

Status of Application of Amines in US PWRs

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INTRODUCTION

A paper on this same subject was presented at the previous conference on Organic Conditioning Agents and Oxygen Scavengers held in Lahnstein in March of 1994 [1]. Interested readers are referred to the Lahnstein paper for a summary of the qualification program that was performed by the US PWR industry to support the transition from ammonia based pH control to other amines. At the time of the Lahnstein conference, 17 US Pressurized Water Reactors (PWRs) had switched to ethanolamine (ETA) for secondary system pH control from morpholine or ammonia and another 30 plants were planning for its implementation. In the 10 or so years since Lahnstein, the use of amines has expanded steadily in US PWRs. Today nearly every US PWR adds one or more amines for secondary system pH control.

The use of alternate amines in PWRs is part of a secondary water chemistry optimization program. Since the early 1990's, there have been major changes in the philosophy of and the additives used for secondary system chemistry control in PWRs. These changes result from an attempt to optimize the secondary water chemistry. Secondary water chemistry programs are generally optimized around the steam generators (SG) since SG corrosion and performance degradation has been the principal life limiting consideration in the secondary system. SG degradation has caused substantial losses of power generation, resulted in large repair and maintenance costs, and contributed to significant personnel radiation exposures in PWRs operating throughout the world. Several water chemistry options have been developed and implemented in US PWRs to eliminate or reduce SG damage, and to minimize corrosion and O&M costs in the remainder of the secondary system. Mitigation strategies reflect a trend towards plant specific solutions to corrosion and performance problems. Accordingly, the focus has shifted from prescriptive water chemistry specifications which all PWRs use to site specific programs. Software tools have also been developed by EPRI and others to help utilities select the most appropriate water chemistry program for their plant.

BACKGROUND

The widespread use of advanced amines followed a number of industry sponsored laboratory and field studies designed to identify the best possible alternative compounds to ammonia for secondary system pH control. This background work is compiled in the Advanced Amine Application Guidelines which were first published by EPRI in 1993 to assist US utilities in evaluating the use of amines [2]. The Advanced Amine Guidelines were subsequently updated in 1994 [3] and 1997 [4] to include the latest laboratory and field data available at that time. The use of advanced amines was first endorsed by the

US PWR utilities in Revision 3 to the EPRI Secondary Water Chemistry Guidelines [5]. This endorsement has continued through the latest revision to the EPRI Guidelines and has been strengthened through secondary water chemistry strategic plans developed by each utility.

Control of pH in the secondary cycle of PWRs is required to minimize corrosion of secondary system components. Corrosion of carbon steel is controlled by a number of factors including pH, temperature, steam quality, and oxygen concentration. Since the temperature and steam quality are governed by design and oxygen is controlled by other restrictions, the carbon steel corrosion rate must be reduced by increasing the pH. The site specific upper pH limit will in most cases be determined by economic considerations (e.g. chemical costs, polisher and/or blowdown regeneration frequency) or other factors (e.g. copper transport). While ammonia can be effective as a pH control agent, there are other amine compounds with more desirable properties. Ammonia is very volatile and 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 flow accelerated corrosion (FAC) of carbon steel components is a serious concern. Ultimately, the level of protection offered by any amine can be predicted from knowledge of the elevated temperature pH throughout the steam cycle. A good example of this is shown in Figure 1 where the measured level of iron in the moisture separator drains is compared to the calculated high temperature pH at that location. It is clear from these and other data that the high temperature pH is the dominating parameter for controlling corrosion not the specific amine (although amine specific effects on FAC are being investigated as part of the optimization process). The actual high temperature pH achieved at any location in the steam cycle is a complex function of the amine properties and the steam cycle design as will be described in the next section.

