

Buffer Intensity of Ammonia and MPA in Water-Steam Cycle of PWRs

In H. Rhee^{1*} and Hyun Kyoung Ahn¹

¹Department of Environmental Engineering, Soonchunhyang University

가압경수로 원전 물-증기 순환영역에서 암모니아와 MPA의 완충세기

이인형^{1*}, 안현경¹

¹순천향대학교 에너지환경공학과

Abstract Amines, ammonia or 3-methoxypropylamine (MPA), are used to maintain the optimized pH for the prevention of corrosion in the secondary side of Pressurized Water Reactors (PWRs). They are differently dissociated as a function of temperature which is not same in each location of the water-steam cycle. pH at the operation temperature depends on temperature of fluid and equilibrium constants of water and amines. Thus, every amine provides the different pH in the entire secondary side so that pH is not only the sufficient parameter in corrosion control. The secondary parameter, i.e., buffer intensity, is the ability to maintain a stable pH when H^+ are added or removed due to the ingress of impurities or the reaction of corrosion.

The buffer intensity is necessary to provide the selection criteria for the best pH control agent for secondary side and the basic understanding of the reason why the flow-accelerated corrosion(FAC) rate may demonstrate the bell-shape curve over temperature. The buffer intensities of ammonia and MPA were reviewed over the entire operation temperature of PWRs. The sufficient buffer intensity is provided for the inhibition of corrosion by ammonia in low temperature (25~100°C) and by DMA in high temperature (150~250°C). In terms of buffer intensity, i) the best pH control agent is an amine with $pK_a(T)$ range of $pH(T) - 1 \leq pK_a(T) \leq pH(T) + 0.5$ and ii) the amine solution should have sufficient buffer intensity, β to inhibit corrosion, and iii) FAC rate may be maximum at the temperature, where β_B/β ratio is lowest.

요약 아민(암모니아 또는 MPA)은 가압경수로 원전 2차측 부식을 방지하는 최적 pH를 유지하기 위해 사용되고, 온도가 동일하게 유지되지 않는 물-증기 순환 영역에서 모든 아민은 평형상수에 따라 2차측에서 서로 다른 pH를 나타낸다. 부식 제어에서 pH는 유일한 인자가 아니므로 두 번째 변수, 즉 불순물의 유입 또는 부식 반응으로 인해 H^+ 가 추가되거나 제거 되었을 때 안정된 pH를 지속하는 능력이 완충세기의 고려가 필요하다.

온도를 고려한 완충세기는 2차측 최적 pH 제어제 선정과 유체가속부식의 특징을 기본적으로 이해할 수 있도록 한다. PWRs의 전체 운전범위에서 암모니아와 MPA의 완충세기를 조사하였다. 낮은 온도(25~100°C)에서는 암모니아 그리고 높은 온도(150~250°C)에서는 MPA가 부식 억제를 위한 충분한 완충세기를 나타내었다. 완충세기 측면에서, i) 최적 pH 제어제 pH 범위는 $pH(T) - 1 \leq pK_a(T) \leq pH(T) + 0.5$, ii) 아민 용액은 부식 억제를 위해 충분한 완충세기(β)를 가져야 하고, iii) 최대 유체가속부식은 β_B/β 비율이 최저인 온도에서 최대를 나타낸다.

Key Words : PWR, Amine, Ammonia, Ethanolamine, Buffer Intensity

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*Corresponding Author : In H. Rhee(ihrhee@sch.ac.kr)

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1. Introduction

The variety of amines are added into the water-steam cycle in the secondary side of PWRs (Pressurized Water Reactors) which plays an important role in generating the electricity in order to prevent the metallic materials from being dissolved [1]. Water and amine are recycled via the conversion between liquid and gas phases in the temperature range of 50 to 300°C in a few minutes. The aqueous solution of amine is evaporated in boiler or steam generator and most of steam is liquidized in the condenser, while the part of steam is fed back to increase the solution temperature. The fluid temperature is not the same at each location of water-steam cycle so that the metallic materials are differently degraded.

