Development of Polymer Gel Systems to Improve Volumetric Sweep and Reduce Producing Water/Oil Ratios

Semi-Annual Report
July 1, 2003 – December 31, 2003

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February, 2004

Contract Number DE-FC26-02NT15363
Contract Dates 7/01/2002 - 6/30/2005

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Abstract

The objectives of the research are to improve the effectiveness of polymer gels to increase volumetric sweep efficiency of fluid displacement processes and to reduce water production in production wells. The research is based on experimental data and conceptual and mathematical models developed from interpretation of experimental data. This report describes two types of mathematical models that were developed. One model type simulates the chemical reactions where polymer molecules are crosslinked to form a 3-dimensional network or gel. The model is based on statistical probabilities of reactions and yields molecular weights averages and distributions as functions of conversion. The second model type simulates the transport of chromium acetate, a common polymer crosslinker, through porous dolomite rock and includes the mechanisms of dolomite dissolution and chromium precipitation. The chromium transport model reasonably agreed with experimental data.

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Executive Summary

The research goals are to improve the effectiveness of polymer gels to increase volumetric sweep efficiency of fluid displacement processes and to reduce water production in production wells. Improvements in these areas have the potential to slow the rate of decline in oil production from existing wells and increase the ultimate oil recovery from existing reservoirs. The research is based on experimental data and conceptual and mathematical models developed from interpretation of experimental data. The program is organized into two major tasks: (1) In-depth Treatment of Matrix Rock from Injection Wells, and (2) Treatment of Production Wells to Control Water Production. These studies will lead to an understanding of the mechanisms of water production and aid in development of methods for designing gelled polymer treatments.

This report covers modeling studies that were conducted between July and December, 2003. Experimental work conducted during this period is not reported here due to its incomplete nature, but will be reported in subsequent reports.

Two types of mathematical models were developed and are presented in this report. One model type simulates the chemical reactions where polymer molecules are crosslinked to form a 3-dimensional network or gel. These chemical reaction models (CRM) will be combined with flow models in future work to describe the placement of gels in oil reservoirs. The second model type is a flow model (FM) that simulates the transport of chromium acetate, a common polymer crosslinker, through porous dolomite rock.

The chemical reaction models (CRM) were developed using the Theory of Branching Processes which is based on statistical probabilities of reaction between functional groups on the reactive species. Two CRM models were developed that include a more realistic description of the polymer than was used in a previous model. Specifically, the carboxyl groups are randomly distributed on the polymer back bone and the polymer is polysidpersed instead of uniformly distributed carboxyl groups and a monodispersed polymer. Model A describes the reaction between functional groups on the polymer backbone (carboxyl groups) with a bi-functional chromium crosslinker. Model A provides results in terms of molecular weights averages as a function of the conversion of reactive groups. Model B describes the reaction between the functional groups on the polymer without using a crosslinker species. Results from Model B are in terms of molecular weight distributions rather than average values. Results that simulate a typical gelled polymer system are presented for both chemical reaction models.

The flow model (FM) developed to simulate the transport of chromium acetate through porous dolomite rock included the mechanisms of dolomite dissolution and chromium precipitation. Twenty-two aqueous species were tracked by solving the transport equation for eight species. Thirteen equilibrium relationships and kinetic rate equations for dolomite dissolution and chromium precipitation were incorporated. The chromium transport FM was used to simulate flow experiments where chromium(III) acetate was flowed through dolomite core material. Model results were comparable to steady-state values of chromium concentration and pH in the effluent of the cores.

Introduction

The research goals are to improve the effectiveness of polymer gels to increase volumetric sweep efficiency of fluid displacement processes and to reduce water production in production wells. Improvements in these areas have the potential to slow the rate of decline in oil production from existing wells and increase the ultimate oil recovery from existing reservoirs. The research is based on experimental data and conceptual and mathematical models developed from interpretation of experimental data.

The research program is organized into two major tasks: (1) In-depth Treatment of Matrix Rock from Injection Wells, and (2) Treatment of Production Wells to Control Water Production. Task 1 seeks to develop design tools to enable the evaluation of gelled polymer systems to treat high-permeability layers that are distant from injection wells when there is crossflow between layers. A component of this task is a fundamental study of the formation and characterization of pre-gel aggregates in commonly used commercial systems. We intend to obtain experimental data and, based on these data, develop mathematical models to predict the placement and post-gelation behavior of polymer systems. Task 2 consists of fundamental studies of disproportionate permeability reduction of porous media by dehydration of gels after placement. These studies will lead to an understanding of the mechanisms of water control in production wells and aid in development of methods for designing these treatments. Task 3 covers technology transfer from this research.

This report covers modeling work that was conducted between July and December, 2003. Experimental work conducted during this period is not reported here due to its incomplete nature, but will be reported in subsequent reports.

