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Phase Equilibrium Studies in the Geothermal Energy Development: The Effect of Hydrogen Bond on the Multi-Component Fluid

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Cite This: *ACS Omega* 2023, 8, 22195−22202

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ABSTRACT: Geothermal energy has become an emerging resource with both large reserves and environmental friendliness and is playing an increasingly important role in the current energy transition progress. In this paper, a thermodynamically consistent *NVT* flash model is developed to consider the effect of hydrogen bond on the phase equilibrium states of multi-component fluid to resolve the challenges of the special thermodynamic characteristic of water as the main working fluid. In order to provide practical suggestions to the industry, a number of possible effects have been investigated on the phase equilibrium states, including the hydrogen bond, environmental temperature, and fluid compositions. The calculated phase stability and phase splitting results can provide thermodynamic foundations for the establishment of the multi-component multi-phase flow model and also help optimize the development process to control the phase transitions for a number of engineering purposes.
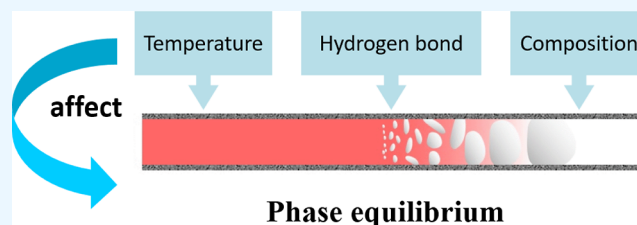
1. INTRODUCTION

With the world's energy crisis and environmental problems becoming increasingly severe, it is urgent to develop new alternative energy sources with both large reserves and environmental friendliness.[1] Recently, geothermal resources have gradually become an emerging and attractive clean energy that is now focused and developed by countries all over the world thanks to the advantages such as high cleanliness, stable operation, and wide spatial distribution.[2] In general, geothermal energy resources can be divided into hydrothermal type and hot dry rock type, in which the latter type of reservoirs takes more than 90% of the discovered resources.[3] This type of geothermal resource is mainly stored in granite or compact metamorphic rocks with a burial depth of 3−10 km and a temperature reaching 420 K.[4] It has been estimated that the amount of available hot dry rock type geothermal resources in the earth's crust is much larger that of all fossil energy sources that can be recovered,[5] and thus has been attracted a number of development projects. In 1974, the United States took the first step in carrying out related research on the development of hot dry rock,[6] and then Britain, France, Germany, Japan, and other countries also carried out related investigations,[7] in which the enhanced geothermal system (EGS) has been proposed and gradually accepted as the potential technique in geothermal energy development.[8] The main working flow of EGS development include the following steps, drilling the injection well, injecting high-pressure water into the reservoir through the injection well to force the rock to crack to form an artificial fracture network structure with high permeability, determining the location of the production well according to the artificial fracture network direction, forming various production types including one injection and one production, one injection and multiple production, or multiple injection and multiple production.[9] The heat recovery of geothermal energy is mainly achieved by injecting low-temperature working fluids such as water and carbon dioxide into the hot dry rock reservoir with an artificial fracture network generated through the injection well. After the heat has been exchanged from the hot dry rock into the working fluid, the hot fluid is produced through the production well.

Although the EGS technique has attracted increasing attention in the current popularity of energy transition, most of the EGS geothermal development projects that have been built up have been closed now, and the existing projects are mostly experimental projects, which have not really realized commercial developments.[10] The main challenges in practical applications are mainly caused by the complex flow and heat transfer process that may occur in the reservoir and wellbores, and the combining mechanisms including seepage flow, chemical reactions, geo-mechanics, and other effects may also play a role.[11] As the current understanding of the complex coupled mechanisms is not clear enough, a huge difference
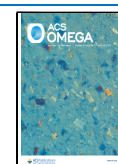
may exist between the designed process and actual production performance. Furthermore, the fracture network formed through the injection well may contain multi-scale geo-formations including bedrock pores, small fractures, and large fractures, with scales varying from nanometer, micrometer to millimeters. The cross-scale characteristics is prominent in the hot dry rock development, and the working fluid flowing through the fractured porous media is more complex as the boundary conditions vary significantly.[12] Moreover, the heat exchange between the working fluid and the hot dry rock may further put thermal stress on the formations, which will cause the "secondary development" of fractures.[13] Meanwhile, the dynamic dissolution and precipitation of rocks and minerals in the working fluid may also gradually modify the geometry and size of the flow channels in the reservoir,[14] and further increases the difficulties in modeling the multi-scale multi-field coupled system.

