



Reinigungswände 2001: Schadstoffe und reaktive Materialien

- Stand der Technik,
Entwicklungen und Grenzen -

Volker Birke



Themenbereiche

- Übersicht reaktiver Materialien
- Nullwertiges Eisen: LCKW
- Metalle: CKW
- Reaktive Materialien, Sorbentien: Schwermetalle
- Reaktive Materialien, Sorbentien: PAK, BTEX
- ORC, HRC



Reviews (1)

- Dahmke, A. (1997), „Aktualisierung der Literaturstudie ‘Reaktive Wände’ pH-Redox-reaktive Wände“. Landesanstalt für Umweltschutz, Baden-Württemberg, Texte und Berichte zur Altlastenbearbeitung, 33/97, Karlsruhe.
- NATO/CCMS Pilot Study (1998), „Special Session on Treatment Walls and Permeable Reactive Barriers“, Vienna, Austria
- Simon, F.-G.; Meggyes, T. (2000), „Removal of Organic and Inorganic Pollutants from Groundwater Using Permeable Reactive Barriers“, Land Contamination & Reclamation, 8, 103-116 (Part I), 175-187 (Part II)

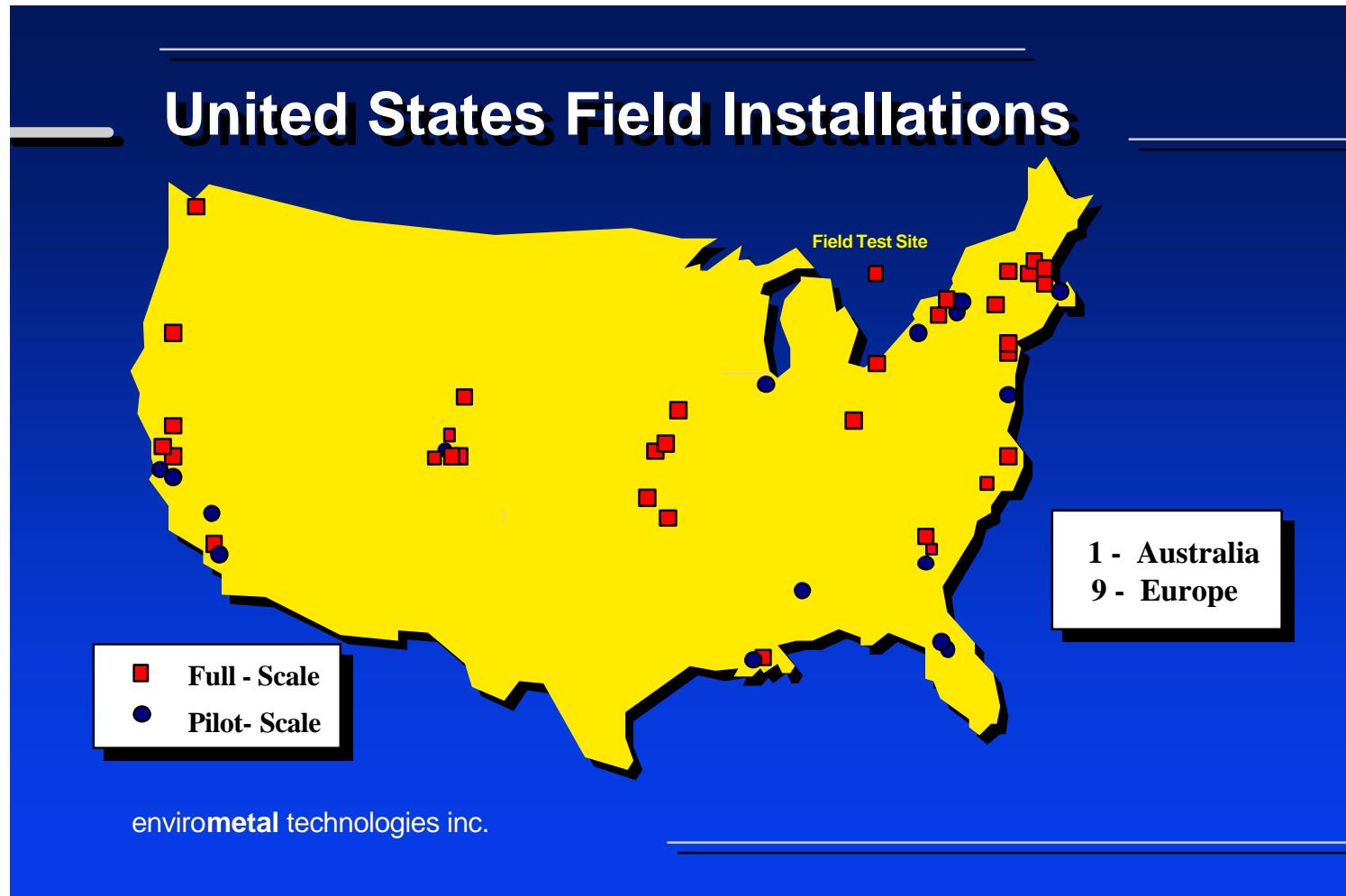


Reviews (2)