I. Statistical Modeling of the Polymer Crosslinking

Gels are formed from an aqueous mixture of large polymer molecules and crosslinker molecules. Aggregates form and grow in size as the crosslinker reacts with two polymer molecules until a bulk gel is formed. One objective of this task is to develop a gelation model that represents the size (or molecular weight) distribution of aggregates as a function of time. This model will be combined with a filtration model to describe the placement of gelants in porous rocks.

The derivation of a simplified model for calculating molecular weight averages of pre-gel aggregates using the Theory of Branching Processes (TBP) was presented in the previous annual report [Willhite et al., 2003]. It was assumed in that model that the polymer charged to the system was monodispersed, that is, all polymer chains had the same degree of polymerization and the initial weight- and number-average molecular weights were equal. Synthetic polymers are mixtures of molecules with different degrees of polymerization. A single polymer molecule is described as an *x-mer* where *x* is the number of monomers in the molecule. Polydispersity of polymers is expressed with different averages of the degree of polymerization (or different molecular weight averages) and distributions of the degree of polymerization (or molecular weight distributions).

Definitions for the number average and weight average of degree of polymerization and molecular weight for polydispersed polymers are:

$P_{n0} = \sum_{x=1}^{\infty} x \cdot n(x)$	number-average degree of polymerization	Eq. 1
$M_{n0} = M_0 \cdot P_{n0}$	number-average molecular weight	Eq. 2
$P_{w0} = \sum_{x=1}^{\infty} x \cdot w(x)$	weight-average degree of polymerization	Eq. 3
$M_{w0} = M_0 \cdot P_{w0}$	weight-average molecular weight	Eq. 4
$PI = \frac{P_{w0}}{P_{n0}} = \frac{M_{w0}}{M_{n0}}$	polydispersity index	Eq. 5

where,

x is the degree of polymerization, the number of monomers for an x-mer,
$n(x)$ is the number fraction of x-mer,
$w(x)$ is the weight fraction of x-mer,
M_0 is the molecular weight of the monomer.

Distributions of the degree of polymerization (or molecular weight) are discrete or continuous functions that are derived from the polymerization mechanism or are experimentally measured. The Schulz-Zimm distribution function was chosen for this work since it covers a range of polymer distributions. This function has two parameters, P_{n0} and σ, and the weight fraction of an *x-mer* is given by:

$$w(x) = \frac{\sigma^{\sigma}}{P_{n0}^{\sigma+1}\Gamma(\sigma)} x^{\sigma} \exp\left(-\frac{\sigma}{P_{n0}} x\right) \qquad \text{Eq. 6}$$

where σ is related to the polydispersity index of the polymer, PI = $(\sigma+1)/\sigma$ and Γ is the standard mathematical gamma function.

The Theory of Branching Processes (TBP) [Vojta and Dusek, 1980] was employed to develop two models for the gelation of a polydispersed polymer. Model A parallels the model presented previously for a monodispersed polymer [Willhite et al., 2003] and the results are the number and weight averages of the gelling polymer. In Model B, the reactants are simplified so that polymer distributions as a function of conversion are obtained. An additional modification in Models A and B was the inclusion of a random distribution of the functional (carboxylate) groups along the polymer chain. Random distribution is more realistic than the uniform distribution of the previous model.

The following general assumptions were applied in the model development using TBP for both cases. (1) The crosslinking reactions are exclusively intermolecular before the gel point. (2) All the functional groups have the same and independent reactivity. Derivations of the two models and computational details will be presented in the next annual report.

Model A: Molecular weight averages of hydrolyzed polyacrylamide-Cr(III) pre-gel aggregates. The reacting system contains two components. Polydispersed hydrolyzed polyacrylamide (HPAM) chains are crosslinked by the reactions between carboxylate groups (randomly distributed on the HPAM) and a bi-functional chromium acetate trimer. Alternating reactions are assumed, which means only HPAM (designated as Unit A) can react with chromium trimer (designated as Unit B). No polymer-polymer or trimer-trimer reactions are allowed.

The weight-average molecular weight of the entire gel system (which averages both polymer and trimer species) is given as a function of conversion by the following equations.

$$M_w = w_A M_{w0} + w_B M_B + \frac{1}{D}\{w_A[M_{w0} x_A P_{w0}(f_B - 1)\alpha_A \alpha_B + M_B x_A P_{w0} \alpha_A] + w_B[M_B x_A (P_{w0} - 1) f_B \alpha_A \alpha_B + M_{w0} f_B \alpha_B]\} \quad \text{Eq. 7}$$

$$D = 1 - x_A (P_{w0} - 1)(f_B - 1) \cdot \alpha_A \alpha_B \quad \text{Eq. 8}$$

$$\alpha_B = \frac{n_A x_A P_{n0}}{n_B f_B} \cdot \alpha_A = r_A \alpha_A \quad \text{Eq. 9}$$

where,

f_B is the functionality of chromium trimer,
n_A, and n_B are the initial number fractions of polymer and chromium trimer, respectively,
r_A is the initial molar ratio of carboxylate groups to chromium functionalities,
x_A is the degree of hydrolysis of primary polymer; molar fraction (which equals the weight fraction) of reactive monomers,
w_A, w_B are the initial weight fractions of polymer and chromium trimer, respectively,
M_B is the molecular weight of the chromium trimer,
α_A, and α_B are the conversions of carboxylate groups on polymer and chromium functionalities, respectively.

