Joint Breakout Session

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

Annual Meeting DOE Field Research Center

10/20/04

Agenda

- Meeting introduction; Bill Burgos, Pennsylvania State University
- HYDROGEOCHEM v. 5 a 3D model of coupled flow, thermal transport, and hydrogeochemical transport under variably saturated conditions, George Yeh, University of Central Florida
- Models of physical non-equilibrium (mass transfer) processes in structured porous media; Tim Scheibe, Pacific Northwest National Laboratory
- U(VI) soprtion to pristine bioreduced and reoxidized FRC sediments; Chongxuan Liu, Pacific Northwest National Laboratory
- Effects of pH and Nitrate on a Consortia of Iron Reducers from Uranium-Contaminated Subsurface Sediments; Lainie Petrie, Florida State University
- Compiled rates of Fe, Mn, uranium(VI), technetium and chromium reduction, and rates of uranium(IV) oxidation; Bill Burgos, Pennsylvania State University
- Group participation/discussion/input

Compiled rates of Fe, Mn, uranium(VI), technetium, and chromium reduction, and rates of uranium(IV) oxidation

Bill Burgos

Penn State University

Working Group Objectives

- 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.

Working Group Deliverable

"Living document" for distribution to NABIR scientists

Current scope of report

Fe(III) reduction	14 citations	6 pure cultures
Mn(III/IV) reduction	12 citations	7 pure cultures 2 enrichment cultures
U(VI) reduction	11 citations	8 pure cultures
Tc(VII) reduction	10 citations	8 pure cultures 2 natural communities
Cr(VI) reduction	8 citations	7 pure cultures 1 mixed culture
Nitrate-dependent Fe(II) oxidation	10 citations	6 pure cultures 4 natural communities
U(IV) oxidation	4 citations	6 pure cultures
FRC rates from push-pull tests	1 citation	natural biostimulated communities

Example of compiled, tabulated data

Table 2. Bioreduction kinetics of solid phase Mn(III/IV) oxides reported in or calculated from data contained in peer-reviewed literature.

Organism [A]	Mn Source [B]	Electron Donor	Buffer/Medium	Rate (uM Mn(II) h^{-1}) [C]	Comments on Source Data	Reference
Geobacter metallireducens C_i = 2 to $4x10^7$ cell mL^{-1}	15 mM MnO_2	10 mM acetate	30 mM HCO_3^-, pH 7.0, 5.0 mM P, defined medium	140	Bacterial growth conditions; T=30°C; Rate estimated from zero-order regression through first 100-h data shown in Figure 5.	Lovley and Phillips, 1988
Shewanella putrefaciens CN32 C_i = 2 to $4x10^8$ cell mL^{-1}	50 mM β-MnO_2 1.2 mM K-birnessite 20 mM Mn_2O_3	25 mM lactate	30 mM HCO_3^-, pH 7.0 (80:20% N_2:CO_2 atm)	16 – β-MnO_2; 0.35 – K- birnessite; 4.5 – Mn_2O_3	Non-growth conditions; T=30°C; Rates calculated from single endpoints reported for no-U(VI) controls in Table 1. β-MnO_2 rate estimated after 50 h, while others estimated after 21 d.	Fredrickson et al., 2002
Shewanella putrefaciens CN32 C_i = 7 to $9x10^7$ cell mL^{-1}	0.5 or 1.0 g sediment per 10 mL; homogenized FRC background sediment; Ringold sediment	10 mM lactate	30 mM HCO_3^-, pH 7.1 (80:20% N_2:CO_2 atm)	15 – FRC sediment; 20-30 – Ringold sediment	Non-growth conditions; T=30°C; Rate calculated for FRC sediment from zero-order regression through first 10-d data shown in Figure 2; Rates calculated for Ringold sediment from zero-order regressions through first 10-d data shown in Figure 4. Rates calculated before Fe(III) reduction commenced.	Fredrickson et al., 2004
Shewanella putrefaciens MR-1 C_i = $9.3x10^5$ to $1.5x10^7$ cell mL^{-1}	0.2 mM δ-MnO_2	15 mM acetate or succinate plus 10% H_2(g)	LO medium included Oneida Lake water with 10 mM HEPES, 2 mM HCO_3^-, pH 7.4. Defined medium had higher buffer index	1.3-10 – in LO medium; 40-150 – in defined medium	Bacterial growth conditions; T=24°C; Rates estimated from zero-order regression through first 6-h data shown in Figures 1A, 1B and 2A.	Myers and Nealson, 1988a
Shewanella putrefaciens MR-1 C_i was unspecified but likely 10^6 to 10^7 cell mL^{-1}	0.2 mM δ-MnO_2	15 mM acetate or succinate plus 10% H_2(g)	LO medium included Oneida Lake water with 10 mM HEPES, 2 mM HCO_3^-, pH 7.4. Defined medium had higher buffer index	2-4 – in LO medium; 8-22 – in defined medium	Bacterial growth conditions; T=24°C; Rates for LO medium estimated from zero-order regression through first 6-h data shown in Figure 2 for no-alternate electron acceptor controls; Rates for defined medium estimated from zero-order regression through first 6-h data shown in Figure 3 for no-alternate electron acceptor controls.	Myers and Nealson, 1988b

