to the potentially high concentration of thiosulfates, thiocyanates, and metal complexes in spent solution and scrap sulfur.

No reliable estimates of the number of units using the alternative sweetening processes could be located. Such systems include potassium carbonate solution systems and variants, caustic wash systems, molecular sieve systems, and Selexol, among others. It is worth noting that Selexol, unlike most other processes, does not produce a regeneration waste. Regeneration of the rich solvent is accomplished through a series of flash tanks which allow recovery of absorbed hydrocarbons before venting waste gases to the atmosphere. According to one source, the materials used are non-toxic and long-lived.

Again, while no systematic study has been released to date, waste management of liquid sweetening wastes is most likely to be by injection. Canadian data indicate that, in that country, spent amines and diluted sludges are deep-well disposed. The API data do show that most "dehydration and sweetening wastes" were reportedly injected in the 1985 Survey (API, 1988). Very little other information was found.

5.3 CONCLUSIONS

While recent data provide an improved understanding of the chemical characteristics of some gas industry wastes, no census of existing facilities, process types, wastes volumes generated, and waste management practices employed appears to exist. In addition, no known environmental monitoring data have been compiled for any gas processing sites to date.

The May 1993 GRI Topical Report on natural gas industry wastes suggests that gas processing waste characteristics are highly variable with waste type, product gas composition, process type and operating conditions, location of the processing unit in the overall treatment train, and other factors. Some wastes, such as regeneration condensate from dehydrators, may contain high concentrations of benzene and other volatile organic compounds with high solubility in water. In the December 1995 Topical Report, GRI concluded that current waste disposal practices for amine-based gas sweetening and Claus sulfur recovery unit wastes are generally adequate for most waste streams. GRI also suggests that operators may want to consider increased testing of their wastes to determine whether they may need to be handled as hazardous wastes in the event of RCRA reauthorization, even if the E&P waste exemption remains in place. GRI's rationale for this is the more stringent definition of hazardousness under CERCLA, which covers the release and cleanup of "hazardous substances," and the possibility of liability problems surfacing later even though the wastes had been disposed in conformance with solid waste regulations.

The API Survey and GRI Survey results as well as data on the Canadian gas industry suggest that the waste management methods used most are deep-well injection of liquid wastes and landfilling of solid wastes. Results of GRI's recently completed survey of the U.S. gas industry provides a better understanding of waste management practices at central gas plants. The practices employed at field/lease operations remain uncertain.

Natural gas processing operations may be amenable to significant pollution prevention opportunities. Operators have implemented optimization of gas conditioning unit operations, addition of sulfur removal systems, substitution of products, and use of regeneration and reclaiming systems. These measures are necessarily site-specific, due to the variability in operating conditions.

Finally, characterization of potential hazards that may be posed by wastes from the natural gas processing industry may not be accurately represented by TCLP data due to matrix interference. Because of their oily matrix, matrix interferences were experienced for many TCLP samples. This required further dilution of the samples producing results that are at best qualitative and unreliable. Additionally, the TCLP test was developed to replicate potential hazards of leachate from wastes disposed in municipal landfills. As discussed previously, dehydration and sweetening wastes typically are not disposed in municipal landfills. Instead, when practical, these wastes are generally disposed by deep well injection. Nevertheless, there currently is no better test method than TCLP available for these types of materials.

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APPENDIX A

Analytical Results of EPA's 1992 Associated Wastes Sampling Program

(Detected Analytes Only)

Dehydration and Sweetening Wastes

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000)

Table A-1. Dehydration and Sweetening Analytical Results - Detected General Chemistry Analytes

