# SPE 100064

# Experimental and Modeling Study on the Transport of Chromium Acetate Solutions Through Carbonate Rocks

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# *Outline*

- Introduction
- Objectives
- Experimental Details
- Mathematical Model
- Results and Discussion
- Conclusions
- Acknowledgements

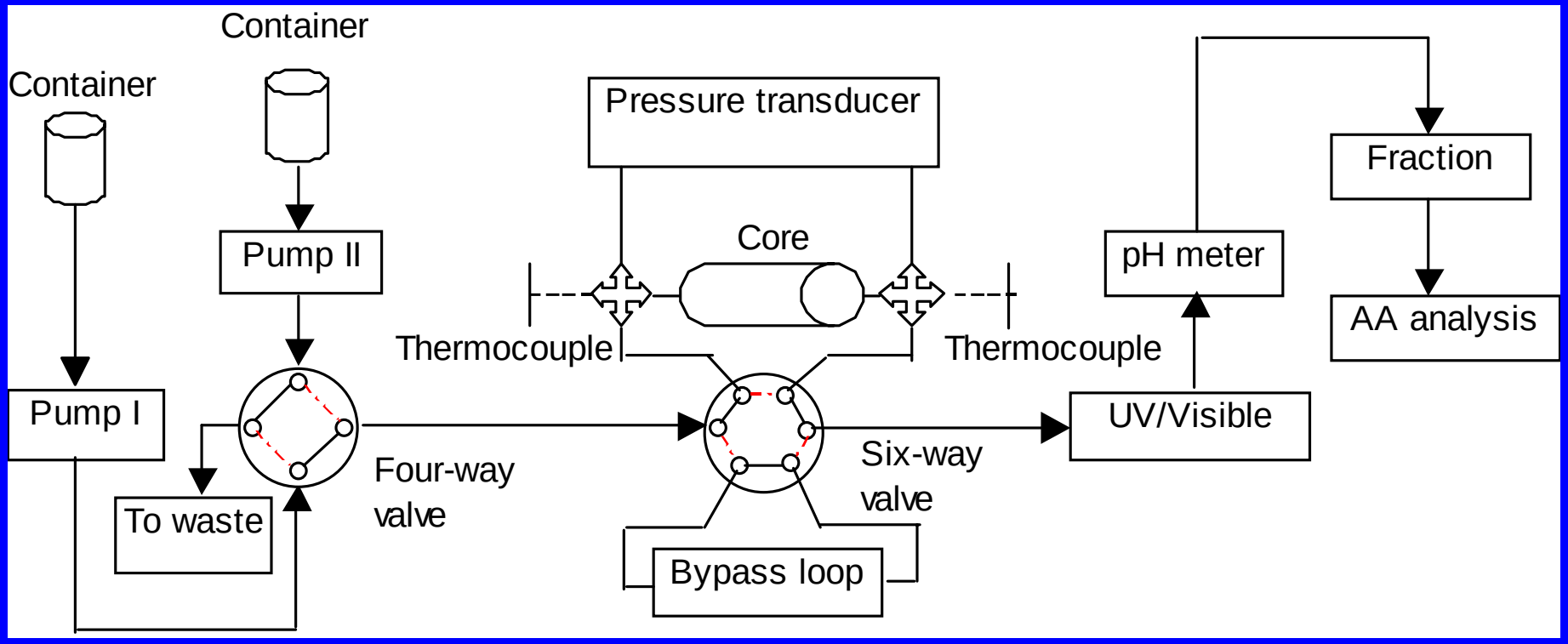
# *Introduction*

- HPAM - chromium(III) acetate gel system is used for permeability modification in oil reservoirs

- Carbonate reservoirs
  - carbonate dissolution raises pH
  - chromium precipitates

# *Objectives*

- Measure Cr(III) transport through carbonate cores
- Simulate Cr(III) transport with a mathematical model




# Experimental set up

# Chemical species and components

<u>10 Independent species:</u>

1: $Ca^{2+}$, 2: $Mg^{2+}$, 3: $CO_3^{2-}$, 4: $H^+$, 5: $K^+$, 6: $Cl^-$, 7: $Cr^{3+}$, 8: $OAc^-$, 9: $SO_4^{2-}$, 10: $H_2O$

<u>14 Dependent species:</u>

11: $OH^-$, 12: $CaOH^+$, 13: $MgOH^+$, 14: $CaCO_3^0$, 15: $MgCO_3^0$, 16: $CaHCO_3^+$, 17: $MgHCO_3^+$, 18: $HCO_3^-$, 19: $H_2CO_3$, 20: $Cr(OH)^{2+}$, 21: $Cr(OH)_2^+$, 22: $Cr(OH)_3^0$ 23: $CrAc(OH)_2$, 24: HOAc

<u>9 material components:</u>

Calcium, Magnesium, Sulfate, Carbonate, Potassium, Chloride, Chromium, Acetate, Water

Transport equation:

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

Numerical dispersion

$$\frac{\Delta t_D}{2} - \frac{\Delta x_D}{2} + \frac{K_{di}\phi}{vL} = 0$$

mixing-cell concept

# Aqueous equilibrium reactions

$$[HCO_3^+] = K_1[CO_3^{2-}][H^+]\frac{\eta_{CO_3^{2-}}\eta_{H^+}}{\eta_{HCO_3^+}}$$

$$CO_3^{2-} + H^+ \overset{K_1}{\leftrightarrow} H_2CO_3^-$$

$$CO_3^{2-} + 2H^+ \overset{K_2}{\leftrightarrow} H_2CO_3$$

$$Ca^{2+} + H_2O \overset{K_3}{\leftrightarrow} CaOH^+ + H^+$$

$$Mg^{2+} + H_2O \overset{K_4}{\leftrightarrow} MgOH^+ + H^+$$

$$Ca^{2+} + CO_3^{2-} \overset{K_5}{\leftrightarrow} CaCO_3^0$$

$$Mg^{2+} + CO_3^{2-} \overset{K_6}{\leftrightarrow} MgCO_3^0$$

$$Ca^{2+} + H^+ + CO_3^{2-} \overset{K_7}{\leftrightarrow} CaHCO_3^+$$

$$Mg^{2+} + H^+ + CO_3^{2-} \overset{K_8}{\leftrightarrow} MgHCO_3^+$$

$$Cr^{3+} + H_2O \overset{K_9}{\leftrightarrow} Cr(OH)^{2+} + H^+$$

$$Cr^{3+} + 2H_2O \overset{K_{10}}{\leftrightarrow} Cr(OH)_2^+ + 2H^+$$

$$Cr^{3+} + 3H_2O \overset{K_{11}}{\leftrightarrow} Cr(OH)_3^0 + 3H^+$$

$$Cr^{3+} + Ac^- + 2H_2O \overset{K_{12}}{\leftrightarrow} CrAc(OH)_2 + 2H^+$$

$$HAc \overset{K_{13}}{\leftrightarrow} H^+ + Ac^-$$

$$H_2O \overset{K_{14}}{\leftrightarrow} H^+ + OH^-$$

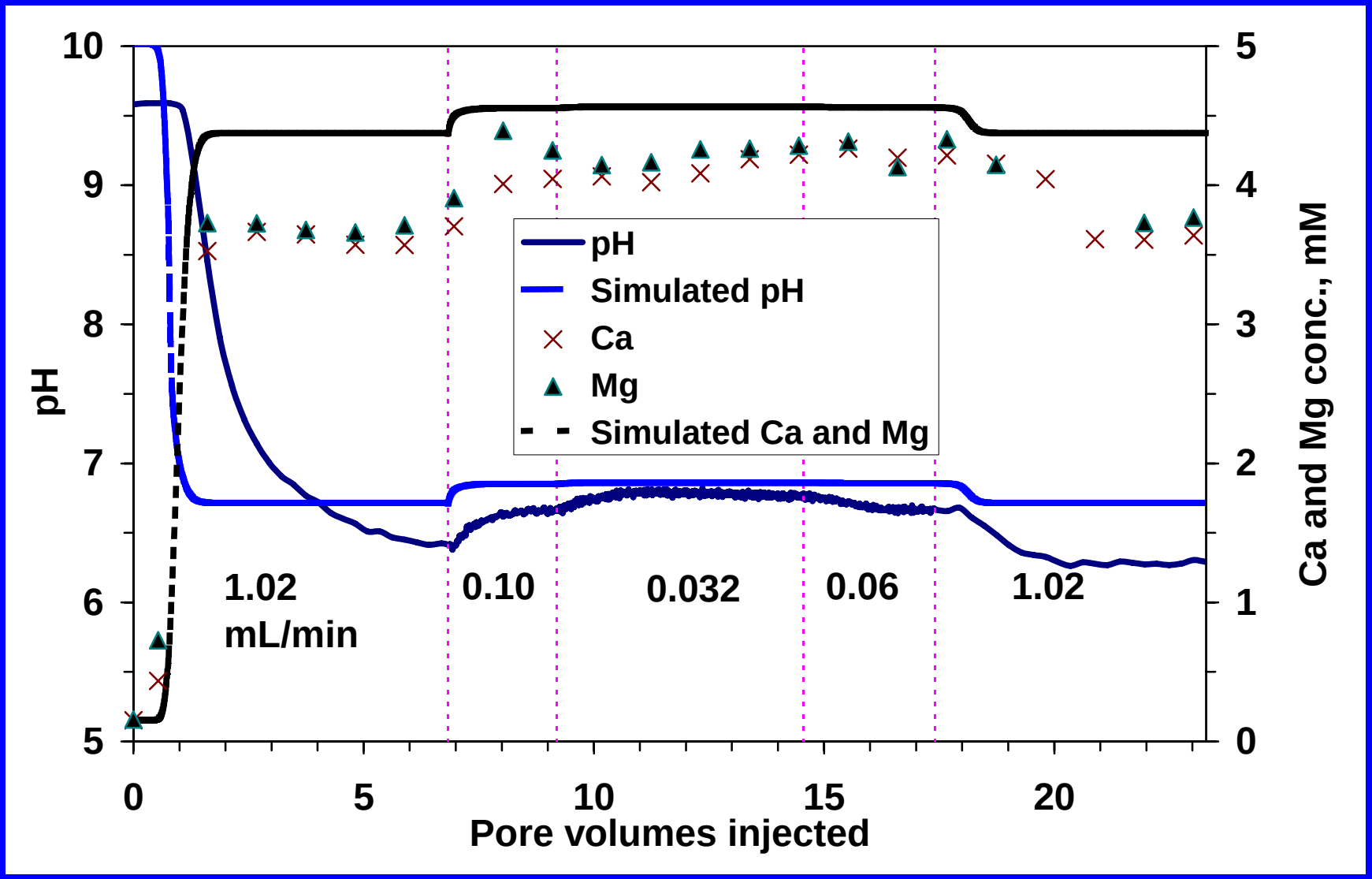
# RRate equation of mineral dissolution:

