

Density and compressibility characteristics of air-water mixtures

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Received December 12, 1975

Accepted June 14, 1976

The density and compressibility of miscible and immiscible air-water mixtures are formulated on the basis of the conservation of mass. Boyle's Law accounts for the compressibility of free air and Henry's Law accounts for the amount of air that goes into solution. The rate of air diffusion into water in the soil is used to choose either the case of complete solution or no solution of air. Formulas are given by which it is possible to predict the density and compressibility of the fluid phase of unsaturated soils.

The difference between the air and water pressures in a soil is of interest only in the compressibility formulation. It is not necessary nor advisable to use Kelvin's capillary model equation to account for the difference in air and water pressure since it incorporates an unmeasurable variable, and gives rise to an anomaly. It is recommended that a measurable pore pressure parameter, B_{aw} or B_{wa} be used in the solution of engineering problems.

La densité et la compressibilité de mélanges eau-air miscible et non miscible sont exprimées à partir du concept de conservation des masses. La loi de Boyle donne la compressibilité de l'air libre, la loi de Henry la quantité d'air entrant en solution. La vitesse de diffusion de l'air dans l'eau dans le sol est utilisée pour distinguer les cas de solution complète et de non solution de l'air. On donne des formules qui permettent de prédire la densité et la compressibilité de la phase fluide de sols non saturés.

La différence entre les pressions dans l'eau et l'air d'un sol présente un intérêt seulement dans la formulation de la compressibilité. Il n'est ni nécessaire ni à conseiller d'utiliser le modèle capillaire de Kelvin pour tenir compte de la différence entre les pressions dans l'eau et l'air puisque ce modèle comporte une variable non mesurable et donne lieu à une anomalie. Il est recommandé d'utiliser un coefficient de pression interstitielle mesurable B_{aw} ou B_{wa} dans la solution des problèmes de Génie.

[Traduit par la revue]

Can. Geotech. J., 13, 386 (1976)

Introduction

When air is mixed with water it is immiscible except for approximately 2% (by volume) that dissolves in the water. Since there is no chemical reaction, the resulting solution is a simple mixture. In the presence of a foreign solid, such as soil particles, the air and water pressures can differ and change at different rates during a process.

Of primary interest from an engineering standpoint is the mathematical formulation of density and compressibility relationships for the fluid phase of an unsaturated soil. An understanding of compressibility is of importance with respect to the pore air and pore water pressures developed under undrained loading of unsaturated soils. In addition to compressibility, a knowledge of the change in the fluid density is required when studying transient flow problems. An understanding of air diffusion through, and air solubility in water is also required.

Koning (1963) treated an air-water mixture

as an immiscible fluid and computed compressibility using Boyle's Law. Bishop and Eldin (1950) and Skempton and Bishop (1954) incorporated Henry's Law to describe the effects of the solubility of air in water. Schuurman (1964; 1966) attempted to account for the surface tension effects by directly applying Kelvin's capillary model equation. In deriving the compressibility equation, it was necessary to assume the number and size of air bubbles. The final equation becomes unusable from an engineering standpoint.

This paper reviews the physical properties of pure water and air, along with the laws governing the behavior of multiphase systems. Then the compressibility and density equations for air-water mixtures are formulated.

Fundamental Laws Describing the Density of Air and Water

Air is a mixture of several gases plus varying amounts of water vapour (Table 1). It behaves essentially in accordance with the Gas Law.

TABLE 1. Composition of dry air*

	Percentage by volume	Density (Mg/m ³)†	Molecular weight
Nitrogen (N ₂)	78.08	0.00125055	28.016
Oxygen (O ₂)	20.95	0.00142904	32.000
Argon (Ar)	0.934	0.0017837	39.944
Carbon dioxide (CO ₂)	0.030	0.0019769	44.010
Neon (Ne)	1.82 × 10 ⁻³	0.00090035	20.183
Helium (He)	5.24 × 10 ⁻⁴	0.00017847	4.003
Krypton (Kr)	1.14 × 10 ⁻⁴	0.003708	83.800
Hydrogen (H ₂)	≈ 5 × 10 ⁻⁵	0.00008988	2.016
Xenon (Xe)	8.7 × 10 ⁻⁶	0.005851	131.300
Ozone (O ₃)	1 × 10 ⁻⁶ to 1 × 10 ⁻⁵	0.002144	48.000
Air	100.0	0.0012929	28.966

*Under standard conditions (1 atm and 0 °C) with no water vapour.
†Mg/m³ = megagrams per cubic metre.

