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Conceptual design and retrofitting of the coal-gasification wastewater treatment process

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Abstract

The coal-gasification wastewater treatment is the most difficult pollution control task for coal-gasification plants. It is identified that there are two serious problems occurring in the current treatment process, i.e., low performance of phenols removal and plugging induced by ammonia salts. A new treatment process is proposed in this paper to solve these severe problems and pursue clean production. Three technical improvements are introduced in the coal-gasification wastewater treatment process. First, ammonia stripping is accomplished before phenols recovery to reduce pH value of the wastewater and to improve the phenols removal performance of extraction. Second, a complex stripper with a side draw is introduced to stripping ammonia and sour gas simultaneously. It is done to eliminate the ionic interaction during stripping and to improve the removal performance of ammonia and sour gas (carbon dioxide and hydrogen sulphide). Finally, methyl isobutyl ketone (MIBK) is used as extraction solvent instead of diisopropyl ether (DIPE) for further improvement of the phenols removal performance.

Conceptual design of the proposed process is accomplished for a large-scale coal-gasification plant based on process simulation. With the proposed process, the concentration of carbon dioxide, hydrogen sulphide and ammonia in wastewater are reduced to trace, less than 10 mg/L, and about 30 mg/L, respectively. As a result, pH value of the wastewater is reduced from >9 to <7 before extraction, thus the phenols removal performance is greatly improved. Compare to the current process, the removal ratios increase from 60% to 99% for carbon dioxide, 96% to 99.6% for ammonia, and 80% to 94% for total phenols using the proposed process. In consequence, the biochemical treatment of wastewater becomes easier. The economical analysis shows that the operating cost of the proposed process is much lower than that of the current process.

Keywords: Coal-gasification; Wastewater; Process development; Sour water stripping

1. Introduction

With the rapid decrease of petroleum resource and increase of crude oil price, the application of coal in energy and chemical industries becomes more and more important. Coal-gasification is a kind of clean technology for high effective utilization of coal, and is widely used in coal gas supply, ammonia synthesis industry, power plant and other industries. Lurgi pressurized coal-gasification is one of the most widely used coal-gasification techniques [1]. In Lurgi coal-gasification process, a great amount of heavy-duty non-biodegradable organic wastewater is produced [2]. The coal-gasification wastewater is contaminated with complex compounds of phenols, hydrogen sulphide, ammonia, carbon dioxide, fatty acid, etc. Concentration of phenols, ammonia, and the chemical oxygen demand (COD) in the wastewater is over 4000 mg/L, 3000 mg/L, and 20,000 mg/L, respectively and pH of the wastewater is usually between 9 and 10.5.

For decades, pollution caused by coal-gasification wastewater has been a serious environmental problem, especially in China [3]. Usually, treatment process consisting of stripping and extracting is adopted to remove most of phenols, ammonia, hydrogen sulphide and carbon dioxide before the following biological treatment. Unfortunately, because the wastewater contains high-concentration complex compounds which fluctuate in a wide range, also there are several design limitations, the current treatment processes do not work well enough in many coal-gasification plants. It is found that there are two main problems occurring in the current treatment process [4,5]. One is low removal performance of phenols, as a result, the concentration of

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Nomenclature

C_{cu1}	cost of cold utility 1
C_{cu2}	cost of cold utility 2
C_{Col}	annualized cost of towers
C_{Ex}	annualized cost of exchangers
C_{hu1}	cost of hot utility 1
C_{hu2}	cost of hot utility 2
C_{S}	cost of solvent
E_{F}	mass flow of solvent make-up
E_i	mass flow of the extract phase that leaves stage i, $i = 1, 2, \ldots, n$
Q_{C}	condenser duty
Q_{EC}	cooler duty
Q_{EH}	heater duty
Q_{R}	reboiler duty
R_i	mass flow of the raffinate phase that leaves stage i, $i = 1, 2, \ldots, n$
tn	operating time per year
x_i	mass fractions of phenols in the raffinate phase that leaves stage i
y_i	mass fractions of phenols in the extract phase that leaves stage i

phenols and COD is too high to be satisfactorily treated to meet the discharge standard by the following biological treatment. The other is the low performance of sour gas stripping which induces high concentration of residual carbon dioxide combined with ammonia during processing, what results in serious plugging of the equipment. Therefore, it is of great significance to improve the treatment process to pursue clean production.

Process simulation is an effective tool for analyzing and improving current processes, or developing new processes with a reasonable reliability. A lot of valuable studies had been reported for development of the similar sour water striping processes using process simulation. Hoogendoorn et al. [6] developed thermodynamic models based on the weak volatile electrolyte compounds such as ammonia, hydrogen sulphide and carbon dioxide, and discussed the applicability of the tray efficiency concept. Yang et al. [7] and Wu and Tang [8] simulated and analyzed a sour water stripping process. The authors [4,5] simulated a wastewater treatment process of a large-scale coal-gasification plant in China, and discussed the feasibility of several improvements without changing the structure of the process. However, several bottlenecks have not been eliminated, e.g. the high pH during extraction process, the ionic interaction between ammonia and sour gas during stripping process.

In this paper, the bottlenecks occurring in the current coal-gasification wastewater treatment process are analyzed. Base on the analysis, a new process is proposed, in which three technical modifications are introduced to solve the severe problems of the current process and pursue clean production. A conceptual design of the proposed process for a large-scale coal-gasification plant is accomplished, and the removal performance of main contaminations is discussed in detail. The operating costs of the current process and the proposed one are compared as well. The results showed that the proposed process creates a solid basis for biochemical decontamination treatment of the coal-gasification wastewater.

Table 1
Main water quality indices of the coal-gasification wastewater

Water quality indices	Measured value[a]	Range
Volatile phenol (mg/L)	3,220	2900–3900
Non-volatile phenols (mg/L)	3,110	1600–3600
Ammonia (mg/L)	7,750	3000–9000
Carbon dioxide (mg/L)	4,200	4000–11,000
Hydrogen sulphide (mg/L)	88	50–200
Fatty acid (mg/L)	–	2000–3500
COD (mg/L)	22,500	20,000–30,000

[a] Data of the current process were collected from the industrial units.

2. Analysis of the current coal-gasification wastewater treatment processes

Coal-gasification wastewater contains high-strength complex compounds which fluctuate in a wide range, as shown in Table 1. There exist several kinds of phenols, including non-volatile and volatile ones, with concentrations of thousands of mg/L. The pH value of the wastewater is typically between 9 and 10.5.

