
Qualification of 5-Aminopentanol for PWRs

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REPORT SUMMARY

Secondary water chemistry control is essential for minimizing costs and maximizing plant availability. This report describes the qualification of a new amine, 5-aminopentanol (5-AP), which may provide some PWR owners with maximum corrosion protection for the least total cost. While this advanced amine is quite expensive, the expense is offset by decreased loading on the deep bed condensate polisher system.

Background

Alkalizing agents are added to the condensate and feedwater to increase pH throughout the secondary system. Because flow-accelerated corrosion and general corrosion are proportional to the hydrogen ion concentration, increased high-temperature pH decreases the production of corrosion products. Historically, ammonia was used for this purpose. Over the past several years, most utilities have adopted advanced organic amines which provide superior protection to all portions of the secondary system while decreasing the condensate polisher loading. The amine examined in this study has been used at Wylfa, an advanced gas cooled reactor in North Wales, for a number of years.

Objective

To qualify and demonstrate a superior amine, 5-AP, for corrosion protection of the secondary system and to expand the options available for optimizing plant secondary chemistry.

Approach

Investigators summarized and extended toxicological and materials compatibility information from Wylfa. Subsequent laboratory testing of 5-AP enabled them to measure its effect on ion exchange resins and plant materials and to determine toxicity. Ultimately, they demonstrated the amine in a full-scale test at Baltimore Gas and Electric Calvert Cliffs Unit 2.

Results

This report summarizes all aspects of the program to qualify the use of 5-AP for pH control in the secondary system of a PWR. Laboratory studies of 5-AP revealed that it possesses some ideal properties of a pH control agent. It exhibits high base strength at

both low and high temperatures and low relative volatility. The high base strength results in minimal dosage of the chemical to the system with maximum effect on high-temperature pH. Low volatility results in significant concentration of the amine in the first condensate from the steam and good protection to the extraction system piping. The low volatility also means that a significant fraction of the amine recirculates to the steam generator via the high-temperature drains. By recycling through the high-temperature drains, this portion of the amine does not pass through the condenser or the condensate polishing system. The reduced load on the polishers, compared to other amines, can significantly improve the economics of advanced amine chemistry. In fact, from a technical viewpoint, the balance of high base strength and low volatility make 5-AP the best choice of amines for plants with deep bed condensate polishing.

Toxicology studies reveal 5-AP to have very low toxicity to aquatic life, much less than either ammonia or hydrazine. Moreover, short-term materials compatibility testing showed that 5-AP does not attack coating, gasketing, and sealing materials.

The full-scale test of 5-AP at Baltimore Gas and Electric Calvert Cliffs Unit 2 successfully demonstrated that 5-AP at 0.8 ppm supplies the same corrosion protection as 2 ppm of ethanolamine, with a considerable decrease in loading of the condensate polishing system and thermal stability exceeding that of ETA. The current report also summarizes successful experience with 5-AP at Wylfa.

EPRI Perspective

EPRI has conducted numerous studies of advanced amines for secondary system pH control. These studies have included basic physical chemistry property measurements, boiler tests, resin selectivity tests, and thermal stability tests (EPRI reports TR-100755, TR-103098, TR-100794, Rev. 1, TR-100756, and TR-102952, Rev. 1). EPRI also took part in the initial demonstration of ethanolamine for use in secondary side treatment (TR-103042). The work reported here will allow utilities to continue to optimize their secondary water chemistry through expanding the allowable choices for amines to include 5-AP.

Interest Categories

Chemistry

Steam generators

Fossil steam plant O&M cost reduction

Key Words

pH control

Amines

Water chemistry

PWR

Oxygen scavenger

ABSTRACT

System corrosion and corrosion product ingress to the steam generators are of paramount importance for protecting the safety and reliability of pressurized water reactors. The work reported here describes the qualification of a new advanced amine for alkalizing the water and steam/water flow paths around the secondary portions of the plant. This amine, 5-aminopentanol (5-AP), offers superior protection throughout the steam and feedwater cycles at minimal dosage. Ion exchange testing, toxicology testing and materials compatibility testing were all performed prior to a full scale test at Calvert Cliffs Nuclear Power Station. This work is all presented here to assist utilities in qualifying 5-AP for use in their systems.

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SUMMARY

Amines are added to the secondary systems of pressurized water reactors (PWR) to increase the pH of the water throughout the system. Since corrosion rates, both bulk corrosion and flow assisted corrosion, are a strong function of hydrogen ion concentration, the increased pH results in improved protection to system materials. Most PWRs have adopted an advanced amine such as ethanolamine or methoxypropylamine due to the superior protection they afford the system, when compared to the traditional addition of ammonia. The work presented here describes the use of another amine, 5-aminopentanol (5-AP), and its properties when used for corrosion protection.

Laboratory studies of 5-AP revealed that it possessed some of the ideal properties of an alkalizing agent. It has high base strength, at both low and high temperatures, and low relative volatility. Its high base strength results in minimal dosage to the system with maximum effect on pH(T). Low volatility results in significant concentration of the amine in the first condensate from the steam and good protection to the extraction system piping. The low volatility also results in a significant fraction of the amine recirculating to the steam generator via the high temperature drains. By recycling through the high temperature drains, this portion of the amine does not pass through the condenser or the condensate polishing system. The reduced load on the polishers, compared to other amines, can significantly improve the economics of advanced amine chemistry.

Toxicological testing was performed using 5-AP to test its environmental effects on fresh water and salt water species. These tests showed that 5-AP is much less toxic to aquatic creatures than either ammonia or hydrazine. Testing was also performed to detect short term materials compatibility. No significant compatibility problems were detected.

A full scale test of 5-AP was performed at Calvert Cliffs Unit 2. The test was a complete success. It showed that 0.8 ppm of 5-AP in the final feedwater provides the same protection as 2 ppm of ETA, with a considerable decrease in the loading of the condensate polishing system. Thermal stability was verified to exceed that of ETA; no compatibility problems arose; no significant differences were observed in the ion exchange resins.

1

INTRODUCTION

A considerable amount of work has been done by the Electric Power Research Institute to develop and implement the use of advanced amines for corrosion protection of the secondary side of PWRs. To date, most utilities that operate PWRs have adopted one or more of these amines as an alkalizing agent(s), injected into the steam generator feedwater (SGFW). The replacement of ammonia, the traditional alkalizing agent, by these advanced amines has resulted in a several fold decrease in iron concentration, as measured in the final feedwater. In addition to the significant increase that this improved corrosion protection provides to personnel safety and balance-of-plant reliability, this reduced iron burden will greatly improve steam generator life and reliability.

1.1 Background

EPRI has conducted research into the use of alternate amines in secondary side treatment. Work has been conducted on the thermal stability¹, the ionization constants^{1,2}, the distribution coefficients^{1,2}, materials compatibility³, effects on condensate polisher resin performance⁴, and support has been supplied to follow in plant testing. Full scale tests of selected advanced amines are currently underway. Revision 3 of the PWR Secondary Water Chemistry Guidelines⁵ approves the use of these amines and a PWR Advanced Amine Application Guideline⁶ has been prepared. Work is also currently underway 1) at Davis Besse, demonstrating alternate amines in the once through steam generator system, 2) at Wylfa, a Magnox station in the United Kingdom, demonstrating 5-Aminopentanol as an advanced amine, and 3) at Millstone 2, demonstrating ETA at a deep bed polisher recirculating steam generator plant. As of this writing, most PWRs have implemented or are in the process of implementing ETA or other advanced amine chemistry.

1.2 Physical Chemistry of 5-AP

The primary purpose of amine addition is to increase the high temperature pH (pH(T)) throughout the system and, as such, decrease the corrosion rate of the system materials. Corrosion is a strong function of system pH(T), as demonstrated by numerous plant and loop studies. Figure 1-1 shows data taken at Catawba during the first use of ethanolamine⁷. The figure shows the decreasing level of iron (corrosion rate) that results from increasing pH(T). One pH(T) unit of increase corresponds to

approximately one order of magnitude decrease in iron. The iron measured during several phases of the test is plotted against the calculated high temperature pH in the moisture separator drains. The pH(T) was calculated from measured final feedwater ammonia, morpholine, and ethanolamine concentrations. These measured values were used to calculate the composition in the moisture separator drains and the resultant pH(T). Data are further characterized as morpholine chemistry, transitional chemistry (ammonia), and ethanolamine chemistry before refueling (ETA-1) and after restart (ETA-2). The iron concentration decreases with increasing pH(T) in the expected logarithmic manner. One pH unit increase corresponds to a factor of 10 decrease in iron. The line drawn through the data is a least squares exponential curve with slope equal to about -1.

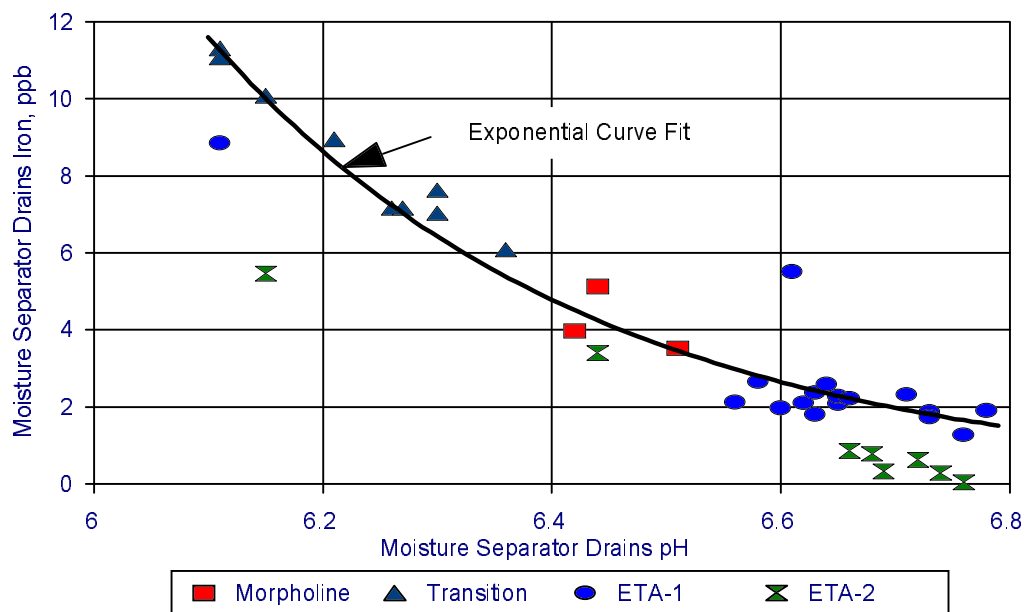


Figure 1-1 MSR Iron vs Calculated MSR pH(T)

The ability of an amine to provide corrosion protection throughout a system is a function of its base strength and its volatility. Base strength, as measured by the negative log of the ionization constant pK_b , is the property that describes the ability of a basic compound to ionize to form free hydroxide. This degree of ionization is a function only of the system pH(T) and the ionization constant. The volatility of the amine controls its concentration in the liquid phase as the steam condenses in the turbine, extraction, and feedwater heating system. Volatility is measured by the distribution coefficient, K_d , which relates the concentration of amine in the vapor phase with the concentration of un-ionized amine in the liquid. The ideal amine would have high base strength and low volatility. Additionally, it would exhibit high thermal

stability, be compatible with system materials, have low toxicity, and be commercially available at low cost. Table 1-1 lists the base strength and distribution coefficient of some common amines at room temperature and at 200 C (392 F).

Table 1-1
Base Strength and Volatility of Common Amines

Amine	pKb(77F)	pKb(392F)	Log Kd(77F)	Log Kd(392F)
NH3	4.748	5.548	1.48	0.84
Morpholine	5.501	5.561	-0.91	0.04
ETA	4.496	5.206	-2.36	-0.63
DMA	3.213	4.077	1.49	1.37
MPA	3.885	4.590	-0.44	0.28
5-AP	3.549	4.598	-3.27	-0.71

Figure 1-2 and Figure 1-3 also show the base strength and vapor/liquid distribution coefficients of these amines as a function of temperature.

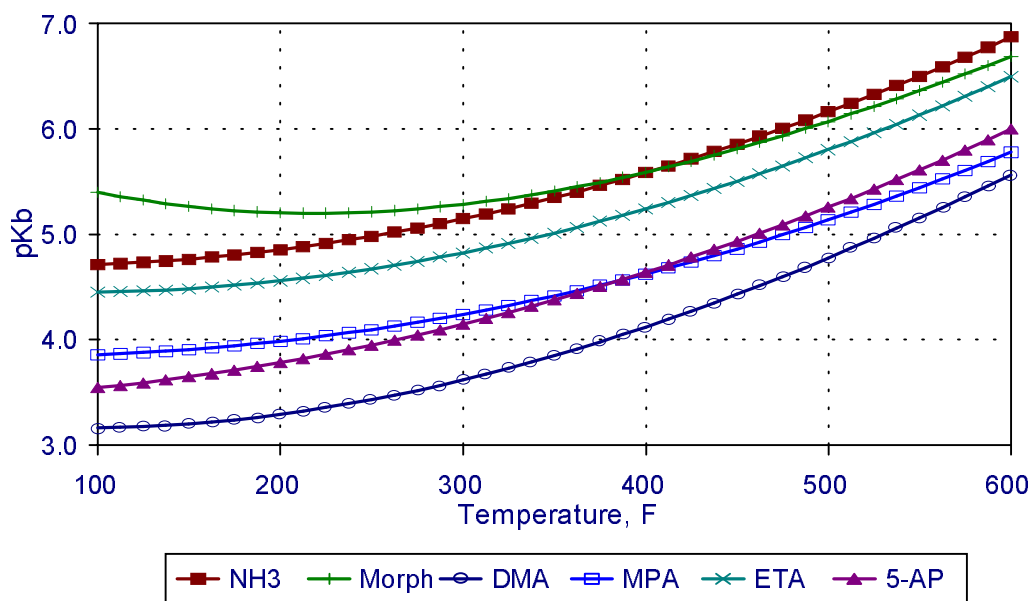


Figure 1-2 Base Strength of Selected Amines vs Temperature

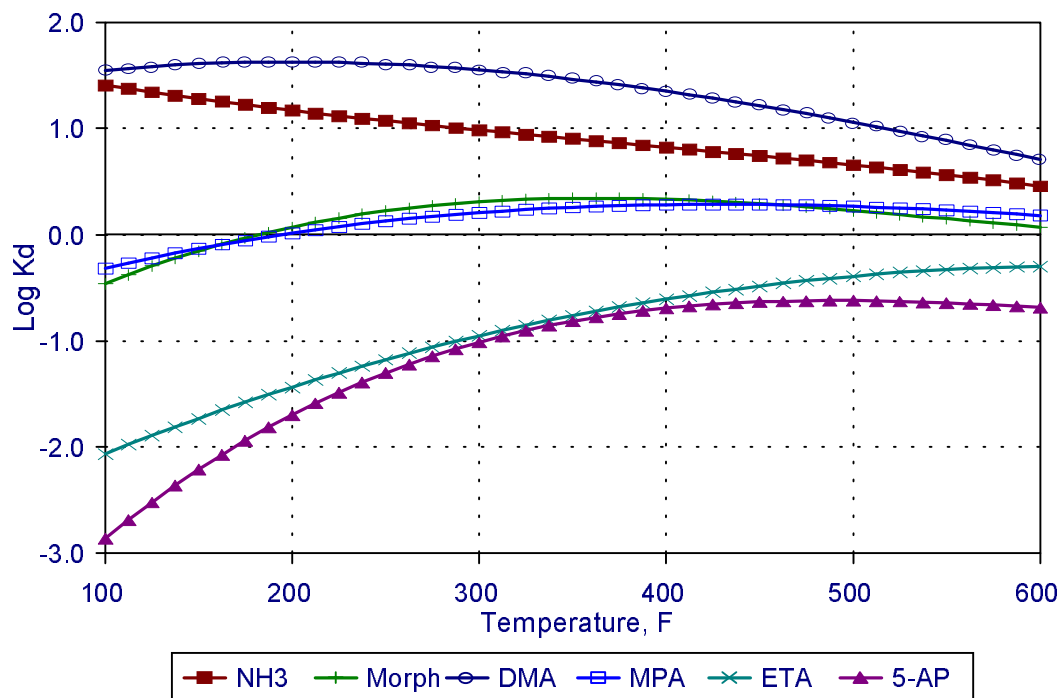


Figure 1-3 Volatility of Selected Amines vs Temperature

The degree that a given amine increases the pH(T) around the steam cycle is a function of both the base strength and the volatility. An amine with high base strength and high volatility may not be as effective as one with lower base strength, but lower volatility. Dimethylamine has very high base strength. It is the strongest amine shown in Figure 1.2-2. However, it has a volatility that is higher than even ammonia. As a result, high concentrations of DMA are required to force enough amine into the liquid phase to get adequate pH elevation and consequent low corrosion rates. 5-AP, on the other hand, has lower base strength than DMA by about 0.5 pKb units. However, 5-AP is about 100 times less volatile than DMA. This hundredfold concentration difference more than makes up for the lower base strength. Figure 1-4 shows the interplay between pKb and log Kd as they relate to the high temperature pH achieved in the moisture separator drains by 30 umolal concentrations in the main steam.

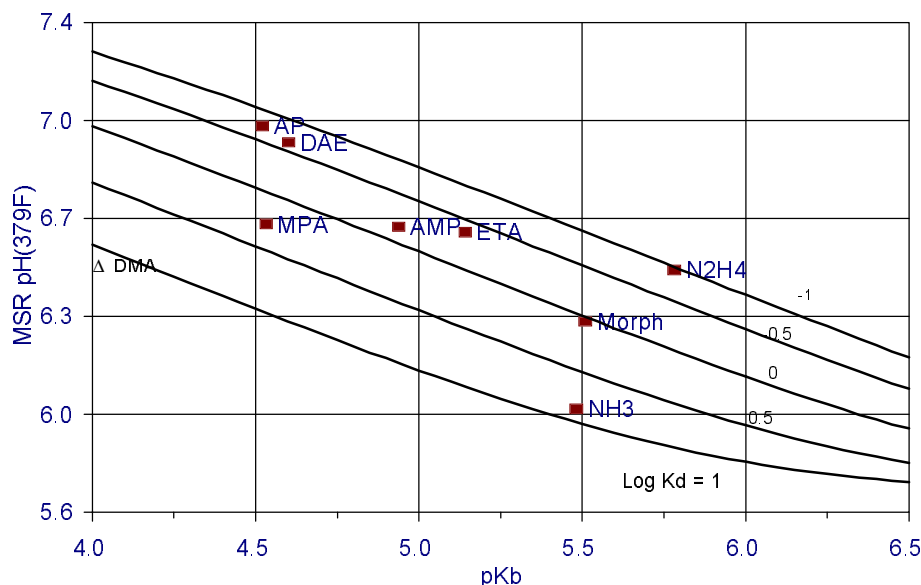


Figure 1-4 Moisture Separator Drains pH(T) vs Base Strength
(30 uMolal Amine in Steam)

Figure 1-5, Figure 1-6, Figure 1-7 and Figure 1-8 show the pH versus concentration curves for ammonia, morpholine, ETA and 5-AP. Ammonia, while showing relatively strong base strength at room temperature, fails to achieve high pH(T) in the MSR or steam generator. This is because its system temperature base strength is not very high and, more importantly, its high volatility limits the concentration in the liquid portions of the system. To attain a minimum pH of 6.6 in the MSR, 12 ppm ammonia is required in the final feedwater. This is acceptable operation for plants that do not use condensate polishers or contain materials incompatible with high ammonia levels. However, these values would lead to unacceptably short run times for condensate polishers. Additionally, the high concentrations of ammonia may have deleterious effects on some materials of construction.

Morpholine has similar base strength to ammonia, but is not as volatile. Morpholine does not concentrate in the vapor phase. It therefore offers better protection to the liquid and two phase portions of the system than ammonia. Still, concentrations for proper system protection preclude operation of condensate polishers, at least with operation of the cation resin in the hydrogen form.

ETA, Figure 1-7, exhibits slightly higher base strength than either ammonia or morpholine, but more importantly, significantly lower volatility. This low volatility not only provides additional protection to the liquid phase of the wet steam, but lowers the load on the polishers. A significant amine bypasses the polishers via the forward-

pumped high temperature drains. This forward-pumped drain water, while comprising only about one third of the total feedwater flow, contains about half of the total ETA mass flow. With ammonia, only about one fourth of the mass flow of amine bypasses the condensate polishers. For these reasons, ETA was rapidly adopted by the industry and currently is the most popular amine for advanced corrosion protection.

Dimethylamine offers the highest base strength of the amines shown in Figure 1-2, but exhibits volatility greater than that of ammonia (Figure 1-3). This very high volatility precludes its use as a primary alkalizing agent in plants with deep bed condensate polishers operating in the hydrogen cycle.

On the basis of its physical chemical properties, 5-AP offers superior protection to the secondary system with minimal loading of the condensate polishers and minimum material concentrations. Both its high base strength and its low volatility act to make it an even better choice than ETA. Less than 1 ppm in the feedwater will achieve the corrosion protection of 2 ppm of ETA, with only about one fourth the condensate polisher loading. Figure 1-8 shows the concentration versus pH behavior for 5-AP.

