

# TEAPREV: A numerical simulation model of Terminal Electron-Accepting Processes in a Representative Elementary Volume of subsurface sediment

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## Introduction

Quantitative models of coupled microbial-geochemical processes are required to predict and interpret the results of in situ biostimulation procedures designed to promote immobilization of metal-radionuclide contaminants. Of particular importance is the development of models which take into account the influence of microbial physiological properties as well as thermodynamic constraints on biological and abiotic reactions. TEAPREV represents a comprehensive synthesis of previously-developed approaches to modeling terminal electron-accepting processes and associated geochemical reactions in ethanol-and/or acetate-stimulated sediments. The choice of ethanol and acetate as carbon/electron donors for biostimulation is based on current U.S. DOE-funded research on metal-radionuclide remediation. The basic structure of the code, however, is completely general and can be adapted to any carbon/electron donor addition. The code is intended for three major uses, the first two of which are illustrated in this poster:

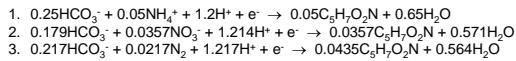
1. Interpretation/synthesis of laboratory-scale experimental data
2. Exploratory modeling of hypothetical laboratory- and/or field-scale reaction systems
3. Incorporation into field-scale reactive transport models for interpretation/synthesis of in situ biostimulation experiments

## Primary dependent variables

Variable	Initial value*	Units
1. Ethanol	0.009	(mol/L)
2. Acetate	0.0	(mol/L)
3. O <sub>2</sub>	0.0	(mol/L)
4. NO <sub>3</sub> <sup>-</sup>	0.0012	(mol/L)
5. NO <sub>2</sub> <sup>-</sup>	0.0	(mol/L)
6. MnO <sub>2</sub> (s)	0.0	(mol/L)
7. FeOOH(s)	0.3	(mol/L)
8. SO <sub>4</sub> <sup>2-</sup>	0.0011	(mol/L)
9. S <sup>0</sup> (s)	0.0	(mol/L)
10. U(VI)	0.00009	(mol/L)
11. HCO <sub>3</sub> <sup>-</sup>	0.005	(mol/L)
12. N <sub>2</sub>	0.0005	(mol/L)
13. NH <sub>4</sub> <sup>+</sup>	0.0001	(mol/L)
14. Mn(II)	0.0	(mol/L)
15. Fe(II)	0.0	(mol/L)
16. HS <sup>-</sup>	0.0	(mol/L)
17. CH <sub>4</sub>	0.0	(mol/L)
18. UO <sub>2</sub> (s)	0.0	(mol/L)
19. TOTH	0.0212	(mol/L)
20. MnCO <sub>3</sub> (s)	0.0	(mol/L)
21. FeCO <sub>3</sub> (s)	0.0	(mol/L)
22. FeS(s)	0.0	(mol/L)
23. AM	0.00005	(g/L)
24. DM	0.00005	(g/L)
25. DRM1	0.000005	(g/L)
26. DRM2	0.0000025	(g/L)
27. DRM3	0.0000025	(g/L)
28. SO4RM	0.000005	(g/L)
29. SORM	0.000005	(g/L)
30. MGM	0.000005	(g/L)

\* For simulation of batch slurry incubation experiment

## Biosynthesis Reactions



## Mineral Precipitation Reactions (MPRs)

1.  $\text{Mn}^{2+}(\text{aq}) + \text{CO}_3^{2-} = \text{MnCO}_3$
2.  $\text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-} = \text{FeCO}_3$
3.  $\text{Fe}^{2+}(\text{aq}) + \text{HS}^- = \text{FeS} + \text{H}^+$
4.  $\text{Fe}^{2+}(\text{ads}) + \text{HS}^- = \text{FeS} + \text{H}^+$
5.  $\text{FeCO}_3 + \text{HS}^- = \text{FeS} + \text{HCO}_3^-$

