MININR: A Geochemical Computer Program for Inclusion in Water Flow Models—An Application Study

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February 1984

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MININR: A GEOCHEMICAL COMPUTER
PROGRAM FOR INCLUSION IN WATER
FLOW MODELS - AN APPLICATIONS STUDY

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ABSTRACT

MININR is a reduced form of the computer program MINTEQ which calculates equilibrium precipitation/dissolution of solid phases, aqueous speciation, adsorption, and gas phase equilibrium. The user-oriented features in MINTEQ were removed to reduce the size and increase the computational speed. MININR closely resembles the MINEQL computer program developed by Westall (1976). The main differences between MININR and MINEQL involve modifications to accept an initial starting mass of solid and necessary changes for linking with a water flow model. MININR in combination with a simple water flow model which considers only dilution was applied to a laboratory column packed with retorted oil shale and percolated with distilled water. Experimental and preliminary model simulation results are presented for the constituents K^+ , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , CO_3^{2-} and pH.

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INTRODUCTION

The inclusion of chemical equilibrium calculations into existing hydrologic water flow models has been a subject of ongoing research. Existing hydrologic models which utilize a distribution coefficient to model chemical interactions are valid only over a very limited set of hydrochemical conditions. Existing geochemical models such as MINTEQ (Felmy et al. 1983a) and PHREEQE (Parkhurst et al. 1980) have the capability of considering precipitation/dissolution of solid phases, aqueous speciation, adsorption and gas phase equilibrium. The purpose of this study was to make an initial attempt at including these complex geochemical calculations into water flow models.

The study was conducted in three phases. In phase one, MININR was constructed by removing user-oriented features from the computer program MINTEQ. A version of MINTEQ was also modified to prepare a small thermodynamic data file to initialize MININR. In the second phase, MININR was incorporated into a simple water flow model. In the third phase, the combined geochemical and water flow model was applied to a system consisting of a laboratory column packed with retorted oil shale and percolated with distilled water.

MININR CONSTRUCTION

MININR was constructed by reducing the computer program MINTEQ. MININR thus includes only the computational structures in MINTEQ. Subroutines SOLID, SOLIDX, SOLVE and SIMQ are identical with those in MINTEQ. Subroutine INPUT was revised to read an initial thermodynamic data file prepared by a modified version of MINTEQ, hereafter termed MINTEQB. The thermodynamic data file contains information for all species types as well as initial starting estimates for the component activities. In preparing the data file, MINTEQB has modified the equilibrium constants for temperature and ionic strength. Therefore, temperature and ionic strength remain fixed for all MININR calculations. In addition to the previously described subroutines, subroutine LINK was added for communicating with the flow model. Subroutine LINK initializes the precipitated solids and mass totals passed from the flow model.

The only adsorption models included in MININR are the "activity" K_d , the "activity" Langmuir and a simple ion exchange model.

USE OF MININR

MININR requires two types of data: 1) thermochemical data and 2) initial aqueous, absorbed and precipitated masses in the actual or hypothetical system to be modeled.

The thermochemical data are passed to MININR by an initial run of MINTEQB. When executing MINTEQB, the formulated chemical model should correspond as closely as possible to the expected conditions in the system being studied. For example, if calcite and gypsum are expected to be present, they should be given an expected finite mass and made precipitated solids in the MINTEQB run. Similar logic applies to adsorption sites and aqueous totals (i.e., the conceptual chemical model should be similar to what is expected for the experimental system).

There are several procedural notes the beginning user of MININR should be aware of:

- 1) There are only two pH options:
 - (a) the pH is fixed at one value for the entire experimental system or
 - (b) the pH is computed by MININR.

The latter option is generally preferred; however, the proton condition must be initialized for each segment. The proton condition (mass of ionizable H^+) is initialized in the flow model data file. If the pH is to remain fixed, it must be initialized in the MINTEQB run.

- 2) In the initial run of MINTEQB, all considered solid phases should be declared as precipitated solids which are subject to dissolution (Type IV) or dissolved solids which are subject to precipitation (Type V). If they are declared Type III (precipitated solids not allowed to dissolve) they will be in equilibrium in every segment.
- 3) If the pE is to be computed, the mass totals of each elemental oxidation state in the specified pE controlling redox reaction(s) must be initialized before the MINTEQB run.

