Role of Heterogeneity in Hindering Assessment and Cleanup of Polluted Groundwater Aquifers

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Abstract**--** **In many regions around the world groundwater serves as the only reliable source for fresh water making it extremely important natural resource. The quality of many groundwater aquifers is threatened by various types of pollution including leaking under ground storage tanks. When such tanks leak, they introduce a liquid organic substance that is usually less dense than water frequently called LNAPL. Usually such source of contamination is not discovered until significant subsurface pollution takes place. To overcome such problem once it exists, proper assessment related to aquifer properties and extent of pollution becomes necessary over which the success of the whole cleanup process depends. The natural heterogeniety is expected to have a big effect on the above attempts. The various processes that influence the fate and distribution of organic contaminants in groundwater after a leak and the transport process itself are presented indicating the complexities that will exist as one attempt to develop flow, transport of dissolved contaminants, and multiphase flow models to come close to representing real life problems indicating the degree of modeling reliability. The role of heterogeneity is examined through the use of a physical model and an idealized heterogeneity. Experimental spills were conducted and experimental observations were compared with model predictions in order to assess the reliability of the mathematical modeling process. The difficulties associated with aquifer remediation from residual LNAPLs are also examined by considering a hypothetical natural heterogeneity and the often low success rate of aquifer restoration programs due to heterogeneity is explained.**

Index Term**--** **Groundwater contamination, LNAPLs, Remediation**

1. INTRODUCTION

Water covers about 73% of our planet with a huge volume of 1.4 billion cubic kilometers most of which is saline. According to the water encyclopedia, (van der Leeden et al, 1990) only about 3-4% of the total water is fresh. Most of the freshwater exists as ice in the polar region leaving about 9 million cubic kilometers of fresh water existing as groundwater and surface water like rivers and fresh lakes. Looking at numbers one will realize that most fresh water on earth exists as groundwater making it arguably the most valuable resource on earth.

The value of this resource can be reduced drastically if its quality deteriorates and there are many sources of groundwater contamination that can be classified into point source and non-point sources. Example of the former is contamination due to hydrocarbon leaks from underground storage tanks which could result because of improper design, human error, accidents or simply due to the natural aging and deterioration of the tank itself or its associated piping and fittings.

An underground storage tank, (UST) or its associated piping may leak due to various reasons releasing a certain volume of light nonaqueous phase liquid, (LNAPL) into the subsurface. Depending on the spill volume, type and subsurface properties, the hydrocarbon may be trapped in the unsaturated zone above the water table. For high LNAPL volume, it will continue to migrate down reaching close to the capillary fringe near the water table. The mobile phase near the water table can migrate laterally in the same direction as groundwater. Part of the LNAPL will dissolve slowly in the groundwater providing a long term source of groundwater contamination by means of a contaminated plume that grows in size with time (Al-Suwaiyan 2010).

The major steps involved in dealing with spills and trying to restore the subsurface have to do, in the initial phase, with source control and development of thorough understanding of the subsurface condition as well as the extent of contamination which should be followed by intensive use of modeling techniques in order to examine and select the most effective means of aquifer restoration and to examine the system behavior under various possible scenarios. Based on the results and understating developed, the actual remediation system is selected and the actual restoration process is started. Throughout these phases extreme difficulties and uncertainties exist which greatly influence the overall success of the remediation effort. The various complicating factors at various stages will be discussed below.

2. POLLUTION ASSESSMENT AND MONITORING

Field investigation at this stage aims at assessing the extent of contamination and knowing the distribution of the released contaminants. It may involve sampling of aquifer material, construction of wells screened in LNAPL zone and wells screened below the water table, which can provide information such as thickness of NAPL in wells, concentration of dissolved contaminants as well as approximate water table elevation. These are the primary data that must be used to evaluate nature and extent of groundwater pollution. Soil samples collected during the field investigation can be taken to the laboratory to get their grain size distribution which may be in turn used in models such as the one presented by Mishra et al. (1989) to generate a first approximation for the hydraulic properties of the subsurface. A review for estimating spill volume is presented by Saleem et al. (2004).

