Recently, the amount of sulfur compounds such as H$_2$S generated in the oil-refining process has increased.\textsuperscript{1,2} Removing such compounds from the process is essential because H$_2$S is the main cause of air pollution and has a fatal effect on the human body. For example, at 0.0057 ppm in the atmosphere, H$_2$S causes eye and nasal symptoms, coughs, and headaches; at 250 ppm, it can damage organs and nervous systems and also deflate cellular metabolism.\textsuperscript{3} Therefore, H$_2$S should be discarded to avoid environmental pollution and increase process efficiency. Most factories use amine gas sweetening to remove sulfur compounds such as H$_2$S generated during the crude-oil refining process.\textsuperscript{4} Amines that absorb H$_2$S in the amine gas sweetening process are degraded using high temperature in the regenerator and reused; this is called the amine regeneration process. The H$_2$S absorption and regeneration mechanism of amines is caused by a difference in pKa; it is absorbed...
at low temperatures in the absorber and removed using the high temperature in the regenerator. Primary, secondary, and tertiary amines are used in the process, and they are divided into monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) and dimethylethanolamine (DEEA). MEA and DEA react more selectively with CO₂ than H₂S, and they have different selectivity for acid gas. The tertiary amines like MDEA and DEEA have a low heat of reaction which lowers energy requirement of the stripper. Especially, the DEEA represents a heat-stable amine salt (HSAS) which corrodes the device and reduces efficiency. Nevertheless, the MDEA is traditionally used to amine gas sweetening process because MDEA is highly selective with H₂S, and is used in several processes because it can effectively remove H₂S and requires a low amount of energy in the regeneration process of amine solutions. In addition, many studies are being investigated on the amine gas sweetening process using MDEA as an H₂S absorbent. Stefania et al proposed the optimal configuration of the acid gas removal section using MDEA, focusing the heat duty at the reboiler of the regeneration column of the plant. As a result, using semi-lean solvent in the absorption and two flash vessels, the heat duty at the reboiler is reduced by 22% compared to base scheme. To determine the influence of recycle stream on the absorption process, S. Moioli et al performed sensitivity analysis in amine gas sweetening process. The best process solution was a split ratio of 50% recycle stream and 50% H₂S-rich product stream which is a benefit for the absorption column through the large diameter and low liquid-gas ratio.

However, in the absorbing process of amine gas sweetening, when amines react with acidic substances other than H₂S, a heat-stable amine salt (HSAS) is produced, which exists in the form of an anion. The HSAS includes formate (CHOO⁻), acetate (CH₃COO⁻), and thiocyanate (SCN⁻), which corrode the device and reduce efficiency because they are deposited inside the heat exchanger. Further, HSAS reacts with amines, thereby reducing the amount of available amines and the efficiency of the desulfurization process. Unlike H₂S, the HSAS has a relatively large pKa with amines; therefore, it is not degraded at the high temperature of the regenerator and needs to be removed through additional processes. In general, HSAS removal methods to solve these problems include ion exchange resin reclamation and electrodialysis reclamation. The ion exchange resin reclamation method removes HSAS through neutralization by ion exchange; the method generates large amounts of waste and has a high chemical and water consumption. An ion exchange resin reclamation unit allows the trapped amine from the cartridge filter to enter the resin column, which then removes HSAS through a reaction with NaOH. The electrodialysis reclamation method removes HSAS through anionic and positive ion permeability membranes. This method has the advantage of using fewer chemicals, such as NaOH, than ion exchange reclamation because the amount used depends on the number of HSAS moles to be removed. Furthermore, the amount of wastewater generated is extremely low, and amine loss is limited; in addition, it has the advantages of modularization and scaling up with a compact unit size. However, this method has the disadvantages of higher water and electricity consumption compared to ion exchange reclamation. The commercial plant targeted for the research in this study uses MDEA, and therefore, electrodialysis reclamation and ion exchange resin reclamation are considered.

Recently, various studies have been conducted to improve the reclamation methods. For example, Bayati et al conducted experimental studies on various variables to increase the efficiency of removing HSAS from the ion exchange resin reclamation unit. Optimal conditions were derived via an experiment that employed different contact times with HSAS and caustic solution, response temperatures, and resin amounts. Burns and Gregory developed a method that improved the conventional electrodialysis reclaiming unit. The developed method is used to (a) reduce unit size by adding the base to the amine without the base tank and (b) vary the arrangement of the permeable membrane inside the stack. The existing method removed only anions; however, the suggested new method is able to remove cations and anions simultaneously.

