

Effect of pH and Temperature on Condensation and dissolution

IN HYOUNG RHEE, HYUN KYOUNG AHN, HYUN JUN JUNG

Department of Environmental Engineering

Soonchunhyang University

646 Eupnae-ri Shinchang-myeon Asan-si Chungcheongnam-do 336-745

Korea

Abstract: The Korean PWR plants replaced ammonia with ethanolamine as a secondary side pH control agent to minimize the sludge production in the moisture drain and heater drain systems and the sludge transport into steam generator. The increase of pH in the secondary system water decreased the sludge deposit in steam generator and prolonged the runtime of ion exchange beds in the condensate polishing plant. The extended lifetime of ion exchange resin led to the reduction in the amount of regenerant used and regeneration waste produced. However the concentration of chemical oxygen demand and nitrogen in the regeneration waste was elevated due to the physico-chemical property of ethanolamine.

The PWR nuclear power plants did not meet intermittently the criterion of release allowance for contaminants and the standard of discharge water quality for wastewater, especially for COD and N. Before the adoption of ethanolamine, the wastewater did not contain the prevailing sources except ammonia so that the existing wastewater treatment plant does not need to include the removal processes. The former pH control agent, ammonia, did not remain in the liquid phase because it is highly volatile. The discharge standard for wastewater is supposed to be strict for COD and T-N: 30 and 60 ppm until 2007, 20 and 40 ppm from 2008 to 2012, 10 and 20 ppm after 2013m respectively. One ppm of ethanolamine is tantamount to 2.36 ppm of COD and 0.23 ppm of N. The treatment technology may be classified as physical, chemical and biological ways. Ethanolamine can be stripped into gas as a function of temperature and solution pH, and oxidized into carbon dioxide and nitrogen gases by electro-chemical and biological oxidation. The electrolysis was hard to meet the regulation standard due to the possible production of nitrate and was expensive to achieve the complete breakdown. Therefore the combined physical, chemical, and biological process may be the best way to meet the discharge standard of COD and N.

Key-World: Water treatment, Chemical Oxygen Demand, Nitrogen, Ammonia, Ethanolamine, Combined process

1. Introduction

All volatile treatment in nuclear power plants, instead of phosphate treatment, was adopted to reduce the fatigue and denting of the steam generator U-tube by inhibiting the precipitation and deposition of sludge. Because ammonia as a first secondary side pH control agent was so volatile that corrosion occurred in the moisture drain and heater drain systems due to low pH, corrosion products were transported into steam generator (SG) and accumulated in U-tube and tubesheet. The pressurized water reactor (PWR) plants all over the world replaced ammonia with ethanolamine (ETA) to minimize the sludge production in the moisture drain and heater drain systems and the sludge transport into steam generator. The increase of pH in the secondary system water decreased the sludge deposit in steam generator and prolonged the runtime of ion exchange beds in the condensate polishing plant. The extended lifetime of ion exchange resin led to the reduction in the amount of regenerant used and regeneration waste produced. However the concentration of chemical oxygen demand and nitrogen in the regeneration waste was elevated due to the physico-chemical property of ethanolamine.

The PWR nuclear power plants in Korea did not meet intermittently the criterion of release allowance for contaminants and the standard of discharge water quality for wastewater, especially for COD and N. Before the adoption of ethanolamine, the wastewater did not contain the prevailing sources except ammonia so that the existing wastewater treatment plant does not need to include the removal processes. The former pH control agent, ammonia, did not remain in the liquid phase because it is highly

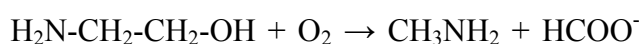
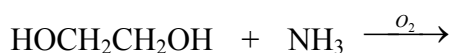
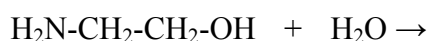
volatile. The discharge standard for wastewater is supposed to be strict for COD and T-N: 30 and 60 ppm until 2007, 20 and 40 ppm from 2008 to 2012, 10 and 20 ppm after 2013 respectively. One ppm of ethanolamine is tantamount to 2.36 ppm of COD and 0.23 ppm of N.

The objective of this study was to review the physico-chemical property of ethanolamine and its treatment technology. The characteristic of volatility and ion exchange were investigated and the combined treatment method was proposed.

