

Evaluation of Dimethylethanolamine (DMEA) as a Pressurized Water Reactor Secondary pH Control Agent

State of Knowledge



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PRODUCT DESCRIPTION

Background

The secondary side at-temperature pH (pH_T) in pressurized water reactors (PWRs) is maintained sufficiently above neutral to limit the corrosion of materials of construction (e.g., due to flow-accelerated corrosion, FAC). The current revision of the EPRI PWR Secondary Water Chemistry Guidelines does not specify the use of a particular pH control agent or a particular pH program, but instructs utilities to optimize their pH control program for their plant-specific circumstances. Most PWRs are operated with both ammonia, either directly added or produced from decomposition of hydrazine and/or amine used, and amine(s) for pH control. A variety of amines are in use, based on differences in their chemical properties, including morpholine, ethanolamine (ETA), dimethylamine (DMA), and methoxypropylamine (MPA). Prior EPRI research has identified N,N-dimethylethanolamine (DMEA) as an amine with the potential advantage of limited interference with condensate polisher resin performance and/or regeneration, as compared to ETA. Specifically, DMEA is considered less likely to react with resin beads in ways that the most currently used amine, ETA, reacts. However, the application of DMEA as a pH control agent in PWR secondary systems has not been qualified.

Objectives

The purpose of this report is to review the state of knowledge regarding the potential use of DMEA as a PWR secondary side pH control agent, to identify existing knowledge gaps, and to identify actions necessary to close those gaps.

Approach

The state of knowledge of DMEA was evaluated in the following areas: (1) physical and chemical properties of DMEA, (2) material compatibility issues, and (3) plant application considerations. In each case, the state of knowledge for DMEA was compared to information available for currently utilized amines and the expected level of knowledge that would be anticipated as required for DMEA prior to a plant demonstration. Each identified knowledge gap generated in this comparison was then categorized based on the anticipated importance of closing that gap prior to a plant trial. As appropriate, testing or other activities were recommended to close each identified knowledge gap.

Results

Dimethylethanolamine (DMEA) may be suitable for application as an amine for the control of secondary side pH in Pressurized Water Reactors (PWRs). In several respects, DMEA is expected to behave in a manner similar to amines that are currently used for pH_T control. However, the availability of DMEA-specific experimental data and industrial experience in conditions comparable to the PWR secondary system is limited. Accordingly, several knowledge gaps were identified in the qualification process. Major knowledge gaps, which are

expected to be addressed before a plant trial, include DMEA's compatibility with metals and elastomers (including corrosion phenomena) and DMEA's cation resin selectivity under representative plant conditions. Moderate knowledge gaps include DMEA's thermal decomposition kinetics (both rate and decomposition products), which are not well characterized. A number of recommended tests are expected to provide improved inputs (i.e., selectivity, decomposition, basicity, and volatility) for modeling the effects of DMEA using EPRI's Plant Chemistry Simulator (PCS), which would improve estimates of secondary circuit chemistry, required amine demand, and resin performance.

Application, Value, Use

DMEA is a potentially beneficial alternative to commonly used amines (i.e., ETA) for controlling PWR secondary side pH_T because DMEA may be less likely to react with resin beads and reduce resin bed performance as experienced by some plant using ETA. This report provides a technical basis for qualifying DMEA for use in the secondary system, by summarizing the state of available knowledge, categorizing knowledge gaps, and recommending testing, where applicable, to close identified gaps. The findings can be used by utility members, EPRI project managers, and plant chemistry personnel, as a basis for qualifying DMEA for pH_T control on the secondary side.

Keywords

DMEA

N,N-dimethylethanolamine

Advanced Organic Amine

pH Control Agent

Secondary Side Chemistry

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PRIMARY AUDIENCE: PWR plant chemist

SECONDARY AUDIENCE: Personnel responsible for monitoring secondary side resin performance

KEY RESEARCH QUESTION

A small number of amines are currently used to control the at-temperature pH (pH_T) in the PWR secondary side. Ethanolamine (ETA) has been observed to have an adverse effect on condensate polisher resin performance and/or regeneration. Research has identified dimethylethanolamine (DMEA) as a possible secondary side amine alternative that is less likely to react with resin beads as compared to ETA. However, DMEA has not been qualified for use in the PWR secondary side.

RESEARCH OVERVIEW

The state of knowledge of DMEA relative to other currently utilized amines was reviewed in a number of key areas considered important to the use of amines for secondary side pH_T control, including physical and chemical properties, material compatibility, and application considerations. Knowledge gaps were identified and characterized by severity where the available technical information for DMEA was found to be limited. Finally, testing or other approaches were recommended to close each identified gap, where applicable.

KEY FINDINGS

DMEA may be suitable as a pH_T control agent on the PWR secondary side. Preliminary estimates based on available information indicate that the addition and control would likely be comparable to other added amines. However, several knowledge gaps indicate that the following additional testing is warranted prior to a plant trial:

- Data for secondary side amines (excluding DMEA) show that the compatibility of the amine with metals and the effects of the amine on associated corrosion phenomena are driven primarily by the pH_T . Additional testing is recommended to demonstrate that DMEA can be similarly characterized as not having an amine-specific effect. As appropriate, this testing may involve bounding materials and environments (e.g., FAC testing of carbon steel).
- The compatibility of secondary side amines with elastomers and seals is known to be amine-specific. Testing is recommended to ensure there are no detrimental effects of DMEA on elastomers in the secondary system. It is noted that this testing should be informed by an audit of the secondary system, followed by a test matrix that focuses on appropriately bounding materials and environments.
- The selectivity of DMEA for cation resins under conditions applicable to the secondary side is not available, though the selectivity is expected to be comparable to other amines (based on measurements under non-representative conditions). Accordingly, testing is recommended to determine the selectivity to allow for an improved estimate of resin performance, as applicable (i.e., for plants with condensate polishers or blowdown demineralizers).
- The thermal decomposition kinetics of DMEA (both rate and products) is not well characterized. Additional testing is recommended to improve estimates of amine demand and the effect of decomposition on the chemistry of the secondary circuit.

WHY THIS MATTERS

The results of this study provide a technical basis of qualification work associated with the implementation of DMEA as a pH_T control agent on the PWR secondary side. The findings can be used by utility members, EPRI project managers, and plant chemistry personnel, to evaluate the application of DMEA.

HOW TO APPLY RESULTS

This evaluation will provide a basis for qualification work associated with the use DMEA as a PWR secondary side pH_T control agent.

LEARNING AND ENGAGEMENT OPPORTUNITIES

- Amine addition guidelines – EPRI Report TR-102952-R2, “PWR Advanced Amine Application Guidelines”
- Assessments of alternate amines in PWRs – EPRI Report 1019042, “Steam Generator Management Program: Effects of Different pH Control Agents on Pressurized Water Reactor Plant Systems and Components”
- Assessments of amine-resin interactions – EPRI Report 1003613 “Investigation of ETA Interactions in Mixed Bed Ion Exchange Systems: Phase II”
- Ongoing EPRI program related to secondary side amine addition, including ETA

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ACRONYMS

APS	Arizona Public Service
DEI	Dominion Engineering, Inc.
DMA	Dimethylamine
DMEA	N,N-dimethylethanolamine
ECP	Electrochemical Potential
EPRI	Electric Power Research Institute
ETA	Ethanolamine
FAC	Flow-Accelerated Corrosion
MPA	Methoxypropylamine
NPP	Nuclear Power Plant
PCS	Plant Chemistry Simulator
PWR	Pressurized Water Reactor
SDS	Safety Data Sheet

CONTENTS

PRODUCT DESCRIPTION	v
EXECUTIVE SUMMARY	vii
ACRONYMS	ix
1 INTRODUCTION	1-1
2 SUMMARY	2-1
2.1 Conclusions.....	2-1
2.2 Knowledge Gap Categorization.....	2-1
2.2.1 Major Knowledge Gaps	2-2
2.2.2 Moderate Knowledge Gaps	2-2
2.2.3 Minor Knowledge Gaps	2-3
2.3 Recommendations	2-3
3 PHYSICAL AND CHEMICAL PROPERTIES	3-1
3.1 Overview	3-1
3.1.1 Formula and Structure	3-1
3.1.2 Identifiers	3-1
3.1.3 Physical Properties.....	3-2
3.1.4 Industrial Uses.....	3-2
3.1.5 Fire and Explosion Hazard Data.....	3-3
3.1.6 Health Hazard Data	3-4
3.1.7 Safety and Storage	3-4
3.1.8 Environmental and Disposal Information.....	3-4
3.2 Factors Affecting Amine Application.....	3-6
3.2.1 Purity	3-6
3.2.2 Basicity	3-7
3.2.3 Volatility	3-12

3.2.4 Thermal Decomposition.....	3-15
3.3 Summary.....	3-18
4 MATERIAL COMPATIBILITY	4-1
4.1 Materials of Construction.....	4-1
4.1.1 Nickel Alloys	4-1
4.1.2 Carbon and Low Alloy Steels	4-2
4.1.3 Stainless Steels	4-3
4.1.4 Copper Alloys	4-3
4.1.5 Titanium and Other Metals	4-4
4.2 Ion Exchange Resins	4-5
4.2.1 Selectivity and Resin Exhaustion	4-5
4.2.2 Resin Fouling Issues	4-8
4.3 Elastomers and Seals	4-10
4.4 Summary.....	4-11
5 APPLICATION CONSIDERATIONS	5-1
5.1 DMEA Program Expectations.....	5-1
5.1.1 Injection	5-2
5.1.2 Chemistry Effects	5-5
5.1.2.1 pH	5-5
5.1.2.2 Cation Conductivity	5-5
5.1.3 Monitoring and Sampling.....	5-8
5.2 Corrosion Phenomena	5-8
5.2.1 General Corrosion	5-8
5.2.2 Flow Accelerated Corrosion	5-9
5.3 Effects on Operation of Plant Equipment.....	5-9
5.3.1 Moisture Carryover.....	5-9
5.3.2 Analytical Instruments	5-9
5.3.3 Corrosion Product Deposition.....	5-10
5.3.4 Ion Exchange Beds	5-10
5.4 Summary.....	5-11
6 REFERENCES	6-1

A PLANT CHEMISTRY SIMULATOR INPUTS.....	A-1
A.1 Plant Settings.....	A-1
A.2 PCS Configuration	A-1
A.3 Input Files	A-2
A.3.1 ixdata.mdb.....	A-2
A.3.2 lxlib.dat.....	A-2
A.3.3 Species.dat	A-3

LIST OF FIGURES

Figure 3-1 Molecular Structure of DMEA	3-1
Figure 3-2 Temperature Dependence of pK_b for Several Common Amines (adapted from Ref [4])	3-9
Figure 3-3 At Temperature pH_T for Several Amine Concentrations Such That $pH_{25} = 9.5$	3-10
Figure 3-4 At Temperature pH_T for Several Amine Concentrations Such That $pH_{25} = 10.5$	3-11
Figure 3-5 Temperature Dependence of K_D for Several Common Amines (adapted from Ref [4])	3-14
Figure 3-6 Thermal Decomposition of Several Common Amines after 10 min Heating (adapted from Reference [28])	3-16
Figure 3-7 Amine Concentrations With or Without Nitrogen Purge of the Test Vessel (10 Minutes at 257°C) [28]	3-17
Figure 4-1 Nucleophilic Attack of an Amine on the Benzylic Carbon of a Benzyltrimethylammonium Group [5]	4-8
Figure 4-2 Nucleophilic Attack of Hydroxide on the Benzylic Carbon of a Benzyltrimethylammonium Group [5]	4-9
Figure 4-3 Product from Attack of DMEA on Benzylic Carbon of Benzyltrimethylammonium Group [5]	4-10
Figure A-1 Chemical Species Dialogue	A-1
Figure A-2 Addition of DMEA Column to IXDATA Table	A-2
Figure A-3 Addition of DMEA to Ixlib.dat	A-3
Figure A-4 Addition of DMEA to Species.dat	A-3

LIST OF TABLES

Table 2-1 DMEA Qualification Matrix.....	2-6
Table 3-1 Toxicological and Environmental Assessment of DMEA and Other Additives.....	3-5
Table 3-2 Concentration of Amine required to reach pH_T (ppm).....	3-11
Table 3-3 At Temperature pH_T for Several Amine Concentrations such that $\text{pH}_{275} = 6.5$	3-12
Table 3-4 Calculated Amine Degradation Half-Lives (Based on Reference [28]).....	3-17
Table 4-1 Loading and Selectivity of Selected Amines [37].....	4-6
Table 4-2 Calculated Cation Exchange Selectivity (<i>KHAmine</i>) for Several Amines Compared to Values Published in Reference [36]	4-7
Table 4-3 Chemical Compatibility of Common Elastomers [38].....	4-13
Table 5-1 PCS Input Concentrations	5-2
Table 5-2 Sample PCS Output for a DMEA Cycle.....	5-3
Table 5-3 Amine Addition Rates (lbm/hr) with and without Condensate Polishing	5-4
Table 5-4 Amine Addition Due to Thermal Decomposition	5-4
Table 5-5 pH_T and pH_{25} With and Without Ammonia.....	5-7
Table 5-6 Cation Conductivity at Various Locations as Estimated by the PCS ($\mu\text{S}/\text{cm}$).....	5-8

1

INTRODUCTION

The use of amines for pH control is a generally accepted practice in secondary chemistry control programs at nuclear power plants. The primary goal is to increase and optimize the at-temperature pH (pH_T) in regions of the secondary loop so as to reduce general corrosion that leads to corrosion product transport to the steam generators, and to mitigate flow-accelerated corrosion (FAC) that leads to thinning of structurally important components [1]. The current revision of the EPRI Secondary Water Chemistry Guidelines [1] does not specify the use of a particular pH control agent or a particular pH program, but instructs utilities to optimize their pH control program for their plant-specific circumstances. Thus, different qualified amines may be selected based on differences in their chemical properties, i.e., volatility and base strength, to achieve a specific pH_T elevation, relative to neutral pH_T , at specific locations in the secondary system with different concentrations of chemical. Amines that are commonly in use include morpholine, ethanolamine (ETA), dimethylamine (DMA), and methoxypropylamine (MPA). These amines are used concurrently with ammonia to control pH, which can be added or generated as a product of hydrazine and/or the amine decomposition.

Dimethylethanolamine (DMEA) is one of many potential amines that have been explored as alternative pH control agents. As early as 1981, MORLEX® DMEA was marketed by Union Carbide as a corrosion inhibitor for condensate steam and boiler systems [2]. However, based on the general lack of technical and commercial literature, use of the chemical in boiler and steam system does not appear to be widespread. During the 1980s, EPRI funded research that characterized 96 different amines for application as pH control agents, including DMEA [3,4]. Those results did not identify DMEA as a top candidate. However, more recent work in 2003 has indicated that DMEA may cause limited interference with condensate polisher resin performance and/or regeneration as compared to ETA [5]. Specifically, DMEA is considered less likely to react with resin beads in ways that the currently most used amine, ETA, reacts. Such reactions have resulted in reduced resin performance characteristics.

The purpose of this report is to review the state of knowledge regarding the potential use of DMEA as a PWR secondary side pH control agent, to identify existing knowledge gaps, and to identify actions necessary to close those gaps. The following general considerations are reviewed in this report:

- Physical and chemical properties of DMEA (Section 3), including fundamental chemical properties, parameters important to plant modeling such as dissociation and volatility, and thermal decomposition
- Materials compatibility (Section 4), including metals, resin, and elastomers and other sealing materials
- Application considerations (Section 5) such as expected concentrations, probable effects on corrosion, and effects on operation of plant equipment

Introduction

It is expected that a subsequent qualification program will address closure or disposition of the knowledge gaps identified in this report before DMEA is used in an initial nuclear power plant (NPP) application. The findings of this report, including knowledge gaps and recommended actions, are summarized in Section 2.

2

SUMMARY

2.1 Conclusions

A review of available literature indicates that dimethylethanolamine (DMEA) may be suitable for application as an amine for the control of secondary side pH in Pressurized Water Reactors (PWRs). In several respects, DMEA is expected to behave in a manner similar to amines that are currently used for pH_T. However, the availability of DMEA-specific experimental data and industrial experience in conditions comparable to the PWR secondary system is limited. Thus, performance expectations are based on limited but favorable experimental data and the behavior of comparable amines. Accordingly, several knowledge gaps were identified in the qualification process. Some of these gaps are expected to be addressed before a plant trial.

2.2 Knowledge Gap Categorization

Table 2-1 summarizes the state of knowledge of each qualification topic that was reviewed for PWR secondary side DMEA application, including the status of associated knowledge gaps and, if applicable, additional work necessary to close each gap. Each knowledge gap is categorized in a relative manner as major, moderate, or minor:

- A major knowledge gap is considered to be a gap with the potential for an uncontrolled or unpredictable effect on plant operations. It is expected that a major knowledge gap would need to be closed before a plant trial would proceed.
- Moderate knowledge gaps are informational gaps that could affect plant operation in a significant way but could be possible to accommodate through appropriate engineering, procurement, or procedural controls. It is expected that a moderate knowledge gap might be left open before starting a plant trial, if the plant trial was expected to provide data that could close the gap without undue risk and if laboratory or modeling work to close the gap was expected to be inconclusive.
- Minor knowledge gaps represent issues that should be monitored during the initial DMEA application or information that would improve plant chemistry modeling. Minor gaps also include issues for which a plant-specific procedure or specification should be written but for which no significant challenges could be identified (e.g., all required inputs are available). It is expected that minor knowledge gaps might be left open before proceeding with a plant trial unless closing them can be readily accomplished.

Note that these definitions do not include consideration of the effort required to close the gap. For example, a major gap might be closed by minimal additional work.

The following subsections discuss each identified gap in order of significance.

2.2.1 Major Knowledge Gaps

The following major knowledge gaps were identified:

- Long-term plant experience with various amines suggests that there are no metal degradation mechanisms that are related to the specific amines or amine concentrations used, beyond a correlation with pH. However, there is no directly relevant information about the specific interaction of DMEA with metals that are typically used in the PWR the secondary system. Insufficient information is currently available to confirm that DMEA behaves in a manner similar to all of the previously investigated amines. This knowledge gap affects several topics concurrently, including material compatibility, corrosion phenomena, and steam generator deposit formation.
- No information regarding the direct interaction of DMEA with elastomers or seals in typical PWR secondary side conditions could be identified. Moreover, there is significant historical experience showing adverse amine-specific effects on elastomers and seals with a possibility of deleterious results. Depending on the elastomeric material / amine combination, several effects have been observed including swelling, hardening due to increased cross-linking, and shorter in-service lifetimes.
- Selectivity data for DMEA exchange with cation resin under relevant PWR secondary side conditions are not available. However, the applicability of this knowledge gap may vary from plant-to-plant (i.e., it is most applicable to plants with full-flow condensate polishing and not applicable to plants without condensate polishers and blowdown demineralizers).
- DMEA is commercially available in industrial quantities that appear to have relatively high purity. However, a publicly available certificate of analysis demonstrating sufficiently low levels impurities important to secondary water chemistry additives could not be identified.

As was noted previously, it is expected that these knowledge gap would be closed before a plant trial would proceed. Recommendations for addressing these gaps, where applicable, are discussed in Section 2.3.

