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MODELING OF LABORATORY TESTS ON THE INTERACTION OF $NaNO_3$-NaOH FLUIDS WITH SANDSTONE ROCKS AT A DEEP RADIONUCLIDE REPOSITORY SITE, USING TOUGHREACT

A.V. Kiryukhin[1], E.P. Kaymin[2], E.V. Zakharova[2], and A.A. Zubkov[3]

[1]- Institute Volcanology and Seismology FEB RAS, Piip-9, P-Kamchatsky, Russia 683006
[2]- Institute of Physical Chemistry and Electrochemistry RAS, Leninsky-31, Moscow, Russia, 119991
[3]- Siberia Chemical Plant, Kurchatova-1, Seversk, Russia
e-mail: avk2@kscnet.ru

ABSTRACT

TOUGHREACT modeling was used to reproduce laboratory tests involving sandstone samples collected from a deep radionuclide repository site at Siberia Chemical Plant. Laboratory tests include injection of alkaline fluids into sandstones samples at 70^{o}C. Some minerals were constrained in the model to precipitate or dissolve according to laboratory test results. Modeling results were compared with observed test data (mineral phase changes, transient concentration data at the outlet of a sample column). Reasonable agreement was obtained between calculated and measured mineral phases (Na-smectite and kaolinite precipitation, quartz, microcline, chlorite, and biotite dissolution). Nevertheless, model generation of sodium was not found possible, although it was clearly observed in the test. Transient chemical concentration data at the outlet of sample column match Na only. Possible improvements to the TOUGHREACT-based model to better match observed data are discussed.

INTRODUCTION

TOUGHREACT is a computer code capable of simulating numerous thermal-hydrodynamic-chemical (THC) processes, including multiphase nonisothermal transport and rock kinetics. Fluid chemical interaction was successfully implemented to reproduce THC processes and associated secondary minerals observed in some geothermal fields within regions of recent volcanic activity (Xu and Pruess, 2001; A.V. Kiryukhin et al., 2004). Similar processes took place during radionuclide-waste fluid injection in sandstones aquifers. When liquid radionuclide waste was injected in layer-type reservoirs (Siberia Chemical Plant [SCP], Seversk; Mining Chemical Plant [MCP], Zheleznogorsk), chemical interaction between natural pore fluids and clay minerals of the repository site took place. New, secondary minerals were created while old, initial minerals dissolved, and temperature increased as a result of radiogenic heat release (Rybalchenko et al., 1994). Monitoring of the hydrogeological parameters in the wells, as well as laboratory experiments at pressure-temperature conditions corresponding to physical and chemical processes in repository sites, were conducted to get reliable information on processes there (Zubkov et al., 2002; Kaymin et al., 2004). Reliable numerical model were needed, both to predict radionuclide migration and to guarantee safety conditions at the repository site as well. In this study, TOUGHREACT was used to reproduce laboratory experiments related to the process of technogenic alteration observed in sandstones (obtained from the deep repository site) as a result of chemical interaction during $NaNO_3$-NaOH fluid injection in rock samples at a temperature of 70^{o}C. Modeling results were calibrated against observed secondary minerals generated during the laboratory experiment and identified based on microprobe analysis, and against the transient chemistry data of fluids discharged from the core outlet during the experiment.

MODEL SETUP

In this study, TOUGHREACT was used to reproduce a laboratory experiment dealing with the process of technogenic alteration observed in sandstones. The model accounts for adjective and diffusive transport of aqueous chemical species. Mineral dissolution/precipitation can proceed at equilibrium and/or under kinetic conditions, according to the following rate law:

$$r = kS\,(1-Q/K)\,\exp(E_a/(R*298.15)-E_a/(RT))$$

where k is the kinetic constant of the chemical dissolution/precipitation at 25 ^{0}C, mole/s·m^2; S is the specific reactive surface area, m^2/m^3; Q is the activity product; K is the equilibrium constant for mineral-water interaction; E_a is the activation energy, kJ/kmole; R is the gas constant, kJ/kmole K, and T is temperature, in K. Temperature effects are also accounted for by geochemical reaction calculations in which equilibrium and kinetic data are functions of temperature.