Despite many contributions to improve the each reclamation method, previous studies didn’t consider the economic feasibility of each methods which is the most important in application to actual commercial plant. The ion exchange resin reclamation unit generates large amounts of waste with high chemical consumption and the electrodialysis reclaiming unit has the disadvantages of higher water and electricity consumption compared to ion exchange reclamation. Thus, since the total cost of each reclaiming unit is varied according to the amount of HSAS reclaimed, it is crucial to derive the economic crossover point when installing the reclaiming unit in the actual process. In addition, through the derived economic crossover point, an economical unit should be selected according to the amount of HSAS reclaimed to reduce total cost.

To deal with this challenge, we proposed the economic crossover point of amine regeneration process with each HSAS reclaiming unit through techno-economic comparison. Figure 1 gives an overview of the optimization of the amine regeneration process with each HSAS reclaiming unit for deriving the economic crossover point. First, we developed a process model for each HSAS reclaiming unit to predict costs for equipment, raw materials, electricity, and water (Section 3.1). We also developed a mathematical model for optimizing the reclamation process costs considering the difference of total annualized cost (Section 3.2). Finally, the economic crossover point was
derived by utilizing the developed models; the obtained crossover point facilitated the identification of economical units based on a quantitative comparison of reclaimed HSAS amount (Section 3.4).

The contributions of this study are as follows. First, considering each HSAS reclaiming unit, the developed process models can be used to predict costs such as equipment, raw materials, electricity, and water costs under various conditions. Second, the proposed mathematical model can be used to calculate all types of costs incurred by the amine regeneration process with the HSAS reclaiming unit, which depends on the amount of HSAS reclaimed per day.
Finally, the economic crossover point derived using the developed models will lead to significant economic improvement when installing an HSAS reclaiming unit in many processes, as shown by our quantitative comparison of the cost according to reclaimed HSAS amount.

2 | PROCESS DESCRIPTION

2.1 | Amine gas sweetening process

Figure 2 shows the simplified workflow of the amine gas sweetening process. Sour gas generated during the refining process of crude oil that contains a large amount of H₂S is passed into the sour gas absorber for removal. The sour gas absorber uses a trayed column and a bubble cap, and each tray is used to facilitate gas–liquid contact. The H₂S is absorbed through an exothermic reaction after a gas–liquid contact with amines. ¹⁸ The chemical equation for absorption of H₂S is as follows:

\[
\text{MDEA} + \text{H}_2\text{S} \leftrightarrow \text{MDEA}^+ + \text{HS}^- \tag{1}
\]

The amine that has absorbed H₂S is discharged into the lower part of the absorber and undergoes the amine regeneration process. Before absorbing H₂S, the amine is referred to as a lean amine, and when it is saturated, it is called rich amine. ¹⁹ The rich amine is regenerated through the H₂S removal process called amine regeneration. ²⁰ In this process, the rich amine that absorbed H₂S through an exothermic reaction is regenerated by supplying heat energy. Then, the rich amine is released from the lower part of the absorber into the rich amine flash drum, which removes hydrocarbons through the weight difference and separates gas components. The rich amine flash drum is operated at a low pressure to maintain the amine flow to the regenerator. The rich amine is preheated through the lean/rich heat exchanger before entering the regenerator, which reduces the heat load on the reboiler and is a preparatory step in the removal process of H₂S. The preheated rich amine is then regenerated in the regenerator. The regenerator is commonly used with a trayed column, and the steam produced in the reboiler adds sufficient heat to the amine solution to improve the removal reaction of the amine solution. After the removal reaction, the acidic gas is cooled using the condenser and released through the treatment process; then, the regenerated amine circulates in the lower part for reuse. The regenerated lean amine is reused by reducing the temperature through the lean/rich heat exchanger; then, it enters the absorber through the lean amine cooler and filter. However, in addition to H₂S, sour gas produced during the refining process of crude oil also includes acetic acid and formic acid. ²¹ When these acidic substances react with amines, HSAS is produced, which can cause problems in the process. The HSAS typically contains acetate and formate. The reaction formula for the salt-production process is as follows ⁵:

\[
\text{MDEA} + \text{CH}_3\text{COOH} \rightarrow \text{MDEA}^+ + \text{CH}_3\text{COO}^-, \tag{2}
\]

\[
\text{MDEA} + \text{HCOOH} \rightarrow \text{MDEA}^+ + \text{HCOO}^- \tag{3}
\]

