International Journal of Engineering & Scientific Research
Vol.6 Issue 11, November2018,
ISSN: 2347-6532 Impact Factor: 6.660
Journal Homepage: http://www.ijmra.us, Email: editorijmie@gmail.com Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

NUMERICAL INVESTIGATION OF GROUNDWATER REMEDIATION USING STEAM INJECTION

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Article Received: 15th October, 2018 Article Revised: 20th October, 2018 Article Accepted: 30th October, 2018

Abstract

Groundwater is of major importance to civilization, because it is the largest reserve of drinkable water in regions where humans can live. The pollution of groundwater by Non Aqueous Phase Liquid (NAPL) has become an increasing concern with industrialization. The effects of these pollutants may remain in the aquifers for many years because the residence time of groundwater is very slow. This work is thus aimed at investigating the remediation of polluted groundwater using steam injection.

The governing equations for simulation of three phase flow in groundwater were developed based on conservation of mass, momentum and energy. The incorporated steam injection as a flux source. Numerical model was subsequently developed by solving the equations using finite element technique. The model was first used to determine recovery efficiency of benzene in an aquifer containing sand of porosity 0.2 and permeability of 1 x $10^{-16}m^{-2}$ with steam injection at $0.01m^3/s$. The numerical model was also used to determine the recovery efficiency of ethanol for all the cases treated in numerical investigations of recovery of benzene.

The numerical results for recovery efficiency of benzene using steam injection at $0.01m^3/s$ was 71.77%. The numerical results for recovery efficiency of ethanol using steam injection at $0.01m^3/s$ was 74.75%.
Steam injection for remediation of porous media contaminated by NAPL has been shown to be an efficient remediation technology.

Keywords: Non Aqueous Phase Liquid, Steam injection, Recovery efficiency, Groundwater Remediation

Introduction

Groundwater is of major importance to civilization, because it is the largest reserve of drinkable water in regions where humans can live. About 40% of drinking water comes from the groundwater, almost 97% of the rural population drinks it and about 30-40% of the water used for agriculture comes from the groundwater (Sherma and Reddy, 2004). Groundwater may appear at the surface in the form of springs or it may be tapped by wells. It can also sustain the flow of surface water during the dry period. It is often preferable to surface water during the dry period because it is less contaminated by wastes and organisms. It is greater in quantity and more economical in distribution.

Groundwater is a valuable resource and it must be protected from any pollution. It is important to conserve not only the quantity of the underground water supply, but even more its quality. The pollution of this major supply has become an increasing concern with increasing industrialization due to numerous human activities. Groundwater quality is endangered by a multitude of contaminants that may enter the ground from leaking disposal dumps, from the disposal of Industrial waste products and through accidental spills. These contaminants are almost immiscible with water and will often be present as Non Aqueous Phase Liquids (NAPLs). The pollution of groundwater by petroleum products is recognized as a major threat to the water resources. There is need for the polluted ground to be cleaned in order to avoid potential hydrocarbon contamination of groundwater aquifer.

Innovative technologies for subsurface remediation, including in situ techniques based on heating the subsurface to enhance the recovery of organic contaminants, are increasingly being evaluated for use at specific sites as the limitations to the conventionally-used techniques are recognized(Davis,1998). With thermal technologies, the contaminated soil/groundwater is heated and this strongly affects the physical-chemical properties of the contaminant to the benefit of the recovery process. Among the thermal technologies, steam injection is being investigated as a potential method for remediation of polluted groundwater. Full scale operations have supported these results suggesting that the techniques ensure rapid and satisfactory clean up of every complicated contamination (Newmark et al. 1994, Newmark et al. 1998). One of the advantages of steam Injection is that various mechanisms may be active in the removal of contaminant from the subsurface. Hence, the technology is very versatile and can be used for highly heterogeneous geologic environments and remediation of both above and below the water table. The process of steam injection for subsurface remediation involves several complex interacting phenomena at the pore level that are not considered in petroleum reservoir engineering (Falta et al; 1992). It is characterized by heat and mass transfer in multiphase flow (gas, water, NAPL) in which the mass transfer of components between the phases is significant. It was originally developed as an enhanced oil recovery where it was the reduction in viscosity that was more important. It is obvious that much of the pioneering work on steam injection as a remediation technology was based on the experiences from steam injection as an enhanced oil recovery technique. There is a slight difference between these two applications. In enhanced oil recovery, the main objective is to remove the maximum amount of oil from the reservoir for as long as it is economically feasible. Small amounts of oil left in the formation are usually ignored. However, the purpose of remediation efforts is to remove as much of the contaminant as possible until clean up levels are achieved.