## Microbial Functional Groups

Description	Abbreviation	Metabolism(s)
Aerobic Microorganisms	AM	O <sub>2</sub> red coupled to ethanol or acetate oxid
Denitrifying Microorganisms	DM	O <sub>2</sub> red, NO <sub>3</sub> <sup>-</sup> red to N <sub>2</sub> coupled to ethanol or acetate oxid
Group 1 Dissimilatory Reducing Microorganisms	DRM1	NO <sub>3</sub> <sup>-</sup> red to NH <sub>4</sub> <sup>+</sup> , Mn(IV), Fe(III), U(VI) red coupled to ethanol ferm (to acetate)
Group 2 Dissimilatory Reducing Microorganisms	DRM2	NO <sub>3</sub> <sup>-</sup> red to NH <sub>4</sub> <sup>+</sup> , Mn(IV), Fe(III), U(VI) red coupled to ethanol ferm or acetate oxid
Group 3 Dissimilatory Reducing Microorganisms	DRM3	NO <sub>3</sub> <sup>-</sup> red to NH <sub>4</sub> <sup>+</sup> ; Mn(IV), Fe(III), U(VI), SO <sub>4</sub> <sup>2-</sup> , S <sup>0</sup> red coupled to ethanol ferm or acetate oxid
Sulfate Reducing Microorganisms	SO4RM	SO <sub>4</sub> <sup>2-</sup> , U(VI) <sup>b</sup> red coupled to ethanol ferm or acetate oxid
Elemental Sulfur Reducing Microorganisms	SORM	S <sup>0</sup> , U(VI) <sup>b</sup> red coupled to ethanol ferm or acetate oxid
Methanogenic Microorganisms	MGM	CH <sub>4</sub> prod coupled to ethanol ferm or acetate oxid

<sup>a</sup> NO<sub>3</sub><sup>-</sup> red by DRM3 can account for NO<sub>3</sub><sup>-</sup> red by SO4RM

<sup>b</sup> U(VI) red by SO4RM and SORM is optional

## Conceptual Overview of Reaction System

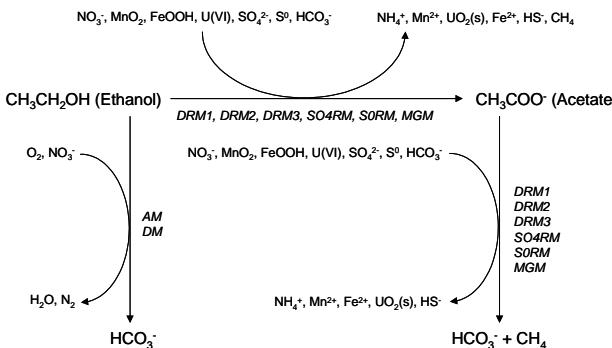


Diagram of substrate metabolism and electron flow in the current implementation of the TEAPREV simulation model.

