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Waste Materials in Construction: Putting Theory into Practice

Using CHEMFRONTS, a geochemical transport program, to simulate leaching from waste materials

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Abstract

A coupled geochemical and transport program, CHEMFRONTS, has been developed for calculating water transport in porous media. The program was developed to handle sharp reaction fronts such as redox and pH fronts. CHEMFRONTS is based on reaction kinetics and can therefore handle non-equilibrium systems such as glass phase dissolution. After modification in the program, we have successfully simulated partially saturated systems with indiffusing carbon dioxide and oxygen. Unsaturated systems are, however, very complex. All the information required to make reliable simulations are not available. Simulations of these systems can, therefore, only be used to show trends and the influence of different variables. In spite of these uncertainties, we find these simulations meaningful to perform.

Introduction

Ashes and slags have physical properties that make these secondary material suitable as gravel substitutes in civil engineering applications. Difficulties in predicting the future leaching from these materials have often led to limitations in utilisation. To assess what will happen with a secondary material in the future, knowledge about the processes controlling the long-term leaching is required. Laboratory experiments can give good information about what will happen in the short-term, but as an experiment rarely lasts for more than a few years (often only for hours) the results cannot be extrapolated to make reliable predictions of long-term behaviour.

Solid materials in a porous medium that comes in contact with mobile water react unless the water already is in equilibrium with the solids. Solid phases dissolve and new phases may form. Dissolved species are transported by advective flow and diffusion. These processes are a natural part of the evolution leading to, for example, weathering of rocks.

With computer programs the leaching processes can be simulated for much longer times than is practical to observe experimentally. Programs can be used to simulate the geochemical evolution in time and space. They are often based on assumptions that there is local thermodynamic equilibrium at every point. Some models include dissolution and precipitation reactions. Examples of equilibrium programs are: HALTAFALL (Ingri et al., 1967), MINEQL (Westall et al., 1976), MICROQL (Westall, 1979), EQ3/6 (Wolery, 1992; Wolery and Daveler, 1992), PHREEQE (Parkhurst et al., 1980), WATEQ (Truesdell and Jones, 1974), and MINTEQA2 (Allison et al., 1991). Transport models, in addition, account for the mass balance. Many computer programs have been developed by combining an equilibrium model and a transport model. Examples hereof are: CHEQMATE (Harworth et al., 1988), TRANQL (Cederberg et al., 1985), PHASEQL/FLOW (Walsh et el., 1984), DYNAMIX (Liu and Narasimhan, 1989), and HYDROGEOCHEM (Yeh and Tripathi, 1991). If the reactions are not fast enough for equilibrium to be reached, dissolution and precipitation kinetics can be used. This approach is used in programs such as CHEMTRNS (Noorishad and Carnahan, 1987), PRECIP (Noy, 1990), MPATH (Lichtner, 1990), and CHEMFRONTS (Bäverman, 1993 and Bäverman et al., 1996).

Simulation of evolution of sharp fronts such as redox fronts and other simultaneously moving fronts has shown to be difficult with equilibrium based transport programs. CHEMFRONTS was originally developed to handle these type of fronts. Such fronts occur, for example, when oxygenated water infiltrates reduced rock. At redox and pH fronts that develop, some minor species can accumulate. These phenomena have been observed in nature, for example in the uranium mine in Poços de Caldas in Brazil, where the uranium ore is located at the redox front (Cross et al., 1991). We have also observed accumulation at a pH front in laboratory experiment where iron has accumulated (Bäverman, 1997a).

As CHEMFRONTS is based on reaction kinetics it can handle non-equilibrium systems, such as glass phase dissolution and reactions with gas phases. We have found it necessary to modify CHEMFRONTS to be able to handle partially saturated systems with indiffusing carbon dioxide and oxygen. These systems are very complicated though and therefore no reliable predictions can be performed at this stage. More knowledge about the processes involved is required for this. Even though these simulations have large uncertainties, they are meaningful to perform. They can give information about what can happen and how variables, such as water infiltration rate, oxygen access etc. influence the leaching and therefore be of use when a construction incorporating waste material is planned.

