New concept to describe three-phase capillary pressure–degree of saturation relationship in porous media

Highlights

- Leverett concept is usually used to model water–nonaqueous phase liquid (NAPL)–air system.
- However, this concept is not applicable in the case of nonspreading NAPLs.
- We discuss limitations of Leverett concept based on state parameter μ.
- New concept applicable to both nonspreading and spreading NAPLs is proposed.
- Proposed concept is validated by comparing experimental and simulation results.

Abstract

The Leverett concept is used conventionally to model the relationship between the capillary pressures and the degrees of saturation in the water–nonaqueous phase liquid (NAPL)–air three-phase system in porous media. In this paper, the limitation of the Leverett concept that the concept is not applicable in the case of nonspreading NAPLs is discussed through microscopic consideration. A new concept that can be applied in the case of nonspreading NAPLs as well as spreading NAPLs is then proposed. The validity of the proposed concept is confirmed by comparing with past experimental data and simulation results obtained using the conventional model based on the Leverett concept. It is confirmed that the proposed concept can correctly predict the observed distributions of NAPLs, including those of nonspreading ones.

Keywords: capillary pressure; degree of saturation; nonspreading nonaqueous phase liquid (nonspreading NAPL); porous media; water–nonaqueous phase liquid (NAPL)–air three-phase system

1. Introduction

Being able to simulate the seepage behavior of water–nonaqueous phase liquid (NAPL)–air three-phase systems in porous media such as soils is of great importance in geoenvironmental engineering, especially when predicting the ground contamination resulting from the leakage of NAPLs as well as when selecting an efficient remediation method. To predict the seepage flow of NAPLs in a three-phase system, a rational model for the permeability coefficients of the three void fluids is crucial. As the permeability coefficients are primarily determined by the degrees of saturation of the three fluids, the relationship between the capillary pressures and the degrees of saturation of the void fluids needs to be described properly.

In the case of the capillary pressure–saturation relationship in three–phase systems, Leverett (1941) assumed that the NAPL spreads across the water–air interface in a water-wet porous medium and separates the water and air phases. This assumption leads to the following conclusions: (a) the water saturation degree depends only on the capillary pressure between the water and the NAPL; and (b) the liquid saturation degree (which is the sum of the degrees of water saturation and NAPL saturation) depends on the capillary pressure between the NAPL and air phases. Based on this assumption, a number of models for the relationship between the capillary pressure and the degree of saturation for three-phase systems (van Genuchten, 1980; Lenhard and Parker, 1987a, 1987b, 1988, 1990; Parker and Lenhard, 1987, 1990; Parker et al., 1987; Farr et al., 1990; Blunt et al., 1995; Zhou and Blunt, 1997) have been proposed.

Meanwhile, it is usually believed that the configuration of the three fluids in a void space will necessarily be influenced by their wettability. A few NAPLs such as hexane will spread over the surface of the water phase, while others such as perchloroethylene (PCE) and decane will form a lens-like structure at the water–air interface (McBride et al., 1992; Hofstee et al., 1997). Thus, the Leverett assumption that the NAPL spreads across the water–air interface will not necessarily hold. Hofstee et al. (1997) determined the PCE–air and water–PCE–air retention curves and suggested that the Leverett concept is not applicable in the case of nonspreading NAPLs. In addition, experimental data (Kalaydjian et al., 1993; Vizika and Lombard, 1996; Zhou and Blunt, 1997) have shown that the residual saturation degree of a nonspreading NAPL in water–NAPL–air systems increases with a decrease in the spreading coefficient.

In this study, we first highlighted the limitations of the classical Leverett concept by proving the existence of a critical ratio of the capillary pressures at which the NAPL layer covering the water–air interface cannot exist stably at the microscale (Keller et al., 1997; Fenwick and Blunt, 1998a, 1998b). Next, we propose a new concept for the capillary pressure–degree of saturation relation for three-phase systems in porous media while considering the effects of the spreading coefficient of the NAPL. The proposed concept employs the relative magnitude of the NAPL pressure with respect to the water and air pressures as defined by Nakamura and Kikumoto (2014) and should be applicable to any capillary pressure–degree of saturation model (e.g., van Genuchten (1980) and Brooks and Corey (1964)). We also propose a method for taking into account the residual NAPL saturation degree in the three-phase system by using the irreducible (or minimum) degree of saturation of NAPL in the same way as is the case for the residual water in the water–air two-phase system. Finally, the performance of the proposed concept is evaluated based on comparisons with experimental data subject to a monotonic drainage path (Zhou and Blunt, 1997).

2. Overview of existing theories for three-phase systems in porous media

In order to propose a new concept for the capillary pressure–degree of saturation relationship that overcomes the limitations of the classical Leverett concept, we first outline the existing theories for three–phase systems in porous media and their limitations.

2.1. Capillary pressure–degree of saturation relationships for two–phase systems in porous media

Using Laplace's equation, the capillary pressure, P_{cij}, between two fluid phases i and j is given by

$$P_{cij} = P_i - P_j = 2\gamma_{ij}/r_{ij} \tag{1}$$

where P_i and P_j are the pressures of the fluid phases i and j, respectively; γ_{ij} is the interfacial tension between the fluid phases i and j; and r_{ij} is the radius of curvature of the i–j phase interface. As r_{ij} can be regarded as being a characteristic of the porous medium, Equation (1) means that the relationship for each combination of phases i and j (i.e., for each i–j system) can be represented by P_{cij}/γ_{ij} (Leverett, 1941; Miller and Miller, 1956).

On substituting the contact angle of the fluid phases i and j, θ_{ij}, and the radius of the capillary tube, a $\left(= r_{ij}\cos\theta_{ij}\right)$, into Equation (1), we obtain the following relationship:

$$\frac{2}{a} = \frac{P_{cij}}{\gamma_{ij}\cos\theta_{ij}} \tag{2}$$

This suggests that the radius, a, is uniquely defined by P_{cij}, γ_{ij}, and θ_{ij}. The degree of saturation is generally determined by the cumulative pore-size distribution, that is, by the pores saturated with the wetting fluid and having an opening radius smaller than a threshold value, a (e.g., Nimmo, J. R., 2004). Thus, as a is a function of the effective degree of saturation, $\bar{S}_j$, we can define a function J using Equation (2) as follows:

$$J(\bar{S}_j) = \frac{2}{a} = \frac{P_{cij}}{\gamma_{ij}\cos\theta_{ij}} \tag{3}$$

where the subscripts i and j denote the nonwetting and wetting phases, respectively. The inverse function, J^{-1} , also exists:

$$J^{-1}\left(\frac{P_{cij}}{\gamma_{ij}\cos\theta_{ij}}\right) = \bar{S}_j \tag{4}$$

For the water–air two-phase system, the effective degree of saturation of water, $\bar{S}_{\mathrm{w}}$, is thus given as

$$\bar{S}_{\mathrm{w}} = \frac{S_{\mathrm{w}} - S_{\mathrm{w}}^{\mathrm{min}}}{1 - S_{\mathrm{w}}^{\mathrm{min}} - S_{\mathrm{a}}^{\mathrm{min}}} = J^{-1}\left(\frac{P_{\mathrm{caw}}}{\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}}\right) \tag{5}$$

where S is the actual degree of saturation, the subscripts w and a denote water and air, respectively, and the superscript $\min$ denotes the minimum (irreducible) degree of saturation. Several equations have been proposed for $\bar{S}_{\mathrm{w}}$. For instance, van Genuchten (1980) proposed the following one:

$$\bar{S}_{\mathrm{w}} = J_{\mathrm{VG}}^{-1}\left(\frac{P_{\mathrm{caw}}}{\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}}\right) = \{1 + (\alpha P_{\mathrm{caw}})^{n}\}^{\frac{1-n}{n}} \tag{6}$$

with two parameters, α and n. As Equation (6) states that $\bar{S}_{\mathrm{w}}$ is a function of $\frac{P_{\mathrm{caw}}}{\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}}$, α is actually a parameter specific to the water–air two phase system and can be represented by

$$\alpha = \frac{a_{\mathrm{VG}}}{2\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}} \tag{7}$$

where a_{VG} is a constant that is specific to the porous media. Meanwhile, Brooks and Corey (1964) proposed that

$$\bar{S}_{\mathrm{w}} = J_{\mathrm{BC}}^{-1}\left(\frac{P_{\mathrm{caw}}}{\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}}\right) = \left(\frac{P_{\mathrm{caw}}}{P_{\mathrm{caw}}^{\mathrm{d}}}\right)^{-\lambda} \tag{8}$$

where λ is a material parameter and $P_{\mathrm{caw}}^{\mathrm{d}}$ is the entry pressure of air in the water–air two-phase system and given by the following equation:

$$P_{\mathrm{caw}}^{\mathrm{d}} = \frac{2\gamma_{\mathrm{aw}}\cos\theta_{\mathrm{aw}}}{a_{\mathrm{BC}}} \tag{9}$$

where a_{BC} is a parameter specific to the porous media.

2.2. Leverett concept and classical capillary pressure–degree of saturation relationships for water–NAPL–air three-phase system in porous media

The Leverett concept (Leverett, 1941) has been usually used to predict the capillary pressure–degree of saturation relationship for three-phase systems based on the relationships for the water–NAPL and NAPL–air two-phase systems. Leverett assumed that, in a water-wet porous medium, the NAPL spreads over the water–air interface, and the water and air phases do not come in contact with each other. This leads to the following: (a) the effective water saturation degree can be determined as a function of the capillary pressure between the water and NAPL phases alone, and (b) the effective degree of total liquid saturation (which is the sum of the degrees of water saturation and NAPL saturation) can be determined as a function of the capillary pressure between the NAPL and air phases alone. Based on Equation (3) and Leverett's assumption stated above, the effective degree of water saturation, $\bar{S}_{\mathrm{w}}$, and the effective degree of total liquid saturation, $\bar{S}_{\mathrm{t}}$, in the three-phase system can be written as

$$J(\bar{S}_{\mathrm{w}}) = \frac{P_{\mathrm{cnw}}}{\gamma_{\mathrm{nw}}\cos\theta_{\mathrm{nw}}} \tag{10}$$

and

$$J(\bar{S}_{\mathrm{t}}) = J(\bar{S}_{\mathrm{w}} + \bar{S}_{\mathrm{n}}) = \frac{P_{\mathrm{can}}}{\gamma_{\mathrm{an}}\cos\theta_{\mathrm{an}}} \tag{11}$$

where J is a function of the effective degree of saturation and describes the capillary pressure for the two-phase fluid, while the subscripts $\mathrm{w}, \mathrm{n},$ and a denote water, the NAPL, and air, respectively. Here, the effective degree of saturation, $\bar{S_j}$, is the effective degree of saturation of the j phase defined by the minimum or irreducible degree of saturation (e.g., Lenhard and Parker (1987)). Equations (10) and (11) indicate that the three-phase capillary pressure–degree of saturation relationship can be simply represented by scaling the two-phase relationships (i.e., the water–NAPL and NAPL–air relationships) in the direction of the capillary pressure.

A number of researchers (van Genuchten, 1980; Lenhard and Parker, 1987a, 1987b, 1988, 1990; Parker and Lenhard, 1987, 1990; Parker et al., 1987; Farr et al., 1990; Blunt et al., 1995; Zhou and Blunt, 1997) have proposed models for the relationship between the capillary pressure and the degree of saturation for three-phase systems, all of which were based on this concept. Parker et al. (1987) and Lenhard and Parker (1988) described a three-phase relationship using van Genuchten's two-phase model (van Genuchten, 1980). This model has been used in numerical simulations of initial-value problems related to soil contamination and remediation. Lenhard and Parker (1987a), Parker and Lenhard (1987), and Lenhard et al. (1989) modified this model to account for the phenomenon of hysteresis in soils. Meanwhile, Wipfler and Van Der Zee (2001), Van Geel and Roy (2002), and Lenhard et al. (2004) extended the existing multiphase constitutive theory to take into consideration the residual NAPL saturation degree.

