Waste Green Sands as Reactive Media for PRBs

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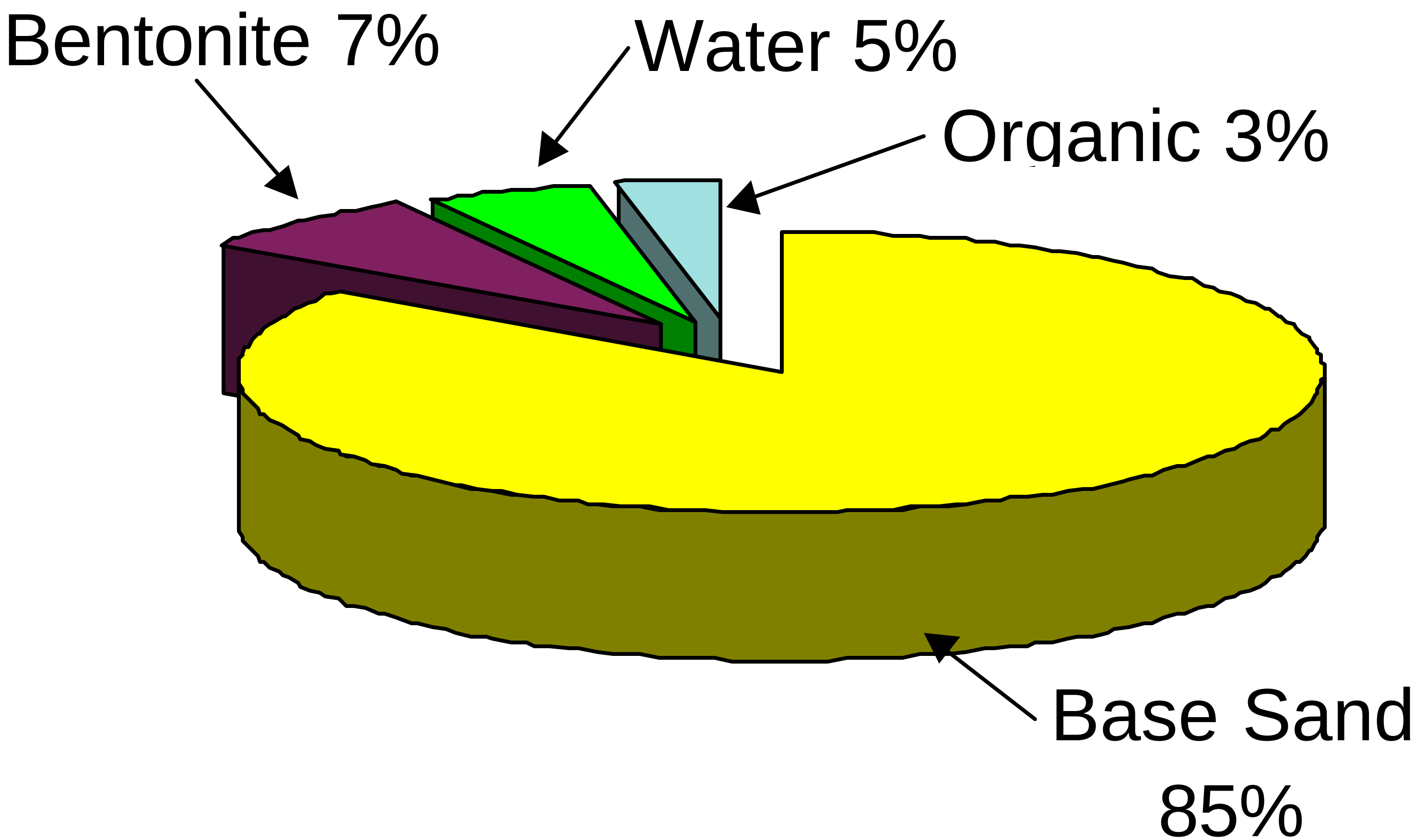
What is waste green sand?