MODEL

In a system where water flows through a solid material, chemical reactions between the solid and the liquid phase occur. The whole system can be defined as consisting of components, at most one for each element. The mass balance of the system is shown in equation 1

$$\frac{\partial}{\partial t}(\phi Y_j) + \nabla W_j = -\sum_{m=1}^{M} v_{mj}\frac{\partial X_m}{\partial t} \qquad (j = 1, \ldots, N) \tag{1}$$

where the first term, the amount of component j that has accumulated in the system, plus the transport of component j by fluid flow and diffusion, ∇W_j, is equal to the changes in the mineral phase. ϕ is the porosity, Y_j is the total aqueous concentration of component j, including that present in the various complexes, M is the number of minerals, v_{mj} is the stoichiometric coefficient for the mineral m and the component j, X_m is the concentration of mineral m in the solid phase, and t is the time.

The quasi-stationary state approximation (Lichtner, 1988), which this model is based on, describes the evolution of geochemical processes as a sequence of stationary states. A single volume of water that flows through a column reacts with the solid phase, dissolves parts of the mineral until the water volume is saturated with the existing minerals, and new minerals form if supersaturation is reached. The reactions of a subsequent volume of water are similar to the previous ones, as the changes in the mineral phase are small.

When the mass of the components in the solution is very small compared to that in the mineral phase, the volume of water that must flow through the system to dissolve a substantial amount of a mineral is very large compared to the total volume of the column and its minerals. The accumulation of species in the water can then be ignored and the first term of equation 1 be neglected without any substantial loss in accuracy.

When there is a large advective flux, the diffusive flux can be small by comparison. In this model the transport by diffusion is not accounted for, which limits the use of the program to systems where the flux is controlled by the advection. Equation 1 then becomes

$$\mathbf{v}\frac{dY_j}{dz} = -\sum_{m=1}^{M} v_{mj}\frac{\partial X_m}{\partial t}(z) \tag{2}$$

for a one dimensional flow. **v** is the water flux in the z direction. Equation 2 states that the change in concentration of a component in the water is equal to the negative change of components in the mineral phase. The mineral precipitation or dissolution rate, $\frac{\partial X_m}{\partial t}$, is given by

$$\frac{\partial X_m}{\partial t}(\mathbf{r},t) = \zeta_m(\mathbf{r},t)\, I_m(\mathbf{r},t) \tag{3}$$

where ζ_m is a logical factor, which is unity both if the solution is supersaturated so that precipitation is possible, and if minerals are present so that dissolution is possible. Otherwise, ζ_m is zero. The rate of dissolution or precipitation, I_m, is

$$I_m(\mathbf{r},t) = \alpha_m(\mathbf{r},t)k_m^f(Q_m(\mathbf{r},t)-K_m^{-1}) \tag{4}$$

the product of the specific surface of the mineral, α_m, the mineral reaction rate, k_m^f, and the driving force of the system $(Q_m(\mathbf{r},t)-K_m^{-1})$. The driving force is the difference between the ion activity product of the water solution, Q_m, and the ion activity product at saturation (the inverse of the equilibrium constant of the formation for the mineral m)

$$Q_m(\mathbf{r},t) = \prod_{j=1}^{J} (a_j(\mathbf{r},t))^{v_{mj}} \tag{5}$$

Expressing the total concentrations in terms of component concentration we finally arrive at equation 6

$$\overline{\overline{A}}\,\frac{d\overline{C}}{dz} = -\frac{1}{\mathrm{v}}\sum_{m=1}^{M} v_{mj}\frac{\partial X_m}{\partial t}(z) = \text{a function of } \overline{C} \tag{6}$$

where $\overline{\overline{A}}$ is the matrix which transforms component concentration C to total concentration Y for any component. The system of equations (6) are solved by a standard solver for systems of stiff differential equations. This gives the concentrations in water along the whole column. From these, the dissolution and precipitation at every point is obtained from equations 3-5. The depletion or accumulation of the minerals at every point is obtained by integrating equation 3 over the time step chosen. In practice, a small time step is taken and bookkeeping of the mineral changes is made. It is then found that in some points a mineral previously present has been depleted. The location where the mineral now starts to appear is the new location of that front. If some mineral has formed which was not there previously, a new front location is formed for that mineral. A new time step is started by solving (6) at the new front locations. This is repeated for as long as needed. It may be noted that the various fronts separate eventually, and the rate of the front movement becomes independent of the mineral reaction rate in the special case when the product of the specific surface and the reaction rate $\alpha_m k_m^f$ is constant (Bäverman, 1993, Bäverman et al., 1996). Figure 1 shows an example where the pyrite and uraninite fronts are coupled and move together. These fronts will not separate. The other fronts in the system are well separated from each other. Then there is no need for further calculations by time stepping. Extrapolation of the front locations in time can then be made.