Rate Summary from FRC Push-Pull Tests

Conditions		Donor Target	Number of	RATES				
				Donor	Nitrate	Sulfate	U	Tc
Nitrate	Donor	Conc (mM)	Tests	(mM/hr)	(mM/hr)	(mM/hr)	(uM/hr)	(pM/hr)
~120mM	Acetate	300-500	2	0.80-24.00	0.51-0.69		0	9-39
~120mM	Acetate	50	2	0.14-0.40	0.12-0.36		0	107
~120mM	Ethanol	300-440	10	0.30-7.60	0.03-3.10		0.00-0.01	4-189
~120mM	Ethanol	30-100	8	0.04-0.25	0.02-0.40	0.00-0.01	0.00-0.03	1-150
~120mM	Glucose	200	3	0.94-4.30	0.04-3.20		0.02-0.03	45-460
~120mM	Glucose	20	4	0.02-0.16	0.44-0.76		0.001	10-143
~120mM	None	0	8		0.00-0.10		0	0
~0.5mM	Acetate	50	1	-	>.01		0.021	-
~0.5mM	Ethanol	15-80	14	0.02-0.30	0.00-0.06	0.00-0.02	0.00-0.04	0-5
~0.5mM	Glucose	200	1	0.31	>.05		0.034	-
~120mM	Glucose	20	1	0.1	0.012		0.041	-
~0.5mM	None	0	8	0	0	0.00-0.001	0.00-0.01	0-1

Challenges Inherent in Comparing Rates

- cell suspension concentration
- speciation of electron acceptor
- electron acceptor concentration
- electron donor and concentration
- incubation temperature
- kinetic sampling frequency

So how do we establish a “universal” rate formulation to extract rates (or rate constants) for comparative purposes?

$$d[\text{e- acceptor}]/dt = k_3[\text{DMRB}][\text{e- acc}][\text{e- donor}]$$

Fe(III) and Mn(III/IV) bioreduction rates in FRC sediments extracted from published data

