

**STUDY TO INVESTIGATE THE MINIMIZATION
OF USE AND DISCHARGE OF
ETHANOLAMINE
AT MILLSTONE POINT**

Millstone Point Nuclear Power Station

NPDES Permit N° CT0003263

Status Report: June 1994

TABLE OF CONTENTS

- 1.0) Introduction
- 2.0) Scope of Study
- 3.0) Background
- 4.0) Millstone Tests
 - 4.1 Millstone 2 Testing
 - 4.2 Millstone 3 Testing
- 5.0) Preliminary Conclusions
- 6.0) Testing and Reporting Schedules
- 7.0) References

Minimization of Use and Discharge of Ethanolamine at Millstone

1.0) INTRODUCTION

On December 14, 1992, the Connecticut Department of Environmental Protection (DEP) reissued NPDES permit CT0003263 to the Northeast Nuclear Energy Company (NNECO), (Reference 7.1). This NPDES permit included an allowance for the use and discharge of ethanolamine (ETA) at Millstone Units 2 and 3. ETA is an amine intended for use as an alternative to ammonia for secondary system water pH control in Pressurized Water Reactors (PWRs), (see Section 3).

Several stipulations included in the new permit require new commitments from NNECO (Reference 7.2). Two of these commitments, pertaining to Millstone Unit 2 secondary system chemistry control, are as follows:

- Submit a scope of study to investigate the minimization of use and discharge of ETA at Unit 2, on or before June 30, 1993.
- Submit an engineering report on the minimization of use and discharge of ETA according to the above scope, of study on or before June 30, 1994.

The scope of study, was submitted June 29, 1993, (006590) (Reference 7.3). This scope of study was subsequently expanded by NNECO to include parallel testing of ETA at Millstone 3.

Due to the fact that the ETA testing is not yet complete at the Millstone site, this document is considered to be a status report intended to meet the intent of the second commitment. A final report will be prepared for submittal to the DEP when the ETA testing has been completed. Completion of this testing at Millstone is presently expected by the end of 1995. Due to the timing of refueling outages at Millstone, this report contains no details on the minimization of ETA for steam generator (SG) wet lay up.

2.0) SCOPE OF STUDY

The scope of study described in Reference 7.3 outlined a plan for in-plant testing of ETA for secondary system pH control at Millstone 2. A summary of this plan is as follows:

- 2.1 ETA will be added until a concentration of 2.0 ppm is achieved in the final feedwater.
- 2.2 After a baseline period, the ETA concentration will be varied.

Minimization of Use and Discharge of Ethanolamine at Millstone

- 2.3 While varying the concentration, all appropriate chemistry parameters and corrosion product parameters will be monitored.
- 2.4 During the study, condensate polisher performance will also be monitored.
- 2.5 The data collected from the study will be used to evaluate the possible continued use of ETA, and to identify the minimum, but necessary, concentrations needed for optimum pH and erosion/corrosion control.

3.0) BACKGROUND

Control of pH in the secondary cycle of PWR plants is essential to minimize corrosion of secondary system components. Corrosion of carbon steel, which typically makes up a large portion of the condensate/feed train, is minimized at a room temperature pH of approximately 10.0, (Reference 7.4). Two of the more critical concerns relative to secondary system chemistry are steam generator corrosion and erosion/corrosion control.

Steam generator corrosion is a serious concern at virtually all PWR plants. Corrosion products, consisting primarily of insoluble ion species, are transported to the steam generators via the feed train. These corrosion products accumulate in low-flow and flow-restricted areas of the steam generators, such as tube/tube support plate intersections and tube/tubesheet crevice regions. Ionic impurities such as sodium and chloride, can concentrate by many orders of magnitude over bulk water concentrations in these areas, resulting in extremely corrosive conditions in localized areas. Many of the steam generator corrosion problems observed in the industry have been linked to this mechanism. It is generally agreed that methods to reduce corrosion produce transport to the steam generators will pay major dividends in terms of long-term plant reliability and steam generator longevity, (Reference 7.5).

Erosion/corrosion is a particular type of corrosive attack which is dependent upon a number of factors, including materials of construction, piping geometry, steam velocity, steam quality, dissolved oxygen content, and pH. Erosion/corrosion has been observed in wet steam areas, such as steam extraction lines, and on an industry wide basis has caused catastrophic failures of piping and severe personnel injury. For example, an unanticipated failure of a high-pressure steam extraction line at Millstone 2 recently resulted in a forced outage. Analysis of the failed line indicated that erosion/corrosion was the causative reason. Studies have shown that pH in wet steam areas has a major impact on the erosion/corrosion rate of carbon steel piping, (Reference 7.6). With all other factors equal, increasing the pH (at 25°C) from 7.0 to 9.0 has been shown to reduce the erosion/corrosion rate by more than a factor of two.