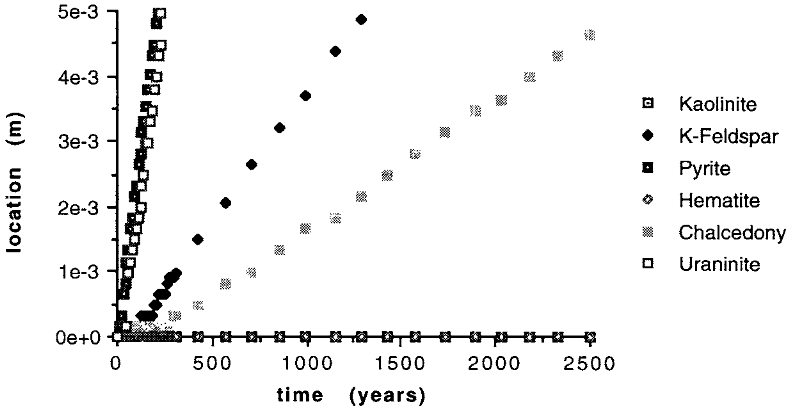

Figure 1. The location of the different fronts versus time. The pyrite and uraninite fronts are coupled, as uraninite is accumulated at the redox front.

The calculation typically starts with a homogeneous one dimensional column where water is flowing through with a constant rate. The calculations are made within a continuous column. The column is sub divided into several regions in each of which the same minerals exist. The regions are separated by "fronts". The positions of the boundaries are moved in every calculation step as the fronts (boundaries) move. As new minerals are formed or old minerals are exhausted, new regions are added or old ones removed. There is no minimum size of the regions, and their sizes can differ considerably.

When the water from one region moves into the next it is generally not in equilibrium and the solid phases react. Some solid phases dissolve and the dissolved species form complexes. Other and new minerals may precipitate. The component concentration profile along the column is calculated by integration of Equations (6). In this process, the mineral dissolution and precipitation rates are also obtained.

The process is illustrated by the following example where K-feldspar ($KAlSi_3O_8$) is dissolved forming a silica mineral (here chalcedony (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$), a clay mineral):

$$KAlSi_3O_8\ (s) + H+\ (aq) + 0.5\ H_2O \rightarrow$$

$$K+\ (aq) + 2\ SiO_2\ (s, l) + 0.5\ Al_2Si2O5\ (OH)_4\ (s) \qquad (7)$$

The dissolution and precipitation rate profile is shown in figure 2 when a front already has propagated a distance downstream in the column. At a front at the distance of 0.1510 m, in the figure, the water first comes in contact with the K-feldspar. The mineral starts to dissolve. This results in supersaturation of both kaolinite and chalcedony that precipitate. Protons are consumed, potassium and some silica are released into the solution. The process stops when the aqueous solution is saturated with respect to K-feldspar, kaolinite and chalcedony. This happens at a distance of about 0.1514 m, in the figure.

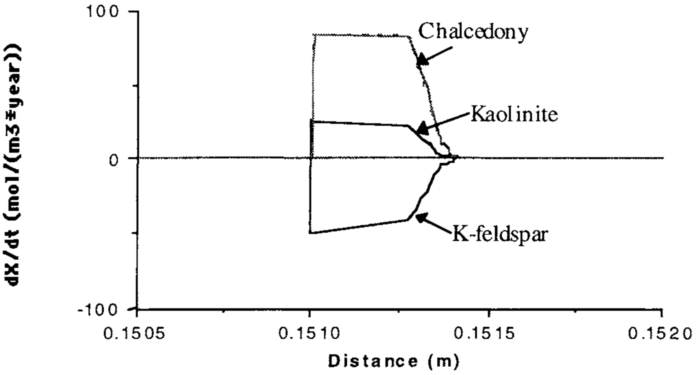

Figure 2. The dissolution (negative) and precipitation (positive) rate of the minerals involved when K-feldspar is dissolved.