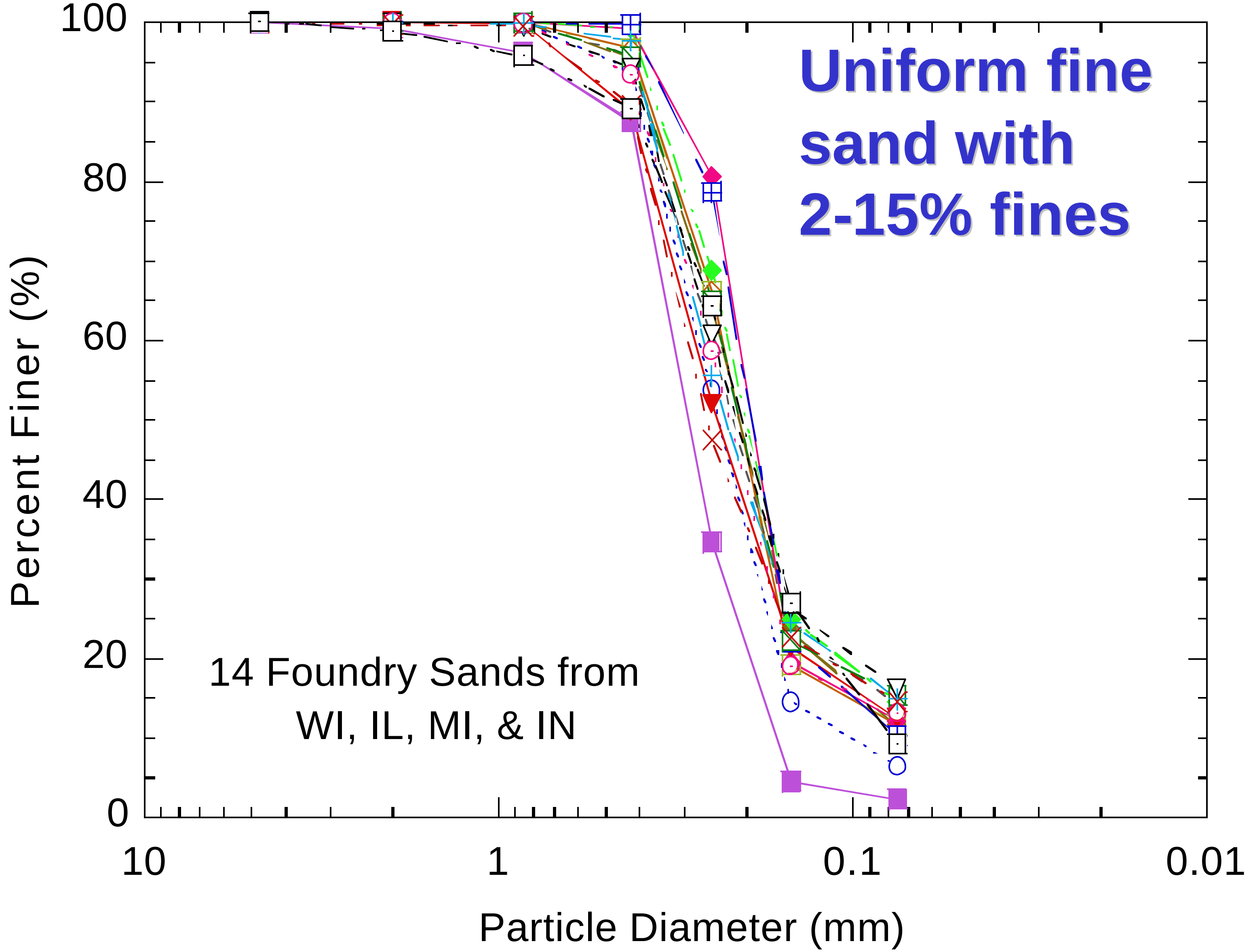
- Granular material used for molds for metal casting
- A blend of sand, binder, organic additive, water
- Generated by addition of components creating excess volume (not truly a waste product)
- Residual iron provides reactivity, organic carbon provides sorptive capacity

Typical Composition



Waste sands also contain *2-12% iron particles* derived from casting process

Particle Size Distribution



Green Sand is Really Black Sand

Usually dry (< 5% water content) and easy to handle, but can contain debris

Why consider green sand?

- Can be obtained at no cost. In some cases, transportation cost is provided by foundry
- Beneficial reuse of industrial byproduct
- Fosters sustainable development
- Appears effective (see presentation)

Objectives

- Assess hydraulic conductivity, reactivity, and sorptive capacity of green sands
- Evaluate long-term reactivity
- Evaluate potential field scenarios
- Assess leaching of metals and PAHs (not in this presentation)