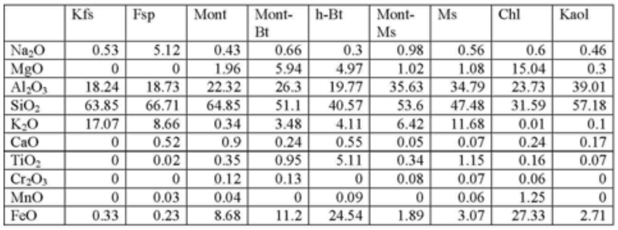
Chemical Input Data (Chemical.inp)

Initial mineral fractions are shown in Table 1. Typical normalized mineral compositions (weight % of oxides) are shown in Table 2. Some of the parameters of kinetic water-rock chemical interaction are assigned the same as in the Kiryukhin et al. (2004) paper (E_a- energy of activation, kJ/kmole), while other parameters were corrected during model calibration (Table 3). The chemical composition of the initial solution (natural pore fluids) and injected fluid are shown in Tables 4 and 5, respectively.

Table 1. Initial mineral fractions observed and assumed in the modeling (run #7).

Mineral Phase (Observed)	Weight %	Mineral Phase (Model)	Vol. % (run#7)
Qtz – quartz	50	Quartz	50
Kfs – K-feldspar	10	Microcline	10
Mont – montmorillonite	10	Na-smectite	10
Kaol – kaolinite	10	Kaolinite	10
Ab – albite	5	Albite (low)	5
Chl – chlorite	3	Chlorite	3
h-Bt – hydrated biotite, Mont-Bt – mont. biotite	5		
Ms – muscovite, Mont-Ms – mont. muscovite	2	Muscovite	12
Sid – siderite	2		
Cc – calcite	<1		
Ap – apathite, Ilm – ilmenite	<1		

Table 2. Typical normalized mineral compositions (weight % of oxides) in initial rock sample (H_2O extracted).



	Kfs	Fsp	Mont	Mont-Bt	h-Bt	Mont-Ms	Ms	Chl	Kaol
Na_2O	0.53	5.12	0.43	0.66	0.3	0.98	0.56	0.6	0.46
MgO	0	0	1.96	5.94	4.97	1.02	1.08	15.04	0.3
Al_2O_3	18.24	18.73	22.32	26.3	19.77	35.63	34.79	23.73	39.01
SiO_2	63.85	66.71	64.85	51.1	40.57	53.6	47.48	31.59	57.18
K_2O	17.07	8.66	0.34	3.48	4.11	6.42	11.68	0.01	0.1
CaO	0	0.52	0.9	0.24	0.55	0.05	0.07	0.24	0.17
TiO_2	0	0.02	0.35	0.95	5.11	0.34	1.15	0.16	0.07
Cr_2O_3	0	0	0.12	0.13	0	0.08	0.07	0.06	0
MnO	0	0.03	0.04	0	0.09	0	0.06	1.25	0
FeO	0.33	0.23	8.68	11.2	24.54	1.89	3.07	27.33	2.71

Table 3. Parameters for chemical interaction of mineral phases (run #7): k – kinetic constant of the mineral dissolution/precipitation at 25 ^{0}C, mole/s·m^2; S – specific reactive surface area, m^2/m^3.

Mineral Phase	Initial mineral fraction, vol.%	Dissolution kS mol/s m^3	Precipitation kS mol/s m^3
Quartz	0.50	1.0e-11	1.0e-11
Microcline	0.10	1.0e-12	0.0
Albite-low	0.05	1.0e-12	0.0
Na-smectite	0.10	0.0	1.0e-5
Kaolinite	0.10	0.0	1.0e-5
Chlorite	0.03	1.0e-12	0.0
Muscovite	0.12	1.0e-12	0.0
Sodium carbonates Na_2CO_3	0.00	0.0	1.0e-5
$NaHCO_3$	0.00	0.0	1.0e-5
Trona $Na_2CO_37H_2O$	0.00	0.0	1.0e-5
Na_3CO_3 HCO_32H_2O	0.00	0.0	1.0e-5

Table 4. Chemical analysis of initial pore fluids and chemical composition assigned in the model.

