

Reactive transport modelling with simulator MODCALIF-CHEM: prediction of the environmental impact of lignite dump waters

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Abstract To evaluate the effect and danger of dump waters from lignite dump sites on surrounding areas (e.g. waterworks, lakes), predictive “reactive modelling” of the transport processes is necessary. The simulator MODCALIF-CHEM was developed to do this. It is an iterative coupling of transport equation solutions and the hydrogeochemical equilibrium model PHREEQC (Parkhurst, 1995). The transport code prevents numerical dispersion for large Peclet numbers by using new algorithms for the discretization of the advection term. This algorithm leads to a drastic reduction in the simulation time. A new scheme for the discretization of the nondiagonal dispersion terms overcomes the problem of numerical oscillation. Thus, the calculation of small negative concentrations is prevented. This is critical for the coupling between transport and chemical reactions. MODCALIF-CHEM was verified by the simulation of different column flow tests. The simulator is able to cover the complexity of the main chemical processes of these tests. Predictive calculations are shown for a lignite open cast mine that is still operating.

INTRODUCTION

The former Eastern Germany was one of the most important lignite producers in the world in the 1970s and 1980s. Since 1990 the majority of the open cast mines have been closed due to a drastic reduction in lignite demand. The process of open cast mining has led to large dump sites containing higher mineralized (sulphate, iron, heavy metals, etc.) and acidic pore waters (phenomenon of Acid Mine Drainage, AMD). This phenomenon is caused by weathering of reduced sulphur compounds which are found in the beds of Tertiary age surrounding the coal seams. Future redevelopment of steady state flow conditions in the dumps will mainly be concerned with the effect and danger for the surrounding areas (e.g. waterworks, lakes). There are different chemical processes which are related to the migration of dump waters into the undisturbed aquifers (mineral dissolution/precipitation, ion exchange, redox reactions, surface complexation). The explanation of the whole migration process requires a reactive transport model. A thermodynamic and geochemical based evaluation is only possible by utilizing such an approach.

The simulator MODCALIF-CHEM was developed for the modelling of such problems. It is an iterative coupling of transport equation solutions and the hydrogeochemical equilibrium model PHREEQC (Parkhurst, 1995).

MATHEMATICAL MODEL

The partial differential equations for the transport of each component are:

$$n \frac{\partial \mathbf{c}}{\partial t} + n \frac{\partial \mathbf{c}^*}{\partial t} = -\text{div}(\mathbf{vc}) + \text{div}(\bar{\mathbf{D}} \text{grad } \mathbf{c}) + \dot{q}\mathbf{c} \tag{1}$$

where \mathbf{c} is the vector of the mobile component concentrations and \mathbf{c}^* represents the concentrations of the immobile form of these components. The total mass of each component can change through the advection–dispersion fluxes and source–sink term. The derivation $\partial \mathbf{c}^* / \partial t$ will be further interpreted as the chemical source–sink term.

For the numerical solution of the transport equation, a program was developed whose user-interface is similar to that of the widely used and acknowledged program MT3D. The contents of the MT3D program were rewritten. The partial differential equation is solved by the finite difference technique with the implementation of the time weighting Crank-Nicolson scheme. The weighting factors of advection and dispersion differ. The discretization schemes are explained below.

Advection Two methods were used to overcome the problem of numerical dispersion, namely the Front-Limitation Scheme (Häfner *et al.*, 1997) and the Total Variation Diminishing schemes ($TVD = \sum_i |c_{i+1} - c_i|$). The TVD schemes are described with reference to Fig. 1.

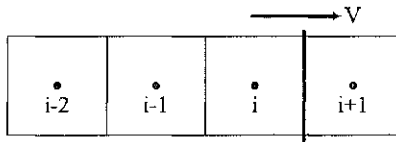


Fig. 1 TVD-schemes.