In order to figure out the mechanisms controlling the multi-scale multi-field coupled flow and heat transfer in the hot dry rock reservoir, at least the thermal-fluid coupling model is needed to describe the physics.[15] This type of two-field models have been widely applied in the past decades to study the effects of fracture opening, reservoir permeability, injection pressure, and physical properties of working fluid during heat transfer and recovery in EGS systems.[16] Based on the basic two-field coupling model, two types of three-field coupling models have been proposed to take into account more complex mechanisms, namely, the "thermal-fluid-mechanical" and "thermal-fluid-chemical",[17] respectively, to achieve a relatively more complete description of the hot dry rock reservoir. In the process of geothermal energy development with injected working fluid flowing through the fractures and exchanging the heat with the surrounding rocks, the sharp change of temperature may result in dramatic phase transitions. Ignoring the possible phase change phenomenon may lead to unreasonable design of the development scheme, which may lead to gas plugging and hydraulic loss. In addition, the occurrence of phase change may also bring challenges to the design of thermal insulation structure in the production well, causing unnecessary heat loss, affecting the prediction of outlet temperature and pressure and leading to the inaccurate prediction on the production performance of EGS. As a result, the design of EGS may fail to achieve the expected effect, and the economic and safety targets cannot be achieved. Therefore, it is necessary to carry out comprehensive investigations on the possible phase transitions during the development of geothermal energy recovery.

At present, in geothermal energy researches, semi-theoretical and semi-empirical models, such as Lee model[18] and Tanasawa model,[19] are used as the governing equations controlling the phase transitions. However, manual selection of certain empirical parameters are needed in solving such models, and there is always a challenge in handling the phase equilibrium problems for multi-component fluids. In practical geothermal energy development, although the injection and production working medium is always considered as purely water or carbon dioxide under ideal conditions, complex geo—chemical reactions may happen when flowing through high-temperature underground porous media, leading to the dissolution of carbonate and other impurities in the working fluid, and multi-component fluid flow can be detected in the produced well. Thus, a thermodynamically consistent phase equilibrium calculation method is essentially needed to accurately describe

the multi-component phase equilibrium states under complex environmental conditions.[20] As a general model describing the relationship between various thermodynamic features, the equation of state, also known as EOS, plays a key role in generating a thermodynamic self-consistent flash algorithm to calculate the phase equilibrium states.[21] The flash algorithm based on the EOS can be divided into two main categories: "flash under the given substance's mole, pressure, and temperature (NPT)" and "flash under the given substance's mole, molar volume and temperature (NVT)". NPT flash has a long history and easy implementations and thus has been widely used in previous phase equilibrium studies.[22] However, since the pressure is a constant environmental condition in the NPT flash algorithm, it may not be suitable for the geothermal energy development process along with violent pressure fluctuations, so that the NVT flash algorithm is obviously more applicable in the designing and production of EGS. In addition, considering that water is usually selected as the main working fluid in geothermal development,[23] it is necessary to introduce the hydrogen bond effect into the flash algorithm. The hydrogen bond is a kind of intermolecular force, which is a force between permanent dipoles.[24] The hydrogen bond occurs between the hydrogen atoms that have been combined with other atomic bonds by covalent bond and another atom. Generally, the atoms on both sides of the hydrogen atom where the hydrogen bond occurs are electronegative protons. Hydrogen bonds can be intermolecular or intramolecular. It is obvious that the effect of hydrogen bond should be considered in the multi-component phase equilibrium studies, as the intermolecular forces can make the thermodynamic correlations more complex. It is worth mentioning that when the working fluid in geothermal exploitation is a mixture of water and carbon dioxide, it is necessary to consider both the self-association of water and the cross association between water and carbon dioxide, which puts forward higher requirements for the stability of the NVT flash model.

In this study, a thermodynamically consistent NVT flash calculation scheme will be developed and applied in the phase equilibrium studies in the geothermal energy. The effect of the hydrogen bond will be coupled with the conventional multi-component phase equilibrium model in order to meet the special demands in the EGS development. The remainder of this paper is organized as follows. In Section 2, the flash calculation scheme will be established, and the application in EGS production is presented in Section 3. The effect of hydrogen bond on the phase equilibrium states of the multi-component fluid will be demonstrated, as well as investigating the effect of temperature and fluid compositions to meet practical engineering demands. Concluding remarks are given in Section 4, with suggestions for the industry and future studies.