The weight-average molecular weight of the pre-gel aggregates (species containing one or more polymer molecules) is given by:

$$M_{w-agg} = \frac{M_w - w_B M_B (1 - \alpha_B)^{f_B}}{1 - w_B (1 - \alpha_B)^{f_B}} \quad \text{Eq. 10}$$

The conversions of the functional groups at the gel point are:

$$\alpha_{crit,A} = \left[\frac{1}{x_A (P_{w0} - 1)(f_B - 1) r_A}\right]^{1/2} \quad \text{Eq. 11}$$

$$\alpha_{crit,B} = \left[\frac{r_A}{x_A (P_{w0} - 1)(f_B - 1)}\right]^{1/2} \quad \text{Eq. 12}$$

The number-average molecular weight of the entire gel system is given by:

$$M_n = \frac{n_A M_{n0} + n_B M_B}{1 - n_A x_A P_{n0} \alpha_A} = \frac{n_A M_{n0} + n_B M_B}{1 - n_B f_B \alpha_B} \qquad \text{Eq. 13}$$

The number-average molecular weight of the pre-gel aggregates is:

$$M_{n-agg} = \frac{n_A M_{n0} + n_B M_B [1 - (1 - \alpha_B)^{f_B}]}{1 - n_B f_B \alpha_B - n_B (1 - \alpha_B)^{f_B}} \qquad \text{Eq. 14}$$

Equations 7 through 14 for Model A are similar to the corresponding relationships that were derived for the model in which the polymer was monodispersed [Willhite et al., 2003]. However, Model A describes the polydispersivity of the starting polymer. The number- and weight-average molecular weights of a typical gel system are given as a function of conversion of the chromium trimer (α_B) in Figure 1. The polydispersivity index of the polymer was 2. As shown in Figure 1, the index increased, along with the weight-average molecular weight of the pre-gel aggregates, as the critical conversion of the system was approached.

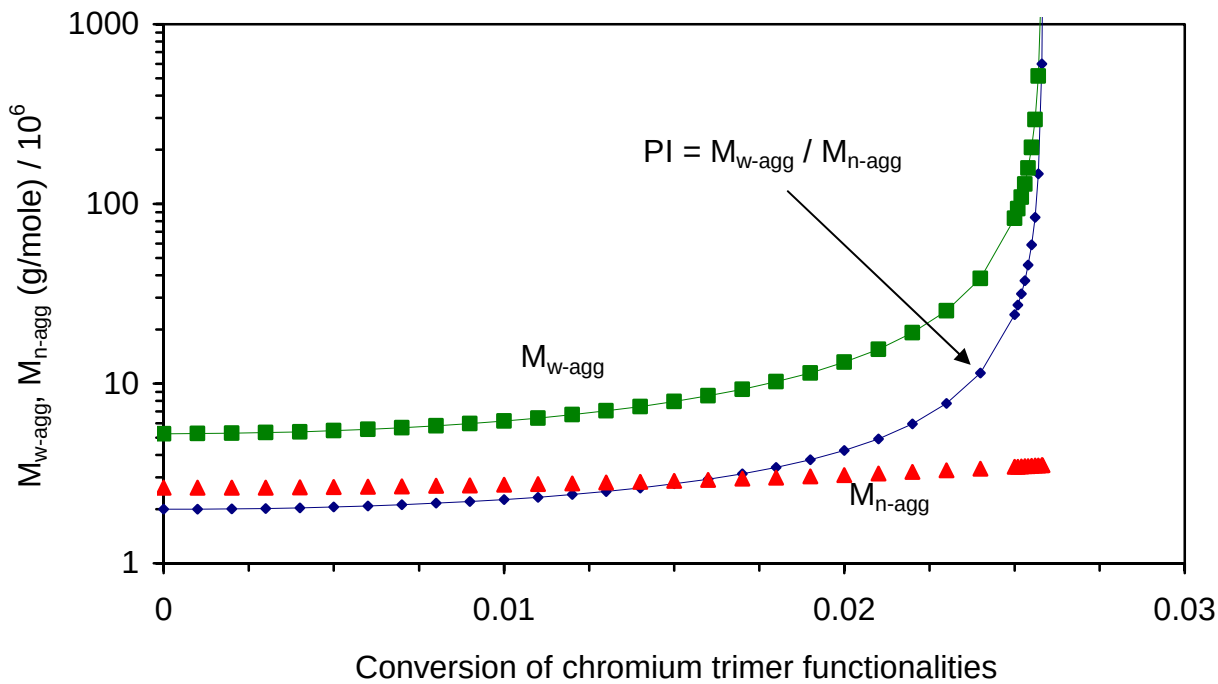

Figure 1 – Weight-average molecular weight, number-average molecular weight and polydispersivity index as a function of conversion. Gelant composition: 45000 ppm HPAM (10% degree of hydrolysis, initial PI =2) and 100 ppm chromium.