Hunt et al. (1988) presented experimental results showing complete removal of volatile organic compounds from a water-saturated column indicating that steam injection could be a very efficient remediation technology. These findings were further developed in two dimensional studies where Itamura (1996) and She and Sleep (1999) showed that heterogeneous porous media could be remediated when steam contacted the contaminant directly. Gudbjerg et al. (2003a) showed that even if a steam zone is not in direct contact with the NAPL rapid clean-up may still occur. Helmig et al. (1998) describe the comparison of one-dimensional steam injection experiments into sand-filled columns with numerical simulations. Based on that Class (1999) gives an example of the numerical simulation of a steam injection experiment into a column that was contaminated with xylene in residual saturation.White et. al (2004) modeled flow of nonvolatile nonaqueous phase liquid (NAPL) and aqueous phases that account for mobile, entrapped, and residual NAPL in variably saturated water-wet porous media and compared against results from detailed laboratory experiments. Yang et. al(2003) carried out numerical modeling for groundwater remediation in Dublin, Ireland. The model was used to characterize contaminants at three dimensional scale. A two-dimensional intermediate scale sand box experiment was performed by Gudbjerg et al.(2004) where an organic contaminant was emplaced below the water table at the interface between a coarse and a fine sand layer. Steam was injected above the water table and after an initial heating period the contaminant was recovered at the outlet. The experiment was successfully modeled using the numerical code T2VOC and the dominant removal mechanism was identified to be heat conduction induced boiling of the separate phase contaminant.

Numerical modeling has also been used at field-scale in predictive studies to support the design of steam remediation schemes (Adenekan and Patzek 1994, Lee 1994, Ochs et al. 2003) and in studies analyzing the lessons learned from full-scale clean –up operations (Kuhlmann 2002, Gudbjerg et al. 2003). Hence, Numerical modeling has played an essential part throughout the development of steam injection as a remediation technology and several numerical multiphase models have been presented (Adenekan et al. 1993, Forsyth 1993, Panday et al. 1995, Class et al. 2002). Falta et al., (1995) performed simulations using the numerical model T2VOC. Numerical modeling gives better understanding of the physical processes. It allows coupling of several processes investigated in small-scale laboratory experiments.

This work has thus investigated numerically the remediation of polluted groundwater using steam injection.

Basic Governing Equations

The basic equations for modeling groundwater pollutant movement as given by Class et al (2002) are presented in eqn (1-5).

$$\frac{\phi\partial(\rho_{w_{mol}} X_w^k S_w + \rho_{g_{mol}} X_g^k S_g + \rho_{n_{mol}} X_n^k S_n)}{\partial t} - div\left\{\frac{k_{rw}}{\mu_w}\rho_{w_{mol}} X_w^k K\left(gradP_w - \rho_{n_{mass}} g\right)\right\} - div\left\{\frac{k_{rg}}{\mu_g}\rho_{g_{mol}} X_g^k K\left(gradP_g - \rho_{g_{mass}} g\right)\right\} - div\left\{\frac{k_{rn}}{\mu_n}\rho_{n_{mol}} X_n^k K\left(gradP_n - \rho_{n_{mass}} g\right)\right\} + div\left\{D_{pm}^k \rho_{g_{mass}} gradX_g^k\right\} - q^k = 0 \quad \text{.....(1)}$$

$$S_w + S_g + S_n = 1 \quad \text{.....(2)}$$

$$(P_{n =} \; P_g - \Theta P_{cgn}(S_g) - (1-\Theta)[P_{cgw}(S_w) - P_{cnw}(S_w = 1) \quad \text{.....(3)}$$

$$P_{w =} \; P_n - \Theta P_{cgw}(S_w) - (1-\Theta)[P_{cnw}(S_w = 1)] \quad \text{.....(4)}$$

$$\frac{\phi\partial(\rho_{w_{mass}} U_w S_w + \rho_{g_{mass}} U_g S_g + \rho_{n_{mass}} U_n S_n)}{\partial t} + \frac{\partial(1-\phi)\rho_R C_R T}{\partial t} - div\lambda_{pm} gradT - div\left\{\frac{k_{rw}}{\mu_w}\rho_{w_{mass}} \mathrm{h}_w K\left(gradP_w - \rho_{w_{mass}} g\right)\right\} - div\left\{\frac{k_{rg}}{\mu_g}\rho_{g_{mass}} h_g K\left(gradP_g - \rho_{g_{mass}} g\right)\right\} - div\left\{\frac{k_{rn}}{\mu_n}\rho_{n_{mass}} h_n K\left(gradP_n - \rho_{n_{mass}} g\right)\right\} +$$

$$div\{D_{pm}^{w}\rho_{g_{mol}}h_{g}^{w}M_{wt}^{w}gradX_{g}^{g}\} + div\{D_{pm}^{a}\rho_{g_{mol}}h_{g}^{a}M_{wt}^{a}gradX_{g}^{a}\} + div\{D_{pm}^{c}\rho_{g_{mol}}h_{g}^{c}M_{wt}^{c}gradX_{g}^{c}\} - q^{h} = 0 \text{……………..(5)}$$

where μ = dynamic viscosity, ρ = fluid density, S =saturation, ∅ = porosity k_w =relative permeability, σ= electric conductivity of the medium, k= fluid phase, p= fluid pressure, X= mole fraction, n =contaminant, w = water ,g= gas.

Determination of Fluid Properties for the Numerical Simulation

There are certain fluid properties in the derived governing equations Eqn (1-5) that needed to be determined before the simulation can be successfully carried out. These properties are density, viscosity, vapour pressures, thermal conductivity, diffusion and enthalpy. The various relationship for these properties are hereby discussed.

Saturated liquid Densities as a Function of Temperature

Racket (1970) proposed that saturated liquid volumes be calculated by

$$V_s = V_c Z_c^{(1-T/T_c)2/7} \text{ ---(10)}$$

$$V_s = \frac{RT_c}{P_c} Z_c^{1+[(1-T/T_c)2/7]} \text{ --(11)}$$

Where $V_s =$ saturated liquid volume, V_c = critical volume, $Z_c =$ critical compressibility factor, $T_c =$ critical temperature.