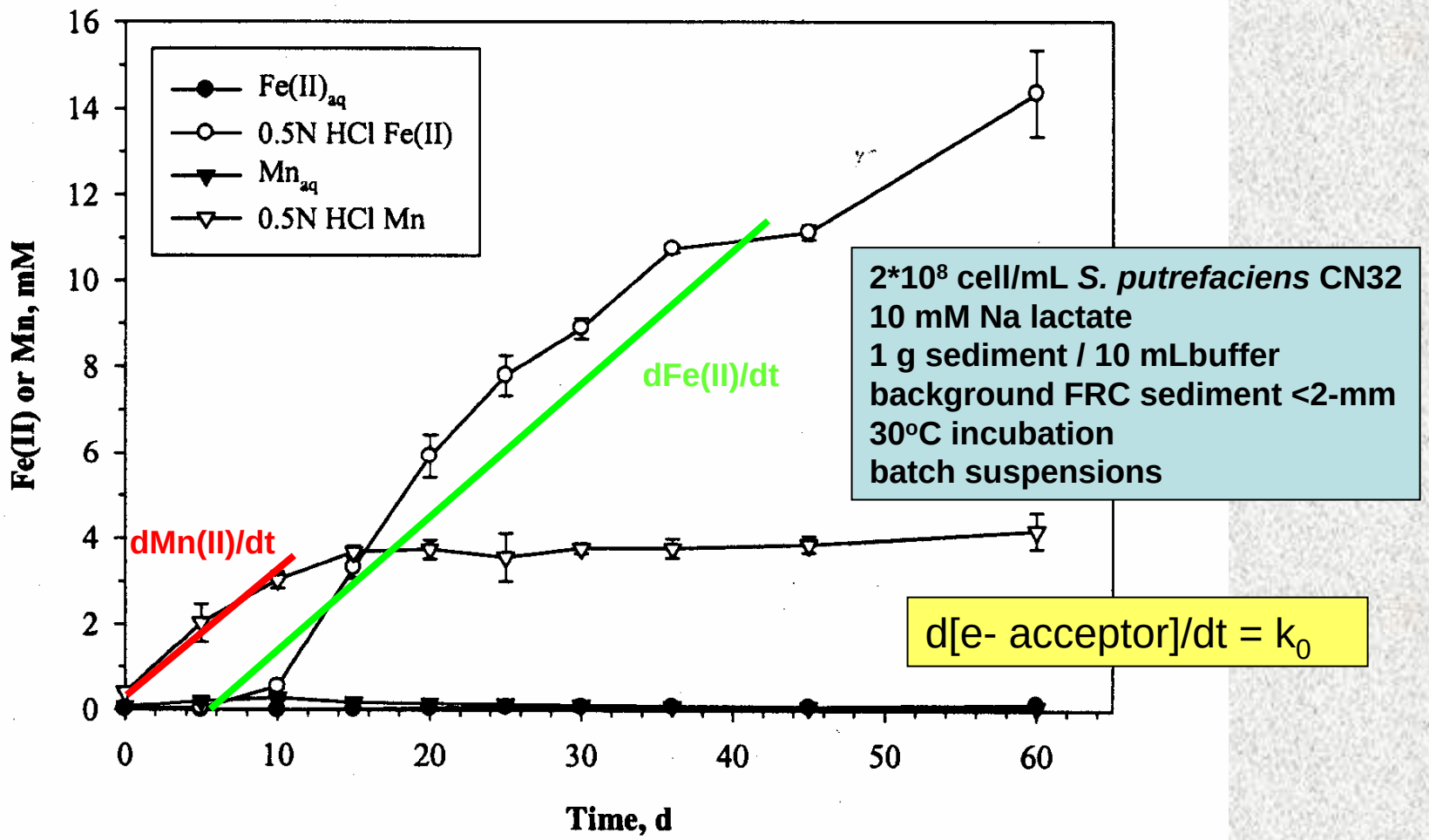


Fig. 2. Concentrations of aqueous (0.2 μm-filtered) and 0.5 N HCl-extractable Mn and Fe(II) during reduction of FRC saprolite by *S. putrefaciens* CN32 in 30 mM $NaHCO_3$, pH 7 buffer with 10 mM Na lactate.

Fredrickson et al. 2004, *GCA*, **68**:3171

One Example of a Comprehensive Comparative Study

- 4 DMRB (Geobacter metallireducens GS-15, Shewanella putrefaciens CN32, S. algae BrY, S. oneidensis MR1)
- 6 electron acceptors (Fe(III)citrate, Fe(III)NTA, Co(III)EDTA, UO_2^{2+}, CrO_4^{2-}, TcO_4^-)
- 2 electron acceptors (lactate vs. H_2, acetate only with GS-15)
- [DMRB] = $2*10^8$ cell/mL
- $[\text{e- acceptor}]_0$ = 500 uM
- [e- donor] never limiting
- 30°C incubations