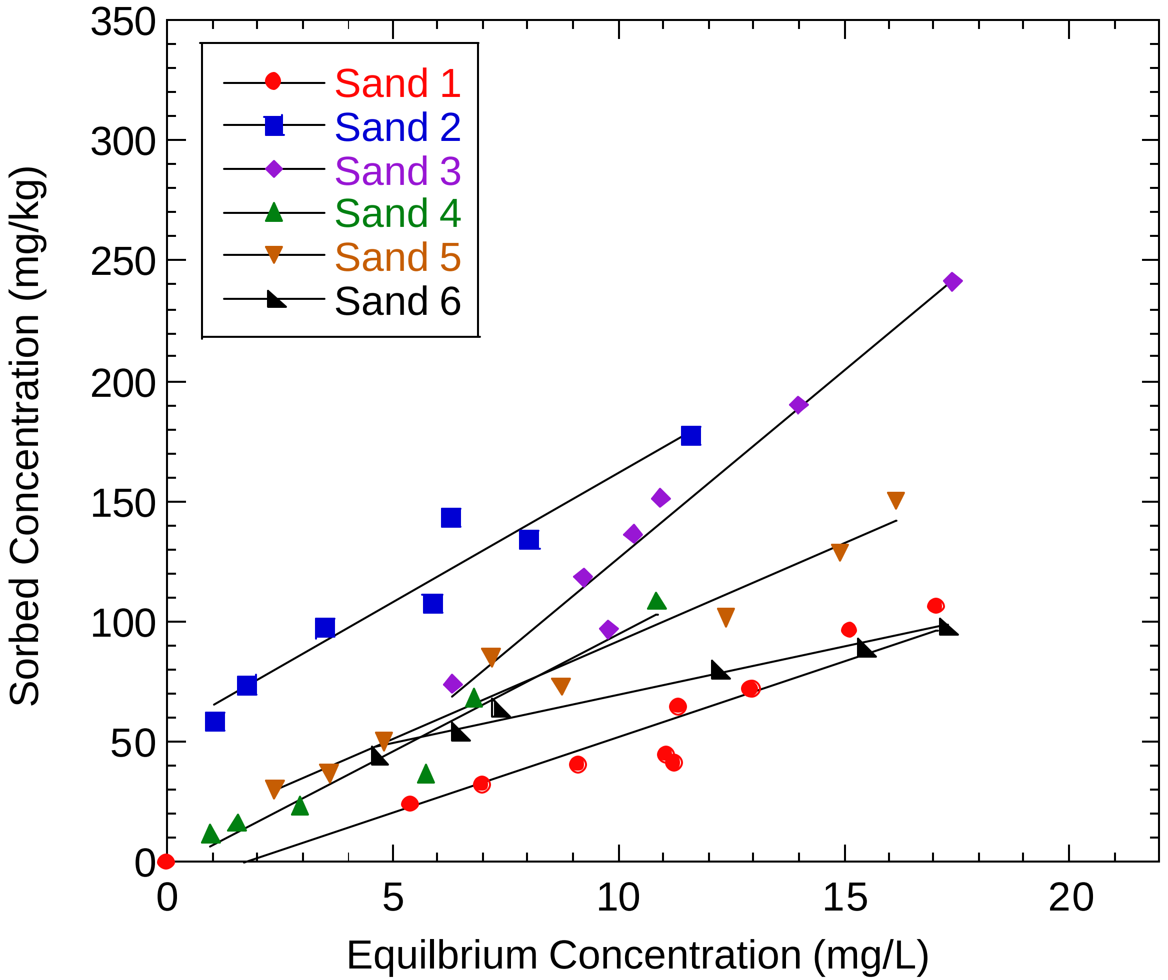
Materials

- 12 greens sands from foundries in Wisconsin, Illinois, and Indiana
- TCE along with vinyl chloride, 1,1-dichloroethylene, trans-1,2-dichloroethylene, and cis-1,2-dichloroethylene
- Alachlor and acetyl alachlor (both from Monsanto Corporation); metolachlor and MBP (both from Novartis Crop Protection)
- ZVI particles from Peerless Metal Powders and Abrasives Co. (mean particle size = 0.7 mm, specific surface area of 0.87 m^2/g)

Hydraulic Conductivity

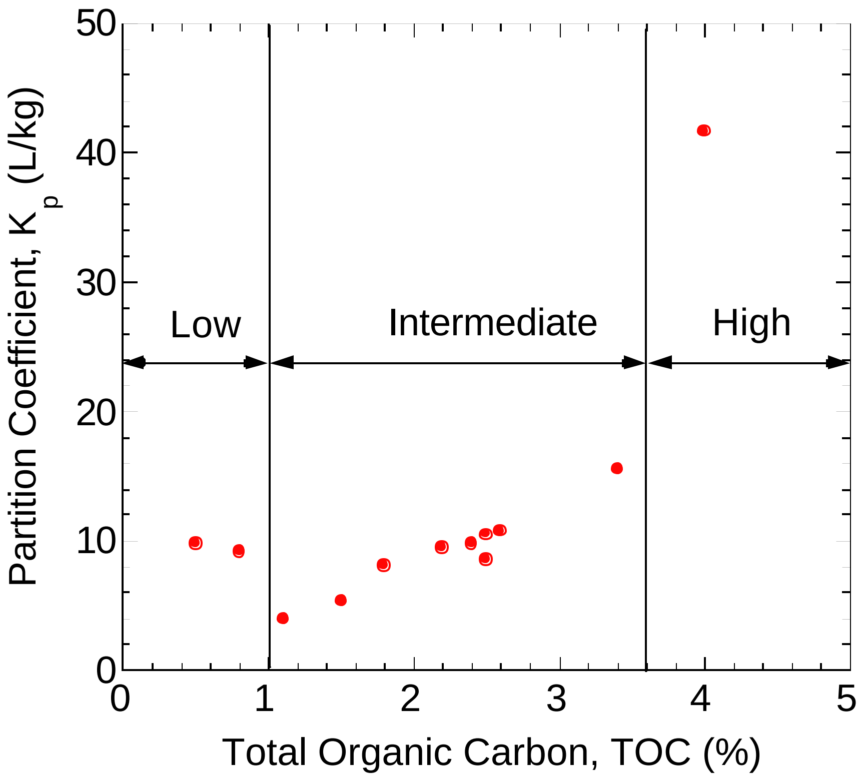
Green Sand	Binder Type	USCS Classification	Total Organic Carbon (%)	Saturated Hydraulic Conductivity (m/d)
1	Clay	SP-SM	1.5	1.35
2	Clay	SM	2.6	1.99
3	Clay	SW-SM	2.5	0.52
4	Clay	SC-SM	0.5	0.00081
5	Clay	SC-SM	1.8	0.24
6	Clay	SP-SM	1.1	0.35
7	Clay	SC-SM	2.2	0.34
8	Clay	SP	2.5	0.0033
9	Chemical	SP	0.8	23.3
10	Clay	SP-SM	2.5	0.47
11	Clay	SM-SC	4.0	0.00079
12	Clay	SP	2.4	1.64

