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Harnessing the complex behaviour of ultra-dense and viscous treatment fluids as a strategy for aquifer remediation

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Abstract This paper examines the possibility of harnessing variable density flow and other processes in the delivery of $KMnO_4$. Specifically, we examined remediating chlorinated solvents as plumes in contaminated aquifers using a semi-passive barrier approach. It is necessary to predict how solutions behave once they are injected into the aquifer. Flow and transport are investigated through experimental and modelling studies. The experimental work of Schincariol and Schwartz is modelled using a finite element code MITSU3D. Simulations revealed that lenses with different permeability enhance mixing and relatively low permeability lenses have the potential to sequester the dense fluids. MITSU3D code is adjusted to simulate the variable density flow of viscous silicate solutions. Fingering in such a heterogeneous system appears to be relatively unimportant. Other possibilities for sequestering $KMnO_4$ at the site of emplacement include increasing the viscosity and forming gels. Dilute silicate solutions can turn into gel through time when they are mixed with dilute bicarbonate solutions. With the addition of permanganate, this gel can act as a slow-release material.

Key words variable density flow; silicate solutions; MITSU3D; time-delayed gelling; slow release material

INTRODUCTION

Remediating dilute plumes of chlorinated solvents (e.g. PCE, TCE) in aquifer and lower permeability zones occurring at depth can be impractical and/or uneconomic using conventional techniques such as pump and treat (P&T) and permeable reactive barriers (PRBs). This study investigates the possibility of using a semi-passive oxidation approach as an alternative. It involves the injection of a hypersaline solution of $KMnO_4$ at extremely high concentrations at strategic points within a contaminated aquifer using wells. Potassium permanganate rapidly oxidizes chlorinated solvents through a series of intermediate reactions which have CO_2 (g), MnO_2 (s), K^+, Cl^- and H^+ as the overall by-products (Yan & Schwartz, 1999; Huang *et al.*, 2001; Waldemer & Tratnyek, 2006). The use of permanganate (MnO_4^-) for the *in situ* chemical oxidation of chlorinated solvents can be advantageous due to its low cost, ease of handling, effectiveness over a wide pH range, and stability in the subsurface (Siegrist *et al.*, 2001).

Although there is some knowledge of variable density flow in groundwater, not much is known about the behaviour of hypersaline fluids in fresh groundwater and how to take advantage of them for remedial purposes. The goal of our study is to understand how hypersaline $KMnO_4$ fluids invade a heterogeneous porous medium and remain in place because of density effects. The hypothesis is that a dense $KMnO_4$ fluid will spread away from the injection wells without wholesale displacement of the contaminated fluid – effectively the $KMnO_4$ will under-ride the less saline groundwater. Moreover, vertical flow of the dense fluid will cause $KMnO_4$ to penetrate less permeable units, which sometimes sequester contaminants from the more active portions of the flow system. Localized reservoirs of $KMnO_4$ sequestered in pools and low permeability lenses would resist advection in the ambient flow and slowly release oxidants in the zone of reaction.

We have explored the efficacy of this idea using a combination of computer modelling and flow-tank experiments. The flow tank experiments provide a physically-based understanding of processes involved and a basis for validating the modelling approach. We tested three concepts in our experiments. The first involves the injection of a saline solution that mimics a dense $KMnO_4$ treatment solution into heterogeneous media and examines the flow of dense solutions. The second approach explores the use of silicate solutions in delivering the $KMnO_4$ into the media as a dense and viscous fluid. Finally, the third approach investigates the "time-delayed gelling" concept and slow-release of treatment fluids *in situ*.

