Literature Review on NAPL Contamination and Remediation

Joint Technical Report

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1 Introduction

Remediation of polluted soils and groundwater is of major concern due to the increasing number of contaminated aquifers. Subsurface aquifers constitute one of the most important sources of drinkable water. In recent years, water needs have been increasing due to increases in development and human population.

Several sorts of contaminants can be found in groundwater: metal ions, pesticides, aliphatic and aromatic hydrocarbons, polycyclic hydrocarbons, chlorinated hydrocarbons, etc. The toxicity of these compounds varies and so do guidelines that establish allowable concentration levels in drinking water. Among the aforementioned types of compounds, a particular importance is assumed by those which exist as a separate phase when their concentrations in water exceed a certain limit. The transport behavior and dynamics of multiphase contaminants are very different from their dissolved counterparts, and are very difficult both to describe and to model. Several phenomena can take place, such as organic phase trapping, formation of ganglia and pools of contaminant, sorption, hysteresis in both soil imbibition and drainage, capillarity, fingering, and mass-transfer. In such cases, our ability to describe and predict the fate of a contaminant plume in which a separate organic phase occurs is limited, and research within this field is quite open. Much effort has been devoted in trying to describe the characteristics of the phenomena occuring in multiphase systems, and several models and formulations have been proposed for predicting the fate of contaminants when present in such systems (see *Miller et al.* 1997) for a review on multiphase modeling in porous media). Work has also been done for modeling human intervention techniques for containing and/or reducing soil contaminantion (*NRC*, 1994), such as pumping, clean water-air-steam injection, soil heating, surfactants, biological methods, etc. Finally, much work has also been done on the numerical solution of mathematical models whose complexity does not allow for an analytical solution.

Among the dozens of remediation methods which have been proposed and which are strongly dependent on site environmental conditions, biological methods are achieving increasing importance, due to their "naturalness" and their low costs (*NRC*, 1993) . It has been noticed that soil microorganisms are able to degrade several classes of compounds, in particular those which partition between an aqueous and an organic phase, or sometimes also gaseous phase, for e.g., hydrocarbons, chlorinated compounds, pesticides. These compounds, or better said, their fractions dissolved in water, are liable to be metabolized by subsurface microrganisms which have the capability to degrade the compounds and to transform them into carbon dioxide and/or other compounds, which are less toxic or unnoxious. Several laboratory and field studies have been conducted for assessing and evaluating the capability and the limits of soil microorganisms to degrade several classes of contaminants (*Mayer et al.*, 1994, 1995, 1996, 1997) . Much work has also been devoted to modeling biodegration of groundwater contaminants.

The outline of this report is as follows: section 2 gives a brief description of the characteristics and properties of NAPLs, including a review of the literature with regards to formulations and modeling; section 3 discusses biodegradation of contaminants and past efforts at modeling biodegradation; section 4 surveys specific remediation technologies and experiences; and section 5 discusses open issues for further research. In the final section possible lines of research for the second phase of the PhD program are indicated.

2 NAPLs

Nonaqueous phase liquids (NAPL) are hydrocarbons that exist as a separate, immiscible phase when in contact with water and/or air. Differences in the physical and chemical properties of water and NAPL result in the formation of a physical interface between the liquids which prevents the two fluids from mixing. The interface is a physical dividing surface between the bulk phases of the two liquids, but compounds found in the nonaqueous phase are not prevented from dissolving into the groundwater under appropriate conditions. Immiscibility is typically determined based on the visual observation of a physical interface in a water- hydrocarbon mixture. There are numerous methods, however, which are used to quantify the physical and chemical properties of hydrocarbon liquids (*Mercer and Cohen*, 1990). NAPLs are typically classified as either light nonaqueous phase liquids (LNAPLs), which have densities less than that of water, or dense nonaqueous phase liquids (DNAPLs), which have densities greater than that of water.

The general chemical categories are halogenated, non-halogenated semi-volatiles, and halogenated volatiles. These compounds are typically found in the following wastes: hydrocarbons (mono-aromatic and aliphatic), polyaromatic hydrocarbons (napthalthene, antracene, benzopyrene), organic solvents, wood preserving wastes (creosote, pentachlorophenol), coal tars, and pesticides. The most frequently cited group of these contaminants to date are the chlorinated solvents (such as trichlorethylene — TCE).

2.1 LNAPLs

LNAPLs affect groundwater quality at many sites in many countries. Generally, major groundwater contaminations due to LNAPLs results from the release of petroleum products. These products are composed of chemicals with varying degrees of water solubility. Some additives (e.g., ethers and alcohols) are highly soluble, while other components (benzene, toluene, ethylbenzene, xylene — BTEX) are much less soluble. The solubility of other compounds is strongly dependent on the range of conditions present at the site. In general, LNAPLs represent potential long-term sources of groundwater contamination (US EPA, 1995) .

Movement of LNAPLs in the subsurface is controlled by several processes which can be described as follows. If a small volume of LNAPL is released, it will move through the unsaturated zone where a fraction of the hydrocarbon will be retained by capillary forces as residual globules in the soil pores, thereby depleting the contiguous NAPL mass until the movement ceases. On the other hand, if the quantity released is sufficient, LNAPL reaches the physical barrier given by the capillary fringe zone, i.e., the water table. At this point, LNAPL begins to spread laterally, floating on top of the capillary fringe zone. A large continuous LNAPL layer can depress the capillary fringe zone and the level of the water table. Finally, LNAPL begins to dissolve (depending on the specific solubility in water) in the groundwater and begins to be transported by the general groundwater motion.

2.2 DNAPLs

Dense nonaqueous phase liquids (DNAPLs) are present at numerous hazardous waste sites and are suspected to exist at many more (*US EPA*, 1991). Numerous variables influence DNAPL transport and fate in the subsurface. DNAPLs are complex, largely undetected, and are likely to be a significant limiting factor in site remediation. Like LNAPLs, DNAPLs produce residual saturation blobs and ganglia, migrate downward until the capillary fringe zone is reached, leaving behind a trace of residual saturation zone. After reaching the saturated zone, DNAPLs can partially spread laterally (when a light fraction is present), partially dissolve in the aqueous phase, and continue to migrate downward due to the gravity effect. Partial dissolution in water causes the organic plume to contaminate a much larger zone, due to the groundwater movement of the saturated zone. Gravity driven migration, on the other hand, causes the dense organic plume to reach the bottom (a possibly present impermeable or semipervious layer of clayey soil) of the phreatic aquifer.

If sufficient amount is present, DNAPL may accumulate at the bottom layer and then move down the slope. The accumulation DNAPL forms a contaminant reservoir that can dissolve and pollute the groundwater for a very long time due to its generally low solubility. Also, their tendency to reach the bottom of the aquifers make their removal difficult.

2.3 Which phenomena are taking place ?

When dealing with multiphase flow in groundwater, knowledge of the phenomena taking place is required. Generally, the most common phenomena one encounters when dealing with multiphase-multispecies transport processes, are the following: advection, dispersion, diffusion, adsorption, dissolution, evaporation, biological activities, thermal effects, capillarity, mass-transfers, etc. As can be understood, the previous list draws a dramatically complex scenario to handle. Thus, it is very important to have some sense of the prevailing conditions in the aquifer, in order to establish a priority list of the importance of the various phenomena taking place. This allows for some simplifications and/or approximations which do not limit our information about the system, but reduce the complexity of the description. For example, when high groundwater velocity and high pressure fields are present, the movement of the organic phase in the aqueous phase can be considered almost exclusively advective, thus dispersion-diffusion can be neglected. On the other hand, when velocities are low, dispersion achieves importance and can be the leading physical phenomena.

Below a list of phenomena characteristic of multiphase flow is given. Each phenomena is briefly described and some references of previous work and research on these topics.

2.3.1 Fingering

Fingering can be described as the set of irregularities which appear when the front of a non-wetting phase substance is moving through a medium saturated with a wetting phase. Experiments measuring the dissolution front of TCE were presented in *Imhoff et al.*, 1993. The dissolution front was found to be unsteady and irregular and it measured between 11 to 20 mm in the experimental systems (measurements were made by means of attenuation of gamma radiation). An interesting theoretical and experimental investigation was conducted by *Imhoff and Miller*, 1996a, *Imhoff et al.*, 1996b: solubilization of TCE was studied and a model proposed for describing the presence of fingering phenomena in 2-D and 3-D experiments. The mechanisms of fingering, i.e., the creation of an irregular dissolution fingers and the presence of dissolution instabilities due to interaction of fluid flow with dissolution-induced porosity changes, was described and the possibility to predict the scaling of fingering was analyzed (*Imhoff and Miller*, 1996a) . A stability analysis performed on the model allowed the authors to evaluate the range of conditions generating concentration and phase front instability. Results compared favourably with experimental investigations. A good agreement was also obtained between model predictions and a series of laboratory experiments (*Imhoff et al.*, 1996b) aimed at evaluating the effect of gravity, porous medium structure, Darcy flux, initial residual saturation, medium particle diameter, and NAPL composition on dissolution fingering. Scaling effects of fingering were also captured quite well. It was found that fingering developed after some time and that the length of the dissolution front before finger development was smaller than the zone of NAPL residual. In the same work, a three-dimensional experiment using a 1-m long cell is documented where front fingers reached up to 30 cm in length, i.e. 30% of the total length of the experimental cell.

2.3.2 Residual saturation, pools, ganglia, and organic trapping

Multiphase flow of immiscible and/or miscible compounds depends upon phase saturation (which can be defined as the volume of the phase to the total pore volume). It has been noticed by many authors (see *Aziz and Settari*, 1979, *Allen et al.*, 1988 and reference listed therein) that phase saturation, partial pressure of the phase, and hydraulic permeability are not completely independent. Several relationships (the so-called p-S-k curves) have been proposed (see *Miller et al.*, 1997 for a complete list). According to these relations and observation, when the saturation of a certain phase exceeds a certain threshold value, this medium becomes completely impermeable to the other phases. This phenomenon causes the so-called phase trapping, which is manifested as small droplets, pools and/or ganglia which cannot be displaced by the movement of another phase. This organic phase presence in soils is called residual saturation or residual organic liquid trapping. *Conrad et al.*, [1992] presented interesting visualizations of residual saturation, ganglia, and phase trapping in porous media. When phase trapping occurs, it has a strong influence on the total transport conditions, due to the impossibility to remove organic trapped liquids at normal pressure gradient conditions. The practical implication of these phenomena will be discussed in section 4.3.2.

2.3.3 Capillarity

Capillarity is the tendency of a fluid displacing another fluid phase occupying the pores. Capillarity is strongly dependent on the properties of the two phases in contact, on surface tension, and on porous medium characteristics. Capillarity is characterized by hysteresis: the saturation of the porous medium is not only a function of pressure conditions and on soil characteritics, but also on previous history, i.e., if the system is under imbibition or drainage. The effect of capillarity was found to be important in lateral spreading in a heterogeneous porous medium in which an accidental release of organic liquid occurs (*Kueper and Gerhard*, 1995) : low capillarity pressures corresponded to an increase of lateral spreading. Effects of capillary forces in a heterogeneous porous medium were also studied by *Van Dujin et al.*, 1995 by means of a 1-D two-phase flow model. In their work in permeability and porosity at the interfaces of the rocks are discontinuous and a regularization technique was employed for making saturation match at both sides of the discontinuity. The application of this condition shows that trapping of the wetting phase may occur near heterogenities. Capillary forces have been found to be important particularly when trying to mobilize organic contaminants. A theoretical analysis was conducted on mobilization of NAPL by *Hunt et al.*, 1988a. The possibility to mobilize NAPL as a separate phase was found to be impossible at reasonable hydraulic gradients due to capillary forces and sorption effects. The only viable possibility of removal was via mass-transfer from the organic to the aqueous phase: this, however, was limited by the very low mass-transfer coefficients. Theoretical results were supported by column experiments (*Hunt et al.*, 1988a) , in which the potential of steam injection for mobilizing NAPL was found to be quite promising, in terms of both results and cost.

