STRATEGY AND MODELLING OF CLEANING CHEMICAL FACTORY CONTAMINATION WITH USE OF NANOTECHNOLOGIES

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Abstract
This paper presents demonstrates the potential for decontamination of soil under a chemical factory using use of metal nanoparticles or palladium-covered nanofibres. A computer model is used to calculate underground water flows and the reaction-diffusion transport of the chemicals. When injected to the porous soil, these materials can eliminate aliphatic and aromatic hydrocarbons, chlorine hydrocarbons, some other carcinogens and heavy metals. The advantage of using small particle size materials is the relatively large surface area available for the activation of chemical decomposition of organic molecules.

Introduction
Nanotechnologies are currently appearing in many applications. In the last decade, the use of nanoparticles in environmental technologies has started to move from testing projects to practical applications. A typical feature of the small particles is the large relative surface area with respect to their mass, which is important for accelerating chemical and biological processes. Examples of applications include the efficient decontamination of groundwater using nanoparticles of suitable material to bond or eliminate contaminants.

In this paper a specific technology for the remediation of soil under a chemical factory is presented. This paper investigates the use of iron particles covered with palladium to eliminate aliphatic and aromatic hydrocarbons, chlorine hydrocarbons, some other carcinogens and heavy metals. The paper also includes the numerical simulation models associated with the complex physical and chemical processes in the underground. The use of a model is necessary to optimise the operation under such conditions. Even if the research in groundwater flow, transport and reaction is adequate and appropriate simulation models exist, then the use of these technologies will provide improvements in the model, particularly in relation to the specific set of chemical reactions and different nanoparticles transport mechanisms with respect to the solutes.

We study the physical description and numerical methods in parallel with preparation of column and in-situ experiments and the full application and comparison will be available in few years. For reference, we present so called zero scenerio (or worst-case scenario), when the sources of contaminant are permanent, the contaminants are transported in the natural water flow and t extraction wells cannot fully capture the contaminants. The numerical experiments indicate how the nanoparticles can eliminate the contaminants, which were not “caught” by the well and transported with natural flow away.

Model Description
Several coupled underground processes have been studied under variable conditions associated with both natural flow and artificial operations. We considered a standard description of underground transport processes (Bear and Verruijt, 1990) with special respect to the remediation technology based on reaction of contaminant and nanoparticles. In this case, the groundwater flow is governed by the Darcy’s law and mass balance condition:

$$v = -\frac{1}{n_m} K \nabla \phi, \quad \nabla \cdot v = q_s^+ + q_s^- \ ,$$

where K is the tensor of permeability, ϕ is the piezometric head, v is the seepage velocity, $q^+_s>0$ is the fluid source intensity, and $q^-_s<0$ is the fluid sink intensity (volume per unit volume of mobile fluid and unit time).

The transport of solute (given by advection, molecular diffusion and hydrodynamic dispersion) is governed by the equation for unknown concentration c of the solute (Bear and Verruijt, 1990):

$$\frac{\partial c}{\partial t} + \nabla \cdot (cv) - \nabla \cdot (D \nabla c) = c^* q_s^+ + c q_s^- + r^\ell \left(c^\ell, c^i, \ldots \right),$$

where D is the matrix of dispersion coefficients (functions of velocity, see e.g. (Bear and Verruijt, 1990)), c^* is the injected solute concentration given, r^l is the chemical reaction rate and v is the seepage velocity, solution of the fluid flow problem. As the simplest approximation, we consider both the dissolved contaminant and nanoparticles are transported by the same mechanism, i.e. the equation holds for concentrations c_{cont} and c_{part}, but with different coefficient of diffusion and dispersion: D_{cont} for contaminant and D_{part} for nanoparticles. A more accurate description will be proposed on the basis of experimental observations. The interaction between the contaminant and palladium surface of particles can be approximated as a kinetic chemical process, i.e. the reaction rate is proportional to the product of concentrations:

$$\frac{\partial c_{cont}}{\partial t} = -k \cdot c_{cont} \cdot c_{part}$$

where k is the rate constant, which will be determined experimentally for each contaminant. This relation is a simplification of the general relation:

$$\frac{\partial c^{\ell}}{\partial t} = -K(c^{\ell}, c^{i}, \ldots, pH, \text{rock}, \ldots) \quad c^{\ell}$$

where the reaction rate depends on several factors including the chemical composition of rock (Brthke, 1996). The exact description of the reactions is complicated (eg. Steefel and Cappellen, 1990) and simplifications are generally used in the computer models (Parkhurst *et al.*, 1980).

Algorithm of the numerical solution:
The fluid flow is solved by the mixed-hybrid finite element method (Maryška *et al*., 1995; Frydrych *et al*., 1998). The advection-diffusion-reaction transport problem is spatially discretized by the finite volume method and the operator splitting method is used for the time discretisation: in each time step the separate problems of advection, diffusion/dispersion, and chemical reaction are sequentially solved. The advantage is a significant simplification of the calculation for large problems of more than 100000 unknowns.

