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This report is a compilation and discussion of the best available information regarding the use, physical and chemical properties, environmental regulations, subsurface transport and fate, and toxicological characteristics relevant to alkanolamines and glycols used in natural gas sweetening and dehydration operations. The wastes generated by these operations and the management of those wastes are also described, and their regulation by the appropriate American and Canadian agencies. The objective of this report was to provide information such that the sources of the waste streams and the routes by which they may be exposed to the subsurface environment could be adequately evaluated by gas industry personnel. The physical and chemical properties relevant to the environmental implications of the selected compounds, particularly those affecting their subsurface transport and fate, are described. The attenuation mechanisms that control the fate of the selected compounds in the subsurface are discussed, with an emphasis on biodegradation. The known toxicological characteristics of the selected alkanolamines and glycols are presented. The basic data, information, and insights that were accumulated are synthesized to provide recommendations for further research regarding the subsurface transport and fate of the compounds of interest.

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RESEARCH SUMMARY

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Objective	To provide background information regarding the use, physical and chemical properties, environmental regulations, subsurface transport and fate, and toxicological characteristics relevant to alkanolamines and glycols used in natural gas sweetening and dehydration operations.
Technical Perspective	Alkanolamines are commonly used by the gas industry to remove acid gases (such H_2S, COS, and CO_2) from the natural gas stream. Likewise, glycols are commonly used for dehydration of the natural gas stream. These operations may result in the production of waste streams that are currently regulated or may be regulated in the foreseeable future under federal or state regulations in the United States and under federal or provincial regulations in Canada. One result is that industry personnel are increasingly faced with assessing the environmental implications associated with alkanolamines and glycols. To provide input to aid the gas industry in making reasonable assessments in this regard, activities were undertaken that resulted in the identification, review, and summary of the currently available data and other information related to the use, physical and chemical properties, environmental regulations, subsurface transport and fate, and toxicological characteristics of selected alkanolamines and glycols.
Results	The uses of selected alkanolamines in acid gas removal units and selected glycols in gas dehydration units are described. The wastes generated by these operations and the management of those wastes are also described, as are their regulation by the appropriate American and Canadian regulatory agencies. The purpose of these descriptions is to provide an informational context in which to evaluate waste stream sources and the routes by which they may be exposed to the subsurface environment. The physical and chemical properties relevant to the environmental implications of the selected compounds, particularly those relevant

to their subsurface transport and fate, are described. The attenuation mechanisms that control the fate of the selected compounds in the subsurface are discussed. Particular emphasis is placed on biodegradation, which the literature suggests is the primary attenuation mechanism controlling the transport and fate of both alkanolamines and glycols. The known toxicological characteristics of the selected alkanolamines and glycols are presented. Finally, the basic data, information, and insights that were accumulated are synthesized to provide recommendations for further research regarding the subsurface transport and fate of the compounds of interest.

Technical Approach

Environment Canada's National Hydrology Research Institute (NHRI) initiated a project to compile and review basic information on the subsurface transport and fate of alkanolamines and glycols used by the gas industry. Previous and concurrent GRI-funded research efforts provided much of that information, and eventually GRI became a joint sponsor of the project. To compile the necessary information, manual and computer-based literature searches were conducted. Discussions were held with other researchers and gas industry personnel familiar with the operational and waste management aspects of natural gas sweetening and dehydration operations. Regulatory personnel were also contacted to obtain information on the regulations relevant to the introduction of alkanolamines and glycols to the subsurface environment.

To provide a context within which to consider the collected data and information regarding the subsurface transport and fate of the selected compounds, discussions of the following topics were documented: 1) the use of alkanolamines and glycols by the gas industry, 2) their physical and chemical characteristics, 3) the generation and management of wastes associated with gas sweetening and dehydration, and 4) the framework within which those wastes are regulated at the relevant federal, state, and provincial levels. Available information pertaining to the subsurface transport and fate of the selected alkanolamines and glycols was also gathered, with an emphasis on the biodegradation of those compounds as the primary attenuation mechanism. These data and information provided the basis for qualitative generalizations regarding the subsurface transport and fate of the selected alkanolamines and glycols.

The literature search included collecting available data on the toxicological characteristics of the alkanolamines and glycols of interest. These data provide basic information regarding the potential health risks associated with the commonly used alkanolamines and glycols.

Finally, recommendations for further research were made based on gaps in the available data and information. Qualitative generalizations regarding the subsurface behavior and fate of the selected chemicals also provided guidance in forming the recommendations.

Project Implications

This document brings together, for the first time, basic background information and data for two classes of chemicals commonly used in the processing of natural gas. This background information has been collected and presented to provide a framework for identifying subsurface environmental issues associated with natural gas sweetening and dehydration operations. While a great deal of research remains to be done on the subsurface transport and fate of the alkanolamines and glycols commonly used by the gas industry, the information and data presented in this document can lead to useful insights into the environmental implications of those substances.

GRI Project Manager
James M. Evans

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GENERAL ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AFIT	Air Force Institute of Toxicology
AGR	acid gas removal
API	American Petroleum Institute
atm	atmosphere
BOD	biochemical oxygen demand
CCME	Canadian Council of Ministers of the Environment
CEQC	Canadian Environmental Quality Criteria
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CFR	Code of Federal Regulations
cm	centimeter
CMOS	completely miscible organic solvents
COD	chemical oxygen demand
COGD	Department of Conservation, Oil & Gas Division
cP	centipoise
CWA	Clean Water Act
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
E&P	exploration and production
EC	effective concentration
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ERCB	Energy Resources Conservation Board
g	gram
GC–MS	gas chromatography–mass spectrometry
GRI	Gas Research Institute
h	hour
H or H_c	Henry's law constant
HOC	hydrophobic organic chemicals
IEC	ion-exclusion chromatography
K_b	basicity constant
K_d	distribution coefficient
kg	kilogram
K_{ow}	octanol–water partition coefficient
K_{oc}	organic carbon–water partition coefficient
L	liter
LADEQ	Louisiana Department of Environmental Quality
LADOT	Louisiana Department of Transportation
LC	lethal concentration
LD	lethal dose
LOAEL	lowest-observed-adverse-effect level
m	meter
Mcf	thousand cubic feet
Mscf	thousand standard cubic feet

MCL	maximum contaminant level
mg	milligram
mm Hg	millimeters of mercury
MMscfd	million standard cubic feet per day
MOGCC	Montana Oil and Gas Conservation Commission
mol	mole
NAP	National Academy Press
NHRI	National Hydrology Research Institute
NOAEL	no-observed-adverse-effect level
NPDES	National Pollutant Discharge Elimination System
OCC	Oklahoma Corporation Commission
OMEE	Ontario Ministry of Environment and Energy
PMOS	partially miscible organic solvents
ppm	parts per million
psia	pounds per square inch absolute
RCRA	Resource Conservation and Recovery Act
SDWA	Safe Drinking Water Act
sec	second
tcf	trillion cubic feet
ThOD	theoretical oxygen demand
TIE	toxicity identification evaluation
TNRCC	Texas Natural Resources Conservation Commission
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TRRC	Texas Railroad Commission
TCLP	toxicity characteristic leaching procedure
μg	microgram
UIC	underground injection control
WQG	Water Quality Guidelines

CHEMICAL ACRONYMS

AEEA	amine ethyl ethanolamine
BHEAE	bis-(hydroxyethylaminoethyl)ether
BHEED	N,N'-bis-(hydroxyethyl)ethylenediamine
BHEI	N,N'-bis-(hydroxyethyl)imidazolidone
BHEP	N,N'-bis-2-(hydroxyethyl) piperazine
BHG	N,N'-bis-(hydroxyethyl)glycine
BHU	N,N'-bis-(2-hydroxyethyl)urea
BTEX	benzene, toluene, ethylbenzene, xylenes
CO_2	carbon dioxide
COS	carbonyl sulfide
CS_2	carbon disulfide
DEA	diethanolamine
DEAE	2-diethylaminoethanol
DEG	diethylene glycol

DEP	diethanolpiperazine
DGA	diethylene glycolamine
DIPA	diisopropanolamine
DMAE	2-(dimethylamino)-ethanol
DMP	1,4-dimethylpiperazine
EG	monoethylene glycol
EO	ethylene oxide
FORMYDEA (II)	N-formyldiethanolamine
H_2CO_3	carbonic acid
H_2O_2	hydrogen peroxide
H_2S	hydrogen sulfide
HCO_3^-	bicarbonate
HEED	N-(hydroxyethyl)-1,2-ethylenediamine
HEI	N-(hydroxyethyl)imidazolidone
HEM	N-(2-hydroxyethyl)ethylenimine
HEO	N-(hydroxyethyl)oxazolidone
HEP	N-(2-hydroxyethyl) piperazine
HMP	N-(hydroxyethyl)methyl piperazine
MDEA	methyldiethanolamine
MEA	monoethanolamine
NDEA	nitrosodiethanolamine
NH_3	ammonia
NO_2^-	nitrite
NO_3^-	nitrate
OX	2-oxazolidinone
O_2	oxygen
RSH	mercaptans
TCA	tricarboxylic acid
TREG	tetraethylene glycol
TEA	triethanolamine
TEG	triethylene glycol
TEHEED	N,N,N',N'-tetra-(hydroxyethyl)-ethylenediamine
THEED	N,N,N'-tris(hydroxyethyl)-ethylenediamine
TMA	trimethylamine

EXECUTIVE SUMMARY

This report includes an overview of the use of alkanolamines and glycols in the processing of natural gas. The alkanolamines are used for the removal of acid gases, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon dioxide (CO_2) from the natural gas stream. The acid gases must be removed or reduced to low concentrations because of their poisonous and corrosive characteristics and to meet interstate and international transport pipeline specifications. The alkanolamines that are typically used by the gas industry for this purpose include monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Triethanolamine (TEA), diethylene glycolamine (DGA), and diisopropanolamine (DIPA) are also used in acid gas removal (AGR) processes, though not as frequently. Glycols are used in the dehydration of a natural gas stream in order to prevent formation of gas hydrates during the transmission of natural gas. The most common glycols used for gas dehydration are triethylene glycol (TEG) and diethylene glycol (DEG), although monoethylene glycol (EG), also known as ethylene glycol, and tetraethylene glycol (TREG) are also occasionally used for dehydration purposes.

The physical and chemical characteristics of the alkanolamines and glycols that relate to their use in natural gas processing/conditioning are discussed in detail. The effects of the chemical and physical characteristics on the effectiveness of the gas industry alkanolamines and glycols under a variety of conditions are also examined.

Other compounds produced during the AGR and dehydration processes are described. These compounds are formed by the degradation of the alkanolamines or glycols, or their reactions with other chemicals, during the AGR or dehydration process. Very little is known about the physicochemical properties and toxicity of many of these compounds, although there is concern that they may be problematic in the subsurface environment. The degradation of alkanolamines and glycols that occurs in the subsurface environment and the compounds produced by that degradation are also discussed. Excessive concentrations of ammonia, nitrite, and nitrate from the degradation of alkanolamines and elevated biochemical oxygen demand levels from the degradation of glycols are other examples of how releases of gas industry alkanolamines and glycols can affect the subsurface and thereby indirectly come under regulation.

The wastes associated with the AGR and dehydration processes are described, with a focus on those wastes that may be released to the subsurface environment. These wastes include spent alkanolamines and glycols, sludges, and system filters. Other components of these wastes besides the alkanolamines, glycols, and their degradation/reaction products include benzene, petroleum hydrocarbons, and trace metals. Benzene can be found at especially high concentrations, particularly in spent glycols and glycol filters. The most common sources of subsurface contamination by alkanolamines and glycols are surface process waste retention pits. Leaks and spills can also release significant volumes of waste to the environment. Landfills are typically used for the disposal of filters and can also be a source of alkanolamine or glycol contamination in the subsurface. Injection wells are another technique used for the disposal of alkanolamine and glycol waste fluids.

The regulatory aspect of the gas processing/conditioning alkanolamines and glycols in both the United States and Canada are discussed at federal, state, and provincial levels. The chemical, physical, and toxicological characteristics of the substances of interest are reviewed in detail. The transport and fate of alkanolamines and glycols are discussed, with a focus on their physicochemical characteristics that relate to subsurface behavior and the attenuation mechanisms that control contaminant persistence and transport. Biodegradation is the primary attenuation mechanism affecting the transport and fate of alkanolamines and glycols. The discussion of transport and fate includes reviews of field and laboratory studies related to the behavior of glycols in the environment. No field or laboratory studies on the behavior of alkanolamines, other than their biodegradability, were available.

1.0 INTRODUCTION

In 1994, the Energy & Environmental Research Center (EERC), with the support of Environment Canada's National Hydrology Research Institute (NHRI), Gas Research Institute (GRI), and the U.S. Department of Energy (DOE), initiated a project to review and compile available basic information of use to the natural gas industry in evaluating and subsequently addressing subsurface contamination related to selected chemicals used in the processing of natural gas. The focus of this study is on alkanolamines used to remove acid gases from "sour" natural gas and glycols used in the dehydration of natural gas.

The use of these compounds for gas conditioning/processing is widespread in both the United States and Canada. Acid gas removal (AGR) units are found at natural gas-processing and conditioning plants and at underground gas storage facilities. At least 394 gas-sweetening facilities exist in the United States (Tannehill and Galvin, 1993) that use amine-based AGR units, and at least 90 gas-sweetening plants exist in Canada that use alkanolamines (Oilweek, 1994). There are as many as 40,000 glycol-based gas dehydrator units in the United States (Graham and others, 1994) and thousands more in Canada. The widespread use of alkanolamines and glycols has resulted in their inadvertent introduction into the subsurface through spills and waste management activities. The potential environmental impact of their presence in the subsurface has become the subject of growing concern. Little research has been done on these issues, and therefore, this effort has been undertaken to gather available research results and basic data that may aid in predicting the behavior of these compounds in the subsurface, their ultimate fate, and the risk they may present, all of which are useful to the gas industry in addressing potential subsurface contamination issues.

Chemical compounds produced as by-products of the gas-sweetening process, which are referred to in this document as reaction products, are also discussed, though in far less detail than the alkanolamines. Preliminary work by researchers in Canada and the United States indicate that the reaction products may be problematic in the subsurface environment. Unfortunately, there are currently very few data on the physicochemical properties of these reaction products, making their behavior in the subsurface difficult to predict. Work is currently being conducted by NHRI and the EERC to characterize the physicochemical properties of the alkanolamine reaction products. Other workers in Canada are examining the potential toxicity of these compounds.

The information and data presented in this report were gathered from an extensive review of the relevant literature pertaining to the chemicals of interest, as well as from discussions with scientists, engineers, and regulatory officials who have worked with, or are otherwise familiar with, alkanolamines and glycols in the context addressed here.

Relevant physical and chemical data for the primary compounds discussed in the report are included in Appendix A.

2.0 OBJECTIVES

The purpose of this report is to provide background information on alkanolamines and glycols used in the processing of natural gas in an effort to aid the natural gas industry in addressing potential subsurface contamination issues related to these chemicals. Specifically, this information will focus on the following topics as they relate to alkanolamines and glycols and their role as subsurface contaminants:

- Use by the gas industry
- Physical and chemical properties, including thermal and chemical reaction products and biological degradation products
- Regulations and guidelines in the United States and Canada, with a special focus on important gas-producing states and provinces
- Subsurface transport and fate (with emphasis on biodegradation)
- Toxicological characteristics

This report will also discuss the environmental implications of the predicted and observed behavior of the alkanolamines, glycols, and their associated wastes. The assessment will include recommendations for the direction of future studies on these substances.

3.0 ALKANOLAMINES AND GLYCOLS IN THE GAS INDUSTRY

3.1 Alkanolamines

The term "sour" gas refers to natural gas that contains acid gases, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon dioxide (CO_2). Sour gas is a significant portion of the natural gas produced in both the United States and Canada. About 13% of the natural gas produced in the United States is sour enough to require treatment (Prouty, 1994). In Canada, about 40% of the annual net production is sour. Alberta produces approximately 83% of the total Canadian gas (Greenaway, 1995) and is the largest producer of sour gas in North America.

The transportation, distribution, and utilization of natural gas require very low concentrations of many impurities, acid gases, and organosulfur compounds. These requirements have been adopted because of the corrosive nature of the acid gases, the toxicity associated with H_2S, and because sulfur oxides, which are acid rain precursors, are formed during combustion of H_2S (Katz and Lee, 1990).

The impurity limit specifications are met largely through the use of alkanolamine-based AGR or "sweetening" processes. These processes are usually based on absorption/stripping technologies and require solutions that have a high capacity for absorbing the acid gases through chemical reaction while exerting a very low equilibrium vapor pressure. The phase reactions between the solutions and the acid gases are usually reversible at a higher temperature to permit regeneration and reuse of the original solution. At least 394 gas-sweetening facilities exist in the United States (Tannehill and Galvin, 1993) that use amine-based AGR units, and at least 90 gas-sweetening plants exist in Canada that use alkanolamines (Oilweek, 1994).

The most commonly used natural gas-sweetening solutions are alkanolamines, specifically monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA). Diisopropanolamine (DIPA) and diethylene glycolamine (DGA) are also used, although less frequently. In addition to removing the above-mentioned acid gases, some of these alkanolamines (i.e., DIPA, DGA) can also be used to remove other impurities, such as carbon disulfide (CS_2), mercaptans (RSH), and thiophenes, to meet product gas specification for total sulfur.

3.1.1 *Physical and Chemical Characteristics*

Alkanolamines can be considered organic derivatives of ammonia and are classified as primary, secondary, or tertiary alkanolamines. The classifications are based on the number of substituent groups attached to the nitrogen atom.

The molecular formula for ammonia is NH_3. Substitution of an organic group, R, for one of the hydrogen atoms gives a primary amine, represented as RNH_2. Similarly, the substitution of two and three hydrogen atoms by organic radicals results in secondary (RNHR) and tertiary (RNRR) alkanolamines, respectively (Solomons and Graham, 1988). Table 1 provides some general physical and chemical properties of alkanolamines commonly used by the gas industry. Depictions of the chemical structures, as well as a variety of physicochemical data with transport and fate implications, can be found in Appendix A for each of the alkanolamines of interest.

TABLE 1

General Physical and Chemical Properties for Selected Alkanolamines[1]

	MEA	DEA	TEA	MDEA
Boiling Point, °F/°C	340/171	514/268	671/355	464/240
Freezing Point, °F/°C	50/10	82/28	71/21	-6/-21.0
Flash Point, °F/°C	210/94	325/163	407/208	270/132
Specific Gravity (@ 25/4°C)	1.01	1.09 @ 30/4°C	1.12	1.05 @ 30/4°C
Vapor Pressure, mm Hg (@ 20°C)	<1	<0.01	<0.01	<0.01
Aqueous Solubility	Completely miscible	Completely miscible	Completely miscible	Completely miscible
Color	Colorless	Colorless	White to pale yellow	White to pale yellow
Odor	Ammoniacal	Slightly ammoniacal	Slightly ammoniacal	Slightly ammoniacal

[1] Dow Chemical Company, 1991.

Alkanolamines are considered weakly to strongly basic, stronger than water, but weaker than hydroxide ions, alkoxide ions, and carbanions. Of the amines used for acid gas removal, the primary alkanolamines (MEA) are stronger bases than secondary (DEA) and tertiary alkanolamines (MDEA and TEA), and are therefore more reactive toward acid gases, forming more stable salts. The strength of the amine–salt bonds is dependent on the heats of reaction between the acid gases and the alkanolamines. The weakly basic alkanolamines react with acid gases, forming salts that are readily decomposed by thermal regeneration. If a stronger acid gas reacts with the alkanolamines, heat-stable salts can form (Skinner and others, 1995).

3.1.2 *Acid Gas Removal Processes*

Several major steps are involved in the removal of acid gases from the natural gas stream by means of absorption/stripping in an amine-based sweetening unit. These steps include prescrubbing and acid gas absorption, solution filtration and heat exchange, and solution regeneration and reclamation. Figure 1 is a schematic diagram of a typical amine-based gas-sweetening unit.

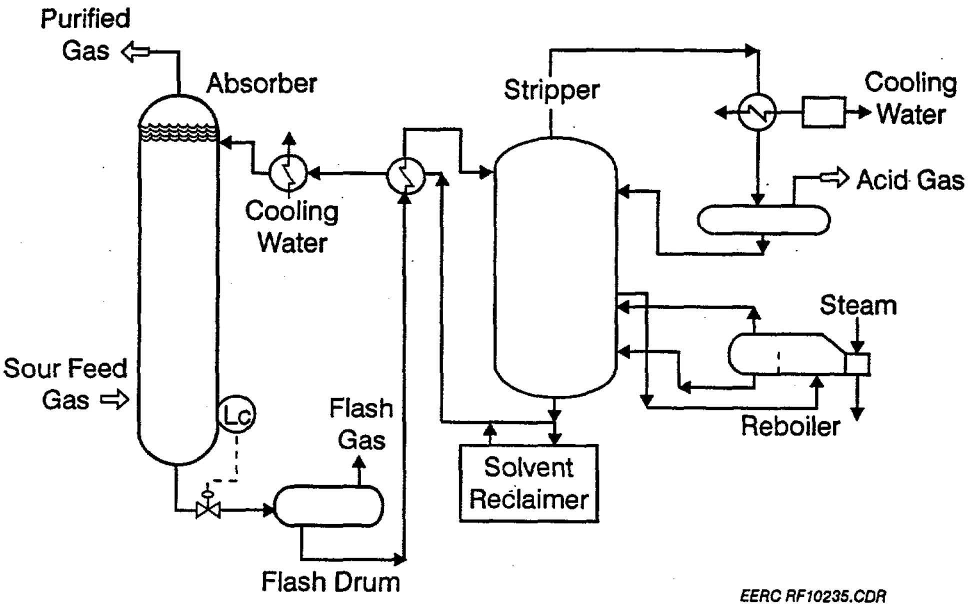


Figure 1. Amine-based gas-sweetening unit.

Prescrubbing of the sour gas takes place in the inlet scrubber, where entrained hydrocarbons, solids, brines, drilling fluids, and other foreign materials are removed to prevent process operation problems, such as foaming. The prescrubbed gas then enters the bottom of the absorber unit, and lean aqueous amine solution is pumped to the top of the absorber. The typical absorber unit is composed of a vertical, high-pressure column containing 18–30 trays. The sour gas rises from the bottom of the absorber, while the amine solution falls from the top of the unit down across the trays. As the sour gas contacts the amine solution in countercurrent flow, the acid gases are chemically absorbed by the lean amine solution. The amount of acid gas absorbed by the amine solution depends on the type of amine used and the operating conditions (Skinner and others, 1995).

The sweetened gas exits the top of the absorber through an outlet scrubber that recovers the amine solution carried over or vaporized from the absorber unit. Additional unit operations, such as a mist eliminator, may be added to prevent amines from passing through the downstream process equipment. The recovered amine, also referred to as "rich" amine because of its high acid gas content, is sent to a flash tank and the sweetened gas is sent either to the next downstream treatment unit, such as a dehydrator, or into the pipeline (Skinner and others, 1995).

Because the reactions between the amines and acid gas components generate heat, the temperature of the rich amine solution leaving the absorber is greater than that of the lean amine solution. A MEA solution that enters the top of an absorber at 110°F will typically exit from the bottom of the absorber at approximately 150°F after absorbing 0.3 mol acid gas/mol MEA. The rich amine solution flows from the bottom of the absorber to a series of unit operations designed to regenerate and reclaim the amine solution for reuse in the absorber unit (Skinner and others, 1995).

If the sour gas contains high concentrations of heavy hydrocarbons (butane and higher), a flash tank is sometimes used as the first regeneration/reclamation step in order to minimize foaming by removing most of the condensed or absorbed hydrocarbons from the amine solution. The flash gas is then treated to remove H_2S before being used as plant fuel (Skinner and others, 1995).

The amine solution is then filtered to minimize operating problems caused by suspended solids and other contaminants present in the stream. In most AGR units, a mechanical filter is used to remove the suspended solids, while activated-carbon bed filters are used to remove the dissolved and condensed organic components. Although the filters remove the suspended material, they cannot remove other contaminants such as heat-stable salts, degradation products, soluble components, or hydrocarbons. The activated carbon filters are used to remove the hydrocarbons and high-molecular-weight degradation compounds (Skinner and others, 1995).

The rich amine solution is then preheated to about 200°F (93°C) by heat exchange with the hot, lean amine from the regenerator. The heat exchanger is usually operated at elevated pressures (100–200 psia) to prevent acid gases from vaporizing. The solution is then sent to the regenerator unit where the acid gases are steam-stripped from the amine solution at temperatures of approximately 240°–260°F (116°–127°C). A reboiler is used to vaporize part of the lean amine solution and generate steam for stripping. Because of the buildup of dissolved and suspended solids in the still bottoms, fouling and corrosion problems can occur in the reboiler (Skinner and others, 1995).

The acid gases, along with the steam, exit the top of the stripper and pass through a reflux condenser where most of the steam is condensed, cooled, and separated from the acid gases. The acid gases are either sent through a sulfur recovery unit or are emitted. The lean amine solution is pumped from the bottom of the regenerator to a surge tank, through the rich/lean amine exchanger, then through a solution-cooling unit before being used again in the absorber (Skinner and others, 1995).

Problems associated with the operation of amine-based AGR units include foaming and corrosion. Foaming is caused by the presence of impurities in the amine solution. Foam-inducing impurities include condensed hydrocarbons, suspended solids, foreign materials, and amine degradation products. Corrosion is generally thought to occur when acid gases react with water to form acids (Blanc and others, 1982), although some of the products of the oxidative degradation of the amines are also thought to be contributors (Skinner and others, 1995). Corrosion usually occurs in areas of high temperature and extremely high flow turbulence and stress, conditions common in amine solution heat exchangers, strippers, and reboilers. The impurities formed from the corrosion are usually responsible for foaming, and this foam in turn causes poor contact between the gas and amine solution, thereby decreasing the efficiency of the acid gas removal process (Congram, 1979). To combat the foaming and corrosion problems, antifoaming agents and corrosion inhibitors are sometimes added to the process. Most antifoamers are either silicone-based or are long-chain alcohols, while inorganic metals are often used as corrosion inhibitors (Pauley, 1991).

3.1.3 *Alkanolamines Used for AGR*

3.1.3.1 MEA

MEA has been one of the most commonly used solvents for treating gas streams having low-to-medium concentrations of H_2S and CO_2, in the absence of COS, CS_2, or O_2. The reasons for its widespread use include its 1) high reactivity with acid gases as a result of its strong basicity; 2) relatively low cost; 3) chemical stability, which increases its resistance to thermal degradation; 4) easy reclamation; 5) production of acid gas with a low hydrocarbon content; 6) high acid gas carrying capacity because of its low molecular weight, which results in a lower process circulation rate; 7) use allows for a lower plant investment, compared with other alkanolamine-based processes (Goar and Arrington, 1979); and 8) enabling of gases to be treated at much lower pressures than any of the other alkanolamines (Batt and others, 1980). Typical concentrations for MEA usage fall in the range of 15–20 wt%; however, concentrations as high as 35 wt% may be required under conditions of high acid gas content (Gagliardi and others, 1989).

Disadvantages of MEA include 1) its irreversible degradation reactions with COS, CS_2, and O_2 in the gas stream; 2) its relatively higher vapor pressure, which results in higher vaporization losses than with any other amine-based process; 3) its ineffectiveness in removing mercaptans; 4) its nonselectivity for H_2S in the presence of CO_2; 5) its relatively high corrosivity; and 6) the relatively high energy requirements for its regeneration as a result of the stability of its reaction products (Batt and others, 1980).

3.1.3.2 DEA

DEA is also used frequently for removing acid gases from natural gas streams. It is most commonly used under conditions of high pressure on streams with high concentrations of acid gases and in the presence of COS and CS_2. Typical concentrations for DEA usage fall in the range of 20–40 wt% (Skinner and others, 1994).

Advantages of DEA include its resistance to degradation by COS and CO_2; relatively low volatility which results in lower vaporization losses; and relatively lower energy requirements for regeneration because of the relative instability of its reaction products (Skinner and others, 1995).

Among the disadvantages of DEA are its relatively low reactivity, requirement of higher solvent circulation rates, and higher solvent cost compared to MEA (Goar and Arrington, 1979). It also tends to be nonselective with respect to CO_2 and H_2S, although with limited contact time it will provide some selectivity for those gases (Pearce, 1995).