Model B: Molecular weight distributions of crosslinked HPAM chains. Model B was simplified in that the starting reactant is polydispersed polymer only, without the chromium crosslinker. Polymer chains are randomly crosslinked by the formation of bonds between two carboxylate groups on two different polymer molecules. The primary (initial) polymer chains are polydispersed according to a Schulz-Zimm distribution and the carboxyl groups are randomly distributed along the polymer molecules.

For Model B, the critical conversion of carboxylate groups at the gel point, α_c, is

$$\alpha_c = \frac{1}{x_A(P_{w0} - 1)} \qquad \text{Eq. 15}$$

In the pre-gel stage, the weight fraction of *x-mer* at conversion α is $w(\alpha, x)$ which is implicitly expressed through the weight-fraction generating function, $W(\alpha, Z)$, given by:

$$W(\alpha, Z) = \int_0^\infty w(\alpha, x) Z^x dx = \int_0^\infty w(0, x) Z^x \left[1 - x_A + x_A(1 - \alpha + \alpha u)\right]^x dx \qquad \text{Eq. 16}$$

$$u = \int_0^\infty w(0, x) Z^x \left[1 - x_A + x_A(1 - \alpha + \alpha u)\right]^{x-1} dx \qquad \text{Eq. 17}$$

where x is the degree of polymerization; Z is the auxiliary variable in generating function; $w(0,x)$ is the initial weight fraction distribution (initial polymer distribution at $\alpha = 0$). $w(\alpha, x)$ was obtained by means of Laplace transform[Vojta and Dusek, 1980]. A computer program was written to solve the problem numerically for the following typical system.

Degree of hydrolysis of HPAM, x_A, was 8%.
The initial polymer distribution, $w(0, x)$, was described by the Schulz-Zimm function, with $\sigma = 1$, making the polydispersity index, PI, equal to 2 ($PI = (\sigma+1)/\sigma$).
$M_{w0} = 5.26 \times 10^6$ g/mol $M_0 = 72.9$ g/mol

$$P_{w0} = \frac{M_{w0}}{M_0} = 72137\,;\ P_{n0} = \frac{P_{w0}}{PI} = \frac{72137}{2} = 36069$$

The critical conversion at the gel point is:

$$\alpha_c = \frac{1}{x_A(P_{w0} - 1)} = \frac{1}{0.08 \times (72137 - 1)} = 0.000173$$

The weight-fraction w(α,x) as functions of the degree of polymerization, x, and molecular weight, xM_0, at different conversions are plotted in Figure 2. With increasing conversion, the weight fraction of the "short" chains ($x < 1.5\times10^5$) decreases, the weight fraction of the "mid-length" chains ($x = 1.5\times10^5 - 3\times10^5$) increases initially then decreases, and the weight fraction of "long" chains increases continually. Numerical values are given in Table 1. The model predicts a long "tail" of crosslinked molecules with high molecular weight.