For the velocity direction, presented in Fig. 1, the concentration at the boundary between the i and $i + 1$ is expressed as:

$$c_{i+1/2} = c_i + \frac{1}{2} \Psi(r_{i+1/2})(c_i - c_{i-1}) \quad r_{i+1/2} = \frac{c_{i+1} - c_i}{c_i - c_{i-1}} \tag{2}$$

with flux limiter $\Psi(r)$. The following limiters were realized in the program: PL-k, Sweby, DPL-k, MPL-k, R-k, MR-k, DR-k (Zijlema, 1997). Therefore, it was possible to overcome the Peclet number constraint. Using these algorithms both minimizes numerical dispersion and suppresses the oscillations, even for coarse grids ($Pe = 100$).

Dispersion Discretization of nondiagonal dispersion fluxes by the common method (Kinzelbach, 1982) leads to numerical oscillations (see e.g. Cirpka, 1997). Cirpka chooses the streamline-oriented grids in order to solve this problem. But this procedure is very complicated, and can only be used for steady state flow. The suggested methods (Cirpka, 1999) for rectangular grids are either non-monotonic (high-order method) or only first-order accurate (low-order method). The scheme applied in this work is based on Demirdzic (1982). It preserves monotonicity and is at

the same time second-order accurate. Figure 2(a) shows the common scheme for the discretization of $q_{yx}^{i+1/2,j}$. This scheme leads to the following result: if at time step t_0 all cells, excluding cell $(i+1, j-1)$, have a concentration equal to 0, then cell (i, j) will have a negative concentration in the next time step. Figure 2(c) presents the corresponding results for a task, where the dispersion tensor ($Pe = 10$, $\alpha_L/\alpha_T = 10^4$) corresponds to the diagonal flow (advection is not taken into account); the cells with negative concentration are not shaded. Figure 2(d) shows the results obtained using the new scheme for the same task. The choice of points for the discretization of $q_{yx}^{i+1/2,j}$ depends on the algebraic sign of $D_{yx}^{i+1/2,j}$ (Fig. 2(b)). For positive coefficients, cells will be chosen which are indicated with "O". For negative coefficients the "□" cells will be chosen:

$$q_{yx}^{i+1/2,j} = -\frac{D_{yx}^{i+1/2,j}}{\Delta x} \left(c^{i+1/2,j+1/2} - c^{i+1/2,j-1/2} \right) = -\frac{D_{yx}^{i+1/2,j}}{2 \Delta x} \begin{cases} \left(c^{i+1,j+1} + c^{i,j} - c^{i+1,j} - c^{i,j-1} \right) \\ \left(c^{i+1,j} + c^{i,j+1} - c^{i+1,j-1} - c^{i,j} \right) \end{cases} \quad (3)$$

It can be shown, that this scheme is second-order accurate (it is symmetric around the point $(i + 1/2, j)$). The other nondiagonal dispersion fluxes were subjected to discretization in a similar way. The scheme can also be extended for the irregular rectangular grids.

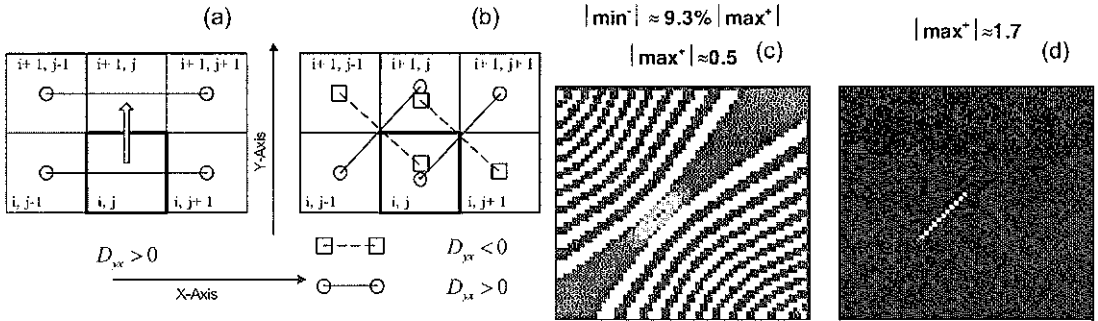


Fig. 2 Comparison between discretization techniques for the dispersion.