2.2.2 Moderate Knowledge Gaps

The following moderate knowledge gaps were identified:

- There is significant uncertainty in DMEA's decomposition rate and decomposition products. The experimental methods used to characterize the decomposition half-life of DMEA yielded results for other amines that were significantly different, by at least a factor of four (4), compared to other studies for those amines (but did not include DMEA). Additionally, the decomposition process for DMEA has not been fully characterized, including the identification of all decomposition products and the kinetics of their formation. This leads to uncertainty in plant chemistry predictions such as amine injection rate, pH, contribution to impurity concentrations, and cation conductivity.
- The effect of DMEA addition on cation conductivity and, as appropriate, the necessary adjustments to baseline values used for monitoring and controlling secondary water chemistry have not been evaluated. The increase in cation conductivity is expected due to the formation of organic acids from DMEA decomposition, which is expected to be less than

ETA. This gap is due, in part, to limited information regarding DMEA decomposition, which would allow for improved estimates of cation conductivity using simulation software.

- The injection rate for DMEA is expected to be comparable to other amines. However, the predicted injection rate is based in part on inputs that have been identified as knowledge gaps, including the thermal decomposition rate and resin selectivity.

As was noted previously, it is expected that these knowledge gaps might be left open before starting a plant trial, if the plant trial was expected to provide data that could close the gap without undue risk and if laboratory or modeling work to close the gap was expected to be inconclusive. Recommendations for addressing these gaps, where applicable, are discussed in Section 2.3.

2.2.3 Minor Knowledge Gaps

Minor knowledge gaps were identified, include:

- DMEA is already used commercially in several industries. Safe handling practices, storage, and disposal considerations are well documented in vendor SDS documents. Plant-specific procedures are expected to be developed or implemented based on available inputs (i.e., SDS documents and applicable regulations) ahead of a plant trial to ensure proper storage and disposal.
- Experimental data for the basicity of DMEA are not available at high temperature. However, the high-temperature ionization behavior of DMEA is believed to be well characterized because the current Gibbs free energy based method for estimating the reaction equilibrium constant has been shown to perform well for similar amines (i.e., ammonia, cyclohexylamine, and morpholine).
- DMEA is unlikely to reduce the performance of cation resin. However, application of DMEA at plant conditions over significant operating times has not been performed.
- DMEA is unlikely to have an adverse effect on plant instrumentation. However, the lack of an adverse interaction of DMEA with plant instrumentation at plant conditions over significant operating times has not been demonstrated.

As was noted previously, it is expected that these knowledge gaps might be left open or simply monitored during initial DMEA application. They may also be addressed with plant-specific procedures or specifications. Recommendations for addressing these gaps, where applicable, are discussed in Section 2.3.

2.3 Recommendations

Recommended additional assessments and testing related to each knowledge gap identified in this review are summarized in Table 2-1. A more detailed description of each recommendation is provided as follows:

- Resin Selectivity Testing (Major Gap Closure) – The selectivity for DMEA by ion exchange resins has not been characterized under conditions relevant to the PWR secondary side, although testing in non-representative conditions suggests the selectivity may be similar to other amines. Testing is recommended to determine the selectivity of DMEA for common

cation resins using in condensate polishing and blowdown demineralizers, under relevant conditions, and with other commonly used amines (for comparison). The measured selectivity parameters would improve models for resin consumption and DMEA's interaction with other exchanged species.

- **Elastomer Testing (Major Gap Closure)** – The potential adverse effects of DMEA on elastomers and seals under PWR secondary side conditions are not characterized. DMEA exposure testing is recommended to characterize the extent of degradation and to identify potential degradation mechanisms. It is noted that this testing should be informed by an audit of the secondary system to identify the location and types of elastomers and seals that may be exposed to DMEA. The resulting test matrix may allow for testing to be optimized, for example, to include only a bounding set of elastomers and environments.
- **Metals Testing (Major Gap Closure)** – Long-term plant experience with various amines suggests that there are no degradation mechanisms that are related to the specific amines or amine concentrations used, beyond a correlation with secondary side pH. Nevertheless, due to the significance of such an effect, if any, and the lack of directly relevant data with DMEA, testing is recommended to confirm or refute any specific effects (i.e., to confirm that the interaction of DMEA with metals can be grouped with the set of amines that have been previously investigated). As appropriate, this testing may be limited to a bounding set of materials and environments, with direct comparisons to other amines that are commonly used (e.g., FAC testing involving DMEA and ETA on carbon steel).
- **Decomposition Testing (Moderate Gap Closure)** – The decomposition of DMEA (rate and products) has not been well characterized. Additional testing is recommended to characterize the rate of decomposition and the formation of decomposition products at conditions relevant the secondary side of a PWR. The additional data could be used to characterize the expected makeup rates of DMEA and the effects of DMEA decomposition products on the secondary circuit.
- **High-Temperature Basicity Testing (Minor Gap Closure)** – More confidence in current plant modeling would be gained from additional measurements of the high temperature dissociation constant. This would provide higher confidence in the calculated pH_T at various locations in the secondary system resulting in higher confidence in the FAC rates. This could provide some cost savings to utilities using DMEA if the results of such testing allowed the elimination of some uncertainty margin in the determination of FAC inspection intervals.
- **Volatility Testing (No Gap)** – Additional data could improve the accuracy of distribution models for DMEA.

It is noted that a number of topics covered in the above-described testing (i.e., selectivity, decomposition, basicity, and volatility) are expected to provide improved inputs for modeling the effects of DMEA using EPRI's Plant Chemistry Simulator (PCS), which would improve estimates of secondary circuit chemistry, required amine demand, and resin performance.

In addition to the above recommended testing, additional utility consideration is recommended to develop/advance plant-specific procedures, programs, or specifications that are expected to be adopted for DMEA addition based on available inputs (e.g., distributor certificate of analysis, plant-specific chemistry program controls, SDS documents, applicable regulations) prior to a plant demonstration. These activities are expected to include the following:

- Purity (Major Gap Closure) – Procedures and controls for procuring appropriately pure quantities of DMEA are expected to be developed by plant personnel based on information provided by chemical distributors and requirements for control of chemical species to the secondary system (i.e., plant-specific chemical impurity limits).
- Handling and Storage (Minor Gap Closure) – Procedures and controls for safe handling, storage, and disposal of DMEA are expected to be developed by plant personnel, if necessary, based on information provided in SDS documents and applicable regulations.
- Cation Conductivity Adjustment (Moderate Gap Closure) – The baseline cation conductivity values used to monitor and control secondary water chemistry will likely need to be adjusted to account for anticipated increases in conductive from the formation of organic acids from thermal decomposition of DMEA. This adjustment will likely be informed by thermal decomposition testing (discussed above), which will improve estimates provided by the PCS software.

Finally, additional precautions and monitoring are expected during the initial application of DMEA. Recommended activities include:

- Increased Feedwater Monitoring – Monitoring and sampling during the initial cycle that DMEA is applied to assess any changes in feedwater iron or other processes related to corrosion phenomenon
- Resin Performance Monitoring – DMEA is less likely to attack the resin backbone for both cation and anion exchange resins as compared to ETA. However, application of DMEA at plant conditions over significant operating times has not been performed.

**Table 2-1
DMEA Qualification Matrix**

Area	Topic	Basis/Rational	Gap Description	Severity	Recommended Testing
Physical and Chemical Properties	Basicity	Sufficient basicity is required to increase the pH _T at key locations without requiring extensive amine addition (i.e., only “low” concentrations required). In general, an increase in the pH _T of at least 1.0 relative to neutral is expected to be effective.	Experimental data for the basicity of DMEA are not available at high temperature. Basicity estimates are available and implemented in MULTEQ. These estimates suggest DMEA’s basicity is bounded by currently utilized amines.	Minor	Additional high-temperature testing would improve models for the DMEA ionization reaction for use in PCS and for comparison to other amines.
	Volatility	Volatility should be relatively “low” (e.g., similar to water) to ensure protection of two-phase systems	Experimental volatility data exists for temperatures between 100° and 262°C. Volatility is implemented in MULTEQ.	N/A	Additional data could improve the accuracy of distribution models for DMEA.
	Thermal Decomposition	Half-life during operation/layup needs to be adequate to ensure cost effective addition schedule. Decomposition products could cause changes in pH, conductivity, or potential that has a negative effect on corrosion rates or pH control.	Experimental results for the decomposition of DMEA include half-lives for other amines that do not agree with published values. Decomposition products are not well defined and production rate data are not available.	Moderate	Additional thermal decomposition testing with an emphasis on both decomposition rate of DMEA and identification of decomposition products would be beneficial, providing improved inputs for plant chemistry modeling.
	Purity	The presence of impurities in DMEA could lead to the addition of unwanted chemicals that significantly contribute to contaminant concentrations.	DMEA appears available at high purity and in industrial quantities. However, a certificate of analysis could not be obtained that demonstrated that the concentrations of impurities of concern were sufficiently low or below detectability.	Major	Plant-specific procedures or specifications will need to be developed or implemented based on available inputs (e.g., distributor certificate of analysis, plant-specific chemistry program controls) to ensure adequate purity feedstocks are acquired for plant application.
	Safety and Storage	Potential safety hazards need to be negligible or sufficiently low, so as to allow for safe/economic storage and handling. Shelf life must be sufficient to allow for storage of acceptable amounts. Note that pure DMEA has a flashpoint of 39°C.	DMEA is commonly used in industrial settings with safety and storage procedures. Handling considerations are comparable to other amines used for PWR secondary side pH control. DMEA is stable under recommended storage conditions. Concentrated DMEA is toxic and corrosive via any contact path. Health hazards may be reduced by use of a dilute form of DMEA.	Minor	Plant specific procedures are expected to be developed or implemented based on available inputs (i.e., SDS documents and applicable regulations) to ensure proper storage and disposal before a plant trial. Additional testing regarding the flash point and extent of water dilution may help establish safe handling procedures.

Table 2-1 (continued)
DMEA Qualification Matrix

Area	Topic	Basis/Rational	Gap Description	Severity	Recommended Testing
Physical and Chemical Properties	Environmental Concerns	Potential environmental hazards need to be negligible or sufficiently low, so as to allow for safe/economic storage, handling, discharge, and/or disposal (include expected volumes, concentrations, discharge, and degradation products)	DMEA is listed under 40 CFR 60 and 40 CFR 63. There may also be applicable local regulations regarding disposal of DMEA. Although regulated, proper disposal pathways are available for DMEA.	Minor	Plant specific procedures are expected to be developed or implemented based on available inputs (i.e., SDS documents and applicable regulations) to ensure proper storage and disposal before a plant trial.
Materials Compatibility	Materials of Construction	Potential to adversely affect nickel alloys, stainless steel (SS), carbon steel (CS), low alloy steel (LAS), copper alloys, or other metals (e.g., Ti).	Little or no data are available for interaction of DMEA with materials of construction at conditions of interest. However, adverse effects are expected to be driven by pH (not the amine). Data are not available to confirm that DMEA interaction with metals is the same as other amines that have been investigated.	Major	Additional testing is recommended to verify that the interaction between DMEA and metals is comparable to other tested amines. As appropriate, this testing may be conducted using a bounding set of materials and environments to confirm the effects of DMEA are comparable to ETA.
	Resins	Potential to increase resin fouling or reduced resin performance	Experimental results show DMEA to be less deleterious to ion-exchange resin than ETA. Reduced fouling is expected compared to ETA. However, DMEA has never been used for an extended period of time under PWR secondary side conditions.	Minor	No additional testing recommended. However, monitoring and assessment of resin performance is recommended during a plant demonstration with DMEA.
	Elastomers and Seals	Potential to reduce elastomer and seal performance	Little or no data are available for interaction of DMEA with elastomers and seals. Adverse effects are expected to be driven by amine-specific interactions.	Major	Additional testing is recommended to determine if any adverse DMEA-specific interactions exist. If appropriate, testing could be limited to elastomers and seal material used within the plant that is considering DMEA use (i.e., a plant-specific evaluation).

Table 2-1 (continued)
DMEA Qualification Matrix

Area	Topic	Basis/Rational	Gap Description	Severity	Recommended Testing
Application Considerations	Program Expectations	Need to specify injection schedule, control bands, target concentrations, monitor and sampling frequency, potential chemistry effects	Modeling is feasible with EPRI Plant Chemistry Simulator but simulation results depend heavily on inputs such as amine basicity, volatility, thermal decomposition, and resin selectivity (which may be the subject of other knowledge gaps).	Moderate	Additional thermal decomposition and resin selectivity data for DMEA would be beneficial for modeling plant chemistry. Cation conductivity baseline values (used for secondary water control) will likely need to be adjusted to account for the formation of DMEA decomposition products.
	Corrosion Phenomena	Need to document potential for corrosion or FAC changes	There is no experimental basis for the effect of DMEA on corrosion phenomenon. Majority of tests indicate that there is no amine-specific effect on corrosion product transport or FAC.	Major	Additional testing is recommended to verify that the interaction between DMEA and metals is comparable to other tested amines.
	Operation of Plant Equipment	Need to evaluate potential non-corrosion related phenomena, including moisture carryover, analytical instruments, and ion exchange beds.	No amine effects on SG moisture carryover. No data plant analytical instruments were found (likely coupled to corrosion phenomena effects). Loading rates for ion exchange beds fall within expected range (but estimate depends on already identified gaps for resin interaction).	Minor	Testing recommended for other knowledge gaps (i.e., corrosion phenomena and resin selectivity) is expected to support this gap.
		Need to evaluate potential changes to corrosion product deposition rate.	Laboratory and plant-based evidence of an amine-specific effect on corrosion product deposition and thermal resistance are limited.	Major	Additional testing is recommended to verify that the interaction between DMEA and metals is comparable to other tested amines (including effects on general corrosion and FAC).

3

PHYSICAL AND CHEMICAL PROPERTIES

In general, a number of basic physical and chemical properties of a candidate amine must be understood before the viability as a pH control agent in the PWR secondary side can be evaluated. This section provides a review of DMEA properties, including key factors related to amine application. A summary is provided in Section 3.3.

3.1 Overview

3.1.1 Formula and Structure

Formula:	C ₄ H ₁₁ NO (CH ₃) ₂ NCH ₂ CH ₂ OH
Molecular Weight [6]:	89.1362 g/mol
Composition:	53.9%C 12.4%H 15.7%N 18.0%O

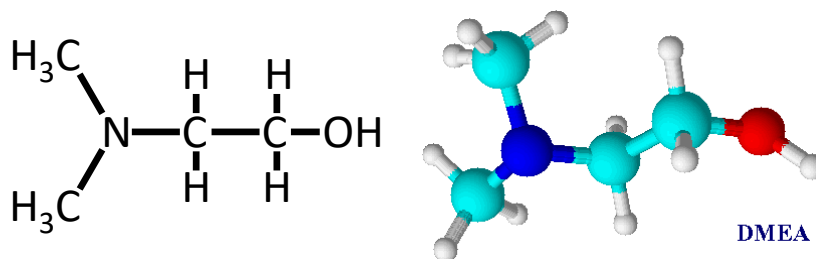


Figure 3-1
Molecular Structure of DMEA

3.1.2 Identifiers

CAS No:	108-01-0
RTECS No [7]:	KK6125000
EC No [8]:	204-542-8
ILO ICSC No [9]:	0654
Common Names [6,7]:	N,N-dimethylethanolamine dimethylethanolamine DMEA N,N-dimethyl-N-(2-hydroxyethyl)amine N,N-dimethyl(2-hydroxyethyl)amine N,N-dimethyl-2-hydroxyethylamine N,N-dimethyl-β-hydroxyethylamine

dimethyl(2-hydroxyethyl)amine
dimethyl(hydroxyethyl)amine
N-(2-hydroxyethyl)dimethylamine
(2-hydroxyethyl)dimethylamine
 β -hydroxyethyl dimethylamine
2-(N,N-dimethylamino)ethanol
N,N-dimethyl-2-aminoethanol
N,N-dimethylaminoethanol
2-(dimethylamino)ethanol
2-dimethylaminoethanol (deanol)
 β -(dimethylamino)ethanol
 β -dimethylaminoethanol
(dimethylamino)ethanol
dimethylaminoethanol
DMAE
ethanol, 2-dimethylamino-
Deanol
Kalpur P

3.1.3 Physical Properties

The following physical properties of DMEA:

Boiling Point [10]:	275°F (134°C at 758 mmHg)
Vapor Pressure [11]:	612 Pa (at 20°C)
Vapor Density [11]:	3.03 (Relative to Air)
Water Solubility [10]:	Miscible
Specific Gravity [12]:	0.887 (at 20°C)
Appearance [13]:	Colorless liquid, with amine/fishy odor

3.1.4 Industrial Uses

DMEA is used in a variety of industries. A literature search showed applications relating to [14,15,16]:

- Production of flocculants for wastewater treatment
- Pulp and paper production
- Manufacture of ion resin and membranes
- Manufacture of flexible and rigid polyurethane foam
- Epoxy resin curing agent
- Acrylic coatings
- Textiles and leather treatment

- Water based paints
- Polyurethane lacquers
- Corrosion control in boiler condensate return lines
- Manufacture of engineered wood products
- Pesticides
- Soil conditioners
- Inks and Dyes
- Drugs and pharmaceuticals

The Dow Chemical Company sold DMEA as recently as 2003 as part of a line of alkyl alkanolamines. Product literature specifically called out DMEA as being used in several water treatment applications. It showed DMEA as used for production of cationic polymeric flocculants and type II anion exchange resins, as well as being used for corrosion inhibition in boiler systems. As a corrosion inhibitor, the literature points out the basicity and volatility giving good pH control in the boiling solution, vapor, and condensate. It also mentions that DMEA does not form solid hydrates or react to form solid products that could cause fouling [17]. DMEA is no longer shown as an available product on the Dow Chemical website. However, it is currently produced by the Huntsman Corporation [15].

Riker Laboratories produced a prescription drug Deaner® (deanol p-acetamidobenzoate, i.e., a salt of DMEA and p-acetamidobenzoate) until 1983 when it was discontinued. This drug was used to treat children with learning and behavior problems. DMEA is currently sold as a dietary supplement, often in the form of DMEA bitartrate. Neither form is trivial to produce from pure DMEA. However, inventory control is always recommended for any obvious pharmaceutical precursor [14]. Additionally, DMEA is a chemical intermediate in the production of procaine and is also used in the production of several antihistamines, analgesics, and the drug Tamoxifen [17].

3.1.5 Fire and Explosion Hazard Data

Flash Point [13]: 39°C (102.2°F)

NFPA Rating [13]: Health = 3.3, Flammability = 2.2, Reactivity = 0

Extinguishing Media [18]: CO₂, dry chemical, or alcohol foam

Toxic Gasses Produced [18]: Nitrogen Oxides

Fire-Fighting Apparatus [13]: Wear self-contained breathing apparatus for firefighting.

Incompatibility [13]: Strong acids, strong oxidizers, copper, zinc, iron

Given the relatively low flash point of DMEA, it would be advantageous for utilities to acquire and store DMEA in a solution with a low enough concentration to reduce its flammability. No information was found during this literature review regarding the relationship between the flash point of DMEA and concentration. The lack of readily available information regarding the specific handling of DMEA with respect to fire and explosion hazards, beyond what is provided

in an SDS document, is considered a minor knowledge gap. Specifically, no unique hazards could be identified. This minor gap is expected to be addressed in plant procedures and specification documents as part of the preparation process for a plant trial. Additional testing regarding the flash point and extent of water dilution may help establish safe handling procedures.

3.1.6 Health Hazard Data

DMEA is acutely toxic through ingestion, inhalation, or skin contact. It is also corrosive to the skin and can cause severe eye damage [11]. Health effects of DMEA and other relevant compounds are provided in Table 3-1. By comparison, the health effects of DMEA appear comparable to or less severe than other secondary side additives (e.g., hydrazine, ETA, ammonia).