Corrosion has been interpreted in terms of the solubility of metal oxides, which in turn depends on pH of amine solutions [2,3]. Even if other chemical properties such as adsorption and complexation are not involved, the corrosion reaction can be initiated in the metal-oxide interface. Under this localized circumstances, OH⁻ may be partially consumed and slowly made up so that the dissolution of oxides proceeds continuously. The mass transport through the fluid boundary layer is known to be the rate-determining step [2,4,5]. But the metal may stop from being released from the solid phase if pH can be hardly changed. That is, the resisting power to change the pH, i.e., buffer intensity, is an important factor to control corrosion, in addition to pH.

The objectives of the study were to review the buffer intensity of ammonia and MPA solutions at each location in the water-steam cycle and to provide the selection criteria for the best pH control agent, and the reason why the FAC rate may demonstrate the bell-shape curve over temperature.

2. Buffer Intensity vs. Corrosion for Amine Solutions

2.1 Buffer Intensity

Alkalinity in the basic environment is the sum of OH⁻ and basic form of amine and is conservative properties of the solution (extensive property). The buffer intensity is

the strength to resist the pH change when H⁺ or OH⁻ is added to the solution (intensive property), i.e., the resisting capacity of the solution to maintain pH. Thus, the buffer intensity, rather than alkalinity, is a more important factor affecting corrosion in which the optimum pH should be kept to protect the metal [3]. Since corrosion may be described as oxide solubility in terms of H⁺ which is a variable in function of the buffer intensity, corrosion can be expressed as the buffer intensity. Alkalinity is a measure of the capacity of a solution to neutralize strong acid (ANC) and can be expressed by integral of buffer intensity over pH of from the solution pH to 4.5 or others.

The buffer intensity can be calculated by differentiating the equation of alkalinity and divided into two parts contributed by water and amine only. Alkalinity of amine (B) solution is the same as the total concentration of amine regardless of temperature because the charge balance equation is related to alkalinity. The maximum buffer intensity of amine is at pH=pK_a where the concentration of the neutral form of amine, [B], is the same as that of the positive form of amine, [BH⁺]. β_B is a bell-shape curve and is known to be high at pK_a - 0.5 ≤ pH ≤ pK_a +0.5. The buffer intensity of water exponentially increases from neutral to moderate to strong base or acid. β_{H₂O} is a U-shaped curve and is minimum at neutral pH, high at the weak base and acidic condition, and highest at pH=0 and 14 regardless of solvent present in the water.

○ Alkalinity = same as total concentration of amine

$$\begin{aligned} C_B = \text{ANC} &= \int_{\text{pH}}^{4.5} \beta \, \text{d pH} = [\text{B}] + [\text{OH}^-] - [\text{H}^+] \\ &= [\text{B}] + [\text{BH}^+] \\ &= \text{total concentration of amine} \end{aligned}$$

Charge balance : [BH⁺] + [H⁺] = [OH⁻]

$$\rightarrow [\text{BH}^+] = [\text{OH}^-] - [\text{H}^+]$$

○ Buffer Intensity

$$\begin{aligned} \beta &= \frac{\text{d}C_B}{\text{d pH}} \\ &= 2.3 \left\{ \frac{[\text{H}^+] K_a}{[\text{H}^+] + K_a} B_T + [\text{OH}^-] + [\text{H}^+] \right\} \end{aligned}$$

$$= 2.3 \left\{ \frac{[B][BH^+]}{[BH^+] + [B]} + [OH^-] + [H^+] \right\}$$

$$\beta_B = 2.3 \frac{[B][BH^+]}{[BH^+] + [B]} ;$$

$$\text{maximum } \beta_B \text{ at pH} = pK_a + \log \frac{[B]}{[BH^+]}$$

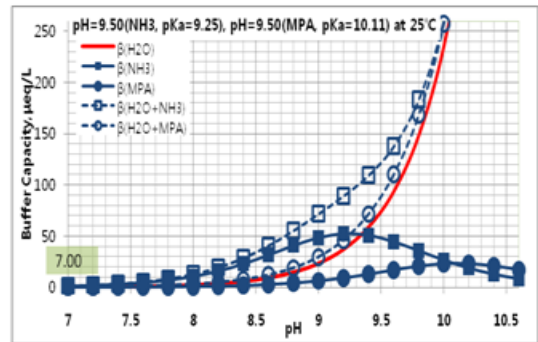
$$\beta_{H_2O} = 2.3([OH^-] + [H^+])$$

where B, K_a , and K_w represent amine, amine dissociation constant, and water dissociation constant, respectively and $[BH^+]$ and $[B]$ are the concentrations for the respective positive and neutral forms of amine.