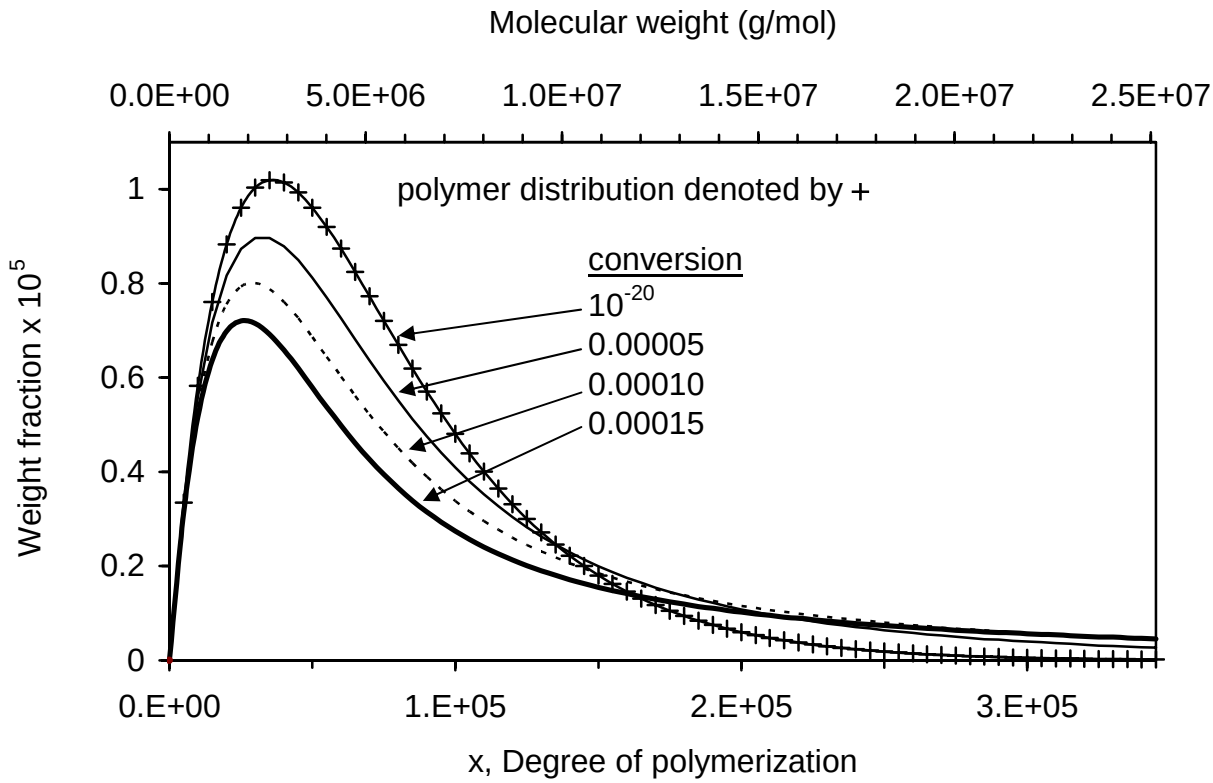

Figure 2 – Distributions of molecular weight and degree of polymerization as a function of conversion

Table 1 – Weight fraction distributions at different conversions for crosslinked HPAM chains with the primary Schulz-Zimm distribution, $\sigma = 1$, $P_{n0} = 36069$; $x_A = 8\%$, $\alpha_c = 0.000173$.

x, Degree of polymerization, 10^5	Molecular weight, 10^6 g/mol	Weight fraction distribution				
		Polymer	Conversion α			
			10^{-20}	0.00005	0.00010	0.00015
< 0.5	< 3.6	0.426	0.426	0.381	0.342	0.308
0.5 – 1.0	3.6 – 7.3	0.349	0.349	0.290	0.239	0.195
1.0 – 1.5	7.3 – 10.9	0.148	0.148	0.140	0.121	0.100
1.5 – 2.0	10.9– 14.6	0.052	0.052	0.072	0.072	0.062
2.0 – 2.5	14.6 – 18.2	0.017	0.017	0.041	0.047	0.043
2.5 – 3.0	18.2 – 21.9	0.005	0.005	0.025	0.034	0.032
3.0 – 3.5	21.9 – 25.5	0.002	0.002	0.016	0.025	0.025
3.5 – 4.0	25.5 – 29.1	0.000	0.000	0.010	0.019	0.020
4.0 – 4.5	29.1 – 32.8	0.000	0.000	0.007	0.015	0.017
4.5 – 5.0	32.8 – 36.4	0.000	0.000	0.005	0.012	0.014
> 5.0	> 36.4	0.000	0.000	0.013	0.074	0.186

II. Modeling the Transport of Chromium(III) through Dolomite Rock

One subtask is to develop a model that can simulate the transport of chromium(III) acetate through dolomite rock. Fluid-rock mechanisms considered in the flow model were dolomite dissolution and chromium precipitation. Both of these mechanisms are dependent on the hydrogen ion concentration, or pH. A description of the model, calculation procedures and initial results are presented.

Model Description

The following assumptions were made to develop the model:

1. The model is written for application at a constant temperature 25°C and the reactions do not change the temperature.
2. A one dimension, incompressible flow is assumed with no transverse gradients. The mobility ratio is unity, i.e., there is no viscous fingering.
3. The core is homogenous with constant permeability and porosity. Dissolution and precipitation do not significantly affect the physical properties of the rock, such as the surface area, or the solution, such as density and volume.
4. Aqueous reactions, other than chromium precipitation, are considered to reach equilibrium instantly.
5. Solid phases are stationary and cannot migrate by entrainment in the flowing phase.
6. Mass-transfer limitations at the dolomite surface are negligible.
7. Water activity is assumed to be unity.

Twenty-two aqueous species considered in the model. The calculation of the concentrations of these species is performed based on the mass conservation (transport equation) of eight species that are referred to here as material components. The chemical species and material components are listed in Table 2.

Table 2 - Summary of the chemical species considered in simulation.

