Joint Breakout Session

Reactive Transport Modeling
and
Rates and Mechanisms of Metal Reduction and Oxidation

Annual Meeting DOE Field Research Center

10/26/05

Compilation of Bacterial Metal Reduction Rates and Kinetic Database Development

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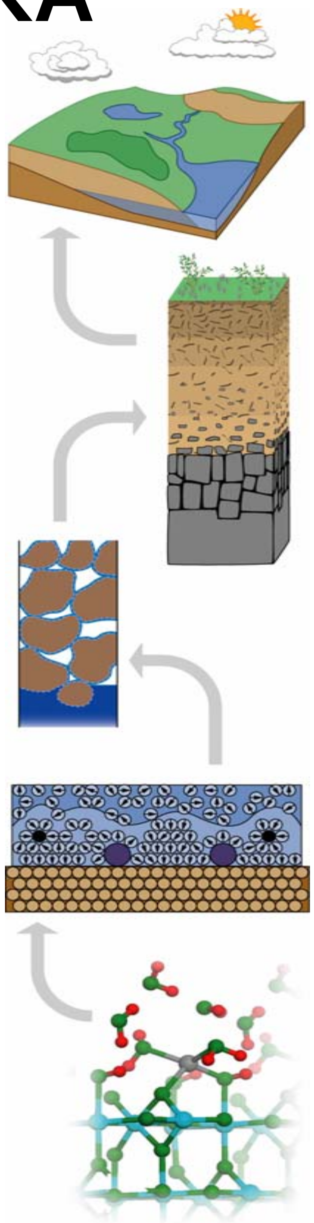
(CEKA)