HSAS exists in anion form and acts as a factor for corrosion and deposition in the actual process; HSAS reduces the efficiency of the process and the amount of available amine. However, the HSAS cannot be degraded even when the regenerator temperature is high; therefore, it must be removed through an additional process. The reaction of H₂S removal depends on the variation in equilibrium constants based on the pKa difference of the two reactants. At a low absorber temperature, the difference in pKa is large, which causes a positive absorption reaction; at a high regenerator temperature, the difference in pKa is smaller, which results in a removal reaction. The difference in pKa between MDEA and acetic acid as well as MDEA and formic acid is relatively large; therefore, there is no removal reaction at a high regenerator temperature. Thus, the salt is called a heat-stable salt. The relationships between the equilibrium constants and pKa are as follows ⁵:

\[
K_{\text{a,acid}} = \frac{[\text{Acid}^-][\text{H}^+]}{[\text{HAcid}]} \tag{4}
\]

\[
K_{\text{a,amine}} = \frac{[\text{Amine}][\text{H}^+]}{[\text{AmineH}^+]} \tag{5}
\]

\[
\log K_{\text{eq}} = \log K_{\text{a,acid}} - \log K_{\text{a,amine}} \tag{6}
\]

\[
\log K_{\text{eq}} = pK_{\text{a,amine}} - pK_{\text{a,acid}} \tag{7}
\]

Table 1 lists the pKa values for MDEA, H₂S, formic acid, and acetic acid at 293 K and 393 K. ⁵

| Component | pKa at 293 K | pKa at 393 K |
|-----------|-------------|-------------|
| MDEA      | 8.52        | 7.03        |
| H₂S       | 7.04        | 6.46        |
| Formic acid | 3.75    | 4.02        |
| Acetic acid | 4.75      | 4.99        |

Table 1
reaction. At 393 K, it is smaller (0.57), which results in the removal reaction. Formic acid and acetic acid have relatively large differences of 3.01 and 2.04 at 393 K, respectively; thus, no removal reaction occurs even if they are heated. They need to be removed through additional processes. Further, there is an effect of pressure, and pKa values vary with temperature. In general, the acid gas absorber in the amine gas sweetening process profits from a higher inlet gas pressure caused by the increase in the H$_2$S partial pressure, which is the greater driving force. Unless H$_2$S is highly decompressed, or the conversion rate of the sorbent is high, the bulk concentration of the liquid sorbent appears large. Assuming that the concentration of the sorbent on the liquid surface is constant, the absorption rate of the amine and H$_2$S is indicated as:

$$r = k \left( C_{\text{H}_2\text{S}} - C_{\text{H}_2\text{S}}^* \right). \quad (8)$$

The concentration of gas within the same volume increases when the pressure of the gas increases, and therefore, it can be expressed as:

$$r = k \left( P_{\text{H}_2\text{S}} - P_{\text{H}_2\text{S}}^* \right). \quad (9)$$

Therefore, as the pressure of the gas increases, the velocity constant ($k$) increases when the equilibrium is reached, thereby increasing absorption efficiency. In the actual process, the pressure is changed during absorption and regeneration. The H$_2$S is absorbed by the acid gas absorber, and therefore, the absorber operates at a relatively high pressure of ~13 bar to increase absorption efficiency. The pressure is then reduced to ~5 bar when the steam phase is flashed out of the rich amine flash drum. Finally, in the regenerator, the operating pressure is set to ~2.1 bar to ensure considerable removal at low pressure. Figure 3 shows the absorption and regeneration mechanism.

### 2.2 Heat-stable salt reclamation

The HSAS generated from the amine gas sweetening process is removed after an additional process because it causes several problems in the process, and the unit used for this process is called the HSAS reclaiming unit. In the amine gas sweetening process, which uses MDEA as an absorbent, the HSAS reclaiming unit comprises equipment for electrodialysis and ion exchange resin reclamation.

#### 2.2.1 Electrodialysis reclaiming unit

The electrodialysis reclaiming unit performs selective separation by placing an ion exchange membrane in an electric field to facilitate the removal of ionizing materials. In electrodialysis reclaimation, the translucent membrane is selectively permeated with either an anion or a positive ion. Figure 4 shows the process diagram of the reaction mechanism inside the electrodialysis stack.

The overall reactant and product are identical to those in the ion exchange resin reclaiming unit; however, in this process, only the basic anion (OH$^-$) is transmitted to the amine solution in addition to the electrodialysis stack, rather than direct addition of NaOH to the amine solution.6

$$\text{MDEAH}^+ + \text{OH}^- \rightarrow \text{MDEA} + \text{H}_2\text{O} \quad (10)$$

Next, a reaction occurs between Na$^+$ that exits the positive ion permeation membrane and HSAS that exits the negative ion permeation membrane. Consequently, they are released as waste.6

$$\text{CH}_3\text{COO}^- + \text{Na}^+ \rightarrow \text{CH}_3\text{COONa} \quad (11)$$

$$\text{HCOO}^- + \text{Na}^+ \rightarrow \text{HCOONa} \quad (12)$$

Figure 5 shows the process workflow for the electrodialysis reclaiming unit.