Therefore, Boyle's Law, Charles' Law, and Avagadro's Law also apply.

$$[1] \quad P \cdot V = W \cdot R \cdot T$$

where P = absolute pressure (kN/m²), V = volume (m³), W = weight (Mg), R = universal molar gas constant (8313.5 kN·m/Mg/°K), and T = absolute temperature (°K).

The Gas Law is often written in terms of specific volume.

$$[2] \quad P \cdot v = R \cdot T$$

where $v = V/W$ (the specific volume is the inverse of the density, γ).

Equation [2] applies for each gas making up air. In accordance with Dalton's Law, the behavior of a particular gas of a mixture of gases is independent of the other gases and the total pressure is the sum of the partial pressures.

$$[3] \quad P = \sum_{i=1}^n u_i$$

where u_i = partial pressure of each gas and n = number of gases in the mixture.

Each gas has a specific gas constant, R_i , and the specific volumes, v_i , are proportioned in accordance with the percentage of each gas by volume. The gas law can be written (Matveev 1967),

$$[4] \quad \sum_{i=1}^n P_i \cdot v_i = T \cdot \sum_{i=1}^n R_i$$

The specific gas constant for air, R , is computed by a proportioning of the molecular weights of each gas. For dry air, the specific

gas constant, R_d , is 287.0 kN·m/Mg/°K. For moist air the specific gas constant is

$$[5] \quad R_m = R_d (1 + 0.608 \cdot s_w)$$

where s_w = weight of water vapour per unit weight of air plus water vapour.

It should be noted that moist air will be slightly lighter than dry air. The density of air (*i.e.* inverse of specific volume) is

$$[6] \quad \gamma_a = \frac{1}{R_m} \cdot \frac{u_a}{T}$$

where u_a = air pressure for the combined gases (absolute).

Water is considered essentially to be a homogeneous substance the world over except for variations produced by salts and isotopes of hydrogen and oxygen (Dorsey 1940). Distilled water under the pressure of its saturated vapour is called pure, saturated water. Its density for various pressures and temperatures is determined experimentally and is published in physics and chemistry handbooks (Fig. 1).

Water molecules unite to form a lattice structure, leaving a 'cage' (approximately 2% by volume) that can be occupied by a gas (Rodebush and Buswell 1958). The water lattice is relatively rigid and stable (Dorsey 1940) and the density of water changes very little as a result of dissolving air in the water (Fig. 2).

Additional Physical Relationships For Air-Water Mixtures

The experimental data on the density of water indicate that air dissolves in water by

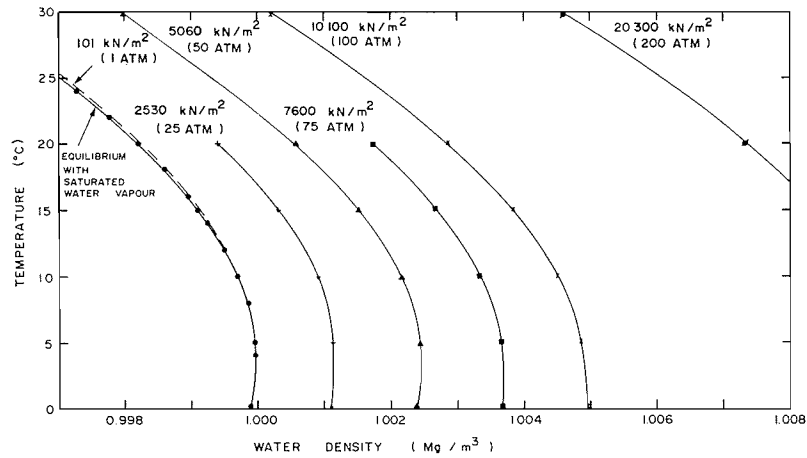


FIG. 1. Density of pure water at various temperatures and pressures.

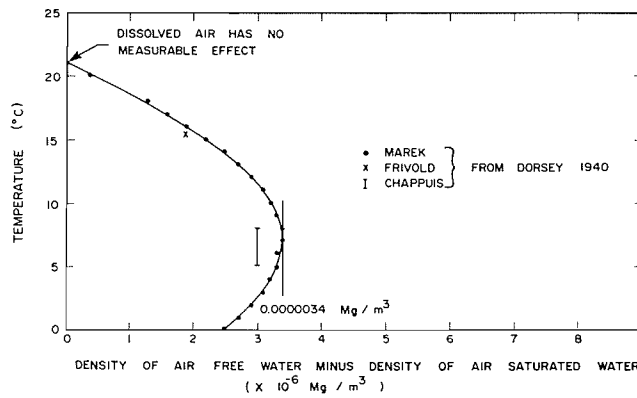


FIG. 2. Effect of dissolved air on the density of water.

fitting within the water structure, causing essentially no disruption. To understand this mechanism further, consider a piston and cylinder arrangement with a porous stone (having a porosity of approximately 2%) at the base of the cylinder (Fig. 3). The porous stone is to simulate the behavior of the water. Let there be an imaginary valve at the contact between the free air and the porous stone. In this way, the movement of air into the stone can be controlled. The air in the porous stone simulates the air dissolved in water. It should be noted that the above analogy lacks in that the air and water pressure cannot differ.