Technology of Remediation

The model compared several possibilities of remediation strategies and subsequent scenarios of long-period transport of contaminants to the environment. The basic analysis is the worst-case scenario of contaminant spreading in natural underground flow. The standard remediation techniques are drawing wells in the areas of contamination or couples of injecting and drawing wells to accelerate the release of contamination. As a novel technology, we considered an "active" decontamination which involved the injected dispersion of nanoparticles to eliminate the contaminants. This process should reduce the necessary operation of extraction wells and also eliminate the contaminants, which could diffuse away from the wells.

The following steps were performed:

- injection of small amount of nanoparticles in relatively dense points covering the contaminated area
- a period of interaction and diffusion of nanoparticles to the whole contaminated area
- extraction of residual solution (both contaminants and nanoparticles)

There are many problems to be solved by modelling. As for standard remediation, we chose the positions of the extraction wells and their pumping rates. Moreover, there is a question of what quantity of nanoparticles to inject and if or how long to wait before the extraction. We must also take into account that the palladium used as the active surface of the nanoparticles is itself a contaminant and must also be extracted. The efficiency of the process is measured both by the cost of the pumping operation and by the amount of residual artificial objects in the underground. We applied these criteria in the model problems below.

Results of Modelling

Characterization of the particular remediation problem
The basic analysis of the contaminated area was calculated with MODFLOW and shows the "worst-case" scenario without any remediation operation (Figures 1 and 2). We present it for reference purposes; as the real-world problem, for which the sophisticated model will be intended.

Test problems for the application of nanotechnology

Here we demonstrate the possible improvements of the remediation, if the nanoparticles are used. Because of unavailability of input data (the exact description of chemical reactions and rate coefficients), we consider few representative models cases: the area with one cloud of contamination, natural piezometric gradient and two possible positions of extracting well and values of pumping rate.

Figure 1. Scheme of the chemical factory with part of the model mesh and isolines of piezometric head.

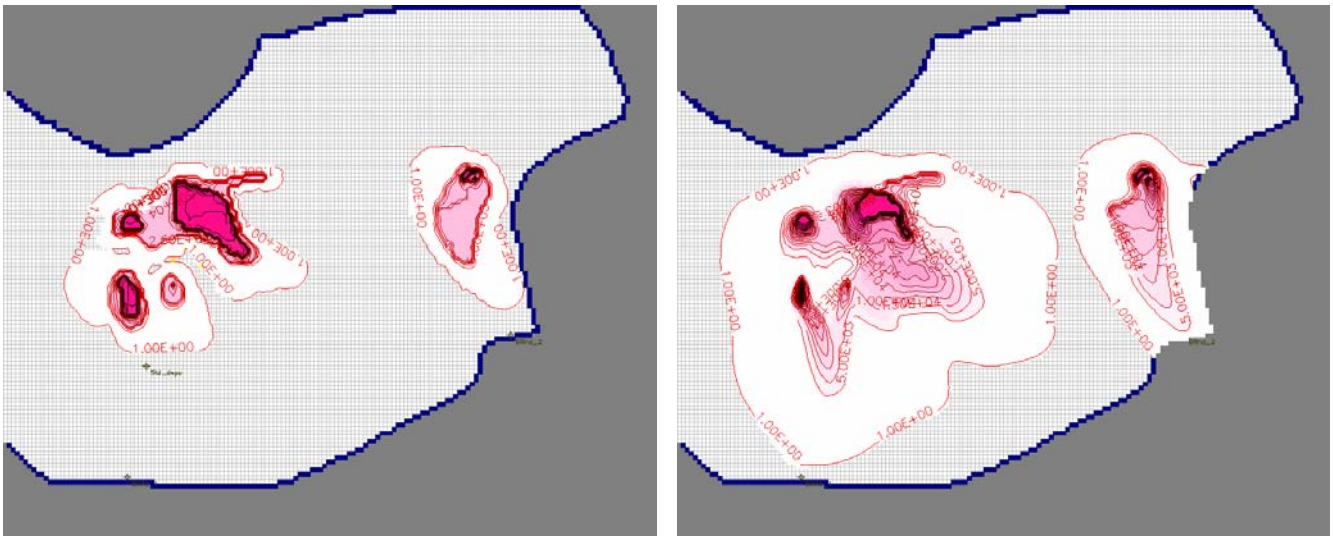

Figure 2. Initial distribution of concentration and the state after 100 years in the whole model mesh.

The problem is defined as follows: The domain is rectangular 500 x 200 m with elementary thickness. The initial contaminated area is about 80 m wide with concentration 10 kg m^{-3} (700 tons of contaminant in total). The natural Darcy velocity in the area is 0.02 m day^{-1}. In the first variant the extraction well is in the centre of contamination (pos. 1) and in the second variant, the well is 100 m in the direction of natural flow (pos. 2). For both cases, we consider four scenarios as combinations of values of pumping rate 50 m^3 day^{-1} and 100 m day^{-1}, and reaction rate k 0.001 and 0.0001 (represent e.g. two different contaminants) (Table 1). The criteria for evaluation are the time to extract given part of contamination and the amount of contamination, which is not extracted but drifted away (out from the modelled area). The exact results are in Table 1 and two of the processes in the scenarios are demonstrated in Figures 3 and 4.