Aqueous species: (22)
Independent species:
1: Ca^{2+}, 2: Mg^{2+}, 3: CO_3^{2-}, 4: H^+, 5: K^+, 6: Cl^-, 7: Cr^{3+}, 8: OAc^-, 9: H_2O
Dependent species:
10: OH^-, 11: $CaOH^+$, 12: $MgOH^+$, 13: $CaCO_3^0$, 14: $MgCO_3^0$, 15: $CaHCO_3^+$, 16: $MgHCO_3^+$, 17: HCO_3^-, 18: H_2CO_3, 19: $Cr(OH)^{2+}$, 20: $Cr(OH)_2^+$, 21: $CrAc(OH)_2$, 22: HOAc

Material components: (9)
Calcium, Magnesium, Carbonate, Hydrogen, Potassium, Chloride, Chromium, Acetate, Water
(Material components calculated by mass balances, except hydrogen which was calculated by a charge balance.)

The partial differential equation describing the transport of the independent species through porous media in the *x* direction is given by

$$\frac{\partial C_i}{\partial t} + \frac{v}{\phi}\frac{\partial C_i}{\partial x} - K_{di}\frac{\partial^2 C_i}{\partial x^2} = R_i(C) \qquad \text{Eq. 18}$$

where

$R_i(C)$ is the rate of reaction per unit volume. (moles/liter-PV/s)
C_i is the concentration of ith species in the fluid phase (moles/liter-PV)
v is the superficial velocity of the injected fluid (cm/s)
K_{di} is the dispersion coefficient (cm^2/s)
t is time (s).

The dispersion term in Eq. 18 was omitted and approximated by numerical dispersion during the solution method.

Dolomite dissolution was described by

$$CaMg(CO_3)_2 \rightarrow Mg^{2+} + Ca^{2+} + 2CO_3^{2-} \qquad \text{Eq. 19}$$

The rate of dolomite dissolution was modeled by the modified Chou's equation [Chou et al., 1989]:

$$R_i(C) = \frac{dC_i}{dt} = (k_1\{H^+\}^n + k_2\{H_2CO_3\}^n + k_3)\left(1 - \left(\frac{\{Ca^{2+}\}\{Mg^{2+}\}\{CO_3^{2-}\}^2}{K_{spDol}}\right)^m\right)\frac{S_0(1-\phi)}{\phi} \qquad \text{Eq. 20}$$

where
{ } stands for activity. k_1= 2.6E-4; k_2=2.0E-5; k_3=2.2E-9; n= 0.75, m=0.01,
S_0, the specific surface area of the solid (cm^2/cm^3).

S_0 was calculated from the modified Kozeny-Carmen equation [Carman, 1937]:

$$S_0 = \sqrt{C_0 \frac{\phi^3}{k(1-\phi)^2}} \qquad \text{Eq. 21}$$

where
C_0 is the Kozeny constant for which Carman [1937] suggested the value of 0.2,
K is permeability (cm^2),
ϕ is the porosity (fraction).

Zou et al. [2000] modeled chromium precipitation in bulk experiments using two equations, one that described an induction time period with no precipitation followed by precipitation according to Equation 22. Induction time periods were not observed in flow experiments so chromium precipitation was modeled with Equation 22 only.

$$\frac{dCr_t}{dt} = -k_0([Cr_t] - [Cr_{eq}])[OH^-]^\gamma[Ac_t]^\beta \qquad \text{Eq. 22}$$

where
$[Cr_t]$is the total chromium concentration in the solution,
$[Ac_t]$ is the total acetate ions concentration in the solution,
$[k_0] = 2.6\text{x}10^{-3}$ (min $M^{\gamma+\beta})^{-1}$; β=0.37, γ=-1.2.
$[Cr_{eq}]$ is the equilibrium chromium(III) concentration hydrolysis and was expressed by Rai et al. [1987] as follows:

$$\left[Cr_{eq}\right] = 10^{\log k_{s1} - 2pH} + 10^{\log k_{s2}} + 10^{\log k_{s3} + pH} \qquad \text{Eq. 23}$$

where

$[Cr_{eq}]$ is the total chromium concentration in the solution including all possible mononuclear chromium species: Cr^{3+}, $Cr(OH)_2^+$, $Cr(OH)^{2+}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$, k_{si} are constants. The values of k_s were 5.96 for log k_{s1}, -6.84 for log k_{s2}, and –18.25 for log k_{s3}.

The solution chemistry was modeled according to the following aqueous reactions.

$$HCO_3^+ \overset{K_1}{\leftrightarrow} CO_3^{2-} + H^+ \qquad \text{Eq. 24}$$

$$H_2CO_3 \overset{K_2}{\leftrightarrow} CO_3^{2-} + 2H^+ \qquad \text{Eq. 25}$$

$$Ca^{2+} + H_2O \overset{K_3}{\leftrightarrow} CaOH^+ + H^+ \qquad \text{Eq. 26}$$

$$Mg^{2+} + H_2O \overset{K_4}{\leftrightarrow} MgOH^+ + H^+ \qquad \text{Eq. 27}$$

$$Ca^{2+} + CO_3^{2-} \overset{K_5}{\leftrightarrow} CaCO_3^0 \qquad \text{Eq. 28}$$