As shown in Figure 5, a lean amine is stored in the amine tank after filtration. Then, the temperature is lowered through the cooler, and the amine is moved to the electrodialysis stack. Similarly, caustic, water, and nitrogen are also stored in the tank, merged, and moved to the stacks. In the stack, each ion reacts between the membranes, the HSAS removal process occurs, and the flow is circulated.6
2.2.2 | Ion exchange resin reclaiming unit

The ion exchange resin reclaiming unit allows the trapped amine from the cartridge filter to enter the resin column, which then removes HSAS through a reaction with NaOH.\(^{24}\)

\[
\text{MDEAH}^+ + \text{CH}_3\text{COO}^- + \text{NaOH} \rightarrow \text{MDEA} + \text{CH}_3\text{COONa} + \text{H}_2\text{O} \quad (13)
\]

\[
\text{MDEAH}^+ + \text{HCOO}^- + \text{NaOH} \rightarrow \text{MDEA} + \text{HCOONa} + \text{H}_2\text{O} \quad (14)
\]

The purified amine solution is stored in the amine storage tank in a low position and then rinsed in the resin. Next, resin regeneration occurs, and alkaline waste produced by the HSAS removal process is discharged.

Figure 6 shows the process diagram of the ion exchange resin reclaiming unit.

3 | OPTIMIZATION

The electrodialysis reclaiming unit and ion exchange resin reclaiming unit are representative devices for removing HSAS generated in the H\(_2\)S absorption process using MDEA. The electrodialysis reclaiming unit is characterized by the advantage of a lower equipment cost compared to the ion exchange resin reclaiming unit. Additionally, the raw material cost is low because the unit uses as much caustic as the number of moles of HSAS to remove. In contrast, the ion exchange resin reclaiming unit has higher equipment and raw material costs than the electrodialysis reclaiming unit; however, its advantages include lower electricity and water consumption. Therefore, when installing the HSAS removal device in the process, it is necessary to consider the cost of each HSAS reclaiming unit. Currently, the amount of reclaimed HSAS changes per day; thus, the cost of each HSAS reclaiming unit also changes accordingly. Hence, it is necessary to derive an economic crossover point for the cost of each HSAS reclaiming unit. The proposed mathematical model for optimization is a nonlinear programming (NLP) problem and was developed to derive an economic crossover point by considering the difference in the total annualized cost of each HSAS reclaiming unit depending on the amount of reclaimed HSAS per day. In the optimization, process models with individual HSAS reclaiming units were developed to calculate the total annualized cost according to the amount of reclaimed HSAS per day. Costs for equipment, raw material consumption, electricity, and water were predicted using the developed model. Figure 7 depicts a flowchart outlining the optimization process for deriving the economic crossover point.\(^{25}\) As the calculation proceeds, the amount of HSAS reclaimed per day gradually increases, and costs of equipment, raw materials, electricity, and water required for the amine regeneration process are predicted through the process model. Next, the costs of equipment, electricity, and raw materials required for the electrodialysis reclaiming unit and the ion exchange resin reclaiming unit are calculated, and the difference in TAC is calculated. The process concludes when the constraints are satisfied.

3.1 | Process model for cost prediction

In this study, to develop a process model for cost prediction, Aspen plus V10 was used to simulate the amine regeneration process.\(^{26}\) And the operating condition and mass balance of a commercial plant in Korea were utilized. The absorption and removal of H\(_2\)S in the amine
regeneration process follow the mechanism of a chemical reaction on the gas and liquid. In addition, the neutralization of the electrolytes during HSAS removal should be considered. Therefore, a thermodynamic model that considers these response mechanisms used the electrolyte nonrandom two liquids (ELEC-NRTL) model with the Redlich–Kwong Equation. The ELEC-NRTL model is based on the fluidity equilibrium of liquid and steam, and it can handle a wide range of concentrations while processing water-soluble substances and mixed solvents. The Redlich–Kwong equation is used to determine the characteristics of the steam phase. The equilibrium constants of the absorption and removal reactions of H₂S and HSAS removal reactions required for modeling are calculated from the standard generation heat of each component as explained below. If chemical reactions occur under isothermal isometric pressure, in the Gibbs free energy formula, \(dG = 0\) and \(dT = 0\). The number of moles of common component \(i\) of a single reaction can be expressed as

\[
dG = -SdT + VdP + \sum_i \mu_i dn_i, \tag{15}
\]

\[
dG = \sum_i \mu_i dn_i, \tag{16}
\]

\[
n_i = n_{i0} + v_i \xi, \tag{17}
\]

\[
 dn_i = v_i d\xi. \tag{18}
\]