Chemical model

PHREEQC was used as a chemical equilibrium model. It includes the following heterogeneous and homogeneous interactions: ion exchange, surface complexation, pure phase equilibrium reactions and aqueous complexation reactions. These reactions lead to a nonlinear system of equations, which is solved by the Newton-Raphson method.

Coupling of transport and chemistry

The transport is described by the linear partial differential equation. The description of the chemical reactions results in a nonlinear system of algebraic equations. Solving both processes simultaneously is very complicated and impractical for realistic

multidimensional tasks. Therefore the iterative “operator split method” (Fig. 3) was implemented in the program.

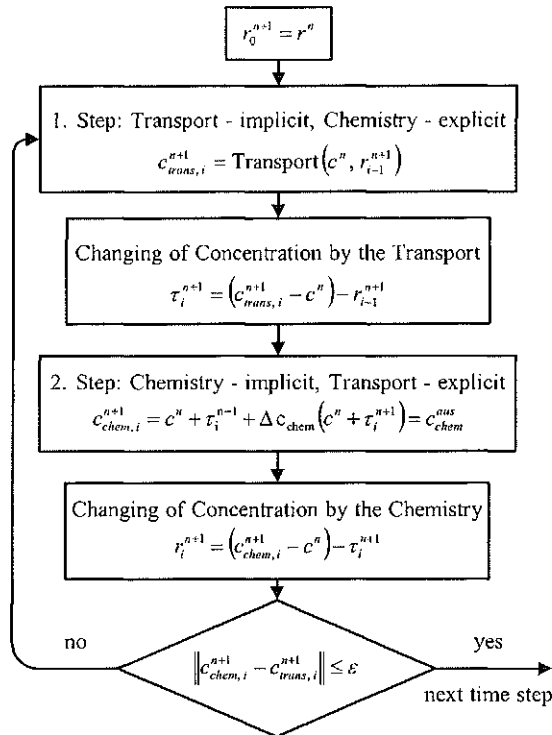


Fig. 3 Coupling of transport and chemistry part.

Data transfer between the transport and the chemistry part has been optimized (Fig. 4) resulting in a sixfold reduction in the expenditure of simulation time (when compared to the simple PHREEQC call). Because solving the “chemistry problem” consumes most of the computing time, the performance of the program can be expressed in terms of the number of PHREEQC-calls per minute. On a Pentium 100 Computer MODCALIF-CHEM is able to call PHREEQC 1200 times per minute.

VERIFICATION

The verification of the model was carried out by the simulation of different column flow tests. This is essential, because such experiments can be measured relatively well (quantification of the reactive phases, CEC and exchanger composition). Figure 5 shows the results for the simulation of a column flow test from Brand (1996). The experiment represents the migration of highly mineralized dump waters in a calcium siderite buffered aquifer. The main buffering processes (precipitation of gypsum, cation exchange) are well represented by the model. Additional column flow tests were simulated by MODCALIF-CHEM. These flow tests emphasize the importance and the

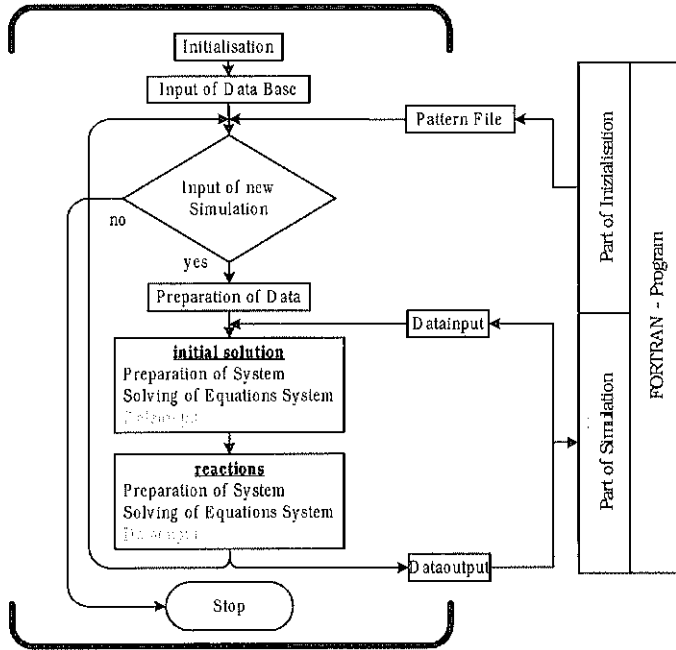


Fig. 4 Data transfer between transport and chemistry part.