3.1.7 Safety and Storage

High concentrations of DMEA are acutely toxic through any method of contact. It is also corrosive to skin. DMEA is a flammable liquid with a flammable vapor so it should not be handled near spark or flame.

Concentrated DMEA (i.e., > 98%) should be stored in non-metal containers¹ at a temperature below 38°C (100°F) [13]. This temperature limit represents an upper bound, as lower concentration solutions (i.e., water-diluted DMEA) would be less flammable. The location should be fireproof, located away from spark or flame, acids, acid chlorides, strong oxidizers, copper, and zinc [11]. Plant personnel handling DMEA should use appropriate personal protection equipment. It is noted that these precautions are not particularly notable for concentrated amine solutions in an industrial setting (i.e., in accordance with SDS documentation).

3.1.8 Environmental and Disposal Information

DMEA is known to be toxic to aquatic life at high concentrations [13]. Environmental toxicity data for DMEA and other PWR secondary side additives are listed in Table 3-1. The data indicate that DMEA is less toxic than hydrazine and similar to ETA.

DMEA is commonly released into water from industrial applications such as the production of plastics, ion exchange resins, flocculants, and pharmaceuticals. A significant portion of the DMEA is distributed to the air during a water release (44% at 10°C, 61% at 20°C). In air, DMEA is known to undergo indirect photolysis in the presence of hydroxide ion. In aqueous environments, it is known to biodegrade. For example, DMEA began to biodegrade after about 5 days when subjected to an oxygen availability that simulated river conditions [14]. DMEA has also been shown to degrade readily in domestic and industrial sewage under aerobic conditions [14].

¹ The restriction on storage in the presence of metal is only mentioned in vendor SDS documents regarding high concentrations of DMEA (≥98%).

Table 3-1
Toxicological and Environmental Assessment of DMEA and Other Additives

Name	GHS Hazard Statements	Carcinogen Status	Acute Toxicity	Environmental Data	Ref
Hydrazine	Flammable liquid and vapor Toxic if swallowed or in contact with skin Causes severe skin burns and eye damage May cause an allergic skin reaction Causes serious eye damage Fatal if inhaled May cause cancer Very toxic to aquatic life with long lasting effects	Probable human carcinogen and confirmed animal carcinogen	LD50 rat (oral): 101-141 mg/kg LD50 rat (inhalation): 0.759 mg/L	Semi-Static EC50: <i>Daphnia magna</i> , 0.17 mg/L, 48 hr	[19]
DMEA	Flammable liquid and vapor Harmful if swallowed or in contact with skin Causes severe skin burns and eye damage Causes serious eye damage Toxic if inhaled Harmful to aquatic life	Not identified as a potential carcinogen	LD50 rat (oral): 1182.7 mg/kg LC50 rat (inhalation): 1641 ppm LD50 rabbit (dermal): 1219 mg/kg	LC50: <i>Leuciscus idus</i> > 100-220 mg/L, 96 hr Static LC50: <i>Leuciscus idus</i> , 146.63 mg/L, 96 hr Static EC50: <i>Daphnia magna</i> , 98.37 mg/L, 48 hr	[13]
ETA	Combustible liquid Harmful if swallowed, in contact with skin or if inhaled Causes severe skin burns and eye damage Causes serious eye damage May cause respiratory irritation Toxic to aquatic life Harmful to aquatic life with long lasting effects.	Not identified as a potential carcinogen	LD50 rat (oral): 1089 mg/kg LD50 rabbit (dermal): 1015 mg/kg	Semi-Static LC50: <i>Cyprinus carpio</i> , 150 mg/L, 96 hr EC50: <i>Daphnia magna</i> , 65.0 mg/L, 48 hr	[20]
Ammonia	Flammable gas Contains gas under pressure; may explode if heated Causes severe skin burns and eye damage Toxic if inhaled Very toxic to aquatic life with long lasting effects	Not identified as a potential carcinogen	LC50 rat (inhalation): 2000 ppm, 4 hrs	LC50: <i>Daphnia magna</i> , 25.4 mg/L, 48 hr	[21]

Federal regulations applicable to the release of DMEA include [14]:

- 40 CFR 60. Subpart YYY – Volatile Organic Compound Emissions from Synthetic Organic Chemical Manufacturing Industry Wastewater.
- 40 CFR 63. National Emission Standards for Hazardous Air Pollutants for Source Categories.
- 40 CFR 63. Subpart F-National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry.

Regulations regarding the release of DMEA will vary by location. Disposal has been recommended via a chemical incinerator equipped with an afterburner and scrubber or through a chemical disposal service [13].

3.2 Factors Affecting Amine Application

3.2.1 Purity

Use of a chemical additive, including amines, involves some risk that one or more unintended species could be introduced as contaminants. In general, industry-wide purity requirements are not established for chemicals that are added to the PWR secondary system. Rather, it is expected that the utility will specify the impurity limits, based on the plant-specific pH program, when a procurement specification is provided to the amine vendor. The ability of the recirculating steam generator to concentrate contaminants means that relatively low contaminant amine solutions must be used. Information concerning typical impurity limits specified in the nuclear industry for chemicals used in PWR secondary systems is included in the EPRI reference document for procurement of bulk chemicals for nuclear plants [22]. Example (for information only) specifications for ETA, MPA, morpholine, and DMA indicate that sodium, chloride, sulfate, lead, copper, iron, fluorine, and TOCs are all impurities of concern. In general, the maximum specified concentration limit for these impurities (excluding TOCs) is between 0.1 and 5 ppm. The plant-specified maximum impurity limit in the procurement specification can be calculated as follows [23]:

$$Am_x [ppm] = 10 \frac{FW_{x,max} [ppb]}{FW_{am} [ppm]} Am [\%] \quad [3-1]$$

Where,

- Am_x – Maximum acceptable impurity concentration in the amine product (ppm)
- $FW_{x,max}$ – Maximum acceptable feedwater concentration of the impurity (ppb)
- Am – Concentration of the amine in the product (%)
- FW_{am} – Feedwater concentration of applied amine (ppm)

Note that the factor of ten addresses unit conversions (ppm impurity in product, ppb impurity in feedwater, % amine in product).

For example, feedwater impurities below 0.01 ppb of the contaminant can be achieved with a 40% amine containing a maximum 2 ppm contamination with an amine feedwater concentration of 20 ppm.

If it is implemented for pH control, similar plant-specific purity requirements will be required for DMEA. A review of commercial chemical vendors indicates that DMEA is available in large volumes and at high purity. For example, one US distributor indicated that 55-gal drums of DMEA (weighing 396.83 lb) were in stock at a cost of \$2.00/lb to \$2.60/lb, depending the quantity ordered [24]. The accompanying certificate of analysis indicated that the chemical contained 100.00-%wt DMEA and 0.01-%wt H₂O, with no other impurities noted (i.e., impurity-free down to ~100 ppm resolution). In addition, a review of information available from different vendors indicated that no specific impurity was common in DMEA. However, a certificate of analysis could not be collected that confirmed that the impurities discussed above (i.e., sodium, chloride, sulfate, etc.) were analyzed for and shown to be exceptionally low or below detectable limits. Therefore, the purity of commercially available DMEA is identified here as a major knowledge gap because it is expected that this gap will be closed prior to a plant trial. However, the limited information that is available indicates that the level of effort to close this gap during procurement will be low.

3.2.2 Basicity

The primary goal of PWR secondary side pH control is to limit the activity of hydrogen ions in solution so as to reduce the potential for corrosion around the secondary loop. Due to this goal, stronger bases are preferred (else high amine concentrations would be necessary).

Amines are defined as derivatives of ammonia in which one or more hydrogen atoms have been replaced with an organic group. The lone pair of electrons on the nitrogen atom has a high affinity for H⁺ ions, which gives amines their basic properties. Amines are weak bases because they do not react fully with water. The basicity or strength of a base is quantified using the base hydrolysis constant, K_b , which is defined as the equilibrium constant of the hydrolysis reaction. The generic dissociation reaction for a basic compound (B) and its conjugate acid (BH^+) is defined as follows:



Here, the amine is the basic compound and the ionized amine is the conjugate acid. The corresponding base hydrolysis constant is:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad [3-3]$$

$$pK_b = -\log_{10} K_b \quad [3-4]$$

Similarly, the acid hydrolysis constant, K_a , for the conjugate acid ion is defined as follows:



$$K_a = \frac{[B][H^+]}{[BH^+]} \quad [3-6]$$

$$pK_a = -\log_{10} K_a \quad [3-7]$$

In solution, the product of the hydrolysis constants for the conjugate acid-base pair, K_a and K_b , are related to the dissociation constant of water, K_w , as follows:

$$K_a K_b = K_w = [H^+][OH^-] \quad [3-8]$$

Lower values of pK_b correspond to an increase in the basicity of the compound. For PWR secondary side pH control, stronger bases (i.e., bases with lower pK_b values) are preferred because lower concentrations are required to control the pH. The use of lower concentrations leads to lower material costs (fewer kilograms of additive must be purchased) and lower consumption of resin used for purification (blowdown demineralizer or condensate polisher resins).

Basicity is known to be temperature dependent due to the increased dissociation of water at higher temperatures (within the range of PWR secondary system operation). This leads to a drop in pH and pK_a and an increase in pK_b with increasing temperature. Figure 3-2 shows the temperature dependence of pK_b values for several common amines, adapted from Reference [4], including DMEA. For DMEA and some other amines shown here, the ionization reaction equilibrium is based on a free energy model that extrapolates from thermodynamic data below 100°C. Moreover, the estimated average heat capacity over the entire temperature range that is used in the calculation is based on both low temperature data and estimated functional group corrections. In the original study, the model results were shown to agree with available high-temperature data for ammonia, cyclohexylamine, and morpholine. Since this work was first published, more recent experimental data have become available that supported the overall validity of the high-temperature equilibrium constants. Note that the temperature dependence of pK_b of DMEA is comparable to other amines and generally bounded by those in service over the temperature range of interest. Thus, the concentration of DMEA required to control PWR secondary side pH should be comparable to other amines (all other factors being equal).

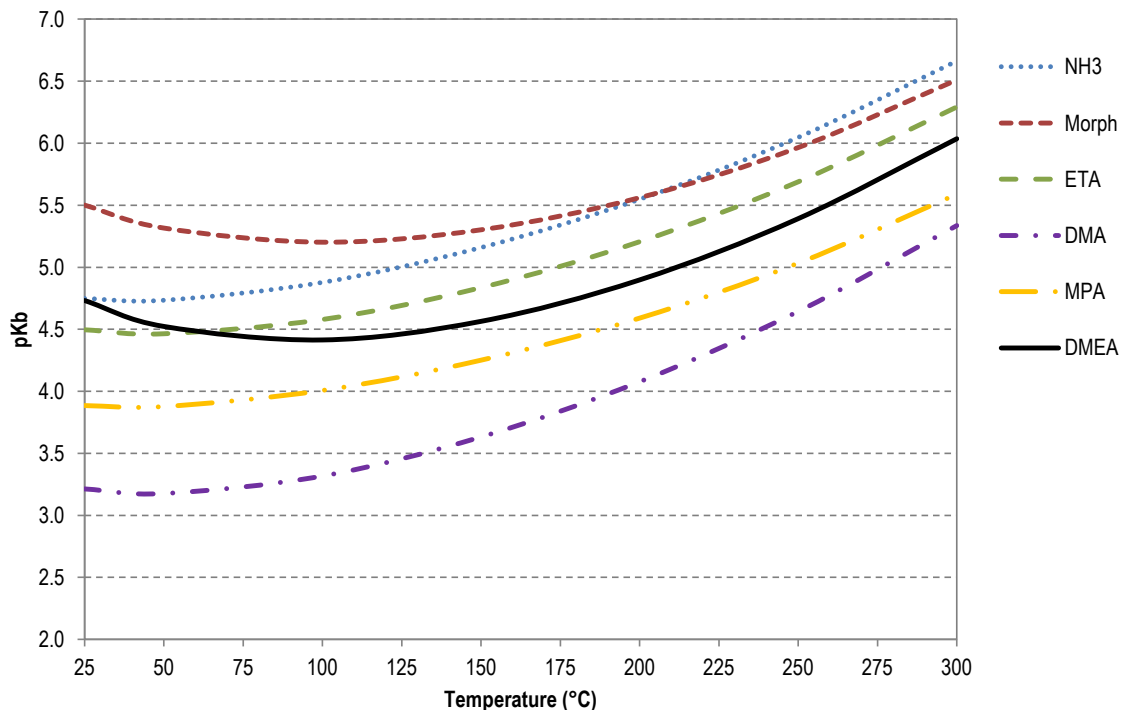


Figure 3-2
Temperature Dependence of pK_b for Several Common Amines (adapted from Ref [4])

The estimated basicity results for DMEA between 50°C and 300°C, discussed above, have been fit using the following MULTEQ formulation [25,26]:

$$\log_{10} K_i = 9.80573 - (2.27860 \times 10^{-2})T + (3.55442 \times 10^{-5})T^2 - (3.35622 \times 10^{-8})T^3 \quad [3-9]$$

Here, T is the temperature in °C and K_i is an equilibrium constant for the following reaction:



$$K_i = \frac{1}{K_a} = \frac{[BH^+]}{[B][H^+]} \quad [3-11]$$

The above correlation is captured in the current Version 8.0² of the MULTEQ Species Database [25]. Thus, the ability to model the ionization of DMEA is currently available in EPRI's ChemWorks Tools™ and Plant Chemistry Simulator software. As was discussed previously, the correlation is expected to be applicable between 25°C and 300°C.

² At the time that this report was written, Version 9.0 of the database was in the late stages of development. No changes to the DMEA entry were planned. Thus, the analyses presented here are expected to be consistent with Version 9.0 of the database even though Version 8.0 was used in preparation of this report.

Because the at-temperature pH (pH_T) depends on both temperature and amine concentration, it is often instructive to normalize the different amines relative to amine-specific concentrations that yield the same pH_T at a specified temperature. This shows the effect of pK_b 's temperature dependence on pH. For example, Figure 3-3 and Figure 3-4 show the pH_T of DMEA and other amines with increasing temperature. Here, the amine concentrations are normalized to the same initial room temperature values of $pH_{25^\circ C} = 9.5$ and $pH_{25^\circ C} = 10.5$, respectively. The pH_T of neutral water is also plotted in each figure for comparison. In addition, the concentration required for each amine to reach a given $pH_{25^\circ C}$ is shown in Table 3-2. These results were generated using MULTEQ in EPRI ChemWorks™ Tools v4.2 supported by Version 8.0 of the MULTEQ Species Database [25].

These results show the trend in decreasing basicity with increasing temperature as, for all cases, the difference in pH_T from the amine to neutral water decreases with increasing temperature. This is expected from the trend in pK_b shown in Figure 3-2. Note that DMEA trends similar to morpholine while requiring a significantly lower concentration to achieve the same pH_T .

Similarly, Reference [27] chose $pH_{275^\circ C} = 6.5$ as a common basis (see concentrations in Table 3-2). The variation in the pH_T of DMEA and other amines using this basis are shown in Table 3-3.

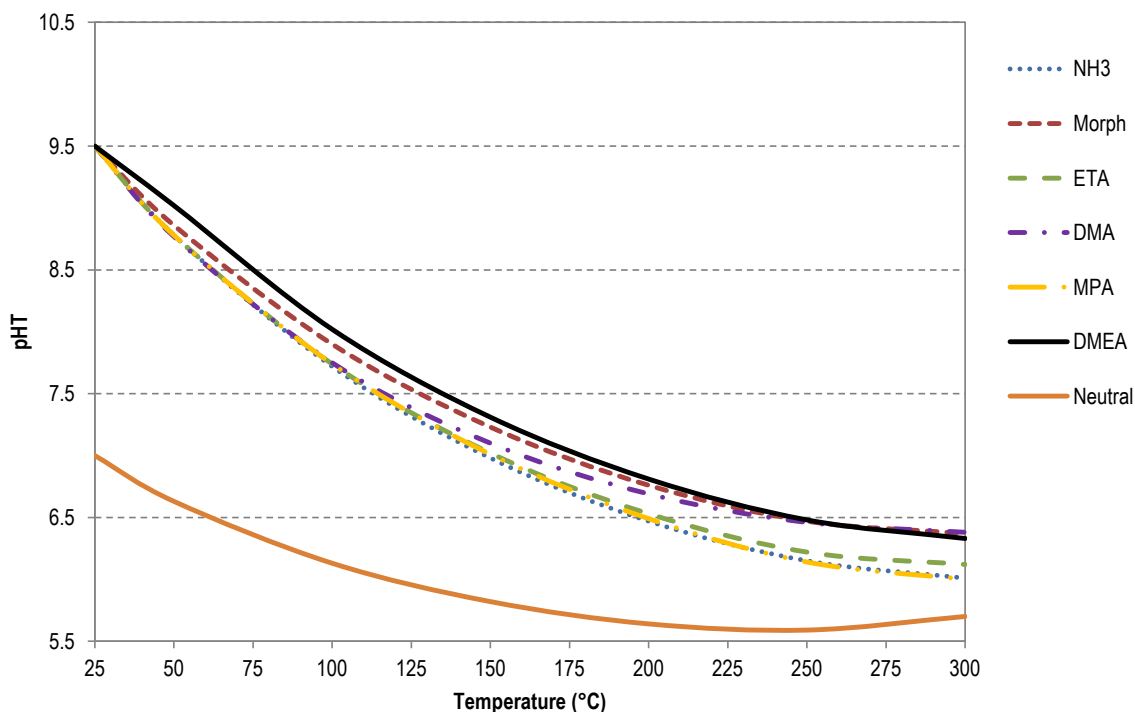


Figure 3-3
At Temperature pH_T for Several Amine Concentrations Such That $pH_{25} = 9.5$

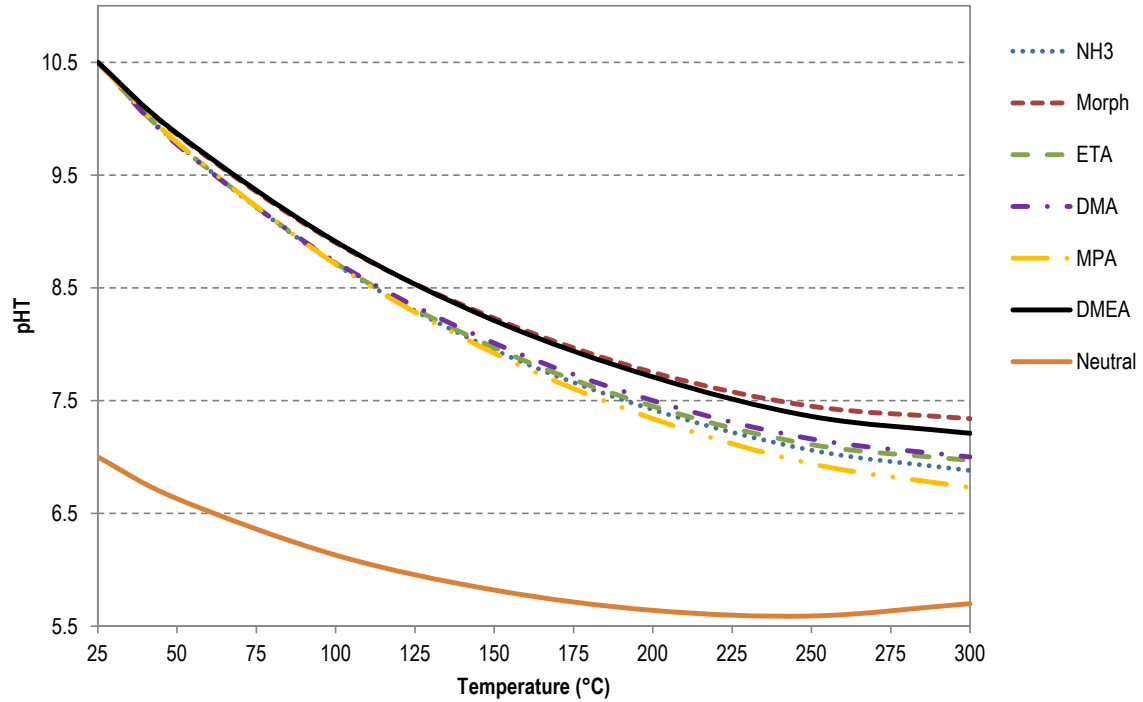


Figure 3-4
At Temperature pH_T for Several Amine Concentrations Such That $pH_{25} = 10.5$

Table 3-2
Concentration of Amine required to reach pH_T (ppm)

Amine	$pH_{25} = 9.5$	$pH_{25} = 10.5$	$pH_{275} = 6.5$
NH_3	1.5	105	13
Morpholine	31	2850	51
DMA	1.5	22	2.3
ETA	3.9	216	21
MPA	4	146	36
DMEA	7.7	521	16.5

Table 3-3
At Temperature pH_T for Several Amine Concentrations such that $pH_{275} = 6.5$

	Neutral	NH ₃	Morph	ETA	DMA	MPA	DMEA
pH_{25}	7.00	10.03	9.61	9.95	9.67	10.15	9.70
pH_{50}	6.63	9.31	8.98	9.24	8.94	9.44	9.06
pH_{100}	6.13	8.24	8.02	8.18	7.92	8.37	8.09
pH_{150}	5.82	7.49	7.35	7.44	7.26	7.60	7.40
pH_{200}	5.64	6.96	6.88	6.92	6.83	7.03	6.92
pH_{250}	5.59	6.61	6.58	6.60	6.57	6.63	6.60
pH_{275}	5.62	6.50	6.50	6.50	6.50	6.50	6.50
pH_{300}	5.70	6.43	6.47	6.47	6.48	6.43	6.46

In summary, experimental data for the DMEA ionization reaction are not available at high temperature. However, the equilibrium constant for the reaction has been extrapolated up to 300°C using a Gibbs free energy relationship based on molar heat capacity estimates. This extrapolation methodology has been validated with high-temperature data for other amines. The results suggest that the basicity of DMEA is comparable to other amines and is generally bounded over the temperature range of interest by other amines that are in service. The extrapolated results for DMEA have also been used to generate a temperature-dependent correlation for the ionization reaction that is currently integrated into EPRI's latest MULTEQ database, allowing the reaction to be modeled in ChemWorks Tools™ or the Plant Chemistry Simulator.