The differential expression is as shown in Equations 15 and 16. If the above expressions are combined,

\[
dG = \sum_i v_i \mu_i d\xi. \tag{19}
\]

In addition, considering the equation of the chemical potential \(\mu_i\) in component \(i\) under constant temperature and pressure conditions,

\[
\left( \frac{\partial G}{\partial n_i} \right)_{T,P} = \sum_i v_i \left[ \mu_i^0 + RT \ln \Pi \left( \hat{f}_i / f_i^0 \right) \right] = 0. \tag{20}
\]

If the expressions for \(\Delta G^0\) and \(K\) are used in the above expressions, the chemical reaction equilibrium constant \(K\) becomes

\[
\Delta G^0 = \sum_i v_i \mu_i^0 \tag{21}
\]

\[
K = \Pi \left( \frac{\hat{f}_i}{f_i^0} \right)^{v_i} \tag{22}
\]

where \(\Delta G^0\) is the standard Gibbs free energy difference between the product and the reactant; the chemical reaction equilibrium constant can be expressed as

\[
K_{eq} = \exp \left( - \frac{\Delta G^0}{RT} \right) \tag{24}
\]

\[
\ln(K_{eq}) = A + \frac{B}{T} + C \ln(T) + DT + ET^2 + FT^3 + GT^4 + HT^5 \tag{25}
\]

Table 2 lists the Gibbs energy of formation for each component to calculate equilibrium constants.

### 3.1.1 Process modeling

Figures 8 and 9 are process flow sheets of the amine regeneration process with an electrodialysis reclaiming unit and ion exchange resin reclaiming unit, respectively. In process modeling, only the amine regeneration process was simulated during the amine gas sweetening process. Therefore, in Stream 1, the rich amine refers to the composition of the actual sour absorber emission flow in the commercial plant. The HSAS was set to formate and acetate, and it entered the model assuming 3 wt% of Stream 1. Table 3 lists the composition of Stream 1, which is a rich amine.

SEP1 was simulated using the separator model as a rich amine flash drum, which entered the split fraction to go to Stream 1OUT as much as the emission flow referenced the actual process. Next, the rich amine passes through PUMP1 to the lean/rich heat exchanger (HX1), and the heat exchange occurs. HX1 used the MHeatX model and entered the temperature of the actual process as an outlet temperature. Stream 3, a preheated rich amine, enters RE-GE, which is simulated using the RadFrac model as a regenerator; the actual number of regenerators, feed stream to the stage, reboiler type, and operating specification are input with a distillate rate. Further, the reaction set is entered into the model considering the removal response of H₂S at the regenerator. In RE-GE, the overhead flow (Stream 7) enters the COND, which uses the heater model as the condenser to cool Stream 7-1, which has undergone COND; then, the overhead flow enters the simulated OVD1 using the Flash2 model and separates the gas phase from the liquid phase. Stream 4 emitted from the lower part of RE-GE is the lean amine with H₂S removed, and the flow is returned to Stream 5 via a heat exchange at HX1. Stream 5 enters the cooler, and cooling is performed. The cooler uses a heater model as a lean amine cooler to input
the temperature and pressure of the actual process into the flash specification. This flow was used to design the model of the amine regeneration process. Table 4 summarizes the specifications of the blocks employed in the simulation.

After the amine regeneration process, Stream 6 is split by a certain percentage and enters each reclaiming unit. First, in the process model comprising the electrodialysis reclaiming unit in Figure 8, Stream ELEC-IN is entered into the AM-TANK and mixed with Stream WATER. The AM-TANK used a mixer model, and it combines the circulating Stream W-3 with the Streams WATER and ELEC-IN. The mixed flow (Stream AT-OUT2) flows in half through SPLIT 1, and the reaction with Stream CAUSTIC occurs in EL-STACK. Stream CAUSTIC is referenced in the commercial plant requirements of NaOH. EL-STACK is an electrodialysis stack simulated using the R-CSTR model. In the EL-STACK, the operating conditions were set to 40°C and 5 atm, thereby assuming equal temperature and equal pressure, respectively. The reactor volume was entered based on the design criterion. The equilibrium constant of Equations 10-12 entered in the EL-STACK was obtained