3.1.3.3 MDEA

MDEA was not commonly used by the natural gas industry until the 1970s because of its higher cost compared to other alkanolamines. However, because MDEA-based processes require less energy, MDEA gained attention during the energy crisis of the 1970s. Typical concentrations for MDEA usage fall in the 30–55 wt% range (Skinner and others, 1995).

The major advantage of the MDEA process over the MEA and DEA processes is the selectivity for H_2S in the presence of CO_2, thus making it more useful for gas streams characterized by a high CO_2:H_2S ratio (Goar and Arrington, 1979). Other advantages of using MDEA include 1) reduced energy requirements because of lower heats of reaction, the absence of CO_2 reaction products and lower circulation rates; 2) its high thermal stability; 3) its nonreactivity with COS and CS_2; 4) its low degradation potential; 5) low changeover requirements because of lower volatility and higher stability; and 6) fewer corrosion problems. The most pronounced disadvantage of using MDEA continues to be its high cost compared to MEA and DEA (Skinner and others, 1995).

3.1.3.4 TEA

TEA has been used to remove acid gases from natural gas streams, although not as frequently as the previously mentioned amines. Its use has generally been confined to bulk removal of CO_2, although it does have good H_2S selectivity (Pearce, 1995).

3.1.3.5 DIPA

DIPA has also been used in the gas sweetening process. DIPA exhibits H_2S selectivity (Goar and Arrington, 1979), has been used to remove COS (Pierce, 1995), and has been used as a primary component of the Sulfinol gas sweetening process licensed from Shell (Maddox, 1977).

3.1.3.6 DGA

DGA, a primary amine, may also be used to remove H_2S from gas streams. It has a relatively low vapor pressure and reacts in a similar manner to MEA (Perry, 1979).

Aqueous solutions of DGA are used in the range of 5–90 wt% DGA. DGA reacts with COS and CO_2 to form urea-type degradation products, which are thermally reversible at elevated temperatures and regenerator pressure. DGA treats gases more efficiently than MEA at higher CO_2-to-H_2S ratios, while operating at higher pressures (Batt and others, 1980). One of the disadvantages of using DGA is that it is usually more expensive than most of the commonly used alkanolamines (Perry, 1979).

3.1.4 *Reaction Products*

In AGR systems, alkanolamines can be involved in a variety of reactions that produce chemical species, which can have an adverse effect on the AGR unit and/or process and may have a role in alkanolamine-related subsurface contamination. Important reactions of this type, as discussed by Skinner and others (1995), include reactions with H_2S, thermal degradation reactions, and chemical degradation reactions. The products formed range from simple "breakdown" products (e.g., ammonia, water, and hydrogen gas) to complex organic compounds.

It can often take several months for concentrations of the products of the reactions of interest to reach significant levels; however, simply from a process standpoint, these products can cost the natural gas industry millions of dollars annually. At the same time, these products can be introduced into the subsurface environment along with the amines from which they are formed and may be an integral part of the "amine contamination problems" that the natural gas industry faces.

In addition to the costs associated with solvent loss, equipment loss cost can be attributed to the corrosive nature of some reaction products. These unwanted compounds may be caused by improper operating temperatures and pressures, inappropriate amine concentrations, and the presence of other acid gases and metal ions (Kennard and Meisen, 1985).

Table 2 provides a list of known alkanolamine reaction products as reported by Skinner and others (1995). This list is almost certainly not comprehensive, considering that reactions involving alkanolamines have not been well studied and alkanolamine-related reaction products can be difficult to identify because of their properties and their tendency to occur in complex chemical mixtures in gas industry settings. These products are difficult to detect and identify because they are usually large organic molecules. The analysis of alkanolamines is further complicated because they tend to have fairly low vapor pressures, decompose at elevated temperatures, and are highly polar. Although gas chromatography and mass spectroscopy have been used to identify certain reaction compounds (Kennard and Meisen, 1985), in general, little information is available concerning the physicochemical properties that relate to subsurface transport and fate. Basic chemical data for some of the reaction products most commonly reported in the literature are included in Appendix A.

TABLE 2

Alkanolamine Reaction Products[1]

Amine	Reaction Products[2]	Reaction
Alkanolamines	Dithiocarbamates, thioureas, thiosulfuric acid, heat-stable salts (i.e., thiosulfate compounds)	Oxidation
	Ammonia	Oxidation
MEA	DEA, pyridine, water, hydrogen, succinic aldehyde, diacetyl	Thermal, oxidation Thermal
	Formic acid, substituted amines, high-molecular-weight polymers	Oxidation
	BHEED, HEED, HEP, BHEI, HEI	CO_2
	OX, HEI, diethanol urea	COS
	Oxazolidone-2-thione	CS_2
DEA	Ammonia	Thermal, Oxidation
	Sulfite, sulfate, thiosulfate, thiocyanate, thiosulfuric acid, thiocyanic acid	Oxidation of DEA + H_2S
	Chloride, cyanide, formic acid, oxalic acid, acetic acid, propionic acid, FORMYDEA (II)	Oxidation
	HEO, THEED, DEP, HEP, BHEP, BHEED, BHEAE	CO_2
	MEA, CarboxyMEA, CarboxyDEA, BHEED, BHEP, HEI, HEO, THEED, CarboxyTHEED	COS
	Substituted dithiocarbamates, thiocarbamates	CS_2
MDEA	Ammonia, formic acid, oxalic acid, acetic acid, propionic acid	Oxidation
	EO, TMA, EG, DMAE, DMP, HMP, TEA, BHEP	CO_2

[1] Skinner and others, 1995.
[2] See Chemical Acronyms list for full chemical names.

3.1.4.1 Reactions with H_2S

Generally, alkanolamines react directly and rapidly with H_2S, forming amine sulfides and hydrosulfides. These reactions occur at a 1:1 molar ratio regardless of whether the amine is primary, secondary, or tertiary (Skinner and others, 1995).

Another mechanism describing the reaction of MEA, DEA, or MDEA with H_2S involves the formation of free sulfur that thermally reacts with alkanolamines in the presence of a strong oxidizer such as oxygen to form dithiocarbamates, thioureas, and other products. Pearce (1995) reports that free sulfur can also react with alkanolamines to form amine polysulfides.

3.1.4.2 Thermal Degradation Reactions

Exposure to excessively high temperatures can cause some alkanolamines to thermally decompose, forming degradation products and reducing process efficiency. The commonly used alkanolamines begin to show accelerated degradation at temperatures above 350°F, and DEA is the most susceptible to thermal degradation. The highest temperatures encountered in the sweetening process occur in the regenerator component of the AGR unit, where temperatures of 240°-260°F are typically sufficient to strip the acid gas from most alkanolamine solutions (Ballard, 1986). However, hot spots may form at a variety of points in the AGR unit where temperatures may exceed 350°F.

Although MEA is the most thermally stable of the gas-sweetening alkanolamines, it is the only one for which thermal degradation product information is available. Specifically, Skinner and others (1995) have indicated that each of four MEA thermal degradation pathways result in some combination of the following products: NH_3, DEA, pyridine, succinic aldehyde, diacetyl, water, and hydrogen gas.

3.1.4.3 Alkanolamine Reactions with Acid Gases

A wide variety of reactions can occur between the alkanolamines and acid gases. The following subsections focus on reactions whose products were most often discussed in the literature available for this report. The occurrence of these reactions is dependent on the alkanolamine used and the operating conditions of the AGR unit, and therefore the presence of the reaction products discussed in these subsections may vary greatly from unit to unit. Some of the reactions discussed below may make up only a small fraction of the overall amine/acid gas reaction, but it is possible that the products may accumulate to levels of concern in some units where operating conditions allow such reactions. A detailed description of the operating conditions under which such reactions may occur is beyond the scope of this paper and are thoroughly discussed in Skinner and others (1995).

Alkanolamines used by the gas industry, as previously noted, are bases that react with acid gases to form salts, the stability of which varies in response to the strength of the respective alkanolamines as bases. Primary alkanolamines (MEA) are stronger bases than secondary (DEA) and tertiary alkanolamines (MDEA and TEA); as a result, they are more reactive toward acid gases and form more thermally stable salts. These salts, such as thiosulfates, can have a negative effect on systems operation, such as neutralizing the amine, increasing the solution viscosity, and decreasing the selectivity of the amine (Skinner and others, 1995). They may also play a rôle in localized subsurface impact if introduced through spills or waste management activities.

3.1.4.4 Chemical Degradation Reactions

Reactions with Oxygen (Acidic)

Acidic reaction products are formed when alkanolamines react with either oxygen in the gas or with an acid stronger than H_2S or CO_2 in the presence of oxygen. The rate of reaction is dependent on concentration, temperature, and pressure. Pauley (1991) reports that primary and secondary amines are easily oxidized. Skinner and others (1995) report that evidence suggests tertiary amines do not usually react with COS or CS_2.

When an alkanolamine (MEA, DEA, or MDEA) reacts with oxygen, free sulfur may form from the H_2S in the gas. As discussed above, the reaction of the free sulfur with the alkanolamine will produce several compounds, including dithiocarbamates, thioureas, and thiosulfuric acid. The thiosulfuric acid will then form heat-stable salts.

MEA. Skinner and others (1995) report that acidic degradation products in the MEA solution have been found at levels that are an order of magnitude greater than those in the DEA and MDEA solutions. Acidic reaction products of MEA include formic acid, ammonia, substituted amines, and high-molecular-weight polymers. The most common heat-stable salt associated with MEA use is MEA thiosulfate (Skinner and others, 1995).

DEA. Acidic DEA reaction products include sulfite, sulfate, and thiosulfate ions, organic acids, and chloride, cyanide, and thiocyanate ions (Skinner and others, 1995). Organic acids reduce the capacity of the amine solution to absorb acid gas by forming heat-stable salts with the amines. If not controlled, the organic acids may also polymerize to form long-chain organic acids or fatty acids.

DEA/MDEA. Other DEA, as well as MDEA, reaction end products formed during oxidative reactions include carboxylic acids (i.e., formic, oxalic, acetic, and propionic), thiosulfuric acid, thiocyanic acids, and diethylene glycol. Further reactions with the compounds may result in other products, such as the formation of N-formyldiethanolamine (FORMYDEA [II]) via formic acid (Skinner and others, 1995).

Reactions with CO_2

The absorption reaction mechanism of CO_2 is dependent on the amine used in the treatment process. For primary and secondary alkanolamines, most of the absorption occurs through carbamate formation. Although it is generally accepted that tertiary amines do not form carbamates, it is thought that CO_2 reactions with tertiary amines occur through the formation of bicarbonates (Skinner and others, 1995).

MEA. When MEA reacts with CO_2, an irreversible reaction involving the intermediate formation of carbamate occurs, followed by formation of an irreversible reaction product, HEED

(N-[hydroxyethyl]-1,2-ethylenediamine) (Skinner and others, 1995). N,N'-bis-(hydroxyethyl)imidazolidone (BHEI) is another reaction product formed through hydration of N-(hydroxyethyl) oxazolidone (HEO), followed by double dehydration of a MEA molecule (Blanc and others, 1982).

DEA. Reaction products of DEA and CO_2, identified by gas chromatography and mass spectroscopy include HEO, N,N,N'-tris(hydroxyethyl)-ethylenediamine (THEED), N-(2-hydroxyethyl) piperazine (HEP), diethanolpiperazine (DEP), bis-(hydroxyethylaminoethyl)ether (BHEAE), and N,N'-bis-(hydroxyethyl)ethylenediamine (BHEED). HEO is formed during DEA reactions in aqueous solutions containing CO_2, through a general condensation reaction that may be reversed through hydrolysis (Kim and Sartori, 1984). This reaction may also produce an amine carbamate (Blanc and others, 1982). HEO further reacts with DEA, in a reversible, nucleophilic displacement reaction to form THEED. This reaction generally regenerates CO_2. THEED accumulates as the major component, reaching a maximum concentration, which is followed by a decline in concentration, at which time HEP begins to form (Kim and Sartori, 1984). The formation of DEP occurs through the internal dehydration of THEED. BHEAE is formed through dehydration of a hydroxyl group (OH^-) on a DEA molecule and a proton (H^+) of the OH^- of another DEA molecule. BHEED is formed through a dehydration reaction between DEA and MEA molecules. Analysis has shown that under certain treatment conditions the production of these basic DEA reaction products are proportional to the concentration of CO_2 dissolved in the solution (Blanc and others, 1982).

MDEA. MDEA has been found to react with CO_2, at elevated temperatures and CO_2 partial pressures, producing reaction products such as ethylene oxide (EO), trimethylamine (TMA), monoethylene glycol (EG), 2-(dimethylamino)-ethanol (DMAE), 1,4- dimethylpiperazine (DMP), N-(hydroxyethyl)methyl piperazine (HMP), TEA, and N,N'-bis-2-(hydroxyethyl) piperazine (BHEP) (Chakma and Meisen, 1989). It is important to note that the products reported by Chakma and Meisen (1989) are from reactions with a formulated MDEA as opposed to MDEA in its "pure" aqueous form.

TEA. The reaction of CO_2 with tertiary amines (TEA) results in the formation of bicarbonate (HCO_3^-) and/or carbonic acid (H_2CO_3).

Reactions with COS and CS_2

Skinner and others (1995) report that alkanolamine solutions are degraded by COS in a manner similar to that of CO_2. They also report that MEA and DEA react with CS_2, but MDEA does not.

MEA. The reaction between MEA and COS involves hydrolysis of the COS to H_2S and CO_2, forming other end products such as 2-oxazolidinone (OX), N-(hydroxyethyl)imidazolidone (HEI), and diethanol urea. Although reactions between MEA and CS_2 have been found to form oxazolidone-2-thione in a 1:1 molar ratio, these reactions occur at a very slow rate, reducing MEA losses. The primary products of MEA reactions with CS_2 are dithiocarbamates which decompose to form thiocarbamates, thermally stable salts (Skinner and others, 1995).

DEA. Reactions of DEA in the presence of COS have been shown to produce a number of products including MEA, carboxyMEA, carboxyDEA, BHEED, carboxyBHEED, BHEI, BHEP, HEI, HEO, THEED, and carboxyTHEED. The number and variety of the products suggest that the reactions are complex (Dawodu and Meisen, 1994). Reactions between DEA and CS_2, like their MEA counterparts, have been found to form substituted dithiocarbamates that decompose to form thiocarbamates (Skinner and others, 1995).

3.2 Glycols

Water in natural gas can cause serious operational problems in both the transmission and processing of the gas. The natural gas industry has found that dehydration ensures smooth operation of gas transmission lines, prevents formation of gas hydrates, and reduces corrosion. Three of the most commonly used dehydration methods include direct cooling, adsorption using solid desiccants, such as molecular sieves, silica gel, and bauxite, and absorption using desiccants such as glycols (Katz and Lee, 1990).

Under normal production conditions, natural gas is saturated with water in the vapor phase. This does not become a problem until the gas reaches its dew point and the water combines with gas molecules (methane, ethane, and propane) to form solid, crystalline-structured hydrates such as $CH_4 \cdot 7H_2O$, $C_2H_6 \cdot 8H_2O$, and $C_3H_8 \cdot 18H_2O$ (Manning and Wood, 1993a). Natural gas hydrates normally consist of hydrocarbons and water, although gases such as hydrogen sulfide, ammonia, carbon dioxide, acetylene, and bromine may also form hydrates (Pearce, 1982).

The formation of gas hydrates in pipelines will usually result in decreased throughput, frozen control valves, plugged orifices, and other operating problems that can result in the complete shutoff of gas flow. Hydrates are likely to form under the following conditions: at high pressure, in the presence of water, and at low temperatures (Pearce, 1982).

Water in natural gas can promote corrosion, especially in the presence of acid gases. When the water condenses on cooling in the pipeline, pipeline corrosion and erosion rates can be accelerated, increasing the pressure drop in the pipeline (Manning and Wood, 1993a).

The most common dehydration process used in the gas industry is the glycol absorption/stripping process. While the actual number of operating glycol units is unknown, it is estimated that as many as 40,000 units exist in the United States and about 100,000 exist worldwide (Grizzle, 1993). In the United States, 90%–95% of the units process less than 10 million standard cubic feet per day (mmscfd) of natural gas (Grizzle, 1993). No estimates were available on the total number of glycol dehydration units operating in Canada, but they are very commonly used in Canadian gas fields. The total volume of natural gas dehydrated in North America each year is approximately 17–18 trillion cubic feet (tcf) (Thompson and others, 1993). While no figures were available on percentage of gas dehydrated by glycol dehydrators, the literature search and discussions with gas industry personnel indicate that a large majority of the dehydration is done using glycol-based units.

Monoethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TREG), and blends of these glycol solutions have all been used in natural gas stream dehydration processes for decades. The earlier glycol dehydration units used DEG but were commonly characterized by the thermal decomposition of the DEG. Around 1950, TEG became the most commonly used glycol because its higher boiling point provided better water removal without being thermally decomposed (Pearce, 1982). EG and TREG are used in some specialized cases; however, TEG remains the most commonly used glycol in natural gas dehydration processes. It has been estimated that TEG is used in approximately 95% of glycol dehydration units (Thompson and others,. 1993).

3.2.1 *Physical and Chemical Characteristics*

Glycols are aliphatic organic compounds and are members of a group of chemicals referred to as the dihydric alcohols (diols). This group has the general formula $C_nH_{2n}(OH)_2$ and is characterized by the presence of two hydroxyl (OH^-) functional groups linked to methylene (CH_2) subunits. Ethylene glycols have the general formula $HO(C_2H_4O)_nH$, where n can be 1 (monoethylene), 2 (diethylene), 3 (triethylene), or 4 (tetraethylene). Table 3 provides some general physical and chemical properties of glycols commonly used by the gas industry. Depictions of the chemical structures, as well as a variety of physicochemical data with transport and fate implications, can be found in Appendix A for each of the glycols of interest.

Glycols are similar to water in that they are clear, colorless, odorless liquids. However, when compared to water, the glycols have a greater specific gravity and viscosity at all temperatures, a higher boiling point, and a lower freezing point. Glycols are completely water-soluble and can also act as solvents for some organic compounds, including most aromatic compounds. They are generally stable in air, under usual storage conditions; however, when heated, glycols tend to oxidize, forming products such as aldehydes and acids (Dow Chemical Company, 1992).

All glycols are hygroscopic; that is, they have the ability to take up water from the atmosphere, a characteristic that makes them useful in removing water from natural gas streams.

TABLE 3

General Physical and Chemical Properties for Selected Glycols[1]

	EG	DEG	TEG	TREG
Molecular Weight	62.1	106.1	150.2	194.2
Boiling Point @760 mm Hg, °F/°C	387.3/197.4	473.8/245.5	550.0/287.8	618.1/325.6
Freezing Point, °F/°C	7.9/-13.4	16.4/-8.7	19.0/-7.2	15.1/-9.4
Flash Point, °F/°C	247/119	281/138	325/163	400/204
Specific Gravity @ 25°C	1.110	1.111	1.120	1.123
Vapor Pressure, mm Hg @ 25°C	<0.1	<0.01	<0.01	<0.01
Aqueous Solubility	Completely miscible	Completely miscible	Completely miscible	Completely miscible
Color	Clear, colorless	Clear, colorless	Clear, colorless	Clear, colorless

[1] Dow Chemical Company, 1992.

The hygroscopic character of glycols is in direct proportion to the solution concentration. The water vapor will be absorbed by the glycol solution as long as the partial pressure of the water vapor in the natural gas exceeds the partial pressure of the water in the solution. Generally, the greater the molecular attraction between the glycol and the water, the lower the water vapor pressure of the solution and the greater the hygroscopicity of the solvent. Water is highly associated through hydrogen bonding, and glycols, having hydroxyl groups, form similar intramolecular associations with water. The glycols, therefore, have a high affinity for water, and the resulting aqueous glycol solutions reduce the water vapor pressure (Pearce, 1982).

3.2.2 *Gas Dehydration Processes*

Water and glycols have a mutual solubility in the liquid phase and their vapor pressures are both very low. As a result, glycols can be used to remove the water vapor from the wet gas stream in the absorber, after which they are regenerated in the stripping column.

The absorption/stripping dehydration process begins by scrubbing compressed, wet, inlet gas to remove liquid and solid impurities. This is followed by sending the scrubbed gas countercurrently through a liquid-glycol absorber. The lean (dry) glycol absorbs the water from the wet gas stream, and the dried gas leaves the absorber for further processing or transport.

The rich glycol exits the bottom of the absorber and on some units is sent through a gas-driven or electric pump to a flash tank, where much of the absorbed natural gas is separated from the glycol solution. The glycol solution is then sent through a series of heat exchangers and filters, after which water is either distilled or stripped from the glycol solution in a regenerator (Thompson and others, 1993). Rising steam in the regenerator strips the water vapor from the rich glycol solution, and the glycol, carried by the rising vapor, is condensed in the reflux section and washed back into the reboiler. The dirty sludge is left in the vessel and eventually removed for disposal, and the uncondensed steam exits the top of the stripper as an air emission off-gas, together with traces of hydrocarbon condensate which may be collected. The regenerated, lean (dry) glycol is then cooled and returned to the absorber (Ballard, 1986). Figure 2 is a schematic diagram of a typical glycol-based dehydration unit.

Of the water and hydrocarbons that enter the regenerator, approximately 1%-10% remain in the lean (regenerated) glycol, while the rest are exhausted in the offgas. Essentially all light hydrocarbons (methane to hexane) and nearly all (90%-99%) benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are stripped from the rich glycol stream in the regenerators (Thompson and others, 1993).

Operating variables that affect the performance of the dehydration process include temperature, pressure, glycol concentration, and glycol circulation rate. The process is especially sensitive to the temperature of the inlet gas. The water content of the gas and glycol vaporization losses increase with temperature at constant pressure. However, a temperature of 50°F (10°C) is considered to be the minimum operating temperature, since glycol becomes very viscous, thus inefficient, and has a greater tendency to foam at lower temperatures (Ballard, 1986).

The efficiency of the dehydration process depends primarily on the amount of water removed in the reboiler/regenerator, although pH control and foam prevention are also important to operation.

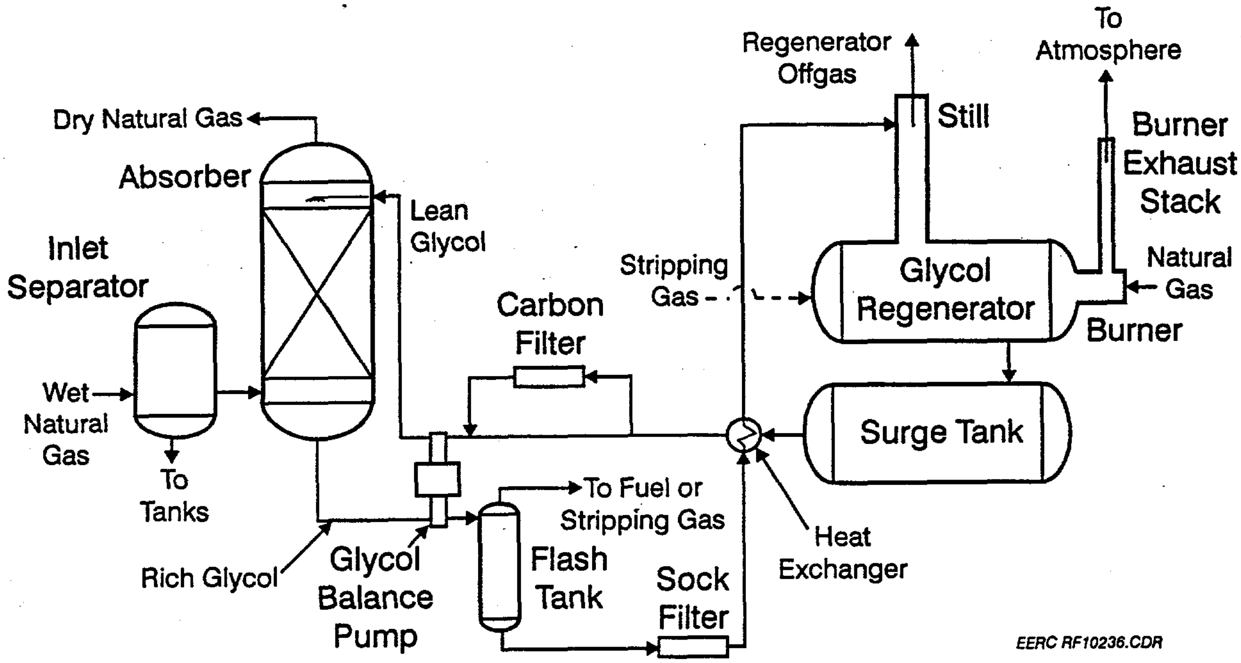


Figure 2. Glycol-based gas dehydration unit.

The leaner (dryer) the glycol returned to the absorber, the more efficient the dehydration. Glycol regeneration is affected by excessive circulation rates, which can overload the reboiler and prevent effective glycol regeneration, as well as increase glycol losses (Ballard, 1986). Foaming caused by hydrocarbons, corrosion inhibitors, salts, and suspended solids will also decrease the efficiency of the glycol dehydration process (Ballard, 1986). Glycol blends may contain propylene glycol and dipropylene glycol, both of which cause severe foaming (Grosso, 1979). Mechanical foaming is caused by operating at excessive gas flow rates. The best preventative method for foaming is to clean the gas prior to contact with the glycol solution, along with proper filtration and carbon purification of the glycol (Ballard, 1986). The pH of the glycol solution also affects the operation of the dehydrator unit. Fresh glycol has a pH ranging from 5.5 to 6.5, but becomes more acidic and corrosive during the dehydration process unless neutralizers or buffers are used. The pH level should be maintained within the range 7.0–7.5. A lower pH accelerates the rate of glycol decomposition, and a higher pH (above 8.0–8.5) can promote foaming and emulsification of the glycol solution. Neutralizing agents generally added to adjust the pH include borax, alkanolamines, or other alkaline compounds (Ballard, 1986).

While solid dessicant dehydration units can also be used to dehydrate gas streams, the absorption/stripping process is the preferred method. This process is run continuously, rather than on a batch or intermittent schedule. Therefore it is better suited for remote sites that are infrequently visited, such as in dehydration at a well site. The cost to install a glycol absorption/stripping unit is about half that of a solid desiccant unit. In addition less heat, and therefore less energy, is required for the regeneration of glycol per pound of water removed.

Glycols have been found to be resistant to degradation by contaminants such as hydrocarbons and produced water, which will quickly render solid desiccants ineffective (Manning and Wood, 1993a). Solid desiccants are generally used when a very low gas water content is desired, such as before the removal of gas liquids in cryogenic units (Evans, 1995).

3.2.3 *Glycols Used for Natural Gas Dehydration*

3.2.3.1 EG

Although it is not normally used for field dehydration, EG is used as a hydrate inhibitor (Pearce, 1995). EG is used as an alternate to solid desiccant units to bring the water vapor in gas to less than a 0°F dew point and, therefore, is primarily used in gas processing plants where cryogenic units are used to separate liquids from natural gas. Its relatively low boiling point indicates that it is more likely to undergo thermal degradation in the reboiler of a reclamation unit.

3.2.3.2 DEG

DEG was commonly used for the dehydration of natural gas prior to 1950 (Pearce, 1982), but is now used on relatively few units. It has a higher boiling point than EG, which indicates greater thermal stability, and can obtain a greater dew point depression than EG, thereby making it a more efficient dehydration agent. However, despite its greater thermal stability, thermal decomposition of the DEG is still common under the operating conditions used (Pearce, 1982).

3.2.3.3 TEG

Since 1950, TEG has been the most commonly used glycol for natural gas dehydration (Pearce, 1982). The higher boiling point of TEG allows it to achieve a greater dew point depression and provide better separation of water without accompanying thermal decomposition. TEG has a theoretical decomposition temperature of 404°F (207°C), which gives it a higher thermal stability than the other glycols. TEG is also characterized by lower vaporization losses than that of DEG and EG.

TEG is generally regarded as the most economical glycol for the dehydration of natural gas, and therefore continues to be the most frequently used glycol in dehydrator units. It has been estimated that approximately 95% of glycol dehydration units use TEG (Thompson and others, 1993).

Because of its physicochemical properties, TEG is commonly added to other glycols for use in dehydration. For example, some DEG solutions consist of 15%-30% TEG, in addition to minor amounts of antifoaming agent, inhibitor, and dye. TREG blends may also contain approximately 20%-30% TEG (Grosso, 1979), although such blends are not common.

3.2.3.4 TREG

TREG has the highest boiling point and the lowest volatility of the glycols used for the dehydration of natural gas. Because of its high cost, it is generally only used in specialized cases. No further information regarding its use was available from the sources utilized in this study.