Initially the cylinder contains a volume that is porous stone and a volume that is air, subjected to equal pressures. Suppose the imaginary valve is initially closed and the load on the

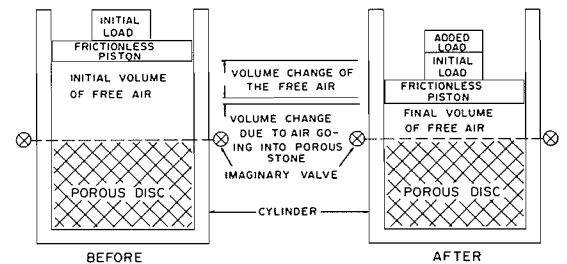


FIG. 3. Piston and porous stone analogy.

piston is increased. The air above the porous stone compresses (Boyle's Law). When the imaginary valve is opened, some additional air passes into the porous stone (Henry's Law). As the piston load is increased this process continues until all the free air has gone into the porous stone. At this point, there is a dis-

TABLE 2. Solubility of air in water*

Temperature	Weight of air per weight of water (H)†			Volume of air per volume of water (h)‡
	Oxygen	Nitrogen argon, etc.	Air (H_a)	
0	14.56×10^{-6}	23.87×10^{-6}	38.43×10^{-6}	0.02918
4	13.06×10^{-6}	21.59×10^{-6}	34.65×10^{-6}	0.02632
10	11.25×10^{-6}	18.82×10^{-6}	30.07×10^{-6}	0.02284
15	10.07×10^{-6}	17.00×10^{-6}	27.07×10^{-6}	0.02055
20	9.11×10^{-6}	15.51×10^{-6}	24.62×10^{-6}	0.01868
25	8.28×10^{-6}	14.24×10^{-6}	22.52×10^{-6}	0.01708
30	7.55×10^{-6}	13.10×10^{-6}	20.65×10^{-6}	0.01564

*From Dorsey (1940).

†At standard atmospheric pressure.

‡ $h = \gamma_a \cdot \gamma_w \cdot H_a$.

continuity since all the applied load is taken by the porous stone.

The above analogy assists in visualizing the density and compressibility of air-water mixtures subjected to various pressures. The density of the mixture is derived based on the conservation of mass. This law is also the fundamental basis for the compressibility relationship since compressibility is, by definition, the inverse of the change in density with respect to a change in pressure. The amount of air going into or coming out of solution is time dependent and is either ignored or taken into account, depending upon the engineering problem being considered.

Air is dissolved in water in accordance with Henry's Law which states that the weight of gas dissolved in a fixed quantity of liquid, at constant temperature, is directly proportional to the pressure of the gas above the solution (Sisler *et al.* 1953). The starting point for applying Henry's Law is given by the coefficient of solubility of each gas in water (Table 2). This coefficient, H , is the total weight of each gas that can be dissolved in water (under 1 atm pressure). If the weights of dissolved air were extracted from the water and compressed at the same pressure as acting on the free air above the water, the volume occupied can be computed using the gas law (*i.e.* volumetric coefficient of solubility, h).

The rate at which air goes into solution is described by Fick's Law of diffusion. The driving force is a concentration or density difference between the free air and the air in the 'cages' in the water. The gases composing air, diffuse individually in water (Table 3).

TABLE 3. Diffusivity of certain gases in water*

Gas	Temperature (°C)	Diffusivity (cm ² /s)
CO ₂	20	1.7×10^{-5}
N ₂	22	2.0×10^{-5}
H ₂	21	5.2×10^{-5}
O ₂	25	2.92×10^{-5}

*From Kohn (1965).

The diffusivity value generally given for air in water is 2.0×10^{-5} cm²/s (U.S. Research Council 1933). Few attempts have been made to measure the diffusivity of air through water in soils (Barden and Sides 1967). However, measurements that have been made show the diffusivity to differ by several orders of magnitude from the above value. The diffusivity appears to decrease considerably with increasing plasticity and decreasing water content of a soil.