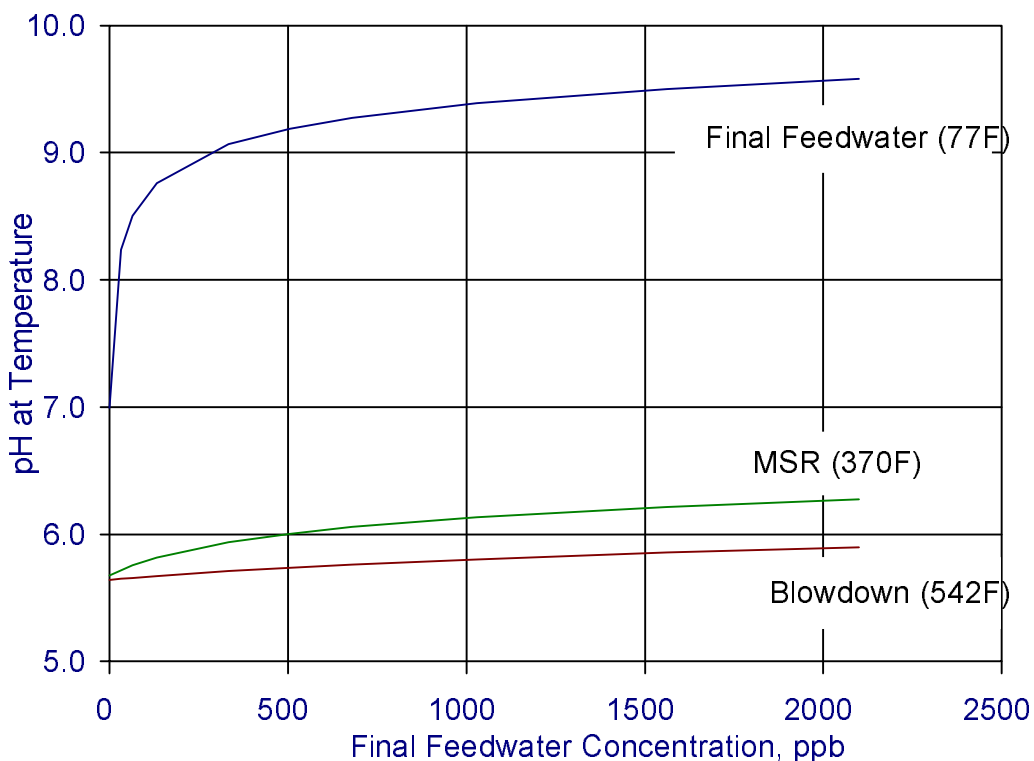


Figure 1-5 Ammonia in FFW versus pH

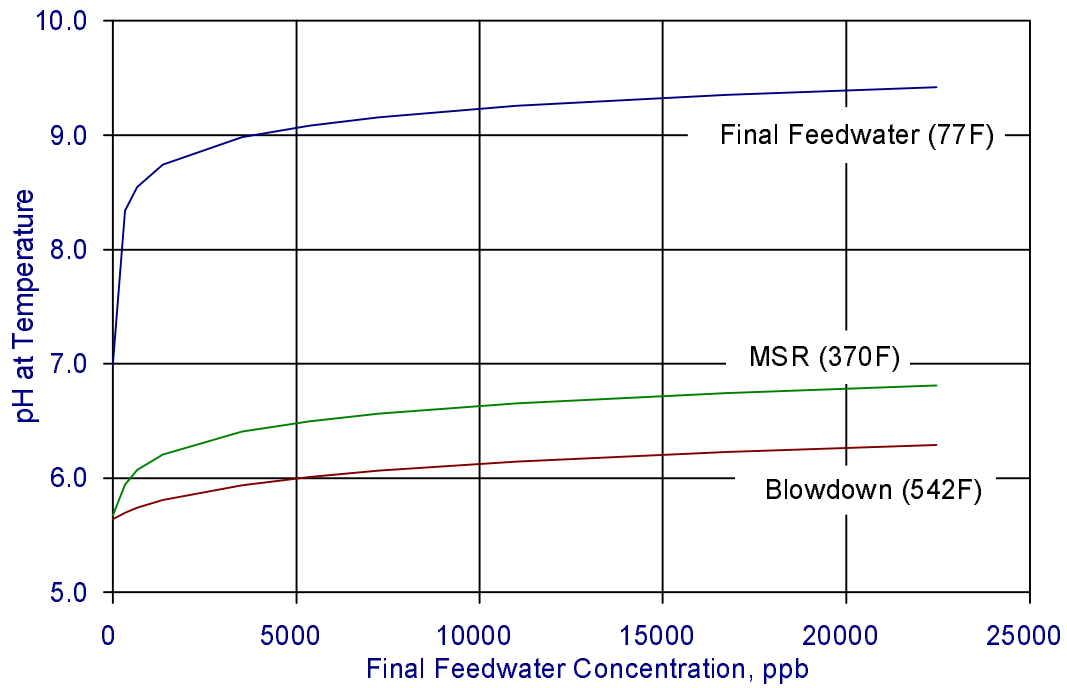


Figure 1-6 Morpholine in FFW versus pH

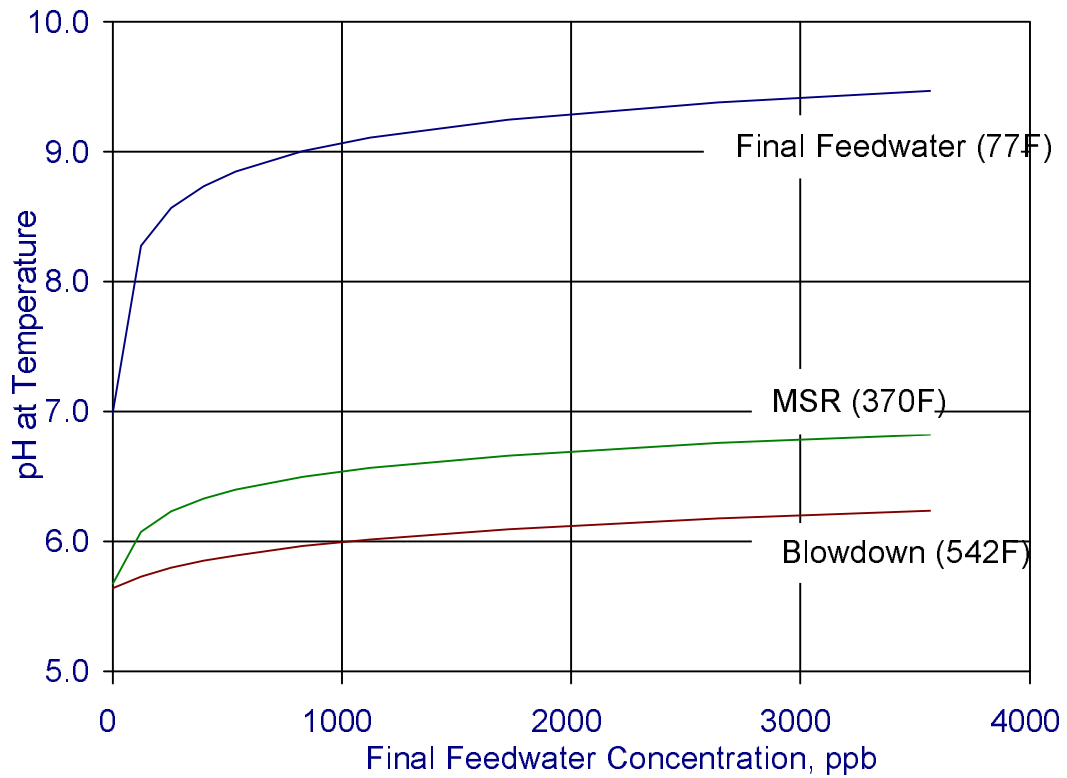


Figure 1-7 Ethanolamine in FFW versus pH

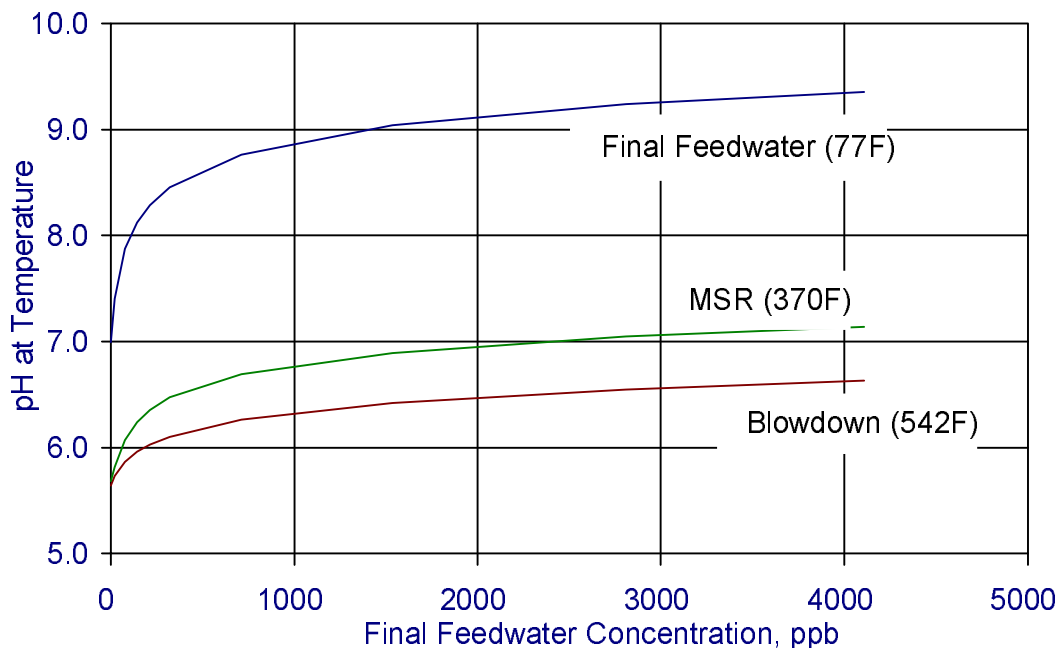


Figure 1-8 5-Aminopentanol in FFW versus pH

Figure 1-9 shows the room temperature specific conductance of 5-AP as a function of concentration for various concentrations of boric acid (as boron). Increased boric acid neutralizes the 5-AP at room temperature, decreasing the specific conductance. Figure 1-10 shows the effect on pH(77). Since boric acid is a very weak acid at high temperature, the effect on high temperature liquid properties is much less marked. The effect of 10 ppm boric acid (as boron) is to decrease the steam generator pH(T) by only about 0.02 pH units and the MSR pH(T) by only 0.04 pH units.

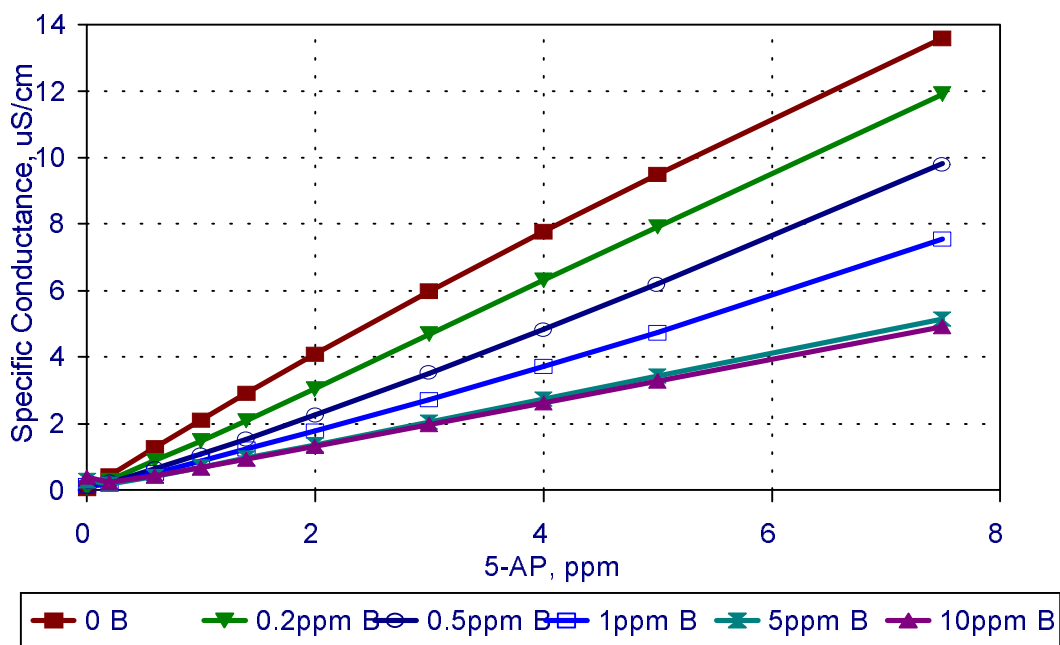


Figure 1-9 Room Temperature Specific Conductance versus 5-AP and Boric Acid (as Boron)

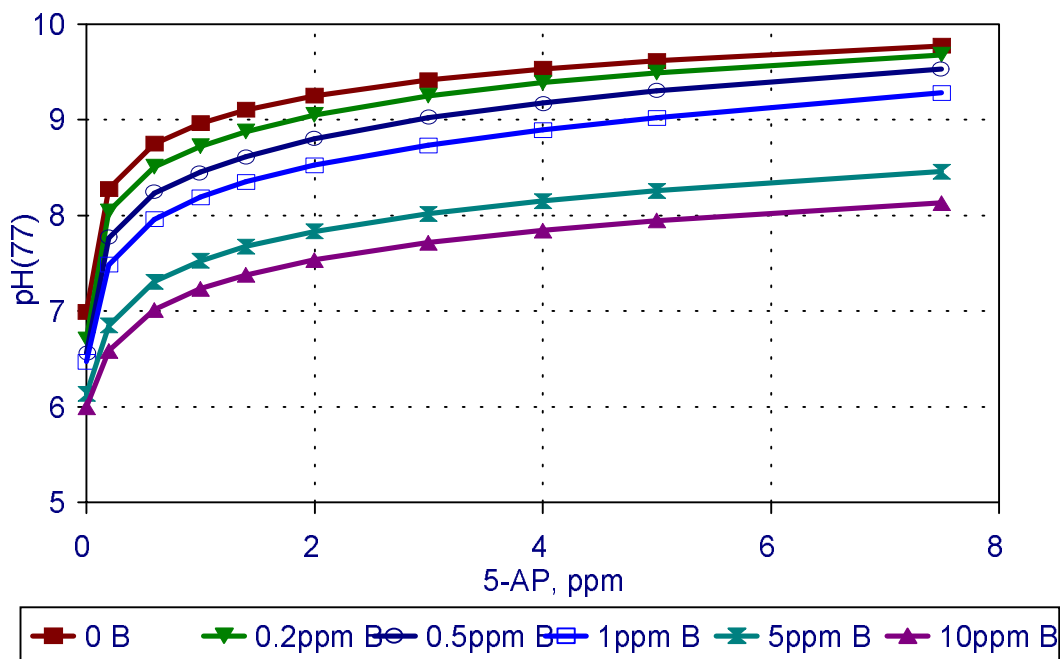


Figure 1-10 Room Temperature pH versus 5-AP and Boric Acid (as Boron)

1.3 Prior Plant Experience

Wylfa Power Station in North Wales has been using 5-AP since November 1992 with excellent results⁸. The site is a two unit Magnox type nuclear power station, located on Anglesey Island in North Wales. The site produces 480 MWe net from each natural uranium fueled unit. The graphite moderated reactors are cooled with carbon dioxide at 400 psia with an inlet temperature of 446 F. Each reactor has two pairs of once through steam generators that produce steam at 515 psia and superheated to 600 F. The serpentine steam generator tubes (mild steel) progress from 18 mm diameter in the economizer to 24 mm in the evaporator section to 30 mm in the superheater. Four identical turbines can be fed steam from either reactor. Each turbine consists of a high pressure turbine, moisture separator and three low pressure turbines. The condenser material is aluminum-brass. Condensate is polished in full flow deep bed demineralizers. Precoat filters are installed for use during startup.

The once-through boilers were suffering severe erosion-corrosion problems in the late 70s while on ammonia chemistry. The full flow condensate polishers and aluminum-brass condenser material limited the concentration of ammonia to values that led to unacceptable corrosion rates in the wet steam regions of the boilers. To decrease the corrosion rate of the boilers, a program was undertaken to find a less volatile, stronger amine that could be dosed at levels compatible with the condensate polishers, yet provide improved protection from erosion-corrosion to the mild steel boilers.

1.3.1 Operational Chemistry at Wylfa

Initial operation with 0.2 ppm NH₃ in the feedwater resulted in erosion-corrosion damage at the 18 mm to 24 mm transition region between the economizer and evaporator. The ammonia concentration was increased to 2 ppm in an unsuccessful attempt to decrease the corrosion. Resin regeneration considerations prevented operation above 2 ppm NH₃.

Amino-methyl-propanol (AMP) was used for pH control at Wylfa, starting in September, 1983. The concentration of AMP was increased from 5 to 10 ppm in March, 1984. This resulted in a condensate polisher loading that required regeneration every 2 days. While its high base strength and low relative volatility gave the expected improvement, its thermal stability led to unacceptably high cation conductance in the high temperature drains that returned to the boiler. This forced the recycle of these drains to the condenser for organic acid cleanup and increased the cation loading on the condensate polishing system.

Other amines were then investigated and tested to define a better amine. This led to the use of 5-Aminopentanol. A full scale test of 5-AP was undertaken at Wylfa in July, 1991. The success of this test led to routine use at both units.

Table 1-2
Chronology of Chemistry and Polisher Resin at Wylfa

Time	Chemistry	Polisher Resin
Startup	0.2 ppm NH ₃	Ambersep 200
	2 ppm NH ₃	
9-83	5 ppm AMP	Ambersep 252
3-84	10 ppm AMP	
86		Ambersep 200
87		Ambersep 252
7-91	3 ppm 5-AP Test	
6-92	3 ppm 5-AP	DOW 650/550

1.3.2 Use of 5-AP at Wylfa

CU Chemie Uetikon GmbH is the manufacturer of 5-AP that is distributed by Becpharm in the UK. 5-AP is made in a batch process that can be scaled up to larger scale production if the demand increases. It is made in a multi-step process from proprietary starting materials and purified in a distillation process. Its only other commercial use is in small amounts used in the manufacture of a Polaroid photographic film.

A solid at ambient temperatures, 5-AP is delivered to Wylfa in 16-18 ton lots by tanker as a 50% solution in demineralized water. Chemical purity (and the purity of dilution water) pose no operational problems at Wylfa. It is stored in two 48 ton tanks with water sealed vents to the atmosphere. Two 400 l tanks supply the 200 l/day system requirement.

The as-installed chemical injection pumps (positive displacement piston pumps from Permutit) are used without modification. Common materials of construction are used throughout. These include mild steel, neoprene gaskets, neoprene valve packing, and natural rubber condensate polisher lining. Two injection points are employed: one just downstream from the condensate polishers and the other at the suction of the feedpumps. The condensate train is thus maintained at about 0.7 ppm 5-AP and the feedwater at 3 ppm. This results in 13-14 ppm 5-AP in the moisture separator drains

(6% of feedwater flow). The low volatility of 5-AP results in relatively small concentration returned to the condenser yielding greater than 50 day run lengths for the condensate polishers. (No ammonia or ammonia producing hydrazine are used at Wylfa. Condensate polisher loading is from the amine only.) Condensate polishers are regenerated on a 42 day cycle for scheduling purposes.

1.3.3 Base Strength and Volatility of 5-AP

The base strength and volatility of 5-AP were measured by Nuclear Electric. Detailed data were supplied to EPRI through the Steam Generator Management Program (SGMP). Reported values were $pK_a=5.8$ at 300C and $K_d=0.174$ at 200C. These are in reasonable agreement with those of Cobble and Turner ($pK_a=5.51$ at 300C and $K_d=0.195$ at 200C). (The Cobble and Turner acid ionization was extrapolated from 25C data of Cobble & Turner and Smith & Martell using entropy estimates from similar amines. The Cobble and Turner distribution coefficient was based on their high temperature data.)

1.3.4 Thermal Stability of 5-AP

The measurement of thermal stability of 5-AP was inconclusive in the loop experiments performed by Nuclear Electric. However, the full scale test and operation at Wylfa show that 5-AP exhibits excellent thermal stability when compared to AMP. During operation with AMP, the moisture separator drains were routed back to the condenser about half of the time, because of high cation conductivity. The MS drains cation conductivity was typically about 3 uS/cm with a formic acid concentration of 300 ppb when using AMP. With operation under 5-AP, the MS drain cation conductivity is about 0.8 uS/cm and the formic acid concentration dropped to below 100 ppb. The MS drains are now normally pumped forward, while easily maintaining the feedwater specification of 0.25 uS/cm cation conductivity. Feedwater cation conductivity is routinely 0.1-0.12 uS/cm (corresponding to about 10 ppb organic acids) with operation at 3 ppm 5-AP (6 uS/cm specific conductance). The expected level of organic acids at PWRs is lower than this. Other impurities are 1-2 ppb Cl^- , 0.5 ppb Na^+ and 0.5 ppb SO_4^{2-} . Copper and iron concentrations in the feedwater remain low. Routine corrosion product analyses are not performed at Wylfa in the same manner as at most US PWRs.

1.3.5 Toxicity

Toxicity tests were performed by Nuclear Electric and are ongoing for 5-AP. A literature search revealed no prior information. One concern was that an interaction between 5-AP and chlorine may take place to produce chloramines. Laboratory tests with 5-AP and chlorine were conducted. No measurable chloramines were detectable by gas chromatography/mass spectroscopy.

Toxicity testing was performed on plaice (*Platichthys platessa*, a flounder-like fish) and brown shrimp. Results, summarized below, indicated that 5-AP was quite non-toxic.

Table 1.3-2
96 Hour Lethal Concentration Test Results

	96 hour LC50*	
Specie	5-AP	AMP
Brown Shrimp	144 mg/l	179 mg/l
Plaice	217 mg/l	184 mg/l

*Lethal concentration where only 50% of the species remains alive for 96 hours.

Since only 50 ton/yr of 5-AP would be discharged to the Irish Sea, compared to 300 ton/yr of AMP, toxicity was not deemed to be a problem. Furthermore, both AMP and 5-AP are considerably less toxic than ammonia. Toxicity tests to predict toxicity to humans is ongoing. Tests on rats indicate a very high tolerated dose of 1500 mg/kg, with no effect observed at 1000 mg/kg. Microtox tests using light emitting bacteria indicated no effect with 3 ppm 5-AP and 0.3 ppm Cl_2 in sea water. 5-AP does not appear to be toxic beyond its effects on alkalinity.

1.3.6 Resin Effects

Wylfa experienced resin cracking problems through their transition to advanced organic amines. To achieve higher resin capacity, the original resin at Wylfa was changed from Ambersep 200 (20% cross linked) to Ambersep 252 (12% cross linked) prior to switching from ammonia to AMP. After 3 years of operation with AMP, regenerating beds at about 2 day intervals, significant resin cracking was observed. The damage could not be reproduced using a simple osmotic shock and attrition test, which cycled the resin between amine and hydrogen forms with an attrition-backwash cycle. The resin was changed back to Ambersep 200 under the recommendation of the resin vendor that the 20% cross linked resin would be more resistant to the bead breakage. On the contrary, the 20% resin suffered significant damage within 3 months of operation, leading to high bed pressure drops and resin fines in the system. The resin was changed back to the 12% cross linked resin and a testing program was undertaken.

This experience initiated the development of a modified osmotic shock test, where the resin was cycled between hydrogen, amine, and sodium forms with molar

concentrations of reagents. The resin was tested with AMP, morpholine, and 5-AP (Table 1-3). A 2 ml sample of resin was dosed at 2 ml/min with 4-5 times its chemical capacity of reagent over a 7.5 minute period. The 45 minute total cycle was repeated 25 times. This test was able to simulate the resin damage. Significant damage occurred to the resin sample:

Table 1-3
Results of Modified Osmotic Shock Test

Amine	20% Cross Link	12% Cross Link
Morpholine	40% damage	5
AMP	70	8
5-AP	95	20

The high cross link resin was damaged even without the NaOH step in the cycle. When the change was made to 5-AP chemistry, all resins were changed to gel type resins (Dow 650/550). It was also noted that some batches of the gel type resin were damaged during manufacture and were rejected under their receipt inspection program.