2. METHODOLOGY

2.1. Thermodynamically Consistent NVT Flash Scheme.
In order to construct a thermodynamically consistent flash calculation model, the dissipation of the system energy should be ensured as required by the second law of thermodynamics, which is equivalent to the consistent decrease of total entropy. The change of entropy can be formulated as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S_{\mathrm{sys}}}{\mathrm{d}t} + \frac{\mathrm{d}S_{\mathrm{env}}}{\mathrm{d}t} = \frac{\mathrm{d}S_{\mathrm{sys}}}{\mathrm{d}t} - \frac{1}{T}\frac{\mathrm{d}\_Q}{\mathrm{d}t}$$
$$= \frac{1}{T}\frac{\mathrm{d}F}{\mathrm{d}t} - \frac{p_c}{T}\frac{\mathrm{d}V^{\mathrm{G}}}{\mathrm{d}t} \tag{1}$$

where S denotes the entropy, F is the Helmholtz free energy, T is the temperature, p_c is the capillary pressure, and V^{G} is the volume of the gas phase. The subscripts sys and env denote the system and environment, respectively. Using the chain rule, the change of Helmholtz free energy over time can be formulated as

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \frac{\partial F}{\partial V^{\mathrm{G}}}\frac{\partial V^{\mathrm{G}}}{\partial t} + \sum_{i=1}^{M}\frac{\partial F}{\partial N_i^{\mathrm{G}}}\frac{\partial N_i^{\mathrm{G}}}{\partial t}$$
$$= (p_{\mathrm{L}} - p_{\mathrm{G}})\frac{\partial V^{\mathrm{G}}}{\partial t} + \sum_{i=1}^{M}(\mu_i(\mathbf{n}^{\mathrm{G}}) - \mu_i(\mathbf{n}^{\mathrm{L}}))\frac{\partial N_i^{\mathrm{G}}}{\partial t} \tag{2}$$

where p denotes the pressure, N is the number of moles, μ_i is the chemical potential of component i, and M is the total number of components in the mixture. The subscripts L and G denote the liquid phase and gas phase, respectively.

According to Onsager's reciprocal principle,[25] there exists a symmetrical matrix, $\mathbf{\Psi} = (\psi_{i,j})_{i,j=1}^{M+1}$, that can construct the time-marching scheme of moles and volume as

$$\frac{\partial N_i^{\mathrm{G}}}{\partial t} = \sum_{j=1}^{M}\psi_{i,j}(\mu_j(\mathbf{n}^{\mathrm{L}}) - \mu_j(\mathbf{n}^{\mathrm{G}})) + \psi_{i,M+1}(p_{\mathrm{G}} - p_{\mathrm{L}} - p_c)$$
$$, \qquad 1 \le i \le M \tag{3}$$

$$\frac{\partial V^{\mathrm{G}}}{\partial t} = \sum_{j=1}^{M}\psi_{M+1,j}(\mu_j(\mathbf{n}^{\mathrm{L}}) - \mu_j(\mathbf{n}^{\mathrm{G}})) + \psi_{M+1,M+1}$$
$$(p_{\mathrm{G}} - p_{\mathrm{L}} - p_c) \tag{4}$$

In order to meet the requirement of the second law of thermodynamics, $\mathbf{\Psi}$ shall be positive definite, and a simple way to construct such coefficient is to take a diagonal positive definite matrix as

$$\psi_{i,i} = \frac{D_i N_i^t}{RT}, \, i = 1, \cdots, M,$$
$$\psi_{M+1,M+1} = \frac{C_V^{\mathrm{G}}C_V^{\mathrm{L}}V^t}{C_V^{\mathrm{L}}p_{\mathrm{G}} + C_V^{\mathrm{G}}p_{\mathrm{L}}} \tag{5}$$

where D_i denotes the diffusion coefficient of component i. The two coefficients, C_V^{G} and C_V^{L}, are selected to ensure that $C_V^{\mathrm{G}}p_{\mathrm{G}} \ge 0$, $C_V^{\mathrm{L}}p_{\mathrm{L}} \ge 0$.

A semi-implicit numerical scheme can be designed to update the mole and volume information as

$$\frac{N_i^{\mathrm{G},k+1} - N_i^{\mathrm{G},k}}{\delta t_k} = \frac{D_i N_i^t}{RT}(\mu_i^{\mathrm{L},k+1/2} - \mu_i^{\mathrm{G},k+1/2}) \tag{6}$$

$$\frac{V^{\mathrm{G},k+1} - V^{\mathrm{G},k}}{\delta t_k} = \frac{C_V^{\mathrm{G}}C_V^{\mathrm{L}}V^t}{C_V^{\mathrm{L}}p_{\mathrm{G}}^k + C_V^{\mathrm{G}}p_{\mathrm{L}}^k}(p_{\mathrm{G}}^{k+1/2} - p_{\mathrm{L}}^{k+1/2}$$
$$- p_c^{k+1/2}) \tag{7}$$

The thermodynamic consistency can be proved by showing

$$F^{k+1} - F^k + p_c^{k+1/2}(V^{\mathrm{G},k+1} - V^{\mathrm{G},k})$$
$$\le -\frac{D_i N_i^t}{RT}(\mu_i^{\mathrm{L},k+1/2} - \mu_i^{\mathrm{G},k+1/2})^2 - \frac{C_V^{\mathrm{G}}C_V^{\mathrm{L}}V^t}{C_V^{\mathrm{L}}p_{\mathrm{G}}^k + C_V^{\mathrm{G}}p_{\mathrm{L}}^k}$$
$$(p_{\mathrm{G}}^{k+1/2} - p_{\mathrm{L}}^{k+1/2} - p_c^{k+1/2})^2$$
$$\le 0 \tag{8}$$