	Chemical analysis	Assign in the modeling	
	mg/l	mg/l	mol/kgH2O
pH	7.3	7.3	
Na^+	26.30	26.30	1.143976E-03
K^+	2.90	2.90	7.417259E-05
Ca^{++}	25.00	25.00	6.237836E-04
Mg^{++}	15.30	15.30	6.295001E-04
Fe^{++}	5.80	5.80	1.038589E-04
AlO^{2-}	0.00	0.00	0.000000E+00
Cl^-	7.10	7.10	2.002651E-04
$SO4^{--}$	3.20	3.20	3.331113E-05
$HCO3^-$	230.00	230.00	3.769441E-03

Table 5. Calculated chemical composition of injected fluid, based on the following initial concentrations (g/L): $NaNO_3$ – 44.3; Na_2CO_3 – 2.08; Al – 0.83, NaOH – 8.9. Chemical composition converted to the primary species concentrations mol/kg H_2O; pH estimations performed by I.B. Slovtsov (software"Selector" used): pH=11.67; and by O.A. Limantseva (software "Gibbs" used): pH= 11.81.

	mg/l	mol/kg$_{H2O}$
pH	11.81	
Na^+	18007	7.832623E-01
K^+	0.00	0.000000E+00
Ca^{++}	0.00	0.000000E+00
Mg^{++}	0.00	0.000000E+00
Fe^{++}	0.00	0.000000E+00
$AlO2^-$	1814	3.075116E-02
Cl^-	0.00	0.000000E+00
$SO4^{--}$	0.00	0.000000E+00
$HCO3^-$	1197	1.961717E-02
$NO3^-$	11987	1.933241E-01

Flow and Solution Input Data (Flow.inp, Solute.inp)

According to the laboratory test data, 70^0C isothermal conditions with mass flux 2.50×10^{-5} kg/s m^2 and pressure 3.0 MPa were assigned in the model. Reservoir porosity assigned 0.2. The length of the model corresponded to the length of test sample, 15 cm. A 1-D numerical grid was generated that included 32 elements: B 1 is the source of injected fluid (element volume $5.00E^{+20}$ m^3; R 1–R 30 elements represent the 15 cm long sandstone column, with each element having a width of 0.005 m; and D 1 is the inactive element with specified pressure 3.0 MPa, which corresponds to the discharge from the column outlet. Figure 1 shows the geometry of the numerical grid corresponding to laboratory test conditions. For chemical analysis, modeling results were printed out at specific times, corresponding to the sampling times of alkaline fluid discharge from the column outlet (9, 16, 23, 30, 32, 58, and 79 days).

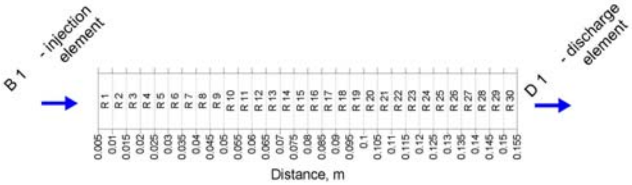


Figure.1. Numerical grid geometry used for modeling alkaline $NaNO_3$-NaOH fluid injection in a sandstone column from the SCP deep repository site.

Calibration Data

Sandstone columns of 15 mm diameter and 150 mm length were used for laboratory tests. The active porosity of sandstones was estimated as 20%. Mineralogical composition includes (in weight %): quartz (55–65), feldspars (albite, plagioclase, microcline) (10–20), micas (2–10), chlorite (up to 2), clay minerals (montmorillonite, kaolinite) (up to 15), carbonates of calcium and magnium (0.5–3.0%) (Table 1). The initial fluid chemical composition corresponds to pore fluids of the deep repository site (Table 6). An alkaline solution was injected into the column at a pressure of 3 MPa and temperature of 70^oC. This solution included the following components (in g/L): $NaNO_3$ – 44.3, Na_2CO_3 – 2.08, Al – 0.83, NaOH – 8.9 (Table 5). Two tests having durations of 79 days and 42 days were performed with injection mass flux at an average level of 2.50×10^{-5} kg/s m^2.

For chemical analysis, at various times during the test (9, 16, 23, 30, 32, 58, and 79 days), sampling of the alkaline fluid took place at the column outlet (Na, Al, Si, Ca, Mg, K, Sr) (Table 6). After testing, we also performed microprobe analysis of the mineral composition of samples. Microprobe analysis was carried out, based on Link INCA ENERGY200 to an electronic scan facility, CamScan MV-2300 (Figure 2). (Note that A.A. Grafchikov, Institute of Experimental Mineralogy RAS, took part in this analysis.)