2.3. Spreading coefficient at thermodynamic equilibrium

The configuration of three fluids in a void space is primarily governed by their wettability, and the spreading coefficient, C_{s}, defined by Adamson (1990) is useful for measuring the tendency of the NAPL to spread across the water–air interface.

$$C_{\mathrm{s}} = \gamma_{\mathrm{aw}} - (\gamma_{\mathrm{nw}} + \gamma_{\mathrm{an}}). \tag{12}$$

NAPLs with a positive spreading coefficient (e.g., hexane) will spread over the surface of the water phase. On the other hand, NAPLs with a negative spreading coefficient, such as PCE and decane, will form a lens-like structure at the water–air interface (McBride et al., 1992; Hofstee et al., 1997). Thus, Leverett's assumption that the NAPL spreads across the water-air interface is invalid for NAPLs having a negative spreading coefficient. Hofstee et al. (1997) determined the PCE–air and water–PCE–air retention curves and also concluded that the Leverett concept is not applicable to nonspreading NAPLs. McBride et al. (1992) stated that the spreading coefficient needs to be incorporated in the numerical models of multiphase flow. Meanwhile, experimental data (Kalaydjian et al., 1993; Vizika and Lombard, 1996; Zhou and Blunt, 1997) have shown that the residual saturation degree of a nonspreading NAPL in water–NAPL–air systems increases with a decrease in the spreading coefficient.

The initial spreading coefficient, $C_{\mathrm{s}}^{\mathrm{I}}$, is defined based on the interfacial tensions of two of the fluids when the third phase is not in contact (Adamson, 1990), as follows:

$$C_{\mathrm{s}}^{\mathrm{I}} = \gamma_{\mathrm{aw}} - (\gamma_{\mathrm{nw}} + \gamma_{\mathrm{an}}). \tag{13}$$

It can be seen from this equation that NAPLs having a positive spreading coefficient ($C_{\mathrm{s}}^{\mathrm{I}} > 0$) will form a continuous film that separates the water and air phases. On the other hand, NAPLs with a negative spreading coefficient ($C_\mathrm{s}^\mathrm{I} < 0$) will form droplets at the water–air interface, such that the NAPL in question will not spread over the boundary of the water and air phases.

The interfacial tension between any two of the phases will be affected by the presence of the third fluid phase (Adamson, 1990). If $C_\mathrm{s} > 0$, the water phase will be fully covered by the NAPL, and the water–air interfacial tension, γ_aw, in the three-phase system will be reduced. The other interfacial tensions, γ_nw and γ_an, will also vary; however, the changes in their values will usually be much smaller than that in γ_aw (Adamson, 1990). When the three phases are at thermodynamic equilibrium, the spreading coefficient at equilibrium can be defined as

$$C_\mathrm{s}^\mathrm{e} = \gamma_\mathrm{aw}^\mathrm{e} - (\gamma_\mathrm{nw}^\mathrm{e} + \gamma_\mathrm{an}^\mathrm{e}), \tag{14}$$

where the superscript e denotes that the three phases are in thermodynamic equilibrium. The spreading coefficient at equilibrium must be either zero or negative (Adamson, 1990). The configuration of the three phases in a pore space will necessarily be governed by the spreading coefficient at thermodynamic equilibrium, C_s^e and this should be properly considered in the model for three-phase pressure–saturation relationship.

2.4. Criterion for NAPL layer stability

The limitations of the Leverett concept is highlighted by previous studies, which have focused on a geometric criterion for NAPL layer stability. Keller et al. (1997) proposed a microscopic model to describe the behavior of the NAPL layer in a crevice (Figure 1). They assumed that the solid is wetted by water. Thus, the water–NAPL contact angle, θ_nw, is equal to or smaller than the NAPL–air contact angle, θ_an. From Equation (1), the ratio of the interfacial curvatures can be defined as

$$R = \frac{r_\mathrm{nw}}{r_\mathrm{an}} = \frac{\gamma_\mathrm{nw}^\mathrm{e} P_\mathrm{can}}{\gamma_\mathrm{an}^\mathrm{e} P_\mathrm{cnw}}. \tag{15}$$

If R is very small, the NAPL layer will be very thick, even though the NAPL layer becomes unstable with a decrease in R. Fenwick and Blunt (1998b) assumed that the NAPL layer will disappear when the water–NAPL and NAPL–air contacts with the solid surface (points A and B in Figure 1, respectively) coincide. Thus, the critical ratio, R_c, at which the NAPL layer on the water–air interface is no longer stable can be defined as

$$R_\mathrm{c} = \frac{\cos(\theta_\mathrm{an} + \phi)}{\cos(\theta_\mathrm{nw} + \phi)} \tag{16}$$

where ϕ is the half-angle of the crevice. Consequently, the Leverett concept is only applicable when $0 \le R \le R_\mathrm{c}$ is satisfied, where the range of R_c is given by equation (17) as $0 \le \theta_\mathrm{nw} \le \theta_\mathrm{an}$ and $\theta_\mathrm{an} + \phi \le \frac{\pi}{2}$ in Figure 1.

$$0 \le R_\mathrm{c} \le \frac{\cos\theta_\mathrm{an}}{\cos\theta_\mathrm{nw}} \tag{17}$$

The constraint condition on the contact angles and interfacial tensions at thermodynamic equilibrium is given by Bartell and Osterhof (1927) as

$$\gamma_\mathrm{aw}^\mathrm{e} \cos\theta_\mathrm{aw} = \gamma_\mathrm{nw}^\mathrm{e} \cos\theta_\mathrm{nw} + \gamma_\mathrm{an}^\mathrm{e} \cos\theta_\mathrm{an}. \tag{18}$$

For a completely water-wet surface, where $\theta_{\mathrm{aw}} = \theta_{\mathrm{nw}} = 0$, we get the following equation from Equations (14) and (18) in the same way as derived by Kalaydjian (1992) and Kalaydjian et al. (1993).

$$\cos\theta_{\mathrm{an}} = 1 + \frac{C_{\mathrm{s}}^{\mathrm{e}}}{\gamma_{\mathrm{an}}^{\mathrm{e}}} \tag{19}$$

Further, the NAPL layer stability has been discussed in detail previously. For example, van Dijke et al. (2007) discussed the criteria for three–fluid configurations while considering the nonuniformity of wettability.

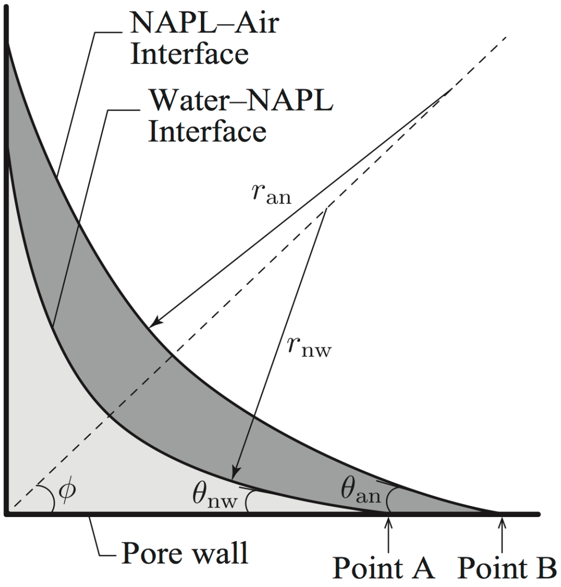

Figure 1. Geometry of a crevice with a stable NAPL layer between the water and air phases (after Zhou and Blunt, 1997).

3. New concept that overcomes limitations of Leverett concept

The limitations of the classical models based on the Leverett concept are first discussed based on a state parameter, μ. Subsequently, a simple approach is proposed to overcome its drawbacks. As we aimed to develop a novel concept to describe the capillary pressure–degree of saturation relationship of the three-phase system at thermodynamic equilibrium, the configuration of the three phases in a pore space is assumed to be governed by the spreading coefficient at equilibrium, $C_{\mathrm{s}}^{\mathrm{e}}$. Further, the simple geometric criterion proposed by Keller et al. (1997) is applied herein.

3.1. State parameter, μ, and interpretation of classical capillary pressure–degree of saturation relationship in three-phase system

In the water–NAPL–air three phase system, when the NAPL spreads over the water–air interface and isolates the water and air phases, it is reasonable to define the degree of water saturation and the degree of saturation of the liquids (water and NAPL) as functions of the water–NAPL capillary pressure and the NAPL–air capillary pressure, respectively. Considering thermodynamic equilibrium state, Equations (10) and (11) can be rewritten as:

$$J(\bar{S}_{\mathrm{w}}) = \beta^{\mathrm{e}}_{\mathrm{nw}} P_{\mathrm{cnw}} \tag{20}$$

and

$$J(\bar{S}_{\mathrm{t}}) = J(\bar{S}_{\mathrm{w}} + \bar{S}_{\mathrm{n}}) = \beta^{\mathrm{e}}_{\mathrm{an}} P_{\mathrm{can}} \tag{21}$$

where β^{e}_{ij} is given as:

$$\beta^{\mathrm{e}}_{ij} = \frac{1}{\gamma^{\mathrm{e}}_{ij} \cos\theta_{ij}}. \tag{22}$$

We introduce the relative magnitude, μ, of the NAPL pressure (P_{n}) with respect to the water pressure (P_{w}) and air pressure (P_{a}) (Nakamura and Kikumoto, 2014) as a parameter that plays a central role in the proposed concept. In case that capillary pressures P_{cnw} and P_{caw} are both positive ($P_{\mathrm{w}} < P_{\mathrm{n}} < P_{\mathrm{a}}$), three phase exists in the system and μ is defined as follows.

$$\mu = \frac{P_{\mathrm{n}} - P_{\mathrm{w}}}{P_{\mathrm{a}} - P_{\mathrm{w}}} \tag{23}$$

Using Equation (1), μ can also be represented by capillary pressures as follows:

$$\mu = \frac{P_{\mathrm{cnw}}}{P_{\mathrm{caw}}} = 1 - \frac{P_{\mathrm{can}}}{P_{\mathrm{caw}}} \tag{24}$$

In other cases, air and/or NAPL phase does not exist in the system and the states in a multiphase system are summarized as follows: (a) $\mu = 0$ when $P_{\mathrm{cnw}} \le 0$ as the NAPL is displaced by water and as the system consists of a water–air two-phase subsystem, and (b) $\mu = 1$ when $P_{\mathrm{can}} \le 0$ as the air is displaced by the NAPL and as the system consists of an NAPL–air two-phase subsystem. Consequently, the possible range of parameter μ becomes $0 \le \mu \le 1$.

On substituting Equation (24) for P_{cnw} and P_{can} in Equations (20) and (21), we obtain

$$J\left(\bar{S}_{\mathrm{w}}\right) = \beta^{\mathrm{e}}_{\mathrm{nw}} \mu P_{\mathrm{caw}} \tag{25}$$

and

$$J\left(\bar{S}_{\mathrm{t}}\right) = \beta^{\mathrm{e}}_{\mathrm{an}} (1 - \mu) P_{\mathrm{caw}}, \tag{26}$$

respectively. As $\bar{S}_{\mathrm{w}} \le \bar{S}_{\mathrm{t}}$ and because the capillary pressure necessarily increases with a decrease in the degree of saturation of the wetting phase (Bear, 1972), we get

$$J(\bar{S}_{\mathrm{w}}) \ge J(\bar{S}_{\mathrm{t}}). \tag{27}$$

Substituting Equations (25) and (26) for $J(\bar{S}_{\mathrm{w}})$ and $J(\bar{S}_{\mathrm{t}})$ in Equation (26), an inequality relation involving μ is derived as follows:

$$\beta^{\mathrm{e}}_{\mathrm{nw}} \mu \ge \beta^{\mathrm{e}}_{\mathrm{an}} (1 - \mu) \tag{28}$$

where P_{caw} is regarded having a nonnegative value.

