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Multiple Species Reactive Chemical Transport in Groundwater: A Verification Exercise

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Abstract

In this work, two multiple-species reactive chemical transport models (FASTCHEM and DYNAMIX) are tested against each other to check for consistency of solutions. For the particular problem studied, FASTCHEM and DYNAMIX led to differences in aqueous concentrations and mineral assemblages primarily because FASTCHEM ignores redox reactions in the transport phase of the calculations. Also, the spatial concentration profiles generated by FASTCHEM tend to be sharper than those generated by DYNAMIX because FASTCHEM is particularly designed to handle advection-dominated transport systems.

Introduction

First generation models capable of handling multiple species reactive chemical transport have begun to appear in the literature. The Electric Power Research Institute (EPRI) has sponsored the development of one such model, FASTCHEM (EPRI, 1989), to permit the thermal power industry to evaluate potential groundwater contamination problems arising from fly ash ponds. Before formally transferring this technology to the industry, EPRI charged a team of hydrogeologists and geochemists to apply FASTCHEM to the solution of problems typically of interest to the thermal power industry, verify the applicability of the model, and evaluate its strengths and weaknesses. This paper deals with one facet of this evaluation exercise, namely, verification of FASTCHEM against an independently developed model, DYNAMIX (Liu and Narasimhan, 1989) with similar capabilities.

We address two aspects of the reactive chemical transport problem. The first involves the ability of the two models to simulate the transport of a single chemical species by advection and longitudinal dispersion. In particular, we consider transport in a tube of non-uniform cross section, for which no analytical solutions are available for verification. The second involves the ability of the two models to handle

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multicomponent transport accompanied by fluid-solid reactions (including reduction and oxidation). Here we consider a uniform flow tube because of the focus on chemistry rather than on transport. The purpose of this paper is to provide insights on the difficult and practical task of refining research tools to solve day to day problems of interest to the industry.

Advective-Dispersive Transport

The two models employ different philosophies to solve the dispersion process. FASTCHEM uses a short memory Markov model involving the transport of a multitude of particles whereas DYNAMIX uses the conventional hydrodynamic dispersivity approach (Freeze and Cherry, 1979). For the simple case of a flow tube of uniform cross section, filled with a single homogeneous material with a steady water flux, the equivalence between dispersivity and the probability density function of the Markov process is well defined. Here, FASTCHEM and DYNAMIX agree very well with each other, and with the equivalent analytical solution.

Under heterogeneous conditions expected at field sites, flow tubes usually exhibit converging and diverging patterns characterized by a variable cross section. Because no analytical solutions are available for advective-dispersive transport in non-uniform flow tubes, we solved this problem using both models and compared the results. We considered a 222-meter long flow tube with cross sectional area varying from 0.222 to 1 m^2. We assumed a linear variation of area between adjacent points, constant flux, $Q = 185$ m^3/yr; porosity = 0.5; longitudinal dispersivity, α_L, spatially variable; initial concentration = 0 everywhere; and concentration of incoming fluid = 1.