3.2.4 *Relevant Uses Outside the Gas Industry*

The airline industry, especially in the northern regions, uses glycols extensively as deicing and anti-icing agents, commonly resulting in their introduction into the environment. Glycol-related subsurface impact has received particular attention in this context, and the insights that have been developed are valuable in understanding glycol behavior in gas industry settings.

A large majority of the aircraft deicing fluids have formulations primarily based on EG or propylene glycol, with DEG sometimes present as a minor component. Deicers are grouped into two categories on the basis of composition and properties. Type I deicers are unthickened anti-icing fluids used to remove ice and snow and prevent refreezing. The Type I fluids contain a minimum of 80 wt% glycols; the remainder is primarily water along with a buffer, a wetting agent, and an oxidation inhibitor. Type II deicers are anti-icing fluids thickened with additives to provide greater protection against refreezing even under conditions of precipitation. These fluids contain a minimum of 50 wt% glycols, with water and polymers as the remaining constituents (Sills and Blakeslee, 1992).

3.2.5 *Reaction Products*

Unlike the alkanolamines, the body of literature obtained for this report revealed little information on the specific reaction products associated with the operation of glycol-based dehydration units. That is not to say that such information does not exist. Several proceedings of the Laurence Reid Gas Conditioning Conference are known to contain such information, but were unable to be obtained at the time of the literature search. The phone survey also indicated that the Dow Gas Conditioning Fact Book (1962) has information on the glycol reaction products, but that book is no longer available from Dow, and interlibrary loan requests were unsuccessful.

What little information that was available for this report indicated that the decomposition of glycols most often results in corrosive acids, salts, and sludges composed of solid particles and tarry substances. These glycol reaction products are associated with oxidative and/or thermal decomposition of the glycols, inadequate pH control, and reactions with contaminants such as salts, hydrocarbons, acid gases, and additives such as pH-controlling agents, corrosion inhibitors, and antifoaming agents (Ballard, 1986). The specific chemical compositions of most of the reaction products formed during the dehydration process were not presented in the available literature.

Grosso and others (1982) describe a variety of reaction and degradation products typically associated with glycol-based gas dehydration units. Sodium and calcium chloride are the salts most commonly found in dehydration glycol solutions. The corrosion of iron in the dehydration unit may produce finely divided, black precipitates such as iron sulfide. Ballard (1986) noted that thermal degradation of TEG will occur at temperatures greater than 404°F (207°C). Such high temperatures may be the result of high heat flux rates or excessive skin temperatures (hot spots) on the fire tube. Thermal degradation is indicated by a burned sugar odor, a decrease in the pH, and a black color. The discoloration may be a result of the coke and tarry products present in the circulating glycol. These products can usually be removed using filtration (Ballard, 1986).

4.0 WASTE GENERATION AND MANAGEMENT

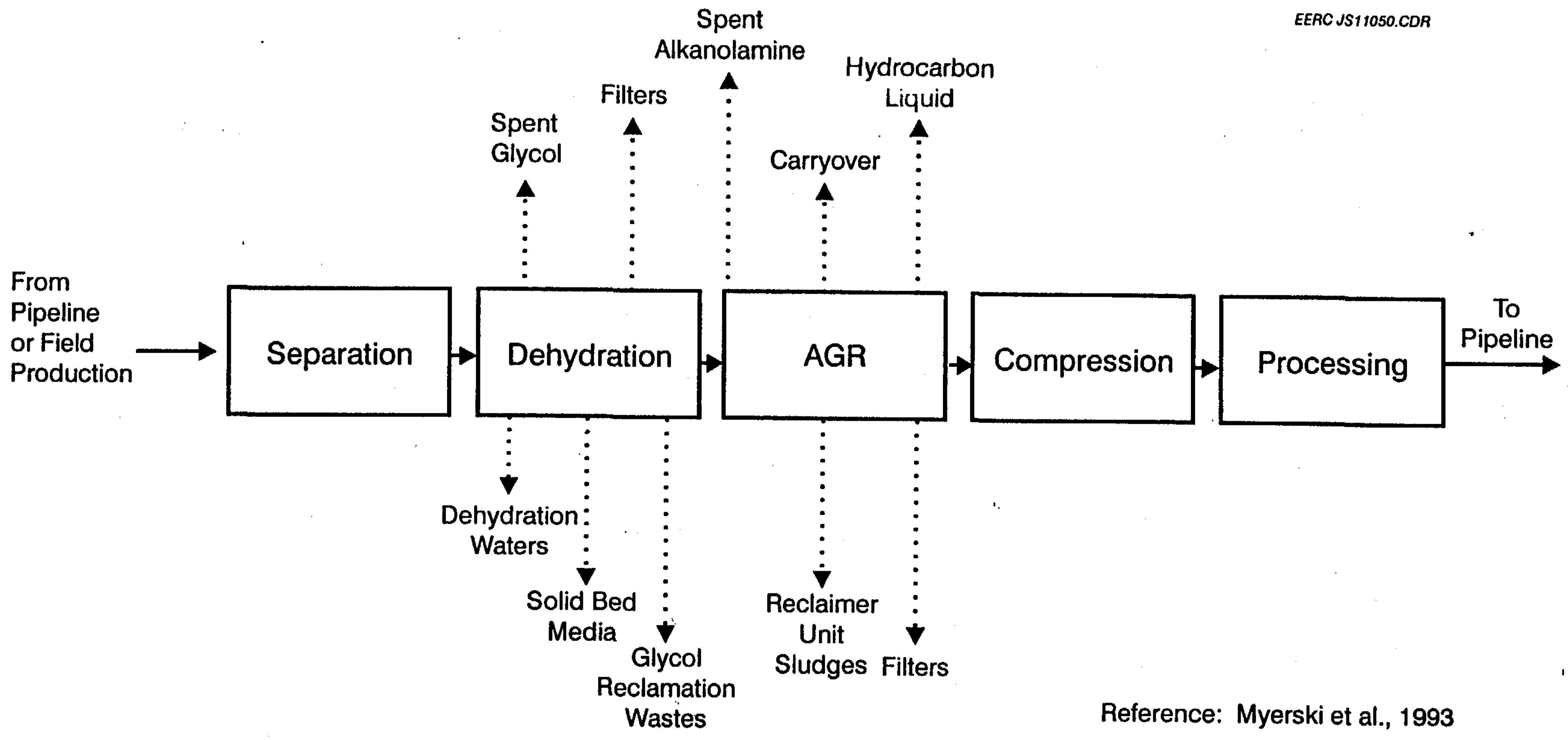
The operation of gas AGR and dehydration units creates a variety of wastes that may be introduced to the environment. Wastes include any residuals or products of the sweetening and/or dehydration process, as well as any stream that is not a part of the process and/or gets away from the system, such as spills or leaks. The gas-processing or conditioning wastes described in this section are the vehicles by which the alkanolamines, glycols, and their related reaction products are introduced into the subsurface environment. Attempts to control these vehicles of contamination include waste management techniques designed to minimize the exposure of gas-processing or conditioning wastes to the subsurface environment; however, wastes generated from accidental exposures such as spills or leaks may go unmanaged. The managed and unmanaged waste streams may be composed of spent alkanolamines and glycols and/or sludges from process unit tank bottoms or system filters. Unmanaged waste streams, particularly spills during changeover operations (the process of exchanging spent chemical for fresh chemical), may also include fresh alkanolamines and/or glycols. The reaction products discussed in the previous section are typically present in the waste streams in varying concentrations, depending on the process conditions. Additional components of the wastes include additives such as corrosion inhibitors and antifoaming agents, benzene and trace metals. Figure 3 is a simplified diagram of a typical gas processing/conditioning plant that illustrates the types of residual or solid or liquid product waste streams which may be generated by AGR and dehydration units. These wastes are generally placed in process wastewater storage pits, but have also been found in sludges and soils as a result of leaks and spills. It is important to note that not all streams associated with AGR and dehydration units are considered to be "wastes." For instance, Scheivelbein (1995) reported that vapors from glycol dehydrator units are typically collected and processed to recover hydrocarbon liquids, a process that precludes them from being classified as a waste stream.

4.1 Wastes Associated with AGR Units

As discussed in Section 1.0, AGR units are found at natural gas-processing and conditioning plants and at underground gas storage facilities. AGR-related waste streams include fresh and spent alkanolamines from changeover operations, sludges from reclaimer units and process filters, carryover from alkanolamine reflux regenerators, and alkanolamine filters. The release of these waste streams to the subsurface environment is generally controlled by waste management techniques, with the exception of spills during changeover operations and leaks or boilovers occurring during operation. Releases due to spills or leaks have often gone unmanaged, except for those occurring as a result of emergency response techniques (which are beyond the scope of this report).

4.1.1 *AGR Changeover Operation Wastes*

Changeover operations are potential sources of fresh and spent alkanolamine spills. The frequency of changeover operations varies from plant to plant and company to company, but they typically occur on a seasonal basis, though some units may go years without being changed over (Myerski, 1994). Spills of fresh alkanolamines are typically composed of aqueous solutions of the alkanolamine in use and may also include any antifoaming agents and/or corrosion inhibitors added to the solution. Spent alkanolamine solutions may contain varying concentrations of the alkanolamine used for sweetening as well as additives and any number of a variety of reaction products formed in varying concentrations during operation (see Section 3.2.3).



Reference: Myerski et al., 1993

Figure 3. Possible waste streams generated by AGR and dehydration units.

The spent alkanolamines (and their associated components) collected during the changeover process are typically disposed into process waste pits but may also be found in storage tanks. Injection wells are also used for the disposal of these wastes, but such wells are designed to prevent the introduction of wastes to the shallow subsurface and any source of drinking water. Newer gas-sweetening facilities typically use catch basins to minimize the amount of fresh and spent alkanolamines spilled directly onto the ground during changeover operations, but many of the older facilities might not have used any management techniques (Myerski, 1994). Such a lack in management may have resulted in varying amounts of these wastes being introduced to the environment. Changeover operations may contribute significantly to subsurface contamination at a gas-sweetening plant, depending on the degree of care taken during changeover operations and the frequency with which such operations occurred at a facility.

In Canada, leaking process waste pits and storage tanks containing spent alkanolamine solutions from changeover operations have been reported to be the most common source of groundwater contamination at gas-processing and conditioning plants. Many of the pits are excavated into surface material and are either lined with compacted natural clay or unlined, a situation more often found at older plants. On-site and off-site landfills have also been used to dispose of spent alkanolamines and thus have also been a common source of contaminants in groundwater (Hardisty and others, 1990).

4.1.2 *Reclaimer Unit Sludges*

Reclamation of alkanolamines after they have removed the acid gas from the gas stream will generally result in the accumulation of sludges in the reclaimer unit and on process filters. This sludge is typically composed of the alkanolamine and its reaction products, solid particles, salts, and corrosion products (Skinner and others, 1995). The reaction products discussed in Section 5.0 are especially prevalent in the sludges of reclaimer bottoms, where the optimum thermal and chemical conditions for their formation exist.

The primary options that have been used for the disposal of alkanolamine-related sludges are landfilling, land treatment, deep-well disposal, surface water discharge, and incineration (Boyle, 1990). Of these options, landfilling provides the greatest potential for the contamination of soil and groundwater. The application of a waste to the soil, where it will then be biodegraded into harmless components, is called land treatment or landspreading. This management technique has been shown to be a viable method of treatment for some AGR process sludges, depending on their composition, though some sludges may require treatment before they can be applied to soil (Boyle, 1990). The use of land treatment is sporadic and will likely continue to be so until further research is done to determine the limits of this management technique. Deep-well disposal of the sludges after filtration has been used in the past and is an option in many areas. Surface water discharge and incineration have also been used to dispose of sludges, but increasing costs for treatment prior to disposal by these methods as well as regulatory restrictions have made these options less viable.

AGR process-related sludges have significant potential to contaminate the subsurface. The composition of these sludges indicates that they may provide a vehicle for significant subsurface contamination by alkanolamines and their reaction products. According to industry and regulatory personnel in both the United States and Canada, disposal of these wastes by deep-well disposal, surface water discharge, and incineration is declining because of regulatory and economic constraints. Consequently, landfills and land treatment facilities are the most likely sources of subsurface contamination by these wastes.

4.1.3 *Carryover from Reclaimer Units*

Carryover is liquid or solid material entrained in and carried by the process stream from an AGR absorber or the reaction vessels of alkanolamine reflux accumulators and regenerators. Carryover occurs in the process stream and may be released to the environment by leaks in absorber units or reaction vessels. Carryover may include alkanolamines and their associated process wastes. These wastes can also be a source of benzene, as shown by the toxicity characteristic leaching procedure (TCLP) analyses on carryover from MDEA and DEA systems (Myerski and others, 1993). The results showed that benzene levels ranged from 560 to 2500 μg/L (Myerski and others, 1993), which are well above any U.S. or Canadian regulatory limits. Carryover from MEA and DEA units have also been found to contain mercaptans (Skinner and others, 1995) and trace metals in varying concentrations (Myerski and others, 1993).

Leaks in the AGR unit have the potential to be a significant avenue for subsurface contamination. The frequency of leaks has varied from plant to plant, depending on the age of the units and their maintenance schedule. Volumes of contaminant generated by a leak can vary greatly, depending on the severity of the leak and the length of time that the leak was active. A significant volume of contaminant can be introduced to the environment by a small leak over a long period of time. While in general these releases are significantly less voluminous and more sporadic than those produced by retention pits, their potential to affect the subsurface should not be overlooked. No information on specific management techniques for carryover wastes was found in the literature.

4.1.4 *Alkanolamine Filters*

The filters used in AGR units may also be a source of subsurface contamination by alkanolamines and their associated compounds, including benzene and trace metals. Wastes from the AGR process filtration systems include spent filters and their media, sludges, backwash, and spilled solution. The filters are periodically regenerated with steam or superheated water to remove the sorbed compounds. Wastes from the regeneration of the filters include spent carbon, regeneration rinse water, and regeneration offgas (Skinner and others, 1995). TCLP analysis of DEA, MDEA, and DGA filters found 11 μg/L benzene in a DEA sock filter. Benzene was not detected in the DGA or MDEA filters. TCLP analyses for metals in the same filters found levels of barium ranging from 0.03 to 0.09 mg/L, chromium ranging from 0.04 to 0.1 mg/L, and 0.01 mg/L selenium in the DEA sock filter (Myerski and others, 1993). While the sample size for the study conducted by Myerski and others (1993) is small (23 plants were surveyed), their data does give an indication of at least some of the contaminants that can be encountered in alkanolamine filters.

Discussions with industry and regulatory personnel indicate that waste filters from the AGR process are typically disposed into off-site commercial landfills as long as they meet all federal, state/provincial, and local standards. If they do not meet those standards, then they typically must go to a hazardous waste disposal facility. Not enough data were available to make a statement about the number of filters generated by an AGR unit in a year of operation. Those numbers depend on how frequently the filters are changed during maintenance, a practice which varies from facility to facility. Waste filters in landfills may be sources of subsurface contamination by alkanolamines and their associated compounds. Backwash and regeneration rinse water are typically placed into process waste pits or deep-injection disposal wells.

4.2 Wastes Associated with Glycol-Based Dehydrators

Glycol dehydration units are found at natural gas-processing and conditioning plants, underground storage facilities, and often at individual well sites. These units generate several waste streams, including fresh and spent glycols from changeover operations and leaks in the unit, glycol reclamation sludges, dehydration water, and used filters. Process reaction products, additives, benzene, and trace metals may occur with the dehydration wastes (Myerski and other, 1993).

4.2.1 *Changeover Operation Wastes*

Changeover operations are likely sources of fresh and spent glycols. The frequency of changeover operations varies from unit to unit and operator to operator, but they typically occur on a seasonal basis, though some units may go years without being changed over (Myerski, 1994). Fresh glycols may be introduced to the environment by spills typically composed of aqueous solutions of the glycol in use and any antifoaming agents and/or corrosion inhibitors that might be added to the solution. Spent glycol solutions can enter the subsurface environment through spills during changeover, through leaks during unit operation, or from a variety of management techniques. The spent glycols may contain the glycol being used for dehydration as well as any number of a variety of substances accumulated in varying concentrations during operation.

Myerski and others (1993) sampled spent glycols from storage tanks and dehydration units and found that they can have very high benzene concentrations. TCLP analysis of the samples indicated that benzene was present in concentrations ranging from 6.5 to 110 mg/kg. However, the number of tanks and units sampled for this study was small, and these concentrations may not be representative of spent glycols in general. Spent glycols may also contain lighter hydrocarbons, such as BTEX, that were absorbed by the glycols. Glycols preferentially absorb aromatics and naphthene components over the paraffinic compounds from natural gas. Absorption of aromatic compounds by glycols increases as the molecular weight of the glycol increases, which means that spent TEG and TREG may contain more of these compounds than spent EG and DEG. The lighter hydrocarbons are usually removed from the glycol solution through the exhaust system. However, if a regeneration unit is used, the BTEX components may be present in the effluent (Smith, 1990). Heavier hydrocarbons can also be absorbed by glycol solutions and, thus, may be components of spent glycol waste, but these components are more typically found in filter systems (Smith, 1990). BTEX will azeotrope with the water from the regenerator stack; thus if the gas contains BTEX, then the glycol will have a residual or equilibrium amount of BTEX at all times (Pearce, 1995).

The spent glycol solutions collected during the changeover process are typically managed by disposal into process waste pits, but they may also be found in storage tanks. Injection wells are also used for the disposal of these wastes, but such wells are designed to prevent the introduction of wastes to the shallow subsurface and, subsequently, any source of drinking water. Catch basins are often placed under the valves and spigots at newer dehydration units to minimize the amount of fresh and spent glycol spilled or leaked directly onto the ground, but some of the older facilities do not use any management techniques (Myerski, 1994). Such lack of management may result in varying amounts of these wastes being introduced to the environment.

Leaking process waste pits have been the most common and the largest sources of groundwater contamination at gas-processing and conditioning plants. Many of the pits are excavated into surface material and are either lined with compacted natural clay or unlined, a situation more often found at older plants (Hardisty and others, 1990). Spent glycols have also been disposed into on-site and off-site landfills which are also potential sources of groundwater contamination (Hardisty and others, 1990). Spills from changeover operations and leaks during operation may contribute to subsurface contamination at a dehydration site, depending on the degree of care taken during changeover and the frequency with which such operations occur at a facility. The frequency of changeover operations varies from unit to unit and operator to operator, but they typically occur on a seasonal basis, though some units may go years without being changed over (Myerski, 1994). The frequency and severity of leaks will also vary from unit to unit depending on their age and maintenance schedule. Volumes of contaminants generated by a leak or spill can vary greatly, depending on the conditions of the spill or leak and the amount of time involved. This is especially true for leaks. A small leak over a long period can introduce a significant volume of contaminant to the environment. Generally speaking, however, these releases are of less volume and more sporadic than those produced by retention pits, as is the case with AGR units, but their potential to affect the subsurface should not be overlooked.

4.2.2 *Glycol Reclamation Unit Sludges*

Wastes from glycol reclamation units include liquids and solids from reclaimer kettle bottoms. These sludges may contain varying concentrations of spent glycol, process reaction products, additives, and benzene. Myerski and others (1993) sampled glycol reclamation wastes for TCLP analysis. Benzene levels were found to range from 0.46 to 1 mg/L, well above the U.S. Environmental Protection Agency (EPA) maximum contaminant level for benzene, which is 0.005 mg/L (American Water Works Association, 1995). Since heavy hydrocarbons have been found to be a component of spent glycols, it may be expected that they can also be a component of glycol-related sludges. Spills of these sludges may occur during maintenance, causing their inadvertent exposure to the ground. For disposal, these wastes are typically placed into on-site process waste pits, or in the case of wellhead units, are transported to retaining pits. The literature search and survey of industry and regulatory personnel indicated that landfilling, land treatment, and deep well injection are the most common disposal techniques for glycol-related sludges.

4.2.3 *Dehydration Water*

The water absorbed from the natural gas and stripped from the glycol is called dehydration water. Myerski and others (1993) collected a sample of dehydration water from a vent pipe at the top of the reboiler. TCLP analysis of the sample found 32 mg/L benzene. This water is typically vented to the atmosphere as steam but may also be released to the land surface by leaks in the reboiler (Myerski and others, 1993). No estimates are available for the volume of dehydration water that may have been introduced to subsurface environments.

4.2.4 *Filters*

Glycol regenerators use sock and charcoal filters. TCLP analyses were performed on both sock- and charcoal-style filters from glycol regenerators. Myerski and others (1993) reported that the sock filters contained benzene concentrations ranging from 6.2 to 38 mg/L, while benzene concentrations in the charcoal filters ranged from 2.6 to 9.1 mg/L. As with the alkanolamine filters, the study examined only a few glycol filters, and these concentrations may not reflect the amount of benzene in most gas dehydration filter systems. Heavy hydrocarbons can also be a component of glycol filters. For example, lean TEG used in dehydrating BTEX-rich inlet gas streams can contain 2–6 mg/L of heavier hydrocarbons, which are preferentially absorbed onto carbon filtration beds (Smith, 1990). Filters from glycol dehydration units are typically discarded into commercial landfills.

5.0 REGULATION OF GAS INDUSTRY AMINES AND GLYCOLS IN THE UNITED STATES AND CANADA

In view of the significance of regulations in determining the climate in which contamination issues are studied and addressed, a survey was conducted to determine current and pending regulations that may be relevant to those contamination issues related to the alkanolamines and glycols used by the gas industry. The survey included gathering information through a series of personal communications with personnel in appropriate U.S. and Canadian government agencies, as well as through a review of pertinent regulatory documents. The survey covered agencies of the U.S. federal government (EPA, Department of Health and Human Services, Health Protection Service), Canadian federal government (Environment Canada and Transport Canada), several leading gas-producing states (California, Texas, Louisiana, Montana, and Oklahoma), and the significant gas-producing provinces (Alberta and Ontario).

5.1 United States - Federal Regulations

Regulatory programs under three federal acts appear to have some significance for alkanolamine- and glycol-related subsurface contamination issues that the gas industry may face in the United States. The regulation of alkanolamines and glycols used by the gas industry in the United States is covered at the federal level by three regulatory acts: the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response Compensation and Liability Act (CERCLA or "Superfund"), and the Safe Drinking Water Act (SDWA), which includes the Underground Injection Control (UIC) Program.

5.1.1 *RCRA*

Originally enacted in 1976, RCRA requires EPA to establish procedures for the identification of wastes as either hazardous or nonhazardous and to promulgate requirements for the management of both. EPA describes a hazardous waste as being either characteristically hazardous (based on the material's reactivity, corrosivity, ignitability, and/or toxicity) or specifically listed as hazardous (known poisons and carcinogens) (American Petroleum Institute, 1989).

In 1980, RCRA was amended by Congress to give special consideration to wastes generated by oil and gas exploration and production (E&P) operations. Under these amendments, E&P wastes became exempt from regulation under RCRA hazardous waste provisions (Subtitle C) (American Petroleum Institute, 1989). In 1988, EPA released a list of E&P associated wastes that it considers exempt from Subtitle C regulation regardless of whether the waste is characteristically hazardous. This list includes alkanolamines used for the removal of acid gas from natural gas as well as glycols used in the dehydration of natural gas. These "exempt" wastes are still subject to regulation under RCRA Subtitle D, which gives EPA the authority to regulate industrial nonhazardous waste. It is important to note that the exclusion of these exempt E&P wastes from the requirements of RCRA Subtitle C does not make any judgment regarding a particular waste's inherent reactivity, corrosivity, ignitability, or toxicity. The exemption also does not remove from the operator or disposer the responsibility of handling and disposing of the waste in a prudent manner. The exemption only gives the operator more latitude in selecting a disposal option other than those required by Subtitle C for what might otherwise be considered a hazardous waste, though the selected option must be in compliance with other state and local requirements (Fitzpatrick, 1990).

The legislation authorizing RCRA is up for reauthorization during the 1995–1996 session of Congress. In several past congressional sessions, serious but unsuccessful attempts have been made by a variety of interest groups to eliminate the E&P exemption from RCRA. No serious attempt of this nature is expected in the 1995–1996 session.

5.1.2 *CERCLA*

CERCLA, also known as "Superfund," was passed into law in 1980 and resulted in EPA establishing a program to identify sites where environmental contamination by hazardous materials has occurred or may occur and to make sure such sites are remediated. Reporting and remediation requirements were imposed on parties responsible for the contaminated sites, and provisions were included to allow the federal government to remediate Superfund sites and recover costs from the liable parties.

CERCLA regulates the release and remediation of "hazardous substances," as opposed to RCRA, which regulates "solid and hazardous waste." The list of substances that fall under CERCLA jurisdiction includes RCRA-regulated hazardous wastes, air pollutants regulated under the Clean Air Act, water pollutants regulated under the Clean Water Act, and substances regulated under the Toxic Substances Control Act. CERCLA includes a provision, called the "Petroleum Exclusion," that specifically exempts petroleum, including crude oil, crude oil fractions, refined products such as gasoline (American Petroleum Institute, 1989), natural gas, natural gas liquids, liquefied natural gas, and synthetic gas usable for fuel (or mixtures of natural gas and synthetic gas) from CERCLA's definition of a hazardous substance (Skinner and others, 1995). The Petroleum Exclusion does not include alkanolamines or glycols.

It is important to note that while gas industry alkanolamine- and glycol-related wastes are exempt from any requirements under RCRA, they are not automatically exempt from CERCLA. Under CERCLA, the operator is still liable for any damage these wastes may cause by their movement off-site and is also responsible for any required remediation (Fitzpatrick, 1990). Because of the persistence and mobility of the alkanolamines and glycols in the subsurface, some potential exists for them to be problematic under CERCLA.

5.1.3 *SDWA*

One of the primary objectives of SDWA is to protect underground water supplies from contamination. To meet that objective, the UIC Program was created by the 1974 SDWA. The UIC program regulates underground injection wells (classified as Class II wells) that are used to dispose of fluids used and produced in the exploration and production of oil and/or natural gas. The fluids eligible for injection into Class II wells include all E&P wastes exempted under Section 3001(b)(2)(A) of RCRA (Knudson, 1993). The EPA has ruled that gas plant dehydration wastes, gas plant AGR wastes, and spent filters and backwash can be injected into Class II wells as long as their physical state allows it (Elder, 1993).

5.2 United States – State Regulations

California, Louisiana, Montana, Oklahoma, and Texas were selected as the focus for state regulations based on their large production of natural gas, especially sour gas. The primary agency with jurisdiction over oil and gas E&P wastes for each state is listed in Table 4.

TABLE 4

Primary State Agencies for the Regulation of Oil and Gas E&P Wastes

State	Primary Agency
California	Dept. of Conservation, Oil & Gas Division (COGD)
Louisiana	Dept. of Environmental Quality (LADEQ)
Montana	Oil and Gas Conservation Commission (MOGCC)
Oklahoma	Corporation Commission (OCC)
Texas	Railroad Commission (TRRC)

5.2.1 *Disposal Regulations*

In the five states surveyed, the disposal of alkanolamines and glycols and their associated wastes are generally not regulated beyond RCRA 40 Code of Federal Regulations (CFR) requirements. These states consider alkanolamines and glycols used in the processing of natural gas to be exempt from classification as hazardous waste, and none of the states specify any management or disposal methods that must be used for wastes with these chemicals. Also, no regulatory limits are set for allowable concentrations of alkanolamines or glycols in soils, groundwater, or surface water.

5.2.1.1 Disposal Regulations for Fluids

The spent alkanolamines and glycols, filter backwash, regeneration rinse water, and any other liquid wastes associated with the operation of AGR and gas dehydration units are typically retained in process waste pits or storage tanks before disposal (Hardisty and others, 1990). Regulatory officials in Louisiana, California, Texas, and Oklahoma indicated that most of the alkanolamine and glycol waste liquids are disposed into Class II injection wells. Most of the alkanolamine and glycol liquid and solid wastes generated in Montana E&P operations are shipped out of state to disposal facilities or recycling plants. Recycling is encouraged in all surveyed states.

5.2.1.2 Disposal Regulations for Solid Waste

Most of the solid wastes generated during the processing of natural gas are in the form of filters used in gas-sweetening and dehydrator units. Landfill disposal of amine and glycol filters is allowed in California, Louisiana, Oklahoma, Montana, and Texas. Only Texas has regulations specific to the disposal of AGR and dehydration unit filters. The other states had no regulations specific to these filters at the time of this report. Solid wastes generated in the surveyed states by the processing of natural gas are generally classified as nonhazardous waste according to RCRA 40 CFR Subtitle C and, therefore, may be handled and disposed as such (American Petroleum Institute, 1989).