$$d[\text{e- acceptor}]/dt = k_1[\text{e- acc}]$$

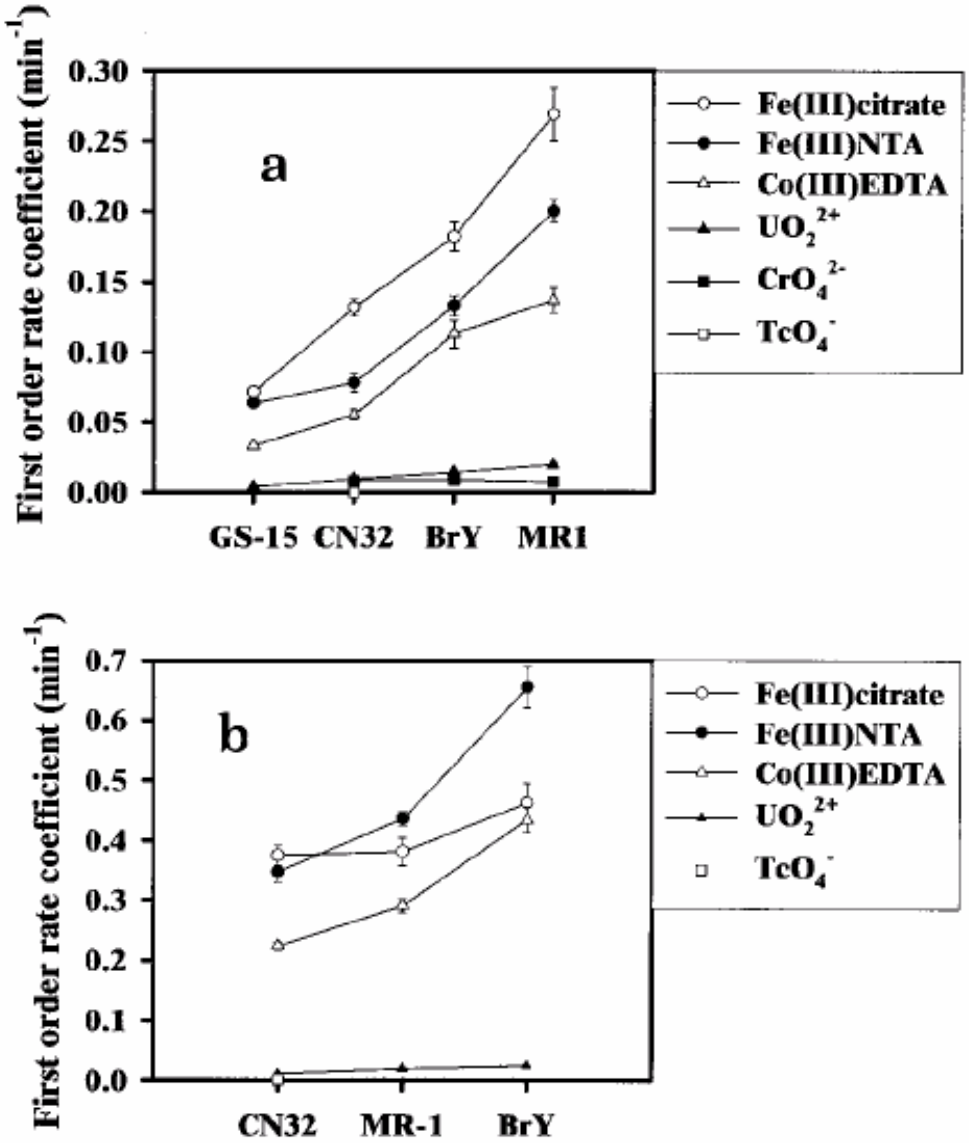
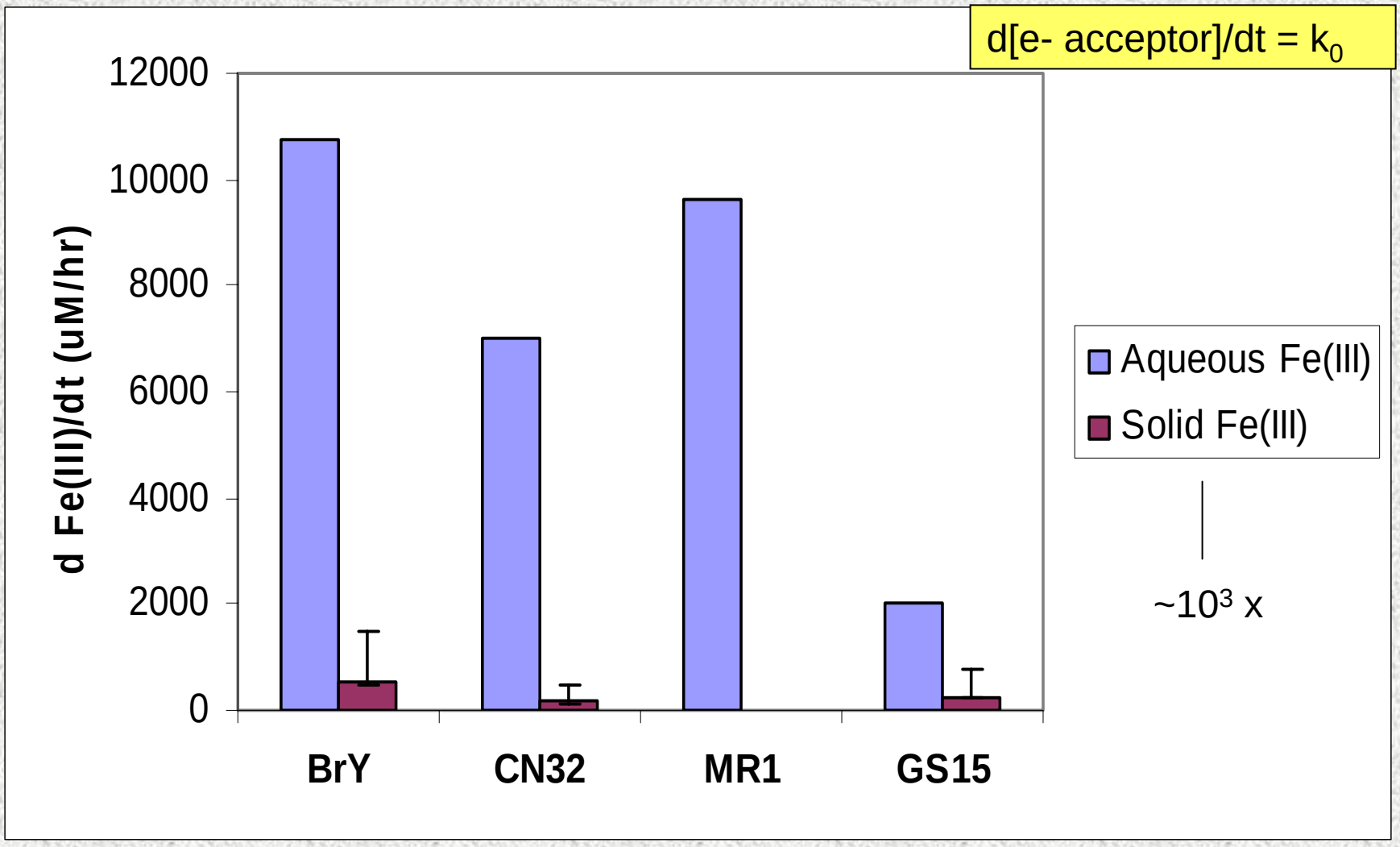