$$R_i = r_i \left( 1 - \left( \frac{IAP}{K_{sp}} \right)^{m_2} \right)^{m_1} \frac{y_i \, S_0 (1 - \phi)}{\phi}$$

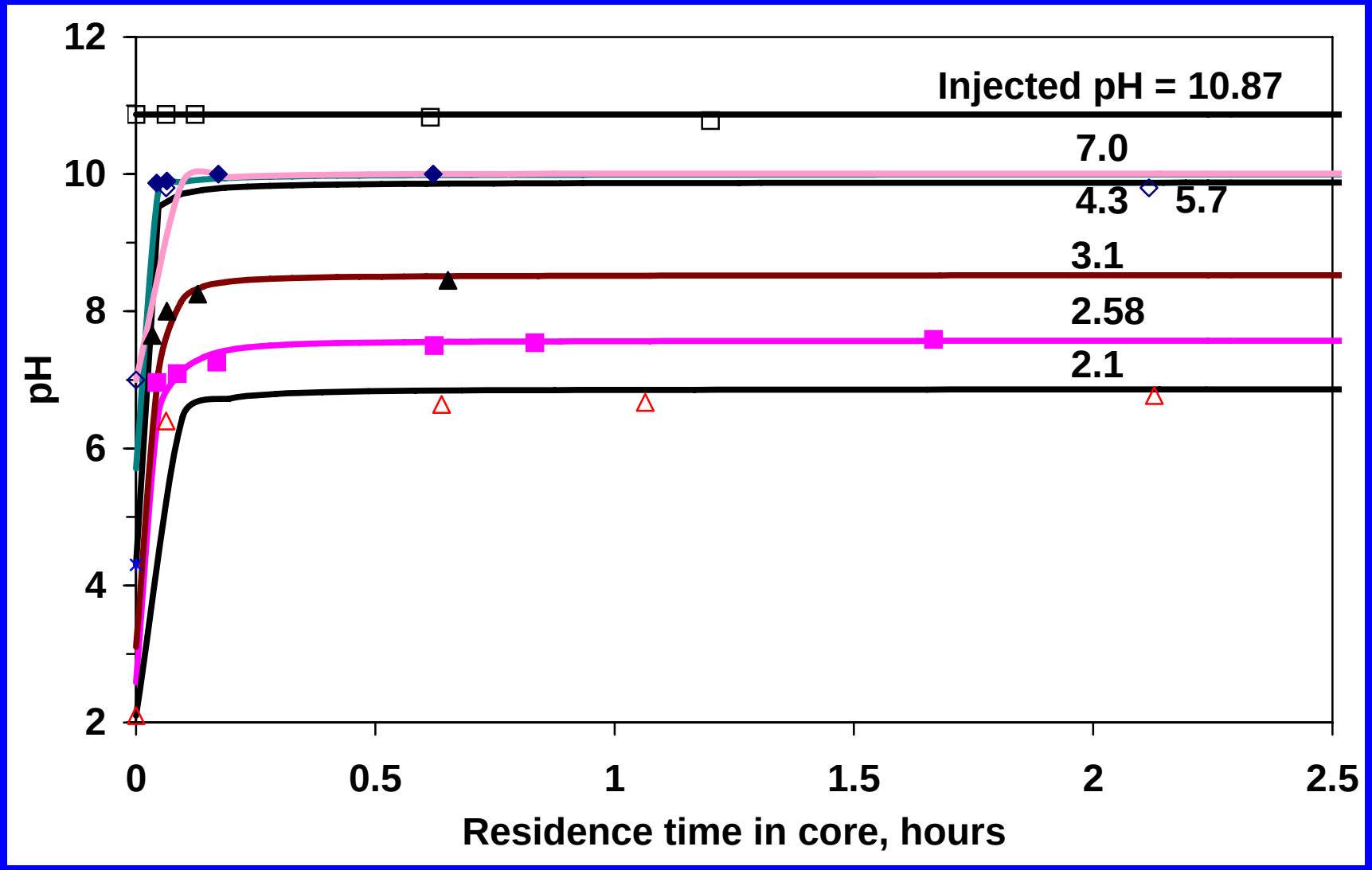
# RRate equation of chromium precipitation:

