

THE THERMODYNAMIC BUBBLE PROBLEM AND ITS RELEVANCE FOR IN-SITU THERMAL REMEDIATION

Bruce C. W. McGee (McMillan-McGee Corp., Calgary, Canada)
Huaxiong Huang (York University, Toronto, Canada)
Rex Westbrook (University of Calgary, Calgary, Canada)
Sean Bohun (Penn State University, Pennsylvania, USA)

ABSTRACT: This paper presents the thermodynamic bubble problem and its relevance for successful design of an in-situ thermal remedy of DNAPL in the water saturated zone. This investigation is relevant to the mass transfer of chemicals that have been volatilized as a result of an in-situ thermal remediation process. The volatilized chemicals exist as numerous entrained bubbles in the water phase within the porosity of the saturated soil. A pressure gradient is created in the soil by the operation of extraction and injection wells. The pressure gradient is towards the extraction wells which operate at a much lower pressure than the initial pressure of the aquifer and the injection wells. This gradient forces the water and entrained bubbles to flow in a horizontal direction towards the extraction wells for recovery of the chemicals from the soil.

In addition to the pressure gradient, a vertical upward force acts on the entrained bubbles. This force is a direct result of the density difference between the water and gas phase and is referred to as the buoyancy force. Consequently, as the entrained bubbles are moving in a horizontal direction towards the extraction wells, they are also moving vertically. If the bubble is not extracted from the soil rapidly it could rise into cooler regions and condense into a liquid phase. This results in a vertical migration of the chemicals and is detrimental to the efficiency of the in-situ thermal remediation process. The thermodynamically aggravated vertical migration of contaminants has been observed in the field. Data from the Turtle Bayou Superfund site provides evidence of the vertical migration of DNAPL.

The design of the extraction system becomes critical to the success of an in-situ thermal remediation process. The distance between extraction and injection wells, the layout of wells, and the rate of extraction are critical design considerations for the prevention of vertical migration of the bubbles. We have derived a simple mathematical model that is based on the physics of a thermodynamically created bubble in porous media. The model tracks the flow path of the bubbles in the soil as a function of temperature and pressure, the distance between wells, and extraction rate. The model can be used by the engineer to optimize the design of an extraction system while accounting for geology and chemical composition of the DNAPL.

INTRODUCTION

Objective: The objective of this paper is to:

1. Introduce in-situ thermal remediation and the mechanism associated with the removal of volatilized chemicals from contaminated soils, in particular low permeability soils,
2. Develop a simple numerical model that can be used to estimate the mass recovery of volatilized chemicals that exist as gas bubbles in the porosity of the soil.
3. Present a case study that uses the model to assist in the design of the extraction system for an in-situ thermal remediation project that uses the Electro-Thermal Dynamic Stripping, (ET-DSP™) technology.

Introduction to the Problem: This investigation is relevant to the mass transfer of chemicals that have been volatilized as a result of an electro-thermal process installed in a low permeability soil. The transfer of heat in the soil by electro-thermal energy does not depend on permeability; however the effectiveness of removing chemical mass from the soil is determined by the flow properties of the flowing phases and the permeability of the soil. The physical process of mass removal in soils such as clays needs to be achieved to complete the in-situ thermal remediation process. It is one thing to heat the soil, yet it is still another to remove the chemical mass and thus remediate it.

In this problem it is assumed that the soil is heated using an electro-thermal process such as Six Phase Heating, SPH™ (Heath, 1992) or the Electro-Thermal Dynamic Stripping Process, ET-DSP™ (McGee, 2001), as shown in Figure 1.

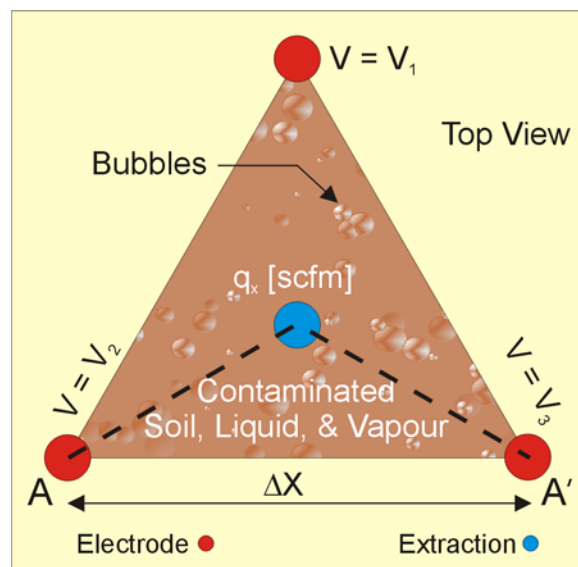


FIGURE 1. Top view configuration of three electrodes and an extraction well of a typical electro-thermal process. The treatment volume is defined by the triangular area and the thickness of the treatment volume. The extraction well is located in the center of the triangle and extends throughout the treatment volume. The treatment and heated volume are approximately the same (see Figure 2).