The example used when CHEMFRONTS was developed was based on the uranium ore development in Poços de Caldas (Cross et al., 1991). The project was an international study of analogue processes. This study concerns redox and hydrolysis fronts and uranium mineralisation propagation at the Osamu Utsumi mine, an open pit uranium mine in Brazil, see figure 3.

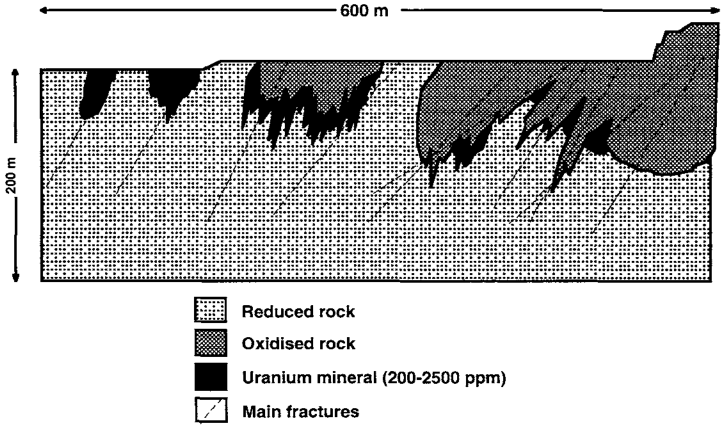

Figure 3. A schematic picture of the uranium mine in Poços de Caldas, Brazil.

The upper part of the pit is oxidised and separated from the deeper-lying reduced rock by a redox front. Uraninite nodules are found in many places just below the redox front in the reduced rock.

The mineral distribution after 38 000 years of water infiltration is shown in figure 4. The front rates in the simulation agree well with the field results (Bäverman, 1993).

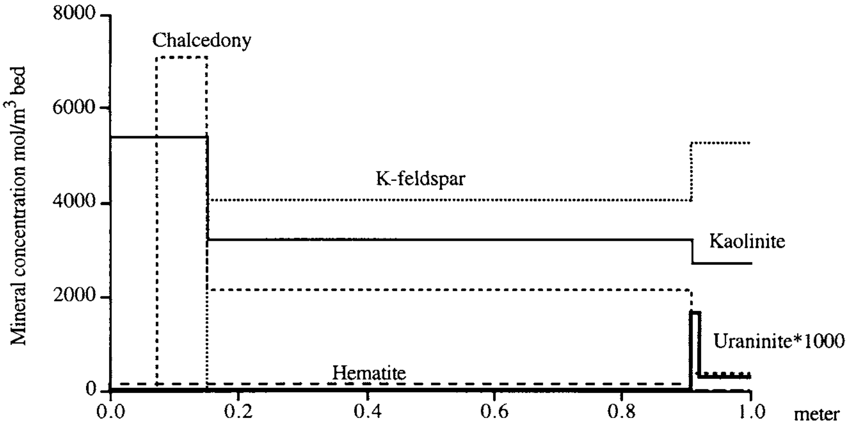

Figure 4. The mineral distribution after 38 000 years of water infiltration.

This is an example where the flow rates are slow and front movements several orders of magnitude slower. The separated fronts can be extrapolated with no loss of accuracy in the calculations, as equilibrium is reached between the fronts. The kinetic approach gives an explanation for the uranium ore formation, just below the redox front, that could be difficult to explain by equilibrium calculations.

Examples of simulations performed with CHEMFRONTS

Weathering of mine waste

In the former case the time scale was hundreds of thousands of years. The front movement were only dependent of the mineral content and the front position could thereby be extrapolated. CHEMFRONTS can also be used to predict geochemical transformations in unsaturated porous media near the atmosphere-geosphere interface. In this case, the time scale is a few years. Extrapolation of front movements is not possible because reaction with the gas phase will take place in all the column.