It is well established that monitoring wells are not reliable for spill detection and quantification since in many field cases, leaks are accidentally discovered by detecting free product in utility manholes not by finding free product monitoring wells. Field as well as laboratory studies showed that free product may not show in a monitoring well even if significant amount of LNAPL is spilled and present in the formation. It was also seen that water table fluctuations and history highly influence the free product thickness in monitoring wells and that no unique relation exists between thickness in monitoring well and amount of spill. It was also observed that sudden appearance and disappearance of LNAPL in the monitoring well can take place. More details related to this issue are given by Marinelli and Dunford, (1996). These points suggest that use of monitoring wells to detect and assess leaks has to be done with care.

3. CONTAMINNATS DISTRIBUTION

Farr et al. (1990) as well as Lenhard and Parker (1990) showed that the vertical distribution of an LNAPL after a spill is expected to be influenced by the spill volume, soil properties like displacement head, distribution index and value of residual saturation. These properties reflect the grain-size distribution in the aquifer material which varies significantly from one location to another. Hydrocarbon properties also influence its distribution including density, surface tension, viscosity, solubility and volatility. In general a hydrocarbon can exist in either of four classes. It can be held by capillary and adsorptive forces in the unsaturated/saturated zone as residual or immobile phase which approximately remain in its place but slowly dissolving part of its mass with any water flow. It can also exist as a vapor phase in the unsaturated zone or as free phase near the water table and in monitoring wells. Finally it can exist as a dissolved phase in groundwater at relatively very low concentrations but note that most of these products are very harmful to humans even at trace levels. According to Suthersan (1997), a typical distribution of the various phases after a spill in a hypothetical aquifer in terms of contaminated volume and contaminant mass shows that in terms of contaminated aquifer volume 79% is accounted for by dissolved phase, and 66% of contaminant mass exists as a free product. The treatment and modeling of each class will be different as will be explained when modeling is discussed adding to the difficulties.

4. MODELING

4.1 Groundwater flow

Based on principle of mass conservation and taking advantage of the well known Law of Darcy, a governing differential equation is established which can be solved numerically to come up with groundwater velocity and pressure at various locations and times (Zheng and Bennett, 1995).

$$\frac{\partial}{\partial x}(K_x\frac{\partial h}{\partial x})+\frac{\partial}{\partial y}(K_y\frac{\partial h}{\partial y})+\frac{\partial}{\partial z}(K_z\frac{\partial h}{\partial z})+q_s=S_s\frac{\partial h}{\partial t}$$

The parameters that appeared in this equation are the coordinate directions, the total head (h), source sink term (q_s) the hydraulic conductivity (K) and specific storage (S_s). The hydraulic conductivity exhibits large variation from one point to another and at the same location which means that we can not come up with a “correct” value that can be used in the model. The velocity field obtained will be as good as the parameters supplied to the mathematical model.

4.2 Transport of dissolved contaminant

Similar to the approach used to model groundwater flow, movement of a dissolved contaminant is modeled by solving the governing equation developed by applying the solute mass balance considering the various mechanisms involved like diffusion, dispersion, advection, retardation, reaction (Zheng and Bennett, 1995). Depending on how rigorous one wants to be the models to describe the various processes is developed/selected and implemented to come up with the governing equation.

$$R\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C}{\partial x_j})-\frac{\partial}{\partial x_i}(v_iC)+\frac{q_s}{\theta}C_s-\lambda(C+\frac{\rho_b}{\theta}\overline{C})$$

Where:

R	retardation factor
C	dissolved concentration
v	seepage velocity
D_{ij}	dispersion coefficient
q_s	flow rate of fluid source
C_s	source concentration
ρ_b	bulk density
θ	porosity
C	sorbed concentration
λ	reaction rate constant

The model prediction will be as good as the degree of closeness of the processes selected in the model to the real problem as well as the closeness to the supplied parameters to the real ones. Groundwater velocity field, hydrodynamic dispersion coefficients are essential but we have seen that velocity obtained from a flow model is not highly reliable. Dispersion was found to be scale dependent meaning that values are not easily approximated. If we include reactions and biotic processes (some of which may be approximated using retardation factor) the case becomes even more complex and modeling results are rarely reliable to a high degree.