When the effective degree of saturation of the NAPL, $\bar{S}_{\mathrm{n}}(=\bar{S}_{\mathrm{t}}-\bar{S}_{\mathrm{w}})$ is 0, the system becomes a water–air two-phase one and Equation (27) satisfies the equality condition:

$$J(\bar{S}_{\mathrm{w}})=J(\bar{S}_{\mathrm{t}})=\beta_{\mathrm{aw}}^{\mathrm{e}}P_{\mathrm{caw}}. \tag{29}$$

Then, as Equation (28) also satisfies the equality condition, μ is equal to μ_{I}, which is given as follows:

$$\mu_{\mathrm{I}}=\frac{\beta_{\mathrm{an}}^{\mathrm{e}}}{\beta_{\mathrm{nw}}^{\mathrm{e}}+\beta_{\mathrm{an}}^{\mathrm{e}}}\left(=\frac{\gamma_{\mathrm{nw}}^{\mathrm{e}}\cos\theta_{\mathrm{nw}}}{\gamma_{\mathrm{nw}}^{\mathrm{e}}\cos\theta_{\mathrm{nw}}+\gamma_{\mathrm{an}}^{\mathrm{e}}\cos\theta_{\mathrm{an}}}\right). \tag{30}$$

Using Equations (25), (26), and (29), $J(\bar{S}_{\mathrm{w}})$ and $J(\bar{S}_{\mathrm{t}})$ as related to the original Leverett concept can be derived in a uniform manner as

$$J(\bar{S}_j)=\beta_j^{\mathrm{e}}(\mu)P_{\mathrm{caw}} \tag{31}$$

while the inverse of function J is written as

$$\bar{S}_j=\frac{S_j-S_{\mathrm{w}}^{\mathrm{min}}}{1-S_{\mathrm{w}}^{\mathrm{min}}-S_{\mathrm{a}}^{\mathrm{min}}}=J^{-1}\left(\beta_j^{\mathrm{e}}(\mu)P_{\mathrm{caw}}\right) \tag{32}$$

where the subscript j denotes water (w) or the total liquid (t) and $\beta_j^{\mathrm{e}}(\mu)$ for the classical capillary pressure–degree of saturation model is given as

$$\beta_{\mathrm{w}}^{\mathrm{e}}(\mu)=\begin{cases}\beta_{\mathrm{aw}}^{\mathrm{e}} & : 0<\mu\le\mu_{\mathrm{I}}\\ \beta_{\mathrm{nw}}^{\mathrm{e}}\mu & : \mu_{\mathrm{I}}<\mu<1\end{cases} \tag{33}$$

and

$$\beta_{\mathrm{t}}^{\mathrm{e}}(\mu)=\begin{cases}\beta_{\mathrm{aw}}^{\mathrm{e}} & : 0<\mu\le\mu_{\mathrm{I}}\\ \beta_{\mathrm{an}}^{\mathrm{e}}(1-\mu) & : \mu_{\mathrm{I}}<\mu<1\end{cases} \tag{34}$$

respectively. The relationships between μ and $\beta_j^{\mathrm{e}}(\mu)$, given by Equations (33) and (34), are shown by the solid lines in Figure 2.

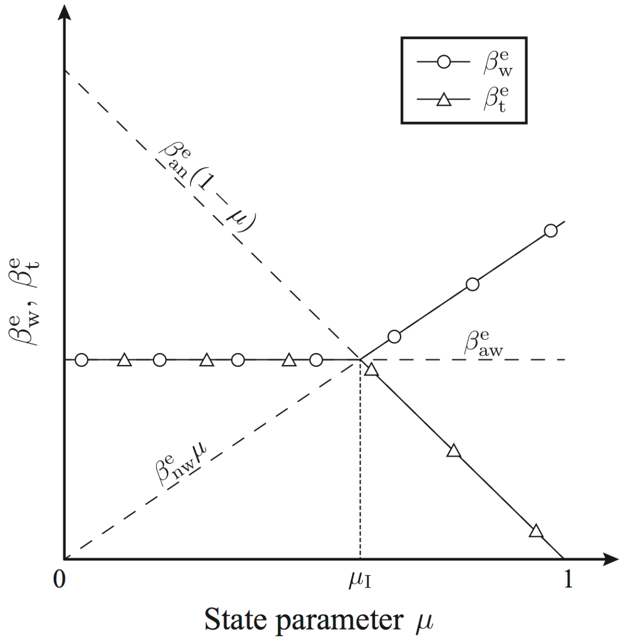

Figure 2. Relationship between μ and β_j^{e}.

Fenwick and Blunt (1998a) theoretically showed that an NAPL layer exists in a crevice when the ratio of the interfacial radius, R, is larger than the critical value, R_{c}. From Equation (7), we obtain

$$\frac{\gamma_{\mathrm{nw}}^{\mathrm{e}} P_{\mathrm{can}}}{\gamma_{\mathrm{an}}^{\mathrm{e}} P_{\mathrm{cnw}}} < R_{\mathrm{c}}. \tag{35}$$

On substituting parameter μ given by Equation (24) for the capillary pressures, the applicable range of the Leverett concept given by Equation (35) becomes

$$\mu \geq \mu_{\mathrm{c}} \tag{36}$$

where μ_{c} is the critical value of μ for $R = R_{\mathrm{c}}$ and is given as follows:

$$\mu_{\mathrm{c}} = \frac{\gamma_{\mathrm{nw}}^{\mathrm{e}}}{\gamma_{\mathrm{nw}}^{\mathrm{e}} + R_{\mathrm{c}} \gamma_{\mathrm{an}}^{\mathrm{e}}}. \tag{37}$$

Conversely, the Leverett concept (Leverett, 1941) is not applicable when $\mu < \mu_{\mathrm{c}}$. From the range of R_{c} given by equation (17) and equations (30) and (37), the range of μ_{c} is given by equation (38).

$$\mu_{\mathrm{I}} \leq \mu_{\mathrm{c}} \leq 1 \tag{38}$$

Figure 3 shows the relationship between μ_{c} and the half-angle of the crevice, ϕ. Figure 4 shows the relationship between μ and $\beta_j^{\mathrm{e}}(\mu)$ for a strongly water-wet system ($\theta_{\mathrm{aw}} = \theta_{\mathrm{nw}} = 0$). To obtain this relationship, we assumed that $\gamma_{\mathrm{nw}}^{\mathrm{e}} = \gamma_{\mathrm{nw}}$ and $\gamma_{\mathrm{an}}^{\mathrm{e}} = \gamma_{\mathrm{an}}$, following the approximation for hydrocarbon systems used by Adamson (1990), and calculated $\gamma_{\mathrm{aw}}^{\mathrm{e}}$ and θ_{an} using Equations (14) and (19), respectively. The values of the other parameters such as $\gamma_{\mathrm{aw}}, \gamma_{\mathrm{nw}}$, and γ_{an} are shown in Table 1. It can be seen from these figures that the range for which the Leverett concept ($\mu_{\mathrm{c}} < \mu < 1$) is applicable is smaller for NAPLs having a smaller spreading coefficients at equilibrium, $C_{\mathrm{s}}^{\mathrm{e}}$; this finding is consistent with the experimental results obtained by McBride et al. (1992). It can also be seen that the original Leverett concept cannot be applied even in the case of an NAPL having a positive initial spreading coefficient (such as hexane), especially when the half-angle, ϕ, in a crevice is large. Thus, the relationships between μ and $\beta_j^{\mathrm{e}}(\mu)$ for $0 < \mu \leq \mu_{\mathrm{c}}$ need to be modified.

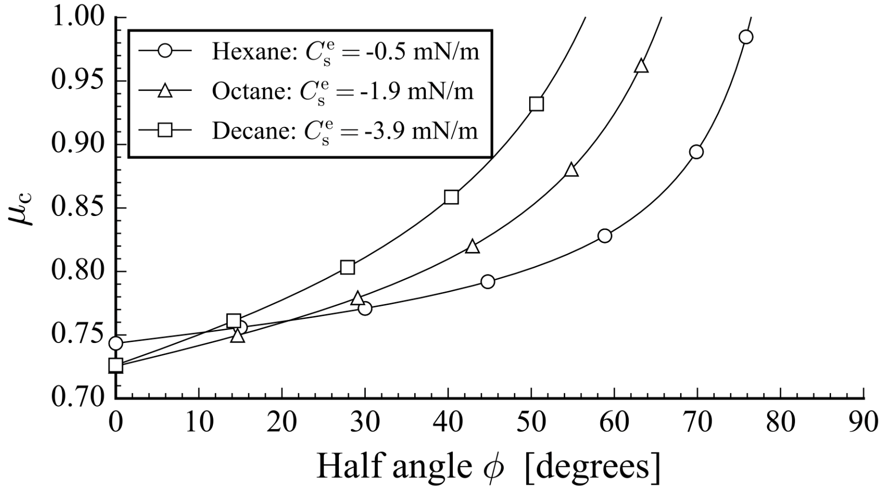

Figure 3. Relationship between ϕ and μ_{c}.