NABIR
Field Research Center

History & Objectives

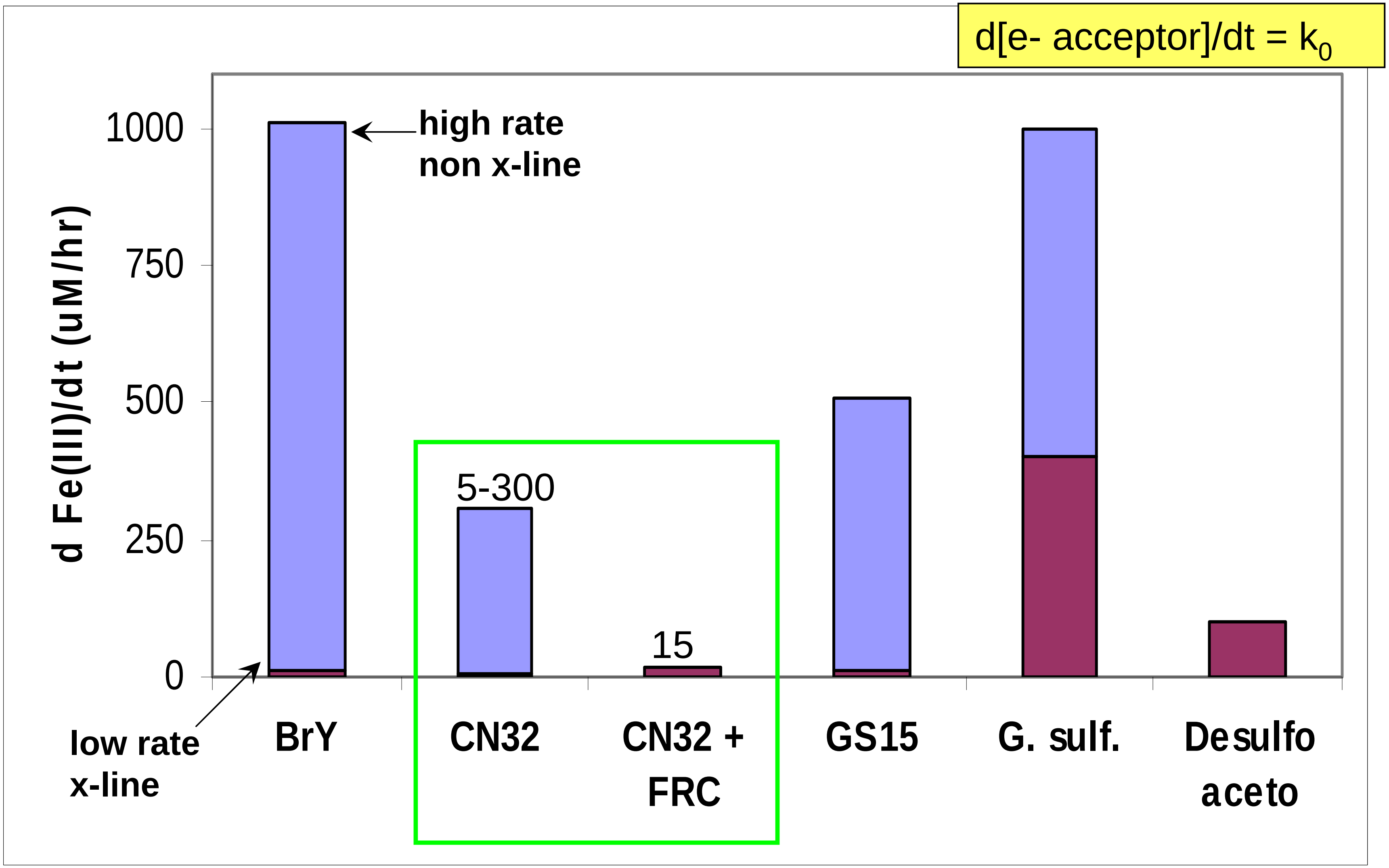
CEKA



NABIR

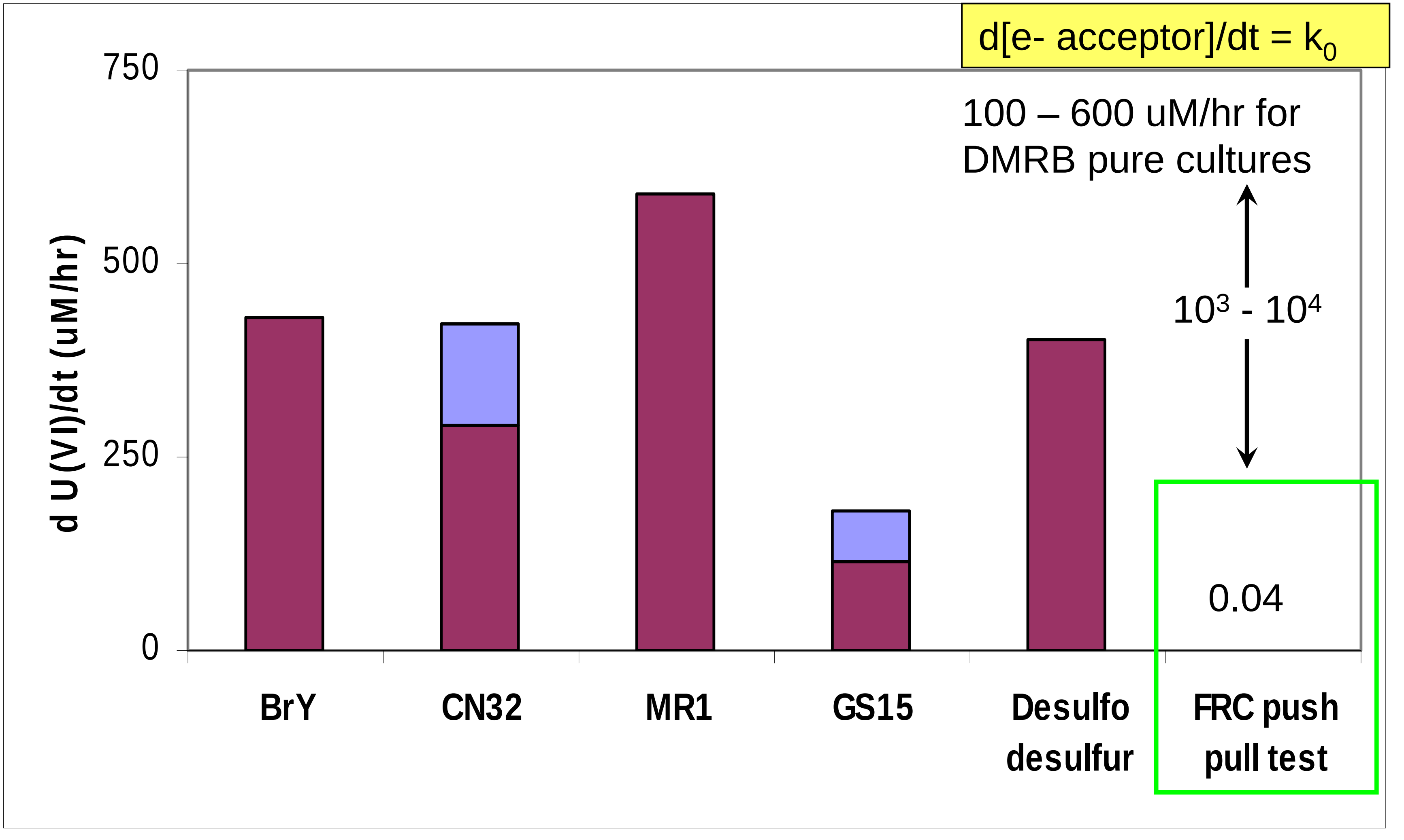
- Compile and synthesize experimental data on metal reduction and oxidation, specifically with FRC sediments.
- Provide support and specific information for reactive transport modeling of the FRC site.
- Encourage collaboration amongst NABIR investigators to establish more direct links to field-scale projects.