The flowchart and measured water quality indices of a coal-gasification treatment process in a large-scale coal-gasification plant are shown in Fig. 1. The wastewater from the stabilization tanks is separated into two parts, one is heated by feed-bottoms heat exchanger and fed to the middle of the sour water stripper T1, and the other is cooled in a cooler and fed to the top of T1. Steam from the reboiler rises and removes the dissolved gases. Sour gas including CO_2 and H_2S, a little amount of steam and ammonia stripped overhead is passed to condenser F1 and partially condensed. The uncondensed gas is incinerated. The stripped wastewater, which leaves as bottoms stream of T1, is cooled to about 45 °C and fed to the top of the extractor E1. Meanwhile, DIPE is fed to the bottom of E1 to remove phenols by countercurrent extraction. The extract stream is pumped into solvent recovery tower T3 to separate the solvent from phenols. The raffinate stream is fed to the ammonia stripper T2, as well as some liquid caustic. Dissolved DIPE in the raffinate is stripped and recovered from the top of T2. Ammonia and some steam drawn from the side of T2 and partially condensed by F2. The uncondensed ammonia-rich gas is pumped to the ammonia purification system. The recovered solvent from T2 and T3 flows into the solvent storage tank for circulating. The bottom stream of T2 is sent to biochemical treatment process.

The two main problems in the process are analyzed in following two sections.

2.1. High residual concentration of carbon dioxide and plugging caused by ammonia salts

As shown in Fig. 1, two single strippers operated at atmospheric pressure are used to strip sour gas and ammonia separately in the current process. The carbon dioxide concen-

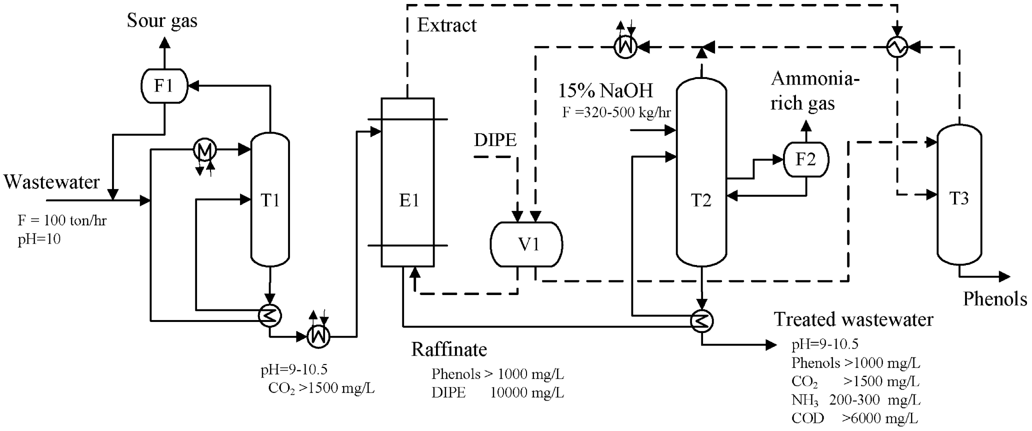

Fig. 1. Flowchart of the current coal-gasification wastewater treatment process: T1, sour water stripper; T2, ammonia stripper; T3, solvent recovery tower; E1, extractor; F1 and F2, partial condenser; V1, solvent storage tank.

tration in the feed and stripped water is about 4200 mg/L and above 1500 mg/L, respectively. High concentration of residual carbon dioxide combines with ammonia and results in serious plugging of the equipment, especially in condenser and seals.

The analysis for the low stripping performance of carbon dioxide is presented below.

Carbon dioxide, ammonia and hydrogen sulphide are weak electrolytes, which are partially dissociated into ions in the liquid phase as follows:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad (1)$$

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad (2)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \quad (3)$$

$$NH_3 + HCO_3^- \leftrightarrow NH_2COO^- + H_2O \quad (4)$$

$$H_2S + H_2O \leftrightarrow HS^- + H_3O^+ \quad (5)$$

$$HS^- + H_2O \leftrightarrow S^{2-} + H_3O^+ \quad (6)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (7)$$

The dissociation equilibrium and vapor–liquid equilibrium is shown in Fig. 2. As for carbon dioxide, reactions (2)–(4) are of interest for this study. In the liquid phase, carbon dioxide exists in two forms, i.e., ions and molecular carbon dioxide. Because CO_2 concentration in the gas phase depends on concentration of molecular carbon dioxide dissolved in liquid phase, shifting the equilibriums of the reactions (2)–(4) to the left is of advantage to strip carbon dioxide. Unfortunately, there is high concentration of ammonia in the wastewater and much OH^- is produced from the ammonia dissociation reaction (7). Much H_3O^+ is neutralized with OH^-, and the equilibriums of the reactions (2)–(4) shift to the right to keep balance. In consequence, more carbon dioxide is ionized. It means that almost all of the residual carbon dioxide in the bottom of T1 is ionized and forms HCO_3^-, CO_3^{2-}, and NH_2COO^- ions, as shown in Table 2. As a result, the residual carbon dioxide becomes hard to be stripped out. It is not economically justified to reduce the residual concentration of carbon dioxide by increasing the stripper trays or lowering pH of wastewater [5].

Similarly, the residual high concentration of carbon dioxide induces more ionized ammonia. Therefore, caustic liquid is fed to the ammonia stripper for improving ammonia removal ratio in the current process. The ionic interaction between ammonia and carbon dioxide strongly affects the removal of both contaminations during the stripping in current two single strippers process. Although the residual concentration of carbon dioxide and ammonia could be reduced to meet the removal specification by increasing the operating pressure [5] and feeding liquid caustic, but operating cost would increase significantly.

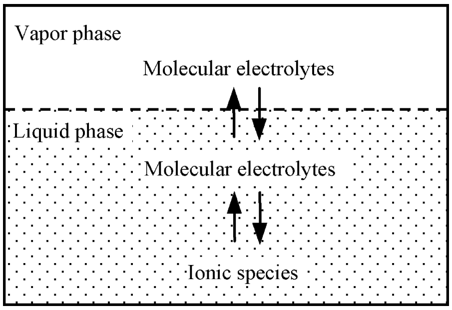

Fig. 2. Vapor–liquid equilibrium in aqueous solution of volatile weak electrolytes.