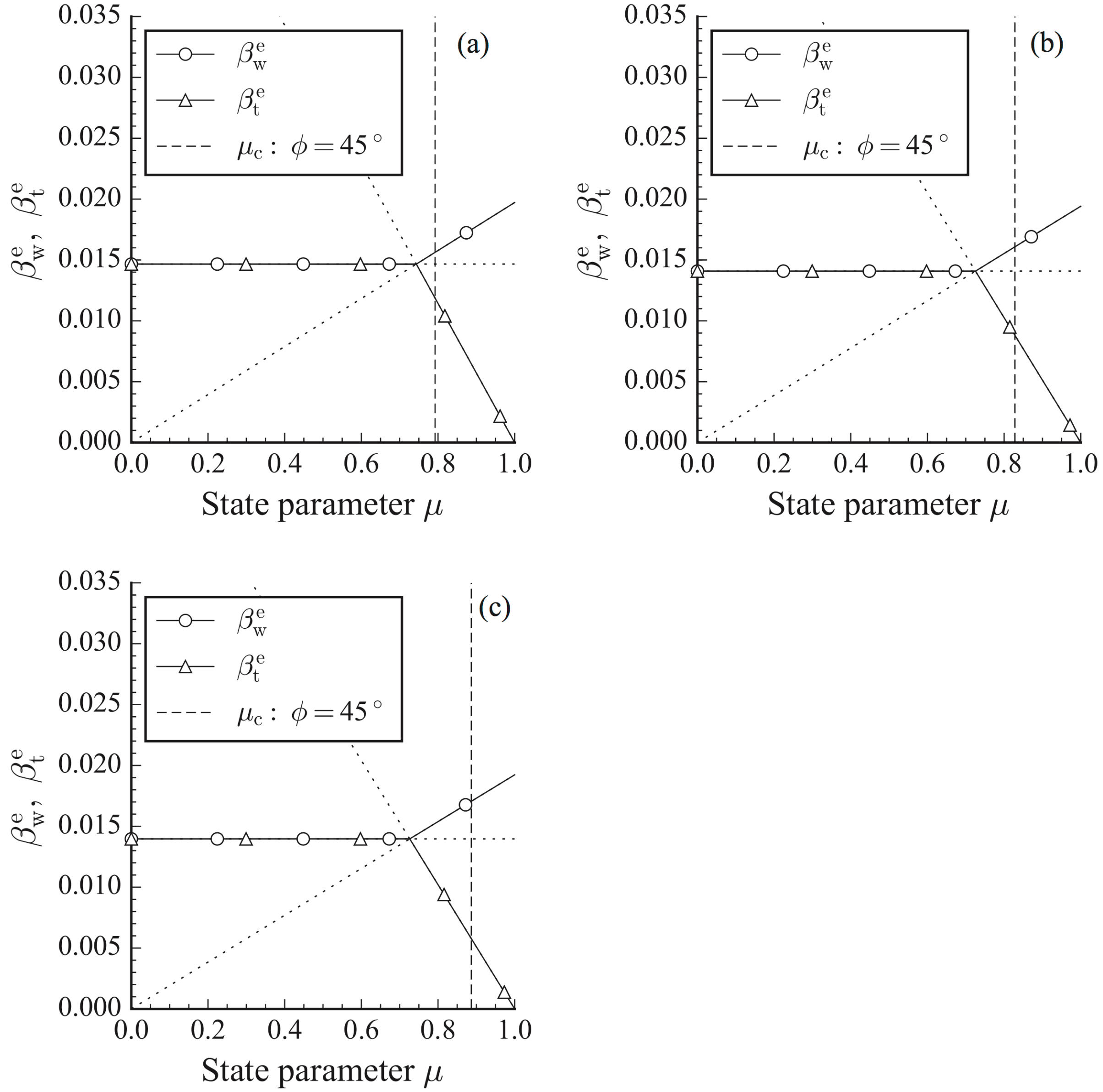

Figure 4. Relationship between μ and β_j^e for (a) hexane, (b) octane, and (c) decane as per the Leverett concept.

Table 1. Fluid properties (after Zhou and Blunt, 1997)

	Hexane	Octane	Decane	Water	Air
$\gamma_{\mathrm{a}j}$ [mN/m]	18.0	21.4	23.5	72.1	
γ_{nw} [mN/m]	50.7	51.5	52.0	72.1	
$C_{\mathrm{s}}^{\mathrm{I}}$ [mN/m]	3.4	-0.8	-3.4		
$C_{\mathrm{s}}^{\mathrm{e}}$ [mN/m]	-0.5	-1.9	-3.9		
ρ_i [kg/m^3]	659	703	730	998.2	1.2

Another issue with the conventional model based on the original Leverett concept is that the model does not take into account the residual degree of saturation of the NAPL, $S_{\mathrm{n}}^{\mathrm{min}}$. It has been suggested by several researchers (Dong et al., 1995; Fenwick and Blunt, 1995; Zhou and Blunt, 1997) that the residual NAPL degree of saturation, $S_{\mathrm{n}}^{\mathrm{min}}$, is positive when $C_{\mathrm{s}}^{\mathrm{e}} < 0$, even though $S_{\mathrm{n}}^{\mathrm{min}}$ in the water–air two-phase system is zero when $C_{\mathrm{s}}^{\mathrm{e}} = 0$. Therefore, we obtain

$$S_{\mathrm{n}}^{\mathrm{min}} = 0 \quad \text{when } \mu_{\mathrm{c}} = \mu_{\mathrm{I}}, \tag{39}$$

and

$$S_{\mathrm{n}}^{\mathrm{min}} > 0 \quad \text{when } \mu_{\mathrm{c}} > \mu_{\mathrm{I}}. \tag{40}$$

As has been pointed out through experimental studies (Kalaydjian et al., 1993; Vizika and Lombard, 1996; Zhou and Blunt, 1997), the amount of the residual NAPL increases with a decrease in the spreading coefficient, that is, $S_{\mathrm{n}}^{\mathrm{min}}$ increases monotonically as μ_{c} increases.

3.2. A new concept taking account of critical μ value, μ_{c}

We herein propose a novel form of the Leverett concept by modifying it such that its drawbacks are overcome. We then apply the unified form of the J function for water and the total liquid in the same way as is the case for the conventional concept:

$$J(\bar{S}_j) = \widetilde{\beta_j^{\mathrm{e}}}(\mu) P_{\mathrm{caw}} \tag{41}$$

where subscript j denotes water (w) or the total liquid (t) and $\widetilde{\beta_j^{\mathrm{e}}}(\mu)$ is a function of μ. Further, we propose the following forms of the effective degree of saturation in order to incorporate the irreducible degree of saturation of the NAPL, $S_{\mathrm{n}}^{\mathrm{min}}$ (i.e., lower limit of the NAPL degree of saturation):

$$\bar{S}_j = \frac{S_j - S_j^{\mathrm{min}}}{1 - \sum_i S_i^{\mathrm{min}}} = J^{-1}\left(\widetilde{\beta_j^{\mathrm{e}}}(\mu) P_{\mathrm{caw}}\right) \tag{42}$$

which means that

$$\bar{S}_{\mathrm{w}} = \frac{S_{\mathrm{w}} - S_{\mathrm{w}}^{\mathrm{min}}}{1 - S_{\mathrm{w}}^{\mathrm{min}} - S_{\mathrm{n}}^{\mathrm{min}} - S_{\mathrm{a}}^{\mathrm{min}}} = J^{-1}\left(\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(\mu) P_{\mathrm{caw}}\right) \tag{43}$$

and

$$\bar{S}_{\mathrm{t}} = \bar{S}_{\mathrm{w}} + \bar{S}_{\mathrm{n}} = \frac{S_{\mathrm{t}} - S_{\mathrm{w}}^{\mathrm{min}} - S_{\mathrm{n}}^{\mathrm{min}}}{1 - S_{\mathrm{w}}^{\mathrm{min}} - S_{\mathrm{n}}^{\mathrm{min}} - S_{\mathrm{a}}^{\mathrm{min}}} = J^{-1}\left(\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(\mu) P_{\mathrm{caw}}\right). \tag{44}$$

Here, $\widetilde{\beta_{J}^{\mathrm{e}}}(\mu)$ is a function of μ that satisfies the requirements listed below.

In the cases where the original Leverett concept is not applicable ($0 < \mu \leq \mu_{\mathrm{c}}$), the NAPL remaining in the porous media tends to continue to remain there (Kalaydjian et al., 1993; Vizika and Lombard, 1996; Zhou and Blunt, 1997). In order to be able to account for this immobile NAPL phase, $\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(\mu)$ and $\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(\mu)$ must satisfy the following conditions:

$$\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(\mu) > \beta_{\mathrm{nw}}^{\mathrm{e}} \mu \tag{45}$$

and

$$\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(\mu) < \beta_{\mathrm{an}}^{\mathrm{e}} (1 - \mu) \tag{46}$$

when $0 < \mu \leq \mu_{\mathrm{c}}$. In addition, it is natural to assume that both $\beta_{\mathrm{w}}^{\mathrm{e}}(\mu)$ and $\beta_{\mathrm{t}}^{\mathrm{e}}(\mu)$ follow the water–air relationship as μ approaches 0 and that the two satisfy the following conditions:

$$\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(0) = \beta_{\mathrm{aw}}^{\mathrm{e}} \tag{47}$$

and

$$\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(0) = \beta_{\mathrm{aw}}^{\mathrm{e}}. \tag{48}$$

In order to satisfy the necessary conditions given by Equations (45)–(48), we describe the μ–$\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(\mu)$ and μ–$\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(\mu)$ relationships using a quadratic Bezier curve (Figure 5). This approach has the following advantages: (a) the capillary pressure–degree of saturation relationships become continuously differentiable functions even at the transition point between the water–NAPL–air three-phase system and the water–air two-phase system—as a result, the implementation of the model using numerical simulations becomes rather straightforward; (b) any kind of suction-based water retention model (e.g., Gardner (1958), Brooks and Corey (1964), van Genuchten (1980), and Fredlund and Xing (1994)) can be used as the J^{-1} function in Equation (42); and (c) the shapes of capillary pressure–degree of saturation relationships can be adjusted readily by varying parameters l_{w} and l_{t} of the quadratic Bezier curves (see Appendix A). In Figure 5, we assume that the system is strongly water-wet ($\theta_{\mathrm{aw}} = \theta_{\mathrm{nw}} = 0$) in the same manner as in Figure 4, and we obtain the following relationship between μ_{c} and $C_{\mathrm{s}}^{\mathrm{e}}$ from equations (16), (19) and (37).

$$\mu_{\mathrm{c}} = \frac{\gamma_{\mathrm{nw}}^{\mathrm{e}}}{\gamma_{\mathrm{nw}}^{\mathrm{e}} + \gamma_{\mathrm{an}}^{\mathrm{e}}(1 + C_{\mathrm{s}}^{\mathrm{e}}) - \tan\phi \sqrt{C_{\mathrm{s}}^{\mathrm{e}}(C_{\mathrm{s}}^{\mathrm{e}} - 2\gamma_{\mathrm{an}}^{\mathrm{e}})}}. \tag{49}$$

The parameters l_{w} and l_{t} can be determined by fitting the shapes of the quadratic Bezier curves for $\widetilde{\beta_{\mathrm{w}}^{\mathrm{e}}}(\mu)$ and $\widetilde{\beta_{\mathrm{t}}^{\mathrm{e}}}(\mu)$ to the $\beta_{\mathrm{nw}}^{\mathrm{e}}\mu$ and $\beta_{\mathrm{an}}^{\mathrm{e}}(1 - \mu)$ of the ordinary Leverett concept, respectively, in μ_{c} ($\phi = 45°$) $< \mu \leq 1$. The determined values of l_{w} and l_{t} are 0.70 and 0.84 for hexane; 0.62 and 0.70 for octane; and 0.52 and 0.69 for decane, respectively. If the spreading coefficient at equilibrium, $C_{\mathrm{s},}^{\mathrm{e}}$ is equal to zero (i.e., μ_{c} is equal to μ_{I}), the Leverett concept does not need any modification. In this case, we may set $l_{\mathrm{w}} \approx 1$ and $l_{\mathrm{t}} \approx 1$.