With reference to Figure 2, electrical energy is introduced to the treatment volume using a multitude of finite length cylindrical electrodes. Current is forced to flow through

the soil by the voltage differentials at the electrodes. The soil is resistive and thus heat is created by an electro-thermal conversion of energy in accordance with ohm's law. The power density distribution is determined by the current flowing between the electrodes. The current is a function of the electrical conductivity of the soil and is independent of its permeability and rheological properties of the fluids.

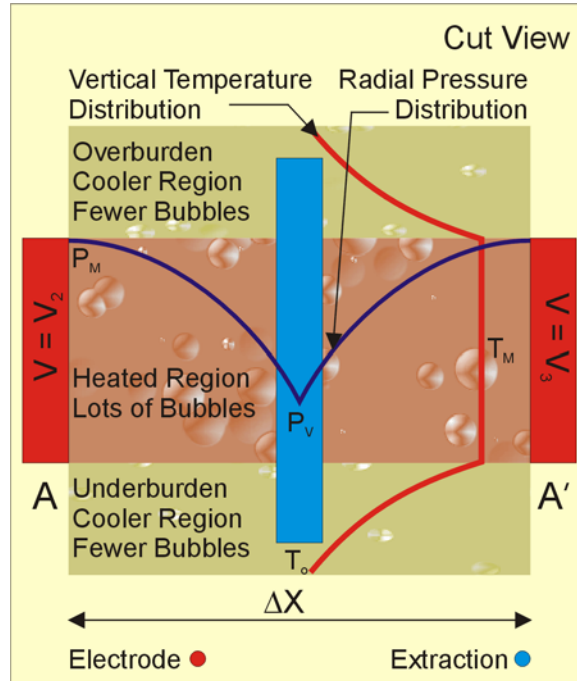


FIGURE 2. Cut view A-A' through two electrodes and the extraction well. Current is forced to flow between the electrodes. The heated volume is defined by the triangular area shown in Figure 1 and the height of the electrodes.

The thermodynamic properties of the chemicals are a function of temperature and pressure. As the soil heats up heated contaminated liquids and vapors are produced at the extraction well. The rate of energy removed from the soil is less than the electrical energy injected so that during extraction the soil will increase in temperature up to some maximum value. This temperature is at the thermodynamic phase boundary for the combined water and chemicals filling the porosity of the soil. The steady state maximum temperature profile is shown in Figure 2 and extends through the heated volume. Outside of the heated volume the temperature decreases at the rate of the heat losses.

A pressure gradient is established in the treatment volume by the difference between the vacuum applied at the extraction well and the ambient pressure of the soil. This gradient forces liquids and entrained bubbles to flow in a horizontal direction towards the extraction wells. The magnitude of the vacuum at the extraction well is a function of permeability and rheological properties of the fluids at the temperature of the soil. Generally, the pressure gradient away from the extraction well is logarithmic. The combination of reduced pressure and increased temperature creates an environment whereby volatile chemicals once in the liquid phase become vaporized.

At initial conditions the pressure and temperature in the soil are at ambient conditions (P_o and T_o respectively). Initially only a liquid phase consisting of water, a

dissolved chemical phase, and possibly a free chemical phase are in the soil. As the temperature increases and the pressure decreases the chemicals transition out of the water and exist in the soil as a vapor, but only to the limited extent of several bubbles of some calculated volume. Since the concentration of chemicals in the soil is small relative to the water, it can be assumed that a continuous gas phase will not occur. This may not be the case where gas is injected into the soil or large amounts of chemicals are present.

The vapour-equilibrium curve for a pure chemical (TCE for example) is shown in Figure 3. Only liquid exists at a temperature and pressure condition above the equilibrium boundary and a bubble phase below it. The volatilized chemicals exist as numerous entrained bubbles in the water phase within the porosity of the saturated soil.