- 4) The initial specified mass of solids which is input in the flow model data file must include the solid ID number and the initial mass of solid in moles/g. These solids are initialized in each segment.
- 5) Adsorption and ion exchange sites are initialized in the same manner as solids with total adsorption sites specified in moles of sites/g.
- 6) The initial concentrations of all dissolved constituents must be initialized in the flow model data file for each segment.

The most difficult problem in the use of MININR is the formation of the conceptual chemical model for each column or experimental segment. An example of formulating conceptual chemical models can be found in Felmy et al. (1983b) and Peterson et al. (1983).

APPLICATION STUDY

The combined geochemical and water flow model was applied to a column packed with Lurgi retorted oil shale. The retorted shale is a calcareous mineral residue, low in organic carbon (~0.3%), derived from surface retorting (at~650°C) of kerogeneous marlstone from the Green River formation in north-western Colorado by the Lurgi process. The purpose was to predict the column effluent concentrations.

EXPERIMENTAL SYSTEM

Dry Lurgi retorted shale (<0.3% moisture by weight) was packed into a 25 cm x 2.5 cm lexan column and leached downward with degassed, deionized distilled H₂O. Saturated conditions were maintained. Maximum particle size of the Lurgi retorted shale was approximately 3.0 mm; 92% by weight was less than 2.0 mm and 42% less than 50 µm. The median particle diameter was 79 µm. Water flux rates to the column were maintained with a peristaltic pump. This provided a slow pore water velocity through the spent shale which is roughly comparable to that anticipated under disposal conditions. The physical and hydrologic characteristics of the column are summarized in Table 1.

TABLE 1. Retorted Shale Column Characteristics

Physical Characteristics^(a)

L = 25 cm	f = 0.55 cm ³ /cm ³
D = 2.5 cm	ρ_b = 1.22 g/cm ³
A = 4.9 cm ²	ρ_s = 2.70 g/cm ³
V_T = 123 cm ³	M_s = 150 g
V_1 = 67.6 cm ³	θ_v = 0.53 cm ³ /cm ³

Flow Data^(b)

Q = 1.62 cm/day	v = 3.06 cm/day	τ = 8.5 days
-----------------	-----------------	-------------------

Parameters: (a) L = column length, D = column diameter, V_T = total column volume, V_1 = pore volume, f = porosity ($1 - \rho_b/\rho_s$), ρ_b = bulk density, ρ_s = particle density, M_s = dry weight of retorted shale, θ = volumetric water content.

(b) Q = total water flux to column, v = average pore water velocity (Q/θ), τ = pore volume residence time = $V_1/(Q \cdot A)$.

Two pore volumes of water were passed through the column of retorted shale. Column leachate was continuously sampled. A fraction collector was used to divert approximate 2 mL increments directly into tubes containing pre-measured volumes of H₂O, conc. HCl, and formaldehyde for preservation of selected chemical constituents. The fraction collector was covered with plastic and purged with N₂ to discourage absorption of CO₂(g) by high pH leachate. Extensive chemical analyses were performed on the leachates but only pH, conductivity, and selected macro ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, CO₃²⁻) are discussed herein.

Leachate samples were removed from the fraction collector as soon as possible after exiting the column (0-12 hr), and pH, Emf (platinum electrode), and specific conductivity were measured immediately. Leachates were diluted to a specific conductivity of less than 3000 μ mho/cm with deionized, distilled, degassed water to minimize precipitation and refrigerated (4°C) until analysis. Major cations and anions were measured within one week of collection. Alkali (Na, K⁺) and alkaline earth metals (Ca²⁺, Mg²⁺) were determined by inductively

coupled argon plasma spectroscopy (Jarrel Ash Model Atom Comp 95 Spectrometer). Sulfate was determined by ion chromatography (Dionex Model 10 Ion Chromatograph) using an ion exchange resin column and an eluate stream of 3 M NaHCO_3 + 2.4 M Na_2CO_3 (McFadden and Garland 1980). Dissolved inorganic carbon ($\text{HCO}_3^- + \text{CO}_3^{2-}$) was quantified by wet oxidation (Oceanographics International Model 0524B-NR Direct Injection Module).

Leachate from the Lurgi retorted shale is high in pH, specific conductivity, and soluble salts (Table 2). These highly soluble constituents are common to other retorted shales (Stollenwerk and Runnels 1981, Garland et al. 1979, Wildung and Zachara 1980). The leaching of these solutes from retorted shale embankments or disposal sites represents a major environmental concern (Routson et al. 1979). The macro ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , CO_3^{2-} , and OH^-) comprise greater than 95% of the cation-anion balance of the leachate. The alkali metals and SO_4^{2-} decrease markedly in concentration in the first 0.25 pore volume indicating rapid leaching of highly soluble salts. In contrast, pH and the concentration of Ca^{2+} and Mg^{2+} remain relative constant, suggesting equilibrium conditions with solid phases present in the retorted shale.

