A numerically efficient approach for solving reactive transport problems

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Abstract

The computational cost associated with transport models can be high depending on the domain size, time scale and complexity of the analysis. Thus there is a need to develop computationally efficient methods of solving such problems. The method proposed here takes a numerical approach to reducing the number of coupled equations to be solved, reducing the computational demand of the simulation. The reduction scheme utilises an indicator species, for which the governing equation of mass balance, including the transport and reaction of the solute, is solved. The transport of the remaining species is then calculated at the end of a time step as a function of the transport of the indicator species, with the reactions being calculated on a point-wise basis. The reduction scheme was tested against an example problem concerning the diffusion of Na^+, Cl^-, K^+ and OH^- into a mortar specimen. An accurate prediction of the concentrations was achieved with a reduction in cost of 52.6% CPU time.

Keywords: Reactive Transport; Porous Media; Reduction of Problem Size; Numerical Simulation

1. Introduction

Transport models are often coupled models which consider the advection, dispersion and in some cases reaction of chemical ions, moisture flow, heat transfer and often mechanical behaviour of the porous medium, through the appropriate mass and energy balance equations. The computational cost of solving these equations can become quite large. According to Cleall et al [2], this is driven by three main areas, the domain size, time scale and complexity of the analysis, which is dependent on the number of variables and degree of coupling between them, the non-linearity of the system and the number of processes considered.

Yeh and Tripathi [9] suggested that the computational cost could be reduced by the use of an operator splitting (OS) scheme, separating the calculation of the transport of the reactions instead of solving them simultaneously; changing the numerical treatment of the problem from a GIA (Global Implicit Approach) to a SIA/SNIA (Sequential Iterative or Sequential Non-Iterative Approach). However, some authors have found that for some chemical systems OS schemes can actually be less efficient [6] and can even lead to mass balance errors [8]. As a result of this many authors have instead proposed reduction schemes that can be applied to the GIA; often through reformulation of the system of equations based on the problem stoichiometry and introducing transformed variables [4,5]. There are, however, some limitations including the condition of equal diffusion for all species which may be inaccurate for some systems [7].

The model presented here reduces the number of governing equations to be solved using a numerical approach. The governing equations are solved for one indicator species, including the advection, dispersion and reaction of the solute. The transport of the remaining species can then be calculated at the end of each time step as a function of the transport of the indicator. The reactions are then taken into account on a point wise basis. The model is tested against an example problem of the diffusion of ions into a mortar specimen and compared to the results of a full (non-reduced) model.

2. Theory

In this section the mathematical formulation of the model will be presented including the governing equation of mass balance for the chemical species and their reaction rates, before describing the problem reduction scheme (PRS). The full description of both the theoretical formulation and the reduction scheme along with two other reduction schemes can be seen in [3]. The governing mass balance equation for a chemical species is given by:

$$\overline{\rho_w}\dot{c} + \nabla.(\overline{\rho_w}cv_w) + \nabla.J_d = -\dot{m}_c \tag{1}$$

where c is the chemical concentration, v_w is the pore water velocity, $\dot{m}_c$ is the source/sink due to chemical reaction, J_d is the dispersive flux, made up of the mechanical dispersion and molecular diffusion, and $\overline{\rho_w}$ is the liquid phase density given as $\overline{\rho_w} = n\rho_w S_w$ where n is the porosity, ρ_w is the water density and S_w is the degree of saturation of the liquid phase. The reactions considered here are of the kinetic chloride binding described here using a Freundlich isotherm:

$$\dot{m}_c = n\rho_p \dot{S}_p = -\frac{(S_p - \mu c^\gamma)}{\tau} \tag{2}$$

where ρ_p is the sorbed mass density, S_p is the degree of salt saturation, μ and γ are rate parameters and τ is a characteristic time.

