

The chemistry beneath our feet – Modeling reacting flow in the Earth's crust

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In this article, Professor Bethke and colleagues from the Ecole des Mines in Fontainebleau give various examples of the importance of careful treatment of chemical reactions in hydrological problems.

In the accurate description of radioactive waste containment, acid drainage from mines or even steam activation of oil fields, reactive transport is shown to play a major role, even though many characteristic values which are needed for a complete treatment are still imperfectly known.

Dans cet article, le professeur Bethke et ses collègues de l'Ecole des Mines de Fontainebleau présentent, par des exemples, l'importance des réactions chimiques dans les problèmes hydrologiques.

Que ce soit pour le stockage des déchets nucléaires, pour les écoulements acides dans les mines ou pour la récupération du pétrole par activation thermique, il convient d'ajouter au simple transport des fluides une modélisation des réactions chimiques. Ceci pose naturellement le problème d'une meilleure mesure des constantes de réactions, aujourd'hui assez mal connues.

The chemical reaction of flowing groundwater with the minerals that make up the Earth's crust occurs continuously, and has done so over geologic time. Subsurface reactions affect aspects of our lives ranging from the purity of the water we drink to the availability of energy and metals needed to sustain our modern lifestyles.

Will traces of toxic metals such as lead appear in our drinking water? Will radioactive waste migrate from nuclear facilities or waste repositories into the

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biosphere and the food chain? How much of the petroleum in a reservoir can be recovered and put to use, and how much will be wasted? Why and where do metallic ores form? Answering these questions requires an understanding of the chemical processes operating within the Earth's crust.

Subsurface reactions occur out of our view, nonetheless, so few people give them much thought. Geoscientists, however, have long been interested in these reactions and have been developing ways to understand them better, even where they occur out of direct observation or over intervals considerably longer than the human time span. An increasingly useful and sophisticated method for studying such reactions is the application of detailed computer simulations (*e.g.*, Bethke, 1997).

In this contribution, we describe various ways in which this type of numerical modeling has begun to lend understanding to the nature of chemical processes in the subsurface. The work described here was initiated in 1994-95 when the senior author served as a professor in the Académie des Sciences at the Ecole des Mines in Fontainebleau. During this period, he also completed a text "Geochemical Reaction Modeling", published by Oxford University Press (Bethke, 1996).

HOW THE MODELING WORKS

There are, as the name suggests, two facets to a reactive transport model. First, the model simulates the chemical reactions that occur within the fluid, between the fluid and the minerals it contacts, and in response to biological activity such as the metabolisms of microbes. Second, the model accounts for the transport of chemicals through the subsurface. Chemical species move along with flowing groundwater, a process known as advection, as well as by molecular diffusion and dispersive mixing.

The models are evaluated numerically over a discretized domain, as shown in Figure 1-1. Unreacted fluid enters the domain at one or more inlets, displacing reacted fluid. Fluid composition at each inlet is specified as a boundary condition, and an initial condition is placed on the chemistry of the system before reaction. The simulation program follows a time marching procedure, evaluating at each time step how transport affects the distribution of chemical components, and how the components are distributed among aqueous species, minerals, sorbed species, and gases.