## Metabolic energy-generating reactions (TEAPs)

Reaction	Catalyzed By
1. $\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$	AM, DM
2. $\text{CH}_3\text{CH}_2\text{OH} + 2.4\text{NO}_3^- + 0.4\text{H}^+ \rightarrow 2\text{HCO}_3^- + 1.2\text{N}_2 + 2.2\text{H}_2\text{O}$	DM
3. $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{NO}_3^- \rightarrow \text{CH}_3\text{COO}^- + 0.5\text{NH}_4^+ + 0.5\text{H}_2\text{O}$	DRM1, DRM2, DRM3
4. $\text{CH}_3\text{CH}_2\text{OH} + 2\text{MnO}_2 + 3\text{H}^+ \rightarrow \text{CH}_3\text{COO}^- + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	DRM2, DRM3
5. $\text{CH}_3\text{CH}_2\text{OH} + 4\text{FeOOH} + 7\text{H}^+ \rightarrow \text{CH}_3\text{COO}^- + 4\text{Fe}^{2+} + 7\text{H}_2\text{O}$	DRM3, SO4RM
6. $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{SO}_4^{2-} \rightarrow \text{CH}_3\text{COO}^- + 0.5\text{HS}^- + 0.5\text{H}^+ + 0.5\text{H}_2\text{O}$	MGM
7. $\text{CH}_3\text{CH}_2\text{OH} + 2\text{S}^0 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + 2\text{HS}^- + 3\text{H}^+$	DRM3, SORM
8. $\text{CH}_3\text{CH}_2\text{OH} + 0.5\text{HCO}_3^- \rightarrow \text{CH}_3\text{COO}^- + 0.5\text{CH}_4 + 0.5\text{H}^+ + 0.5\text{H}_2\text{O}$	AM, DM
9. $\text{CH}_3\text{COO}^- + \text{O}_2 \rightarrow 2\text{HCO}_3^- + \text{H}^+$	DRM2, DRM3
10. $\text{CH}_3\text{COO}^- + 1.6\text{NO}_3^- + 0.6\text{H}^+ \rightarrow 2\text{HCO}_3^- + 0.8\text{N}_2 + 0.8\text{H}_2\text{O}$	DRM2, DRM3
11. $\text{CH}_3\text{COO}^- + \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+ \rightarrow 2\text{HCO}_3^- + \text{NH}_4^+$	DRM2, DRM3
12. $\text{CH}_3\text{COO}^- + 4\text{MnO}_2 + 7\text{H}^+ \rightarrow 2\text{HCO}_3^- + 4\text{Mn}^{2+} + 4\text{H}_2\text{O}$	DRM2, DRM3
13. $\text{CH}_3\text{COO}^- + 8\text{FeOOH} + 15\text{H}^+ \rightarrow 2\text{HCO}_3^- + 8\text{Fe}^{2+} + 12\text{H}_2\text{O}$	DRM3, SO4RM
14. $\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{HS}^-$	MGM
15. $\text{CH}_3\text{COO}^- + 4\text{S}^0 + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 4\text{HS}^- + 5\text{H}^+$	DRM3, SORM
16. $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{CH}_4$	DRM2, DRM3
17. $\text{CH}_3\text{CH}_2\text{OH} + 2\text{UO}_2(\text{CO}_3)^{2-} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + 4\text{HCO}_3^- + 2\text{UO}_2(\text{s}) + \text{H}^+$	DRM2, DRM3, [SO4RM, SORM]*
18. $\text{CH}_3\text{COO}^- + 4\text{UO}_2(\text{CO}_3)^{2-} + 4\text{H}_2\text{O} \rightarrow 10\text{HCO}_3^- + 4\text{UO}_2(\text{s}) + \text{H}^+$	DRM2, DRM3, [SO4RM, SORM]*

\* Reduction of U(VI) by SO4RM and SORM is optional

## Substrate Partitioning

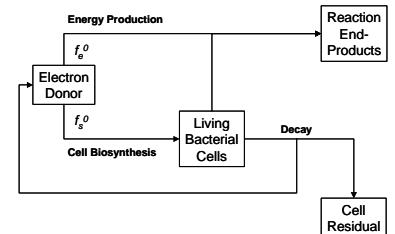


Diagram of substrate partitioning between energy production and cell biosynthesis during microbial respiration. Modified from Fig. 2.1 in Rittmann, B.E. and P.L. McCarty. 2001. Environmental Biotechnology. McGraw-Hill, Boston.

Substrate partitioning is determined by the computed free energy of a given metabolic reaction, assuming a fixed energy transfer efficiency ( $\varepsilon$  value) of 0.6, and that pyruvate is the central carbon compound used in biosynthesis (Rittmann and McCarty, 2001).