FACILITY		B	F	F	R	R	B	F	R	Q	R	B
SAMPLE TYPE		AMINE	AMINE	AMINE	AMINE	AMINE	GLYCOL	GLYCOL	RICH-GLY	GLY-COND	GLY-COND	CAUSTIC
SAMPLE NUMBER		23138	23159	23162	23646	23647	23137	23160	23648	23643	23649	23139
ANALYTE	UNITS			Dup-159		Dup-646						
Acidity	mg/L CaCO3	ND	ND	ND	ND	ND	ND	ND	ND	59.80	ND	ND
pH	std. units	8.80	11.24	11.21	10.76	10.75	10.69	9.75	8.81	6.52	7.58	13.12
Carbon, total organic	mg/L	303600	159640	193440	188000	14700	290400	442800	741000	4220	28100	10540
Chloride	mg/L	619.64	2336.38	2174.00	923.00	925.00	671.70	219.00	ND	6.82	12.50	66610
Corrosivity	mmpy	NA	ND	ND	ND	ND	NA	ND	ND	0.09	0.01	10.85
Cyanide, Total	mg/L	0.03	ND	ND	ND	ND	0.11	0.01	ND	0.03	ND	ND
Flashpoint, closed cup	deg. F	>140	>140	>140	210.00	210.00	>140	>140	210.00	210.00	210.00	128.00
Fluoride	mg/L	ND	12.40	11.70	ND	0.21	6.40	ND	0.40	ND	ND	ND
Nitrogen, ammonia	mg/L	1.33	0.44	0.16	127.00	153.00	1.80	0.46	7.60	22.30	12.80	ND
Oil & Grease, Total	mg/L	187.00	69.00	63.00	1.90	3.50	3626	6300	633	211	127	ND
Oxygen Demand, Biochemcial 5-day Tot.	mg/L	10800	ND	ND	17.70	22.10	2064000	ND	505000	6910	1190	6900
Oxygen Demand, Chemical	mg/L	1226000	829000	820000	451550	354500	645000	1856000	1572000	31580	92100	59400
Phenols	mg/L	0.07	0.24	0.25	0.41	0.34	1.59	1.39	0.41	1.23	0.65	0.02
Salinity	Salinity #	0.29	1.36	1.33	0.53	0.53	0.16	0.00	0.02	0.13	0.71	0.00
Solids, Total Dissolved	mg/L	ND	ND	ND	17740	14230	ND	ND	44700	198	434	82670
Solids, Total Suspended	mg/L	19	207	243	22	20	125	ND	ND	ND	ND	534
Specific Conductance	umhos/cm	532	2370	2330	NA	NA	300.00	9.00	NA	NA	NA	ND
Sulfate	mg/L	ND	447.00	326.00	11.40	31.30	ND	ND	64.50	ND	299.00	ND
Sulfide	mg/L	0.04	50.60	52.90	258.00	200.00	18.80	ND	162.00	165.00	25.80	1800.00

NU = Not Used DS = Detector Saturation

Due to laboratory problems caused by sample matrices, Total Dissolved Solids analysis results could not be obtained for samples 23137, 23159, 23160, and 23162.