Yamada and Gunn (1973) proposed that Z_c in Eq. (11) be correlated with the acentric factor:

$$V_s = V_c(0.29056 - 0.08775w)^{(1-T/T_c)2/7} \text{ ---(12)}$$

Densities of Liquid Mixtures at their Bubble Point

In order to extend equations of Eq. (12) to mixtures, mixing rules are required. Li (1971) and Spencer and Danner (1973) recommended

$$V_m = R \ (\textstyle\sum_i \frac{x_i T_{ci}}{P_{ci}}) Z_{RAm}^{[1+(1-T_r)0.2857]} \text{ --(13)}$$

$$Z_{RAM} = \sum x_i Z_{RAI} \text{ ---(14)}$$

With the relation of Yamada and Gunn (1973)

$$Z_{RAI} = 0.29056 - 0.08775 w_i \tag{15}$$

Where $T_r = T/T_{cm.}$ Spencer and Danner (1973) recommend the mixing rules of Chueh and Prausnitz (1976).

$$T_{cm} = \sum_i \sum_j \varphi_i \varphi_j T_{cij} \tag{16}$$

$$\varphi_i = \frac{x_i V_{ci}}{\sum_j x_j V_{cj}} \tag{17}$$

$$1 - k_{ij} = \frac{8(V_{ci} V_{cj})^{1/2}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \tag{18}$$

$$T_{cij} = \left(1 - k_{ij}\right)(T_{ci} T_{cj})^{1/2} \tag{19}$$

Li,s method sets $k_{ij} = 0$ for Eq.(19). The HBT method of Eq. (16) to (19) has been extended to mixtures by Hankinson and Thomson (1979) with

$$T_{cm} = \frac{[\sum_i x_i (V_{ci} T_{ci})^{1/2}]^2}{V_{cm}} \tag{20}$$

$$V_{cm} = 0.25[\sum_i x_i V_i^* + 3(\sum_i x_i V_i^{*2/3}](\sum_i x_i V_i^{*1/3})] \tag{21}$$

$$w_m = \sum_i^n x_i w_{srki} \tag{22}$$

$$V_m = V^* V^{(0)}\left(1 - w_m V^{(\delta)}\right) \tag{23}$$

Vapor Pressures and Enthalpies of Vaporization

This section covers method for estimating and correlating vapor pressures of pure liquids. Since enthalpies of vaporization are derived from vapor pressure-temperature data, the estimation of this property is also included.

Correlation and Extrapolation of Vapour-Pressure Data

When the vapor phase of a pure fluid is in equilibrium with its liquid phase, theequality of chemical potential, temperature, and pressure in both phases leads to the Clapeyron equation (Smith, et al., 1996).

$$lnP_{vp} = A$$

(24)

Vapor pressures have been measured for various substances. Boublik (1984) presents tabulations of experimental data that have been judged to be of high quality for approximately 1000 substances. Antoine in 1888 proposed a simple modification of Eq. (24) which has been widely used over limited temperature ranges.

$$log_{10}P_{vp} = A - \frac{B}{T+C-273.15}$$

(25)

Where T is in kelvins, Values of A, B and C are tabulated for a number of materials in Appendix A with P_{vp} in bars and T in K. Additional tabulations of Antoine constants may be found in Boublik, et al. (1984), Dean (1999) and Yaws (1992).

Enthalpy of Vaporization at the Normal Boiling

A pure-component constant that is occasionally used in property correlations is the enthalpy of vaporization at the normal boiling point $\Delta H_{vb.}$ Vetere (1995) determined an expression to correlate vapor pressures so that acentric factor is eliminated. When applied to the normal boiling point:

$$\Delta H_{vb} = RT_b \frac{(1-T_{br})^{0.38}(\ln P_c - 0.513 + 0.5066/(P_c T_{br}^2))}{1-T_{br} + F(1-(1-T_{br})^{0.38})lnT_{br}}$$

(26)

F is 1.05 for C_2+ alcohols and dimerizing compounds such as SO_3, NO and NO_2. For all other compounds investigated by Vetere, F is 1.0. When T_c and P_c are not available, Vetere proposed

$$\Delta H_{vb} = RT_b = (A + BlnT_b + \frac{CT_b^{1.72}}{M'})$$

(27)

M' is a fictitious molecular weight that is equal to the true molecular weight for most compounds.

Estimation of Low-Pressure Gas Viscosity

Essentially all gas viscosity estimation techniques are based on either the Chapman-Enskog theory or the law of corresponding states. Experimental values of low-pressure gas viscosities are compiled in Landolt-Bornstein (1955), Stephan and Lucas (1979), and Vargaftif, et al. (1996). Literature references for a number of substances along with equations with which to calculate gas viscosities based on critically evaluated data may be found in Daubert, et al. (1997). Gas phase viscosity information can also be found in Dean (1999), Lide (1999), Perry and Green (1997), and Yaws (1995).