2.2. Effect of Hydrogen Bond. With the development of Wertheim's thermodynamic perturbation theory,[26] Cubic-Plus-Association type equations of state have been introduced into the phase equilibrium calculation scheme of water thanks to their ability to accurately describe hydrogen bond interactions. In order to correspond to thermodynamic models developed based on classical cubic equations of state (such as the Peng–Robinson equation of state, PR EOS [PR]) to facilitate the construction of coupling models, the Helmholtz free energy of aqueous mixtures is defined as

$$F = F^{\mathrm{PR}} + F^{\mathrm{ASSOC}} \tag{9}$$

where the PR-type Helmholtz free energy can be calculated using the PR EOS as

$$F^{\mathrm{PR}} = NRT\left(\ln\frac{N}{V} - 1\right) - NRT\ln\left(\frac{V - bN}{V}\right)$$
$$+ \frac{aN}{2\sqrt{2}\,b} \times \ln\left(\frac{V + (1 - \sqrt{2})bN}{V + (1 + \sqrt{2})bN}\right) \tag{10}$$

and the association-type Helmholtz free energy can be calculated as

$$F^{\mathrm{ASSOC}} = NRT\sum_A\left(\ln X_A - \frac{1}{2}X_A + \frac{1}{2}\right) \tag{11}$$

The unbounded site fractions, X_A, in eq 11 can be obtained by

$$X_A = \frac{1}{1 + \frac{1}{V}N\sum_B X_B \Delta^{AB}} \tag{12}$$

and the association strength can be calculated by

$$\Delta^{AB} = g\beta^{AB}\left[\exp\left(\frac{\varepsilon^{AB}}{RT}\right) - 1\right]b \tag{13}$$

In this study, considering the practical working fluid in realistic geothermal energy development is a mixture containing water and other components, the targeting fluid studied in phase equilibrium is selected as a combination of water and carbon dioxide. The key thermodynamic features of the two components are listed in Table 1. The acentric factor is a conceptual number that is proposed as a measure of the non-sphericity (centricity) of molecules, and works as a key feature in flash calculations along with other thermodynamic properties like critical temperature and pressure.
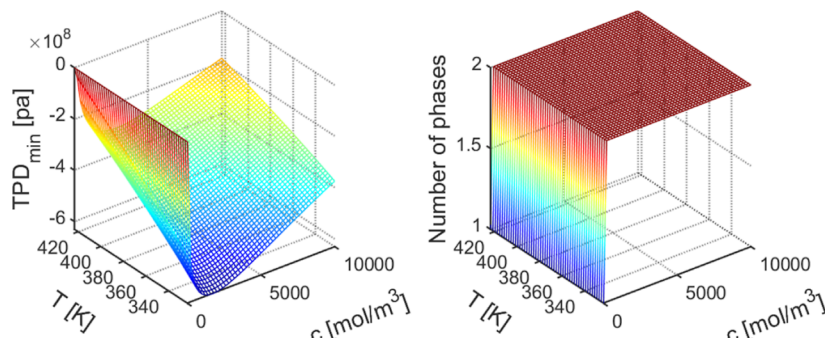
Table 1. Key Thermodynamic Features of the Working Fluid Mixture in Geothermal Energy Development

component	critical temperature [K]	critical pressure [MPa]	acentric factor
water	647.45	22.05	0.3449
carbon dioxide	304.22	7.3864	0.2250
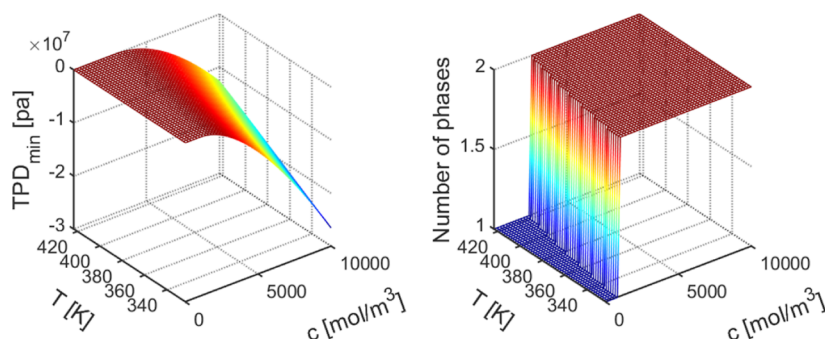
Figure 1. TPD function (left) and number of phases at equilibrium (right) if the hydrogen bond is taken into account.