## Key end-products of equilibrium speciation reactions

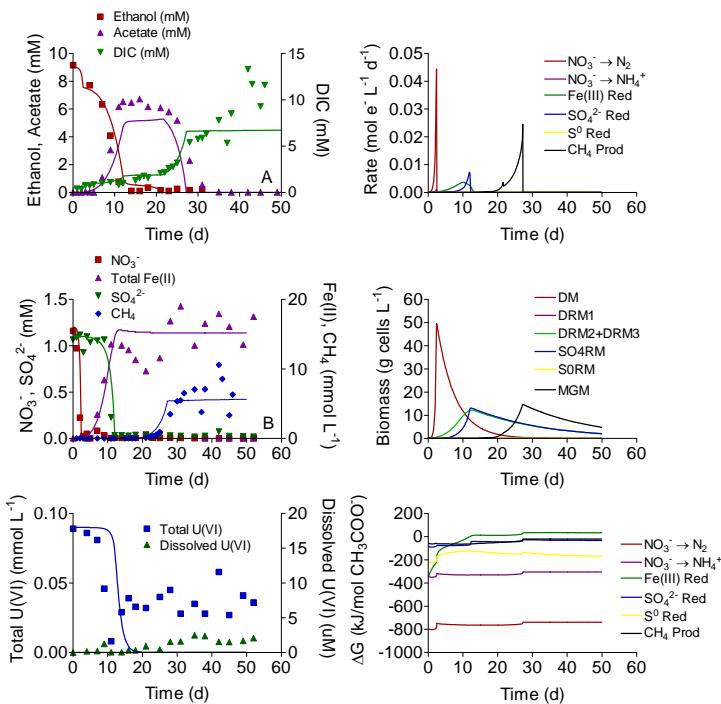
Name	Description	Role in Simulation
Mn <sup>2+</sup> (aq)	Conc of aqueous Mn <sup>2+</sup>	Participation in SRRs, MPRs
Mn <sup>2+</sup> (ads)	Conc of adsorbed Mn <sup>2+</sup>	Attenuation of MnO <sub>2</sub> reduction; SRRs
Fe <sup>2+</sup> (aq)	Conc of aqueous Fe <sup>2+</sup>	Participation in SRRs, MPRs
Fe <sup>2+</sup> (ads)	Conc of adsorbed Fe <sup>2+</sup>	Attenuation of Fe(III) reduction; SRRs, MPRs
{CH <sub>3</sub> COO <sup>-</sup> }	Activity of CH <sub>3</sub> COO <sup>-</sup>	Free energy of TEAPs
{NO <sub>3</sub> <sup>-</sup> }	Activity of NO <sub>3</sub> <sup>-</sup>	Free energy of TEAPs, SRRs
{UO <sub>2</sub> (CO <sub>3</sub> ) <sup>2-</sup> }	Activity of U(VI)-carbonate	Free energy of TEAPs, SRRs
{SO <sub>4</sub> <sup>2-</sup> }	Activity of SO <sub>4</sub> <sup>2-</sup>	Free energy of TEAPs, SRRs
{NH <sub>4</sub> <sup>+</sup> }	Activity of NH <sub>4</sub> <sup>+</sup>	Free energy of TEAPs, SRRs
{H <sup>+</sup> }*	Activity of H <sup>+</sup>	Free energy of TEAPs, SRRs
{Mn <sup>2+</sup> }	Activity of Mn <sup>2+</sup> (aq)	Free energy of TEAPs, SRRs, MPRs
{Fe <sup>2+</sup> }	Activity of Fe <sup>2+</sup> (aq)	Free energy of TEAPs, SRRs, MPRs
{HS <sup>-</sup> }	Activity of HS <sup>-</sup>	Free energy of TEAPs, SRRs, MPRs
{HCO <sub>3</sub> <sup>-</sup> }	Activity of HCO <sub>3</sub> <sup>-</sup>	Free energy of TEAPs, SRRs, MPRs
{CH <sub>4</sub> (aq)}	Activity of CH <sub>4</sub> (aq)	Free energy of TEAPs, SRRs, MPRs