Kelvin's equation for a single capillary tube, relates the difference in the air and water pressure to the surface tension, T_s , and effective radius of curvature of the air-water interphase, r . Attempts have been made to use this equation in the compressibility relationships for air-water mixtures (Schuurman 1966). However, this equation does not assist in solving practical problems since it incorporates a new unmeasurable quantity. In fact, an anomaly and conceptual difficulties arise when it is incorporated (see Appendix A). Since Kelvin's equation is not required in the derivation of density or compressibility, it is omitted except to demonstrate that its usage is unnecessary.

Density of Air-Water Mixtures

The density of air-water mixtures (miscible and immiscible) can be evaluated by a direct proportioning of the air and water fractions. Consider a cubic element with impervious sides. All sides are fixed with the exception of the top which is in the form of a sealed, frictionless piston. Let the volume of water be V_w and the volume of free air be V_a' . Applying the conservation of mass to the element gives

$$[7] \quad \gamma_m \cdot V = \gamma_w \cdot V_w + \gamma_a \cdot V_a'$$

where V = total volume of the element (*i.e.* free air and water), γ_m = density of the air-water mixture, γ_w = density of water, and γ_a = density of air.

Now suppose the force on the piston is increased. Assume that the volume of water remains constant and the total mass of air (*i.e.* free and dissolved air) remains constant. The density of the air in terms of any air pressure is given by [6]. Boyle's Law is applied to the free and dissolved air.

$$[8] \quad dV_a = dV_a' + dV_d = \frac{(V_{ai}' + V_{di}) \cdot du_a}{u_a}$$

Here,

$$[9] \quad u_a = u_{ai} + du_a$$

where u_{ai} = initial air pressure, du_a = change in air pressure, V_a = volume of free and dissolved air, V_d = volume of dissolved air, V_{ai}' = initial volume of free air, and V_{di} = initial volume of dissolved air.

The new volume of free air corresponding to a pressure, u_a , is

$$[10] \quad V_a' = V_{ai}' - (V_{ai}' + V_{di}) \cdot \left(1 - \frac{u_{ai}}{u_a}\right)$$

Substituting [10] into [7] and writing the volumes of air and water in terms of the initial degree of saturation gives

$$[11] \quad \gamma_m = \frac{\gamma_w \cdot S}{S + (1 - S) \cdot \frac{u_{ai}}{u_a} + S \cdot h \cdot \frac{u_{ai}}{u_a}}$$

where S = initial degree of saturation and h = volumetric coefficient of solubility.

For the case where the air has not had time to dissolve in the water, the $S \cdot h \cdot u_{ai}/u_a$ term can be omitted. It should be noted that the difference between the air and water pressure never comes into the derivation.

Compressibility of Air-Water Mixtures

Isothermal compressibility is defined as,

$$[12] \quad \beta = \frac{-1}{v} \cdot \frac{dv}{du}$$

where v = specific volume at temperature, t and u = fluid pressure.

The specific volume of air is given by the gas law.

$$[13] \quad v = \frac{R_m \cdot T}{u_a}$$

The specific volume can be differentiated with respect to pressure. Substituting into the compressibility equation [12] shows that the compressibility of air is inversely proportional to the absolute air pressure.

$$[14] \quad \beta_a = \frac{1}{u_a}$$

The compressibility of water can be obtained from the density results previously presented. It also has been directly measured (Dorsey 1940) (Fig. 4).

The compressibility of air-water mixtures is derived using a direct proportioning of the air and water, and in accordance with the compressibility definition.

The total volume, V , is composed of water, V_w , and free air, V_a' . Note that the volume of dissolved air is within the volume of water.

$$[15] \quad \beta_m = - \frac{1}{V_w + V_a'} \cdot \left[\frac{dV_w}{du} + \frac{dV_a'}{du} \right]$$

where u = a reference pressure for the mixture.

Applying the chain rule of differentiation gives,

$$[16] \quad \beta_m = - \frac{1}{V_w + V_a'} \cdot \left[\frac{dV_w}{du} \cdot \frac{du_w}{du} + \frac{dV_a'}{du_a} \cdot \frac{du_a}{du} \right]$$

Either the air or water pressure can be used as a reference pressure. If the water pressure is used as a reference, the following pore pressure parameter can be defined:

$$[17] \quad B_{aw} = \frac{du_a}{du_w}$$

The pore pressure parameter can also be written as the ratio of the B_a and B_w pore pres-