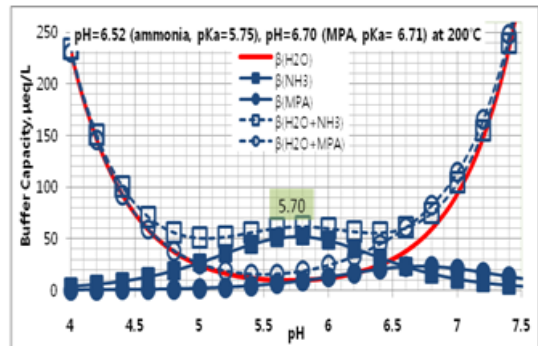
2.2 Buffer Intensity of Weakly Basic Solution at High Temperature

pH for the maximum buffer intensity of ammonia and 3-MPA at 25, 200, and 300°C are not the same because $pK_a(T)$ depends on temperature, as shown in Figure 1 [6,7]. In the low temperature of below 200°C, the solution buffer intensity of ammonia is greater than that of 3-MPA due to the bigger contribution of ammonia but, vice versa above 200°C. The solution pH for ammonia, is 9.5 at 25°C ($pK_a=9.25$), 6.52 at 200°C ($pK_a=5.75$), and 5.99 at 300°C ($pK_a=4.64$) and the solution pH for 3-MPA, is 9.5 at 25°C ($pK_a=10.11$), 6.70 at 200°C ($pK_a=6.71$), and 6.27 at 300°C ($pK_a=5.71$). In addition, $pH(T)-pK_a(T)$ for ammonia, is 0.25 at 25°C, 0.77 at 200°C, 1.35 at 300°C and $pH(T)-pK_a(T)$ for 3-MPA is -0.61 at 25°C, -0.01 at 200°C, -0.44 at 300°C. $pK_a(T)$ of ammonia is greater than that of $pK_w(T)$ at the temperature of <200°C, similar to $pK_w(T)$ around 200°C, and less than that of $pK_w(T)$ at the temperature of >200°C. $pK_a(T)$ of 3-MPA is still less than that of $pK_w(T)$ up to the temperature of 300°C and the difference between $pH(T)-pK_a(T)$ is within +0.5 at >200°C. Ammonia provides some contribution to the solution buffer intensity below 200°C, where pK_a of ammonia is less than $pH(T)-1$ ($pK_a(T)>pH(T)+1$). However, the buffer intensity of 3-MPA is significant in the condition of $pK_a(T)<pH(T)+0.5$ above 200°C. In conclusion, there is no amine with $pK_a(T)=pH(T)$ to provide the maximum contribution to the solution buffer in the temperature range of 25 ~ 300°C (no ideal pH control agent for PWR secondary side). Thus, the best pH control agent should

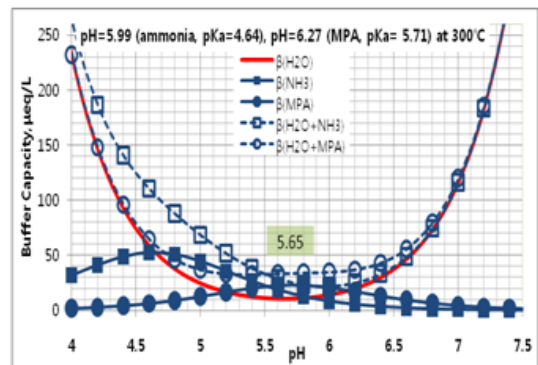
be chosen of which pK_a is greater than $pH(T)-1$ and less than $pH(T)+0.5$, that is, $pH(T)-1 \leq pK_a(T) \leq pH(T)+0.5$.



