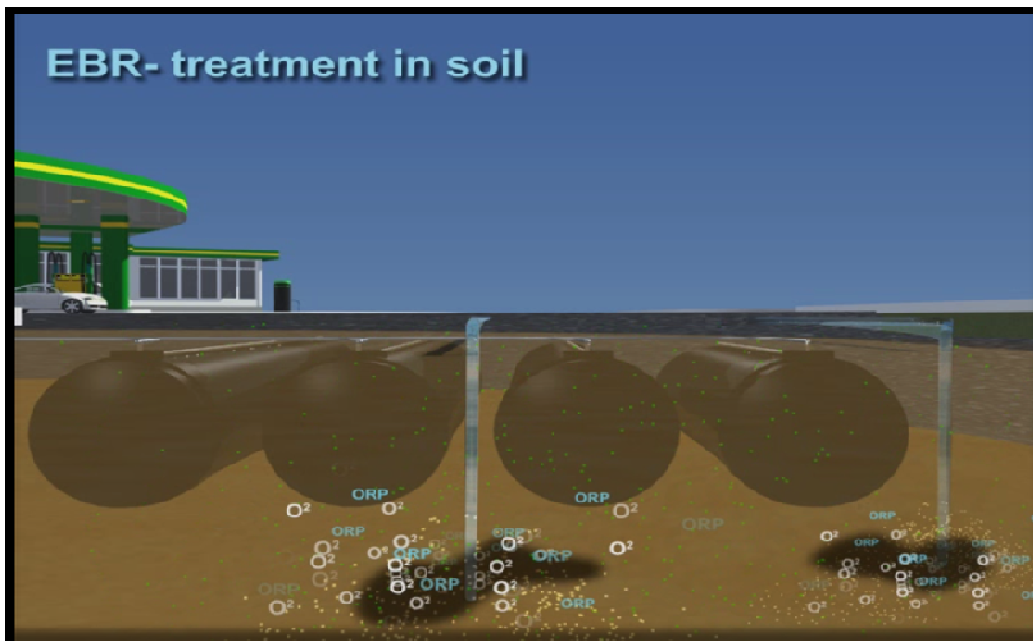


Computation of the dissolution time of dissolved oxygen in the unsaturated zone.

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EBR- (Electro-bioremediation)



The **EBR** system developed by the **E.Elgressy Ltd** Company injected dissolved oxygen (DO) by sparkling in the unsaturated soil. One of the requirements is to compute the time of dissolution of the dissolved oxygen (DO) into the soil or into the water existing in the vadose zone. In this report, we present a computation based on the Henry law that permits to evaluate the time required for dissolution of the DO, after the **EBR** system is stopped.

1. Henry's Law

The amount of air that can be dissolved in water increase with the system pressure and decrease with the temperature.

Deaeration

When fresh water is heated up, air bubbles start to form. The water can obviously not hold the dissolved air with increasing temperature. At 100°C (212°F) water starts to boil - the bubbles are formed by evaporated water or [steam](#). If the water is cooled down at then again reheated, bubbles will not appear until the water starts to boil. The water is [deaerated](#).

Solubility Ratio

The solubility of air in water can be expressed as a solubility ratio:

$$S_a = m_a / m_w \quad (1)$$

where

S_a = solubility ratio

m_a = mass of air (lb_m , kg)

m_w = mass of water (lb_m , kg)

