

A SYSTEMATIC APPROACH TO UNCOVERING SCALE- INDEPENDENT RATE FORMULATIONS FOR BIOREDUCTION OF HEMATITE IN SEDIMENTS AT A FIELD SITE

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ABSTRACT

This presentation focuses on a systematic modeling approach in search of scale-independent rate formulations for biological reduction of hematite. Biological and chemical processes controlling Fe(III) reduction are very complex including direct bioreduction of ferric iron, microbial growth, secondary reactions of biogenic ferrous iron adsorptions, iron complexation, precipitation of ferrous minerals, and re-oxidation. A reaction network of five reactions was proposed to describe these processes under laboratory-controlled batch and column experiments which were conducted using sediments taken from a field site. The key reaction in the experiments is the direct bioreduction of hematite. Four possible rate formulations were proposed to describe this key reaction. Two kinds of simulations were conducted to verify the rate formulations and reaction parameters: the first one is batch modeling and the second one is column modeling. Simulation results indicated that while all rate formulations can adequately model batch experiments, only the formulation based on dual Monod kinetics with inhibition of ferrous iron and the effect of DMRB is “universal”. Furthermore, only this rate formulation can be upscaled to column experiments. Iterative modeling between batch and column experiments revealed that the equilibrium assumptions for surface hydration of hematite and adsorption of biogenic ferrous iron onto hematite may have to be revoked and substituted with kinetic rate formulations.

1. INTRODUCTION

Hematite (Fe_2O_3) is the most important ore of iron on earth and deposited as sediment from streams and rivers; however, the bioreduction of hematite and of associated contaminant interaction is very complicated and difficult to describe because multiple simultaneous reactions often occur under Fe(III)-reducing conditions. The dissimilatory metal reducing bacteria (DMRB) can be employed to dissolve ferric oxides and the biogenic Fe(II) can then chemically react with other reducible compounds in the biologic-chemical reactions (Burgos et al., 2003). Reducible compounds of concern comprise both organic and inorganic pollutants and can be “directly” (biologic) or “indirectly” (combined biologic-chemical) reduced by DMRB. Because the reactions are complicated, an appropriate biogeochemical numerical model is needed to properly evaluate and design the bioreduction system of Fe(III).

Our study was to analyze the bioreduction of natural hematite and to determine the rate formulations and parameters of the reaction network via modeling. A reaction network of five reactions was proposed to describe the bioreduction of natural hematite under laboratory-controlled batch and column experiments which were conducted using sediments taken from a field site. The key reaction in the experiments is the direct bioreduction of hematite; hence, four possible rate formulations were proposed to describe this key reaction, and two kinds of simulations were conducted to verify the rate formulations and reaction parameters: the first one is batch modeling with BIOGEOCHEM 1.0 (Yeh et al., 2005a) and the second one is column modeling via HYDROGEOCHEM 4.0 (Yeh et al., 2004). Furthermore, the results of simulations were compared with both batch and column experimental data to see if the employed approach and models could be used to adequately determine the reaction rate formulations and parameters for the biological reduction of hematite.

2. SIMULATION APPROACH AND EXPERIMENTAL CONDITIONS

2.1 Modeling Methods for Batch Systems

A biogeochemical system is completely defined by specifying reaction networks (Yeh et al., 2001), and the production-consumption rate of every species is resulted from all reactions that produce or consume that species:

$$r_i|_N = \sum_{k=1}^N (v_{ik} - \mu_{ik})R_k \quad \text{so that} \quad \frac{dC_i}{dt} = \sum_{k=1}^N (v_{ik} - \mu_{ik})R_k, \quad i \in M \quad (1)$$

where $r_i|_N$ is the production-consumption rate of the i -th species due to N biogeochemical reactions, v_{ik} is the reaction stoichiometry of the i -th species in the k -th reaction associated with the products, μ_{ik} is the reaction stoichiometry of the i -th species in the k -th reaction associated with the reactants, R_k is the rate of the k -th reaction, C_i is the concentration of the i -th chemical species, t is time, and M is the number of chemical species. Moreover, for facilitating numerical integration, Eq. (1) can be converted into a matrix form to decouple equilibrium (“fast”) reactions from kinetic (“slow”) reactions and enforces mass conservation of chemical components via using Gauss-Jordan elimination. In addition, the decomposition of Eq. (1) also determines the number of linearly independent reactions (N_I) and selects the mass-conserved chemical components (N_C). Furthermore, based on certain assumptions, the researcher can identify the number of linearly independent equilibrium reactions (N_E).