2.3.4 Mass transfer phenomena and description

Mass transfer is one of the fundamental phenomena taking place in groundwater, particularly in connection with the problem of removing trapped NAPLs. It is not possible to remove residual NAPLs by means of simple soil flushing, due to the fact that the relative permeability approaches zero under residual conditions (*Allen et al.*, 1988). Under such conditions, mass transfer becomes the only way for removing NAPLs by means of solubilization in water. Solubilization is also very important for making organic matter available to microorganisms which can degrade them. An experimental investigation (*Miller et al.*, 1990) was conducted for measuring mass-transfer coefficients between toluene and water in glass bead media systems. The rate of interphase mass transfer was investigated in two-fluid (water and oil) systems as a function of aqueous phase velocity, aqueous- and nonaqueous phase fluid saturations, and porous media characteristics. Mass transfer was found to be directly proportional to aqueous phase velocity and nonaqueous saturation level, but no effects were found for different particle sizes. Some adimensional correlations were determined for mass transfer coefficients and compared to those found in the literature. It was also found that equilibrium was achieved quite rapidly (at least for the case of two fluid phases) for a wide range of conditions (phase saturations and velocities), and this was confirmed by the mass-transfer coefficients determined by measurement. Mass-transfer coefficients by means of experimental investigation were also determined for TCE (*Imhoff et Jaffè*, 1993) . In this case the mass transfer coefficients were found to be a function of Darcy flux, TCE volumetric content, and of the distance into the region of residual TCE. This work also reports the presence of some TCE (0.002 g/l) after 290 pore volumes of water flushing the experimental system, thus confirming the difficulty of a fast and complete removal of NAPLs from porous media.

Another experimental investigation on NAPL mass-transfer coefficients was performed by means of a laboratory 1-D column (*Powers et al.*, 1994). Some experiments of NAPL dissolution were performed for studying the removal of NAPLs trapped in a sandy porous medium. It was found that the number of pore volumes of water flushing the porous medium was much higher than that predicted by the local equilibrium conditions. In this case, it was found that grain size was affecting the rate of NAPL removal and that large blobs were more difficult to flush, probably for the irregularity of the large blobs of residual organic contaminant. In the same work (*Powers et al.*, 1994), a mathematical model was calibrated by means of experiments on styrene, and it was found that this calibration was sufficient to predict the dissolution rates of experiments conducted on TCE in the same sandy porous medium.

Mass-transfer between liquid and gaseous phases is also important, since organic pollutants can evaporate into the gaseous phase. This change of phase can have relevant consequences, in characterizing both the movement and the possibility of removal of an organic substance in saturated and unsaturated porous media.

A mathematical model was developed to examine the impact of gas advection, diffusion, gas-water mass-transfer, gas-water partitioning, sorption, and intra-aggregate diffusion on the subsurface movement of organic vapors (*Gierke et al.*, 1992) . Laboratory experiments using toluene were performed to determine the validity of this model and to investigate the impact of the various mechanisms on the transport. Results of these experiments showed the following: 1) gas diffusion and advection had the greatest impact on the phenomena; 2) intra-aggregate diffusion was important for gas phase velocities greater than 0.05 cm/s; 3) gas sorption was found to be negligible when liquid water was present. These findings support the assumption that nonequilibrium should be accounted for in soil vapor extraction models.

2.3.5 Local equilibrium and nonequilibrium conditions

Mass-transfer is strongly related to equilibrium and to nonequilibrium phenomena. Mass-transfer becomes important when local equilibrium assumptions cannot be invoked. Nonequilibrium has been studied by several authors both by means of numerical investigation and laboratory experiments. A theoretical investigation was conducted for assessing the importance of nonequilibrium in dissolution of NAPLs (*Powers et al.*, 1991) . This study was conducted by means of a 1-D advection-dispersion mass balance equation incorporating first order interphase mass-transfer rate relationships and temporal changes in blob configuration. Both analytical and numerical solutions were computed and a sensitivity analysis performed for evaluating the importance of mass-transfer coefficient, blob size and shape, and Darcy velocity on the results. Nonequilibrium was found to be relevant, as expected, for high Darcy velocity, and for large blob sizes. The effects of these parameters on possible remediation scenarios are also discussed and compared to the case of contaminant removal under ideal LEA (local equilibrium assumption) conditions.

Other nonequilibrium studies dealt with application of the mobile-immobile model or the dual porosity approach to the organic immobile contaminant which was assumed to be at residual saturation acting as a sorbing phase(*Brusseau*, 1992). The fraction of organic contaminant which is dissolved in water was considered as a desorbed pollutant from the organic immobile phase. Some curves from the literature were successfully predicted by the model, and through a series of simulations it was found that the phenomena resulted to be mass-transfer limited, particularly in cases in which some induced gradient conditions, such as those superimposed by the classical pump-and-treat systems (PAT) systems, hold (*Brusseau*, 1992).

A two-dimensional model was developed (*Mayer and Miller*, 1996) for studying the effects of mass transfer and porous media heterogeneity on NAPL dissolution. Simulations were performed to observe dissolution rate variations and the degree of NAPL-aqueous phase nonequilibrium as a function of two aqueous phase velocities and five forms of the NAPL-aqueous phase mass transfer formulations. The authors introduced an integral form of the Damkohler number for evaluating the degree of nonequilibrium present in the system under study. Variations in mass elution rates were investigated in homogeneous and heterogeneous media. Generally, mass removal was found to be quite insensitive to the mass-ransfer formulation, yielding results similar to those obtained using a local equilibrium approach for all but one of the mass-transfer formulations. This last formulation showed the most nonequilibrium behaviour. In the case of heterogeneous soils, dissolution rates were found to be smaller than in the previous cases: this was explained as a result of the presence of relatively immobile regions of NAPL, in which the mimimum residual saturation was reached and some immobile pools were formed. These results support the importance of statistical characterization of porous media.

2.4 Issues in description of multiphase flow

2.4.1 Standard approach

The mathematical formulation of multiphase flow and transport is very complex, due to the number and the complexity of phenomena involved. The starting point is to write the standard continuum balance equations (mass, momentum, and energy conservation) for general compositional multiphase flow (*Aziz and Settari*, 1979, *Allen et al.*, 1988, *Miller et al.*, 1997, *Gray and Hassanizadeh*, 1998) of n_p phases and n_s chemical species. Generally, the most advanced models account for the nonaqueous, water, solid, and gas phases, but some other phases can be included as well (colloidal, microemulsion, etc). The mass balance transport equations are supplied with separate momentum balance equations for determining the pressure and velocity fields. Darcy's law is invoked to establish a relationship between pressure and velocity fields. Darcy's law, however, holds for a restricted range of conditions, i.e., for low value of Reynolds number (generally lower than unity), and some open issues still remain about the validity of its extension to the multiphase case, as e.g. *Hassanizadeh and Gray*, 1993. The dispersion mass phase of solute is modeled by an estension of the Fick's first law. The energy balance equation is added to the model to account for temperature effects. This equation, however, is often neglected due to the low variations in thermal conditions normally encountered in groundwater. It is taken into account, for instance, when modeling thermal treatments such as steam injection and soil heating, or when strong evaporation occurs. The closure of the mass-momentum-energy system of equations is obtained by means of a set of constitutive relationships.

The complete set of balance equations is very complex and extremely difficult (and sometimes impossible) to be solved in practice. Some assumptions are made in order to reduce the complexity of the problem and to make the system of equations amenable to numerical solution. Some of the most common simplifying assumptions (*Miller et al.*, 1997) are: 1) nondeformable porous medium; 2) inert solid phase (no sorption); 3) possibility of neglecting some species which do not affect the phenomenon and the solution; 4) use of a subset of lumped chemical species representing the whole set of components present in the system; 5) local equilibrium conditions (this is generally related to different time scales of the phenomena taking place); 6) different time scale variations for some variables. These simplifications can be very helpful in some cases, but are unacceptable in others for which an almost complete formulation is necessary. A proper understanding of which phenomena are important in the system under study is fundamental for properly simplifying the full formulation of the multiphase-multicomponent system.

Determination of the constitutive relationships is still a matter of much discussion. In particular, the most important uncertainties regard the p-S-k curves which relate pressure, phase saturation, and hydraulic conductivity of a porous medium (*Bear*, 1972) . Two main problems are generally encountered: 1) the determination of these relationships is generally made for the two-phase case, and then for three-phase systems it is generally obtained by combining sets of different two-phase relationships; 2) these relationships are not unique, particularly when hysteretic conditions occur. p-S-k relationships can also sometimes violate thermodynamic constraints (*Hassanizadeh and Gray*, 1993).

2.4.2 Integral continuum approach

Due to the aforementioned problems, some alternative solution approaches have been attempted for solving these thermodynamic paradoxes, and one of the most promising is based on "contact lines"(*Hassanizadeh and Gray*, 1993, *Weeber*, 1996) . In this approach balances of mass, momentum, energy, and entropy are made and a rigorous and complete set of equations is obtained. The balance equations describe the conservation of the aforementioned properties across contact areas, contact lines, and contact points. Actually, this approach is aimed at provinding insights and understanding for theories of two-phase flow. Also, interfacial areas which play an important role in two-phase flow are brought into macroscale models. Unfortunately, this approach is very expensive in terms of memory and computational load, since it generates 35 primary unknowns and 111 secondary unknowns simply for the two-phase case (*Miller et al.*, 1997). The complexity of this formulation generates a computational load that is definitely beyond the current most powerful supercomputer available.

2.4.3 Upscaling

Some considerations are worth making with regards to upscaling. Let us consider the determination of the p-S-k curves: measurements are generally made at laboratory scale, but the values of the parameters obtained are applied to field scale, i.e., at a scale at which the types of heterogeneities and anisotropy are generally much different (*Lenhard*, 1994, *Steffy*, 1997), and see the discussion in *Miller et al.*, 1997) . It is often not possible to discretize the domain under study and include heterogeneities explicitly, because of the limitation in memory and computational load. Furthermore, the problem of scaling is related to all the parameters of the models, such as permeabilities, dispersivities, etc. One theoretically possible solution would be also a sort of multiscale approach in which a coarse scale problem would contain a set of embedded finer scale problems: however this would be unfeasible in terms of computational complexity. Some approximations are then necessary in order to "transfer" all the information embedded in a smaller scale to a larger and coarser scale. Antoher approach is to replace the heterogeneous medium with an equivalent homogeneous medium. Then, original p-S-k relationships have to replaced with "effective" relationships for the "homogeneous" medium (see e.g. *Braun et al., 1998*).

2.4.4 Stochastic approach

The aforementioned problems related to computational complexity, upscaling, limits of approximations, and generally the impossibility to perfectly characterize groundwater or a subsurface environment, have led some researchers to turn to stochastic modeling and solution approaches.

A stochastic approach can be applied in different ways. For example, *Kueper and Gerhard*, 1995 performed results of two-phase flow simulations in which the distribution of hydraulic conductivity was stochastic for each cell of the computational domain. On the other hand, a stochastic approach can imply the solution of a set of stochastic partial differential equations, such as in the Lattice Boltzmann method which is one of the most common methods for solving partial differential equations. This method seems quite promising, from both the phenomenological and computational points of view (*Miller et al.*, 1997).

Another quite promising method is the diagrammatic perturbation method (*Christakos et al.*, 1994) which is based on a particular representation of flow: it has been applied successfully to single phase flow and could be quite attractive in extension to multiphase flow. Also, the solution of the diagrammatic multiphase flow systems can be obtained by a decomposition of the stochastic equations into a deterministic part that can be solved using both analytical and/or numerical techniques plus a random component including fluctuation effects. Another quite promising technique is the spatial transformation of stochastic PDEs which leads to a set of monodimensional ODEs that can be efficiently solved on parallel computers.