The lack of high-temperature ionization data is identified as a knowledge gap. However, the severity of this gap is considered minor because the method currently used to predict the ionization behavior of DMEA at high temperature (i.e., a Gibbs free energy based extrapolation) has been shown to perform well for similar amines (i.e., ammonia, cyclohexylamine, and morpholine). Stated alternatively, the predicted behavior of DMEA is expected to remain largely unchanged if additional data were to be made available. Even so, the additional high-temperature data could facilitate more accurate modeling of the distribution of DMEA around the PWR secondary system.

3.2.3 Volatility

The volatility of pH control agents is important because PWR secondary coolant systems contain many components where liquid-vapor equilibrium exists. In general, volatility similar to that of water gives the best distribution throughout the secondary system because the agent is equally distributed in both phases at all condensation points. This is particularly important in early condensate, where only some very small fraction of steam is condensed to a liquid phase that should maintain an elevated pH_T relative to neutral. Additionally, amines can have a significant influence on the lifetime and effectiveness of the ion exchange resins used in condensate polishing or blowdown demineralization. Choosing a pH control agent with an appropriate plant-optimized volatility can help mitigate any negative affect. For example, lower volatility amines may be ideal for plants with condensate polishers because much of the amine may

separate to the liquid phase in the moisture separator reheater and thus bypass the condensate system on its return to the steam generators.

In general, the volatility is quantified using an equilibrium ratio, defined as the ratio of the mole fraction of the species present in the two phases. The distribution coefficient is defined as follows:

$$K_D = \frac{y_B}{x_B} = \frac{[B]_v}{[B]_{aq}} \quad [3-12]$$

Note that at these relatively low amine concentrations (i.e., water dominant phases) the concentration of the amine can effectively be used interchangeably with the mole fraction. The parameter $[B]_{aq}$ in Equation [3-12] is the concentration of the neutral species in the liquid phase, i.e., it does not include any charged species. At low concentrations, the distribution coefficient, K_D , will only be dependent on temperature and, by definition, will not change due to other factors that shift the chemical equilibrium. Stated alternatively, a change in pH leading to a decrease in the neutral species concentration will also decrease the equilibrium vapor phase concentration of the amine (but not change K_D).

If the total concentration in the liquid phase is known independent of ionization, it is convenient to define an *apparent* distribution coefficient, as follows:

$$K_{D,app} = \frac{y_B}{\sum x_{B,i}} = \frac{[B]_v}{\sum [B_i]_{aq}} \quad [3-13]$$

Here, the denominator defines the total liquid phase concentration of the species under consideration, including both neutral and ionized species. Note that the apparent distribution coefficient is a less fundamental parameter. Specifically, $K_{D,app}$ will be dependent on pH as well as temperature (for a given vapor phase concentration and temperature, the liquid phase concentration of the neutral species, $[B]$, is fixed but the amount of ionized species and thus the sum in the denominator of Equation [3-13] is affected by pH).

Figure 3-5 shows the temperature dependence of K_D values for several common amines adopted from Reference [4], including DMEA. The K_D of DMEA is calculated up to 300°C as part of the same Gibbs free energy calculation performed for Figure 3-2 [4].

For some of the amines shown in Figure 3-5, as with basicity, the K_D presented is based on a Gibbs free energy model that extrapolates from thermodynamic data below 100°C. Moreover, the estimated average heat capacity over the entire temperature range that is used in the calculation is based on both low temperature data and estimated functional group corrections. In the case of DMEA, volatility data exist between 100°C and 262°C but do not cover the full range presented. In the original study, the model results were shown to agree with available high-temperature data for ammonia, cyclohexylamine, and morpholine. Since this work was first published, more recent experimental data have become available that support the overall validity of the high-temperature equilibrium constants. Note that the temperature dependence of K_D for DMEA is comparable to other amines and generally bounded by those in service over the temperature

range of interest. Moreover, the volatility is similar to that of MPA, which means that it will tend to distribute around the secondary system in essentially constant concentrations (all other factors being equal). Note that the horizontal line at $\text{Log } K_D = 0$ (or $K_D = 1$) in Figure 3-5 corresponds to the equal distribution of nonvolatile species between the liquid and vapor phase.

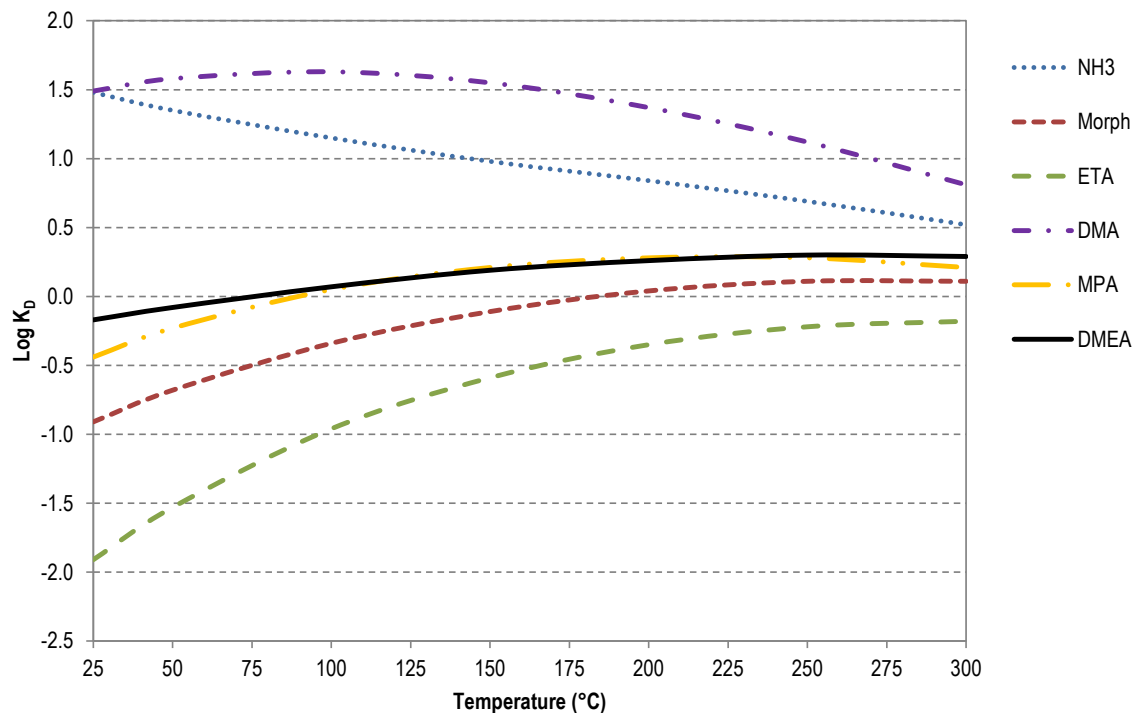


Figure 3-5
Temperature Dependence of K_D for Several Common Amines (adapted from Ref [4])

The volatility results for DMEA between 50°C and 300°C, discussed above, have also been fit using the following MULTEQ formulation [25]:

$$\begin{aligned} \log_{10} K_D = & -0.12 - (2.15333 \times 10^{-3})T + (8.53333 \times 10^{-5})T^2 \\ & - (6.13333 \times 10^{-7})T^3 - (1.86667 \times 10^{-9})T^4 \\ & - (2.13333 \times 10^{-12})T^5 \end{aligned} \quad [3-14]$$

Here, T is the temperature in °C and K_D is an equilibrium ratio for the following reaction:



$$K_D = \frac{[DMEA]_v}{[DMEA]_{aq}} \quad [3-16]$$

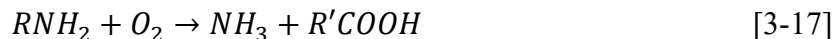
The above correlation is captured in the current Version 8.0³ of the MULTEQ Species Database [25]. Thus, the ability to model liquid-vapor phase partitioning of DMEA is currently available in EPRI's ChemWorks Tools™ and Plant Chemistry Simulator software. As was discussed previously, the correlation is expected to be applicable between 25°C and 300°C.

In summary, experimental data for the DMEA volatility are available between 100°C and 262°C. However, the equilibrium constant for the reaction has been extrapolated up to 300°C using a Gibbs free energy relationship based on molar heat capacity estimates. This extrapolation methodology has been validated with high-temperature data for other amines. The results for DMEA suggest that its volatility is bounded by other amines and comparable to MPA. Specifically, DMEA is expected to partition (generally) almost equally between the liquid and vapor phases in the PWR secondary system. The extrapolated results for DMEA have also been used to generate a temperature-dependent correlation for the liquid-vapor phase equilibrium ratio that is currently integrated into EPRI's latest MULTEQ database, allowing the partitioning of DMEA to be modeled in ChemWorks Tools™ or the Plant Chemistry Simulator.

Although experimental data do not cover the full range of temperatures relevant to PWR secondary side chemistry, the extrapolation necessary is small and mostly at the low temperature end of the range. Due to this, no knowledge gap is identified here. Even so, additional information could be helpful to provide more accurate modeling of the distribution of DMEA around the PWR secondary system.

3.2.4 Thermal Decomposition

Thermal stability of any pH control amine is an important consideration as this determines the rate of amine loss, ammonia formation, and the forming of organic acid decomposition products in the PWR secondary coolant. Typical decomposition processes involve oxidation of the amine through a reaction similar to the one shown below [27]:



Amines, such as DMEA, with multiple organic (*R*) groups bonded to the amino nitrogen may undergo many decomposition steps before ammonia is produced. These intermediate amines may have different volatility and basicity than the original amine used for pH control. This, combined with the production of organic acids, could possibly lead to local pH excursions in the PWR secondary system or additional stress on the ion exchange beds. Understanding decomposition paths and rates is thus important prior to use of a new amine for pH control.

Reference [28] examined the thermal degradation of DMEA along with several other amines over a range of temperatures and pressures. Figure 3-6 shows the data collected for DMEA compared with the data for several common amines.

³ At the time that this report was written, Version 9.0 of the database was in the late stages of development. No changes to the DMEA entry were planned. Thus, the analyses presented here are expected to be consistent with Version 9.0 of the database even though Version 8.0 was used in preparation of this report.

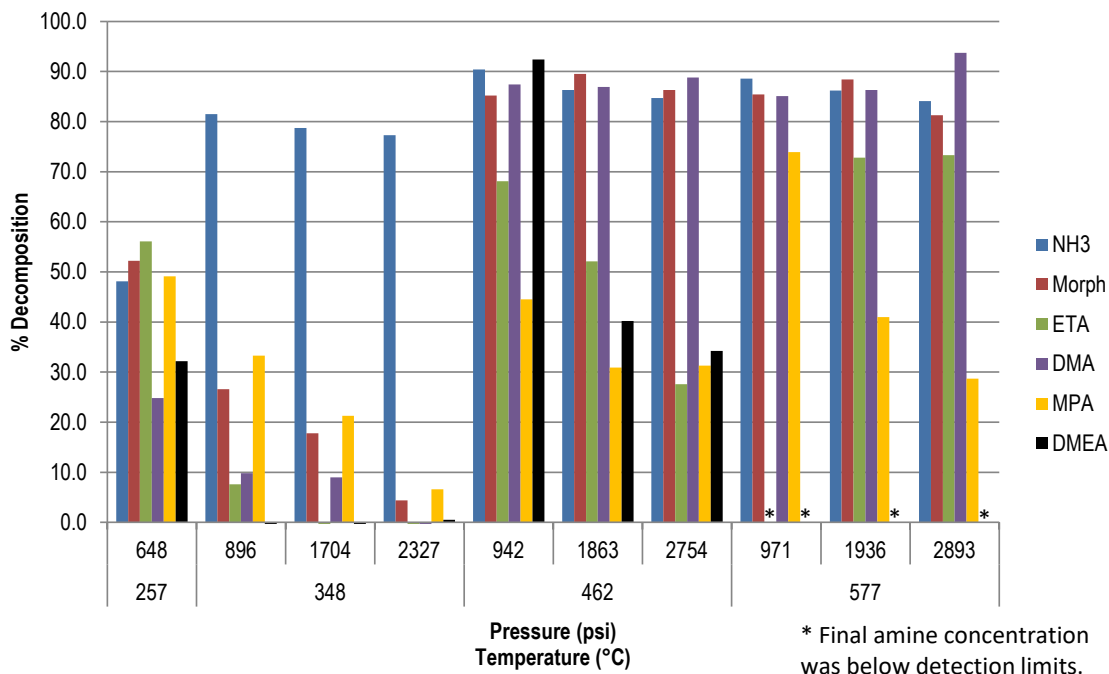


Figure 3-6
Thermal Decomposition of Several Common Amines after 10 min Heating⁴ (adapted from Reference [28])

These results show DMEA to have generally similar (or sometimes better) thermal stability than the other amines surveyed in the 257°C, 348°C, and 462°C tests. Based on these results, DMEA decomposition at PWR secondary chemistry conditions is expected to be similar to other amines currently in use.

The same Reference [28] reports a first order reaction rate constant for each amine using the same data presented in Figure 3-6. The calculated half-lives for each amine at 257°C, based on the reported decomposition rates in Reference [28], are presented in Table 3-4. For comparison, half-lives presented in another reference [29] for the same amines under similar conditions are also presented in this table. As can be seen in the table, the calculated degradation half-life values for ETA, MPA, and morpholine are all at least a factor of 4 lower than the previously reported values for 10 ppm solutions at 285°C [27,29]. Note that data in Reference [28] were viewed as not being well suited for an Arrhenius-type fit, so no attempt was made to adjust the reported rates to the same temperatures (i.e., 285°C). Ultimately, the mismatch in the predicted decomposition rates for other amines and the negative degradation values seen for several samples call into question the applicability of these decomposition results for DMEA.

⁴ It is believed the decomposition of ammonia was over estimated throughout all tests due to ammonia's high room temperature volatility compared to other amines causing loss during the opening / depressurization of each sample. Oxygen is also known to catalyze the decomposition of ammonia in the presence of metals, which may be an additional factor. Additionally, measurement error led to a few samples showing negative decomposition. This was true for the 896 and 1704 psi samples of DMEA at 348°C. Samples with a negative value are expected to have had minimal decomposition.

Table 3-4
Calculated Amine Degradation Half-Lives (Based on Reference [28])

Amine	$t_{1/2}$ (hr)	Condition	Reference
Morph	2.67	10 ppm, 257°C, 648 psi	Based on [28]
	12	10 ppm, 285°C	[29]
ETA	2.38	10 ppm, 257°C, 648 psi	Based on [28]
	99	10 ppm, 285°C	[29]
DMA	6.88	10 ppm, 257°C, 648 psi	Based on [28]
MPA	2.92	10 ppm, 257°C, 648 psi	Based on [28]
	12	10 ppm, 285°C	[29]
DMEA	5.07	10 ppm, 257°C, 648 psi	Based on [28]

In general, half-lives for amines have a wide range of reported values in the literature. One explanation for this may be differences in the quantity of dissolved oxygen in the sample during testing. The same study as discussed above performed decomposition tests for several amines at varying levels of dissolved oxygen. The quantity of dissolved oxygen was not well-controlled (atmospheric conditions versus nitrogen purging of the test vessel) and DMEA was not one of the amines studied. Nevertheless, Figure 3-7 shows that the presence of oxygen has a dramatic effect on the decomposition rate of ETA and MPA. Based on this knowledge gap (i.e., limited decomposition data), additional decomposition testing of DMEA at secondary side conditions would be beneficial.

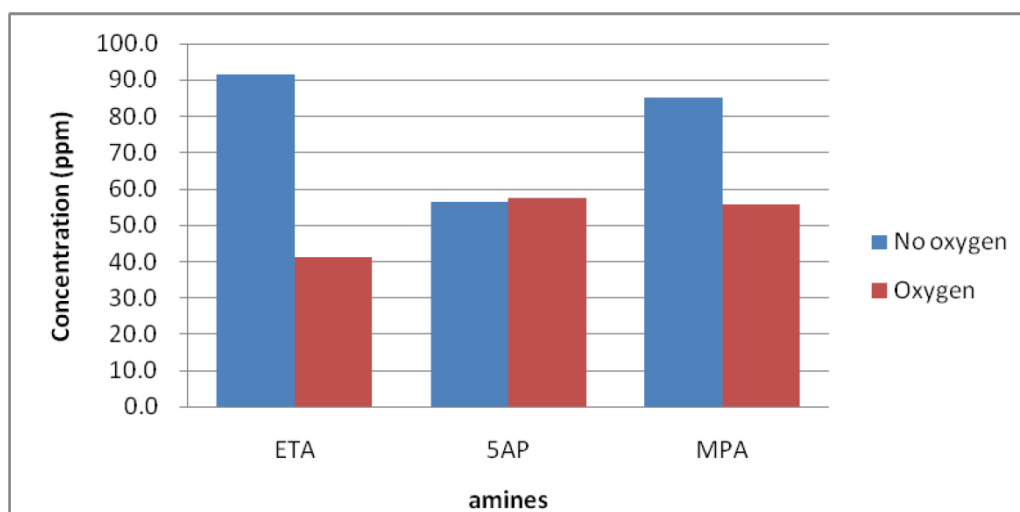


Figure 3-7
Amine Concentrations With or Without Nitrogen Purge of the Test Vessel (10 Minutes at 257°C) [28]

In general, amines are known to decompose to lower molecular weight amines, organic acids (such as formic acid and acetic acid) and ammonia. The resulting ionic species are expected to have minor effects on the pH, conductivity, and electrochemical potential of the secondary

coolant. However, when considering local pH, it is important to recognize that, due to differences in volatility, the amines and their decomposition products can be distributed differently in the PWR secondary system [27]. DMEA has been estimated to decompose into ethylmethanamine, trimethylamine, propylamine, and ammonia based on comparing decomposition product molecular weights to known amine degradation mechanisms [28]. Acetate has also been identified as a decomposition product via ion exchange chromatography (IC) [28]. Here, the IC column was insensitive to formic acid, so it cannot be excluded as a potential decomposition product.

