**Generalization of Vapor Pressure Lowering Effects in an
Existing Geothermal Simulator**

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ABSTRACT

Thermodynamic properties of pore water are shown to be different from those of bulk water because of interfacial forces between the aqueous and solid phases. This "vapor-pressure lowering" (VPL) effect is described through Kelvin's equation, which relates VPL to properties of the liquid phase.

An algorithm that accounts for VPL had previously been implemented in the geothermal simulator TETRAD. This algorithm applies to a narrow range of reservoir properties, and in some cases leads in inconsistencies. This report presents a generalization of the VPL algorithm which removes many of its limitations. The governing equations for the generalization are presented, assumptions and limitations of the method are discussed, and the modifications are validated.

Generalization of Vapor Pressure Lowering Effects in an Existing Geothermal Simulator

INTRODUCTION

This report describes a proposed modification to TETRAD, the multipurpose simulator used by INEL's geothermal reservoir technology program. The current version of TETRAD has an option for adsorption of water on rock. However, the algorithm for adsorption as currently implemented applies to a narrow range of properties and cannot be used in many field scale studies. The modifications proposed in this report generalize the adsorption algorithm and allow for its broader use.

Thermodynamic properties of water in porous media are different from those of bulk water because of interfacial and surface forces between the aqueous phase and the rock surface. Liquid water wets the rock preferentially compared to water vapor, and liquid adsorbs onto the rock surface as multi-layers that are a few molecules thick. Liquid is also held in smaller pores and fractures by capillary forces, again because liquid wets the rock surface. These phenomena cause the vapor pressure of the liquid phase to be lower than that of the vapor phase by an amount typically referred to as capillary pressure, P_c , thus reducing the liquid's tendency to boil. Therefore, saturation pressure becomes a function of both temperature and liquid saturation (through the capillary pressure/liquid saturation relation). This "vapor pressure lowering" (VPL) effect is described by Kelvin's equation (Edlefsen and Anderson, 1943):

$$\beta = \frac{P'}{P_{\text{sat}}} = \exp\left(-\frac{M_{\text{H}_2\text{O}} P_c}{\rho_w R T}\right)$$

where P_{sat} is the "flat surface" saturation pressure, P' is the "porous media" saturation pressure, and β is referred to as the relative vapor pressure. See Nomenclature for a complete definition of terms.

EXISTING ALGORITHM

The algorithm currently implemented in TETRAD to account for VPL effects is a direct extension of the work presented by Holt and Pingol (1992). In their work, β was expressed in terms of the adsorbed mass fraction of water, X , and a Langmuir isotherm:

$$X = \frac{\beta}{A + B\beta} \quad (1)$$

Nghiem and Ramey (1991) suggest that Langmuir parameters $A=31$ and $B=53$ are suitable for a variety of reservoir rocks. By assuming that all liquid water is adsorbed (or held by capillarity), then the adsorbed mass of water may be expressed in terms of a liquid saturation, S_w :

$$\chi = \frac{\phi \rho_w S_w}{(1-\phi)\rho_r} \quad (2)$$

where ϕ is porosity and ρ_w and ρ_r are liquid and rock densities, respectively. Substituting Eq. 2 into Eq. 1 gives β in terms of S_w :

$$\beta = \frac{S_w A \frac{\phi \rho_w}{1-\phi \rho_r}}{1 - S_w B \frac{\phi \rho_w}{1-\phi \rho_r}}, \text{ with } \beta \leq 1 \quad (3)$$

In this formulation, A , B , S_w , ρ_w , and ρ_r are all that are needed to quantify VPL.

Two limitations exist with the above formulation for VPL effects. However, it should also be noted that the VPL algorithm as currently implemented was regarded as a short-term fix (personal communication, Paul Atkinson, UNOCAL, April, 1993), and the limitations of the method were known. The suggested modifications discussed herein are not meant as a criticism of the existing VPL implementation, merely as a means of generalizing the method.