Minimization of Use and Discharge of Ethanolamine at Millstone

Thus, it is very advantageous from the standpoint of erosion/corrosion control and personnel safety to increase the pH in wet steam areas of the plant.

Beginning in the early 1970's, most U.S. PWRs utilized ammonia for secondary system pH control. Feedwater pH is typically maintained between 8.8 and 9.2 depending on the use of copper alloys in the secondary cycle. While ammonia is effective as a pH control agent, there are other amine compounds with more desirable properties. For example, ammonia is very volatile, i.e., the ammonia tends to stay with the steam phase as opposed to the water phase. As a result, very little protection is provided in wet steam areas where erosion/corrosion is a serious concern. The use of higher levels of ammonia creates significant difficulties with effective operation of the full flow condensate polishers including very short polisher run lengths. Most plants have been unable to effectively operate past the ammonia break through point without unacceptable increases in sodium leakage and subsequent SG corrosion concerns.

Beginning in 1986, studies were conducted using morpholine as an alternate to ammonia for secondary system pH control, (Reference 7.7). Morpholine has been used for pH control at Beaver Valley Unit 1 since startup and fewer steam generator problems were observed at this unit when compared to similar units. Morpholine is also less volatile than ammonia and, therefore, provided better protection of wet steam areas. Studies conducted at Beaver Valley and Prairie Island showed reductions of approximately a factor of two in feedwater corrosion product transport with morpholine as compared to ammonia pH control. Based on this data and the favorable experience of French PWRs, many U.S. PWRs have converted to morpholine over the past five years. There are currently 31 U.S. PWR units and 36 French PWR units that employ morpholine for secondary cycle pH control.

Although morpholine has proven effective in reducing corrosion product transport, there are other amine compounds with more favorable properties for secondary system pH control. The Electric Power Research Institute (EPRI) has evaluated several of these amines and has selected three for in-plant evaluation. Based on certain selection criteria, ETA was chosen for initial plant testing at Millstone.

The major goal of the proposed test programs at Millstone is to evaluate actual plant performance of the ETA in reducing corrosion product transport and erosion/corrosion, while maintaining effective operation of the condensate polishers.

4.0) MILLSTONE TESTS

The following is a summary of the testing at Millstone. The information derived from this testing is expected to be interchangeable between Millstone 2 and Millstone 3.

Minimization of Use and Discharge of Ethanolamine at Millstone

The sum of this information will be used to define the optimum ETA concentration necessary to minimize erosion/corrosion in the secondary water system at both units and to minimize the use and discharge of ETA.

4.1 Millstone 2 Testing

Erosion/corrosion wear rate data was developed from an EPRI computer model called CHECWORKS, (Reference 7.8). This model showed theoretically that the optimum feedwater ETA concentration for a significant decrease in erosion/corrosion of secondary system components, such as the reheater drains, was of the order of 1-3 ppm. Therefore, a concentration of 1-3 ppm ETA in the final feedwater was established as a target value in order to achieve the required at temperature pH in the heater drains, (Reference 7.9).

On April 23, 1993, the unit began ETA addition. For a few days, the ETA was kept at about 1.0 ppm in the final feedwater while cation conductivity was being evaluated. No concerns were identified, and the ETA concentration was subsequently increased to about 2 ppm. This ETA concentration has been maintained through the current test period with the exception of some downpowers, reactor trips, and a mid cycle outage.

Throughout the current test period, the impact of ETA on corrosion product transport was being evaluated by routine bi-weekly corrosion product samples at Millstone 2. By drawing various side stream samples through multiple filters, both the insoluble and soluble fractions can be identified.

Preliminary results showed that by early June 1993, the total feedwater iron transport had dropped from about 6-7 ppb to about 1-2 ppb, with the greatest change being observed in the soluble fraction.

Due to the success of ETA in reducing secondary system mass transport, Millstone 2 Chemistry will implement procedural changes for continued operation with ETA, once the special test procedures have expired. At present, there are no plans to return to the previous ammonia-based pH control.

Under a "Tailored Collaboration Program" (shared cost) with EPRI, NU plans to monitor the electrode potential (ECP) in the secondary system feedwater at Millstone 2, (Reference 7.10). The main objective of this program is to more precisely demonstrate the relationship (via ECP)

Minimization of Use and Discharge of Ethanolamine at Millstone

between feedwater ETA and/or hydrazine concentration, condensate oxygen concentration and corrosion product transport. The ECP program and measurements are now underway.