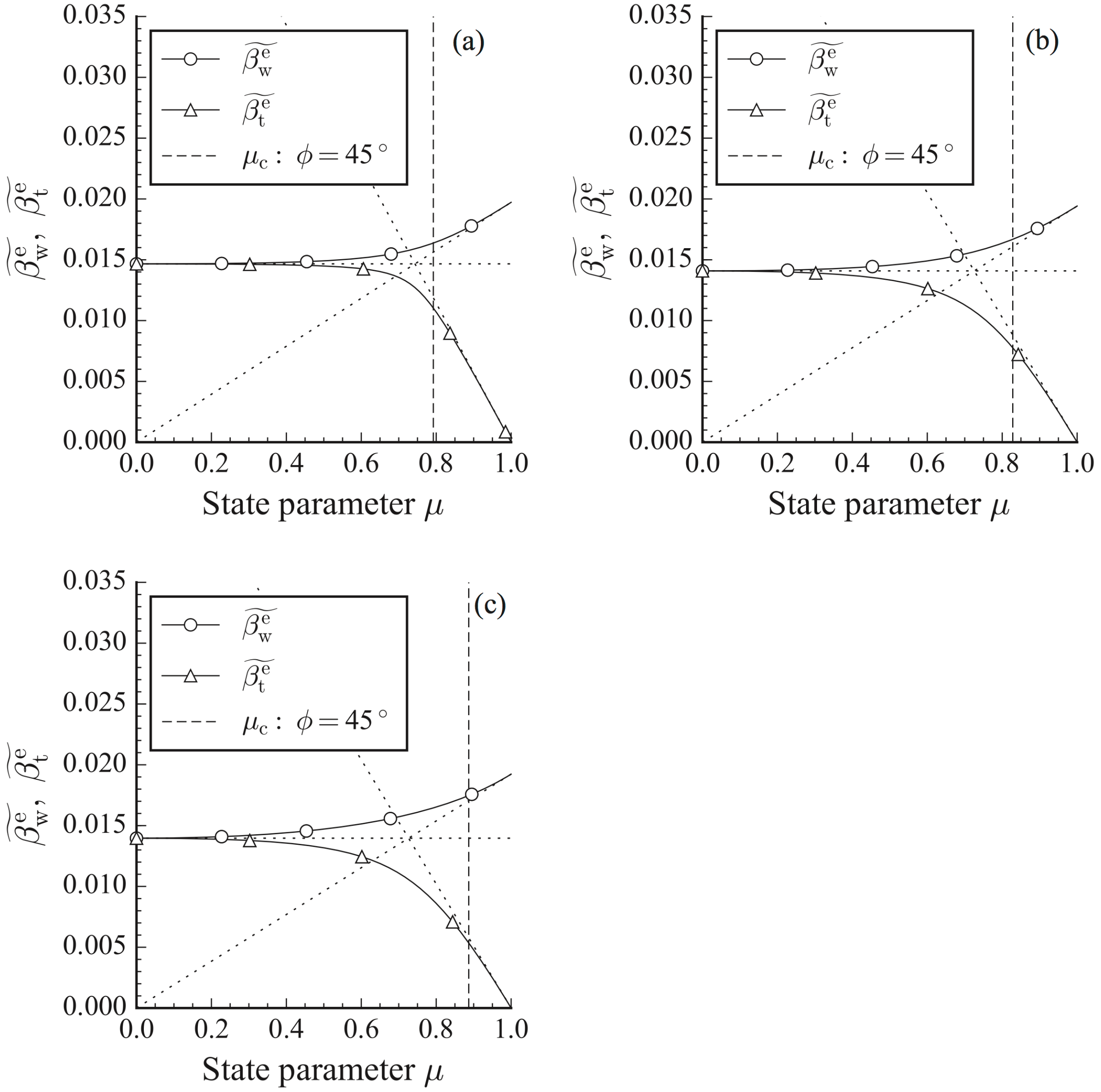

Figure 5. Relationship between μ and β_j^{e} for (a) hexane, (b) octane, and (c) decane as per the proposed concept.

3.3. Application of the proposed concept

The procedure for evaluating saturation degrees of three-phase fluids by the proposed concept is summarized herein. For given pressure of three-phase fluids, P_w, P_n and P_a, we first calculate P_{caw} and μ. As most existing models for two-phase relationship between degree of saturation, S_j, and capillary pressure, P_{cij}, such as Equation (6) (van Genuchten, 1980) or Equation (8) (Brooks and

Corey, 1964) do not incorporate negative value of P_{cij}, we evaluate P_{caw} and μ through the following steps.

In case that $P_{\mathrm{w}} < P_{\mathrm{n}} < P_{\mathrm{a}}$ (the capillary pressures P_{cnw} and P_{can} are both positive), three phase exists in the system. For this case, P_{caw} is given as:

$$P_{\mathrm{caw}} = P_{\mathrm{a}} - P_{\mathrm{w}} \tag{50}$$

and μ is given by equation (23). In other cases, air and/or NAPL phase does not exist in the system and we evaluate P_{caw} and μ as follows: (a) $P_{\mathrm{caw}} = P_{\mathrm{a}} - P_{\mathrm{w}}$ and $\mu = 0$ when $P_{\mathrm{n}} < P_{\mathrm{w}} \leq P_{\mathrm{a}}$ (water–air two-phase); (b) $P_{\mathrm{caw}} = P_{\mathrm{n}} - P_{\mathrm{w}}$ and $\mu = 1$ when $P_{\mathrm{w}} \leq P_{\mathrm{n}}$ and $P_{\mathrm{a}} < P_{\mathrm{n}}$ (NAPL–air two-phase); and (c) $P_{\mathrm{caw}} = 0$ and μ is any value when $P_{\mathrm{a}} < P_{\mathrm{w}}$ and $P_{\mathrm{n}} < P_{\mathrm{w}}$ (water phase). This procedure is summarized in Figure 6.

Figure 6. Procedure for calculating P_{caw} and μ.

```
IF ($P_w < P_n < P_a$)
    $P_{caw} = P_a - P_w$ and calculate $\mu$ by eq. (23).    (water–NAPL–air three phase)
ELSE IF ($P_n < P_w \leq P_a$)
    $P_{caw} = P_a - P_w$ and $\mu = 0$.                      (water–air two phase)
ELSE IF ($P_w \leq P_n$) and ($P_a < P_n$)
    $P_{caw} = P_n - P_w$ and $\mu = 1$.                      (water–NAPL two phase)
ELSE
    $P_{caw} = 0$ and $\mu$ is any value.                     (water phase only)
ENDIF
```

Next, we evaluate $\widetilde{\beta_j^{\mathrm{e}}}(\mu)$ ($j = \mathrm{w}, \mathrm{t}$) in Equation (42) from μ. By solving quadratic equation $at_j^2 + bt_j + c = 0$, the intermediate parameter t_j that controls the curvature of the Bezier curve for $\widetilde{\beta_j^{\mathrm{e}}}(\mu)$ (see Appendix A) is given by μ and l_j as:

$$t_j = \frac{-b_j + \sqrt{b_j^2 - 4a_j c}}{2a_j} \tag{51}$$

where

$$\begin{aligned} a_j &= 1 - b_j \\ b_j &= d_j \mu_1 + \mu\left(2 - d_j\right) \\ c &= -\mu \\ d_j &= \frac{2l_j}{1 - l_j} \end{aligned} \quad . \tag{52}$$

Substituting t_j for Equation (53), we can calculate weighting parameters k_{1j}, k_{2j} and k_{3j} for phase j (w : water, t : liquid), respectively.

$$\begin{cases} k_{1j} = \left(1 - t_j\right)^2 \\ k_{2j} = \dfrac{2l_j}{1 - l_j} t_j\left(1 - t_j\right) \\ k_{3j} = {t_j}^2 \end{cases} \tag{53}$$

$\widetilde{\beta_w^e}$ and $\widetilde{\beta_t^e}$ are given as follows.

$$\widetilde{\beta_w^e} = \frac{(k_1 + k_2)\beta_{aw}^e + k_3\beta_{nw}^e}{k_0} \tag{54}$$

$$\widetilde{\beta_t^e} = \frac{(k_1 + k_2)\beta_{aw}^e}{k_0}. \tag{55}$$

Using $\widetilde{\beta_j^e}(\mu)$ and P_{caw}, we finally obtain saturation degrees of water and liquid by Equations (43) and (44), respectively. For the inverse of function J in these equations, several functions were proposed. For instance, van Genuchten (1980) proposed:

$$\bar{S}_j = J_{\mathrm{VG}}^{-1}\left(\widetilde{\beta_j^{\mathrm{e}}}(\mu)P_{\mathrm{caw}}\right) = \left\{1 + \left(\frac{a_{\mathrm{VG}}}{2}\widetilde{\beta_j^{\mathrm{e}}}(\mu)P_{\mathrm{caw}}\right)^n\right\}^{\frac{1-n}{n}} \tag{56}$$

with parameters specific to the porous media, n and a_{VG}, while Brooks and Corey (1964) proposed:

$$\bar{S}_j = J_{\mathrm{BC}}^{-1}\left(\widetilde{\beta_j^{\mathrm{e}}}(\mu)P_{\mathrm{caw}}\right) = \left(\frac{a_{\mathrm{BC}}}{2}\widetilde{\beta_j^{\mathrm{e}}}(\mu)P_{\mathrm{caw}}\right)^{-\lambda} \tag{57}$$

where λ and a_{BC} are parameters specific to the porous media. Finally, saturation degrees of NAPL and air are given as follows.

$$\bar{S}_{\mathrm{n}} = \bar{S}_{\mathrm{t}} - \bar{S}_{\mathrm{w}} \tag{58}$$

$$\bar{S}_{\mathrm{a}} = 1 - \bar{S}_t \tag{59}$$

4. Validation

We hereafter discuss the applicability of the proposed concept by comparing it with the ordinary Leverett concept and the past experimental data. Zhou and Blunt (1997) performed gravity drainage column experiments for water–air two-phase system and water–NAPL–air three-phase system on two kinds of sands (purified sand and red sand), for which the vertical distributions of the pressure of each fluid can be explicitly given as a stationary state is reached. For the experiments for three-phase system, three kinds of NAPLs (hexane, octane and decane) are used. In the simulation, we selected a model proposed by Brooks and Corey (1964) for the capillary pressure–degree of saturation relationship (Equation (57)).

First, we simulated the water–air two-phase system to determine the material parameters for soils. For the water–air two-phase system, the water pressure and air pressure are given by Equations (60) and (61), respectively.

$$P_{\mathrm{w}} = -\rho_{\mathrm{w}} g z, \tag{60}$$

$$P_{\mathrm{a}} = P_{\mathrm{caw}}^{\mathrm{d}} - \rho_{\mathrm{a}} g z. \tag{61}$$

Here, ρ_{w} and ρ_{a} are densities of water and air, respectively; $P_{\mathrm{caw}}^{\mathrm{d}}$ is the capillary pressure for the entry of the air into the water-saturated porous medium; and g is the gravitational acceleration. As shown in Figure 7, vertical distributions of water saturation for two kinds of sand are well captured by the simulation. The material parameters for the water–air two-phase system are calibrated as Table 2 and the same sets of parameters are applied to the simulation of the three-phase system.

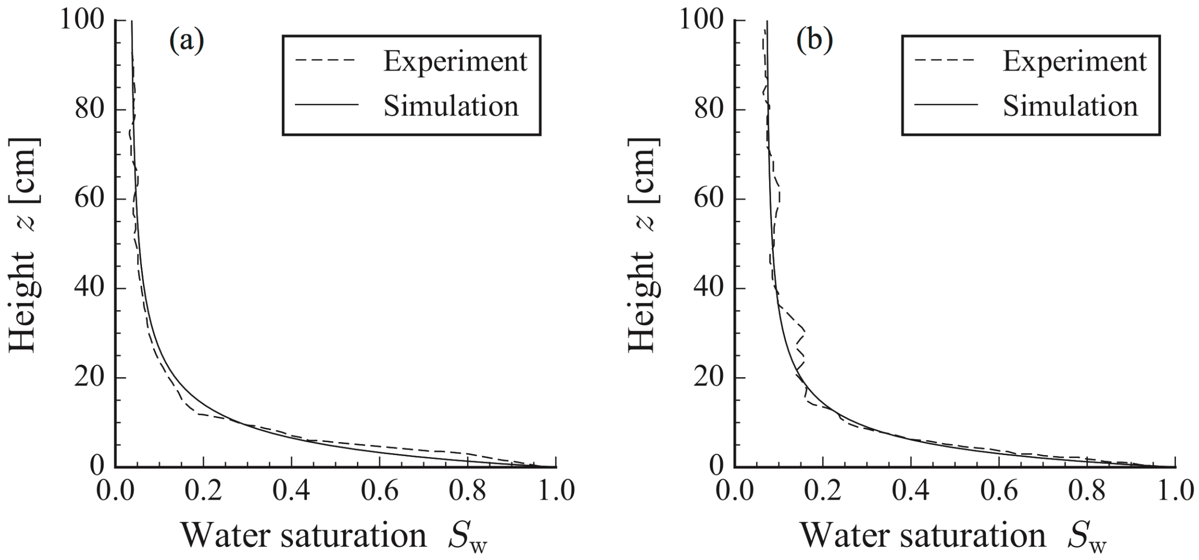

Figure 7. Water–air two-phase capillary pressure–degree of saturation relationships for (a) purified sand and (b) red sand as determined experimentally (Zhou and Blunt, 1997).