\* pH was fixed at 6.9 for all simulations

## Secondary Redox Reactions (SRRs)

1.  $0.5\text{Mn}^{2+}(\text{aq}) + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} \rightarrow 0.5\text{MnO}_2 + \text{H}^+$
2.  $0.5\text{Mn}^{+} + 0.25\text{O}_2 + 0.25\text{H}_2\text{O} \rightarrow 0.5\text{MnO}_2 + 0.5\text{H}^+$
3.  $0.5\text{MnCO}_3 + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} \rightarrow 0.5\text{MnO}_2 + 0.5\text{HCO}_3^- + 0.5\text{H}^+$
4.  $\text{Fe}^{2+}(\text{aq}) + 0.25\text{O}_2 + 1.5\text{H}_2\text{O} \rightarrow \text{FeOOH} + 2\text{H}^+$
5.  $=\text{Fe}^{+} + 0.25\text{O}_2 + 1.0\text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{H}^+$
6.  $\text{FeCO}_3 + 0.25\text{O}_2 + 1.5\text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{HCO}_3^- + \text{H}^+$
7.  $\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$
8.  $\text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$
9.  $\text{FeS} + 2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$
10.  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$
11.  $\text{Fe}^{2+}(\text{aq}) + 0.2\text{NO}_3^- + 1.4\text{H}_2\text{O} \rightarrow \text{FeOOH} + 0.1\text{N}_2 + 1.8\text{H}^+$
12.  $=\text{Fe}^{+} + 0.2\text{NO}_3^- + 1.4\text{H}_2\text{O} \rightarrow \text{FeOOH} + 0.1\text{N}_2 + 0.8\text{H}^+$
13.  $\text{FeCO}_3 + 0.2\text{NO}_3^- + 1.4\text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{HCO}_3^- + 0.1\text{N}_2 + 0.8\text{H}^+$
14.  $\text{HS}^- + 1.6\text{NO}_3^- + 0.6\text{H}^+ \rightarrow \text{SO}_4^{2-} + 0.8\text{N}_2 + 0.8\text{H}_2\text{O}$
15.  $\text{S}^0 + 1.2\text{NO}_3^- + 0.4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 0.6\text{N}_2 + 0.8\text{H}_2\text{O}$
16.  $\text{FeS} + 1.6\text{NO}_3^- + 1.6\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 0.8\text{N}_2 + 0.8\text{H}_2\text{O}$
17.  $\text{Fe}^{2+}(\text{aq}) + 0.5\text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{FeOOH} + 0.5\text{Mn}^{2+} + \text{H}^+$
18.  $=\text{Fe}^{+} + 0.5\text{MnO}_2 + 0.5\text{H}_2\text{O} \rightarrow \text{FeOOH} + 0.5\text{Mn}^{2+} + \text{H}^+$
19.  $\text{FeCO}_3 + 0.5\text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{FeOOH} + 0.5\text{Mn}^{2+} + \text{HCO}_3^-$
20.  $0.5\text{HS}^- + 0.5\text{MnO}_2 + 1.5\text{H}^+ \rightarrow 0.5\text{S}^0 + 0.5\text{Mn}^{2+} + \text{H}_2\text{O}$
21.  $\text{FeS} + 1.5\text{MnO}_2 + 3\text{H}^+ \rightarrow \text{FeOOH} + \text{S}^0 + 1.5\text{Mn}^{2+} + \text{H}_2\text{O}$
22.  $0.5\text{HS} + \text{FeOOH} + 3\text{H}^+ \rightarrow 0.5\text{S}^0 + \text{Fe}^{2+} + 2\text{H}_2\text{O}$
23.  $4\text{S}^0 + 4\text{H}_2\text{O} \rightarrow 3\text{HS}^- + \text{SO}_4^{2-} + 5\text{H}^+$
24.  $0.125\text{NH}_4^+ + 0.25\text{O}_2 \rightarrow 0.125\text{NO}_3^- + 0.125\text{H}_2\text{O} + 0.25\text{H}^+$
25.  $\text{UO}_2(\text{s}) + 0.5\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + \text{H}_2\text{O}$
26.  $\text{UO}_2(\text{s}) + 0.4\text{NO}_3^- + 2\text{HCO}_3^- + 0.4\text{H}^+ \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + 0.2\text{N}_2 + 1.2\text{H}_2\text{O}$
27.  $\text{UO}_2(\text{s}) + \text{MnO}_2 + 2\text{HCO}_3^- + 2\text{H}^+ \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + \text{Mn}^{2+} + 2\text{H}_2\text{O}$

## Model Calibration: Simulation of FRC Area 2 Sediment Slurry Experiment



Results of simulation of the ORNL Area 2 sediment slurry experiment. Data points show means of duplicate slurries; solid lines show simulation results.

## Key Kinetic Equations

### TEAPs: Soluble electron acceptors

$$\text{RTEAP(i,j)} = V_{\max}(i,j) * \text{FED}(i,j) * \text{FEA}(i,j) * \text{FTTEAP}(i) * \text{FIED}(i,j) * \text{FIEA}(i,j) * \text{BM}(i) \text{ (mol e^-/L/d)}$$

$$V_{\max}(i,j) = \mu_{\max}(i,j) / Y_{\text{Cells}}(i,j)$$

$\mu_{\max}$  = maximum specific growth rate for cells catalyzing RTEAP(i,j) (1/d)  
 $Y_{\text{Cells}}(i,j)$  = Yield coefficient for RTEAP(i,j) (mol cells/electron)  
 $= f_{\text{SO}_4^{2-}}(i,j) * \text{gmwcells}/\text{biomasscofdenom}(i,j)$