Figure 2. TPD function (left) and number of phases at equilibrium (right) if hydrogen bond is not taken into account.

3. RESULTS AND DISCUSSION

In this section, the results of phase equilibrium calculations are presented using the developed *NVT* flash scheme. The effect of hydrogen bond, temperature and compositions will be studied by comparisons on both the phase stability test and the phase splitting calculation. Given the critical temperature and pressure of the two components, a large range of temperate conditions is set as [323.15 K, 423.15 K] to capture the possible phase transitions, especially for the hot dry rock reservoirs where the temperature can be higher than 420 K, while the overall mole concentration range is set as [0 mol/m³, 10,000 mol/m³] to represent the concentrations found in practical production systems and the corresponding pressure conditions.

3.1. Effect of Hydrogen Bond. In this study, considering the fact that water is the dominant species in the working fluid in geothermal energy development, the mole fraction of water in the feed compositions is set as 0.9, while that of carbon dioxide is set as 0.1. Generally, the phase stability test is the first step in phase equilibrium studies, as this process can give the information of whether the fluid mixture can remain stable in the single phase region or phase transition may occur. The tangent plane distance (TPD) function[27] is an effective approach indicating the number of phases at equilibrium and has been widely applied in a number of numerical scenarios representing various engineering applications.[28] Considering the *NVT* flash scheme derived based on Helmholtz free energy in this paper, the following equation is used to calculate the TPD function with respect to the Helmholtz free energy surface

$$D_{\mathrm{E}}(d) = \sum_{i=1}^{nc} d_i[\mu_i(d) - \mu_i(d_0)] - (p(d) - p(d_0)) \qquad (14)$$

where d denotes the vector of component molar densities and D_{E} the TPD with respect to the Helmholtz free energy density E. Generally speaking, the fluid mixture can remain stable in the single phase region if the TPD function under that condition is calculated to be zero, while phase transition may occur if TPD is negative. The TPD function of the sample mixture is calculated and shown in Figure 1, as well as the corresponding number of phases at equilibrium.

It can be referred from the images that phase transition occurs for the fluid mixture if the effect of hydrogen bond is considered, and the mixture changes from the single-vapor-phase region to the vapor−liquid-two-phase region with the increase of overall mole concentrations. This is explainable as a larger overall mole concentration corresponds to a larger pressure, which may liquidize the gas. Moreover, a large single-vapor-phase region can be observed at a larger temperature, as the molecule motions are accelerated and the liquid phase may be gasified.

The effect of hydrogen bond can be observed from Figure 2, in which the TPD function and the corresponding number of phases at equilibrium plotted are calculated considering no hydrogen bond. As can be seen from the figures, there is no single-phase region within the computational domain if hydrogen bond is not taken into account, and the TPD function is much smaller than in Figure 1 with the hydrogen bond. The extremely high critical temperature of water is usually believed as a consequence of hydrogen bond effect, and thus, the conventional *NVT* flash scheme without special treatment on the hydrogen bond may overestimate the effect by considering only the critical features. A stronger interaction between the molecules can lead to an easier transition into the liquid phase. In other words, the thermodynamic perturbation modeling is a correction to better describe the effect of hydrogen bond.

The changing curve of the number of phases at equilibrium with respect to the overall mole concentration plotted in Figure 3 shows more clearly on the effect of hydrogen bond on
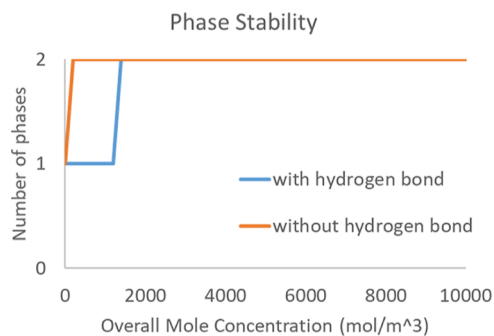

Figure 3. Number of phases at constant $T = 363.15$ K.

the phase stability. At the constant temperature as 363.15 K, the phase stability conditions tested by the flash scheme with hydrogen bond represents the existence of single-vapor-region at lower overall mole concentrations, and then transition to the vapor−liquid-two-phase region with the increase in mole concentrations. However, if hydrogen bond is not considered in the *NVT* flash scheme, no single-phase region can be obtained in the domain. Thus, the phase transition temperature is underestimated if no accurate treatment on the hydrogen bond effect is taken in the flash scheme. For the geothermal energy industry, if the working fluid is expected to remain in the single-phase region to avoid unexpected damages to the structure integrity of the production facilities as a consequence of violent phase transitions, a larger pressure conditions can be accepted using the proposed algorithm. A more accurate description on the thermodynamic features of water is obtained using the Cubic-Plus-Association-EOS-based thermodynamic models compared with solely based on the critical features. However, phase transition can also be enforced for special engineering purposes, for example, to separate certain species, and a larger pressure is needed compared to the simple description of water only by the critical thermodynamic features.