2.4.5 Network models

Modeling of NAPLs implies the treatment of multiphase systems which, in the past, were always represented as a set of PDE equations coupled in different fashions. The numerical solution of these systems is quite difficult and computationally demanding, particularly when many of the usual simplifications are revoked. A different method of approaching multiphase problems is to represent the porous medium (pore space and pore solid) as a network of capillary tubes which are interconnected to eachother (see *Blunt et al.*, 1992a, *Celia et al.*, 1995 for a review of the state-of-the-art of network modeling). A rough description of the porous medium in a network model approach is as a set of balls and sticks which are interconnected.

Network models offer a systematic approach to estimating NAPL ganglia sizes and shapes, estimating interfacial areas, modeling mass transfer at interfaces to study processes such as evaporation and NAPL dissolution, and modeling heterogeneities to study scaling relationships in multiphase porous media systems.

In the work of *Celia et al.*, 1995 some comments are made about the real capabilities and possibilities of network models of describe properly multiphase flow in porous media. Network models have demonstrated that pore-level spatial correlation allows the generation of Pc-S (Pc

is the capillary pressure) curves with relatively gradual slopes. This may be important to model many real soils, and provides directions for small-scale measurement studies. Modeling studies based on recent observations concerning imbibition mechanisms have highlighted the important role that snap-off and piston displacement play in imbibition processes, although some care must be exercised because the physical experiments on which the models are based have been performed on the relatively simple geometry of etched-plate micromodels. Such studies point to the importance of the wetting-phase films, and recent theoretical and modeling studies have provided some directions for proper inclusion of wetting films in pore-scale multiphase flow models. Some new results are found in the work of *Reeves and Celia, 1996* . On the basis on a hypothesis for predicting a functional relationship between capillary pressure, saturation, and interfacial area, a network model was developed to test this hypothesis. By simulating microscale physical processes using volume averaging to derive the macroscopic measures of saturation and fluid-fluid interfacial area per volume of porous media, interesting results were obtained. These indicate that a smooth, though complex, functional relationship exists at the continuum scale. These results have direct relevance to constitutive theory and the modeling of nonaqueous phase liquid dissolution processes.

2.5 Modeling NAPL movement

Mathematical and numerical modeling of NAPLs has been a challenging issue. In the last two decades much effort has been devoted to modeling groundwater flow and transport, for both multispecies and multiphase reactive systems. Basically, two main motivations have led researchers to modeling multiphase flow: first, the need to improve the yields of petroleum reservoirs (*Allen et al.*, 1988, *Trangestein and Bell*, 1989, *Aziz and Settari*, 1979), by optimizing water injection for oil displacement towards extraction points, by fluidification, etc.; secondly, and recently, groundwater pollution and remediation problems, with regard to the possibility of monitoring contamination from organic compounds and of correctly predicting the effects of soil remediation interventions.

The petroleum and groundwater classes of models are quite similar, since the set of equations describing the phenomena are fundamentally the same. However, substantial differences are present with regards to the relative importance of the phenomena that are taken into account, the range of conditions (concentration, pressures, temperatures, etc) considered, and the time scales involved in the processes. These issues lead to strongly different model formulations and simplifications and, as one could expect, to different numerical solution techniques. The gap between these two classes of approaches has been reduced in recent years: current models can be applied to increasingly wider sets of conditions such as those encountered when performing soil remediation. Pump and treat systems (PATs), injection of hot water, steam and/or different gases (air, oxygen, methane, etc), soil heating, and chemical oxydating and reducing compound injections, are only a few examples of applications common to both subsurface and oil recovery scenarios (*Aziz and Settari*, 1979, *Allen et al.*, 1988, *Trangestein and Bell*, 1989) .

It is not the purpose of the current work to list all the models and/or numerical solution techniques available in the field of multiphase flow. However, in the following sections a brief summary is given, starting with simple formulations up to much more sophisticated ones.

2.5.1 Two-phase flow

Two-phase flow in porous media has been widely studied, since it is the least complex polyphasic system in porous media. The easiest formulation of two-phase flow is the Buckley-Leverett model, or, as widely known, the phase displacement model. When considered in 1-D, the two-phase flow equation set can be directly integrated analytically (*Allen et al.*, 1988) and it represents a classical problem against which numerical models can be tested. Since the Buckley-Leverett equation is quite unsatisfactory for treating the generality of problems and conditions encountered in real scenarios, increasingly complex formulations have been considered. Several two-phase flow simulators have been proposed in the literature and several numerical formulations have been adopted for computing an accurate numerical solution. *Kueper and Frind*, 1991 proposed a two-phase flow solver (organic and aqueous phase) in which primary variables were wetting phase pressure and saturation, which allowed for the disappearance of the non-wetting phase without numerical problems of low-saturation superimposition of the non-wetting phase. The numerical solution was computed by means of finite differences and fully implicit Newton-Raphson iteration. The performance of the iterative solver was also discussed (Dupont-Kendall-Rachford iterative solver). The model was tested using a 2-D example with 22500 cells and random heterogeneous permeability (*Kueper and Frind*, 1991b): it was found that migration of nonwetting liquid was extremely sensitive to subtle variations in the capillary properties in the porous medium and physical properties of the fluids. A numerical scheme of two phase flow (water and air) in porous media was presented by *Celia and Binning*, 1992. The scheme was found to be oscillation-free and mass conservative and was tested on the case of air and water two-phase flow, within the range of validity of the Richards equation (which approximates two-phase flow — air-water system — by means of a single nonlinear flow equation). With respect to the Richards equation, the two-phase flow model is capable of dealing with a wider set of conditions, such as scenarios in which air pressure cannot be assumed to be atmospheric (such as air injection, soil venting, air sparging). Air sparging was simulated by means of a two-phase flow model (*van Diske et al.*, 1995) in an axially homogeneous porous medium. The numerical model, based on the mixed form of the Richards equation, is compared with two different analytical solutions which approximate the phenomenon under some simplifying assumptions (steady-state, 1-D models, etc.) Computations, in good agreement with the analytical solutions, enable the determination of the radius of influence of air sparging. Air sparging simulations suggested that steady state was achieved in a short time.

2.5.2 Three-phase flow

Three and, more generally, multiphase flow is the logical extension of two-phase flow and can be considered as a "must" for a full description of subsurface NAPL contamination phenomena as close as possible to real field conditions. Organic compounds, when in contact with the aqueous phase, can partially dissolve in it, but they are also liable to evaporate and diffuse into the gaseous/air phase. On the other hand, when, as it commonly occurs, a mixture of hydrocarbons is present in the aqueous and/or organic phase, lighter hydrocarbons tend to pass more easily into the gaseous phase, while the heavier ones remains in the liquid phases. Among the many investigations conducted in this field, *Huesemann*, 1995 proposed a model for predicting the mixture of hydrocarbon distribution among different phases. The determination of phase compositions is quite complex and has been widely studied in the literature (*Kikic and Fermaglia*, 1991), even if results thus far cannot be considered conclusive. The strong dependence of phase presence on phase composition has led to the development of several compositional models in which the transport of several phases was coupled with variations in the compositions of the phases themselves.

The complexity of the mathematical formulation of multiphase flow models, and, as a consequence, of its numerical solution, has led researchers to devote their effort to two main directions: use of simplifying assumptions for making the model less general but more tractable; formulation of increasingly efficient and robust numerical algorithms to reduce the amount of computations which makes use of models prohibitive in many cases. In the following section a brief review of the work on general multiphase codes is presented.

2.5.3 Simplifying assumptions in modeling multiphase flow

A three-phase flow solution method was proposed for contamination of subsurface porous media by *Abriola and Pinder* 1985. The model treated organic, aqueous, and gaseous phases, and included capillarity, gravity, mass-exchange, and matrix and fluid compressibilities. This work is often referred to as one of the earliest works on compositional models in the field of groundwater hydrology. A numerical model was developed for providing areal analysis of the 3-D spreading of immiscible liquids in groundwater systems (*Wu et al.*, 1994). The mathematical formulation was based on vertical integration of the three-dimensional two-phase flow equations and incorporation of the concept of gravity-capillarity vertical equilibrium (GCVE) in which a vertical balance of gravitational and capillary forces is assumed. The leading assumptions were that under the state of GCVE, the vertical gradients of fluid potentials are zero and that the knowledge of capillary pressure at any point on the reference surface establishes the variation of capillary pressure along the vertical line through that point. An overview of different numerical techniques for solving the nonlinear governing equations was presented together with some special schemes for handling production wells. The solution obtained by this approach was compared with that obtained by rigorous and complete three-phase models. The model was shown to be robust and accurate in three test cases presented and appropriate for personal computers and workstations.

A different approximation approach was presented for modeling the removal of volatile organic carbon by means of soil vapor extraction in the unsaturated zone in the case of a semipervious soil lens (*Ng and Mei*, 1997). Each layer of soil was modeled as a periodic array of spherical aggregates (*Ng and Mei*, 1996a, *Ng and Mei*, 1996b) and the layers were assumed to be shallow. A quasi 1-D model was obtained by means of these simplifying assumptions. The importance of lens permeability, retardation factors, and diffusivity were assessed by means of a set of simulations which were much more efficient than the case of rigorous modeling.

A three-dimensional model was presented for modeling steam flush for DNAPL site remediation (*Forsyth*, 1995) . The model under study, multiphase-multicomponent, was based on a 3-D tetrahedral model. Flux limiters for limiting the artificial dispersion were described, together with the primary variables selection and the thermodynamic state transition rules which regulate, depending on the set of conditions present in the system, which variables are to be assumed as primary and which ones are to be computed in a second phase. A comparison of the model with other formulations was also presented on some numerical test cases of steam flush scenarios.

A powerful model has been developed for simulating fluid flow and transport in variably saturated porous media by *White et al.*, 1995a. The system under study may be nonvolatile three-phase flow. The simulator presented, STOMP, is based on an integrated-volume finite difference solver. The model can treat: multiphase flow, compositional NAPLs, and nonisothermal conditions. The model can be piloted by means of a compilation selection menu from which the chosen version of the code can be produced and compiled. Hysteretic behavior and fluid entrapment are also included in the model. Phase transition algorithms are integrated in the model for handling phase disappearances. Results obtained with STOMP are compared on the basis of some test cases (*Lenhard et al.*, 1995b) with those obtained with the model MODFAT-2D (*Kaluarachchi and Parker*, 1989, *Kaluarachchi and Parker*, 1990).

A model for thermal venting of less volatile hydrocarbons for the unsaturated zone was proposed by *Kaluarachchi and Islam*, 1995a. The model includes nonisothermal gas flow, thermal energy transport, multicomponent mass transport in a multiphase porous medium, and temperature-dependent properties (viscosity, density, diffusion, etc.). The model was tested on a series of numerical simulations in one and two dimensions. Simulations (*Kaluarachchi and Islam*, 1995b) were performed on a mixture of four hydrocarbons differing in their volatility in order to evaluate the effect of thermal venting on the efficiency of removal of contaminant. An increase of 33% in removal of naphthalene (which was the most heavy hydrocarbon) was found with respect to isothermal venting. On the other hand, more volatile compounds did not show any significant increase in removal.

Local equilibrium was the leading assumption of a three-phase compositional simulator (immiscible oil, water, and gas) presented in *Corapcioglu and Baehr*, 1987. The model could treat: mixture of hydrocarbons, several compounds in the water phase, biodegradation (considered as a sink term), saturated and unsaturated zone, and sorption. Local equilibria were assumed between phases and the model was solved by means of finite differences with forward projection method (see *Celia et al.*, 1989) for more details) for evaluating nonlinear coefficients. A sensitivity analysis of the model was also performed by means of some test problems.