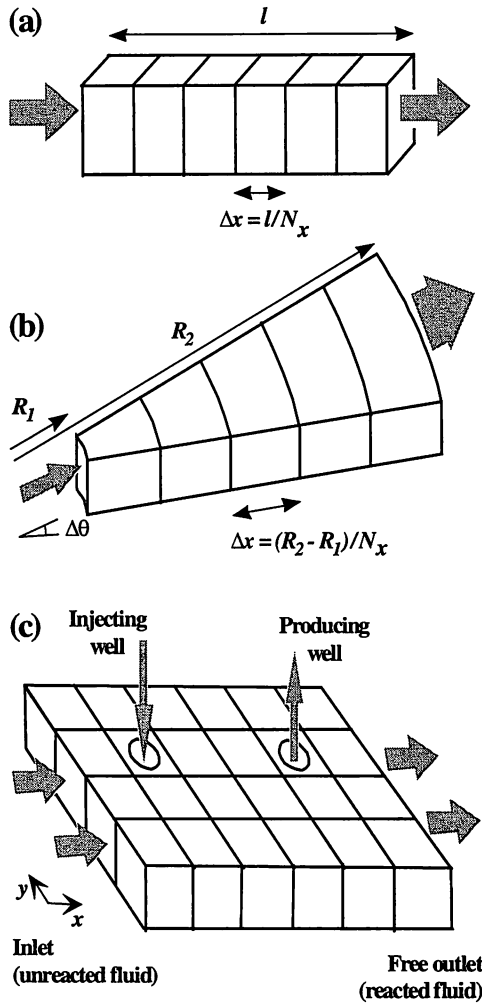


Figure 1-1 – Conceptual basis for calculating a reactive transport model in (a) one dimension, (b) one radial dimension, and (c) two dimensions. Unreacted fluid enters the domain inlet (or inlets), displacing reacted fluid toward a free outlet (or outlets).

CLEANING HEAVY METAL CONTAMINATION FROM GROUNDWATER

Owing to poor appreciation of the Earth’s hydrologic cycle, industries world-wide in the twentieth century have disposed of many of their most toxic wastes by dumping them into the subsurface and burying them in landfills. Many of these wastes contain heavy metals that contaminate groundwater migrating