### TEAPs: Solid-phase electron acceptors

$$\text{RTEAP(i,j)} = V_{\max}(i,j) * \text{FED}(i,j) * \text{FEA}(i,j) * \text{FTTEAP}(i) * \text{FIED}(i,j) * \text{FIEA}(i,j) * \text{BM}(i) / (\text{KmDRM}(i) + \text{BM}(i))$$

$$V_{\max}(i,j) = V_{\max}\text{EA}(i,j) * \text{EAfss}$$

$V_{\max}\text{EA}(i,j)$  = maximum reduction rate constant at high biomass (mol/mol sites/d)  
 $\text{EAfss}$  = concentration of free surface sites (mol/L)

$$\text{KmDRM}(i) = \text{half-saturation constant for the biomass-dependent rate of e- transfer to free surface sites (g cells/mol free surface sites)}$$

$$\text{FED}(i,j) = \text{ED}(i,j) / (\text{KmED}(i,j) + \text{ED}(i,j))$$

$$\text{ED}(i,j) = \text{concentration of e- donor for TEAP}(i) \text{ (mol/L)}$$

$\text{KmED}(i,j)$  = half-saturation constant for uptake of ED(i,j) via RTEAP(i,j) (mol/L)

$$\text{FEA}(i,j) = \text{EA}(i,j) / (\text{KmED}(i,j) + \text{EA}(i,j))$$

$$\text{EA}(i,j) = \text{concentration of e- acceptor TEAP}(i) \text{ (mol/L)}$$

$$\text{KmEA}(i,j) = \text{half-saturation constant for uptake of EA}(i,j) \text{ via RTEAP}(i,j) \text{ (mol/L)}$$

$$\text{FTTEAP}(i) = \max(0, (1 - \exp(d\text{GrxnTEAP}(i) * \text{nelecTEAP}(i) * \text{Gmin}(i))) / 0.008314 / (273 + \text{Temp}))$$

$d\text{GrxnTEAP}(i)$  = free energy for TEAP(i) (kJ/electron)  
 $\text{nelecTEAP}(i)$  = number of e- transferred in TEAP(i)  
 $\text{dGmin}(i)$  = minimum free energy for biological energy conservation (-20 kJ/rxn)  
 $\text{Temp}$  = temperature (K)

$$\text{FIED}(i,j) = \prod_k \text{KmIED}(i,j,k) / (\text{KmIED}(i,j,k) + \text{EDI}(i,j,k))$$

$$\text{KmIED}(i,j,k) = \text{half-saturation concentration of e- donor k inhibiting RTEAP}(i,j)$$

$\text{EDI}(i,j,k)$  = concentration of e- donor k inhibiting RTEAP(i,j)

$$\text{FIEA}(i,j) = \prod_k \text{KmIEA}(i,j,k) / (\text{KmIEA}(i,j,k) + \text{EA}(i,j,k))$$

$$\text{KmIEA}(i,j,k) = \text{half-saturation concentration of e- acceptor k inhibiting RTEAP}(i,j)$$

$$\text{EA}(i,j,k) = \text{concentration of e- acceptor k inhibiting RTEAP}(i,j)$$

$$\text{BM}(i) = \text{Biomass of microorganisms catalyzing TEAP}(i) \text{ (g cells/L)}$$

$$\text{BM}(i) = \text{BM}(i) / \text{ESfss} \text{ (g cells/mol free surface sites)}$$

### TEAPs: Microbial Biosynthesis

$$\text{RBM}(i) = \sum_i \text{fsO}(i,j) * \text{RTEAP}(i^*, j^*) * \text{ProdcofBS}(i, j^*) * \text{gmwcells}$$

$$\text{RBM}(i) = \text{Total rate of BM}(i) \text{ biosynthesis (g cells/L/d)}$$

$$\text{fsO}(i,j) = \text{Fraction of e- donor used to produce biomass in RTEAP}(i^*, j^*)$$

$$\text{RTEAP}(i^*, j^*) = \text{Rate of electron transfer coupled to RTEAP}(i^*, j^*) \text{ (mol e^-/L/d)}$$

$$i^*, j^* \text{ refer to RTEAPs that involve BM}(i)$$

$$\text{ProdcofBS}(i, j^*) = \text{fNNH4}(i,j) * 0.05 + \text{fNNO3}(i,j) * 0.0357 + \text{fNN2}(i,j) * 0.0435$$

$$\text{biomasscofdenom}(i,j) = \text{fNNH4}(i,j) * 20.0 + \text{fNNO3}(i,j) * 28.0 + \text{fNN2}(i,j) * 23.0$$