The FASTCHEM model is so set up that for flow tubes of non uniform cross section, dispersivity must be provided as proportional to "bin length". As a result, actual dispersivities must vary from bin to bin. Moreover, to assure mass balance, these "bin-space dispersivities" must meet certain numerical constraints. A consequence is that the dispersivities must be fairly small, as is typical of advection-dominated systems. We therefore let the dispersivities be spatially variable in the DYNAMIX simulations and used harmonic mean dispersion coefficients between adjoining elemental volumes. The results from FASTCHEM and DYNAMIX are compared in Figure 1.
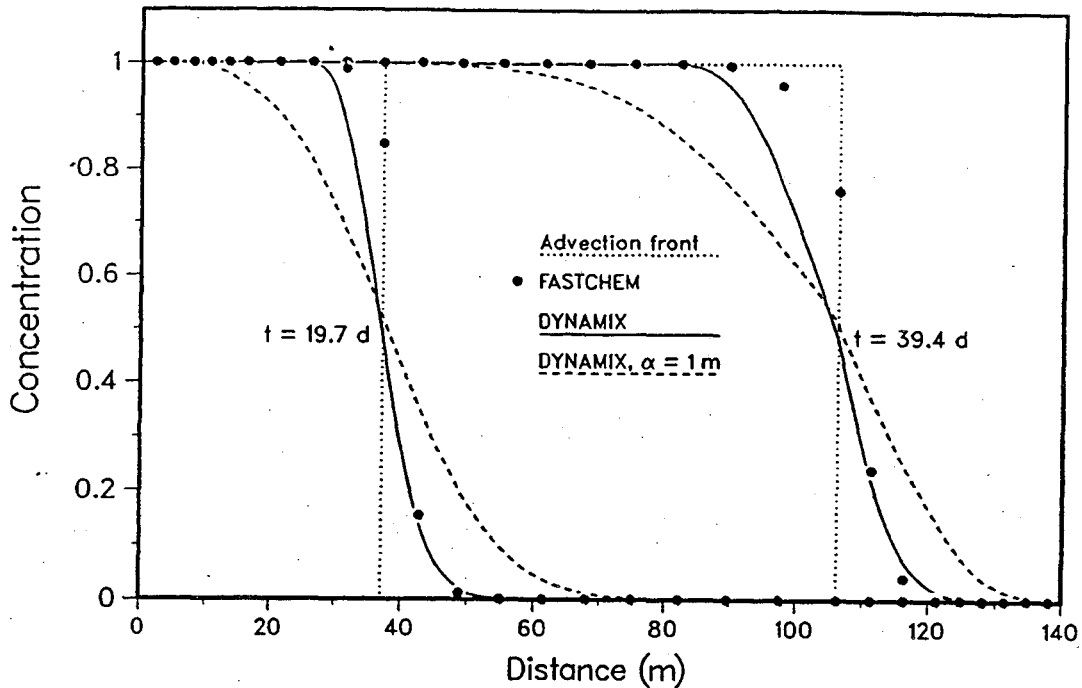
Figure 1: Advective-dispersive transport in a non
uniform tube: Comparison of FASTCHEM and DYNAMIX
for t = 19.7 and 39.4 d.

Both solutions agree fairly well except that
FASTCHEM is sharper and less diffuse. It is interest-
ing that whereas the DYNAMIX front intersects the
hydrodynamic front at C = 0.5, the FASTCHEM profile
intersects C = 0.5 line a little ahead of the hydro-
dynamic front.

For flow tubes of about 200 m, dispersivities
should be expected to be at least a meter or so. How-
ever, FASTCHEM constraints restrict the dispersivities
to be considerably smaller, 0.04 to 0.18 m. With a
more realistic dispersivity of 1 m, DYNAMIX produces a
profile shown by the dashed line in Figure 1. This
suggests that in systems with large dispersivities
resulting from heterogeneities, FASTCHEM may force the
prediction of sharper and later breakthroughs.

Redox-Controlled Chemical Transport

DYNAMIX and FASTCHEM have different geochemical
data bases. The two codes therefore yield somewhat
different aqueous concentrations for identical mineral
assemblage under assumed equilibrium. Yet, this does
not critically influence the modest insights which we
seek. DYNAMIX permits redox reactions whereas FASTCHEM

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presently does not possess such a capability. There-
fore, the major question we address in this work is
whether coupled redox reactions could give rise to
significant differences in aqueous concentrations of
affected species. In other words, how reasonable is
it to ignore redox in transport simulations as is done
in FASTCHEM?

We considered the transport of 12 chemical
species through a saturated 10-meter flow tube of uni-
form cross section, filled with a homogeneous porous
medium. Initially in the porous medium, the porewater
is in equilibrium with gibbsite, quartz, hematite and
calcite under Eh = 10 mV and pH = 7.5. At t = 0, a
more oxidizing acidic sulfate leachate (Eh = 300 mV,
pH = 4.1, SO_4 = 1300 ppm) continuously enters the tube
at one end. This leachate also contains 185 ppm of Fe^{2+}
and 20 ppm of Cu^{2+}. The simulation problem is to
predict the chemical evolution within the tube over
time.