2

RESULTS

An extensive tailored collaboration project was undertaken by EPRI, Baltimore Gas and Electric and Public Service Electric and Gas to evaluate 5-AP for its suitability for use as an alkalizing agent in US PWRs. Testing was performed on resin at bench scale and pilot scale, to evaluate the toxicity to aquatic species, and to measure effects on system materials of construction. The culmination of this testing was a full scale test employing 5-AP at Calvert Cliffs.

2.1 Bench Scale Resin Testing

Because of the work the Nuclear Electric had reported on resin cracking under advanced amine chemistry, a short set of cycling experiments were performed on various cation resins. Nuclear Electric had experienced severe cracking of ion exchange resin at Wylfa when using amino-methylpropanol (Section 1.3.6). To confirm this testing and extend it to other resins, a small bench scale testing program was undertaken.

In this evaluation, 1.5 ml of cation resin of various types was put into a plastic column and subjected to repeated cycling among chemical forms with 2 N reagent solutions. A four way valve and ion chromatograph gradient pump were used to cycle the cation resin to hydrogen form, sodium form, and amine form with reagent grade H_2SO_4 , NaOH, and amine. These solutions were pumped at 1.5 ml per minute through parallel resin columns. Demineralized water was used to rinse the columns prior to changing reagents. A schedule operated by a computer fed the columns the respective reagents and rinse water automatically. After a series of twenty five cycles, the resin columns were dis-assembled for inspection of the resin. Table 2-1 lists the resin types tested in this series of tests.

Results of the bench scale resin cracking tests were consistent with the tests performed by Nuclear Electric. Cation beads can easily be cracked by the stresses caused by rapidly changing their chemical form from amine to hydrogen to sodium to amine, etc. While the more complex amines such as 5-AP cause more severe cracking, beads can be significantly cracked by ammonia. Figure 2-1 shows a photo-micrograph of 8% crosslinked gel type strong acid cation resin after 25 cycles with 5-AP. A significant fraction of the bead have been cracked by this treatment. Figure 2-2 shows an increased magnification of a single bead.

Table 2-1
Resins Used for Bench Scale Cracking Tests

Resin	Type	Cross Linkage
Purolite C106	Weak Acid Macro	16 %
Amberlite 200C	Strong Acid Macro	20 %
Amberjet 1200C	Strong Acid Gel	8 %
Dowex HGRW2	Strong Acid Gel	10 %

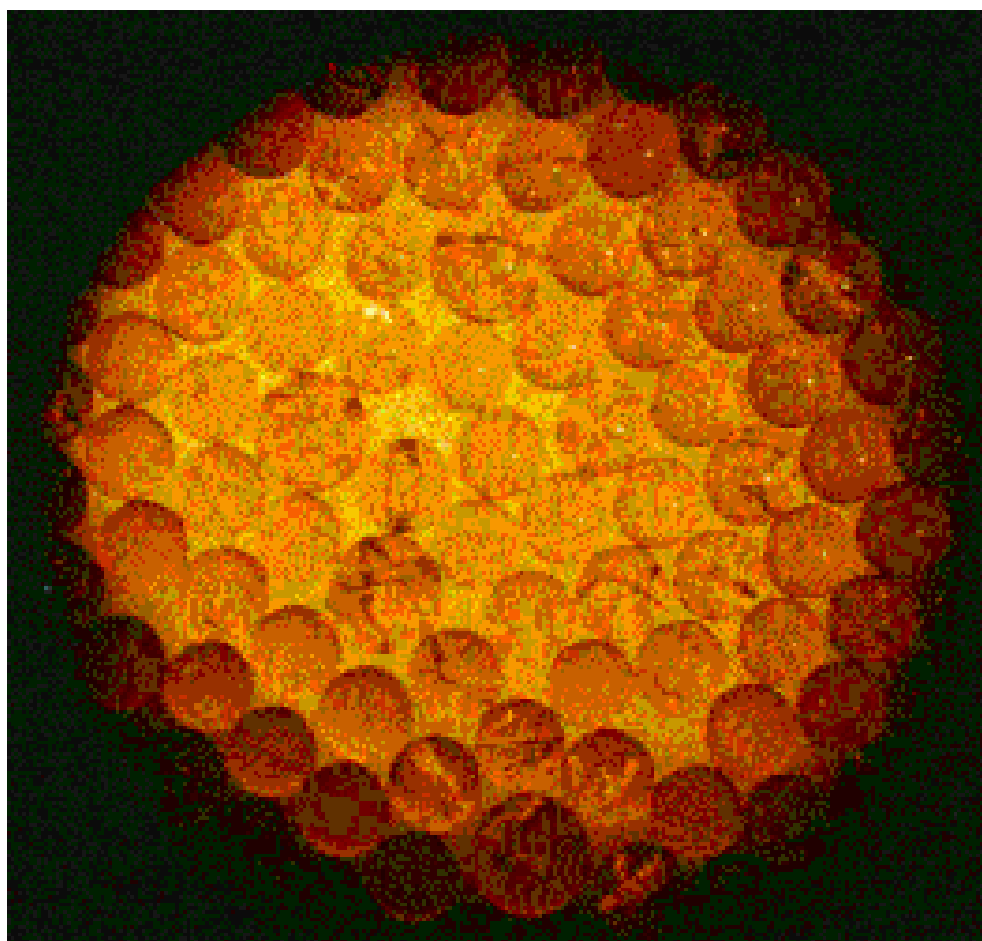


Figure 2-1 Gel Type Resin Cracked by Cycling with 5-AP



Figure 2-2 Gel Type Resin Bead Cracked by Cycling with 5-AP

Figure 2-3 and Figure 2-4 show the effects of cycling on macroporous resin. While effects are more difficult to see, since the beads are not transparent, broken and cracked beads are apparent. Figure 2-4 shows a magnification of some broken and cracked beads.



Figure 2-3 Macroporous Resin Cracked by Cycling with 5-AP

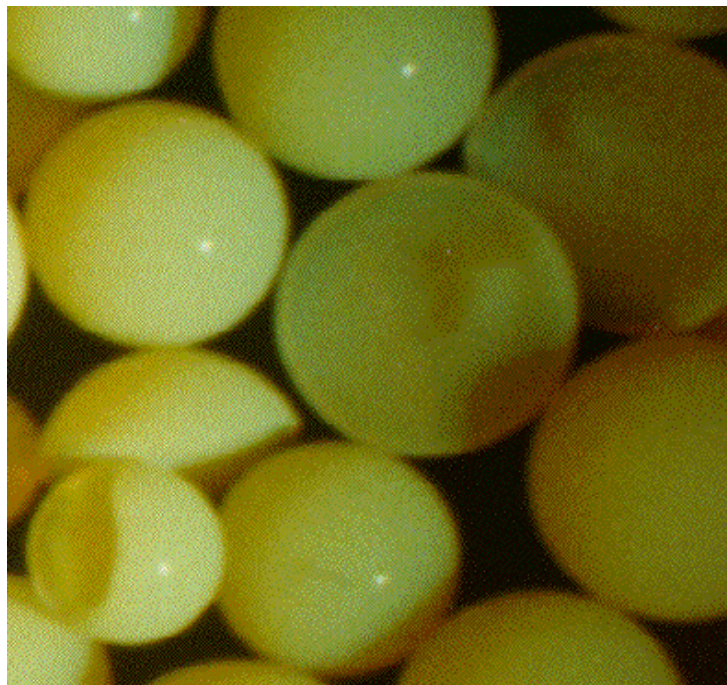


Figure 2-4 Macroporous Resin Beads Cracked by Cycling with 5-AP

While these tests confirm that 5-AP can cause severe cracking of cation resin, in particular the macroporous resins, careful operation of the regeneration system can limit this affect. The sodium portion of the cycling is necessary for the severe cracking. If care is exercised in the separation step of regeneration, only a small fraction of the resin exchange sites will be in the sodium form. This will limit the extent of cracking, when the resin subsequently converts to the amine form.

2.2 Pilot Scale Resin Performance

To test performance of condensate polishing resin with 5-AP, a test run was performed in the CenTec test loop. The test loop, shown in Figure 2-5, consists of a 600 liter feed tank, chemical addition system, main pump, five 4 inch diameter glass resin test columns, and large capacity cation and mixed bed ion exchangers for complete removal of any impurities and/or amines. The large capacity cation and mixed beds columns allow for a “once through” type test operation. A nitrogen cover is maintained on the feed tank to preclude carbon dioxide absorption and a refrigeration system removes pump heat.

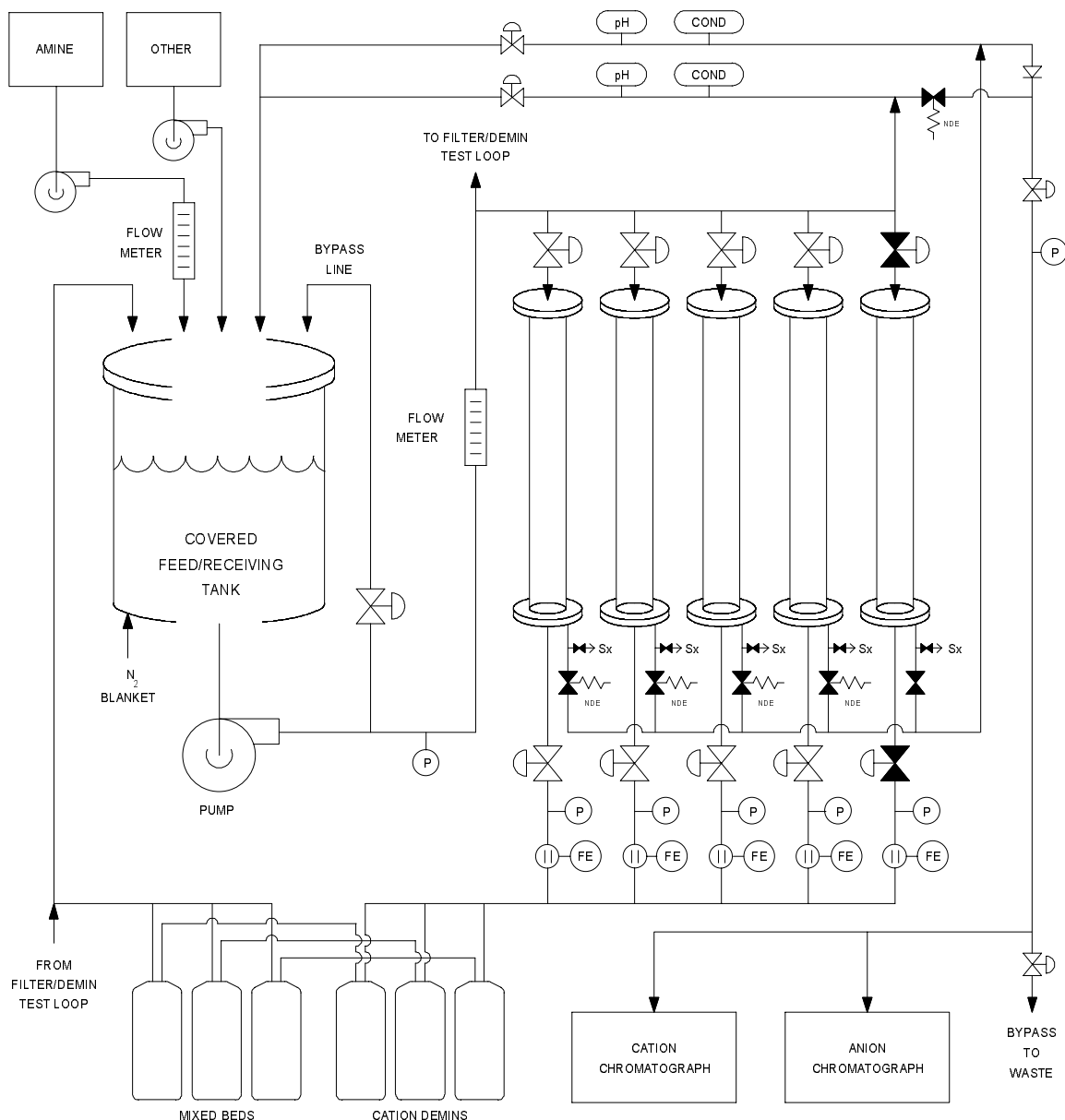


Figure 2-5 CENTEC Resin Pilot Loop

Water is fed to the resin test columns at 50 gallons per minute (gpm) per square foot of column cross sectional area. This matches the normal design flow in condensate polishing systems at power plants. After passing through the columns, the water passes through the 3 cubic foot cation exchange bed and mixed bed before returning to the feed tank. Amines or simulated impurities are metered into the feed tank to the desired chemical test conditions. For example, to test resin performance at 10 ppm

feed, 0.7 grams per minute of amine is added to the feed tank to feed four resin columns at 50 gallons per minute per square foot (4.65 gpm each) spacial velocity. (The exact feed rate of amine is controlled by measuring it via ion chromatography, not by measuring flow rates.) Initially, the test beds remove the added amine or impurities. After the test beds have been exhausted, the ionic material is removed by the large ion exchange beds so that only high purity water is returned to the feed tank. In this manner steady state is maintained in the feedwater chemistry, independent of the performance of the test resins.

The feed is continuously monitored for pH, specific conductance, and temperature. The inlet and four outlets of the resin columns are monitored sequentially for pH, specific conductance, and temperature. The sequence is controlled by a programmable controller and solenoid valves. The same solenoid valves sequentially direct the column common influent and each effluent to two on line ion chromatographs; one set up for anion analysis and the other set up for cation analysis. A bypass flow, extracted near the ion chromatograph sample pumps, assures sufficient flow through sample lines to prevent cross contamination between samples. The equipment is capable of analyzing to the sub-part-per-billion level of impurities at intervals of 10 to 50 minutes. The analysis interval is controlled by the ions of interest and the ion chromatography method required for this analysis. For an easily eluted ion such as ammonium ion, a short interval of 10 minutes between analyses can be maintained. For a more strongly retained ion such as diaminoethane cation, the analysis interval must be extended to 50 minutes.

Resins chosen for testing were regenerated according to procedures consistent with those in use at operating PWRs. In all experiments, two columns each of gel type and macroporous type resins were used. While procured in the regenerated (hydrogen-hydroxide) forms, the resins were regenerated and rinsed to verify their chemical form. To simulate actual regeneration practice, a measured amount of cation resin was added to the anion resin and a measured amount of anion resin was added to the cation resin before their respective regenerations. This resin cross contamination was set at 1.0% for all resins tested for the 5-AP test. Thus, cation resin corresponding 1.0% of the total volume of anion resin was in the sodium form, and similarly, anion resin corresponding to 1.0% of the volume of cation resin was in the sulfate form. Since a 2:1 cation to anion resin mix was chosen for this work, 0.5% of the cation resin was in the sodium form and 2% of the anion resin was in the sulfate form. Resins types for the 5-AP run are shown in the Table 2-2 below.

Table 2-2
Resins for Alternate 5-AP Test

Col.	Resin Type	Volume Ratio Cation:Anion	Cross- Contamination	%Cross Linkage
#1	Macroporous (Rohm & Haas IR 200/900C)	2:1	1.0%	20
#2	Premium Gel (Dow HGRW/550A)*	2:1	1.0%	12
#3	Weak Acid Cat (Rohm & Haas IRC86-550A)	2:1	1.0%	
#4	Gel (Rohm & Haas IRC 1200/4300)	2:1	1.0%	8

The four 4-inch diameter columns were loaded with 8.5 liters (0.3 cubic feet) of resin each. Thus, 5.66 liters of cation resin and 2.83 liters of anion resin were used in each column. For 1 % cross contamination, 57 cc of anion resin was added to the cation resin before regeneration, while 28 cc of cation resin was added to the anion resin. The bed depth was approximately 42 inches, typical of plant systems. A shorter bed was used for column 3 to allow expansion of the weak acid cation resin.

2.2.1 LABORATORY TEST RESULTS

The 5-AP experiment was the eighth experimental run in the alternate amine series. Table 2-3 summarizes the experimental runs that were performed. The concentration of amine chosen for these runs was above the concentrations that would normally be used in practice. This was so that the resins could be depleted within a reasonable short time and run beyond exhaustion to collect selectivity data. These experiments are discussed in detail in the following sections:

Table 2-3
List of Experimental Runs

Chemistry	Concentration	pH(25C)
Ammonia	2 ppm	9.6
Morpholine	60	9.6
Morpholine	10	9.2
2-Amino-2-methylpropanol	12	9.8
Ethanolamine	10	9.8
1,2-Diaminoethane	8	9.9
3-Methoxypropylamine	10	9.9
5-Aminopentanol	10	9.9

2.2.2 Resin Selectivity

Ion exchange performance is governed by several factors: equilibrium relationships, kinetics, and flow phenomena. When resin kinetics are reasonably fast and flow distribution is uniform, the effluent quality is determined by equilibrium processes. Effluent sodium concentration will be proportional to the fraction of resin that is in the

sodium form, the amine ionic concentration and the resin selectivity. Resin selectivity is defined in these terms in Eq 1, below:

$$K[\text{Na}, \text{Amine}] = \frac{[\text{Na}(\text{Resin})][\text{Amine}+(\text{Liquid})]}{[\text{Amine}(\text{Resin})][\text{Na}+(\text{Liquid})]} \quad (\text{Eq. 1})$$

Where: [Na(Resin)] is the fraction of resin in the sodium form.

[Amine(Resin)] is the fraction of resin in the amine form.

[Amine+(Liquid)] is the concentration of amine ion in the liquid.

[Na+(Liquid)] is the concentration of sodium ion in the liquid.

The degree of ionization for the amines used in the experiments performed are listed in

Table 2-4. From these data and the results of the experimental runs listed in Table 2-5, the resin selectivity coefficients can be calculated. These results are shown in Table 2-6. Selectivity for sodium over the 5-AP was the lowest of any amine tested. However, since only a small amount of amine will be used, sodium throw at the time of amine breakthrough should be lower than for ETA. Estimated sodium levels at amine breakthrough for comparable levels of amines are shown in

Table 2-7. Values are calculated for a pH(T) elevation of 1 pH unit in the MSR from each amine. The effluent concentrations are calculated at 100 F. As shown, 5-AP breakthrough results in the lowest sodium concentration in the condensate polisher effluent.

Table 2-4
Ionization of Amines for Experimental Runs

Chemistry	Conc.	pH(77)	% Ionized
Ammonia	2 ppm	9.55	33
Morpholine	10 ppm	9.23	15.2
Morpholine	60 ppm	9.65	6.5

2-Amino-Methyl-1Propanol	12 ppm	9.78	45
Ethanolamine	10 ppm	9.75	35
1,2 Diaminoethane	8 ppm	9.85	54
3-Methoxypropylamine	10 ppm	9.85	64
5-Aminopentanol	11 ppm	9.87	78

Table 2-5
Condensate Demineralizer Sodium Sloughage During Alternate Amine Tests

Chemistry (pH)	Gel Resins		Macroporous Resins	
	#1 (0.2%)	#2 (1%)	#3 (0.2%)	#4 (1%)
2 ppm Ammonia (9.6)	1.6 ppb	7.0 ppb	2.2 ppb	7.4 ppb
60 ppm Morpholine (9.6)	0.8 ppb	3.4 ppb	0.15 ppb	0.20 ppb
10 ppm Morpholine (9.2)	0.6 ppb	1.5 ppb	0.15 ppb	0.25 ppb
12 ppm AMP (9.8)	1.1 ppb	6.0 ppb	0.08 ppb	0.14 ppb
10 ppm ETA (9.78)	1.4 ppb	6.7 ppb	0.5 ppb	1.9 ppb
8 ppm DAE (9.85)	>10 ppb	>10 ppb	>10 ppb	>10 ppb
10 ppm MPA (9.85)	1 ppb	4 ppb	0.05 ppb	0.15 ppb
11 ppm 5-AP (9.87)		12/22.5* ppb		

*10 / 8 % cross linked resin

Table 2-6
Sodium/ Amine Selectivity Coefficients

	Gel (10% xl)		Macroporous	
Experiment	0.2%	1%	0.2%	1%
2 ppm NH ₄	0.5	0.6	0.4	0.6
10 ppm Morpholine	0.7	1.4	2.7	8.3
60 ppm Morpholine	1.3	1.2	7	27
12 ppm AMP	1.3	1.2	18	52
10 ppm ETA	1.0	1.0	2.7	3.6
8 ppm DAE	NA	NA	NA	NA
10 ppm MPA	1.7	2.1	34	57
10 ppm 5-AP		0.8/0.4*		