In this example, we simulate the breakthrough of copper in drainage water from mining waste, using data from the Aitik site in northern Sweden. Sulphide weathering, pH-buffering and copper (im)mobilisation are included. The principal processes in this case are as follows. The waste rock dump is partially saturated and the air in the pore-space contains oxygen (3-21%; Bennett et al., 1994). Sulphide minerals oxidise in this environment, which produces acidity, sulphate and dissolved metal species. The release of dissolved copper is of environmental interest and as its mobility is influenced by pH, it is necessary to include the processes affecting pH conditions. The acidity reacts with pH-buffering minerals, for example, calcite.

The simulated breakthrough curves for the waste rock heap are shown in figure 5. During the first 13 years, the effluent pH is near neutral and aqueous concentrations are close to the measured concentrations of effluents from large experimental columns filled with fresh waste rock (Strömberg et al., 1994). The effluent pH then declines as a consequence of the calcite depletion. pH is for a short period buffered near 5.5 as a result of copper mobilisation. After this phase the pH stabilises near 3.5. The peak concentration of copper is obtained between 14 and 15 years, which is the result of the release of previously accumulated copper.

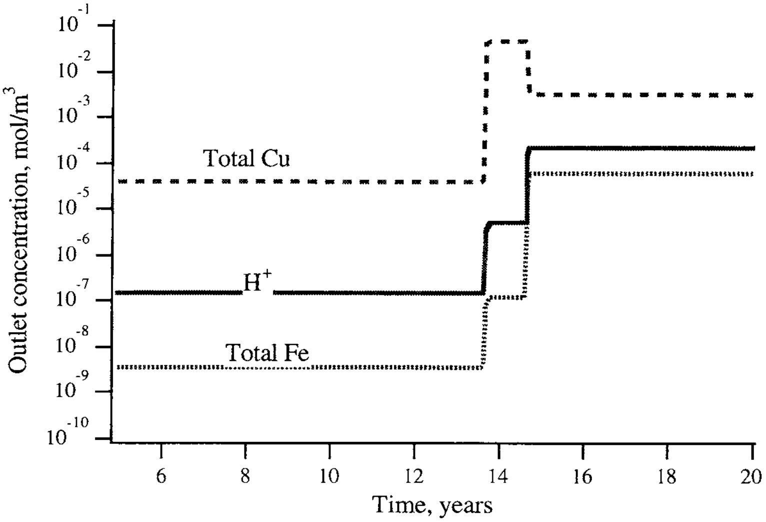

Figure 5. The leachate concentration in the effluent from the waste rock heap.

Simulation of a leaching experiment

CHEMFRONTS has been used to simulate a serial batch experiment where leach water has been flowing through a series of bottles containing waste material. The flow-through rate has been L/S=1 in 20 days. The simulation and experiment has been carried out with electric arc furnace steel slag, blast furnace slag and municipal waste combustion bottom ash (Bäverman, 1997 a, b). The input data to the simulation has been chosen based on total composition of the materials, minerals identified with X-ray diffraction analysis, Scanning electron microscopy has been included in the simulations, both primary minerals and secondary minerals formed in leaching experiments. Trace minerals have been chosen to be the most probable, using an equilibrium program EQ3/6 and discussion with a geologist. The aqueous complexes included in the simulation are chosen from the results of the EQ3/6 simulation. In the simulation only the most important elements are included. The basic components, original minerals, and secondary minerals for the simulation with EAF steel slag are shown in table 1. In addition, 38 different aqueous species were included in the simulation.

Table 1. The components and minerals used in the simulation with MSWIBA.

Components:

calcium, hydrogen, iron, sulphur, copper, silicon, chlorine, sodium, lead, chromium, oxygen and carbon dioxide

Original minerals:

larnite (β-Ca_2SiO_4), ferrous oxide (FeO), halite ($NaCl$), cuprous oxide (Cu_2O), $Ca(OH)_2$, anglesite ($PbSO_4$), chromic oxide (Cr_2O_3) and anhydrite ($CaSO_4$)

Secondary minerals:

calcite ($CaCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$), cupric oxide (CuO), goethite ($FeOOH$), lead chromate ($PbCrO_4$), Ca-ferrite and andradite ($Ca_3Fe_2(SiO_4)_3$)

Figure 6 shows the simulated results of the EAF slag experiment, for the iron, copper, chromium and silicon concentrations in the first leach water. The strange profile of the silicon concentration is caused by dissolution of one mineral and precipitation of another. In the whole column larnite (β-Ca_2SiO_4) dissolves. When the concentrations of iron and calcium, together with silicon, have reached saturation level, andradite ($Ca_3Fe_2(SiO_4)_3$) starts to precipitate. As the concentration of calcium continues to increase, the precipitation of andradite continues. This causes the decrease in iron concentration. As the silicon concentration in the steel slag leach water is below the detection limit, it is impossible to compare the results from the simulation with the experimental results.