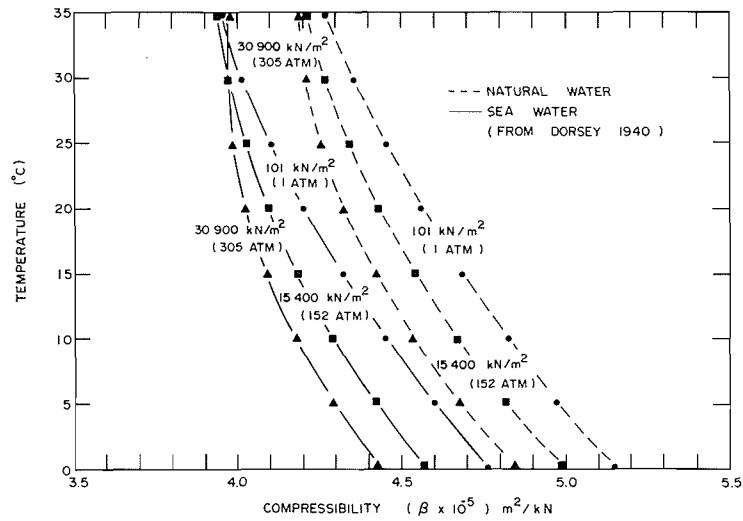


FIG. 4. Isothermal compressibility—saturated and salt water.

sure parameters proposed by Bishop and Henkel (1962)

$$[18] \quad B_{aw} = \frac{B_a}{B_w}$$

The B_{aw} pore pressure parameter should always be less than 1 for undrained loading, becoming equal to 1 at saturation.

At this point, Kelvin's equation could be incorporated; however, it will not assist in solving for the new pore pressure parameter. Differentiating Kelvin's equation gives,

$$[19] \quad \frac{du_a}{du_w} = 2 \cdot T_s \cdot \frac{d(r^{-1})}{du_w} + 1$$

This exercise merely incorporates another unknown variable, the radius of curvature of the air-water meniscus, r .

If the air pressure is used as a reference, another pore pressure parameter can be defined.

$$[20] \quad B_{wa} = \frac{du_w}{du_a}$$

When the air-water mixture is in the absence of a solid, the pore pressure parameters will equal 1. On the other hand, in the presence of a solid, the surface tension effects will result in differing rates of pore air and pore water pressure change. The B_{wa} pore pressure parameter should always be greater than 1 for undrained loading, becoming equal to 1 at saturation.

Using the water pressure, u_w , as a reference,

compressibility [16] becomes,

$$[21] \quad \beta_m = -\frac{1}{V_w + V'_a} \cdot \left[\frac{dV_w}{du_w} + \frac{dV'_a}{du_a} \cdot B_{aw} \right]$$

The compressibility of the free air can be envisaged in terms of applying Boyle's Law to the free air and Henry's Law to a portion going into solution. (A detailed derivation is presented in Appendix B).

$$[22] \quad \frac{dV'_a}{du_a} = \frac{(V_{ai}' + V_d)}{u_a}$$

Substituting into the compressibility [21] and writing the volumes of air and water in terms of initial degree of saturation gives,

$$[23] \quad \beta_m = S \cdot \beta_w + B_{aw} \cdot \frac{(1 - S)}{u_a} + B_{aw} \cdot \frac{S \cdot h}{u_a}$$

The first term in the equation accounts for the compressibility of the water, the second term accounts for Boyle's Law being applied to the free air and the third term accounts for the air driven into solution in accordance with Henry's Law.

Engineering Significance

Figure 5 shows the significance of the variables contributing to compressibility for the case of B_{aw} equal to 1 and the initial air pressure equal to 202.6 kN/m² (i.e. 2 atm). The compressibility due to the solution of air in water is approximately two orders of magni-

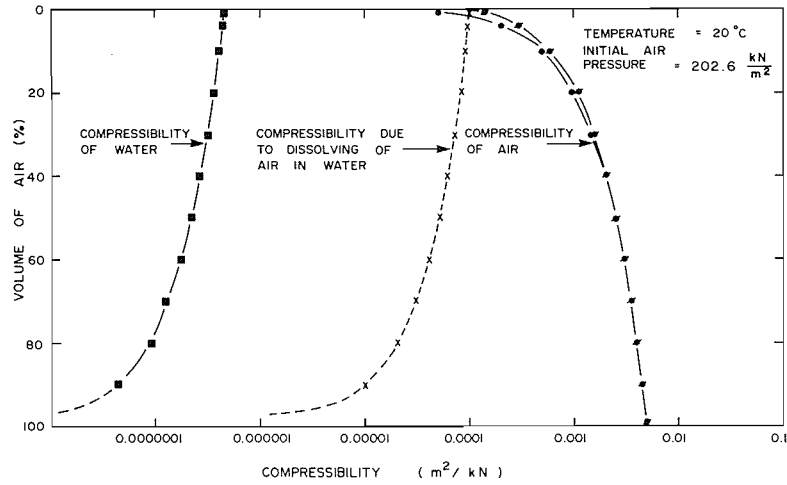


FIG. 5. Components of compressibility of miscible and immiscible air-water mixtures.