In summary, available laboratory data suggest that the thermal stability of DMEA is similar to other amines. However, the estimated half-lives for several amines (including DMEA) generated from experimental data [28] were inconsistent with previously reported values for ETA, MPA and morpholine [29], by a factor of at least four (4), calling into question the results for DMEA. This discrepancy may have been due to the effect of dissolved oxygen (as there was significant uncertainty in the level of dissolved oxygen in the experiments of Reference [28]), which has been shown to influence the decomposition of ETA and MPA under similar conditions. In addition, the decomposition products of DMEA are not well characterized. Accordingly, the decomposition of DMEA, including the decomposition kinetics and the decomposition reaction products, are identified here as a moderate knowledge gap. Improved characterization of the decomposition process would be beneficial prior to application in a NPP in order to determine the anticipated demand for DMEA additions and the effect of subsequent DMEA decomposition on PWR secondary side pH control.

3.3 Summary

This section considered the chemical and physical properties of DMEA relevant to application of DMEA as a PWR secondary side pH control agent. The results of these topics are summarized below:

- DMEA is already used commercially in several industries. Safe handling practices, storage, and disposal considerations are well documented in vendor SDS documents. Utilities will need to ensure that disposal pathways for DMEA are compliant with applicable regulations. The safe handling and disposal of DMEA is identified as a minor knowledge gap because plant-specific procedures are expected to be developed or implemented based on available inputs (i.e., SDS documents and applicable regulations) ahead of a plant trial to ensure proper storage and disposal.
- DMEA is commercially available in industrial quantities that appear to have relatively high purity. However, a publicly available certificate of analysis demonstrating sufficiently low levels impurities important to secondary water chemistry additives could not be identified. Accordingly, the purity of DMEA is identified here as a major knowledge gap because utilities are expected to close this gap prior to a plant trial. The limited information that is available suggests that the level of effort to close this gap during procurement will be low.
- Experimental data for the basicity of DMEA are not available at high temperature. Gibbs free energy based estimates have been calculated up to 300°C using low temperature data. These estimates suggest that the behavior of DMEA is bounded by currently utilized amines. Moreover, the estimates have been used to generate a temperature-dependent ionization reaction equilibrium constant that is implemented in the latest version of the MULTEQ

database. The lack of high-temperature ionization data is identified as a knowledge gap. However, the severity of this gap is considered minor because the method currently used to predict the ionization behavior of DMEA at high temperature (i.e., a Gibbs free energy based extrapolation) has been shown to perform well for similar amines (i.e., ammonia, cyclohexylamine, and morpholine).

- Volatility data for DMEA are experimentally available for most of the temperature range of interest (100-262°C). A Gibbs free energy based calculation has been used to extrapolate the data to the full range of temperatures relevant to PWR secondary side chemistry (25-300°C). The current MULTEQ database includes a function for DMEA volatility that is based on these data. The volatility of DMEA is similar to that of MPA, with DMEA expected to partition near equally between the liquid and vapor phases around the PWR secondary system. No knowledge gap is identified regarding volatility. However, additional information could be helpful to provide more accurate modeling of the distribution of DMEA around the PWR secondary system.
- Experimental results regarding the thermal decomposition of DMEA show similar thermal stability to other commonly used amines (ETA, morpholine). However, the experimental methods used to characterize the decomposition half-life of DMEA yielded results for other amines that were significantly different, by at least a factor of four (4), compared to other studies. Additionally, the decomposition products of DMEA (i.e., chemical species and reaction kinetics) are not well characterized. Therefore, the decomposition rate and decomposition products of DMEA are identified here as a moderate knowledge gap. Improved characterization of the decomposition process would be beneficial prior to application in a NPP in order to determine the anticipated demand for DMEA additions and the effect of subsequent DMEA decomposition on PWR secondary side pH control.

4

MATERIAL COMPATIBILITY

Suitable physical and chemical properties of an amine (i.e., basicity, volatility, thermal stability) are not sufficient to justify its use as a pH control agent. The interaction of the amine with all the potentially wetted materials in the PWR secondary system must also be shown to be satisfactory at expected operating conditions. Accordingly, the following sections discuss the compatibility of DMEA with various PWR secondary side materials. The following three general categories of material are considered:

- Metals (Section 4.1)
- Ion exchange resin (Section 4.2)
- Elastomers and other sealing materials (Section 4.3)

A summary is provided in Section 4.4.

4.1 Materials of Construction

In general, there is little or no laboratory data or reported plant experience regarding the interaction of DMEA with metal surfaces that are typically found in the PWR secondary system. The following sections discuss the expected interaction of DMEA with each material type. Due to data limitations, the expectations for DMEA are based on a broader review of other amines. As will be discussed, long-term industry experience shows no amine-specific effects regarding the degradation of metallic surfaces in the secondary system, beyond a correlation with pH, which is controlled by the amine concentration. Accordingly, DMEA is expected to have a similar interaction with metal surfaces (i.e., no amine-specific effects). Nonetheless, the lack of data specific to DMEA is considered a major knowledge gap because the similarity of DMEA to the already investigated set of amines has not yet been confirmed. Thus, additional testing is recommended to demonstrate that the effects of DMEA are comparable to other amines that have been previously investigated. It may be appropriate to limit this testing to bounding materials and environments (e.g., materials and conditions that are known to be more sensitive to corrosion).

4.1.1 Nickel Alloys

There is no evidence of amines causing corrosion of nickel alloys commonly used for SG tubing (Alloys 600, 690, and 800) despite their widespread use for PWR secondary side pH control [1]. However, amines may contribute to nickel alloy degradation processes through their decomposition products, by degradation of ion exchange resins, or by increasing copper transport.

The primary decomposition species of concern are organic acids such as acetate and formate. These have been shown to contribute to IGA/SCC in the presence of acid sulfates and lead doped

sludge [30]. This is believed to be due to the presence of reduced sulfur species in possibly locally acidic conditions. However, despite the increase in organic acid concentrations from the breakdown of amines, plant experience has not shown increases in IGA/SCC when using amines in place of ammonia for pH control [1]. As the decomposition of DMEA is expected to be similar to other commonly used amines (Section 3.2.4), there is no reason to expect that the use of DMEA will have an undesirable effect on IGA/SCC rates for nickel alloys.

The possibility of increased degradation of ion exchange resin due to the presence of DMEA is discussed in Section 4.2. As discussed therein, no additional release of sulfur species from ion exchange resin is expected from DMEA use. Therefore, no increase in nickel alloy degradation is expected from this effect.

The compatibility of copper alloys with DMEA is discussed in Section 4.1.4. As discussed therein, copper corrosion is not expected to be accelerated by DMEA use. Therefore, no increase in nickel alloy degradation is expected from this effect.

A significant concern regarding the effect of various chemical species on the degradation of steam generator tubes is the ability of boiling to drive the concentration of some species to very high concentrations despite only trace concentrations in the bulk water. As discussed in Section 3.2.3, the volatility of DMEA is close to that of water. Therefore, significant concentrations are not expected to develop in the steam generator.

Although an amine-specific effect is not expected, the lack of direct laboratory compatibility data for DMEA with nickel alloys is identified as a major knowledge gap. Accordingly, testing is recommended to verify the interaction of DMEA with nickel alloys is comparable to other amines. It is further noted that testing specifically with nickel alloys may not be necessary if similar and bounding testing is performed (e.g., positive results from FAC testing with carbon steel).

4.1.2 Carbon and Low Alloy Steels

The corrosion rate of carbon and low alloy steel is dependent on the solubility of iron, which is dependent on pH. Flow accelerated corrosion (FAC) occurs when the flow of coolant over a surface increases the diffusion of corrosion products into solution that would otherwise have limited the rate of corrosion. Any chemical that increases the solubility of iron or mobility of iron corrosion products could therefore accelerate the corrosion rate. Such an increase in the corrosion rate would be observed as an increase in the iron concentration in the feedwater [27].

Although no known data exist regarding the direct effect of DMEA on iron transport, there is a significant body of research showing that iron transport is primarily dependent on pH [23,27,31]. Therefore, the expectation is that DMEA will not affect corrosion of carbon and low alloy steels. However, if corrosion rates were to increase due to the presence of DMEA, it would likely be due to DMEA forming coordination compounds with iron cations in solution. Amines readily form complexes with small highly charged cations such as Ti^{4+} , Fe^{3+} , Co^{3+} , and Al^{3+} . This is supported by research showing iron(III) N-methyl diethanolamine complexes being used as sol-gel precursors [32]. Iron coordination compounds are likely common in PWR secondary coolant as there are several compounds with a basic lone pair that can act as a ligand (water, hydrazine, ammonia). Such coordination compounds are only problematic if they increase the mobility of the iron cation (i.e., increasing iron transport) or if the resulting compound is

insoluble (leading to increased iron deposition rates). Observed correlations between feedwater iron concentrations and amine concentrations are no stronger than the correlation between feedwater iron and feedwater pH. Moreover, regardless of the amine used for pH control, lower iron transport is generally observed with higher pH [27,31]. Vendor literature regarding the use of DMEA for corrosion inhibition in boiler systems also states that DMEA does not react to form solid products (precipitates) [17]. Therefore, iron coordination compounds are likely not an issue for DMEA.

In addition to FAC and fouling concerns, the interaction of DMEA with carbon steel has been studied in the context of concrete rebar corrosion inhibition. Specifically, simulated pores containing sodium chloride at near ambient conditions have confirmed DMEA is an efficient corrosion inhibitor at relatively high concentration (i.e., 0.125 mol/L or about 1%). Here, the inhibition mechanism is a Langmuir-type adsorption process that generates a protective DMEA film on the metal surface. These results, although not representative of operating conditions, indicate that DMEA does not have a detrimental effect on carbon steel at high concentrations [33].

Nevertheless, the consequence of FAC and the lack of directly relevant compatibility data for DMEA and carbon / low alloy steel at PWR secondary side condition cause this to be identified as a major knowledge gap that would be expected to be addressed prior to plant application of DMEA. Accordingly, confirmatory FAC testing with carbon steel in comparison to ETA is recommended to demonstrate that there are no adverse interactions between DMEA and carbon steel. As is noted elsewhere, this testing may be appropriately bounding for other metal interactions and by providing sufficient evidence that DMEA can be categorized with amines that have been previously studied and shown to have no amine-specific effect on metal degradation.

4.1.3 Stainless Steels

The general corrosion and FAC rates for stainless steel are much lower than that of carbon or low alloy steels. There is currently no evidence that the use of amines for pH control has any effect on the corrosion rate of stainless steel [34]. The same arguments regarding SCC of nickel alloys also apply to localized corrosion (SCC, pitting) of stainless steels. Nevertheless, the lack of directly relevant compatibility data for DMEA and stainless steel is identified as a major knowledge gap. Accordingly, testing is recommended to verify the interaction of DMEA with stainless steel is comparable to other amines. As was the case for other metals, testing with stainless steel may not be necessary if similar bounding testing is performed with other metals (e.g., positive results from FAC testing with carbon steel).

4.1.4 Copper Alloys

Corrosion of copper alloys results in copper transport, which can increase the risk of IGA/SCC in susceptible SG tubes. This is in addition to issues of fouling and deposition similar to those seen from iron transport.

Aminoethanols (e.g., ETA, DMEA) are known to attack copper at high concentrations (greater than 5%) and form copper complexes in aqueous solutions [17]. However, at the concentrations used for PWR secondary side pH control, plant operating data along with the limited laboratory data available do not support an amine-specific effect on copper transport. In general, feedwater

copper concentrations are often correlated with feedwater iron concentrations and therefore feedwater pH. Moreover, plant data indicate that most of the copper in the feedwater is in particulate form, which implies that amines-specific effects are not likely to be a primary factor (i.e., amine-copper complex formation are likely not important) [27]. Thus, adverse interactions between DMEA and copper in the secondary system are expected to be limited or comparable to other amines, i.e., based on pH and not an amine-specific effect. Nevertheless, the limited directly relevant compatibility data for the DMEA and copper interaction is identified as a major knowledge gap. Accordingly, testing is recommended to verify the interaction of DMEA with copper is comparable to other amines. As was indicated for other metals, testing specifically with copper may not be necessary if bounding testing is performed with other metals (e.g., positive results from FAC testing with carbon steel). Additionally, testing regarding copper alloys would not be expected to be necessary prior to application at a unit with an all-ferrous balance of plant.

4.1.5 Titanium and Other Metals

Titanium alloys are commonly used in turbine components and condenser tubing. One way in which DMEA could affect titanium alloy corrosion is through an effect from the decomposition products. Low molecular weight amines, such as DMEA, are known to decompose to the organic acids acetate and formate, which will raise the cation conductivity. However, testing at 10 times the organic acid concentrations expected from the use of pH control amines, but not including DMEA, has shown no negative effects on titanium alloys used in turbine components [35]. Comparable or lower decomposition (see Section 3.2.4) is expected for DMEA and, thus, less production of decomposition products like acetate and formate is expected compared to ETA. Conversely, the use of lower volatility amines for pH control has been shown to prevent chloride pitting of turbine parts compared to pH control by ammonia. This is believed to be due to the lower volatility of the amine giving better pH control of early condensates where the temperature is higher [1].

An amine-specific effect on titanium is also possible. However, the mechanism for such an effect would be expected to be similar to those postulated for iron and copper. Iron and copper are more susceptible to corrosion in typical PWR secondary system environments. Therefore, the lack of an amine-specific effect for copper and iron is a reasonable indicator that there is no amine-specific effect for titanium.

In general, the corrosion rates of titanium and other alloys present in the secondary system or balance of plant are expected to be lower than those of iron and copper. Therefore, any effect from DMEA would also be expected to be lower on titanium and other alloys than on iron or copper.

Based on this information, the lack of directly relevant compatibility data for DMEA and other metals in the secondary system is identified as a major knowledge gap. As was noted previously, this gap may be addressed by using bounding tests with other more metals that are more sensitive to corrosion (e.g., positive results from FAC testing with carbon steel). Additionally, testing of compatibility of DMEA with titanium alloys would not be relevant for a unit with no titanium alloys in the balance of plant.

4.2 Ion Exchange Resins

Amines used for pH control can have a variety of effects on ion exchange resins used for PWR secondary side coolant purification. Generally, the amine is likely to be at a much higher concentration than the impurities the resins are designed to remove, which can lead to shorter resin service times. Since ion exchange is a reversible process, amine loading on the cation resin can lead to release of previously exchanged impurities, further reducing the effectiveness of the resin [27].

There are several methods that can be employed to lengthen the life of ion exchange resins when using amines. Most of these methods center around reducing the amine exposure of the ion exchange resin. Examples of this would be partial flow condensate polishing or running ion exchange beds only when specific ion concentrations exceed a given threshold. Alternately, the choice of an amine with a distribution coefficient (K_d) that partitions the amine away from the ion exchange resin can minimize exposure of the resin (e.g., for plants that only have condensate polishers or only blowdown demineralizers). For example, an amine with a low K_d would preferentially partition to the early condensate in the moisture separator. This would reduce the amine concentration in the condenser thereby reducing the effect on the condensate polisher ion exchange resin. Conversely, higher K_d amines would reduce the exposure for blowdown polishers. Choosing an amine with a high basicity will allow for lower overall amine concentrations throughout the entire PWR secondary coolant system. Partial flow polishing or periodic polishing based on impurity concentrations can also be effective [23].

ETA is suspected of attacking the cation resin leading to fouling of the anion resin [5]. Ideally, the selected amine is less likely to chemically attack or foul the resin. A 2003 report identified DMEA as a possible amine for pH control that could reduce the effect on ion exchange resins as compared to ETA [5]. The following sections explore the available data regarding the interaction of DMEA with ion exchange resins.

4.2.1 Selectivity and Resin Exhaustion

Strongly acidic cation resins will form ionic bonds with cationic species. However, the strength of these bonds is different for each cation. For example, divalent cations generally form a stronger bond than monovalent cations. This means there are differences in selectivity for different cation resin formulations [36].

The exchange reaction between monovalent cations in solution, bound cations, and binding sites can be represented as follows [27]:



Here, C^+ is a cation in solution, R is the resin binding site, and X is the initial cation species associated with the resin. In the case of a hydrogen (acid) form resin, X would be the hydrogen ion (H^+). At equilibrium, the proportional amount of free and bound competing ions in this reaction can be quantified with an ion selectivity coefficient, as follows:

$$K_X^C = \frac{[RC][X^+]}{[RX][C^+]} \quad [4-2]$$

Here, K_X^C is the selectivity coefficient for ions C^+ and X^+ , $[X^+]$ and $[C^+]$ are the liquid phase concentration of the two ions (mol/kg), and $[RC]$ and $[RX]$ are the concentrations of absorbed species, C and X , respectively, in the resin (mol/L). Note that a higher value of K_X^C corresponds to increased selectivity for species C over species X (i.e., species C is preferentially exchanged). Also, by definition, the selectivity for X over species C is simply the inverse or $K_C^X = 1/K_X^C$. If sodium is chosen as the cation of interest (C) and the resin is operating in amine form (i.e., saturated in amine ions), Equation [4-2] can be rearranged as:

$$[Na^+] = \frac{1}{K_{Am}^{Na}} \frac{[RNa][Am^+]}{[RAm]} \quad [4-3]$$

where Am represents an amine used for pH control. Equation [4-3] shows that a higher selectivity for sodium versus the pH control amine is required to minimize sodium concentration in the ion exchange bed effluent (i.e., ensure sodium is removed in the exchange process).

In general, the selectivity coefficient of ions, including amines, are different for different resin. The selectivity of a new ion, in pairs with known ions, can be derived once the selectivity of the new ion is determined relative at least one previously studied ion. This means that the selectivity coefficient of each new amine must be derived experimentally, and often for each resin type of interest. Table 4-1 shows the results, from 1998, that investigated the selectivity of a range of amines, including DMEA, of two cationic resins – Thermax Tulsion T-42 and Ambersep -252. In these tests, the resins were first washed with an excess of 5% NaCl (to saturate them with sodium). Then, the resin was mixed with the amine (stirred for 1 hour) and allowed to equilibrate overnight [37].