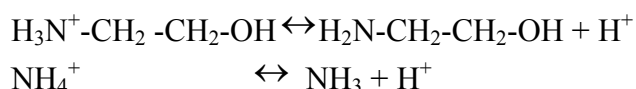
2. Physico-Chemical Properties of ETA

Compared with ammonia, ETA is more basic due to the high pKa, easy to be handled due to the high boiling point, less diffusive due to the high viscosity, more dissociative due to the high dielectric constant, and more comparable to the polar chemical due to the high dipole moment as shown Table 1.

ETA can be broken down formate, acetate and glycolate and the degree of thermal decomposition is less than 2% per hour at 270 .



ETA and ammonia are weak basic. The degree of their dissociation is a function of temperature and the reactions are as follows.



Volatility can be expressed as relative volatility (RV), distribution ratio (K_D), and Henry constant (K_H) which are the ratios of molality in the vapor phase (M_s) to molality in the liquid phase (M_L), molality in the vapor phase to molality of undissociated species in the liquid phase, and molality in the liquid phase and partial pressure in the vapor pressure, respectively.

$$RV = \frac{M_s}{M_L} = \frac{\text{ppm}(\text{steam})}{\text{ppm}(\text{water})}$$

$$K_D = \frac{M_s}{\alpha_1 M_L} = \frac{RV \cdot M_L}{\alpha_1 M_L} = \frac{RV}{\alpha_1} = \frac{RV}{1 - \alpha_0}$$

$$K_H = \frac{M_L}{P}$$

As temperature rises, ETA is more volatile due to the increased relative volatility that the concentration in the vapor phase is elevated as shown Table 2.

3. Ion exchange Characteristics

When ion exchange resin in condensate polishing demineralizer is exhausted, cation and anion exchange resin is mainly present as ETA and chloride (or sulfate) forms, respectively. COD and T-N are

produced due to ETA as a result of regeneration of spent cation exchange resin with H_2SO_4 . Although the nitrogen in ETA can be oxidized into N_2 , NO_2^- and NO_3^- , the specific removal of ETA into CO_2 and N_2 is difficult to be practical. Thus alternative way may be the volume reduction of bulky wastewater by ion exchange. The recovery of ETA in the spent resin can be achieved by NaOH regeneration. As illustrated in Figures 1, 2 the regeneration efficiency is increased with the concentration of NaOH and the stripping of nitrogen gas.

4. Combined Process of ETA

ETA cannot be so easily decomposed into CO_2 and N_2 that the best way is the combined process of physical, chemical, and biological treatments. Figure 3 shows the combined process in which ion exchange, stripping, biological denitrification were selected as chemical, physical, and biological methods.

Reference:

- [1] Handbook of Chemistry and Physics 3, 4, 1996-1997
- [2] The Merck Index 375, 684, 686, 1996
- [3] Dorfner, K. Ion Exchanges, Properties and Applications. 3rd ed. Ann. Arbor, Mich; Ann Arbor Science Publishers, 1971.
- [4] Dow Chemical Co. Ion Exchange. Midland, Mich;Dow Chemical Co., 1964.

Table 1. Physico-chemical Properties of ETA and Ammonia

	unit	Ammonia	ETA
Molecular weight	g	17.03	61.08
Density	g/ml	0.6818 (-33.5)	1.0180 (20)
Molting point		-77.75	10.5
Boiling point		-33.35	170.8
Viscosity	mN·S·m ⁻²	0.254 (-33.5)	21.1 (25)
Dielectric constant		22.4(-33.5)	31.94 (20)
Dipole moment	3.33561×10 ⁻³ C·m	1.471	2.27
Conductivity	10 ⁻⁴ m ² ·S/mol	73.5	47.2
Diffusivity	10 ⁻⁵ ·cm ² /s	1.957	1.124
Surface tension	mN/m	1453.11 (-40)	48.3175 (25)

Table 2. Volatility and Basicity of ETA and Ammonia as a function of temperature

Temp ()	pKa		Log RV		pKw
	NH ₃	ETA	NH ₃	ETA	
25	9.244	9.496	1.41	-2.1	13.992
50	8.537	8.807	1.28	-1.72	13.271
100	7.384	7.684	1.08	-1.13	12.262
150	6.482	6.805	0.94	-0.71	11.641
200	5.752	6.094	0.81	-0.46	11.300
250	5.148	5.506	0.67	-0.26	11.195
300	4.637	5.008	0.51	-0.21	11.300