Table 6. Initial fluid chemical composition and transient data of chemical composition from fluid sampling at column outlet

Time, days	Volume of injection, ml	pH	Concentration, ppm						
			Na	Al	Si	Ca	Mg	K	Sr
Initial fluid		11.8	17300	955	<0.5	<0.1	<0.01	7.95	<0.01
9	12.5	7.55	12100	≤0.1	47.1	1140	106	85.1	86.9
16	11	8.78	15300	≤0.1	30.6	14.7	11.7	73.8	3.92
23	10.2	8.98	15100	≤0.1	42.4	8.92	7.92	68.9	2.16
30	10	8.84	15500	≤0.1	42.4	6.4	4.24	65.9	1.42
32	12	8.20	17000	≤0.1	40.0	2.5	2.03	57.1	1.35
58	31.5	8.92	17500	≤0.1	1.58	1.46	0.65	44.5	0.29
79	30.5	8.85	17500	≤0.1	2.13	2.32	0.84	64.3	0.34

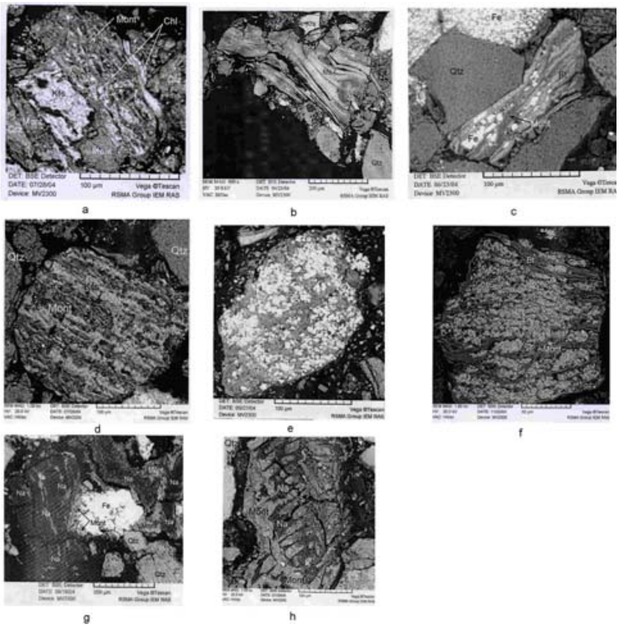


Figure 2. Electron-scan images of samples (E.P. Kaymin data). a- chlorite (Chl) replacement by montmorillonite (Mont), b- muscovite (Ms) replacement by kaolinite (Kaol), c- biotite (Bt) replacement by montmorillonite (Mont), d- K-feldspar (Kfs) replacement by montmorillonite (Mont) , e- grains of magnetite hosted in clay minerals, f- magnetite (white) inside of montmorillonite (grey) replaced biotite grain, g- sodium or trona (Na) release in form of crust and regions in montmorillonite (Mont), h- sodium or trona (Na) release in form of regions in montmorillonite (Mont).
Note: black space is polymeric matrix.

Laboratory testing of the sandstone column yields the following results:

(1) Biotite, chlorite and feldspars are replaced by Na-smectites, (2) Muscovite are replaced by kaolinite, (3) Na-smectite precipitation is greater then kaolinite precipitate, (4) Insignificant siderite change, (5) Magnetite precipitate, (6) Sodium precipitate

($Na_2CO_3 \times 10H_2O$ (or trona $Na_3H(CO_3)_2 \times 2H_2O$) is found in inflow zone, (7) Test duration increase does not cause an increase in the degree of hydrothermal alteration within the sandstone sample column (which means that secondary minerals formed cover, isolating other minerals from participation in chemical reactions) (Figure 2).

MODELING RESULTS

Quartz, microcline, albite-low, Na-smectite, kaolinite, chlorite, muscovite, and sodium (Na_2CO_3) were used for geochemical system definition (modeling run #7). Chemical interaction parameters were assigned as shown in Table 3. Some minerals were constrained in the model to precipitate or dissolve according to laboratory test results (see above). In particular: (1) K-feldspar, albite, chlorite and muscovite were constrained from precipitation, (2) Na-smectite (montmorillonite) and kaolinite were prevented from dissolution. TOUGHREACT modeling of the laboratory test (run #7) yielded the following results (Figure 3 and 4):

(1) Mineral phase fractions change (Figure 3). By the end of the day 79 alkaline solution injection: quartz dissolves (from 9.2 10^{-5} to 9.8 10^{-5}), microcline dissolves (from 3.1 10^{-6} to 3.2 10^{-6}), albite dissolves slightly (to 1.4 10^{-6}), Na-smectite (montmorillonite) precipitates in the middle and outlet parts of column (up to 1.8 10^{-3}), kaolinite precipitates in the middle and outlet part of column (up to 1.1 10^{-5}), chlorite dissolves (3.0 10^{-9}), muscovite dissolves throughout (from 6.3 10^{-5} to 7.3 10^{-5}). Secondary mineral phases (Na-smectite and kaolinite) were formed only during the first 9 days. In general, these results match with laboratory test results, except that no sodium was obtained in the model (while abundant sodium carbonates were observed during the laboratory test).