4.3 Contaminants as distinct phases

For modeling distinct phases the problem becomes much more involved but the basic principle is the mass balance of each phase combined with auxiliary equations that reflect the properties of various phases as well as porous media properties. Example of the governing equations for multi-phase problem for three phase system of water(w), oil(o) and air and assuming that the pressure in air remains constant as given by Segol (1994) are:

$$\frac{\partial}{\partial x_i}[K_{wij}(\frac{\partial \psi_w}{\partial x_j}+u_j)]-C_{ww}\frac{\partial \psi_w}{\partial t}-C_{wo}\frac{\partial \psi_o}{\partial t}=0$$

$$\frac{\partial}{\partial x_i}[K_{oij}(\frac{\partial \psi_o}{\partial x_j}+\rho_{ro}u_j)]-C_{oo}\frac{\partial \psi_o}{\partial t}-C_{ow}\frac{\partial \psi_w}{\partial t}=0$$

Where:

Ψ	pressure head
ρ_r	specific gravity for oil
u_j	gravity vector
Kwij, Koij	hydraulic conductivities for water and oil
C_{pq}	fluid capacities between phase p and q

$$C_{pq}=\varepsilon\frac{\partial S_p}{\partial \psi_q}$$

S	saturation of phase p
ε	porosity

In addition auxiliary or constitutive equations relating phase saturation, pressure head and relative permeability for the three phases like the ones given by Brooks and Corey(1966), Corey(1986), van Genuchten(1980) and Parker et al.(1987) are needed before the modeling processes can be started. Constitutive relations used currently involve many assumptions and are usually scaled up from the simpler two phase constitutive relations. These relations are sometime developed by extending results from laboratory studies for simple cases and assuming them to represent the more complex situation. All of this combined indicates that it is extremely difficult to carry a modeling study that closely resembles and predicts what could take place in a real life situation.

4.4 Boundary and initial conditions:

Boundary and initial conditions are very important for a meaningful solution of any partial differential equation and unfortunately for this class of problems its is practically impossible to know in reasonable details the existing conditions for heads and the original distribution of the different phases.

5. EXAMINATION OF HETERGENEITY ROLE

5.1 Experimental examination

To demonstrate the significant role of heterogeneity of aquifer material on the distribution and remediation of LNAPLs, an experimental set up was fabricated in order to examine physically this process in a simple one dimensional layered aquifer. The physical model shown in figure 1 consists of a tank containing two end reservoirs to control the water table, a left reservoir through which the LNAPL is spilled, monitoring wells and a right reservoir through which the free product is extracted. This tank was filled with uniform porous media consisting of glass beads of size 8/12 (passing #8 and retained on # 12). An idealized heterogeneity is created by introducing a thin layer of uniform sand having an approximate diameter of 1.2 mm (retained on # 16). Figure 2 gives the mathematical model prediction for the LNAPL saturation along a vertical profile which is presented by the smooth curve indicating the expected uniformity. However the physical model clearly indicate a non-uniform behavior and LNAPL fingering as shown in figure 3 which could not be predicted by sophisticated mathematical models described above. **5.2**

Hypothetical examination

Consider the hypothetical vertical profile of the subsurface shown in figure 4. This could be the case after a uniform wide spread contamination and the removal of as much free product as possible. It can be noted that near the water table and at the clay lenses, hot spots, which contain discontinuous free product, are created. Since vapor extraction is a popular technique for treating the residual contamination it could be selected as means for clean up. However, during the vapor extraction process, shown in figure 5, it would be difficult for air to flow close to these hot spots due to the reduction in the relative permeability resulting from heterogeneity as well as reduced air saturation. The logical result of this is the inefficient cleanup particularly near the hot spots even after long time of remediation.