For our case, the proposed reaction network for the bioreduction of hematite is exhibited in Table 1. According to the reaction network, we can then conduct the matrix decomposition as shown in Table 2 by using BIOGEOCHEM 1.0. Nevertheless, based on the reference (Burgos et al., 2002), R2 is relative to certain crystalline oxide surfaces, so Eq. (2) was employed to substitute for Eq. (13), the mass action for R2:

$$[\equiv \text{FeOOH}]_T = [\equiv \text{FeOOH}] + [\equiv \text{FeOOFe(II)}^+] = K_{\text{TSS}}^e [\text{Fe}_2\text{O}_3] \quad (2)$$

where $K_{\text{TSS}}^e = \frac{S_A N_S}{N_A} \text{MW}_{\text{Fe}_2\text{O}_3}$

where $[\equiv \text{FeOOH}]_T$ is the total hematite surface site concentration (mol sites L^{-1}), K_{TSS}^e is the

TABLE 1. Reaction Network of Bioreduction of Hematite.

No.	Reaction	Type
R1	$2\text{Fe}_2\text{O}_3 + \text{lactate}^- + 7\text{H}^+ \Leftrightarrow 4\text{Fe}^{2+} + \text{acetate}^- + \text{HCO}_3^- + 4\text{H}_2\text{O}$	slow
R2	$\text{Fe}_2\text{O}_3(\text{bulk}) + \text{H}_2\text{O} \Leftrightarrow 2[\equiv\text{FeOOH}](\text{surface})$	fast
R3	$\equiv\text{FeOOH} + \text{Fe}^{2+} \Leftrightarrow \equiv\text{FeOOFe(II)}^+ + \text{H}^+$	fast
R4	$5\text{lactate}^- + 4\text{CO}_2 + \text{H}_2\text{O} + \text{NH}_4^+ \Leftrightarrow \text{DMRB} + 5\text{acetate}^- + 4\text{HCO}_3^- + 5\text{H}^+$	slow
R5	$\text{HPIPES} \Leftrightarrow \text{PIPES}^- + \text{H}^+$	fast

TABLE 2. Matrix Decomposition form the Reaction Network.

$(N_I - N_E)$ Kinetic-variable Equations:

$$\frac{d([\text{Fe}^{2+}] + [\equiv\text{FeOOFe(II)}^+])}{dt} = 4R_1 \quad (3)$$

$$\frac{d[\text{DMRB}]}{dt} = R_4 \quad (4)$$

N_C Mass Conservation Equations:

$$\text{Total } [\text{Fe}_2\text{O}_3] = [\text{Fe}_2\text{O}_3] + 0.5 [\text{Fe}^{2+}] + 0.5 [\equiv\text{FeOOH}] + [\equiv\text{FeOOFe}^+] \quad (5)$$

$$\text{Total } [\text{lactate}^-] = [\text{lactate}^-] + 0.25 [\text{Fe}^{2+}] + 0.25 [\equiv\text{FeOOFe}^+] + 5 [\text{DMRB}] \quad (6)$$

$$\text{Total } [\text{H}^+] = [\text{H}^+] + 1.75 [\text{Fe}^{2+}] + 0.75 [\equiv\text{FeOOFe}^+] - 5 [\text{DMRB}] - [\text{PIPES}^-] \quad (7)$$

$$\text{Total } [\text{acetate}^-] = -0.25 [\text{Fe}^{2+}] + [\text{acetate}^-] - 0.25 [\equiv\text{FeOOFe}^+] - 5 [\text{DMRB}] \quad (8)$$

$$\text{Total } [\text{HCO}_3^-] = -0.25 [\text{Fe}^{2+}] + [\text{HCO}_3^-] - 0.25 [\equiv\text{FeOOFe}^+] - 4 [\text{DMRB}] \quad (9)$$

$$\text{Total } [\text{CO}_2] = [\text{CO}_2] + 4 [\text{DMRB}] \quad (10)$$

$$\text{Total } [\text{NH}_4^+] = [\text{NH}_4^+] + [\text{DMRB}] \quad (11)$$

$$\text{Total } [\text{HPIPES}] = [\text{HPIPES}] + [\text{PIPES}^-] \quad (12)$$