The first limitation concerns the explicit dependence of VPL effects on porosity and on the use of the Langmuir parameters A and B . Figure 1 shows β vs. S_w for a variety of different porosity values. This figure is a plot of Eq. 3 using $A=31$ and $B=53$. For these values of A and B , β does not reach unity even at $S_w = 1.0$ for values of porosity less than about 0.04. The implication of this error is that the Langmuir parameters A and B must depend on porosity, and must therefore vary from grid block to grid block in a field scale model. As A and B are currently scalars, VPL effects cannot be correctly simulated at the field scale unless porosities are held constant throughout the domain.

The second concern regarding the current formulation is the lack of interdependence between β and capillary pressure, P_c . According to Kelvin's equation, these two cannot be varied independently. This dependence is not considered in the existing formulation.

One way to generalize VPL effects is to use Kelvin's equation directly to determine β . This proposed modification has several advantages over the existing method, including:

- β does not rely on a Langmuir isotherm to describe the VPL effects. Continuing research (Shang et al., 1993) suggests that adsorption cannot always be represented well by a Langmuir isotherm.

- VPL is made dependent on P_c , consistent with Kelvin's equation.

- VPL is no longer an explicit function of ϕ , and VPL can therefore be used in field scale problems where porosity changes spatially.

This balance of this report discusses the modifications required to implement a more general approach to VPL effects.

REVISED FORMULATION

In order to correctly resolve pressures and saturations for pure water in cases where VPL effects are important, a correction factor must be applied to the saturation pressure as determined from a steam table. This correction factor is the relative vapor pressure, β . This technique is preferred because it is relatively easy to implement in an existing simulator. Another, more difficult option would be to develop a new simulator that takes VPL effects into account by their explicit incorporation in the governing equations.

As noted above, the relative vapor pressure can be expressed as

$$\beta = \frac{P'}{P_{\text{sat}}} = \exp\left(-\frac{M_{\text{H}_2\text{O}} P_c}{\rho_w R T}\right) \quad (4)$$

which is known as Kelvin's equation. Inspection of this equation shows that relative vapor pressure is a function of temperature, saturation (through the capillary pressure), molecular weight, and density of the liquid.

In order to implement Kelvin's equation, β must be expressed in terms of fundamental thermodynamic variables (P , T , S_g , ω_i). The following parametric equations are used to achieve this:

$$P_c = A_{p_c} (1 - S_w)^{B_{p_c}} \quad (5)$$

$$\rho_w = \frac{\rho_w^{\circ} [1 + c_T(T - T^{\circ})]}{[1 + c_p(P - P^{\circ})]} \quad (6)$$

Eq. 5 can be generalized to include scaling due to permeability and porosity variations (Leverett, 1941) and temperature (Lange, 1956):

$$P_c = A_{p_c}^{\circ} (1 - S_w)^{B_{p_c}} \left\{ \frac{T_c - T}{T_c - T^{\circ}} \right\}^{1.2} \sqrt{\frac{k^{\circ}}{k} \frac{\phi}{\phi^{\circ}}} \quad (7)$$

The superscript "°" in the above equations refers to a reference property or condition, and T_c is the critical temperature. When Eqs. 6 and 7 are substituted into Eq. 1, β can be written as

$$\beta = \exp \left\{ - \frac{M_{\text{H}_2\text{O}} A_{p_c}^{\circ} (1 - S_w)^{B_{p_c}} \left\{ \frac{T_c - T}{T_c - T^{\circ}} \right\}^{1.2} \sqrt{\frac{k^{\circ}}{k} \frac{\phi}{\phi^{\circ}}}}{R T \frac{\rho_w^{\circ} [1 + c_T(T - T^{\circ})]}{[1 + c_p(P - P^{\circ})]}} \right\} \quad (8)$$

which is completely in terms of reference and fundamental thermodynamic properties of the system.