**FIGURE 7** Flowchart of optimization for deriving the economic crossover point

**TABLE 2** Gibbs energy of formation of components

| Component | Gibbs energy of formation [kJ/mol] | Component | Gibbs energy of formation [kJ/mol] |
|-----------|-----------------------------------|-----------|-----------------------------------|
| MDEA      | -169.000                          | HCOO⁻     | -335.000                          |
| H₂S       | -33.0536                          | NaOH      | -379.494                          |
| MDEAH⁺    | -155.760                          | CH₃COONa  | -607.700                          |
| HS⁻       | -12.0450                          | HCOONa    | -599.900                          |
| CH₃COO⁻   | -369.310                          | Water     | -237.130                          |
through the minimization of Gibbs free energy using the value in Table 2. After completing the response at the EL-STACK, Stream ELEC-OUT is split at the same rate, and the flows rotate into AM-TANK, BR-TANK, and CA-TANK. In Stream BT-OUT from BR-TANK, a certain percentage is split into the EL-STACK, and the rest that is not considered in the modeling is processed back into the stack. Stream AT-OUT2, the flow that does not enter EL-STACK in AM-TANK, is separated from SEP1 and divided into Stream TR-AMINE and Stream AT-OUT3. Stream TR-AMINE is treated as a lean amine with HSAS removed. Second, in the process model comprising the ion exchange resin reclaiming unit in Figure 9, the cooled lean amine enters the ion exchange resin reclaiming unit, during which the flow is separated through a split model to control the throughput of the salt removal process. The separated stream then enters the HSAS removal device (ION-EX) to eliminate the HSAS, and the combined stream (TR-AMINE) with the remaining stream (6-1) returns to the absorption tower. The Rstoic model was used as the ION-EX, and fractional conversion was input considering the operating conditions of a
commercial plant. Table 5 lists the specifications of each heat-stable salt reclaiming unit.

### 3.1.2 Simulation results and validation

Table 6 presents the simulation results of the process model with the electrodialysis reclaiming unit, while Table 7 presents those of the process model with the ion exchange reclaiming unit. In this study, to validate the developed model, the mass balance of the commercial plant and simulation results were compared because empirical verification is necessary for developing the model. First, there is a lapse pertaining to H$_2$S in both the models because HSAS reduces the stripping efficiency of MDEA in the actual process, resulting in leftover H$_2$S that has not been stripped. Because this study did not consider the effect of HSAS on absorption and stripping efficiency, the errors arising from MDEA and MDEAH$^+$ were relatively high in the two process models with each reclaiming unit. Next, from the simulation results of the process model with the electrodialysis reclaiming unit, Stream TR-AMINE and Stream B-RETURN confirm that HSAS has been removed in response to NaOH, which is a caustic solution. However, it can be inferred that there is an error in the removal amount of each heat-stable salt. This is attributed to the difference in the values calculated using the equilibrium constant obtained by minimizing the Gibbs energy, which is influenced by other factors such as temperature and pressure in the actual process. Therefore, in the future, the model will be modified, considering other factors that affect the reaction. Finally, the simulation results of the process model with the ion exchange resin reclaiming unit show that a majority of the mass composition is consistent, with an error of ~0.1%.

### 3.2 Mathematical model for deriving the economic crossover point

In this section, we describe a mathematical model for deriving the economic crossover point by calculating the
total annualized cost of each heat-stable salt removal unit. The proposed mathematical model for optimization is a nonlinear programming (NLP) problem. The economic crossover point was derived by considering the difference in the total annualized cost of each HSAS reclaiming unit, depending on the amount of reclaimed HSAS per day. The process models developed to calculate the total annualized cost according to the amount of reclaimed HSAS per day were used to predict the cost of raw materials, water, electricity, equipment, etc. And the detailed description of overall equation of EAC and TPC, parameter, and variable was given in Appendix S1.

3.2.1 | Equivalent annual cost (EAC)

The EAC is the cost to be considered when evaluating other investments with an economic lifetime. It is equal to the annual cost of an investment that has the same value as the present value of the cost incurred by the investment. It can be calculated by dividing the net present value (NPV) by the net present value of the annuity factor (AF)\(^{31-33}\):

\[
EAC = \frac{NPV}{AF}. \tag{26}
\]

Because the NPV of the cost is the same as the total capital investment (TCI), EAC can be expressed as follows:

\[
EAC = \frac{TCI}{AF}. \tag{27}
\]

\[
DPC = C_{\text{raw materials}} + C_{\text{water}} + C_{\text{steam}} + C_{\text{electricity}} + C_{\text{maintenance}} + C_{\text{labor}} + C_{\text{supervision}} + C_{\text{operating supplies}} + C_{\text{laboratory}}. \tag{32}
\]

First, the variable, AF can be calculated as follows:

\[
AF = \frac{1}{\left(1 + RP\right)^{NP}}, \tag{28}
\]

where RP and NP are the rate per period and number of periods and were set to 10\% and 20 years, respectively, in this study.