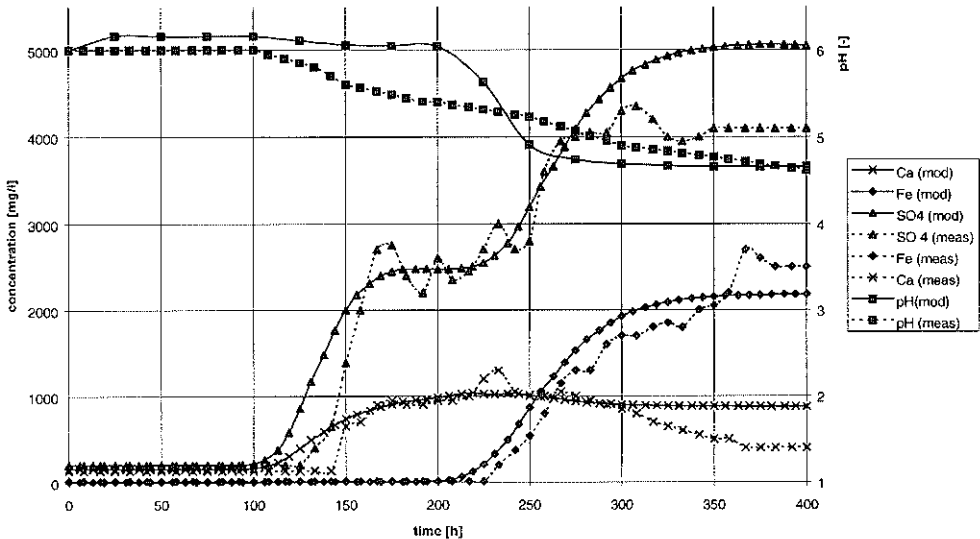


Fig. 5 Comparison of the model results (MODCALIF-CHEM) with the measurements from a column flow test from Brand (1996)

difficulties of determining the initial chemical conditions (quantification of the reactive phases, exchanger composition–extraction methods) of the percolated sample.

CASE STUDY

The predictive calculations for a currently operating open cast mine are given as an example. The primary issue for this site is also the effect and danger on the surrounding areas (e.g. waterworks, lakes) after redevelopment of steady state flow conditions in the dump. Two dimensional reactive simulations for the most important pollution pathways were carried out. Table 1 shows the chemical initial and boundary conditions for the dump and the Quaternary aquifer. These values result from extensive investigations and simulations of the chemical processes within the water unsaturated dump zone. For the reactive transport calculations the thermodynamic data within the "phreeqc.dat" file was used (Parkhurst, 1995).

Table 1 Initial and boundary conditions: chemical concentrations and parameter conductivity

	Dump layer 1-2	Dump layer 3-8	Dump layer 9	Quaternary aquifer
CEC (mol l ⁻¹)	0.62	0.62	0.29	0.04
Ca ²⁺ (mg l ⁻¹)	524	682	441	94.4
Fe ²⁺ (mg l ⁻¹)	473	4.6	135	0.26
Fe ³⁺ (mg l ⁻¹)	8.38×10^{-3}	8.7×10^{-4}	7.93×10^{-3}	1.9×10^{-4}
TIC (mg l ⁻¹) as HCO ₃	380	796	373	152.5
SO ₄ ²⁺ (mg l ⁻¹)	2010	1280	2180	123
Calcite (mol l ⁻¹)	0	7.7×10^{-2}	0	8×10^{-2}
Gypsum (mol l ⁻¹)	1.8×10^{-1}	2.8×10^{-2}	6.0×10^{-3}	0
Fe(OH) _{3(a)} (mol l ⁻¹)	5.54×10^{-7}	6.9×10^{-7}	3.77×10^{-8}	3.2×10^{-6}
Siderite (mol l ⁻¹)	2.06×10^{-2}	1.97×10^{-2}	0	0
pH	5.49	6.52	5.51	7.58
pE	4.37	3.35	4.88	1.14
k _f (m s ⁻¹)	2×10^{-5}	2×10^{-5}	8×10^{-4} – 5.8×10^{-7}	1.2 – 3.5×10^{-4}