*10 / 8% crosslinked resin

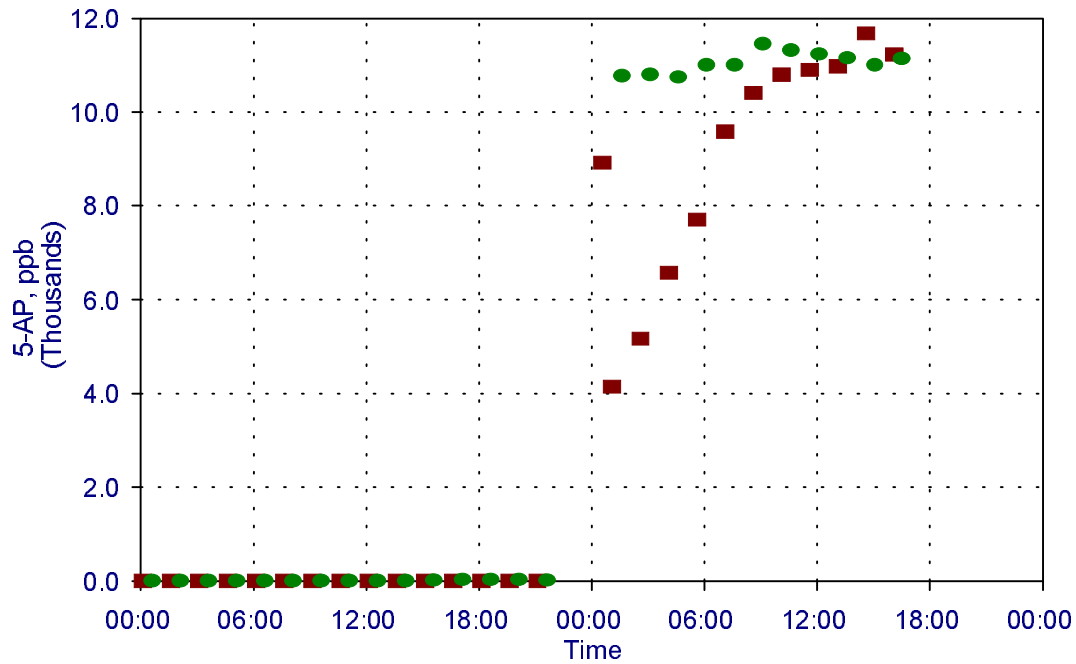


Figure 2-6 Breakthrough Curves for 5-AP during 5-AP Run

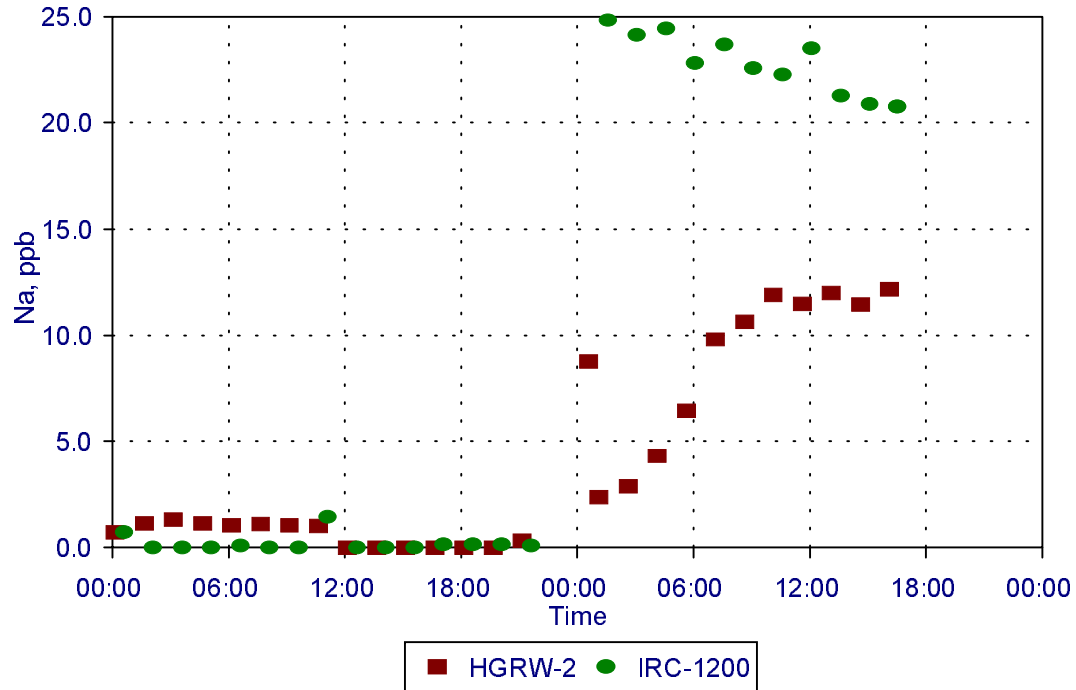


Figure 2-7 Breakthrough Curves for Sodium during 5-AP Run

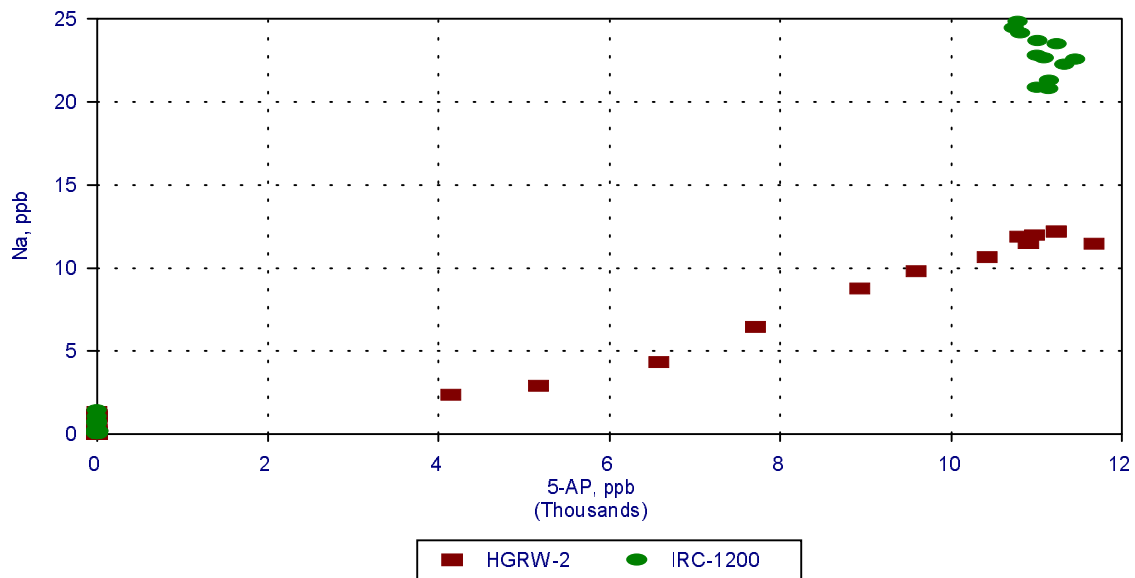


Figure 2-8 Sodium Leakage vs 5-AP

Table 2-7
Sodium Throw from Equivalent Amine Concentrations

Amine	FFW Conc. ppm*	CPD Conc., ppm	Na, ppb
NH3	12.0	13.2	22
MPA	5.5	5.6	2.6
Morpholine	11.5	11.3	1.8
ETA	1.1	0.7	1.1
5-AP	0.7	0.3	0.4

Basis: 0.5 % of cation resin in Na form.

Amine concentrations to give +1 pH(T) elevation.

Ionization fraction calculated at 100 F.

2.3 Toxicology Testing

As part of the tailored collaboration project, toxicological testing was performed to determine the toxicity of 5-AP to freshwater and saltwater species typically used for NPDES biomonitoring. EA Engineering, Science and Technology, Inc. was contracted to perform acute and chronic toxicity tests using fathead minnows (*Pimephales promelas*) and water fleas (*Ceriodaphnia dubia*) for freshwater testing and opossum shrimp (*Mysidopsis bahia*) and sheepshead minnows (*Cyprinodon variegatus*) for saltwater testing in conformance with accepted practices. Additional details on this work is available in Appendix A.

Organisms in the water flea definitive acute test were exposed for 48 hours to a graded concentration series of 8.7, 32, 75, 180 and 420 ppm and a laboratory control. In the sheepshead minnow test, the organisms were exposed for 96 hours to a graded concentration series of 155, 370, 870, 2100, 4900 ppm and a laboratory control. The fathead minnow and opossum shrimp acute organisms were both exposed to a graded concentration series of 32, 75, 180, 420, 1000 ppm and a laboratory control for 96 hours. The objective of the acute tests was to determine the median lethal concentration (LC50) of 5-AP. The definitive chronic tests were short-term daily renewal toxicity tests. In the water flea chronic test, the organisms were exposed to a concentration series of 8.7, 32,, 75, 180, and 420 ppm and a laboratory control until three broods of young were reproduced (6 days). The fathead minnow and opossum shrimp chronic toxicity tests consisted of a concentration series of 32, 75, 180, 420, and 1000 ppm and a laboratory control and an exposure duration of 7 days. In the sheepshead minnow test chronic toxicity test, the organisms were exposed for 7 days to a concentration series of 65, 155, 370,870, 2100, 4900 ppm and a laboratory control. The objectives of the chronic tests were to assess the chronic lethality of the product to the test organisms and to determine the inhibition of reproduction potential (water flea), growth (fathead minnow, sheepshead minnow, and opossum shrimp), and the fecundity (opossum shrimp) of the test organisms as compared to the controls.

2.3.1 Test Organisms

Ceriodaphnia dubia were cultured in EA's laboratory using dilute mineral water as described below. The cultures were kept in an environmentally controlled room at 25 ±2 C with a 16-hour light/8-hour dark photoperiod. Organisms were fed daily as described in Weber et al. (1989) and thinned as necessary to maintain healthy, productive cultures. Adults were separated from the bulk cultures at least one week prior to test initiation, placed in individual 30-ml plastic cups (15-ml volume) in brood boards, and fed heavily. Gravid adults were re-isolated and fed the evening before the test. The neonates (young) were < 24 hours old at test initiation in the acute test. The neonates used for the chronic toxicity test were < 26 hours old at initiation. All neonates used in the chronic test were released within the same 4-hour time period

from broods of eight or more, and were randomly assigned to the treatment chambers using a transfer pipette.

Pimephales promelas were obtained from embryos spawned in EA's Aquatic Culture Facility. Lot FH5-4/17-18, used in the chronic test, were hatched on 17-18 April 1995 and maintained at $25 \pm 1^\circ\text{C}$ in dechlorinated water. The fathead larvae were < 24 hours old when used to initiate the chronic test on 18 April 1995. Lot FH5-4/9-10, hatched on 9-10 April 1995, were 8-9 days old (hatched within a 24-hour window) when used to initiate the acute test on 18 April 1995. The larvae were hatched in dechlorinated tap water. The larvae were maintained at $20 \pm 1^\circ\text{C}$ and were fed brine shrimp nauplii (*Artemia sp.*, < 24 hours old) a minimum of once daily during this rearing period. At initiation of the acute and chronic definitive tests the fathead larvae were slowly siphoned into I-L culture bowls from which the larvae were randomly assigned to the treatment chambers, using a transfer pipette.

Mysidopsis bahia (opossum shrimp) were acquired from Chesapeake Cultures (Hayes, Virginia). The organisms represented by the EA designation Lot #Mb-315, were two days old when received at EA on 18 April 1995. The shrimp were 4 days old when used to initiate the acute test. *M. bahia* Lot #Mb-318 was used in the chronic toxicity test. The organisms were 6 days old when received at EA on 3 May, and were 7 days old when used to initiate the chronic toxicity test. The temperature and salinity of the shipping water upon receipt at EA, for Mb-315 were 19.5°C and 21.5 ppt, and for Mb-318, 21.4°C and 20.3 ppt, respectively. The shrimp were maintained at the testing temperature of $20 \pm 1^\circ\text{C}$ (acute) and $26 \pm 1^\circ\text{C}$ (chronic), 20 ± 2 ppt salinity, and were fed brine shrimp nauplii (*Artemia sp.*, < 24 hours old) twice daily during the holding period. At initiation of both the acute and chronic tests, the shrimp were slowly siphoned into I-L culture bowls and randomly placed into treatment vessels using a transfer pipette.

Cyprinodon variegatus (sheepshead minnow) were acquired from Aquatic Biosystems (Colorado). Lot CV-202 was received on 18 April 1995. The temperature and salinity of the shipping water upon receipt at EA was 19.5 and 20.5 ppt, respectively. The larvae were 12 days old when used to initiate the acute toxicity test on 20 April 1995. Lot CV-203 was received at EA on 20 April 1995. The temperature and salinity of the receiving water were 21.3°C and 22.0 ppt, respectively. The larvae at test initiation were less than 24 hours old. During the acclimation period, *C. variegatus* were maintained at testing temperatures of $20 \pm 1^\circ\text{C}$ (acute) and $25 \pm 1^\circ\text{C}$ (chronic) and 20 ± 2 ppt salinity and were fed < 24 hour old brine shrimp (*Artemia sp.*) nauplii twice daily.

2.3.3 Toxicity Test Operations And Performance

Toxicity tests were performed in accordance with EA's protocols (EA 1992) which are included in Reference 1. Prior to preparation of test solutions, 1 g/L (1000 ppm) stocks were made by diluting one gram of product into one liter of dechlorinated water. This

stock was used for preparing solutions for *C. dubia*, *P. promelas*, and *M. bahia* acute and chronic toxicity tests. A 5 g/L (5000 ppm) stock was made by diluting 5 grams of product into one liter of dechlorinated water and used to prepare solutions for the *C. variegatus* acute and chronic toxicity tests. Test concentrations were prepared using Class A glassware. Small volumes of stock were first measured in pipettes and graduated cylinders, then added to a volumetric flask and brought to final volume with dilution water. For the freshwater toxicity tests, the pH of the dilutions was adjusted to 7.5 ± 0.2 as they were outside (e.g., 10.7) the acceptable range of 6-9, prior to transferring of organisms into testing vessels. The dilutions of the saltwater tests were pH adjusted to 8.3 ± 0.2 after the addition of the appropriate amount of synthetic sea salts and prior to transferring organisms into testing vessels. The test solutions were mixed, then split equally into the replicate tests chambers.

The short-term chronic toxicity testing endpoints reported are expressed as the No Observed Effect Concentration (NOEC), the Lowest Observed Effect Concentration (LOEC), and the Chronic Value (ChV). The definitions of these chronic endpoints follow Weber et al. (1988) and are as follows:

The NOEC is the highest concentration of toxicant to which organisms are exposed in a full life-cycle or partial life-cycle test, which cause no statistically significant adverse effect on the observed parameter (usually hatchability, survival, growth, and reproduction), as compared to the controls.

The LOEC is the lowest concentration of toxicant to which organisms are exposed in a life-cycle or partial life-cycle test, which causes a statistically significant adverse effect on the observed parameters (usually hatchability, survival, growth, and reproduction), as compared to the controls.

The ChV is a value lying between the NOEC and the LOEC, derived by calculating the geometric mean of the NOEC and LOEC. The term ChV is sometimes used interchangeably with Maximum Acceptable Toxicant Concentration (MATC).

2.3.4 Results And Discussion

All acute and chronic toxicity tests were conducted on the 5-aminopentanol (5-AP) sample received by EA on 28 March 1995 from CenTec-21, Inc. Water quality parameters (temperature, pH, dissolved oxygen, conductivity, and salinity) measured during the duration of the acute and chronic tests were within acceptable ranges, with minor exceptions. The minor exceptions did not affect the acute and chronic toxicity test results.

Results

The 48-hour *Ceriodaphnia dubia* static acute test exhibited 100 percent survival in the laboratory control at test termination. There was greater than 95 percent survival in concentrations 8.7 ppm through 75 ppm. There were no surviving organisms in the 180 and 420 ppm concentrations at 48 hours. The LC50 value calculated from the survival data at 48-hours was 116.2 ppm product.

The short-term chronic *C. dubia* test was terminated on Day 6, per EPA guidelines, at which time 100 percent of the laboratory control females had produced three broods of neonates (young). Both the 180 and 420 ppm concentrations significantly affected ($P=0.05$) survival and the 75 ppm concentration significantly affected ($P=0.05$) reproduction. By Day 6, there was 100 percent survival in the laboratory control through the 75 ppm concentration. Mean young production ranged from 12.2 to 27.4 young per female in the treatment concentrations compared to 24.7 young per control female. The NOEC was 32 ppm product. The LOEC and ChV were 75 and 49 ppm product, respectively. The IC25 value was calculated to be 48.4 ppm product.

The *Pimephales promelas* acute toxicity test was terminated after 96 hours of exposure to 5-AP with 100 percent control survival. The 32, 75, 180, and 420 ppm concentrations also exhibited 100 percent survival, but the 1000 ppm had 20 percent survival. The LC50 value calculated from the survival data was 763.6 ppm product.

Statistical analysis of the survival data from the *P. promelas* short-term toxicity test showed a significant difference ($P=0.05$) from the control in the 1000 ppm concentration. The 1,000 ppm concentration at test termination had 40 percent survival compared to 85 percent control survival. There was no statistical difference ($P=0.05$) based on the growth data found between the control and the evaluated sample concentrations. (Those concentrations which have significant mortality are not statistically analyzed for growth, per EPA guidelines). Mean dry weight of the larvae exposed to the effluent treatments ranged from 0.90 to 1.04 mg/fry. The control organisms had a mean dry weight of 0.98 mg/fry. The NOEC was 420 ppm product. The LOEC and ChV were 1,000 and 648.1 ppm, respectively. The IC25 value was 562.3 ppm product.

After 96 hours of exposure to the product 5-AP, the *Cyprinodon variegatus* acute toxicity test exhibited 100 percent survival in the laboratory control. At test termination, the 4,900 ppm concentration had 35 percent survival. The LC50 value was calculated as 4,218.3 ppm product.

After 7 days of exposure the highest concentration evaluated in the *C. variegatus* chronic toxicity test (4,900 ppm) was significantly affected ($P = 0.05$) compared to the control, as there were no surviving organisms. The laboratory control exhibited 100 percent survival with a mean dry weight of 0.81 mg/organism. When the growth data was statistically analyzed, both the 870 ppm and the 2,100 ppm concentrations were found to be statistically different ($P=0.05$) from the control. The adversely affected

concentrations (870, 2100 ppm) had mean dry weights of 0.72 and 0.45 mg/organism, respectively. The NOEC was 370 ppm product and the LOEC was 870 ppm product. The ChV and IC25 values were 567.4 and 1,308.1 ppm product, respectively.

The 96-hour acute toxicity test utilizing *Mysidopsis bahia* exhibited 100 percent survival in the laboratory control. The 1000 ppm concentration had only 20 percent survival at test termination. The LC50 value was calculated based on this survival data and found to be 725.4 ppm product.

The *M. bahia* short-term chronic toxicity test had 95 percent control survival at test termination. The highest concentration tested (1,000 ppm) was found to be statistically different ($P=0.05$) from the control as it exhibited only 8 percent survival of the test organisms by Day 7. Based on EPA guidelines, treatments which have no surviving organisms, or have significant mortality, are not statistically analyzed for growth or reproduction. There was no statistical difference ($P=0.05$) based on the growth data found between the control and the evaluated sample concentrations. Mean dry weight of the organisms exposed to the effluent treatments ranged from 0.31 mg/fry to 0.39 mg/fry. The control organisms had a mean dry weight of 0.36 mg/organism. Statistical analysis of the reproductive potential also showed no statistical differences from the control. The NOEC was 420 ppm and the LOEC was 1,000 ppm. The ChV and IC25 were found to be 648.1 ppm product and 492.2 ppm product, respectively.

Table 2-8 and Table 2-9 provides a summary of the acute and chronic toxicity of 5-AP to selected freshwater and saltwater species evaluated as part of this study. 5-AP appears to be more toxic to invertebrate species as compared to fish species. *C. dubia* was the more sensitive freshwater species to 5-AP as well as the most sensitive species evaluated during this study. 5-AP was approximately 6.5 times more acutely toxic and, based on the chronic value, 13 times more toxic to *C. dubia* as compared to *P. promelas*. *P. promelas* and *M. bahia* appeared to be similarly sensitive to 5-AP with regards to acute toxicity, while *M. bahia* were somewhat more sensitive than *P. promelas* with respect to chronic effects. *M. bahia* were approximately 6 times more acutely sensitive and 2 to 3 times more chronically sensitive to 5-AP as compared to *C. variegatus*.

Table 2-8
Summary of Acute Toxicity of 5-AP to Selected Freshwater and Saltwater Species

	Acute Toxicity, ppm	
Specie	48 hr LC50	96 hr. LC50
<i>Ceriodaphnia dubia</i>	116.2 (75-180)1")	----
<i>Pimephales promelas</i>	----	763.6 (420-1,000)
<i>Cyprinodon variegatus</i>	----	4,218.3 (2,100- 4,900)
<i>Mysidopsis bahia</i>	----	725.4 (616.7- 884.6)

Table 2-9
Summary Of Chronic Toxicity Of 5-AP To Selected Freshwater and Saltwater Species

	Chronic Toxicity, ppm			
Specie	NOEC	LOEC	ChV	IC25
<i>Ceriodaphnia dubia</i>	32	75	49	48.4 (42.6- 55.3)
<i>Pimephales promelas</i>	420	1,000	648.1	562.3 (486.0- 628.5)
<i>Cyprinodon variegatus</i>	370	870	567.4	1,308.1 (1,106.8-1,437.3)
<i>Mysidopsis bahia</i>	180	420	275.0	492.2 (432.9- 544.1)

Acute and chronic toxicity data for other corrosion inhibiting chemicals are presented in Table 2-10. However, it should be cautioned that a comprehensive literature search for available toxicity data on corrosion inhibitors was not performed for this study. 5-

AP is considerably less acutely and chronically toxic to aquatic organisms than ammonia at normal reference pH and temperature values used in this study. The data also show that 5-AP is less acutely toxic to freshwater organisms than hydrazine. Based on the freshwater (*P. promelas*) and saltwater (*C. variegatus*) acute and chronic toxicity tests performed in this study, 5-AP is also less toxic than ethanolamine and morpholine given the available comparative toxicity data for fish. However, toxicity data on invertebrate species were not readily available for these compounds.

Table 2-10
Acute And Chronic Toxicity Of Selected Chemicals Used As Corrosion Inhibitors

		LC50	Chronic	Reference
Ammonia (mg/L NH ₃)				
	<i>Ceriodaphnta dubia</i> (water flea)	1.96(c)		EPA 1985
	<i>Daphnia Magna</i> (water flea)	1.91(c)		EPA1985
	<i>Pimephaks promelas</i> (fathead minnow)	2.07(c)	.13-0.2(d)	EPA 1985
	<i>mysidopsis bahia</i> (opossum shrimp)	1.02(e)		EPA 1989
	<i>Cypronodon variegatus</i> (sheepshead minnow)	2.74(e)		EPA 1989
Ethanolamine (mg/L)				
	<i>Carassius auratus</i> (goldfish)	170(f)		Verschueren 1983
Hydrazine (mg/L)				
	<i>Poecilia reticulata</i> (guppy)	0.61(g)		Verschueren 1983
	<i>P. reticulata</i> (guppy)	3.85(h)		Verschueren 1983
Morpholine (mg/L)				
	<i>Lepomis Macrochirus</i> (bluegill)	350		Verschueren 1983
	<i>Menidia beryllina</i> (inland silverside)	400		Verschueren 1983

(a) The LC50 is the lethal concentration that causes 50 percent mortality in the test population. Typically cladocerans (water fleas) are expressed as 48-hour LC50's and the remaining species as 96-hour LC50 values.

- (b) The chronic value is the geometric mean of the no observable effect concentration (NOEC) and the lowest observable effect concentration (LOEC).
- (c) Reference Species Mean Acute Value for each species in the national database is calculated at a reference pH of 8 and temperature of 20°C due to the relationship that pH and temperature have on the percentage of unionized ammonia concentration. Un-ionized ammonia is the toxic fraction of the total ammonia concentration (See EPA 1984).
- (d) Range of fathead minnow chronic values for life-cycle and early life-cycle tests.
- (e) Species Mean Acute Value
- (f) Test performed at pH 10. I
- (g) Test performed in soft water at 22-24.5°C.
- (h) Test performed in hard water at 22-24.5°C.

In summary, based on these acute and chronic toxicity results, 5-AP is less toxic than traditionally utilized corrosion inhibiting chemicals such as ammonia, ethanolamine, hydrazine, and morpholine. Since a smaller dosing of 5-AP is required for corrosion protection than the chemicals in current use, the overall environmental impact of 5-AP usage should be significantly less than current practice.