The local equilibrium assumption was removed in the numerical compositional simulator developed in *Adenekan et al.*, 1993 for modeling 3-D transient, nonisothermal, and multiphase transport of multicomponent organic contaminants in the subsurface. The model was solved numerically by applying the integral finite difference method (IFDM) which supports the use of irregular meshes. The model included advection in response to pressure, capillary, and gravity forces; interphase mass-exchange for every component; diffusion; and transport of sensible and latent heat energy. The model allowed for phase disappearance and could deal with virtually any number of compounds for each phase. Another compositional simulator of groundwater contamination by organic compounds was presented by *Sleep and Sykes*, 1993. The model included three phases, interphase partitioning, phase density functions of pressure and phase composition, and variable time integration schemes (implicit pressure -explicit saturation). The model was tested against available analytical solutions for simplified multiphase flow and transport test problems. The model was used to investigate the effect of field scale heterogeneity on movement of organic compounds: 3-D simulations of soil vacuum extraction demonstrated the difficulty of removing dissolved organic compounds from the saturated zone with this process.

Considerations for robust compositional simulations of subsurface nonaqueous phase liquid contamination and remediation were presented in *Panday et al.*, 1995. These considerations are implemented in a compositional simulator for nonisothermal problems in which several possibilities are built-in for different configuration scenarios. Some test simulations are presented and the results/performance are compared with those obtained with other solution approaches, whose weak points are discussed.

Variable spatial and time weighting of the advective contaminant mole fraction term were explored as a means of reducing numerical dispersion of contaminant plumes in a multiphase compositional simulator (*Unger et al.*, 1996). The performance of various weighting schemes was considered, in terms of Newton scheme iterations and computational costs. It was found that in homogeneous permeability fields best performance was obtained by means of a nonlinear flux limiter along with fully implicit weighting. For heterogeneous permeability fields, the macrodispersion imparted by heterogeneity dominates numerical dispersion so that smearing of contaminant mole fraction fronts did not appear to be a serious problem.

2.5.4 Oil-reservoir modeling experience

Petroleum engineers have often been interested in modeling multiphase flow for problems which were generally much different from those related to pollution and soil remediation. Differences between petroleum engineers and hydrologists are generally interested in different ranges of saturations of the organic compounds in the subsurface: actually, the concentration values which are of interest for hydrologists are generally several order of magnitude lower than those which are of interest for petroleum engineers. However, soil-monitoring/remediation and oil-reservoir problems are becoming increasingly similar.

Mulder and Meyling, 1991 presented a two-phase flow model using locally refined grids in 3-D. The model implemented a finite-difference multigrid approach in which an operator splitting technique was applied for separating convection and diffusion. The method of characteristics (MOC) was used for the grid-block tracking and for computing movement of the coordinates and/or insertion/deletion of grid points. The conservativity of the flow was assured by means of the mixed finite element method.

A variation of the black-oil model (see *Allen et al.*, 1988 for a detailed presentation of the model) was presented in a new fully implicit fashion (*Huan*, 1985) based on the phase equilibrium concept. At each timestep a flash (nonisothermal compositional equilibrium between liquid and vapor phases) calculation is performed.

Fung, 1994 presented a hybrid control volume finite element method for flexible grid reservoir simulations. This method was used to construct hybrid grids for handling wells. The method considered the use of local cylindrical or elliptical grids for representing near-well flow accurately while honoring complex reservoir boundaries. A control volume finite element model was presented also by *Forsyth*, 1990 for thermal reservoir simulations. The focus of this work was on mesh refinement on structured meshes.

A compositional simulator based on mixed finite elements was presented for modeling oil reservoir multiphase movement (*Durlofsky*, 1993). The simulator, based on mixed finite element/finite volume solution techniques, was developed for handling complex geometries and highly heterogeneous oil reservoirs. The numerical solution is IMPES-type (Implicit Pressure Explicit Saturation) and some 2-D applications are presented.

An analytical exposition of the relationship between two forms of fully compositional isothermal three-phase numerical simulator was presented (*Wong*, 1989). The methods considered are the standard Newton-Raphson solution of the mass/mole conservation equations and associated constraints and the volume balance method, where for each simulator block the pore volume is equated with the combined fluid volume of all the phases. The methods were proved to be essentially the same, although starting from different viewpoints and assumptions.

A control volume finite element method was presented for reservoir simulation (*Fung*, 1992). The technique adopts the usual finite-element shape functions to evaluate flow potentials at the control volume boundaries and uses the conservation equations for each control volume. The technique can handle quite easily local grid refinement for well calculations and can offer some advantages in terms of computational costs.

Local grid refinement techniques were investigated for reservoir flow problems (*Dahle et al.*, 1992). Using a sequential time-marching approach, an effective solution strategy for solving equations governing immiscible displacement in porous medium was described. Numerical solution is computed by combining grid refinement with an operator-splitting technique based on the modified method of characteristics. Grid refinements are performed only across steep phase wavefronts, both for preserving front steepness and accurately describing phase movement in heterogeneous environments.

Several commercial codes (e.g. *ECLIPSE*, 1988) are available. Generally, these codes offer several features and switches for enabling/disabling some calculations, but are not very sophisticated in terms of numerical solution techniques and accuracy of the solution computed.

3 Modeling transport with biodegradation in groundwater

In the last decades, the study of biodegradation of contaminants in the subsurface has achieved increasing importance, particularly when evaluating viable alternatives for groundwater clean-up. Much work has been devoted to mathematical modeling of biodegradation on the basis of laboratory and field investigations. For this purpose, various methodologies have been considered, based on different assumptions, such as: 1) biodegradation takes place in the same phase as the bulk flow; 2) biodegradation takes place in a separate or bacterial phase that is accessible only via mass-transfer from the bulk flow; 3) biofilm models; 4) multiphase flow models.

The first class of models arose from the practical consideration that in several cases the characteristic time of mass exchange between aqueous solution and microbial colonies is much smaller than the characteristic time of concentration variation in bulk flow. There are several examples of this class of models: *Sykes et al.*, 1982 modeled single substrate consumption via a Monod or first kinetics; *Corapcioglu and Haridas*, 1985 included a single substrate plus microbial transport; *Borden and Bedient*, (1986 accounted for a single substrate, an electron-acceptor possibly limiting the degradation kinetics, and microbial transport. A two-dimensional biodegradation model was considerd by *Rifai et al.*, 1988 which accounted for a single degradable substrate and an electron-acceptor whose reaction was, however, instantaneous (i.e., proportional to the total concentration within the bulk phase). *Srinivasan and Mercer*, 1988 proposed a monodimensional biodegradation model including single substrate, dual electron-acceptors, and constant biomass, in which the kinetics of degradation could be alternatively Monod or first order. *Kindred and Celia*, 1989 considered multiple substrates, dual electron-acceptors, and cellular nutrient limitation, while the degradation kinetics was Monod. *Frind et al.*, 1990 presented a case study of transport and biodegradation in which the two-dimensional model included microbial transformation with denitrification and desulfonation. *MacQuarrie and Sudicky*, 1990a presented a two-dimensional model including a single substrate, a single electron acceptor, and Monod degradation kinetics for organic substrate. *Lindstrom*, 1992 considered single substrate, a single electron acceptor, and a Monod kinetics monodimensional biodegradation model. *Chen et al.*, 1992 presented multiple substrates, multiple electron-acceptors including Monod and first-order degradation kinetics, while *Malone et al.*, 1993 considered monodimensional multiple substrate, single electron-acceptor, and Monod degradation kinetics models: both these last two models were monodimensional. An alternative monodimensional model was presented by *McCarty and Semprini*, 1993 which considered methanotrophic degradation and cometabolism of chlorinated ethenes via a Monod kinetic relationship. *Wood et al.*, 1994 considered a two-dimensional biodegradation transport model including dual substrates and a single electron acceptor with metabolic lag (i.e., an initial time in which biodegradation shows a sort of "stand-by" condition). *McNab and Narasimhan*, 1994 presented a three-dimensional biodegradation model including multiple substrate and electron-acceptors, geochemical equilibrium reactions, and Monod degradation kinetics for the organic substrate.

The second class of models arose due to diffusive limitation in substrate delivery to bacteria which resides in microcolonies which are accessible only via mass-transfer phenomena. *Molz et al.*, 1986 presented a microcolony-based concept transport and biodegradation monodimensional model including a single substrate, a single electron-acceptor, and a Monod degradation kinetics. The model presented by *Molz et al.*, 1986 was extended in *Widdowson et al.*, 1988 including a single substrate, two competing electron-acceptors, and cellular nutrient limitation. *Chen et al.*, 1992 presented a monodimensional transport and biodegradation model including two substrates, two electron acceptors, cellular nutrient limitation and two microbial population degrading the contaminant.

The third class of models are those including biofilm limitation. Within this class the following models are worth mentioning. *Taylor and Jaffè*, 1990d presented a monodimensional model including organic substrate and microbial transport and Monod degradation kinetics. *Kinzelbach et al.*, 1991 presented a two-dimensional model including a single substrate and two electron acceptors and Monod degradation kinetics. *Zysset et al.*, 1994 considered a monodimensional model including single susbtrate and electron-acceptor with first-order degradation kinetic. *Lensing et al.*, 1994 presented a single substrate, multiple electron-acceptors, geochemical equilibrium monodimensional model including Monod degradation kinetics. *Nicol et al.*, 1994 presented a monodimensional model including multiple substrates, dual-electron, and nutrients. The model accounts for hydrocarbon residual saturation and Monod degradation kinetics. *Wood et al.*, 1995 presented a monodimensional model including a single substrate, a single electron-acceptor, and metabolism lag for both the bulk and microcolony phase. *Essaid et al.*, 1995 presented a two-dimensional, multispecies reactive solute transport model with sequential aerobic and anaerobic degradation processes, including also manganese and iron-reduction, and methanogenesis. *Dykaar and Kitanidis*, 1996 modeled transport and biodegradation in two dimensions by considering a macropore in which biofilm was present. Biofilm growth distribution and transformation rate were studied at different Reynolds numbers.

The last class of models regards multiphase flow which includes biodegradation of contaminants. Biodegradation is accounted for as a zero- or first-order reaction decay instead of using some more complex, and often more realistic, nonlinear degradation kinetics. Some useful references for these models are *Corapcioglu and Baher*, 1987, *Sleep and Sykes*, 1991, 1993. Other authors have also developed models for accounting for the effects of vegetation in biodegradation of organic compounds: *Tracy et al.*, 1993, 1994 presented an unsaturated two-phase (mobile and immobile) 1-D flow model coupled with multispecies transport.

3.1 Numerical solution approaches to biodegradation models

A wide variety of numerical approaches for solving biodegradation models is documented in the literature. Numerical techniques have been generally related to the degree of complexity of the solvers and to the number of dimensions for which the transport of biodegradable compounds is solved. Generally, biodegradation is considered for one-dimensional test cases and is solved using finite differences (*Molz et al.*, 1986, *Widdowson et al.*, 1988), with some iterative procedure for solving the coupling between the various transport equations for the species accounted for and for biomass. *Kindred and Celia*, (1989) used the optimal test function method and avoided the internal iteration for coupling the different equations by evaluating nonlinear coefficient for the current iteration by using a linear extrapolation of the concentration values obtained at the two last previous time steps. *Chen et al.*, 1992 solved transport plus biodegradation using finite elements as well as *Tracy et al.*, 1993,1994 which, however, included the solution of the flow equations for both the mobile and immobile region. Finally, one-dimensional solutions for transport plus biodegradation was presented by *Wood et al.*, (1994, 1995) which applied finite elements with modified characteristic method (MMOC, *Chiang et al.*, 1989).