2.2. High residual concentration of phenols

The performance of phenols removal is poor in the current process. Since phenols are resistant to biological oxidation, the residual concentration of total phenols should be reduced to below 400 mg/L according to the specification of the bio-

Table 2
Conformations of carbon dioxide in the bottom of the sour water stripper

Conformations	Concentration (mg/L)
Molecular CO_2	11
HCO_3^-	2118
CO_3^{2-}	69
NH_2COO^-	343

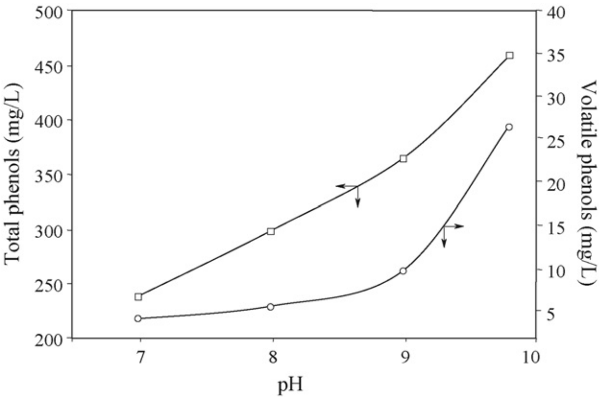

Fig. 3. Effect of pH on extraction of phenols from wastewater by MIBK: $x_0 = 5410$ mg/L; solvent ratio = 1:1.

logical treatment process. However, it was observed that the residual concentration of phenols is still above 1000 mg/L. It was found that the residual phenols could not be reduced to less than 400 mg/L by increasing solvent flow rate and/or extractor stages in the current process [5]. The reasons for low phenols removal performance are following:

(1) Since ammonia is not yet stripped out, pH value of the wastewater in the extraction process is between 9 and 10.5. At such high values of pH, a significant fraction of phenols is ionized, $PhOH \leftrightarrow PhO^- + H^+$. The effect of pH on extraction of phenols from the coal-gasification wastewater is shown in Fig. 3 [2]. It is clear that the removal performance of phenol decreases dramatically when the pH value is over 7 and especially poor if pH is greater than 9.

(2) Forty percent of total phenols in the coal-gasification wastewater are non-volatile dihydric and trihydric phenols. It was found that the distribution coefficient of DIPE on the non-volatile dihydric and trihydric phenols is small [2,9]. Thus, quite a lot of residual non-volatile phenols were found in the treated wastewater after DIPE extraction.

3. Development of new process

Base on the bottleneck analysis, a new process is proposed for treatment of coal-gasification wastewater. To solve the severe problems occurring in the current process and pursue a clean production process, three technical innovations are proposed:

(1) Separation sequence of contaminations is changed in the proposed process—ammonia stripping is accomplished before phenols recovery to reduce pH value of the wastewater and to improve the phenols removal performance.

(2) It was found that the complex stripper technique had high efficiency for simultaneous separating of ammonia and sour gas in refinery wastewater treatment [7,8]. In the proposed process, instead of the current two single strippers, a complex stripper with a side draw is introduced to strip ammonia and sour gas (carbon dioxide and hydrogen sulphide) simultaneously. It is proposed to eliminate the ionic interaction during stripping and improving the removal performance of ammonia and carbon dioxide.

(3) Instead of diisopropyl ether, methyl isobutyl ketoneis used as extraction solvent for further improvement of the phenols removal performance in the proposed process. It was found that MIBK was more suitable for phenols recovery from coal-gasification wastewater [2].

3.1. Flowsheet of new coal-gasification treatment process

The proposed treatment process is shown in Fig. 4. Sour water from the stabilization tank is separated into two streams. The first one is heated by feed-bottom exchanger and fed to the middle of the sour water stripper T1′, and the second stream is cooled in a cooler and fed to the top of T1′ to reduce the top temperature. The sour gas, a little amount of steam and ammonia stripped overhead is incinerated. Ammonia and some steam drawn from the side of T1′ are partially condensed. The uncondensed ammonia-rich gas is pumped to the ammonia purification system. The stripped wastewater is cooled to about 45 °C and fed to the top of the

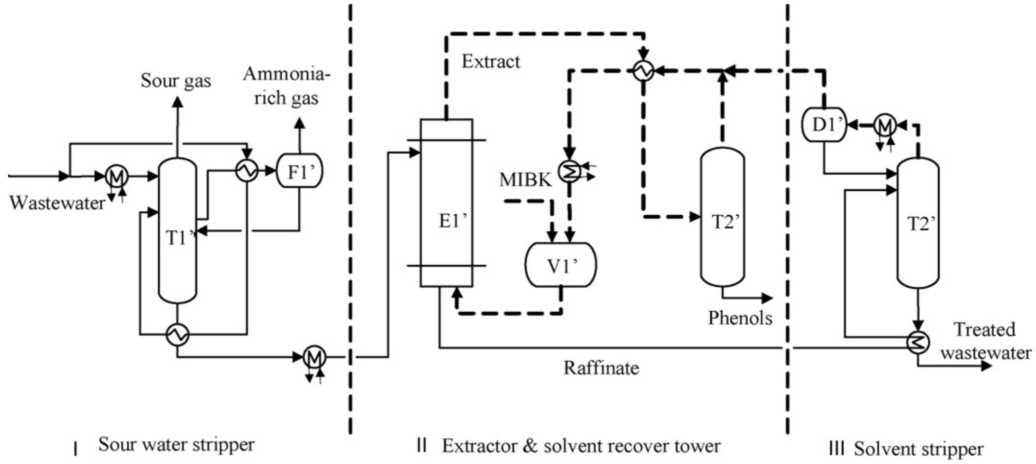

Fig. 4. Flowchart of the proposed coal-gasification wastewater treatment process: T1′, sour water stripper; T2′, solvent recovery tower; T3′, solvent stripper; E1′, extractor; F1′ and F2′, partial condenser; V1, solvent storage tank.

extractor E1′ to remove phenols by extraction with MIBK. The extract stream is pumped into solvent recovery tower T2′ to separate the solvent from phenols. The raffinate stream is fed to the solvent stripper T3′ to recover dissolved MIBK in the raffinate by stripping and following decanting. Recovered MIBK from T2′ and T3′ is pumped to the solvent store tank for circulating. The treated water from T3′ bottom is sent to biochemical treatment process.