Texas was found to have the most stringent requirements for disposal of solid wastes with which gas processing/conditioning alkanolamines and glycols and their reaction products are associated. A TRRC minor permit is required for the disposal of any alkanolamine or glycol filters into landfills. These filters are required to be drained, air dried for 48 hours, and then tested for total petroleum hydrocarbons (TPH) and total benzene level before a permit for commercial landfilling will be issued. The TPH limit is 1500 mg/kg, and the total limit for benzene is 10 mg/kg. If total benzene exceeds 10 mg/kg, then TCLP analysis must be performed, for which the limit is 0.5 mg/L (Railroad Commission of Texas, 1994a). According to the data reported by Myerski and others (1993) and discussed in Section 4.0, the alkanolamine filters would be granted a permit for landfill disposal under these regulations, but the glycol filters would be denied because of their benzene content, thereby causing the operator to treat them as hazardous waste. Disposal of a hazardous waste in Texas requires a special permit and placement in a designated hazardous waste landfill. Texas is also the only state among those surveyed that permits land treatment of alkanolamine- and glycol-related liquids and sludges.

5.2.2 *Remediation Regulations*

Discussions with regulatory personnel from the surveyed states revealed that the remediation levels for a site with soil or groundwater contamination from alkanolamine- or glycol-related wastes are handled on a case-by-case basis. In many cases, elevated levels of the associated wastes such as, NO_2^-, NO_3^-, benzene, TPH, and biodegradation products are the impetus for any of the states to require remediation.

Regulatory limits have been set on contaminants that may be associated with AGR and dehydration wastes. As discussed in Section 4.0, wastes from glycol-based dehydration units may contain benzene and petroleum hydrocarbons. All the states surveyed have set limits for concentrations of benzene and the TPH in groundwater and soils, and, therefore, contamination of the subsurface by glycol-based dehydration wastes may be subject to regulatory action under those regulations. Regulations dealing with contaminants associated with alkanolamines include limits for NH_3 in surface water, groundwater, and soil. The presence of ammonia in particular has been used as an indicator of alkanolamine contamination at gas industry sites. Both glycols and alkanolamines undergo biodegradation (see Section 6.0 for a detailed discussion on biodegradation), and some of the products of their biodegradation are regulated by the surveyed states. The alkanolamine biodegradation products for which there are regulatory limits include NO_2^- and NO_3^-. Effects of glycol biodegradation for which regulatory limits exist include the production of ethanol and increases in biochemical oxygen demand (BOD).

5.3 Canada – Federal Regulations

Canadian federal guidelines for levels of contamination in soils and waters are set by the Canadian Council of Ministers of the Environment (CCME). These guidelines are often followed by the provinces but may be altered by the provinces to suit the circumstances of each. For instance, population density, land use, climate, and geological setting may dictate more stringent requirements or allow less restrictive measures than those set by the CCME. None of the federal or provincial regulations related to oil and gas dealt specifically with alkanolamines, though some of the wastes in which they and their reaction or biodegradation products can be expected are regulated. Specific levels have been set for EG and DEG in surface and groundwaters because of their use in aircraft deicing operations, but none have been set for TEG or TREG.

In 1991, the CCME issued the Canadian Environmental Quality Criteria (CEQC) for Contaminated Sites. These criteria are numerical limits for contaminants in soil and water, including surface and groundwater, intended to provide general guidance for the general maintenance, improvement, or protection of environmental quality and human health at contaminated sites. This set of criteria addresses soil and water contaminants associated with agricultural, residential, parkland, and commercial/industrial land uses.

5.3.1 *Alkanolamines*

The concentrations of alkanolamines in water and soil are not addressed specifically by these criteria. However, the CEQC do include some guidelines for ammonia, nitrate, and nitrite, all of which are known degradation products of the alkanolamines used by the gas industry. Those criteria are listed in Table 5.

5.3.2 *Glycols*

The Canadian Water Quality Guidelines (WQG) were prepared by the Task Force on Water Quality Guidelines under the authority of the Canadian Council of Ministers of the Environment and issued by Environment Canada (revised June 1995). These guidelines are meant to be used in a complementary fashion with the CEQC guidelines. Earlier versions included guidelines for allowable concentrations of EG and DEG. The WQG were given interim status and were updated as new information became available. However, based on a reevaluation of the available toxicity data, it was determined by the CCME that there was insufficient information for the issuance of a full or interim water quality guideline for DEG. At the time of this writing, EG was the only glycol used by the gas industry for which WQG have been set in Canada. Federal and provincial regulators emphasized that the use of these guidelines will greatly depend on local conditions (i.e., climate, geologic setting, vegetation, wildlife habitat, population density, and land use) and that the values provided in the guidelines are not uniform national water quality requirements.

The Canadian WQG were developed in part for the protection of aquatic life from EG which could contribute to oxygen depletion in surface waters. Acceptable EG concentrations in surface waters are, therefore, considered in conjunction with guidelines for dissolved oxygen. Canadian WQG (Section 3.2.1.10) reported dissolved oxygen guidelines of 6 mg/L for early life stages and 5 mg/L for other life stages for warm-water species. For cold-water species, the guidelines were 9.5 and 6.5 mg/L for early life stages and other life stages, respectively (CCME, 1994). The Canadian WQG for EG concentrations is 192 mg/L. This level is considered sufficient for the protection and maintenance of freshwater aquatic life (CCME, 1994). While these regulations were developed with the protection of surface water in mind, large discharges of glycol-contaminated groundwater can affect the water quality of the receiving surface water body, and therefore, these guidelines may apply to groundwater in some cases.

TABLE 5

CEQC Criteria for Alkanolamine Degradation Products, mg/L (water by use)

	Freshwater Aquatic Life	Livestock Watering	Drinking Water
Ammonia (NH_3)	1.37–2.2	---[1]	---
Nitrate (NO_3^-)	---	---	45
Nitrite (NO_2^-)	0.06	10	4.5
Nitrate + Nitrate	---	100	---

[1] Criteria values not established.

5.4 Canada - Provincial Regulations

Since over 90% of the gas production in Canada is in Alberta, its provincial regulations, as set forth by Alberta Environment and the Alberta Energy Resources Conservation Board (ERCB), are particularly important. Ontario, which also has a significant amount of natural gas production, is known as the regulatory "trendsetting" province in Canada. As a result, Ontario regulations relevant to alkanolamines and glycols will also be briefly discussed as an indication of where future regulations may be heading.

5.4.1 *Alberta*

5.4.1.1 Alberta Water Quality Guidelines

The province of Alberta uses the criteria set forth by the CCME Canadian WQG as its standards for surface and groundwater quality (see Section 5.3.1). These standards are enforced by Alberta Environment.

5.4.1.2 Alberta Treatment and Disposal Guidelines

The ERCB has issued a set of oil field waste management recommendations. These recommendations currently do not have the full force of law, but regulators are holding operators accountable under these guidelines. These recommendations were scheduled to become legal requirements by the end of 1996.

Alkanolamines and Related Wastes

Spent sweetening agents, including DEA, MEA, and MDEA, are not normally classified as dangerous oil field waste. Testing to determine flash point and other leachate characteristics must be performed. Spent sweetening agents may be reclassified as dangerous oil field waste, depending on the results of those tests. The only disposal options allowed for these wastes are injection down a Class I well (wells used for the disposal of oil field or industrial waste streams [Energy Resource Conservation Board, 1994]) after the pH has been adjusted to 4.5–12.5, and injection down a Class II well (wells used for the injection or disposal of produced water or brine equivalent [Energy

Resource Conservation Board, 1994]) after pH adjustment to 6.0–9.0. These disposal options apply to both dangerous and non-dangerous oil field waste (Energy Resource Conservation Board, 1993). The criteria for the classification of dangerous oil field waste are given in Table 6.

Amine filter backwash liquids may be classified as a dangerous oil field waste, depending on their composition and particularly BTEX content. These liquids need to be tested for leachate characteristics. The leachate characteristics, with a notable focus on BTEX, along with ignitability, flash point, and toxicity, will determine the hazardousness of the waste liquids. Injection down an ERCB-approved Class I or Class II disposal well is the acceptable industry disposal practice (Energy Resource Conservation Board, 1993).

Amine filters are classified as dangerous oil field waste, as are any entrained liquids recovered from the filters. This material must be tested for ignitability, and spontaneous combustion potential, and flash point and leachate characteristics must be determined. Acceptable management and disposal practices include recycling, thermal treatment, and landfilling in an ERCB-approved Class I or Class II oil field landfill after entrained liquids have been removed. Recycling of the entrained liquids is encouraged; otherwise, they must be either injected down a Class I well if the organic fraction is <10% or incinerated or, if the organic fraction is greater than 10%, then the liquids must be incinerated or treated before injection (Energy Resource Conservation Board, 1993).

Sludges from amine gas-sweetening units are classified as dangerous oil field waste. Flash point, leachate characteristics (especially with regard to BTEX), and toxicity must be determined on these sludges, and the selection of disposal options must be based on their characteristics of the waste or from historical data. Disposal options include physical or chemical treatment, placement in approved landfills, land treatment, and thermal treatment (Energy Resource Conservation Board, 1993).

Glycols and Related Wastes

Glycol solutions used for the dehydration of natural gas are normally not classified as dangerous oil field waste. However, leachate characteristics, flash point, and toxicity must be determined, because these characteristics may lead to the classification of these glycols as dangerous oil field waste. Regardless of their classification, glycols may be recycled or injected in ERCB-approved Class I or Class II disposal wells if the glycol content is <40% by mass. If the glycol content is >40% by mass, then it must be treated before disposal (Energy Resource Conservation Board, 1993).

Glycol filters are classified as dangerous oil field waste, as are any entrained liquids recovered from the filters. This material must be tested for ignitability and spontaneous combustion potential, and the flash point and leachate characteristics must be determined. Acceptable management and disposal practices include recycling, thermal treatment, and landfilling in an ERCB-approved Class I or Class II oil field landfill after entrained liquids have been removed. Recycling of the entrained liquids is encouraged; otherwise, they must be injected down a Class I well if the organic fraction is <10% or incinerated. If the organic fraction is >10%, then the liquids must be incinerated or treated before disposal (Energy Resource Conservation Board, 1993).

TABLE 6

Criteria for the Classification of E&P Wastes as Dangerous Oilfield Wastes According to Alberta ERCB (Energy Resource Conservation Board, 1993)

Flammability	Waste has a flash point less than 61°C, and/or waste ignites and propagates combustion in a test sample.
Spontaneous Combustion Potential	Waste generates heat at a rate greater than it loses heat and reaches the autoignition temperature.
Water Incompatibility	Waste generates flammable or explosive gases in contact with water.
Oxidizing Potential	Waste contributes oxygen for combustion at a rate that is equal to or greater than that provided by either ammonium persulfate, potassium perchlorate, or potassium bromate.
Toxicity	Waste has an oral toxicity LD_{50} not greater than 5000 mg/kg and has an inhalation toxicity LC_{50} not greater than 10,000 mg/kg at normal atmospheric pressure.
Corrosivity	Waste has a pH less than 2.0 or greater than 12.5.
PCB Content	Waste contains polychlorinated biphenyls at a concentration equal to or greater than 50 mg/kg.
Leachate Toxicity	Waste is a liquid, a solid that passes a 9.5-mm mesh opening, or a friable solid that can be reduced by grinding a mortar and pestle to a particle size that passes a 9.5-mm mesh opening, or a mixture of these and: 1) Contains at a concentration of 100 mg/L or higher any substance listed in Table 1 of the Schedule to the Alberta Users Guide for Waste Managers published by Alberta Environmental Protection Agency; 2) The leachate contains any substance listed in Table 2 of the Alberta Users Guide for Waste Managers, in excess of the concentrations listed in that table; or 3) Contains any of the following substances in a concentration greater than 0.001 mg/L: Hexachloro-dibenzo-p-dioxins Pentachloro-dibenzo-p-dioxins Tetrachlor-dibenzo-p-dioxins Hexachloro-dibenzofurans Pentachloro-dibenzofurans Tetrachloro-dibenzofurans

Sludges from glycol dehydration units are classified as dangerous oil field waste and must be characterized as to flash point, leachate components (especially with regard to BTEX), and toxicity. The selection of disposal options must be based on characteristics of the waste as determined from historical or analytical data. Disposal options include physical or chemical treatment, land treatment, thermal treatment, injection in ERCB-approved Class I or Class II disposal wells if glycol content is <40% by mass, and approved landfill disposal. If the sludge has a glycol content >40% by mass then it cannot be injected unless it is treated to reduce the glycol (Energy Resource Conservation Board, 1993).

5.4.1.3 Tier I Criteria for Remediation

Alberta Environmental Protection (AEP) states that contaminated soil is required by the province of Alberta to be remediated by the polluter or owner of the contaminated site (Alberta Environmental Protection, 1994). AEP subscribes to a two-tier approach to setting acceptable concentrations of contaminants in soil. Tier I values approximate acceptable concentrations of soil contaminants for all site conditions and land uses without defining actual risk. The Tier II criteria are site-specific and focus on the protection of human health and the environment. These criteria are based on acceptable risk specific to the site in question considering such variables as soil, geology, surface and groundwater, climate, and land use. Tier I criteria are set by AEP and have been developed from the scientific literature, existing guidelines, and current practices in Alberta and other jurisdictions in Canada and abroad. Tier II criteria are offered by the proponent as an alternative and must be supported by credible risk-based scientific documentation (Alberta Environmental Protection, 1994).

The Alberta Tier I criteria for soil and groundwater remediation do not currently include values for allowable concentrations of alkanolamines, glycols, or their associated wastes. Their exclusion does not mean that their remediation is not regulated, but rather that remediation criteria for these wastes would be dealt with on a case-by-case basis.

5.4.2 *Ontario*

5.4.2.1 Ontario Water Quality Guidelines

Sources of water contamination are regulated by the Ontario Ministry of the Environment and Energy (OMEE). Regulated sources of water contamination are those created by activities which require specific approval under the Ontario Water Resource Act or the Environmental Protection Act, including oil- and gas-related activities (OMEE, 1984).

Water quality requirements for proposed regulated waste discharges are established on a case-by-case basis. Water quality criteria are set by OMEE to protect reasonable uses, existing or proposed, of both ground and surface waters. The ministry will issue a certificate of approval for each discharge source that will specify the quantity and quality of the discharge, as well as stipulate any control measures which the ministry deems necessary. Applicants for waste disposal facilities may be required to monitor groundwater quality and provide background data on natural water quality (OMEE, 1984).

The Provincial Water Quality Objectives issued in July 1994 include interim guidelines for allowable concentrations of MEA, EG, and DEG in surface and groundwater. The guidelines were set at 200 μg/L for MEA, 2000 μg/L for EG, and 11,000 μg/L for DEG. Other regulatory limits have been set for many parameters that may be directly affected by releases of alkanolamine, glycol, or related wastes. These parameters include alkalinity and pH, ammonia (not ionized), dissolved oxygen, and hydrogen sulfide (OMEE, 1984). The basicity of both glycols and alkanolamines can have considerable effects on the pH of surface and groundwaters.

5.4.2.2 Ontario Treatment and Disposal Options

The requirements for the treatment and disposal of alkanolamines and glycols used by the gas processing industry and their related wastes in Ontario are promulgated under the General Waste Management Regulations (Regulation 347) of the Ontario Provincial Environmental Protection Act. At the time of this study, the regulations were being revised by OMEE, and updated specific requirements were not available. However, general information on disposal options was provided verbally by OMEE personnel (Ward, 1994).

Allowable disposal options for gas industry-related wastes, including spent alkanolamines, glycols, and their associated wastes, include landfilling, landfarming, stream discharge, and deep-well injection. All of these disposal options require a permit from OMEE, which is granted on the basis of testing of hazardous characteristics, primarily toxicity. If the waste is deemed to be hazardous, then it must be removed to a hazardous waste disposal facility. As of 1994, only one hazardous waste disposal facility existed in the province of Ontario. Waste sent to this facility may be incinerated or stabilized and buried in a landfill. Landfilling of wastes deemed to be nonhazardous is a viable disposal option. Some landfarming of nonhazardous alkanolamine- and glycol-related wastes occurs, but the use of this practice has been reduced drastically in recent years. Deep-well injection, while allowed for disposal of nonhazardous waste, is not a standard practice. The situations where injection is permitted are very restricted, depending on the proximity of the well to populated areas and on the geologic setting. Many oil and gas industry wastes are transported to Quebec or the United States for disposal. Recycling is encouraged and done wherever and whenever feasible (Ward, 1994).

5.5 Indirect Implications of Regulations

While very few regulations exist in the United States and Canada that are specifically aimed at the gas industry amines and glycols, there are circumstances under which a release of these chemicals to the environment may be indirectly regulated. For example, in both the United States and Canada, wastes associated with AGR units and gas dehydrators often must be tested for benzene before disposal. High benzene concentrations, such as those reported by Myerski and others (1993), could cause the waste to be classified as being hazardous in many states and provinces. Excessive concentrations of ammonia from the degradation of alkanolamines and elevated BOD levels from the degradation of glycols are other examples of how releases of gas industry alkanolamines and glycols can indirectly come under regulation. These types of scenarios must be taken into serious consideration when determining the regulatory framework within which disposal is practiced.

6.0 TRANSPORT AND FATE OF ALKANOLAMINES AND GLYCOLS

The transport and fate of any substance released into the subsurface environment is primarily dependent on the physicochemical characteristics of the substance and the attenuation processes to which it is subjected. As a result, physicochemical properties can provide insight into transport and fate. These properties, coupled with the results of research, can provide insight into significant attenuation processes. The nature (e.g., porosity, permeability, mineralogy, organic content) of the material into which the substance is introduced is an important aspect of attenuation processes and, therefore, also important in determining the behavior and persistence of the substance in the environment. The type of point source from which the substance is released can also affect the extent and severity of soil and groundwater contamination.

The relationships between physicochemical properties and subsurface behavior and the effects of attenuation processes can be used to predict the potential for the persistence and transport of alkanolamines and glycols in the subsurface. Laboratory and field case studies on the transport and fate of EG provide complementary information that supports those predictions. While the glycol field studies reviewed for this report examine the environmental effects of glycol-based deicer fluids rather than those of dehydration glycols, enough information is provided in these studies to make inferences applying to glycol releases from dehydrator units and pits. Neither laboratory nor field studies dealing with the behavior of alkanolamines in soil, sediment, or groundwater could be obtained for this report.

6.1 Physicochemical Properties Used to Predict Subsurface Behavior of Alkanolamines and Glycols

The physicochemical properties of alkanolamines and glycols can provide useful insights into their transport and fate. Aqueous solubility, octanol-water partitioning coefficients (log K_{ow}), organic carbon-water partitioning coefficients (log K_{oc}), Henry's law constant, diffusivity coefficients in water, vapor pressure, and viscosity can all provide clues about the potential mobility and attenuative tendencies of alkanolamines and glycols. Appendix A contains values obtained for these physicochemical properties for the gas industry alkanolamines and glycols, as well as the reaction and degradation products for which such data were available. Values for some of these properties were not available for many of the compounds, especially for the reaction and degradation products. No information was available regarding any of these physicochemical properties for several of the alkanolamine reaction products. Compounds for which no physicochemical data were available are not included in Appendix A.

6.1.1 *Specific Gravity*

Specific gravity is defined as the ratio of a chemical's density to the density of distilled water at 4°C. Specific gravity is particularly important in the case of immiscible fluid, as the specific gravity will be an indication of the fluid's tendency to "float" if it has a specific gravity less than that of water or "sink" if it is greater than that of water. Miscible fluids with a specific gravity greater than that of water, such as most of the alkanolamines and glycols of interest, will move down through the water as they dissolve. The alkanolamines and glycols of interest have specific gravity values that are greater than water, though in some cases only slightly (see Appendix A).

6.1.2 *Aqueous Solubility*

The solubility of a substance is a measure of its capability to dissolve in a particular solvent, usually water. Values mentioned in this report describe the solubility of the pure single compound in distilled, deionized water. Solubility in natural waters can be significantly affected by such factors as pH, temperature, naturally occurring organic substances, and dissolved anions and cations. In general, the higher a compound's solubility the more likely that compound is to dissolve in and, hence, contaminate groundwater (Harju and Schmit, 1993).

The gas-sweetening alkanolamines and gas-dehydrating glycols are all known to be completely miscible in water. The high solubility of the alkanolamines and glycols, coupled with specific gravities that are near that of water, will cause these compounds to readily mix with the groundwater once they reach the water table.

6.1.3 *Octanol-Water Partitioning Coefficient*

The octanol-water partitioning coefficient (K_{ow}), which is usually expressed as a logarithmic value, is the ratio of the concentration of a compound in octanol to the concentration of that compound in water at equilibrium (e.g., Harju and Schmit, 1993). Negative or low K_{ow} values are indicative of high subsurface mobility (McKay, 1991).

6.1.3.1 Alkanolamines

MEA, DEA, and TEA are all characterized by negative K_{ow} values, which indicate that these alkanolamines will tend to partition into water and, thus, may be expected to be highly mobile in the subsurface (Harju and Schmit, 1993). No K_{ow} values were available for MDEA or DIPA, but may be expected to be similar to MEA, DEA, and TEA as a group (Pearce, 1995).

For alkanolamines, K_{ow} values are dependent on pH. Alkanolamines will be more soluble in an acidic system. This requires that careful attention be paid to the pH of the system being evaluated if the partitioning of these contaminants to or from the aqueous phase are to be predicted (Harju and Schmit, 1993).

6.1.3.2 Glycols

EG, DEG, and TEG are all characterized by negative K_{ow} values, indicating that these glycols will tend to partition into water and be highly mobile in the subsurface.

6.1.4 *Organic Carbon-Water Partitioning Coefficient*

The organic carbon-water partitioning coefficient (K_{oc}) is the ratio of the concentration of a compound attenuated by organic carbon to its concentration in water at equilibrium. K_{oc} is usually expressed as a logarithmic value. These values are usually obtained by 1) using an observed distribution coefficient (K_d) that accounts for the ratio of the concentration adsorbed onto soil/sediment surfaces to that in water at equilibrium, normalized on the basis of the soil/sediment organic carbon content or 2) estimating the value of K_{oc} from equations based on solubility and/or K_{ow} (Harju and Schmit, 1993).

Normalizing this distribution coefficient to the organic carbon of the soil/sediment may not be completely accurate because a variety of other factors also contribute to the distribution. Some of these factors include the mineralogy, the surface area, and the nature of the organic matter of the soil/sediment. When K_{oc} values are used, it is important to keep in mind that these values are describing the behavior of a compound in a material generally regarded to have organic matter as a homogeneous mass, whereas in reality the material is a heterogeneous mixture of organic materials, each of which will attenuate various organic compounds to a different extent (Dragun, 1988). It is also important to remember that these values were obtained in a laboratory under conditions that are not necessarily reflective of conditions in the field.

6.1.4.1 Alkanolamines

K_{oc} values for the alkanolamines could not be found in the literature.

6.1.4.2 Glycols

Both EG and DEG have low organic carbon-water partitioning coefficients (−2.14 and −2.19, respectively). Such a lack of adsorption of glycols from water into organic matter indicates that these glycols would not be retained by dissolved or particulate organic matter in soils and freshwater sediments (Sabeh, 1991; Transport Canada, 1989b). These glycols will have a tendency to remain dissolved in water and will, thus, be mobile in the subsurface environment (Transport Canada, 1989b).

6.1.5 *Henry's Law Constant*

The Henry's law constant (H or H_c) is the ratio of the concentration of a compound in the gaseous phase to the concentration of that compound at equilibrium in the aqueous phase. This value (typically dimensionless, but also frequently expressed in atm • m^3/mol) is closely related to the vapor pressure of a compound but is also dependent on its aqueous solubility and molecular weight and, therefore, can be used to make a more accurate prediction of volatility than one based solely on vapor pressure. A higher value of H will translate to a higher rate of volatilization.

Henry's law constants can be used to make generalizations about the volatilization of organic substances including (Lyman and others, 1982):

- H values $<10^{-7}$ atm • m^3/mol (4.2×10^{-6} in the dimensionless form) indicate that the substance is less volatile than water and can be considered essentially nonvolatile.

- H values in the range of $10^{-7} < H < 10^{-5}$ atm • m^3/mol ($4.2 \times 10^{-6} < H < 4.2 \times 10^{-4}$ in the dimensionless form) indicate that the substance may volatilize slowly at a rate directly dependent on H. However, the substance will still tend to partition into the aqueous phase.

- H values from $10^{-5} < H < 10^{-3}$ atm • m^3/mol ($4.2 \times 10^{-4} < H < 4.2 \times 10^{-2}$ in the dimensionless form) indicate that volatilization is a significant contaminant transfer mechanism.

- H values $> 10^{-3}$ atm • m^3/mol (4.2×10^{-2} in the dimensionless form) indicates that volatilization may be significant to the point that the majority of the compound will tend to reside in the gaseous phase with the highest values of H.

6.1.5.1 Alkanolamines

MEA and DEA each have low Henry's law constants (1.667×10^{-6} and 2.229×10^{-12} in dimensionless form, respectively). Such low H values indicate that MEA and DEA are less volatile than water and can, therefore, be considered essentially nonvolatile (Harju and Schmit, 1993). Henry's law constants were not available for TEA, MDEA, or DIPA, but it would be expected that their H values are similar to MEA and DEA (Pearce, 1995).

6.1.5.2 Glycols

EG and TEG are characterized by low Henry's law constants (2.5×10^{-6} and 5.31×10^{-9} in dimensionless form, respectively). Such low H values indicate that EG and TEG are less volatile than water and can, therefore, be considered essentially nonvolatile (Harju and Schmit, 1993). No values of H were available for DEG, but it would be expected to fall somewhere in the range of EG and TEG.

6.1.6 *Diffusivity Coefficient in Water*

The diffusivity coefficient is a measure of the tendency for a compound to spread from areas of high concentration to areas of lower concentration. A compound characterized by a high diffusivity coefficient can be expected to be very mobile in the subsurface. Observed diffusion in porous media suggests that there will be a considerable departure in groundwater systems from the experimentally obtained diffusion values for water because of the longer diffusion flow paths caused by the presence of particles in the solid matrix and by adsorption on the solids (Harju and Schmit, 1993). Diffusion coefficient values have been observed in groundwater systems to typically range from 0.5 to 0.01 times the diffusivity coefficient in water (Freeze and Cherry, 1979). The lower values are due to the longer diffusion flow paths caused by the presence of particles in the solid matrix and by adsorption on the solids.

6.1.6.1 Alkanolamines

Diffusivity coefficients for alkanolamine in water were not available. However, the complete miscibility of the alkanolamines in water, as well as their slightly higher densities relative to water, suggest that they are likely to exhibit a tendency to diffuse readily.

6.1.6.2 Glycols

Reported diffusivity coefficients in water for glycols ranged from 7.6×10^{-6} cm^2/sec for TEG to 1.16×10^{-5} cm^2/sec for EG. These values suggest that the mobility of the glycols may be enhanced by diffusion. No diffusivity coefficients were located for the other glycols of interest, however their relatively high densities compared to water suggest that they may also diffuse readily.

6.1.7 *Vapor Pressure*

Vapor pressure is the pressure that a compound's vapor phase will exert when in equilibrium with its liquid phase. Substances with relatively higher vapor pressures will be more likely to volatilize than those with lower vapor pressures. Generally speaking, as vapor pressure values increase so does the likelihood that vapor-phase transport will play a significant role in the transport and fate of a substance (Harju and Schmit, 1993). Vapor-pressure values are temperature-dependent and are usually determined at 77°F (25°C).

6.1.7.1 Alkanolamines

The alkanolamines of interest tend to have very low vapor pressures. Specifically, the vapor pressures of MEA, DEA, TEA, and MDEA at 20°C are <1 mm Hg, <0.01 mm Hg, <0.01 mm Hg, and <0.01 mmHg, respectively. Such low vapor pressures indicate that these alkanolamines do not readily volatilize, and, therefore, vapor-phase transport will not be expected to play a significant role in their subsurface transport.

6.1.7.2 Glycols

EG, DEG, and TEG have very low vapor pressures (<0.1 mm Hg, <0.01 mm Hg, and <0.001 mm Hg @ 25°C, respectively). Such low vapor pressures indicate that these glycols do not readily volatilize, and, therefore, vapor-phase transport will not be expected to play a significant role in their subsurface transport.