$$\text{gmwcells} = \text{molecular weight of cell biomass (g/mol)}$$

## Secondary Redox Reactions

$$\text{RSRR}(i) = k_{\text{RedOxid}} \times \text{Red} \times \text{Oxid} \times \text{FTSRR}(i, j)$$

$$k_{\text{RedOxid}} = \text{second-order reaction rate coefficient 1/(mol/L/d)}$$

$$\text{Red} = \text{Concentration of reducing reactant}$$

$$\text{Oxid} = \text{Concentration of oxidizing reactant}$$

$$\text{FTSRR}(i) = \max(0, (1 - \exp(d\text{GrxnSRR}(i))) / 0.008314 / (273 + \text{Temp}))$$

$$d\text{GrxnSRR}(i) = \text{free energy for SRR}(i) \text{ (kJ/electron)}$$

$$\text{Temp} = \text{temperature (K)}$$

## Mineral Precipitation Reactions

$$\text{RMPR}(i) = k_{\text{precip}}(i) \times (\text{OMEGA}(i) - 1.0), \text{OMEGA}(i) \geq 1$$

$$\text{RMPR}(i) = k_{\text{diss}}(i) \times \text{Min}(i) \times (\text{OMEGA}(i) - 1.0), \text{OMEGA}(i) < 1$$

$$k_{\text{precip}}(i) = \text{mineral i precipitation rate constant (mol/L/d)}$$

$$k_{\text{diss}}(i) = \text{mineral i dissolution rate constant (1/d)}$$

$$\text{Min}(i) = \text{concentration of mineral i (mol/L)}$$

$$\text{OMEGA}(i) = \exp(d\text{GrxnMPR}(i)) / 0.008314 / (273 + \text{Temp})$$

$$d\text{GrxnMPR}(i) = \text{free energy for RMPR}(i) \text{ (kJ/mol)}$$

$$\text{Temp} = \text{temperature (K)}$$

## TOO MUCH

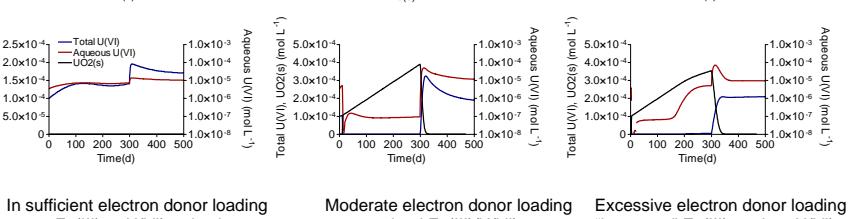
In sufficient electron donor loading  
=> no Fe(III) or U(VI) reduction

## JUST RIGHT

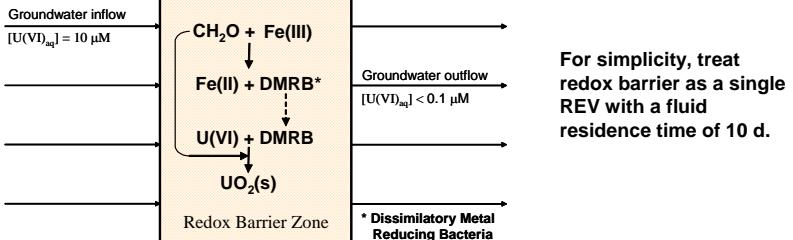
Moderate electron donor loading  
=> sustained Fe(III)/U(VI) reduction throughout reduction phase

## TOO MUCH

Excessive electron donor loading  
"burns out" Fe(III) pool => U(VI) scavenging failure after ca. 150 d; extra FeS produced does not really retard UO<sub>2</sub>(s) oxidation



## Exploratory Simulation: Effect of Electron Donor Loading on In Situ Redox Barrier Performance



### Simulation conditions:

Initial concentrations: O<sub>2</sub> = 200 μM; NO<sub>3</sub><sup>-</sup> = 1 mM; FeOOH = 50 mmol/L; SO<sub>4</sub><sup>2-</sup> = 1 mM

Input concentrations: O<sub>2</sub> = 200 μM; NO<sub>3</sub><sup>-</sup> = 1 mM; SO<sub>4</sub><sup>2-</sup> = 1 mM, Ethanol = 0.1-10 mM

Stop ethanol input after 300 days and allow system to reoxidize