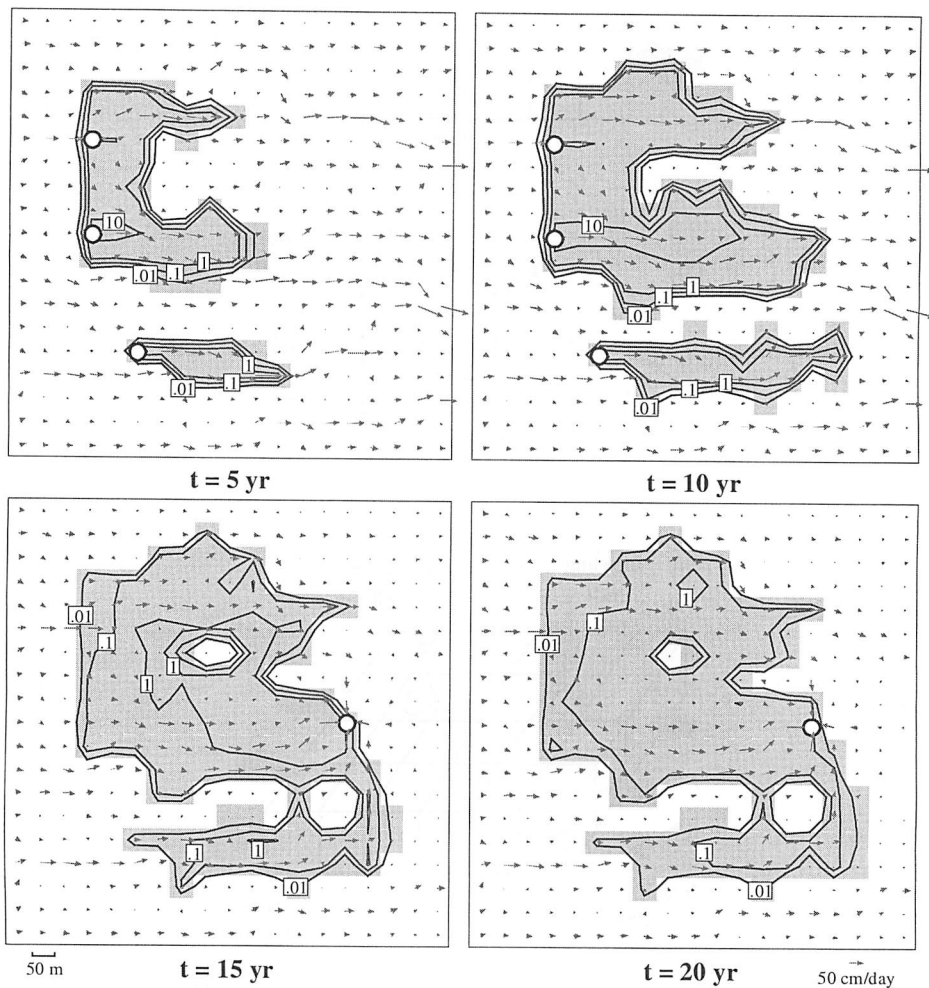


Figure 1-2 – Simulation of the contamination of an aquifer with inorganic lead, and its attempted remediation by the “pump and treat” method. Three storage tanks (circles to left) leak lead into aquifer, where it is entrained by natural groundwater flow (arrows, see scale). Contours show lead concentration (mg/kg; note logarithmic spacing) in the groundwater, and shading represents area where lead has sorbed to ferric oxide in the aquifer, contaminating it. After ten years, the tanks are removed and a remediation well (circle to right) begins pumping water from aquifer. After ten years of pumping the well, the aquifer remains contaminated and groundwater contains lead in concentrations considerably in excess of health standards (.015 mg/kg in USA).

through and below disposal sites, as well as the sediments the groundwater contacts. In the USA, for example, about two-thirds of the roughly 1,300 sites identified as priorities for cleanup are contaminated with heavy metals, including lead, chromium, copper, and nickel.

Early theoretical analyses of cleanup schemes suggested that flushing clean water through the sites (the “pump and treat” method) could displace from the subsurface most of the heavy metals sorbed to minerals. The calculations were based on a particularly simplified chemical theory known as the distribution coefficient or K_D approach. Experience in the laboratory and field, however, seems to contradict these calculations. Heavy metals have proved difficult to displace and water flushed through the sites continues to contain metals at unhealthy levels long after the calculations suggest it should be clean.

Much of the discrepancy between calculation and experience appears to result from inadequacies in the K_D approach (Bethke and Brady, 1999). As such, there is considerable interest in developing more realistic models of the subsurface transport of heavy metals. Figure 1-2 shows the results of such a simulation, calculated using surface complexation theory, rather than the K_D approach. The model simulates the contamination of a groundwater flow system with inorganic lead, which sorbs strongly to ferric oxide minerals within the aquifer, and attempted remediation of the system by the “pump and treat” method.

In the simulation, three tanks leak waste containing 100 μmolal Pb (20 mg/kg) into the aquifer, where it is entrained by local groundwater flow. The leaking tanks contaminate groundwater within the aquifer as well as the aquifer itself. After 10 years, the tanks are removed and a remediation well is installed to pump groundwater from the aquifer. The remediation well displaces groundwater from the contaminated zone several times over ten years of pumping.

The remediation scheme succeeds in displacing the groundwater most concentrated in lead from the aquifer. Little of the lead sorbed to aquifer minerals, however, is displaced, and lead concentrations in groundwater from within the contaminated zone remain well in excess of health standards (0.015 mg/kg in the USA). The simulation, contrary to calculations employing the K_D approach, suggests that continued pumping will do little to remediate the aquifer. Alternative strategies for environmental protection such as containment or natural attenuation might be more profitably pursued in this case.

HOW COLLOIDS MIGHT DISPERSE RADIOACTIVE WASTE

One of the most critical current applications of reactive transport modeling is assisting in the design of radioactive waste repositories. These repositories, which will accept materials from civilian and military activities, are designed to isolate waste containing actinide elements and fission products from the bios-

phere for thousands of years. Man-made structures (concrete and steel, backfill, etc.) cannot be assumed capable of holding the waste over such long time periods. For this reason, designers call upon the subsurface geologic environment as a natural barrier to the migration of radionuclides.

The concept of a natural barrier relies on the low solubility of many radionuclides combined with their tendency to sorb onto mineral surfaces, which might render them immobile. The subsurface, however, is complex: it contains zones of high permeability such as fractures through which groundwater can migrate relatively rapidly. As well, radionuclides can exist in various forms with a groundwater.