Henry's Law

Solution of air in water follows **Henry's Law** - "the amount of air dissolved in a fluid is proportional with the pressure of the system" - and can be expressed as:

$$c = k_H p_g \quad (2)$$

where

c = solubility of dissolved gas

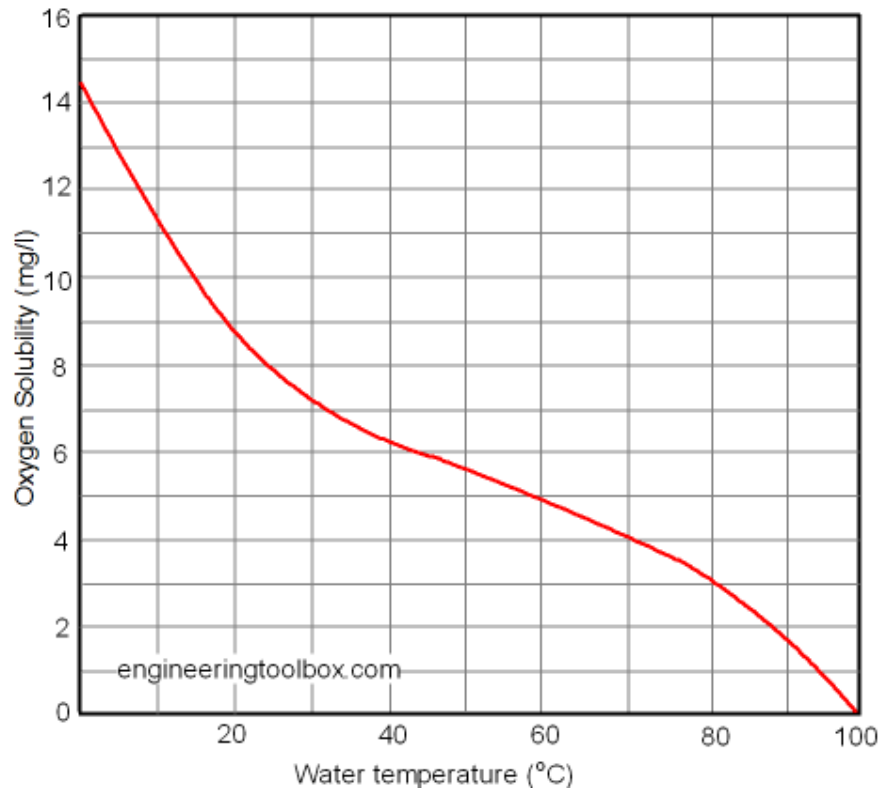
k_H = proportionality constant depending on the nature of the gas and the solvent

p_g = partial pressure of the gas

The solubility of oxygen in water is higher than the solubility of nitrogen. Air dissolved in water contains approximately 35.6% oxygen compared to 21% in [air](#).

Dissolved Air in Water (25°C)						
Gauge Pressure (atm)	0	1	2	3	4	5
Dissolved Air (g/kg)	0.023	0.045	0.068	0.091	0.114	0.136

Dissolved Oxygen in Fresh Water



2. THE MODEL BASIS

2.1 The ideal gas and Henry's laws

The ideal gas and Henry's laws are expressed by the following equations:

$$U_g V_g = nRT \quad \text{Ideal gas law} \quad [1]$$

$$U_g = Hx \quad \text{Henry's law} \quad [2]$$

In these equations, U_g = absolute pressure, V_g = volume, T = absolute temperature, n = number of moles, R = universal gas constant, x = mole fraction of the dissolved gas in a liquid and H = Henry's constant. An ideal or perfect gas is a gas that obeys the perfect gas law. For an isothermal process, the perfect gas law reduces to the Boyle's law, i.e. $U_g V_g = \text{CONSTANT}$.

Mass of the dissolved air in water is obtained from the Henry's law. The mole fraction of the dissolved air in water, x , is expressed by:

$$x = \frac{\frac{M_{da}}{m_a}}{\frac{M_{da}}{m_a} + \frac{M_w}{m_w}} \quad [7]$$

In this equation M_{da} = mass of the dissolved air in water at equilibrium conditions and m_w = molecular mass of water. Other symbols in Equation 7 have already been introduced. Eliminating x from Equations 2 and 7 results in a suitable form of the Henry's law (Equation 8), which will be used in the proposed constitutive formulation.