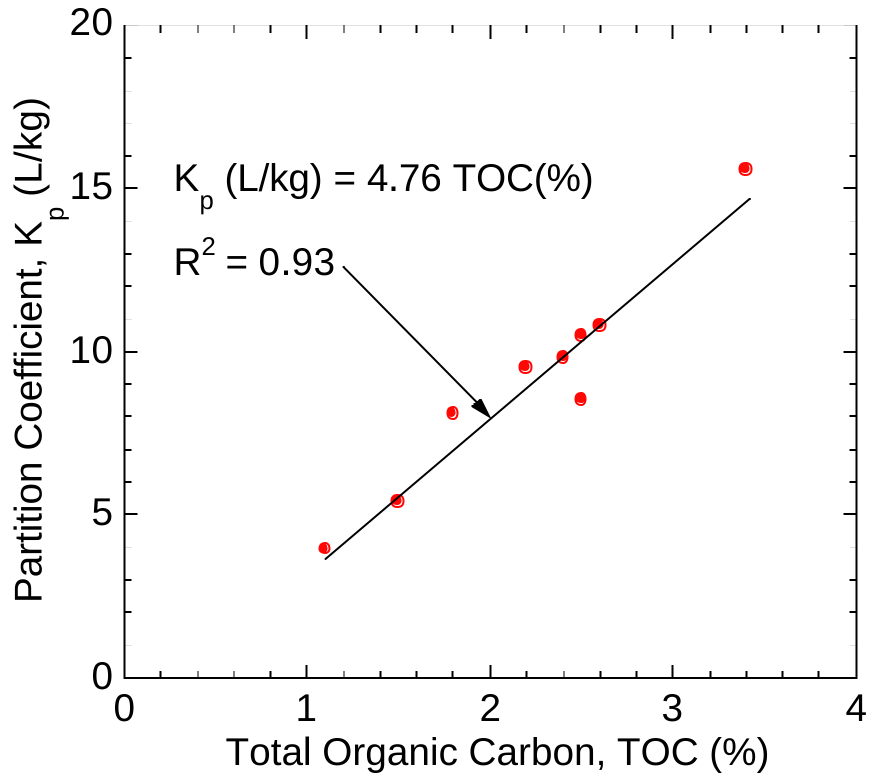
TCE Sorption Isotherms



- Linear within range of concentrations used
- Intercepts indicate non-linearity at low concentrations

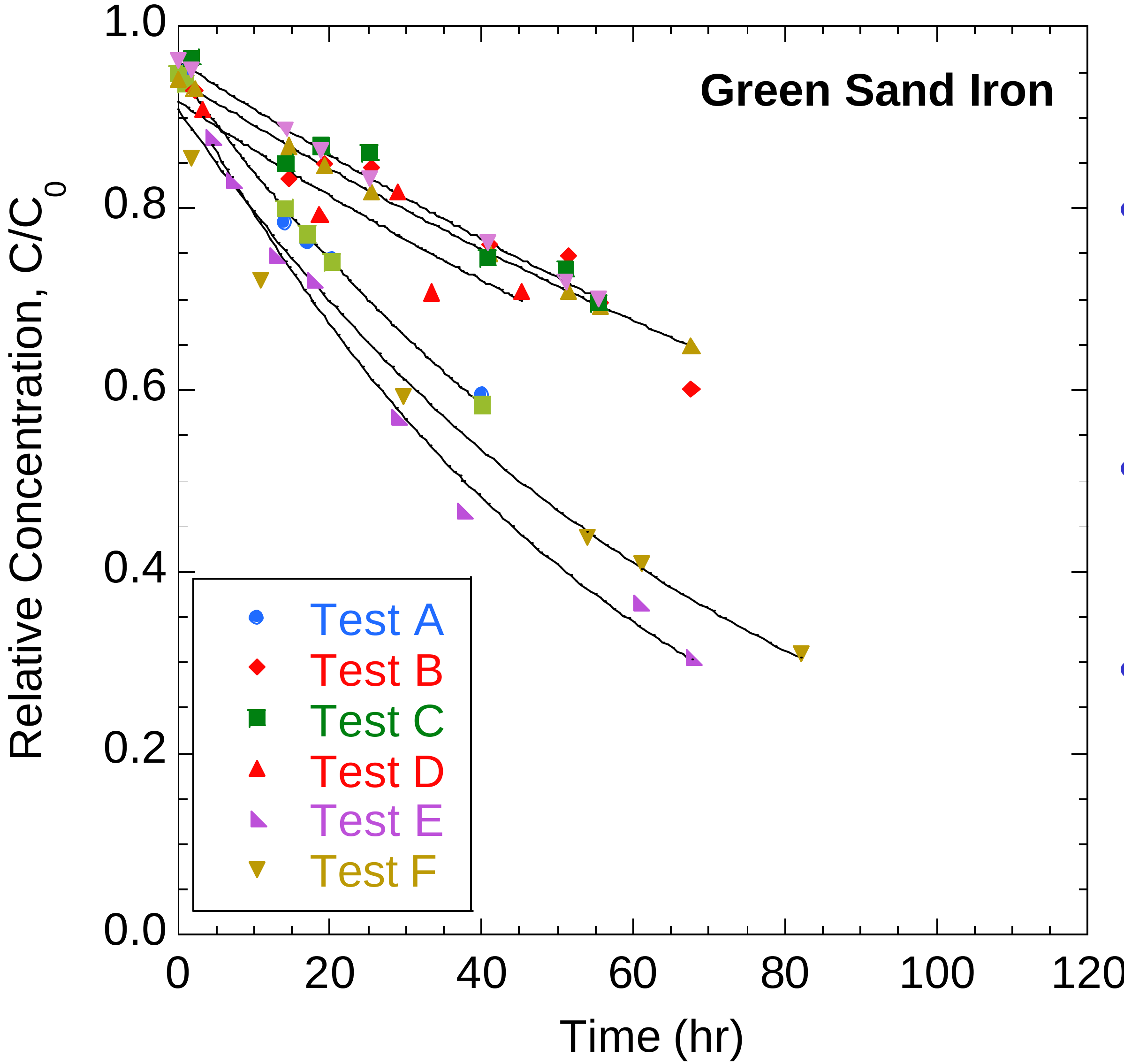
TCE Partition Coefficients vs. TOC





Linear K_p-TOC relationship in intermediate TOC range. K_p is approx. 2x higher than expected based on K_{oc} and f_{oc}