Next, vertical arrangement of fluids for the water–NAPL–air three-phase system at capillary/gravity equilibrium is schematically shown in Figure 8. NAPL and air exist above the level of $z = 0$ and $z = H$, respectively. We can set the vertical distribution of the pressure of each phase as:

$$P_{\mathrm{w}} = -\rho_{\mathrm{w}} g z, \tag{62}$$

$$P_{\mathrm{n}} = P_{\mathrm{cnw}}^{\mathrm{d}} - \rho_{\mathrm{n}} g z \tag{63}$$

and

$$P_{\mathrm{a}} = P_{\mathrm{can}}^{\mathrm{d}} + P_{\mathrm{cnw}}^{\mathrm{d}} - (\rho_{\mathrm{n}} - \rho_{\mathrm{a}}) g H - \rho_{\mathrm{a}} g z \tag{64}$$

where ρ_{n} is density of the NAPL; and $P_{\mathrm{cnw}}^{\mathrm{d}}$ and $P_{\mathrm{can}}^{\mathrm{d}}$ are the capillary pressure for the entry of the NAPL into the water-saturated porous medium and the capillary pressure for the entry of air into the NAPL-saturated porous medium, respectively. $P_{\mathrm{cnw}}^{\mathrm{d}}$ and $P_{\mathrm{can}}^{\mathrm{d}}$ are calculated as follows.

$$P_{\mathrm{cnw}}^{\mathrm{d}} = \frac{\beta_{\mathrm{aw}}^{\mathrm{e}}}{\beta_{\mathrm{nw}}^{\mathrm{e}}} P_{\mathrm{caw}}^{\mathrm{d}} \tag{65}$$

$$P_{\mathrm{can}}^{\mathrm{d}} = \frac{\beta_{\mathrm{aw}}^{\mathrm{e}}}{\beta_{\mathrm{an}}^{\mathrm{e}}} P_{\mathrm{caw}}^{\mathrm{d}} \tag{66}$$

In this simulation, we assume a completely water-wet medium ($\theta_{\mathrm{aw}} = \theta_{\mathrm{nw}} = 0$), as did Zhou and Blunt (1997). For the Leverett concept, Equation (57) is applied to Equation (32), with the μ–β_j^{e} relationship being given by Equations (33) and (34) as shown in Figure 4. On the other hand, in the proposed concept, Equation (57) is applied to Equation (42) (Equations (43) and (44)), with the μ–$\widetilde{\beta_j^{\mathrm{e}}}$ relationship being evaluated through the procedure explained in the section 3.3 as shown in Figure 5.

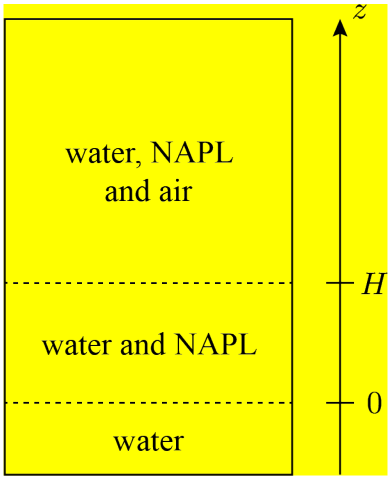

Figure 8. Arrangement of water, NAPL and air in equilibrium (after Zhou and Blunt, 1997).

Table 2. Material parameters for water–air two-phase system.

	Purified sand	Red sand
$S_{\mathrm{w}}^{\mathrm{min}}$	0.032	0.070
$S_{\mathrm{a}}^{\mathrm{min}}$	0.0	0.0
λ	2.45	2.5
a_{BC} [mm]	0.1091	0.1227

Figure 9 shows the μ–z relationship obtained by the vertical distribution of pressures (Equations 62, 63 and 64) for purified sand–hexane. In this figure, we can define a critical height, z_{c} which corresponds to the critical μ value, μ_{c}. As stated in Section 3.1, the Leverett concept is not applicable when $\mu < \mu_\mathrm{c}$. Since μ decreases monotonically as z increases based on the linear distribution of pressures, the Leverett concept is not applicable in the range of $z > z_\mathrm{c}$.

Figures 10 and 11 show comparisons of the observed vertical distributions of the degrees of saturation of the three fluids and their corresponding values as calculated based on the original Leverett concept and the proposed concept, respectively. The height, H, detected from the experimental data for purified sand (Zhou and Blunt, 1997), is 14.0 cm for hexane, 16.9 cm for octane, and 17.6 cm for decane. For red sand, the heights, H, for hexane, octane, and decane are 11.1 cm, 17.4 cm, and 15.5 cm, respectively. In the case of the proposed concept, we set the irreducible degree of saturation of the NAPL, $S_\mathrm{n}^\mathrm{min}$, as per the values used by Zhou and Blunt (1997). For purified sand, the value of $S_\mathrm{n}^\mathrm{min}$ is 0.13% for hexane, 1.13% for octane, and 1.49% for decane. For red sand, the value of $S_\mathrm{n}^\mathrm{min}$ is set to 0.35% for hexane, 3.11% for octane, and 5.25% for decane.

It is seen from Figure 10 that the Leverett concept underestimate the NAPL saturation degree especially in the region above the critical height, z_c. This is because the original Leverett concept cannot consider the existence of the NAPL in the region of $z > z_\mathrm{c}$. On the other hand, the proposed concept can predict the measured distributions of saturation degrees of three fluids including the residual saturation degree of the NAPL well. To highlight this, we show comparisons of the observed vertical distributions of the NAPL saturation and the corresponding simulation results based on the Leverett concept and the proposed concept in Figure 12 and 13, respectively. As the ordinary Leverett concept fails when $z > z_\mathrm{c}$, the predicted NAPL saturation degree tends to be much lower than the experimental results. The proposed concept, in contrast, predicts the measured NAPL saturation precisely even in the region of $z > z_\mathrm{c}$. From Figures 10 and 11, it can be seen that the proposed concept can be applied regardless of the value of the spreading coefficient by controlling the shape of the quadratic Bezier curves. The residual saturation degree of the NAPL can be predicted well by the new concept as shown Figure 13(e) and 13(f) as the concept can consider the residual saturation degree of the NAPL by Equation (42). It is deduced that the difference between the calculated results and the measured ones seen in Figures 10(f) and 11(f) is primarily due to the heterogeneity of the sand ground used in the experiment, as suggested by Zhou and Blunt (1997).

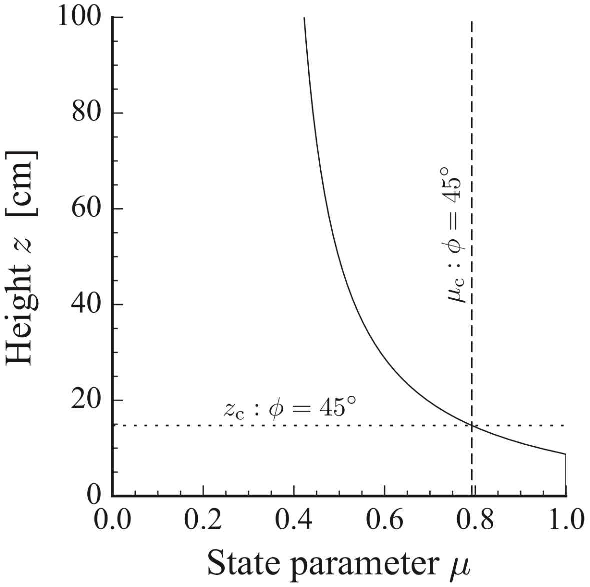

Figure 9. Relationship between μ and z for purified sand–hexane.

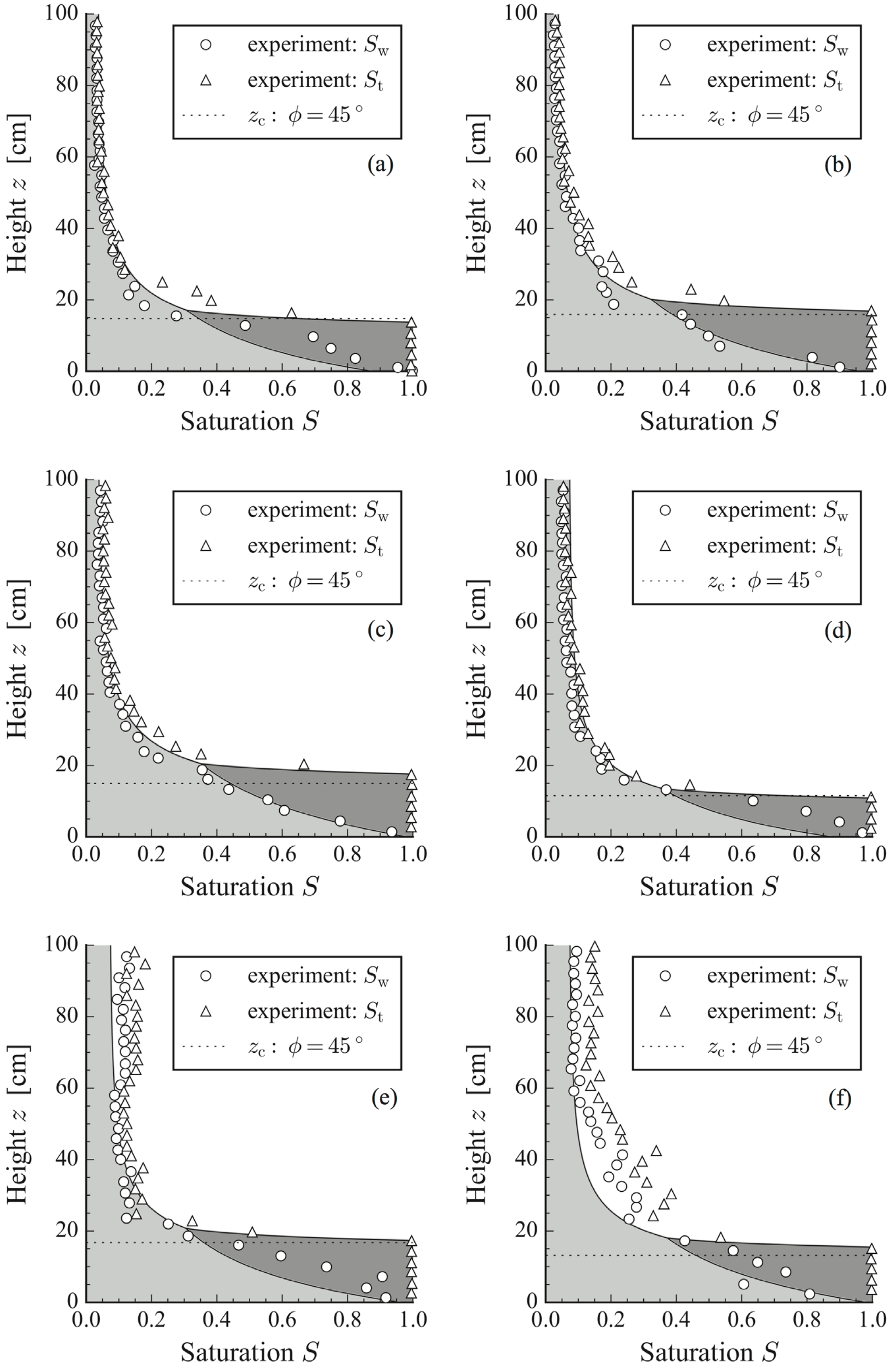

Figure 10. Three-phase capillary pressure–degree of saturation relationship as determined by experiments (Zhou and Blunt, 1997) and simulations based on the Leverett concept for (a) purified sand–hexane, (b) purified sand–octane, (c) purified sand–decane, (d) red sand–hexane, (e) red sand–octane, and (f) red sand–decane systems.

