

ETA Recovery Process with Ion Exchange and Evaporation

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Abstract: The PWR plants have replaced 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 discharge standard of wastewater quality, especially for COD and 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 difficult to meet the regulation standard due to the possible production of nitrate and was expensive to achieve the complete breakdown. Therefore the total decomposition or recovery of ethanolamine by physical, chemical, or biological processes is the best way to meet the discharge standard of COD and N.

Key-Words: PWR, ethanolamine, COD, T-N, regulation, physical, chemical, biological, processes

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 almost 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 objectives of this study were to review the physico-chemical property of ethanolamine and its treatment technology, to investigate the characteristic of ethanolamine on evaporation, condensation, adsorption, and ion exchange, and finally to propose the possible removal and recovery processes of ethanolamine.

2 Physico-Chemical Properties of ETA

Compared with ammonia, ETA is more basic due to the high pKa, easier 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.

Table 1. Physico-chemical Properties of ETA and Ammonia

	unit	Ammonia	ETA
Molecular weight	g	17.03	61.08
Density	g/ml	0.787 (25°C)	1.0180 (20°C)
Melting/ Boiling point	°C	-77.75/-33.35	10.5/170.8
Surface tension	mN/m	2.338×10^{-4} (11.1°C)	48.3175 (25°C)
Viscosity	mN·S·m ⁻²	0.13 (25°C)	21.1 (25°C)
Dielectric constant		16(25°C)	31.94 (20°C)
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
Relative Volatility	log@25°C	1.41	-2.10
pKa	25°C	9.244	9.496

3 Evaporation and Condensation Characteristics

The evaporation of ETA depends on the heating temperature, the applied pressure, and the solution pH. As shown in Figure 1, the increased temperature and the decreased pressure make larger the vaporization ETA the rate of which becomes exponentially

increased with time. However, it is not much affected by the solution pH especially at the vacuum pressure. The condensation of ETA is increased at the lower temperature and the lower pressure (vacuum), as illustrated in Figure 2.

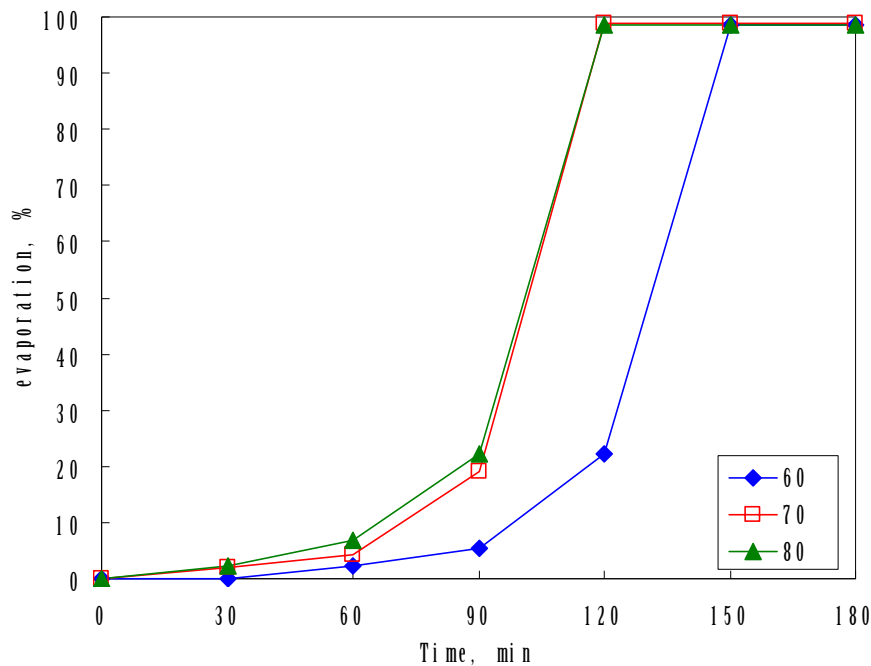


Figure 1. Evaporation rate of ETA with temperature and time (vacuum pressure=650mmHg , solution pH= 9)