3.2. *Process development based on simulation*

The new process is developed based on simulation performed on Aspen Plus platform. Many study results show that the rate based approach is to be preferred for distillation simulations which involve reactions because of the difficulty in the accurate prediction of tray efficiency for the equilibrium model [10,11]. However, the rate based approach involves more strongly non-linear equations, that makes the simulation and sensitivity analysis for weak volatile electrolyte system difficult. Moreover, the rate based approach involves much more data including surface tension, diffusion coefficients, viscosities, etc. These data are difficult to be collected and accurately estimated in this complex industrial case. Therefore, up to now, most of the industrial units including sour water strippers are still designed with the equilibrium approach. Since the objective of this study is to developing an industrial-scale process and the Murphree efficiency can be determined accurately from similar industrial units, the operating units are represented by equilibrium stage-based modules incorporated with Murphree stage efficiencies. The RadFrac module is selected for all strippers, and the Extract module for the extraction column. For simplicity, the volatile phenols are represented by phenol, and non-volatile phenols are represented by hydroquinone. Since long-chain fatty acids and poly-aromatic hydrocarbons have little effect on the simulation results, they are neglected in process simulation.

The wastewater is volatile weak electrolyte aqueous solution system. For this kind of systems, a wide variety of electrolyte activity coefficient models have been proposed [12,13]. The electrolyte non-random two liquid (ELECNRTL) model is recognized as universal one for the calculation of activity coefficients. Using binary and pair parameters, aqueous electrolyte systems covering the entire range of electrolyte concentrations can be represented by the ELECNRTL model, as well as mixed solvent electrolyte systems. In the ELECNRTL model, the unsymmetric Pitzer–Debye–Hückel model and Born equation are selected to represent the contribution of the long-range ion–ion interactions, and the NRTL theory is used to represent the local interactions. The mathematical expression of the ELECNRTL model is [14]:

$$\ln \gamma_i^* = \ln \gamma_i^{*\mathrm{PDH}} + \ln \gamma_i^{*\mathrm{Born}} + \ln \gamma_i^{*\mathrm{lc}} \tag{8}$$

where γ_i^* is the unsymmetrical activity coefficient of ionic species i. The first, second and third terms on the right side of the equation are the activity coefficients introduced by the Pitzer–Debye–Hückel, Born equation, and NRTL local composition models, respectively. Since the Born contribution is applicable to mixed aqueous–nonaqueous electrolyte solvents, only the Pitzer–Debye–Hückel and NRTL expressions are used in this work. The expression for the Pitzer–Debye–Hückel equation and local composition activity coefficients of cation and anion are given in Appendix A. The complete form of the model can be found in literature [14–16].

The ELECNRTL model is conveniently embedded in the Aspen Plus software with built-in parameter estimation facility, and coupled with a general process-modeling tool. The property methods for the strippers are taken as ELECNRTL, and for the solvent recovery tower as NRTL. Missing binary interaction parameters are estimated with UNIFAC model. The vapor phase properties are calculated using the Redlich–Kwong equation. The models and approach of simulation was verified by simulating the current process, it has been found that the simulating results are consistent with actual industrial data, and the comparison of simulating results and actual industrial data for some key components of treated wastewater are showed in Table 3 [4].

Liquid–liquid equilibrium during extracting process is strongly non-ideal, it cannot be described exactly by standard thermodynamic methods such as NRTL, UNIFAC, UNIQUAC. Since water–MIBK system has only limited miscibility with about 1.8% MIBK in water and 2% water in MIBK, a simplified equation, which was obtained in this work from experimental data, can be used to describe the liquid–liquid equilibrium. When ammonia is less than 100 mg/L and all of carbon dioxide is removed, the liquid–liquid equilibrium correlations between phenols mass fraction in the extract phase and in the raffinate phase is as follows:

$$y_i = 62,752 \ln(x_i) - 350,028 \quad (x_i > 240) \tag{9}$$

The liquid–liquid equilibrium equation is developed as a subroutine of the user module, and complied into the Extract module of Aspen Plus system for calculating liquid–liquid equilibrium distribution coefficients.

The proposed process consists of three parts: (I) a sour water stripper, (II) an extractor and a solvent recovery tower, and (III) a solvent stripper, as shown in Fig. 4. The three parts can

Table 3
Comparison of simulation results and actual data for treated wastewater of the current process [4]

	Carbon dioxide	Hydrogen sulphide	Ammonia	Phenols
Original wastewater (mg/L)	4200	88	7750	5123
Treated wastewater of current process				
Actual industrial value (mg/L)	1683	71	273	1017
Simulating value (mg/L)	1805	76	262	1017

be designed and simulated simultaneously or separately. The design variables of the parts I and III are determined directly with using Aspen Plus. In the part II, on the other side, design variables are determined preliminarily with the non-linear programming which will be presented in the next paragraph. Next these values should be rectified with rigorous simulation using Aspen Plus.

The model of part II, extractor and solvent recovery tower, has many variables, e.g. the number of theoretical stages or the extractor, solvent flow rate, recovery ratios of solvent and solute in solvent recovery tower, the number theoretical trays of the solvent recovery tower and reflux ratio. The design problem is to determine the optimal values of those variables according to composition of wastewater and separation specification of phenols. The objective is to minimize the operating cost. The relationships between these variables are so complicated that it is difficult to determine the optimal design directly by simulation using Aspen Plus system. In this study, the original optimal values for these variables are determined using the improved method for global optimization design of extraction and solvent recovery systems [17]. Then the original values are rectified with rigorous simulation using Aspen Plus. The steps of the procedure are following:

(1) The design problem for the extractor and solvent recovery tower is stated as a non-linear programming with an objective of minimizing the operating cost. Fig. 5 shows the superstructure for the extractor and the solvent recovery tower. The total annualized cost (TAC) mainly consists of annualized costs of extractor, solvent recovery tower, heat exchangers, utility and solvent supplement. The objective function of this problem is given by

$$\min \mathrm{TAC} = \min((C_{\mathrm{cu1}}Q_{\mathrm{C}} + C_{\mathrm{hu1}}Q_{\mathrm{R}} + C_{\mathrm{cu2}}Q_{\mathrm{EC}} + C_{\mathrm{hu2}}Q_{\mathrm{EH}} + C_{\mathrm{S}}E_{\mathrm{F}}) \times tn + C_{\mathrm{Col}} + C_{\mathrm{Ex}}) \tag{10}$$

The equality constraints include mass balance, the relationships among design variables and relationships between design variables and costs. The inequality constraints include the purity and recovery specifications and the engineering constraints [17].