$$R_{chromium} = -882.9([Cr_t] - [Cr_{eq}])^2 [OH^-]^{0.65} [Ac_t]^{-0.75}$$

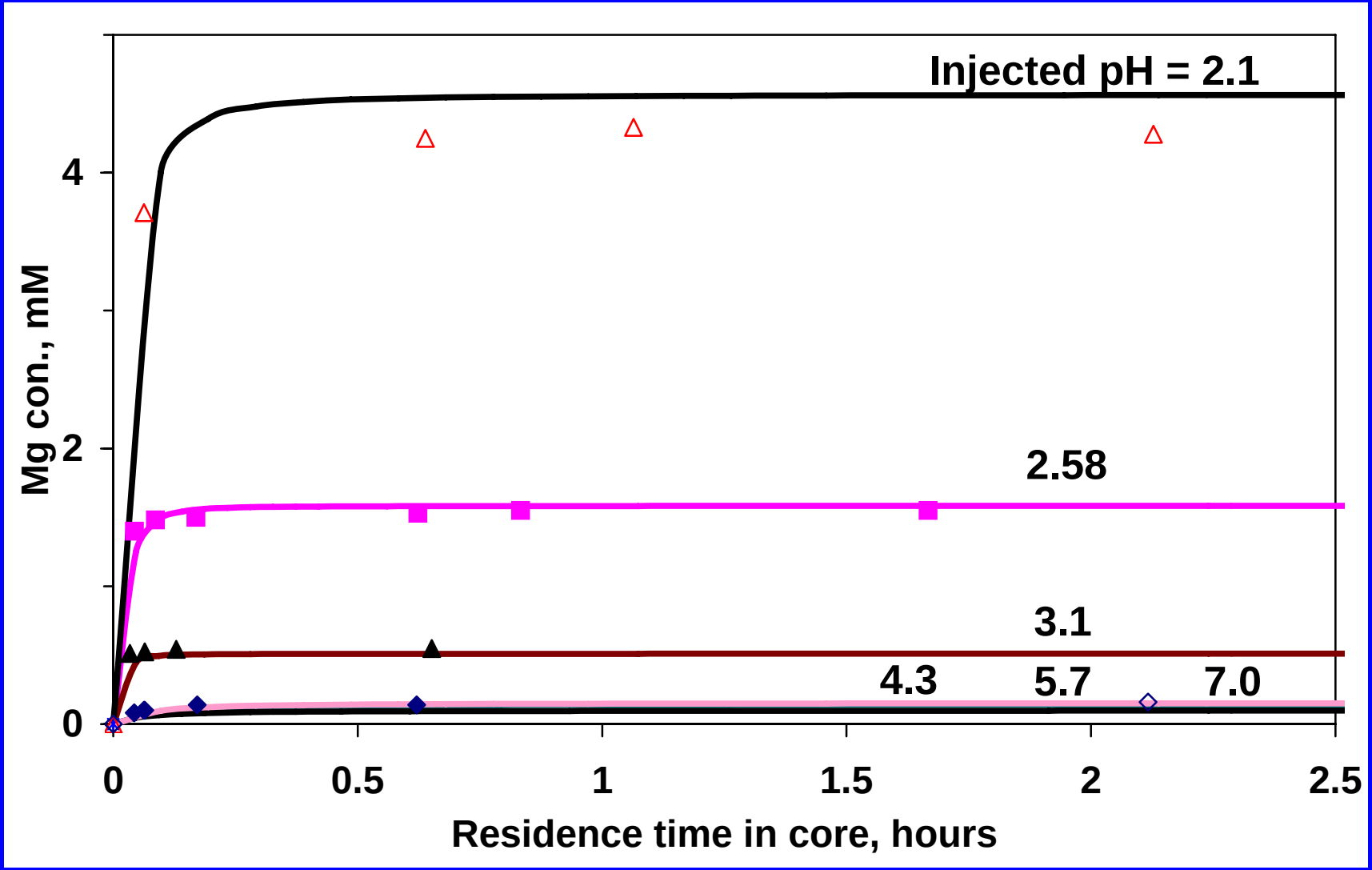
Rate equation



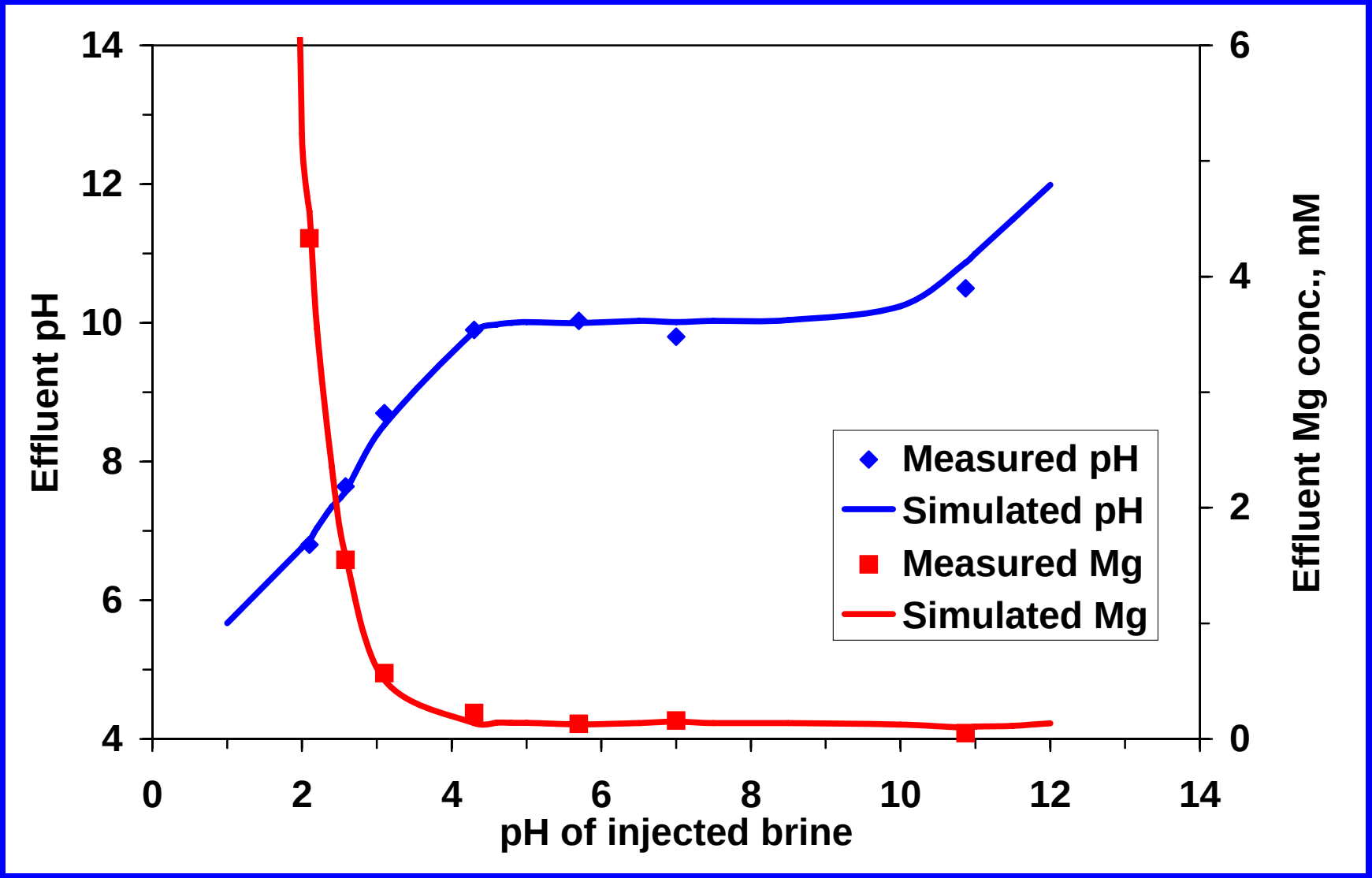

Injected brine pH = 2.1



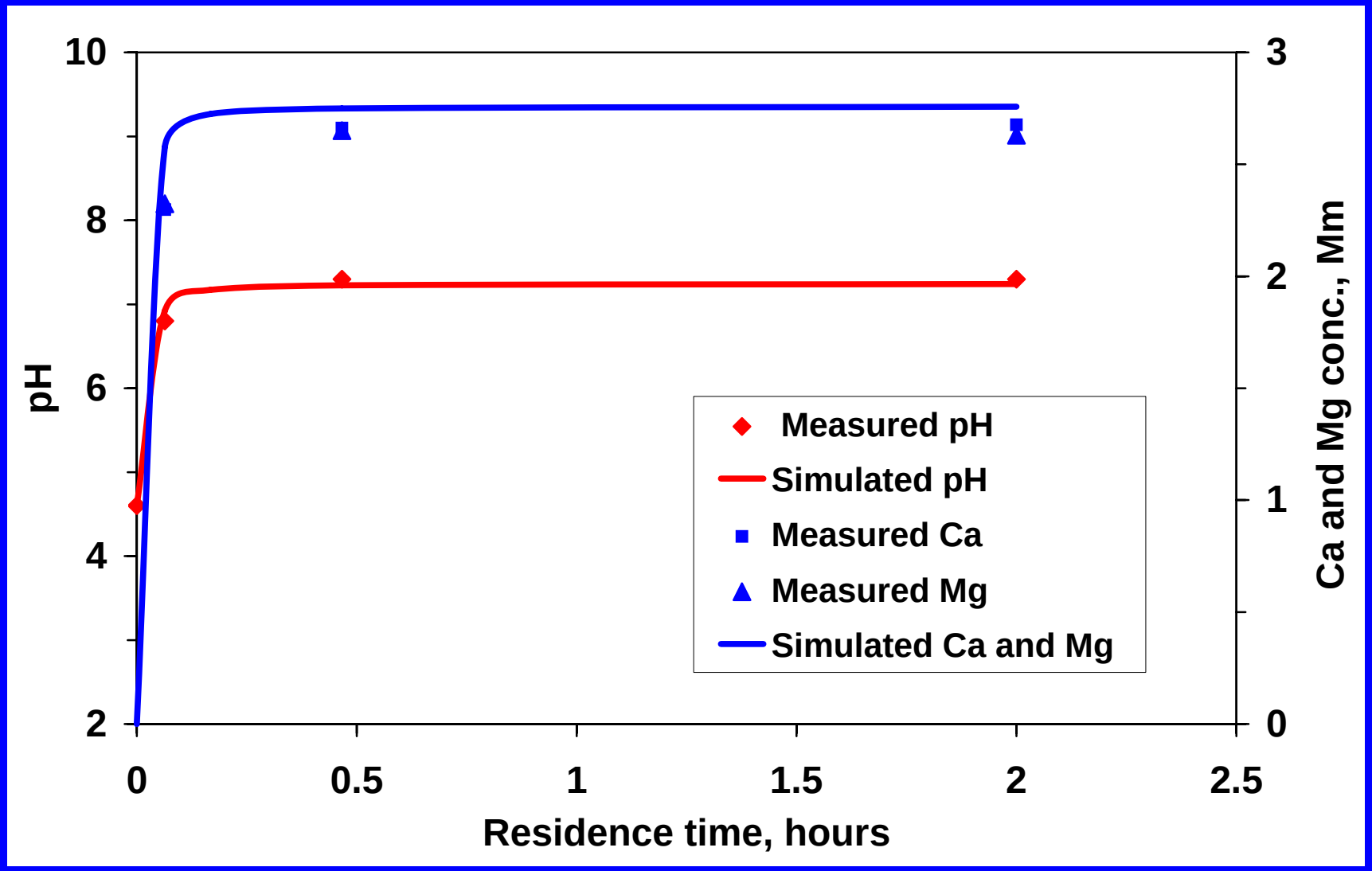

# Steady-state pH




Steady-state Mg conc.