2.4 Materials Compatibility

Three elastomers (Viton A, Red Rubber and EPDM) were tested for compatibility with 5-aminopentanol (5-AP). A second amine, ethanolamine (ETA) was used as the control, and was tested using an identical protocol. ETA has previously been tested in the laboratory and has been used extensively in plants. As such it is a good candidate for control. The three elastomers were immersed in 100 ppm concentrations of 5-AP and ETA for 30 days at a temperature of 93 °C (200 °F). Material properties of the elastomers were measured before and after the immersion test with the purpose of determining if the elastomers were compatible with 5-AP.

For EPDM and Red Rubber, both amines caused similar changes in properties. On average, one of the parameters for Viton A was affected differently by 5-aminopentanol than by ethanolamine, but the differences are not statistically significant.

For EPDM and Viton A there is data from other laboratory studies with ethanolamine.⁹ The differences in results for ethanolamine from the current study and previous studies

are on the same order of magnitude as the differences between ethanolamine and 5-aminopentanol in the current study.

It is concluded, therefore, that the laboratory studies did not detect any significant differences in materials properties caused by 5-aminopentanol compared to ethanolamine.

2.4.1 Experimental Methods

The objective of the tests described below was to examine the compatibility of three elastomeric materials used at Calvert Cliffs Nuclear Power Plant with 5-aminopentanol, a pH control chemical. The study used ethanolamine as a study control, as ethanolamine has been used at the Plant and its compatibility with elastomers has been studied.

2.4.1.1 Elastomers

Viton A: Viton A is a copolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene. It was formulated by PARCO, Inc., Ontario, CA using bisphenol cure system, and supplied as 6" x 6" x 1/16" black slabs, marked compound 9062-95, lot B-11975.

EPDM: EPDM (ethylene propylene diene monomer) is a copolymer of ethylene, propylene, and a diene crosslinking agent. It was formulated by PARCO, Inc., Ontario, CA, using a peroxide cure, and supplied as 6" x 6" x 1/16" black slabs, marked compound 5611-80, lot B-11464.

Red Rubber: A 11" x 15" x 1/16" piece of Red Rubber was received from Ms. Evelyn Eshelman at Calvert Cliffs Nuclear Power Plant. It is part of the stockroom supply, from which gaskets are made.

2.4.1.2 Chemicals

Ethanolamine (2-aminoethanol) was Baker Analyzed grade, 99.5%, Lot 021628, density 1.012 grams/mL

5-Aminopentanol was obtained from the CenTec supply, indicated to be from CU CHEMIE UETIKON GMBH, as an 80% (w/w) solution in water, density 0.956 grams/mL.

2.4.1.3 Procedures

Dumbbell-shaped coupons were cut using a modified ASTM die C, which generated coupons 4.5" long and 1 wide at the ends, and with a ¼" wide and 2" long constricted section in the center. The coupons fit in the 230-mL jars. The samples weighed 4 to 7 grams. Immersion testing was based on ASTM Standard D471⁹. The ASTM method recommends using 75-80 mil samples, but in these tests the thicknesses were determined by the materials received. The thickness of the middle section of each sample was measured with a micrometer. The coupons were labeled by punching small holes in one end (1 to 6 holes). The samples were weighed, strung together in threes on a Teflon string that was knotted on each side of the coupon so they would hang separately, and immersed in 220 mL of solution in 230-mL jars.

Each of the exposure solutions contained 100 ppm of either ethanolamine or 5-aminopentanol. There were three coupons per solution.

The jars were placed in a water bath maintained at 93 °C (200 °F). After 15 days had elapsed, the samples were cooled briefly and the solutions replaced with fresh 100 ppm solutions.

After the immersion period, the heating bath was cooled, and the jars were removed. Materials testing was performed at Burke Rubber Company, San Jose, CA. Testing was performed the same day that the solutions were cooled. Samples were removed from the solutions, rinsed with DI water, blotted dry, and loose deposits removed. The samples were weighed and tested at ambient temperature within one hour of removal from the solutions. Hardness testing was performed according to ASTM Procedure D2240¹⁰ using instantaneous (one second) readings (Shore A scale). Tensile strength and elongation at break were measured on an Instron using a pull rate of 20"/minute (ASTM Procedure D412)¹¹. Tensile strength calculations were based on the coupon cross sections before immersion (ASTM Procedure D412).

2.4.2 Results and Discussion

Results from the current study and from earlier experiments conducted for EPRI(1) were evaluated to reach these conclusions.

Table 2-11 is a summary of results for the three elastomers tested in the current study Table 2-12 is a summary of results of similar testing of Viton A performed in 1992 for EPRI, wherein Viton A and EPDM were exposed to 100 ppm ETA and to high purity water.

Table 2-11
Summary of Results from Low Temperature Test Material Coupons Heated at 93° C
(200° F) for 30 Days June 1995

<u>MATERIAL</u>	<u>UNEXPOSE</u>	<u>5-AMINOPENTANOL</u>		<u>ETHANOLAMINE</u>	
	<u>D</u>	100 PPM		100 PPM	
		Value	% Change	Value	% Change
<u>Viton A</u>					
Weight increase, %			0.5%		0.5%
Tensile strength at break, psi	2100	1736	-17%	1919	-8%
Elongation at break, %	60	50	-16%	70	16%
Hardness, Shore A	95	95	0%	95	0%
<u>Red Rubber</u>					
Weight increase, %			14.9%		14.9%
Tensile strength at break, psi	880	600	-31%	543	-38%
Elongation at break, %	300	250	-16%	230	-23%
Hardness, Shore A	82	70	-12%	70	-12%
<u>EPDM</u>					
Weight increase, %			1.1%		1.1%
Tensile strength at break, psi	2597	2900	11%	2797	7%
Elongation at break, %	150	180	20%	170	13%
Hardness, Shore A	83	83	0%	84	1%

Table 2-12
Summary of Results from Low Temperature Test Material Coupons Heated at 93° C
(200° F) for 30 Days
(From EPRI TR-1007794, Rev 1)

Material	Unexposed	Water		Ethanolamine 100 ppm	
		Value	% Change	Value	% Change
Viton A					
Weight increase, %			0.4%		0.4%
Tensile strength at break, psi	1930	1790	-7.2%	1729	-10.4%
Elongation at break, %	67	75	11.9%	72	7.5%
Hardness, Shore A	95	94	-1.1%	94	-1.1%
EPDM					
Weight increase, %			1.4%		1.4%
Tensile strength at break, psi	2523	2358	6.5%	2428	-3.8%
Elongation at break, %	183	165	-9.8%	178	-2.7%
Hardness, Shore A	80	81	1.2%	81	1.2%

Viton A: Using data from this study and data from previous studies, it is seen that water, ethanolamine and ETA affect the properties of Viton A similarly, except for the elongation at break parameter. Both ethanolamine and water cause Viton A to become more elongated (compared to unexposed material) before breaking whereas 5-aminopentanol causes Viton A to break earlier in the elongation process. There was no visual indication of change, nor was there a change in the weight of the elastomer.

Red Rubber: Ethanolamine and 5-aminopentanol had similar effects on red rubber. This elastomer became more brittle in both of the amines, as indicated by a reduced tensile strength at break and decreased elongation at break. Visual inspections of the exposed coupons support the laboratory measurements, as the material looked brittle and had a whitish appearance. The rubber gained 14.9% in weight in both amines.

Red rubber was not tested with ethanolamine in the 1992 study. However, a different red rubber (product of Boston Bultrite Company) obtained from Alabama Power Company, was exposed for 20 days at 93 °C (200 °F) to distilled water and to a 50% morpholine solution. These are the results for those two exposures:

	<u>Water</u>	<u>50% Morpholine</u>
Weight Increase, %	8.6%	5.1%
Tensile strength at break, psi (Unexposed = 860)	301 (-65%)	332 (-61%)
Elongation at break, %	305	433

The Garlock Red Rubber had a greater weight increase than the Boston Bultrite red rubber, but Garlock had a lesser effect on the tensile strength by either ETA or 5-AP than was noted for either water or 50% morpholine for the Boston Bultrite rubber.

EPDM: Ethanolamine and 5-aminopentanol had similar effects on EPDM, both amines causing an increase in tensile strength at break and an increase in elongation at break. In the 1992 study (Table 2.4-2) where EPDM was exposed to water and to ethanolamine under similar conditions as in the current study, the trends were somewhat different but within the margins of variability of these types of experiments.

In this study, as in previous immersion exposure studies, several additional factors should be included in assessing whether the elastomers are useable in the plant environment, and are worth mentioning.

Applicability of laboratory studies to plant experience. Properties that may appear to be negative from the exposure study may be unimportant or even positive properties when elastomers are used in the secondary system. Swelling, as evidenced by weight increase, probably increases the sealing ability of elastomers used as gaskets. Laboratory exposure studies are one factor in considering whether certain amines and elastomers are compatibility. Plant experience, if it exists, should be considered also.

Exposure conditions for the study necessarily have been modified so that data are obtained in a reasonable time period. Effects that are time-dependent may not be discovered in a 30-day test, although higher than usual concentrations are used to accelerate time-dependent effects. Extrapolating results to temperature and concentrations higher than test conditions is not valid.

Variability of elastomer materials. For the laboratory immersion studies, some materials have been specially formulated for the test, and may not represent the actual material used at the plant. Properties of these materials may vary somewhat from formulation

to formulation, such as the Viton A or EPDM. Some elastomers may contain fillers that are not part of the elastomer used in the tests. Red rubber may be one of several types of red rubbers, each having its own properties.

2.5 Full Scale Test at Calvert Cliffs

The culmination of the 5-AP testing program was a full scale test using 5-AP in place of ethanolamine at Calvert Cliffs Unit 2. The purpose of this test was to verify the corrosion protection offered by 5-AP was equivalent to ETA, but at a much lower chemical dosing, and determine whether any unforeseen operational problems might arise.

Calvert Cliffs is a two unit Combustion Engineering PWR located in Calvert County Maryland on the lower Chesapeake Bay. Unit 1 started operation in 1975, followed by Unit 2 in 1977. The two units have somewhat different secondary systems in that Unit 1 has a General Electric turbine, while Unit 2 uses a Westinghouse turbine. Figure 2-9 and Figure 2-10 show simplified flow diagrams for the two units. The Westinghouse unit (Unit 2) has a significantly larger extraction system. For example, it has four moisture separator/reheaters compared to the two that the GE unit (Unit 1). As such, a considerably higher surface area is available for corrosion in Unit 2, exemplified by the higher final feedwater iron levels routinely experienced by that unit. Figure 2-11 shows the final feedwater iron for the two units from September 1994 through October 1995. Unit 2 consistently tracks at higher iron levels than Unit 1. The site goal was to maintain iron in the final feedwater less than 3.5 ppb. Unit 1 routinely maintained the iron at this goal, as shown in Figure 2-11. Unit 2 iron values were usually above this level. For this reason and also outage timing considerations, Unit 2 was chosen for the 5-AP test.

The testing protocol was to inject 5-AP at a concentration that would maintain the system at an equivalent corrosion protection that had been supplied by the normal corrosion inhibitor, ethanolamine. This meant injecting 5-AP equivalent to the 1.8 ppm ETA that had been present. Only 0.8 ppm 5-AP was required in the final feedwater to match the protection in the high temperature drains that was supplied by 1.8 ppm ETA in the FFW.

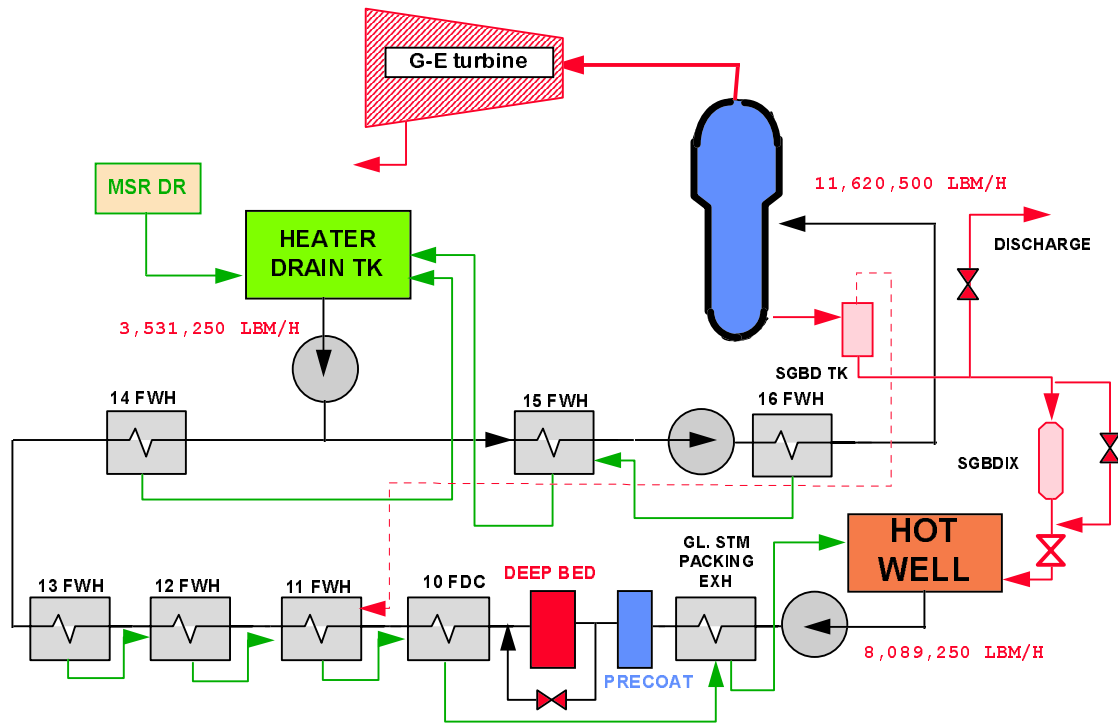


Figure 2-9 Secondary Flow Diagram for Unit 1

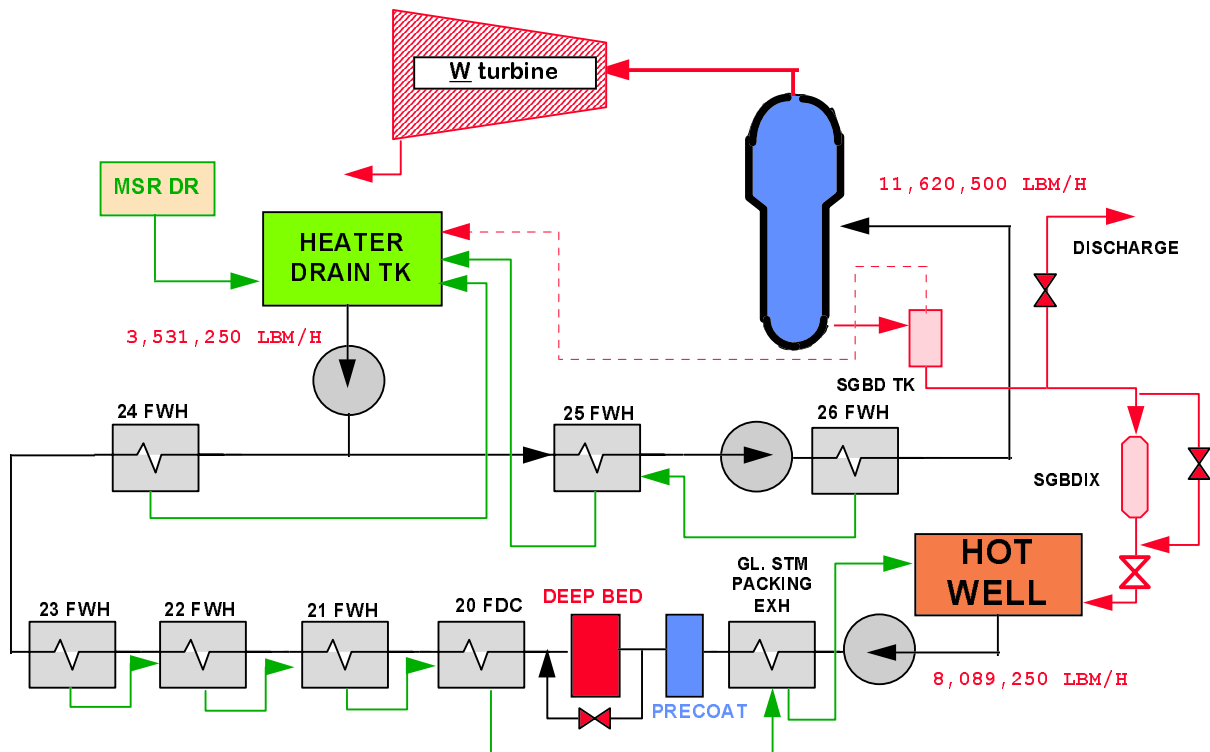


Figure 2-10 Secondary Flow Diagram for Unit 2

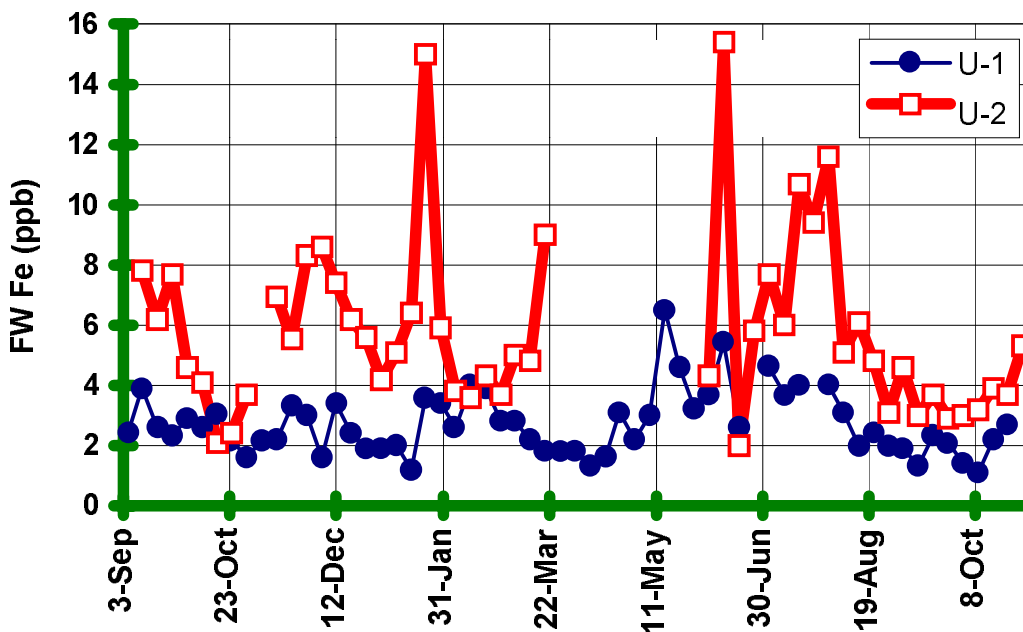


Figure 2-11 FFW Iron Levels at Calvert Cliffs from September 1994 through October 1995

Figure 2-12 trends the 5-AP concentrations measured during the test. As shown, the test began on December 19, 1995 and extended until February 4, 1996. The 45 day test was conducted with an average of 0.8 ppm 5-AP in the final feedwater, 0.35 ppm in the condensate, 2.3 in the blowdown and 4.3 ppm in the moisture separator drains. One condensate polisher was in service (out of five total) at a flow rate of 3200 gpm. Over the test period, about 610 lb of 5-AP was removed by the polisher, while about 60 lb were removed from the system via the blowdown. Blowdown was routed to drain throughout the test. This nearly completely accounts for the 500 kg of 80% 5-AP that was made available for the test by Becpharm.

Figure 2-13 shows the distribution of 5-AP around the secondary system at Calvert Cliffs. The solid lines are drawn from data taken from the EPRI PWR Secondary Chemistry Simulator. As shown, this theoretical data matches the experimental data from Calvert Cliffs very well. Less than half of the final feedwater concentration of 5-AP returns to the condenser. Thus, since about 2/3 of the total flow travels through the condenser, only about 1/4 of the total 5-AP in the final feedwater is removed (and must subsequently be replaced) by full flow condensate polishing. These values confirm the expected performance of 5-AP and verify its chief advantage as an alkalizing agent. With a plant such as Calvert Cliffs, about 15 lb/hr of 5-AP would be input to the steam generator, while only about 4 lb/hr would come out of the condenser for demineralization. With ETA, about 30 lb/hr of chemical would be required to be fed to the steam generator, while 13 lb/hr would flow into the condensate polishers. Accounting for molecular weight differences, this represents a reduction in condensate polisher loading of over 80%. This improvement could be used as cost savings or to

improve corrosion protection. A typical condensate polisher regeneration costs about \$1,000. With full flow polishing, the annual regeneration costs are nearly \$200,000 for a modern PWR using full flow condensate polishing. 5-AP could be used to decrease this cost to about \$50,000, depending on the level of hydrazine that is employed. Calvert Cliffs uses high hydrazine levels that, coupled with partial flow polishers, lead to ammonia levels of about 1 ppm. With full flow polishing, this concentration would be decreased to about 0.2 ppm. This concentration of ammonia would add additional loading on the condensate polishers and decrease the relative benefit achieved through usage of 5-AP. A significant cost savings over the use of ETA would still be obtained. This cost savings would help offset the cost of 5-AP. Alternatively, a higher concentration of 5-AP could be added to the system to significantly improve the corrosion protection and decrease iron concentrations throughout the system.

Figure 2-14 and Figure 2-15 show the total iron levels before and through the 5-AP test. As shown, the final feedwater during the test was about the same as that before the test. Scatter in the data over the relatively short test preclude any conclusion of relative protection. The design basis of the test was to match the protection given by 2 ppm ETA. The data show that this was accomplished.