N_E Mass Action Equations:

$$\frac{d[\equiv\text{FeOOH}]}{dt} = R_2 - R_3; \quad R_2 = \infty \quad \Rightarrow \quad \frac{[\equiv\text{FeOOH}]^2}{[\text{Fe}_2\text{O}_3]} = K_2^e \quad (13)$$

$$\frac{d[\equiv\text{FeOOFe}]}{dt} = R_3; \quad R_3 = \infty \quad \Rightarrow \quad \frac{[\equiv\text{FeOOFe}][\text{H}^+]}{[\equiv\text{FeOOH}][\text{Fe}^{2+}]} = K_3^e \quad (14)$$

$$\frac{d[\text{PIPES}^-]}{dt} = R_5; \quad R_5 = \infty \quad \Rightarrow \quad \frac{[\text{PIPES}^-][\text{H}^+]}{[\text{HPIPES}]} = K_5^e \quad (15)$$

“lumped” equilibrium constant for the total surface sites, S_A is the hematite unit surface area ($\text{m}^2 \text{g}^{-1}$), N_S is the surface site density (sites m^{-2}), N_A is Avagadro’s number (sites mol^{-1}), and $\text{MW}_{\text{Fe}_2\text{O}_3}$ is the molecular weight of hematite (160g mol^{-1}). In our case, we have assumed a site density of 52 sites nm^{-2} (Jeon et al., 2001). Using the estimated N_S value of 52 sites nm^{-2} and the measured surface area of $9.04 \text{m}^2 \text{g}^{-1}$ (Burgos et al., 2002); thus, K_{TSS}^e for Eq. (2) is calculated as 0.125. Similarly, for R3, the “Freundlich equation” is proposed to substitute for Eq. (14) based on the concept of the attachment of the material to be adsorbed to adsorbent at an available adsorption site (Snoeyink and Summers, 1999); thus, R3 can be described as:

$$[\equiv\text{FeOOFe(II)}^+] = K[\text{Fe}^{2+}]^n \quad (16)$$

where K is the Freundlich capacity factor, and n is the Freundlich intensity parameter. For our study, because both Fe^{2+} and total $[\text{Fe}^{2+}] = [\text{Fe}^{2+}] + [\equiv\text{FeOOFe(II)}^+]$ were measured, the parameters, K and n , can be determined via the “best fit” equation using a spreadsheet. Finally, the logarithm equilibrium constant for PIPES buffering ($\log K_5^e$) is equal to -6.8 according to the product information (Sigma-Aldrich, St. Louis, MO).

The most important task in batch simulation is to determine the rate formulations and parameters for the kinetic reactions. Four rate formulations for R1 will be tested: (1) a physically-based formulation proposed to be first-order with respect to “free” hematite surface sites, $\equiv\text{FeOOH}$, (Eq. 17), (2) a dual Monod kinetic rate formulation with respect to the concentrations of lactate and $\equiv\text{FeOOH}$ (Eq. 18), (3) a dual Monod kinetic with inhibition of ferrous iron (Eq. 19), and (4) a dual Monod kinetics with inhibition of ferrous iron and the effect of DMRB (Eq. 20).

$$R_1 = K_{\text{fss}} [\equiv \text{FeOOH}] \quad (17)$$

$$R_1 = U_{\text{max}} \frac{[\text{lactate}]}{(k_L + [\text{lactate}])} \times \frac{[\equiv \text{FeOOH}]}{(K_F + [\equiv \text{FeOOH}])} \quad (18)$$

$$R_1 = V_{\text{max}} \frac{[\text{lactate}]}{(k_{\text{La}} + [\text{lactate}])} \times \frac{[\equiv \text{FeOOH}]}{\{[\equiv \text{FeOOH}] + K_{\text{Fe}} (1 + \frac{[\text{Fe}^{2+}]}{K_I})\}} \quad (19)$$

$$R_1 = W_{\text{max}} \frac{[\text{lactate}]}{(k_{\text{Lb}} + [\text{lactate}])} \times \frac{[\equiv \text{FeOOH}]}{\{[\equiv \text{FeOOH}] + K_{\text{Fe}\alpha} (1 + \frac{[\text{Fe}^{2+}]}{K_{\text{I}\alpha}})\}} \times [\text{DMRB}]^\alpha \quad (20)$$