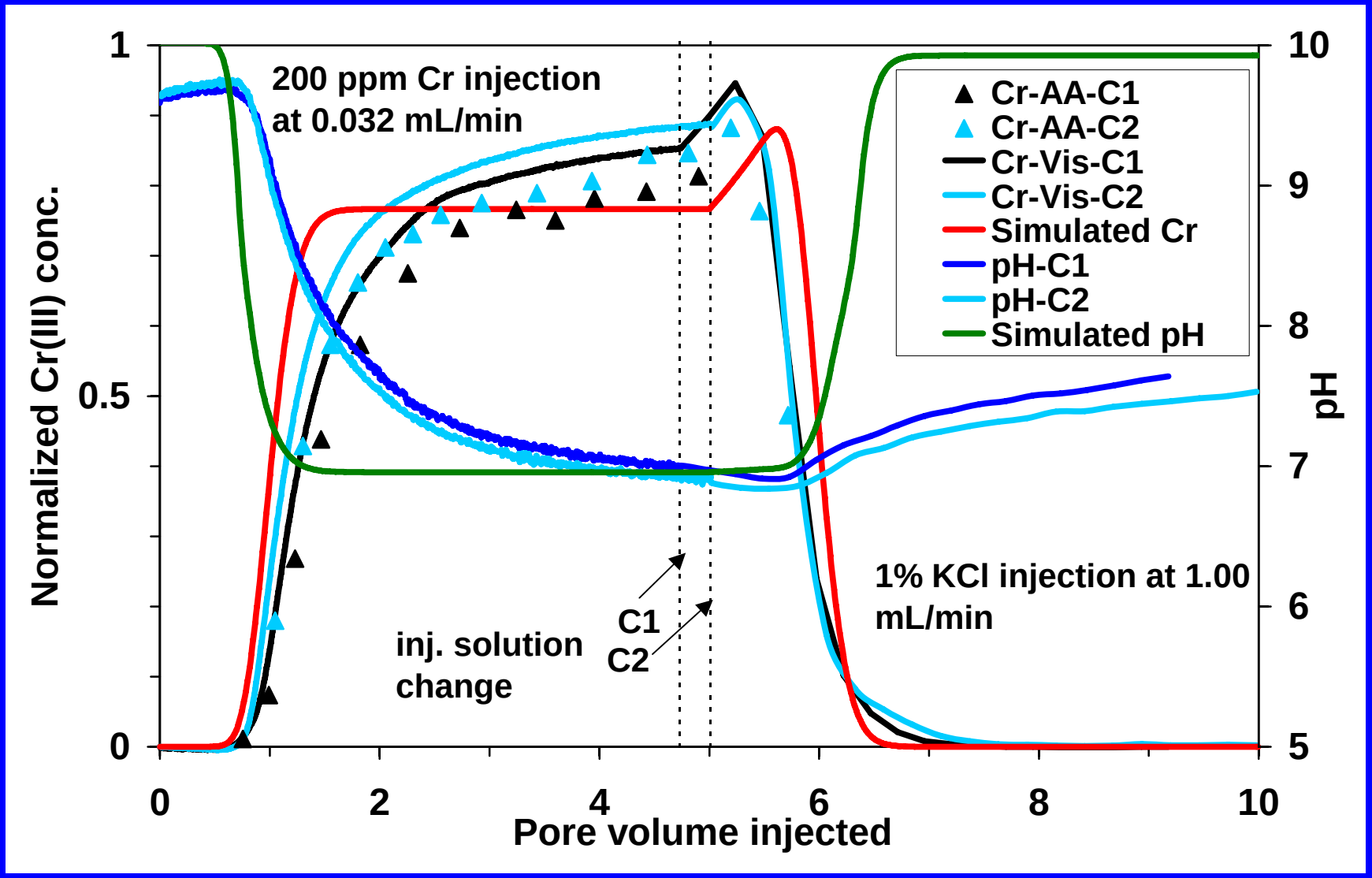



# Equilibrium data

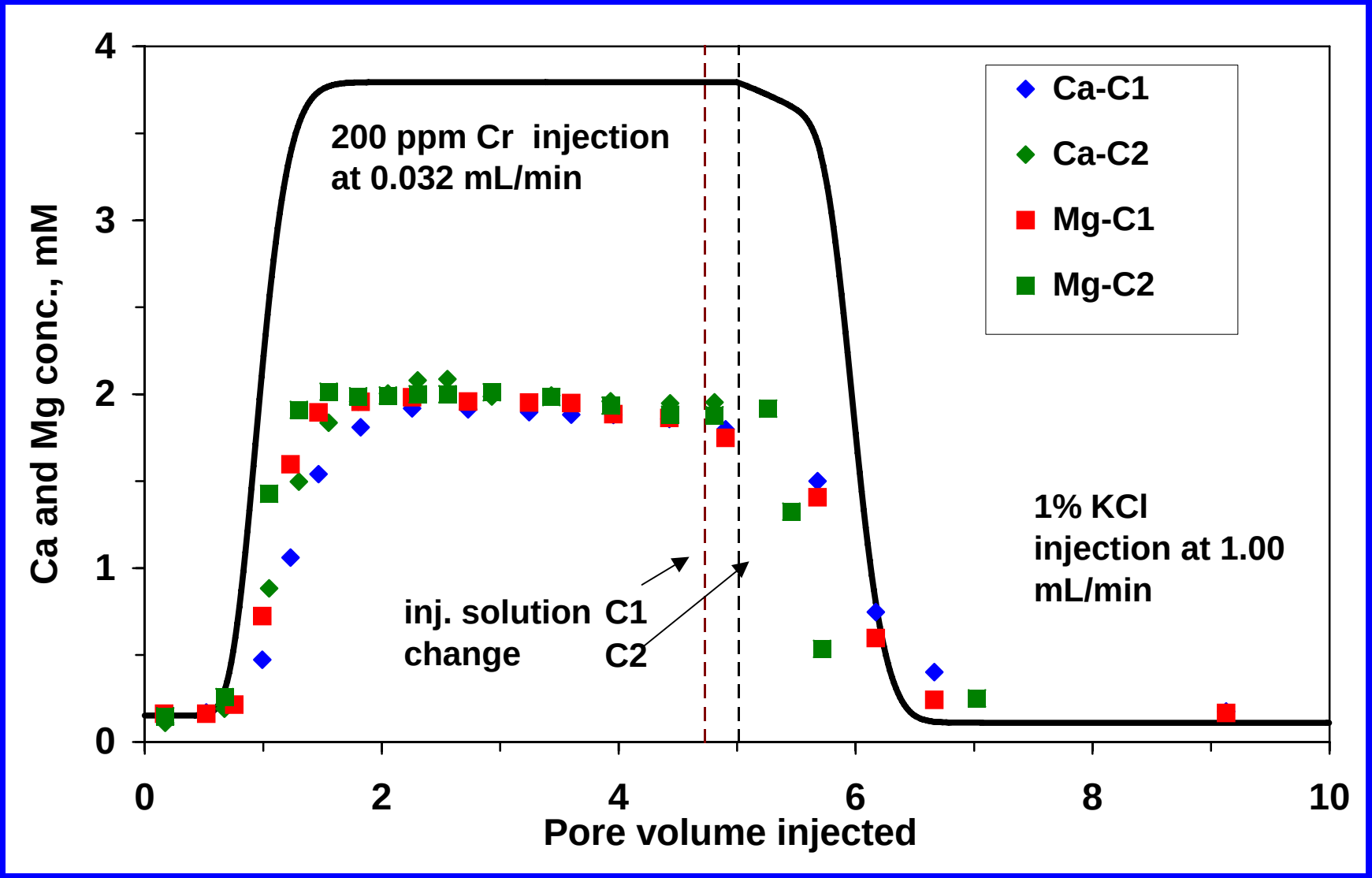



Injected solution: 0.0114 M KOAc, pH=4.6

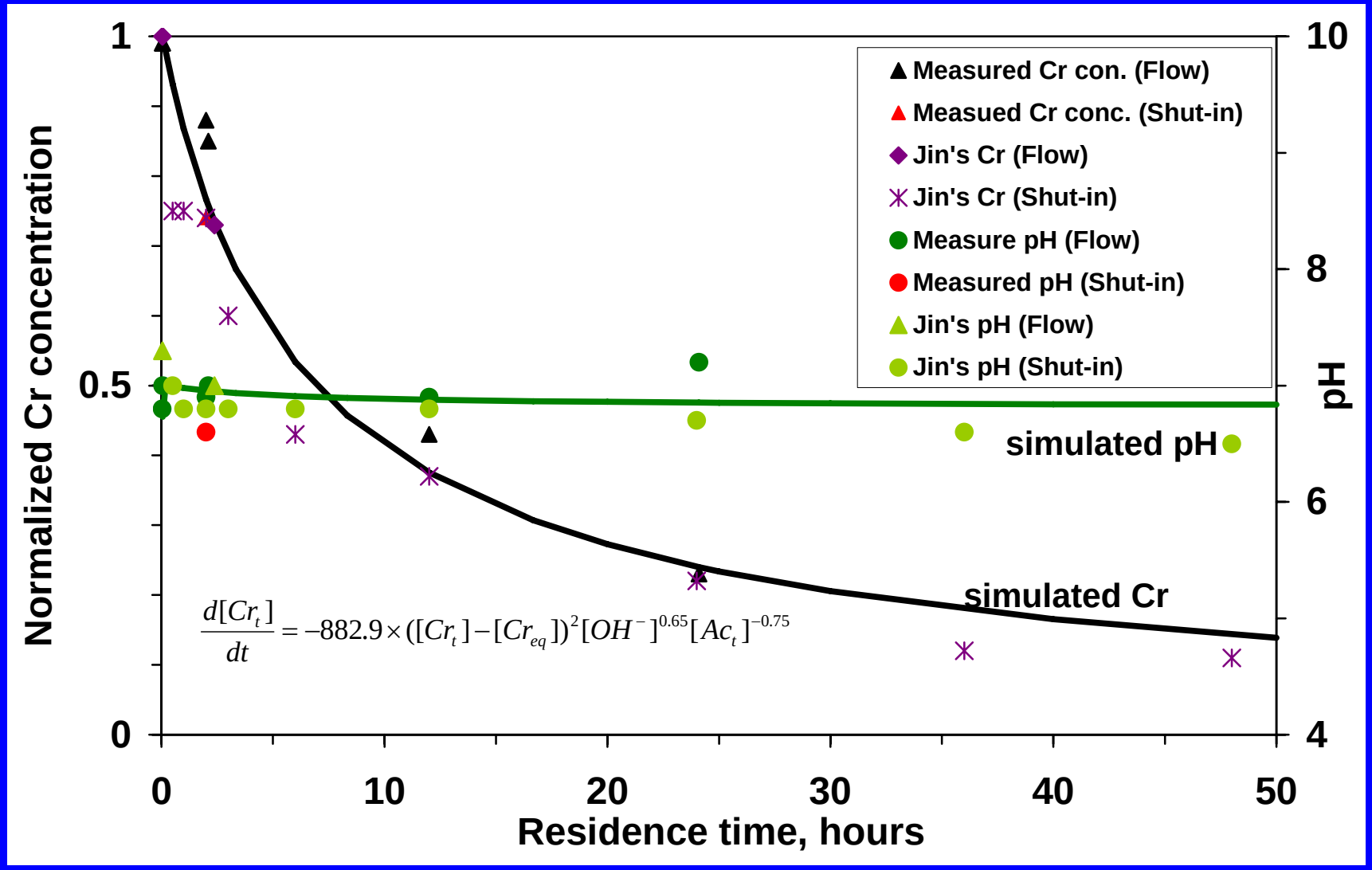
Steady-state data