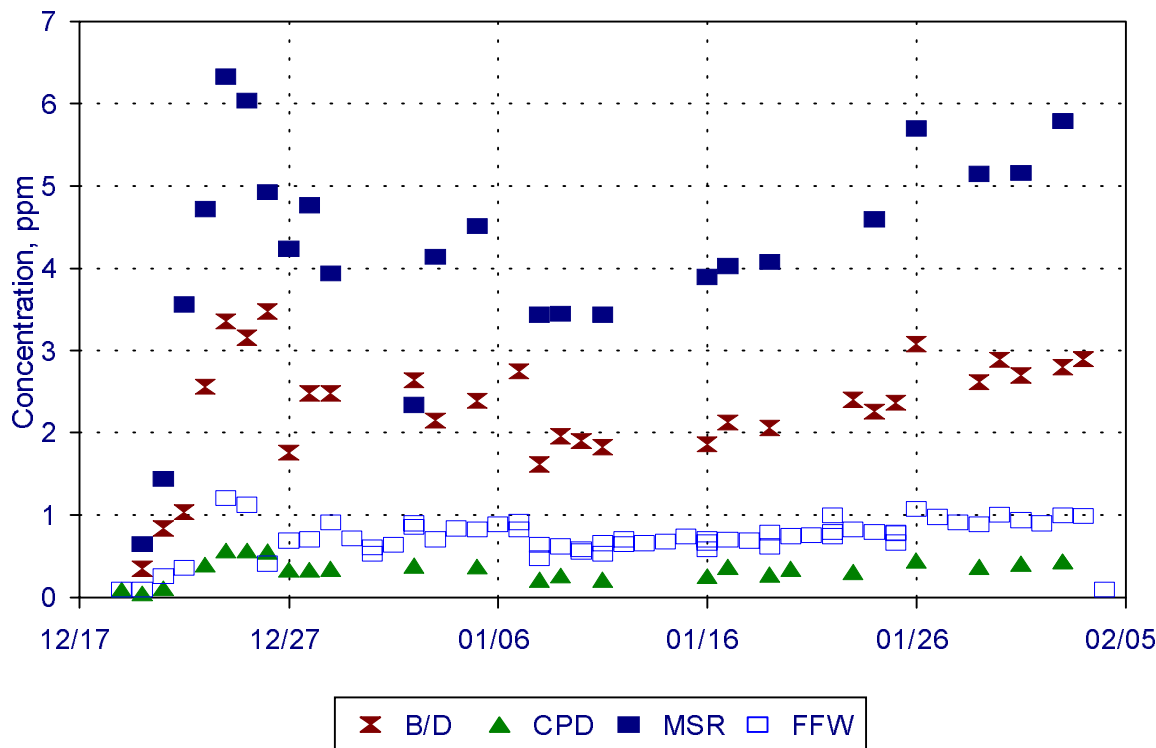
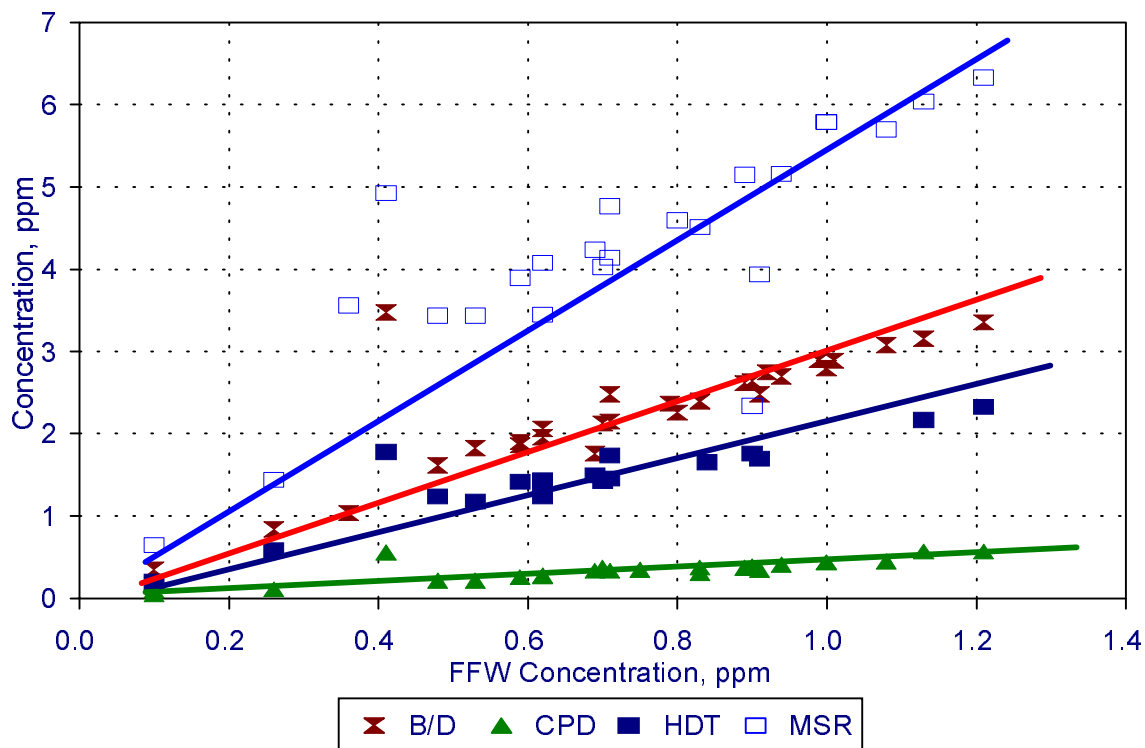


Figure 2-12 5-AP Trend at Calvert Cliffs



Lines are drawn from EPRI PWRSCS data.

Figure 2-13 Distribution of 5-AP at Calvert Cliffs

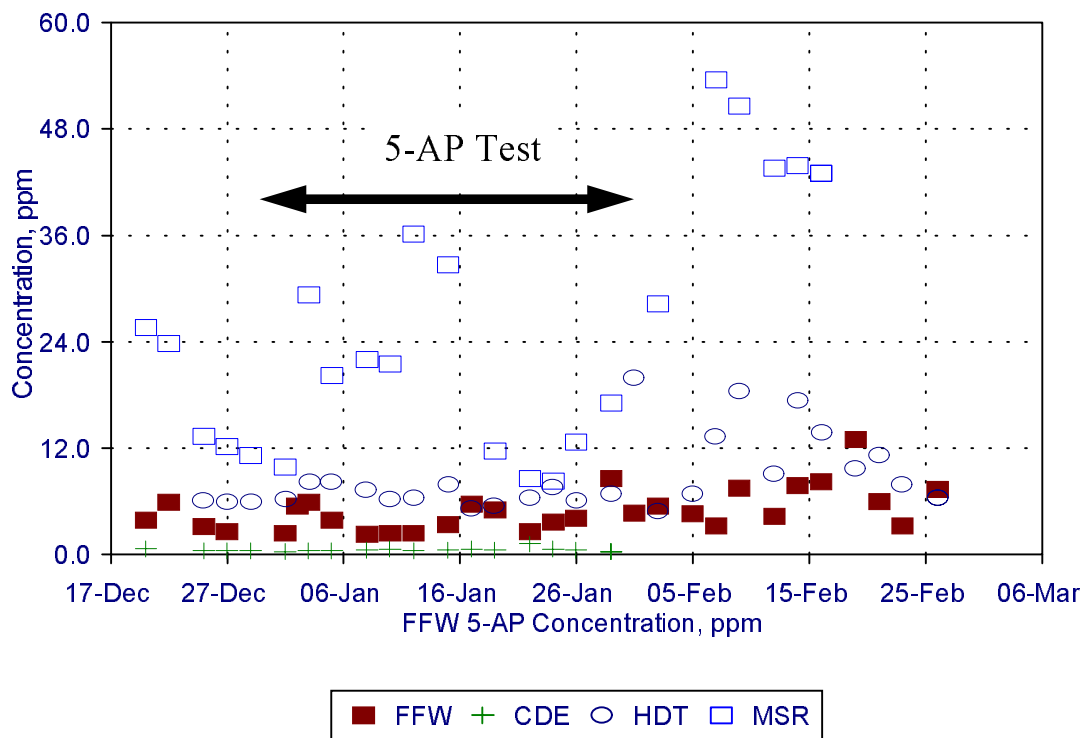


Figure 2-14 Iron Concentrations at Calvert Cliffs

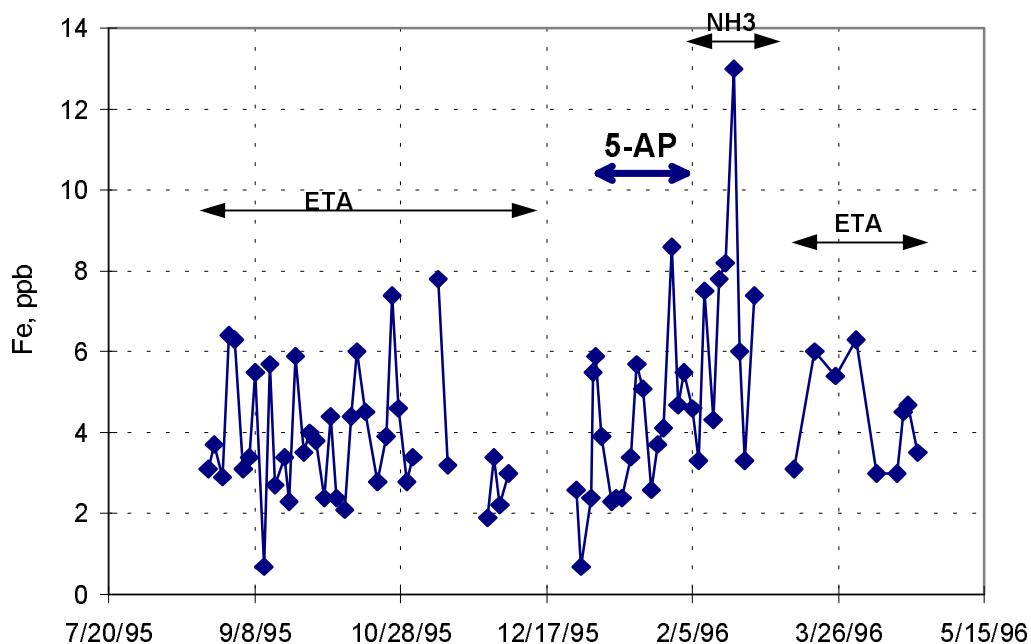


Figure 2-15 Final Feedwater Iron Concentrations at Calvert Cliffs

Figure 2-16 and Figure 2-17 show the cation conductance in the blowdown, condensate and final feedwater as a function of time and the final feedwater 5-AP concentration. If 5-AP were decomposing to any appreciable extent to form the expected organic acids, this figure would be expected to show a correlation between the cation conductance and the 5-AP concentration. No such correlation is apparent. Furthermore, the cation conductance is very low, indicating that the organic acid and other anionic content of the three streams is also low. Calvert Cliffs, when operating on ETA exhibited a blowdown cation conductance of 0.2 to 0.5 uS/cm. This implies that 5-AP is about twice as thermally stable as ETA under the operational conditions at Calvert Cliffs.

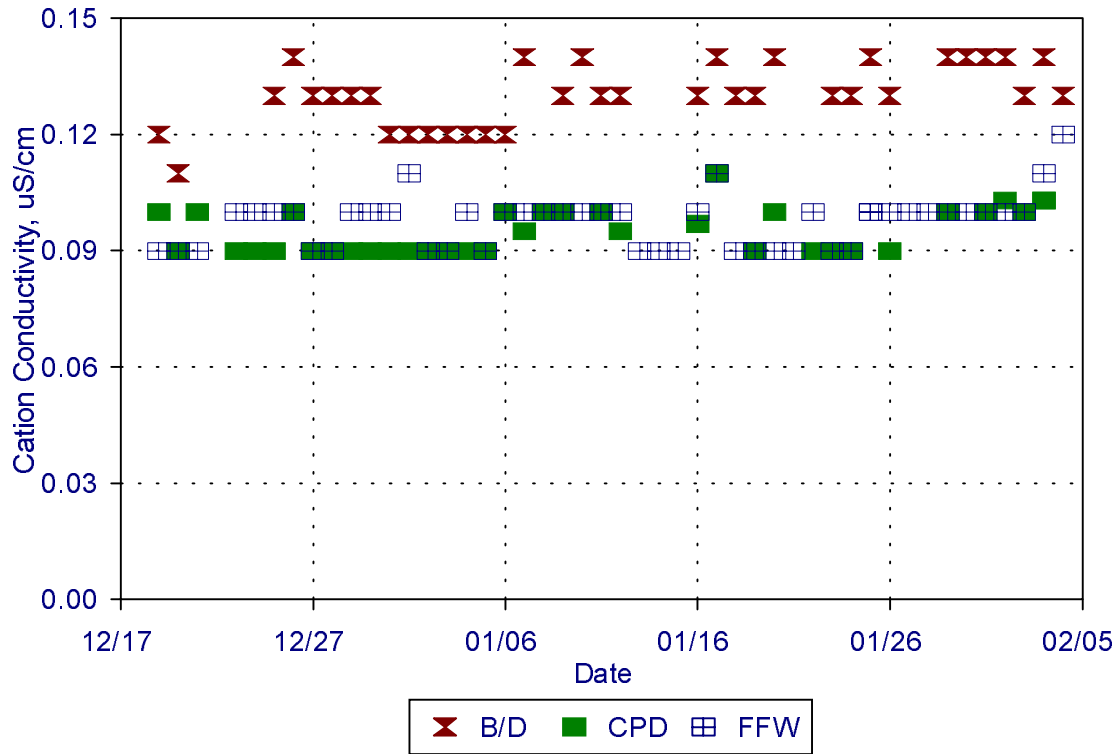


Figure 2-16 Cation Conductance Trend Plot

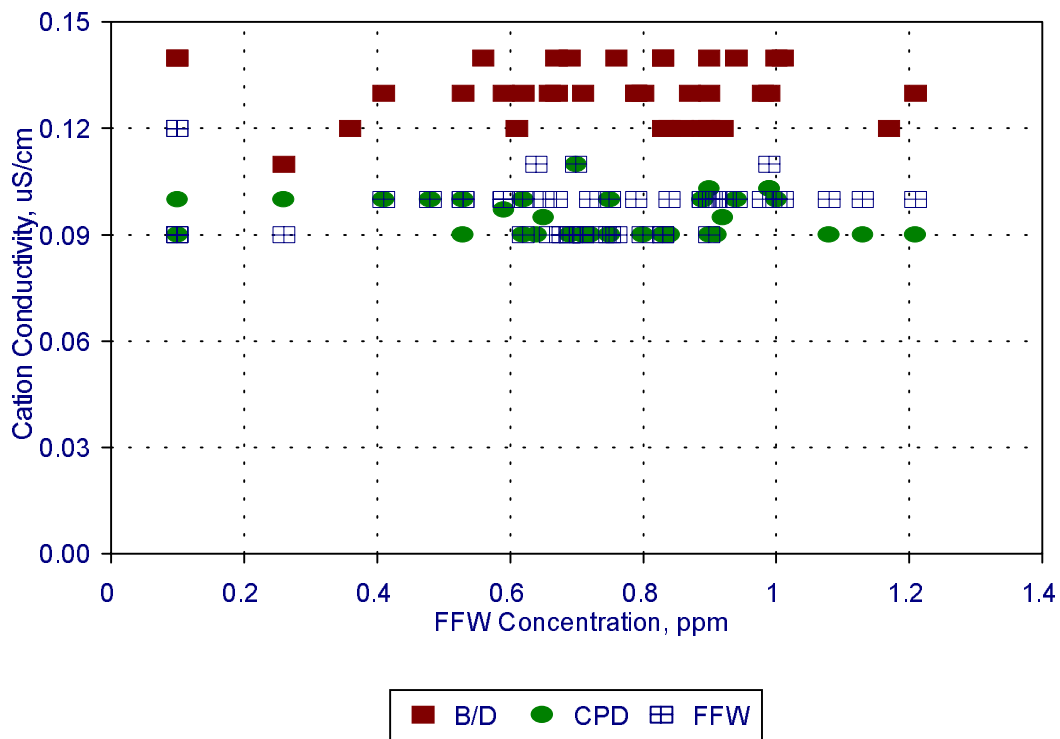


Figure 2-17 Cation Conductance vs 5-AP

3

CONCLUSIONS

The extensive work reported here qualifies 5-AP as an excellent choice for alkalizing agent in the secondary system. Its high base strength results in a low dosage of chemical, while its low volatility provides excellent protection to the two phase flow regions of the secondary plant. This balance of high base strength and low volatility make 5-AP the best choice of amines for plants with deep bed condensate polishing. The use of 5-AP provides the most corrosion protection with the least condensate polishing loading.

Toxicology studies reveal it to have very low toxicity to aquatic life and the materials compatibility study shows that it does not attack coating, gasketing and sealing materials. Full scale testing verified it behaved as expected, yielding the same corrosion protection with considerably less chemical dosing. It is more thermally stable than ETA and should provide a significant improvement in water quality.

4

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A

DETAILED TOXICOLOGY REPORT

As part of the tailored collaboration project, toxicological testing was performed to determine the toxicity of 5-AP to freshwater and saltwater species typically used for NPDES biomonitoring. EA Engineering, Science and Technology, Inc. was contracted to perform acute and chronic toxicity tests using fathead minnows (*Pimephales promelas*) and water fleas (*Ceriodaphnia dubia*) for freshwater testing and opossum shrimp (*Mysidopsis bahia*) and sheepshead minnows (*Cyprinodon variegatus*) for saltwater testing in conformance with accepted practices. Initially, rangefinder tests were performed to establish appropriate concentration series for the acute and chronic toxicity tests.

Organisms in the water flea definitive acute test were exposed for 48 hours to a graded concentration series of 8.7, 32, 75, 180 and 420 ppm and a laboratory control. In the sheepshead minnow test, the organisms were exposed for 96 hours to a graded concentration series of 155, 370, 870, 2100, 4900 ppm and a laboratory control. The fathead minnow and opossum shrimp acute organisms were both exposed to a graded concentration series of 32, 75, 180, 420, 1000 ppm and a laboratory control for 96 hours. The objective of the acute tests was to determine the median lethal concentration (LC50) of 5-AP. The definitive chronic tests were short-term daily renewal toxicity tests. In the water flea chronic test, the organisms were exposed to a concentration series of 8.7, 32,, 75, 180, and 420 ppm and a laboratory control until three broods of young were reproduced (6 days). The fathead minnow and opossum shrimp chronic toxicity tests consisted of a concentration series of 32, 75, 180, 420, and 1000 ppm and a laboratory control and an exposure duration of 7 days. In the sheepshead minnow test chronic toxicity test, the organisms were exposed for 7 days to a concentration series of 65, 155, 370, 870, 2100, 4900 ppm and a laboratory control. The objectives of the chronic tests were to assess the chronic lethality of the product to the test organisms and to determine the inhibition of reproduction potential (water flea), growth (fathead minnow, sheepshead minnow, and opossum shrimp), and the fecundity (opossum shrimp) of the test organisms as compared to the controls.

A.1 Methods And Materials

A.1.1 Sample Description

One gallon of 5-aminopentanol (5-AP) was shipped from CenTec-21, Inc. to EA's Aquatic Toxicology Laboratory in Sparks, Maryland. Upon receipt at EA, the product was logged in and assigned an Aquatic Toxicology Laboratory accession number. The

product was handled according to the specified handling outlined in the MSDS guidelines. The sample was stored in the laboratory at 20 C when not in use.

A.1.2 Test Organisms

Ceriodaphnia dubia were cultured in EA's laboratory using dilute mineral water as described below. The cultures were kept in an environmentally controlled room at 25 ± 2 C with a 16-hour light/8-hour dark photoperiod. Organisms were fed daily as described in Weber et al. (1989) and thinned as necessary to maintain healthy, productive cultures. Adults were separated from the bulk cultures at least one week prior to test initiation, placed in individual 30-ml plastic cups (15-ml volume) in brood boards, and fed heavily. Gravid adults were re-isolated and fed the evening before the test. The neonates (young) were < 24 hours old at test initiation in the acute test. The neonates used for the chronic toxicity test were < 26 hours old at initiation. All neonates used in the chronic test were released within the same 4-hour time period from broods of eight or more, and were randomly assigned to the treatment chambers using a transfer pipette.

Pimephales promelas were obtained from embryos spawned in EA's Aquatic Culture Facility. Lot FH5-4/17-18, used in the chronic test, were hatched on 17-18 April 1995 and maintained at $25 \pm 1^\circ\text{C}$ in dechlorinated water. The fathead larvae were < 24 hours old when used to initiate the chronic test on 18 April 1995. Lot FH5-4/9-10, hatched on 9-10 April 1995, were 8-9 days old (hatched within a 24-hour window) when used to initiate the acute test on 18 April 1995. The larvae were hatched in dechlorinated tap water. The larvae were maintained at $20 \pm 1^\circ\text{C}$ and were fed brine shrimp nauplii (*Artemia sp.*, < 24 hours old) a minimum of once daily during this rearing period. At initiation of the acute and chronic definitive tests the fathead larvae were slowly siphoned into I-L culture bowls from which the larvae were randomly assigned to the treatment chambers, using a transfer pipette.

Mysidopsis bahia (opossum shrimp) were acquired from Chesapeake Cultures (Hayes, Virginia). The organisms represented by the EA designation Lot #Mb-315, were two days old when received at EA on 18 April 1995. The shrimp were 4 days old when used to initiate the acute test. *M. bahia* Lot #Mb-318 was used in the chronic toxicity test. The organisms were 6 days old when received at EA on 3 May, and were 7 days old when used to initiate the chronic toxicity test. The temperature and salinity of the shipping water upon receipt at EA, for Mb-315 were 19.5°C and 21.5 ppt, and for Mb-318, 21.4°C and 20.3 ppt, respectively. The shrimp were maintained at the testing temperature of $20 \pm 1^\circ\text{C}$ (acute) and $26 \pm 1^\circ\text{C}$ (chronic), 20 ± 2 ppt salinity, and were fed brine shrimp nauplii (*Artemia sp.*, < 24 hours old) twice daily during the holding period. At initiation of both the acute and chronic tests, the shrimp were slowly siphoned into I-L culture bowls and randomly placed into treatment vessels using a transfer pipette.

Cyprinodon variegatus (sheepshead minnow) were acquired from Aquatic Biosystems (Colorado). Lot CV-202 was received on 18 April 1995. The temperature and salinity of the shipping water upon receipt at EA was 19.5 and 20.5 ppt, respectively. The larvae were 12 days old when used to initiate the acute toxicity test on 20 April 1995. Lot CV-203 was received at EA on 20 April 1995. The temperature and salinity of the receiving water were 21.3 C and 22.0 ppt, respectively. The larvae at test initiation were less than 24 hours old. During the acclimation period, *C. variegatus* were maintained at testing temperatures of $25 \pm 1^{\circ}\text{C}$ (acute) and $25 \pm 1^{\circ}\text{C}$ (chronic) and 20 ± 2 ppt salinity and were fed < 24 hour old brine shrimp (*Artemia* sp.) nauplii twice daily.

A.1.3 Dilution Water

The dilution water used in the acute and chronic toxicity testing of the *C. dubia* was dilute mineral water (DMW) consisting of 20 percent Perrier water. Batches of DMW were made by passing deionized water through activated carbon, adding bottled Perrier water, and aerating overnight. The water was stored at 20°C under gentle aeration until needed. This water is also used for the culturing of *C. dubia*.

The laboratory water used in the *P. promelas* toxicity tests was dechlorinated tap water. The source of the tap water was the Baltimore municipal water supply, which upon entry into the laboratory passed through a high capacity activated carbon dechlorination unit which removed chlorine and other potential contaminants such as hexane soluble compounds. The dilution water used in the testing of the *M. bahia* and *C. variegatus* was 20 ppt artificial seawater which was made by adding dry synthetic sea salts (Forty Fathoms, Marine Enterprises, Towson, Maryland) to dechlorinated tap water. A summary of the water quality characteristics associated with Forty Fathoms artificial seawater is presented in Table A-1.

