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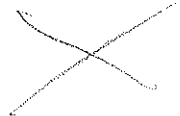
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Optimization of Groundwater Remediation Strategies
in Aquifers Affected by Slow Desorption Processes

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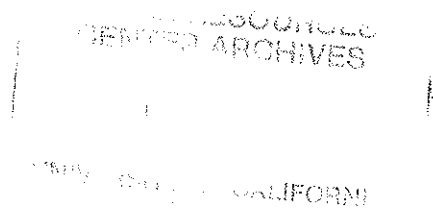
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Optimization of Groundwater Remediation Strategies
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ABSTRACT

Most of the major groundwater contamination in California, including that inundating the San Fernando, San Gabriel and San Bernadino Valleys, will be addressed using some variation of the pump-and-treat technology. The pump-and-treat strategy is often judged to be unsuccessful because of difficulties encountered in recovering the contaminants from relatively stagnant zones within stratified aquifer systems. These zones can exist at the particle scale, as intraparticle or intra-aggregate porosity, and at the larger scales, as low permeability layers or lenses interspersed in substantially more permeable layers. This work focuses first on achieving an efficient numerical solution to a system of groundwater flow and contaminant transport equations that sufficiently captures the dynamics of slow desorption in a two-dimensional porous medium. The upstream-weighted, multiple cell balance (UMCB) method is developed and verified here to provide such a solution. Next, this work focuses on coupling the simulation model with a management model to provide a design tool for pump-and-treat remediation of real aquifer systems. Zeroth, first and second moments are calculated for mobile and immobile aqueous concentration distributions, and tested as potential design objectives. In a departure from conventional approaches, spatial moment analysis is also applied to local differences between simulated mobile and immobile aqueous concentrations.

Results suggest that pump-and-treat systems in heterogeneous domains might best be designed as two phase operation. The first phase addresses the early time removal of mobile (i.e., readily accessible) phase contaminant, and suggests the conventional approach of placing extraction wells slightly downgradient of the plume centroid. The second attacks fractions of the contaminant plume that are either harbored within immobile porosity, or that have penetrated impermeable layers. The latter stage can be accomplished through maximizing the desorption driving force distribution, or be minimizing the spreading (variance) of this distribution. It is recommended that the techniques developed in this research be applied to one or more of California's on-going pump-and-treat systems.

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1. PROBLEM AND RESEARCH OBJECTIVES

Remediation of groundwater supplies impacted by sparingly soluble organics becomes an inefficient process once these chemicals have achieved a dilute and widespread state. The most common remediation strategy is groundwater extraction followed by conventional treatment (e.g., activated carbon adsorption) of the extracted water, a technology referred to as pump-and-treat. Most of the major groundwater contamination scenarios in California, including those inundating the San Fernando, San Gabriel and San Bernadino Valleys, will be addressed using some variation of the pump-and-treat technology.

Despite its widespread usage, it is well-known that the typical pump-and-treat project is only partially successful in that it succeeds in extracting large amounts of contaminant during the early stages of implementation, but fails to achieve and maintain targeted cleanup levels within a reasonable timeframe (Mackay and Cherry 1989; Travis and Doty 1990). Instead, projected timeframes for large scale pump-and-treat efforts are commonly discussed in terms of decades. The characteristic "tailing" in concentration histories has been observed in field experiments (Roberts et al. 1986; Bahr 1989; Mackay and Cherry 1989; Harmon et al. 1992; Thorbjarnarson and Mackay 1994), and indicates that desorption processes are slow relative to induced groundwater velocities.

The popularity of the pump-and-treat technology is due to the following considerations: (1) pump-and-treat guarantees an immediate reduction in groundwater contaminant levels; (2) the remediation is based primarily on hydraulic capture zone considerations that are relatively straightforward to implement; and (3) treatment at the surface can be accomplished using conventional technologies, which are generally easier to implement than *in situ* treatment strategies, due to a combination of technological or regulatory issues. The consensus among researchers is that several interrelated flow and transport phenomena are responsible for the shortfall of pump-and-treat strategies, including: (1) the existence nonaqueous phase liquid (NAPL) serving a contaminant reservoirs at unknown locations of the subsurface domain; (2) nonequilibrium desorption phenomena limiting the rate contaminant release from aquifer solids; and (3) relatively impermeable hydrogeologic units harboring aqueous and sorbed contaminants. The first of these problems, the presence of NAPL, is the most serious, and must be dealt with before the final pump-and-treat design is emplaced. However, even with the elimination of a NAPL presence, the optimal management of a relatively large contaminant plume in the face of the latter two problems is a difficult task.

The objectives of this research were two-fold:

- (1) To formulate and solve the governing equations representing a multi-dimensional flow and transport model capable of simulating the essential rate-determining desorption processes affecting the remediation of contaminated stratified aquifers systems.
- (2) To couple the flow and transport model with a management model capable of providing optimal pump-and-treat designs.

2. METHODOLOGY

The research methods employed in this project are discussed in the following sections: (2.1) Flow and Transport Model Formulation; (2.2) Numerical Solution; (2.3)

Simulated Domain; (2.4) Moment Analysis and (2.5) Remediation Management. A detailed accounting to the methods used in (2.1) through (2.3) may be found in a recent publication (Kong and Harmon 1996). Because the physical parameters used in this project are important for understanding the results section, they are discussed here in some detail in (2.3). The methods applied in (2.4) and (2.5) are currently being prepared for submittal to a refereed journal (Kong 1995; Harmon et al. 1996).

2.1 Flow and Transport Model Formulation

Because of the issue of flow field heterogeneity, adequate modeling of contaminant transport in a nature porous medium requires the solution of both flow and transport equations. The coupled equations allow for modeling of sorption/desorption dynamics at both the particle- and layer-scales. The layer-scale mass transfer resistance is exhibited in zones with relatively small pore water velocities, as determined by the flow equation. The mass transfer resistance at the particle-scale is modeled using a rate-dependent solute source/sink term in the transport equation (i.e., invoking the mobile-immobile porosity concept). These equations are detailed in Kong and Harmon (1996).

2.2 Numerical Method

The simulation model developed here is used as part of a remediation management model. As such, repetitive solution is required, and computational efficiency is a concern. With this in mind, a combined finite difference, finite element method, referred to here as the upstream-weighted, multiple cell balance method (UMCB), was selected for solving the governing equations. The UMCB method combines a finite-element basis function with a finite-difference local mass balance. The technique used in this paper is an extension of the method of Sun and Yeh (1983), who introduced the method to solve the flow and transport equations in two-

dimensions, assuming equilibrium sorption. Later, Wang et al. (1986) extended the equilibrium version of the Sun and Yeh's model to three-dimensions. This work extends the algorithm to encompass a nonequilibrium approach. The MCB method, as applied to this research, is presented in Kong and Harmon (1996).