(2) The original optimal values for these variables are obtained by solving this programming problem.

(3) Because there are several simplified assumptions in this programming model, the original optimal values should be rectified, which can be accomplished with rigorous simulation using Aspen Plus.

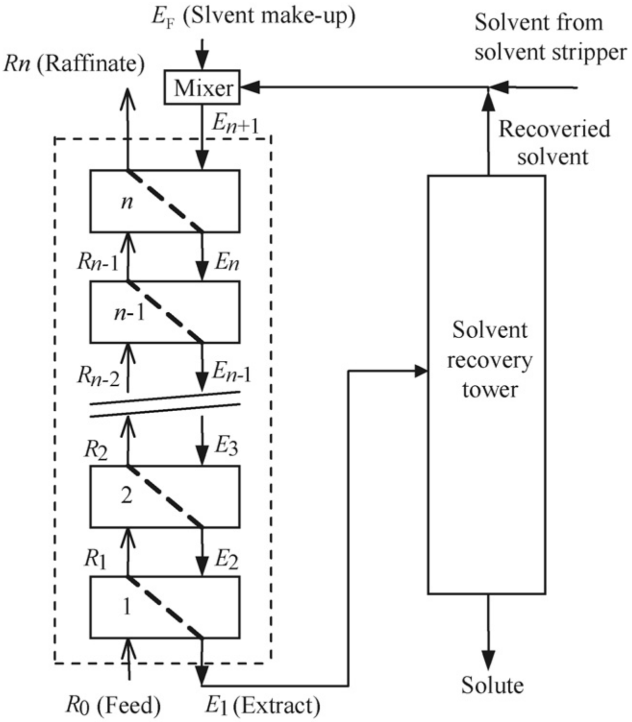

Fig. 5. Superstructure of the extraction and solvent recovery system.

3.3. Design specifications for the proposed process

According to the demands of biological treatment and ammonia purification system, the design specifications for the proposed process are as follows:

(1) The flow rate of the wastewater is 100 t/h. The concentrations of contaminants are set to peak historical values of the coal-gasification plant, i.e., volatile phenols 3500 mg/L, non-volatile phenols 3500 mg/L, carbon dioxide 9000 mg/L and ammonia 11,000 mg/L.

(2) After treatment, ammonia, phenols and hydrogen sulphide in the wastewater should not exceed 200 mg/L, 400 mg/L and 50 mg/L, respectively. During the design of the new process, concentrations of these contaminants are required to be less than 30 mg/L, 300 mg/L and 10 mg/L, respectively.

(3) Ammonia is 14–16 wt.% and carbon dioxide is less than 2.5 wt.% in the ammonia-rich gas of sour water stripper.

(4) Water and ammonia is requested to be less than 1 wt.% in sour gas stripped from the top of the sour water stripper. Because when the concentration of water is less than 3 wt.% and ammonia less than 5 wt.%, plugging will not form [18].

(5) The concentration of MIBK in treated water is less than 5 mg/L.

4. Result and discussion

Base on the simulation results, the conceptual design of an improved treatment process for the large-scale coal-gasification plant is accomplished. The sensitivity analysis is conducted to understand how the operation conditions affect the performance of the process.

4.1. Sour water stripper

The Murphree tray efficiencies are different for every component. Hoogendoorn et al. reported that the efficiency for NH_3

Table 4
Operating conditions of the base-case for the sour water stripper

Parameters	Value
Number of trays	55
Side draw tray	21
Cold feed temperature	35 °C
Cold feed/hot feed ratio	0.25
Top pressure	0.41 MPa
Top temperature	40 °C
Side draw mass flow rate	8340 kg/h

usually had a value between 0.65 and 0.85, for H_2S between 0.15 and 0.4, for CO_2 between 0.01 and 0.05, and for phenol between 0.65 and 0.9 [6]. Based on the comparison of several industrial complex sour water strippers, the values of the Murphree efficiencies in this study for NH_3, H_2S, CO_2 and phenol are set to 0.61, 0.07, 0.05 and 0.9, respectively.

The stripping performance is affected by many operation conditions such as top temperature, operating pressure, the cold feed/hot feed ratio, number of trays, side draw placement and side draw mass flow rate. The basic operation conditions for the sour water stripper are determined by simulation, as shown in Table 4. When the residual ammonia in bottom stream is set to 30 mg/L and ammonia concentration in ammonia-rich gas is set to 15 wt.%, based on the nominal operation conditions. A set of different operation conditions is compared for illustrating how the operation conditions affect the performance of the sour water stripper.

4.1.1. The top temperature and the feed temperature

Concentrations of water and ammonia in sour gas are influenced by the top temperature of the sour water stripper. When the top temperature is below 40 °C, the concentrations of water and ammonia are less than 1 wt.%. Considering the industrial cooling problems, the top temperature is set at 40 °C and is controlled by the cold feed with a temperature of 35 °C. Since the hot feed is heated before feeding to the stripper, its temperature depends on the temperature and flow rate of the side draw and the bottom stream. For the basic case, the hot feed temperature is about 134 °C.

4.1.2. The cold feed/hot feed ratio and the operating pressure

Fig. 6 shows the effect of the top pressure and cold feed/hot feed ratio on the reboiler duty and CO_2 concentration in the ammonia-rich gas. It indicates that operating pressure has a strong effect on the reboiler duty, higher operating pressure results in higher bottom temperature, even after heat transfer between bottom stream and feed, more un-recovered heat is generated. Therefore, lowering the top pressure of sour water stripper is advantageous for saving heat utility. Also heat utility can be saved by reducing the cold feed flow rate, but the effect is not so remarkable as the top pressure. Whereas, Fig. 6 also indicates that CO_2 concentration in the ammonia-rich gas increases with the lowering of operating pressure and cold feed/hot feed ratio. According to the ammonia purification system, CO_2 concentration in the ammonia-rich gas should be less than 2.5 wt.%. Considering the CO_2 concentration limitation and the operating cost, the top pressure is determined as 4.1 MPa and cold feed/hot feed ratio as 0.25.