Table A-2. Dehydration and Sweetening Analytical Results - Detected Metals

FACILITY	B	F	F	R	R	B	F	R	Q	R	B
SAMPLE:	23138	23159	23162	23646	23647	23137	23160	23648	23643	23649	23139
TYPE:	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN GLYCOL	LEAN GLYCOL	RICH GLYCOL	GLYCOL COND.	GLYCOL COND.	CAUSTIC
			Dup-159		Dup-646						
METAL	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Aluminum	37.0	ND	88.3	4710.0	3030.0	73.6	ND	443.0	796.0	ND	119.0
Antimony	ND	121.0	63.4	ND	ND	ND	172.0	ND	79.4	ND	ND
Arsenic	ND	ND	ND	ND	71.0	ND	ND	25.3	4.8	ND	ND
Barium	33.7	30.9	28.9	ND	ND	ND	20.8	ND	ND	6.8	27.2
Boron	70.7	756.0	731.0	6240.0	3670.0	952.0	2230.0	1320.0	ND	ND	23.0
Cadmium	ND	968.0	ND	ND	ND	ND	ND	150.0	ND	ND	ND
Calcium	8290.0	ND	912.0	340.0	1020.0	ND	431.0	2730.0	2680.0	14900.0	1460.0
Chromium	102.0	ND	ND	ND	ND	27.3	ND	ND	39.0	ND	ND
Copper	ND	ND	ND	ND	ND	24.9	ND	67.2	166.0	ND	183.0
Iron	3250.0	2110.0	1900.0	1210.0	660.0	ND	348.0	4540.0	45800.0	969.0	2620.0
Lead	ND	70.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Magnesium	921.0	ND	ND	ND	281.0	ND	ND	ND	ND	391.0	ND
Manganese	1050.0	75.9	73.4	19.2	5.8	ND	27.2	113.0	440.0	16.4	105.0
Mercury	ND	ND	ND	ND	ND	ND	ND	ND	ND	54.0	ND
Molybdenum	11.6	102.0	75.4	108.0	77.3	20.9	195.0	253.0	ND	17.4	10.6
Nickel	82.4	ND	ND	ND	ND	ND	ND	193.0	55.0	ND	ND
Sodium	7820.0	349000.0	350000.0	20900.0	13700.0	1700.0	42800.0	40100.0	ND	3020.0	19200000.0
Strontium	57.0	230.0	22.0	ND	ND	28.0	ND	23.5	24.2	206.0	69.0
Sulfur	963000.0	21500.0	23000.0	48200.0	34700.0	23200000.0	17800.0	60200.0	449000.0	6030.0	627000.0
Thallium	ND	ND	ND	ND	ND	ND	ND	ND	ND	208.0	14.4
Tin	74.3	455.0	266.0	2950.0	854.0	231.0	1230.0	4950.0	ND	ND	34.8
Titanium	3.5	ND	ND	3560.0	2060.0	4.2	ND	306.0	10.2	ND	3.3
Vanadium	ND	ND	ND	213.0	118.0	12.7	ND	ND	ND	ND	ND
Zinc	ND	39.4	46.7	ND	ND	ND	ND	145.0	658.0	ND	127.0

ND = Non Detect

NA = Not Analyzed

Table A-3. Dehydration and Sweetening Analytical Results - Detected Volatile Organic Compounds

FACILITY	B	F	F	R	R	B	F	R	Q	R	B
SAMPLE TYPE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN GLYCOL	LEAN GLYCOL	RICH GLYCOL	GLYCOL COND	GLYCOL COND	CAUSTIC
SAMPLE NUMBER	23138	23159	23162	23646	23647	23137	23160	23648	23643	23649	23139
			Dup-159		Dup-646						
COMPOUND	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
ACETONE	ND	ND	ND	ND	ND	ND	ND	ND	7186.0	627.0	ND
BENZENE	ND	ND	ND	ND	ND	505.0	99853.0	81581.0	43332.0	1657.0	ND
CARBON DISULFIDE	ND	ND	ND	ND	ND	ND	ND	ND	25947.0	ND	ND
ETHYLBENZENE	ND	ND	ND	ND	ND	855.0	55255.0	879.0	15531.0	21.0	ND
METHYL CHLORIDE (CHLOROMETHANE)	ND	ND	ND	ND	ND	ND	ND	ND	136.0	ND	ND
METHYLENE CHLORIDE	ND	15.0	15.0	ND	ND	ND	1769.0	ND	ND	ND	ND
M-XYLENE	ND	ND	ND	ND	ND	1472.0	54286.0	4829.0	24444.0	95.0	ND
O- + P-XYLENE	ND	ND	ND	ND	ND	919.0	31497.0	1575.0	222057.0	41.0	ND
TOLUENE	ND	11.0	15.0	ND	ND	2866.0	356570.0	74699.0	91192.0	866.0	ND
TRICHLOROFLUOROMETHANE	ND	49.0	51.0	ND	ND	ND	2937.0	ND	ND	ND	ND

NU = Not Used NA = Not Analyzed

Table A-4. Dehydration and Sweetening Analytical Results - Detected Semivolatile Organic Compound