where K_{fss} is the rate constant, U_{max} , V_{max} , and W_{max} are the maximum specific reaction rate, K_L , K_F , k_{La} , K_{Fe} , k_{Lb} , and $K_{\text{Fe}\alpha}$ are the half-velocity constant, K_I and $K_{\text{I}\alpha}$ are the inhibition coefficient, and α is the effort coefficient of DMRB. In addition, a formal bacteria growth kinetic with cell decay was used to describe R4 (Eq. 21; Metcalf and Eddy, 2003).

$$R_4 = \frac{B_{\text{max}}}{Y_s} \frac{[\text{lactate}]}{(K_b + [\text{lactate}])} \times [\text{DMRB}] - K_d [\text{DMRB}] \quad (21)$$

where B_{max} is the maximum specific growth rate of DMRB, Y_s is the substrate consumed coefficient, K_b is the half-velocity constant of bacteria growth rate, and K_d is the endogenous decay coefficient.

2.2 Modeling Methods for Column Systems

For the reactive transport system, the ordinary differential equations in a reactive batch system can be replaced with the transport equation as shown by Fang et al (2003):

$$\theta \frac{\partial C_i}{\partial t} - L(C_i) + QC_i = \theta r_i \Big|_N = \sum_{k=1}^N (v_{ik} - \mu_{ik}) R_k, \quad i \in M; \quad \text{where } L(C_i) = \frac{\partial}{\partial x} (\theta D \frac{\partial C_i}{\partial x}) - v \frac{\partial C_i}{\partial x} \quad (22)$$

TABLE 3. Initial Concentrations in the Batch Experiments.

Batch Experiment	[Sediment] (g/ml)	[Fe(III)] (mM)	[lactate] (mM)	[DMRB] (cells/mL)
#4	0.0682	25	0.69	10^8
#5	0.0683	25	3.75	10^9
#6	0.0683	25	3.75	10^7

TABLE 4. Column Experimental Conditions.

Column	Feed Solution			Column Packed		
	Flow Rate (PV/day)	Lactate (mM)	pH	PIPES (mM)	SANDS (grams)	DMRB (Cells/ml)
A-D	2.72	8.63	7	45	9.069	10^8
K-N	1.50	6.00	7	45	9.009	10^8
G-J	0.40	1.45	7	45	9.007	10^8

where θ is the effective moisture content, L is the advection-dispersion/diffusion operator, Q is the flow rate, D is the hydrodynamic dispersion coefficient, x is the distance, and v is the velocity. In batch system, we defined R1 and R4 as kinetic reactions and defined R2, R3, and R5 as equilibrium reactions; however, in column system we have to change R2 and R3 into a kinetic reaction. The reason is that the influent solution does not permeate throughout the entire column immediately. Therefore, Eq.(2) and Eq (16) are modified as:

$$R_2 = K_2^b \left\{ K_{TSS}^e [Fe_2O_3] - \left([\equiv FeOOH] + [\equiv FeOFe(II)^+] \right) \right\} \quad (23)$$

$$R_3 = K_3^b \left(K [Fe^{2+}]^n - [\equiv FeOFe(II)^+] \right) \quad (24)$$

where K_2^b and K_3^b are the backward rate constant. In addition to R2 and R3, the rest of rate formulations and parameters are the same as the batch simulation in order to inspect the accuracy of the resolved parameters and our proposed rate formulations.

2.3 Experimental Conditions

In our study, four species, Fe(II), H^+ , lactate, and acetate (incomplete), and one operational quantity, total $[Fe^{2+}] = [Fe^{2+}] + [\equiv FeOFe(II)^+]$, were measured in batch experiments. Table 3 specifies the initial concentrations in the batch experiments. In addition, three species, Fe(II), lactate, and acetate (incomplete), were measured in column experiments. The column experimental condition is shown in Table 4.

3. RESULTS

From Figures 1 to 3, we can know that our proposed formulations with the determined parameters (shown in Table 5) are reasonably good to express the R1 rate in batch system. We also observe that the parameters' values of fourth proposed formulation are identical for each batch experiments. For column simulation, the determined values for K_2^b is represented

TABLE 5. Determined Value of Parameters in Batch System.