(2) Space distributions of chemical elements in liquid phase. Figure 4 shows pH and chemical concentration distributions for Na^+, NO_3^-, HCO_3^-, Ca^{++}, and AlO_2^- along the streamline of injected fluid by day 79 of the laboratory test. Quasi-stationary distribution of chemical component concentrations was observed along the streamline.

(3) Figure 5 shows the match between observed and modeled transient chemical-concentration data of fluid sampled from the sandstone column outlet (run #7). A pH match shows the same trend between model and experiment, while absolute modeling values are 2.6 units larger than the measured pH. The calculated Na matches the experimental data reasonably well, whereas the K values are underpredicted by the model. The Ca match between model and experiment show the same trend, while the absolute values in the model are 2–3 orders less than the experiment. The Mg match shows the same trend between model and experiment, while model absolute values are 1–2 orders of magnitude less. The Al match shows a model yield 4 orders of magnitude greater than experimental values.

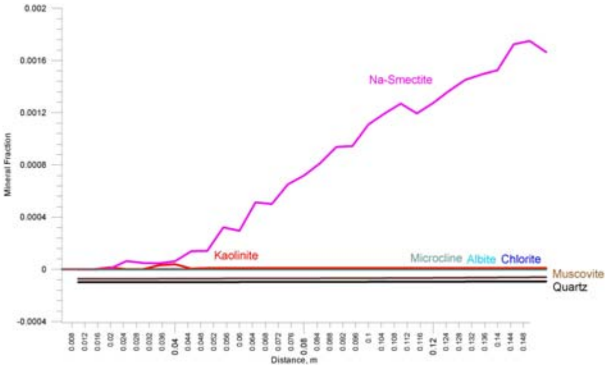


Fig. 3a Modeling results (run #7). Mineral fractions change along injection streamline in the sandstone column sample by 79 days of modeling time.

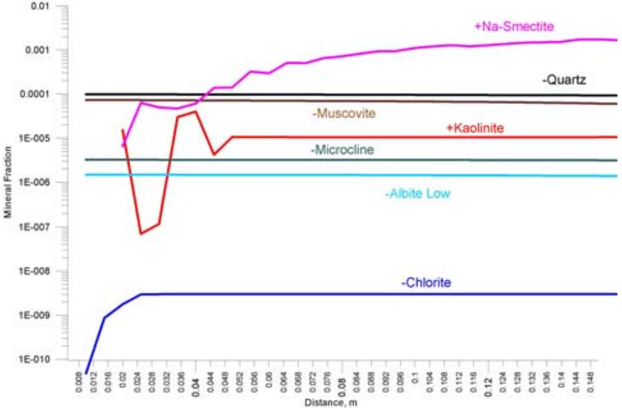


Fig. 3b Modeling results (run #7). The same as Fig. 3a, except Y-axes represented in log scale, and mineral fractions changes are represented in absolute values (dissolved phases denoted with «-» symbol).

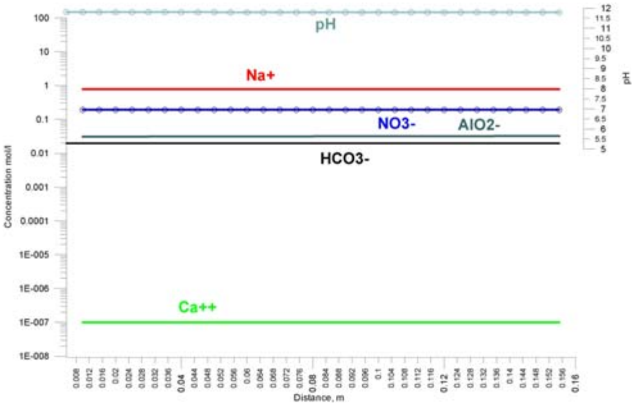


Fig. 4 Modeling results (run #7). pH and concentrations Na^+, NO_3^-, HCO_3^-, AlO_2^- , Ca^{++} distributions along a streamline of injected fluid by day 79 of modeling time.