COMPUTER MODELING OF ADVANCED AMINES

All of the amines used for secondary system pH control are classified as weak base compounds. The base dissociation constant, K_b , for all of the advanced amines is highly temperature dependent. An equally important consideration in the selection of an amine for pH control is volatility. The volatility of the advanced amines determines their distribution in the secondary system. An amine with a low relative volatility (RV) will tend to distribute with the water phase. More of the amine is carried into the wet steam piping, resulting in a higher pH and better protection in these areas. It must be recognized however, that amines with low RVs will result in a lower pH in condensate and low-temperature feedwater sections of the plant. Mixed amine treatment, i.e., addition of a small quantity of ammonia or another amine, can be used to increase the condensate pH in this case. In many plants, breakdown of hydrazine to ammonia will provide sufficient ammonia for condensate pH control.

Detailed models have been developed in order to evaluate the impact of a given amine or mixture of amines on the secondary system chemistry. The AminMod computer code and the PWR Secondary Chemistry Simulator were both developed by EPRI for this purpose. AminMod calculates the distribution of amines, amine decomposition products and boric acid at key points in a steam cycle. Based on these distributions, the code calculates the pH and neutral pH at temperature, specific conductivity, cation conductivity at 25°C and species concentrations at pre-determined points of interest. The primary purpose of this program is to assist chemistry personnel in evaluating the use of various amine compounds for secondary system pH control. As an example of the AminMod output, Figure 2 shows the calculated pH at temperature throughout the steam cycle for 1 ppm feedwater (FW) ethanolamine (ETA).

The user supplies input data for system flow rates, temperature and feedwater species concentrations. Calculations of species distributions are based on published thermodynamic data for the ionization constants (K_b) and distribution coefficients (K_d) of the input species. Values for $pH(t)$ and $pH(n)$ are obtained by iteratively solving the multi-component equilibrium equations for all input species. Specific conductivity is calculated by resetting the temperature to 25°C, recalculating the equilibrium ionic concentrations (based on the calculated distribution at system temperatures) and applying the appropriate equivalent conductance constants. The PWR Chemistry Simulator is also capable of performing all of the same simulations as AminMod. In addition, the simulator can calculate the distribution of other impurities and additives throughout the steam cycle. The simulator also predicts polisher performance and can be used to model the decomposition of amines to organic acids.

FIELD EXPERIENCE WITH ADVANCED AMINES

The initial experience with amines was with the use of morpholine. Morpholine was first adopted in nuclear plants based on experience in fossil stations. Calculations using the computer models described above showed that other amines had superior base strength and volatility for PWR pH control applications. For example, Table 1 shows the distribution of several amines and the resultant pH at temperature throughout a typical PWR steam cycle. The common feature for all of the calculations is a MSR pH of 6.6 at temperature. As shown in Table 1, there is a large carryover of morpholine to the condensate polishers. PWR's operating with full-flow deep bed polishers were reluctant to operate the polishers in the morpholated form because of the potential for impurity leakage. Widespread adoption of amines did not occur until it became understood that other amines such as ETA could be used for pH control while continuing to operate cation resins in the hydrogen form.

ETA was first used in a full scale test at the Catawba 1 station in early 1992 [6]. ETA was selected based on laboratory data indicating that system pH's would be increased and organic acid concentrations would be lowered from operation with morpholine. Additionally, since ETA is a decomposition product of morpholine, concerns regarding side effects in the plant were reduced. After the successful implementation of ETA in Unit 1, an ETA test was performed at Catawba Unit 2 in late 1992. Duke Energy subsequently adopted ETA for pH control on a full time basis in both Catawba units, as well as their other 4 PWRs¹. After the successful tests at Catawba, many additional US PWRs adopted ETA and other amines.