IMPLEMENTATION

In order to implement the above formulation, several changes are required in the simulation code. These changes impact two areas of the code: relative permeability (subroutines INREL and RELP) and secondary fluid properties (subroutines ADSORB and SDRYTH). These modifications have been implemented in a test version of TETRAD, but have not been made in a general release of the code.

Modifying Relative Permeabilities and Capillary Pressures

The existing version of TETRAD uses capillary pressure tables rather than a parametric expression; therefore, an expression for P_c must be incorporated. This involves changing the input for analytical relative permeabilities (RELANAL).

Relative permeabilities are defined in terms of dimensionless, mobil saturations

$$\begin{aligned} S_{wD} &= (S_w - S_{wr}) / (1 - S_{wr} - S_{or} - S_{gr}) \\ S_{oD} &= (S_o - S_{or}) / (1 - S_{wr} - S_{or} - S_{gr}) \\ S_{gD} &= (S_g - S_{gr}) / (1 - S_{wr} - S_{or} - S_{gr}) \end{aligned}$$

all constrained to within $[0,1]$, then

$$k_{rw} = k_{rw}^o (S_{wD})^{e_w}$$

$$k_{ro} = k_{ro}^o (S_{oD})^{e_o}$$

$$k_{rg} = k_{rg}^o (S_{gD})^{e_g}$$

Capillary pressures can be written parametrically as

$$(P_c)_{wo} = A_{wo} (1 - S_w)^{B_{wo}}$$

$$(P_c)_{og} = A_{og} (1 - S_o)^{B_{og}}$$

Phase residual saturations (S_{wr} , S_{or} , S_{gr}), relative permeability exponents (e_w , e_o , e_g), and capillary pressure exponents (B_{wo} , B_{og}) can be temperature dependent. Interpolation for these parameters is discussed in the TETRAD 10.0 Users' Manual (Vinsome, 1993).

The endpoint capillary pressures (A_{wo} , A_{og} above) are not temperature dependent. Instead, the temperature dependence of capillary pressure is through its influence on interfacial tension, σ (Lange, 1956):

$$\frac{\sigma(T)}{\sigma(T^o)} = \left\{ \frac{T_c - T}{T_c - T^o} \right\}^{1.2}$$

Capillary pressures are also proportional to porosity and permeability, through the Leverett-j function (Leverett, 1941):

$$\frac{P_c}{P_c^\circ} = \sqrt{\frac{k^\circ}{k} \frac{\phi}{\phi^\circ}}$$

Therefore, capillary pressures can be written in a general form as

$$P_{cwo} = A_{wo}^\circ (1 - S_w)^{B_{wo}} \left\{ \frac{T_c - T}{T_c - T^\circ} \right\}^{1.2} \sqrt{\frac{k^\circ}{k} \frac{\phi}{\phi^\circ}}$$

$$P_{cog} = A_{og}^\circ (1 - S_o)^{B_{og}} \left\{ \frac{T_c - T}{T_c - T^\circ} \right\}^{1.2} \sqrt{\frac{k^\circ}{k} \frac{\phi}{\phi^\circ}}$$

For non-thermal simulations, the temperature dependence on interfacial tension is neglected. Leverett-j scaling can also be neglected by setting the input ϕ° to zero on the RELANAL input line, as discussed below.

In order to implement the above changes, input for RELANAL must be changed. First, four new matrices are required (in file SPECS.INC) to store capillary pressure parameters. These are

AWO(2,NRELMX), BWO(2,NRELMX), AGO(2,NRELMX), BGO(2,NRELMX).

These matrices are dimensioned to be consistent with other relative permeability input data (2 data per table to account for temperature effects; NRELMX is the maximum number of different relative permeability tables).