6.1.8 *Viscosity*

The resistance of a fluid to shearing forces is termed viscosity. High values of flow resistance are indicative of more viscous, less fluid substances. Lower values of viscosity are, therefore, generally indicative of greater subsurface mobility (Harju and Schmit, 1993). Viscosity is most useful in predicting infiltration rates of a compound through the vadose zone. It is less important when predicting the behavior of compounds in water, especially highly soluble compounds, because the viscosity of a substance will change as it dissolves into water. Viscosity is also very dependent on temperature.

6.1.8.1 Alkanolamines

The viscosities of alkanolamines vary over a broad range. Pure MEA, MDEA, and TEA have viscosities of 24.1, 83, and 1013 centipoise (cP) at 20°C (68°F), respectively, while pure DEA and DIPA have viscosities of 380 and 870 cP at 30°C (86°F), respectively. These viscosities would apply in the case of spills of pure alkanolamines. However, alkanolamines at gas industry sites would more likely be introduced into the environment in solution, in which case the viscosity would be dependent on the concentration of the alkanolamines in solution. Typical solution strengths for the alkanolamines most commonly used to process natural gas vary, as previously noted (Section 3.1.3). To reiterate, MEA concentrations generally range from 15 to 20 wt%, DEA ranges from 20 to 40 wt%, and MDEA solution strengths range from 30 to 55 wt% (Skinner and others, 1995). At these concentrations, viscosity is still significant (with the exception of DEA), and infiltration of these solutions through the vadose zone would be expected to be much slower than that of water. However, viscosity would become less important as the alkanolamine solution moved across the water table and began to mix with and dissolve into the groundwater. The same effect will also be caused by water moving through the vadose zone. The alkanolamine will become more dilute and lower the viscosity of those solutions, which will result in an increase in the rate of infiltration of the alkanolamines in the vadose zone.

6.1.8.2 Glycols

The viscosities of glycols tend to be lower than those of the alkanolamines. Pure EG and DEG have viscosities of 19.9, 38, and 34 cP at 20°C (68°F), respectively, while pure TREG has a viscosity of 43 cP at 25°C (86°F). These viscosities would apply in the case of spills of pure glycols. Pure EG will take about 130 days to infiltrate 6 m of silty sand (Environment Canada, 1984). However, glycols at gas industry sites would more likely be introduced into the environment in solution, in which case the viscosity would be dependent on the concentration of the glycol in solution. For instance, a 10% solution of EG has been observed to penetrate 6 m of unsaturated silty sand in about 10 days, a rate very similar to the movement of pure water (Environment Canada, 1984). However, typical glycol concentrations used in gas dehydration units are 86 wt% EG, 91 wt% DEG, and 92 wt% TEG (Dow, 1990). Typical concentrations of TREG were not available. The infiltration of these solutions through the vadose zone would be expected to be much slower than that of water and closer to the movement of pure glycol. Because of the high solubility of the glycols, the amount of water that moves through the vadose zone will also significantly affect their movement. Water moving through the vadose zone will dilute the glycol, thereby lowering its viscosity, which will result in an increase in the rate of infiltration. Viscosity would become less important as an attenuation mechanism as the glycol solution moved from the vadose zone across the water table and began to dissolve into the groundwater.

6.2 Summary of the Effects of Physicochemical Properties on Transport and Fate

6.2.1 *Alkanolamines*

The high solubility of alkanolamines in water and their low K_{ow} values suggest that the alkanolamines of interest tend to be mobile in the aqueous phase. The low Henry's law constants and vapor pressure values indicate that the alkanolamines do not readily volatilize, and, therefore, vapor-phase transport, a primary mechanism for transport in the vadose zone, is not expected to be significant. Water moving through the vadose zone will dilute any alkanolamines in the vadose zone, thereby lowering their viscosity and increasing their rate of infiltration. Once in the saturated zone, the miscibility of the alkanolamines suggests that the rate of their transport is likely to be a function of the hydraulic conductivity of the aquifer material and the hydraulic gradient.

6.2.2 *Glycols*

Based on their high solubility in water and their low K_{ow} and K_{oc} values, it is not likely that significant quantities of EG, DEG, or TEG would be adsorbed onto soils or sediments. The values for these parameters indicate that these glycols may be quite mobile and readily transported in the aqueous phase. The low Henry's law constants and vapor pressure values indicate that EG, DEG, and TEG do not readily volatilize, and, therefore, their movement in the vadose zone because of transport in the vapor phase is expected to be minimal. Because of their high solubility, water moving through the vadose zone will dilute the glycols, which will lower their viscosity and increase their rate of infiltration. The high solubilities, coupled with the low partitioning coefficients, lead to the prediction that the rate of transport of the glycols through the saturated zone is primarily a function of the hydraulic conductivity of the saturated aquifer material and the hydraulic gradient. While few physicochemical data exist on which to base predictions on the subsurface transport and fate of TREG, the similarity of its molecular structure to the other glycols and its miscibility indicate that it is likely to behave in a manner similar to the other glycols. The results of three studies of EG behavior in soils and sediments support the transport and fate predictions based on physicochemical characteristics.

Lokke (1984) carried out laboratory experiments that showed that EG in concentrations of 137 and 220 g/L was only slightly adsorbed into a sandy till soil, while a sandy soil and a clayey soil showed no adsorption of EG. The same study indicated that EG closely followed the movements of water in sand and sandy soil. The movement of EG in clayey soil was not examined.

Abdelghani and others (1990) analyzed soils, sediments, and water from areas near bridges in Louisiana where EG was sprayed in deicing operations. The results of these analyses showed that concentrations of EG in all samples were below the detection limit of 1 mg/L. According to the authors, the lack of EG in the samples could be as a result of the small volume (between 10 and 20 gallons per application) of EG applied to the bridges and the high dilution in streams and precipitation runoff. Adsorption and desorption tests were also conducted on five different soils ranging in texture from clay to sandy clay, four from fields near sprayed bridges and one commercial laboratory clay. The results of this study showed that the percent adsorbed ranged from 0 to 0.5 for both sandy clay and clay soils. The sorption study also indicated that neither the concentration of EG nor the total organic carbon (TOC) of the soil had any effect on the adsorption capacity of the tested soils. The results of this study provide insight to the interactions between glycols and soils and sediments, particularly with respect to sorption. The conclusions of this research may be applicable to gas industry sites where spills or leaks occur.

The Airports Authority Group of Transport Canada commissioned a study to examine the potential for groundwater contamination caused by the use of glycol-based aircraft deicing fluids at Ottawa International Airport. Monitor wells were installed adjacent to the airport apron area, where deicing operations are performed. Groundwater samples were analyzed for EG and DEG, both of which are major components of deicing fluids. Significant migration of EG in groundwater was observed at Ottawa International Airport, as peak concentrations were recorded in late June at a site 500 m away from the source (Transport Canada, 1987). EG concentrations decreased as summer progressed, as did concentrations of the EG biodegradation products ethanol and acetaldehyde, until they fell below detection limits in August. The timing suggests a lag period after deicing had ended during which the glycols infiltrated through the sandy soils. The lack of EG in late summer is likely a result of either complete biodegradation or off-site transport by groundwater, though the absence of biodegradation products indicates that off-site transport is more likely.

While the results of this study are noteworthy for their information on the subsurface transport and fate of glycols, it must be pointed out that significant differences exist between the circumstances surrounding the release of glycol from an airport versus a gas dehydration unit.

Glycol concentrations in the deicing fluids are not as high as solutions used in gas dehydration units, and the applicability of the information from the airport study to the transport and fate of highly concentrated glycol solutions may be limited. The annual loading of glycols into the environment at Ottawa International Airport occurs over the course of a 5-month period and involves large volumes of glycol. Releases of glycols into the environment from process waste pits at gas-processing plants would presumably be less intensive over longer periods, while releases from leaks or spills at a dehydration unit would be considerably less in volume and more sporadic. With respect to biodegradation, significant differences also may occur at gas industry sites. Other contaminants can be expected to occur with glycols at gas industry sites, such as alkanolamines and organosulfur compounds, which may be toxic to the microbes that biodegrade glycol. On the other end of the spectrum, such pits may be more conducive to biodegradation, depending on the microbes present and the conditions in the pit.

6.3 Attenuation Mechanisms

The transport and ultimate fate of any contaminant in the environment is determined by processes that are referred to as attenuation processes. Attenuation processes include physical, chemical, and biological processes that generally result in lowering the concentration of a contaminant in groundwater and soil. Table 7 lists the primary attenuation processes that may affect a contaminant in the subsurface.

Many of the attenuation processes listed in Table 7 will not have an effect on the subsurface transport and fate of alkanolamines and glycols because of their physical and chemical properties, which are discussed above. Chemical precipitation of solids from contamination in the liquid state occurs when solubility constraints for the aqueous contaminant species have been exceeded (Harju and Schmit, 1993). Because of the high solubility of the alkanolamines and glycols in water, chemical precipitation and coprecipitation are not expected to occur. The dissolved nature of alkanolamines and glycols will also prevent filtration from being a significant mechanism of attenuation. Vaporization will not be an important attenuation process because of the low vapor pressures and low Henry's law constants that are characteristic of the alkanolamines and glycols. Photolysis, the process by which sunlight causes chemical decomposition, occurs only in the top few millimeters of the land surface (Harju and Schmit, 1993) and, therefore, does not merit attention in this context with its emphasis on the subsurface environment. Neither alkanolamines nor glycols are radioactive, and therefore they will not be subject to attenuation by radioactive decay.

Of the remaining attenuation processes, dilution will obviously play a significant role in the subsurface transport and fate of both the alkanolamines and glycols of interest, as will biodegradation, which has been the focus of a notable amount of research. Ion-exchange reactions, and oxidation may also have a role, but little information concerning the relationship of these processes to alkanolamine and glycol subsurface transport and fate was available.

6.3.1 *Biodegradation*

Microorganisms are ubiquitously distributed in the environment. They have broader capabilities to withstand environmental changes in pH, salinity, oxygen, heat, nutrients, and water than other forms of life. Additionally, virtually every compound that has some energy available in it will be metabolized by a microorganism. A large amount of research has been done which examines the biodegradation of alkanolamines and glycols. That body of research, which will be discussed in detail in the following subsections, comes to the general conclusion that the alkanolamines and glycols used by the gas-processing and conditioning industry are readily biodegradable under a wide variety of conditions. When the effectiveness of biodegradation on the subsurface transport and fate of alkanolamines and glycols is compared with the effectiveness of the other attenuation processes, it becomes obvious that biodegradation stands out as the most significant process at work. With this in mind, it merits particular attention in this context.

TABLE 7

Subsurface Attenuation Processes

Dilution (dispersion and diffusion)	Biotransformation
Chemical Precipitation and Coprecipitation	Sorption
Oxidation–Reduction Reactions	Ion Exchange
Filtration	Photolysis
Volatilization	Hydrolysis
Biodegradation	Radioactive Decay

6.3.1.1 Methodology

Biodegradation rates and processes have been determined by a number of different methods. The method used may be indirect, such as a measure of change in the BOD, or direct, as in the loss of added compound. The implications of the method used can be profound. For example, if an indirect measurement, such as evolution of carbon dioxide (CO_2) is used, the investigator may note a rapid evolution of CO_2 and a final mass balance of, say, 40% of the total found. Analysis by parent compound might determine that very little of the parent compound has been degraded, and the CO_2 found might have been the result of toxic effects on the biomass.

Table 8 summarizes the most frequently used methods of determining biodegradation of a compound. Note that all indirect methods are susceptible to errors because of impurities in the test compound. Frequently, a compound cannot be purchased in purities greater than about 90% (although the alkanolamines and glycols of interest are typically available in purities near 99%). Additionally, many compounds use carrier solvents to solubilize them or additives. For example, pesticides are often mixed with emulsifiers, oils, and detergents. These other compounds may falsely indicate that biodegradation has occurred or overestimate the amount of degradation.

It is important to distinguish between types of biodegradation processes. The test compound added in a biodegradation test may simply be transformed to a slightly different form, without utilization of oxygen, loss of carbon, etc. This transformation may be important since it may

TABLE 8

Methods for Determining Biodegradation
(Zitco, 1984; Painter and King, 1985; Baker and Herson, 1994)

Method	Type	Comments
Biochemical Oxygen Demand (BOD) usually reported as 5-, 10-, or 20-day BOD	Indirect – measures consumption of oxygen over an incubation period	Requires high concentrations of test compounds
Chemical Oxygen Demand (COD)	Indirect – measures amount of oxygen required for chemical oxidation	Requires high concentrations of test compounds
Total Organic Carbon (TOC)	Indirect – measures total soluble carbon	Requires high concentrations of test compounds
Respirometry	Indirect – measures CO_2 evolution	Requires high concentrations of test compounds
Radiorespirometry	Indirect – usually a mass balance of radioactivity from the test compound	Can be performed with low concentrations; allows a mass balance
Electron Acceptors	Indirect – measures concentrations of electron acceptors (i.e., sulfate, methane)	High concentrations of test compounds
Metabolite Concentrations	Indirect – measures release of halogen or other part of the test compound	Medium-to-high concentrations of test compounds
Growth	Indirect – measures changes in turbidity or cell numbers	High concentrations of test compounds
Parent Compound	Direct – analysis of loss of test compound	Medium-to-low concentrations – depends on analytical method

increase or decrease toxicity, but it may also suggest biodegradation if monitoring is only performed by loss of test compound. The complete degradation of a compound to its mineral components (e.g., water, CO_2, ammonia, sulfate) is known as mineralization. A fraction of the test compound is usually converted into cell mass; hence, even a readily degraded compound will not result in 100% degradation based on a measurement such as BOD. Analysis of test compound would, however, indicate complete degradation. Mineralization is the biodegradation process usually assumed and desired in biodegradation testing. However, it cannot be assumed to have occurred without a careful mass balance and chemical analysis.

The inocula used to supply the microbes for biodegradation is very important, both in terms of the numbers of microbes and with respect to the metabolic capabilities of the population. If the metabolic capacity is not known, it is best to acclimate the microbes to the test compound prior to inoculation.

Another important factor to be considered in biodegradation testing is the use of killed microbial populations as controls. These controls allow the separation of biotic and abiotic effects and can be a check on the methods used for estimating biodegradation.

6.3.1.2 Microbial Types

Review of the literature clearly shows that the metabolic capacity to degrade alkanolamines and glycols is widely distributed, although the segment of the microbial population that can degrade these chemicals in an environment without previous exposure is probably very small. The degradation mechanism is, however, inducible, and exposure results in rapid growth of the appropriate population of microbes.

Alkanolamine-Utilizing Microorganisms

The review of the literature indicates that a variety of bacterial genera are capable of biodegrading alkanolamines, including the following: *Achromobacter*, *Arthrobacter*, *Clostridium*, *Enterobacter*, *Erwinia*, *Escherichia*, *Klebsiella*, *Pseudomonas*, and *Salmonella*. Some of these bacteria can grow without oxygen (either by fermentation or by nitrate respiration) or in the presence of oxygen.

Glycol-Utilizing Microorganisms

All glycols used by the gas industry for dehydration, that is EG, DEG, TEG, and TREG, have been observed to be readily biodegradable (Harada and Nagashima, 1975; Kersters and De Ley, 1963). A review of the literature indicates that a wide variety of microbial types have been shown to biodegrade glycols, including acetic acid bacteria, anaerobes, salt-requiring bacteria, and others. Specifically, these microbes include members of the following genera: *Acetobacter*, *Achromobacter*, *Acinetobacter*, *Alcaligenes*, *Bacillus*, *Bacteroides*, *Clostridium*, *Desulfovibrio*, *Flavobacterium*, *Glucobacter*, *Klebsiella*, *Micrococcus*, *Mycobacterium*, *Pseudomonas*, *Sarcina*, and *Xanthomonas*.

6.3.1.3 Pathways

A review of the pathways of biodegradation of alkanolamines and glycols provides information on the biological mechanisms used by microorganisms to biodegrade these chemicals, as well as on the ultimate products of their biodegradation. Such information offers insight into what may be expected to be found in a setting where alkanolamine or glycol biodegradation has occurred, and, thus, what to test for. While many of these pathways were derived from bacteria operating under optimal conditions for biodegradation, such as in an activated sludge reactor where oxygen and nutrients are plentiful, the products produced by the same bacteria in a natural setting can generally be expected to be the same.

Aerobic Alkanolamine Biodegradation

Williams and Calley (1982) reported on the metabolism of DEA and TEA by a gram-negative bacterium. The bacterium used was isolated from an activated sludge reactor treating cutting fluid wastes containing alkanolamines. The bacterium could grow with MEA, DEA, or TEA as the sole carbon source. A biodegradation pathway was proposed based on the identification of intermediate chemical species and the determination of enzyme activities (Figure 4).

Narrod and Jakoby (1964) proposed a pathway of alkanolamine (MEA) biodegradation. They isolated an *Arthrobacter* sp. using enrichment culture. MEA served as the sole source of carbon for this bacterium but was inhibitory at concentrations $>0.15\%$. The initial products of the biodegradation were glycolaldehyde and ammonia. Further reactions convert the glycolaldehyde to glycollate and glyoxylate.

Anaerobic Alkanolamine Biodegradation

The biodegradation of alkanolamines under anaerobic conditions would most likely occur at a slower rate than if oxygen were available. Therefore, in an anaerobic environment the potential for alkanolamines to persist and be transported is greater than that in an aerobic environment. This should be considered when predicting the potential transport and fate of alkanolamines in the subsurface, as many subsurface environments are characterized by anoxia. Even an initially aerobic environment can experience a rapid depletion of oxygen if biodegradation of contaminants is associated with a high oxygen demand, subsequently becoming anaerobic. In such a case, anaerobic degradation processes would become the predominant factor in the persistence of any present alkanolamines.

Bradbeer (1965) conducted investigations with an anaerobic *Clostridium* isolated in earlier work. The *Clostridium* was able to grow on MEA as the sole carbon source. Evidence was presented that showed the MEA was deaminated to ammonia and acetaldehyde. The primary end products of this anaerobic biodegradation were ammonia, acetaldehyde, glycolaldehyde, and hydrogen peroxide (H_2O_2). A pathway that was proposed for anaerobic MEA degradation is shown in Figure 5.

Products of Alkanolamine Biodegradation

Based on data available in the literature, ammonia and CO_2 are the only alkanolamine biodegradation products that would be expected in areas of dilute alkanolamine contamination because of the likelihood of complete biodegradation. High concentrations of alkanolamines in soils and/or groundwater might result in the production of acetaldehyde, ammonia, CO_2, and H_2O_2. Glycolaldehyde may also be found as a biodegradation product, but it may in turn be converted to glycollate and glyoxylate, which are themselves metabolized by a wide variety of microorganisms and, therefore, not likely to accumulate in the environment.

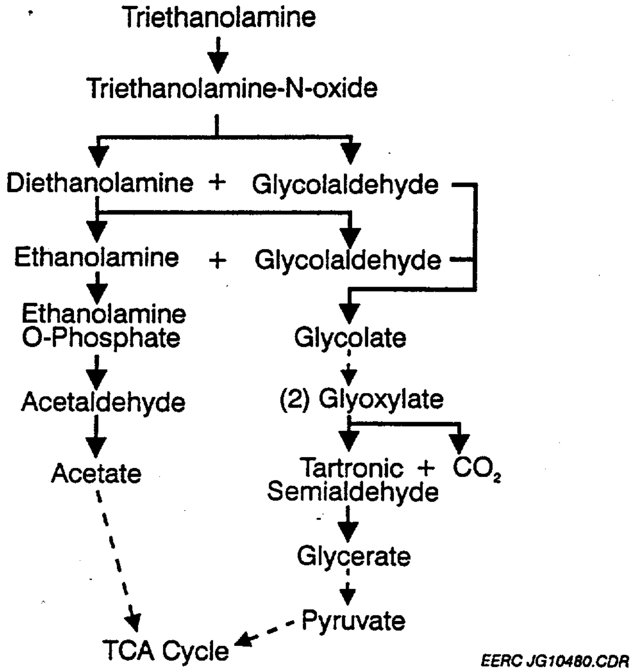


Figure 4. Proposed pathway for the metabolism of the mono-, di-, and triethanolamines by a gram-negative bacterium (after Williams and Calley, 1982).

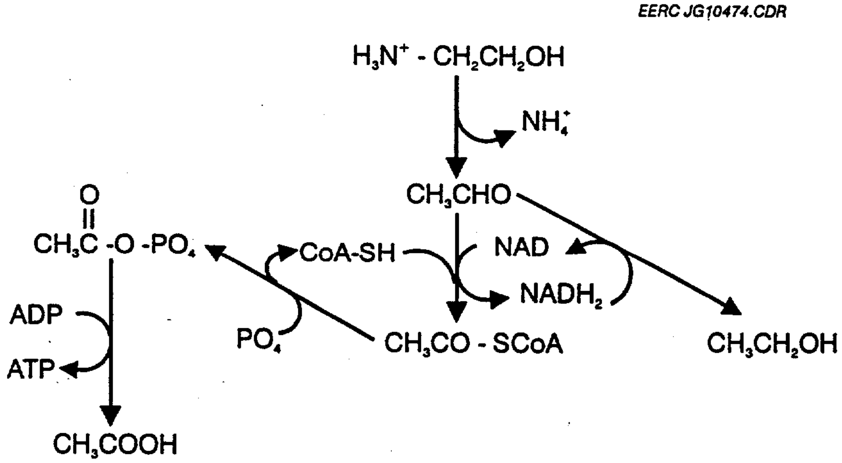


Figure 5. Pathway proposed for ethanolamine biodegradation in a *Clostridium* (after Bradbeer, 1965).

One additional concern that has been expressed with regard to environmental contamination by alkanolamines is the formation of N-nitrosamines. This reaction can occur involving secondary amines (including DEA) and nitrite in natural waters and sewage (Yordy and Alexander, 1981). The ammonia produced by the biodegradation of alkanolamines provides a source of nitrogen for the formation of nitrite, thereby increasing the potential N-nitrosamine formation. These conditions may occur in some gas industry settings. This scenario is worthy of consideration as some N-nitrosamines are carcinogenic, mutagenic, teratogenic, and resist biodegradation (Tate and Alexander, 1976; Yordy and Alexander, 1980).

Aerobic Glycol Biodegradation

Gonzalez and others (1972) suggest that an aerobic EG degradation pathway went from EG to glycerate via glycollate, glyoxylate, and tartronic semialdehyde. Caskey and Tabor (1981) confirmed that the same bacterium degraded EG via the same pathway. Child and Willets (1978) examined aerobic EG biodegradation by a *Flavobacterium* isolated from pond water and enriched with EG. The *Flavobacterium* was found to grow on EG and produce glycollate, glyoxylate, tartronic semialdehyde, and glycerate (Child and Willets, 1978).

Pearce and Heydeman (1980) describe an aerobic EG biodegradation pathway for unspecified bacteria from soil, sewage, and river water. The end products are ethanol, acetate, and traces of acetaldehyde. Willets (1981) examined the effects of oxygen availability on the metabolism of EG by *Flavobacterium* NCIB 11171. Under strongly aerobic conditions, the primary mechanism of EG metabolism was oxidative via EG oxidase to glycollate, glyoxylate, tartronic semialdehyde, glycerate, etc. (see Figure 6). A pathway for EG biodegradation by this bacterium under conditions of low oxygen availability is shown in Figure 7, with acetaldehyde, acetate, and ethanol as the end products.

Harada and Nagashima (1975) observed that bacterium MC11, isolated with ethylene glycol monomethylether, could also grow on EG, DEG, TEG, and TREG, while another unspecified bacterium, isolated with TEG, could also grow on EG, DEG, TEG, and TREG. Bacterium PE18 could grow on TEG and TREG but not on EG or DEG. In addition, these isolates could also grow on glycollate and acetate. The bacteria were all tentatively identified as members of the genus *Alcaligenes*.

The capabilities of the acetic acid bacteria for oxidation of glycols was studied by Kersters and De Ley (1963). They found that *Glucobacter oxydans* (suboxydans) could oxidize a wide variety of glycols, including EG, DEG, and TEG. Resting cells of *G. oxydans* (suboxydans) and *Acetobacter aceti* (liquifaciens) produced glycolic acid from EG.

Anaerobic Glycol Biodegradation

Many studies indicate that glycol biodegradation can also occur under anaerobic conditions. As with the alkanolamines, anoxia may affect glycol degradation rates in groundwater. Aerobic glycol degradation is associated with a high oxygen demand and may result in a rapid depletion of the dissolved oxygen in groundwater, thereby creating anaerobic conditions. Anaerobic biodegradation would then become the dominant process acting on glycols. Anaerobic biodegradation of glycols is generally slower than aerobic biodegradation (Cox, 1978; Kaplan and others, 1982), and, therefore, glycols would be more persistent under anaerobic conditions.

Toraya and others (1979) examined several genera of the bacterial family *Enterobacteriaceae* to determine the mode of metabolism of EG they used under anaerobic conditions. They found that, under those conditions, *Klebsiella pneumoniae* (ATCC 8724) readily metabolized EG. The enzyme involved appeared to be a diol dehydratase using a pathway essentially as described above by Child and Willets (1978).

Eichler and Schink (1985) tested the anaerobic fermentation of several compounds, including EG, with a variety of anaerobic bacteria. The bacterial strains used were isolated from sewage sludge, freshwater mud, and marine sediments. The authors reported that EG was found to be metabolized in the presence of a diol dehydratase enzyme to acetaldehyde, and then to ethanol, acetylphosphate, and other unspecified end products.

Additional anaerobic testing of glycol degradation was done by Dwyer and Tiedje (1986). They identified a *Bacteroides* sp. and *Desulfovibrio desulfuricans* from an anaerobic polyethylene glycol-degrading culture. The *D. desulfuricans* culture could metabolize EG, DEG, TEG, and TREG. The *Bacteroides* culture metabolized DEG, TEG, and TREG.

Products of EG biodegradation by *Flavobacterium* NCIB 11171 (Willets, 1981) and *Clostridium glycolicum* (Gaston and Stadtman, 1963) under anaerobic conditions include acetaldehyde, acetate, and ethanol. Those same compounds and hydrogen were found by Dwyer and Tiedje (1986) as products of the utilization of EG, DEG, TEG, and TREG in an anaerobic environment by *Bacteroides* sp. and *Desulfovibrio desulfuricans*. Dwyer and Tiedje (1983) also observed the production of methane, along with ethanol and acetate, from the biodegradation of EG and DEG by methanogenic consortia. The pathway they suggested is essentially the same as the one described by Wiegant and de Bont (1980) and is shown in Figure 8.

Evidence for anaerobic biodegradation in groundwater has been observed in the field in a shallow aquifer at Ottawa International Airport. High concentrations of iron, which is indicative of reducing (anaerobic) conditions, as well as the presence of ethanol and acetaldehyde, which are known to be the products of anaerobic breakdown of EG, were identified in groundwater at that site (Transport Canada, 1987).

Products of Glycol Biodegradation

The available literature indicates that the most likely products of aerobic biodegradation of EG, DEG, TEG, and TREG to be found in the environment are ethanol, acetate, and acetaldehyde. While there are several other compounds produced by glycol biodegradation (glycollate, glyoxylate, tartronic semialdehyde, and glycerate), these are not likely to accumulate in the environment because of the ease with which they themselves are biodegraded by a wide variety of microorganisms. Anaerobic biodegradation was found to produce the same compounds, as well as methane, when biodegradation was by methanogenic consortia.

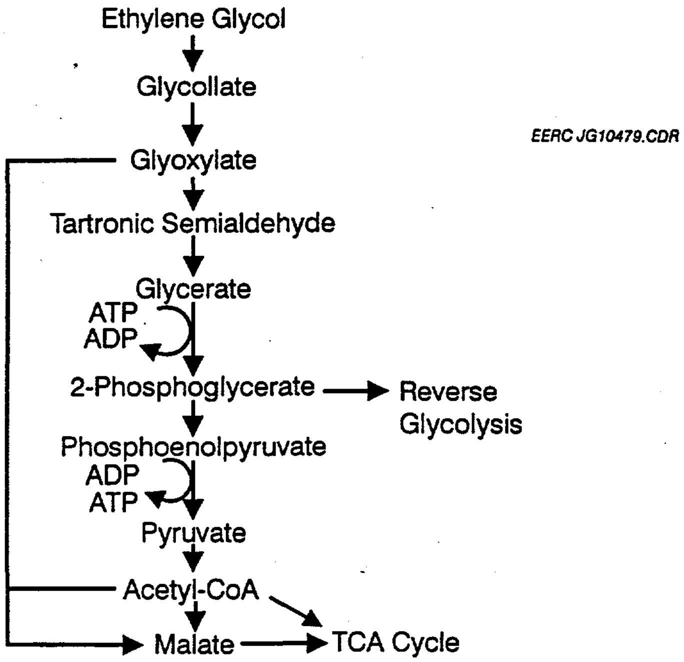


Figure 6. Aerobic metabolism of ethylene glycol by *Flavobacterium* NCIB 11171 primarily uses EG oxidase (after Willets, 1981).