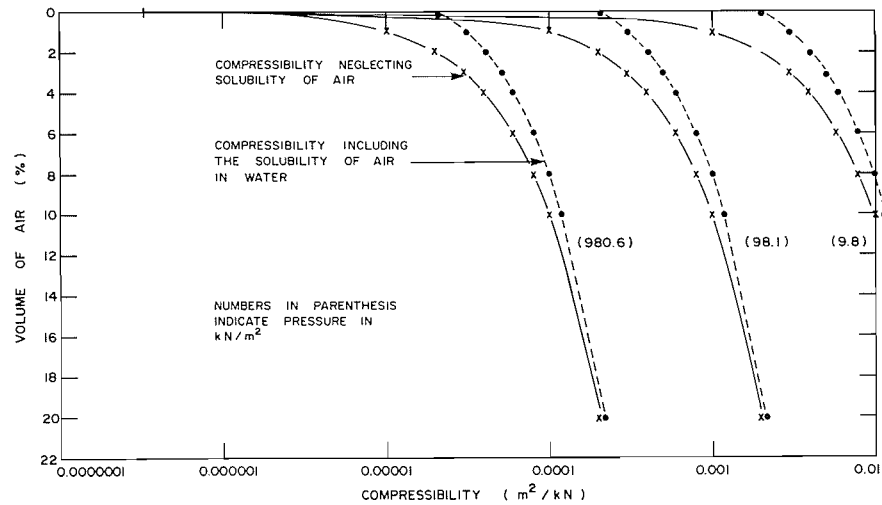


FIG. 6. Effect of solubility of air in water on the compressibility.

tude greater than the compressibility due to the water. The plot also shows that the compressibility of the water is of significance only for the case of a fully saturated soil and that the effect of air dissolving in water becomes significant for air volumes less than approximately 20% of the total void volume. Figure 6 shows an amplification of the effect of air solubility in water for several values of initial air pressure. The effect (at any percentage of air) of the solution of air is the same, (on a logarithmic scale) regardless of the air pressure. The overall compressibility of the mixture does

not have a smooth transition back to that of pure water. Rather, there is a discontinuity at the point where the free air is zero. At this point, there is no air to be driven into solution and the last term must be dropped. Here the compressibility abruptly decreases to that of water. On the other hand, if the air does not have time to go into solution, the transition back to the compressibility of water is smooth.

The dramatic increase in compressibility due to the presence of a small amount of air is of significance in studying the pore pressure reaction of soils (Black and Lee 1973). The pore

pressure parameter, B , depends on the compressibility of the pore fluid (Skempton 1954).

$$[24] \quad B = \frac{1}{1 + \frac{n \cdot \beta_m}{\beta_s}}$$

where n = porosity, β_m = compressibility of the air-water mixture, and β_s = compressibility of the soil structure.

If the soil is completely saturated, the compressibility of the pore fluid is equal to that of pure water (*i.e.* approximately $4.7 \times 10^{-7} \text{ m}^2/\text{kN}$). The inclusion of even 1% air at a pressure of 1 atm, results in a pore fluid compressibility of $3.0 \times 10^{-4} \text{ m}^2/\text{kN}$ or an increase of almost three orders of magnitude. This compressibility approaches that of the soil structure and has a significant effect upon the B parameter.

The density and compressibility characteristics of air-water mixtures are also required when considering the mathematical formulation of transient processes associated with unsaturated soils. They are necessary for the prediction of the initial pore air and pore water pressures when an unsaturated soil is loaded and for the description of the consolidation or swelling processes. The mathematical description of the rate of development of swelling pressure in an unsaturated soil also requires the above formulations. An assumption must generally be made as to whether sufficient time has elapsed to have complete air movement in or out of the water phase.

Conclusions

1. The density equation for an air-water mixture can be written as follows.

$$\gamma_m = \frac{\gamma_w \cdot S}{S + (1 - S) \cdot \frac{u_{ai}}{u_a} + S \cdot h \cdot \frac{u_{ai}}{u_a}}$$

The surface tension membrane has no effect on the above equation.

2. The compressibility equation for an air-water mixture can be written as follows:

$$\beta_m = S \cdot \beta_w + B_{aw} \cdot \frac{(1 - S)}{u_a} + B_{aw} \cdot \frac{S \cdot h}{u_a}$$

The first term accounts for the compressibility of the water, the second term accounts

for the compressibility of the free air and the third term accounts for the amount of air that could go into solution.