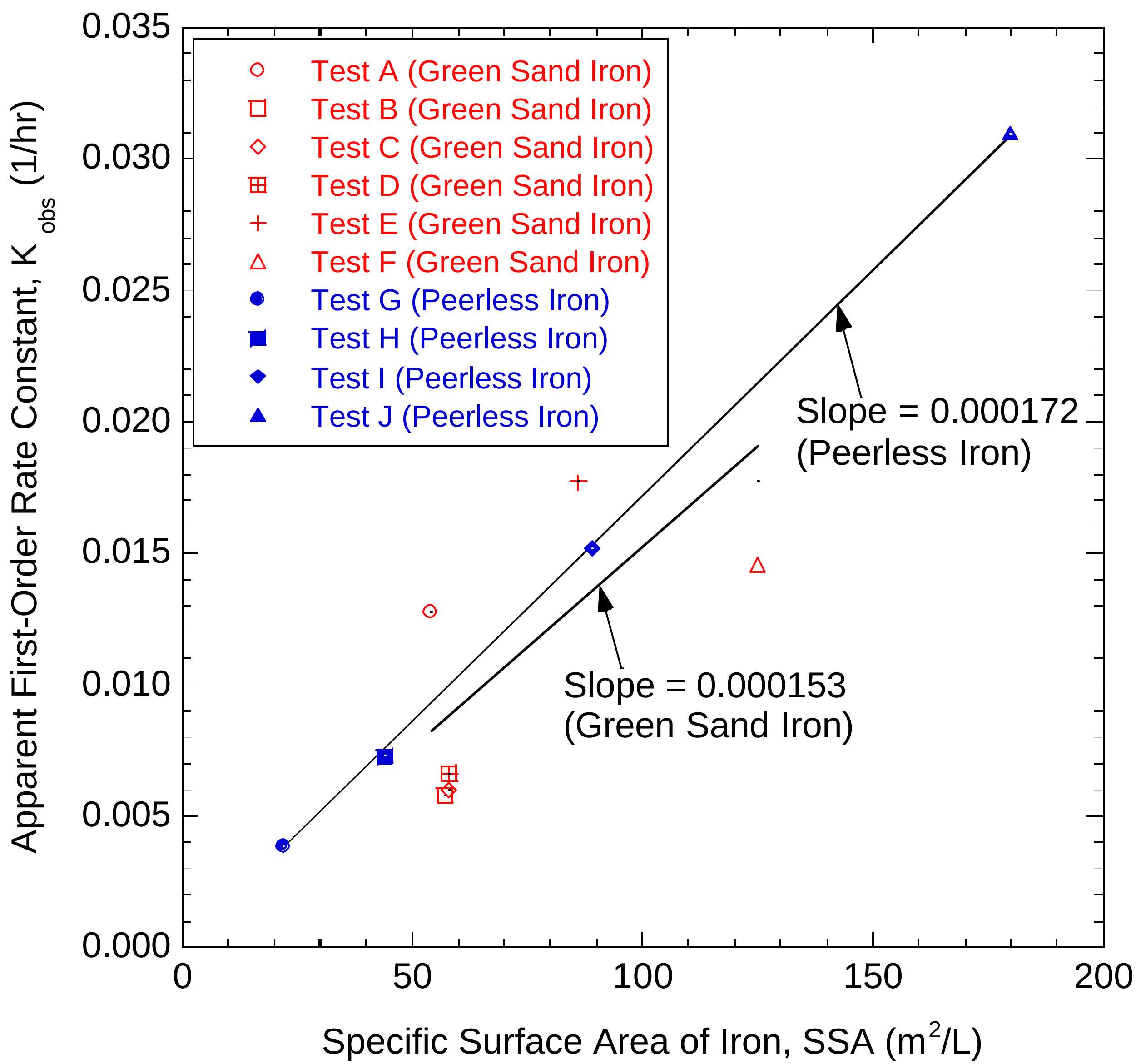
Batch Reactivity Tests



- Conducted on iron extracted from sand
- Approximately first order
- Similar rate coefficients as Peerless iron