The rate of transport of an ion is dependent on the pore water velocity, the molecular diffusion coefficient and the concentration gradient. The pore water velocity acts on all species equally; any difference in transport rate between species therefore is due to the fact that each species has different diffusion coefficients and may have different concentration gradients. The proposed reduction scheme takes the ratios of diffusion coefficients and maximum concentration gradients (considered here as the difference between the initial and boundary concentration), of the species under consideration to the indicator species, and uses them to scale the transport of the indicator species over each time step. The equation is given as:

$$c_s^{t+1} = c_s^t + \frac{(c_s^0 - c_s^b)}{(c_{ind}^0 - c_{ind}^b)}\frac{D_s}{D_{ind}}\Delta c_{ind} \tag{3}$$

where c_s is the concentration of a chemical species, D_s and D_{ind} are the diffusion coefficients where the s and ind subscripts represent a species and an indicator respectively, Δc_{ind} is the change of the indicator species over a time step and c^0 and c^b refer to the initial and boundary concentrations respectively.

3. Test Problem

In order to test the ability of the reduction scheme to accurately predict concentration profiles a test problem was considered. The test problem considered here was presented by Baroghel-Bouny et al. [1] and concerns the diffusion of Na^+, OH^-, K^+ and Cl^-, ions into a mortar specimen from a solution with all other surfaces sealed. The reactions considered were kinetic binding of the chloride ions to the mortar matrix as describe by the Freundlich isotherm, eqn. (2) and the releases of hydroxide ions in equal amount to maintain the charge neutrality of the solution. The initial and boundary coefficients along with the diffusion coefficients are given in Table 1. The problem geometry can be seen in Fig. 1. The full details of the material and reaction parameters can be found in [1,3]. The chosen indicator species here was Na^+. The geometry was divided into a finite element mesh consisting of 42 nodes and 20 bilinear quadrilateral elements of size $\Delta x = 1mm$ and a time step of $\Delta t = 36s$ were used.

Table 1: BC's, IC's and Diffusion Coefficients of Species

Chemical Species	Initial Conc. (kg/kg)	Boundary Conc. (kg/kg)	D_{mol} ($10^{-10} m^2/s$)
Na^+	0.000299	0.01352	1.33
OH^-	0.001105	0.00188	5.3
K^+	0.002028	0.00319	1.96
Cl^-	0.0	0.01954	2.1
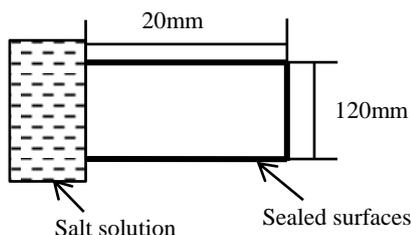
Figure 1: Boundary conditions and specimen size (not to scale)

The concentration profiles after 12hrs as predicted by (1) and the reduced model can be seen in Fig. 2. As can be seen from the profile, the predictions of the PRS are very close to those of the full model. The biggest difference can be seen in the OH^- profile with the difference being in the peak concentration where the hydroxide ions are being released due to the chloride adsorption.

An investigation into the computational cost was also made. The analysis of the test problem was performed on a laptop with an Intel Core i5-3230M @2.60GHz and 5.88GB useable RAM. The CPU time of the time step loop was measured for a number of runs and an average taken. The averaged CPU times were 620.1s and 293.9s for the full model and PRS respectively, equating to a reduction of 52.6%.
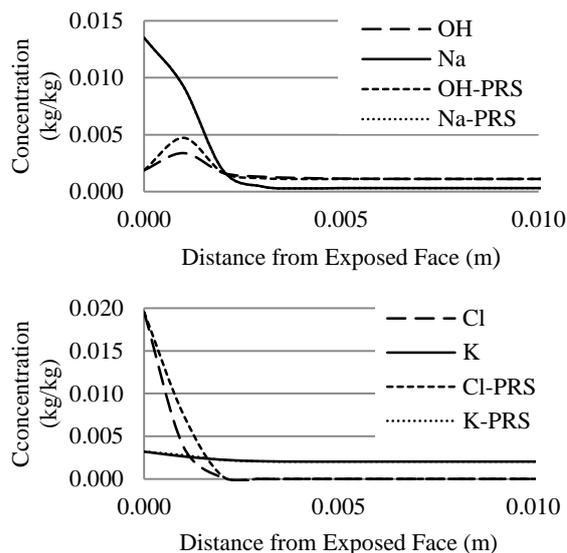
Figure 2: Concentration profiles predicted by (1) and PRS

5. Conclusions

The computational cost of an example problem has been successfully reduced whilst maintaining a suitable level of accuracy using the PRS presented. The reduction in cost equated to 52.6% CPU time and was achieved by reducing the number of governing equations to be solved from four to one.

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