$$M_{da} = \frac{M_w m_a U_a}{m_w (H - U_a)} \quad [8]$$

2.2 Conservation of Mass

A constitutive formulation for partially saturated soils, which accounts for variation of the degree of saturation due to changes in the pore fluid pressure, should, in principle, comply with the law of conservation of mass. In fact, the air in a partially saturated soil can exist either in free gas or as dissolved in water. According to the law of conservation of mass, the total mass of the gas phase, i.e. sum of the free and dissolved gas should remain constant and not depend upon the variation of the pore fluid pressure. It is very important to note the Henry's law is valid only for an equilibrium condition in which under a constant pressure no further mass of gas is exchanged between the gas and water phases in the mixture. This can be true for long term loading conditions such as static and slow monotonic loads, where there is sufficient time for the dissolvable mass of the free gas to be dissolved in the water phase.

Consider a soil element subjected to a pore fluid pressure change from u_0 to u after that the **EBR** system is stopped. This results in a change in the soil degree of saturation from its initial value, i.e. s_0 to a final value, s . The law of the conservation of mass implies that the difference in the mass of the free gas at initial and final states is equal to the mass of gas that dissolved in water. Using Equation 6 and 8, mathematically, this law can be expressed as Equation 16 or Equation 17:

$$\frac{m_a M_w U_0 (1 - S_0)}{\rho_w R T S_0} - \frac{m_a M_w U (1 - S)}{\rho_w R T S}$$

$$= m_d^* \left(\frac{M_w m_a U}{m_w (H - U)} - \frac{M_w m_a U_0}{m_w (H - U_0)} \right) \quad [16]$$

Or,

$$\frac{m_a M_w U_0 (1 - S_0)}{\rho_w R T S_0} - \frac{m_a M_w U (1 - S)}{\rho_w R T S}$$

$$= m_t^* \frac{m_a M_w U_0 (1 - S_0)}{\rho_w R T S_0} \quad [17]$$

In the above equations, the difference in the mass of the free gas at the initial and final states due to a pressure change from U_0 to U (right hand sides of equations 16 and 17), is written either in terms of a mass fraction of the total dissolvable gas at the corresponding equilibrium condition, i.e., m_d^* in Equation 16, or a mass fraction of the total initial gas, m_t^* in Equation 17. Simplifying Equations 16 and 17 results in Equations 18 and 19, respectively, which express changes in the soil degree of saturation as a function of absolute pressure.

$$S = \frac{U}{\left\{ \frac{1 - S_0}{S_0} U_0 + U - \frac{m_d^* \rho_w R T H (U - U_0)}{m_w (H - U) (H - U_0)} \right\}} \quad [18]$$

Or,

$$S = \frac{U}{\left\{ (1 - m_t^*) \frac{1 - S_0}{S_0} U_0 + U \right\}} \quad [19]$$

Equation 18 is used to obtain the lower and upper limits of the soil degree of saturation. Conditions $m_d^* = 0$ and $m_d^* = 1$ refer to the lower and upper bounds of the soil degree of saturation, expressed by Equations 20 and 21, respectively.

$$s = \frac{U}{\left\{ \frac{1-s_0}{s_0} U_0 + U \right\}} \quad [20]$$

$$s = \frac{U}{\left\{ \frac{1-s_0}{s_0} U_0 + U - \frac{\rho_w RTH(U-U_0)}{m_w(H-U)(H-U_0)} \right\}} \quad [21]$$

Under certain conditions, due to the application of a pore fluid pressure change, the entire mass of the gas phase can be dissolved in water. In this case, the soil element is fully saturated. The absolute pressure at which the soil element becomes saturated is called saturation pressure and is shown as U_{sat} . This pressure is obtained from Equation 21 by substituting $s = 1$. This results in the following expression:

$$U_{sat} = \frac{\left\{ \frac{1-s_0}{s_0} U_0 m_w H(H-U_0) + \rho_w RTH U_0 \right\}}{\left\{ \frac{1-s_0}{s_0} U_0 m_w (H-U_0) + \rho_w RTH \right\}} \quad [22]$$

It is readily noted from Equation 22 that for an initially saturated soil ($s_0 = 1$) U_{sat} is equal to U_0 .