A special concern is that radionuclides might form colloids, or sorb onto colloids already present in local groundwater. Colloids are polymers and small particles in solution that range in size from 0.001 to 1 μm . Since they can move with flowing groundwater freely through fractures, commonly faster than aqueous species, colloids may present a means by which radionuclides can escape quickly to the biosphere. There is evidence, in fact, that such a process may operate. At Los Alamos National Laboratory (USA), plutonium and americium have migrated in colloidal form for several tens of meters downward from a low-level liquid waste repository (Travis and Nuttall, 1985). Radionuclides, some or all of which were associated with colloidal particles, moved at least 300 meters in seven years from a cavity created at the Nevada Test Site (USA) by a nuclear explosion (Buddemeier and Hunt, 1988). Finally, naturally occurring radionuclides at the Nevada Test Site are observed to be associated with colloidal particles (Kersting *et al.*, 1999). Plutonium, for example, would be virtually insoluble there in the absence of colloids.

There is, therefore, considerable need in repository design to account for colloidal transport in reactive transport modeling. Such models are complicated by the necessity to account for processes occurring on a microscopic or molecular scale at the solution-colloid interface (*e.g.*, van der Lee, 1997; van der Lee *et al.*, 1997; van der Lee, 1998). For example, colloidal surfaces are charged electrically and thus interact with ionic species in solution as well as the surfaces of minerals and other colloids.

Figure 1-3 shows the results of a reactive transport simulation that attempts to account for colloid transport in a rigorous fashion. The goal of the simulation is to reproduce a bench-top experiment by Warwick *et al.* (1996). In the experiment, a solution containing europium and a silica colloid passes through a column of quartz sand that has already been flushed with a solution containing silica colloid.

If the europium were to sorb to the sand surface, its arrival in the effluent would be delayed relative to a conservative tracer. The observed arrival, however, is not delayed, although only a fraction of the europium introduced passes through the experiment. This result indicates that although some of the element sorbs to sand, a fraction sorbs to colloids, which pass through the column. Apparently, electrical repulsion between colloid and quartz holds the colloid particles near the center of pore channels, where they are free to migrate. The numerical model reproduces this complex behavior well.

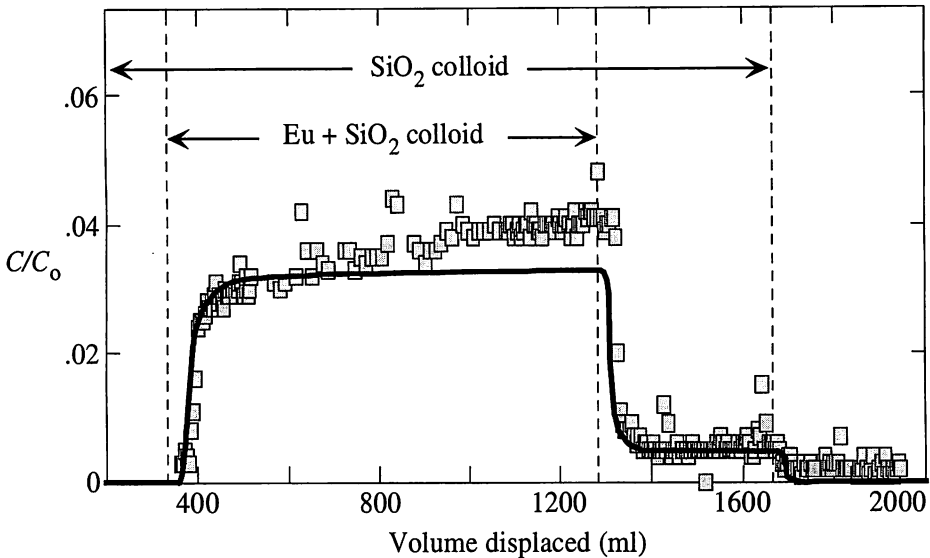


Figure 1-3 – Concentration (C/C_0 , where C_0 is the inlet concentration) of europium in the effluent of a bench-top experiment in which a solution containing a silica colloid and, for an interval, europium are passed through quartz sand. Squares are observed data (Warwick et al., 1996) and line shows the result of a reactive transport simulation (van der Lee, 1997).

ACID DRAINAGE FROM MINING DISTRICTS

Acid drainage from historic mining districts is an acute environmental problem worldwide, in large part because of the high concentrations of heavy metals, iron, and aluminum – up to tens of thousands of mg/kg – commonly observed. The metal concentrations make the drainage a threat to water supplies, agriculture, and recreational and commercial fisheries.