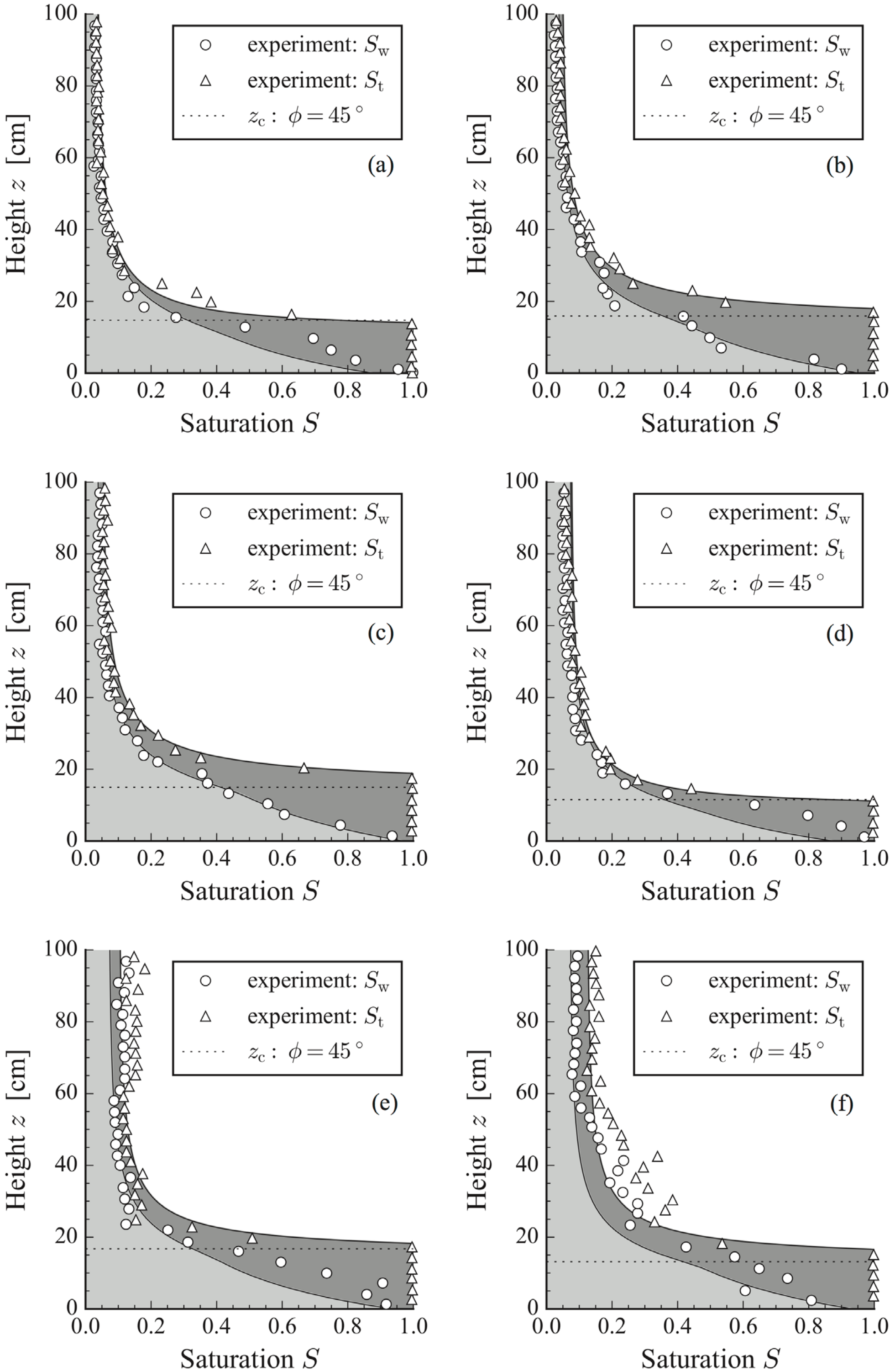

Figure 11. Three-phase capillary pressure–degree of saturation relationship as determined by experiments (Zhou and Blunt, 1997) and simulations based on the proposed concept for (a) purified sand–hexane, (b) purified sand–octane, (c) purified sand–decane, (d) red sand–hexane, (e) red sand–octane, and (f) red sand–decane systems.

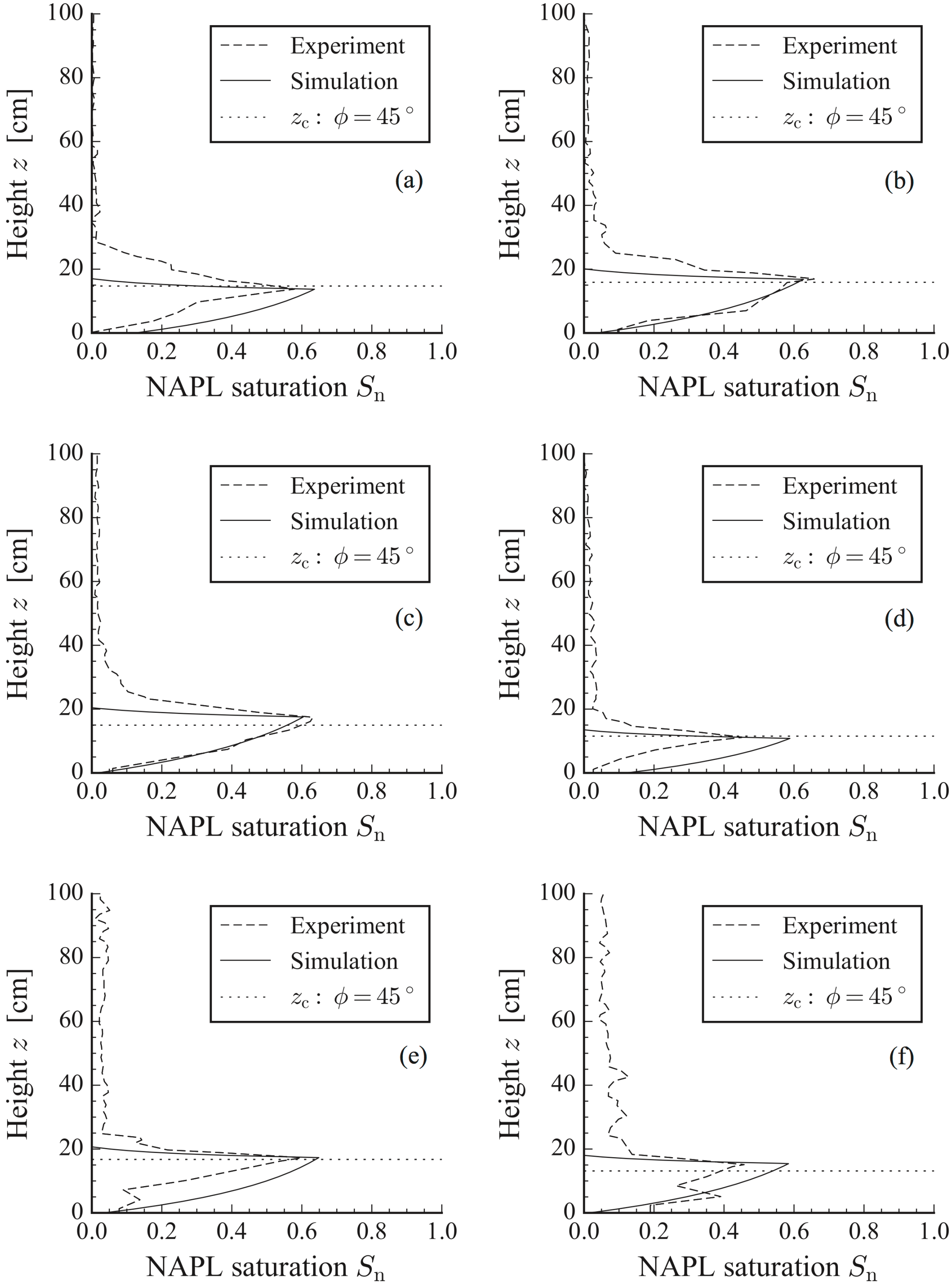

Figure 12. Distributions of the NAPL saturation as determined by experiments (Zhou and Blunt, 1997) and simulations based on the Leverett concept for (a) purified sand–hexane, (b) purified sand–octane, (c) purified sand–decane, (d) red sand–hexane, (e) red sand–octane, and (f) red sand–decane systems.

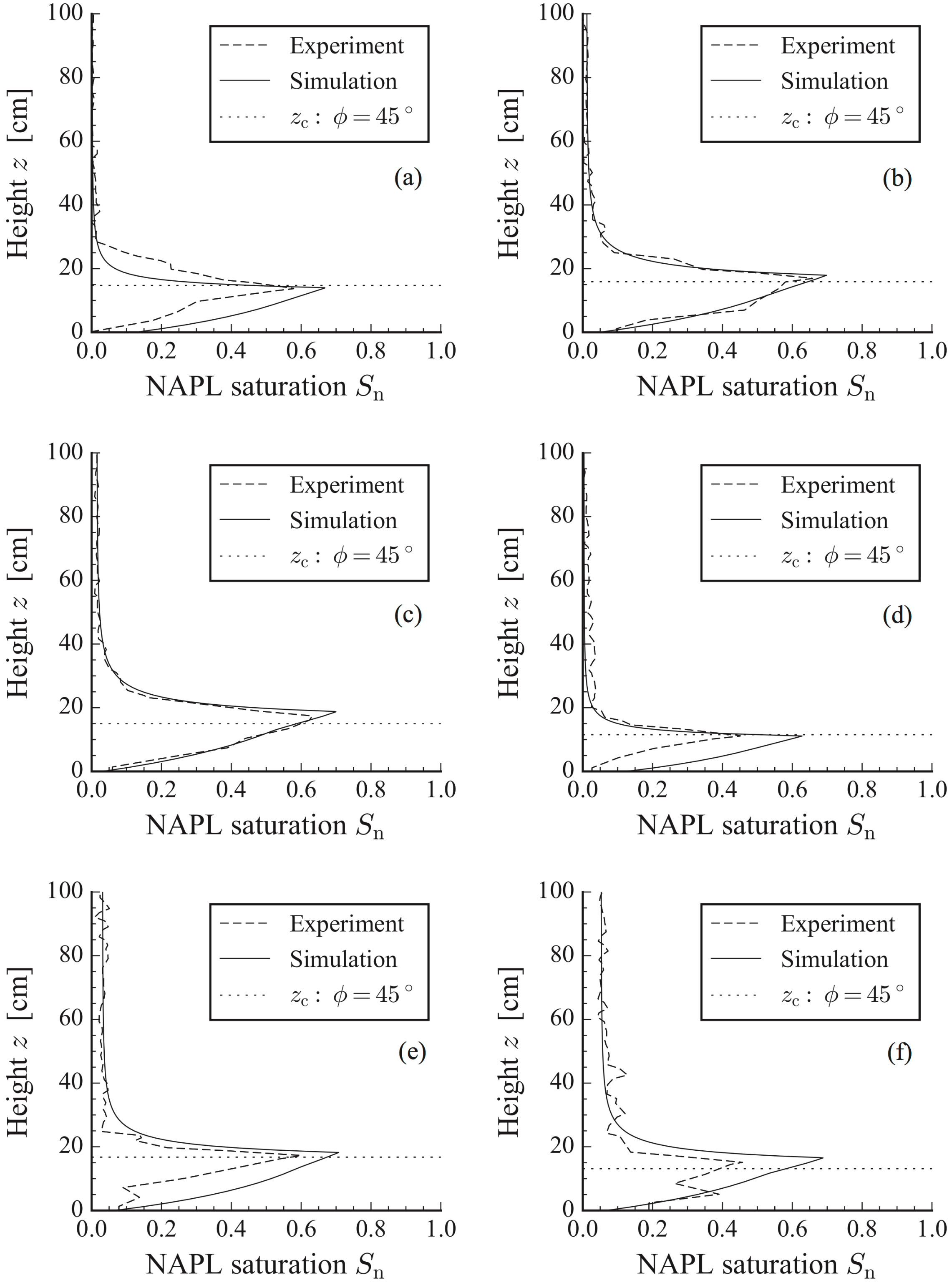

Figure 13. Distributions of the NAPL saturation as determined by experiments (Zhou and Blunt, 1997) and simulations based on the proposed concept for (a) purified sand–hexane, (b) purified sand–octane, (c) purified sand–decane, (d) red sand–hexane, (e) red sand–octane, and (f) red sand–decane systems.