2.3 Simulated Domain

The set of simulations presented here illustrates the sensitivity of the two-dimensional pump-and-treat simulation to changes in the number and location of pumping wells. The overall goal of the analyses is to demonstrate the potential usefulness of spatial moment analysis in optimizing well location in complex hydrogeologic regimes. The simulations focused on the two systems depicted in Figure 1: (1) a homogeneous, sandy aquifer, and (2) an ideally stratified aquifer-aquitard system. The domains were chosen to allow for comparison of long-term contamination scenarios in which mass transfer resistances at different length scales (i.e., particle and layer scales) impact the success of remediation efforts.

The heterogeneous domain is composed of a system of three hydrogeologic units, or layers. This configuration was chosen to reflect current site characterization strategies, which typically implement a zonation approach due to data sparsity. The parameter requirements for the simplified flow regime may be considered reasonable, with the possible exception of the intraparticle mass transfer rate parameter which is typically not available and may need to be estimated from literature values (e.g., Ball and Roberts 1991; Fry and Istok 1994; Harmon and Roberts 1994). The center layer, characterized by a low permeability, serves as a hydraulic barrier between the upper and lower aquifers. However, the center layer is amenable to contaminant flux.

2.3.1 Flow and Transport Parameters. In Figure 1, the upper and lower layers are considered as conductive zones, and the middle layer is considered as an aquitard,

characterized by a hydraulic conductivity that is four orders of magnitude lower than that of the upper layer. The hydraulic conductivity distribution was assumed to be homogeneous and isotropic in each layer. The horizontal Darcy velocities for the three layers, under a constant hydraulic gradient of 0.0002, are approximately 21, 0.0021 and 2.1 m/yr, for the upper, middle and lower layers, respectively. Under natural flow conditions, the vertical component of the velocity is negligible in all layers.

The longitudinal dispersion coefficient (D_L) values are the product of a longitudinal dispersivity (α_L) value of 10 m and the local groundwater velocity. According to the Gelhar et al. (1992) correlation with groundwater velocity, the longitudinal dispersion coefficient values for the given natural velocities range are 0.57, 5×10^{-5} and 0.057 m²/d for the upper, middle and lower layers, respectively. The transverse dispersivity value was chosen as one-fifth of the longitudinal value (Freeze and Cherry 1979).

The sorption capacity, given in terms of the equilibrium distribution coefficient (K_d), was assumed to be distributed homogeneously within the individual layers. This parameter determines the degree of retardation of the solute in both the inter- and intraparticle pore spaces (equations 3 and 4). The upper and lower layer parameters represent those of a sandy deposit, with relatively weak to moderate sorption capacities for relatively mobile organic solutes, such as halogenated alkenes. For the base simulation, the sorption capacity of the center layer was selected to be relatively high, compared to the adjacent layers. The K_d value (4.5 mL/g) was intended to be representative of that for a silt or clay deposit, which might contain a significantly greater amount of natural organic matter than the neighboring sands. Roberts et al. (1990) encountered confining solids with similar sorption characteristics in core samples taken from the a small scale experimental field site.

The particle-scale sorption/desorption rate characteristics were also assumed to be distributed homogeneously within each of the layers. The base simulation values for the

rate constants (α) for the three layers were calculated using observed pore diffusion coefficients measured for sandy (Harmon and Roberts 1994) for the upper and lower layers, and for silty particles (Harmon 1992) for the middle layer. The physical characteristics shown in Figure 1 were measured previously for the same materials (Ball et al. 1990; Harmon 1992). The rate constant values for the upper and lower layers were substantially lower than the value used for the middle layer. This result reflects a presumed particle size effect, with the sand-sized particles of the upper and lower layers being substantially larger than the silt-sized particles of the center layer. Thus, particle scale desorption limitations are presumed to be less significant in the middle layer.

The homogeneous flow domain was assumed to be of the same size as the heterogeneous domain, but all parameters in the homogeneous domain were equivalent to those of the uppermost layer of the heterogeneous domain.

2.3.2 Initial and Boundary Conditions. Contaminant transport was simulated under natural and forced gradient conditions. Conditions of no flow or mass flux were imposed at the top and bottom of the lower boundaries of the two computational domains. Such conditions are reasonable for the lower boundary condition, which might be interpreted as a bedrock formation, and somewhat artificial for the upper layer. The latter would more likely be composed of a porous layer allowing some mass flux. To simplify calculations, vertical mass flux was allowed only within the domains. Under the imposed natural gradient conditions, the domains were subject to constant head vertical boundaries, providing a hydraulic gradient of 0.0002. The forced gradient conditions were implemented by inserting a pumping well (a column of fluid sink nodes) in the upper region of the two domains, as indicated in Figure 1. For the heterogeneous domain, this well fully penetrated the uppermost layer. In subsequent simulations, the location of the pumping well was varied in the longitudinal direction, and, finally, in the

vertical direction. In all cases, the pumping well was simulated using three fluid sink nodes with flow rates of $50 \text{ m}^3/\text{d}$ for a total pumping rate of $150 \text{ m}^3/\text{d}$.

A constant source term was used to simulate contaminant release into the simulation domains. A source term was situated at a column of vertical nodes in the upper portions of the computational grids (Figure 1), and was meant to simulate a steady concentration flux. This term represents a steady state dissolution process as might occur with a steady flow of groundwater through a column of residual nonaqueous phase liquid (NAPL) entrapped in the porous medium (Powers et al. 1991; Anderson et al. 1992). The natural hydraulic gradient that was imposed drove groundwater flow during the contamination phase of the simulation. The constant concentration of 1 mg/L was maintained at the source nodes. This steady state concentration is roughly 100 to 1000 times less than the aqueous solubility of common halogenated alkenes (e.g., TCE 1100 mg/L), yet 100 to 1000 times greater than the regulatory limit for such compounds (e.g., MCL for TCE is $5 \text{ } \mu\text{g/L}$).

The simulated contaminant distributions for the natural flow simulations were used as initial conditions for the remediation simulations (i.e., pumping case). This approach differs from that employed in many related studies, which simply assumed an initial contaminant concentration distribution that is in equilibrium with the aquifer solids (Goltz and Oxley 1991, Rabideau and Miller 1994). The approach employed here enables simulations to address the relationship between contamination history and remediation, which is particularly important in the heterogeneous case (Kong and Harmon 1996).