METHODOLOGY

Computer modelling

We used the finite element code MITSU3D (Ibaraki, 1998) to model our experimental work to gain insight into variable density flow in multi-dimensional systems. MITSU3D simultaneously solves the transient groundwater flow equation and the advection–dispersion equation. The transient groundwater flow equation can be written mathematically as:

$$\frac{\partial}{\partial t}(n\rho) = -\nabla \cdot \{\rho q\} \tag{1}$$

where t is time, n is porosity, ρ is fluid density, and q is groundwater velocity, described by:

$$q = \frac{k}{\mu_f}(\nabla P - \rho g \nabla Z) \tag{2}$$

where k is intrinsic permeability, μ_f is fluid viscosity, P is pressure, g is the gravitational constant and Z is distance from datum. The advection-dispersion equation is written as:

$$\frac{\partial}{\partial t}(nc) = \nabla \cdot (nD_{ij}\nabla c) - \nabla \cdot (cq) \tag{3}$$

where c is solute concentration and D_{ij} is the dispersion coefficient, described by Bear (1972).

MITSU3D solves equations (1) and (3) simultaneously given some simulation domain, associated boundary, initial conditions and a set of parameters, which include intrinsic permeability, porosity, diffusion coefficient, and longitudinal, transverse and vertical transverse dispersivities, initial solute conditions (source location, initial concentration, and release rate), and initial pressure conditions.

The code has been applied in other studies of variable density flow. Ibaraki *et al.* (2000) studied the development of instabilities in layered media using the experimental results, described by described by Swartz & Schwartz (1998). Ibaraki & Schwartz (2001) used MITSU3D to study the efficiency of $KMnO_4$ flooding in the destruction of DNAPLs in source zones in heterogeneous media. Indications are that the solver in MITSU3D is up to five times faster than other popular codes, such as SUTRA (Voss, 1984) and SWIFT (Ward *et al.*, 1984).

Experimental work

Experiments involving dense, viscous silicate solutions were conducted in a 33 cm tall and 80 cm wide glass flow tank where a simple layered set up composed of high and low conductivity media. Uniform flow was created through the tank using a peristaltic pump. Sodium silicate solution was produced by PQ Corporation with a viscosity of 180 cp. This solution has a high density of 1.38 g/cm^3 with silica to sodium weight ratio of 3.22. We added 300 mg/L Rhodamine Wt dye to observe the solution in a flow tank.

RESULTS

Given the limited scope of this paper, we present illustrative results that show how modelling is being used to understand processes, to interpret the results of laboratory experiments, and to shed light on the three remedial concepts. Much is known both experimentally and theoretically concerning the migration of dense plumes in unstable configurations that lead to instability development. As will be evident, most of our experimental results are manifested by the formation of instabilities. In modelling practice, such instabilities are difficult to create in a realistic manner (Schincariol & Schwartz, 1993; Ibaraki *et al.*, 2000). Previous studies (Schincariol *et al.*, 1994) suggest that explicit creation of instabilities is unnecessary in heterogeneous media because the heterogeneity disrupts their formation. We explore this behaviour using experimental results from Schincariol & Schwartz (1990).

Saline solutions

Schincariol & Schwartz (1990) performed a series of experiments on the transport of saline solutions through a lenticular media. We show model results of the 10 g/L NaCl experiment by using MITSU3D and the grid shown in Fig. 1. The top and bottom boundary conditions were no flow for flow and transport. The left and right boundaries were constant flux for flux and transport.

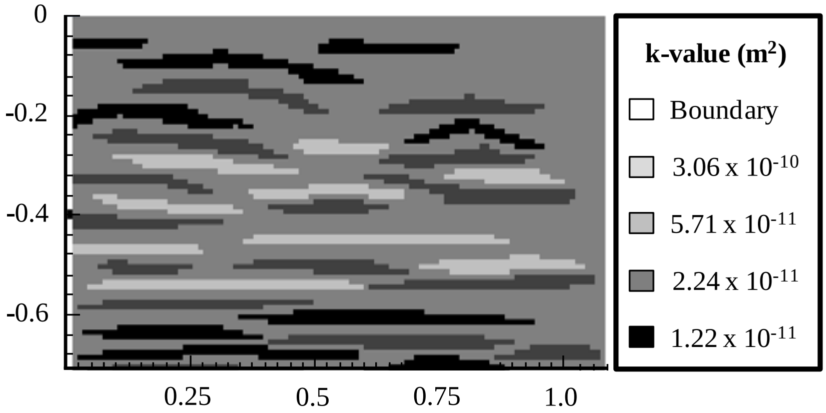

Fig. 1 Grid system applied to the heterogeneous media of Schincariol & Schwartz (1990). “Boundary” mil size has an intrinsic permeability value of 3.06×10^{-8} m^2 and is intended to simulate injection and withdrawal reservoirs.