(a)



(b)



(c)

[Fig. 1] Buffer Intensity of Ammonia and 3-MPA at (a) 25°C, (b) 200°C, (c) 300°C

2.3 Best Amine in terms of Buffer Intensity

Buffer intensity may be too low for corrosion to occur in the particular metal surface where OH is locally consumed and not sufficiently supplied due to its slow mass transfer. However, corrosion under this circumstance

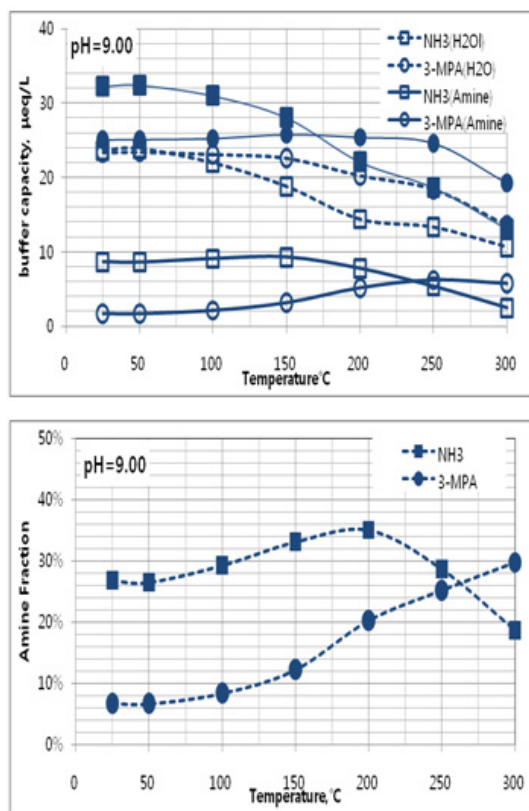
can be relatively reduced by the increased mass transfer of OH^- or amine species when the concentration of amine is high and its pH is in the region for the high buffer capacity. The solution buffer intensity should be increased to inhibit corrosion by increasing pH which in turn raises the buffer intensity of water alone or by adding the proper amine which thereby enhances the buffer intensity of amine alone, given that pH cannot be elevated due to the degradation of other components in system. In conclusion, corrosion may be generally and locally protected by choosing the amine with higher β and β_B at optimum pH. pK_a of ideal amine is the same as $\text{pH}(T)$ to ensure the maximum β and β over the temperature range of concern and $\text{pK}_a(T)$ of best or optimized amine should be in the range of $\text{pH}(T)-1 \leq \text{pK}_a(T) \leq \text{pH}(T)+0.5$. Since iron is often dumped into steam generator (SG), an amine with pK_a suitable to the low temperature region such as low-temperature feedwater (FW), moisture separator and reheater (MSR), de-aerator, and condensate may be preferred as best pH control agent.

2.4 Best Amine in terms of β_B/β or $\beta_{\text{H}_2\text{O}}/\beta$ ratios

The buffer intensity of amine solution can be composed of two parts: portion of amine and water alone. As shown in Figure 2, the solutions of ammonia and 3-MPA with $\text{pH}(25^\circ\text{C})=9.00$ have the different values from 25 to 300°C for β , β_B , and $\beta_{\text{H}_2\text{O}}$ (except for $\beta_{\text{H}_2\text{O}}$ at 25°C). For ammonia solution, the region of temperature over which β and $\beta_{\text{H}_2\text{O}}$ diminish abruptly is $100 \sim 300^\circ\text{C}$ and that which β_B decreases is 150°C . For 3-MPA solution, the region of temperature over which β diminishes is $>250^\circ\text{C}$ and that which $\beta_{\text{H}_2\text{O}}$ reduces is $>100^\circ\text{C}$. But β_B for 3-MPA rises at $100 \sim 250^\circ\text{C}$. β for both amine solutions decreases at $>100^\circ\text{C}$ mainly due to $\beta_{\text{H}_2\text{O}}$ and $\beta_{\text{H}_2\text{O}} > \beta_B$. β_B/β ratio is maximal at $\sim 180^\circ\text{C}$ for ammonia solution and is rising $>100^\circ\text{C}$ for 3-MPA solution.