Fig. 1. Physical model

6. SUBSURFACE RESTORATION

After controlling contamination source and stopping bleeding quickly and spending sometime to understand the subsurface condition and to figure out the extent of contamination, the dissolved phase could be a priority since it may directly affect water supply. A technique such as pump-and-treat could de used here. Selection of number of wells, their locations, flow rate and time variations are selected solely based on model predictions

Dealing with potential sources for groundwater contamination in the form of residual hydrocarbon in the unsaturated zone must be done through designing a treatment system that promotes mass transfer into the vapor phase and/or enhancing the biodegradation of hydrocarbon mass by subsurface microorganisms. Both processes are expected to take long time due to the nature of these processes. Incorporating conditions related to the subsurface heterogeneity and initial moisture and contaminant phase distribution into models is very important factor that influences the success of the restoration effort. Free phase product near the water table acts as a continuous source of groundwater contamination which may be dealt with using extraction wells or trenches but this process will remove only part of the product converting the other part into residual form. This process is always incomplete and costly and sometimes time consuming. Modeling is a common technique utilized heavily in designing, evaluation and operating the treatment of such phases of contaminants in the subsurface and any problems in the modeling used will be reflected on the resulting treatment.

Subsurface restoration is rarely attained using conventional treatment and further this inherently complex task requires long time in ten years and extremely high cost. The committee on groundwater cleanup alternative, in National Research Council (1994), estimates that the cost of clearing up sites in the US where groundwater and soil are contaminated could reach $1 trillion over a period of 30 years. To evaluate performance of pump-and-treat systems they reviewed 77 sites throughout the US where such systems are in use. At 69 of these sites the cleanup goals have not been reached.

Subsurface treatment could even make a bad situation even worse by creating new channels through which contaminant transport may be facilitated. National Research Council (1994) describe the case of south Brunswick, NJ where a computer manufacturing facility carried a cleanup process for six years and stopped thinking that the process was complete. After three years the contamination was back and worse than ever in some locations.

To measure the success of the site remediation one must assure the elimination of any potential contamination source in the residual phase. Obviously, heterogeneity made it essentially impossible to have a successful remediation.