2.4 Moment Analysis

Normalized masses were calculated from the simulated concentration distributions discussed in the previous section. For each distribution, the total mass (aqueous and sorbed) was calculated as the zeroth spatial moment of the simulated distribution,

normalized by the total amount of mass delivered to the subsurface prior to the onset of remediation (MT). Spatial and temporal moment analyses have been used with some frequency for quantifying observed and simulated contaminant distributions in groundwater. The zeroth, first and second spatial moments are representative of the amount of mass, the center of mass, and the degree of spreading about the center of mass of a contaminant distribution. Detailed expressions used for the various moment calculations are presented in a forthcoming publication (Harmon et al 1996). These moments are typically calculated for the mobile aqueous concentration, which is the only directly observable concentration value. In a departure from previous approaches, this study demonstrates the usefulness of zeroth and first spatial moments as calculated from simulated spatial distributions of the local concentration gradient ($C_m - C_{im}$).

2.5 Remediation Management Model

2.5.1 Background

As expected, the initial management models focused on simple conditions (e.g. non-reactive solutes, steady flow, homogeneous porous medium, etc.), while subsequent models gained in complexity. Willis (1976) formulated a mixed integer optimization model for disposal of wastes to minimize costs of surface waste treatment. The simulation model assumed no dispersion, and steady flow and transport conditions. Gorelick (1982) developed a linear programming model to maximize the disposal of a non-sorbing solute in an aquifer, subject to water quality constraints at specific locations. Gorelick et al. (1983) applied least squares regression and linear programming for absolute error to identify the sources and magnitudes of chloride and tritium in a hypothetical two-dimensional, heterogeneous and anisotropic aquifer, under steady and transient conditions. Alhfeld et al. (1988) utilized nonlinear optimization formulations and sensitivity theory to maximize the removal of contaminant and to minimize the cost of remediation to specified levels over a fixed time period. Their simulation model

assumed steady flow with transient transport pollutant response for a sorbing contaminant using the local equilibrium assumption.

More recently, Lee and Kitanidis (1991) formulated a stochastic optimization model, which minimized the expected cost from the limited information available. Their optimization method applied a combination of constrained differential dynamic programming with perturbation approximations, while the simulation model assumed equilibrium sorption in a two-dimensional aquifer under unsteady flow and transport conditions. Culver and Shoemaker (1992) applied a successive approximation linear quadratic regulator (SALQR) with flexible management periods to minimize the remediation cost in a homogeneous and isotropic aquifer with equilibrium sorption. Their work showed that the flexibility in changing the duration during which the pumping rates remained constant reduced the computational effort by as much as 85 percent. Wang and Ahlfeld (1994) developed a model that optimized the location of wells and pumping rates, treating them as continuous variables in a two-dimensional aquifer under steady flow and transient transport of a single contaminant under equilibrium sorption conditions. Haggerty and Gorelick (1994) formulated a model to minimize total pumping by finding the optimal well locations and pumping rates for multiple contaminant remediation. These investigators used a simulation model which incorporated non-equilibrium (rate-limited) sorption for three organic contaminants. Harvey et al. (1994) analyzed the effect of pulse pumping in the remediation of contaminants subject to rate-limited mass transfer. In a recent study of soil vapor extraction system design, Sun (1994) introduced a mixed integer nonlinear optimization scheme to provide optimal well locations and pumping schedules. In order to reduce the computational requirements in the system design, a k-change local search algorithm was employed to solve the combinatorial optimization problem.

2.5.2 Management Algorithm The present work focuses in the development of a sound and efficient management model for groundwater flow and contaminant transport.

The management model will help establish the optimal pumping rates and pump well locations that maximize the mass of contaminant extracted from an aquifer over a fixed time period or that minimize the time required to attain a desired level of cleanup. The optimization scheme is accomplished by coupling the groundwater flow and contaminant transport model developed by Kong and Harmon (1996) with the well established nonlinear optimization programming system MINOS (Murtagh and Saunders 1978; 1982). MINOS conducts several evaluations of the mass remaining in the aquifer at different pump rate combinations by calling the groundwater flow and contaminant transport simulation program, and MINOS iteratively seeks the combination that produces the optimum cleanup effort. The nonlinear gradient searching techniques used by MINOS significantly reduce the number of simulations required to find the optimum solution, when compared with a standard trial and error approach.

The link between the optimization model and the simulation model has been accomplished and simple solutions are now possible. The current management model will be expanded to optimize the pumping rates and well locations for multiple extraction/injection well systems, multiple remediation periods, and large scale aquifers. The current solutions are limited to the determination of the optimum pumping rate combination of fixed-locations two-well systems that will extract the maximum mass of contaminant in a fixed time period.

An example optimization problem is one which is constrained by the aquifer system represented in the simulation model, which includes initial conditions, boundary conditions, and the spatially distributed parameters. In this study, the spatial domain represents a vertical cross section of a three-layer, small scale aquifer with a low permeability middle layer and subject to diffusion-limited sorption at the particle scale. The extraction system consists of two pumping wells with fixed locations, but variable pumping rates. Well 1 is located in the middle of the aquifer ($x = 50$ m, See Figure 1), while well 2 ($x=10$ m) is closer to the source of contamination ($x = 0$ m), which travels

towards the wells by a natural gradient. The wells pump from the upper layer of the aquifer at rates Q_1 and Q_2 . Also, upper and lower bounds are specified for the pumping rates at each well. An additional constraint is incorporated that limits the cumulative pumping rate of the wells to be under a maximum cumulative pumping rate. This later constraint may be related to the operating budget of the cleanup effort, which limits the total amount of water that may be extracted from the site at a given time, or to prevent aquifer overdrafting. The optimization goal of this problem is to maximize the mass extracted from the aquifer, which is the same as minimizing the mass remaining in the aquifer. The optimization is conducted by minimizing the zeroth moment M_{00} of the mobile concentrations (the objective function) of contaminant in the porous medium, which is equivalent to minimizing the mobile mass remaining in the aquifer and is obtained from Spatial Moment Analysis in the simulation model. The decision variables, which will result in the optimization of the objective function, are the extraction rates at each well. Mathematically, this optimization problem is formulated as follows:

$$\text{Min } M_{00}$$

Subject to:

$$Q_1 + Q_2 \leq U_1$$

$$U_{\min} \leq Q_1 \leq U_2$$

$$U_{\min} \leq Q_2 \leq U_3$$

Flow and Transport Simulation Model
(Initial and Boundary Conditions, Parameters, etc.)