Experiments	Rate Eq. (1)	Rate Eq. (2)	Rate Eq. (3)	Rate Eq. (4)
#4	$K_{fss} = 0.0038$	$U_{max} = 5.24E-5$ $K_L = 7.93E-4$ $K_F = 4.26E-3$	$V_{max} = 8.50E-5$ $K_{La} = 9.00E-3$ $K_{Fe} = 3.50E-5$ $K_I = 6.00E-4$	$W_{max} = 1.5E-3$ $K_{Lb} = 5.0E-3$ $K_{Fea} = 3.5E-5$ $K_{Ia} = 6.0E-4$ $\alpha = 0.65$
#5	$K_{fss} = 0.0095$	$U_{max} = 5.50E-5$ $K_L = 7.00E-4$ $K_F = 4.00E-3$	$V_{max} = 3.20E-5$ $K_{La} = 9.80E-3$ $K_{Fe} = 6.00E-6$ $K_I = 1.00E-5$	$W_{max} = 1.5E-3$ $K_{Lb} = 5.0E-3$ $K_{Fea} = 3.5E-5$ $K_{Ia} = 6.0E-4$ $\alpha = 0.65$
#6	$K_{fss} = 0.0042$	$U_{max} = 2.20E-5$ $K_L = 5.50E-4$ $K_F = 3.30E-3$	$V_{max} = 1.80E-5$ $K_{La} = 9.60E-3$ $K_{Fe} = 2.00E-6$ $K_I = 1.00E-5$	$W_{max} = 1.5E-3$ $K_{Lb} = 5.0E-3$ $K_{Fea} = 3.5E-5$ $K_{Ia} = 6.0E-4$ $\alpha = 0.65$

TABLE 6. Determined Values of the R2 Rate Backward Constant.

Experiment	K_2^b (M/hr)			
	Rate Eq.(1)	Rate Eq. (2)	Rate Eq. (3)	Rate Eq. (4)
Column A-D	23.83E-4	23.83E-4	0.635E-4	0.635E-4
Column K-N	3.971E-4	7.943E-4	0.953E-4	0.953E-4
Column G-J	1.588E-4	1.588E-4	1.191E-4	1.194E-4

in Table 6, and K_3^b is identical (1.0 M/hr) for all column simulations. From Figures 5 to 7, we can clearly observe that only the fourth proposed R1 rate formulation could provide the best overall fit with the experimental data for all flow rates. In addition, as mentioned above, we changed R2 and R3 from equilibrium to kinetic reactions for column simulations; therefore, we employed the data of batch experiment #4 with the fourth proposed R1 rate formulation to justify the consistency of our entire simulations between batch and column system. From Figure 4, we demonstrate that Eq. (23) and Eq. (24) are applicable to the batch system.

4. CONCLUSIONS

In our research, four rate formulations were proposed to describe the key reaction of direct bioreduction of hematite in sediments from a field site, and these formulations were examined by conducting the simulations in both batch and column systems. Simulation results indicated that while all rate formulations can adequately model batch experiments, only the formulation based on dual Monod kinetics with inhibition of ferrous iron and the effect of DMRB is “universal”. Besides, only this rate formulation can be upscaled to column experiments. Furthermore, iterative modeling between batch and column experiments revealed that the equilibrium assumptions for surface hydration of hematite and adsorption of biogenic ferrous irons onto hematite may have to be revoked and substituted with kinetic rate formulations.

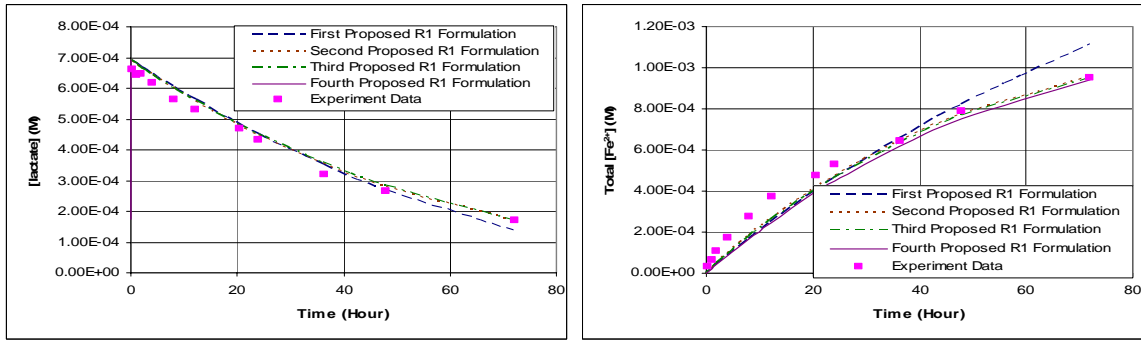


FIGURE 1. Simulation Results for Batch Exp. #4.