In addition to including these matrices in the SPECS.INC file, the input for RELANAL is modified as

```
'RELANAL' ITABLE ISTONE T1 T2 K° φ°
SWR KRW° EW
SOR KRO° EO AWO° BWO°
SGR KRG° EG AOG° BOG°
```

If $T2 > T1$, the last three lines above are repeated. Each of the above parameters are in fact specific to a particular relative permeability table, and different relative permeability tables can be used in different parts of a simulation domain. This allows residual saturations (for example) to vary in portions of a reservoir, or differ between fractures and rock matrix. If Leverett-j effects are not desired, ϕ° is set to zero, and that scaling is not done.

Modifications Required for VPL

Using the relative permeability/capillary pressure changes discussed above, additional changes required for VPL effects are straightforward. Liquid density is estimated as

$$\rho_w = \frac{\rho_1^0 [1 + c_T(T - T^0)]}{[1 + c_p(P - P^0)]}$$

Reference properties ρ_1^0 , T^0 , and P^0 , and isothermal and isobaric compressibilities are already required input (line LIQDEN). Liquid density is estimated from the liquid density of component 1 (pure water) because water is the largest component in the aqueous phase and because the effects of salts or non-condensable gases on adsorption have not yet been quantified.

Capillary pressure is implemented in the VPL routine (ADSORB) exactly as described above. The molecular weight of water is also required input (line DENCS), and the real gas constant, R , is set internally in TETRAD. The final parameter in Eq. 1 is the temperature, T . The manner of handling T depends on the phase status, as described below.

In single-phase situations (100% liquid or 100% vapor), primary variables are P , T , and aqueous mole fractions of components 2 through the total number of components, NC . VPL for either of these cases is readily determined from the primary variables. For $S_g = 0$, VPL is zero ($P_c = 0$; $\beta = 1$); for $S_g = 1$, β has its minimum value (VPL effects largest), which depends on the values of P_c and T .

In a two-phase situation, temperature is not a primary variable; it is replaced by S_g . This is not to say that T is not a fundamental thermodynamic variable, only that T is obtained from P , S_g , and equilibrium relationships. See Vinsome and Shook (1993) for details regarding variable switching in TETRAD. Temperature is found iteratively by evaluating the phase distribution of mole fractions in a flash algorithm. VPL effects also determine the phase behavior of the components, and β is also a function of temperature. Therefore, the adsorption routine must be included in the temperature iteration. Code changes for including this modification for VPL can be summarized as follows. The call to the VPL routine is moved inside the temperature iteration for two-phase conditions; for either single-phase state, no change is required. Sufficient changes are required in the VPL routine itself so that a new routine replaces the existing one.

LIMITATIONS OF THE PROPOSED MODIFICATIONS

While the proposed modifications render VPL effects in a more general manner, they are not without limitations. The following statements should be considered as assumptions, limitations, and observations that apply to this implementation of VPL effects:

- Liquid density is estimated using the density of pure water. This estimation is very good, considering the limitations placed on the VPL option. TETRAD currently allows VPL only when pure water and water tracers (e.g., tritium) are used in the simulation. VPL cannot currently be used in conjunction with the CO₂/SALT options. As experimental results become available regarding the effect of VPL on brine phase behavior, this estimation of ρ can be relaxed. A more general approach would be to estimate liquid density in terms of each species' molar density, summed over aqueous mole fractions.
- The liquid density calculation for VPL further assumes that the reference density data (LIQDEN) was input at standard conditions of temperature and pressure. This is not required by TETRAD, except in the VPL calculations. This could be relaxed easily by changing the input on the ADSORB line to include standard conditions (P° and T°).
- Currently several input data exist that are not used in any simulation. The ADSORB input line consists of four data; however, only the first is used (VPL effects considered if $\text{ADSORB}(1) > 0$). Also, in RELANAL, ISTONE is still read in, despite there being no option to use Stone's model (Stone, 1970) for three-phase relative permeability. These superfluous input will be removed when these modifications are implemented in a general release of TETRAD.
- The critical temperature for component 1 (pure water) is used in the temperature scaling of interfacial tension. Again, this is a good assumption for the current application. This could also be relaxed by obtaining a pseudo-critical temperature, T_{pc} , where $T_{pc} = \sum(T_{ci} \cdot \omega_i)$.
- In geothermal mode, oil-gas capillary pressure must be set to zero ($A_{og} = 0$). If this is not done, capillary pressure is not calculated correctly, since $P_w = P_g - P_{cog} - P_{cwo}$. Also, oil phase residual saturation should be set to zero, as an oil phase does not exist in a geothermal simulation.
- The current analytic relative permeability option allows for temperature dependence of all of the parameters. This has been continued in this implementation. However, as was noted above, the endpoint capillary pressures are not temperature dependent, except through the interfacial tension. Therefore, if $T_2 > T_1$ on the RELANAL input line, a second value for A_{wo}° and A_{og}° must be read in (to remain consistent with the other data read in); however, **these second values are not ever used.**