3.2. Effect of Temperature. In practical geothermal energy development, the change of temperature along the flow of working fluid is usually the main cause of phase transition. Especially, the sudden change of temperature when the working fluid entering the production well may result in a violent phase transition. Using the developed *NVT* flash scheme, the effect of temperature on the phase stability is first tested, and the result is plotted in Figure 4. Generally speaking, with the increase of the overall mole concentration, the number of phases at equilibrium changes from 1 to 2, which indicates the transition from the single-vapor-phase region into the vapor−liquid-two-phase regions. Moreover, a larger temperature may result in a larger single-vapor-phase region, which corresponds to a higher overall mole concentration for the phase transition into the two-phase region. This is reasonable as a higher temperature is always preferable for the mixture to remain in the vapor phase. For the geothermal energy industry, such findings can help optimize the heating and cooling processes of the working fluid when injection and extraction to avoid unnecessary phase transitions that may damage the facilities. Moreover, loss on the heat and hydraulic
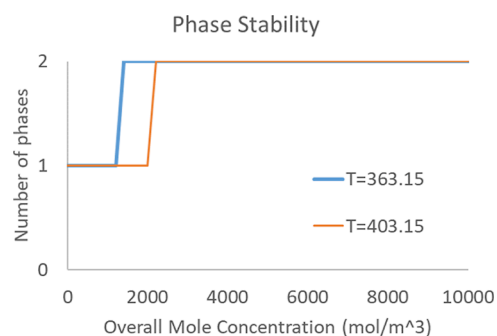

Figure 4. Phase stability test at different temperatures.

potential can also be controlled if the fluid flow along the EGS process remains in a single phase.

In addition to the phase stability test, phase splitting calculations are also important in describing the phase equilibrium states, as the compositional mole fractions in each phase can be obtained. The phase splitting results at the constant temperature as 363.15 K are shown in Figure 5. It can be referred that the compositional mole fractions in the vapor phase almost keep the same with the increase in overall mole concentration, with only a slight change at the phase transition point. The mole fraction of water in the vapor phase will slightly increase, and that of carbon dioxide may slightly decrease at that point. In general, due to the large ratio between the feed mole fractions of the two components, there is a huge difference between the compositional mole fractions in the vapor phase. On the contrary, a significant change can be captured for the compositional mole fractions in the liquid phase. For both components, the fraction remains at zero in the single-vapor-phase region, and then, the fraction of water sharply increases after entering the two-phase region. The mole fraction of carbon dioxide in the liquid phase will gradually increase, when that of water gradually decreases. This phenomena is also reasonable as more water is fed into the mixture, so that the mole fraction is higher at first. However, carbon dioxide is easier to be liquidized due to the lower critical pressure; thus, its fraction can be higher than that of water at a higher pressure when more water remains in the vapor phase.