Acid drainage forms when sulfide minerals react with atmospheric oxygen in the presence of water. Where air circulates into old mine workings or through waste dumps, sulfide minerals oxidize, adding acid and metal to solution. The oxidation reaction is catalyzed by acidophilic bacteria such as *Thiobacillus*. The strong temperature dependence of the reaction rate, which increases ten-fold between 0°C and 20°C (Lizama & Suzuki, 1989), serves to emphasize the biological control on sulfide oxidation.

Drainage water varies significantly in chemistry, and hence in its environmental threat, depending on a number of factors including the availability of oxygen, the ability of country rocks to buffer acidity, temperature, and microbial activity. Due to the complex nature of the problem, reaction modeling is becoming an important tool for analyzing metal mobility in mining districts (e.g., Schmitt & Combes, 1996; Berger et al., 1999).

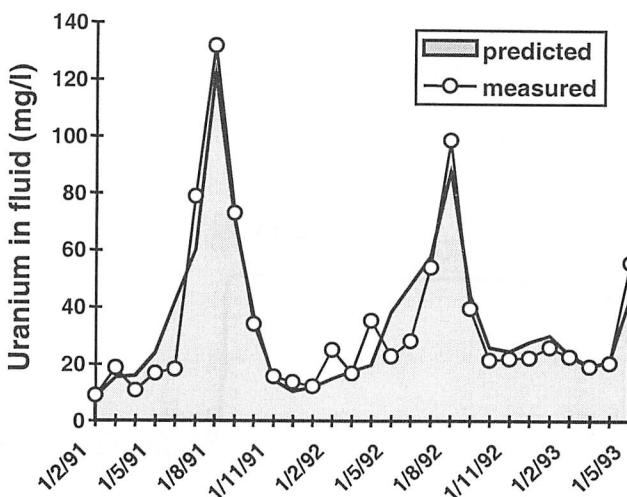


Figure 1-4 – Uranium concentration (mg/l) observed over time (day/month/year) in acid drainage from a waste dump near an abandoned mine, compared to predictions of a reactive transport model.

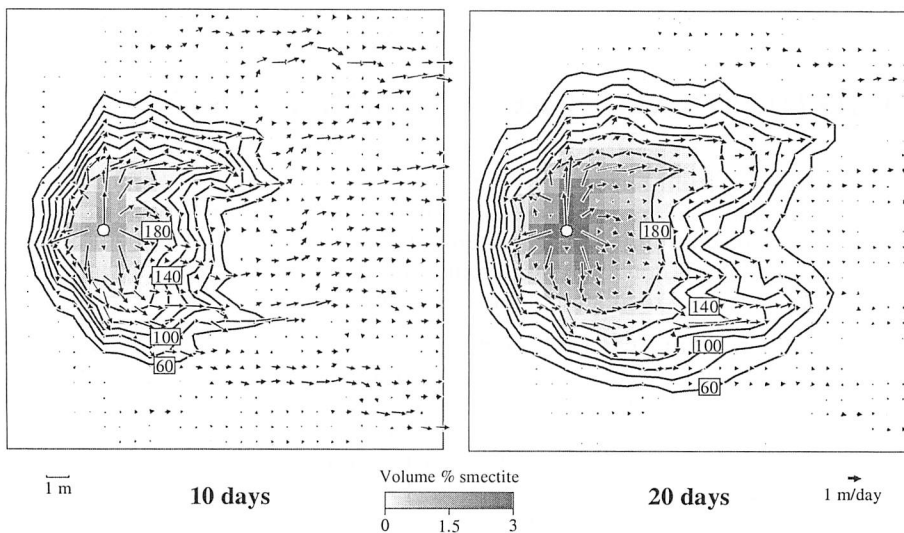


Figure 1-5 – Simulated effect of steam flooding a sandstone petroleum reservoir, shown in plan view after 10 and 20 days. Natural groundwater flow (arrows, see velocity scale) is from left to right. Hot water entering the formation at the well (circle) drives a thermal pulse, as represented by contour lines ($^{\circ}\text{C}$). The sandstone reacts with the hot water, producing the swelling clay smectite (volume % of formation; see scale).