Fe(III) Reduction Rates



batch incubations

U(VI) Reduction Rates



Compiling Kinetic Data

Geochimica et Cosmochimica Acta Vol. 52, pp. 2727–2732

0016-7037/88/$3.00 + .00

Microbial reduction of manganese oxides: Interactions with iron and sulfur

CHARLES R. MYERS and KENNETH H. NEALSON*
Center for Great Lakes Studies, University of Wisconsin—Milwaukee, Milwaukee, WI 53201, U.S.A.

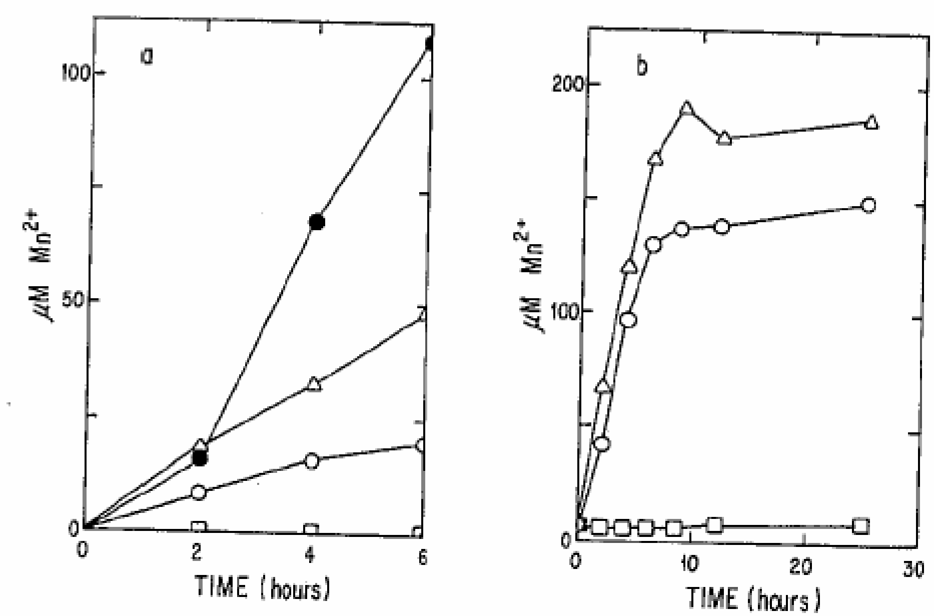
Meta-Data in text

MATERIALS AND METHODS

Isolation of MR-1

Alteromonas putrefaciens strain MR-1 was isolated from the anaerobic zone of sediments of Oneida Lake, N.Y., as outlined in Fig. 1 (see also MYERS and NEALSON, 1988). These Oneida Lake sediments are aerobic on the surface, but become rapidly anaerobic (within millimeters of the surface). During the summer months, a rapid flux of manganese upward into the water column occurs (DEAN *et al.*, 1981; NEALSON and ENZIEN, unpublished data).

Rate Data in time series plots



Scope of Compilation

Fe(III) reduction	14 citations
Mn(III/IV) reduction	12 citations
U(VI) reduction	11 citations
Tc(VII) reduction	10 citations
Cr(VI) reduction	8 citations
FRC rates from push-pull tests	1 citation

Example Compilation of Meta-Data

Source	
Reference	Other Identifier
Myers and Nealson (1988) Geochim Cosmochim Acta 52:2727-2732	Fig 2A

Organism				
Strain	ATCC #	Concentration (cells/L)	Culture preperation	Other Notes
Shewanella oneidensis MR-1		$9.3*10^8$ to $1.5*10^{10}$	cells grown aerobically in batch mode in LO medium, and directly inoculated into subsequent experiments	

Electron Donor			
Type	Co-Ion	Concentration (mol/L)	Other Notes
succinate	Na	15 e^{-3}	

Electron Acceptor							
Metal	Form	Specific Surface Area (BET) (m^2/g)	Concentration (g/L)	Particle Size (m)	Natural sediment characteristics	Synthesis Technique	Other Notes
Mn(IV)	MnO2	NR	0.2 mM	NR		NR	