Results

Figures 6, 7 and 8 show concentration distributions after 200 years of steady state dump outflow. The three columns on the right side of the model represent the dump body (vertical divided—compare Table 1). Figure 6 represents the iron content distribution for the reactive modelling, while Fig. 7 represents the distribution for the "tracer approach" (no chemical interactions). The model clearly shows that the ion exchange drastically buffers the iron content in the Quaternary aquifer. The calcite content of the aquifer material leads to a good buffering of the pH values (Fig. 8). The model also shows that the sulphate plume will have the most important influence on the aquifer. Sulphate will be suppressed only in small amounts by the process of gypsum precipitation in the direct vicinity of the dump. The phenomena of surface complexation were not considered. The calculations make clear that the complexity of the migration processes can only be understood and predicted by a reactive transport model.

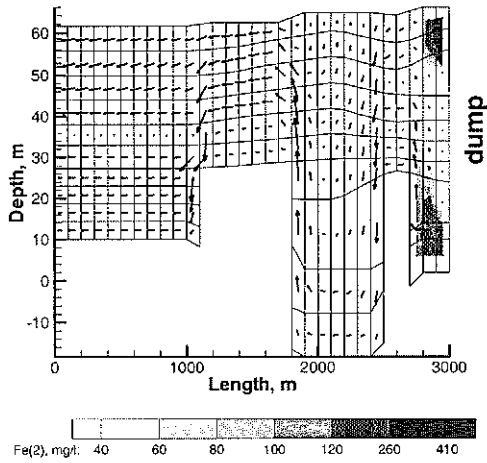


Fig. 6 Predicted iron concentrations (reactive modelling) after 200 years.

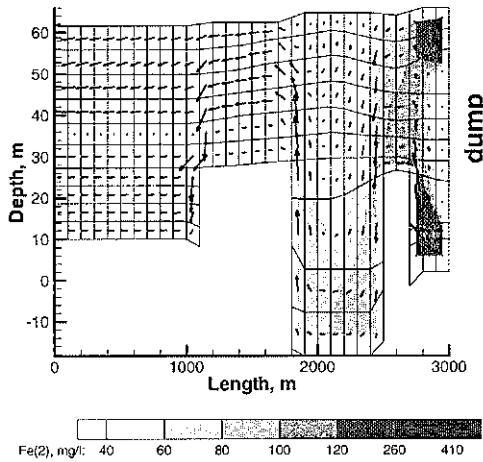


Fig. 7 Predicted iron concentrations (non reactive modelling) after 200 years.

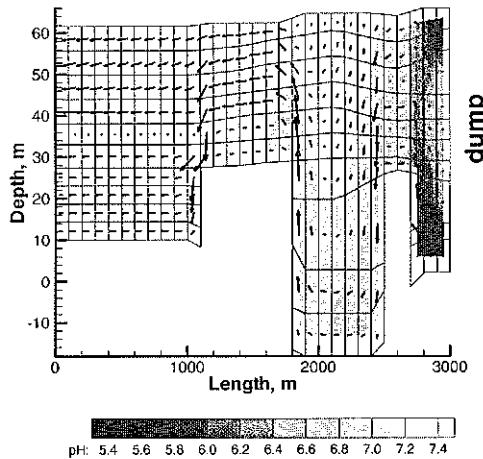


Fig. 8 Predicted pH values (reactive modelling) after 200 years.

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