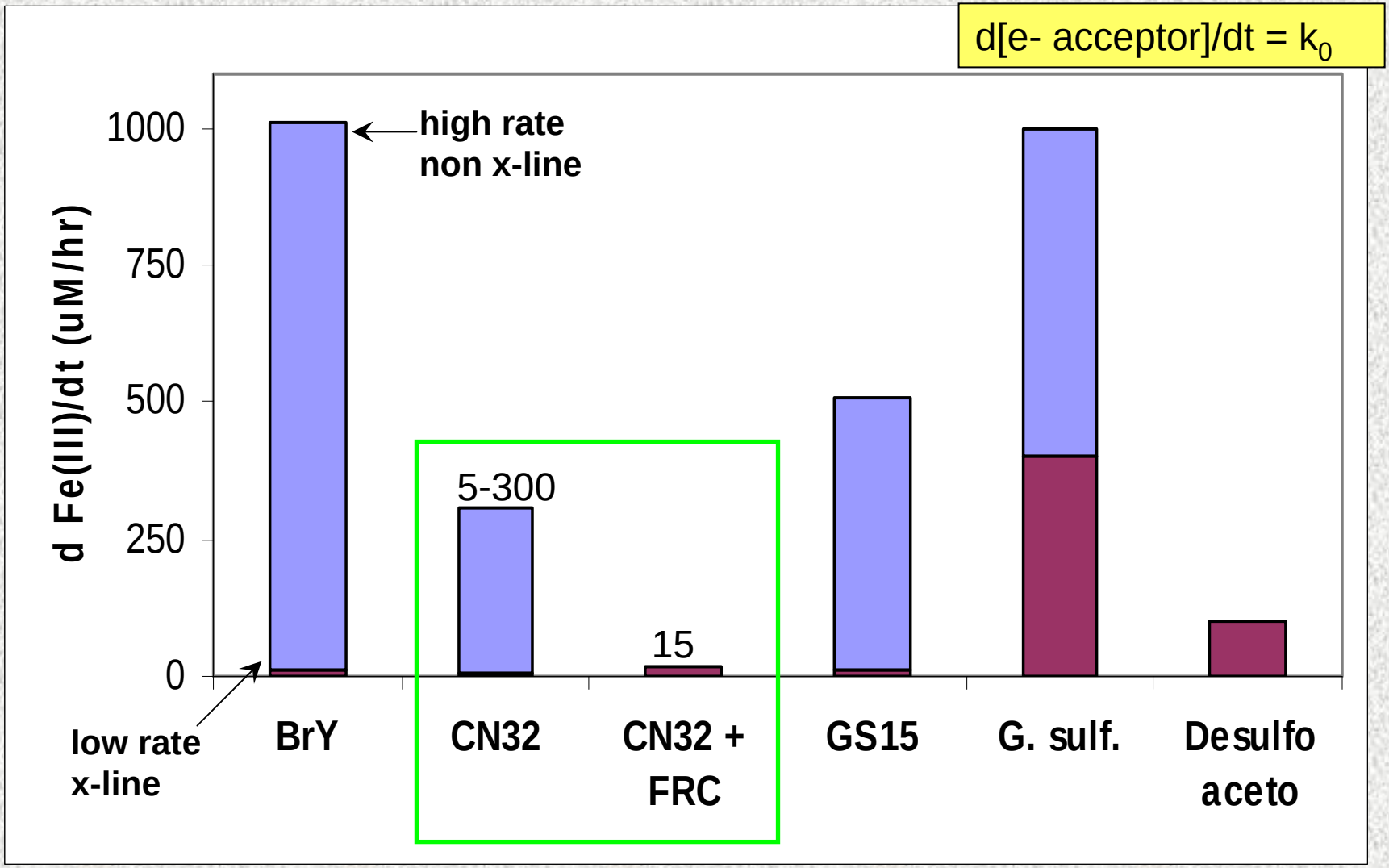
Figure 7. Observed trends in first-order rate coefficients for different metals and DMRB with lactate⁻ (a) or H_2 (b) as electron donor.