Extension in 2-D are somewhat less common than in 1-D: *Frind et al.*, 1990 implemented a two-dimensional simulator using finite differences and first order degradation kinetics for the substrate. *Kinzelbach et al.*, 1991) used finite differences in two dimensions and the nonlinearities of biodegadations were solved using an internal iteration procedure. Finally, *Gallo and Manzini*, (1998). presented a two-dimensional mixed-finite element/finite volumes approach for solving advective-dominant transport and biodegradation of organic contaminants. In this last case, no internal iteration for solving the nonlinear coupling was implemented, since the explicit time integration scheme was sufficient to guarantee an accurate solution for the different species.

Much work has also been devoted to modeling biodegradation kinetics and its parameter calibration (*Taylor and Jaffè*, 1990a, *Chen et al.*, 1992, *Malone et al.*, 1993, *Wood et al.*, 1994, *Wood et al.*, 1995, *Essaid et al.*, 1995).

3.2 Which compounds undergo biodegradation?

A wide variety of contaminants can be found in groundwater and many of them are good candidates for biodegradation, as evidenced by the many studies, investigations, and experiments that have addressed this topic. Generally, the possibility for compounds to be degraded by microorganisms is strongly environment-dependent, i.e., on particular conditions such as temperature, previous history, soil moisture, pH, particle size, presence of other compounds which can work as inhibitors and/or nutrients, availability of other organic compounds and/or energy, capability of the bacterial strains to adapt to the new chemical conditions, etc.

Generally bacteria need a source of organic carbon (which is used for cell reconstruction) and energy for their metabolism (*NRC*, 1993). Their availability can strongly influence the success of contaminant degradation. Some *a-priori* indications on the possibility of a certain compound to be degraded are obtained on the basis of previous experience. Depending on the class of compounds considered, an energy surplus and/or a further organic carbon supply could be necessary, and could be provided by soil heating and/or addition of suitable substances.

Some groups of groundwater pollutants are listed below and their likelihood of being degraded is discussed on the basis of investigations and laboratory experiments documented in the literature (see *Leathy and Colwell*, 1990 for a comprehensive review of factors affecting microbial activities).

3.2.1 Aromatic hydrocarbons

Aromatic hydrocarbons are generally synonymous for benzene, toluene, ethylbenzene, and xylene (BTEX, which are the major constituents of car fuels), and styrene. This class of pollutant is generally found in the proximity of fuel stations from which they could have accidentally spilled, and in military bases.

BTEX compounds are partially soluble in water (700g/l for benzene, 540 g/l for toluene) and they are strongly degradable under oxic conditions (*Kelly et al.*, 1996). Several investigations were performed for determining degradation kinetics and some measurements of attenuation rates demonstrated the suitability of fitting by a Monod kinetic equation (*Wiedemeier et al.*, 1996). In some cases biodegradation of BTEX compounds were extremely sensitive to initial bacterial concentration and nutrient availability (the influence of these compounds in bioremediation is discussed below). In some cases a second order kinetic model seemed to fit better the kinetics of degradation of this class of hydrocarbons, particularly under oxygen-limited conditions (*Freijer*, 1996). Toluene was found to be anaerobically transformed and mineralized in mixed methanogenic cultures (*Vogel and Grbic-Galic*, 1986). It was also demonstrated by *Volkering et al.*, (1992) that bacterial growth on crystalline or adsorbed polycyclic hydrocarbons can result in a linear increase of biomass concentration. They presented a mathematical model which showed that under these circumstances mass transfer from the solid phase to the liquid phase is rate-limiting for growth.

3.2.2 Nitrocompounds

Some examples of nitrocompounds are: acetonitrile (ACN), chloroacetonitrile (CCN), chloroacetic acid (ACA), and chloroacetamide (ACM). These compounds can derive from septage-treatment facilities (*Desimone and Howes*, 1996) and their biodegradation is strongly affected by organic carbon limitation. 2,4,6-trinitrotoluene (TNT) and its derivatives are also commonly found in groundwater, and their source is strongly related to the production of explosives for both army and tunnel works. Nitrocompounds are generally liable to be biodegraded, and their transformation kinetics do not suffer inhibition of concentration excess (*Bruns-Nagel et al.*, 1996).

Examples of aerobic and anoxic biotransformation of 2,4-dinitrotoluene (DNT) by *Pseudomonas aeruginosa* strain isolated from a plant treating propellant manufacturing wastewater was documenteed (*Noguera and Freedman*, 1996). Both DNT nitro groups were reduced by P. *aeruginosa*, which demonstrated the ability to degrade also the 4-amino-2-nitrotoluene and 2-amino-4-nitrotoluene formed by DNT reduction. 2-*sec*-butyl-4,6-dinitrophenol was found to be degraded by *Clostridium bifermentans* KMR-1 up to 90% for a wide range of TNT (*Hammill and Crawford*, 1996), when percolated with potassium phosphate, glucose and/or glucose ammonium sulfate, which were providing the necessary nutrient supply for the degrading bacteria.

3.2.3 Phenol and poliaromatic hydrocarbons

Polyaromatic hydrocarbons (PAHs) are generally obtained by distillation of petroleum and constitute the heavy fractions of these chemical processes. Some examples of those compounds are naphthalene, benzopyrene, antracene, thiophene, and their intermediary metabolites (2 dihydroxy-1,2-dihydronaphthalene). This class of compounds (as well as phenols) is also used in color industries because of the property of some of these compounds to selectively absorb different wavelengths. The biodegradability of phenol and all isomers of six different functional groups of monosubstituted phenols were examined under denitrifying and methanogenic conditions (*Connor and Young*, 1996). It was found that the type of anaerobic condition and the nature of the substituting group could influence both metabolism and toxicity of phenolic compounds. In some cases some reaction and degradation paths have been found to be predominant with respects to others (*Selifonov et al.*, 1996). They are often present in mixtures whose degradation liability was investigated (*Chelly and Cerniglia*, 1995) for determining possible reaction selectivity.

3.2.4 Pesticides

A consistent portion of groundwater pollution is due to the presence of herbicides and pesticides which are used in farming and agriculture for limiting and/or eliminating undesired insects and/or parasites. These compounds are sulfur and/or chlorine based (atrazine, metolachlor, metazachlor, sulfolame, DDT, DDD, bentazon, chloramphenicol, cyclehexemide, isoproturon, vinclozolin, rimsulfuron, carbazole, etc), and are poisonous when present in drinking water and in fruits and vegetables. Their degradation can be affected by the presence of dissolved oxygen and nutrients, as was investigated, for example, by *Fedorak and Coy*, 1996. These compounds have also been found to be particularly sensitive to soil temperature variations (*Veeh et al.*, 1996) whose effect was adequately described and fitted by an Arrhenius-like equation.

3.2.5 Halogenated compounds

Chlorinated hydrocarbons are quite common in contaminated soils, due to the extensive use of these compounds in industry (solvents, metal degreasers, etc). Generally, their density is higher than that of water and they move downward toward the saturated zone and continue their path throughout the saturated zone until they reach an impervious layer (i.e., they can be classified as DNAPLs). Chlorinated compounds are very toxic and their concentration limits in drinking water are very low. Due to their low solubility in water, their presence is generally accompanied by a separate phase. These characteristics make their removal very complicated: their value of residual saturation in groundwater in quite high, so their removal by means of simple PAT systems is very complicated and ineffective, particulary due to their tendency to reach the bottom of the aquifer thus making them practically unreachable. Some common examples of these compounds are trichloetylene (TCE), dichloroetylene (DEC), trichloroethane (TCA), perchloroetylene (PCE) deriving from aliphatic hydrocarbons, and trichlorophenol from aromatic hydrocarbons.

Like aromatic hydrocarbons, chlorinate compounds also undergo biodegradation by soil microorganisms, but they require much more favourable conditions in order for the kinetics to be acceptably fast. It has been found that biodegradation of chlorinated compounds requires the presence of other compounds which supply the organic carbon necessary for the reaction to take place (*Doong and Wu*, 1996). These compounds are also particularly sensitive to the electron acceptor available for the reaction. Several investigations were conducted on chlorinated hydrocarbon biodegradability and some interesting results were found: methanogenic, oxygen enriched, iron reducing, sulfate reducing, and nitrate reducing conditions favour degradation and can significantly increase the rate of transformation, while compounds like phenol, toluene, lactate, glucose, amino acids, and acetate were found to work properly as organic carbon suppliers (*Leathy and Colwell*, 1990, *Sharma and McCarty*, 1996).

On the other hand, chlorinated hydrocarbons are liable to be transformed to metacompounds which are more dangerous and toxic than the original ones. Also, some inhibitory effects on the degradation of other compounds were measured (TCE inhibited toluene degradation). Experiments showed that the leading factor in biodegradation of chlorinated compounds was the redox potential of the reaction.

3.2.6 Metals and other compounds

The presence of metallic ions in groundwater can have multiple sources, due to the common use of these substances in industry. They can be reduced during biodegradation of other compounds: an example is the microbially mediated Cr(VI) reduction during anaerobic degradation of benzoate that was studied in a series of microcosms and enrichments (*Sehn et al.*, 1996). Cr(VI) was found to influence quite strongly the degradation of benzoate whose degradation process was reversely promoting Cr(VI) reduction to Cr(III).

The ability of microorganisms to degrade trace levels of hydrofluorocarbons ($CHCl_2F$ and $CHCl_2CF_3$) was investigated (*Oremland et al.*, 1996). It was found that $CHCl_2F$ was biodegradable in both aerobic and anaerobic soils, while $CHCl_2CF_3$ was biodegradable only under anaerobic conditions.

4 Remediation

Remediation is one of the most important research topics in groundwater hydrology of recent years, due to the increased political and social importance this issue has achieved.

4.1 How to exploit biodegradation and demonstrate its effectiveness

Biodegradation is appealing because of the "naturalness" of the method, its attractive economics in terms of installation costs, and the minimal environmental damage it inflicts (unlike, for instance, methods requiring injection of solvents or steam). Two bioremediation approaches can be delineated: intrinsic and enhanced.

Intrinsic bioremediation (or natural attenuation) can be described by means of a simple motto: "leave the enviroment to clean itself". Intrinsic remediation is obviously very cheap from an economical point of view, but it requires a careful evaluation of the characteristics of the aquifer and subsurface scenario. Intrinsic bioremediation cannot be applied to all contaminated sites: a typical candidate is a site in which the contaminant has a very low probability to spread further, or an aquifer that is not a source for drinking water in the short term, or, in the extreme case, a site that does not allow for any other type of intervention at acceptable costs. Costs are generally related to the installation of a monitoring network for checking the distribution and the progress of the remediation. Intrinsic bioremediation generally implies long remediation times.

Enhanced bioremediation can be applied in several ways, depending on the type of technique chosen. Some of the most common enhanced bioremediation techniques are: 1) bioventing; 2) peroxide injection; 3) microbe injection; 4) nutrient injection; 5) soil heating; 6) surfactant injection (fluidification of the organic matter trapped in pools and ganglia). In this case remediation generally takes less time since the sorption kinetics are increased from two to 10 times (*Lesage et al.*, 1996). Costs are higher, however, and when pumping stations are installed or when a fluidification of organic phase is obtained, the risk of artificial spreading of contaminant is increased.

A rather new approach is the passive well injection technique (*Wilson and Mackay*, 1996). This technique consists of introducing nutrients and/or other substances into a number of wells in a contaminated zone. The substances penetrate the soil surrounding the wells by means of natural dispersion-diffusion, with no expense of power supply for forced injection. This can be considered a middle-way solution that seems to be very promising (*Chapman et al.*, 1996).

4.2 Combining biodegradation with other remediation techniques

One of the major open issues in remediation deals with the possibility of combining technical/engineered methods, such as pump-and-treat, with bioremediation. One of the appealing aspects of such hybrid methods is the different time scales at which individual techniques act.