Second, the TCI is an expense paid to generate future profits and includes the cost of purchasing fixed assets or investing in fixed assets. TCI is calculated by summing the fixed capital cost (FCI), start-up cost (SUC), and working capital investment (WCI)\(^{34,35}\):

\[
TCI = FCI + SUC + WCI. \tag{29}
\]

3.2.2 | Total product cost (TPC)

The TPC is the cost related to production and includes labor, raw material, and utilities. The TPC can be calculated by summing fixed charges (FC), direct production cost (DPC), plant overhead cost (OVHD), and general expenses (GE)\(^{36}\):

\[
TPC = FC + DPC + OVHD + GE. \tag{30}
\]

First, the fixed charges are calculated as the sum of local taxes (\(C_{\text{local tax}}\)) and insurance cost (\(C_{\text{insurance}}\)). Local tax and insurance costs were calculated as 4\% of the FCI\(^{36}\):

\[
FC = C_{\text{local tax}} + C_{\text{insurance}}, \tag{31}
\]

\[
C_{\text{local tax}} = C_{\text{insurance}} = 0.04 \times FCI. \tag{32}
\]

Second, the DPC is directly related to production and can be calculated by summing utility costs, such as raw material cost, water, and electricity cost\(^{36}\):

\[
DPC = C_{\text{raw materials}} + C_{\text{water}} + C_{\text{steam}} + C_{\text{electricity}} + C_{\text{maintenance}} + C_{\text{labor}} + C_{\text{supervision}} + C_{\text{operating supplies}} + C_{\text{laboratory}}. \tag{33}
\]

Third, the overhead cost is the cost related to the operation of the business, including factory rental, advertising, insurance, and repair costs. The overhead cost was calculated as 60\% of the sum of the maintenance, labor, and supervision costs\(^{36}\):

\[
\]

| Block                  | Used model | Operating condition                      |
|-----------------------|------------|-----------------------------------------|
| EL-STACK (Electrodialysis stack) | R-CSTR     | - Temperature: 40°C                      |
|                       |            | - Pressure: 5 atm                        |
|                       |            | - Reactor volume: 13.5 cum               |
|                       |            | - Reaction: Equations 10-12              |
| IO-EX (Ion exchange resin reclaiming unit) | R-CSTR     | - Temperature: 54°C                      |
|                       |            | - Pressure: 13.4 bar                      |
|                       |            | - Reaction: Equations 13-14              |
|                       |            | - Fractional conversion                  |
|                       |            | Equation 13 (0.027), Equation 14 (0.523) |
Finally, general expenses (GE) are incurred as part of the operation of a business and can be calculated as the sum of the administrative cost ($C_{\text{administrative}}$), market-
ing cost ($C_{\text{marketing}}$), and research and development cost ($C_{\text{R&D}}$):\(^{24}\)

$$\text{GE} = C_{\text{administrative}} + C_{\text{marketing}} + C_{\text{R&D}}. \quad (35)$$

### Objective function and constraints

The objective function that can be expressed by the mathematical model was set to minimize the difference in total annualized cost ($\Delta\text{TAC}$) between the process with the electrodialysis reclaiming unit and that with the ion exchange resin reclaiming unit. The equation is as follows:

Minimize $\Delta\text{TAC}$

$$\Delta\text{TAC} = \text{TAC}_{\text{eru}} - \text{TAC}_{\text{iru}}. \quad (36)$$

The constraints for optimization are as follows. First, the amount of reclaimed HSAS was set to less than 10% of MDEA in the target process for safe operation. In the target process, MDEA is operated at 1357.21 kg-mol/h. Therefore, the constraint equation is as follows:

$$\sum_i N_{\text{HSAS}}^{\text{reclaimed}} < 135.721. \quad (37)$$

Second, during optimization, the amount of reclaimed HSAS per day is changed, the difference of each total annualized cost is minimized, and as the calculation proceeds, the economic crossover point is gradually approached. Therefore, to derive the economic crossover point, the TAC of the process with the electrodialysis reclaiming unit and that of the process with the ion exchange resin reclaiming unit must be equal:

$$\text{TAC}_{\text{eru}} = \text{TAC}_{\text{iru}}. \quad (38)$$
TABLE 8  Optimization results according to the amount of HSAS reclaimed per day