Liu et al. 2002, *Biotech Bioeng*, **80**:637

Fe(III) Reduction Rates

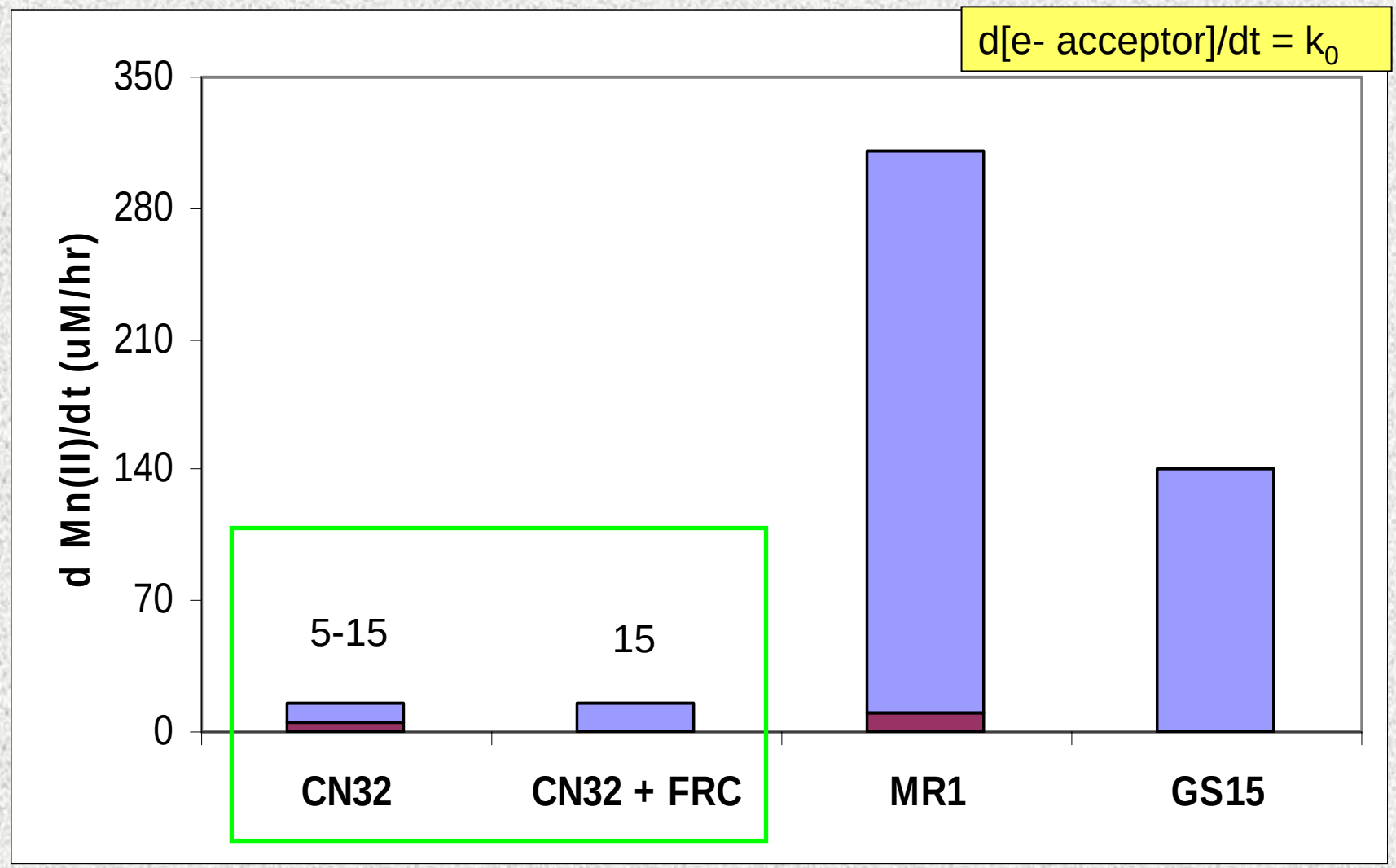


Fe(III) Reduction Rates