The number of OH^- in the ammonia solution decreases with increasing temperature and the contribution of OH^- concentration to the solution buffer intensity is minimal at $\sim 180^\circ\text{C}$. In the localized area of this temperature in the oxide-water interface, OH^- may be consumed to form $\text{M}(\text{OH})_n^{+(n-1)}$ in corrosion reaction so that the solution pH

diminishes. pH in the interface boundary may continue to fall down if OH^- cannot be timely fed through the mass transfer of OH^- or the production of OH^- from amine. The resistance of amine solution to change pH may be reduced at $\sim 180^\circ\text{C}$ where corrosion occurs. In conclusion, amine solution should have the minimum buffer intensity to achieve the corrosion inhibition, while the resisting power to pH change in the metal-water interface may be lowest at the highest ratio of β_B to β (minimum $\beta_{\text{H}_2\text{O}}/\beta$ ratio) over the temperature of $100 \sim 250^\circ\text{C}$.



[Fig. 2] Buffer Intensity of ammonia and 3-MPA as a function of temperature at $\text{pH}=9$: β , β_B , $\beta_{\text{H}_2\text{O}}$, β_B/β .

2.5 Effect of Amine Nature and Temperature on FAC Rate in terms of Buffer Intensity

The flow-accelerated corrosion (FAC) rate of carbon and low alloy steels has been investigated in terms of the nature of amine, the at-temperature pH and temperature under the one-phase flow conditions [7,8,9,10]. The loop and rotating disc tests were concluded that

- The FAC rate decreases as at-temperature pH increases.
- The FAC rate varies with temperature. The effect of temperature on the FAC rate is demonstrated by the bell-shaped curve. The temperatures of maximum FAC rate were $\sim 150^{\circ}\text{C}$ and $\sim 180^{\circ}\text{C}$, and $\sim 225^{\circ}\text{C}$ obtained by the loop and rotating disc tests.

3. Summary and Conclusions

Ammonia and MPA are reviewed in terms of buffer intensity to provide the selection criteria for the best pH control agent for secondary side since there is no amine with $\text{pK}_a(\text{T})=\text{pH}(\text{T})$ and the basic understanding of the reason why the FAC rate may demonstrate the bell-shape curve over temperature. The sufficient buffer intensity is provided for the inhibition of corrosion by ammonia in low temperature ($25 \sim 100^{\circ}\text{C}$) and DMA in high temperature ($150 \sim 250^{\circ}\text{C}$).

In conclusion, i) the best pH control agent is an amine with $\text{pK}_a(\text{T})$ range of $\text{pH}(\text{T}) - 1 \leq \text{pK}_a(\text{T}) \leq \text{pH}(\text{T}) + 0.5$ and ii) the amine solution should have sufficient buffer intensity, β , to inhibit corrosion, and iii) FAC rate may be maximum at the temperature, where $\beta_{\text{H}_2\text{O}}/\beta$ ratio is highest. The critical temperature in the bell-shape curve, calculated using dissociation constants of water and amines, is usually between 150°C and 250°C depending upon the solution pH and the type of amine. It is shifted to the higher value from 150°C to 250°C and finally disappear, as $\text{pH}(\text{T})$ of the solution and $\text{pK}_a(\text{T})$ of amine are to be higher.

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In H. Rhee

[Regular member]



- Aug. 1990 : Cornell University, civil and environmental engineering, MS
- Nov. 1996 : Carnegie Mellon University, civil and environmental engineering, PhD

<Research Interests>

Water Chemistry, Waste Water Treatment

Hyun Kyong Ahn

[Regular member]



- Feb. 2003 : Soonchunhyang University, environmental engineering, MS
- Feb. 2003 ~ current : Soonchunhyang University, environmental engineering, Ph.D. candidate

<Research Interests>

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