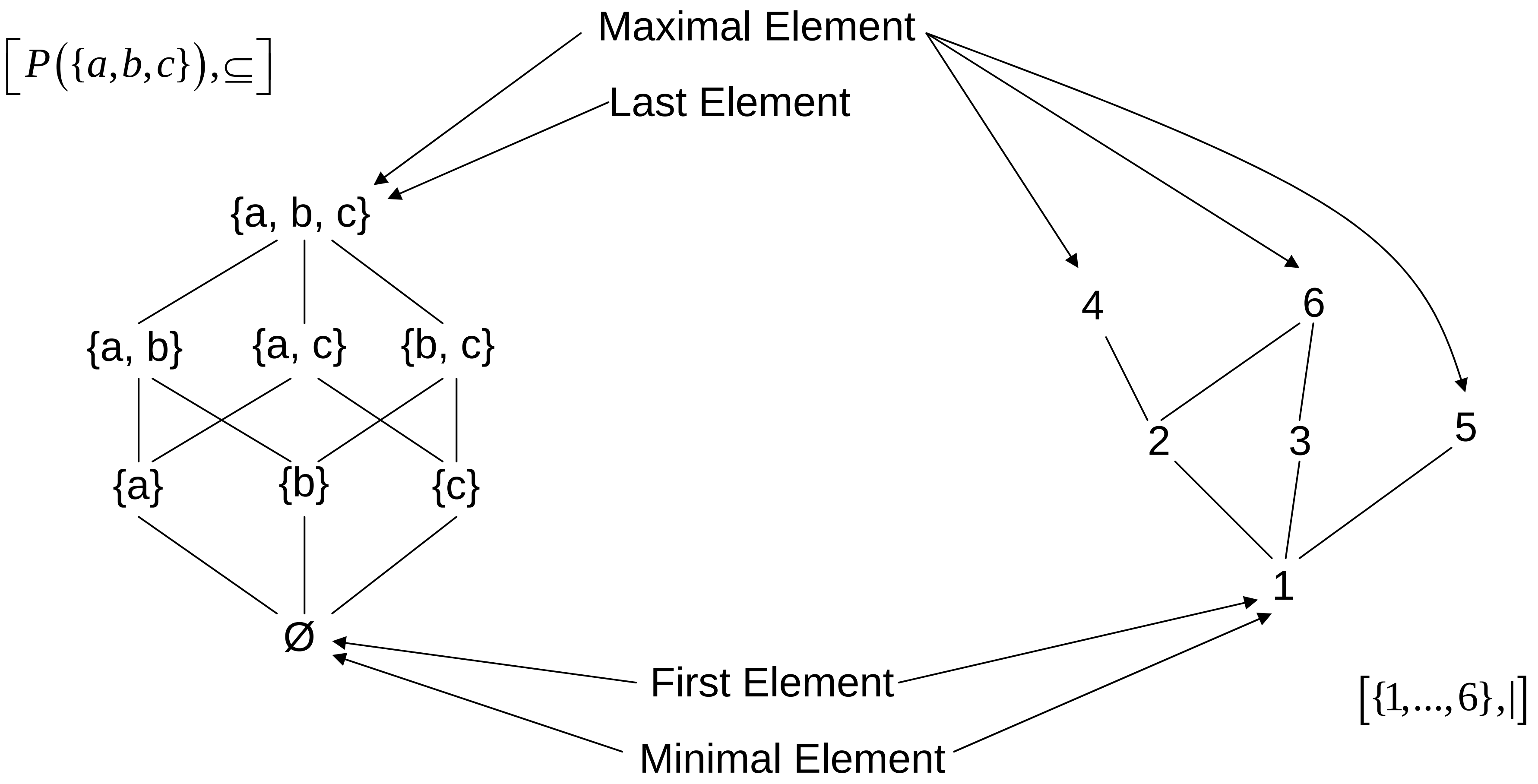
Solution Chemistry			
pH	Buffer	Ionic Strength (mol/L)	Other Solution Notes
7	LO medium included Oneida Lake water with 10 mM HEPES, 2 mM HCO3, pH 7.4; Defined medium had higher pH buffer index		

Products
MnCO3 ?

Reactor Conditions		
Temperature (°C)	Reactor Design	Mixing Rate (rpm)
24	Batch	75

Rate			
element monitored	equation	rate constants	notes
Mn(II), cell number	r = k	3.55 microM/hr	

Partially Ordered Set (POSET)



Rate Laws as a POSET

Global Rate Law?