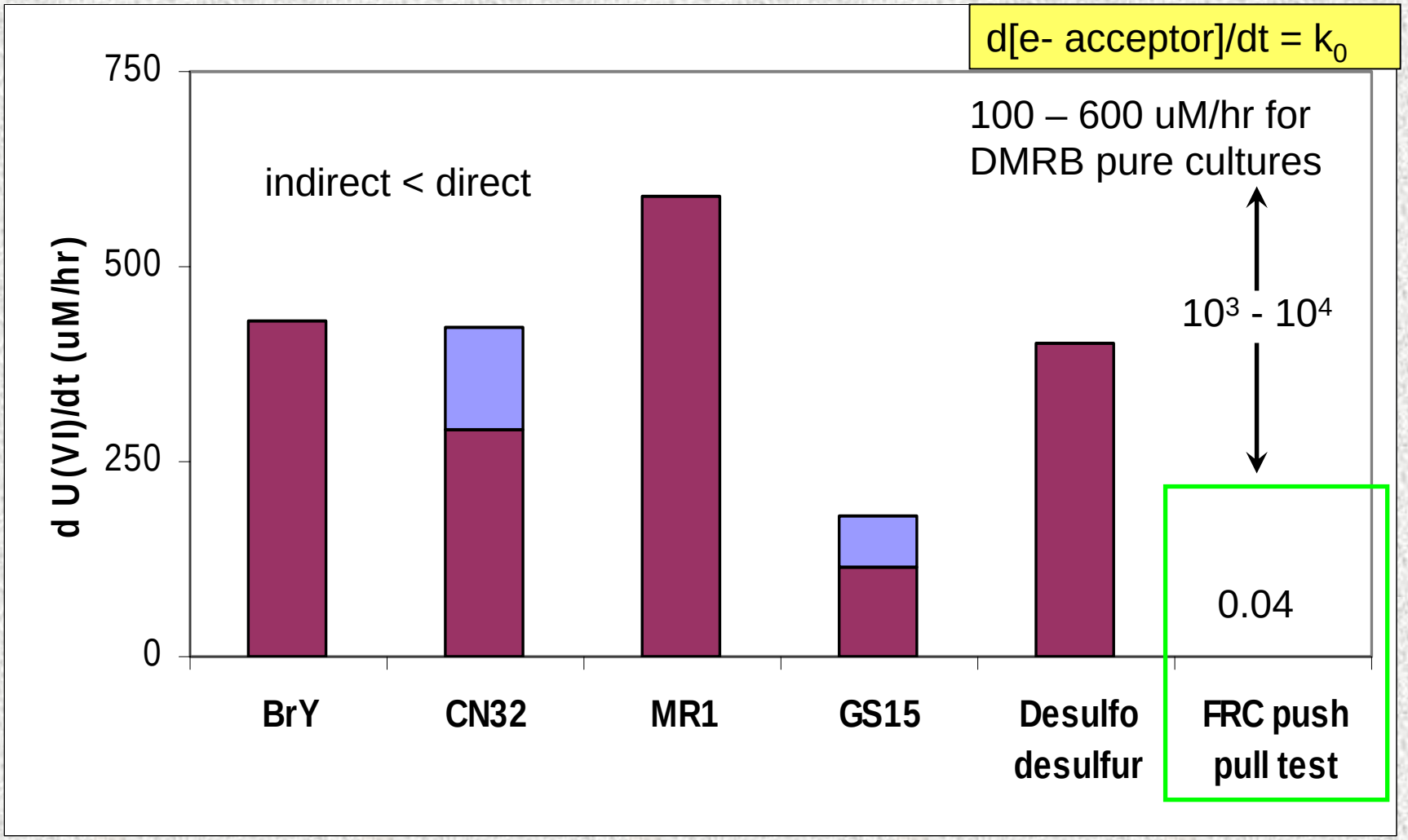
batch incubations

Mn(III/IV) Reduction Rates

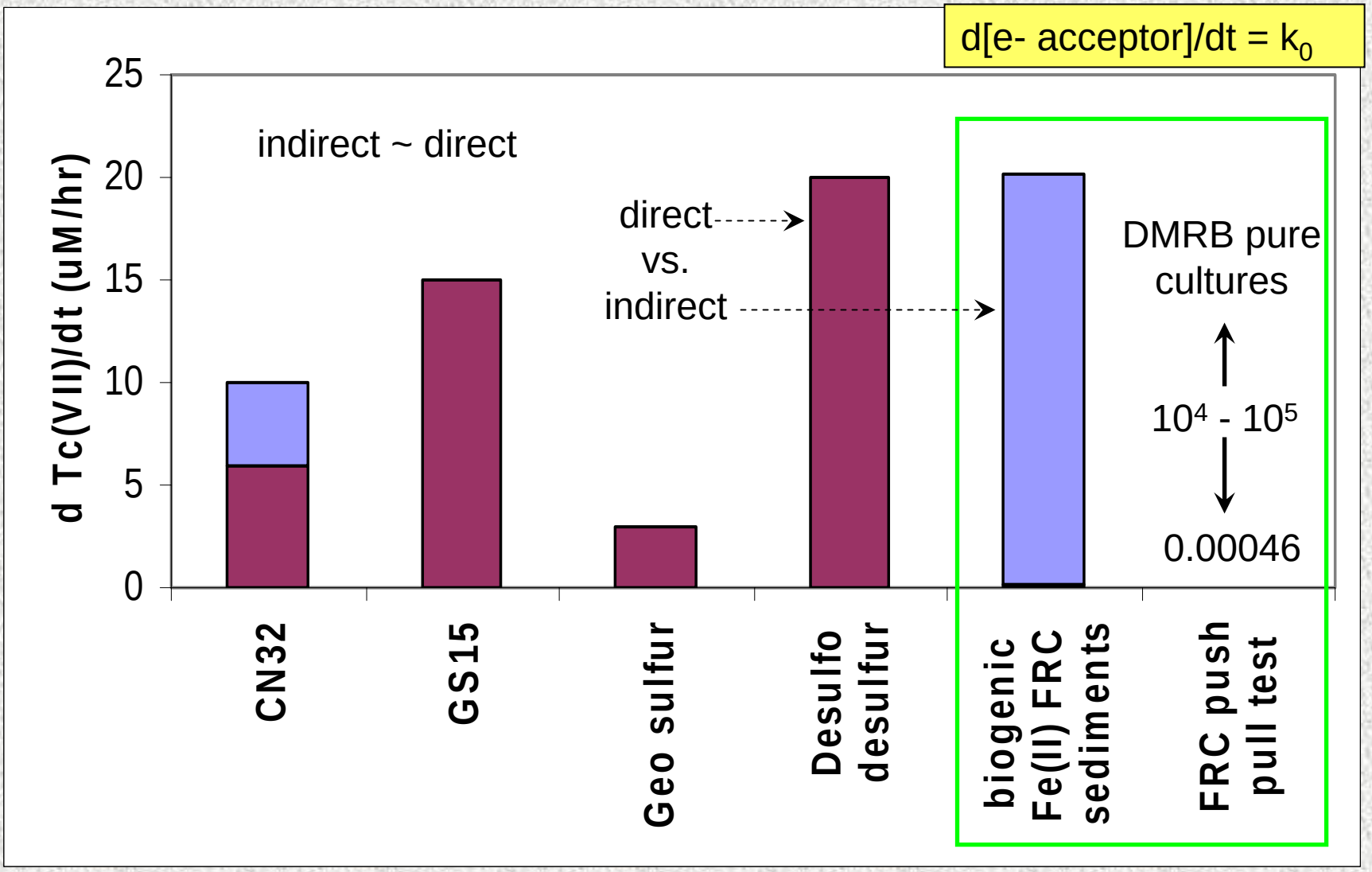