Table A-1
Summary Forty Fathoms Marine Mix Hydrated To A Density Of 1.025 Using Distilled Water

Parameter	Mol. Wt.	Conc, ppm	Parameter	Mol. Wt.	Conc, ppm
Aluminum	27.0	0.06	Lithium	6.9	0.24
Antimony	121.7	0.0005	Magnesium	24.3	1,290
Arsenic	74.9	0.01	Manganese	54.9	0.008
Barium	137.3	0.12	Mercury	200.6	0.0007
Bicarbonate	61.0	174.0	Molybdenum	95.9	0.005
Beryllium	9.0	0.0002	Nickel	58.7	0.009
Boron	10.8	2.1	Nitrogen	14.0	0.85
Bromide	79.9	62.0	Phosphorus	31.0	0.04
Cadmium	112.4	0.009	Potassium	39.1	380
Calcium	40.0	410.0	Silicon	28.1	4.5
Carbonate	60.0	10.0	Sodium	23.0	10,400
Cerium	140.0	0.0007	Strontium	87.6	12.4
Chromium	52.0	0.02	Sulfur (SO ₄)	96.1	2,600
Chloride	35.4	18,600	Thallium	204.4	0.000007
Cobalt	58.9	0.0025	Tin	118.7	0.006
Copper	63.5	0.007	Titanium	47.9	0.004
Fluorine	19.0	1.9	Tungsten	183.9	0.004
Gallium	69.7	0.0004	Vanadium	50.9	0.0009
Germanium	72.6	0.00005	Zinc	65.4	0.24
Iodine	126.9	0.03	Vanadium	50.9	0.0009
Iron	55.8	0.03	Zinc	65.4	0.24

A.1.4 Toxicity Test Operations And Performance

Toxicity tests were performed in accordance with EA's protocols (EA 1992) which are included in Reference 1. Prior to preparation of test solutions, 1 g/L (1000 ppm) stocks were made by diluting one gram of product into one liter of dechlorinated water. This stock was used for preparing solutions for *C. dubia*, *P. promelas*, and *M. bahia* acute and chronic toxicity tests. A 5 g/L (5000 ppm) stock was made by diluting 5 grams of product into one liter of dechlorinated water and used to prepare solutions for the *C. variegatus* acute and chronic toxicity tests. Test concentrations were prepared using Class A glassware. Small volumes of stock were first measured in pipettes and graduated cylinders, then added to a volumetric flask and brought to final volume with dilution water. For the freshwater toxicity tests, the pH of the dilutions was adjusted to 7.5 ± 0.2 as they were outside (e.g., 10.7) the acceptable range of 6-9, prior to transferring of organisms into testing vessels. The dilutions of the saltwater tests were pH adjusted to 8.3 ± 0.2 after the addition of the appropriate amount of synthetic sea salts and prior to transferring organisms into testing vessels. The test solutions were mixed, then split equally into the replicate tests chambers.

A.2 Acute Toxicity Tests

The 48-hour static definitive acute *C. dubia* test (IN-95-269) was initiated at 1415 hours on 18 April 1995. The test was terminated at 1438 hours on 20 April 1995. Five neonates (< 24 hours old) were randomly added to each of the four replicate test chambers per concentration and control. Each test chamber contained 15 ml of test solution. The *C. dubia* were fed a 0.2 ml solution of trout chow/yeast/cereal leaves supplemented with algae (*S. capricornutum*) once daily for the duration of the toxicity test.

The 96-hour static definitive acute *P. promelas* test (TN-95-270) was initiated at 1525 hours on 18 April 1995. The test was terminated at 1553 hours on 22 April 1995. Test chambers for the fathead minnow acute test were I-L beakers containing 250 mls of test solution. Each test concentration and control had two replicate test chambers with 10 organisms per replicate. The *P. promelas* were not fed during the 96-hour exposure period.

The 96-hour static definitive acute *C. variegatus* test (M-95-275) was initiated at 1730 hours on 20 April 1995. The test was terminated at 1703 hours on 24 April 1995. Test chambers used for the *C. variegatus* test were I-L beakers containing 250 ml of test solution.

The 96-hour static definitive acute *M. bahia* test (TN-95-273) was initiated at 1755 hours on 20 April 1995. The test was terminated at 1700 hours on 24 April 1995. Test chambers used for the *M. bahia* acute test were 20 cm glass culture bowls containing I L

of test solution. There were 10 organisms placed randomly in each chamber. The *M. bahia* were fed < 24 hour old brine shrimp (*Artemia* sp.) nauplii daily during the 96-hour exposure period.

All acute test chambers were maintained at 20 ± 1 °C with a 16-hour light/8-hour dark photoperiod. Water quality measurements and mortality observations were made daily. Temperature, dissolved oxygen (DO), pH, salinity, and conductivity were measured in one replicate of each concentration daily for the duration of the tests. Table A-2 reports the water quality ranges measured during the tests.

Table A-2
Water Quality Ranges Measured During Testing

Test	Organism	Type	Temp, °C	pH	DO	Salinity, ppt	Cond., uS/cm
269	<i>C. dubia</i>	Acute	19.6 - 22.5 ^(a)	7.4-8.7 ^(b)	8.1-9.4	N/A	178-482
270	<i>P. promelas</i>	Acute	18.1 - 21 ^(a)	7.4-8.3 ^(b)	6.4-9.1	N/A	237-817
275	<i>C.variegatus</i>	Acute	19.2 - 20.4	7.6-8.3 ^(b)	3.5-8.7 ^(c)	19.0-21	N/A
273	<i>M. bahia</i>	Acute	19.5 - 20.6	8.0-8.3 ^(b)	6.5-8.0	18.9-21.2	N/A
271	<i>C. dubia</i>	Chronic	24.2 - 26.5 ^(e)	7.3-8.3 ^(b)	7.2-8.1	N/A	171-394
272	<i>P. promelas</i>	Chronic	23.3 - 26.3 ^(f)	7.2-7.9 ^(b)	3.5-7.9 ^(d)	N/A	231-1,234
276	<i>C. variegatus</i>	Chronic	21.3 - 26.3 ^(f)	7.7-8.4 ^(b)	2.6-8.7 ^(d)	17.7-20.8	N/A
308	<i>M. bahia</i>	Chronic	24.4 - 26.9 ^(g)	7.4- 8.3 ^(b)	3.7-7.1 ^{(c) (h)}	18.0-22.4	N/A

- (a) Temperature was outside of the target range of 20 ± 1 °C. This short term deviation did not appear to impact the results of the acute toxicity test.
- (b) pH was adjusted to 7.5 ± 0.2 for freshwater tests, 8.3 ± 0.2 for saltwater tests at initiation for acute tests and daily for chronic tests on new solutions.
- (c) Dissolved oxygen measurement below the target range of 4.0 mg/L.
- (d) Test placed under gentle aeration due to low dissolved oxygen increments.

- (e) Temperature was outside of the target range of 25 ± 1 C (but within 25 ± 2 C) for old test solutions at the 96-hour observation period. This short term deviation did not appear to impact the results of the chronic toxicity test.
- (f) Temperature was outside of the target range of 25 ± 1 C. The lower temperatures were a result of aeration of the test chambers due to low dissolved oxygen. This short term deviation did not appear to impact the results of the chronic toxicity test.
- (g) Temperature was outside of the target range of 26 ± 1 C (but within 26 ± 2 C) for old test solution at the 72 hour observation period. This short term deviation did not appear to impact the results of this chronic toxicity test.
- (h) The *M. bahia* chronic toxicity test could not be aerated due to minimal volume in each test chamber. Dissolved oxygen levels < 4.0 mg/l were only observed in two treatments (420 ppm- day 7 and 1,000 ppm- day 6). These two values did not appear to effect the results of the chronic toxicity test.

Using the total number of dead organisms per concentration at the end of the exposure period (e.g., 48 or 96 hours), the median lethal concentration (LC50 value) was calculated by the binomial, moving average, and probit analysis methods as described by Stephan (1977).

A.3 Chronic Toxicity Tests

The *C. dubia* definitive short-term chronic toxicity test (TN-95-271) was initiated at 1455 on 18 April 1995 and terminated at 1500 on 24 April 1995. At initiation, neonates were < 26 hours old, and released within a 4-hour window from broods of 8 or more. They were randomly loaded into the test chambers for a total of ten replicates of one organism per concentration and control. Test chambers were 30 ml plastic cups with 15 ml of test solution per cup. Renewal of test solution was performed by transferring the test organisms to new cups containing freshly prepared test solution. During testing, organisms in each test chamber were fed daily with 0.2 ml trout chow/yeast/cereal leaves solution, supplemented with algae (*S. capricornutum*). Observations of mortality were recorded daily. Measurements of temperature, pH, DO, and conductivity were taken on one replicate of each treatment and the control daily on the new and old test solutions and are summarized in Table A-2.

Fisher's Exact Test was used on the survival data of the *C. dubia* chronic test and the Bonferroni t-Test adjustment was used on the parametric reproduction data to determine which of the treatment groups were statistically ($P=0.05$) different from the controls.

The *P. promelas* definitive short-term chronic toxicity test (TN-95-272) was initiated at 1600 hours on 18 April 1995 and terminated at 1630 hours on 25 April 1995. This test was conducted at $25 \pm 1^\circ\text{C}$ with a 16-hour light/8-hour dark photoperiod. The organisms were randomly loaded into 1-L polypropylene beakers each containing 250 ml of test solution, for a total of four replicates of ten organisms for each concentration and control. Daily renewal of the test solution was performed by siphoning 80 percent of the old test solution from each test chamber taking care to remove any debris from the bottom of the chamber, and then slowly siphoning new test solution into the chamber. The larvae were fed 0.15 to 0.30 ml (ration increased with age) of a 0.05 g/ml suspension of newly hatched brine shrimp nauplii (*Artemia* sp., < 24 hours old) three times daily. Temperature, pH, DO, and conductivity were measured in a minimum of one replicate of each concentration daily on old test solutions and new, unsplit test solutions. These water quality ranges are summarized in Table A-2.

At the end of the test period surviving larvae were placed in pre-weighed oven-dried pans and dried at 100°C for 24 hours. Dunnett's Mean Comparison Test was used to statistically evaluate the parametric survival and the growth data.

The *C. variegatus* definitive short-term chronic test (TN-95-276), initiated at 1625 hours on 20 April 1995 and terminated at 1700 hours on 27 April 1995, was performed in 1-L polypropylene beakers containing 250 ml of test solution with four replicates of ten organisms per concentration. During testing, the larvae were fed < 24-hour old brine shrimp nauplii (*Artemia* sp.) three times daily. Each feeding per replicate test vessel consisted of 0.15 to 0.30 ml (ration increased with age) of a 0.05 g/ml concentration of brine shrimp nauplii. Renewal of test solution (80 percent replacement) was performed daily by carefully siphoning the old solution from the beakers. During the renewal procedure, uneaten and dead brine shrimp and other debris were removed from the bottom of the test chamber. New test solution was then added to the test chamber by slowly siphoning the new solution into the beaker. The *C. variegatus* test was conducted at $25 \pm \text{C}$ with a 16-hour light/8-hour dark photoperiod.

Temperature, pH, DO, and salinity were measured in a minimum of one replicate of each concentration daily on old test solutions and new, unsplit test solutions. Table A-2 summarizes the water quality ranges measured during testing. The number of surviving larvae were recorded daily on the test data sheets.

At the end of the test period, surviving larvae were rinsed with deionized water, placed in preweighed, oven dried pans (one pan per replicate) and dried at 100°C for 24 hours. Mean dry weights were calculated for each replicate. Survival data which was nonparametric was analyzed using Steel's Many-One Rank Test and Dunnett's Test was used to analyze the parametric growth data.

The *M. bahia* definitive short-term chronic toxicity test (TN-95-308), initiated at 1145 hours on 4 May 1995 and terminated at 1400 hours on 11 May 1995, was performed in 10 cm glass culture bowls containing 150 ml of test solution. Organisms were

randomly loaded into the test chambers for a total of eight replicate bowls with five organisms each, per concentration. The organisms were fed 0.25 ml of a 0.05 g/ml suspension of < 24-hour old brine shrimp nauplii (*Artemia* sp.) twice daily. Daily renewal of test solution was performed by siphoning approximately 80 percent of the old test solution from each test chamber taking care to remove uneaten and dead brine shrimp and other debris from the bottom of the chamber. New test solution was then poured slowly into the chamber avoiding excessive turbulence for the organisms.

The *M. bahia* test was conducted at $26 \pm 1^\circ\text{C}$ with a 16-hour light/8-hour dark photoperiod. Temperature, pH, DO, and salinity were measured daily on a minimum of one replicate for every concentration on old test solutions and on the new, unsplit test solutions. The ranges of the water quality parameters measured during testing are included in Table A-2. The number of surviving organisms was also recorded daily.

At test termination, each organism was viewed under a microscope to determine its sex, sexual maturity, and in the case of females, the number of individuals with eggs in the oviducts or brood pouch. Surviving organisms from each replicate test chamber were rinsed with deionized water and placed in pre-weighed, oven-dried pans (one pan for each replicate) and dried at 100°C for approximately 16 hours in order to obtain a total dry weight of each replicate. The average growth, expressed as mg dry weight per organism, was calculated for each replicate by dividing the total net dry weight by the number of surviving opossum shrimp in that replicate.

Wilcoxon's Rank Sum Test with Bonferroni adjustment was used on the nonparametric survival, growth, and reproduction data to determine which of the treatment groups (if any) were statistically ($P=0.05$) different from the laboratory water control.

The short-term chronic toxicity testing endpoints reported are expressed as the No Observed Effect Concentration (NOEC), the Lowest Observed Effect Concentration (LOEC), and the Chronic Value (ChV). The definitions of these chronic endpoints follow Weber et al. (1988) and are as follows:

The NOEC is the highest concentration of toxicant to which organisms are exposed in a full life-cycle or partial life-cycle test, which cause no statistically significant adverse effect on the observed parameter (usually hatchability, survival, growth, and reproduction), as compared to the controls.

The LOEC is the lowest concentration of toxicant to which organisms are exposed in a life-cycle or partial life-cycle test, which causes a statistically significant adverse effect on the observed parameters (usually hatchability, survival, growth, and reproduction), as compared to the controls.

The ChV is a value lying between the NOEC and the LOEC, derived by calculating the geometric mean of the NOEC and LOEC. The term ChV is sometimes used interchangeably with Maximum Acceptable Toxicant Concentration (MATC).

A.4 Reference Toxicant Tests

In conformance with EA's quality assurance/quality control program, reference toxicant tests were performed with each species tested. The *C. dubia* were exposed to the reference toxicant sodium chloride (NaCl), *P. promelas* were exposed to cadmium chloride (CdCl₂), and *M. bahia* and *C. variegatus* were exposed to sodium dodecyl sulfate (SDS). With each reference toxicant test, the 48-hour acute response of the organisms was determined. The results were compared to the established control chart limits set by EA based on historical reference toxicant data. Results of reference toxicant tests for the tested lots are included in Table 13.

A.5 Archives

Original data sheets, records, memoranda, notes, and computer printouts are archived at EA's Mid-Atlantic Office in Sparks, Maryland. These documents will be retained for a period of 5 years unless a longer period of time is requested by CenTec-21 or the Electric Power Research Institute.

A.6 Results And Discussion

All acute and chronic toxicity tests were conducted on the 5-aminopentanol (5-AP) sample received by EA on 28 March 1995 from CenTec-21, Inc.. Constituents comprising the synthetic sea salts utilized for the salt water testing are listed in Table 2.3-1. Water quality parameters (temperature, pH, dissolved oxygen, conductivity, and salinity) measured during the duration of the acute and chronic tests were within acceptable ranges, with the minor exceptions as noted in Table A-2. The minor exceptions did not affect the acute and chronic toxicity test results.

The 48-hour *Ceriodaphnia dubia* static acute test exhibited 100 percent survival in the laboratory control at test termination. There was greater than 95 percent survival in concentrations 8.7 ppm through 75 ppm. There were no surviving organisms in the 180 and 420 ppm concentrations at 48 hours. The LC50 value calculated from the survival data at 48-hours was 116.2 ppm product. The results of this acute test are summarized in Table A-3.

Table A-3
RESULTS OF ACUTE TOXICITY TEST WITH *Ceriodaphnia dubia* ON PRODUCT 5-AP

QC Test TN-95-269
Number:

Test Initiation: 1415, 18 April 1995

Test 1438, 20 April 1995
Termination:

Test Conc, ppm	% Survival 48 hrs
Control	100
8.7	100
32	95
75	100
180	0
420	0

LC50 Value (ppm product): 116.2 (75 - 180)

The short-term chronic *C. dubia* test was terminated on Day 6, per EPA guidelines, at which time 100 percent of the laboratory control females had produced three broods of neonates (young). Both the 180 and 420 ppm concentrations significantly affected ($P=0.05$) survival and the 75 ppm concentration significantly affected ($P=0.05$) reproduction. By Day 6, there was 100 percent survival in the laboratory control through the 75 ppm concentration. Mean young production ranged from 12.2 to 27.4 young per female in the treatment concentrations compared to 24.7 young per control female. The NOEC was 32 ppm product. The LOEC and ChV were 75 and 49 ppm product, respectively. The IC25 value was calculated to be 48.4 ppm product. The results of this chronic toxicity test are summarized in Table A-4.

Table A-4
RESULTS OF CHRONIC TOXICITY TEST PERFORMED WITH *Ceriodaphnia dubia* ON
PRODUCT 5-AP

QC Test Number: TN-95-271

Test Initiation: 1455, 18 April 1995

Test Termination: 1500, 24 April 1995

Test Conc, ppm	% Survival 48 hrs	Mean Young Production
Control	100	24.7 (± 3.4)
8.7	100	27.4 (± 3.5)
32	100	24.0 (± 2.8)
75	100	12.2(± 4.9) ^(a)
180	60	--- (b)
420	0	--- (b)

NOEC (ppm product): 32

LOEC (ppm product): 75

ChV (ppm product): 49

IC25 (ppm product): 48.4

95 percent confidence limits (42.6 - 55.3)

(a) Significantly different from the control ($P=0.05$) indicating an adverse effect.

(b) Treatments which have no surviving organisms or have significant mortality are not statistically analyzed for growth or reproduction, per EPA guidance.

The Pimephales promelas acute toxicity test was terminated after 96 hours of exposure to 5-AP with 100 percent control survival. The 32, 75, 180, and 420 ppm concentrations also exhibited 100 percent survival, but the 1000 ppm had 20 percent survival. The LC50 value calculated from the survival data was 763.6 ppm product. These results are summarized in Table A-5.

Table A-5
RESULTS OF ACUTE TOXICITY TEST WITH *Pimephales promelas* ON PRODUCT 5-AP

QC Test Number: TN-95-270

Test Initiation: 1525, 18 April 1995

Test Termination: 1553, 22 April 1995

Test Conc, ppm	% Survival 48 hrs
Control	100
32	100
75	100
180	100
420	100
1000	20

LC50 Value (ppm product): 763.6 (420 - 1,000)

Statistical analysis of the survival data from the *P. promelas* short-term toxicity test showed a significant difference ($P=0.05$) from the control in the 1000 ppm concentration. The 1,000 ppm concentration at test termination had 40 percent survival compared to 85 percent control survival. There was no statistical difference ($P=0.05$) based on the growth data found between the control and the evaluated sample concentrations. (Those concentrations which have significant mortality are not statistically analyzed for growth, per EPA guidelines). Mean dry weight of the larvae exposed to the effluent treatments ranged from 0.90 to 1.04 mg/fry. The control organisms had a mean dry weight of 0.98 mg/fry. The NOEC was 420 ppm product. The LOEC and ChV were 1,000 and 648.1 ppm, respectively. The IC25 value was 562.3 ppm product. The results of this chronic test are summarized in Table A-6.

Table A-6
RESULTS OF CHRONIC TOXICITY TEST PERFORMED WITH *Pimephales promelas* ON
PRODUCT 5-AP

QC Test Number: TN-95-272

Test Initiation: 1600, 18 April 1995

Test Termination: 1630, 25 April 1995

Test Conc, ppm	% Survival 7 day	Mean Growth as mg/org (+ SD)
Control	85	0.98 (± 0.13)
32	85	1.04 (± 0.16)
75	68	1.02 (± 0.06)
180	90	0.92 (± 0.05)
420	93	0.90 (± 0.03)
1000	40(")	--- (b)

NOEC (ppm product): 420

LOEC (ppm product): 1000

ChV (ppm product): 648.1

IC25 (ppm product): 562.3

95 percent confidence limits (486.0 - 628.5)

(a) Significantly different from the control ($P=0.05$) indicating an adverse effect.

(b) Treatments which have no surviving organisms or have significant mortality are not statistically analyzed for growth or reproduction, per EPA guidance.

After 96 hours of exposure to the product 5-AP, the *Cyprinodon variegatus* acute toxicity test exhibited 100 percent survival in the laboratory control. At test termination, the 4,900 ppm concentration had 35 percent survival. The LC50 value was calculated as 4,218.3 ppm product. The results of this acute toxicity test utilizing *C. variegatus* are summarized in Table A-7.

Table A-7
RESULTS OF ACUTE TOXICITY TEST WITH *Cyprinodon variegatus* ON PRODUCT 5-AP

QC Test Number: TN-95-275

Test Initiation: 1730, 20 April 1995

Test Termination: 1703, 24 April 1995

Test Conc, ppm	% Survival 96 hrs
Control	100
155	95
370	100
870	100
2,100	100
4,900	35

LC50 Value (ppm product): 4,218.3(2,100 - 4,900)

After 7 days of exposure the highest concentration evaluated in the *C. variegatus* chronic toxicity test (4,900 ppm) was significantly affected ($P = 0.05$) compared to the control, as there were no surviving organisms. The laboratory control exhibited 100 percent survival with a mean dry weight of 0.81 mg/organism. When the growth data was statistically analyzed, both the 870 ppm and the 2,100 ppm concentrations were found to be statistically different ($P=0.05$) from the control. The adversely affected concentrations (870, 2100 ppm) had mean dry weights of 0.72 and 0.45 mg/organism, respectively. The NOEC was 370 ppm product and the LOEC was 870 ppm product. The ChV and IC25 values were 567.4 and 1,308.1 ppm product, respectively. The results of this *C. variegatus* chronic toxicity test are summarized in Table A-8.