| Variable                        | Description                        | Process with electrodialysis reclaiming unit | Process with ion exchange resin reclaiming unit |
|---------------------------------|------------------------------------|---------------------------------------------|------------------------------------------------|
| $C_{\text{equipment}}$         | Equipment cost ($)                 | 2 594 507                                  | 269 686                                        |
| $C_{\text{raw materials}}$      | Raw material cost ($)              | 19 631.83                                  | 331 556.0                                      |
| $C_{\text{water}}$              | Water cost ($)                     | 18 862.48                                  | 17 384.39                                      |
| $C_{\text{electricity}}$        | Electricity cost ($)               | 426 629.1                                  | 16 543.29                                      |
| $EAC$                           | Equivalent annual cost ($)         | 11 675 280                                 | 12 133 739                                     |
| TPC                             | Total product cost ($)             | 14 939 394                                 | 14 885 543                                     |
| TAC                             | Total annualized cost ($)          | 16 310 768                                 | 16 310 768                                     |
| $\sum_{t=1}^{24}\Sigma_{\text{HSAS reclaimed}}$ | Amount of HSAS reclaimed ($t = 1, \ldots, 24$) (kg-mol) | 36.61111 (Economic crossover point)          |                                                 |

FIGURE 10  Difference in the total annualized cost according to the amount of HSAS reclaimed per day

**Optimization result**

Table 8 lists the optimization results according to the amount of HSAS reclaimed per day. At the economic crossover point, the amount of HSAS reclaimed per day was derived as 36.6111 kg-mol. Further, at this point, the process with the electrodialysis reclaiming unit had a relatively high water cost and electricity cost, and the process with the ion exchange resin reclaiming unit had a high equipment cost and raw material cost. From the economic crossover point, it can be seen that the TAC satisfies the constraints of 16 310 768 in both processes.

Figure 10 shows the difference in the total annualized cost according to the amount of HSAS reclaimed per day. It is evident from Figure 10 that the difference of total annualized cost gradually decreases as the amount of HSAS reclaimed per day increases, until it is approximately 10 kg-mol/d. This is because if the amount of HASA reclaimed is low, the effect of electricity cost, water cost, and raw material cost is small, and the effect of equipment cost is large. The decrease in this section can be interpreted as the effect of an increase in the capacity of the ion exchange resin reclaiming unit, which has a higher equipment cost. Thereafter, the amount of HSAS reclaimed tends to increase.
from approximately 10 kg-mol/d or higher and continues to increase after the economic crossover point. Initially, the increase in raw material cost and equipment cost has a greater effect on the total annualized cost of the ion exchange resin. However, after the economic crossover point, the increase in electricity and water cost has a greater effect on the total annualized cost of the ion exchange resin. Therefore, the conclusion that can be drawn from the results is that if the amount of HSAS reclaimed in the process is ~36.6111 kg-mol/d or higher, the cost of the ion exchange reclaiming unit is low, thereby rendering it more economical. If it is below this value, the cost of the electrodialysis reclaiming unit is low, making it more economical.

4 CONCLUSION

During amine gas sweetening, HSAS is generated in a negative reaction, which reduces process efficiency. Therefore, ion exchange resin and electrodialysis reclaiming methods are employed for HSAS removal. Because the cost of each reclaiming unit differs according to the amount of HSAS reclaimed, efficient cost estimation is necessary. In this study, we derived the economic crossover point by technological comparison of the amine regeneration process employing each heat-stable salt reclaiming unit. The economic crossover point is derived as 36.6111 kg-mol/d by utilizing the developed models. The point can be employed to deduce the economic feasibility of units according to the amount of HSAS reclaimed. At the economic crossover point, the process with the electrodialysis reclaiming unit had relatively high water cost and electricity cost, while the process with ion exchange resin reclaiming unit had high equipment cost and raw material cost. From the economic crossover point, it can be seen that the TAC satisfies the constraint of $16,310,768 in both processes. We believe that the economic crossover point derived using the developed models will lead to significant economic improvement when installing the HSAS reclaiming unit in various processes because it is based on the quantitative comparison of cost according to the amount of HSAS reclaimed.

This paper focuses on the economic feasibility of ion exchange resin and electrodialysis reclaiming to reclaim the HSAS in amine regeneration process. However, another reclaiming method, thermal reclaiming, is addressed in many literatures. The thermal reclaiming is performed semi-periodically in the slipstream extracted from the reboiler of stripper. The amine solution is vaporized in the recliner vessel and returned as steam to the main process and it has high energy consumption but low capital cost. Thus it will be crucial to compare the economic feasibility of HSAS reclaiming unit considering thermal reclaiming method in the further study.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SUPPORTING INFORMATION

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