Table 1. Evaluation of remediation efficiency for various scenarios of pumping

Treatment (explained in the text)	Time to eliminate 90% of contaminant (years)	Lost (escaped) mass of contaminant (kg)
Pos. 1, rate 100, k=1e-3	2	3651
Pos. 1, rate 100, k=1e-4	5	12680
Pos. 1, rate 50, k=1e-4	41	98165
Pos. 1, rate 100, k=0	12	23935
Pos. 2, rate 100, k=1e-3	3	1.1
Pos. 2, rate 100, k=1e-4	10	3.2
Pos. 2, rate 50, k=1e-4	4	12744
Pos. 2, rate 100, k=0	21	4.35

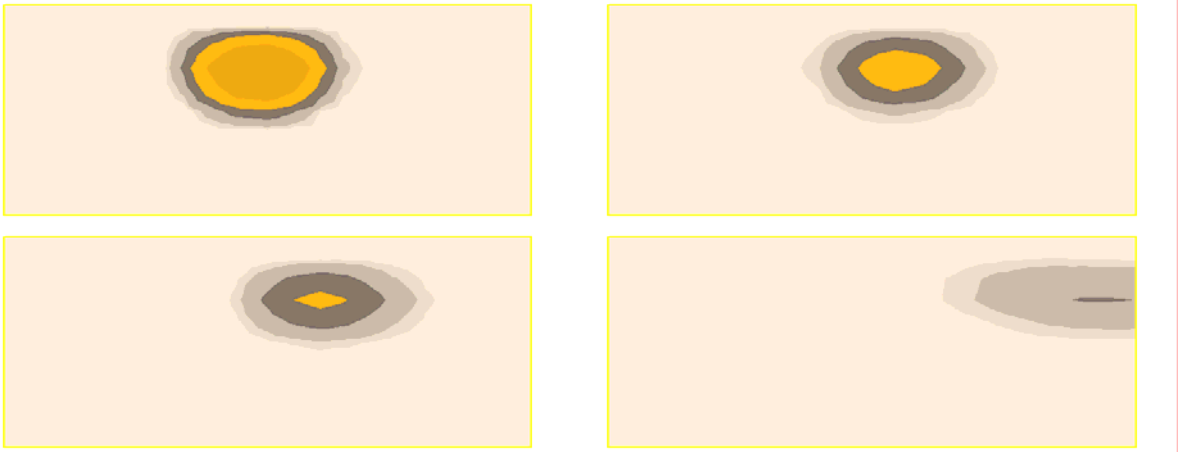

Figure 2. Distribution of concentration in the years 1, 5, 10, 40 after start of extraction, for the scenario with well position 1 and pumping rate 50 m^3 day^{-1}.

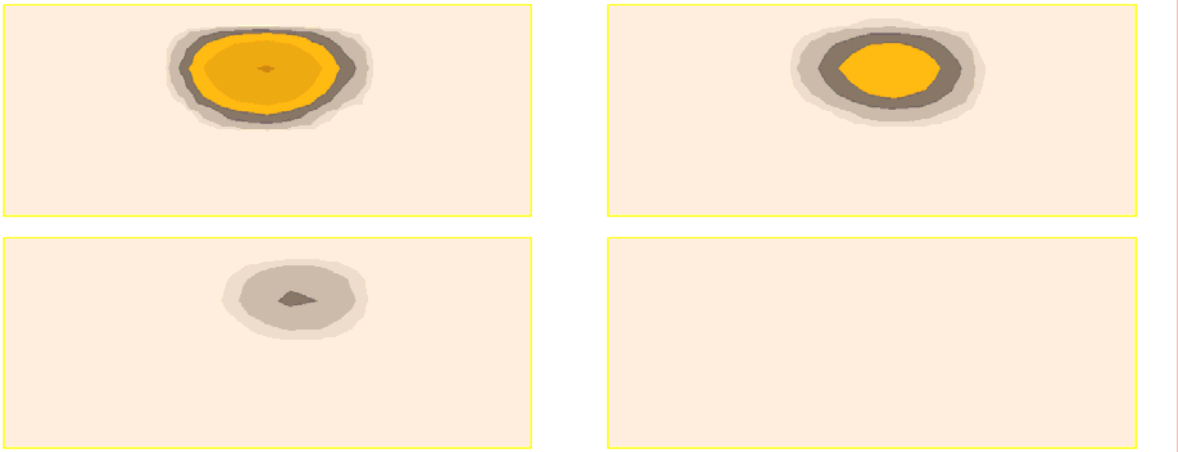

Figure 3. Distribution of concentration in the years 1, 5, 10, 40 after start of extraction, for the scenario with well position 2 and pumping rate 100 m^3 day^{-1}.

Conclusions

The technology of remediation based on the use of nanoparticles appears to be promising. The presented information and results are a starting point for our future research, which will be devoted to experimental work in this field and accurate evaluation of the improvements with respect to the standard technologies. Comparisons of the model scenarios show the strong sensitivity to the rate constant in the chemical interaction between the nanoparticles and the contaminant.

Acknowledgements

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