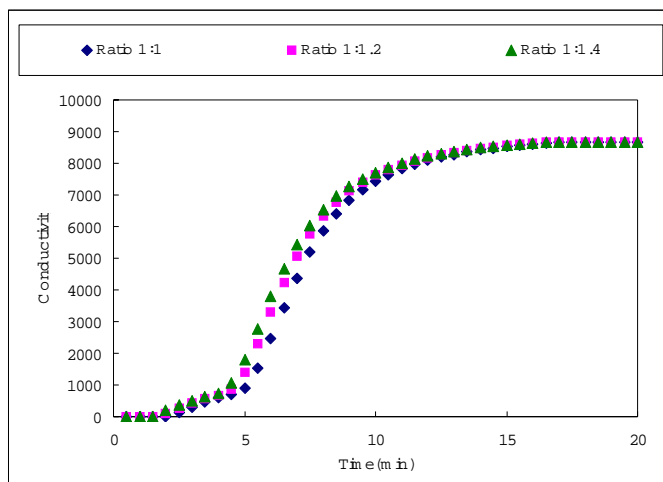


Figure 1. Breakthrough curve (ETA and NaOH ratio 1:1, 1:1.2, 1:1.4)

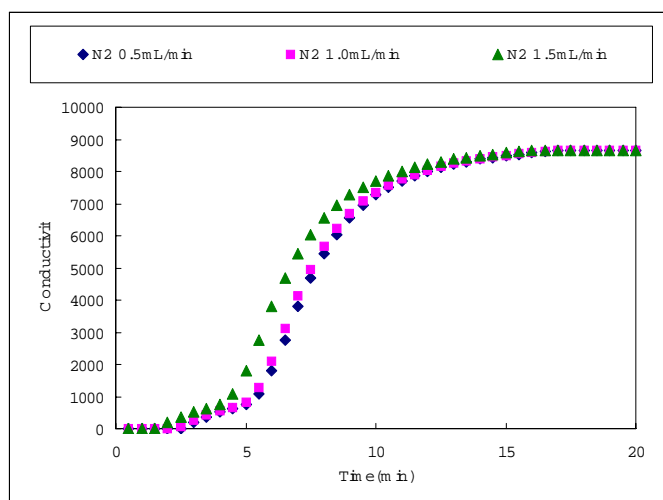


Figure 2. Breakthrough curve (N₂ gas 0.5, 1.0, 1.5mL/min)

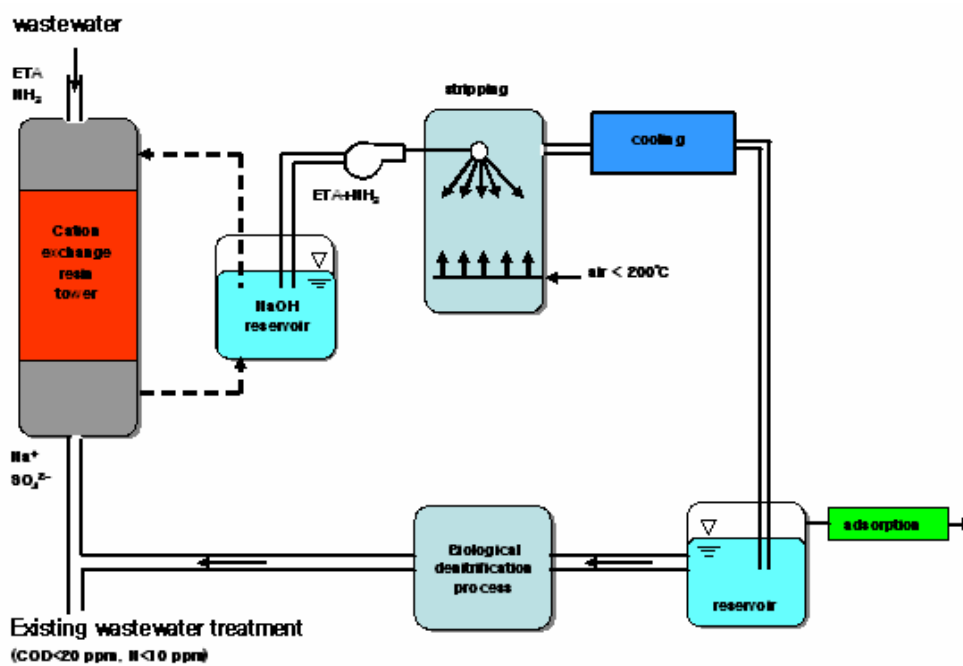


Figure3. Combined process