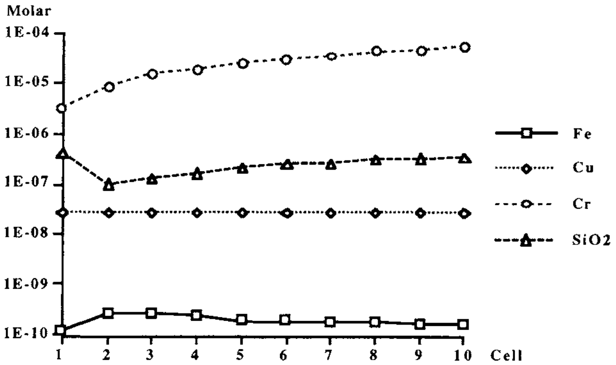

Figure 6. The concentration of iron, copper, chromium and silicon in the simulated column with steel slag.

The concentration at the end of the simulated column was compared with the experimental column. For most of the components the agreement was satisfying, but for copper and sodium the results disagree. There may be many reasons for this mismatch. The simulation was performed with only 12 elements whereas there were many more in the experiment. Some important elements may have been left out of the simulation that would considerably affect the result of the simulation. There may also be some solid phase or aqueous complex of importance for the solubility, of the elements included in the simulation, that were left out of the simulation. Some elements are very sensitive to the redox potential. As it is difficult to measure reducing Eh in an oxic environment, the redox potential in the simulation may be wrong compared to the real value in the experiment, as it was based on the measured value.

The simulations using experimental data for validation can be continued for longer time to simulate the long-term leaching from a waste material. This has been done and is reported elsewhere (Bäverman et al., 1997a). The simulation conditions, flow rate, access to oxygen, concentration of inflowing water etc., can be varied.

Discussion

There are several difficulties encountered when making computer simulations of long-term processes in waste materials. The materials are heterogeneous and formed under extreme conditions. Large parts of the waste materials are glasses. Geochemical computer models are developed for calculations of problems in geological systems. They often require well defined systems with thermodynamic data to make reliable simulations. These data are often not available for waste materials, especially not for the glass phases. It is therefore difficult to make reliable simulations in space and time for systems containing waste materials.

CHEMFRONTS has been found to be a reliable program for studying reactions along advective water flow paths through porous bedrock systems. We have also been able to use CHEMFRONTS to simulate unsaturated flow in ashes, slags and mine waste. The program cannot, at this stage, be used to make good predictions of what will happen in an unsaturated system, as more knowledge about the processes is required. It can, however, be used to give an indication of potential risks etc. Even though these simulations have large uncertainties, we find them meaningful to perform.

Acknowledgments

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References

Allison, J.D., D.S. Brown and K.J. Novo-Gradac (1991) MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems, EPA/600/3-91/021, March.

Bennett J. W., Gibson D. K., Ritchie A. I. M., Tan Y., Broman P. G. and Jönsson H. (1994) Oxidation rates and pollution loads in drainage, Correlation of measurements in a pyritic waste rock dump, Bureau of Mines Special Publications SP06A-94, 400-409.

Bäverman, C. (1993) Development of "CHEMFRONTS", a coupled transport and geochemical program to handle reaction fronts, SKB Tech. Report 93-21, Swedish Nuclear Fuel and Waste Management CO, Box 5864, S-102 48 Stockholm, Sweden.

Bäverman, C. (1997a) The importance of the pH buffering capacity – Comparison of various methods to estimate the pH properties of a waste material, Fifth Annual North American Waste-to-Energy Conference, Research Triangle Park, North Carolina, USA, April 22-25, 1997.

Bäverman, C. (1997b) Long-term leaching mechanisms of ashes and slags; Combining laboratory experiments with computer simulations, Ph.D. thesis, TRITA-KET R65, ISSN 1104-3466.