Where: M_{00} = zeroth moment of the aqueous concentration (mass /L³)

Q_1, Q_2 = Pumping rates at wells 1 and 2 respectively (ft³/day)

U_1, U_2, U_3 = the allowable total and individual pumping rates, respectively (ft³/day)

U_{\min} = the minimum allowable individual pumping rate (ft³/day)

The constraints are specified in files in the MINOS optimization program, while the simulation model is linked as a subroutine of MINOS. In addition, an estimation of the gradients of the objective function (M_{00}) with respect to the decision variables (Q_1 and

Q₂) must be performed to aid MINOS in finding the trajectory of the optimization solution(s). These gradients are calculated by perturbing the decision variables one at a time by a small amount (0.01-0.1 ft³/day) and calling the simulation model to determine the corresponding change in the decision variable.

3. PRINCIPLE FINDINGS AND SIGNIFICANCE

Results from the simulations are presented in the form of simulated spatial distributions, or "snapshots", of the mobile and immobile aqueous concentrations. The spatial distributions were also integrated over the computational domain to provide contaminant mass histories. A final set of analyses detail the temporal behavior of the spatial moments of the simulated mobile concentrations (C_m), immobile concentrations (C_{im}) and local concentration gradients ($C_m - C_{im}$) to provide new insight into the problem of pump-and-treat strategies. However, discussion of the spatial moments becomes rather involved and is abbreviated here. The spatial moment calculations and results will be presented in detail in a forthcoming publication (Kong 1995; Harmon et al. 1996).

3.1 Simulated Spatial Distributions

For brevity, this section details the results for the heterogeneous case with reference to the results for the homogeneous domain, which are not explicitly presented. The isoconcentration plots in Figure 2 represent (a) the progression of the mobile contaminant plume under natural flow conditions (i.e., the contamination scenario), and (b) the progression of the same plume after pumping begins. The final spatial distribution in column (a) of the figure represents the plume after 20 years, and is the point of departure for the pump-and-treat simulations. The corresponding immobile contaminant distributions are plotted in Figure 3.

It is important to recall that the immobile zone aqueous concentration is coupled to the mobile aqueous concentration in these simulations, limiting the rate at which a large portion of the sorbed mass can enter or leave the mobile aqueous phase. Given the transport parameters selected, the local equilibrium assumption is less appropriate when pumping increases the groundwater flow rate. Thus, the discrepancy between the mobile and immobile zone concentrations is greatest early in the pump-and-treat phase of the simulation.

A second observation regarding the plots in Figures 2 and 3 pertains to the amount of mass in each of the three geologic units of the heterogeneous domain. As the sequence of plots for natural flow conditions in Figures 2a and 3a suggests, the majority of the contaminant mass remains in the uppermost layer. However, as the 10 year isoconcentration contours indicate, contaminant mass slowly enters the low conductivity layer. As the 20 year plots depict, this layer can accumulate a significant amount, given adequate time. At the onset of pumping, the concentrations in the upper layer are immediately reduced. However, the lower layers, largely unaffected by the pumping, continue to receive an influx of contaminant. Indeed, in the 15 year plots in the pumping simulations Figures 2b and 3b, a lower lobe of the plume is evident, indicating penetration of a substantial amount of the contaminant into the relatively conductive lower layer.

3.2 Simulated Mass Recovery

The historical reduction in total mass in the heterogeneous aquifer system (aqueous and sorbed) for various locations of a single pumping well was analyzed by integrating the concentration distributions. A comparison of the relative success of the different locations clearly indicated that the locations just down-gradient of the initial plume centroid (approximate location $x = 15$ m) are optimal. Well locations located relatively further down-gradient of the plume are more conservative, but will extend the

pump-and-treat project lifetime substantially. These results are in accord with previous groundwater quality management studies (e.g., Harvey et al. 1994). The final stages of the simulations indicate that even the preferred well locations suffer from the mass transfer limitations imposed by the large particles and the low conductivity layer.

3.3 Moment Analysis

The results from the analysis of the spatial moments of the simulating mobile, immobile concentration distributions and desorption driving force (C_{m-im}) distribution provided insight into the management of pump-and-treat remediation (for details, see Kong 1995; Harmon et al. 1996 and section 3.5 below). In particular, it became evident that (1) optimization schemes might be best based on the mobile zone concentrations relatively early in the remediation process, and (2) the variance (i.e., second moment) of the driving force distribution provides an excellent gauge of cleanup progress at later times.

3.4 Two Phase Pumping Scheme

The results from the heterogeneous case simulations suggest that a two-phase approach will provide an efficient pump-and-treat design in a heterogeneous domain. In the first phase, the more accessible portions of the plume are extracted. After the majority of the accessible mass has been recovered, a second phase is begun to target the residual portions of the plume with additional extraction wells. The key considerations in this design strategy are the timing of the second phase, and the location of the additional extraction wells. The results from the first and second moment calculations suggest criteria for these design considerations. The case of the nearly optimal extraction well ($x=20$ m) from the previous battery of simulations served as a point of departure for an illustrative example of the two phase approach. Again, this case is presented in its entirety in a forthcoming publication (Harmon et al 1996).

Mass is effectively removed by pumping at $x = 20$ m for the first decade of the simulated pump-and-treat operation. This time period corresponds to the first phase of the remediation. After ten years, as was discussed previously, the majority of the mass remaining cannot be recovered because of the flow field heterogeneity. According to the two phase approach, a second well should be developed to capture the remaining mass, and the question becomes one of locating this well. The best location, in the absence of a second well, the centers of mass will behave as follows: (1) the driving force distribution will migrate to $x = 50$ m over the next decade; and (2) the mobile and immobile distribution will migrate to approximately $z = 10$ m (i.e., below the middle layer) over the same time period. Thus, it would appear that situating the second well at $x = 50$ m and $z = 10$ m would be an effective strategy.

The pump-and-treat simulations for the proposed two-phase pumping strategy are compared with the optimal single well simulation in Figure 4. The second well clearly addresses the problem of escaping mass. Optimal pumping schedules for the two phase system are discussed in the following section.