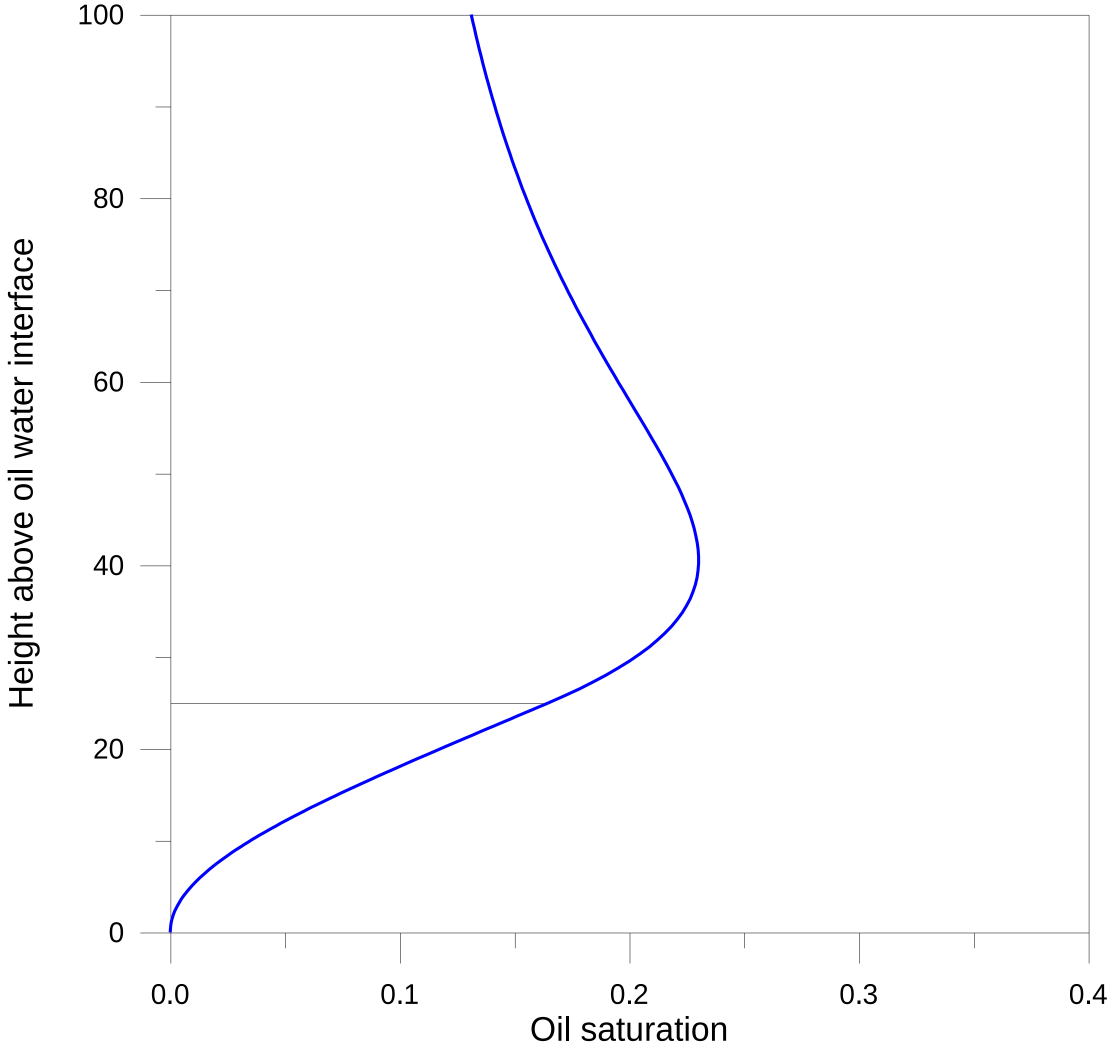

Fig. 2. Model predicted LNAPL saturation along the vertical

Fig. 3. Effect of heterogeneity on flow and distribution of LNAPL

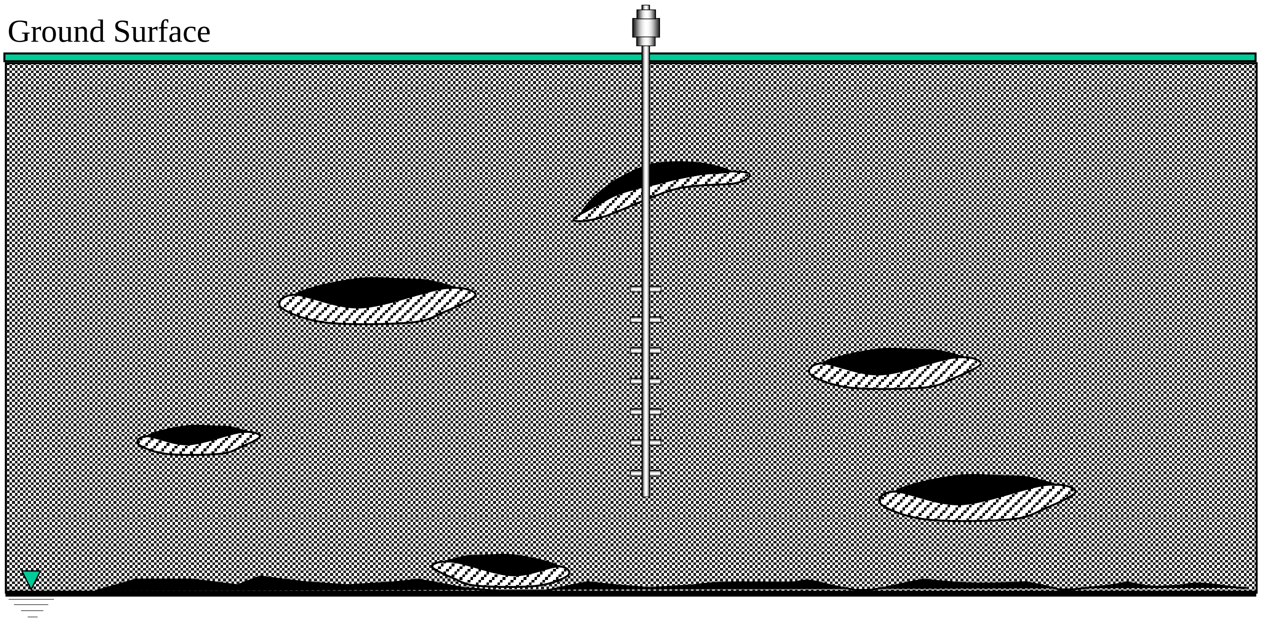

Fig. 4. Vertical profile in a polluted aquifer with clay lenses

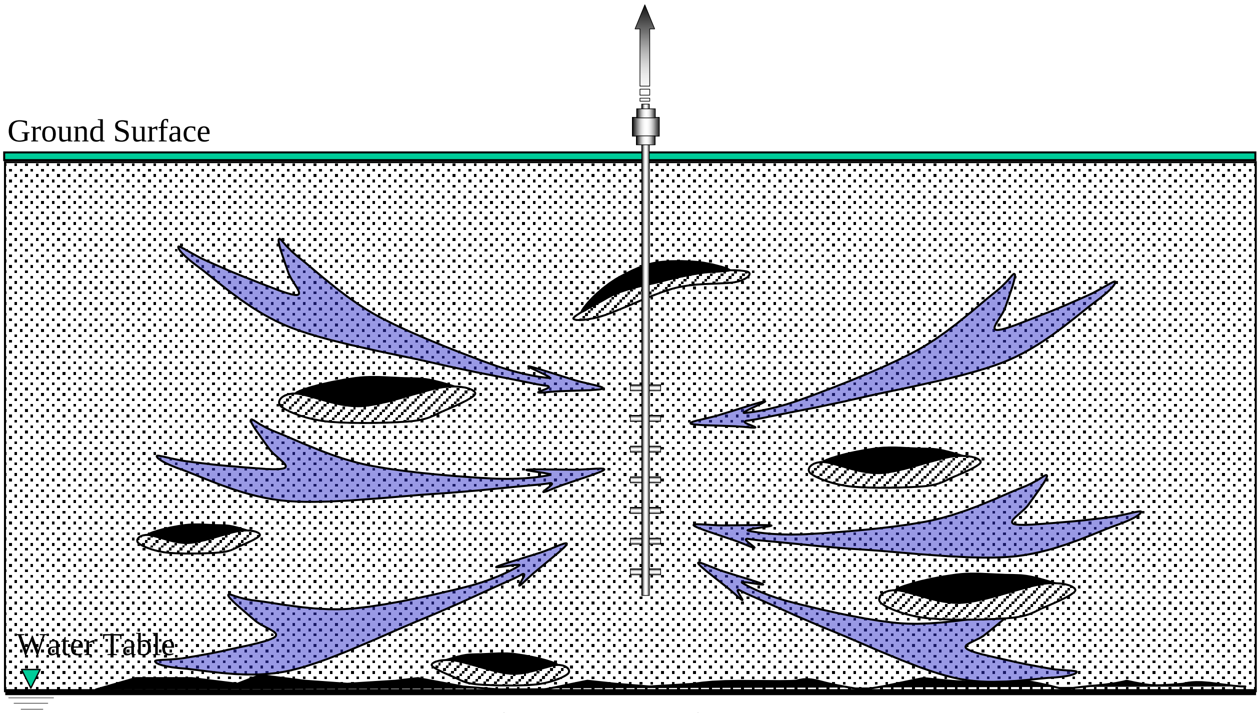

Fig. 5. Aquifer during late stages of soil vapor extraction

7. SUMMARY AND CONCLUSION

Characterization, analysis, design and operation of an aquifer remediation operation involve many challenges and difficulties created by the nature of the subsurface being hidden and full of heterogeneity and difficult to explore in detail. It is extremely difficult to accurately predict the fate and distribution of contaminants once they are released in the subsurface due to the inherited natural heterogeneity of this environment. As a result, any effort to clean up the subsurface would have limited effectiveness. Modeling is an essential part of such projects and any design or selection of operating condition and in turn the overall performance will be influenced by how accurately real conditions were presented in the model. This accounts for the fact that remediation of contaminated aquifers is rarely successful. One way to try to avoid such problem could be through reducing or preventing, if possible, groundwater contamination in the first place by regulating USTs and requirement of continuous maintenance and monitoring.

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