FACILITY	B	F	F	R	R	B	F	R	Q	R	B
SAMPLE TYPE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN AMINE	LEAN GLYCOL	LEAN GLYCOL	RICH GLYCOL	GLYCOL COND	GLYCOL COND	CAUSTIC
SAMPLE NUMBER	23138	23159	23162	23646	23647	23137	23160	23648	23643	23649	23139
			Dup-159		Dup-646						
COMPOUND	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
ACENAPHTHENE	ND	ND	ND	ND	ND	ND	ND	ND	27158	ND	ND
ACETOPHENONE	ND	ND	ND	ND	ND	194250	ND	ND	ND	ND	ND
BENZO(A)ANTHRACENE	ND	ND	ND	ND	ND	ND	ND	ND	11566	ND	ND
BENZO(A)PYRENE	ND	ND	ND	ND	ND	ND	ND	ND	7059	ND	ND
BENZO(B)FLUORANTHENE	ND	ND	ND	ND	ND	ND	ND	ND	4888	ND	ND
BENZO(K)FLUORANTHENE	ND	ND	ND	ND	ND	ND	ND	ND	4888	ND	ND
BIPHENYL	ND	ND	ND	ND	ND	ND	ND	ND	181307	ND	ND
BIS(2-ETHYLHEXYL)PHTHALATE	ND	ND	ND	ND	ND	ND	ND	ND	5086	ND	ND
CHRYSENE	ND	ND	ND	ND	ND	ND	ND	ND	11115	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND	ND	ND	30933	ND	ND
FLUORANTHENE	ND	ND	ND	ND	ND	ND	ND	ND	36865	ND	ND
NAPHTHALENE	35419	ND	ND	ND	ND	ND	ND	ND	1750844	ND	ND
N-DECANE (N-C10)	ND	ND	ND	ND	ND	ND	ND	1421	ND	6381	ND
N-DOCOSANE (N-C22)	ND	ND	ND	ND	ND	ND	ND	ND	26124	12780	ND
N-DODECANE (N-C12)	ND	ND	ND	ND	ND	ND	ND	ND	56889	ND	ND
N-EICOSANE (N-C20)	ND	ND	ND	ND	ND	ND	ND	ND	72847	ND	ND
N-HEXACOSANE (N-C26)	ND	ND	ND	ND	ND	ND	ND	ND	11642	ND	ND
N-HEXADECANE (N-C16)	ND	ND	ND	ND	ND	ND	ND	ND	134829	19184	ND
N-OCTADECANE (N-C18)	ND	ND	ND	ND	ND	ND	ND	ND	134920	18388	ND
N-TETRACOSANE (N-C24)	ND	ND	ND	ND	ND	ND	ND	ND	18170	ND	ND
N-TRIACONTANE (N-C30)	ND	ND	ND	ND	ND	ND	ND	ND	39618	ND	ND
PHENANTHRENE	ND	ND	ND	ND	ND	ND	ND	ND	90893	ND	ND
PYRENE	ND	ND	ND	ND	ND	ND	ND	ND	32556	ND	ND
TRIPROPYLENE GLYCOL METHYL ETHER	27706	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-METHYLNAPHTHALENE	ND	ND	ND	ND	ND	ND	ND	ND	1085409	ND	ND
4-CHLOROANILINE	10596	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = Non Detect NA = Not Analyzed

APPENDIX B

Summary Table of Samples Collected and Analyzed During

Gas Research Institute Sampling Program

GRI Samples Included in this Report

Associated Waste Report: Dehydration and Sweetening Wastes (U.S. EPA, January 2000) Page 1

Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
1	Processing/conditioning plant, booster station in San Juan Basin NM	1	Regeneration condensate from (solid, silica bead) dry bed dehydrator prior to mainline (regenerated with steam). pH 5.3	AB-02PC	06	See Sweetening and Dehydration, Section 2.2.4
		2	Carryover from DEA scrubber. pH 6.8		12	See Sweetening and Dehydration, Section 2.4.9
2	Associated gas (oil, oil/gas fields) processing/ conditioning plant (including NGLs), booster station in Delaware Basin NM	1	Engine jacket cooling water drainings from chromate system (400 ppm chromate). pH 7.5	AB-03PC	10	Not Included in Associated Waste Report. Not associated waste.
		2	Condensed stripping steam from lean oil stripping. pH 10.7		12	See Sweetening and Dehydration, Section 2.4.11
		3	Reflux accumulator carryover in acid gas removal system (MEA absorption). pH 6.3		17	See Sweetening and Dehydration, Section 2.4.9
3	Underground storage facility (including conditioning, processing) in Michigan Basin MI Methanol injected intermittently [Pipeline quality and casinghead gas]	1	Kettle bottoms from glycol reclaimer (EG injection). pH 6	AD-03US	03	See Sweetening and Dehydration, Section 2.2.6
		2	Spent oil from engines/compressors. pH 6		07	Not Included in Associated Waste Report. Not associated waste.
		3	Waste oil sock filters (cloth around plastic core) from engines/compressors. pH 6		08	Not Included in Associated Waste Report. Not associated waste.
		4	Spent glycol from dehydration unit (TEG contacting). Unit not in use at time of sampling. pH 7		16	See Sweetening and Dehydration, Section 2.2.7
		5	Waste sock filter (cloth around plastic core) from ethylene glycol regeneration unit (follows TEG contacting).		19	See Sweetening and Dehydration, Section 2.2.5
		6	Liquids from compressor room floor drains. pH 5		02	Not Included in Associated Waste Report. Not associated waste.

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
4	Mainline compressor station in Michigan Basin MI	1	Used waste oil filter (sand-like in wire mesh in cloth bag) from compressors/turbines.	AE-01ML	02	Not Included in Associated Waste Report. Not associated waste.
		2	Used oil from compressors/turbines.		04	Not Included in Associated Waste Report. Not associated waste.
		3	Inlet gas scrubber liquid (pipeline cleaning waste).		07	Not included in Associated Waste Report. Not associated waste.
5	Processing/conditioning plant (sweetening, dehydration, Claus sulfur recovery) in Red Desert Basin WY Samples collected 3-5 weeks prior to sampling visit, stored in sealed plastic bags.	1	Used amine sock filters (string-wound cartridge filter) from MDEA sweetening unit (CO_2, H_2S)	AF-01PC	03	See Sweetening and Dehydration, Section 2.4.6
		2	Used activated carbon filters from MDEA sweetening unit		04	See Sweetening and Dehydration, Section 2.4.6
		3	Spent alumina catalysts from sulfur plant Claus unit		13	See Sweetening and Dehydration, Section 2.4.12
		4	Spent filters (cloth cartridge) from inlet gas separator		20	See Sweetening and Dehydration, Section 2.2.1
6	Processing/conditioning (of processed gas and NGLs) plant, compressor station in Kindt Basin WY	1	Sock filter (cloth media) from glycol regeneration unit	AF-02-PC	03	See Sweetening and Dehydration, Section 2.2.5
		2	Sock filter (cloth media) from engine/compressor lubricating system		11	Not Included in Associated Waste Report. Not associated waste.
7	Underground storage, compressor station in Denver Basin CO. Methanol and corrosion inhibitors used [Pipeline quality gas]	1	3-phase separator wastewater effluent (to evaporation pond). pH 7	AF-03US	02	Not Included in Associated Waste Report. Produced water not associated with dehydration process.
		2	Kettle bottoms from glycol reclaimer. pH 11		15	See Sweetening and Dehydration, Section 2.2.6