Also, another important relationship, which will be used later to discuss the limitations of the model, is the relationship between m_d^* and m_t^* . Comparing Equations 18 and 19, the desired relationship between m_d^* and m_t^* is as follows.

$$m_d^* = \frac{m_w U_0 (1-s_0)(H-U)(H-U_0)}{s_0 \rho_w RTH(U-U_0)} m_t^* \quad [23]$$

2.3 TRANSIENT AIR DISSOLUTION

In Equation 19 (or 18), it is required to know the value of the transient mass fraction of the dissolved gas, m_t^* (or m_d^*). This requires that an analogy be considered for the mechanism of air dissolution in water. Since in soils with high degrees of saturation, the air phase exists as

discrete bubbles, the proposed analogy includes a single spherical air bubble and its surrounding water as shown in Figure 1. As stated in the previous section, the dissolution phenomenon is explained by the diffusion equation. However, since the radius of the air bubble in this analogy varies with respect to time, the corresponding diffusion equation is a moving boundary type Partial Differential Equation (PDE). Based on the Fick's diffusion law (Crank 1975), the PDE related to the dissolution of air in water in spherical coordinates with radial symmetry is written in the form of Equation 24. The boundary and initial conditions of Equation 24, considered within the period between two successive time steps, are expressed by Equations 25 to 27. The function $C(r, t)$ represents concentration of the dissolved air in water (i.e., mass of the dissolved air per unit volume of water), and D is the coefficient of diffusion. Also, $C_s(t)$ = concentration at the interface between air and water at $r = a$, and $C_{i-1}(r)$ = concentration at the beginning of the time step.

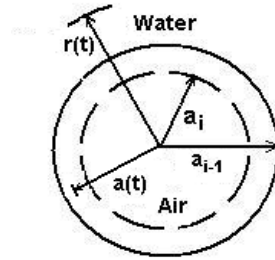


Figure 1. An analogy used to compute the transient mass fraction of the dissolved air in water.

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad 0 < t < \Delta t \quad [24]$$

$$C(a, t) = C_s(t) \quad t > 0 \quad [25]$$

$$C(\infty, t) = C_\infty \quad t > 0 \quad [26]$$

$$C(r, 0) = C_{i-1}(r) \quad r \geq a_{i-1} \quad [27]$$

The boundary condition expressed by Equation 26 is arbitrary and as it can be seen later, it does not affect the results for computing the transient dissolved gas mass fraction. For this type of diffusion problems the following change of variable is considered (Crank 1975):

$$z = \frac{r}{\sqrt{Dt}} \quad t > 0 \quad [28]$$

Using Equation 28 results in the following form for the diffusion equation (Crank 1975):

$$\frac{\partial^2 C}{\partial z^2} = -\left(\frac{z}{2} + \frac{2}{z}\right) \frac{\partial C}{\partial z} \quad [29]$$

Equation 29 is a first order Ordinary Differential Equation (ODE) in terms of $\frac{\partial C}{\partial z}$. The solution of Equation 29 is:

$$\frac{\partial C}{\partial z} = B z^{-2} \exp\left(\frac{-z^2}{4}\right) \quad [30]$$

The coefficient **B** is the integration constant of the ODE and can be obtained from boundary conditions.