The first-order Chapman-Enskog viscosity equation was given as

$$\eta = \frac{(26.69)(MT)^{1/2}}{\sigma^2 \Omega_v}$$

(28)

In order to use this relation to estimate viscosities, the collision diameter σ and the collision integral σ and the collision integral Ω_v must be found. For any potential curve, the dimensionless temperature T^* is related to ε by

$$T^* = \frac{kT}{\varepsilon}$$

(29)

Where k is Boltzmann's constant and ε is the minimum of the pair-potential energy.

Neufeld, et al. (1972) proposed an empirical equation which is convenient for computer application:

$$\Omega_v = [A(T*)^{-B}] + C[\exp(-DT^*)] + \mathrm{E}[\exp(-\mathrm{F}T^*)]$$

(30)

Where $T^* = kT/\varepsilon$, A = 1.16145, B = 0.14874, C = 0.52487, D = 0.77320, E = 2.16178 and F = 2.43787. Equation (30) is applicable from $0.3 \leq T^* \leq 100$ with an average deviation of only 0.064%.

Chung, et al. (1984, 1988) have employed Eq. (30) with

$$\frac{\varepsilon}{k} = \frac{T_c}{1.2593}$$

(31)

$$\sigma = 0.809 V_c^{1/3}$$

(32)

Where ε/k and T_c are in kelvins, σ is in angstroms and V_c is in cm^3/mol.

$$T^* = 1.2595 T_r$$

(33)

Their final result can be expressed as:

$$\eta = 40.785 \frac{F_{c(MT)^{1/2}}}{V_c^{2/3} \Omega_v}$$

(34)

Where η = viscosity, μ M = molecular weight, g/mol T = temperature, K $V_c =$ critical volume, cm^3/mol Ω_v = viscosity collision integral from Eq. (34) and T^*= 1.2593T_r

$$F_c = 1 - 0.275\omega + 0.059035\mu_r^4 + \kappa$$

(35)

Where ω is the accentric factor and κ is a special correction for highly polar substances such as alcohols and acids. When V_c is in cm^3/mole, T_c is in kelvins and μ is in debyes,

$$\mu_r = 131.3\frac{\mu}{(V_c T_c)^{1/2}}$$

(36)

Viscosities of Gas Mixtures at Low Pressures

The rigorous kinetic theory of Chapman and Enskog can be extended to determine the viscosity of low-pressure multicomponent mixtures (Chapman and Cowling, 1939; Hirschfelder, et al., 1954; Kestin, et al., 1976). In a further simplification of the kinetic theory approach, Wilke (1950) neglected second-order effects and proposed:

$$\eta_m = \sum_{i=1}^{n} \frac{y_i\eta_i}{\sum_{j=i}^{n} y_j\varphi_{ij}}$$

Where

$$\varphi_{ij} = \frac{[1+(\eta_i/\eta_j)^{\frac{1}{2}}(M_j/M_i)^{1/4}]^2}{[8(1+M_i/M_j)]^{1/2}}$$

(37)

φ_{ij} is found by interchanging subscripts or by

$$\varphi_{ji} = \frac{\eta_j}{\eta_i}\frac{M_i}{M_j}\varphi_{ij}$$

(38)

For a binary system of 1 and 2, with Eqs. (37) to (38),

$$\eta_m = \frac{y_{i\eta_1}}{y_1 + y_{2\varphi_{12}}} + \frac{y_{2\eta 2}}{y_2 + y_{2\varphi_{12}}}$$

(39)

Where η_m = viscosity of the mixture, $\eta_i, \eta_{2,}$= pure component viscosities

y_1, y_2 = mole fractions

and

$$\varphi_{ij} = [1 + (\eta_1/\eta_2)^{1/2}(M_2/M_1)^{1/4}]^2$$

(40)

$$\varphi_{21} = \varphi_{12}\frac{[1+\eta_{1/\eta_2})^{1/2}(M_2/M_1)^{1/4}]^2}{\{8[1+(M_1/M_2)]\}^{1/2}}$$

(41)

$$\varphi_{21} = \varphi_{12}\frac{\eta_2 M_1}{\eta_1 M_2}$$

(42)

As an approximate expression for φ_{ij} of Eq. (42) the following is proposed (Herning and Zipperer, 1936)

$$\varphi_{ij} = (\frac{M_j}{M_i})^{1/2} = \varphi_{ji}^{-1}$$

(43)

Estimation of Low-Temperature Liquid Viscosity

The estimation methods for low-temperature liquid viscosity often employ structural-sensitive parameters which are valid only for certain homologous series or are found from group contributions. Orrick and Erbar (1974) employs a group contribution technique to estimate A and B in Eq. (44).

$$\ln\frac{\eta_L}{p_L^M} = \mathrm{A} + \frac{B}{T}$$

(44)

where η_L = liquid viscosity, c p_L = liquid density at 20°C, g/cm^3

M = molecular weight, T = temperature, K

Prezdziecki and Sridhar (1985) Method

In this technique, the authors propose using the Hildebrand-modified Batschinski equation (Batschinski, 1913; Hildebrand, 1971; Vogel and Weiss, 1981)

$$\eta_L = \frac{V_o}{E(V-V_o)}$$

(45) Where η_L = liquid viscosity, cP V = liquid molar volume, cm^3/mol

And the parameters E and V_o are defined below.

$$\mathrm{E} = -1.12 + \frac{V_c}{12.94+0.10M-0.23P_c+0.024T_{fp}-11.58(T_{fp}/T_c)}$$