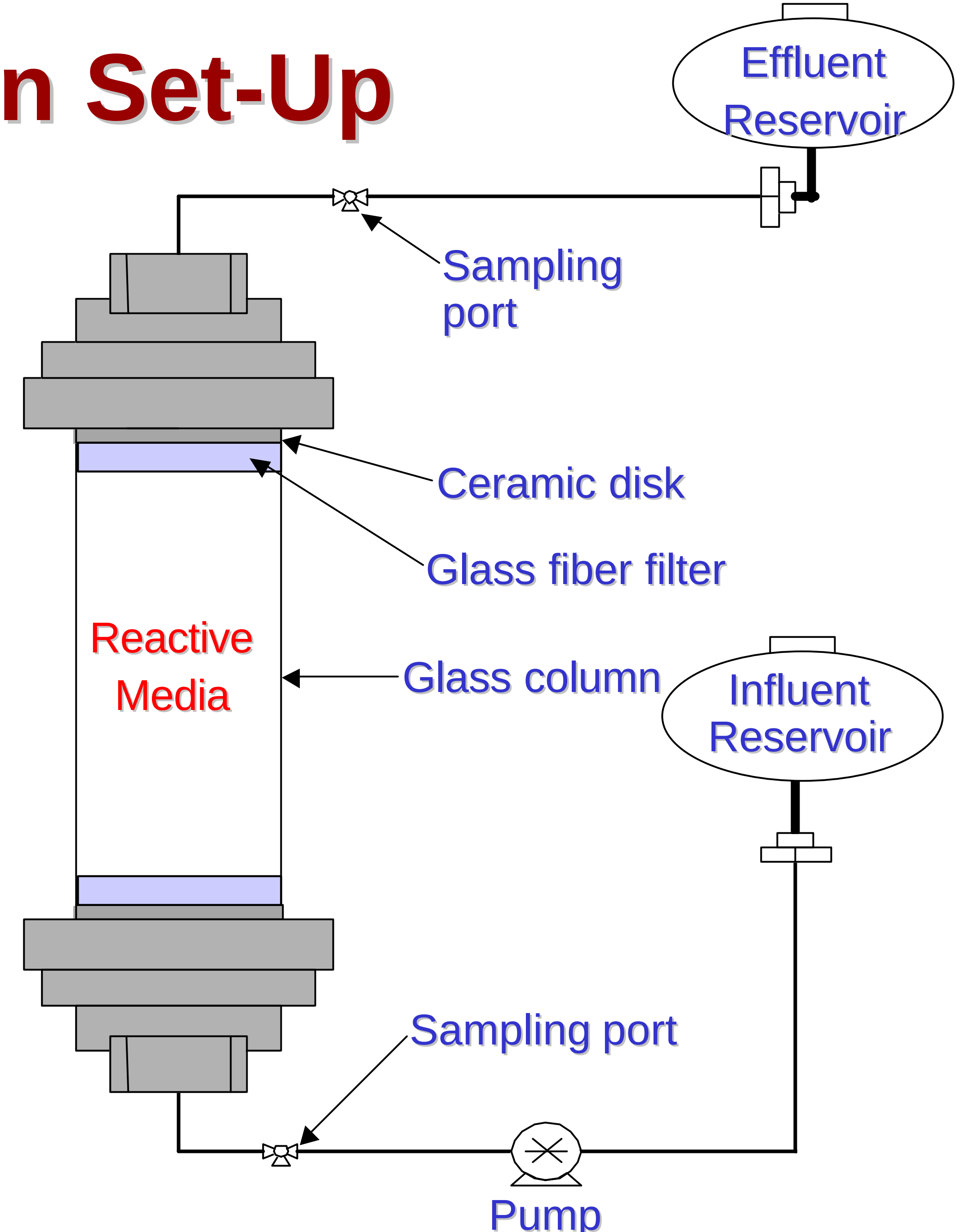
Test	Iron Source	Initial Conc. (mg/L)	Iron Surface Area/Volume (m^2/L)	Dissolved Oxygen (mg/L)	NaCl (M)	Rate Constant (L/m^2-hr)	Partition Coefficient (L/kg)
A	Green Sand	5.2	54	5.4	0.00	2.37×10^{-4}	2.13
B	Green Sand	31.9	57	< 0.6	0	1.02×10^{-4}	1.22
C	Green Sand	31.9	58	5.4	0.02	1.03×10^{-4}	0.77
D	Green Sand	8.8	58	< 0.6	0	1.14×10^{-4}	1.76
E	Green Sand	15.2	86	6.0	0	2.06×10^{-4}	1.72
F	Green Sand	40.3	125	5.8	0	1.17×10^{-4}	2.41
G	Peer-less Iron	40.3	22	5.6	0	1.76×10^{-4}	2.12
H	Peer-less Iron	40.3	44	5.6	0	1.65×10^{-4}	1.79
I	Peer-less Iron	40.3	89	5.6	0	1.71×10^{-4}	1.52
J	Peer-less Iron	40.4	180	5.6	0	1.72×10^{-4}	1.61