3. An experimentally measured pore pressure parameter, B_{aw} or B_{wa} , is recommended to account for surface tension effects. The B_{aw} parameter should be less than 1 for undrained loading, becoming equal to 1 as the air bubbles become occluded.

4. Air volumes in the order of a few percent of the total void volume can increase the compressibility of the pore fluid by several orders of magnitude.

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Appendix A. Air-Water Mixture Anomaly

Consider a sample of unsaturated soil contained in a sealed piston and cylinder arrangement. As the load on the piston is increased (*i.e.* total stress), the free air is compressed in accordance with Boyle's Law (Fig. A1). Under the new increased air pressure, air goes into solution in accordance with Henry's Law. This results in a further decrease in the size of the free air bubbles. At high degrees of saturation, this volume decrease may be a significant percentage of the total volume of free air.

If the radius of curvature is decreasing during the decrease in free air volume, Kelvin's equation would indicate that the difference between the air and water pressures must increase. Since a positive total stress was initially applied, it is logical to assume that the water pressure underwent a positive increase. Therefore, the air phase must have undergone a positive increase. In fact, the air phase must have undergone a larger increase to satisfy

Kelvin's equation. This increase in air pressure (due to the surface tension effect) would result in a further decrease in volume in accordance with Henry's Law. Once again, Kelvin's equation must be satisfied and the air bubble tends faster and faster towards self destruction as the air pressure goes to infinity.

The above description is the result of strictly applying Boyle's Law, Henry's Law, and Kelvin's equation. It certainly does not appear feasible and compatible with observed behavior. The above apparent anomaly is partly overcome by assuming that although the free air volume is decreasing, the radius of curvature is increasing as shown in zone 1 of Fig. A.1. (Fredlund 1973)

However, increased compression of the sample will eventually result in the air bubbles being occluded (zone 2). At this time the self destructing mechanism takes over and Schuurman (1966) proposed a bubble collapse theory to account for this mechanism.

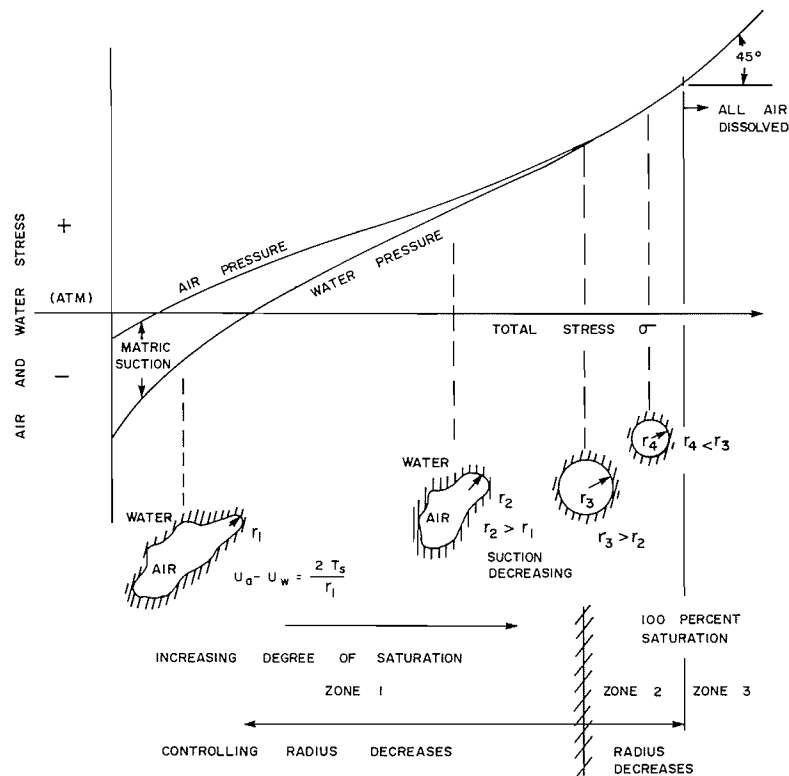


FIG. A1. Pore air and pore water responses to a change in the total pressure for undrained conditions.

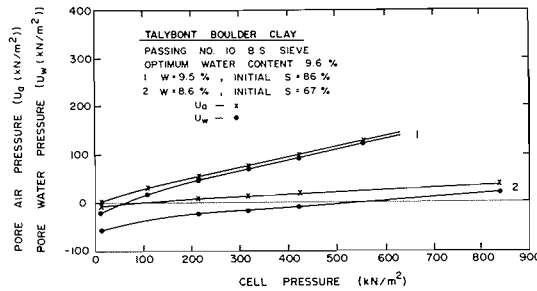


FIG. A2. Air and water pressure changes under undrained loading (from Bishop and Henkel 1962).