Table A-8
RESULTS OF CHRONIC TOXICITY TEST PERFORMED WITH *Cyprinodon Variegatus*
ON PRODUCT 5-AP

QC Test Number: TN-95-276

Test Initiation: 1625, 20 April 1995

Test Termination: 1700, 27 April 1995

Test Conc, ppm	% Survival 7 day	Mean Growth as mg/org (+- SD)
Control	100	0.81(±0.01)
65	100	0.82 (±0.02)
155	100	0.85 (±0.05)
370	100	0.77 (±0.03)
870	100	0.72 (±0.07)(“)
2100	98	0.45 (±0.02)(“)
4900	0 (9)	--- (b)

NOEC (ppm product): 370

LOEC (ppm product): 870

ChV (ppm product): 567.4

IC25 (ppm product): 1,308.1

95 percent confidence limits (1, 106.8 -1,437.3)

(a) Significantly different from the control (P=0.05) indicating an adverse effect.

(b) Treatments which have no surviving organisms or have significant mortality are not statistically analyzed for growth or reproduction, per EPA guidance.

The 96-hour acute toxicity test utilizing *Mysidopsis bahia* exhibited 100 percent survival in the laboratory control. The 1000 ppm concentration had only 20 percent survival at test termination. The LC50 value was calculated based on this survival data and found to be 725.4 ppm product. These results are summarized in Table A-9.

Table A-9
RESULTS OF ACUTE TOXICITY TEST WITH *Mysidopsis bahia* ON PRODUCT 5-AP

QC Test Number: TN-95-273

Test Initiation: 1755, 20 April 1995

Test Termination: 1700, 24 April 1995

Test Conc, ppm	% Survival 96 hrs
Control	100
32	100
75	95
180	100
420	95
1000	20

LC50 Value (ppm product): 725.4 (616.7 to 884.6)

The *M. bahia* short-term chronic toxicity test had 95 percent control survival at test termination. The highest concentration tested (1,000 ppm) was found to be statistically different ($P=0.05$) from the control as it exhibited only 8 percent survival of the test organisms by Day 7. Based on EPA guidelines, treatments which have no surviving organisms, or have significant mortality, are not statistically analyzed for growth or reproduction. There was no statistical difference ($P=0.05$) based on the growth data found between the control and the evaluated sample concentrations. Mean dry weight of the organisms exposed to the effluent treatments ranged from 0.31 mg/fry to 0.39 mg/fry. The control organisms had a mean dry weight of 0.36 mg/organism. Statistical analysis of the reproductive potential also showed no statistical differences from the control. The NOEC was 420 ppm and the LOEC was 1,000 ppm. The ChV and IC25 were found to be 648.1 ppm product and 492.2 ppm product, respectively. The results of this chronic toxicity test are summarized in Table A-10.

Table A-10
RESULTS OF CHRONIC TOXICITY TEST PERFORMED WITH *Mysidopsis Bahia* ON
PRODUCT 5-AP

QC Test Number: TN-95-308

Test Initiation: 1145, 4 May 1995

Test Termination: 1400, 11 May 1995

Test Conc, ppm	% Survival 7 day	Mean Growth, mg/org	Reproductive Potential (% females with eggs)
Control	95	0.36 (± 0.05)	0.97 (± 0.09)
32	98	0.39 (± 0.07)	0.91 (± 0.19)
75	93	0.36 (± 0.05)	1.00 (± 0.00)
180	98	0.36 (± 0.04)	0.82 (± 0.2)
420	98	0.31 (± 0.04)	0.96 (± 0.12)
1000	8 (a)	--- (b)	--- (b)

NOEC (ppm product): 420

LOEC (ppm product): 1,000

ChV (ppm product): 648.1

IC25 (ppm product): 492.2

95 percent confidence limits (432.9 - 544.1)

(a) Significantly different from the control ($P=0.05$) indicating an adverse effect.

(b) Treatments which have no surviving organisms or have significant mortality are not statistically analyzed for growth or reproduction, per EPA guidance.

Table A-11 and Table A-12 provides a summary of the acute and chronic toxicity of 5-AP to selected freshwater and saltwater species evaluated as part of this study. 5-AP appears to be more toxic to invertebrate species as compared to fish species. *C. dubia* was the more sensitive freshwater species to 5-AP as well as the most sensitive species evaluated during this study. 5-AP was approximately 6.5 times more acutely toxic and, based on the chronic value, 13 times more toxic to *C. dubia* as compared to *P. promelas*. *P. promelas* and *M. bahia* appeared to be similarly sensitive to 5-AP with regards to acute toxicity, while *M. bahia* were somewhat more sensitive than *P. promelas* with respect to chronic effects. *M. bahia* were approximately 6 times more acutely sensitive and 2 to 3 times more chronically sensitive to 5-AP as compared to *C. variegatus*.

Table A-11
Summary of Acute Toxicity of 5-AP to Selected Freshwater and Saltwater Species

	Acute Toxicity, ppm	
Specie	48 hr LC50	96 hr. LC50
<i>Ceriodaphnia dubia</i>	116.2 (75-180)1")	----
<i>Pimephales promelas</i>	----	763.6 (420-1,000)
<i>Cyprinodon variegatus</i>	----	4,218.3 (2,100- 4,900)
<i>Mysidopsis bahia</i>	----	725.4 (616.7- 884.6)

Table A-12
Summary Of Chronic Toxicity Of 5-AP To Selected Freshwater and Saltwater Species

	Chronic Toxicity, ppm			
Specie	NOEC	LOEC	ChV	IC25
<i>Ceriodaphnia dubia</i>	32	75	49	48.4 (42.6- 55.3)
<i>Pimephales promelas</i>	420	1,000	648.1	562.3 (486.0- 628.5)
<i>Cyprinodon variegatus</i>	370	870	567.4	1,308.1 (1,106.8-1,437.3)
<i>Mysidopsis bahia</i>	180	420	275.0	492.2 (432.9- 544.1)

Acute and chronic toxicity data for other corrosion inhibiting chemicals are presented in Table A-13. However, it should be cautioned that a comprehensive literature search for available toxicity data on corrosion inhibitors was not performed for this study. 5-AP is considerably less acutely and chronically toxic to aquatic organisms than ammonia at normal reference pH and temperature values used in this study. It also appears that 5-AP is less acutely toxic to freshwater organisms than hydrazine. Based on the freshwater (*P. promelas*) and saltwater (*C. variegatus*) acute and chronic toxicity tests performed in this study, it appears that 5-AP is also less toxic than ethanolamine and morpholine given the available comparative toxicity data for fish. However, toxicity data on invertebrate species were not readily available for these compounds.

Table A-13
Acute And Chronic Toxicity Of Selected Chemicals Used As Corrosion Inhibitors

		LC50	Chronic	Reference
Ammonia (mg/L NH ₃)				
	<i>Ceriodaphnta dubia</i> (water flea)	1.96(c)		EPA 1985
	<i>Daphnia Magna</i> (water flea)	1.91(c)		EPA1985
	<i>Pimephaks promelas</i> (fathead minnow)	2.07(c)	.13-0.2(d)	EPA 1985
	<i>mysidopsis bahia</i> (opossum shrimp)	1.02(e)		EPA 1989
	<i>Cypronodon variegatus</i> (sheepshead minnow)	2.74(e)		EPA 1989
Ethanolamine (mg/L)				
	<i>Carassius auratus</i> (goldfish)	170(f)		Verschueren 1983
Hydrazine (mg/L)				
	<i>Poecilia reticulata</i> (guppy)	0.61(g)		Verschueren 1983
	<i>P. reticulata</i> (guppy)	3.85(h)		Verschueren 1983
Morpholine (mg/L)				
	<i>Lepomis Macrochirus</i> (bluegill)	350		Verschueren 1983
	<i>Menidia beryllina</i> (inland silverside)	400		Verschueren 1983

(a) The LC50 is the lethal concentration that causes 50 percent mortality in the test population. Typically cladocerans (water fleas) are expressed as 48-hour LC50's and the remaining species as 96-hour LC50 values.

- (b) The chronic value is the geometric mean of the no observable effect concentration (NOEC) and the lowest observable effect concentration (LOEC).
- (c) Reference Species Mean Acute Value for each species in the national database is calculated at a reference pH of 8 and temperature of 20°C due to the relationship that pH and temperature have on the percentage of unionized ammonia concentration. Un-ionized ammonia is the toxic fraction of the total ammonia concentration (See EPA 1984).
- (d) Range of fathead minnow chronic values for life-cycle and early life-cycle tests.
- (e) Species Mean Acute Value
- (f) Test performed at pH 10. I
- (g) Test performed in soft water at 22-24.5°C.
- (h) Test performed in hard water at 22-24.5°C.

In summary, based on these acute and chronic toxicity results, it appears that 5-AP would be less toxic than traditionally utilized corrosion inhibiting chemicals such as ammonia, ethanolamine, hydrazine, and morpholine. Thus, 5-AP would be an adequate substitution as a corrosion inhibiting chemical for power generating facilities. However, it should be cautioned that this study only evaluated acute and chronic toxicity to aquatic organisms and did not attempt to evaluate parameters necessary for the overall recommendation of the use of 5-AP as a corrosion inhibitor.

B

EXAMPLE 50-59 REPORT ON 5-AP

Proposed Activity:

This activity provides justification, from a safety standpoint, that the addition of 5 aminopentanol (5-AP) is acceptable as a chemical additive to the Condensate and Feedwater System for pH control in order to reduce formation of corrosion products which result in sludge formation when transported to the steam generators. During initial startup and operation, ammonia/hydrazine was added at Calvert Cliffs as an all volatile treatment (AVT) for condensate pH control. At that time, AVT was the industry standard for treatment of PWR secondary chemistry and ammonia/hydrazine were the pH additives of choice. In time, after extended periods of PWR operation, it became apparent that ammonia/hydrazine had various shortcomings for pH control. Ammonia is a very weak base at high temperatures (i.e. above 400 F) and is quite volatile at system temperatures relative to other chemical additives. These characteristics resulted in inadequate pH control in the condensate, ultimately leading to high corrosion rates in condensate systems and flow-assisted corrosion in wet-steam piping. To address these inherent problems, ammonia was replaced with the less volatile pH additive morpholine. This change was made because morpholine substantially reduces the corrosion product generation which results in sludge formation when transported to the steam generators.

Although morpholine proved effective in reducing corrosion product transport, the high molecular weight and low basicity require high dosing rates in order to achieve sufficiently high pH levels to reduce corrosion. This has the negative effect on plant economics due to the high morpholine usage rates and the frequent condensate demineralizer resin regeneration. Morpholine also undergoes thermal decomposition at PWR condensate and feedwater operating temperatures, generating small quantities of organic breakdown products. Some fouling and/or loss of condensate polisher resin capacity has also been observed at a number of plants including Calvert Cliffs. As a result, Calvert Cliffs has limited use of morpholine since 1992 and has also used ammonia / hydrazine for pH control.

Based on these considerations, BGE approved use of monoethanolamine (ETA) in 1994 for Units 1 and 2. It was expected that compared with morpholine, ETA would provide greater corrosion protection in wet steam areas, extend polisher run lengths due to lower concentrations in the condensate and result in significantly lower product usage. Although these predictions were largely confirmed, some fouling of the polisher resin, whose cause has not yet been identified, was observed. As a result, Calvert Cliffs

switched back to ammonia/hydrazine for Unit 1 after a performance test was completed. Calvert Cliffs recently began feeding ETA to Unit 2 and thus far has observed the benefits which were seen during the Unit 1 test without the resin fouling which also occurred.

Reason for Activity:

The purpose of this activity is to allow use of 5-AP as an alternative chemical for pH control in the Condensate and Feedwater Systems and the Steam Generators. The basis for considering 5-AP is improved volatility characteristics which should result in greater corrosion protection in wet steam areas, potentially lower product usage and lower concentrations in the condensate resulting in increased condensate polisher run lengths and fewer regenerations.

Currently, the Calvert Cliffs UFSAR Section 10.2.2 states that chemicals (hydrazine and ammonia or morpholine) are added to the condensate flow for oxygen scavenging and pH control. Since this Safety Evaluation proposes to allow the use of 5-AP, the UFSAR is affected and must be revised as necessary.

Function(s) of Affected Systems, Structures, or Components:

The affected SSCs include the Chemical Addition System equipment currently in use for adding morpholine, hydrazine, ammonia or ETA for secondary plant system pH control and the components of the Condensate and Feedwater System that will be treated by 5-AP including the steam generators, steam turbines and condensers. The Chemical Addition System is being modified in response to an INPO Commitment, which is unrelated to the subject MCR and Safety Evaluation and is covered under a separate FCR. As discussed in this FCR, this activity is essentially a component upgrade which does not introduce any new system interactions.

The function of the secondary plant chemistry control equipment is to maximize the lifetime of the steam generators and other secondary plant piping and components by minimizing corrosion mechanisms. The secondary plant chemistry control additives do not provide a safety function and the chemical addition equipment affected by this activity are classified as non-safety related components in the Calvert Cliffs Quality-List since they perform no safety related functions. However, secondary plant chemistry is important for maintaining the steam generators and has a direct bearing on the useful life of the remainder of the secondary plant equipment.

SAR Sections Reviewed:

UFSAR Sections 1.2, 1.4, 4.1.3, 9.3, 9.6, 10.1, 10.2, 10.5, 10A.1, 10A.4, and Chapter 14 and associated UFSAR Tables and Figures.

1. *The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety previously evaluated in the SAR is not increased.*

___ Yes ☒ No *May the probability of occurrence of a malfunction of equipment important to safety previously evaluated in the SAR be increased?*

Probability of Malfunction:

A malfunction of the secondary system related to safety could occur due to corrosion of the Alloy 600 steam generator tubes, feedwater piping, or main steam piping. Any slow developing corrosion or material degradation which is typically observed in operating PWRs from corrosion product transport data or equipment performance is monitored and the appropriate maintenance can be performed during refueling and other planned outages. The probability of malfunctions from rapid corrosion or degradation of these systems caused by use of 5-AP is not increased and is very remote.

The decomposition products of morpholine, ETA, and 5-AP are predominantly acetic and formic acids. Since ETA and morpholine are used at higher dosages than 5-AP will be used, the expected amount of acetic and formic acids from 5-AP decomposition is expected to be less than that seen with ETA or morpholine. Acetic and formic acids have no deleterious affects on Alloy 600 in the concentrations found in PWR secondary systems. The Intergranular Stress Corrosion Cracking/Intergranular Attack (IGSCC/IGA) rate of Alloy 600 steam generator tubing is strongly dependent on crevice pH. As long as the crevice pH is maintained at the current near neutral value, the IGSCC/IGA rate will be unaffected. Based on these considerations, it is concluded that the probability of failure of Alloy 600 steam generator tubes or other metallic components in the presence of 5-AP is not increased.

The impact of amines on non-metallic materials such as seals and gaskets has also recently been evaluated by EPRI. The following amines were evaluated in addition to ETA and morpholine:

1,3-diaminopropane

1,2-diaminoethane

3-methoxypropylamine

piperazine

The evaluations were performed by immersing specimens of the various materials in test solutions containing 1, 10 and 50 wt% amine and are therefore difficult to

extrapolate to condensate / feedwater conditions in which the amine concentration would typically be in the range of 1 to 10 ppm. However, even under these extreme conditions only one material (Viton) was visibly degraded and only when the amine concentration was increased to 50 wt%. There is no evidence that any of the above amines would initiate a failure of synthetic materials in the secondary system under actual service conditions. Since the above list, although small, covers a broad range of amines, it is also very unlikely that any other amines could initiate a failure of synthetic materials under actual service conditions. As discussed in the MCR, 5-AP has been used for a number of years at Wylfa and no adverse impact on synthetic materials was reported.

☐ Yes ☒ No *May the consequences of a malfunction of equipment important to safety previously evaluated in the SAR be increased?*

Consequences of Malfunction:

No equipment is being installed or modified as a result of this change. The scope of this safety evaluation is limited to the change from morpholine, ammonia or ETA to 5-AP for pH control of the Calvert Cliffs secondary systems. There are no new malfunctions postulated with this change since, as discussed above, 5-AP is not expected to have deleterious effects on Feedwater or Main Steam piping, Alloy 600 steam generator tubes or synthetic materials used for seals and gaskets. Since there are no new malfunctions, the existing analyzed malfunctions and associated consequences are unchanged. The only potential effects associated with 5-AP would be to impact the useful life of the various components of the secondary plant systems due to the effectiveness in controlling corrosion rates. The effectiveness of 5-AP and any negative side effects associated with its use are enveloped by morpholine, ammonia and ETA which are already approved chemical additives for Calvert Cliffs secondary plant system pH control. The offsite dose consequences resulting from any postulated malfunctions will not be affected in any way by the subject activity. Therefore, based on the above discussion, the consequences due to malfunctions previously analyzed in the SAR are unaffected by the subject activity.

☐ Yes ☒ No *May the probability of occurrence of an accident previously evaluated in the SAR be increased?*

Probability of Accident:

Previously evaluated accidents which need to be considered as part of this activity include steam generator tube rupture (SGTR) event, feedline break (FLB) event, and main steam line break (MSLB) event. The probability of a SGTR event is not increased based on the fact that 5-AP is expected to reduce steam generator sludge accumulation as a result of reduced corrosion product transport. In addition, steam generator tube

wear/corrosion performance is closely monitored and inspected during each refueling outage and any adverse trends will be noted and corrective action taken as appropriate. Also, the probability of a FLB is not increased since the predominant mechanism which could initiate a FLB, erosion/corrosion, is a function of pH rather than the specific amine used for pH control. The pH will continue to be maintained in accordance with the current Plant Chemistry limits and the EPRI guidelines which apply to erosion/corrosion. There have been no reports of a FLB attributed to ETA at an operating PWR in the US or attributed to AMP or 5-AP which have been used in the Wylfa power station for several years. Similarly, the probability of a MSLB is not increased since the predominant mechanism would be erosion-corrosion and 5-AP would provide similar or better pH protection in wet steam areas. Therefore, the subject activity will not increase the probability of occurrence of an accident previously evaluated in the SAR.

___ Yes ☒ No *May the consequences of an accident previously evaluated in the SAR be increased?*

Consequences of Accident:

The consequences of a SGTR, a MSLB, or a FLB event are not in any way affected by the subject activity. There would be no change to the plant or operator response to any of these accidents. The subject activity will not affect any of the accident assumptions, accident sequences of events, operator information, or plant/operator responses to any of the accidents (including the SGTR, FLB and MSLB events) previously evaluated in the SAR. The offsite dose consequences resulting from any of the postulated events that involve radiological releases analyzed in Chapter 14 of the UFSAR would not be affected in any way as a result of replacing ammonia, morpholine or ETA with 5-AP. Therefore, it is concluded that the consequences of any of the accidents previously evaluated in the SAR will not be increased as a result of the subject activity.

2. *The possibility for an accident or malfunction of a different type than any evaluated previously in the SAR is not created.*

___ Yes ☒ No *May the possibility of a malfunction of a different type than any previously evaluated in the SAR be created?*

Possibility of New Malfunction:

There is no new equipment being added or modified as a result of this activity. The use of 5-AP as a pH control additive to the secondary cycle has been shown in some cases to reduce corrosion product transport which results in less sludge formation in the steam generator. Any negative effects associated with the use of 5-AP will be enveloped by the ammonia, morpholine and ETA chemical use which are currently approved chemical additives for secondary cycle pH control. There are no new spatial

or systems interactions as a result of the subject activity. As such, any failures for the steam generators, feedwater piping or main steam piping pressure boundary would not constitute a new malfunction of a different type than previously evaluated. Therefore, it is concluded that possibility of a malfunction not previously analyzed in the SAR is not created.

___ Yes ☒ No *May the possibility of an accident of a different type than any previously evaluated in the SAR be created?*

Possibility of New Accident:

As discussed previously, there is no new equipment being added as a result of this activity. 5-AP functions in essentially the same manner as ammonia, morpholine and ETA, produces similar degradation products (i.e. acetic and formic acid) and should provide equal or better corrosion protection in the secondary system. As such, any failures for the steam generators, feedwater piping or main steam piping pressure boundary would not constitute a new accident of a different type than previously evaluated. 5-AP is of relatively low volatility, low acute toxicity and low flammability at ambient temperatures and therefore poses a smaller risk than the presently used chemicals (ammonia, hydrazine, morpholine and ETA). Therefore, the new activity poses no increased possibility of a new accident.

3. *The margin of safety as defined in the basis for any Technical Specification is not reduced.*

___ Yes ☒ No *Will the margin of safety as defined in the basis for any Technical Specification be reduced?*

<u>Bases</u>	<u>Discussion of why the margin of safety is not reduced</u>
--------------	--

Secondary water chemistry and/or the use of chemical additives or chemical controls for the secondary cycle is not addressed in the Calvert Cliffs Technical Specifications. Therefore, the margin of safety as defined in the Bases for any of the Technical Specifications is not changed in any way as a result of the subject activity.

Summary: (For NRC Report, provide a brief overview)

The scope of this activity is limited to an assessment of 5 amino-pentanol (5-AP) which is expected to be used at Calvert Cliffs in a trial demonstration in late 1995 or early 1996. The purpose of this Safety Evaluation is to demonstrate that 5-AP would not compromise the integrity of the secondary system which could potentially impact plant safety. To date, ETA has been used at a number of operating PWRs in the US and AMP and 5-AP have been used at the Wylfa power station in the UK without deleterious effects on plant materials. EPRI studies with several alternative amines have

demonstrated that physical degradation of synthetic materials used for seals and gaskets does not occur except at extremely high concentrations (i.e. 50 wt%) several orders of magnitude greater than those which would be maintained in the secondary system. Although the EPRI work and actual plant experience has only included a small number of amines, the results should be applicable to 5-AP based on the expected application at similar, low ppm dosages and similar decomposition products (e.g. acetic and formic acids) in the steam generator. Therefore, it is concluded that any differences in corrosion or material degradation rates such as those which can be observed in corrosion product transport studies, pose an economic rather than a safety issue. It is also, therefore concluded, that use of 5-AP will not increase the probability of an accident or the consequences of a malfunction.

The existing Chemical Addition System can be used to feed 5-AP into the secondary system, therefore there are no new system interactions. Also, 5-AP is of relatively low volatility, low acute toxicity, and low flammability at ambient temperatures and poses a smaller risk than the presently used chemicals (ammonia, morpholine, hydrazine and ETA). Therefore, it is further concluded that 5-AP could not cause an accident of a different type from those which have already been evaluated. Since there is no effect on offsite dose consequences due to use of 5-AP and the margin of safety, as defined in the Technical Specifications, is not affected, there are no unreviewed safety questions associated with the subject activity defined in this Safety Evaluation.

Currently, the Calvert Cliffs UFSAR states that chemicals (hydrazine and ammonia or morpholine) are added to the condensate flow for oxygen scavenging and pH control. Since this Safety Evaluation proposes to allow the use of 5-AP for pH control, a UFSAR change is necessary and is included as part of the scope of this activity.