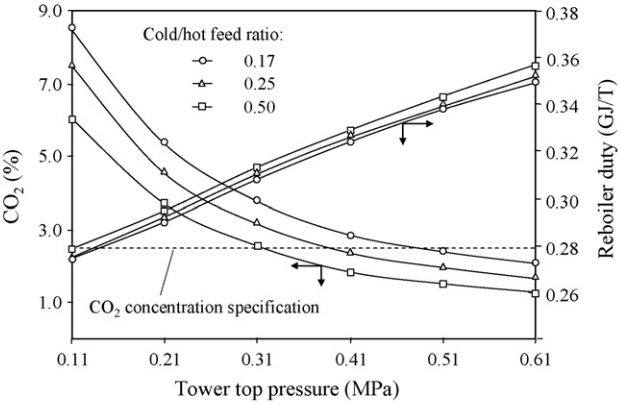

Fig. 6. Effect of the top pressure of the sour water stripper on CO_2 concentration in ammonia-rich gas and reboiler duty.

4.1.3. Number of total trays and side draw location

According to simulation results, the number of trays above side draw location (N_A) does not influence heat duty and the concentration of ammonia in bottom, whereas the number of trays below side draw location (N_B) does not affect CO_2 concentration in ammonia-rich gas.

The relationship between N_B and cost of trays and heat utility is estimated, as shown in Fig. 7. It indicates that the total cost decreases with the increase of N_B and reached a lower limit, and this tendency is clearly visible when N_B is less than 30.

The wastewater is easy to froth, thus the sufficient distance between trays is needed to prevent liquid entrainment in sour water stripper. However, considering engineering practicalities, there is a limit for the height of stripper. Usually, the total number of trays (N_T) of the sour water stripper is less than 55. When N_T is determined, increase of N_B, i.e., heightening the side draw location, is advantageous for saving utility, but CO_2 concentra-

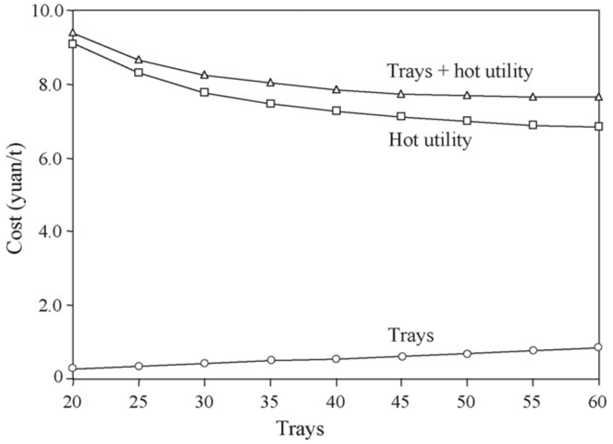

Fig. 7. Number of the sour water stripper trays under side draw vs. operating cost.

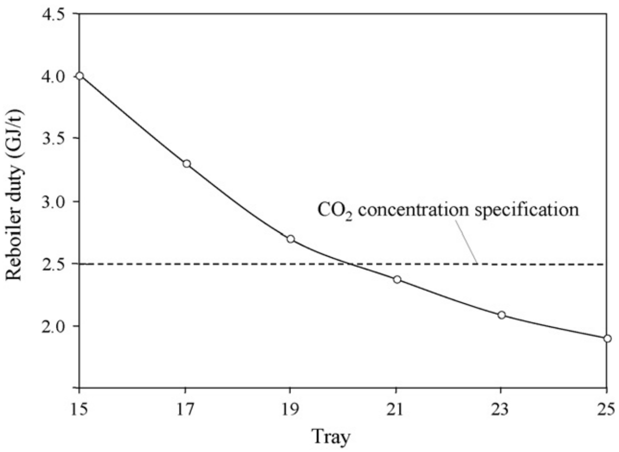

Fig. 8. Influence of the sour water stripper side draw location on the concentration of CO_2.

Table 5
Optimal designing results for the extractor and the solvent recovery tower

Parameters	Origin value	Rectified value
Extractor theoretical stages	4	4
Distillation tower theoretical trays	27.7	28
Reflux ratio	0.177	0.177
Solvent (MIBK) flow rate (kg/h)	5090	5090
Solvent (MIBK) recovery ratio (%)	99.9992	99.9992
Solute (phenols) recovery ratio (%)	0.0988	0.0859

tion in the ammonia-rich gas will increase, as shown in Fig. 8. Conforming to the design specifications, the side draw location is selected at $N_B = 21$.

The ammonia concentration in stripped wastewater reduces to a quite low value of 30 mg/L. Because there are many fatty acids in the wastewater, the pH value of the wastewater decreases from above 9 to less than 7. This is promising for improving the phenols removal performance of solvent extraction.

4.2. Extractor and solvent recovery tower

With the method mentioned in Section 3.2, the design problem for this part is defined as a non-linear programming. The original optimal values of the variables are determined by solving this non-linear programming problem and the optimal values obtained using rigorous simulation are shown in Table 5. The main cost items for the extraction and solvent recovery system are shown in Table 6.

Table 6
Annual equipments and utility costs of the optimal design for the extractor and the solvent recovery tower

Item	Cost ($\times 10^3$ yuan/year)
Solvent recovery tower	95.3
Extractor	214
Heat exchangers	11
Utility	384.4
Solvent make-up	4.5
Sum	709.2

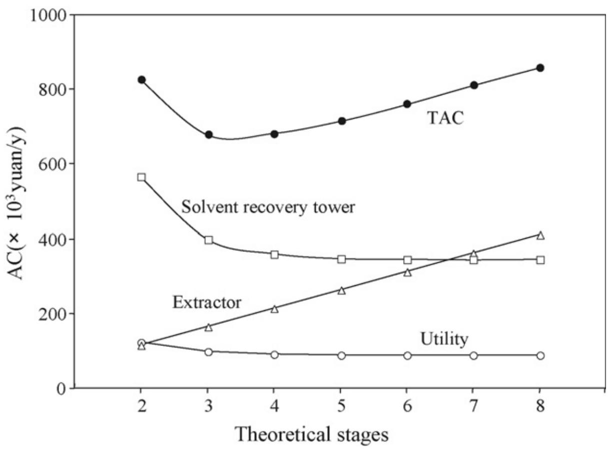

Fig. 9. Annual costs as a function of number of the extractor theoretical stages.