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
8	Underground storage, compressor station in Rodessa Fault Zone TX [Mainline storage]	1	Sock filter (cloth media) from glycol regeneration unit (TEG)	AG-01US	12	See Sweetening and Dehydration, Section 2.2.5
		2	Charcoal (carbon) filter from glycol regeneration unit (TEG)		19	See Sweetening and Dehydration, Section 2.2.5
		3	Regenerated condensate (dehydration water) from glycol regeneration unit		06	See Sweetening and Dehydration, Section 2.2.4
9	Underground storage, compressor station in Mississippi Arch IA methanol and corrosion inhibitor injected and/or batch fed [Pipeline quality gas]	1	Used gas filter (cloth wound around metal core) from horizontal inlet separator (formation 1)	AG-05US	10	See Sweetening and Dehydration, Section 2.2.1
		2	Sock filter (cloth and string wound around metal core) from methanol recovery system after dehydration (formation 3)		26	See Sweetening and Dehydration, Section 2.2.10
		3	Charcoal filter media from methanol recovery system (formation 3)		26	See Sweetening and Dehydration, Section 2.2.10
		4	Pigging solids (formation 3)		32	Not Included in Associated Waste Report. Separate associated waste category.
		5	Pigging liquids (formation 3). pH 6.0		31	Not Included in Associated Waste Report. Separate associated waste category.
10	Underground storage, compressor station in Appalachian Basin WV [Pipeline quality gas]	1	Oil/water separation pond sludge. Assumed produced water pond (report unclear). Facility is central treatment/disposal facility for surrounding areas	AI-01US	12	Not Included in Associated Waste Report. Produced water and miscellaneous pit wastes outside scope of this report.

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
11	Processing/conditioning plant in Appalachian Basin WV Molecular sieve samples taken 6/90, "archived" in sealed plastic bags and boxed until sampling visit in 9/90.	1	Spent molecular sieve from mol sieve dehydration towers	AI-02PC	08 +dupe	See Sweetening and Dehydration, Section 2.2.8
		2	Dehydration water from mol sieve regeneration knockout drum. pH 8.4		03 +dupe	See Sweetening and Dehydration, Section 2.2.4
		3	Spent mol sieve from drip gasoline dryers		31	See Sweetening and Dehydration, Section 2.2.3 and 2.4.11
		4	Spent mol sieve from isobutane sweetener		27 +dupe	See Sweetening and Dehydration, Section 2.4.11
12	Mainline compressor station, booster station in Appalachian Basin WV	1	Glycol and hydrocarbon liquids from glycol dehydrator skim tank (glycol contacting dehydration). pH neutral	AI-03ML	01	See Sweetening and Dehydration, Section 2.2.7
13	Underground storage, compressor station in Appalachian Basin PA [No information on gas quality]	1	Dehydration water from distillate tank used for storage of gasoline tank bottoms. pH 4.8	AI-04US	02 +dupe	Not Included in Associated Waste Report. Not associated waste. See discussion in Sweetening and Dehydration, Section 1.4
		2	Oil/water spill from floor drain sumps in engine buildings. pH neutral		10	Not Included in Associated Waste Report. Not associated waste.
14	Underground storage, compressor station in Appalachian Basin PA [Pipeline quality and wet gas]	1	Glycol/water (55%/45%) from engine cooling system (and duplicate). pH $>$ 10	AI-06US	17 +dupe	Not Included in Associated Waste Report. Not associated waste.
		2	Oily sludge from "forced evaporation water/waste pond"		12	Not Included in Associated Waste Report. Miscellaneous pit wastes outside scope of report.

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
15	Processing/conditioning plant (and NGL recovery) in Appalachian Basin WV. Sample 1 collected and bagged 5 days prior to sampling visit. Sample 2 collected earlier in day and stored in open air.	1	Composited spent molecular sieve packing material from two dehydration towers	AJ-03PC	11	See Sweetening and Dehydration, Section 2.2.8
		2	Used sock filter (coated with 1/8 inch of carbon fines) from lean oil absorption unit		12	See Sweetening and Dehydration, Section 2.4.11
16	Processing/conditioning plant in Appalachian Basin WV. (CO_2 sold off-site.) Gas filter collected and wrapped in plastic 13 days prior to sampling visit Methanol and corrosion inhibitors used	1	Used gas filter (outer cloth wrap, inner paper wrap, metal core) from inlet filter separator.	AJ-04PC	04	See Sweetening and Dehydration, Section 2.2.1
		2	Kettle bottoms from mobile glycol regeneration unit (spent glycol comes from trucks/drums and from TEG contacting unit used for CO_2 stream)		11	See Sweetening and Dehydration, Section 2.2.6
17	Processing/conditioning plant (for offshore gas) in South Louisiana Salt Basin LA	1	Sock filter (cloth) from TEG contacting dehydration unit	AL-02PC	04	See Sweetening and Dehydration, Section 2.2.5
		2	Charcoal (carbon) filter (in perforated metal canister) from TEG contacting dehydration unit		05	See Sweetening and Dehydration, Section 2.2.5
		3	Regeneration condensate (dehydration water) from glycol regeneration unit (TEG). pH 6.1		06	See Sweetening and Dehydration, Section 2.2.4