$$Mg^{2+} + CO_3^{2-} \overset{K_6}{\leftrightarrow} MgCO_3^0 \qquad \text{Eq. 29}$$

$$Ca^{2+} + H^+ + CO_3^{2-} \overset{K_7}{\leftrightarrow} CaHCO_3^+ \qquad \text{Eq. 30}$$

$$Mg^{2+} + H^+ + CO_3^{2-} \overset{K_8}{\leftrightarrow} MgHCO_3^+ \qquad \text{Eq. 31}$$

$$Cr^{3+} + H_2O \overset{K_9}{\leftrightarrow} Cr(OH)^{2+} + H^+ \qquad \text{Eq. 32}$$

$$Cr^{3+} + 2H_2O \overset{K_{10}}{\leftrightarrow} Cr(OH)_2^+ + 2H^+ \qquad \text{Eq. 33}$$

$$Cr^{3+} + Ac^- + 2H_2O \overset{K_{11}}{\leftrightarrow} CrAc(OH)_2 + 2H^+ \qquad \text{Eq. 34}$$

$$HAc \overset{K_{12}}{\leftrightarrow} H^+ + Ac^- \qquad \text{Eq. 35}$$

$$H_2O \overset{K_{13}}{\leftrightarrow} H^+ + OH^- \qquad \text{Eq. 36}$$

The above equilibrium reactions and the equilibrium constants were taken from literature [Bhuyan, 1989 and Stavland et al., 1993]. Equilibrium constants are given in Table 3.

Calculation Procedures

A two stage procedure was followed for each time-step. The first stage was a calculation of the mass conservation for the material components (except hydrogen). Transport equations for the eight material components were written in finite difference form for distance and time. The inlet boundary condition was the concentrations of the injected species. These equations were solved numerically across a time-step to determine the concentration of material components. This stage included the calculation of the kinetic dissolution of dolomite and precipitation of chromium(III). In this simulation, the numerical dispersion was used to approximate the physical dispersion term in the transport equations [Midha, 1994].

Table 3 - Equilibrium constants for equilibrium reactions.

K_1	2.138 E+10
K_2	3.981 E+16
K_3	1.205 E-13
K_4	3.887 E-12
K_5	1.675 E+03
K_6	9.550 E+02
K_7	3.548 E+10
K_8	5.888 E+11
K_9	6.310 E-05
K_{10}	7.940 E-11
K_{11}	3.450 E-07
K_{12}	5.560 E+04
K_{13}	1.0 E-14

The second stage, 'equilibrium calculation', was the calculation to determine the equilibrium concentration for all 22 species in the solution when the concentrations of the material components (except hydrogen) were known. Each material component is the sum of all the species that contain that material component according to a mole balance. For example, [Calcium] = $[Ca^{2+}]$ + $[CaOH^{+}]$ + $[CaCO_3^{0}]$ + $[CaHCO_3^{+}]$. This was an iterative calculation with the initial concentration values of the dependent species equal to the corresponding material components (i.e. $[Ca^{2+}]$ = [Calcium]), an initial guess for the hydrogen concentration and the dependent species calculated by Equations 24-36. A charge balance equation was used for calculating the hydrogen concentration. This set of nonlinear equations (8 material component equations and the charge balance) was solved by Newton-Raphson iterations. Since the concentrations of the chemical species participating in various reactions typically vary over several orders of magnitude, the molar concentrations of the independent species are transformed into logarithmic variables as:X_n= log C_n. The logarithmic transformation was found to aid the convergence of the Newton-Raphson iterations and also prevented negative concentrations values during iterations.

Non-ideal behavior of the solution was considered in this model. Davies equation was used to calculate activity coefficient. To compute ion strength at Ith iteration of the Newton-Raphson method given only the concentrations of the species, an iterative procedure using successive substitution was employed. At first, all activity coefficients were assumed to be unity to calculate activities. Then ion strength was calculated. From this ion strength, activity coefficients were calculated using Davies equation. Continue this iterative process until there is no appreciable difference of the ion strength between the two iteration steps. This successive substitution was inside the Newton-Raphson iterative method of solution.

Auxiliary programs were also developed to provide solutions that were at equilibrium for the initial conditions for the flow model. One program solved the aqueous equilibrium relations relating to chromium species (Equations 32-36) to provide equilibrated solutions at selected chromium concentrations and pH values for injection into the flow system. A second program

provided a 1% KCl solution that was in equilibrium with dolomite rock using Equations 24 -31 and 36. This solution was resident in the core model. The pH of the equilibrated KCl solution was about 10, consistent with lab measurements.

Results and discussion

The model was used to simulate flow experiments where chromium(III) acetate was flowed through Baker dolomite cores [Jin et al., 2002]. Model results were compared to chromium concentration and pH values measured in the effluent. Properties of the dolomite core used in the experiments are shown in Table 4.

Table 4 - The properties of dolomite core in Jin's experiments.