Generally, pump and treat (PAT) methods modify the flow field in the subsurface and can recover a significant bulk of the pollutant in a relatively short time. However these methods cannot deal favourably with trapped pollutants at residual saturation. When the organic phase saturation approaches residual saturation, phase entrapment, pools, and ganglia make these zones completely pervious to water flow and the flushing of the organic phase is impossible. As previously mentioned, in this case, organic phase can be removed by means of mass-transfer between two phases, and/or by means of different remediation techniques. Bioremediation can be an effective technique to use in a second, longer term phase of remediation.

4.2.1 Active bioremediation

Several studies and field investigations have been conducted to assess and measure the enhanced biodegradation obtained by means of several techniques (oxygen, nutrients, or sulfate injection, soil heating, oxygen release). As discussed previously, some classes of compounds have been particulary targeted by researchers and investigators. In many cases bioremediation has been implemented and applied to large scale spills of contaminant.

The greatest part of these remediation studies have been carried out at military installations and by governments, under a variety of climatic conditions. It is interesting to note that soil microorganisms can degrade fuel in soils under extreme climatic conditions (e.g. investigation conducted for the fuel-contaminated soil at McMurdo Station, Antarctica by *Wardell*, 1995), even if enhancement by means of nutrient injection may not be as effective as expected at temperate climate conditions.

Several oxygen releasing products have been developed for enhanced aerobic degradation and many field experiments support these studies (*Chapman et al.*, 1996, *Johnson and Methvin*, 1996). However, oxygen injection into an aquifer for stimulating biodegradation of target PAH and pentachlorophenol might be jeopardized by the demand exerted by uncontaminated oxygen sediments, causing significant increase of remediation costs of additional oxygen delivery for sediment oxidation (*Hess et al.*, 1996).

Positive results were obtained in cleanup of residual solvents (perchloroetylene) in the saturated zone. Using vitamin B_{12} increased degradation rates and because of enhanced anaerobic bacteria survival. The degradation was found to be independent of the concentration range of PCE (*Lesage et al.*, 1996).

Another technique that is achieving importance is bioaugmentation, i.e., injection of bacteria into subsoil in order to increase their concentration in the subsurface and to assist potential forces acting towards organic contaminant degradation. Some experiments were performed in this area and positive results were found for biodegradation of CCl_4 at Schoolcraft, MI (*Mayotte et al.*, 1996). Sometimes, however, problems are encountered due to excessive biomass growth which can strongly depress hydraulic conductivity. Within this context, some studies were made for assessing this problem in a phenol-contaminated aquifer (*Essa et al.*, 1996). Some correlations in the number of soil bacteria and hydraulic conductivity have been found theoretically and in laboratory experiments (*Taylor and Jaffè*, 1990a, *Taylor and Jaffè*, 1990b, *Taylor and Jaffè*, 1990c). A convenient alternative to bypass aquifer clogging due to bacteria proliferation surrounding injecting wells is pulse mixing injection of oxygen and/or nutrients in a contaminated aquifer. *Devlin and Barker*, 1996 presented a field investigation of nutrient pulse mixing in an *in-situ* biostimulation experiment in a portion of the Borden aquifer. Results indicated that large-period pulsed injections of a substrate could be useful for promoting injected and ambient water mixing in bioremediation programs.

Some problems could arise when even small amounts of trapped gas occur in the pore spaces in saturated porous medium, as was investigated in experiments conducted in a large aquifer (*Fry et al.* 1996). Results showed that the presence of even a small amount of a trapped gas phase in an aquifer would significantly affect the distribution and transport of dissolved oxygen with a consequent depression of aerobic degradation of contaminant.

4.2.2 Passive release technique

A passive oxygen delivery technique is achieving increasing importance in groundwater remediation. In this case no power supply for forced injection of air and/or pure oxygen (e.g., air venting, air sparing) are required. The technique consists of exploitation of wells for letting air and oxygen penetrate soil and being transported by the general bulk flow (*Wilson and Mackay*, 1996). Characteristics and limitations of the technique were discussed and some suggestions for a correct application were also given. This technique is expected to combine low costs associated with intrinsic bioremediation with active-enhanced bioremediation benefits obtained by artificial air and/or oxygen injection in groundwater (bioventing, air-sparging, injection of hydrogen-peroxide).

A field study of oxygen injection was carried out in a sandy iron-rich groundwater system contaminated with gasoline hydrocarbons for evaluating enhancement of intrinsic bioremediation (*Gibson et al.*, 1996). Results indicated enhancement of both bacterial population and rate of aerobic degradation, especially of benzene and ethylbenzene which were recalcitrant to intrinsic remediation under low oxygen conditions.

One of the risks connected with this remediation approach is that concentration decreases can be registered for reasons other than contaminant removal, as was investigated in plot infiltration tests and a conservative tracer test at Eglin Air Force Base, FL (*Sweed et al.*, 1996). The potential transport of solutes to the subsurface via recharging water was tested and results indicated dilution as the dominant attenuation mechanism associated with high surface application rates.

4.2.3 Intrinsic bioremediation

As previously mentioned, natural or intrinsic bioremediation can be considered an open matter of discussion insofar as it is quite different from what is generally intended by "soil remediation".

A survey was conducted on 119 dissolved hydrocarbon plumes in California to evaluate evidence of natural attenuation (*Buscheck et al.*, 1996). It was found that petroleum hydrocarbon plumes were stabilizing at relatively short distances, rarely exceeding 260 feet in length. Sulfate-reduction biodegradation of petroleum hydrocarbons appeared to play a major role in many of the sites investigated. Another informal survey of over 125 regulators from environmental agencies was conducted to determine each agency's position regarding natural attenuation (*Ritz et al.*, 1996). The results of the inquiry indicated that natural attenuation could be more expensive (in terms of: impossibility of using a contaminated aquifer; very long-term monitoring expenses and analysis, etc.) and risky than proactive remediation methods, but that no general evaluation could be made since remediation was found to be strongly site specific.

An evaluation of intrinsic bioremediation in support of risk-based corrective action (RCBA) was presented (*Douthit et al.*, 1996). A comparison of regulatory outcomes with and without intrinsic bioremediation considerations was presented, and the relevance of intrinsic bioremediation to RCBA was discussed on a set of data from a site located in New York State.

Screening models are achieving increasingly importance. They are based, generally, on analytical or semi-analytical solutions of simplified flow and transport equations and very simple expressions for describing complex phenomena such as: chemical reactions, chemical equilibria, sorption, etc. These models are not intended to furnish highly accurate solutions of a complex set of equations, but are aimed at providing some understanding of the phenomena considered and giving some insights on possible interactions of the different components (such as advection, diffusion-dispersion, chemical reactions) which are present in a system.

A screening model approach was presented for evaluating BTEX natural attenuation in groundwater (*McAllister*, 1996). The estimation of the maximum extent of the soluble contaminant plume, the determination of soluble plume attenuation rates, and estimations of the time required for the plume to stabilize were the aims of the two methods proposed. A review was presented on regulatory progress toward risk-based remediation together with a description of the successful application of RCBA at two fuel contaminated sites on Air Force installations (*Downey et al.*, 1996). A user-friendly screening tool, BIOSCREEN, for simulating natural attenuation of dissolved hydrocarbons at petroleum fuel release sites was described (*Newell et al.*, 1996). The program was aimed at estimating the plume extension without human intervention and evaluating the plume residence time before natural attenuation occurred. An approach for evaluating the use of intrinsic remediation in conjunction with other technologies for implementing an optimal site-dependent remedial strategy was developed (*Norris et al.*, 1996). The method relied basically on a multiple application of models with successively increasing levels of engineering and cost requirements in order to tailor the final intervention to the site under study. A spreadsheet model was developed to project adsorbed and dissolved phase concentrations at any distance from a two-dimensional "line" source considering both natural and biological degradation (*Henry and Herman*, 1996). Similar spreadsheet models were developed, based on the Domenico analytical model and provided results in close agreement with the numerical model BIOPLUME II (*Ollila*, 1996).

A screening study of chlorinated aromatic hydrocarbons (CAHs) intrinsic bioremediation at a southern New Hampshire site was conducted (*Shaffner et al.*, 1996). Results showed the occurrence of reductive dehalogenation and co-metabolism of CAHs, and it was found that the latter process was dissolved-oxygen and CH_4-limited. Incorporation of the intrinsic bioremediation potential of CAHs as part of a site's remediation strategy was discussed (*Lee and Swindoll*, 1996). A careful evaluation of the factors affecting biodegradation of aquifers as well as an assessment of potential human and environmental risk was strongly recommended for avoiding excessively optimistic predictions. Two case histories of natural attenuation in New Jersey were documented (*Valdes*, 1996). Measurements of indicator parameters suggested that BTEX compounds were rapidly degrading, both aerobically and anaerobically, with no assistance. Resident bacteria showed marked preferences for some of the available specific electron-acceptors in the attenuation process, namely oxygen, nitrate, manganese, ferric iron, sulfate and carbon dioxide.

A discussion was presented regarding the real advantages and disadvantages of active soil cleanup interventions, and an evaluation of the related indirect financial and environmental costs was discussed (*Hicks and Rizvi*, 1996).

4.3 U.S. EPA national policies and demonstration of *in-situ* groundwater remediation

4.3.1 Ongoing studies

Numerous studies and experiences at contaminated groundwater sites have shown that remediation of contaminated aquifers using conventional PAT systems furnish unsatisfactory results and are expensive and time consuming. Particularly when dealing with DNAPLs, factors such as residual saturation and/or downward migration (especially in fractured rocks or in deep aquifers), low solubility in water, and high toxicity make remediation a real challenge to experts, engineers, and technicians. Some alternatives to classical PAT systems are "a must" condition which is to be fulfilled by introducing new technical solutions.

Due to the costs related to soil excavation and external soil/water/gas treatments, in recent years several studies and investigations have been conducted to assess the feasibility of *in-situ* treatments. These studies have taken two main though not entirely opposite directions. On the one hand, an increase of solubility of NAPL is believed to play a major role in organic mobilization and, consequently, removability via PAT techniques. On the other hand, soil microbial population metabolism is accelerated in degrading organic pollutants, and an increased solubility in water could make these pollutants more easily available to degrading bacteria.

Mobilization of DNAPLs can be obtained generally by either increasing solubility or by decreasing viscosity. An increase of solubility is obtained by addition of surfactants, i.e., compounds which decrease the surface tension between water and organic compounds and which have the characteristics of both classes of compounds (aqueous and nonaqueous). Viscosity can be decreased by an increase in temperature.

An increase in microbial activity can be obtained by addition of oxygen, nutrients, nitrogen, and other electron-acceptors (such as methane, sulfates, etc.). A moderate rise in soil temperature can also enhance bacterial activity (being a enzymatic reaction, the temperature can vary only within a narrow range).

When soil injection of substances other than oxygen is to be performed, regulatory and/or procedural measures can prohibit the application of a technology. Examples can be found in USA regulations: nitrate concentrations in drinking water are restricted by the Safe Drinking Water Act, but some states can also impose stricter guidelines. It can be understood that regulations and restrictions are not uniform in the country. Injection wells for soil remediation are regulated by the Underground Injection Control (UIC) program under the Federal Safe Drinking Water Act. Not all states apply the UIC guidelines in the same manner — some consider them to be guidelines while other states treat them as regulations and ask for UIC permission before injecting surfactants or other substances which could affect drinking water quality. Some states have policies that discourage use of injection technologies in general, others tends to accept them on a case-by-case basis, and still others accept injections only in closed systems, in which the injectant can eventually be completely captured and removed. A summary of the state policies concerning the use of injectants for groundwater remediation can be found in *US EPA*, 1996a.