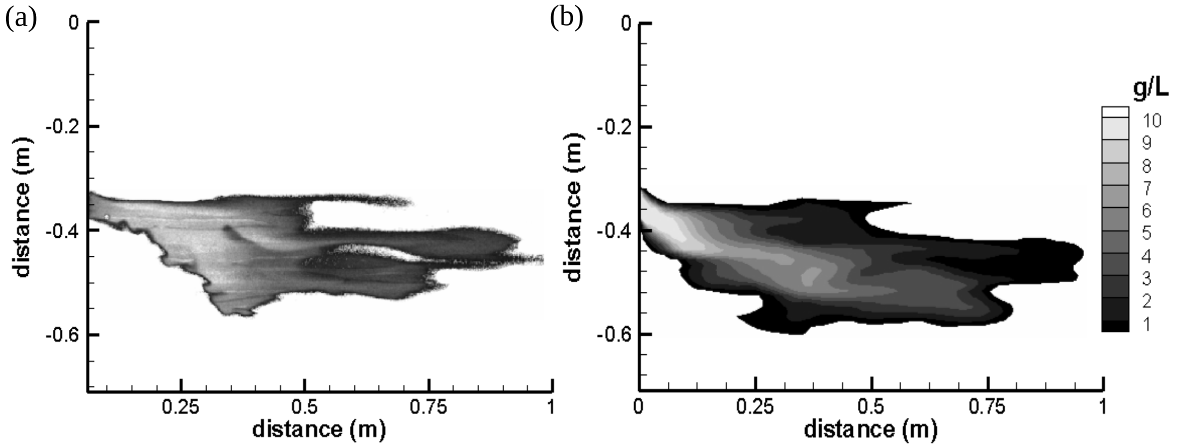

Fig. 2 Experimental results (a) with simulation results (b) for 10 g/L after 2 days. Plume concentrations below 0.5 g/L were not plotted for the experimental or the simulated plumes.

A photograph of 10 g/L experiment was processed using the method described by Schincariol *et al.* (1993). The results of the image analysis provided the concentration distribution (Fig. 2(a)) that was used as the calibration target for the simulations (Fig. 2(b)). The experimental plume was simulated reasonably well with the prominent features similar. For the most part, the lateral extent of both plumes matched well.

The experimental plume sank 7.3 cm further than the simulated plume. Moreover, the experimental plume began sinking about 14 cm sooner than the modelled plume. These problems might be attributed to 3D effects within the experiment flow tank. These 3D effects could either be caused by the solute plume moving differently in the unobservable middle of the tank or slight imperfections in lens construction (i.e. the lenses may not be the same shape throughout).

The pattern of heterogeneity clearly influences the pattern of migration of the dense plume. Much of the transport was through lenses with high intrinsic permeability and a relatively high hydraulic conductivity background matrix. The lower conductivity lenses tended to divert or partition the flow. This phenomenon produced the obvious patterning of concentrations in the plume and the tendency for preferential migration along certain axes of spreading (Fig. 2). When dense solutions were evident in the lower conductivity lenses, it is likely that density-driving forces rather than advection alone were responsible. This result is significant in the context of a remediation system because it suggests that dense fluid can be sequestered in low permeability lenses, which could potentially provide a long-term source of remediation chemicals.

Indications in the simulation results are that no obvious instabilities developed in time. Nothing special was done to trigger their growth, nor did they generate spontaneously because of the porous medium structure. This result is in keeping with the results of the experiment. It appears that this heterogeneous structure of the porous medium tended to severely minimizing the growth of instabilities. This result suggests that in some cases this process is a second order effect.