--(46)

$$V_o = 0.0085wT_c - 2.02 + \frac{V_m}{0.342(T_{fp}/T_c)+0.894}$$

--(47)

Where T_c = critical temperature, K P_c = critical pressure, bar

V_c = critical volume, cm^3/mol M = molecular weight, g/mol

T_{fp} = freezing point, K ω = acentric factor, V_m = liquid molar volume at $T_{fp,}$ cm^3/mol

The authors recommend that V_m and V be estimated from T_{fp} and T by the Gunn-Yamada (1971) method. In this method, one accurate value of V is required in the temperature range of applicability of Eq. (48). The datum point is defined as V^R at T^R, then at any other temperature T,

$$V(T) = \frac{f(T)}{f(T^R)} V^R$$

(48)

Where

$$f(T) = H_I(1 - \omega H_2)$$

(49)

$$H_1 = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4$$

(50)

$$H_2 = 0.29607 - 0.09045T_r - 0.04842T_r^2$$

(51)

Liquid Mixture Viscosity

Based on a corresponding-states treatment for mixture compressibility factors (Teja, 1980; Teja and Sandler, 1980), Teja and Rice proposed an analogous form for liquid mixture viscosity.

$$\mathrm{Ln}(\eta_m \varepsilon_m) = \ln(\eta\varepsilon)^{(R1)} + [\ln(\eta\varepsilon)^{(R2)} - \ln(\eta\varepsilon)^{(R1)}] \frac{\omega_m - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}}$$

(52)

Where the superscript (R1) and (R2) refer to two reference fluids. η is the viscosity, ω the accentric factor, and ε is a parameter defined here as :

$$\varepsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}}$$

(53)

The rules suggested by the authors to compute these mixture parameters are:

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij}$$

(54)

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j V_{cij}}{V_{cm}}$$

(55)

$$M_m = \sum_i x_i M_i$$

(56)

$$w_m = \sum_i x_i \, w_i$$

(57)

$$V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})}{8}$$

(58)

$$T_{cij} V_{cij} = \Psi_{ij} (T_{ci} T_{cj} V_{ci} V_{cj})^{1/2}$$

(59)

Ψ_{ij} is an interaction parameter of order unity which must be found from experimental data.

Thermal Conductivity

Through rather elementary arguments, the thermal conductivity of an ideal gas was found to be equal to $vLC_v n/3$, where v is the average molecule velocity, L is the mean free path, C_v is the constant volume heat capacity per molecule, and n is the number densities of molecules. It is quite inaccurate. For monatomic gases, which have no rotational or vibrational degrees of freedom, a more rigorous analysis yields

$$\lambda = \frac{25}{32} \; (\pi m K T)^{1/2} \frac{C_v/m}{\pi \sigma^2 \Omega_v}$$

(60)

or, written for computational ease, with $C_v = \frac{3}{2} k$,

$$\lambda = 2.63 \times 10^{-23} \frac{(T/M')^{1/2}}{\sigma^2 \Omega_v}$$

(61)

Where λ = thermal conductivity, W/(m.k)

T = temperature, K k = Boltzmann's constant = 1.3805 × 10^{-23}J/k

M' = molecular weight, kg/mo σ = characteristic dimension of molecule, m

Ω_v = collision integral dimensionless

Thermal Conductivities of Polyatomic Gases

The reduced thermal conductivity may be expressed as

$\lambda_r = \lambda\Gamma$ -- (62)

$\Gamma = [\frac{T_c(M')^3 N_o^2}{R^5 P_c^4}]^{1/6}$ -- (63)

In SI units, if R = 8314J/(kmol K), N_o (Avogadro's number) = 6.023 × 10^{26} $(\text{kmol})^{-1}$, and with T_c in kelvins, M' in kg/mol, and P_c in N/m^2, Γ has the units of m.K/W or inverse thermal conductivity. In more convenient units,

$\Gamma = 210\,(\frac{T_c M^3}{P_c^4})$ -- (64)

Where Γ is the reduced, inverse thermal conductivity,T_c is in kelvins, M is in g/mol, and P_c is in bars.

The reduced thermal conductivity was employed by Roy and Thodos (1970), who, however, separated the $\lambda_r = \lambda\Gamma = (\lambda\Gamma)_{tr} + (\lambda\Gamma)_{int}$

Where λ = low-pressure gas thermal conductivity, W/(m.K) and Γ is defined in Eq. (65).

$(\lambda\Gamma)_{tr} = 8.757[\exp(0.0464T_r) - \exp(-0.2412T_r)]$ --- (65)

$(\lambda\Gamma)_{int} = Cf(T_r)$ -- (66)

Chung, et al. developed an approach similar to that of Mason and Monchick (1962) to obtain a relation for λ. By using their form and a similar one for low-pressure viscosity [Eq. (67), one obtains

$\frac{\lambda M'}{\eta C_v} = \frac{3.75\Psi}{C_v/_R}$ --- (67)

Where λ=thermalconductivity/(m.K) M' = molecular weight, kg/mol

η = low-pressure gas viscosity, N.s/m^2 C_v = heat capacity at constant volume, J/(mol.K)

R = gas constant, 8.314 J/(mol.K)