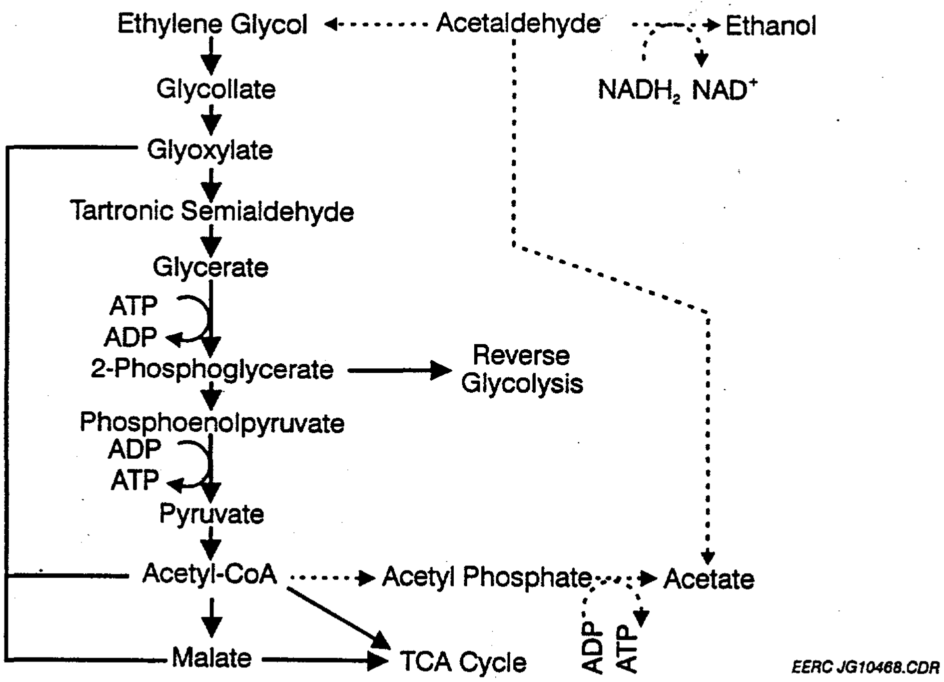


Figure 7. Microaerophilic metabolism of ethylene glycol by *Flavobacterium* NCIB 11171 uses EG dehydratase as the primary enzyme (after Willets, 1981).

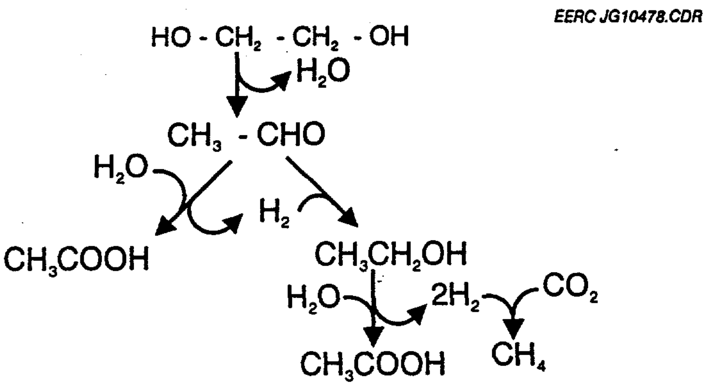


Figure 8. Metabolism of ethylene glycol under anaerobic conditions using a methanogenic consortium (after Dwyer and Tiedje, 1983).

6.3.1.4 Factors Influencing Biodegradation Rates

Studies done on activated sludges, soils, sediments, and natural waters (both groundwaters and surface waters) have demonstrated varying, but generally rapid, rates of biodegradation of the alkanolamines and glycols of interest. The rates of biodegradation of these chemicals vary, depending on the temperature of the environment; the pH of the soil, sediment, or water; their initial concentration; the acclimation status of the local microbial population to the chemicals; the availability of nutrients in the soil, sediments, or water; the availability of oxygen; and the species of microorganisms involved. Section 6.3.1.3 has already addressed the issue of oxygen availability by discussing the aerobic and anaerobic biodegradation of the alkanolamines and glycols of interest. The species of microorganisms that may be involved in the biodegradation of these chemicals are presented in Section 6.3.1.2.

A consideration of the role of these factors is important in developing a soundly based understanding of the biodegradation of the alkanolamines and glycols of interest. The information relating to these factors obtained from the available literature is selective, and many instances exist where pieces of information important for predicting the transport and fate of these chemicals are missing. It is also important to note that most of the available information was primarily generated in laboratory settings, with little or no verification in the field.

Temperature

Lower temperatures will generally decrease the activity of a microbial population, thereby reducing the biodegradation rate. The rate of decrease in activity with temperature will vary from species to species. The effects of varying temperatures on the biodegradation of alkanolamines was not specifically examined in the literature reviewed for this report. However, several workers studied the biodegradation of glycols over a wide range of temperatures, with reduced temperatures leading to overall reduced rates of biodegradation in some, but not all, cases.

As part of an EERC project focused on the subsurface fate of MEA at an AGR plant site in Alberta, Gallagher and others (1995a) examined the biodegradation of MEA in soil/sediment from Alberta at various temperatures. Data from this study indicated that temperature was the most important variable affecting biodegradation. Lag times for the initiation of biodegradation decreased with an increase in temperature, averaging 24 days at 6°C, 9.5 days at 14°C, and 5.3 days at 25°C. Corresponding maximum average degradation rates were 2.37, 4.55, and 6.65 mg of carbon per kg soil per day at 6°, 14°, and 25°C, respectively. Biodegradation rates for MEA were found to increase by a factor of 1.67 for every 10°C increase in temperature (Gallagher and others, 1995a).

Evans and David (1974) studied the biodegradation of EG, DEG, and TEG in river waters at different temperatures. They collected water from four different river sources and tested the biodegradation of the glycols at doses of 0, 2, and 10 mg/L and at temperatures of 4°C (39°F), 8°C (46°F), and 20°C (68°F). The study showed that at 20°C (68°F) EG was completely biodegraded in 3 days in all river waters, while EG in the samples at 4°C (39°F) and 8°C (46°F) required more than 3 days, but less than 14 days, for complete degradation, in spite of some variability between waters. Biodegradation rates obviously slowed at lower temperatures. DEG and TEG degradation at the lowest temperatures was more complex, varying from sample to sample. Biodegradation of DEG and TEG in some river waters was complete in approximately 4 days, regardless of the temperature, while in other samples no significant degradation was observed during the 14-day incubation period. The variability in the DEG and TEG biodegradation may be due to differences in nutrient concentrations in the different river waters.

Klečka and others (1993) found EG to be biodegraded in soil near aircraft deicing operations at all temperatures ranging from −2°C (28°F) to 25°C (77°F), although rates were very low at temperatures below freezing. Average biodegradation rates were 19.7–27.0 mg/kg soil per day at 8°C (46°F) and 66.3–93.3 mg/kg soil per day at 25°C (77°F). Rates observed at −2°C (28°F) ranged from about 2.5 to 4.5 mg/kg soil per day.

McGahey and Bouwer (1992) also found that decreasing the temperature from 25°C (77°F) to 10°C (50°F) for a given soil retarded the rate of EG biodegradation by a factor of 2.44. Even at the reduced temperature, EG removal was >99% in less than 7 days of incubation.

The results of these studies indicate that lower temperatures will generally cause a decrease in the rate of biodegradation of the glycols of interest. Similar effects may be expected for the biodegradation rates of the alkanolamines of interest.

pH

The effect of pH on a microbial population is dependent on the species comprising the population. The ranges of pH within which microbes can thrive varies from species to species. While no studies were located that specifically examined the effect of pH on the biodegradation of either alkanolamines or glycols of interest here, the literature did offer some insight into biodegradation at various pHs.

Sandin and others (1990) reported that the toxicity of DEA to microorganisms was enhanced at high pHs. These data imply that biodegradation may be inhibited in the presence of DEA in high-pH environments. While this study indicates that a relationship may exist between pH and toxicity to microbes, it did not focus specifically on that potential relationship and, therefore, its usefulness in this regard is limited.

Biodegradation of glycols has been observed to occur over a variety of pH. The rate of dehydrogenation of TEG by some microbial populations was measured with respect to pH and found to be fastest at a pH of 8.0, but did occur at more acidic pHs (Fincher and Payne, 1962). Gonzalez and others (1972) observed EG biodegradation at a neutral pH. Jones and Watson (1976) reported on the activities of an *Acinetobacter* sp. that could grow on EG, DEG, and TEG as the sole carbon sources in an environment with a pH as high as 9.8.

Acclimation

Adaptation of the microorganisms to the chemicals present is required before they can utilize these chemicals. Acclimation is of two types. The first requires the induction of enzymes necessary for biodegradation, and acclimation usually occurs within a matter of hours. The second type involves allowing the growth of the biodegrading population to numbers large enough to be measured. The time period for the second type is usually described in terms of days for aerobic microorganisms but may take months for anaerobic microbes. In most cases, both types of acclimation are necessary. The microbial population will not be able to utilize the chemicals until the microorganisms have developed the necessary enzymes. The subsurface transport of a compound can be dependent on the acclimation of a microbial population to the compound. The longer it takes for a population to be able to utilize a compound, the further the distance that compound will be transported in the subsurface. This tendency is especially true for highly soluble and less volatile compounds such as alkanolamines and glycols.

Gallagher and others (1995a) found that acclimation was necessary before significant biodegradation of MEA could occur. Acclimation times for MEA were found to range from about 1 to 34 days, depending on the temperature of the soil and the concentration of MEA.

It can be reasonably assumed that wherever alkanolamines are introduced to an environment that has never been exposed to them, a period of time is likely during which no biodegradation takes place while the microbial population becomes acclimated. While none of the available studies provided data on the lag times associated with acclimation to alkanolamines, Gannon and others (1978) did note that the rates of DEA, MDEA, and TEA biodegradation were faster in an acclimated sewage sludge than in an unacclimated pure culture.

For the glycols of interest, the lag time for acclimation in sludges has been demonstrated to range from several hours to a few days (Hatfield, 1957), and acclimation occurred in a matter of a few days for populations in simulated subsurface environments (McGahey and Bouwer, 1992). In the natural subsurface environment, however, where conditions are likely to be less conducive to biodegradation, it would more likely take a few weeks for the microbial population to become acclimated to the glycols of interest. The differences in times for adaptation are due to the nature of the materials involved. Sludges are generally high in oxygen and high in microbe population, characteristics which facilitate acclimation. Sediments and groundwater, on the other hand, generally have less oxygen available and relatively sparse populations of microbes compared to activated sludges.

The erratic rates of biodegradation observed by Evans and David (1974), and noted above in the discussion of temperature, may be either a reflection of the lag time involved in the acclimation of the microbial population to the DEG and TEG or the lack of the necessary nutrients. This illustrates the point that a variety of conditions can exist under which biodegradation can be inhibited and that such instances of inhibition can be difficult to predict.

Acclimated microbial populations have been shown to biodegrade EG and DEG at high rates. ARCO Chemical Company (1990) performed batch bioreactor tests for degradation of EG and DEG using acclimated biomass. Initial concentrations of 2000 and 2100 mg/L were reduced after 24 hours by 92% and 24%, respectively (as COD).

Effects of Contaminant Levels

Concentrations of contaminants above certain levels can be toxic to the microorganisms involved in their biodegradation. The initiation of biodegradation will be prevented altogether where the initial contaminant concentration is at a toxic level, while ongoing biodegradation can be halted by an increase in contaminant concentration to a toxic level. In both cases, biodegradation will not occur as long as a toxic concentration of the contaminant is maintained. However, as the contaminant moves away from such an area and disperses, the concentrations will decrease until the levels are no longer toxic to microbes. At that point, the remaining microbial population may begin biodegrading the compound, though perhaps after a period of acclimation.

Gallagher and others (1995a) found that concentrations of MEA in soil/sediment equal to or greater than 1500 mg/kg inhibited microbial growth and/or metabolism. Some instances have existed where DEA has been observed to be toxic to microorganisms (Sandin and others, 1990). The toxicity of DEA was found to be such that the authors even suggested its use in high concentrations as an antimicrobial agent in metalworking fluids. Data obtained by Gannon and others (1978), and shown in Table 9, on the inhibition of alkanolamine biodegradation support those findings. DEA was found to be toxic to the microbial population at a concentration of 2000 mg/L, and TEA was found to be toxic at a concentration of 5000 mg/L. Below these concentrations, the alkanolamines studied were described to be nontoxic to the microbes. No data were available on the toxic concentrations of MEA, MDEA, or DIPA.

High concentrations of EG (>500 mg/L) have been shown to be inhibitory to some microbial populations in activated sludge treatment. The principal effects were reduced COD removals and, in the case of sludge experiments, poor sludge settling. McGahey and Bouwer

(1992) showed that increasing EG concentrations, 100, 1000, and 10,000 mg/L, in simulated subsurface environments resulted in decreased biodegradation rates. They found a 13.3-day half-life for the 10,000-mg/L dose, as opposed to a range of 0.35 to 0.92 days for the 100–1000-mg/L dosages. Bieszkiewicz and others (1979) found that concentrations of EG exceeding 1000 mg/L were inhibitory to the treatment of activated sludge. Decreasing COD removals were noted as EG concentrations increased above about 500 mg/L. No data were available on the toxic levels of DEG, TEG, or TREG.

While several studies showed the inhibition of EG biodegradation at concentrations greater than 1000 mg/L, ARCO Chemical Company (1990) performed batch bioreactor tests for biodegradation using initial EG and DEG concentrations of 2000 and 2100 mg/L, respectively, on an acclimated biomass. Despite these relatively high concentrations, no evidence of inhibition due to toxicity was observed since the concentrations (after 24 hours) had been reduced by 92% and 24%, respectively (as COD).

The concentration level at which a particular alkanolamine or glycol becomes toxic to a microbial population is likely to be primarily dependent on the species of the microbes as well as on their acclimation or lack thereof. However, the available literature suggests that, in general, concentrations measured in the thousands of mg/L of either the alkanolamines or glycols of interest could be toxic to microbial populations, and therefore, inhibit biodegradation.

Diauxie

Another phenomenon that may hinder the biodegradation of the alkanolamines and glycols of interest is diauxie. Diauxie occurs when a microorganism is capable of utilizing more than one compound but preferentially utilizes one over another. In an environmental situation where other compounds may be preferred as carbon sources over alkanolamines or glycols, the likelihood is that the alkanolamines and glycols will persist in the system and perhaps might be transported a significant distance before they begin to undergo biodegradation.

TABLE 9

Inhibition and Biodegradation of Some Alkanolamines (Gannon and others, 1978)

Compound	Complete Inhibition[a], mg/L	BOD_5, mg O_2/mg	ThOD[b], %
DEA	2,000	1.48	97.3
MDEA	---	0.70	40.0
TEA	5,000	0.41	22.1

[a] Lowest concentration in which no viable organisms remained after 72 hr.

[b] Percent of theoretical oxygen demand observed.

No incidents of diauxie were noted in the available alkanolamine biodegradation studies, but diauxie was observed in two glycol studies. Gonzalez and others (1972) showed that the presence of glucose in a mixture of EG reduced the metabolism of EG to near zero until the glucose was consumed. Fincher and Payne (1962) found that EG, DEG, and TEG were not utilized by a glycol-consuming bacterium if yeast extract was available. Once the glucose and yeast extract were consumed, then the glycols were readily biodegraded. While no evidence exists of glucose or yeast extract occurring with glycols from natural gas dehydrators, other compounds associated with glycol-containing wastes may be preferentially biodegraded thereby inhibiting the biodegradation of the glycols. The same is probably true for alkanolamines in gas industry wastes.

Key Nutrients

The availability of nutrients to a microbial population is a key factor in determining the rate of biodegradation of a substance. A few studies of alkanolamine and glycol biodegradation illustrate this point. McGahey and Bouwer (1992) suggest that nutrients may affect the rate of glycol degradation in aquifers. The addition of nutrients in a simulated groundwater experiment resulted in a 30% increase in EG metabolism. Omitting the nutrients resulted in a slightly longer lag period and reduced removal rate. Vitamin B_{12}, in particular, was singled out in several papers as being necessary for the biodegradation, by at least a few microorganisms, of both alkanolamines (Chang and Chang, 1975; Scarlett and Turner, 1976) and glycols (Abeles and Lee, 1961; Toraya and others, 1979). These studies indicated that both aerobic and anaerobic metabolizing of at least some alkanolamines and glycols may use an enzyme that requires vitamin B_{12} (cobamide). Vitamin B_{12} is an enzyme cofactor that contains cobalt, introducing the possibility that the initial degradation of alkanolamines and glycols may be limited in environments that are low in cobalt. The erratic rates of DEG and TEG biodegradation in river waters reported by Evans and David (1974) could be caused in part by a lack of such necessary nutrients.

Other Factors

Soil Types. McGahey and Bouwer (1992) examined the biodegradation of EG in simulated subsurface environments. As part of their study, they compared EG biodegradation in two soils: a Mississippi sandy loam and a Texas sandy silt loam. EG concentrations of 100, 1000, and 10,000 mg/L were used. From the data collected, including biomass, EG concentrations, and CO_2 evolution, they were able to calculate first-order kinetic rate constants for biodegradation in the soils. The first-order kinetic rate constants were 1.01 for the Mississippi sandy loam (0.94% organic carbon), and 2.90 for the Texas sandy silt loam (3.25% organic carbon). The authors concluded that the type of soil used for inocula had a clear effect on biodegradation.

Artificial Seawater. Price and others (1974) determined the biodegradability of EG in freshwater and in artificial seawater. Domestic sewage was the seed, and batch tests were conducted using doses of 3, 7, and 10 mg/L. Dissolved oxygen depletion was followed for twenty days. The results, which compare biodegradation in the two waters by showing percent EG biodegradation over time, are presented in Table 10.

The data clearly show that seawater has an inhibitory effect on EG biodegradation; though inhibition is not complete, and biodegradation is still significant in the seawater. The implications of these data may have some relevance to the gas industry. The composition of produced water from natural gas production is often very similar to that of seawater. In fact, the average dissolved solid concentrations in onshore produced water from nonassociated gas are, on the average, significantly higher than typical concentrations for seawater. If such produced water brines should become mixed with glycols in the environment, those brines will probably have an inhibitory effect on the biodegradation of the glycols, though how much of an effect remains to be seen.

Alkanolamines

Studies indicate that biodegradation plays a major role in determining the transport and fate of alkanolamines. The alkanolamines MEA, DEA, MDEA and TEA all appear to be readily biodegraded by adapted aerobic and anaerobic microbial cultures. No information on the biodegradation of DIPA was available. MEA and DEA are degraded more completely, and probably more easily, than MDEA and TEA. Lower temperatures will likely result in lower rates of alkanolamine biodegradation. Inhibition of biodegradation due to high concentrations of alkanolamines has not been observed except when concentrations have been at or near 1500 mg/L or more. Inhibition by DEA may be greater at high pHs. In instances where the microorganisms are acclimated to alkanolamines, and the soil temperatures are favorable, it is quite possible that a significant portion of an alkanolamine released to the environment may be biodegraded before it reaches the water table. However, a lack of nutrients in the soil, especially vitamin B_{12}, or diauxie may prevent or delay the biodegradation. The prevention or delay of biodegradation will allow the alkanolamines to be further transported in the subsurface.

TABLE 10

Biodegradation of EG in Freshwater and Synthetic Seawater (Price and others, 1974)

	Freshwater, % Biodegraded	Seawater, % Biodegraded
Day 5	34	20
Day 10	86	60
Day 15	92	65
Day 20	100	77

6.3.1.5 Summary of Alkanolamine and Glycol Biodegradation

Some useful work has been done on the biodegradation of alkanolamines in wastewater, sludges, soils, and sediments. However, additional systematic laboratory and field studies on the biodegradation of alkanolamines in natural waters, soils, and sediments are critically necessary before reliable predictions can be made on the full impact of biodegradation on the transport and fate of these chemicals in the subsurface.

Glycols

Studies have been done on activated sludges, soils, and natural waters (ground and surface waters) that demonstrate the biodegradability of gas processing/conditioning glycols. While the results from a study of biodegradation in an activated sludge or sewage might not be completely applicable to predicting the biodegradability of glycols in a typical gas industry setting, such data do provide information on their potential biodegradability and, therefore, their potential for persistence and transport within the subsurface. More applicable data were found in a few studies performed on natural waters (river and groundwater), simulated seawater, soils, and sediments. These studies indicate that the gas dehydrator glycols are readily biodegradable by a wide variety of microbial organisms in a variety of soils over wide ranges of glycol concentrations and temperature. The studies showed that under laboratory conditions using acclimated microbial populations in nutrient-rich soil, glycols were biodegraded in a matter of days or, at most, weeks. The time for biodegradation to occur in the natural subsurface, where conditions are not likely to be as optimal, could be significantly longer.

Generally speaking, the high biodegradability of the glycols indicates that they are not likely to be persistent in the environment. In fact, biodegradation has been used by Flathman and others (1989) to remediate groundwater that had been contaminated by EG. However, some factors that may inhibit the biodegradation of glycols include oxygen availability, cold temperatures, toxic effects due to concentrations of glycol greater than 1000 mg/L, unacclimated microbial populations, a lack of the necessary nutrients, and diauxie. The introduction of produced water brines to the system is another inhibitory factor that may be of particular concern to the biodegradation of glycols at gas dehydration sites. The inhibition of biodegradation by any of the above factors will favor the persistence of glycols in the subsurface.

Based on the knowledge available at present, it appears that biodegradation is the most significant process influencing the fate of EG, DEG, and TEG in the subsurface, although it appears to occur more slowly than in aerobic surface waters. Degradation rates of EG in groundwater have been predicted to be about half those observed in surface waters (Syracuse Research Corp., 1989). Jerger and Flathman (1990) found that up to 93% of the EG (initial concentration of 1440 mg/L) in contaminated groundwater was degraded in 26 days, which indicates a half-life of about 9 days.

6.3.2 *Dilution*

The dispersion and diffusion of a compound in water is referred to as dilution, which results in the lowering of that compound's concentration. The dilution process typically occurs at a much slower rate in the subsurface environment than it does in surface water. This tendency is because of the more convoluted pathways of dispersion and diffusion that the molecules of a contaminant must take because of the presence of soil/sediment grains, as well as whatever sorption occurs between the contaminant and the grains. It is important to note that while dilution reduces the point concentration of a contaminant in the subsurface, it also acts as a transport mechanism, increasing the area of contamination by means of contaminant movement.

Dilution may play a significant role in the transport and fate of alkanolamines and glycols. The high water solubilities of these compounds suggest that they may be readily dissolved and diffused in subsurface water. The diffusivity coefficients in water for EG and TEG are further evidence for the effectiveness of dilution on glycols. In a scenario where water is readily available in the subsurface (e.g., shallow depth to water table or high rainfall), the process of dilution will cause the alkanolamines and glycols to disperse away from the point source of contamination. The contaminant concentrations will decrease as dilution moves the compound further from the point source, leading to a significant decrease in concentration with increased distance away from the source of contamination. This effect can have a significant impact on biodegradation. High concentrations of a chemical may be toxic to the microbial population, and biodegradation may not be able to occur until high initial concentrations of a chemical have been lowered by dilution. However, a negative effect of dilution with regard to alkanolamines and glycols is that diffusion will act as a transport mechanism. Diffusion may be the primary transport mechanism in subsurface areas where water movement is stagnant, such as in clays. This phenomena has been demonstrated in percolation experiments involving high concentrations of glycol in clayey soils, where EG was observed moving into areas of stagnant water in the soil column because of diffusion (Lokke, 1984).

6.3.3 *Sorption*

Adsorption (assimilation by a surface) and absorption (assimilation into a structure) are collectively referred to as sorption and are partially dependent on the hydrophobicity (tendency not to dissolve in water) of compounds. The high solubilities of the alkanolamines in water and their low K_{ow} values suggest that they are not likely to be attenuated by sorption processes. However, recent data indicate that adsorption may be a significant attenuation process for at least one alkanolamine. Gallagher and others (1995b) examined the adsorption of MEA in soil/sediment ranging in pH from 6.5 to 8.5. The distribution coefficients (K_d values) reported by Gallagher and others (1995b) for MEA indicate that adsorption of MEA onto soil/sediment may occur under the pH conditions examined. The K_d results for MEA in soil/sediment under the examined pH conditions ranged from 3.61 to 2.64, which fall within the low mobility class ($2 < K_d < 10$) as defined by Dragun (1988) and thereby indicate a tendency for MEA to be adsorbed under typical subsurface pH conditions. Gallagher and others, (1995b) also reported, however, that kinetic experiments performed at a pH of 9.4 as part of their work indicate that at that pH or greater the K_d values for MEA are less than 1. Thus at very high pH, MEA would not be expected to be adsorbed onto soil/sediment. Considering the high basicity of MEA, a plume of highly concentrated MEA could theoretically raise the pH of the subsurface such that MEA is highly mobile. It is important to note that the data reported by Gallagher and others (1995b) is preliminary, and that more research focused on the sorptive tendencies of alkanolamines is required to properly assess the effectiveness of sorption as an attenuation mechanism for alkanolamines.

The high solubilities of the glycols in water, as well as their low K_{ow} and K_{oc} values, indicate that they are not likely to be attenuated by sorption processes. However, while the physicochemical characteristics of the glycols of interest suggest that adsorption will not be a significant attenuation mechanism, it is important to note that there may be some conditions under which it may occur. For instance, if the pH of the subsurface system is sufficiently high (perhaps due to hydrolysis), the hydroxyl groups associated with some organic chemicals, such as glycols, may dissociate and acquire a negative charge. After the negatively charge molecules are formed, they may be adsorbed by surfaces that possess a positive charge that can absorb organic ions by ionic exchange. However, it is important to note that soils typically have more negative than positive surface charges. The negatively charged soil surfaces will repulse the negatively charged organic anions, resulting in a net decrease in adsorption that yields an increase in mobility (Dragun, 1988). Based on this information, this mechanism of adsorption would be expected to exert, at the most, only a minor effect on the glycols of interest.

6.3.4 *Ion-exchange Reactions*

Ion-exchange reactions involve the replacement of ions in a solid structure with the ions of a dissolved compound. These reactions often occur in the subsurface environment and are highly dependent on the site-specific variables such as temperature, pH, chemical and physical characteristics of the subsurface media, and the nature of the contaminant of interest. This attenuation process is typically more important for inorganic species, though ion-exchange reactions can exert a pronounced effect on some organic species following hydrolysis or other reactions that result in the contaminant species being charged (Harju and Schmit, 1993).

6.3.5 *Oxidation*

Reactions where the transfer of electrons occurs are referred to as oxidation–reduction reactions. Biological activity often mediates these reactions, particularly oxidation. The mobilities of compounds in the subsurface may be either enhanced or inhibited by oxidation or reduction, depending on the physical and chemical properties of the oxidation or reduction reaction products (Harju and Schmit, 1993).

No information on the abiotic oxidation of alkanolamines or glycols in the environment was available. In the AGR and dehydration processes, the alkanolamines and glycols are known to undergo oxidation reactions in situations where oxygen is present. However, the temperatures and pressures in the process units are much higher than would normally be found in a soil or groundwater environment, and it is apparently these high temperatures and pressures that facilitate oxidation. With this in mind, it is still possible, but not likely, that abiotic oxidation may be an attenuation process for alkanolamines and glycols in subsurface environments where oxygen is available.

6.4 Transport and Fate Discussion

6.4.1 *Effects of Physicochemical Properties and Attenuation Mechanisms*

The physical and chemical properties of both the alkanolamines and glycols suggest that they would be highly mobile in the subsurface environment because of their low vapor pressures, low Henry's law constants, high solubilities, low partitioning coefficients, and high diffusivity coefficients in water. The vapor pressure and Henry's law constants suggest that the alkanolamines and glycols are not likely to volatilize and, therefore, be transported in the vapor phase. The high solubilities of both alkanolamines and glycols indicate that they would easily and quickly dissolve in water, and thereby lose the higher viscosities that characterize both groups of compounds at high concentrations. Low partitioning coefficient (K_{oc} and K_{ow}) values suggest that neither alkanolamines nor glycols are likely to adsorb to soil or sediment. This was shown to be true for EG in laboratory soil experiments by Lokke (1984) and Abdelghani and others (1990). Alkanolamines and glycols are likely to diffuse easily in water according to their high diffusivity coefficients in water. These properties lead to the conclusion that the alkanolamines and glycols used for natural gas processing/conditioning may be highly mobile in the subsurface environment, especially groundwater.