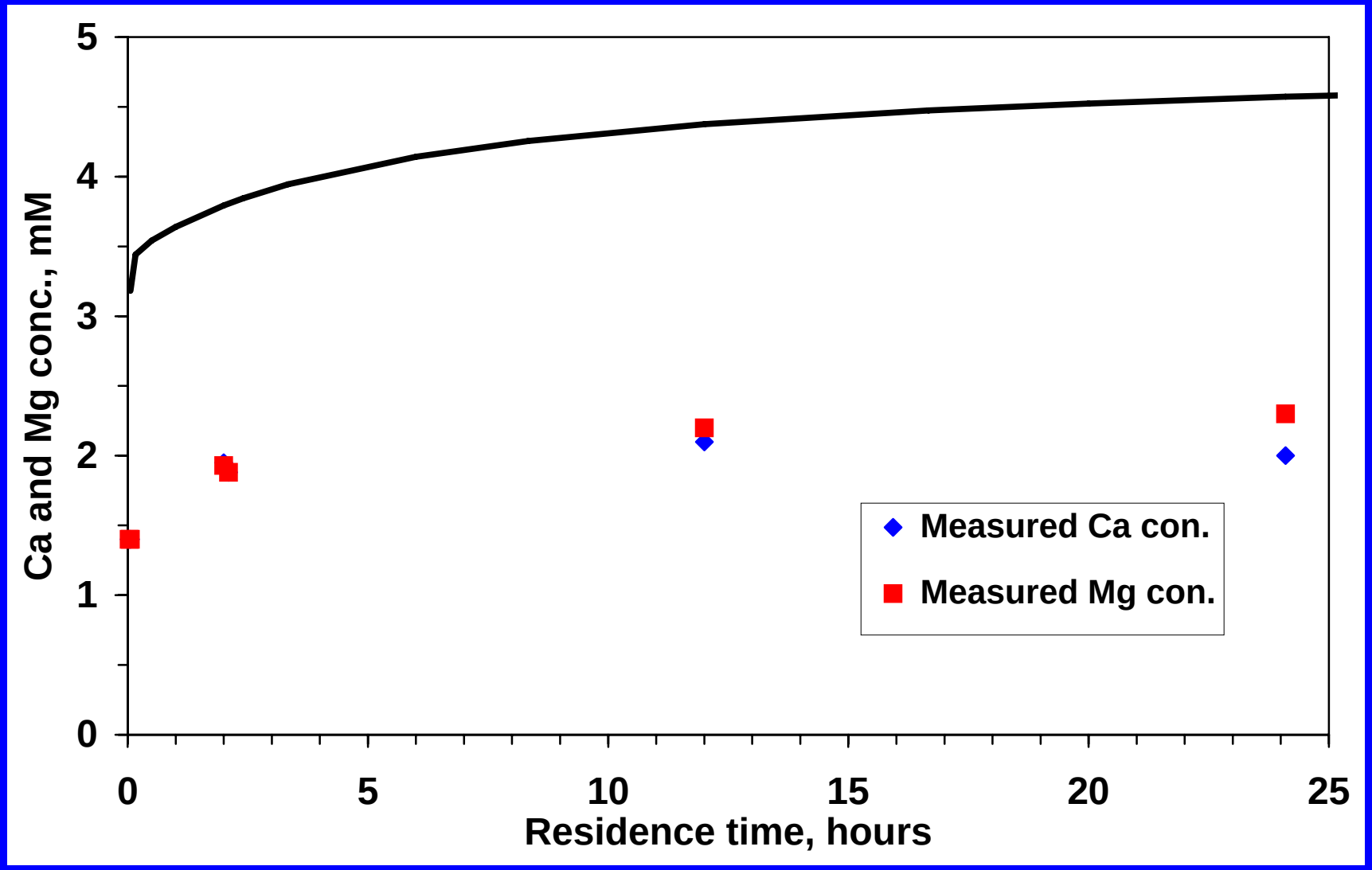

200 ppm Cr(III), residence time = 2 hours



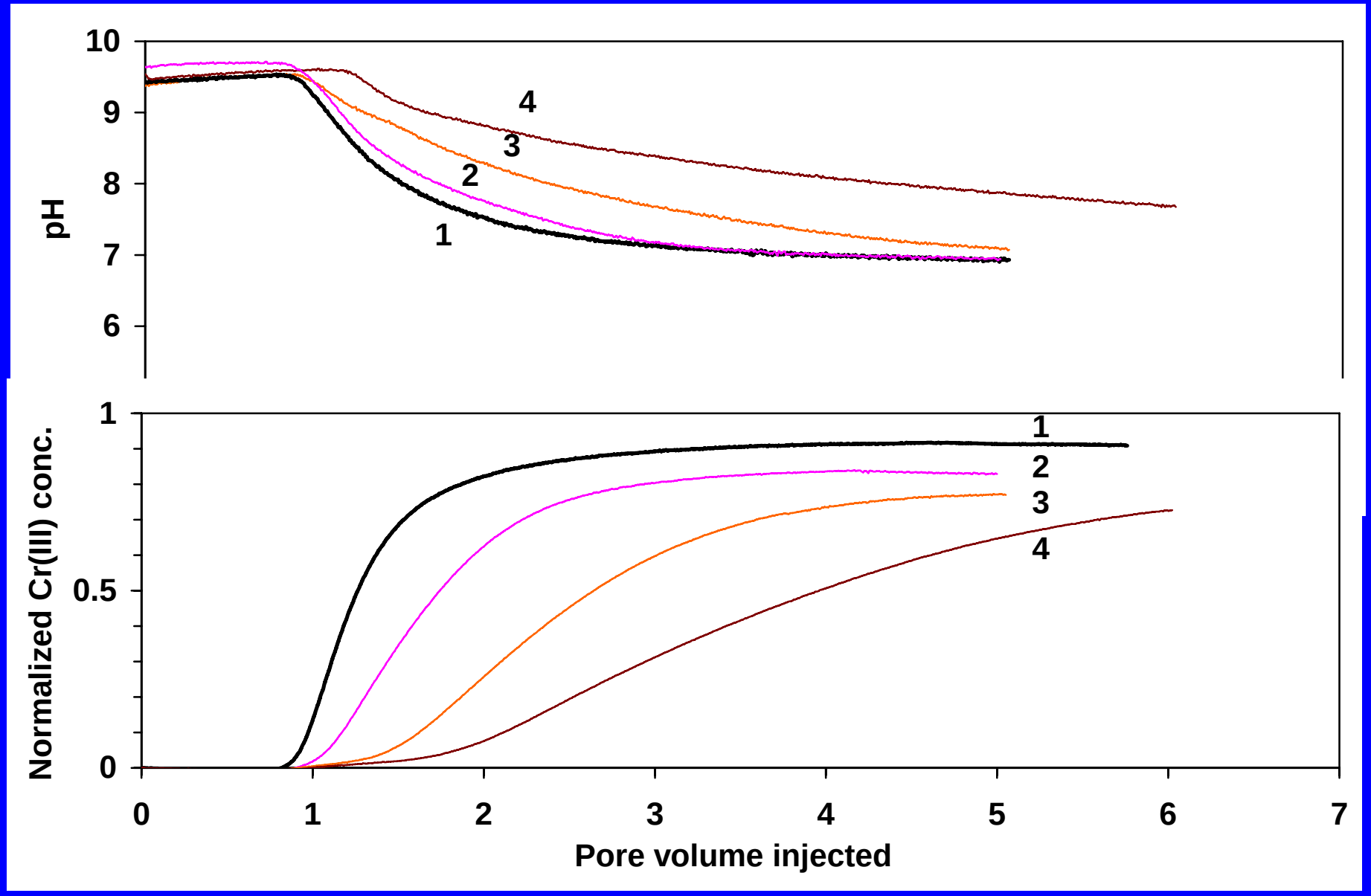

200 ppm Cr(III), residence time = 2 hours




# Steady-state pH and Cr conc.




Steady-state Ca and Mg conc.