$$r_{\text{Red}} = \frac{V_{\max}[\text{cell}][\text{don.}]}{K_{1/2} + [\text{don.}]} \qquad \frac{d[\text{cell}]}{dt} = \alpha \cdot r_{\text{Red}}$$

$$r_{\text{Red}} = k''[\text{acc.}][\text{cell}] \qquad \frac{d[\text{cell}]}{dt} = \alpha \cdot r_{\text{Red}}$$

$$r_{\text{Red}} = \frac{V_{\max}[\text{cell}][\text{acc.}_{aq}]}{K_{1/2} + [\text{acc.}_{aq}]}$$

$$r_{\text{Red}} = \frac{V_{\max}\Gamma_{\equiv\text{acc.}}\rho_{SA}\mathrm{M}_{solid}[\text{cell}]}{K_{1/2} + [\text{cell}]}$$

$$r_{\text{Red}} = k''\Gamma_{\equiv\text{acc.}}\rho_{SA}\mathrm{M}_{solid}[\text{cell}]\left(1 - \exp\left(\frac{\Delta G}{RT}\right)\right)$$

$$r_{\text{Red}} = k''\Gamma_{\equiv\text{acc.}}\rho_{SA}\mathrm{M}_{solid}[\text{cell}]$$

$$r_{\text{acc}_1} = k'_{\text{Mn}}[\text{acc}_1] + k''[\text{acc}_2][\text{acc}_1] \qquad r_{\text{acc}_2} = k'_{\text{Fe}}[\text{acc}_2] - k''[\text{acc}_2][\text{acc}_1]$$

$$r_{\text{Red}} = k'[\text{don.}] \qquad \frac{d[\text{don.}]}{dt} = -\alpha \cdot r_{\text{Red}}$$

$$r_{\text{Red}} = k''[\text{cell}][\text{don.}]$$

$$r_{\text{Red}} = k'[\text{cell}] \qquad \frac{d[\text{cell}]}{dt} = \alpha \cdot r_{\text{Red}}$$

$$r_{\text{Red}} = k''[\text{acc.}][\text{cell}]$$

$$r_{\text{Red}} = k'[\text{acc.}] \qquad \frac{d[\text{acc.}]}{\text{dt}} = -r_{\text{Red}}$$

$$r_{\text{Red}} = k'[\text{don.}]$$

$$r_{\text{Red}} = k'[\text{cell}]$$

$$r_{\text{Red}} = k'[\text{acc.}]$$

$$r_{\text{Red}} = k$$

The First (and Minimal) Element

$$r_{\text{Red}} = \frac{V_{\max}[\text{cell}]}{K_{1/2} + [\text{cell}]}[\text{acc.}]$$

$$\frac{d[\text{cell}]}{dt} = \alpha \cdot r_{\text{Red}} - \alpha_{dth}[\text{cell}]$$

$$\frac{d[\text{acc.}]}{\text{dt}} = -r_{\text{Red}}$$

$$r_{\text{Red}} = k'[\text{acc.}]$$

$$\frac{d[\text{acc.}]}{\text{dt}} = -r_{\text{Red}}$$

$$r_{\text{Red}} = \frac{V_{\max}[\text{cell}]}{K_{1/2} + [\text{cell}]}$$

$$\frac{d[\text{cell}]}{dt} = \alpha_{grwth} \cdot r_{\text{Red}} - \alpha_{dth}[\text{cell}]$$

$$r_{\text{Red}} = k'[\text{acc.}]$$

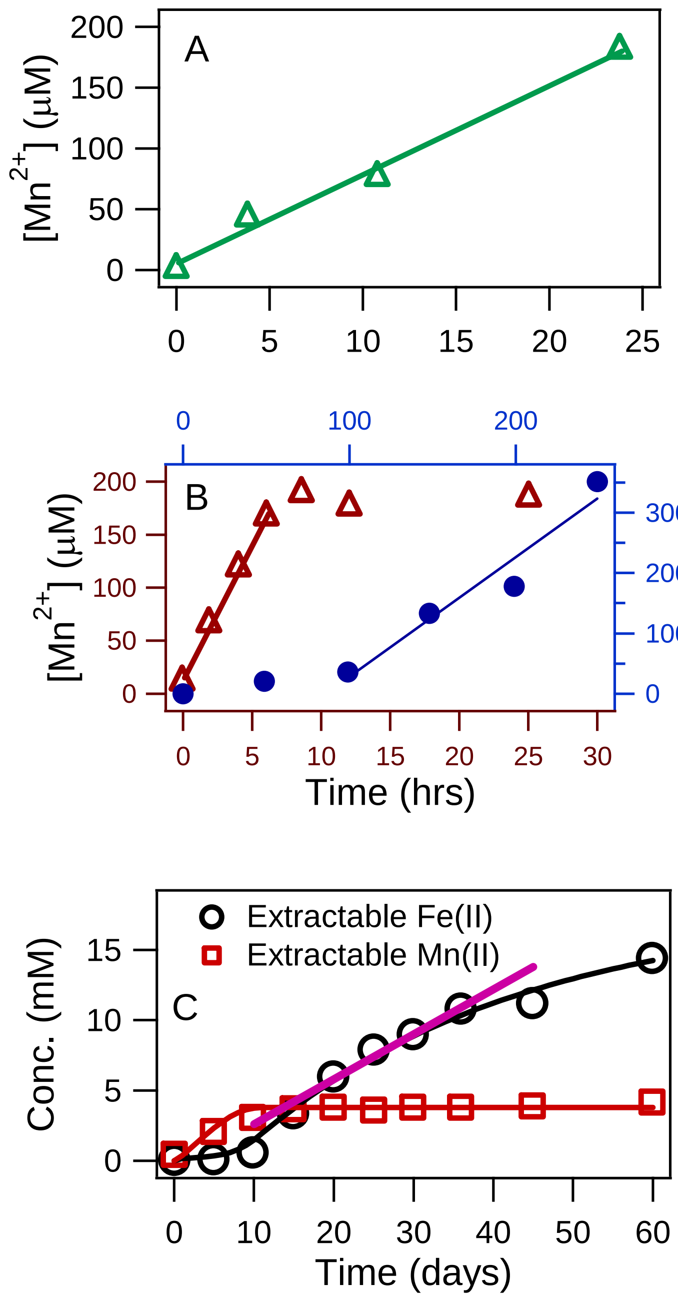
$$r_{\text{Red}} = \frac{V_{\max}[\text{cell}]}{K_{1/2} + [\text{cell}]}$$