3.6 Optimal Management of Two Phase Pumping

A short time horizon of 50 days was arbitrarily chosen to compare the different remediation alternatives. The results shown in Figure 5 demonstrate the progression of the optimization process from a feasible but inferior initial solution to the final optimum solution. Initially, both pumps start at their lower bounds ($20 \text{ ft}^3/\text{day}$). This initial set of pumping rates extracts the minimum amount of water, which in turn results in a relatively low amount of mass extracted and a large amount of mass remaining in the aquifer (as represented by M_{00}). MINOS uses this initial solution to estimate the gradients of the objective function and find a trajectory for the next set of pumping rate candidates, which will improve the objective function by the greatest amount. After several iterations, the objective function can no longer be improved, because an optimum

solution has been found. This solution corresponds to $Q_1 = 20 \text{ ft}^3/\text{day}$, $Q_2 = 80 \text{ ft}^3/\text{day}$. This final solution implies that all of the available pumping rate (except for the minimum requirement for Q_1) is allocated to the more efficient well .

Even if a problem is properly formulated, non-linearities in the simulation model may prevent MINOS from obtaining a global optimum, and may limit the solution to the determination of a local optimum. However, for this particular problem MINOS did determine the global optimum. This was verified by simulating all possible discretized pumping rate combinations for this two-well extraction system. Furthermore, MINOS arrived at the same optimum even when different initial pump rates were specified, which exemplifies that the management model is quite robust in searching the optimum. Figure 6 presents a contour plot of the objective function with respect to the pumping rates. This contour map shows that the global optimum for this problem occurs at $Q_1 = 20 \text{ ft}^3/\text{day}$, $Q_2 = 80 \text{ ft}^3/\text{day}$, regardless of the initial pumping conditions selected.

Finally, the time required by the computer (IBM RS6000/590 work station) to obtain the optimum solution was in the order of one to two minutes, which is quite convenient for this test problem. However, as the management problem is faced with the substantial complexity characteristic of increasingly realistic cases, the program run-time will increase considerably.

4. CONCLUSIONS AND RECOMMENDATIONS

This research present the general framework for implementing a design and management strategy for applying the pump-and-treat technology to complex hydrogeologic domains. The approach is based on reasonably accessible parameter requirements, and is meant to be applicable to real aquifer systems. The approach is meant to address the long-term recovery problem and possible escape of plumes in heterogeneous formations. Specific conclusions from the work can be summarized by the following:

C1) The adaptation of upstream-weighted, multiple cell balance (UMCB) algorithm provides a reasonably accurate representation of the governing equations for two-dimensional groundwater flow and nonequilibrium solute transport (Harmon and Kong 1996).

C2) The UMCB nonequilibrium sorption algorithm is computationally efficient. For example, twenty year simulations involving 121 nodes (200 elements) consumed approximately three minutes of CPU time on an IBM RS6000/590 workstation (Harmon and Kong 1996).

C3) Simulations for an ideally stratified aquifer system demonstrate that, in addition to defining the flow regime, low conductivity layers can significantly impact contaminant transport. If such layers adsorb sufficient quantities of contaminant mass, they serve as contaminant sources for the adjacent geological units (above and below) during pump-and-treat remediation operations (Harmon and Kong 1996).

C4) The two-phase strategy effectively reduces the amount of tailing caused by mass transfer limitation and/or escaping portions of the original plume (Harmon et al. 1996).

C5) Optimization schemes might be best based on the mobile zone mass (i.e., zeroth moment) relatively early in the remediation process, and the variance (i.e., second moment) of the driving force distribution provides an excellent gauge of cleanup progress at later times. *This design strategy can also be viewed as one that maximizes mass extraction in a first phase of pumping, and maximizes the desorption gradient in a second phase of pumping.*

Recommendations based on this research are as follows:

R1) The first recommendation stemming from this work relates to the proper execution of the pump-and-treat technology in real aquifer systems. *Current pump-and-treat design strategies are usually base solely on groundwater flow modeling results. That is, hydraulic capture zones are determined, but little or no regard is given to the duration of the cleanup.* According the results of this study, it is clear that low conductivity zones, which might be considered merely as no flow boundary conditions in flow models, should be given greater consideration during site characterization studies. In particular, these zones should be considered as porous media impacted by either low flow or diffusion-dominated transport. *This recommendation is applicable to the Superfund sites located in the San Fernando, San Gabriel and San Bernadino Valleys, based on their hydrogeology, and likely to be applicable to many other sites in California and the rest of the United States.*

R2) It is further recommended that the techniques developed in this project be applied to one or more large-scale test cases, such as the San Fernando, San Bernadino or San Gabriel Valley basins. The techniques can be used to improve contaminant extraction efficiency (thereby reducing project lifetime). The economic benefit of the increased efficiency could be substantial, given the enormous pumping requirements and treatment costs associated with these large projects.

5. SUMMARY

One objective of this work was to develop and verify an efficient numerical algorithm for simulating two-dimensional groundwater flow and contaminant transport of a solute subject to nonequilibrium sorption. The upstream-weighted, multiple cell

balance (UMCB) technique, previously used to solve the flow and equilibrium transport equations, was adapted for this purpose. Analytical solutions to a two-dimensional, equilibrium, and a one-dimensional, nonequilibrium transport models were used to verify the resulting numerical model's performance (see Kong and Harmon 1996). Finally, an illustrative two-dimensional simulation was used to demonstrate the model's robustness, and suggests site characterization and modeling directives for pump-and-treat practitioners.

The second objective of this work was more applicable to remediation: to develop a management scheme capable of optimizing pump-and-treat strategies in aquifer systems affected by slow desorption. More basically, these aquifer systems may be characterized as vertically alternating strata of sandy (aquifer) and clayey (aquitard) material. To this end, the simulation model has been successfully coupled to MINOS, a well known optimization module, and is ready for implementation. More specific results will be available in the forthcoming publication related to this aspect of the work (Harmon et al. 1996).

6. PH.D. DISSERTATIONS:

Kong, D. 1995. *Remediation Strategies for Contaminated Aquifers Affected by Slow Desorption Processes*. Ph.D. Dissertation, Department of Civil and Environmental Engineering, University of California, Los Angeles, California.

Dr. Kong is currently employed at the Los Angeles County Sanitation District's Solid Waste Research and Development group.

Saez, J. A. 1997 (expected). *Optimization of Pump-and-Treat Remediation Design in Stratified Aquifer Systems*. Ph.D. Dissertation, Department of Civil and Environmental Engineering, University of California, Los Angeles, California.

Mr. Saez is also currently employed at the Los Angeles County Sanitation District's Solid Waste Research and Development group. He will continue work on his dissertation at no additional cost to the project, and expects to complete his dissertation in the summer of 1997.