VERIFICATION

The test problem used to verify the modifications to VPL effects in TETRAD consists of radial flow of vapor to a geothermal well. A radial grid of 30 blocks was used, with grid spacing fine near the well and increasing away from the well. The outer radius is such that boundary

effects are not seen in the time frame of interest. Reservoir thickness is 1000 m, porosity is 0.05, and permeability is input as 50 md ($49.3 \times 10^{-12} \text{ m}^2$).

Two different cases were simulated in order to compare results with and without VPL. Initial pressure in each case was 1000 kPa, and temperature was 206.46°C. This temperature was determined to lie on the saturation curve for the adsorption case, as discussed below. For the case of no VPL effects, these conditions result in superheated steam.

For the case with VPL effects, initial liquid saturation was 0.05. The capillary pressure curve used in this study is given in Figure 2. Selection of this capillary pressure curve and a liquid saturation of 0.05 resulted in the initial temperature of 206.46°C. Other properties were those of pure water, with a few exceptions. For example, thermal conductivities were all set to zero, as was the heat of vaporization of water. These changes were made to ensure isothermal flow. Also, vapor viscosity was held at a constant 0.016 mPa-s (i.e., independent of temperature and pressure).

Mass was withdrawn from the center of the grid at a constant rate of 5 kg/s. Pressure variations were measured at three locations near the production well. From Mathews and Russel (1967), pressure in the reservoir can be expressed as

$$P^2(r,t) = P_i^2 - \frac{q_m \mu}{2\pi K H} \frac{ZRT}{M_{H_2O}} \left[\ln\left(\frac{t}{r^2}\right) + \ln\left(\frac{k}{\phi \mu c}\right) + 0.80907 \right] \quad (9)$$

A plot of P^2 vs. the similarity variable t/r^2 is given in Figure 3 for both test cases (with and without VPL). The data points represent results of the simulation, and curves drawn are least squares fits to the data. These curves have the same slope of $-1.25 \times 10^5 \text{ kPa}^2$, confirming the validity of the similarity variable. From Eq. 9, this slope translates into a permeability of 50.3 md ($49.6 \times 10^{-12} \text{ m}^2$), in good agreement with the input value of 50 md. Also from Eq. 9, an apparent compressibility, c , can be calculated for each case. With VPL, $c = 1.35 \times 10^{-1} \text{ kPa}^{-1}$; without VPL, $c = 1.2 \times 10^{-3} \text{ kPa}^{-1}$. The increase in apparent compressibility with VPL is consistent with other studies (e.g., Pruess and O'Sullivan, 1992). The magnitude of the increase is appreciably larger than that noted by these authors; however, the increase is due in part to VPL and in part to phase change, and is quite sensitive to the level of VPL in the simulation. The apparent compressibility is bounded from above by that arising from vaporization, as determined by Grant and Sorey (1979).

SUMMARY

A new algorithm for vapor pressure lowering effects has been presented. This algorithm allows VPL to be treated in a more general manner than the current implementation. Most importantly, the explicit relationship between VPL effects, porosity, and adsorption isotherm

parameters have been removed, thus allowing VPL to be studied at the field scale where porosity varies spatially. The modifications require changes to four subroutines in TETRAD and include new input options for capillary pressures and relative permeabilities.