Comparison of Normalized Rate Coefficients

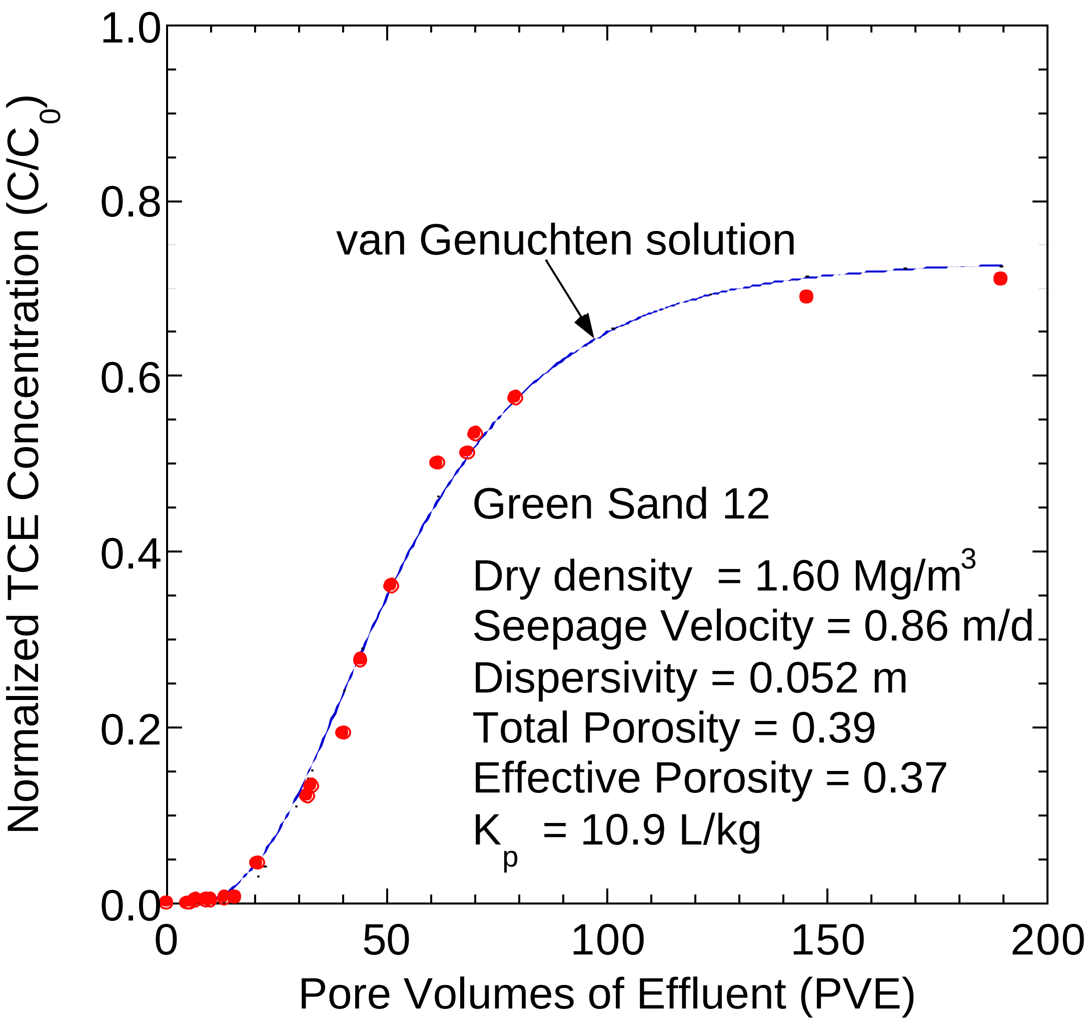


- K_{obs} vs. SSA approximately linear for both green sand iron and Peerless iron
- Comparable normalized rate coefficients

Column Set-Up



Typical Breakthrough Curve



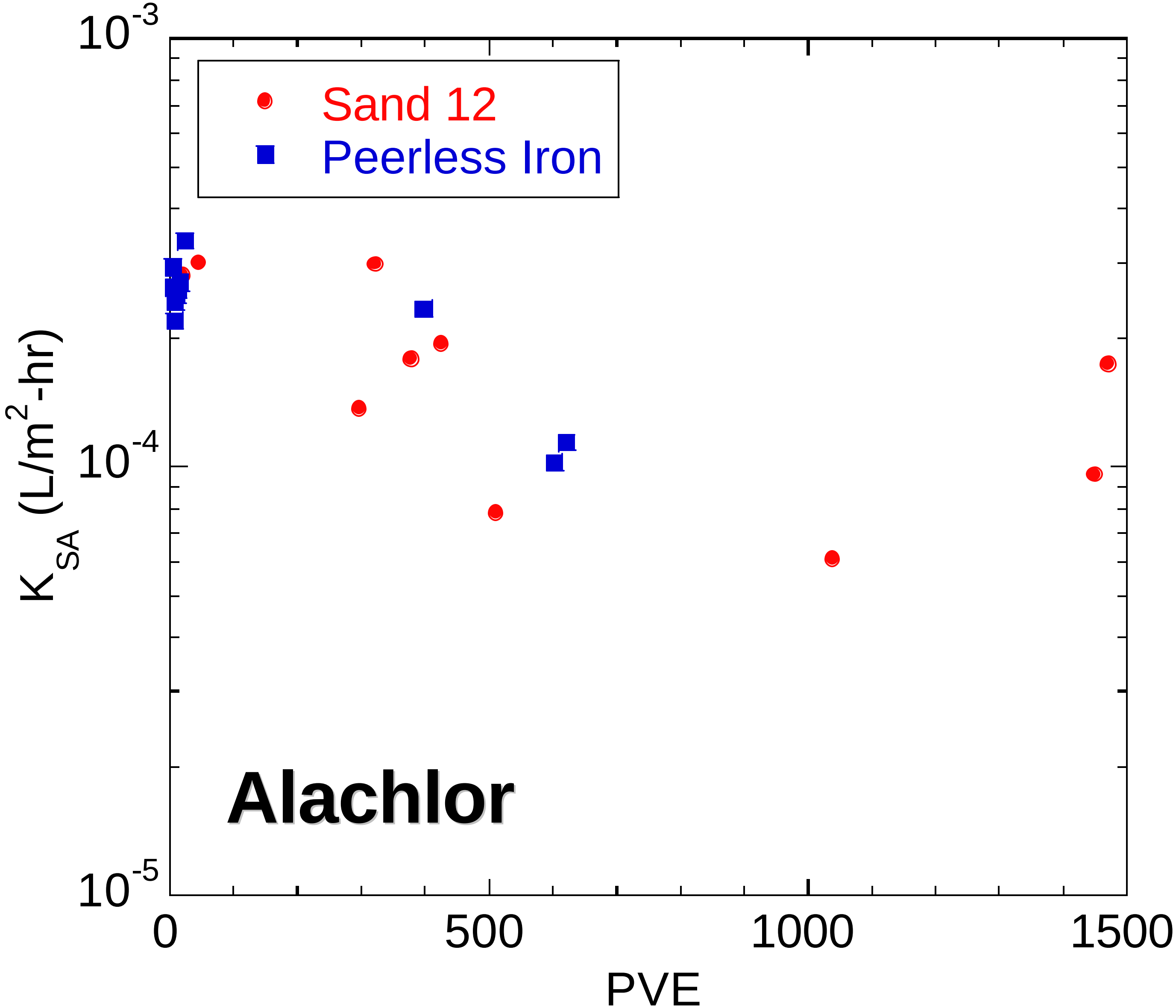
- Breakthrough data analyzed using van Genuchten solution to ADRE with instantaneous sorption and first-order reactions
- Fit by least-squares minimization