Core length	4.8 cm
Diameter	1.9 cm
Pore volume	2.85 cm^3
Porosity	0.21
Specific surface area*	3468 1/cm
Solid density	2.64 g/cm^3

* Specific surface area is calculated from the modified Kozeny-Carmen equation.

Two types of experiments, continuous flow and shut-in, were conducted. In continuous-flow experiments, solutions containing 200ppm chromium(III) (acetate salt) and 1% KCl were injected through the dolomite core that was initially saturated with 1% KCl. Two runs were conducted at flow rates of 1 and 0.02 mL/min, corresponding to contact times in the core of 3 and 142 minutes. Steady-state values of chromium concentration and pH in the effluent (after several pore volumes injected for the low injection rate) were used for comparison with the model. In the shut-in experiments, a solution of 200ppm chromium(III) (acetate salt) and 1% KCl was quickly injected into a dolomite core until the effluent concentration equaled the injected concentration, after which the core was shut in for a selected time period. This was followed by a second quick injection of the chromium solution to displace the resident chromium acetate solution from the core. This procedure was repeated for selected time intervals, or contact times, between the injections. Measured values of chromium concentration and pH in the effluent that represented values in the core after different contact times were compared to the results of the model. Data from the two types of experiments correlated in terms of contact times as shown in Figure 3.

Runs were conducted to simulate the injection of a solution containing 200ppm chromium (III) (acetate salt), 1% KCl and a pH of 4.5 through the brine-saturated dolomite core. Runs were conducted at a selected flow rate until the effluent chromium(III) concentration and pH reached steady state. Several runs at different flow rates were conducted to span the range of contact times used in the experimental runs. The simulated steady-state values of chromium concentration and pH are presented as a function of the residence, or contact, time in the core in Figure 3. The agreement between simulated and measured values of the chromium concentration

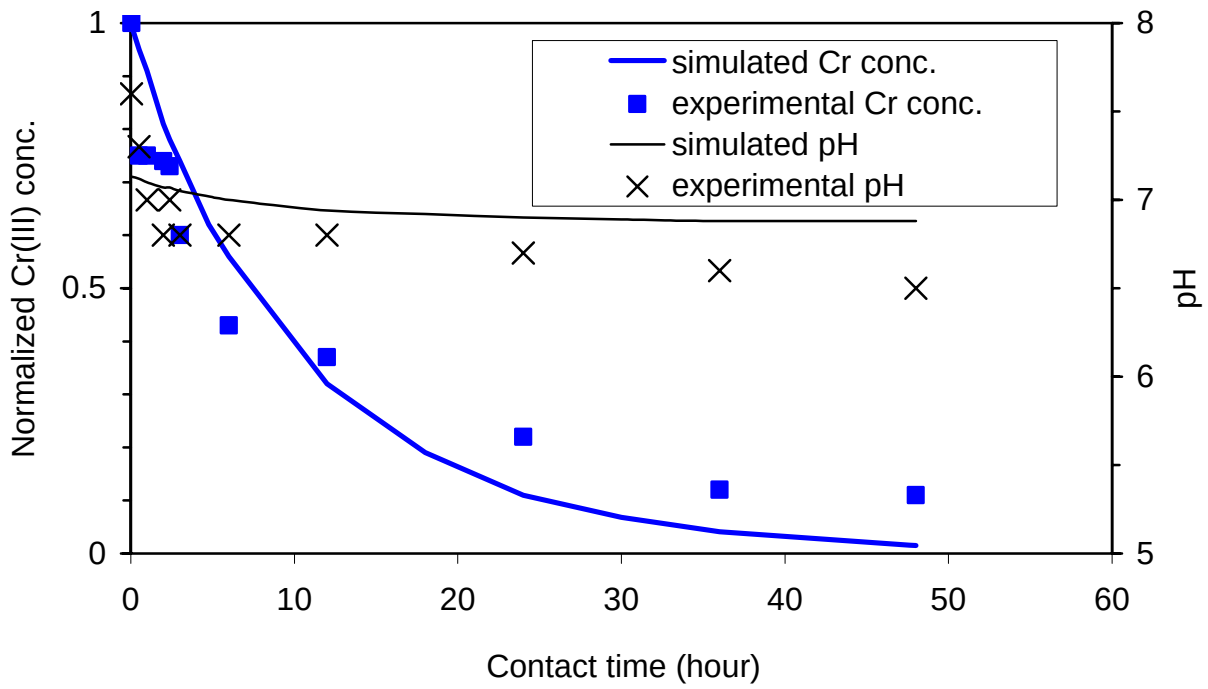

Figure 3 – Comparison of simulated and measured pH and chromium concentration as functions of contact time.

and pH profiles was reasonable, considering the chromium precipitation model was based on a portion of a model for precipitation in bulk solutions. We plan to compare the model to transient effluent data next. Further refinement of the model will most likely require acquisition of additional experimental data.

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