At a different temperature, 403.15 K, the phase splitting calculation is also carried out and the compositional mole fractions in each phase are plotted in Figure 6. Similarly, the mole fraction of water in the vapor phase slightly increases with the increase in overall mole concentration, while that of carbon dioxide slight decreases. The trend in the liquid phase is also similar, with a sharp increase and gradual decrease of water fraction and a gradual increase of carbon dioxide fraction. An obvious difference with the phase equilibrium states at 363.14 K can be observed that the increase of carbon dioxide mole fraction in the liquid phase is much slower, as well as the decreasing rate of water. In other words, at a higher temperature, less carbon dioxide will be liquidized under the same pressure conditions. The importance of phase equilibrium studies is demonstrated that flash calculations should be carried out if the environmental conditions have been changed, in order to figure out the number of phases at equilibrium and compositional mole fractions in each phase. These information can be helpful for the industry to optimize the geothermal energy development, including whether to adjust the operation conditions to ensure the single-vapor-phase flow.
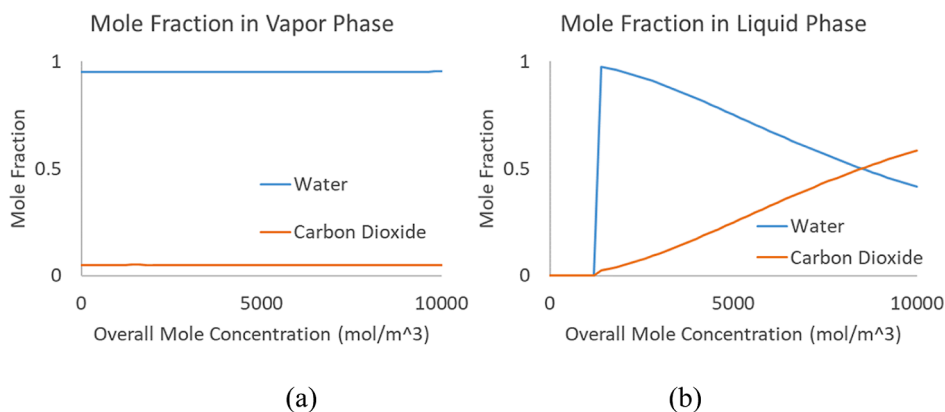
Figure 5. Compositional mole fractions in the vapor phase (a) and liquid phase (b) of the fluid mixture at constant $T = 363.15$ K.
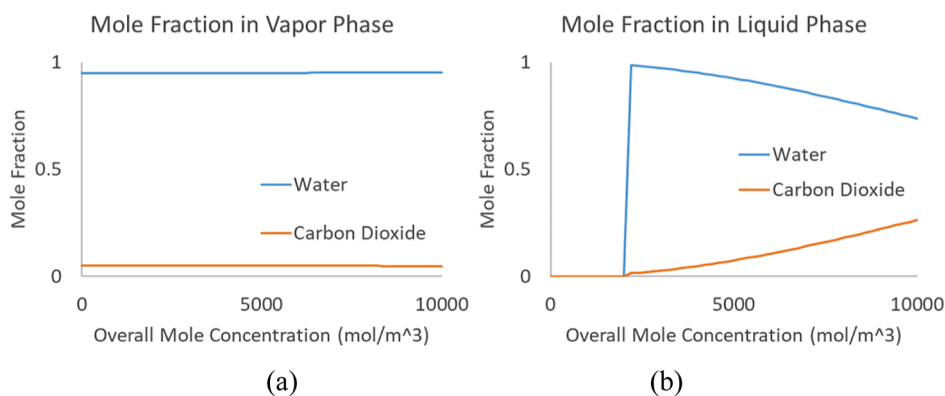

Figure 6. Compositional mole fraction in the vapor phase (a) and liquid phase (b) of the fluid mixture at constant $T = 403.15$ K.
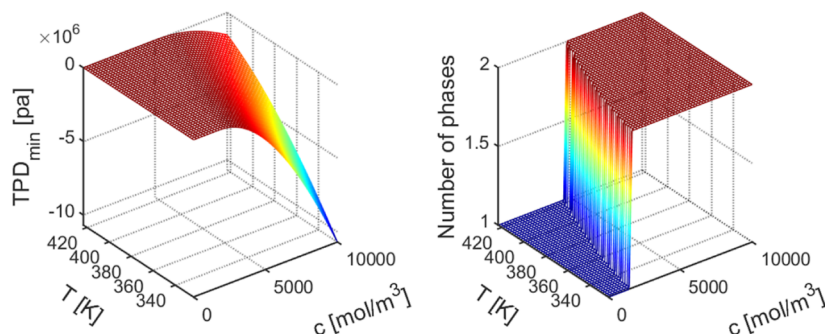

Figure 7. TPD function (left) and number of phases at equilibrium (right) for composition 2.

3.3. Effect of Compositions. In the development of geothermal energy resources, the compositions of the working fluid may vary with the different environmental conditions. Complex geo-chemical reactions may occur with dynamic dissolution and precipitation processes.[29] Thus, another feed composition of the targeting fluid is designed to test the robustness of the developed flash algorithm, and the effect of compositions on the phase equilibrium states is investigated. In the new composition, named as composition 2, the mole fraction of water is set as 0.5, while that of carbon dioxide is set as 0.5 as well. Within the same temperature and overall mole concentration conditions, the TPD function and the corresponding number of phases at equilibrium for the composition 2 mixture are presented in Figure 7. Compared with Figure 1, it is easy to find that a larger single-vapor-region can be obtained, which indicates a lower temperature and higher pressure for the mixture to be liquidized. In other

words, a higher requirement on the environmental conditions are needed to liquefy the mixture. This finding is reasonable as carbon dioxide is more preferable to remain in the vapor phase under the same environmental conditions, and more carbon dioxide has been fed into the mixture in this composition.

The number of phases at equilibrium changing with the overall mole concentrations at the constant temperature as 363.15 K can be obtained for both the two components, as illustrated in Figure 8. A larger single-phase region can be captured clearly with a larger overall mole concentration entering the two-phase region for composition 2. Thus, if more carbon dioxide exists in the working fluid in geothermal energy development, a larger range of environmental conditions can be tolerated to keep the mixture in the single-vapor-phase region.