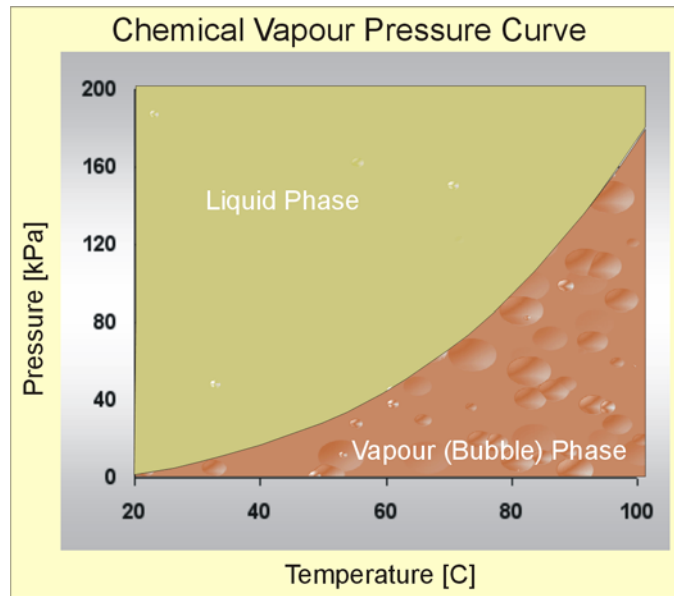


FIGURE 3. The transition from the liquid phase to the vapor phase is assumed to be by the creation of bubbles in the porosity of the soil and occurs along the phase boundary determined by the thermodynamic properties of the chemical (hence the thermodynamic bubble effect).

Given the temperature and pressure in the soil it is possible to approximate where the bubbles will exist. Figure 4 shows a bubble in the porosity of the soil created at conditions below the equilibrium curve (Figure 3). There is a pressure gradient in the soil created by the extraction well of finite length. This imposes a horizontal force on the bubble towards the extraction well. The other force acting on the bubble is buoyancy, which is a function of temperature, acting in the vertical direction. At this time an equation needs to be derived to determine the momentum or flow path of the bubble in the porous media as it moves about the pressure and temperature distribution through the chaotic path of pore throats. The extraction objective is to capture the bubble at the extraction well before it rises vertically and escapes from the heated volume and possibly re-condenses on cooler surfaces. If this occurs it becomes difficult or impossible to remove the chemical from the soil. *The effectiveness of an in-situ thermal remediation process is based upon the ability to extract the bubbles from the heated volume.*

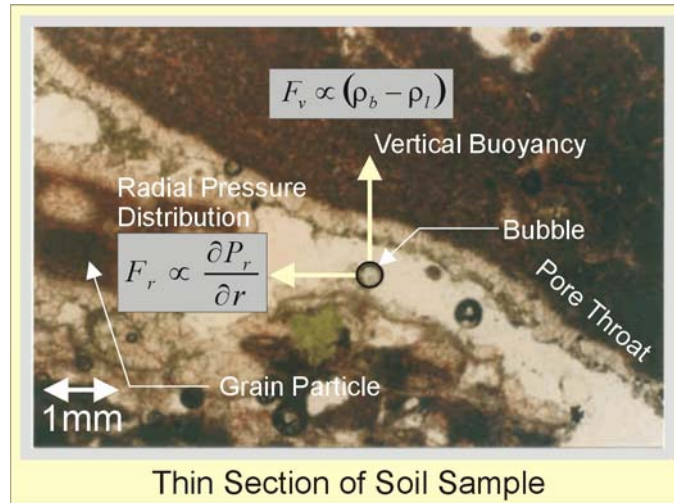


FIGURE 4. The horizontal force created by pressure gradients and vertical force due to buoyancy acting on the bubble in the pore space.

The objective of in-situ thermal remediation is to determine the necessary extraction rate so that the chemical bubble is removed before it rises above the heated volume and condenses into a liquid. Given the micro-porosity and low permeability of clays it is difficult to imagine a condition of liquid or vapour mobility in the soil under even extreme vacuum pressures at the extraction well. Figure 5 shows a sample of clay that was removed from 8 meters (25 feet) below ground surface after just 60 days of ET-DSP™ operations. Initially the clay was impermeable as evidenced by the operating conditions at the extraction well (high vacuum - low flow rate). As electro-thermal energy was established in the clay, a dramatic reduction in vacuum pressure and associated increase in extraction rate was observed. Close inspection of Figure 5 show that the geomechanical properties of the clay have been thermally altered. Forces associated with differential thermal expansion and pressure release at steam temperatures created micro-fractures in the clay. Large vugular porosity due to steam release interconnected with striated micro-fractures has resulted in a very permeable soil type.