At the interface of air and water, $r = a$, equilibrium condition is satisfied and concentration is:

$$C_s = \frac{M_{da}}{V_w} \quad [31]$$

Substituting Equation 8 in 31 results in:

$$C_s = \frac{\rho_w m_a U}{m_w (H - U)} \quad [32]$$

Also, from Equation 28:

$$\frac{\partial C}{\partial t} = \frac{\partial C - z}{\partial z 2t} \quad [33]$$

Substitution Equations 28 and 30 in 33 gives:

$$\frac{\partial C}{\partial t} = \frac{-B \sqrt{Dt}}{2rt} \exp\left(\frac{-r^2}{4Dt}\right) \quad [34]$$

At the interface of air and water, the following condition exists:

$$\left(\frac{\partial C}{\partial t}\right)_{r=a} = \frac{dC_s}{dt} \quad [35]$$

From Equation 32:

$$\frac{dC_s}{dt} = \frac{m_a \rho_w H}{m_w (H - U)^2} \frac{dU}{dt} \quad [36]$$

Therefore, from Equations 34, 35 and 36, the integration constant, **B**, is expressed in the following form:

$$B = \frac{Hm_a \rho_w (-2at)}{m_w (H-U)^2 \sqrt{Dt} \exp\left(\frac{-a^2}{4Dt}\right)} \frac{dU}{dt} \quad [40]$$

Using the Fick's law, the mass flow rate of the gas passing through the interface area, **A**, is obtained by the following Equation (see Fredlund and Rahardjo 1993):

$$\frac{dM_{da}}{dt} = -DA \left(\frac{\partial C}{\partial r}\right)_{r=a} \quad [41]$$

In Equation 41, **A** = $4\pi a^2$ is the surface of air bubble. Also, from 28:

$$\left(\frac{\partial C}{\partial r}\right)_{r=a} = \left(\frac{\partial C}{\partial z} \frac{1}{\sqrt{Dt}}\right)_{r=a} \quad [42]$$

Expanding Equation 42 based on Equations 28, 30 and 40 and substituting the resultant equation in 41 will result in the following relationship for the transient (time) mass rate of air, dissolved in water.

$$\frac{dM_{da}}{dt} = \frac{8\pi DHm_a \rho_w t a}{m_w (H-U)^2} \frac{dU}{dt} \quad [43]$$

Also, $\underline{M_{da}}$ is a fraction of the initial air mass M_0 , which can be written in terms of the initial absolute pressure and volume of the air bubble, i.e. U_0 and V_0 (see Equation 4). Therefore:

$$M_{da} = m_t^* M_0 = m_t^* m_a \frac{U_0 V_0}{RT} \quad [44]$$

$$V_0 = 4\pi a_0^3 / 3 \quad [45]$$

$$\frac{dM_{da}}{dt} = \frac{4\pi a_0^3 / 3 U_0 m_a}{RT} \frac{dm_t^*}{dt} \quad [46]$$

Moreover, at any time m_t^* as a fraction of the initial air mass can be written in the following form:

$$m_t^* = \frac{\frac{m_a U_0 V_0}{RT} - \frac{m_a U V_a}{RT}}{\frac{m_a U_0 V_0}{RT}} = 1 - \frac{U V_a}{U_0 V_0} \quad [47]$$

Since $V_a = 4 \pi a^3 / 3$, m_t^* will be:

$$m_t^* = 1 - \frac{U a^3}{U_0 a_0^3} \quad [48]$$

From Equation 48, the radius of air bubble is:

$$a = \sqrt[3]{\frac{(1 - m_t^*) U_0}{U}} a_0 \quad [49]$$

In general, U can be written as a piecewise linear function of time as shown in Figure 2.

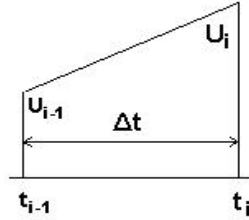


Figure 2. Absolute pressure, U , as a piecewise linear function of time.