$$r_{\text{Red}} = k$$

A) Myers & Nealson 1988

B) Myers & Nealson 1988
Rusin et al. 1991

C) Fredrickson et al. 2004



Building Up from the First Element

$$r_{\mathrm{Red}} = \frac{V_{\max}[\mathrm{cell}]}{K_{1/2} + [\mathrm{cell}]}[\mathrm{acc.}]$$

$$\frac{d[\mathrm{cell}]}{dt} = \alpha \cdot r_{\mathrm{Red}} - \alpha_{dth}[\mathrm{cell}]$$

$$\frac{d[\mathrm{acc.}]}{\mathrm{dt}} = -r_{\mathrm{Red}}$$

$$r_{\mathrm{Red}} = k'[\mathrm{acc.}]$$

$$\frac{d[\mathrm{acc.}]}{\mathrm{dt}} = -r_{\mathrm{Red}}$$

$$r_{\mathrm{Red}} = \frac{V_{\max}[\mathrm{cell}]}{K_{1/2} + [\mathrm{cell}]}$$

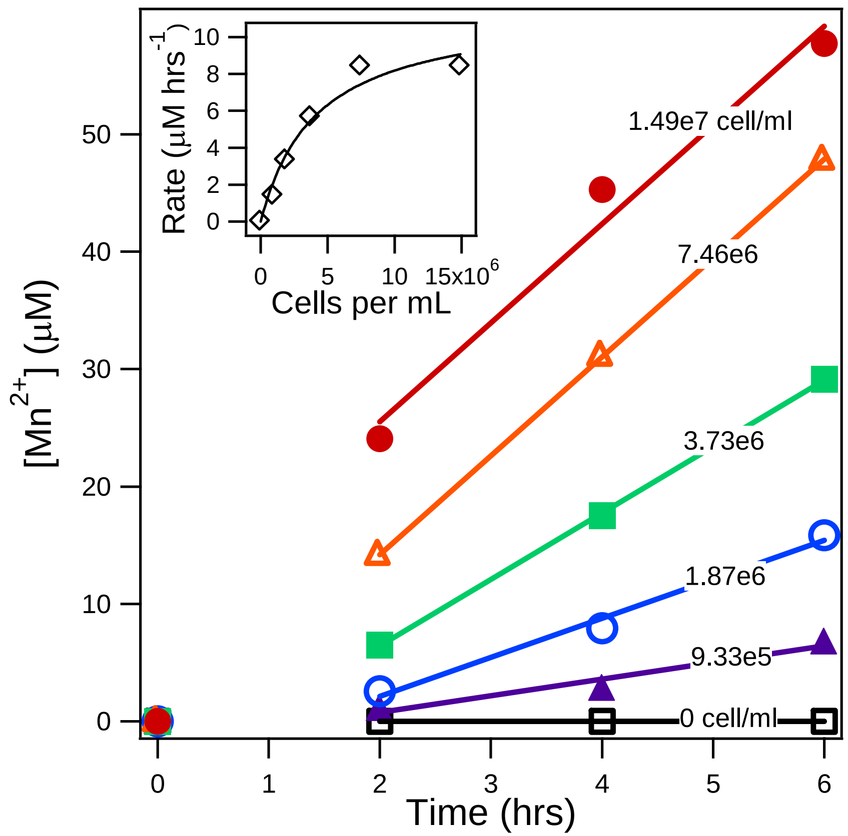
$$\frac{d[\mathrm{cell}]}{dt} = \alpha_{grwth} \cdot r_{\mathrm{Red}} - \alpha_{dth}[\mathrm{cell}]$$