Table 4-1
Loading and Selectivity of Selected Amines [37]

Amine	Thermax Tulsion T-42		Ambersep-252	
	% Loading	K_{Na}^{Am}	% Loading	K_{Na}^{Am}
Ammonia	14.34	0.012	9.00	0.007
Morpholine	12.89	0.010	7.00	0.005
ETA	16.12	0.016	10.00	0.009
MPA	9.90	0.005	17.00	0.017
DMEA	13.01	0.010	9.60	0.007

The data in Table 4-1 show that the two resins have similar selectivity (relative to sodium) for all of the amines studied. The DMEA selectivity also appears to be comparable to morpholine, ammonia, and ETA, depending on the resin used. Note that the selectivity values presented in this table are based on equilibrium conditions where the amine loading is only 10% to 15%, so

that the sodium loading is about 85% to 90%. This amount of sodium loading is substantially more than typically observed in plant conditions and, in this measurement, is likely to affect the selectivity of other species.

It is possible to express the selectivity values in Table 4-1 relative to hydrogen, which is the preferred presentation for PWR secondary side applications involving hydrogen form beds. The *Condensate Polishing Guidelines for Pressurized Water Reactor and Boiling Water Reactor Plants – 2004 Revision* gives sodium selectivity values (K_H^{Na}) in the range of 1.4 – 1.5 for 8% crosslinked strong acid gel resins like the Thermax Tulsion T-42 [36]. Unlike the previously discussed data set in Table 4-1, these selectivities were likely measured at a very low initial sodium loading. Using a value of $K_H^{Na} = 1.41$ (cited for Amberlite 120H, the most similar resin discussed in the *Condensate Polishing Guidelines*), K_H^{Amine} can be calculated based on the selectivity values presented in Table 4-1. The calculated values for K_H^{Amine} are presented in Table 4-2 compared to published values from the *Condensate Polishing Guidelines*. The differences in selectivities of the same amines between the different resins are likely due to the extent of sodium loading on the resin during the measurement. Thus, the high sodium loading selectivity measurement that is available for DMEA cannot be extended to low sodium loading conditions. Accordingly, the lack of sufficient selectivity data for DMEA under conditions relevant to PWR secondary side is identified as a major knowledge gap.

Table 4-2
Calculated Cation Exchange Selectivity (K_H^{Amine}) for Several Amines Compared to Values Published in Reference [36]

Amine / Species	Thermax Tulsion T-42	Condensate Polishing Guidelines (Amberlite 120H)
Sodium	-	1.41
Ammonia	0.017	1.77
Morpholine	0.014	1.26
ETA	0.023	1.19
MPA	0.007	-
DMEA	0.014	-

In summary, the laboratory data under non-representative conditions (i.e., high sodium loading) show that DMEA has a selectivity to common cation exchange resins that is similar to MPA or ammonia depending on the type of cation exchange resin. However, data are not available for DMEA selectivity under representative PWR secondary side conditions. This is identified as a major knowledge gap because the potentially inaccurate value may limit the ability to model the resin bed behavior, even though it is expected to be comparable to other amines. In addition, it is noted that this knowledge gap is applicable to plants with partial and full flow condensate polishing (i.e., where the interaction with significant amounts of resin is important).

4.2.2 Resin Fouling Issues

Another concern with resin compatibility is chemical attack by the amine (or its decomposition products) on the structure of the cation resin. Attack of the cation resin backbone can lead to reduced functionality and breakdown of the resin. Fragments from the breakdown of the cation resin will load and foul the anion resins in mixed bed systems [5]. Additionally, some of the resin breakdown products are anionic sulfur compounds, which are known to contribute to nickel alloy corrosion phenomenon (see Section 4.1.1) [27]. It is believed that the additional steric hindrance provided by the fully alkylated amino group within DMEA (as compared to ETA) helps to reduce the rate of nucleophilic attack on the cation resin backbone [5]. This is a principle reason for consideration of DMEA, in lieu of ETA, for pH control in the PWR secondary system.

Amines will also often attack the resin backbone of anion exchange resin. The proposed mechanism for this is substitution of the trimethylammonium groups of the anion resin by the pH control amine.⁵ This is through a nucleophilic attack of the benzylic carbon to which the trimethylammonium is attached as shown in Figure 4-1.

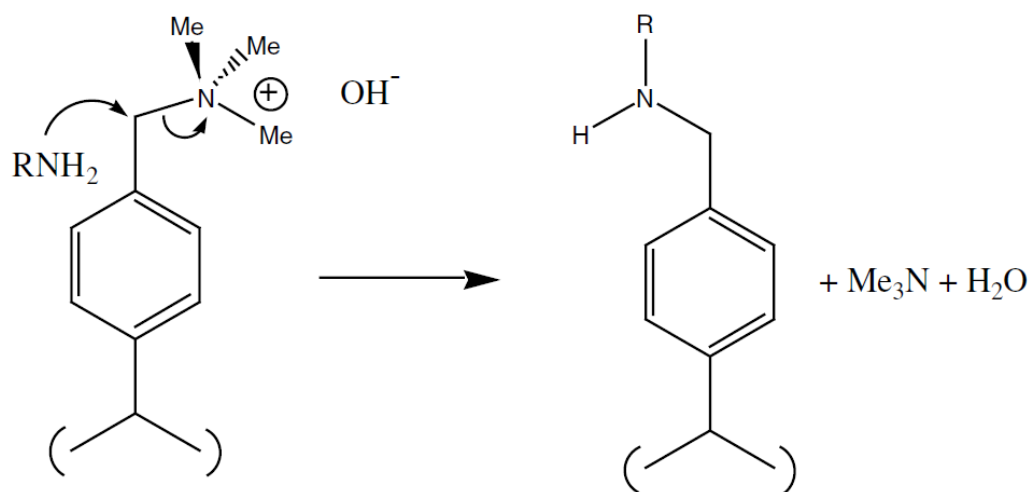


Figure 4-1
Nucleophilic Attack of an Amine on the Benzylic Carbon of a Benzyltrimethylammonium Group [5]

Such attack generally leads to a permanent kinetic degradation of the anion exchange resin as strongly acidic sites would be displaced by weakly acidic sites. A similar displacement at the same site can also occur through the nucleophilic attack of hydroxide ion (OH^-) leaving a non-exchangeable alcohol group in place of the trimethylammonium group (Figure 4-2).

⁵ Experiments with deuterated ETA have confirmed that ETA integrates with the cation resin backbone. The reaction mechanism for this was not identified but suspected to include nucleophilic attack by the amino nitrogen. This integration was shown to be catalyzed by iron in the presence of oxygen [EPRI 1003613]. Similar integration is expected, but not confirmed, for anion resin.

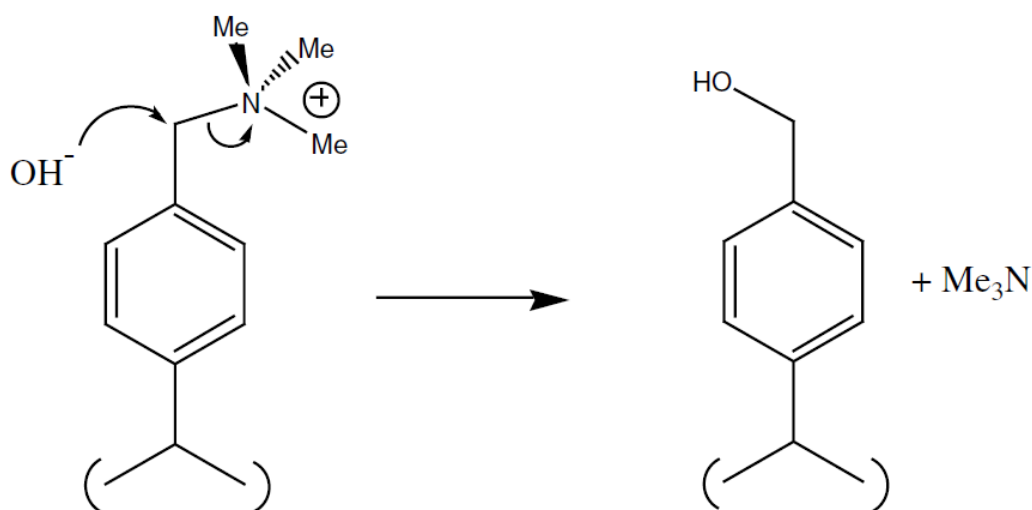


Figure 4-2
Nucleophilic Attack of Hydroxide on the Benzylic Carbon of a Benzyltrimethylammonium Group [5]

Regardless of whether the trimethylammonium group is displaced by a hydroxide or a pH control amine, the susceptibility of the final product (a benzyl alcohol or amine) to oxidative attack will be increased. There is also research showing that the de-trimethylaminated polymers undergo oxidation to form aldehyde and other acid groups with eventual oxidation of the polymeric backbone occurring [5].

One advantage of DMEA is that nucleophilic attack on the benzylic carbon leads to the fully alkylated active group shown in Figure 4-3. This retains the strong acid exchange characteristics of the resin. There is also no evidence of increased oxidative attack following displacement of the trimethylamine group by DMEA [5].

Some pH control amines also attack the methyl groups of the benzyltrimethylammonium. In this process, the nucleophile is methylated. Since the amino group is already fully alkylated, this prevents such attack by amines like DMEA [5].

Susceptibility of the resin backbone to oxidation is a problem for both cation and anion exchange resins. Steam generator corrosion considerations require that reducing conditions be maintained in the PWR secondary coolant. The primary oxidant present in the condensate ion exchange beds is very low levels of dissolved oxygen (typically ≤ 10 ppb). Although oxygen has a high activation barrier for reaction with saturated organics or aromatics, elevated temperature, radiation, or the presence of catalysts (such as iron) can increase the rate of resin oxidation. It is believed that some pH control amines could aggravate oxidation of the ion exchange resins through the propagation of radical species. No evidence has been found that DMEA participates in or exacerbates such reactions. [5].

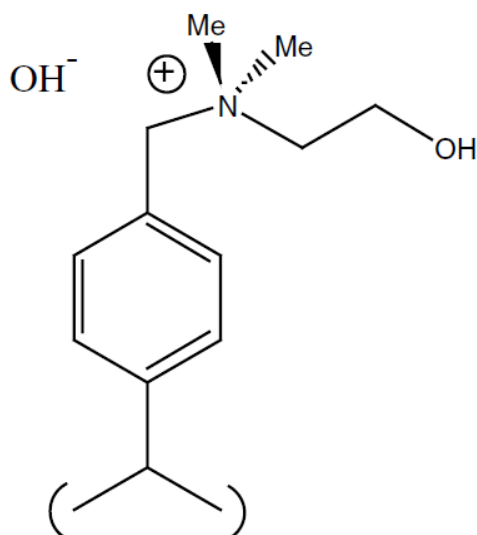


Figure 4-3
Product from Attack of DMEA on Benzylic Carbon of Benzyltrimethylammonium Group [5]

In summary, the research into ETA derivatives identified DMEA as a possible choice for pH control due to its reduced effect on ion exchange kinetics and fouling compared to ETA. It is believed that the fully alkylated amino group provides steric hindrance thereby reducing nucleophilic attack by DMEA on the cation resin backbone. There is also no evidence that DMEA exacerbates or participates in the oxidation reactions known to degrade the resin backbone of both cation and anion exchange resins. Additionally, DMEA, after displacement of trimethylamine in anion exchange resins, acts as a strong acid with no evidence of increased oxidative attack on the resin due to this displacement. All three of these effects should lead to less degradation and fouling of ion exchange resins by DMEA when compared to ETA [5]. These results combined with the relative sodium selectivity shown in Section 4.2.1 indicate that it should be possible to run cation exchange beds in either acid (H^+) or amine form successfully. Nonetheless, because DMEA has not been used for extended periods of time under PWR secondary side conditions, the interaction between DMEA and resin performance is identified here as a minor knowledge gap.

4.3 Elastomers and Seals

EPRI's Elastomer Handbook (Reference [38]) catalogues plant experience with various elastomers. Amine exposure can result in several chemical processes depending on the elastomer exposed. The result of these processes can include swelling of the elastomer, increased cross-linking of the polymer leading to hardening of the elastomeric material, and chemical attack by the amine leading to a shorter in-service life. Table 4-3 shows chemical compatibility for several commonly used elastomers. Natural rubber, polysulfide rubber, nitrile rubber, and urethane rubber are all shown to have low chemical resistance to amines. Additionally, acrylic rubber is not recommended for use with diethylamine (DEA) or ETA due to significant swelling concerns. Finally, fluorocarbon rubbers undergo hardening in the presence of amines [38].

A search of the literature did not reveal any direct research into the interaction of DMEA with elastomers under conditions applicable to a PWR secondary side environment. Previous work regarding the interaction of morpholine and ETA with elastomers showed significant differences in elastomer compatibility between the different amine species [39]. Accordingly, the interaction of DMEA with elastomers is identified as a major knowledge gap. Testing is expected to be completed regarding DMEA interactions with elastomers prior to a plant application. It is noted that this testing would likely require an audit of the secondary system regarding the location of elastomers and seals and their importance, in order to generate an informed test matrix. Subsequent testing may be optimized to include, for example, a bounding set of elastomers and environments (e.g., temperature / flow rates) that ensure adequate performance.

4.4 Summary

This section investigated the available information about the interaction of DMEA with common secondary side materials. Specifically, a literature search was performed to investigate the compatibility of DMEA with materials of construction (metals), ion exchange resins, and elastomers and seals. The results are summarized below:

- There is no directly relevant information about the specific interaction of DMEA with metals that are typically used in PWR the secondary system. However, long-term plant experience with various amines suggests that there are no degradation mechanisms that are related to the specific amines or amine concentrations used, beyond a correlation with secondary side pH. Nevertheless, due to the significance of such an effect, if any, and the lack of directly relevant data with DMEA, the interaction of DMEA with metals is identified as a major knowledge gap. Accordingly, testing is recommended to confirm or refute any specific effects (i.e., to confirm that the DMEA can be grouped with the set of amines that have been previously investigated). As appropriate, this testing may be limited to a bounding set of materials and environments, with direct comparisons to other amines that are commonly used (e.g., FAC testing involving DMEA and ETA on carbon steel).
- The selectivity of DMEA for cation resin has been shown to be comparable to ammonia and morpholine under non-representative conditions (i.e., high sodium loading). Selectivity data for conditions relevant to the PWR secondary side are not available. Accordingly, the selectivity of DMEA for resin under PWR secondary side conditions is identified as a major knowledge gap. However, it is noted that the importance of this knowledge gap may vary from plant-to-plant (i.e., it is most applicable to plants with full-flow condensate polishing and would not likely be considered a major gap for a unit that does not use condensate polishers).
- It is believed that the fully alkylated amino group of DMEA significantly reduces the attack of the resin backbone for both cation and anion exchange resins as compared to ETA. Additionally, substitution of the anion exchange active site by DMEA should not suppress the anion exchange capability of the resin. However, application of DMEA at plant conditions over significant operating times has not been performed. Therefore, a minor knowledge gap exists regarding DMEA's effect on resin performance. It is expected that this gap would be addressed by monitoring and assessing resin performance during a plant demonstration.

- No information regarding the direct interaction of DMEA with elastomers or seals in typical PWR secondary side conditions was found during this investigation. Previous plant experience with similar amines indicates that effects on elastomers and seals are heavily dependent on the specific amine. This lack of experience regarding the interaction of DMEA with common plant elastomers and seals is considered a major knowledge gap because the severity will depend on which elastomers are in use at a given plant. Accordingly, testing is expected to characterize the effects of DMEA on elastomers prior to a plant demonstration.

**Table 4-3
Chemical Compatibility of Common Elastomers [38]**

Category	Chemical or Environment	Neoprene (CR)	Ethylene-propylene rubber (EPR)	Fluorocarbon rubber (FKM)	Styrene butadiene rubber (SBR)	Isoprene rubber (IR)	Nitrile rubber (NBR)	Butyl rubber (IIR)	Silicone rubber (VMQ)	Acrylic rubber (ACM)	Epichlorohydrin (ECO)	Urethane rubber (AU)	Natural Rubber (NR)	Fluorosilicone (FVMQ)	Hydrogenated nitrile rubber (HNBR)	Polysulfide rubber (T)
Plant Water Chemistry	Ammonia	6-8	6-8	1-6	2-8	2-8	1-8	6-8	2-9	D	-	2-8	2-8	1-8	B	2-8
	Boric Acid	8	8	8	8	8	8	8	8	D	A	A	8	8	A	2
	Carbamates	6	6	8	2	2	4	6	-	D	-	2	2	8	-	6
	Diethylamine	2-4	6	1	2	1-6	4-6	6	6	D	-	4	1-6	1-2	-	6
	Ethanolamine (ETA)	2-9	6	2-6	6	6-9	2-9	6	6	D	B	2-4	6-9	2	-	2-6
	Ethylene glycol	8-9	8-9	8	8	8-9	8-9	8	8	C	8	6	8-9	8-9	A	4
	Hydrazine	6-9	6-8	1-2	6-8	2-8	2-9	6-8	4	-	-	2	2-8	1-3	D	2
	Hydrogen peroxide	8	8	9	6		6	8	8	-	-	-	6	8	B	4
	Morpholine	2	-	-	-	-	-	-	-	-	-	-	5-6	-	-	-
	Sodium borate	8	8	8	6	8	8	8	8	-	A	-	8	8	A	8
	Sodium hydroxide	6	8	6	8	8	6	8	6	C	B	6	8	6	B	2
	Sodium hypochlorite	5-8	6-8	8	4	4	6	6	6	D	8	2	4	6	B	2
	Sodium silicate	8	8	8	8	8	8	8	-	-	-	-	8	-	A	-
	Titanium dioxide (elevated temperature)*	-	-	8	-	-	-	-	-	-	-	-	-	-	-	-
	Triethyl amine	-	-	8	-	-	-	-	-	-	-	-	-	-	-	-
	Trisodium phosphate	8	8	-	-	-	-	-	-	8	-	-	-	-	-	-
Zinc oxide*	-	-	9	-	-	-	-	-	-	-	-	-	-	-	-	
Lubricants and Oils	Grease	2-6	2	8	2	2	8	2	2-9	-	-	8	2	8	-	8
	Hydraulic oil [96]	6	1-2	8	2	2	6-8	2	4-6	A	8	6-8	2	8	A	6-8
	Machine lubricating oils (petroleum)	4-6	1-2	8	2	2	6-8	2	1-6	A	8	6	2	6-8	D	4
	Mineral oil	6-8	2-4	8	2	2	8	2	2-6	7	8	8	2	8	A	6-8
	Molybdenum disulfides	-	-	-	-	-	-	-	9	-	-	-	-	9	-	-
	Petroleum oils and gels	6	2	8	2	2	8	2	2	B	8	8	2	8	-	2
	Silicone grease	8	8	8	8	8	8	8	4	A	A	8	8	-	A	8
	Silicone oil	8	8	8	8	8	8	8	4	A	A	8	8	-	A	8
	Turbine oil	2-6	2	8	2	2	6-8	2	2	A	8	2-8	2	6-8	A	8
Transformer oil	6	1-2	8	2	2	8	2	2-8	B	-	6-8	2	8	A	2-8	
Aqueous Solutions	Bleaches (sodium hypochlorite)	4	8	8	2	2	1-8	8	6	D	-	2-5	2	6-8	B	2
	Cleaning products - detergents	6	8	8	6	6	8	8	8	D	A	2	6	8	A	-
	Ethylene glycol (antifreeze)	8-9	8-9	8	8	8-9	8-9	8	8	C	8	6	8-9	8-9	A	4
	Seawater	8	8	8-9	A	A	8	A	8	8	-	B	A	8	A	D
	Terpeneol	2	4	8	2	2	6	4	-	-	-	6	2	8	B	8
	Water	6-8	8-9	8-9	8	8	8	8	8-9	A	6	2	8	8	A	2