Therefore:

$$U = \alpha_i t + U_{i-1} \quad [50]$$

Or:

$$t = \frac{U - U_{i-1}}{\alpha_i} \quad [51]$$

$$\alpha_i = \frac{U_i - U_{i-1}}{t_i - t_{i-1}} \quad [52]$$

Substituting Equations 49 and 51 in Equation 43 and comparing this equation with Equation 46 results in the following separable ODE for m_t^* :

$$\frac{dm_t^*}{\sqrt[3]{1-m_t^*}} = \frac{6RTDH\rho_w}{a_0^2 U_0^{2/3} m_w \alpha_i} \frac{(U-U_{i-1})}{\sqrt[3]{U}(H-U)^2} dU \quad [53]$$

The Henry's constant, H , is a very large number ($H=55000$ atm at a temperature of 10°C) and $H-U \approx H$. Therefore, Equation 53 becomes:

$$\frac{dm_t^*}{\sqrt[3]{1-m_t^*}} = \frac{6RTD\rho_w}{a_0^2 U_0^{2/3} m_w H \alpha_i} \frac{(U-U_{i-1})}{\sqrt[3]{U}} dU \quad [54]$$

Integration of Equation 54 within the period between two successive time steps, i.e. from $m_{t_{i-1}}^*$ to $m_{t_i}^*$ and from U_{i-1} to U_i on both sides of Equation 54, respectively, will result in the following expression for m_t^* in terms of U .

$$1 - m_{t_i}^* = \quad [55]$$

$$\left\{ (1 - m_{t_{i-1}}^*)^{2/3} - \frac{Q}{\alpha_i} \left[\frac{(U_i^{5/3} - U_{i-1}^{5/3})}{5} - \frac{U_{i-1}(U_i^{2/3} - U_{i-1}^{2/3})}{2} \right] \right\}^{3/2}$$

3. MODEL CONSTANTS AND PARAMETERS

3.1. Model constants

Independent constants: Independent constants in the proposed constitutive formulation are those, whose values do not change due to a change in temperature. Values of these constants can be found in many references such as Perry and Green (1997). Independent constants, considered in the model are:

Universal gas constant: $R = 8314.472 \text{ J/kmol.K}$

Molecular mass of water: $m_w = 18.0153 \text{ kg/kmol}$

Dependent constants: The proposed formulation is valid for an isothermal process. Some factors like the Henry's constant are dependent upon the temperature. These factors are considered as the dependent

constants of the model. For example, at a temperature of 10°C , these constants are listed below:(See Perry and Green 1997)

Henry's constant: $H = 5.5 \times 10^9 \text{ Pa}$

Coefficient of diffusion: $D = 2.2 \times 10^{-9} \text{ m}^2/\text{S}$

3.2 Model Parameters

The introduced model, in principle, has three parameters: initial degree of saturation, S_0 , absolute temperature, τ , and initial radius of a representative air bubble, a_0 .

Temperature and initial degree of saturation are measurable parameters. However, initial radius of the representative air bubble should be selected in such a way that represents the effects of the air dissolution phenomenon on the compressibility of the pore fluid. The smaller the initial air bubble radius is selected, the higher rate of air dissolution will be. This is due to the fact that for the same volume of air in the soil, assuming smaller air bubbles radii results in a higher total interface surface between the air and water phases, and consequently, this increases the rate of air dissolution in water.

In fact, the initial volume of air in soil, V_0 , should be proportional to the initial volume of the representative air bubble $\frac{4}{3}\pi a_0^3$ or simply a_0^3 . Also, V_0 is related to the volume of water, V_w , assumed to be constant:

$$V_0 = \frac{1-S_0}{S_0} V_w \quad [57]$$

Therefore, a_0^3 is proportional to $\frac{1-S_0}{S_0}$. This results in the following expression for the initial radius of the representative air bubble:

$$a_0 = \lambda \sqrt[3]{\frac{1-S_0}{S_0}} \quad [58]$$

Parameter λ is the coefficient of proportionality of Equation 58. The greater values of λ results in a smaller total interface area between air and

water phases and consequently, lower dissolution rate. In fact, λ can be considered as an adjusting parameter and provides the model with a desired versatility to match with any experimental data.

4.

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