The compositional mole fractions at equilibrium can also be obtained for composition 2 by phase splitting calculations, as
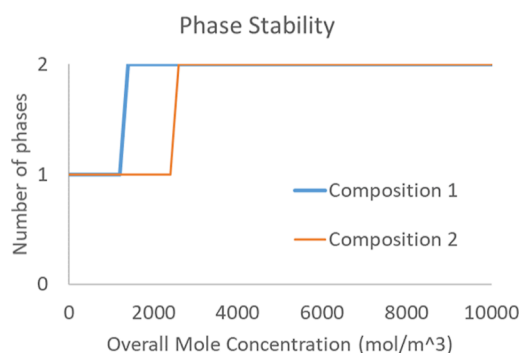
Figure 8. Phase stability test at constant T = 363.15 K for composition 1 and composition 2, respectively.

shown in Figure 9. At the constant temperature as 363.15 K, the mole fraction in the vapor keep consistent with half the water and half the carbon dioxide, which is the same as the feed composition as only the vapor phase exists under certain conditions. With the increase of the overall mole concentration entering the two-phase region, the fraction of water in the mixture sharply decreases and then gradually increases, while that of carbon dioxide sharply increases and then gradually decreases. Correspondingly, the mole fractions in the liquid phase are maintained at zero for both the two components, and then, the fraction of water sharply increases and then gradually decreases. This phenomena further indicates the easier liquefaction of water when entering the two-phase region, and the faster liquefaction of carbon dioxide with the increase of pressure. Thus, in practical geothermal energy development, if the compositions in the working fluid varies with the recovery progress, it is important to carry out phase equilibrium studies to obtain the information regarding phase stability and phase splitting to suggest the development processes.

4. CONCLUSIONS

In this work, a thermodynamically consistent *NVT* flash algorithm is developed with the effect of hydrogen bond taken into account to study phase equilibrium states in the geothermal energy development. Considering the complex conditions in practical production, including the special thermodynamic properties of water, the varying temperature along the process and the changing fluid compositions as a consequence of dissolution and dissipation, the effect of hydrogen bond, environmental temperature, and fluid

compositions on the phase equilibrium states have been investigated.

Based on the phase stability test and phase splitting calculations, the energy industry can optimize the development process to ensure that the working fluid remains in the single-phase region or enforce the phase transitions of the working fluid for different engineering purposes, for example, to avoid unnecessary damages to the facilities or to enforce the separation of unexpected species. Moreover, the calculated phase equilibrium states can also provide helpful information to generate a more efficient and accurate multi-component multi-phase flow model, for example, to simplify the model into single-phase models if only single phase exists at equilibrium.[30] A number of multi-phase flow algorithms have been developed in the past decades to study the heat transfer and phase transition,[31] with which the phase equilibrium calculations can be incorporated to establish a comprehensive scheme. Using the phase equilibrium information, a solid thermodynamic foundation can be established for further hydraulic, geochemical, and mechanical description in the geothermal energy development system, and can be used directly as the initial sates for phase evolutions. It should also be pointed out that the iterative flash algorithms cannot be widely applied in practical geothermal energy development, as it could be very time-consuming as the equilibrium states may vary with the changing temperature and pressure conditions. Repeated flash calculations in a large spatial and temporal domain with rapid changes in the environmental conditions are calling for an efficient and robust phase equilibrium algorithms. The emerging big data techniques[32] and deep learning algorithms[33] are expected in future studies to accelerate phase equilibrium calculations to make it useful in practical geothermal energy development.

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(a)

(b)
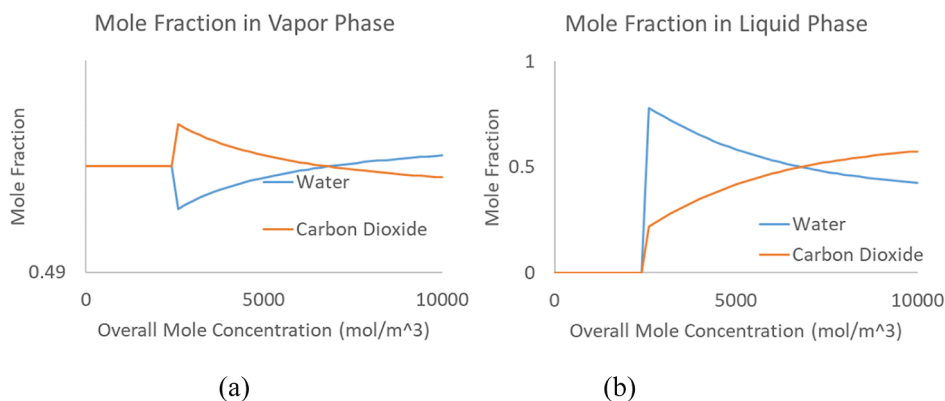
Figure 9. Compositional mole fractions in the vapor phase (a) and liquid phase (b) for the composition 2 at constant T = 363.15 K.

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Notes

The authors declare no competing financial interest.

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