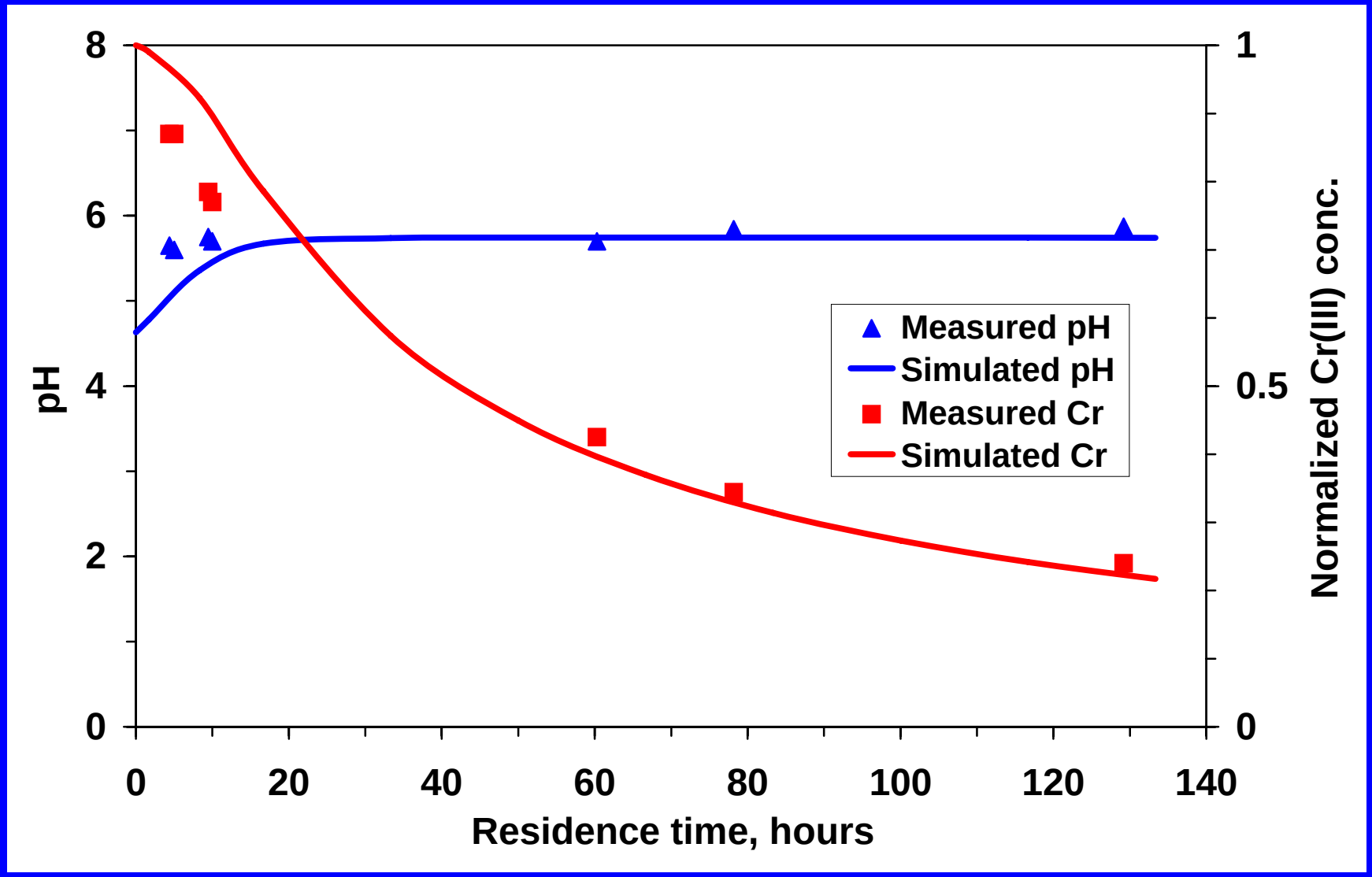



# Used core experiments

# San Andres dolomite cores [McCool et al., 2000]

| Injected solution and residence time | Effluent solution | |
|---|---|---|
| | Experimental data | Simulation results |
| 3.0 % KCl<br>pH = 6.9<br>residence time = 23 mins | pH = 9.5<br>Ca Conc. = 3.88-1.55 mM<br>Mg Conc. = 0.20-0.10 mM | pH = 9.51<br>Ca Conc. = 4.14 mM<br>Mg Conc. = 0.29 mM |
| 3.0 % KCl, 50 ppm Cr<br>pH = 7.0<br>residence time = 138.5 mins | pH = 7.9<br>Normalized Cr Conc. = 0.40 | pH = 8.0<br>Normalized Cr Conc. = 0.39 |
| 3.0 % KCl, 215 ppm Cr<br>pH = 4.4<br>residence time = 120 mins | pH = 6.8<br>Normalized Cr Conc. = 0.79 | pH = 6.8<br>Normalized Cr Conc. = 0.79 |

**San Andres dolomite includes anhydrite ranging from 0.5-5%. [Anderson, 1991]**




Injected solution: 400 ppm Cr in artificial seawater [Stavland et al., 1993].

# *Conclusions*

- One kinetic equation described Cr retention rate in three types of carbonate-containing rocks (Baker dolomite, San Andres dolomite, and Brent sandstone)

Effluent Cr and pH

- The steady-state values--- reasonably well
- The transient period--- less satisfactory

# *Conclusions (Cont'd)*

- Chromium precipitation increased

  increasing pH

  increased residence time

  a decrease in the injected Cr conc.

  in used cores than in virgin cores.

- Results from shut-in experiments approximated the flow experiments at the same residence times.

# *Conclusions (Cont'd)*

- The presence of Cr in fluids injected into Baker dolomite cores significantly reduced the dissolution of Ca and Mg.

# *Acknowledgement*


- US Department of Energy

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- State of Kansas

  Tertiary Oil Recovery Project

# *Experimental Details*

- Chemicals:
  - Chromium solution:

    Chromium(III) acetate, 100 or 200 ppm Cr(III)
  - Tracer: 0.1M $KNO_3$
  - Blank: 1% KCl solutions
- Displacement experiments:
  - Continuous flow
  - Shut-in

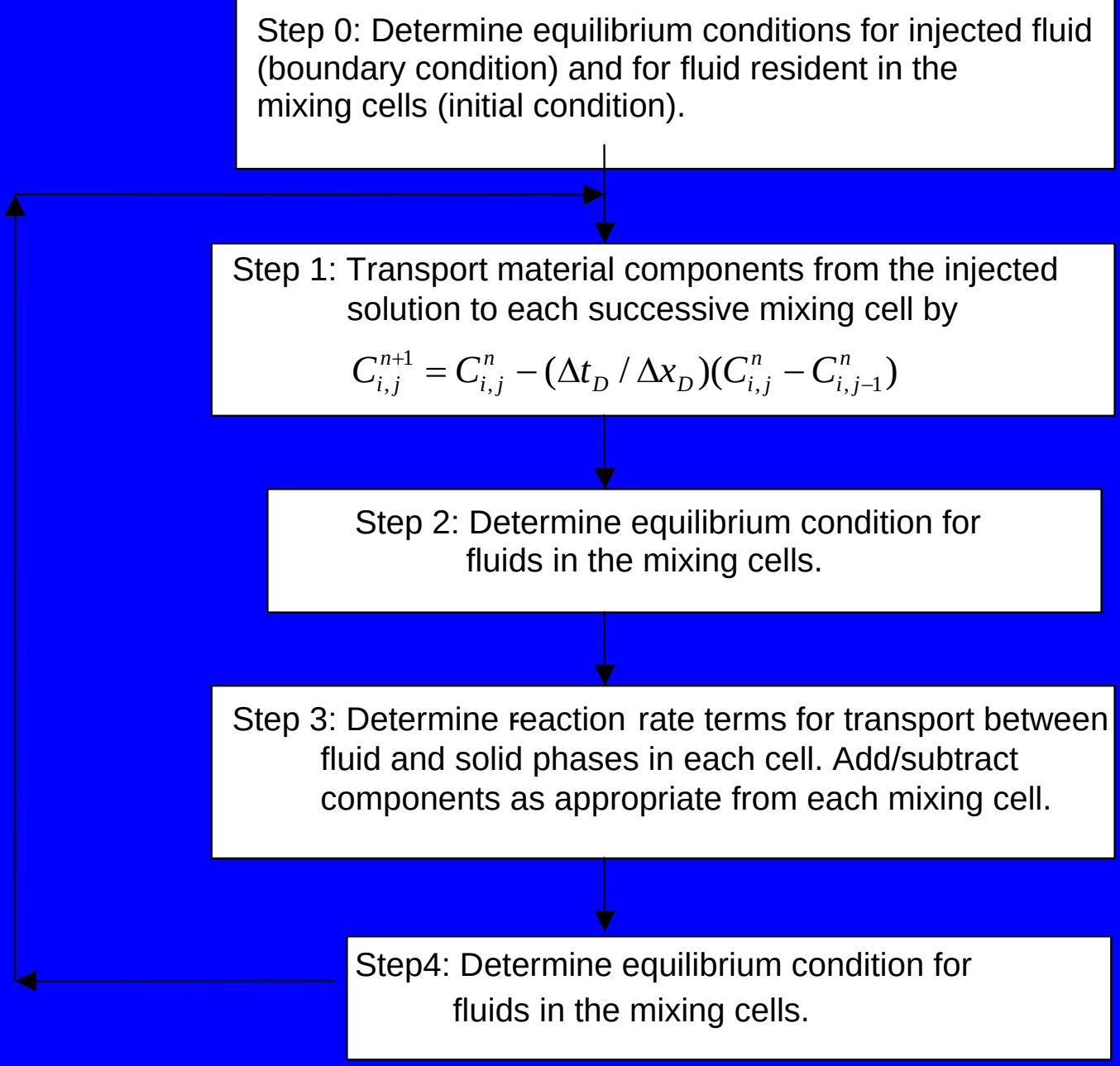


Figure A1- Schematized flow chart of mixing-cell concept.