Dense/viscous fluids

Silicate solutions are inorganic, non-toxic chemical grouts that have been used for geotechnical applications such as soil stabilization. They are considered to be free of health hazards and environmental effects (PQ Corp., 2011). We postulate that the use of silicate solutions can help remediation in two ways. First, they can be used as a delivery medium for transporting oxidants into deeper portions of the aquifer due to their high density. Also, the aquifer heterogeneity provides an *in situ* long-term source of oxidants. Second, the silicate permanganate solution would create a viscosity much greater than water. This could effectively reduce the hydraulic conductivity aiding in sequestration.

The silicate solution could be injected into the uppermost high conductivity layer but the delivery of this solution had limitations due to its high viscosity. Once it was delivered, pooling occurred. This is due to the high viscosity of the silicate solution close to the injection zone. The silicate solutions then sank slowly and the concentrations of the viscous solutions decreased significantly in relatively short distances due to the dilution of the solution. There were small undulations at this boundary between the high conductivity layer and the low conductivity layer below, which caused pooling of the solutions and their subsequent sinking. The presence of such undulations triggered the development of instabilities. As instabilities grew and sank further down, their concentrations also decreased due to further dilution, with time the dilute end of the plume entered the lower high conductivity layer after 6 h. Then, the diluted solutions spread laterally in this layer (Fig. 3).

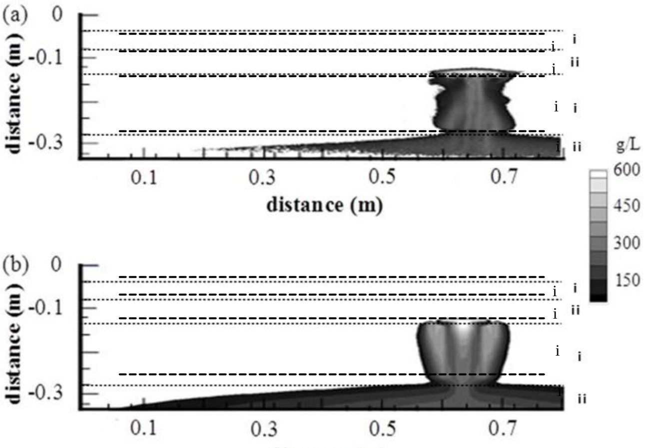

Fig. 3 Comparison of dense, viscous fluid experimental (a) and simulated (b) plumes, after 8 hours. Plume concentrations below 60 g/L are not shown for either experimental or simulated plumes. i and ii represent hydraulic conductivities of 1.6×10^{-4} and 2.9×10^{-3} m/sec, respectively.

We modelled the experiments involving the viscous solution using MITSU3D, which requires new equations to represent the density and viscosity of the silicate solutions. Published properties of sodium silicate solutions (PQ Corp., 2011) with a SiO_2 to Na_2O weight ratio equals to 3.22 yielded the following concentration-dependent equations developed for solving viscosity and density in order to model viscous fluid experimental results:

$$\rho = 0.7463c + 998.2 \tag{4}$$

$$\mu = 0.001e^{0.003481c} + 2.383x10^{-6}e^{0.02149c} \tag{5}$$

where ρ is the density (kg/m^3) , μ is the dynamic viscosity (Pa sec) and c is the concentration (kg/m^3) of the sodium silicate solution.

Modelling of the dense viscous fluid was successful in reproducing the shape of experimental plumes, especially in later times. For instance, the modelled plumes at 8 h had only slight and negligible differences in shape from the corresponding experimental plumes (Fig. 3). This experiment suggests that silicate solutions can be useful in delivering oxidants to the deeper zones of contaminated aquifers.

Time-delayed gelling

Silicate solutions are stable at high pHs (i.e. pH > 11) but once the pH of the solution is lowered, the solubility of the silica is reduced and it polymerizes. Many chemical compounds modify the pH and can be used as setting agents. However, most of these compounds result in permanent gels, with the exception of bicarbonate (PQ Corp., 2011). We used this idea to prepare a time-delayed gel that serves as a slow-release material *in situ* for delivering oxidants such as permanganate. This concept, in theory, would facilitate the initial emplacement of the treatment chemicals in wells to ultimately provide a slow release, reactive barrier.