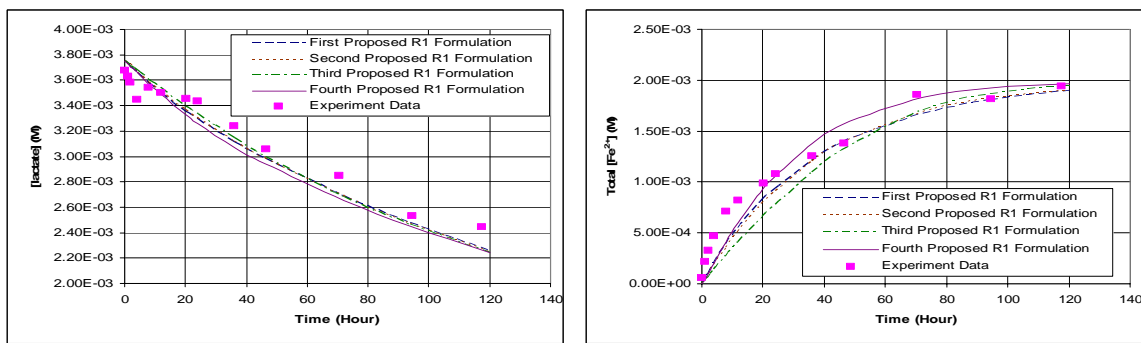


FIGURE 2. Simulation Results for Batch Exp. #5.

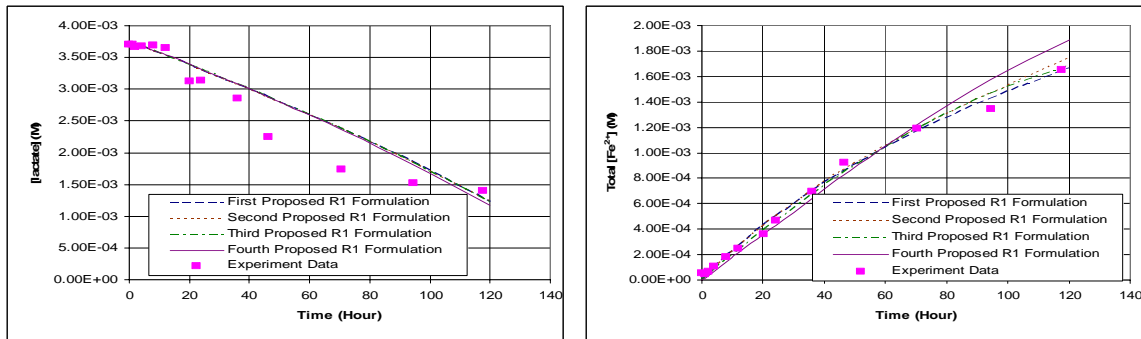


FIGURE 3. Simulation Results for Batch Exp. #6.