As an example of reaction modeling applied to study acid drainage, we consider an abandoned uranium mine in the province of Aveyron, France. A waste dump left in a nearby valley contains the country rock (granite), marginal ore, and processing sludge. Reaction within the waste pile produces acidic (pH \approx 1.5), sulfate-rich groundwater that contains significant concentrations of uranium, aluminum, iron, and manganese. Discharge from the dump is collected in a small basin for treatment.

Monitoring of the discharge shows a close correlation between air temperature at the site and uranium concentration, which increases ten-fold from winter to summer. Figure 1-4 shows the results of using a geochemical model to predict seasonal variation in the chemical composition of discharge from the waste pile. The model accounts for water filtering into the pile, the dissolution rates of reactive minerals (pyrite, albite, uraninite, and pyrolusite) in the waste, thermal variation in microbial activity, and the depletion of reacting minerals with time. The model results have been used for several years to predict metal fluxes from the dump and to design and test remediation schemes for the site.

STEAM FLOODS OF PETROLEUM RESERVOIRS

An important concern in developing energy resources is producing from a reservoir as much petroleum as possible. In practice, perhaps two-thirds of the oil contained in a typical reservoir does not flow readily to a well and cannot be recovered directly. Secondary recovery techniques such as steam flooding and chemical treatments are designed to increase production, and in many cases are effective in doing so. The methods, however, can actually damage an oil field by driving chemical reactions that precipitate harmful scales. Reservoir engineers increasingly apply reactive transport modeling to predict and avoid such damage.

In steam flooding, hot water is pumped into a reservoir to lower the viscosity of petroleum and thus increase its ability to flow to a well. Figure 1-5 shows the results of a simulation in two dimensions of reactive transport during a steam flood. The reservoir rock is a sandstone composed of quartz, calcite, and kaolinite; porosity and permeability vary across the sandstone.

The 200°C flood enters the formation, which is initially at 40°C, driving a thermal pulse from the well outward into the formation, especially along the direction of natural groundwater flow. Reaction with the reservoir rock produces smectite, a swelling clay that is especially detrimental to permeability in the subsurface, and CO₂. Although the thermal pulse lowers fluid viscosity, favoring flow, the smectite produced sharply lowers permeability. The overall effect of the flood is to reduce the ability of fluid to flow to the wellbore, and hence undesirable.

THE FUTURE OF REACTION MODELING

The examples in this and other recently published contributions (*e.g.*, Lichtner *et al.*, 1996) serve to emphasize the growing power and scope of reactive transport modeling in a variety of applications. Like any integrative endeavor, however, the modeling points out deficiencies in our quantitative understanding of fundamental processes, as well as gaps in the data needed to apply quantitative theories.

Fundamental data such as the thermodynamic stability of many minerals important near the Earth's surface – clays, oxides and oxy-hydroxides, zeolites, and so on – are not known exactly. Likewise, data describing the reaction of dissolved species with mineral surfaces and colloids of geologic interest are in many cases lacking.

The field of geochemical kinetics has advanced considerably in recent years (*e.g.*, Lasaga, 1998). Even so, predicting the rates at which minerals react with fluids in the Earth's crust, as opposed to laboratory conditions, is not straightforward. Rate constants for individual minerals determined in different laboratories commonly agree only to within a factor of 30, and reaction rates in nature may differ from those observed in the laboratory by as much as four orders of magnitude. These differences may result in large part from variation in the state of a mineral's surface, rather than its inherent properties.

Finally, the role of biology in controlling geochemical reactions is poorly represented in current reactive transport models. As much as half of the prokaryotic biomass on Earth exists beneath the soil zone (Whitman *et al.*, 1998), and the metabolism of these microbes has a profound effect of the chemistry of subsurface fluids (*e.g.*, Chapelle, 1993). These effects can be integrated into reaction models (*e.g.*, Rittmann and VanBriesen, 1996), but improved understanding of the microbes living in the subsurface, their metabolic rates, and how differing strains interact as communities will be necessary to successfully apply such models to the spectrum of problems that exist in geoscience.

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