$$r_{\mathrm{Red}} = k'[\mathrm{acc.}]$$

$$r_{\mathrm{Red}} = \frac{V_{\max}[\mathrm{cell}]}{K_{1/2} + [\mathrm{cell}]}$$

$$r_{\mathrm{Red}} = k$$

Myers & Nealson Science 1988



Finding a Maximal Element

$$r_{Red} = \frac{V_{max}[\text{cell}]}{K_{1/2} + [\text{cell}]}[\text{acc.}]$$

$$\frac{d[\text{cell}]}{dt} = \alpha \cdot r_{Red} - \alpha_{dth}[\text{cell}]$$

$$\frac{d[\text{acc.}]}{\text{dt}} = -r_{Red}$$

$$r_{Red} = k'[\text{acc.}]$$

$$\frac{d[\text{acc.}]}{\text{dt}} = -r_{Red}$$

$$r_{Red} = \frac{V_{max}[\text{cell}]}{K_{1/2} + [\text{cell}]}$$

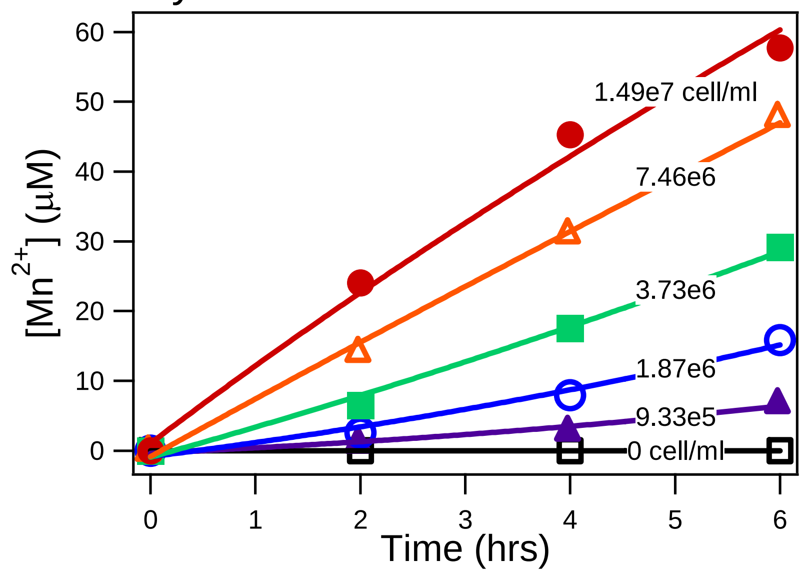
$$\frac{d[\text{cell}]}{dt} = \alpha_{grwth} \cdot r_{Red} - \alpha_{dth}[\text{cell}]$$