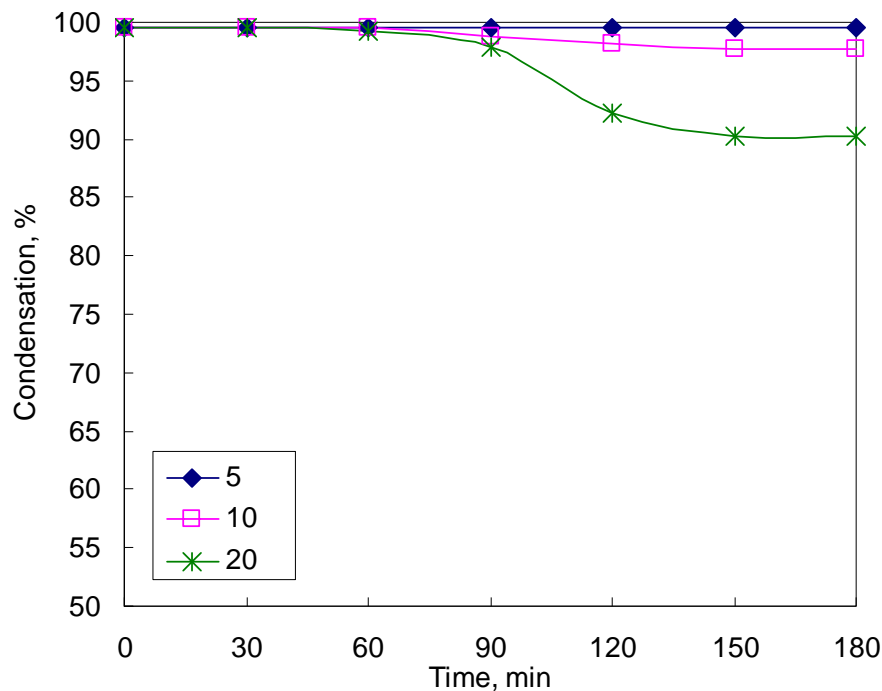


Figure 2. Condensation rate of ETA with temperature and time (vacuum pressure=650mmHg)

4 Ion Exchange and Adsorption 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 the 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 3 and 4, the regeneration efficiency is increased with the concentration of NaOH and the stripping of nitrogen gas. The gaseous ETA was adsorbed onto activated carbon and zeolite at the

lower temperature, while ETA was released out of activated carbon over $80^\circ C$ and maintained on zeolite even at $170^\circ C$ as shown in Figure 5.

The resin regeneration process was carried out by injecting NaOH solution at 25mL/min into the ion exchange bed of R-ETAH. The concentration of NaOH solution was 10~20 %, which is tantamount to 1, 1.2, and 1.5 in chemical equivalent of ion exchange resin. The effluent was taken for IC analysis to determine the regeneration efficiency

The resin regeneration process is shown in Table 2. The process was modified to recover pH control agent by adding NaOH to detach pH control agent from exhaust resin and then H_2SO_4 to make R-H form resin.

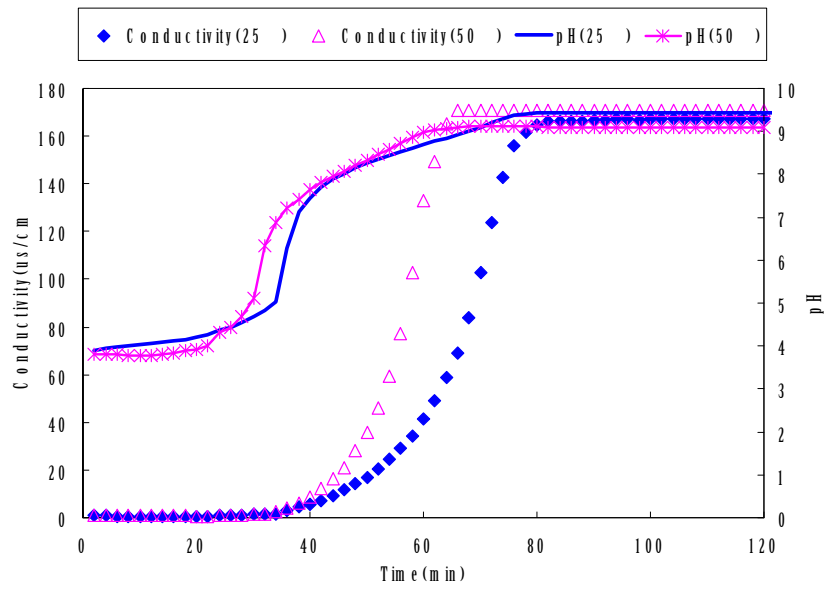


Figure 3. pH and conductivity at temperatures of 25 and 50°C (ETA=1000ppm)