Figure 3 shows the trend of the use of amines in US PWRs over time. As shown in Figure 3, the use of amines increased rapidly after Catawba in 1992 approaching 75% of all US PWRs by the mid 1990's. Some plants using ETA began experiencing problems with their condensate polishers and the adoption of amines slowed down for a period of time. Laboratory investigations to try to understand this issue identified several factors contributing to the apparent fouling mechanism and several plants have began implementing improved regeneration protocols that are mitigating this fouling issue. Additional improvements in condensate polishing were also implemented that reduced the negative impact of amines. Subsequently as shown in Figure 3, the adoption of amines continued until today where nearly every US PWR is adding one or more amines for pH control. As of the publication of this paper, 54 of 55 US PWRs or 98% of plants responding to an informal EPRI survey indicated they were using one or more amines for secondary system pH control.

¹ Other advanced amines are currently being used in the Duke Energy plants.

The breakdown of different amines being used in US PWRs as of 2005 is shown in Figure 4. ETA is the mostly widely used (close to 50% of all plants). MPA and DMA are being used in 27% and 20% of US PWRs, respectively. Nearly 20% of the plants are adding a mixture of one or more amines. The remaining plants are indirectly controlling pH with two or more amines since ammonia is always present in PWR steam cycles either as a direct additive or from the breakdown of hydrazine. The amines are added at different concentrations to achieve the most desirable distribution of pH throughout the steam cycle while minimizing the loading on demineralizers. Computer codes such as AMINMOD and the PWR Secondary Chemistry Simulator have been indispensable in the effort to determine the optimum amine addition rates on a plant specific basis.

As discussed in the Introduction, the use of alternate amines is only part of an overall optimized secondary water chemistry strategy. In addition to minimizing impurity concentrations, PWR operators add hydrazine as an oxygen scavenger and to maintain low electrochemical potentials in the SG's. PWRs typically do not practice Oxygenated Water Treatment as is practiced in many fossil stations. The use of Inconel alloys for SG tubing prohibits this approach. The current EPRI Guideline indicates that hydrazine or a qualified alternative should be maintained at feedwater concentrations $>8x$ the condensate dissolved oxygen concentration. In the early 1990's, many plants operated with feedwater concentrations of >100 ppb hydrazine as shown in Figure 5. Today nearly 60% of plants operate at this level and almost all plants ($>90\%$) operate with feedwater hydrazine levels above 50 ppb. This is an important consideration with respect to pH control since hydrazine decomposes to ammonia under operating conditions. The actual ammonia concentrations generated from hydrazine decomposition varies from plant to plant depending on materials of construction in the plant as well as the use of condensate and blowdown demineralizers. The important point is that all US PWRs have developed an operating strategy that combines the use of elevated hydrazine with amines for pH control which both minimize iron transport to the SG's and insure that reducing conditions are maintained.

The effectiveness of a pH control program can be directly measured by the corrosion product transport levels in the plant. Current EPRI Guidelines recommend that US PWRs maintain FW iron levels at <5 ppb. The levels of FW iron in US PWRs have been reduced steadily since alternate amines were adopted in the 1990's. Today, most plants are easily able to achieve 1-3 ppb FW iron with many reporting levels below 0.5 ppb. As was shown in Figure 1, this can be attributed to direct reductions in corrosion product generation throughout the steam cycle, primarily in two phase regions of the plant.

Early on there were some concerns primarily from the turbine vendors associated with the increased levels of cation conductivity from organic acid production that are experienced with the use of organic amines. All amines thermally decompose under operating conditions to some extent. Typical decomposition products include acetate and formate with concentrations on the order of a few to 20 ppb. The actual levels observed in any plant cannot be predicted a priori so direct measurements are initially made when an amine is first used. Calculations can be performed to show that even with the observed levels of organic acids in the secondary system, the pH(t) is greater throughout the steam cycle (including local regions of the turbine) with the combination of organic amine plus organic acid compared to ammonia pH control alone. Of course, the observed reductions in FW iron concentration is also direct evidence of this

prediction. Based on these calculations and the fact that no apparent increase in turbine corrosion has occurred in US PWRs, the concern has been diminished.

ACKNOWLEDGMENTS

The authors would like to acknowledge and thank the US PWR utilities for contributing their experience and data for this paper.