The algorithm has been validated by comparing numerical results against a known solution. Agreement between input and calculated permeabilities is very good. Apparent compressibility due to phase change and VPL effects was much larger than has been noted in other studies on VPL, but are still within values that considered increases due to phase change.

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NOMENCLATURE

English

A	Langmuir parameter [=] 0
A_{og}°	Endpoint capillary pressure for oil-gas phases at reference conditions [=] kPa
A_{pc}	Endpoint capillary pressure in parametric expression for P_c [=] kPa
A_{wo}°	Endpoint capillary pressure for water-oil at reference conditions [=] kPa
B	Langmuir parameter [=] 0
B_{pc}	Exponent for capillary pressure in parametric expression for P_c [=] 0
B_{wo}	Exponent for water-oil capillary pressure [=] 0
B_{og}	Exponent for oil-gas capillary pressure [=] 0
c	Apparent isothermal compressibility [=] kPa^{-1}
c_p	Isothermal coefficient of compressibility [=] kPa^{-1}
c_T	Isobaric coefficient of thermal expansion [=] K^{-1}
e_j	Relative permeability exponent for phase j, j = water, oil, gas
H	Thickness [=] m
k	Permeability [=] m^2
kr_j	Relative permeability of phase j, j=water (w), oil (o), gas (v)
k_{rj}°	Endpoint relative permeability for phase j, j = water, oil, gas
k°	Reference permeability; permeability at which P_c is measured [=] m^2
M_{H_2O}	Molecular weight of pure water [=] kg/kg.mol
NC	Number of components
P_i	Initial pressure [=] kPa
$P(r,t)$	Pressure as a function of time and position [=] kPa
P'	Saturation pressure of pure water in porous media [=] kPa
P_c	Capillary pressure, $P_v - P_w$ [=] kPa
P_{sat}	Saturation pressure of bulk water [=] kPa
P°	Reference pressure; pressure at standard conditions (101.3 kPa) [=] kPa
P_v	Vapor pressure [=] kPa
P_w	Liquid pressure [=] kPa
q_m	Mass flow rate [=] kg/s
r	Radius [=] m

R	Real gas constant [=] (kPa m ³)/(kg.mol K)
S _g	Vapor saturation [=] vol vapor/vol pore space
S _{gD}	Dimensionless gas saturation
S _{gr}	Residual gas saturation
S _o	Oil saturation [=] vol oil/vol pore space
S _{oD}	Dimensionless oil saturation
S _{or}	Residual oil saturation
S _w	Liquid saturation [=] vol liquid/vol pore space
S _{wD}	Dimensionless water saturation; mobil saturation
S _{wr}	Residual water saturation
t	Time [=] s
T	Temperature [=] K
T _c	Critical temperature [=] K
T ^o	Reference temperature; temperature at standard conditions (288.7 K) [=] K
X	Adsorbed mass fraction of water [=] kg H ₂ O/kg rock
z	Real gas compressibility factor

Greek

β	Relative vapor pressure [=] 0
φ	Porosity [=] vol. pore space / bulk volume
φ ^o	Reference porosity; porosity at standard conditions [=] vol. pore space / bulk volume
μ	Viscosity [=] mPa-s
ρ _w	Density of liquid phase [=] kg/m ³
ρ _w ^o	Density of liquid phase at reference conditions [=] kg/m ³
ρ _l	Density of pure water in liquid phase [=] kg/m ³
ρ _r	Density of rock [=] kg/m ³
σ	Interfacial tension [=] dynes/cm
ω _i	Mole fractions of component i in aqueous phase

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Figure 1. VPL effects for various values of porosity.

Figure 2. Capillary pressure - saturation relationship used in verification study.

Figure 3. Transient test response with and without VPL effects.