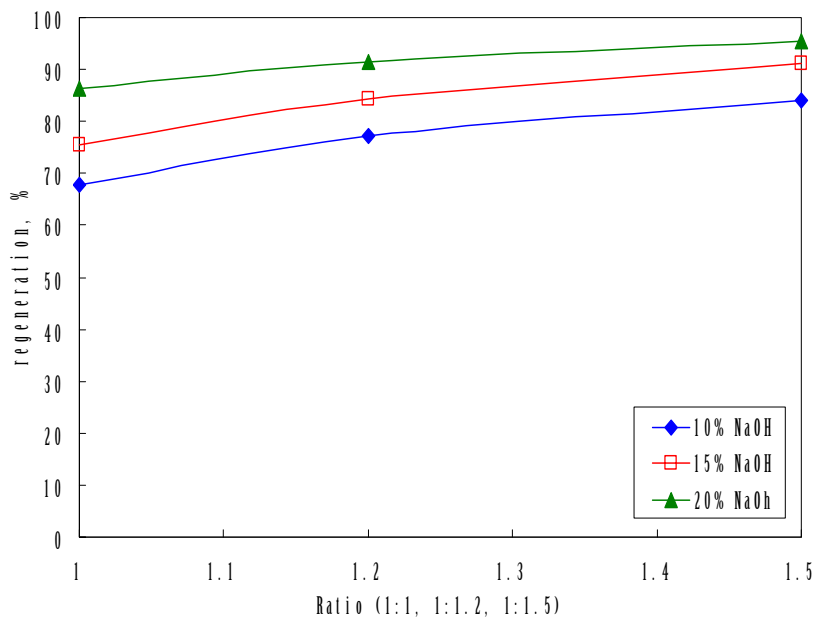


Figure 4. Regeneration efficiency with NaOH concentration (regeneration time=60minute)

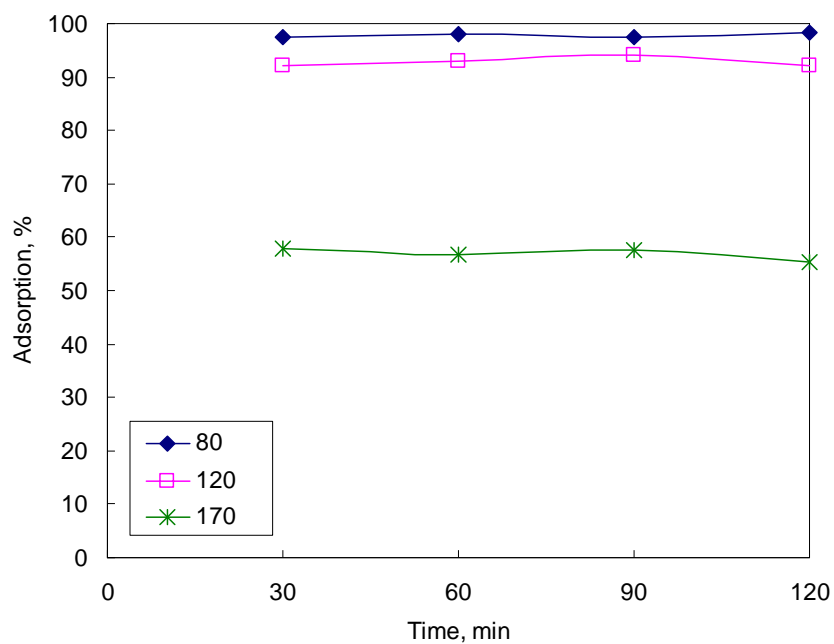


Figure 5. Adsorption of ETA with zeolite with temperature