A handy reference is version 2.0 (February 1996) of EPA's Bioremediation in the Filed Search System (BFSS) database which contains information on the 450 sites at which bioremediation techniques are being applied. The database contains a list of 153 sites where *in-situ* groundwater treatment, via bioremediation, has occurred, or is planned. A detailed description of the contaminants and treatments applied is given together with the number of the sites in which a certain treatment has been applied.

4.3.2 Injection of cosolvents

In situ solvent flushing involves a solvent mixture (water plus organic solvent such as alcohol) in the vadose and/or saturated zone for extracting the contamintant (*US EPA*, 1995). The mixture is injected upgradient and is extracted downgradient and treated above ground for contaminant recovery. The solvent acts in two ways: by increasing apparent solubility of the contaminant in water, which improves the ratio of mass removed to pore volume injected; and by reducing the interfacial tension between the water and the contaminant, which may result in direct mobilization of NAPLs. Some cases have been reported in which co-solvents were used by microbes as organic carbon sources, thus promoting bioremediation if used under toxic levels of concentration. Some successful examples of remediation by means of injections of methanol-water mixtures have been obtained in the supercritical CO_2 extraction of DDT from soil, and cosolvents added to potassium permanganate ($KMnO_4$) improved the degradation (by oxidation) of the common dense NAPLs TCE and PCE (tri- and per-chloroethylene). Investigations on removal of residual DNAPLs by means of cosolvents were also conducted for evaluating the possibility of remediation (*Imhoff et al.*, 1995).

4.3.3 Air sparging, biosparging, soil vapor extraction

Air sparging (*NRC*, 1993) is an *in situ* groundwater remediation technology that involves the injection of a gas (usually air/oxygen) under pressure into a well installed into the saturated zone. Air sparging technology extends the applicability of soil vapor extraction to saturated soils and groundwater through physical removal of volatilized groundwater contaminants and enhanced biodegradation in the saturated and unsaturated zones. Oxygen injected below the water table volatilizes contaminants that are dissolved in groundwater, that exist as a separate aqueous phase, and/or that are sorbed onto saturated soil particles. The volatilized contaminants migrate upward into the vadose zone, where they are removed, generally using soil vapor extraction techniques. This process of moving dissolved and nonaqueous volatile organic compounds (VOCs), originally located below the water table, into the unsaturated zone has been likened to an *in situ*, saturated zone, air stripping system. In addition to this, air sparging promotes biodegradation by increasing oxygen concentrations in the subsurface, stimulating aerobic biodegradation in the saturated and unsaturated zones.

Air sparging systems must be designed with air flow rates and pressures to provide adequate coverage of the area of contamination, while minimizing the potential for uncontrolled releases of contaminated vapors to the atmosphere, into buildings, etc. The target of a careful design of the system is the elimination of the needs of surface vapor treatment together with a complete coverage of the zone to be remediated.

A variation on vertical wells is horizontal well technology which makes for more efficient air delivery in the subsurface. In other studies hydraulic containment was realized by air injection to create a sort of air-sparge curtain for mitigating downgradient transport of contaminant. Further improvements are obtained by means of soil heating, hot air injection, steam injection, gas phase nutrients, and alcohol flooding.

An interesting variation (even if sometimes used interchangeably with air sparging) is biosparging, applicable to volatile or semi-volatile biodegradable organic contaminants. Air sparging is generally applied when dewatering (for applying soil vapor extraction) is not feasible. In particular, this could be one of the few alternatives when dealing with DNAPL contaminantion for which the requested level of dewatering would be impractical. Air sparging (and its derivatives) is particularly recommended for strengthening soil vapor extraction techniques (e.g., when strongly-sorbed contaminants are to be treated). Some of the contaminants that have been treated with air sparging include: BTEX, general fuels, oils and greases, and chlorinated solvents.

The applicability of air sparging is strongly connected to some requirements of the site under treatment: coarse-grained (high permeability), homogeneous soils. Clay lenses, fractures, and anything creating strong preferential paths can jeopardize or strongly limit the effectiveness of this remediation technique. Also, relatively large saturated thicknesses and depths to groundwater greater than 5 feet may be required for determining a sufficiently large area of influence of the area injected. In case of shallow aquifers the area of influence of any injection well is limited, and an increased number of injection wells (which could be cost-prohibitive) could be required to properly cover the zone under remediation.

As for many other remediation techniques, a detailed site investigation (including site-specific determination of air flow patterns in the unsaturated zone and conditions relating to the feasibility of bioremediation, such as nutrient concentration and contaminant level of toxicity for microbes) is necessary before applying air sparging. Also, pilot studies could be necessary for determining the feasibility and correctness of any assumptions made.

One key factor for a successful application of air sparging/vapor extraction systems in connection with bioremediation is the network of wells that is to be installed. Deep wells (saturated zone — air sparging) and shallow wells (vadose zone — vapor extraction) are to be properly installed and designed. Air pressure and vacuum pump characteristics are also critical to the correct application of the system whose tuning is strongly site-specific. Bioremediation rates can also influence the work of pumps and compressors (generally, bioremediation become more important in a second phase of remediation, while the first phase is dominated by evaporation of the light fractions of organic contaminants). It has been noticed that a proper turning on/off of compressors for air/oxygen injection can maximize the biodegradation rate and limit or eliminate the presence of contaminants in the vapor phase. It should be remarked that very strict regulatory constraints are imposed on emission of organic pollutants into the air, making it necessary to treat above ground any vapors extracted from the soil (and thereby also increasing the remediation costs).

The Savannah River site in Aiken, Carolina is an example of successful application of air sparging/soil vapor extraction systems. Remediation has been performed for eliminating TCE and PCE from 500-1800 mg/kg to 0.67-6.29 mg/kg. Costs were within $ 15.60 per pound of volatile organic carbon (VOC) removed.

Limitations of air sparging/soil vapor extraction include: contaminants that form complexes with the soil matrix (limited or no volatilization); fine-grained, low-permeability soils (difficult flow); heterogeneous soils in which strong channeling occurs; superficial contaminant distribution (for which an excessive number of wells would be required).

4.3.4 Bioventing

Bioventing (BV) is quite similar to soil vapor extraction and the same technology and installation can be used. This only difference is in the air flow rate that, in this case, is lower. BV is aimed to stimulation of indigenous microorganisms through increased oxygen content in the subsurface.

This technique is predicted to be very successful for sites where the water table is below 10 feet. For very surficial soils (0-2 feet) it can be applied only by soil capping of the surface.

4.3.5 Thermal enhancements

Soil heating (*US EPA*, 1995) is achieving increasing importance because of the following: 1) it increases contaminant vapor pressure and diffusivity; 2) it increases the effective permeability of impervious soils (e.g. clays) with the release of both vapor and water; 3) it increases the volatility of the contaminant from in-situ steam stripping by the water vapor; 4) it improves the mobility of the contaminant by a reduction of viscosity. Soil heating can be performed in different ways, depending on the permeability of the soil under study: for impervious or clayey soils heated up by means of electromagnetic waves (kind of microwave) or electricity current are common; for more permeable soils steam injection can be useful. In other cases, injection of heated water is preferred to steam injection. In fact, heated water can really promote bioremediation, since it does not create strong shocks to the microbial environment but it accelerate the kinetics of degradation (mild increase in soil temperature).

There are several examples of successful applications of thermal enhancement techniques. Steam heating and pre-heating of nutrients was applied to the soil at an AT&T site. 18000 pounds of solvent in both water and vapor phase were extracted from the contaminated site. At Bell Lumber and Pole, New Brighton, MN, hot water was applied for removing oil wastes, and 80% of the contaminants were removed. At the Annex Terminal, San PEDRO, CA, steam heating and soil vapor extraction were applied for removing VOCs and SVOCs (semi-volatile organic carbons). Results obtained were the removal of 85% of VOCs, and more than 55% SVOCs were removed at a rate of 3 yards^3 per hour. An identical remediation technique was applied at Huntington Beach, CA. BTEX were the contaminants to be removed, but results were less successful than predicted: 16,000 gallons extracted of 70,000-135,000 estimated for the oil spill. Some problems were found for soil heating, but the costs were kept low, i.e., $ 29-46 per cubic yard of contaminant.

4.3.6 Surfactant enhancements

The application of surfactants (*US EPA*, 1995) can enhance remediation in three ways: 1) by increasing contaminant mobility and solubility to improve PAT performance (hydrophilic surfactants); 2) by decreasing the mobility of contaminants to prevent their migration (increasing the compounds' sorbability); 3) by enhancing the rate of biodegradation of contaminants in soil.

Surfactants increase the apparent solubility of the contaminant in water, which improves the mass removal per pore volume, and reduce the interfacial tension between water and NAPL. This can require a higher concentration of surfactants than normally used for simple solubilization enhancement, but the increased NAPL mobility can justify this. It should be taken into account that this increased solubility can increase the potential spreading of the contaminant. Cationic surfactants have been shown to improve the sorbability of hydrophobic organic contaminants, such as PAHs. Other investigations found that an increase of bioremediation could be promoted by low surfactant concentrations, particularly in the case of hydrophobic pollutants (very low solubility in water).

An example of successful application of surfactant enhancement took place at the Corpus Christi Dupont site where DNAPLs at shallow soil depths were present. A large reduction of CCl_4 was obtained and the initial high costs of surfactant supplies were recovered by the acceleration in solvent recovery. The final operational costs were lower than those for standard PAT systems. At General Motors NAO Research & Developement, Warren, MI, PCBs and oils were treated by surfactant injection into wells. Good results were otained and the possibility of reusing the surfactants was examined. Organic pollutants were removed by means of ultrafiltration: membranes retained more thant 89% of the contaminant.

5 Open issues

As previously mentioned, NAPL and remediation problems are very complex and many open issues remain in this field. In the following, some possible research topics will be listed together with some related comments.

5.1 Modeling

5.1.1 *P-s-k* relationships

Some questions remain to be answered: in developing the large scale percolation models, an algebraic relationship between Pc and S is assumed. However, when large scale heterogeneities are present, "slow-drainage" phenomena are expected to occur on a larger scale. This would undermine the instantaneous responses between these two variables and lead toward a differential relationships relating capillary pressure and saturations which would seem more close to physical reality.

5.1.2 PDE numerical models

Several numerical models have been developed for studying biodegradation and bioremediation in contaminated porous media (see *Rathfelder et al.*, 1996 and reference listed therein). These models generally approximate the organic substrate as a dissolved compound, and the classical transport equation is adopted for describing the organic plume motion. On the other hand, multiphase flow models accounts for biodegradation as a linear kinetics sink term. Two models, however, are worth mentioning for the approach used in coupling multiphase flow and biodegradation. *Sleep* *and Sykes*, 1991 proposed a multiphase flow-transport-biodegradation model that is based on local equilibrium between all the fluid phases and with no diffusion limitation considered between the bacterial colonies. *Chen et. al.* 1992 presented a nonequilibrium model for mass-transfer between the bulk flow and the biophase: however, it does not account for residual NAPL, equilibrium between the liquid and the gas phase is assumed, and transport in the gas phase is only diffusive. This last approach seems to be quite promising with regards to the description of the biodegradation kinetics (some interesting results in agreement with laboratory experiments are presented therein), but only an approximate description of the multiphase flow of the organic substrate is given. However, a comprehensive formulation of multiphase flow plus biodegradation phenomena involving complex kinetics, bacterial population dynamics, and chemical equilibria has not yet been presented, at least at author's knowledge. Such a model would allow to study the combination of remediation techniques with natural or forced bioremediation.

5.2 Remediation — Soil vapor extraction and bioventing

As observed in *Rathfelder et al.*, 1995, some open issues remain in SVE applications. Mass-transfer mechanisms and limitations of hydrocarbon volatility have begun to be understood by means of modeling and laboratory experiments. Further contributions in this area could be beneficial, particularly with regards to field application of SVE design and management.