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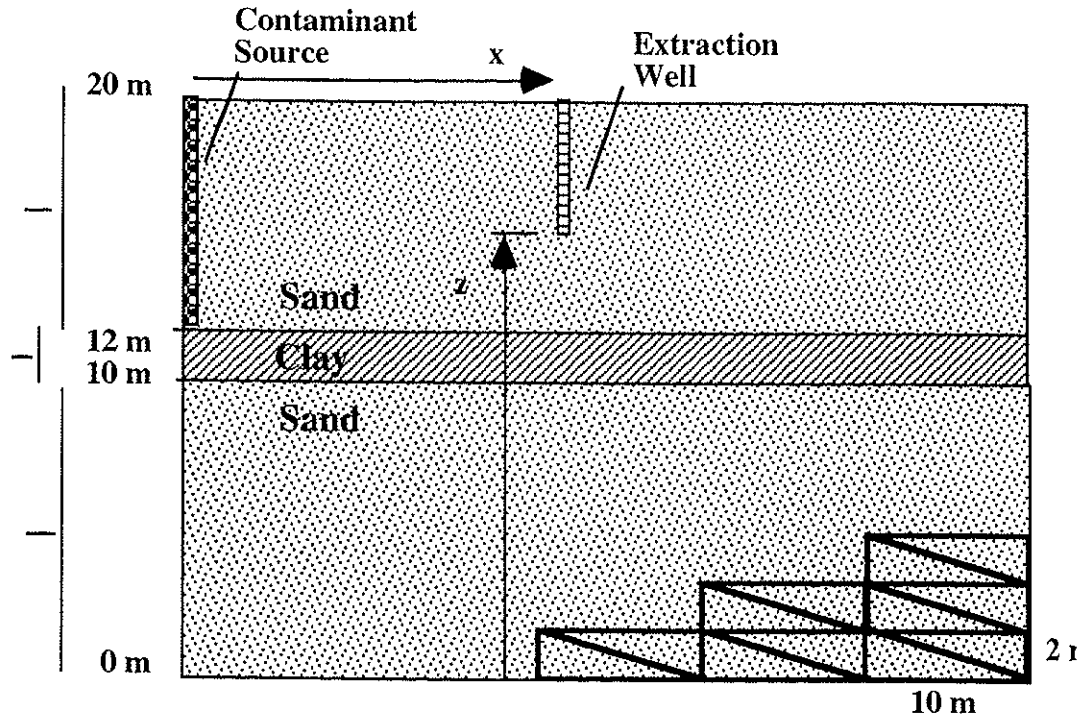
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Heterogeneous Domain:

α 0.03 d⁻¹
 K_d 1.0 ml/g
 K 100 m/d
 R_m 6.2
 R_{im} 37

 4.8 d⁻¹
 4.5 ml/g
 0.01 m/d
 19
 286

 0.2 d⁻¹
 0.5 ml/g
 10 m/d
 3.5
 34



Homogeneous Domain:

α 0.03 d⁻¹
 K_d 1.0 ml/g
 K 100 m/d
 R_m 6.2
 R_{im} 37

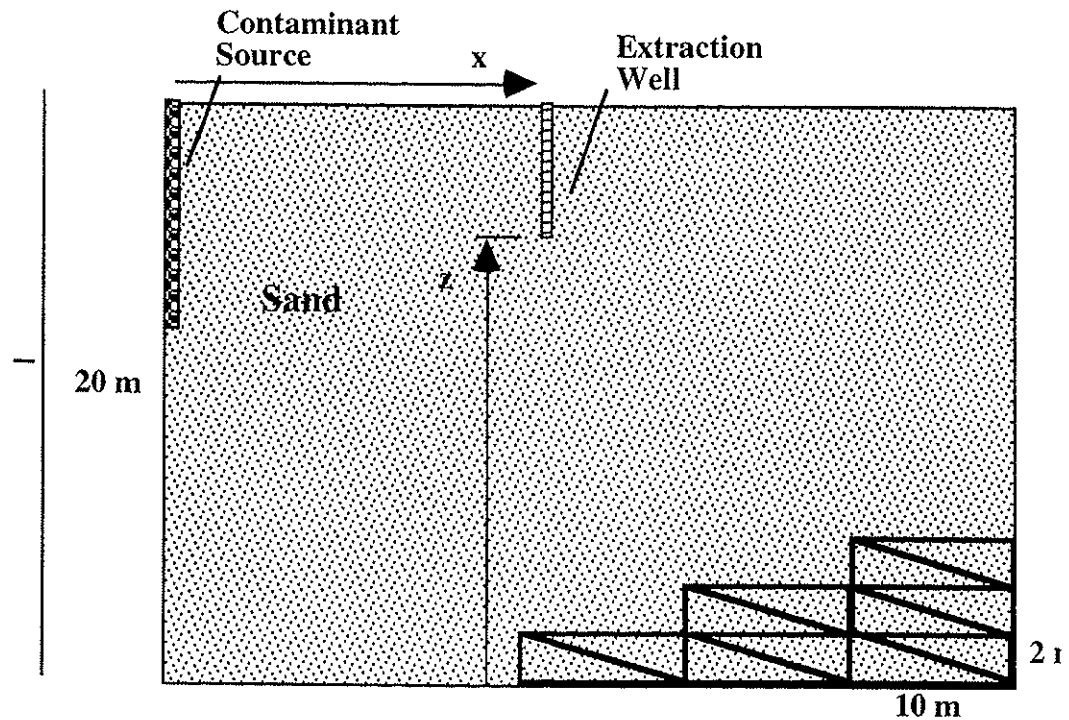


Figure 1. Computational domains, parameter zonation and extraction well location for heterogeneous and homogeneous cases. Triangular finite elements shown are at the approximate resolution used for sandy zones; regions in and around the clay layer were modeled using a substantially finer grid in the same configuration.