A = Little to Minor, 0 to 5% Vol. Swell; B = Minor to Moderate, 5 to 10% Vol. Swell; C = Moderate to Severe, 10 to 20% Vol. Swell; D = Not Recommended
Volume Swell Data from Los Angeles Rubber Group, Inc. & Dupont Elastomers
PDL Chemical Resistance Guide Rating (0 = Low - 9 = High Resistance)

Table 4-3 (continued)
Chemical Compatibility of Common Elastomers [38]

Category	Chemical or Environment	Neoprene (CR)	Ethylene-propylene rubber (EPR)	Fluorocarbon rubber (FKM)	Styrene butadiene rubber (SBR)	Isoprene rubber (IR)	Nitrile rubber (NBR)	Butyl rubber (IIR)	Silicone rubber (VMQ)	Acrylic rubber (ACM)	Epichlorohydrin (ECO)	Urethane rubber (AU)	Natural Rubber (NR)	Fluorosilicone (FVMQ)	Hydrogenated nitrile rubber (HNBR)	Polysulfide rubber (T)
Acids	Acetic acid	2-9	4-9	1-6	2-6	2-9	2-8	2-6	4-9	2	2	2	2-9	1-7	B	2-6
	Boric acid	8	8	8	8	8	8	8	8	7	8	8	8	8	A	2
	Hydrochloric acid	2-9	4-8	8-9	2-4	2-9	2-9	8	2	D	B	D	2-9	4-6	-	2
	Hydrofluoric acid	5	1-4	1-8	D	D	1	C	1	D	-	C	D	D	-	-
	Sulfuric acid	2-8	1-8	6-8	2-4	2-4	1-4	2-4	1-2	3-8	2-6	2-4	2-4	1-4	-	2
Solvents	Acetone	3-8	6-8	1-3	6	4-8	1-6	8	4-6	2	2	2-8	4-8	1-2	D	4
	Xylene	1-4	1-2	7-9	2	1-2	1-8	2	1-4	2	2	D	1-2	4-8	D	6
	Alcohols	8	8	8	8	8	8	8	8	-	8	2	8	8	-	4
	Turpentine	1-9	1-2	8	2	1-2	7-9	2	1-7	4	8	2	1-2	1-6	A	6
	Natural gas	8	1-2	8	4	4	8	2	8	B	8	6	4	4	A	6
	Propane	6	1-2	6-9	2	2	8	2	1-2	A	A	4	2	6	A	8
	Fuel Oil	2-6	1-2	8	2	2	6-8	2	1-8	A	8	2-6	2	8	A	8
Fuels	Diesel	6	1-2	8	2	2	8	2	1-2	A	8	4	2	8	A	8
	Gasoline	1-8	1-4	6-9	2	1-2	6-9	2	1-7	4	8	2-6	1-2	4-8	A	6-8
	Kerosene	2-9	1-2	8-9	2	1-2	8-9	2	1-2	5	8	6	1-2	8	A	6
	Acetylene	5-6	8	8	6	6	6-8	8	6	D	6	D	6	-	-	4
Miscellaneous	Air (elevated temperature)	2-6	2-6	8	2	2	2-6	2-6	8	-	-	2-4	2	6-8	-	2
	Amines	6	6	-	6	6	2	6	6	-	-	2	6	2	-	2
	Borax	8	8	8	6	6	6	8	6	B	-	8	6	6	A	2
	Ethers	2	4	-	2	2	2	2	2	-	-	6-8	2	4	-	8
	Hydrogen	8	8	8	6	6	8	8	4	7	-	8	6	4	-	2-4
	Methane	6	1-2	6-9	2	2	8	2	1-8	A	8	4	2	6	A	8
	Nitrogen	2-8	2-8	2-8	2-8	2-8	2-8	4-8	2-8	A	8	2-8	2-8	2-8	A	2-8
	Ozone	4	8	8	2	2	1-2	6	8	B	8	8	2	6	D	8
	Refrigerant (Freon 12)	8-9	5-6	5-6	8	6	8-9	6	1-2	6	8	8	6	2-4	A	8
	Sodium chloride	8	8	8	8	8	8	8	8	8	8	8	8	8	A	4
	Steam under 300°F (149°C)	C	A	D	D	D	D	B	C	D	-	D	D	D	D	D
	Steam over 300°F (149°C)	D	C	D	D	D	D	D	D	D	D	D	D	D	D	D
	Sulfur hexafluoride	8	6-8	6	2	2	6	8	6	-	8	-	2	6	-	4
	Aqueous Solutions	Bleaches (sodium hypochlorite)	4	8	8	2	2	1-8	8	6	D	-	2-5	2	6-8	B
Cleaning products – detergents		6	8	8	6	6	8	8	8	D	A	2	6	8	A	-
Ethylene glycol (antifreeze)		8-9	8-9	8	8	8-9	8-9	8	8	C	8	6	8-9	8-9	A	4
Seawater		8	8	8-9	A	A	8	A	8	8	-	B	A	8	A	D
Terpineol		2	4	8	2	2	6	4	-	-	-	6	2	8	B	8
Water		6-8	8-9	8-9	8	8	8	8	8-9	A	6	2	8	8	A	2

A = Little to Minor, 0 to 5% Vol. Swell; B = Minor to Moderate, 5 to 10% Vol. Swell; C = Moderate to Severe, 10 to 20% Vol. Swell; D = Not Recommended
 Volume Swell Data from Los Angeles Rubber Group, Inc. & Dupont Elastomers
 PDL Chemical Resistance Guide Rating (0 = Low – 9 = High Resistance)

5

APPLICATION CONSIDERATIONS

In addition to the material compatibility and chemical properties of DMEA, the expected application considerations of DMEA as a pH control amine should be investigated. Accordingly, the following section discusses some of the programmatic expectations for DMEA along with expected corrosion phenomena and other effects on plant systems. Section 5.4 provides a summary of these issues.

5.1 DMEA Program Expectations

EPRI's Plant Chemistry Simulator (PCS) is a valuable tool for predicting PWR secondary water chemistry conditions resulting from the use of DMEA [40]. The PCS uses a mass balance approach to model the distribution of chemical additives and contaminants in the steam cycle. For PWRs, the model is based on a steam loop consisting mainly of SG, HP turbine, moisture separator, LP turbine, condenser, and feedwater heaters. The output from the condenser is returned to the SG via the feed train. Additional connections and components are then defined to match the configuration of a given plant based upon that plant's heat and mass balance. This section describes how the PCS software was used to simulate the effects of implementing a DMEA-based pH control program, and compares those results to currently implemented amines. A sample plant was selected for demonstration purposes. A detailed description of the simulation inputs is provided separately in Appendix A.

Table 5-1 shows the concentrations that were input into PCS to simulate three different amine chemistries – morpholine, ETA, and DMEA. The feedwater concentration of each amine was chosen to match the $\text{pH}_{25} = 9.5$ values calculated using MULTEQ (per Table 3-2). Representative feedwater concentrations of hydrazine, sodium, chloride, and sulfate (for all three amine cases) were assumed fixed and equal to industry averages adapted from Reference [27]. The concentration of the ammonia, acetate, and formate decomposition products were assumed proportional to the concentration of the amine concentration based on ratios provided in Reference [27]. These ratios were used because stoichiometric reactions for the decomposition process are not currently available. In addition, due to the lack of available data, the decomposition product ratios for ETA were used for DMEA. The application of ETA ratios to DMEA is expected to be conservative because the thermal decomposition of ETA is expected to be greater than DMEA (see Section 3.2.4).

For all modeling described in this section, the concentrations of acetate and formate were input as blowdown concentrations. All others were input as feedwater concentrations. The hideout calculation was also disabled. Unless otherwise stated for specific cases of interest, the decomposition calculation was only tracking the decomposition of hydrazine in the steam generator, the SG blowdown was not recycled, and the condensate polishers were bypassed.

Table 5-1
PCS Input Concentrations

Input Species	Location	Morpholine	ETA	DMEA
Hydrazine (ppb)	Feedwater	100	100	100
Na (ppb)	Feedwater	0.0036	0.0036	0.0036
Cl (ppb)	Feedwater	0.01	0.01	0.01
SO4 (ppb)	Feedwater	0.01	0.01	0.01
Acetate	Blowdown	$(10/40) \times [\text{Morph}] / 1000$	$(10/3) \times [\text{ETA}] / 1000$	$(10/3) \times [\text{DMEA}] / 1000$
Formate	Blowdown	$(10/3) \times [\text{Morph}] / 1000$	$1 \times [\text{ETA}] / 1000$	$1 \times [\text{DMEA}] / 1000$
NH3	Feedwater	$(3.6/40) \times [\text{Morph}] / 1000$	$(3.6/3) \times [\text{ETA}]$	$(3.6/3) \times [\text{DMEA}]$
Amine (ppm)	Feedwater	31.0	3.9	7.7

The outputs at select locations for a DMEA cycle with the above-described parameters are shown in Table 5-2. The predicted concentrations of DMEA and NH₃ at various points around the cycle agree with what would be expected based on the relative distribution coefficient of each amine as presented in Figure 3-5 (ammonia being more volatile than DMEA). The concentration of DMEA is also relatively constant across the entire secondary system highlighting the similar volatilities of DMEA and water.

5.1.1 Injection

Amine injection is required to maintain the target feedwater concentration (e.g., pH₂₅ 9.5). The amine injection rate needs to balance amine loss through three processes: (1) loss to SG blowdown (or blowdown demineralizers); (2) loss to condensate polishers; and (3) thermal decomposition of the amine. All three of these processes can be modeled using the PCS software, allowing one to estimate the effect of each loss mechanism on the overall injection rate or amine demand.

The PCS software can be used to characterize the amine addition required to make up removal by condensate polishing. Table 5-3 presents simulation results, with and without condensate polishing (inputs from Table 5-1). The *SGBD Only* column shows the addition rate required for each amine to offset loss due to the SGBD being overboard (i.e., not recycle to the feedwater train). Note that the model uses an assumed SGBD mass flow rate of 50,000 lbm/hr (~22,700 kg/hr). The effects of the blowdown demineralizer are not simulated here because the process (when simulated) reduces amine concentrations by more than five orders of magnitude and gives essentially the same result as the overboard simulation (effectively equivalent to overboarding the SGBD in terms of the required amine addition rates). The *SGBD + Full Flow CP* column shows the effects of the blowdown and full-flow condensate polishing on amine demand. Note that significantly more amine is required when plants are operating with full-flow condensate

polishers and the results represent a bounding case. Here, the condensate polisher was modeled with the cation exchange resin initially in hydrogen form. Subsequent ion exchange in the condensate polisher was modeled in the PCS software based on ion selectivity. Default PCS values for 8% cross-linked cation resin (gel type, strong acid) were used for the selectivity for each amine relative to hydrogen (i.e., 1.26 for morpholine and 1.1925 for ETA). A default selectivity value for DMEA was not available in the PCS software. Therefore, based on similarities between morpholine and DMEA discussed in Section 4.2.1, the selectivity of DMEA was assumed equal to morpholine. Note that the PCS also calculates the MTC for each species on the resin. The inputs for this come out of two files: *ixlib.dat* and *Species.dat*. DMEA entries were added to these files and the selectivity was added to the *ixdata.mdb* (MS Access database). A gives details on the specific modifications to these files.

Table 5-2
Sample PCS Output for a DMEA Cycle

	SG Blowdown	Main Steam	Moisture Separator	Drain Tank	Condenser Inlet	Condensate (CP Disabled)	Final Feedwater
pH(t)	6.41	6.33	6.85	6.9	9.47	11.59	6.94
pH(n)	5.62	5.62	5.66	5.63	6.88	7.9	5.63
pH(25°C)	9.82	9.98	9.66	9.93	10.01	10.01	9.98
pH(25°C) w/o cations	6.18	6.16	5.96	6.1	6.21	6.21	6.16
Specific Conductivity (uS/cm)	17.26	25.49	11.52	22.61	27.46	27.13	25.44
Cation Conductivity (uS/cm)	0.26	0.28	0.43	0.32	0.25	0.25	0.28
Ionic Strength	1.54E-05	1.29E-05	3.43E-05	4.50E-05	5.48E-05	6.36E-05	4.90E-05
Saturated Steam Pressure (psia)	848.08	848.08	184.31	247.31	0.69	0.02	247.3
Na (ppb)	4.26E-01	1.49E-03	8.80E-03	3.69E-03	1.16E-05	2.19E-05	3.60E-03
Cl (ppb)	1.18E+00	4.14E-03	2.45E-02	1.03E-02	3.22E-05	6.09E-05	1.00E-02
SO4 (ppb)	1.18E+00	4.14E-03	2.44E-02	1.02E-02	3.22E-05	6.08E-05	1.00E-02
OAc (ppb)	2.57E+01	8.63E+00	5.21E+01	2.00E+01	8.12E-01	1.02E+00	8.72E+00
HCO2 (ppb)	7.70E+00	2.44E+01	1.15E+01	2.10E+01	2.66E+01	2.65E+01	2.43E+01
NH3 (ppm)	4.34E+00	9.27E+00	1.59E+00	7.27E+00	1.08E+01	1.05E+01	9.24E+00
N2H4 (ppb)	3.29E+02	9.39E+01	4.02E+02	1.75E+02	3.58E+01	3.96E+01	1.00E+02
DMEA (ppm)	5.37E+00	7.72E+00	6.58E+00	7.41E+00	7.92E+00	7.86E+00	7.70E+00

Table 5-3
Amine Addition Rates (lbm/hr) with and without Condensate Polishing

	SGBD Only	SGBD + Full Flow CP
Morpholine	1.32	133.00
ETA	0.49	11.00
DMEA	0.27	36.20

The PCS software can also be used to characterize the required amine addition due to decomposition. Amine decomposition is not expected to lead to losses comparable to full-flow condensate polishing. However, decomposition rates can still have a noticeable effect on amine addition rates. Table 5-4 presents the simulation results for amine addition due to SGBD and decomposition, respectively, without condensate polishing (inputs from Table 5-1). The results for two different sets of decomposition half-lives are presented for each amine, using values from Table 3-4 and from Reference [29], respectively. The half-life of DMEA is not included in the Reference [29] analysis, so the half-life of ETA was used for DMEA due to its similarity in chemistry. Finally, decomposition is only modeled in the steam generator, where a large volume of liquid water and high temperatures are present. Percent decomposition, used in the PCS simulation for each amine, is calculated with the first order thermal decomposition half-lives and an assumed SG residency time of 3 minutes. Note that the residence time of DMEA in the SG is assumed equal to that of water (e.g., 167 klbm SG volume with 3300 klbm/hr feedwater), assuming a DMEA volatility similar to water (see Section 3.2.3) and rapid equilibrium mixing between the liquid and vapor phases.

Table 5-4
Amine Addition Due to Thermal Decomposition

Amine	Assumed Half-Life (hrs)	SG Thermal Decomposition (%)	Total Amine Addition (lbm/hr)	SGBD Loss (lbm/hr)	Thermal Decomposition Loss (lbm/hr)
Morpholine	2.67	1.29	5.330	1.310	4.020
	30	0.115	1.680	1.320	0.358
ETA	2.38	1.45	1.050	0.486	0.568
	99	0.035	0.507	0.493	0.014
DMEA	5.07	0.681	0.794	0.267	0.527
	99*	0.035	0.296	0.268	0.027

* ETA's half-life used due to ETA having the most similar chemistry to DMEA of the amines presented.

As is shown in Table 5-4, based on the assumed decomposition percentages, the loss from thermal decomposition are expected to be the same order of magnitude as SGBD losses, except in one case (i.e., the assumed 99-hr half-life) where the losses to thermal decomposition are much less. For DMEA, the expected addition rate due to thermal decomposition is less than

1 lbm/hr at typical operating conditions. Amine addition rates at or below 1 lbm/hr agree with the fleet survey information presented in Reference [27].

In summary, the required injection rate to maintain the proper concentration of DMEA can be calculated using EPRI's Plant Chemistry Simulator (PCS). Uncertainty in the cation exchange resin selectivity and thermal decomposition of DMEA (previously identified knowledge gaps) add uncertainty to the DMEA addition rate modeled by the PCS. However, available estimates for these values appear to give reasonable estimates for an upper and lower bound to the DMEA addition rate. These estimates are further corroborated by reasonable addition rates predicted using the same methodology for morpholine and ETA. The addition rate of DMEA is considered a moderate knowledge gap because the underlying inputs have not been adequately characterized.

5.1.2 Chemistry Effects

pH and cation conductivity are the most likely to be affected by DMEA addition (and DMEA decomposition products).

5.1.2.1 pH

The primary effect on pH from the addition of DMEA (aside the desired pH control) is expected to be due to the organic acids, ammonia, and amines produced as decomposition products. Effects on pH due to ammonia and amine production will raise the pH so they are not of primary concern. Of particular concern would be the low volatility of the organic acid decomposition products that could reduce the pH of the early condensate. Section 3.8.2 of Reference [27] discusses calculations that show organic acid concentrations would need to be 500 ppb or higher in order lower the early condensate pH below acceptable levels. Organic acids are not expected to be a problem with DMEA as the decomposition rate is expected to be less than that of ETA, which should lead to lower production of organic acids (Section 3.2.4). DMEA is also less volatile than ammonia, ETA, and morpholine, which will provide better protection in the early condensate than is seen with pH control by those amines. This expected behavior is demonstrated by simulations using the PCS. For example, Table 5-5 presents the pH_T and pH_{25} for morpholine, ETA, and DMEA both with and without ammonia (based on the concentrations taken from Table 5-1).

In general, DMEA is expected to provide similar pH control around the secondary cycle to that of ETA and morpholine. This suggests that cycle pH_T can be controlled and monitored using methods that are already in place for current amine pH control programs.

5.1.2.2 Cation Conductivity

Cation conductivity is used for monitoring anions, such as chloride and sulfate in PWR secondary cycle water chemistry. Organic acids, such as acetic acid or formic acid, produced through the decomposition of amines will also elevate the cation conductivity. This is an issue for all amines used for pH control [27]. There has not yet been a test program measuring the effect of DMEA on cation conductivity. However, cation conductivity can be modeled based on the estimated species concentrations in Table 5-1. The cation conductivity values from the PCS are shown in Table 5-6.

The results in Table 5-6 suggest that the cation conductivity will be increased relative to ETA and morpholine. However, this increase is likely an artifact of the conservative way decomposition products are being modeled here. Experimental data suggest that DMEA thermally decomposes at a rate less than that of ETA (Section 3.2.4) and DMEA has a higher molecular weight compared to ETA. Since decomposition products are being modeled based on a mass-concentration ratio and using the concentration ratios for ETA for modeling both amines, it is likely that the decomposition product concentrations are overestimated for DMEA.