FORMULATION OF CONCEPTUAL CHEMICAL MODEL

Chemical (solid phase elemental analysis and batch aqueous extraction) and mineralogical (x-ray diffraction) analyses of the Lurgi retorted shale (discussed elsewhere) indicate that the major solid phases influencing solution composition were magnesium and calcium oxides and carbonates as well as soluble potassium and sodium salts. In addition, ion speciation/solubility calculations were performed with MINTEQ on selected effluent volumes indicating that leachates were in equilibrium with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and portlandite [$\text{Ca}(\text{OH})_2$]. The importance of the above solid phases is supported by limited solubility calculations performed for alkaline groundwaters in contact with naturally retorted Mideastern oil shales (Barnes 1981). With this information and some preliminary modeling of the equilibrium dissolution of selected assemblages of solids into water to simulate batch aqueous extractions of the

TABLE 2. Major Ions in First 0.3 Pore Volume of Leachate

Leachate Volume		Solution Parameters							
Cumulative Volume (mL)	Pore Volume Fraction	pH	Conc mmho/cm	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO ₄ ²⁻	CO ₃ ²⁻
				μg/mL					
5.0	0.074	11.68	24,622	489	BD	4,140	2,763	10,760	615
7.0	0.104	11.30	25,664	474	BD	3,330	2,379	9,680	196
8.5	0.126	11.53	21,626	447	BD	2,931	2,259	8,660	261
10.0	0.148	10.83	20,453	450	BD	2,454	1,912	7,810	165
11.5	0.170	10.89	18,499	471	BD	2,096	1,791	7,050	75.5
13.0	0.192	11.16	18,499	462	BD	1,855	1,605	6,670	98.5
14.5	0.214	11.14	17,848	504	0.06	1,886	1,608	6,220	144
16.0	0.237	11.05	17,327	504	0.30	1,685	1,410	6,010	134
17.5	0.259	9.94	14,200	453	BD	1,752	1,452	5,630	ND
19.0	0.281	10.13	14,330	492	0.39	1,671	1,344	5,610	57.5
20.5	0.303	10.54	13,679	489	0.06	1,611	1,299	5,340	205

BD = Below Detection, ND = Not Determined.

retorted shale, a conceptual chemical model of the retorted shale/water system was formulated. The solid phases included in the conceptual model are given in Table 3.

TABLE 3. Solid Phases in the Conceptual Chemical Model

Solid	Mass (Moles/g)	Comments
Brucite	1.30×10^{-3}	Estimated from Chemical and Mineralogic Analyses
Gypsum	3.91×10^{-4}	Estimated from Chemical and Mineralogic Analyses
Mg-Calcite	4.1×10^{-4}	Estimated from Chemical and Mineralogic Analyses
Portlandite	2.65×10^{-6}	Estimated from Column Effluent pH

Direct quantification of the solid phases in the conceptual model is problematic as some are present in low concentration and others are amorphous. Hence, masses were estimated indirectly from 1) total chemical analysis of the retorted shale (e.g., Ca, Mg, SO_4^{2-} , and inorganic carbon), 2) mineralogic analysis by x-ray diffraction [e.g., peak location and height ratios of CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$], and 3) aqueous batch extraction of the retorted shale under inert atmosphere and over a large range in solids to solution ratio (1:1 - 1:1000). Batch extraction combined with modeling of the dissolution of different hypothetical mineral assemblages was particularly useful in estimation of the masses (e.g., mg/g or moles/g of retorted shale) of important, soluble solid phase constituents.

Use of MINTEQ to calculate saturation indices for carbonate minerals in the batch extractions suggested that a high Mg-calcite was present and in equilibrium with solution. A close agreement between analytical data and model simulations of batch extractions was obtained when a high magnesium calcite ($\text{Ca}_{0.76}\text{Mg}_{0.24}\text{CO}_3$, $\log K = -7.2$) (Thorstenson and Plummer 1977), was used as the dissolving/precipitating carbonate phase. This high Mg calcite was used in model simulations of the column leaching experiment.