Higher MIBK recovery ratio means less MIBK supplement, and lower phenols concentration in the recovered MIBK means smaller solvent ratio needed for phenol recovery at same extracting stages. However, such situation requires more solvent recovery tower stages or larger reflux ratio. According the calculated optimal results, the reasonable concentration of phenols in the recovered MIBK is about 170 mg/L, and MIBK in phenols is about 45 mg/L.

The influence of the number of the extracting theoretical stages on the annualized costs is shown in Fig. 9. It indicates that cost of the extractor increases with the increase of the number of stages, and cost of the solvent recovery tower and utility are continually decrease with the increase of the number of stages. When the number of extracting theoretical stages is 4 then the operating cost becomes lowest.

4.3. Solvent recovery stripper

The wastewater leaving the extractor contains about 1.8 wt.% of MIBK which should be recovered. The T–x–y phase diagram of water–MIBK system is shown in Fig. 10. It indicates that there is an azeotropic point at about 88 °C for the MIBK–water system.

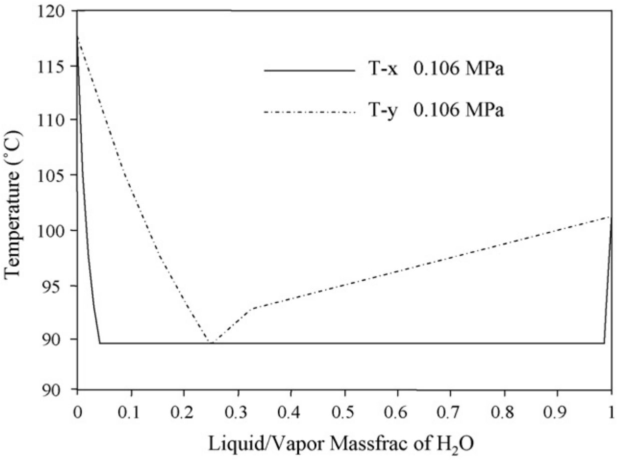

Fig. 10. T–xy for H_2O–MIBK system.

Table 7
Comparison of treated water quality between the current and the proposed process

	Carbon dioxide	Hydrogen sulphide	Ammonia	Phenols
Original wastewater (mg/L)	4200	88	7750	5123
Treated wastewater				
Measured value (mg/L)	1683	71	273	1017
Current process				
Remove ratio (%)	60	19.3	96.5	80.1
Value (mg/L)	Trace	<2	30	<300
Proposed process				
Remove ratio (%)	100	>97	99.6	>94

The azeotropic mixture contains about 75.7 wt.% of MIBK and 24.3 wt.% of water. The solubility of MIBK in water is less than 2 wt.%, and the density of MIBK is 0.78 g/cm^3. It means that MIBK is much lighter than of water. Thus, the dissolved MIBK can be recovered by stripping and decanting.

The design for the solvent stripper also involves a balance between stages and heat duty. The total annual cost (TAC) as a function of the number of the solvent stripper theoretical stages is shown in Fig. 11. The residual concentration of MIBK is fixed at 10 mg/L. It indicates that the TAC is the lowest when the number of theoretical stages is 11.

5. Comparison between the proposed process and the existing installation

The material balance is summarized in Fig. 12 for the proposed process. The wastewater quality indices, after treatment by the proposed process and the existing installation, are presented in Table 7. It is shown that the proposed process is more efficient than the current process for treatment of the coal-gasification wastewater. The carbon dioxide and ammonia removal performance is greatly improved. There is only a trace of carbon dioxide and less than 50 mg/L of residual ammonia in wastewater after sour water stripping. Therefore, plugging of ammonia salts will be prevented.

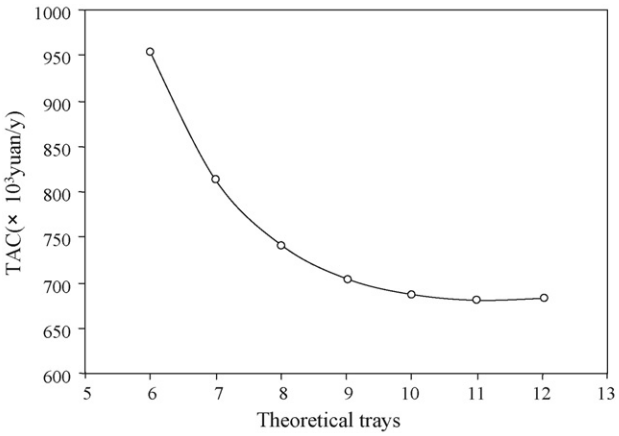

Fig. 11. Annual costs as a function of number of the solvent stripper theoretical trays.

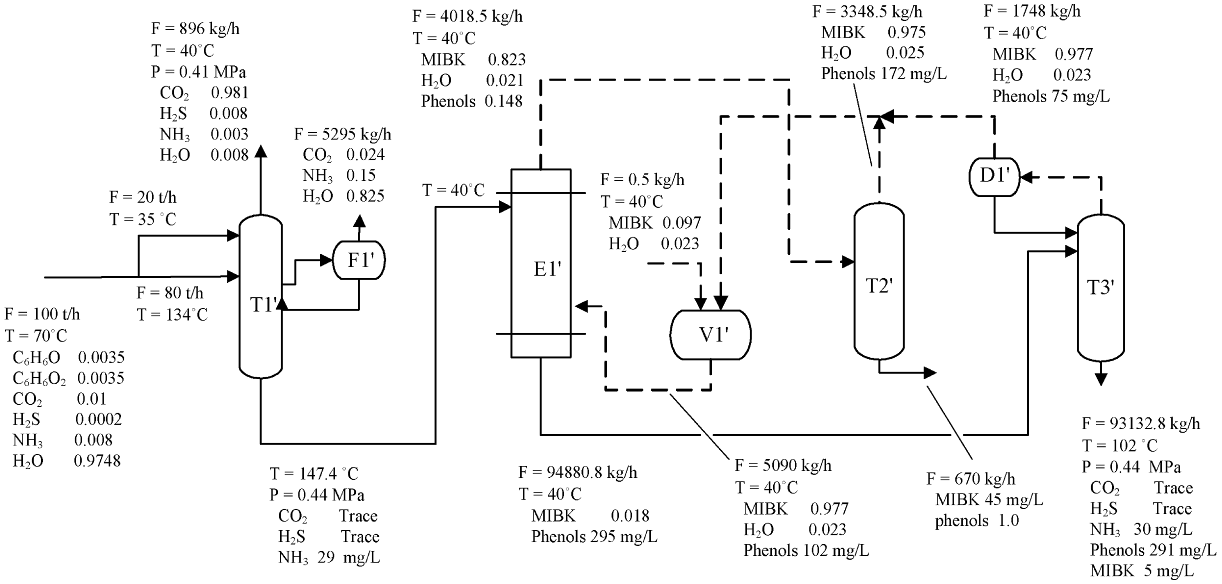

Fig. 12. Results of material balance for the proposed process.