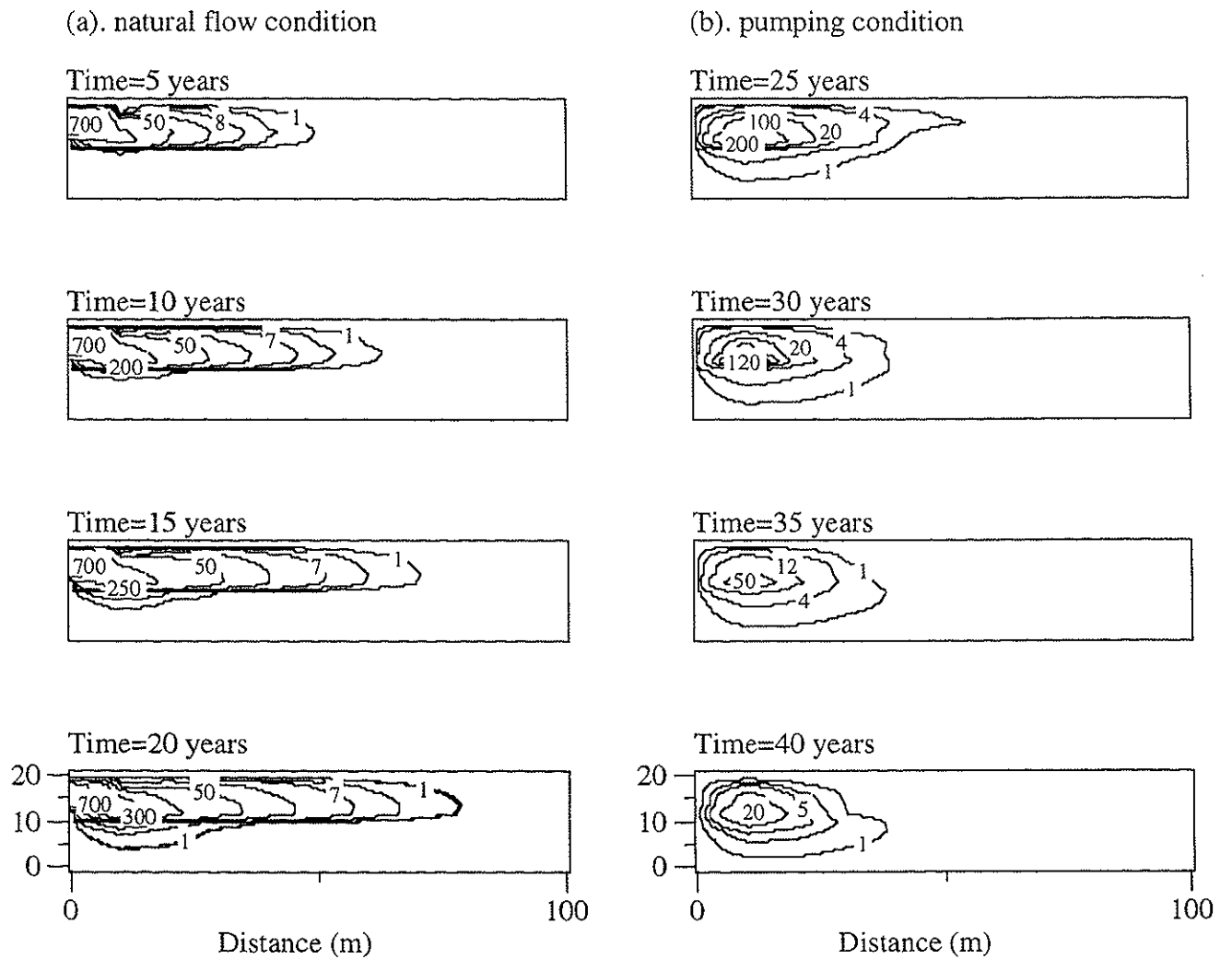


Figure 3. Heterogeneous domain simulated immobile zone concentrations lines under (a) 20 year source term under natural-gradient flow conditions for 20 years mobile zone concentrations, and (b) 20 years forced gradient flow conditions (pumping $Q = 150 \text{ m}^3/\text{d}$ at $x = 20 \text{ m}$, $z = 16 \text{ m}$) after contaminant source is removed.

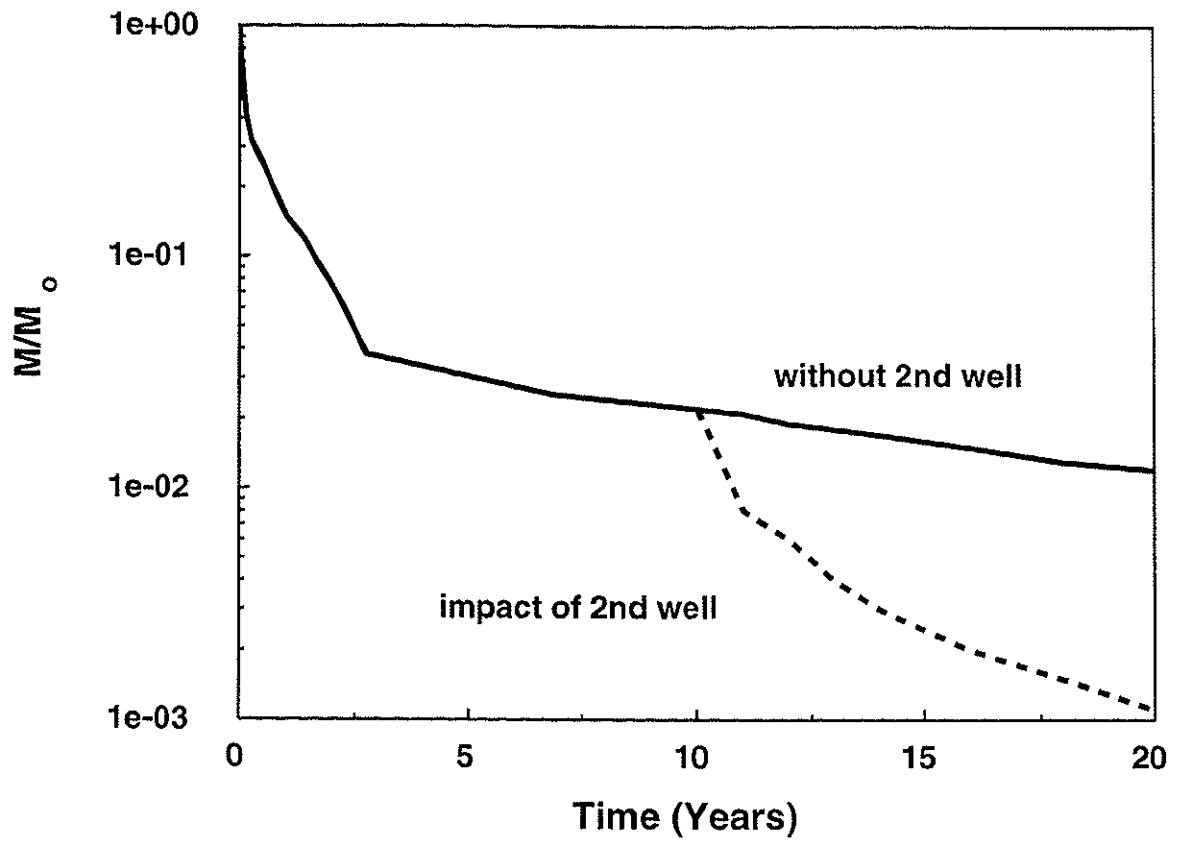


Figure 4. Normalized contaminant mass remaining in the heterogeneous domain during twenty years of pumping ($150 \text{ m}^3/\text{d}$). Pumping follows simulation of 20 years of contaminant input by constant source under natural flow conditions. Calculations are based a single pumping well located at $x = 20 \text{ m}$ and $z = 16 \text{ m}$ for ten years (Phase 1), followed by ten years of pumping from a well at $x = 50 \text{ m}$ and $z = 10 \text{ m}$ (Phase 2).