4.2 Millstone 3 Testing

At Millstone 3, a different approach was adopted for the testing of ETA. For this test, ETA was added to the secondary system in small increments over a relatively long period of time. While making these additions, various side streams were monitored for both soluble and insoluble iron using similar techniques to those used at Millstone, (see Section 4.1).

ETA was first injected at Millstone 3 on January 26, 1994, until a final feedwater concentration of 0.25 ppm was achieved, (Reference 7.11). This level of ETA was maintained for several days while assessing the impact on various chemistry parameters. Concentrations of ETA were then increased in increments, until a feedwater concentration of 1.2-1.5 ppm was reached on March 11, 1994.

Evaluation of corrosion product transport within the secondary system show that levels of iron were decreasing considerably. Current results show a decrease in total feedwater iron transport from about 10-12 ppb to about 6 ppb, when changing from ammonia chemistry to a feedwater ETA concentration of about 1.5 ppm.

Testing at higher concentrations of ETA is planned for Millstone 3 after the nature of a neutral organic by-product has been adequately explained. This observation has not been currently identified at Millstone 2.

5.0) PRELIMINARY CONCLUSIONS

The following preliminary conclusions can be drawn from the testing so far:

- 5.1 ETA appears to be a successful alternative amine to ammonia for wet steam area chemistry and erosion/corrosion control.
- 5.2 By using ETA, the reduction in the formation, mass transportation and accumulation of corrosion products can significantly reduce the risk of damage to major system components such as piping, heat exchangers, and steam generators.

Minimization of Use and Discharge of Ethanolamine at Millstone

- 5.3 The reduction of corrosion products also leads to other significant advantages, such as reduced condensate polisher ion-exchange fouling, reduced ion exchange backwash demands, and subsequent reduction in waste discharge at the Millstone site.
- 5.4 The current experience with the use of ETA warrants further testing and optimization at both Millstone PWR units.

6.0) TESTING AND REPORTING SCHEDULE

The following is a tentative schedule for testing and reporting of the minimization of use and discharge of ETA at Millstone. These target dates are subject to change due to future plant operational needs.

- 6.1 ECP Monitoring at Millstone 2:
 - December 1994.
- 6.2 Increasing ETA additions at Millstone 3:
 - April 1995
- 6.3 Final report on the minimization of use and discharge of ETA at Millstone:
 - Submittal of report to DEP, December 1995

Minimization of Use and Discharge of Ethanolamine at Millstone

7.0) REFERENCES

- 7.1 NPDES Permit CT0003263, dated December 14, 1992.
- 7.2 T.P. Arcari to Distribution. NPDES Permit CT0003263 — Millstone Nuclear Power Station New Permit Commitments. ESD/GEL-92-125, dated December 23, 1992.
- 7.3 M.J.B. Hudson to T.P. Arcari. Scope of Study for Minimization of ETA Use and Discharge at MP2. MCE-CM-93-146, dated June 9, 1993.
- 7.4 C.S. Welty, et.al. Steam Generator Reference Book, Chapter 18 — Corrosion Product Control, Electric Power Research Institute, Palo Alto, CA, May 1985.
- 7.5 D.P. Siegworth, et.al. PWR Water Treatment Improvements: Cost Benefit Analysis, Electric Power Research Institute. Research Project N^o. 1571-5, Palo Alto, CA, May 1988.
- 7.6 K.V. Chexal. CHECKMATE Version 1.1. Users Manual, Electric Power Research Institute, Palo Alto, CA, April 1991.
- 7.7 J.M. Riddle, et.al. On-Line Monitoring of Secondary-Cycle Chemistry with Morpholine at Beaver Valley Power Station, Electric Power Research Institute, Research Project N^o 2647-1, Palo Alto, CA, June 1987.
- 7.8 CHECWORKS Computer Program Users Guide, Electric Power Research Institute Publication TR-103496, dated December 1993.
- 7.9 B.A. Luthanen, et.al., to J.W. Klisiewicz. Alternate Amine Preliminary Experience Summary - Millstone 2. NU Memo MCE-CM-93-207, dated September 1, 1993.
- 7.10 Babcock and Wilcox Technical Proposal For Electrochemical Test Program at Millstone 2. Electric Power Research Institute document EPRI RFP S414-07/03, dated February 26, 1993.
- 7.11 V.W. Jones to J.J. Waters. Interim Report on ETA Addition at Millstone 3. NU Memo ES-WC-94-075, dated April 14, 1994.