In Figures 2, 3 and 4 the results of the two
models are compared. Figure 2 illustrates pH and Eh
along the stream tube after 5 years. FASTCHEM arbi-
trarily calculates Eh from the Fe^{3+}/Fe^{2+} redox pair
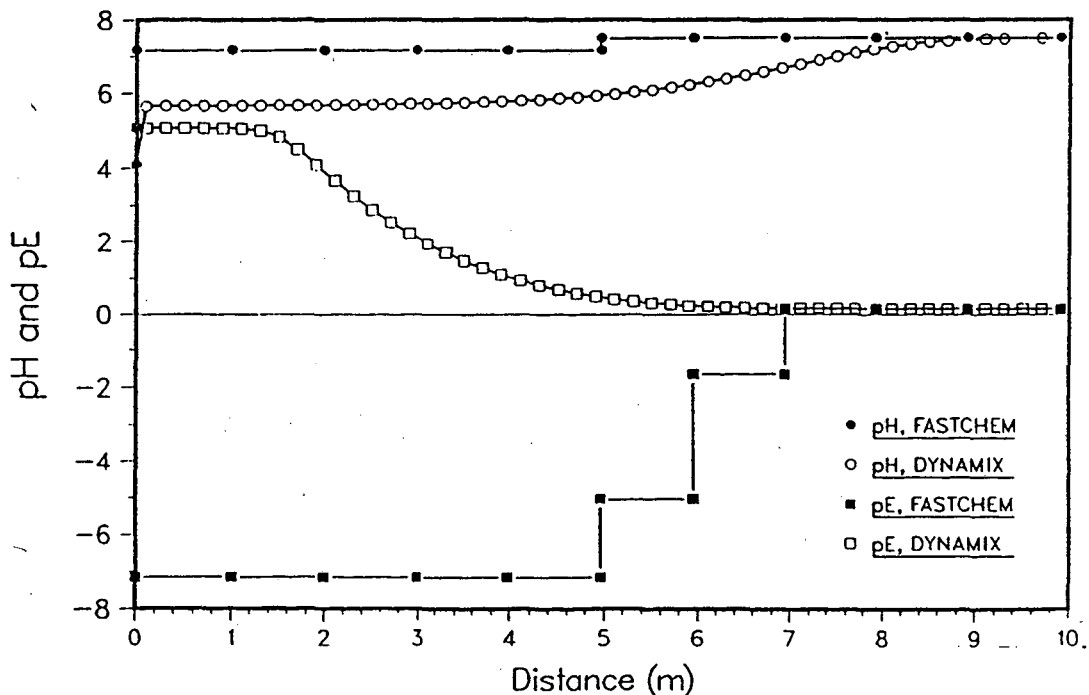while ignoring redox reactions, whereas with DYNAMIX

Figure 2: Redox-driven chemical transport: Comparison of
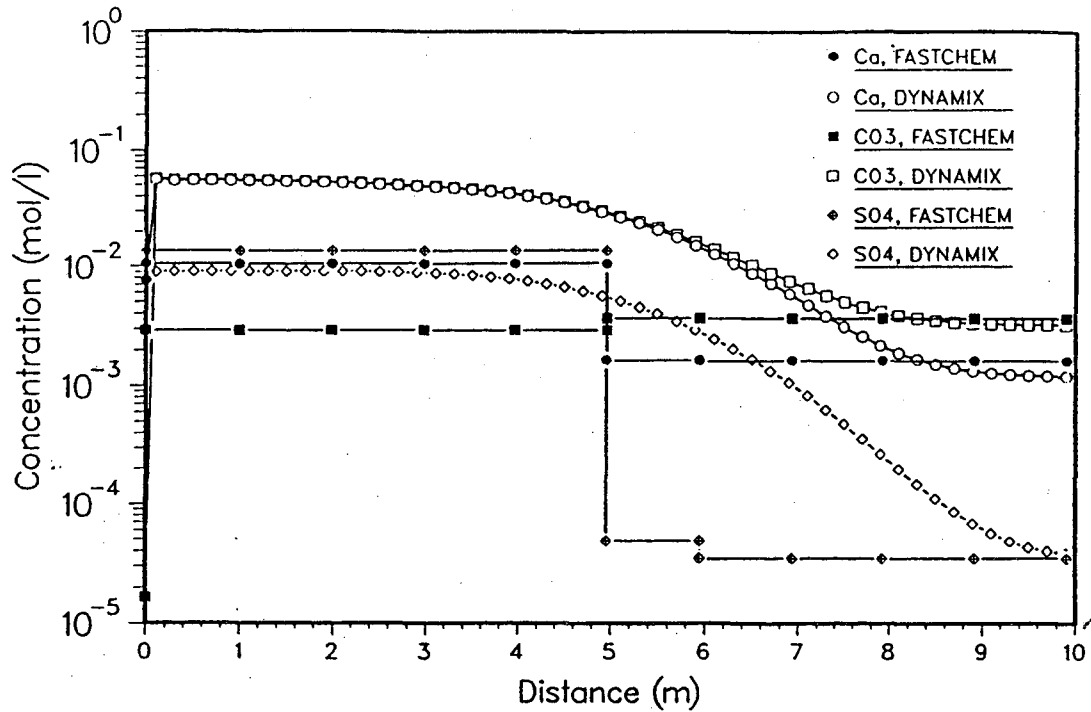FASTCHEM and DYNAMIX for pH and pE at t = 5 yr.