At this stage of the study, we are not close to modelling this effect. However, the results of preliminary experiments illustrate the potential of this approach and the modelling challenges involved. We prepared a solution by mixing diluted sodium silicate solution (N-clear) with sodium bicarbonate solution that transforms into a soluble silicate gel through time. We also added 300 mg/L Rhodamine Wt as tracer to this solution. The initial viscosity of such a mixture is low and the gelation is not immediate (i.e. several hours). These conditions are useful for easy injection of this solution into the targeted layer. We set up a small flow tank with a higher conductivity unit

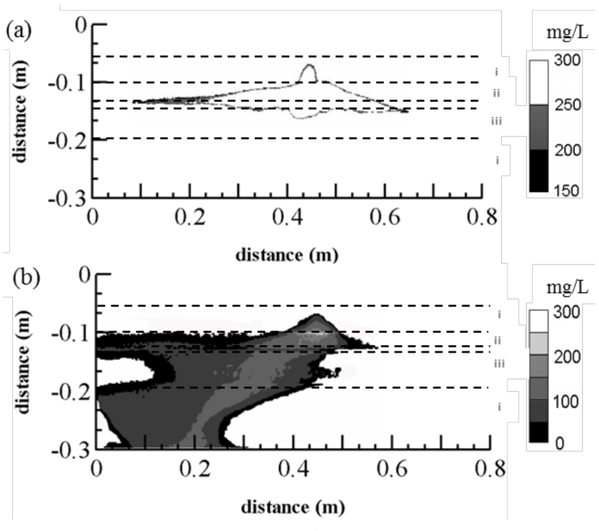

Fig. 4 Concentration maps for the time-delayed gelling experiments representing the Rhodamine Wt concentrations. The image analyses procedure of McNeil *et al.* (2006) was followed. (a) Immediately after injection of the solution into 3 cm thick high conductivity layer, (b) 20 days after the injection. i, ii and iii represent hydraulic conductivities 1.6×10^{-4}, 2.9×10^{-3} and 5.0×10^{-5} m/sec, respectively.

sandwiched among lower conductivity units (Fig. 4). The high conductivity layer was flooded with this solution so that parts of the higher conductivity layer would have a solution capable of gelling (Fig. 4). Because this solution is more viscous than water, downward flow into the lower layers was slow. Some portions of this solution sank below before gelling which took place after several hours. Tracer slowly diffused out gel. After 20 days, less than 60% of the initial tracer concentration was left in the gelled zone. This experiment showed the potential for creating a slow-release material that releases the necessary oxidants into the reaction zone through time.

The modelling challenge with a system that is gelling is substantial. It will be necessary to consider time varying viscosity/concentration relationships up to the point at which the material gels. At this point, there is a transition in the behaviour of the gelled material that behaves more like a solid than a liquid.

CONCLUSIONS

We presented the results of modelling dense solution transport using the code MITSU3D, which build confidence in the ability of the code in modelling dense solution transport. MITSU3D enables us to investigate not only the properties of the porous medium but also the processes that can affect the movement and mixing of treatment chemicals.

Our lenticular media modelling results indicate that lenses enhance mixing and density-driving forces allow dense solutions to be sequestered in low permeability lenses, which could be potentially used as long-term sources of remediation chemicals. Fingering appears not to develop in highly heterogeneous systems, under the conditions that we tested. Viscous silicate solution modelling showed us that it is possible to model systems with highly variable density and viscosity solution transport in various media. Such solutions can be useful in delivering the oxidants into deeper portions of the aquifers and increasing the residence time of oxidants in the targeted zone due to their higher viscosity. Investigating the slow release of permanganate out of the time-delayed silicate gel and the mathematical modelling of this concept remains a challenge.

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