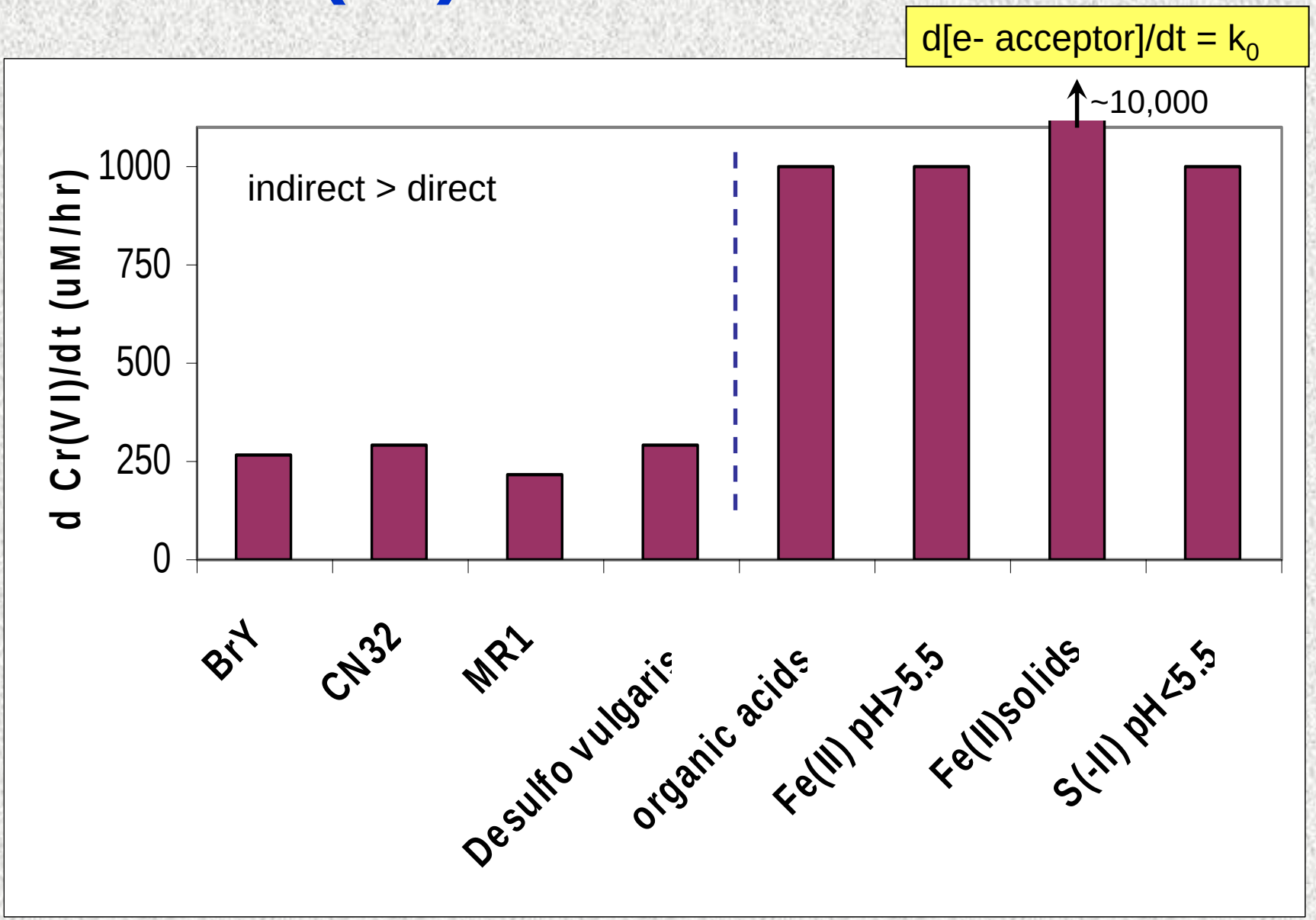


batch incubations

U(VI) Reduction Rates



Tc(VII) Reduction Rates



Cr(VI) Reduction Rates