Microbial degradation processes occurring in BV systems are not completely understood. In particular, much of the research has addressed saturated systems, while laboratory experiments for unsaturated scenarios are still lacking. A deeper knowledge on biodegradation in unsaturated systems would help in understanding the importance of various design and field parameters, such as contaminant distribution, nutrient and electron-acceptor supply and distribution, temperature effects, system configuration, and operational conditions.

Models describing transport and biodegradation have been presented together with analytical and numerical solution methods. However, they have been used for homogeneous scenarios only; a realistic description of the effects of heterogeneous soil properties on fluid distributions is needed. Further work is expected to be made on descriptions of nonequilibrium mass-exchange between phases and microbial degradation kinetics. This last issue is expected to increase the mathematical and numerical complexity of the models, in turn spurring development of efficient and robust algorithms for solving the aforementioned models. This is expected to improve the capability of numerical codes for optimal design and management in SVE and BV applications.

5.3 LEA validity - multiphase equilibria - dissolution kinetics

The range of validity of LEA for NAPL dissolution is unresolved at this time and is an area of active research. There does appear to be a trend toward greater departure from LEA in heterogeneous media. One can therefore speculate that models of NAPL remediation in realistic field formations, with a hierarchy of scales of heterogeneity, will often require nonequilibrium partitioning. As discussed below, the implications of this for practical modeling can be profound. As for the case of NAPL dissolution, the range of validity of LEA for VOC mass transfer is uncertain at this time, but it appears that nonequilibrium phenomena will be important in at least some applications.

Multiphase equilibria have been studied in petroleum industries for decades and a state-of-the-art summary of the best correlations, obtained by comparing published correlations to the Core Laboratories database, is available (*McCain*, 1991). Because component (refined as opposed to crude), phases (NAPL and water instead of liquid and vapor hydrocarbon), and conditions (e.q., much lower pressures) are different in groundwater modeling, these equilibria cannot be applied explicitly, but an analogue would be desirable.

Some numerical studies have been made for simulating dissolution kinetics of NAPL compounds with high volatility and dissolution (*Zaidel and Russo*, 1993). These studies made for a homogeneous domain, confirmed that LEA hold if the Damkohler number (mass-transfer coefficient times vertical extent of NAPL, divided by advective velocity of water), or an analogue in diffusion-dominated flows, is sufficiently large. A modified expression of LEA equilibrium was proposed for simulating nonequilibrium: the modification introduced was a constant lower than unity which was exposing NAPL to less water (*Mackay et al.*, 1991). For multiple components with distinct solubilities, the approximation became more complicated as the dissolution of one component would affect NAPL concentration of others. To compute the transfer of a component, the authors grouped the remaining ones into those of greater solubility, which were assumed to be rapidly lost from NAPL phase, and those of lesser solubility, which were assumed to remain fully in the NAPL phase. Column experiments were consistent with the theory. Further investigation on approximated kinetics is an important tool for future modeling of nonequilibrium models.

5.4 Subsurface characterization

Open questions about subsurface characterization concern the correct sampling methods, the choice of the most "effective" parameters, heterogeneity of aquifer properties and the scale at which this heterogeneity is distributed and is to be considered (upscaling), the level of characterization, and proper three-dimensional characterization with a reduction in the cost related to measurement and sampling (*NRC*, 1994).

Another problem which is hard to solve is the location of pure phase in the subsurface, due to the difficulty and the costs of making direct measures, particularly for deep layers of the subsurface. In this regard, ground-penetrating radar is assuming increasing importance as a non-intrusive technique for estimating, for example, water phase saturation (see *Greaves et al., 1996*).

5.5 Contaminant distribution

Several problems arise when trying to evaluate the contaminant distribution, due to the complexity of the phenomena taking place. Generally, the contaminants which are found in the groundwater are those which are searched for, but it is quite easy to figure out that several others can be present. The choice of the critical parameters really affecting the contaminant transport is a problem, and how and how much these parameters affect contaminant spreading is not straightforward to be determined. Another problem is connected with the possibility of inferring contaminant mass distribution from soil characterization. Also, the proper interpretation of well and sampling measurements is not straightforward for locating the contaminant distribution, since this is often an ill-posed inverse problem whose solution can easily be non-unique.

5.6 Reaction pathways and rates

Research is needed to answer a series of open issues, such as: determination of which are the critical chemical and biological reactions affecting the contaminants in relation to the subsurface conditions, and what are the kinetics pathways. Laboratory measurements can furnish data on kinetics, but their extrapolation to field conditions is a matter of discussion, due to the different conditions occurring in the two environments.

Bioremediation is achieving increasing importance, since it represents a "clean way" to get rid of subsurface contamination. For a contaminated site it is important to know whether indigenous microorganisms are able to degrade the pollutant or some external "engineered" ones are to be supplied; whether contaminant degradation is effectively caused by subsurface bacteria or by some abiotic degradation processes; how subsurface conditions (temperature, pH, other contaminants, etc) affect biodegradation kinetics.

5.7 Subsurface clean-up

Remediation of groundwater has to solve the following problems: 1) a proper evaluation of the contaminant, such as its location, entity, distribution, set of reactions, etc; 2) choice of the proper remediation methods; 3) correct evaluation of the clean-up process, i.e., the correct determination of the effectiveness of the cleanup. Research should be directed to the previous topics.

Of concern is also what could be a good (in terms of remediation/associated costs) configuration for injecting and pumping wells. This depends on several other factors, such as relation between velocity and equilibrium (soil vapor extraction), diffusion-limited processes, turbulent flow (air sparging, steam injection, etc.), steady state or transient, presence of multicomponent solutions, correct modeling of the two-phase flow taking place (air-sparging), effect of turbulence on biodegradation and on contaminant degradation, opportunity and convenience of contaminant containment (flow regime, walls) and their long term-large scale effects.

The availability of a complete dataset for pollution and biodegradation could be useful for trying to use different formulations found in the literature and fitting them to see which of them seem to furnish better results. In this framework a new, flexible module could be built to be easily integrated within existing models.

5.8 Approximations

The need for making the mathematical models tractable requires some simplifications. Such simplifications require approximations, the effects of which are not always clear. These approximations can be very useful in saving memory and computations, but it is not trivial to understand which approximations can be made without affecting the accuracy of the solution.

With regards to the mass-transfer between different phases, several models have also been presented: generally equilibrium was assumed between the phases, but some first order mass-transfer models have been presented. Some improvements could be achievable in terms of mass transfer coefficients and expressions for this phenomena.

Complex systems are one of the most challenging issues in subsurface modeling. Within this domain, surfactant systems are especially significant because they require the consideration of balance equations for additional phase(s). The standard approach for such systems is to formulate balance equations for a microemulsions phase in addition to the other phases present. This complexity, together with the dramatic effects of surfactants on constitutive relations, leaves many unresolved issues. The most widely discussed and critical issue is the modeling of the macroemulsion transport. Macroemulsions have a characteristic dimension larger than one micron and are either unstable or mesostable, while microemulsions have a characteristic dimension smaller than one micron and are thermodynamically stable. If macroemulsion transport is important, balance equations will need to be formulated and solved to describe such cases accurately.

Some questions remain to be answered: in developing the large scale percolation models, an algebraic relationship between Pc and S is assumed. However, when large scale heterogeneities are present, "slow-drainage" phenomena are expected to occur on a larger scale. This would undermine the instantaneous responses between these two variables and lead toward a differential relationships relating capillary pressure and saturations which would seem more close to physical reality. An important issue is the upscaling of the p-S-k relationships, since studies have always been performed at laboratory scales, but these relationships are used at field scales. Scaling approaches are also requested for modeling sorption effects, especially when moving from grain scale to larger scales. Scaling is necessary, since grain scale for large domains would be excessively demanding. Fields simulations, on the other hand, need proper relationships more than the classical parameter fitting which does not really upscale the phenomena.

Mass-transfer obtained as a combination of nondimensional parameters (based on dimensional analysis) suffers in that it derives only from a mathematical combination of dimensional parameters in order to obtain some new lumped parameters. The choice of groups is rather arbitrary since the dimensional analysis provide some dimensionally correct combinations which are fitted on experimental data using linear or nonlinear regression. However, very few of these parameters have been experimentally measured and for only a very limited range of conditions.

Natural porous media are usually more heterogeneous than the systems examined in the theoretical and experimental (laboratory) study, in which simplified configurations are considered. This heterogeneity may lead to unpredicted behaviour of transported single- or multi-phase plumes, and to phenomena like fingering, whose complete knowledge is far to come.

Since existing mass-transfer models are all based on saturation levels lower than or equivalent to the maximum initial-residual saturation levels, existing relationships are inadequate to describe mass transfer in pooled regions. Yet these pools will be long-lived in the subsurface environment and hence of significant concern. In summary, the dynamics of DNAPL pool formation and mass-transfer from DNAPL pools in markedly and subtly heterogeneous porous media are worthy of further investigation.

6 Possible research topics of the ongoing PhD

In this section a possible line of research is identified, based on consideration of the literature review and the "Open Issues" presented in this report.

The research topics mentioned could all be good candidates for characterizing future research within this PhD. However some constraints must be accounted for, due to the lack of a laboratory in which measurements can be made, so no experimental work could be included in the thesis. However, this work should not focus solely on mathematical development of a multiphase model. It is not the main scope of this PhD work to produce a super-efficient code. A focus on the development of some computational modules able to describe certain sets of phenomena is preferred.

A possibility could be to focus on the development of a two-phase code for treating remediation techniques such as air-sparging and or bioventing in connection with other remediation techniques. Including multiphase flow is deemed important also beacuse of the novel and complex issues it encompasses. Modeling of surfactant injection in groundwater could be quite appealing since it produces a colloidal phase and is not trivial to model. The work could be restricted to the set of surfactants which are compatible with survival of subsurface bacteria. Biodegradation effects could/should also be included; a formulation similar to that considered by *Molz et al.*, 1986, *Widdowson et al.*, 1988, *Chen et al.*, 1992 is suggested, with sorbing phase outside the range of linear retardation. On the other hand, there is still much discussion on mathematical formulations of biodegradation of contaminants. A "biofilm model" formulation seems appropriate for several real field applications, due to evidence of aquifer clogging in the surroundings of wells injecting oxygen and nutrients into the subsurface.

The choice of model to develop will be conditioned by the availability and the type of data set with which the model could be calibrated and validated. Depending on data availability, an improved chemical module(s) could be developed and tested to get a better understanding on how to model correctly biodegradation reaction in contaminated soils.

There has been much recent work on natural attenuation, and it should be a viable option to include something on this topic. However, this last is still conditioned by the availability of detailed data. The literature contains several applications of "screening models" (*Weaver et al.*, 1996a, 1996b) in which a very simplified model is applied to get a rough estimate of the distribution of the plume. The estimates are often considered good when errors in concentration prediction are within one order of magnitude with respect to field measures. This seem to be consistent with accuracy of field measurements.

A third and maybe more viable alternative (which could more easily fulfill the 2-$2^{1/2}$ year time constraint of the PhD resesearch) is the possibility of exploiting the STOMP code (*White et al.*, 1995). This is a possibility that has been discussed already. The use of STOMP would allow the bypassing of the realization of a multiphase flow code (STOMP has been sufficiently benchmarked and debugged), to focus instead on the problem of coupling of several remediation techniques with bioremediation and/or natural attenuation. A possible work plan could be:

1. obtain, install, and learn the STOMP model;

2. Develop a theoretical description and mathematical formulation of some biodegradation kinetics;

3. Realization of a "biodegradation module" suitable to be plugged into the STOMP code;

4. Benchmarking of several options of the code and application of this updated STOMP (i.e., STOMP + biodegradation module) to a dataset eventually available. Some work could be dedicated to simulations of different scenarios in which the coupling of different remediation techniques could be implemented at the same time;

5. Summary of results and final thesis.

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