The conceptual chemical model also included soluble potassium and sodium sulfates; their masses were estimated from batch extraction data. The column study indicated that these salts were rapidly solubilized in water and were removed in approximately the first quarter pore volume of leachate. Since the

oil shale column was initially dry, all of the soluble sodium and potassium sulfate was placed in the last segment to simulate the accumulation of solubles that occurred as the wetting front moved through the column. The aqueous concentrations of Na, K and SO_4^{2-} in the first four column segments were initialized at the 19.0 mL effluent value to simulate a slow dissolution of readily soluble salts. A schematic of the column is shown in Figure 1.

FLOW MODEL CONSTRUCTION

The initial efforts to link a flow code to the chemical model were done by creating a simple code to simulate a segmented, saturated, one-dimensional soil column. The purpose of the code was to aid in developing a computational interface between the flow and chemical codes. The larger objective is to link the chemical code to the unsaturated water flow code, UNSAT1D, (Bond et al. 1982, Gutknecht and Bond, 1983).

The UNSAT1D flow code is a large, complex code which simulates not only the unsaturated flow through the soil column, but also includes daily variations in rainfall, potential evapotranspiration (PET) as well as a moisture sink term, which simulates changes in plant root depth and density. The simpler flow model SATCOL and linking subroutines SETUP and ALCHEMY, use the conventions of the larger model. The program structure was designed to permit replacement of the flow code. The combined chemistry and flow code is identified as MINICUP, representing the coupling of MININR with a flow code, either SATCOL or UNSAT1D.

The conceptual hydrologic model used to simulate the laboratory flow column consisted of a column of shale with properties as described in Table 1, in which one-dimensional flow occurred. The flow column was divided into five equal segments (Figure 1). The driver program, SATCOL, reads the initial data and defines the segmented saturated soil column and at each time step adds an aliquot of water to the column. The code first calls the Subroutine SETUP, which reads the chemical data file created by MINTeqB and initializes each cell with the species in solution and the precipitates present in each cell. SETUP makes an initial call to the MININR model to read the thermodynamic data file and initialize the chemistry for each cell.

FIGURE 1. Schematic of Flow Column Modeled Using MINICUP (MININR and SATCOL) to Simulate the Water Chemistry of Effluent Water from a LURGI Oil Shale Column

SATCOL then adds an aliquot of water to the top of the column and sends the pulse through each segment of the column. The flux passing between segments is passed to the subroutine ALCHMY which is the primary linking subroutine between the flow and chemical codes. From the concentrations of soluble species in the volume of fluid transferred between segments, ALCHMY calculates a new total soluble mass for the soluble species and converts mass to concentrations.

One can express the change taking place in each segment due to the flow as follows:

$$\frac{\partial C_i^t}{\partial t} = \frac{C_i^{t-1} V_i^{t-1} - C_i^{t-1} Q_{out} + C_{i-1}^{t-1} Q_{in}}{\Delta t V_i^t}$$

where C_i represents the concentration in segment i ,
 V_i^t represents the volume in segment i at time t ,
 Q_{out} represents the flux moved out of segment i to $i+1$,
 Q_{in} represents the flux moved into segment i from $i-1$.

Once the adjustment of the concentration is made, due to the flow between segments, the chemical model MININR is called.

A new equilibrium between soluble and precipitated mass is determined. MININR returns the new concentrations for both soluble species and precipitates, which ALCHEMY stores for the next time step. The primary difficulty in developing the link was the fact that MININR re-orders the solution matrix to optimize matrix calculations and returns the chemical species in a seemingly random order. The species in the next segment passed to the chemical model must be in the order last used in the matrix solution. Simple sort routines are used to identify and re-order subscripts to accomplish this. A schematic of the flow code and linking subroutines are shown in Figure 2.

FLOW MODEL USAGE

Simulation of a column requires two files. The thermodynamic data from the required MINTEQB run is written to a file called PASS.DAT. The second file, whose name is assigned at run time, initializes each segment of the column with the lengths of each segment and the mass totals of both soluble and precipitated species present.

The program is interactive and when run from the terminal the program asks for:

- 1) the number of time steps,
- 2) the flux of water in each time step in cm^3 ,
- 3) the column cross section, and
- 4) the bulk density and porosity of the soil in each column segment.

Under control of the UNSAT1D program, the flux will come from the simulation of the flow and the porosity will be replaced with moisture content. Input will be significantly changed for the flow code only. It is anticipated that the data for the chemical model and linking subroutines will remain the same.