$\Psi = 1 + \alpha\{[0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z]/[0.6366 + \beta Z + 1.061\alpha\beta]\}$---- (68)

$\alpha = (C_v/R) - {}^3/_2$-- -(69)

$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$-- -(70)

$Z = 2.0 + 10.5T_r^2$-- -(71)

Thermal Conductivities of Low-Pressure Gas Mixtures

The theory for calculating the conductivity of for rare-gas mixtures has been worked out in detail (Hirschfelder, et al., 1954; Mason, 1958; Mason and von Ubisch, 1960, Muckenfuss, 1958). The major problem is how to modify monatomic mixture correlations to apply to polyatomic molecules. In a form analogous to the theoretical relation for mixture viscosity,

$\lambda_m = \sum_{i=1}^{n} \frac{y_i\lambda_i}{\sum_{j=i}^{n} y_j A_{ij}}$ -- -(72)

Where $\lambda_m =$ thermal conductivity of the gas mixtur $\lambda_i =$ thermal conductivity of pure i

$y_{i,}y_j =$ mole fraction of components i and j $A_{ij} =$ a function, as yet unspecified $A_{ii} = 1.0$

Mason and Saxena (1958) suggested that A_{ij} in Eq. (72) could be expressed as

$A_{ij} = \frac{\varepsilon[1+\lambda_{tri}/\lambda_{trj})(\frac{M_i}{M_j})^{1/4}]^2}{[8\left(1+\frac{M_i}{M_j}\right)]^{1/2}}$ -- -(73)

Where M = molecular weight, g/mol $\lambda_{tr} =$ monatomic value of the thermal conductivity $\varepsilon =$ numerical constant near unity

Mason and Saxena proposed a value of 1.065 for ε, and Tandon and Saxena (1965) later suggested 0.85. As used here, ε = 1.0.

Noting that for monatomic gases that $C_v = C_{tr} = 3R/2$

$\frac{\lambda_{tri}}{\lambda_{trj}} = \frac{\eta_i M_j}{\eta_j M_i}$ -- (74)

Substituting Eq. (72) into Eq. (73) and comparing with Eq. (68) gives

$A_{ij} = \varphi_{ij}$ -- (75)

Where φ_{ij} is the interaction parameter for gas-mixture viscosity.

Thermal Conductivities of Gas Mixtures at High Pressures

Equations (106) to (115) were suggested as a way to estimate the high-pressure thermal conductivity of a pure gas. This procedure may be adapted for mixture given that mixing and combining rules are available to determine$T_{cm,}$ $P_{cm,}$ $V_{cm,}$ $Z_{cm,}$ M_m. Yorizane, et al (1983) have examined this approach and recommend the following:

$$T_{cm} = \frac{\sum_i \sum_j y_i y_j V_{cij} T_{cij}}{V_{cm}}$$

(76)

$$V_{cm} = \sum_i \sum_j y_i \, y_j V_{cij}$$

(77)

$$w_m = \sum_i y_i w_i$$

(78)

$$Z_{cm} = 0.211 - 0.08 w_i$$

(79)

$$P_{cm} = Z_{cm} R T_{cm} / V_{cm}$$

(80)

$$M_m = \sum_i y_i M_i$$

(81)

$$T_{cii} = T_{ci}$$

(82)

$$T_{cij} = (T_{ci} T_{cj})^{1/2}$$

(83)

$$V_{cii} = V_{ci}$$

(84)

$$V_{cij} = \frac{[(V_{ci})^{1/3} + [(V_{cij})^{1/3}]^3}{8}$$

(85)

Estimation of the Thermal Conductivities of Pure Liquids

In an examination of the thermal conductivities of many diverse liquids, Latini and his coworkers (Baroncini, et al., 1981,1983, 1984); (Latini and Pacetti, 1977) suggest a correlation of the form:

$$\lambda_L = \frac{A(1-T_r)^{0.38}}{T_r^{1/6}}$$ --

(86) Where $\lambda_L =$ thermal conductivity of the liquid,W/(mk)

T_b= normal boiling temperature (at 1 atm), T_c = critical temperature, K

M = molecular weight, g/mol

$$T_r = T/T_c$$ --

(87)

$$A = \frac{A^* T_b^{\alpha}}{M^{\beta} T_c^{\gamma}}$$ --

(88)

Diffusion Coefficient for Binary Gas Systems at Low Pressure

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. The theory results from solving the Boltzmann equation and the results are usually credited to both Chapman and Enskog, who independently derived the working equation

$$D_{AB} = \frac{3}{16} \frac{(4\pi kT/M_{AB})^{1/2}}{n\pi\sigma^2 AB\Omega_D} f_D$$ --

(89)

Where M_A, M_B = molecular weights of A and B

$M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$---

(90)

n = number density of molecules in the mixture K = Boltzmann's constant

T = absolute temperature Ω_D = the collision integral for diffusion, is a function of temperature

σ_{AB} is the characteristic length of the intermolecular force law

f_D is a correction term, which is of the order of unity and n is expressed by the ideal-gas law, Eq. (90) may be written as

$$D_{AB} = \frac{0.00266 T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}$$ ---

(91)

Where D_{AB} = diffusion coefficient, cm^3/s T = temperature, k P = pressure, bar

σ_{AB}= characteristic length, A Ω_D = diffusion collision integral, dimensionless and M_{AB} is defined under eq. (91). To use Eq. (91) some rule must be chosen to obtain the interaction value σ_{AB} from σ_A and σ_B. Ω_D is a function only of $\frac{KT}{\epsilon_{AB}}$.