Bäverman, C., A. Sapiej, L. Moreno and I. Neretnieks (1997) Serial Batch Tests Performed on Municipal Solid Waste Incineration Bottom Ash and Electric Arc Furnace Slag, in Combination With Computer Modelling, Waste Management and Research, in press.

Cederberg, G.A., R.L. Street, and J.O. Leckie (1985) A groundwater mass transport and equilibrium chemistry model for multicomponent systems, Water Resour. Res. 21(8), 1095-1104.

Bäverman, C., Strömberg, B., Moreno, L. and Neretnieks, I. (1996) CHEMFRONTS: a coupled geochemical and transport simulation tool, KAT 96/36, submitted to Journal of Contaminant Hydrology.
Cross, J.E., A. Harworth, I. Neretnieks, S.M. Sharland, and C.J. Tweed (1991) Modeling of redox front and uranium movement in a uranium mine at Poços de Caldas, Radiocim. Acta, 52/53, 445-451.
Harworth, A., S.M. Sharland, P.W. Tasker and C.J. Tweed (1988) A guide to the coupled chemical equilibria and migration code CHEQMATE, Harwell Laboratory Report, NSS R113.
Ingri, N., W. Kakolowicz, L.G. Sillen, and B. Warnquist (1967) High speed computers as a supplement of graphical methods - V. HALTAFALL: A general program for calculating the composition of equilibrium mixtures, Talanta, 14, p 1261.
Lichtner, P. (1988) The quasi-stationary state approximation to coupled mass transport and fluid-rock interactions in a porous medium, Geochim. Cosmochim. Acta 52, 143-165.
Lichtner, P. (1990) Redox front geochemistry and weathering: theory with application to the Osamu Utsumi uranium mine, Poços de Caldas, Brazil, Submitted to Chemical Geology, Special issue on the Poços de Calds, December 3.
Liu, C.W., and T.N. Narasimhan (1989) Redox-controlled multiple reactive chemical transport, 1. Model development, Water Resour. Res., 25(5), 869-882.
Noorishad, J., and C.L. Carnahan (1987) Development of the non-equilibrium reactive chemical transport code CHMTRNS, DE-AC03-76SF00098; LBL-22361.
Noy, D.J. (1990) PRECIP: A program for coupled groundwater flow and precipitation/dissolution reactions, National Environment Research Council British Geological Survey, Technical Report WE/90/38C.
Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer (1980) PHREEQE - A computer program for geochemical calculations, Report USGS/WRI 80-96, NTIS Tech. Rep. PB81-167801.
Strömberg B., S. Banwart, J.W. Bennett and A.I.M. Ritchie (1994) Mass balance assessment of initial weathering processes derived from oxygen consumption rates in waste sulfide ore. Bureau of Mines Special Publication SP 06B-94, 363-370.
Truesdell, A.H., and B.F. Jones (1974) WATEQ, a computer program for calculating chemical equilibria of natural waters, J. Res. U.S. Geol. Surv. 2(2), 233-248.
Walsh M.P., S.L. Bryant, R.S. Schechter, and L.W. Lake (1984) Precipitation and dissolution of solids attending flow through porous media, AIChE J., 30(2), 317-328.
Westall, J.C., J.L. Zachary, and F.M.M. Morel (1976) MINEQL: A computer program for the calculation of chemical equilibrium composition of aqueous system, Tech. Note 18, 91 pp., Dep. of Civ. Eng., MIT, Cambridge, Mass.
Westall, J. (1979) MICROQL: 1 A chemical equilibrium program in BASIC, EAWAG, Swiss Fed. Inst. of Technol., Duebendorf, Switzerland.
Wolery, T.J. (1992) EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide and related documentation (Version 7.0), Lawrence Livermore National Laboratory, September 14.
Wolery, T.J., and S.A. Daveler (1992) EQ6, A computer program for reaction path modeling of aqueous geochemical systems: Theoretical manual, user's guide and related documentation (Version 7.0), Lawrence Livermore National Laboratory, October 9.
Yeh, G.T., and V.S. Tripathi (1991) A model for simulating transport of reactive multispecies components: model development and demonstration, Water Resour. Res., 27(12), 3075-3094.