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
18	Compressor station (for storage field and purchased gas) in Michigan Basin MI [Purchased and mainline gas]	1	Waste oil from main plant compressors	AM-01ML	06	Not Included in Associated Waste Report. Not associated waste.
		2	Waste oil from BTU plant compressors		07	Not Included in Associated Waste Report. Not associated waste.
		3	Used oil filter (paper) from main plant compressor		10	Not Included in Associated Waste Report. Not associated waste.
		4	Used oil filter (paper) from BTU plant compressors		12	Not Included in Associated Waste Report. Not associated waste.
19	Underground storage, compressor station in Los Angeles Basin CA [Pipeline quality gas]	1	Sludge from central knockout tank (sump) of brine treatment system. Sour "flash" gas recovered from system, said to be from anaerobic bacteria.	AN-01US	09	See Tank Bottoms and Oily Debris Chapter 2
20	Underground storage, compressor station in Santa Barbara/Ventura Basin CA [No information on gas quality]	1	Engine room washdown water from sump adjacent to compressor room. pH neutral	AN-02US	05	Not Included in Associated Waste Report. Not associated waste.
		2	Waste glycol from TEG contactors taken from storage tank. pH neutral		07	See Sweetening and Dehydration, Section 2.2.7
		3	Sludge bottoms from produced water storage tanks. Had been pumped to roll-off box 5 days prior to sample collection		10	See Tank Bottoms and Oily Debris Chapter 2

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Appendix B: Samples Collected and Analyzed During Gas Research Institute Sampling Program

Facility	Plant	Number	Samples	Stream code		Status of Sample in Associated Waste Report
				Facility number	Sample number	
21	Processing/conditioning plant in Mississippi Salt Basin AL	1	Used filter (corrugated paper media) from DGA contacting tower (CO_2 and H_2S removal). Some carbon fines.	AW-01PC	09	See Sweetening and Dehydration, Section 2.4.6
	Corrosion inhibitors added	2	Used oil filter (corrugated cardboard in metal exterior) from inlet gas compressor		13	Not Included in Associated Waste Report. Not associated waste.
22	Processing/conditioning plant in Central Platform Basin TX	1	Spent TEG from TEG contacting dehydration unit (in conjunction with DGA unit, all in Nitrogen Rejection Facility). pH 11.1	AX-01PC	01	See Sweetening and Dehydration, Section 2.2.7
		2	TEG reboiler condensate. pH 8.7		02	See Sweetening and Dehydration, Section 2.2.4
		3	Sludge from lined evaporation pit used for miscellaneous process waters		03	Not Included in Associated Waste Report. Miscellaneous pit wastes outside scope of report.
23	Processing/conditioning plant in East Texas Salt Basin TX	1	Sock filter from amine sweetening unit (DEA)	BB-02PL	01	See Sweetening and Dehydration, Section 2.4.6
	Sample 1 collected 2 days prior to sampling visit, stored in plastic bags	2	Charcoal (carbon) filter media from amine sweetening unit (DEA)		02	See Sweetening and Dehydration, Section 2.4.6

SOURCE: ENSR Consulting and Engineering. 1993 (May). *Sampling and Analysis of Wastes Generated from Natural Gas Industry Operations--Topical Report* . Prepared for Gas Research Institute under contract 5091-253-2160