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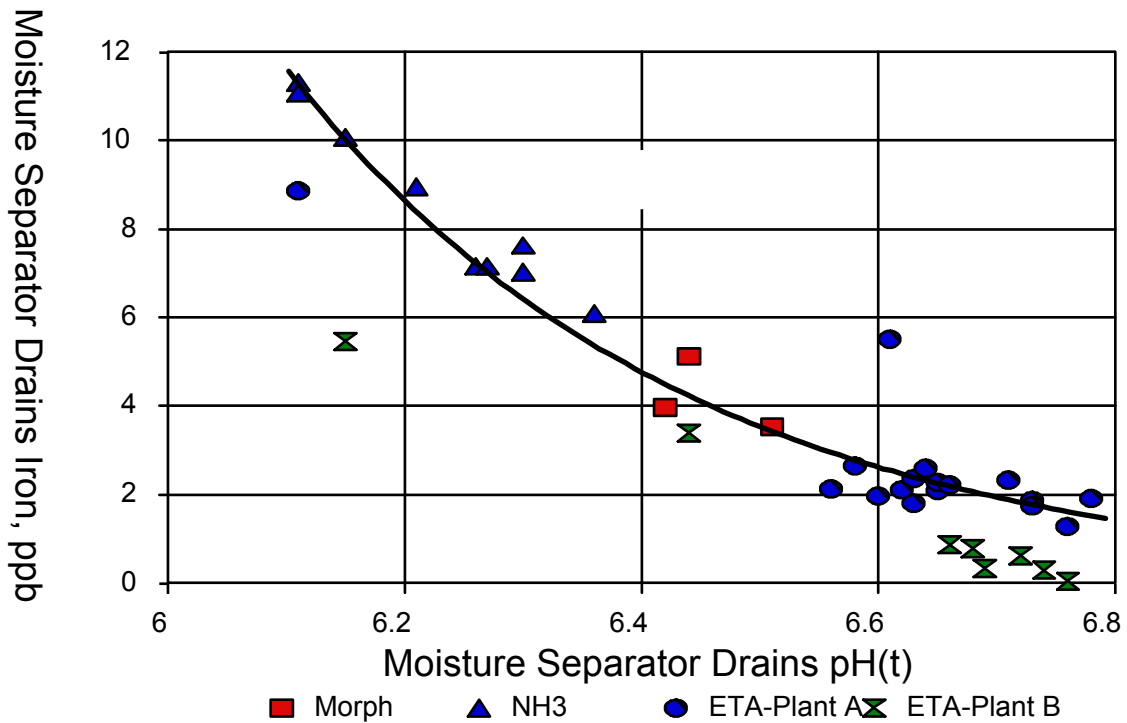


Figure 1: Moisture Separator Iron Transport as a function of pH at temperature.