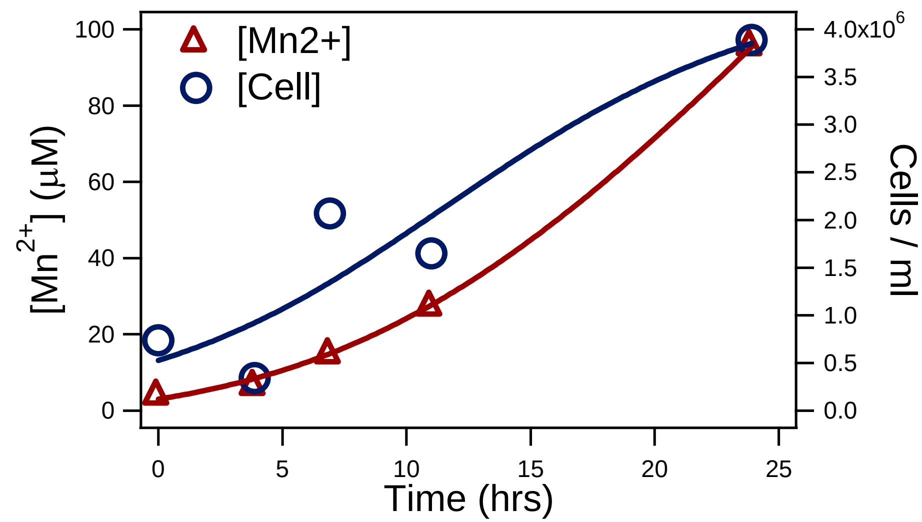
$$r_{Red} = k'[\text{acc.}]$$

$$r_{Red} = \frac{V_{max}[\text{cell}]}{K_{1/2} + [\text{cell}]}$$

$$r_{Red} = k$$

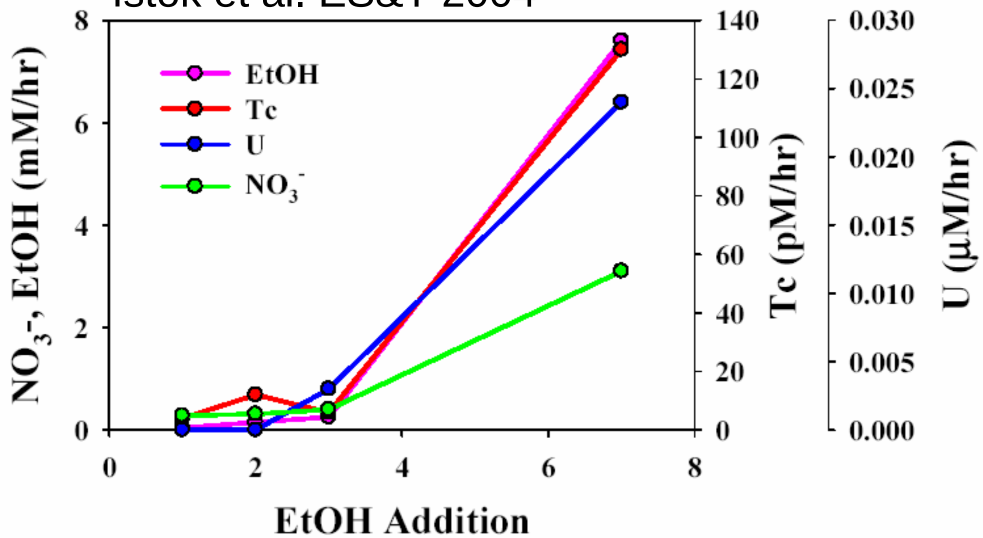
Myers & Nealson Science 1988





Challenge for Field Up-Scaling

Istok et al. ES&T 2004

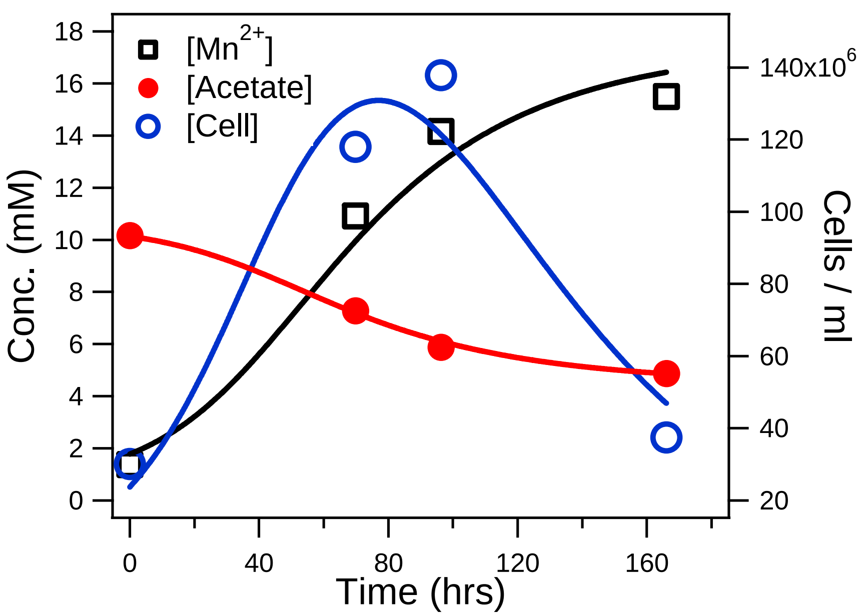


Donor Limited Rate

$$r = k[\text{cell}][\text{don.}]$$

$$\frac{d[\text{cell}]}{dt} = \alpha_{grth} \cdot r - \alpha_{dth}[\text{cell}]$$

$$\frac{d[\text{don.}]}{dt} = \beta \cdot r$$



Lovley & Phillips Appl. Env. Microbiol. 1988

Scaling Law for Successive Additions

$$\frac{d[\text{cell}]}{dt} = \frac{\alpha_{grth} \cdot r - \alpha_{dth}[\text{cell}]}{\beta \cdot r} \cdot \frac{d[\text{don.}]}{dt}$$

$$\frac{r_N}{k \cdot [\text{don.}]_0} = [\text{cell}]_0 + N \cdot \left(\begin{array}{l} \frac{\alpha_{grth}}{\beta}[\text{don.}]_0 (\chi - 1) \\ -\frac{\alpha_{dth}}{k} \ln(\chi) \end{array} \right)$$