FIGURE 5. The porosity created in a clay soil as a result of micro-fracturing (the cross bedded striations and large holes from steam pressure)..

MATHEMATICAL MODEL

A mathematical model based on the problem description in the previous section is now developed. The main component in the system is water and water vapor and therefore the problem will be treated as a one-component system with two phases: liquid and vapor. Secondly, we assume that the vapor bubble generated by the heating moves in the horizontal direction with the liquid phase. Thus a single-phase model can be used for the horizontal velocity component. Furthermore, the mass exchange happens mainly in the radial \mathbf{r} direction due to an applied vacuum at the extraction. Therefore, conservation of mass will be applied to the horizontal velocity component only. In the vertical \mathbf{z} direction the bulk of the liquid phase is at rest, except the part displaced by vapor due to buoyancy force. The \mathbf{r} -component of the velocity is determined by Darcy's law;

$$u = -\frac{k}{\mu} \frac{\partial P}{\partial r}$$

Where k and μ are permeability and viscosity. The conservation of mass, assuming most of the mass flows in the radial direction (only bubbles rise) is given by;

$$\frac{\partial \rho_f}{\partial t} + \frac{1}{r} \frac{\partial (r \rho_f u)}{\partial r} = 0, \quad \rho_f = \alpha \rho_l + (1 - \alpha) \rho_v, \quad \rho_f u = \alpha \rho_l u_l + (1 - \alpha) \rho_v u_v$$

The mixture density is ρ_f and \mathbf{r} -velocity u is defined as in the above equation. The subscripts v and l are for vapor and liquid respectively and α is the liquid volume fraction. The temperature of the soil, liquid and vapor mixture is determined by the energy conservation law;

$$\rho c \frac{\partial T}{\partial t} + \rho_f c_f u \frac{\partial T}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left(\kappa r \frac{\partial T}{\partial r} \right) + \sigma |E|^2 - LM$$

Where $\sigma |E|^2$ is the electro-thermal heating of the soil with an electrical conductivity σ and electric field \mathbf{E} . The term LM represents the heat lost in the formation of the bubbles with L is the latent heat of vaporization of the fluid and M the mass rate of vaporization. The soil fluid mixture is characterized by a heat capacity ρc and thermal conductivity κ . Note that we have assumed that there is no temperature variation in the vertical \mathbf{z} direction since heat capacity of the bubbles is relatively small.

The conservation of mass and energy are coupled though the velocity term \mathbf{u} , which is calculated using Darcy's Law. The density distribution is coupled by the term α which is the volume fraction of the components in the vapor phase. The transfer of mass from the liquid to the vapor phase (temperature and pressure dependent) is calculated using K-values based on Antoine Vapor Pressure Correlation for ideal mixtures and Dalton's law of partial pressures;

$$K = \frac{y}{x} = \frac{VP}{p}, \quad \ln(VP) = 10 \left(-A + \frac{B}{T+c} \right)$$

Where y is the molar concentration of the component in the liquid phase and x is the molar concentration of the component in the vapor phase. Now that the radial

components of mass and energy transfer are accounted for and from which the mass transport to the vapor or bubble phase can be calculated, the vertical rise rate of the bubbles must now be determined. We use the motion of a long gas bubble inside a small channel to describe the relative vapor rising velocity in the vertical z direction due to buoyancy force. This problem was first investigated by Taylor (Liao, 2003) and studied subsequently by many researchers as a model to gain insights into slug multi-phase flows (in oil and gas recovery). Experimental investigations in micro non-circular channels have shown that the elongation bubbles always rise to a terminal velocity. This is as a function of the effective diameter and is given in a non-dimensional form as

$$C_a = c_1 Eo^{d_1} + c_2 Eo^{d_2}, \quad v_b = \frac{\gamma}{d} C_a$$

Where C_a is the capillary number, v_b is the vertical terminal velocity, γ is the surface tension of water, d is the mean pore throat diameter, Eo is the Eötvös number and c_i and d_i are fit using numerical results (please see Liao, 2003 for more detail). For a square, $c_1 = 6.7 \times 10^{-5}$, $c_2 = 2.3 \times 10^{-5}$, $d_1 = 1.03$, $d_2 = 2.61$. It is assumed that the bubbles reach terminal velocity rapidly in comparison to the duration of remedial operations. Assuming that the buoyancy force is proportional to the density difference between the liquid and vapor phase, then it can be treated as a pressure gradient. The vertical flow velocity, v_v , based on soil properties is thus;

$$v_v = \tau \phi(1-\alpha)v_b = \tau \frac{\phi(1-\alpha)\gamma}{d} (c_1 Eo^{d_1} + c_2 Eo^{d_2})$$