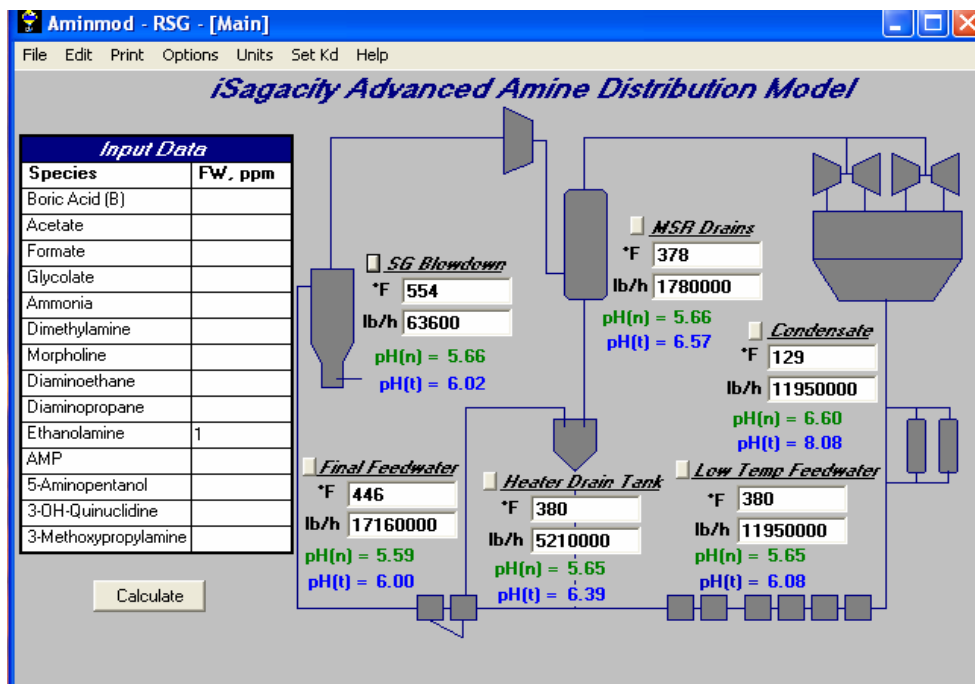


Figure 2: Steam Cycle pH with 1ppm FW ETA

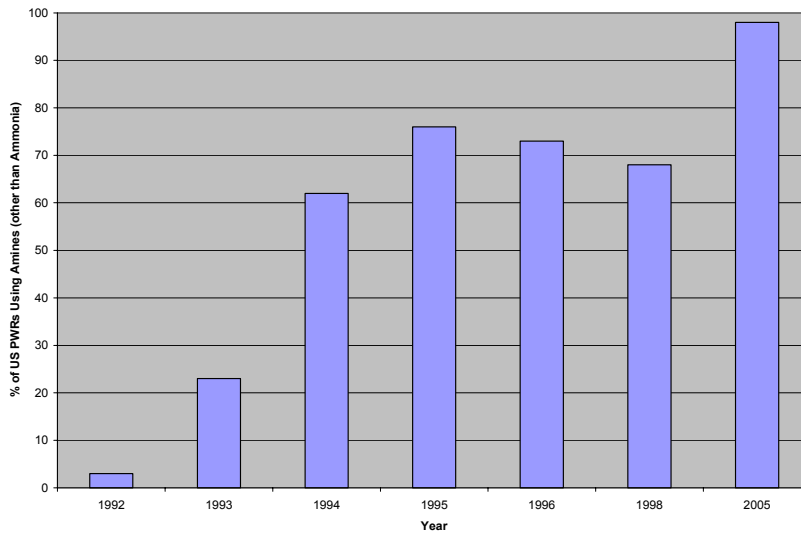


Figure 3: Use of Advanced Amines in US PWRs

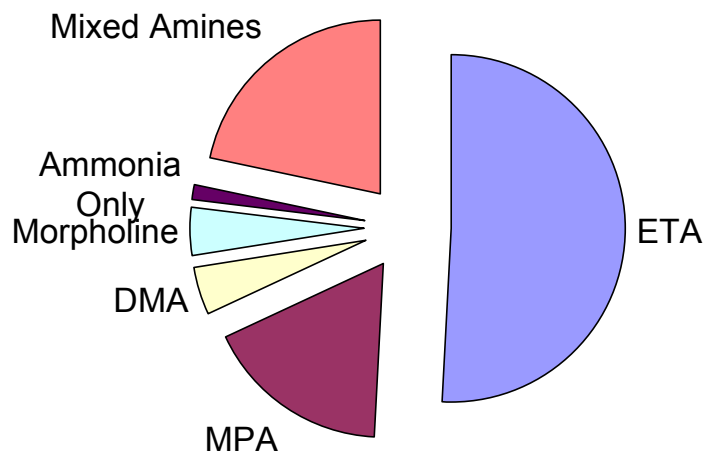


Figure 4: Distribution of Amines used in US PWRs (2005).