The Si match shows convergence at early times, while later model concentrations are three times greater in the experiment. It was also found that a change of rate constants in mineral precipitations (kS) for Na-smectite and kaolinite (Table 3) had no effect on the pH and outlet discharge of transient chemical concen-trations.

CONCLUSIONS

(1) TOUGHREACT modeling was used to reproduce laboratory tests on sandstones samples collected from a deep radionuclide repository site in the Siberia Chemical Plant. Laboratory tests include injection of alkaline fluids into sandstones samples at 70°C. Based on laboratory test results, some minerals were not allowed to precipitate or dissolve in the model. Modeling outputs were matched against observed test data (specifically mineral-phase change and transient concentration data at the outlet of the sample column).

(2) Model and test convergence in mineral phases (Na-smectite and kaolinite precipitation in the model, quartz, microcline, chlorite and biotite dissolution in the model) were obtained through restrain orders on some minerals, preventing them from precipitating or dissolving. Nevertheless, it was not found possible to generate sodium in the model (even through sodium is clearly observed in the test). Transient chemical concentration data at the outlet of the sample column matches Na only. The pH match shows the same trend of model and experiment, whereas absolute modeling values are 2.6 units greater. Ca and Mg matches between model and experiment show the same trend, while absolute values in the model are 2–3 orders less than in the experiment.

(3) The main reason for mismatches between model and laboratory tests seems to be TOUGHREACT's not taking into account mineral/mineral chemical reactions. In laboratory tests, K released to solutions, and Al was consumed by secondary minerals due to biotite, K-feldspars, and muscovite being replaced by clay minerals. If such reactions are implemented into TOUGHREACT, convergence of modeling and laboratory test data may improve.

(4) Additional improvement of modeling and laboratory test matches may be achieved through extension of the existing thermodynamic database by adding biotite, sodium ($Na_2CO_3 \times 10H_2O$), trona $Na_3H(CO_3)_2$ x $2H_2O$) and others minerals (see Table 2). Moreover, the conceptual model for chemical interaction during laboratory testing needs to be improved, and primary and secondary minerals need to be more accurately identified.

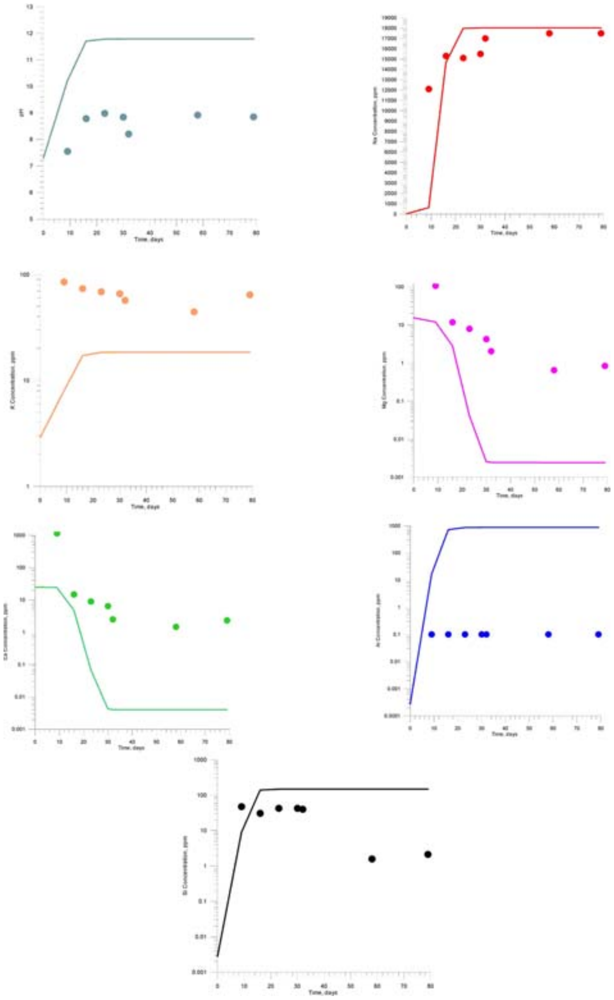


Figure 5. Modeling and laboratory test match (transient chemical concentrations of fluids sampled from the outlet of the testing column): solid circles represent laboratory test data, continuous lines represent modeling results (run #7).

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