Results of Column Tests

- Tests conducted on two sands with very little (<0.1%) iron and two sands with moderate to high amounts of iron
- K_{SA} and K_p are comparable to those obtained from batch tests

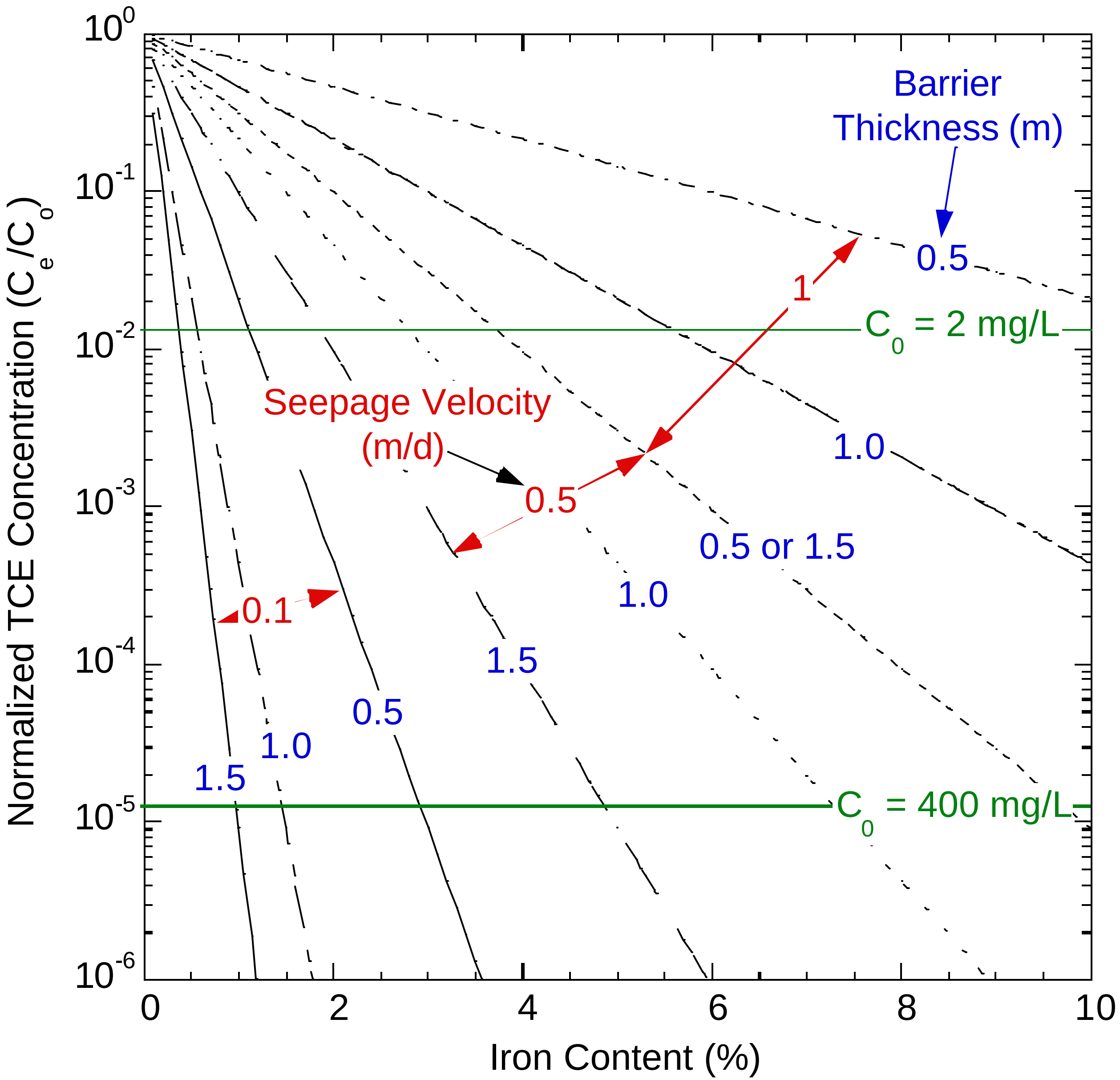
Green Sand	Total Porosity (n)	Effective Porosity (n_e)	n_e/n	K_p (L/kg)	K_{obs} (1/hr)	SSA (m^2/L)	K_{SA} (L/m^2-hr)
1	0.36	0.37	1.03	9.1	0.063	327	0.000193
9	0.39	0.46	1.18	7.23	-	0.0	-
11	0.43	0.46	1.07	41.0	-	0.0	-
12	0.39	0.37	0.95	10.9	0.126	1034	0.000122

Long-Term Column Tests



- Modest reduction in K_{SA} (2-3x) over 1500 pore volumes
- Comparable effect on Peerless iron

Field Scenarios



- Based on van Genuchten's steady-state solution
- PRBs 1 m wide are practical for lower seepage velocities (<0.1 m/d) and modest iron contents (>2%)
- Higher seepage velocities (1 m/d) required a thicker barrier or higher iron content

Summary

- Green sands have high sorptive capacity for TCE and chlorinated herbicides (4.0 L/kg to 50 L/kg).
- Isotherms are approximately linear and partition coefficient is linearly related to TOC (1 < TOC < 4%).
- Reactivity of green sand iron determined from batch tests (iron alone) or column tests (in green sand) is comparable to that of Peerless iron.
- Comparable partition coefficients and rate coefficients obtained using column and laboratory tests.
- Long-term reactivity appears to be comparable to that of Peerless iron.

Acknowledgement

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