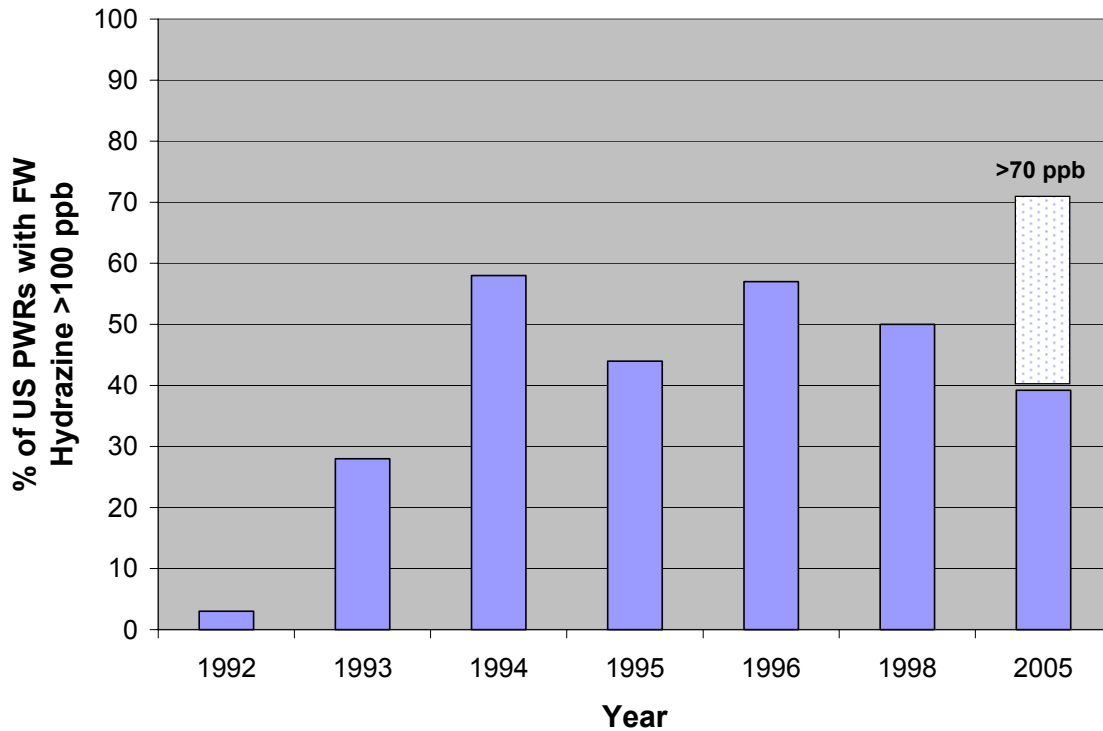


Figure 5: Use of Elevated Hydrazine in US PWRs

	<u>FW,ppm</u>	<u>BD,ppm</u>	<u>MSR, ppm</u>	<u>HDT, ppm</u>	<u>Polisher Loading, eq/hr</u>	<u>FW pH(t)</u>	<u>Condensate pH(t)</u>
ETA	1.5	3.5	5.5	2.86	78.9	6.1	8.2
DAE	0.5	1.29	2.27	1.10	41.7	6.0	7.7
AMP	3.0	3.89	5.88	3.98	155.5	6.3	8.5
MPA	2.5	2.11	3.10	2.71	146.2	6.3	8.5
3-HQ	0.9	4.68	4.77	2.21	12.9	5.9	7.5
Morph	15	12.11	15.96	15.34	922.0	6.4	8.6
Ammonia	15	4.33	2.18	10.82	5360.6	6.7	9.3

Notes: Calculations assume single amine only. FW-Feedwater, BD-blowdown, HDT-Pumped Forward Heater Drains, MSR-Moisture Separator Reheater. For all amines the MSR pH(t) is equal to 6.6

Table 1: Calculated Distribution of Advanced Amines in a Typical PWR Secondary System (using AminMod)