5. Conclusions

In this study, we first discussed the limitations of the ordinary Leverett concept, by which the capillary pressure–degree of saturation relationship for three-phase systems can be simplified to a combination of the water–NAPL and NAPL–air two-phase relationships. We pointed out that the limitations of the concept arise owing to the assumption that the NAPL spreads on the water surface as well as the fact that the concept needs to be modified, especially when the relative magnitude of the NAPL pressure (μ) is lower than its critical value (μ_{c}).

In order to extend the Leverett concept, $\widetilde{\beta}^{\mathrm{e}}_{\mathrm{w}}$ and $\widetilde{\beta}^{\mathrm{e}}_{\mathrm{t}}$ are both described by quadratic Bezier curves. The spreading coefficient is incorporated into the three-phase capillary pressure–degree of saturation relationship by controlling the curvature of the quadratic Bezier curves through the parameters l_{w} and l_{t}. In the new concept proposed in the present study, the residual NAPL is further taken into account by its using irreducible (or minimum) saturation degree in the same way as is the case for the residual water in the water–air two-phase system.

As the proposed concept is a generalized one, any two-phase capillary pressure–degree of saturation model can be applied to the concept. The validity of the proposed concept is demonstrated by comparing the simulation results obtained using the model proposed by Brooks and Corey (1964) with the experimental data reported by Zhou and Blunt (1997). In contrast to the case for the original Leverett concept, the predictions obtained using the proposed concept match well with the experimental data, including the amount of residual NAPL. Finally, it should be noted that we discuss the capillary pressure–degree of saturation relationship subject to a monotonic saturation path in the present paper. For the phenomenon of hysteresis and strongly NAPL-wet media, the proposed concept would need to be modified further.

For the further application of the proposed concept to initial-boundary-value problems of water–NAPL–air three-phase flow in porous media, it is necessary to solve governing equations of mass conservation of three fluids with the pressure–saturation relationship given by the proposed concept. The details of the application of the proposed concept is explained in Appendix B.

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Appendix

A. Quadratic Bezier curve

The quadratic Bezier curve shown in Figure A1, which is described using three control points $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, and $\boldsymbol{r}_3$, has the following properties: (a) the curve interpolates $\boldsymbol{r}_1$ and $\boldsymbol{r}_3$ and its curvature is controlled by the middle control point, $\boldsymbol{r}_2$; (b) the curve connects to $\boldsymbol{r}_1$ and $\boldsymbol{r}_3$ smoothly, that is, the tangential vector of the curve is parallel to $\boldsymbol{r}_1$–$\boldsymbol{r}_2$ and $\boldsymbol{r}_2$–$\boldsymbol{r}_3$ at $\boldsymbol{r}_1$ and $\boldsymbol{r}_3$, respectively. Point

$\boldsymbol{r}$ on the Bezier curve can be derived via a geometric construction and can be easily written as a linear combination of the control points.

$$\boldsymbol{r} = \frac{k_1\boldsymbol{r}_1 + k_2\boldsymbol{r}_2 + k_3\boldsymbol{r}_3}{k_1 + k_2 + k_3} \tag{A1}$$

Here, k_1, k_2, and k_3 are functions of intermediate variable t $(0 \leq t \leq 1)$, which are modified with an additional parameter l $(0 < l < 1)$ so that the curvature of the Bezier curve can be controlled.

$$\begin{cases} k_1 = (1-t)^2 \\ k_2 = \dfrac{2l}{1-l}t(1-t) \\ k_3 = t^2 \end{cases} \tag{A2}$$

The position of the Bezier curve $t = 0.5$ is controlled by l as follows.

$$l = \frac{h}{H} \tag{A3}$$

In this study, the curve is applied in order to describe the μ–$\widetilde{\beta}_J^{\mathrm{e}}$ relationship. As shown in Figure A2, the control points $\boldsymbol{r}_{\mathrm{w1}}$, $\boldsymbol{r}_{\mathrm{w2}}$, and $\boldsymbol{r}_{\mathrm{w1}}$ are used for the μ–$\widetilde{\beta}_{\mathrm{w}}^{\mathrm{e}}$ relationship while $\boldsymbol{r}_{\mathrm{t1}}$, $\boldsymbol{r}_{\mathrm{t2}}$, and $\boldsymbol{r}_{\mathrm{t3}}$ are used for the $\mu - \widetilde{\beta}_{\mathrm{t}}^{\mathrm{e}}$ relationship. Parameters, l_{w} and l_{t} are set separately as the parameter l for the μ–$\widetilde{\beta}_{\mathrm{w}}^{\mathrm{e}}$ and μ–$\widetilde{\beta}_{\mathrm{t}}^{\mathrm{e}}$ relationships, respectively.

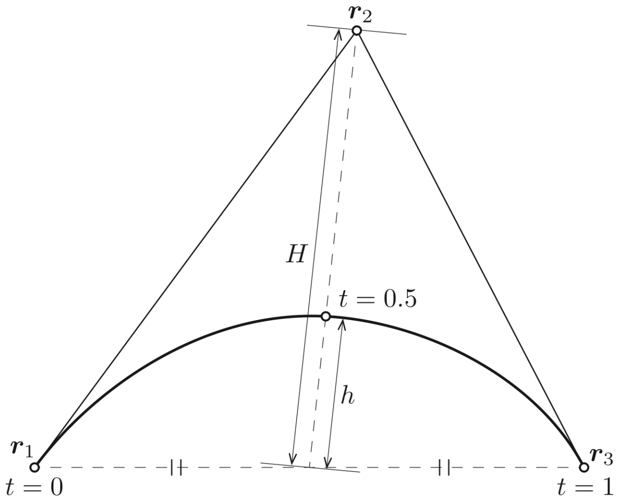

Figure A1. Quadratic Bezier curve with three control points.

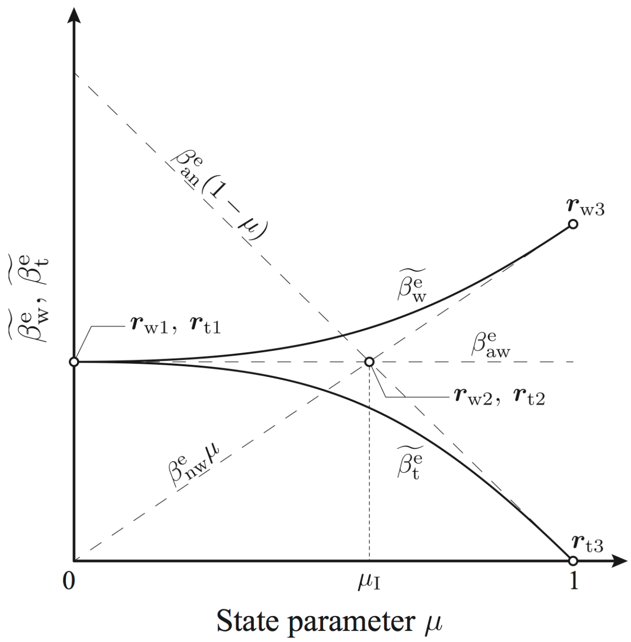

Figure A2. Description of the μ–$\widetilde{\beta}^{\mathrm{e}}_{j}$ relationship using a quadratic Bezier curve.

B. Role of the pressure-saturation relationship in the simulation of initial boundary-value problems of water-NAPL-air three-phase transport in porous media

In solving initial-boundary-value problems of water–NAPL–air three-phase transport in non-deformable porous media, the mass of each fluid i (w : water; n : NAPL; a : air) must be conserved everywhere.

$$\phi_{\mathrm{s}}\dot{S}_i + \frac{\phi_{\mathrm{s}}S_i}{K_i}\dot{P}_i + \nabla\cdot\boldsymbol{v}_i = 0 \qquad \text{(B1)}$$

where ϕ_{s} is the porosity of the porous media, and S_i, P_i, K_i and $\boldsymbol{v}_i$ are volumetric saturation of pores, pressure, the bulk modulus and the flow rate of the fluid i, respectively. “ $\dot{}$ ” denotes the time derivative and “ $\cdot$ ” denotes an inner product of two vectors. By assuming Darcy’s law, $\boldsymbol{v}_i$ is given as:

$$\boldsymbol{v}_i = -\frac{k_i}{\eta_{\mathrm{r}i}}\nabla\left(\frac{P_i}{\rho_{\mathrm{w}}g} + \rho_{\mathrm{r}i}z\right) \qquad \text{(B2)}$$

where k_i, $\eta_{\mathrm{r}i}$ $(=\eta_i/\eta_{\mathrm{w}})$ and $\rho_{\mathrm{r}i}$ $(=\rho_i/\rho_{\mathrm{w}})$ are the permeability, the relative viscosity and the specific gravity of fluid i, respectively, and z is the elevation potential.

As the permeability of air, k_{a}, is practically a few order larger than k_{w} and k_{n}, we may assume that the air will immediately flow without significant change in the pore air pressure P_{a} from the atmospheric pressure. Thus, the mass conservation for air is automatically satisfied and only the mass conservation for water and NAPL needs to be considered. By assuming that water and NAPL are both incompressible, governing equations becomes:

$$\begin{aligned} &\phi_{\mathrm{s}}\dot{S}_i - \frac{k_i}{\eta_{\mathrm{r}i}}\nabla\cdot\nabla\left(\frac{P_i}{\rho_{\mathrm{w}}g} + \rho_{\mathrm{r}i}z\right) = 0 \quad \text{in } \mathcal{B} \\ &P_i = P_i^* \quad \text{on } \partial\mathcal{B}_{P_i} \\ &\boldsymbol{v}_i\cdot\boldsymbol{n} = q_i \quad \text{on } \partial\mathcal{B}_{q_i} \end{aligned} \tag{B3}$$

where $\mathcal{B}$ denotes an analysis domain and $\partial\mathcal{B}$ represents the surface of the domain. In order to solve the first equation under Dirichlet and Neumann boundary given by the second and the third equation, we additionally need relationships that link the saturation degree, S_i, and the pressure, P_i, for three liquids. For this, a model for capillary pressure–saturation relationship as the Leverett concept or the proposed concept is required.

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