Actual measurements of air pressure have been made in samples under undrained compression by Bishop and Henkel (1962) (Fig. A.2). Air pressure measurements are valid only as long as the air phase is continuous or unoccluded. In the continuous zone, they show the air and water pressures tending toward the same value. What happens in the air phase beyond this point (zone 2) is of limited engineering significance since the air bubbles do not affect the soil structure. They merely render the pore fluid compressible.

Since it is impossible to directly apply Kelvin equations and obtain meaningful and reliable results, it is postulated that air and water pressures should be experimentally measured in the continuous air zone (zone 1). In the occluded zone (zone 2) it is recommended that the air and water pressures be assumed equal. Thus, the effect of surface tension is taken into account by methods other than attempting to directly apply Kelvin's equation.

Appendix B. Boyle's and Henry's Laws Applied to Air-Water Mixtures

The piston and porous stone analogy can be used to help visualize the rigorous application of Boyle's and Henry's Laws.

Under the initial pressure conditions, u_{ai} , the volume of free air is V_{ai} , and the dissolved air is V_d . Suppose the imaginary valve between the free air and the porous stone is closed and the pressure on the piston is increased to u_a . Boyle's Law can be applied to the free air and the new volume computed is

$$[B.1] \quad u_{ai} \cdot V_{ai} = V_a \cdot u_a \quad \text{or} \quad V_a = \frac{u_{ai}}{u_a} \cdot V_{ai}$$

If the imaginary valve is now opened, some

air passes into the porous stone, resulting in a further volume decrease. According to Henry's Law, the total weight of air to pass into the porous stone is directly proportional to the applied pressure.

$$[B.2] \quad \frac{w_{di}}{w_d} = \frac{u_{ai}}{u_a} \quad \text{or} \quad w_d = w_{di} \cdot \frac{u_a}{u_{ai}}$$

where w_{di} = the weight of gas dissolved at a pressure, u_{ai} , and w_d = weight of gas that would be dissolved under the new pressure, u_a .

The weight of free air that passes into the porous stone is the difference between the initial and final weights (*i.e.* $dw_d = w_d - w_{di}$). The volume represented by this weight change (under pressure conditions, u_a) can be computed from the gas law.

$$[B.3] \quad \Delta V_d = \frac{dw_d \cdot R \cdot T}{u_a}$$

This additional volume change must be added to the previous volume change in order to obtain the total volume change of the free air.

$$[B.4] \quad V_a = V_{ai} - \Delta V_d$$

Although the weight of gas dissolved is proportional to the pressure, the volume occupied by a gas is inversely proportional to the pressure (*i.e.* Gas Law). In other words, the volume of a gas decreases with increasing pressure, just as rapidly as the weight dissolved increases. Therefore, the volume of gas dissolved in a given volume of liquid is independent of pressure. This can be proven as follows:

$$[B.5] \quad u_{ai} \cdot V_{di} = w_{di} \cdot R \cdot T$$

and

$$[B.6] \quad u_a \cdot V_d = w_d \cdot R \cdot T$$

In addition, Henry's Law states that

$$[B.7] \quad \frac{w_{di}}{w_d} = \frac{u_{ai}}{u_a}$$

From [B.5]

$$[B.8] \quad V_{di} = w_{di} \cdot R_d \cdot T / u_{ai}$$

Substituting [B.7] into [B.6] gives,

$$[B.9] \quad V_d = \frac{w_d \cdot R_d \cdot T}{u_a} = \frac{u_a \cdot w_{di}}{u_{ai}} \cdot \frac{R_d \cdot T}{u_{ai}}$$

or

$$V_d = \frac{w_{di} \cdot R_d \cdot T}{u_{ai}}$$

Therefore

$$V_{di} = V_d$$

Since the volume of dissolved air remains a constant, it is also possible to combine the free and dissolved air, and apply Boyle's Law to the entire volume. To separate the air into its dissolved and free phases at any point, the

volume of dissolved air can be subtracted from the total volume of air.

As additional load is applied to the piston, the free air is compressed and a small portion goes into the porous stone. Eventually, all the air is driven into the porous stone. At this point, no further load can be applied to the air phase since additional load is transmitted directly to the porous stone. Therefore, once the air is driven into solution (the porous stone), the air-water mixture behaves as a fluid with a compressibility equal to that of pure water (porous stone).