

Appendix C Derivation of Equations for an Air-Water Mixture

The following assumptions were made for this analysis. We will assume initial saturation levels are greater than 85 percent, which implies that all air bubbles are occluded. Surface tension effects will be neglected, which allows us to assert that the air bubbles within the water will be at the same pressure as the water. The air is soluble in water and observes Henry's Law, and the rate of increase in pore water pressure from any simulation is slower than the rate of diffusion of air in water. Finally, prior to full saturation, the compressibility or bulk modulus of water is a constant. We will first develop the equations for an air-water system with a rigid porous skeleton, then one with a compressible porous skeleton.

The following terms are used in the derivation of the compressibility of an air-water mixture.

Let

V denote the total volume of air and water,

V_v the volume of the void space,

V_w the volume of water,

V_d the volume of dissolved air,

V_a the total volume of air,

V'_a the volume of free air, which is equal to $V_a - V_d$,

P_w the pore water pressure,

P_a the pore air pressure and

H Henry's constant.

A subscripted "o" is used to indicate an initial value. The total mass of air and water remains constant. Substituting expressions for porosity (n) and saturation (S), the initial volumes of water V_{wo} and free air V'_{ao} may be expressed as

$$V_{wo} = S_o V_{vo} = n_o V_o S_o \quad \text{C.1}$$

and

$$V'_{ao} = (1 - S_o) V_{vo} = n_o V_o (1 - S_o) \quad \text{C.2}$$

Using Henry's Law and Equation C.1, the initial volume of dissolved air may be expressed as

$$V_{do} = V_{wo} H = n_o V_o S_o H \quad \text{C.3}$$

The sum of Equations C.2 and C.3 yields an expression for the initial total volume of air in the system

$$V_{ao} = n_o V_o (1 - S_o + S_o H) \quad \text{C.4}$$

Expressions for the compressibility of water and an air-water mixture may be written as

$$C_w = - \frac{1}{V_w} \frac{dV_w}{dP_w} \quad \text{C.5}$$

and

$$C_m = - \frac{1}{V'_a + V_w} \left(\frac{dV'_a}{dP_w} + \frac{dV_w}{dP_w} \right) \quad \text{C.6}$$

respectively. Substituting Equation C.5 into Equation C.6 one obtains

$$C_m = - \frac{1}{V'_a + V_w} \left(\frac{dV'_a}{dP_w} - V_w C_w \right) \quad \text{C.7}$$

We will now use Boyle's Law to develop an expression for the derivative in Equation C.7. Boyle's Law may be written as

$$V_a P_a = V_{ao} P_{ao} \quad \text{C.8}$$

If we assume the pore and air pressure are equal and $V_d = V_{do}$, we can write the following

$$\frac{P_{ao}}{P_a} = \frac{P_{wo}}{P_w} = \frac{V'_a + V_d}{V'_{ao} + V_d} \quad \text{C.9}$$

from which we write

$$\begin{aligned} \frac{dP_w}{dV'_a} &= - \frac{V'_{ao} + V_d}{(V'_a + V_d)^2} P_{ao} \\ &= - \frac{V_{ao} P_{ao}}{V_a^2} \end{aligned} \quad \text{C.10}$$

Substituting the latter expression in Equation C.10 into Equation C.7, one obtains

$$C_m = \frac{1}{V'_a + V_w} \left(\frac{V_a^2}{V_{ao} P_{ao}} + V_w C_w \right) \quad \text{C.11}$$

which is an expression for the compressibility of an air-water mixture. By judiciously substituting for the volume terms in Equation C.11, we will develop a final expression for the compressibility of the mixture.

By combining Boyle's Law (Equation C.8) and Equation C.4, we may write an expression for the current total volume of air

$$V_a = \frac{P_{ao}}{P_a} n_o V_o (1 - S_o + S_o H) \quad \text{C.12}$$

The current volume of water may be expressed as

$$V_w = V_{wo} (1 - C_w \delta P) \quad \text{C.13}$$

and, after substituting for V_{wo} , as

$$V_w = n_o V_o S_o (1 - C_w \delta P) \quad \text{C.14}$$

The current volume of dissolved air, which is a function of Henry's Law and the current volume of water, is written as

$$V_d = n_o V_o S_o H (1 - C_w \delta P) \quad \text{C.15}$$

Subtracting Equation C.15 from Equation C.12, one obtains an expression for the current volume of free air

$$V_a' = n_o V_o \left\{ \frac{P_{ao}}{P_a} (1 - S_o + S_o H) - S_o H (1 - C_w \delta P) \right\} \quad \text{C.16}$$

Adding Equations C.16 and C.14, one obtains

$$V_a' + V_w = n_o V_o \left\{ \frac{P_{ao}}{P_a} (1 - S_o + S_o H) + S_o (1 - H) (1 - C_w \delta P) \right\} \quad \text{C.17}$$

which will eventually be substituted back into Equation C.11. Combining Equations C.4 and C.12, one may write

$$\frac{V_a^2}{V_{ao}} = \left(\frac{P_{ao}}{P_a} \right)^2 n_o V_o (1 - S_o + S_o H) \quad \text{C.18}$$

and, by multiplying Equation C.14 by the compressibility of water and dropping the higher order terms, one obtains

$$V_w C_w = n_o V_o S_o C_w \quad \text{C.19}$$

Substituting Equations C.17, C.18, and C.19 into Equation C.11 yields the final expression for the compressibility of an air-water mixture

$$C_m = \left\{ \frac{P_{ao}}{P_a} (1 - S_o + S_o H) + S_o (1 - H) (1 - C_w \delta P) \right\}^{-1} \quad \text{C.20}$$

$$\times \left\{ \frac{P_{ao}}{P_a^2} (1 - S_o + S_o H) + S_o C_w \right\}$$

In a similar manner, an expression for the level of saturation may be developed and written as

$$S = \frac{V_w}{V_a' + V_w} \quad \text{C.21}$$

$$= \frac{S_o (1 - C_w \delta P)}{\frac{P_{ao}}{P_a} (1 - S_o + S_o H) + S_o (1 - H) (1 - C_w \delta P)}$$

When the porous skeleton is compressible, the current void volume may be expressed as

$$V_a' + V_w = V_o (n_o - \varepsilon_{kk}) \quad \text{C.22}$$

where V_o is the initial total volume of voids and solids and ε_{kk} is the effective volumetric strain.

Substituting the above and Equation C.14 into the first expression in Equation C.21, one obtains

$$S = \frac{V_w}{V_a' + V_w} = \frac{n_o S_o (1 - C_w \delta P)}{n_o - \varepsilon_{kk}} \quad \text{C.23}$$

which is an expression for the level of saturation in a deforming porous skeleton. An equation for the compressibility of an air-water mixture within a deforming porous skeleton may be obtained by combining Equations C.11, C.18, C.19, and C.22 to yield

$$C_m = \frac{n_o}{n_o - \varepsilon_{kk}} \left\{ \frac{P_{ao}}{P_a^2} (1 - S_o + S_o H) + S_o C_w \right\} \quad \text{C.24}$$

In the process of a calculation, one must first evaluate Equation C.23. If the level of saturation is less than one, Equation C.24 is used to calculate the bulk modulus of the pore fluid. If the level of saturation is equal to one, the bulk modulus of the pore fluid is calculated from the EOS of water.