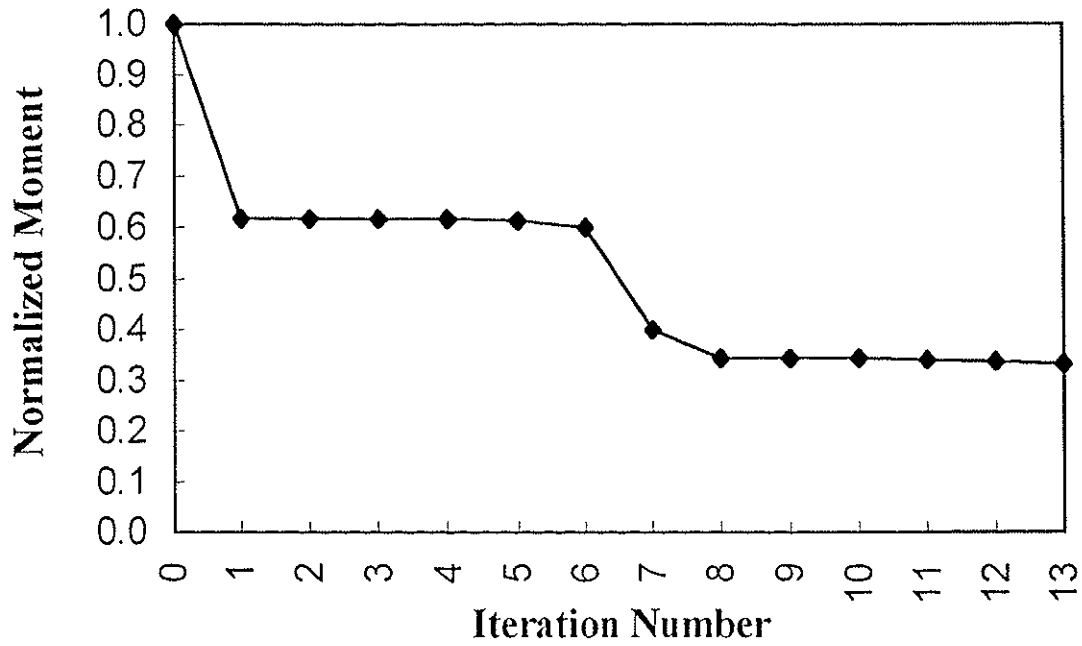


Figure 5. Improvement in the objective function (normalized zeroth-moment of mobile concentrations) versus iterations for simulated heterogeneous aquifer under steady state pumping conditions and a time horizon of 50 days. Each iteration involves new candidates of the decision variables (the pumping rates Q_1 and Q_2). The optimum occurs at $Q_1=20$ ft³/day and $Q_2=80$ ft³/day.

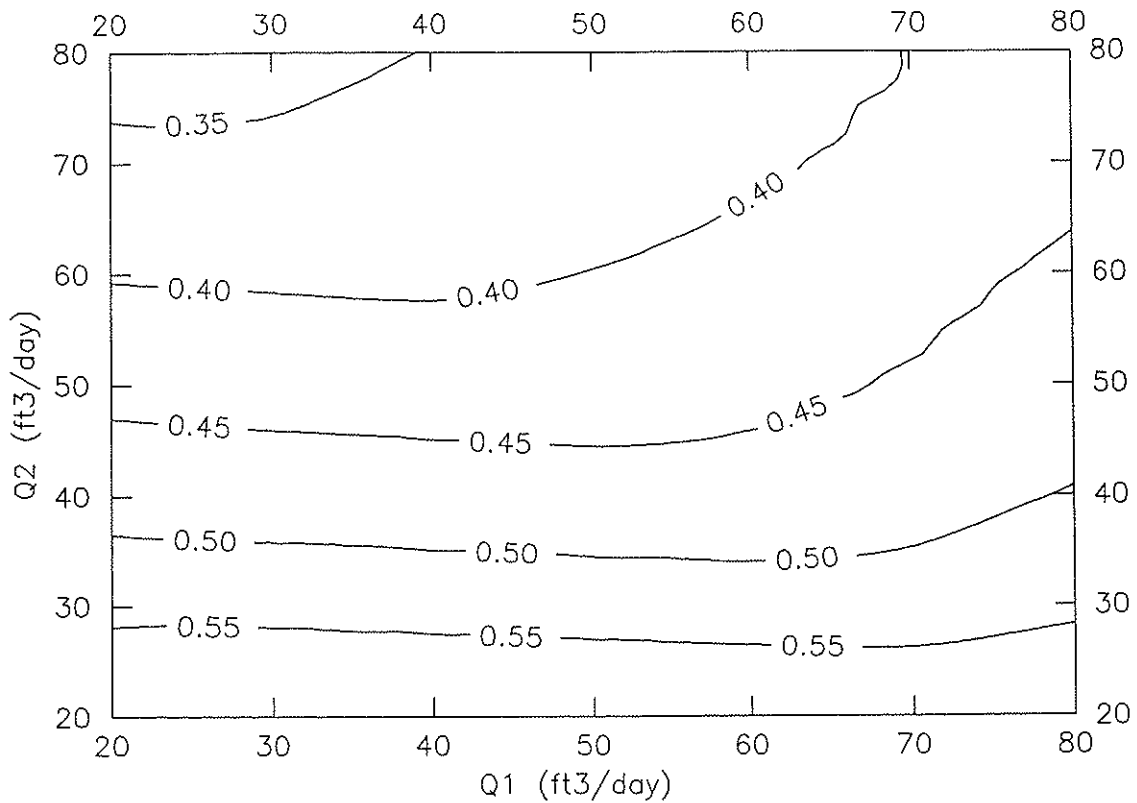


Figure 6. Map of feasible solution space of the decision variables (pumping rates) showing contours of the objective function (normalized zeroth-moment of mobile concentrations) for the simulated heterogeneous aquifer under steady state pumping conditions and a time horizon of 50 days. The figure shows that the minimum occurs at $Q_1=20$ ft³/day and $Q_2=80$ ft³/day.