Table 5-5
pH_T and pH₂₅ With and Without Ammonia

		SG Blowdown	Main Steam	Moisture Separator	Drain Tank	Condenser Inlet	Condensate (CP Disabled)	Final Feedwater
Morph	pH _T	6.36	6.35	6.85	6.73	9.59	10.96	6.73
	pH ₂₅	9.47	9.50	9.51	9.50	9.50	9.50	9.50
Morph + NH ₃	pH _T	6.40	6.37	6.87	6.81	9.60	11.35	6.82
	pH ₂₅	9.63	9.75	9.57	9.72	9.78	9.77	9.75
ETA	pH _T	6.35	6.39	6.89	6.60	9.61	11.03	6.49
	pH ₂₅	9.76	9.50	9.82	9.63	9.33	9.35	9.50
ETA + NH ₃	pH _T	6.41	6.42	6.91	6.78	9.63	11.47	6.77
	pH ₂₅	9.86	9.86	9.85	9.86	9.86	9.86	9.86
DMEA	pH _T	6.26	6.23	6.77	6.68	9.42	10.93	6.69
	pH ₂₅	9.40	9.49	9.46	9.49	9.50	9.50	9.49
DMEA + NH ₃	pH _T	6.41	6.33	6.85	6.90	9.47	11.59	6.94
	pH ₂₅	9.82	9.98	9.66	9.93	10.01	10.01	9.98
—	pH _N	5.62	5.62	5.66	5.63	6.88	6.80	5.63

Table 5-6
Cation Conductivity at Various Locations as Estimated by the PCS ($\mu\text{S}/\text{cm}$)

	SG Blowdown	Main Steam	Moisture Separator	Drain Tank	Condenser Inlet	Condensate (CP Disabled)	Final Feedwater
Morph	0.12	0.10	0.15	0.11	0.10	0.10	0.10
ETA	0.16	0.15	0.22	0.17	0.14	0.14	0.15
DMEA	0.26	0.28	0.43	0.32	0.25	0.25	0.28

Ultimately, the formation of organic acids from DMEA decomposition has the potential to change plant-specific cation conductivity values that are used established a baseline for action level entry [1]. As discussed in Section 3.2.4, the thermal decomposition of DMEA is expected to be less than ETA, so the expected increase in cation conductivity due to organic acids should be less. Consequently, the need to evaluate the effect of DMEA addition on cation conductivity and, as appropriate, adjust baseline values for action level entry is identified here as a moderate knowledge gap. As indicated above, improved thermal decomposition data should improve the accuracy of the cation conductivity calculated using the PCS.

5.1.3 Monitoring and Sampling

Additional pH monitoring and grab samples to measure DMEA and decomposition product concentrations are recommended at multiple points around the secondary system for the initial application of DMEA. This is due to the uncertainty in the decomposition rate of DMEA and in the uncertainty in the expected decomposition products. Considering the concentrations of DMEA and cation conductivity values predicted by the PCS at various points in the secondary system (see Table 5-1 and Table 5-6), the need for additional monitoring and sampling may not be needed beyond the initial cycle.

5.2 Corrosion Phenomena

As discussed in Section 4.1, the only correlation observed between corrosion rate and amine concentration has been the reduction of corrosion rates with increasing pH [27,31]. With pH being the strongest correlated factor to corrosion rate, local pH becomes a primary consideration in any amine application. However, these interactions are based a set of amines that does not include DMEA. Accordingly, as discussed in Section 4.1, the interaction of DMEA with metals has been identified as major knowledge gap and additional testing is recommended to demonstrate that the behavior of DMEA is comparable to other amines.

5.2.1 General Corrosion

Local pH at various points around the secondary system depends heavily on the basicity and volatility of the amine or combination of amines used. Amines with volatilities similar to that of water will have the most consistent coverage over the entire secondary system. Table 5-2 and Table 5-5 show the concentrations and pH at various points around the secondary system as modeled by the PCS. These tables show a relatively consistent concentration of DMEA around the steam cycle with pH control similar to that of ETA and morpholine. Based on these estimates, DMEA is expected to be as effective as currently used amines at controlling general

corrosion processes. However, as discussed above, the effect of DMEA on general corrosion is identified as a major knowledge gap because data are not available to confirm that the interaction of DMEA with metals is comparable to previously tested amines.

5.2.2 Flow Accelerated Corrosion

Flow accelerated corrosion (FAC) is known to depend on the local solubility and diffusion rate of iron at the site of corrosion. This is known to be dependent on pH, as discussed above. However, any substance that increases the solubility of iron independently of pH could increase the rate of FAC in the secondary system. An increase in the solubility (and therefore mobility) of iron in the secondary system would likely correspond to an increase in the iron content in the feedwater. Amine addition at plants has been correlated to a reduction in feedwater iron consistent with increases in pH [27,31]. DMEA is expected to have a similar positive effect. However, as discussed above, the effect of DMEA on FAC is identified as a major knowledge gap because data are not available to confirm that the interaction of DMEA with metals is comparable to previously tested amines.

5.3 Effects on Operation of Plant Equipment

5.3.1 Moisture Carryover

The rate of moisture carryover at a plant is important, as this is a pathway for non-volatile species to distribute around the steam cycle. Any chemical additive added to the PWR secondary coolant has the potential to change the coolant surface tension and therefore the carryover rate. In general, adding any amine to water will reduce the surface tension. However, a literature search found no data regarding the effect of dissolved DMEA (or other common pH control amines) on solution surface tension under typical secondary side conditions. This is considered a minor knowledge gap.

5.3.2 Analytical Instruments

The addition of DMEA could potentially have two effects on analytical instrumentation in use for secondary side monitoring. The addition of a new amine could interfere with or change the baseline readings for analytical methods that are sensitive to DMEA. There is also the potential for transport of deposits that could foul or block online analytical instruments.

It is possible that the addition of DMEA will change the baseline readings for cation conductivity and electrochemical potential as this would be consistent with other amines used for pH control [27]. However, the change in ECP relative to ETA is expected to be insignificant (e.g., less than ~40 mV difference at an amine concentration of 0.0165 mol/L, which is equivalent to 1000 ppm ETA [5]). As was discussed in Section 5.1.2.2, change in the cation conductivity due to DMEA will need to be accounted for in the baseline values used for action level entry (i.e., to ensure that changes in chloride or sulfate can be appropriately detected).

Fouling of online analytical instruments could theoretically be caused by DMEA forming insoluble compounds or by DMEA increasing the mobility of corrosion products in the secondary system. Such fouling could affect a wide range of chemical analysis and process monitoring equipment. However, DMEA is not known to form solid hydrates or products in boiler systems [17]. Additionally, the type of corrosion product transport necessary to foul

analytical instruments is equivalent to the type of process that would lead to an increase in FAC. As DMEA is not expected to increase corrosion product transport, increased fouling of analytical instrumentation is not expected. The effects of DMEA on analytical instruments are considered a minor knowledge gap due to the lack of plant experience with DMEA.

5.3.3 Corrosion Product Deposition

The rate of corrosion product deposition in the steam generator depends on a variety of factors. This includes factors influencing corrosion rate, corrosion product transport, and the local conditions at the deposition site. Some laboratory results have shown the deposition rate can be amine specific. In general, amine concentration strongly influences the general corrosion rate and FAC rates through the effect on pH_r. There is also some evidence supporting an amine-specific difference in deposition rate in laboratory test with a fixed iron concentration and pH. In these tests, ETA was shown to have a deposition rate of 4 times that of DMA [1]. The mechanism for this is not well defined. Without a more detailed understanding of the amine-specific factors influencing corrosion product deposition, it is not possible to predict effects of DMEA in similar conditions. Accordingly, the effect of DMEA on corrosion product deposition in the steam generator is identified as a major knowledge gap. Testing is recommended to demonstrate that the effects of DMEA on general corrosion and FAC rates are comparable to other amines (i.e., primarily due to pH_r changes). It is likely that this recommended testing could be combined with testing that has already been recommended in Section 4.2 to determine the interaction of DMEA with metals.

5.3.4 Ion Exchange Beds

Amines can affect ion exchange beds through exchange onto the cation resin and attack of the resin backbones of both anion and cation exchange resins. Section 4.2 discusses these processes. In general, DMEA is expected to have a reduced negative effect on resin performance compared to ETA. This is believed to be due to DMEA being less likely than ETA to participate in a variety of processes deleterious to ion exchange resins.

An estimate of the cation-loading rate can be derived from the addition rates modeled by the PCS. Based on the amine addition rates in Table 5-3 for DMEA, full flow condensate polishing removed 35.93 lbm/hr (16.30 kg/hr). Given the parameters from the PCS model of a bed volume of 4500 gallons (17000 L), a cation resin capacity of 1.875 meq/mL, and a bed composition of 66.67% cation resin, this would lead to 95% DMEA loading of the cation resin in 4.6 days. For comparison, a similar calculation for ETA based on a removal rate of 10.51 lbm/hr (see Table 5-3) yields 10.8 days. Resin exhaustion would likely occur before these times as other cations such as ammonia and sodium occupy binding sites. Of course, for different percent cross link resin and capacity, these values will change slightly.

As was noted in Section 4.2, the effect of DMEA on resin bed is dependent on two knowledge gaps – bed performance (minor gap) and resin selectivity (major gap). Improved estimates of ion exchange bed effects using the PCS are expected to be available once these two gaps are addressed.

5.4 Summary

This section investigated application considerations regarding the use of DMEA as a PWR secondary side pH control amine. The EPRI *Plant Chemistry Simulator* (PCS) was used to estimate secondary water chemistry parameters based on a sample plant configuration. These simulation results, in combination with results of the literature search presented in Sections 3 and 4, were used to investigate expected application parameters. The results are summarized below:

- EPRI's PCS software can be used to model the application of DMEA as PWR secondary side amine for pH control. The results are reasonable compared to similar simulations for ETA and morpholine. The ability to model DMEA with the PCS is considered a knowledge gap because many of the necessary inputs are based on data identified as knowledge gaps earlier in this report.
- The expected injection rate for DMEA is comparable to other amines. The injection rate of DMEA without condensate polishing, as modeled by the PCS, is calculated to be between 0.3-0.8 lbs/hr (2.2-6.0 g/hr). These results are based on assumed values for thermal decomposition and resin selectivity, which were identified as knowledge gaps in previous sections. Accordingly, the injection rate of DMEA is identified as a moderate knowledge gap, due to the additional necessary refinement of model inputs before plant application.
- DMEA is expected to provide better pH protection in the early condensate than ammonia, morpholine, or ETA due to its lower volatility.
- Additional monitoring and sampling is recommended during the initial application of DMEA due to uncertainty in thermal decomposition rate and products.
- Long-term plant experience indicates a lack of amine-specific effects on corrosion phenomena. However, there are no direct experimental data or plant experience regarding general corrosion or FAC with DMEA as a pH control agent. Therefore, the effect of DMEA on corrosion phenomena is identified as a major knowledge gap. It is expected that this gap will be addressed concurrently with the previously identified gap regarding the interaction of DMEA with metals in Section 4.1 (i.e., using confirmatory testing to demonstrate DMEA can be categorized with other previously studied amines).
- The potential effect of DMEA on moisture carry over is considered a minor knowledge gap. Operating experience with amines suggests that no amine or amine-specific effects have been identified relating to moisture carryover.
- DMEA and DMEA decomposition products are expected to affect the baseline cation conductivity that are established and are used to monitor and control secondary water chemistry. The lack of adequate estimates of cation conductivity changes caused by DMEA, due in part to limited decomposition testing, is identified as a moderate knowledge gap.
- The effect of DMEA on plant analytical instruments is considered a minor knowledge gap. DMEA is not expected to participate in any of the chemical processes known to lead to analytical instrument fouling.
- Data are not available concerning the effects of DMEA on corrosion product deposition within the steam generator. This is identified as a major knowledge gap. Available data suggests that an amine-specific effect is expected and that the phenomenon is primarily

dependent on general corrosion and FAC effects, which are driven by pHr changes. Testing is recommended to address this knowledge gap, which can likely be accomplished with other recommended testing suggested previously for metal capability evaluations.

- Modeling of ion exchange bed loading predicted 95% loading of the cation bed in about 5 days for a sample plant under full flow condensate polishing. This agrees with available plant experience. These estimates are based on a number of assumptions that will likely be improved once knowledge gaps related to PCS inputs are addressed, including improved estimates of resin selectivity.

6

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A

PLANT CHEMISTRY SIMULATOR INPUTS

The run specific inputs to the Plant Chemistry Simulator (PCS) are discussed in Section 5. However, there were several modifications to the PCS input files that should be covered to allow the results in this report to be reproduced.

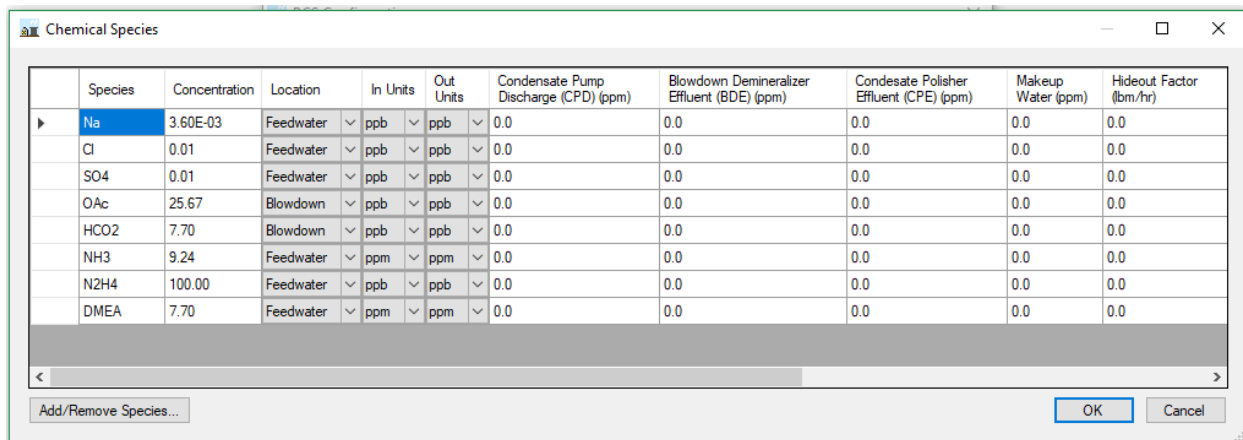
The PCS calculations performed in this report used the sample model installed with the PCS for a PWR with a recirculating steam generator [40]. The default settings were maintained unless noted.

A.1 Plant Settings

From the *Plant Settings* dialogue accessed through the *Tools* menu, the steam generator (SG) and condenser were configured. For the SG, the blowdown destination was set to *Drain/Vent* and the *Fraction Demineralized* was set to 0%. For the condenser, the condensate polisher was turned on and off by adjusting the *Fraction of Condensate Polished* to either 0% or 100%.

A.2 PCS Configuration

The *PCS Configuration* dialogue was accessed by double-clicking on *PCS* under *Modules* in the item tree. Under *Calculation Options* both *Decomposition* and *Injection* were enabled. Under *Decomposition Reactions* the default decomposition reaction of hydrazine to ammonia was moved from the feedwater to the steam generator. The chemical species were then entered to match the values in Table 5-1. An example is shown for DMEA in Figure A-1.



Species	Concentration	Location	In Units	Out Units	Condensate Pump Discharge (CPD) (ppm)	Blowdown Demineralizer Effluent (BDE) (ppm)	Condensate Polisher Effluent (CPE) (ppm)	Makeup Water (ppm)	Hideout Factor (lbm/ft ³)
Na	3.60E-03	Feedwater	ppb	ppb	0.0	0.0	0.0	0.0	0.0
Cl	0.01	Feedwater	ppb	ppb	0.0	0.0	0.0	0.0	0.0
SO4	0.01	Feedwater	ppb	ppb	0.0	0.0	0.0	0.0	0.0
OAc	25.67	Blowdown	ppb	ppb	0.0	0.0	0.0	0.0	0.0
HCO2	7.70	Blowdown	ppb	ppb	0.0	0.0	0.0	0.0	0.0
NH3	9.24	Feedwater	ppm	ppm	0.0	0.0	0.0	0.0	0.0
N2H4	100.00	Feedwater	ppb	ppb	0.0	0.0	0.0	0.0	0.0
DMEA	7.70	Feedwater	ppm	ppm	0.0	0.0	0.0	0.0	0.0

Figure A-1
Chemical Species Dialogue

A.3 Input Files

There are several input files included as part of the sample model. These files can be found in the directory */PCS Projects/Sample*, which is installed in the user's *Documents* directory as part of the install. Three files were modified to allow DMEA to be treated by the ion exchange beds modeled by the PCS, as discussed in the following subsections.

A.3.1 *ixdata.mdb*

The MS Access database *ixdata.mdb* contains resin selectivity constants in the *IXDATA* table. Based on the selectivity of DMEA being equivalent to morpholine for gel type, strong acid cation exchange resins with 8% cross linkage, the value for morpholine was used for DMEA. A new column in the table was created with the value for morpholine inserted. A placeholder value of 1 was input for other cation resins in the database (not used in simulations). Tab shows a screen capture of the modification to *ixdata.mdb*.

Resin	Type	Resin Name	Morph	DMEA
1	C	Gel Strong Acid Cation, 10% Crosslinkage	1.06	1
2	C	Gel Strong Acid Cation, 8% Crosslinkage	1.26	1.26
3	C	Macroporous Strong Acid Cation, 20% Crosslinkage	0.245	1
4	C	Macroporous Strong Acid Cation, 12% Crosslinkage	0.68	1
5	A	Gel Strong Base Anion, Type I	0	0
6	A	Gel Strong Base Anion, Type II	0	0
7	A	Macroporous Strong Base Anion, Type 1	0	0
8	A	Gel Weak Base Anion, Type II	0	0
*				0

Figure A-2
Addition of DMEA Column to IXDATA Table

A.3.2 *lxlib.dat*

The file *lxlib.dat* gives equivalent weight (molecular weight), diffusivity, and the binding ion for species. This file is organized by MULTEQ database number. The molecular weight and binding ion were taken from the MULTEQ database and the diffusivity was based on analytical work from Reference [41]. Figure A-3 shows the inline modification to *lxlib.dat*.

```

79) Pyrrol      4) Equivalent Weight = +71.12
                  Diffusivity      = 1.
                  Binding ion:      HPyrrol      E

82) DMEA        4) Equivalent Weight = +89.00
                  Diffusivity      = 0.878
                  Binding ion:      HDMEA        E

99) H2          4) Equivalent Weight = 0.0
                  Diffusivity      = 0.0
                  Binding ion:      none         E

```

Figure A-3
Addition of DMEA to lxlib.dat

A.3.3 Species.dat

The file *Species.dat* contains a subset of the MULTEQ database and is organized by MULTEQ database number. The MULTEQ entry for DMEA was inserted inline at the appropriate location. A screen capture of modification is shown in Figure A-4.

```

79) Pyrrol      1) Charge          = 0
                  2) M.W.          = 71.12
                  5) Distribution Coefficient :
                      5.a) Default value @ 25 = 0.51
                      5.b) Temperature Coeff. :
                          A = 2.60775E-01      B = 1.13178E-02
                          C = -4.89448E-05     D = -2.27911E-08
                          E = 4.16807E-10     F = -5.99180E-13

                                                    2001 Jun 29 16:00:00

82) DMEA        1) Charge          = 0
                  2) M.W.          = 89.0
                  5) Distribution Coefficient :
                      5.a) Default value @ 25 = 0.6761
                      5.b) Temperature Coeff. :
                          A = -1.20000E-01     B = -2.15333E-02
                          C = 8.53333E-05      D = -6.13333E-07
                          E = 1.86667E-09     F = -2.13333E-12

                                                    1991 Aug 13 16:50:05

99) H2          1) Charge          = 0
                  2) M.W.          = 2.0
                  5) Distribution Coefficient :
                      5.a) Default Value @ 25 = 6.330000E+00
                      5.b) Temperature Coeff. :
                          A = 6.94554E+00     B = -2.62353E-02
                          C = 6.80258E-05     D = -1.97199E-07
                          E = 3.82525E-10     F = -3.71184E-13

```

Figure A-4
Addition of DMEA to Species.dat



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