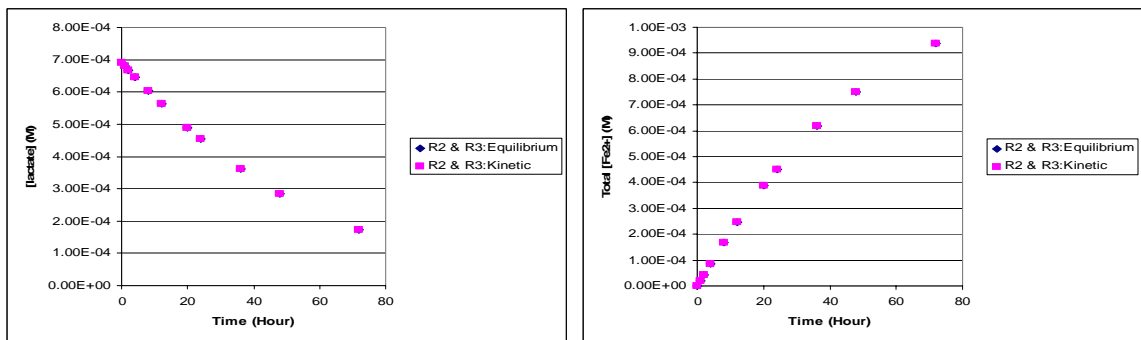


FIGURE 4. Comparison between the Equilibrium and Kinetic Rate Formulation for R2 and R3 with Forth Proposed R1 rate Formulation.

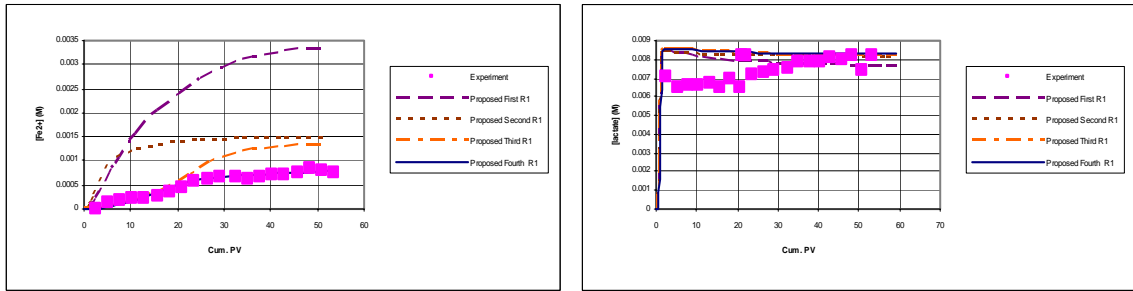


FIGURE 5. Simulation Results for Column A-D.

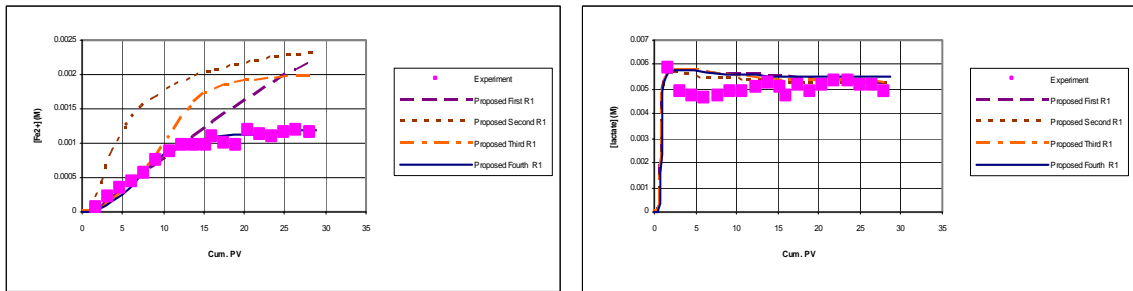


FIGURE 6. Simulation Results for Column K-N.

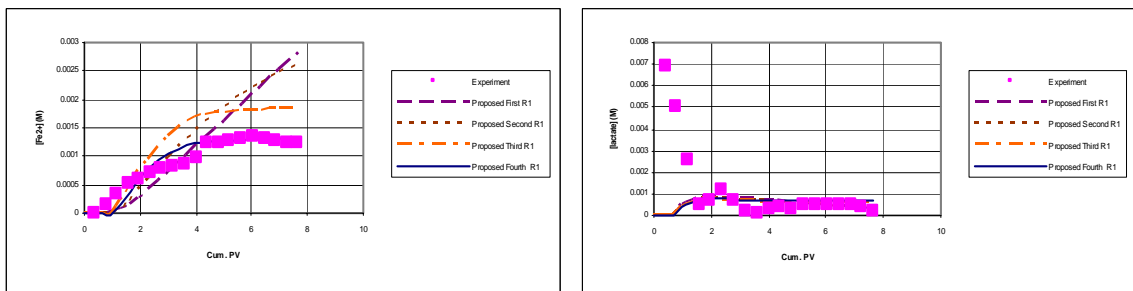


FIGURE 7. Simulation Results for Column G-J.

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