Table 8
Comparison of annualized operation cost between the current and the proposed process

Items[a]	The current process		The proposed process		Cost saving (Myuan/year)
	Consumption[b] ($\times 10^3$ t/year)	Cost ($\times 10^6$ yuan/year)	Consumption[c] ($\times 10^3$ t/year)	Cost ($\times 10^6$ yuan/year)	
Steam (0.5–1.0 MPa)	122.6	6.13	121.1	6.06	0.07
Steam (2.5 MPa)	15.7	0.86	7.0	0.39	0.47
NaOH	0.5	1.0	0	0	1.0
Phenols	–	–	0.5	−1.0	1.0
Sum	–	–	–	–	2.54

[a] Only the main cost items are listed.
[b] Data of the current process were collected from the industrial units.
[c] Data of the proposed process were estimated from the simulation results and efficiency coefficient.

Because most of ammonia has been stripped out, pH value of the wastewater feeding into the extractor reduces to below 7, thus the extraction performance is expected to be improved. The use of MIBK as extracting solvent gives further improvement of the phenols removal performance. Therefore, the residual phenols in treated wastewater are reduced to less than 400 mg/L, and become easy to be treated by biological methods.

The comparison of the main operating costs between the proposed process and the current process is shown in Table 8. It indicates that the annual operation cost of the proposed process is about 2.6 million yuan lower than that of the current process.

This study is based on rigorous process simulation, and all basic data are collected from the industrial units. Therefore, the results of this study are reasonably reliable and have been positively confirmed by several engineering experts and a Chinese patent has been published as well [19].

6. Conclusions

It is identified in this work that low performance of removal of contaminants is one the serious problems occurring in the current coal-gasification wastewater treatment processes. It results in too high phenols concentration and COD value of treated wastewater to meet the discharge standard needed for the subsequent biological treatment. It also induces serious plugging caused by ammonia salts.

A new coal-gasification wastewater treatment process is proposed. Ammonia stripping is accomplished before phenol removal, a complex stripper with a side draw is introduced to strip ammonia and sour gas simultaneously, and MIBK is used as extracting solvent. No NaOH is needed to feed into the stripper for improving the removal ratio of ammonia in the proposed process. Because the ionic interaction between sour gas and ammonia during stripping is greatly reduced by simultaneously removal using the complex stripper, the removal ratios of ammonia and sour gas are remarkably improved—more than 99%. After very efficient removal of ammonia, pH value of the treated wastewater reduces from above 9 to less than 7 in the proposed process.

The performance of phenols removal is greatly improved in the proposed process because of the pH reduction and substituting MIBK for DIPE as extracting solvent. The phenols removal ratio increases from about 80% in the current process to above 94% in the proposed one. This makes the subsequent biochemical treatment more effective. The comparison shows that the problems occurring in the current treatment method can be successfully eliminated by applying the proposed process. The operating cost of the proposed process is much lower than that of the current process.

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Appendix A

The Pitzer–Debye–Hückel equation is given as

$$\ln \gamma_i^{*\mathrm{PDH}} = -\left(\frac{1000}{M_\mathrm{W}}\right)^{1/2} A_\varphi \left[\left(\frac{2z_i^2}{\rho}\right) \ln(1+\rho I_x^{1/2}) + \frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right] \quad \text{(A.1)}$$

where I_x is the mole fraction ionic strength of the mixture and ρ is the “closest approach parameter”. The local composition activity coefficients of cation and anion in a multi-component solution were given as [14]:

$$\frac{1}{z_c} \ln \gamma_c^{\mathrm{lc}} = \sum_{a'} \left[\frac{X_{a'}}{\sum_{a''} X_{a''}}\right] \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_{B'} \frac{X_B G_{cB}}{\sum_k X_k G_{kB}} \left[\tau_{cB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}}\right] + \sum_a \sum_{c'} \left[\frac{X_{c'}}{\sum_{c''} X_{c''}}\right] \frac{X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}} \times \left[\tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right] \quad \text{(A.2)}$$

$$\frac{1}{z_a}\ln\gamma_a^{\mathrm{lc}} = \sum_{c'}\left[\frac{X_{c'}}{\sum_{c''}X_{c''}}\right]\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_B \frac{X_{Bm}G_{aB}}{\sum_k X_k G_{kB}}\left[\tau_{aB} - \frac{\sum_k X_k G_{kB}\tau_{kB}}{\sum_k X_k G_{kB}}\right] + \sum_c\sum_{a'}\left[\frac{X_{a'}}{\sum_{a''}X_{a''}}\right]\frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}} \times \left[\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right] \tag{A.3}$$

where

$$G_{ji} = \mathrm{e}^{-\alpha_{ji}\tau_{ji}}, \qquad G_{ji,ki} = \mathrm{e}^{-\alpha_{ji,ki}\tau_{ji,ki}},$$

$$G_{cB} = \frac{\sum_a X_a G_{ca,B}}{\sum_{a'}X_{a'}}, \qquad G_{aB} = \frac{\sum_c X_c G_{ca,B}}{\sum_{c'}X_{c'}}$$

g_{ji} and g_{ii} are energies of interaction between species j and i, and i and i, respectively. $X_j = x_j z_j$ is the effective mole fraction of species j (x_j and z_j are the mole fraction and charge number of ion j, respectively). α_{ji} is nonrandomness factor:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}, \qquad \tau_{ji,ki} = \frac{g_{ji} - g_{ki}}{RT},$$

$$\tau_{cB} = -\frac{\ln G_{cB}\sum_{a'}X_{a'}}{\sum_a X_a \alpha_{B,ca}}, \qquad \tau_{aB} = -\frac{\ln G_{aB}\sum_{c'}X_{c'}}{\sum_c X_c \alpha_{B,ca}}$$

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