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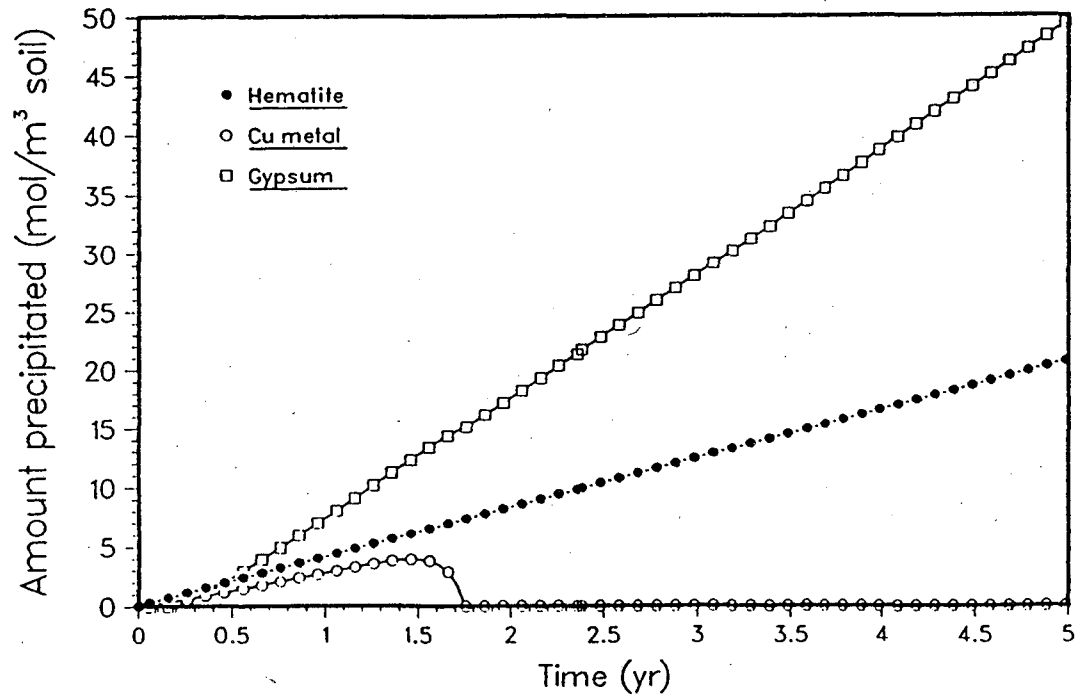Figure 3: Redox-driven chemical transport: Comparison of FASTCHEM and DYNAMIX for major ions at t = 5 yr.

Figure 4: Redox-driven chemical transport: Evolution of mineral phases at x = 0.2 m, obtained with DYNAMIX.

Eh falls gradually from the influent value. Also with DYNAMIX, some of the Fe^{2+} brought in by the influent fluid is oxidized to Fe^{3+} and then precipitated as hematite, producing H^+. DYNAMIX thus predicts a lower pH for the transition zone. This also results in significant differences in the dissolution of calcite as the acid invades the soil (Figure 3). By only considering initial and boundary conditions, FASTCHEM fails to identify gypsum and copper metal as potential mineral precipitates. As a result, it overestimates the sulfate concentration in solution. In DYNAMIX, the oxidation of the initially reducing soil causes transient precipitation and re-dissolution of copper, accompanied by precipitation of hematite; and gypsum precipitates as a result of calcite dissolution and sulfate intrusion (Figure 4).

Conclusions

Comparison between FASTCHEM and DYNAMIX shows that with tubes of non-uniform cross section, there are slight differences between the results generated by the two models. FASTCHEM is set up in such a way that it is difficult to control the input values of dispersivity and the model accepts only relatively small magnitudes of that parameter. The reactive chemical transport results generated by DYNAMIX illustrate how redox reactions may modify the fate of contaminants. Because FASTCHEM does not dynamically account for changes in Eh, it may, under certain conditions, predict higher mobilities for certain elements, when in fact they may be less mobile due to redox precipitation.

Acknowledgement

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