The simple rules shown below are usually employed:

$\varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{1/2}$--(92)

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$ ---(93)

Ω_D is tabulated as a function of KT/ε for the Lennard-Jones potential (Hirsch-felder, et al., 1954), and various analytical approximations also are available (Johnson and Colver, 1969; Kestin, et al., 1977; Neufeld, et al., 1972). The accurate relation of Neufield, et al. (1972) is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(DT^*)} + \frac{G}{\exp(\mathrm{FT}^*)} \quad \text{---}(94)$$

Where $T^* = KT/\varepsilon_{AB}$

A= 1.06036 B=0.15610 C=0.19300 D=0.47635 E =1.03587

F=1.52996 G=1.76474 H=3.89411

These equations were then used to develop computer program which was then used to investigate the groundwater remediation using steam injection.

A model was developed through solving the equations using finite element technique. The contaminants that are used for the numerical investigation are benzene and ethanol.

Computer Implementation

The governing equations for each case were solved through a COMSOL Multiphysics interphase for a 1m x 1m x1m aquifer. The numerical code automatically maximizes the time step according to the specified convergence and accuracy criteria. The equations were solved using the listed data for each case. The simulation is used to obtain the pressure, saturations and temperature in the domain of interest.

Geometric Representation of the Domain for Simulation

The geometric configuration of the domain for simulation is shown in Fig. 1.

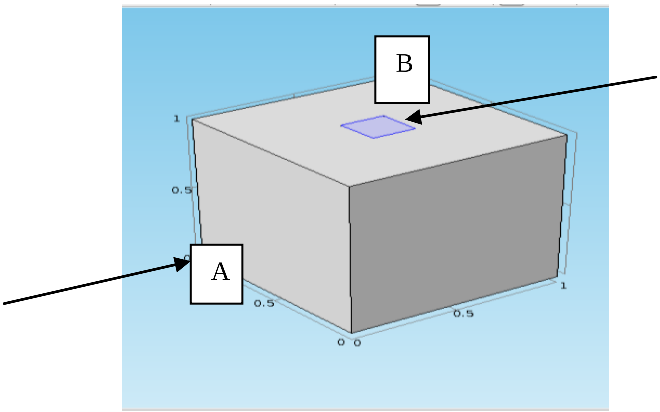

Fig. 1 Geometric Representation of the Domain

Notably steam injection occurs at A while the contaminant is at B. The sand box was considered as a three-dimensional system and was discretized into cells with dimensions 1m x 1m x1 m. The measured steam injection rate was used as a flux boundary condition at the injection side of the sand box. At the right hand side of the sand box, a mixed boundary condition was specified that allowed outflow of a phase when the phase pressure exceeded atmospheric pressure and otherwise the boundary was a no-flux boundary.

Result and Discussions

The numerical results for removal of benzene from groundwater using steam injection are reported. The operation practice used and the recovery efficiency in the numerical investigation were listed in Table 1-2.

Table 1 Numerical Result for Groundwater Remediation of Benzene at Steam Injection Rate of 0.01m^3/s

Numerical no	1
Contaminant	Benzene
Operation	Steam Injection
Recovery Efficiency	71.77%

Table 2 Removal of Benzene from Groundwater using Steam Injection

Time (s)	Recovery Efficiency (%)
0	0
3800	4.47
7600	11.61
11400	26.23
15200	49.08
19000	71.77

The injection of steam created a zone with steam temperature in the upper part of the coarse sand layer with convection as the dominant heat transfer process. A vertical steam front, where the temperature rapidly changed from steam temperature to the temperature of the surroundings, moved with a constant velocity through the sand box. As the contaminated area was heated, the vaporized benzene was transported to the heat front where it condensed and accumulated. The emplaced benzene recovered as separate phase liquid from the top of the water table was 71.77%. The results presented are illustrated in Fig. 1 which shows the graph of recovery efficiency against time of treatment. The recovery efficiency increased with time of treatment and it reached a maximum value at the end of treatment.

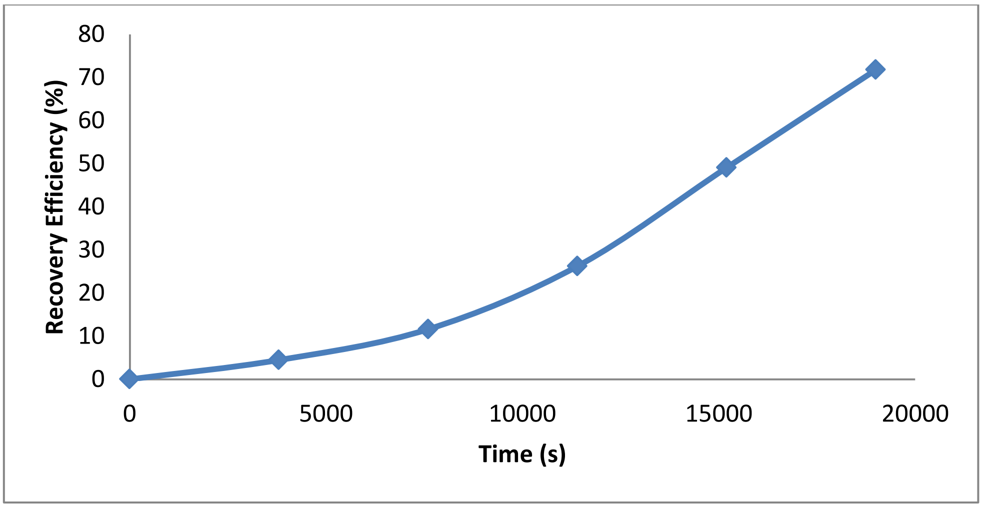

Fig. 2 Benzene Removal efficiency vs Time for Numerical Investigation at steam injection rate of 0.01m^3/s