Biodegradation is the primary attenuation mechanism for the alkanolamines and glycols used for gas processing/conditioning. Both the alkanolamines and glycols appear to be readily biodegradable by a wide variety of organisms under a wide variety of conditions in both aerobic and anaerobic environments. Both groups of compounds have been shown to have the potential to undergo rapid and complete biodegradation. Rates of biodegradation have been observed in the laboratory that indicate complete biodegradation occurring as quickly as days or weeks. However, many factors exist that may inhibit biodegradation in the field. Low temperatures have been shown to lower the rates of biodegradation. In many cases, the microbial population must become acclimated to a compound before it can begin biodegradation. High concentrations of alkanolamines and glycols may be toxic to some microbial populations, thereby preventing biodegradation until such levels fall. The presence of nutrients, such as vitamin B_{12}, is essential. Diauxie may occur, whereby another compound that is present in the soil or groundwater along with the alkanolamine or glycol, is preferentially utilized by the microbial population until that compound is completely gone.

Dilution will be a significant factor in the transport and fate of the gas industry alkanolamines and glycols and will likely be the primary attenuation mechanism under circumstances where biodegradation is inhibited. Adsorption may be an effective attenuation mechanism for alkanolamines under certain conditions, but the degree to which it is effective has yet to be determined. Adsorption is not expected to be an effective attenuation mechanism for glycols. Hydrolysis, ion exchange, and perhaps oxidation, are other attenuation processes that may have an effect on the subsurface transport and fate of the alkanolamines and glycols. These attenuation processes are expected to have minor-to-inconsequential roles in directly determining the transport and fate of the contaminants of interest. These processes can, however, exert significant influences over the effectiveness of biodegradation, thereby indirectly affecting the attenuation of the alkanolamines and glycols.

In general, the alkanolamines and glycols used by the natural gas industry are probably not long-term problems at sites where they have been introduced into the subsurface environment, as over time (a few months to a few years), they are expected to biodegrade and/or dilute toward innocuous levels. However, in a situation where the hydrogeologic conditions are favorable for transport (shallow depth to water table, high transmissivity of the aquifer material), and the environmental conditions are such that biodegradation is inhibited, then dilution would be the primary attenuation mechanism at work, and the alkanolamines and glycols of interest could be transported significant distances.

Some alkanolamine and glycol process reaction products, though present in much lower concentrations, may be nonbiodegradable and, therefore, tend to persist in the environment. Unfortunately, little is known about the biodegradability of many alkanolamine and glycol process reaction products (see Table 2 for list of these compounds). As far as the transport and fate of the process reaction products are concerned, with little to no knowledge of their physicochemical properties or their relationship to the attenuation mechanisms, particularly biodegradation, it is difficult to predict how they will be affected by the processes that determine transport and fate.

6.4.2 *Cosolvency Effects of Alkanolamines and Glycols*

So far, the discussion of the behavior of alkanolamines and glycols in the subsurface has, for the most part, focused on the chemodynamics of single compounds in water. However, in the real world, a release of contaminants into the environment will rarely consist of a single compound and water. As discussed above in Section 4.1, many of the alkanolamines and glycols used for the processing of natural gas that have been released to the environment have been done so via waste pits, ponds, and landfills (Hardisty and others, 1990). These point sources normally consist of a complex mixture of chemicals related directly and indirectly to the gas-processing industry. The transport and fate of contaminants associated with AGR and dehydration wastes, as well as those not associated with these wastes but which may coincidently occur in the same subsurface environment, will be determined not only by the various attenuation mechanisms discussed above but also by the effect of cosolvents. In examining cases where a complex mixture of chemicals may be involved in a release to the environment, it is important to address the issue of cosolvency.

Cosolvency is the effect of completely miscible and/or partially miscible organic solvents on the solubility and sorption of hydrophobic organic chemicals (Rao and others, 1990). As the concentrations of organic cosolvents increase, sorption will decrease, and organic contaminants are therefore likely to be present at higher concentrations in pore water. Consequently, transport of the organic contaminants would be greater than predicted by a strictly aqueous-based transport model (Rao and others, 1991).

The alkanolamines and glycols used by the gas industry may be categorized as being completely miscible organic solvents (CMOS). As described in Sections 3.0, 4.0, and 6.0, both gas-sweetening and dehydration wastes include a wide variety of compounds besides alkanolamines and glycols. In a simple aqueous-based transport model, some of these compounds may have a tendency to adsorb to soil and be expected to move slowly through the subsurface. However, the principles of cosolvency indicate that the presence of CMOS, such as alkanolamines and glycols, may increase the solubility and decrease the sorption of other waste compounds, thereby facilitating their transport beyond that previously predicted. In this sense, the subsurface behavior and persistence of alkanolamines and glycols may also have a direct impact on the transport and fate of other, more toxic, compounds.

Glycols have been detected in the sludges of brine treatment tanks at natural gas processing/conditioning facilities that use glycol dehydration units (Myerski and others, 1993). The significance of finding glycols mixed with the contents of a brine treatment tank is that the glycols might act as a cosolvent for compounds in the sludges that might otherwise have low solubilities. If the glycols act as a cosolvent, then the potential for those compounds to become mobile in the subsurface upon exposure to the environment will increase.

7.0 TOXICOLOGY

Once a release of AGR or gas dehydration contaminants is determined to be in the subsurface environment, an increasingly important aspect of determining the corrective action necessary for dealing with the contamination is to undertake a risk assessment of the site. A key part of that risk assessment is determination of the toxicity of the substances involved to humans and other organisms in the potentially affected environment. The toxicity determination includes considerations of nonlethal exposure effects; lethal exposure effects, both chronic and acute; and long-term effects such as carcinogenicity, mutagenicity, and teratogenicity. Toxicological effects are typically described in terms of lethal concentration (LC), lethal dose (LD), effective concentration (EC), and lowest-observed-adverse-effect level (LOAEL).

Lethal concentration$_{(LO)}$ (LC_{LO}) is defined as the lowest concentration of a chemical in air that has been reported to cause death in humans or animals. The LC_{50} is the calculated concentration to which exposure for a specific length of time is expected to cause death in 50% of an experimental animal population (Clement International Corporation, 1993).

The lethal dose$_{(LO)}$ (LD_{LO}) is the lowest dose of a chemical introduced through a pathway other than inhalation (i.e., ingestion or dermal contact) that is expected to have caused death in humans or animals. The LD_{50} is the dose calculated to cause death in 50% of an experimental animal population (Clement International Corporation, 1993).

The effective concentration$_{(LO)}$ (EC_{LO}) is defined as the lowest concentration of a chemical that causes a noted effect in humans or animals. The effect a researcher is looking for must be defined prior to the test for EC. The EC_{50} is the concentration calculated to cause 50% of an experimental animal population to display the predefined effects (Kallow, 1995).

Another term used in describing toxicological effects is the LOAEL. This level is the lowest dose of a chemical that produces statistically or biologically significant increases in frequency or severity of adverse effects between an exposed population and its control. If no adverse effects are produced at this level, the level is called a no-observed-adverse-effect level (NOAEL) (Clement International Corporation, 1993).

Acute and chronic toxicological effects are often used to measure the potential hazards of a particular chemical to humans. Acute toxicity (short-term) studies are used for several purposes: 1) to provide information on effects of different exposure routes (i.e., inhalation, ingestion, or dermal contact); 2) to compare substances having different mechanisms and sites of action; 3) to estimate the effects of chronic exposures to low concentrations of chemicals; and 4) to determine local effects of chemicals on the skin or in the eyes (Air Force Institute of Technology, 1985). Data on acute toxic symptoms and effects of many chemicals on humans and laboratory animals are readily available, especially acute LD_{50} values. Large LD_{50} values indicate low acute toxicity, and small values indicate a potent chemical (Air Force Institute of Technology, 1985).

Chronic toxic effects are changes resulting from intermittent or continual exposure to low concentrations of a chemical. Symptoms of chronic exposure include detectable impairments in functional capacity (pathological, physiological, biochemical, or behavioral) as well as the inability to maintain homeostasis. Because most human exposures to chemicals are long-term exposures to low concentrations, chronic toxicity studies are particularly valuable (Air Force Institute of Technology, 1985).

Toxicological assessments also involve the determination of carcinogenicity, mutagenicity, and teratogenicity. Carcinogenicity is the inherent characteristic of a chemical to cause cancer. Carcinogenesis is a biological process involving the unrestrained growth of daughter cells that were altered by one or more events in which the DNA or other cellular regulatory mechanisms were modified (Air Force Institute of Technology, 1985).

Mutagenicity is the ability of a chemical to cause stable and heritable changes in cells or organisms. These changes can range from base DNA modifications, which result in point mutations in a single gene, through major structural or numerical chromosomal changes that may involve entire sets of genes or chromosomes (Air Force Institute of Technology, 1985).

Teratogenicity describes the lethality of a chemical to an embryo. Teratogenic effects are complex and difficult to differentiate from one type of effect to another. Embryonic reactions to a particular chemical depend on metabolic differences, excretion rates, placental variations, age of mother, and nutritional status. The dose, route, and the point in gestation time at which the embryo is exposed are also important factors in determining the teratogenicity of a chemical to a species (Air Force Institute of Technology, 1985).

7.1 Alkanolamines

Very little information exists regarding the toxic effects of alkanolamines on humans and other organisms in the environment. The following information provided for MEA, DEA, TEA, and MDEA is based on LD_{50}, LC_{50}, and EC_{50} values. Because of the lack of available information, no NOAELs or LOAELs have been reported for the alkanolamines. No information about the toxicity of DIPA was available.

7.1.1 *MEA*

MEA may cause severe eye irritation with corneal injury, which may result in blindness. Moreover, it is considered corrosive under DOT classification and may cause burns on the skin after only a short, single exposure. The LD_{50} for skin absorption in rabbits is reported as approximately 1000 mg/kg. The LD_{50} for single-dose oral toxicity in rats is low, between 1720 and 2740 mg/kg. Other LD_{50} values for different mammals and exposures can be found in Table 11. Ingestion may cause gastrointestinal irritation or ulceration and burns to the mouth and throat. A single, prolonged, excessive inhalation exposure may cause respiratory irritation and liver and kidney injury in a matter of hours (Dow Chemical Company, 1991). The Committee on Amines for the National Research Council found MEA to be weakly toxic to mammals. No LD_{50}s were observed at levels <700 mg/kg for any species studied for any route of administration (National Academy Press, 1981).

Potential chronic effects from repeated exposures include liver and kidney injury. Lethargy may also be a symptom of excessive exposure. MEA has been reported to cause birth defects in rats following oral ingestion; however, inadequate information exists to confirm this. Results of in

TABLE 11

LD_{50} Values[1] of Alkanolamine Exposures

	MEA	DEA	MDEA	TEA
Rabbits oral	1000			2200
Rabbits, dermal	1000	12,000	>2000	
Rats, oral	1720-2740	710-1820	2000-3980	8680
Rats, dermal				2000
Mice, oral	700			7400

[1] Values in mg/kg.

vitro mutagenicity tests have been negative (Dow Chemical Company, 1991). No information was available regarding the potential carcinogenicity of MEA.

Toxicity work is currently being done for risk assessment at a contaminated sour gas processing site where one of the subsurface contaminants has been identified as MEA. The results of this work may provide significant insight to the toxicity of MEA at concentrations found in the subsurface environment (Environmental Management Associates, 1994).

7.1.2 *DEA*

DEA may cause severe irritation with corneal injury. Although DEA is considered noncorrosive under the U.S. Department of Transportation (DOT) classification, it may result in skin irritation as a result of prolonged or repeated exposure. The LD_{50} for skin absorption in rabbits is reported as approximately 12,000 mg/kg. The LD_{50} for single-dose oral toxicity in rats is low, between 710 and 1820 mg/kg. At room temperature, exposures to DEA vapors are uncommon because of its low vapor pressure; however, at higher temperatures, vapor levels may be sufficient to cause irritation and other effects. Excessive exposure may cause liver and kidney injury (Dow Chemical Company, 1990). The National Research Council's Committee on Amines found DEA to be weakly toxic to mammals. No LD_{50}s were observed at levels <700 mg/kg for any species studied for any route of administration (National Academy Press, 1981).

Chronic effects associated with repeated exposures to DEA include anemia (as seen in rats) and chronic effects on kidneys (rats and mice), livers (mice), hearts, and nervous systems (exaggerated doses in rats and mice). Results of in vitro mutagenicity tests have been negative (Dow Chemical Company, 1990). Information on DEA carcinogenicity or teratogenicity was not available.

7.1.3 *MDEA*

MDEA may cause severe eye irritation and result in skin irritation after prolonged or repeated exposure. The LD_{50} for absorption in rabbits is >2000 mg/kg. The oral LD_{50} for rats ranges from 2000 to 3980 mg/kg. Ingestion may cause gastrointestinal irritation or ulceration and may cause irritation of mouth and throat. Excessive inhalation may cause irritation to the upper respiratory tract (Dow Chemical Company, 1993).

7.1.4 *TEA*

TEA inhalation is not considered hazardous unless it is sprayed or heated. Vapors are irritating to the eyes and upper respiratory tract. Prolonged or repeated skin contact can be moderately to highly irritating, but does not seem to present a significant hazard under reasonable industrial conditions. Ingestion of TEA can cause irritation to the mouth, throat, and the gastrointestinal tract, resulting in nausea, vomiting, and abdominal pain. The Committee on Amines for the National Research Council reports TEA to be weakly toxic to mammals. No LD_{50}s were observed at levels <700 mg/kg for any species studied for any route of exposure (National Academy Press, 1981). TEA has been shown to cause liver and kidney damage in laboratory animals (Genium Publishing Corporation, 1986).

7.1.5 *Amine Reaction Products*

Alkanolamine reaction products are of potential concern with respect to their toxicity. Unfortunately, little information exists regarding the toxicity of these substances. Of the potential degradation products, described in Section 3.0, at least one (HEED) is considered toxic. HEM and possibly OX have been reported to be animal carcinogens (Skinner and others, 1995).

Ammonia and nitrates present as the result of alkanolamine degradation are also of concern in this regard. LC_{50} values for ammonia generally fall in the range of 1–10 mg/L, indicating that the acute toxicity of ammonia to aquatic life is relatively high. Excessive exposure of humans to nitrates impairs the ability of blood hemoglobin to transport oxygen. In infants, this condition has been given the name blue baby syndrome, also known as methemoglobinemia (Sills and Blakeslee, 1992).

It is possible that aliphatic alkanolamines used in AGR processes or produced as a result of degradation can be nitrosated to nitrosamines. Some nitrosamines have been suspected of being genotoxic with a potential for mutagenicity, teratogenicity, and carcinogenicity, producing acute and long-term toxic effects. Some nitrosamines have been identified as potent carcinogens, the ingestion of which in food and water has been determined to present health hazards (National Academy Press, 1981).

TEA may be converted by nitrosating agents to N-nitrosodiethanolamine (NDEA), which has been identified as a weak carcinogen, inducing tumors in rats and hamsters. It is suspected specifically of causing stomach and esophageal cancer. NDEA has also been shown to be absorbed through the skin of humans and rats (National Academy Press, 1981).

7.1.6 *Toxicity Identification Evaluation*

A study was conducted in Canada to determine the toxicity of wastewater pond sludge from sour gas plants using MEA and DEA for sweetening. The sludge samples were centrifuged, separating the centrifugate from the dewatered sludge, which was then extracted with water to generate a leachate. The centrifugate and the sludge leachate were analyzed using the toxicity identification evaluation (TIE) procedure, which involves chemical and physical manipulation of samples followed by aquatic toxicity testing to verify the presence of acute toxicity. The aquatic toxicity tests used in this study were *Daphnia magna* and Microtox (Enviro-test Laboratories, 1992).

Results from the MEA-using plant showed the raw centrifugate to be very toxic with the *Daphnia* (LC_{50} 0.8%-1.8%) and Microtox (EC_{50} 0.73%-1.4%) tests. Filtering the centrifugate rendered the same sample virtually nontoxic (EC_{50} 47%-60%). The leachate from the dewatered sludge was found to be relatively nontoxic (EC_{50} 91%-100%) as well (Enviro-test Laboratories, 1992).

Toxicity tests results for the DEA-using plant showed the raw centrifugate to be extremely toxic with the *Daphnia* (LC_{50} 0.53 ±/-0.67%) and the Microtox (EC_{50} 0.08 ±/-0.02%). As in the case with the MEA-using plant, filtration of this sample reduced the toxicity by factors of 6- to -12 fold, under a pH of 3. For tests conducted under pH 6.2 and 11.0 conditions, filtration reduced the toxicity of the raw centrifugate by 12- to -16 fold and 57- to -59 fold, respectively. The toxicity test results for the dewatered sludge leachate suggested that the leachate was slightly toxic; however, the toxicities are 430-fold less toxic than the centrifugate (Enviro-test Laboratories, 1992).

Results from further chemical analyses showed that the most toxic compounds were removed by elution with 100% methanol. Gas chromatography identified the major components of the contaminated methanol as sulfur-containing polycyclic aromatic hydrocarbons, i.e., substituted dibenzothiophenes (Enviro-test Laboratories, 1992).

7.2 Glycols

A significant amount of information regarding the toxic effects of the glycols and their biodegradation products to humans and a broad variety of organisms was reviewed. The effects of these chemicals on aquatic fauna are discussed here because groundwater systems typically feed streams, lakes, and wetlands, and therefore, may act as conduits for the delivery of subsurface contaminants to aquatic ecosystems. In this context, the toxicities of these chemicals to aquatic fauna are important.

7.2.1 *EG*

In humans, EG does not seem to present a significant hazard from the inhalation of vapors at room temperatures or from skin or oral contact under reasonable industrial conditions. However, an industrial inhalation hazard could be generated if EG was heated or vigorously agitated or if appreciable skin contact or ingestion occurred over a period of time. EG is considered to be very toxic in particulate form upon inhalation (Hazard Data Bank, 1985). The American Conference of

Governmental Industrial Hygienists (ACGIH) recommended value for EG aerosol and vapor exposure is 100 mg/m^3 and 125 mg/m^3, respectively. The lowest published LD_{LO} for human toxicity by inhalation is reported at 10,000 mg/m^3 (Abdelghani and others, 1990). Ingestion of EG usually manifests itself with symptoms of alcohol intoxication, with drowsiness and mental confusion. More severe symptoms include a severe headache, vomiting, muscle spasms, shortness of breath due to congestion of the lungs, unconsciousness, and convulsions. Subsequent kidney failure may stop the urine flow (Hazard Data Bank, 1985).

Abdelghani and others (1990) looked at crawfish that were exposed to increasing concentrations of EG for the purposes of studying bioaccumulation and its possible health effects on humans. It was found that the tissues did not concentrate EG to levels higher than the concentration in the water. This study showed that the amounts of EG accumulated in edible crawfish tissues do not pose an acute health hazard to humans. It was determined that a human would have to consume approximately 63,900 contaminated crawfish at one time to be affected by EG. This finding was based on a worst-case situation in which the crawfish were continuously exposed to 1000 mg/L EG (Abdelghani and others, 1990).

EG has been the cause of a number of deaths due to either accidental or intentional poisoning. The minimal lethal dose of EG for humans has been estimated at 100 mL; although individuals have survived ingestion of 240 mL (Winek and others, 1978). Another estimate of the minimum lethal dose for adults has been reported as 1.4 mL/kg of 95% EG. Although EG is considered to have a low toxicity rating, it is metabolized to a variety of toxic chemicals, including glycolaldehyde, glycolic acid, glyoxylic acid, and oxalic acid. The deposition of oxalate crystals has been linked with cerebral and renal damage (Godolphin and others, 1980).

EG has been reported to be teratogenic in experimental animals, but is not carcinogenic or mutagenic in humans. The available literature provided no information regarding the teratogenicity of EG to humans.

Limited data are available for acute and chronic toxicity of EG to marine and estuarine fish species. Acute toxicity effects on three species of marine and estuarine invertebrates suggest that these species are relatively insensitive to EG, responding only to high concentrations. However, data from longer-term studies show that 7- to 28-day exposure of adult sand worms (*Ophryotrocha labronica*) resulted in extreme mortality (80% to > 95%). A 10-day exposure of 557 mg/L and 55.7 mg/L resulted in a 50% and 20% mortality rate, respectively. The EG concentrations of 55.7 mg/L represents the LOAEL for marine and estuarine organisms (MacDonald and others, 1992). Data on the toxicity of EG to freshwater fauna were presented by Abdelghani and others (1989), who reported that acute toxicity studies determined a 96-hour LC_{50} for crawfish and bluegill sunfish to be 91,430 mg/L and 27,540 mg/L, respectively. The LC_{50}s for soil microorganisms were also determined in this study, by the Bauer assay method, to be around 114,300 mg/L.

7.2.2 *DEG*

Browning (1965) reports that DEG is less toxic than EG, but more toxic than TEG. As with EG, its hazard lies in its pathway of ingestion. In humans and animals, DEG is a depressant in the central nervous system and produces changes in the kidney and urinary tract that are similar to those caused by EG (Browning, 1965). A LOAEL of 1700 mg/L was reported for DEG, which was the concentration that caused a reduction in the population growth of the blue-green alga, *Anacystis aeruginosa* (MacDonald and others, 1992). In animal studies, the toxicity of DEG to one salt-tolerant invertebrate species, brine shrimp nauplii, was found to occur for concentrations greater than 10,000 mg/L for a 24-hour LC_{50} (MacDonald and others, 1992). DEG is not suspected to be carcinogenic or mutagenic in humans (ARCO Chemical Company, 1990). No information on the teratogenicity of DEG to humans was available.

7.2.3 *TEG*

Very little general information and no specific data were available with regards to the toxic effects of TEG. The available information suggests that TEG is the least toxic of the gas dehydration glycols. Browning (1965) reports that ingestion of TEG does not result in the formation of the calcium oxalate crystals, as is the case for EG and DEG. Most of the TEG ingested is excreted unchanged, with the exception of the formation of certain metabolites, such as dicarboxylic acid. This same study states that pure TEG has very low acute and chronic toxicities and is not irritating to eyes or skin.

7.2.4 *TREG*

TREG has been reported to cause skin and eye irritation on rabbits at concentrations greater than 550 mg. The LD_{50} for rats has been reported to be 29 g/kg. No information on the toxicities of TREG to humans was available.

7.2.5 *Glycol Degradation Products*

7.2.5.1 Formaldehyde

Information on the toxic effects of formaldehyde on humans, as well as a wide variety of fish, algae, and invertebrate species, indicates that it is considerably more toxic than EG, DEG, TEG, or any of their other biodegradation products. Verschueren (1983) reports that formaldehyde is known to cause an irritation of eyes, nose, and throat at concentrations as low as 2-3 mg/L. It is also reported to cause symptoms of illness in humans at concentrations of 30 mg/L and severe toxic effects, that may lead to death in humans, at concentrations of 100 mg/L or greater.

Acute toxicity data for formaldehyde has been determined for some freshwater fish species, including 96-hour LC_{50} values ranging from 15 mg/L for striped bass (*Morone saxatilis*) to 329.6 mg/L for the American eel (*Anguilla rostrata*). Sublethal effects and egg mortalities have been determined at concentrations of 0.17 mg/L for rainbow trout (*Oncorhynchus mykiss*) and 0.25 mg/L for mirror carp (*Cyprinus carpio*). Acute toxicity data for two marine fish species have produced LC_{50} values ranging from 69.1 to 330 mg/L. For marine invertebrates, LC_{50} values have ranged from 235 to 1000 mg/L for various species of shrimp and from 0.37 to 3.7 mg/L for the eggs of sea urchins (*Anthocidaris crassispina*). Data for toxicity of formaldehyde to freshwater invertebrates are extremely limited; however, one study has reported significant reductions in the population growth of the flagellate euglenoid (*Entosiphon sulcatum*) following a 72-hour exposure to a formaldehyde concentration of 22 mg/L. It was also found that formaldehyde concentrations as low as 0.39 mg/L caused significant mortality and reduced population growth of blue-green algae (*Anacystis aeruginosa*) (MacDonald and others, 1992).

7.2.5.2 Acetaldehyde

Generally, acetaldehyde is considered to be less toxic than formaldehyde but more toxic than EG and DEG. Verschueren (1983) reports that acetaldehyde can cause eye irritation in humans at levels of 50 mg/L, and irritation of the respiratory tract at levels of 134 mg/L. MacDonald and others (1992) presented data from five studies on three species of freshwater fish that suggest that the fish are relatively sensitive to acetaldehyde, with reported 96-hour LC_{50} concentrations ranging from 30.8 to 372 mg/L for the fathead minnow (*Pimephales promelas*). For freshwater invertebrates, an EC_{50} for acetaldehyde based on immobilization was determined to be 48.25 mg/L for a species of water flea (*Daphnia magna*). The LC_{50} for the *Daphnia magna* and for the *Ceriodaphnia dubia* was found to range from 3715 to 14,221 mg/L.

7.2.5.3 Ethanol

Of the three biodegradation products of the glycols of interest, ethanol is the least toxic to humans. Concentrations of at least 8000 mg/L are required to cause severe toxic effects, and a concentration of 2000 mg/L is necessary to produce symptoms of illness in humans. Headaches and numbness are generally felt after consumption of concentrations exceeding 1300 mg/L (Verscheuren, 1983).

Ethanol has been shown to have some severely toxic effects on some animals, but not on others. Data suggest that toads (*Bufo arenarum*) may be severely affected (100% mortality rate) by ethanol concentrations as low as 144 mg/L. On the other hand, acute toxicity data for ethanol on freshwater fish suggest that fish are relatively insensitive to the chemical, with 96-hour LC_{50} values ranging from 13,000 to 14,700 mg/L. The LOAEL for a change in the respiration of a rainbow trout was found to occur at a concentration of 2930 mg/L (MacDonald and others, 1992).

8.0 RECOMMENDATIONS FOR FURTHER RESEARCH

While much of the discussion of gas industry alkanolamines and glycols appears to indicate that these chemicals, in and of themselves, are not likely to be problematic in the subsurface environment, issues must be clarified before a complete and clear picture of their transport and fate can be presented. As the state of information on these chemicals and their associated reaction and degradation products stands today, no such complete picture can be offered.

The least understood and perhaps most potentially problematic components of wastes associated with the AGR and gas dehydration units are the reaction products created during the AGR and dehydration processes (see Section 3.0 for a list of reaction products). Almost no information is available on many of the physicochemical characteristics of many of these compounds, and even less data are available on the effectiveness of attenuation mechanisms. With such a lack of information, it is not possible to make any confident predictions about their transport and fate in the subsurface environment. The pertinent physicochemical properties of these compounds need to be determined before predictions about their transport and fate can be made. The toxicity of these compounds also needs to be examined in order to evaluate the risks that may be associated with them.

Another issue that should be examined in detail is the compositions of the wide variety of additives that are used in both the AGR and gas dehydration processes, such as corrosion inhibitors, antifoaming agents, and pH stabilizers. The composition of these additives, their potential threat from a human health and safety standpoint, and the frequencies and quantities of these chemicals that are used are important pieces of information that need to be known to assess their potential for detrimental impact on the environment. Such information is beyond the scope of this report but is likely to be available for many of these additives. Like the reaction and degradation products, these chemicals could very well be more problematic than the alkanolamines and glycols they are associated with.