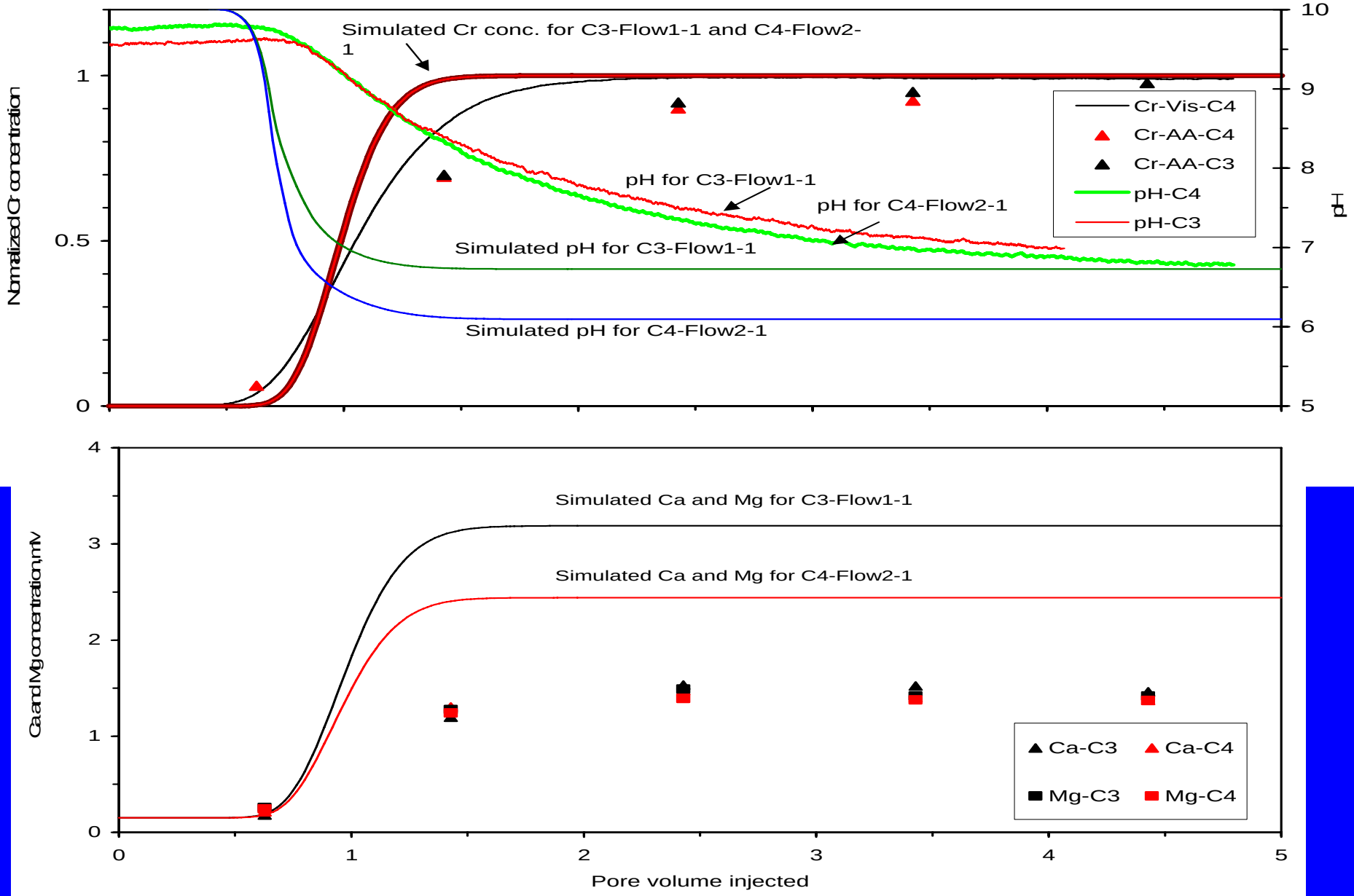


Figure A2- The comparison of simulation results and the experimental data from runs C3-Flow1-1 and C4-Flow2-1.

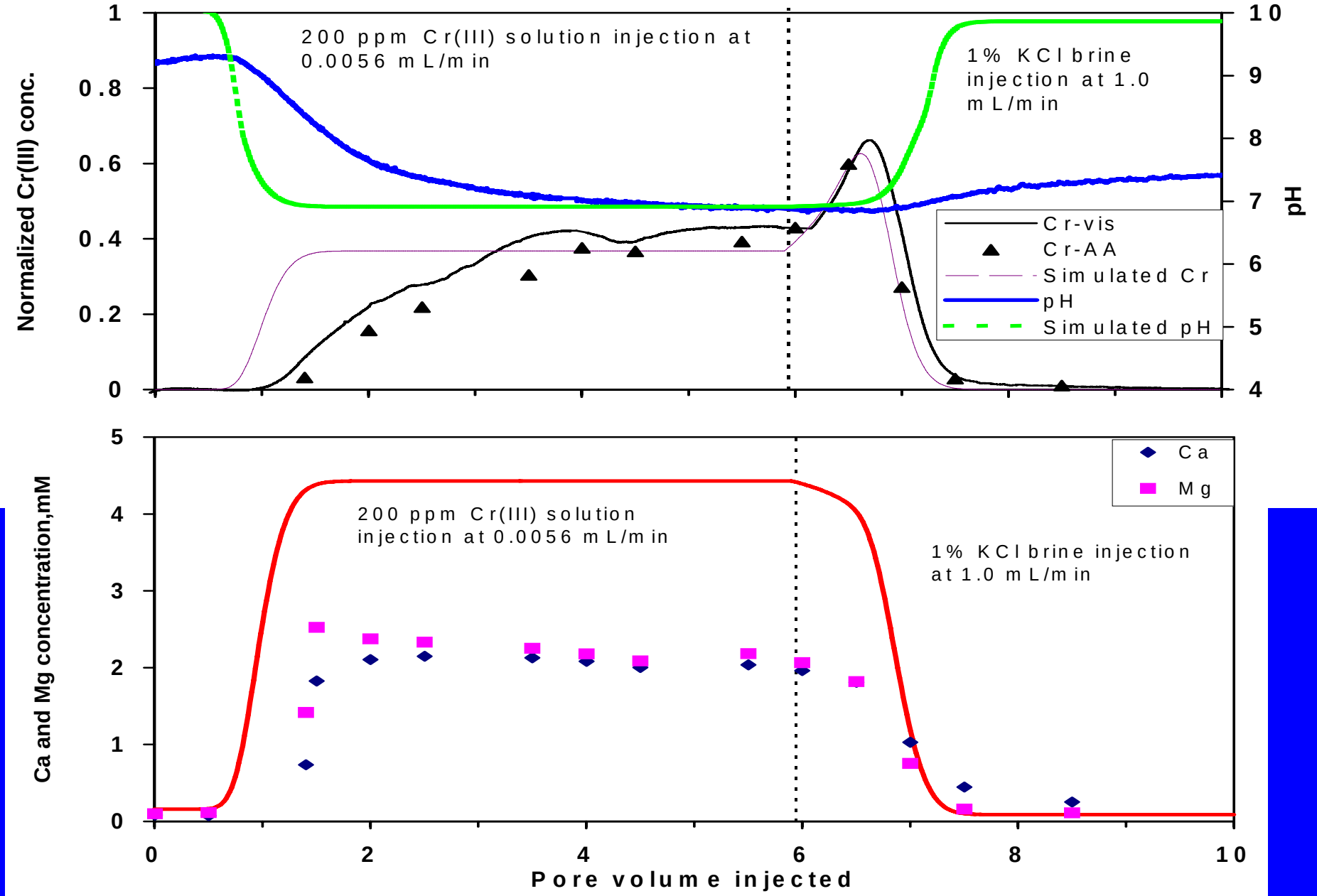


Figure A3- The comparison of simulation results and the experimental data from run C6-Flow0.0056-1 and the following brine postflood.

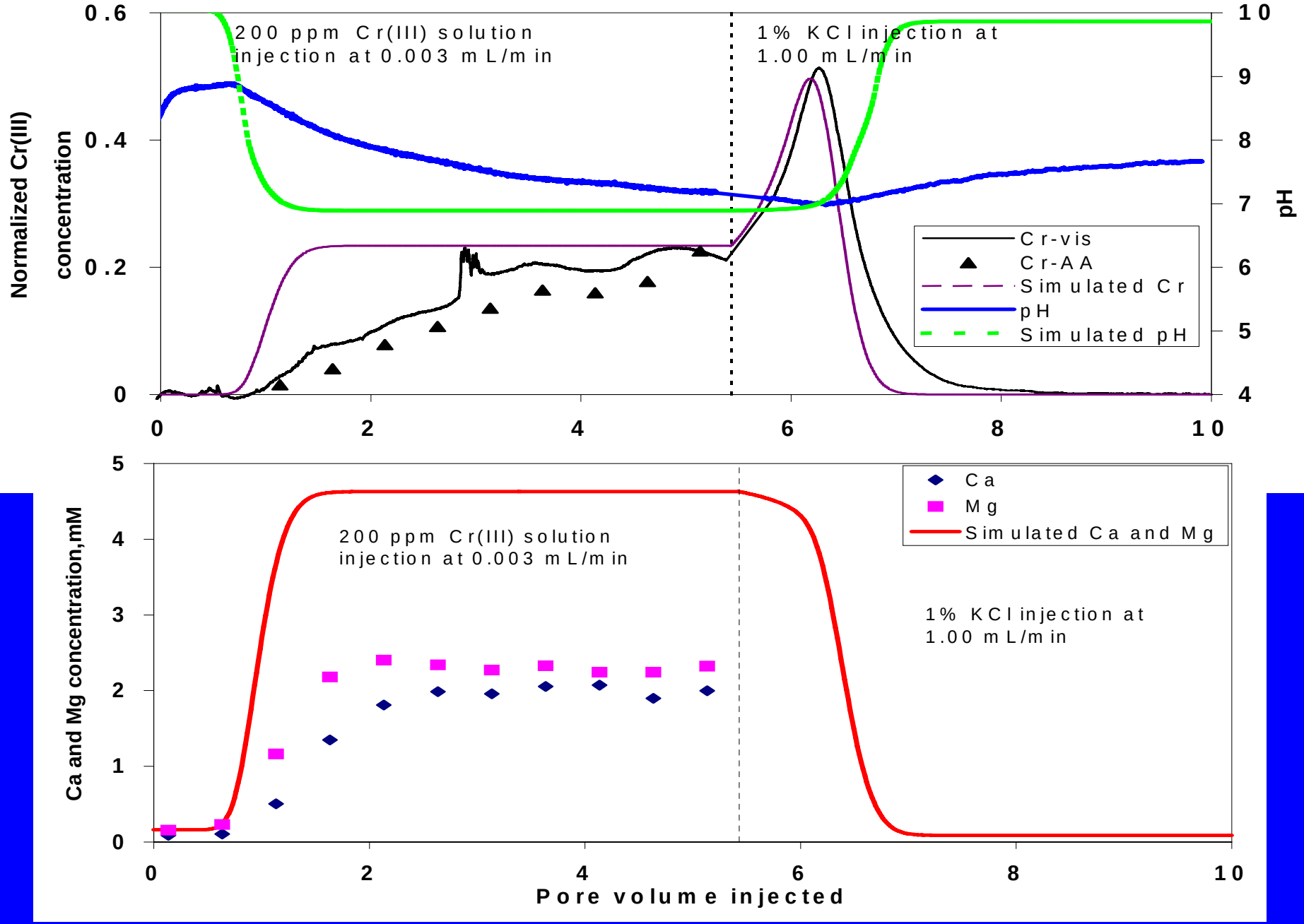


Figure A4- The comparison of simulation results and the experimental data from run C5-Flow0.003-1 and the following brine postflood.