*ENTRY 0 READ THERMODYNAMIC DATA
ENTRY 1 SOLVES CHEMISTRY CODE

FIGURE 2. Schematic of Flow Code SATCOL and Linking Subroutines Connecting the Geochemistry Code, MININR to SATCOL

RESULTS

The predicted leaching trend of Na^+ and K^+ closely follow that observed in the column study (Figures 3 and 4), suggesting that the dilution model is correct. However, the predicted effluent concentrations of Na^+ and K^+ are consistently lower than the experimental observations, with K^+ most distinctive in this respect. The predicted K^+ values are consistently 17-20% lower than the experimental data suggesting an underestimate in 1) the quantity of soluble K^+ present, or 2) the rate of K_2SO_4 dissolution used in the model calculations.

The predicted and experimental sulfate concentrations are given in Figure 5. The predicted concentrations are quite close to the experimental data. Thus, the assumption of chemical equilibrium with gypsum, $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$, combined with leaching of soluble Na^+ and K^+ sulfates provide an accurate representation of the data. The decrease in sulfate concentration with effluent volume reflects leaching and dilution of SO_4 associated with amorphous salts of K and Na.

The predicted and experimental calcium concentrations are shown in Figure 6. The predicted concentrations are lower than the experimental values at early effluent volumes. This is a result of a low estimate in the original mass of portlandite $[\text{Ca}(\text{OH})_2]$ in the column. It was assumed that portlandite was not present in a mass high enough to lead to equilibrium conditions with the leachate, and therefore influenced leachate pH and Ca^{2+} levels by dissolution. Thus, a low estimate in the mass of $\text{Ca}(\text{OH})_2$ would result in low predicted Ca^{2+} concentrations by the model.

The predicted and experimental effluent pH values are shown in Figure 7. The predicted values were obtained by estimating the initial mass of portlandite from the initial effluent pH. Decreasing pH at later volumes is a result of dilution of this initially redissolved mass of portlandite, while maintaining equilibrium with brucite. The modeling results successfully predict very high pH values which are comparable to those measured experimentally. Additionally, the predicted pH values follow the same trend as the experimental values.

FIGURE 3. Predicted and Experimental Effluent Potassium Concentrations

FIGURE 4. Predicted and Experimental Effluent Sodium Concentrations

FIGURE 5. Predicted and Experimental Sulfate Concentrations

FIGURE 6. Experimental and Predicted Calcium Concentrations

FIGURE 7. Predicted and Experimental Effluent pH Values

The predicted and experimental magnesium concentrations are shown in Figure 8. The predicted values are very low as are the experimental values until approximately 10 mL of effluent. At later effluent volumes (10 to 20.5 mL), the model predicts a gradual decrease in pH which accompanies dissolution and removal of portlandite [$\text{Ca}(\text{OH})_2(\text{s})$]. Under these conditions, the solubility of brucite and magnesium calcite increase leading to higher predicted Mg concentrations. Additional experimental evidence developed since the completion of the modeling study suggests that the pH internal to the column may have been higher than measured in the effluent samples. An input of a higher pH to the model would significantly reduce predicted Mg concentrations because of equilibrium conditions with brucite [$\text{Mg}(\text{OH})_2$]. These would more favorably compare with the experimental observations.

The predicted and experimental carbonate concentrations are given in Figure 9. The experimental values are always higher than the predicted values. There are two obvious possibilities for the disagreement: 1) diffusion of atmospheric CO_2 into the high pH leachates during sampling or analysis, or 2) a more soluble carbonate phase exists in the column. The first possibility is the most likely since the effluent samples were undersaturated with respect to atmospheric $\text{CO}_2(\text{s})$.

FIGURE 8. Predicted and Experimental Magnesium Concentrations

FIGURE 9. Predicted and Experimental Carbonate Concentrations

CONCLUSIONS AND RECOMMENDATIONS

The modeling methodology proved effective in defining important chemical mechanisms. Although the results presented here are only preliminary, the conceptual chemical model could be used to predict the pH, Ca^{2+} , SO_4^{2-} , Na^+ and K^+ concentrations with good accuracy. The methodology will prove even more satisfactory when analytical inaccuracies are resolved in the leachate data and the initial mass of solid phases, particularly portlandite and soluble sodium and potassium sulfates, can be more accurately determined.

The reduced geochemical computer code MININR should be incorporated into an unsaturated flow code to avoid the need to adjust the concentrations of solids in each column segment. In addition, the modeling methodology should be applied to other retorted oil shales to more accurately define the initial conceptual chemical model developed here.

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