The numerical results for removal of ethanol from groundwater using steam injection are reported. The recovery efficiency was also determined for incidence of steam injection at 0.01m^3/s. The operation practice used and the recovery efficiency in the numerical investigation were listed in Table 3-4. The numerical results for recovery efficiency of ethanol using steam injection only at 0.01m^3/s yielded 74.75 %. The results presented are illustrated in Fig. 3 which shows the graph of recovery efficiency against time of treatment. The recovery efficiency also increased with time of treatment and it reached a maximum value at the end of treatment.

Table 3 Numerical Result for Groundwater Remediation of Ethanol at Steam Injection Rate of 0.01m^3/s

Numerical no	1
Contaminant	Ethanol
Operation	Steam Injection
Recovery Efficiency	74.75%

Table 4 Removal of Ethanol from Groundwater using Steam Injection

Time (s)	Recovery Efficiency (%)
0	0
4000	3.71
8000	9.72
12000	21.66
16000	41.53
20000	74.75

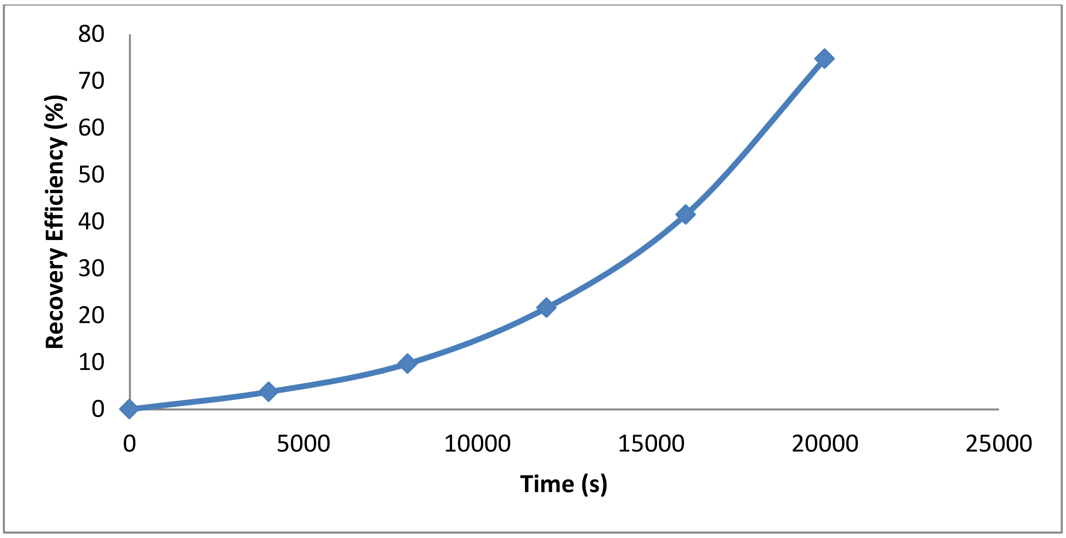

Fig. 3 Ethanol Removal efficiency vs Time for Numerical Investigation at steam injection rate of 0.01m^3/s

Comparison of the Present Work on Groundwater Remediation with Similar Works by other Researchers

In Table 5, the recovery efficiency of the contaminants (benzene and ethanol) show that steam injection technique for remediation of polluted groundwater using steam injection only is an efficient technology. The numerical results for recovery of pollutant from groundwater were in agreement with the similar work by other researchers using DCB and kerosene as contaminants with a deviation of -1.87–6.65% and 1.64–10.36% respectively.

Table 5 Comparison of Recovery Efficiency for Numerical Investigation of Groundwater Remediation using Steam Injection

Parameter	**Present Work**	**Gudbjerg *et al.*, 2003**	**Dare and Sasaki 2012**	**Percentage Deviation**
Contaminant	Benzene Ethanol	DCB	Petrol	
Steam Injection Rate	0.01	0.01	0.01	0.00
% Recovery	71.77%	67%	73.11%	-1.87 - 6.65
	74.75%	67%	73.11%	1.64 - 10.36

Conclusions

The numerical investigation was performed to investigate the recovery efficiency of ethanol and benzene at steam injection of 0.01 m^3/s. The numerical results for recovery efficiency of benzene using steam injection only at $0.01m^3/s$ yielded 71.77 % . The numerical results for recovery efficiency of ethanol using steam injection only at $0.01m^3/s$ yielded 74.75 %. Steam injection for remediation of porous media contaminated by NAPL has been shown to be an efficient technology. The result demonstrated the ability of steam injection to effectively recover contaminants from the subsurface.

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