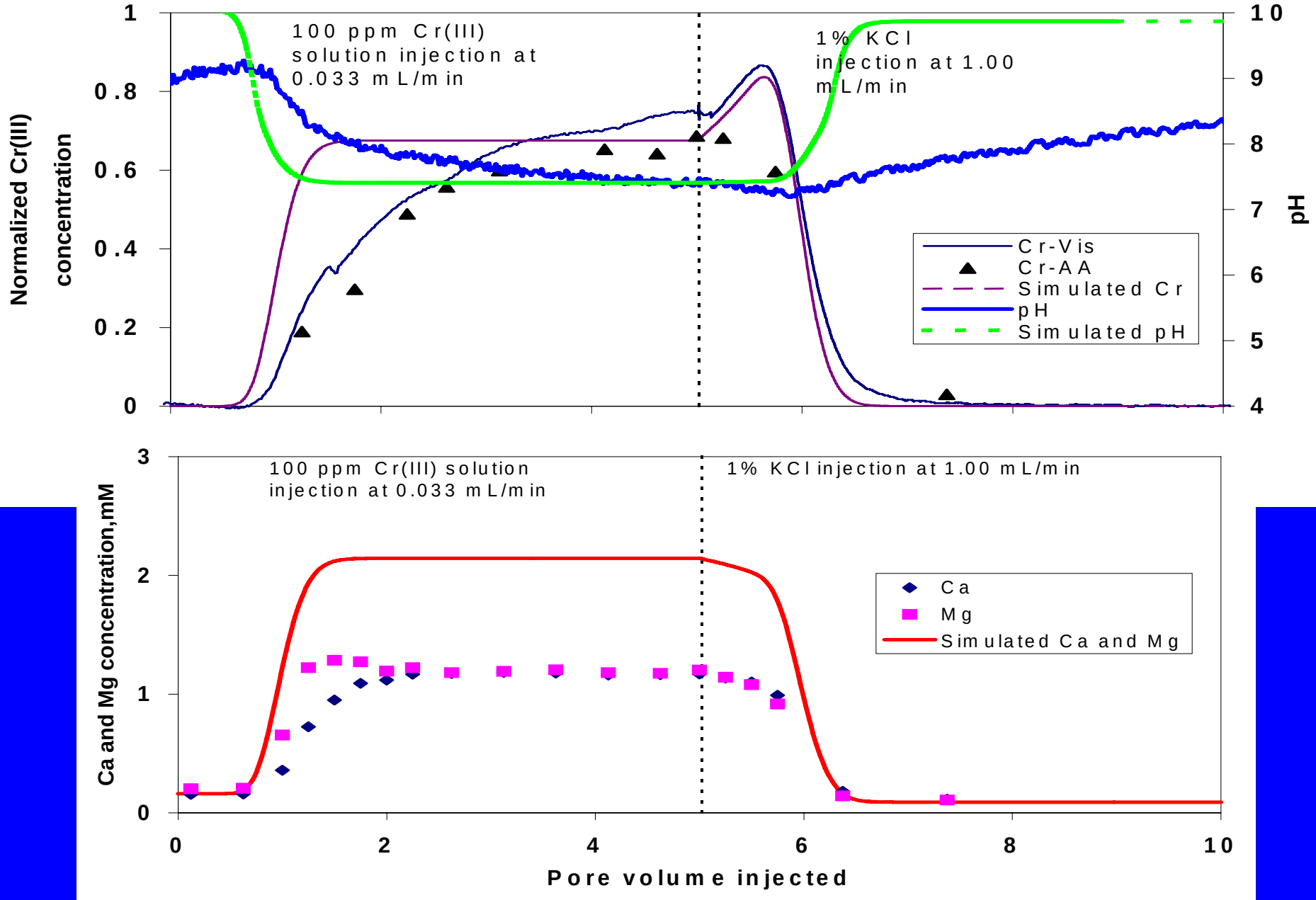


Figure A5- The comparison of simulation results and the experimental data from run C7-Flow0.033-1 and the following brine postflood.

**Table A1 - Properties of dolomite cores used in this project.**

| Core name | B | C1 | C2 | C3 | C4 | C5 | C6 | C7 |
|---|---|---|---|---|---|---|---|---|
| Diameter (cm) | 1.86 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 |
| Length cm) | 6.50 | 6.55 | 6.02 | 6.00 | 6.42 | 7.15 | 6.83 | 6.62 |
| Porosity | 0.23 | 0.22 | 0.23 | 0.22 | 0.23 | 0.22 | 0.21 | 0.21 |
| Pore volume (mL) | 4.14 | 4.06 | 3.83 | 3.61 | 4.13 | 4.34 | 4.03 | 3.94 |
| Permeability (md) | 42 | 30 | 27 | 23 | 55 | 24 | 17 | 36 |

**Table A2 – Experimental parameters and results for flow experiments in virgin cores.**

| Run No. | C4-Flow2-1 | C3-Flow1-1 | C2-Flow0.0 32-1 | C1-Flow0.03 2-1 | C6-Flow0.00 56-1 | C5-Flow0.0 03-1 | C7-Flow0.03 3-1 |
|---|---|---|---|---|---|---|---|
| Chromium conc. (ppm) | 200 | 200 | 200 | 200 | 200 | 200 | 100 |
| Residence time (hours) | 0.034 | 0.060 | 2.0 | 2.1 | 12.0 | 24.1 | 2.0 |
| PV injected | 5.0 | 6.9 | 5.01 | 4.74 | 5.94 | 5.43 | 5.02 |
| Steady-state norm. Cr conc. | 0.99 | 0.99 | 0.88 | 0.85 | 0.43 | 0.23 | 0.75 |
| Steady-state pH | 6.8 | 6.9 | 6.9 | 7.0 | 6.9 | 7.2 | 7.4 |
| Steady-state Mg conc. (mM) | 1.4 | 1.4 | 1.93 | 1.88 | 2.2 | 2.3 | 1.2 |
| Steady-state Mg/Ca molar ratio | 1.00 | 1.00 | 0.99 | 1.00 | 1.05 | 1.15 | 1.00 |
| Amount of chromium retention* (mg) | - | - | 0.903 | 0.888 | 3.469 | 3.660 | 0.711 |

* The amount of chromium retention = the amount of chromium injected – the amount of chromium detected by spectrophotometer.

## Table A3 – Results of experiments to test for co-precipitation.

| | Initial condition | | | | Measured value after 25 hours | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample No | Cr con. Ppm | Ca con. mM | Mg con. mM | pH | Contact time, hours | Cr con. ppm | Ca con. mM | Mg con. mM | pH |
| 1 | 200 | 6.39 | - | 9.06 | 25 | 90 | 6.14 | - | 6.55 |
| | | | | | 142 | 56 | 6.19 | - | 6.04 |
| 2 | 200 | - | 5.51 | 9.07 | 25 | 94 | - | 5.21 | 6.54 |
| | | | | | 142 | 58 | - | 5.43 | 6.05 |
| 3 | 200 | 5.63 | 5.13 | 9.04 | 25 | 98 | 5.40 | 5.14 | 6.54 |
| | | | | | 142 | 58 | 5.46 | 5.13 | 6.01 |
| 4 | 200 | 2.21 | 1.78 | 9.05 | 142 | 56 | 2.20 | 1.78 | 6.06 |

**Table A4 - Parameters and results of shut-in and flow experiments; chromium(III) acetate solution (200 ppm Cr, 1% KCl).**

| Run | Residence or shut-in time (hrs) | Volume of chromium acetate injected prior to exp (PV) | Norm. Cr conc. | Mg conc. (mM) | Ca conc. (mM) | Mg/Ca molar ratio | pH |
|---|---|---|---|---|---|---|---|
| C3-Shutin2-2 | 2.0 | 6.9 | 0.74 | 2.2 | 1.9 | 1.16 | 6.6 |
| C4-Shutin2-2 | 2.0 | 5.0 | 0.74 | 2.2 | 1.8 | 1.22 | 6.6 |
| B-Shutin2-1 | 2.0 | 15.8 | 0.67 | 2.4 | - | - | 6.9 |
| B-Shutin 2-2 | 2.0 | 25.9 | 0.64 | 2.5 | - | - | 6.8 |
| C1-Flow0.032-1 | 2.1 | 0 | 0.85 | 1.88 | 1.88 | 1.00 | 7.0 |
| C2-Flow0.032-1 | 2.0 | 0 | 0.88 | 1.93 | 1.95 | 0.99 | 6.9 |