Where, τ , the tortuosity factor is related to the permeability of the soil. For convenience we define;

$$v_v = \tau F \frac{\Delta\rho g d^2}{3\mu_l}, \quad F = \frac{3\phi(1-\alpha)\gamma\mu_l}{\Delta\rho g d^3} (c_1 Eo^{d_1} + c_2 Eo^{d_2})$$

The transport of the chemicals now needs to be determined. Let x and y be the concentration of the chemicals in the vapor and liquid phase. The total amount of contaminant is conserved and satisfies

$$\frac{\partial}{\partial t}(x+y) + \nabla \cdot (\bar{u}_v x + \bar{u}_l y) = 0$$

Using $K=y/x$ from Antoine's equation and substituting K into this equation and using the Method of Characteristics results in the following curve of solutions,

$$\frac{dr}{dz} = \frac{u_v + Ku_l}{v_v + Kv_l}$$

From the flow and temperature model we have.

$$u_l = u_v = -\frac{q}{2\pi r H}, \quad v_l = 0, \quad v_v = \tau F \frac{\Delta\rho g d^2}{3\mu_l}$$

Assume that the height h has been heated up by the electrodes and is the minimum distance that bubble must travel ($h < H$), then the characteristic which starts from $z=0$ and the boundary r is

$$z = \frac{2\pi H v_v}{q} \int_{r_w}^r \frac{r}{1+K} dr$$

Let $z_e = z(r_e)$, the height of the characteristic when it reaches the extraction well $r=r_e$. The condition for all the contaminant being extracted is then simply $z_e < h$, or

$$q \geq \frac{\pi \tau F H \Delta \rho g d^2}{3 \mu_l h (1+K)} (r_e^2 - r_w^2)$$

The above equation is our final result. It simply states that to ensure capture of the bubble from the heated zone we must produce at a rate q at the extraction well. The following case study will be useful in clarifying the utility of this equation.

CASE STUDY

The example problem demonstrates the use of the model as an engineering design tool. This example problem is shown in Figure 1 with the electrodes spaced 10 meters apart. Based on this geometry the design engineer must estimate the minimum liquid extraction rate to ensure that all the bubbles are captured at the extraction well before they rise out of the heated volume. The following table summarizes the calculations.

Parameter	Data	Units	Comments
Operating Temperature	100.00	[C]	
Target Thickness	5.00	[m]	
Minimum Thickness	1.00	[m]	Minimum flow path for bubble
Electrode Spacing	10.00	[m]	
Distance to Extraction Well	4.33	[m]	In Center of Electrode Triangle
Water Viscosity	1.00	[cp]	
Surface Tension of Water	71.70	[dyne/cm]	
Density of Water	1.00	[gm/cc]	
Mean Pore Throat Diameter	0.10	[mm]	Post heating
Eo	0.001370	□	Eovtos number
Ca	0.075190	[u m ² s/kg]	Capillary number
F	0.000160	□	Vertical discharge factor
A	7.089		Antoine Constants
B	1238.710		
C	217.000		
K - Factor	0.025	□	Molar ratio of vapor to liquid phase
Alpha	0.050	□	Critical Gas Saturation Worst Case
Qmin	1.200	[gpm]	Minimum Extraction Rate

REFERENCES

- Heath; William O. ; Richardson; Richard L.; and Goheen; Steven C.** 1994 “Heating of Solid Earthen Material, Measuring Moisture and Resistivity.”, United States Patent Number 5,330,291, US Patent Office File date May 13, 1992
- McGee, Bruce C. W.** 2003 “Electro-thermal Dynamic Stripping Process”, United States Patent Number 6,596,142, US Patent Office File date March 22, 2001
- Liao, Q and Zhao T.,** 2003 “Modeling of Taylor bubble rising in a vertical mini mon-circular channel filled with a stagnant liquid”. *Int. J. Multiphase Flow*, 29, pp. 411-434 (2003).