With regards to the alkanolamines and glycols, field data are lacking on their subsurface behavior, especially in gas industry settings. While some work has been done on the transport and fate of glycol-based deicing fluids in a variety of environments, such cases do not involve high concentrations of glycol, such as those associated with gas dehydrator units. These studies also do not involve glycols as part of complex mixtures of sludges and other organic compounds, situations that are very common to the gas industry. As far as alkanolamines are concerned, even less data exist, as no studies were found that address their subsurface behavior. While the literature that examines the biodegradation of both the alkanolamines and glycols is extensive, it is far from complete. A few studies have examined the biodegradation of glycols at airport deicing sites, as well as a variety of natural water settings, but these are not necessarily indicative of how biodegradation may occur in a gas industry setting. The available literature on alkanolamines is completely lacking data on their biodegradation in any environmental setting. The biodegradation of both the alkanolamines and glycols in typical gas industry settings needs to be examined by a systematic coordination of laboratory and field efforts before their transport and fate can be fully understood. This kind of work, with a focus on MEA, has been and continues to be undertaken by the EERC at a gas processing site in Alberta. The initial results of the MEA study have provided some useful information on the biodegradation of MEA as well as the abiotic interaction of MEA with soil/sediment, which is discussed in Section 6.1.4. However, one site study will not answer all the questions surrounding the transport and fate of the gas industry alkanolamines and glycols. Laboratory studies of the movement of alkanolamines and glycols through various types of soils under a variety of simulated subsurface conditions are also necessary to provide much needed insight on the effects of abiotic attenuation mechanisms on subsurface transport and fate. Laboratory work should also be performed to examine the potential for the alkanolamines and glycols of interest to act as cosolvents for more toxic and environmentally damaging compounds such as BTEX.

Field and laboratory studies on the topics discussed in this section are key to understanding the transport and fate of the gas industry alkanolamines, glycols, and their associated contaminants. Some work has recently been done by NHRI to examine the potential for cosolvents to enhance the mobilization of benzene in groundwater at gas sweetening facilities (Gong and others, 1995). Studies currently under way at the EERC are examining the biodegradation of MEA, as well as developing analytical techniques for some of the alkanolamine reaction products. These studies will begin to shed light on some of the issues related to the transport and fate of the gas industry alkanolamines, glycols, and their reaction products, but more work clearly needs to be done to provide a more complete picture of their behavior in the subsurface environment. A determination of the toxicity of these substances is also essential in order to assess the risk, if any, that they may pose to the environment.

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APPENDIX A

PHYSICOCHEMICAL DATA RELEVANT TO THE TRANSPORT AND FATE OF THE GAS INDUSTRY ALKANOLAMINES, GLYCOLS, AND SELECTED PROCESS REACTION AND DEGRADATION PRODUCTS

EXPLANATORY NOTES

All values are reported directly from the literature; no attempt was made to normalize significant figures.

Any value accompanied by an * was reported in the literature as a calculated rather than an experimentally obtained value.

Values of Henry's law constant are presented here in the dimensionless form, although in some cases, they may have been reported in the literature with units of atm · m^3/mol. Dimensionless values were obtained by dividing the dimensioned value by 0.024.

An absence of values for individual constants indicates that no values could be located in the literature surveyed during the search activities.

References for data sources are listed at the end of the appendix.

Acetaldehyde C_2H_4O **CAS # 75-07-0**

Synonym:

Molecular Mass: (grams/mole)

44.05 (8)

Boiling Point: (°C)

21 (8)

Freezing Point: (°C)

-125 (8)

Specific Gravity: (20 °C/4 °C)

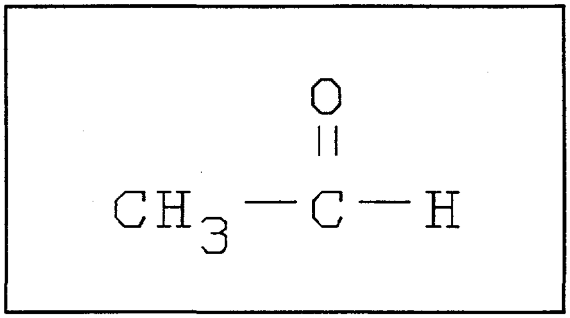
0.788 (8)

Aqueous Solubility: (mg/l @ 25 °C)

miscible (19)

Vapor Pressure: (mm Hg @ 25 °C)

748 @ 20 (19)



$CH_3-C(=O)-H$

Viscosity: (Centipoise)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

0.43 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Acetic acid $C_2H_4O_2$ **CAS # 64-19-7**

Synonym: ethanoic acid; methanecarboxylic acid, glacial acetic acid; vinegar acid; ethylic acid

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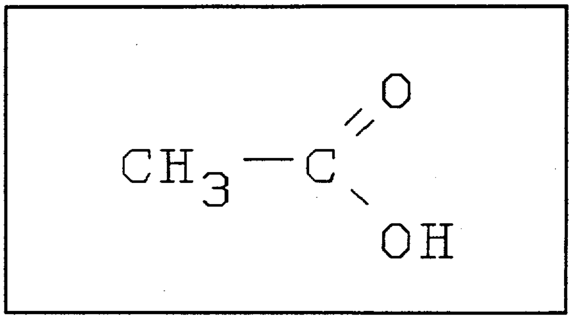
Molecular Mass: (grams/mole)

60.05 (8)

Boiling Point: (°C)

116-118 (8); 118.1 (3)



Freezing Point: (°C)

16.2 (8); 16.7 (3)

Specific Gravity: (20°C/4°C)

1.049 (3)

Aqueous Solubility: (mg/l @ 25°C)

miscible (6)

Vapor Pressure: (mm Hg @ 25°C)

11.4mm @ 20°C (3)

Viscosity: (Centipoise)

1.22 @ 20°C (6)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-0.31 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

-0.52 (19)

Acid Dissociation Constant: (dimensionless)

Diethanolamine **$C_4H_{11}NO_2$** **CAS # 11-42-2**

Synonyms: DEA; Diethylolamine; 2,2'-aminodi-ethanol; 2,2'-Iminodiethanol; Bis(2-Hydroxyethyl)amine; 2,2'-Dihydroxydiethylamine

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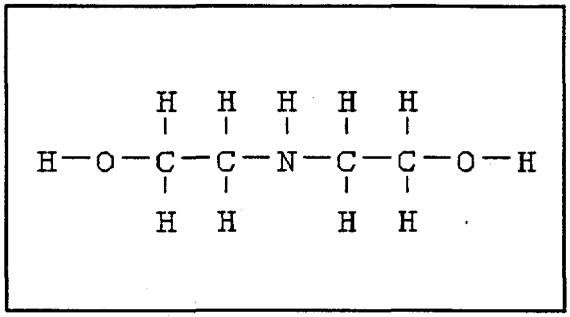

$$H-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{N}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$$

Molecular Mass: (grams/mole)

105.14 (3,5); 105.16 (7)

Boiling Point: (°C)

269.1 (3); 268.8 (5)

Freezing Point: (°C)

28 (3,5); 27-30 (8)

Specific Gravity: (20°C/4°C)

1.092 @ 30/20°C (5); 1.097 (8)

Aqueous Solubility: (mg/l @ 25°C)

9.54E5 (3); miscible (5,6)

Vapor Pressure: (mm Hg @ 25°C)

<0.01 @ 20°C (3); 2.8E-4 (5)

Viscosity: (Centipoise)

380 @ 30°C (13)

Henry's Law Constant: (dimensionless)

2.229 E-12 (5)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-1.43 (3,5)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

8.97 @ 20°C (5)

Diethylene Glycol $C_4H_{10}O_3$ **CAS # 111-46-6**

Synonym: DEG; 2,2′-Oxydiethanol; 2,2′-Dihydrowyethylether; Glycolethylether; bis(2-hydroxyethyl)-ether; Diglycol; Ethylene Diglycol; 3-oxa-1,5-penanediol; 2,2′-oxybisethanol; 3-Oxapentane-1,5-diol

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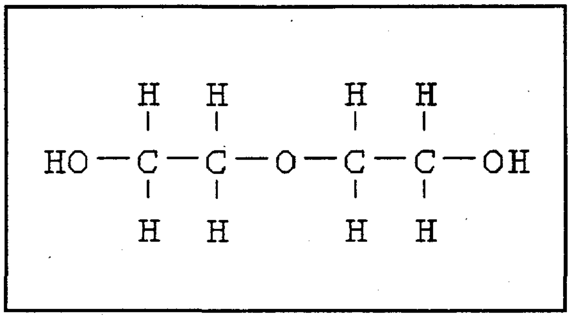


$$HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$$

Molecular Mass: (grams/mole)

106.12 (3)

Boiling Point: (°C)

245 (3,8); 245.8 (7)

Freezing Point: (°C)

-10/-8 (3); -10 (8)

Specific Gravity: (20 °C/4 °C)

1.118 (3,8)

Aqueous Solubility: (mg/l @ 25 °C)

miscible (12,6)

Vapor Pressure: (mm Hg @ 25 °C)

<0.01 (3)

Viscosity: (Centipoise)

50 @ 15 °C (6); 38 @ 20 °C (6); 30 @ 25 °C (6)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-1.98* (3)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Diisopropanolamine $C_6H_{15}O_2N$ **CAS # 110-97-4**

Synonym: DIPA; 1,1′-iminodi-2-propanol

Molecular Mass: (grams/mole)

133.19 (8)

Boiling Point: (°C)

249-250 @ 745mm Hg (3)

Freezing Point: (°C)

44.5-45.5 (3)

Specific Gravity: (20°C/4°C)

1.004 (8)

Aqueous Solubility: (mg/l @ 25°C)

1200g/100g H_2O (6)

Vapor Pressure: (mm Hg @ 25°C)

70 @ 20°C (6)

Viscosity: (Centipoise)

870 @ 30°C

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Diethylene Glycolamine $C_4H_{11}NO_2$ **CAS # 929-06-6**

Synonym: 2-(2-Aminoethoxy)ethanol, DGA

Molecular Mass: (grams/mole)

105.14 (8)

Boiling Point: (°C)

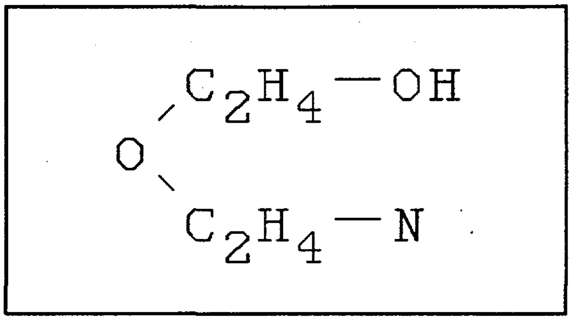
218-224 (8)

Freezing Point: (°C)

-10.5 (22)

Specific Gravity: (20°C/4°C)

1.048 (8)



Aqueous Solubility: (mg/l @ 25°C)

Vapor Pressure: (mm Hg @ 25°C)

Viscosity: (Centipoise)

Henry's Law Constant: (dimensionless)

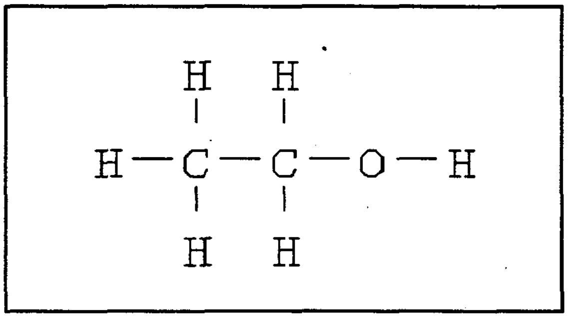
Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Ethanol C_2H_6O **CAS # 64-17-5**

Synonym: Ethyl alcohol



Molecular Mass: (grams/mole)

46.07 (8)

Boiling Point: (°C)

78 (8)

Freezing Point: (°C)

-130 (8)

Specific Gravity: (20 °C/4 °C)

0.785 (8)

Aqueous Solubility: (mg/l @ 25 °C)

miscible (19)

Vapor Pressure: (mm Hg @ 25 °C)

40 @ 19 °C (19)

Viscosity: (Centipoise)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-0.32 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Ethyl Acetate $C_4H_8O_2$ **CAS # 141-78-6**

Synonym: Ethyl alcohol

Molecular Mass: (grams/mole)

88.11 (8)

Boiling Point: (°C)

76.5-77.5 (8)

Freezing Point: (°C)

-84 (8)

Specific Gravity: (20 °C/4 °C)

0.902 (8)

Aqueous Solubility: (mg/l @ 25 °C)

7.9 E4 @ 20 °C (19)

Vapor Pressure: (mm Hg @ 25 °C)

100 @ 20 °C (19)

Viscosity: (Centipoise)

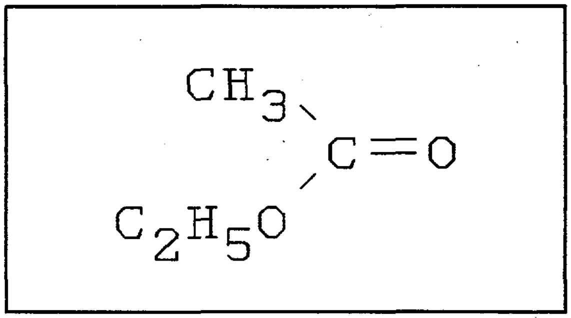
Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

0.73 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)



Ethylene Glycol $C_2H_6O_2$ **CAS # 107-21-1**

Synonym: EG, MEG; 1,2 Ethanediol; 1,2-Dihydroxyethane; monoethylene glycol

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Molecular Mass: (grams/mole)

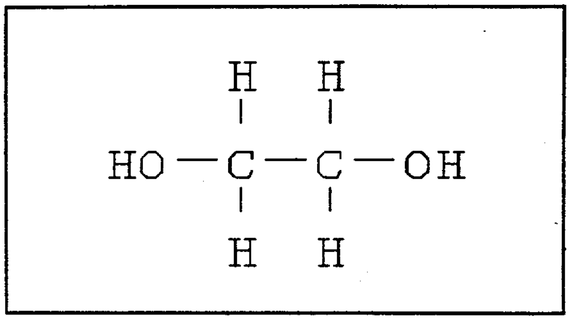
62.1 (3); 62.07 (5)

Boiling Point: (°C)

198 (3); 197.6 (5); 196-198 (8)

Freezing Point: (°C)

-17/-12.6 (3); -13 (5,8)



Specific Gravity: (20°C/4°C)

1.113 (3,8)

Aqueous Solubility: (mg/l @ 25°C)

miscible (5,12)

Vapor Pressure: (mm Hg @ 25°C)

0.05 @ 20°C (3); 0.0878 (5)

Viscosity: (Centipoise)

19.9 @ 20°C (20); 20* (21)

Henry's Law Constant: (dimensionless)

2.5E-6 (5)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-1.93 (3); -1.36 (5)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

-1.57* (11)

Acid Dissociation Constant: (dimensionless)

14.22 (1)

Formic acid **CH_2O_2** **CAS # 64-18-6**

Synonym: Methanoic acid

Molecular Mass: (grams/mole)

46.03 (8)

Boiling Point: (°C)

100-101 (8)

Freezing Point: (°C)

8.2-8.4 (8); 8.4 (3)

Specific Gravity: (20°C/4°C)

1.220 (3)

Aqueous Solubility: (mg/l @ 25°C)

miscible (6)

Vapor Pressure: (mm Hg @ 25°C)

35mm @ 20°C (6)

Viscosity: (Centipoise)

2.2469 @ 10°C (6)

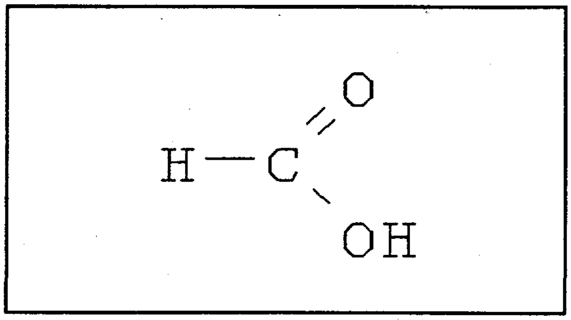
Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-0.54 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)



Methyl Alcohol **CH_4O** **CAS # 67-56-1**

Synonym: Methanol

Molecular Mass: (grams/mole)

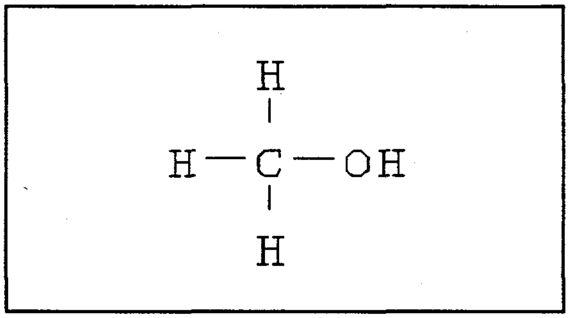
32.04 (19)

Boiling Point: (°C)

64.7 (19)

Freezing Point: (°C)

-97.8 (19)



Specific Gravity: (20 °C/4 °C)

0.791 (19)

Aqueous Solubility: (mg/l @ 25 °C)

miscible (19)

Vapor Pressure: (mm Hg @ 25 °C)

92 @ 20 °C (19)

Viscosity: (Centipoise)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-0.66 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Methyldiethanolamine $C_5H_{13}NO_2$ **CAS # 105-59-9**

Synonym: MDEA; 2,2'-Methyliminodiethanol; n-methyl-2,2'-iminodiethanol

Molecular Mass: (grams/mole)

119.16 (8); 119.19 (7)

Boiling Point: (°C)

246-248 (8); 247.2 (6)

Freezing Point: (°C)

-19 (6)

Specific Gravity: (20°C/4°C)

1.038 (8); 1.037 (6)

Aqueous Solubility: (mg/l @ 25°C)

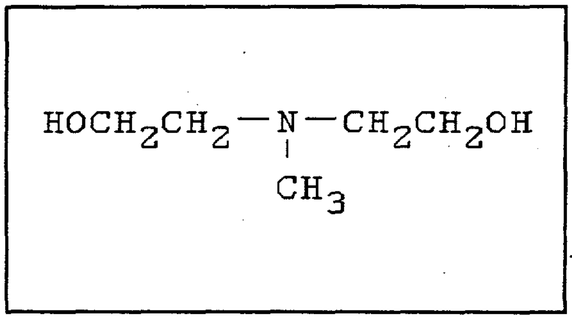
miscible (6)

Vapor Pressure: (mm Hg @ 25°C)

<0.01 @ 20°C (6)

Viscosity: (Centipoise)

101 @ 20°C (6)



$$HOCH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2CH_2OH$$

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

8.52 (15)

Monoethanolamine **C_2H_7NO** **CAS # 141-35-5**

Synonyms: MEA; ethylolamine; 2-Aminoethanol; Beta-Aminoethylalcohol; ethanolamine; Beta-Hydroxyethylamine; Colamine

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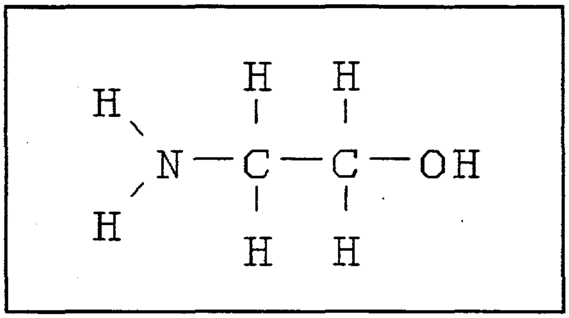


Molecular Mass: (grams/mole)

61.08 (3,5)

Boiling Point: (°C)

172 (3); 170.8 (5); 170 (8)

Freezing Point: (°C)

11 (3); 10.3 (5); 10.5 (8)

Specific Gravity: (20°C/4°C)

1.02 (3); 1.012 (8)

Aqueous Solubility: (mg/l @ 25°C)

miscible (5,6)

Vapor Pressure: (mm Hg @ 25°C)

0.4 @ 20°C (3); 0.26 (5)

Viscosity: (Centipoise)

24.14 @ 20°C (6)

Henry's Law Constant: (dimensionless)

1.667E-6* (5)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-1.31 (3,5)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

9.48 (5)

Oxalic acid $C_2H_2O_4$ **CAS # 144-62-7**

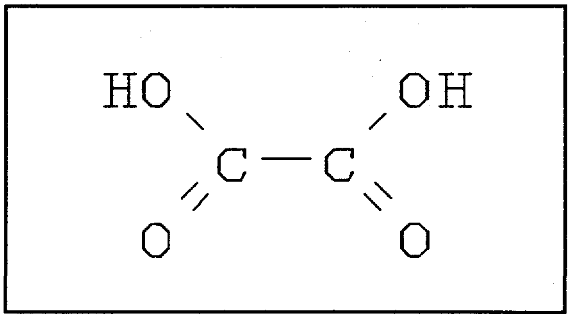
Synonym: ethanedioic acid; ethanedionicacid

Molecular Mass: (grams/mole)

90.04 (8)

Boiling Point: (°C)

157 (8)



Freezing Point: (°C)

190 (8)

Specific Gravity: (20°C/4°C)

1.653 (3)

Aqueous Solubility: (mg/l @ 25°C)

95,000 mg/l @ 15°C (24)

Vapor Pressure: (mm Hg @ 25°C)

0.0003mm @ 30°C (24)

Viscosity: (Centipoise)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Propionic acid $C_3H_6O_2$ **CAS # 79-09-4**

Synonym: propanoic acid; methylacetic acid; metactonic acid, ethylcarbonic acid

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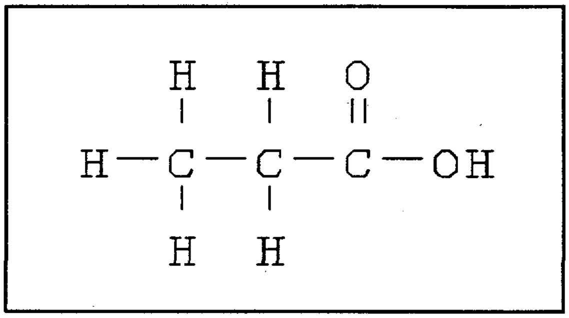
Molecular Mass: (grams/mole)

74.08 (8); 74.1 (3)

Boiling Point: (°C)

141 (8)



Freezing Point: (°C)

-24 to -23 (8)

Specific Gravity: (20°C/4°C)

0.993 (8)

Aqueous Solubility: (mg/l @ 25°C)

miscible (6)

Vapor Pressure: (mm Hg @ 25°C)

2.9mm @ 20°C (6)

Viscosity: (Centipoise)

1.175 @ 25°C (18)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

0.25 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Propylene Glycol $C_3H_8O_2$ **CAS # 57-55-6**

Synonym: 1,2-Propanediol

Molecular Mass: (grams/mole)

76.10 (8)

Boiling Point: (°C)

187 (8)

Freezing Point: (°C)

-60 (8)

Specific Gravity: (20 °C/4 °C)

1.036 (8)

Aqueous Solubility: (mg/l @ 25 °C)

Miscible (8)

Vapor Pressure: (mm Hg @ 25 °C)

0.13 (8)

Viscosity: (Centipoise)

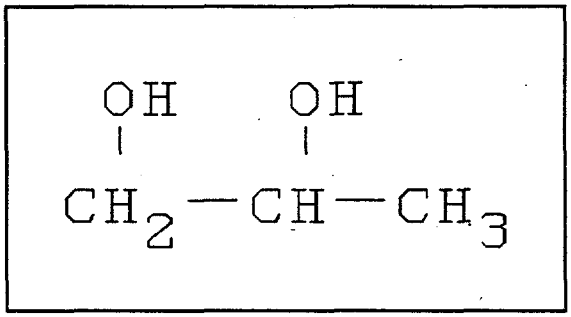
48.6 @ 25°C (8)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)



$$\overset{\overset{OH}{|}}{CH_2}-\overset{\overset{OH}{|}}{CH}-CH_3$$

Tetraethylene Glycol $C_8H_{18}O_3$ **CAS # 112-60-7**

Synonym:

Molecular Mass: (grams/mole)

164.23 (8)

Boiling Point: (°C)

314 (8)

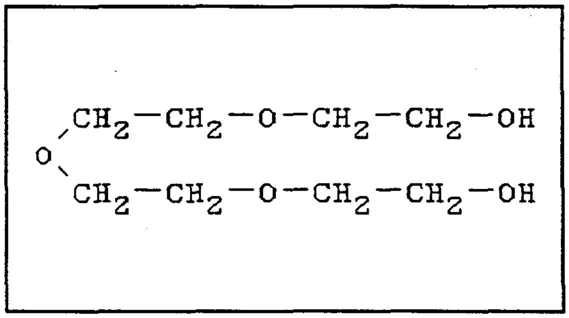
Freezing Point: (°C)

-6 (8)

Specific Gravity: (20 °C/4 °C)

1.125 (8)

Aqueous Solubility: (mg/l @ 25 °C)



Vapor Pressure: (mm Hg @ 25 °C)

<0.01 (8)

Viscosity: (Centipoise)

43 @ 25°C (8)

Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)

Triethanolamine $C_6H_{15}NO_3$ **CAS # 102-71-6**

Synonyms: TEA; 2,2',2"-nitrilotriethanol; Tris(2-hydroxyethyl)amine

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Molecular Mass: (grams/mole)

149.1 (8)

Boiling Point: (°C)

335.4 (1)

Freezing Point: (°C)

17.9-21 (8)

Specific Gravity: (20°C/4°C)

1.124 (8)

Aqueous Solubility: (mg/l @ 25°C)

miscible (6)

Vapor Pressure: (mm Hg @ 25°C)

10 @ 20°C (6)

Viscosity: (Centipoise)

1013 @ 20°C (17)

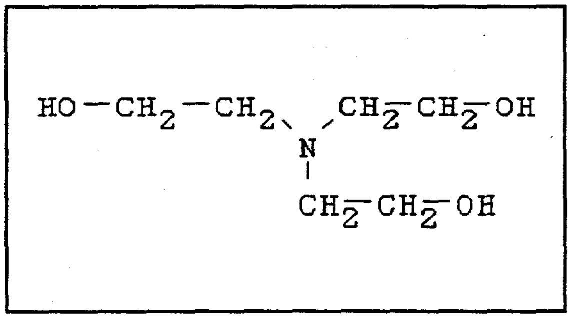
Henry's Law Constant: (dimensionless)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-1.75 (19)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

Acid Dissociation Constant: (dimensionless)



Triethylene Glycol $C_6H_{14}O_4$ CAS # 112-27-6

Synonym: TEG; 2,2(ethylenedioxy)diethanol; Triglycol;
Glycol bis(hydroxyethyl)ether

Molecular Mass: (grams/mole)

150.2 (3); 150.17 (8)

Boiling Point: (°C)

287.4 (3); 285 (8)

Freezing Point: (°C)

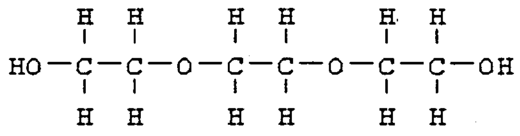
-4/-7 (3); -7 (8)

Specific Gravity: (20 °C/4 °C)

1.1254 (3); 1.125 (8)

Aqueous Solubility: (mg/l @ 25 °C)

miscible (12,6)



$$\begin{array}{ccccccccccccccccccc} & & H & & H & & & & H & & H & & & & H & & H & & \\ & & | & & | & & & & | & & | & & & & | & & | & & \\ HO & - & C & - & C & - & O & - & C & - & C & - & O & - & C & - & C & - & OH \\ & & | & & | & & & & | & & | & & & & | & & | & & \\ & & H & & H & & & & H & & H & & & & H & & H & & \end{array}$$

Vapor Pressure: (mm Hg @ 25 °C)

<0.001 @ 20 °C (3)

Viscosity: (Centipoise)

34 (6)

Henry's Law Constant: (dimensionless)

5.31E-9 (5)

Log Octanol-Water Partitioning Coefficient: (dimensionless)

-2.08/1.32* (3); -2.08 (11)

Log Organic Carbon Partitioning Coefficient: (dimensionless)

-2.29 (11)

Acid Dissociation Constant: (dimensionless)

14.5 (2)

Commonly Reported Alkanolamine Reaction Products

Bis(hydroxyethylaminoethyl)ether
$C_8H_{20}N_2O_3$
Synonym: BHEAE
Molecular Mass (grams/mole): 192.23

N,N'-bis(hydroxyethyl)ethylenediamine
$C_6H_{16}N_2O_2$
Synonym: BHEED
Molecular Mass (grams/mole): 148.18

N,N'-bis(hydroxyethyl)imidazolidone
$C_7H_{14}N_2O_3$
Synonym: BHEI
Molecular Mass (grams/mole): 174.17

N-(hydroxyethyl)imidazolidone
$C_5H_{10}N_2O_2$
Synonym: HEI
Molecular Mass (grams/mole): 130.12

N-(2-hydroxyethyl)piperazine
$C_6H_{14}N_2O$
Synonym: HEP
Molecular Mass (grams/mole): 130.16

N,N,N'-tris(hydroxyethyl)ethylenediamine
$C_8H_{20}N_2O_3$
Synonym: THEED
Molecular Mass (grams/mole): 192.23

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