- Scherer, M.M.; Richter, S.; Valentine, R.L.; Alvarez, P.J.J. (2000), „Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean Up“, Critical Reviews in Environmental Science and Technology, 30, 363-411.
- Gavaskar, A.; Gupta, N.; Sass, B.; Janosy, R.; Hicks, J. (2000), „Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation“, Battelle, Columbus, Ohio

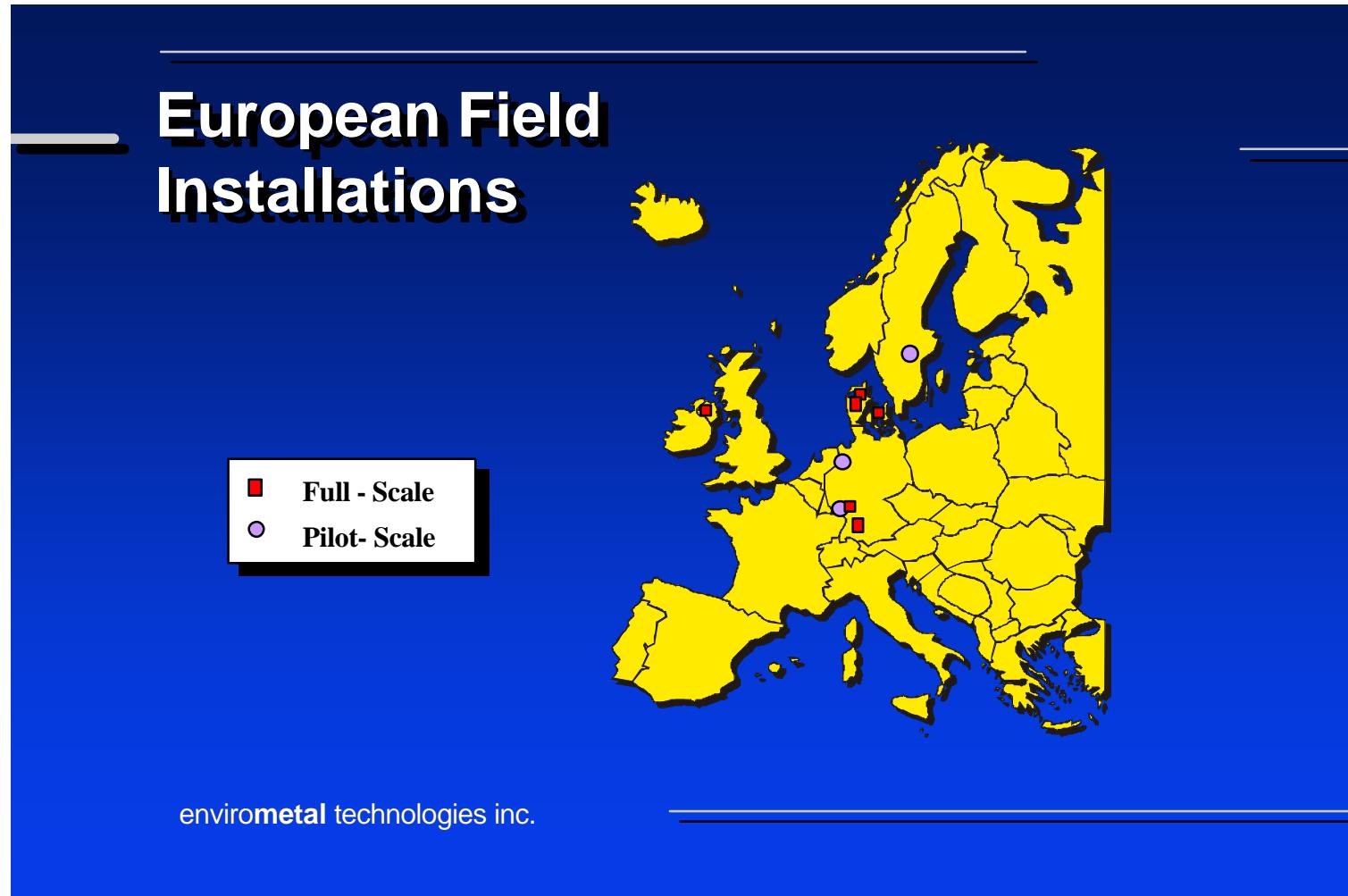


Reaktive Wände in Nordamerika



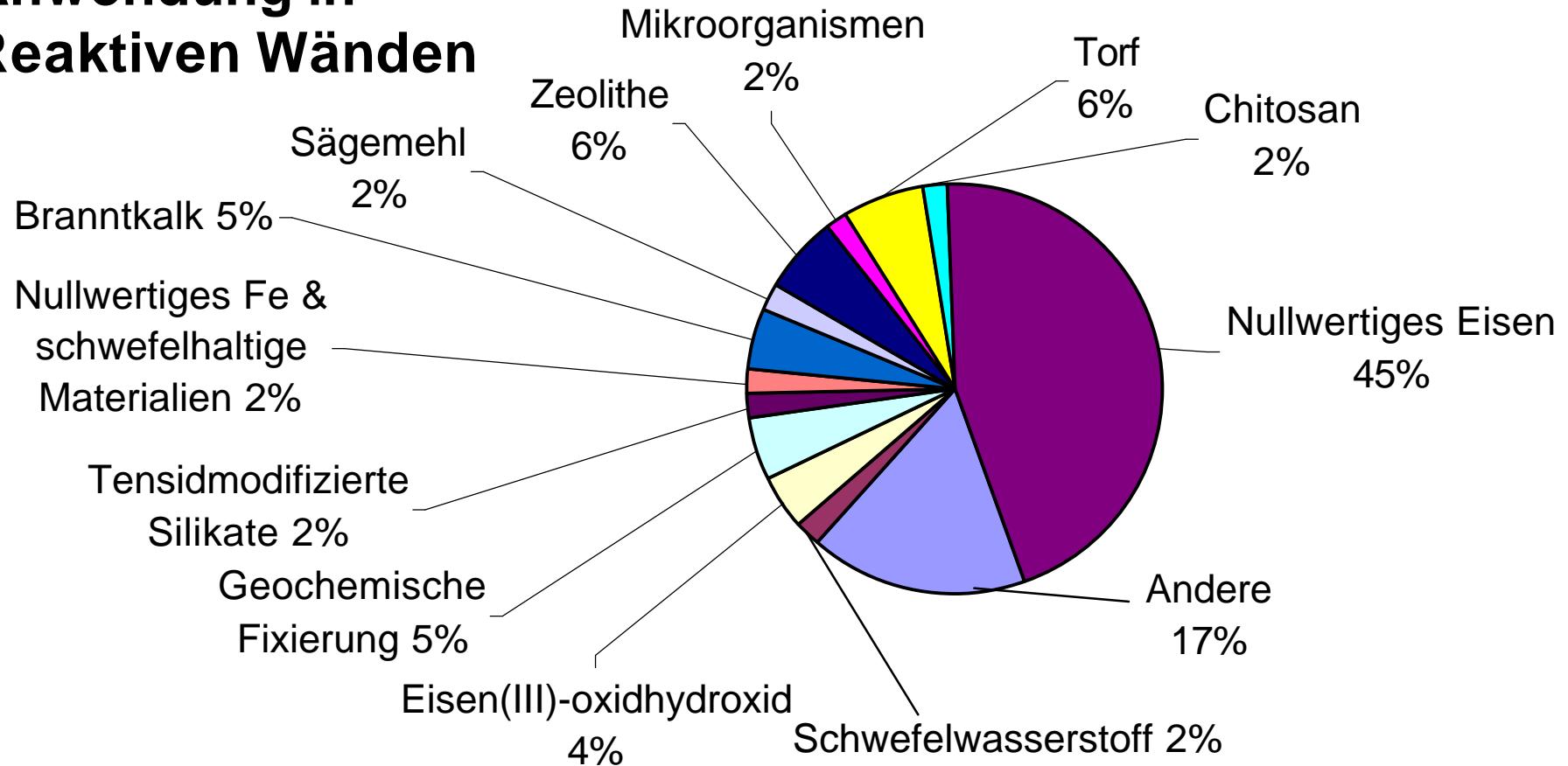


Reaktive Wände in Europa





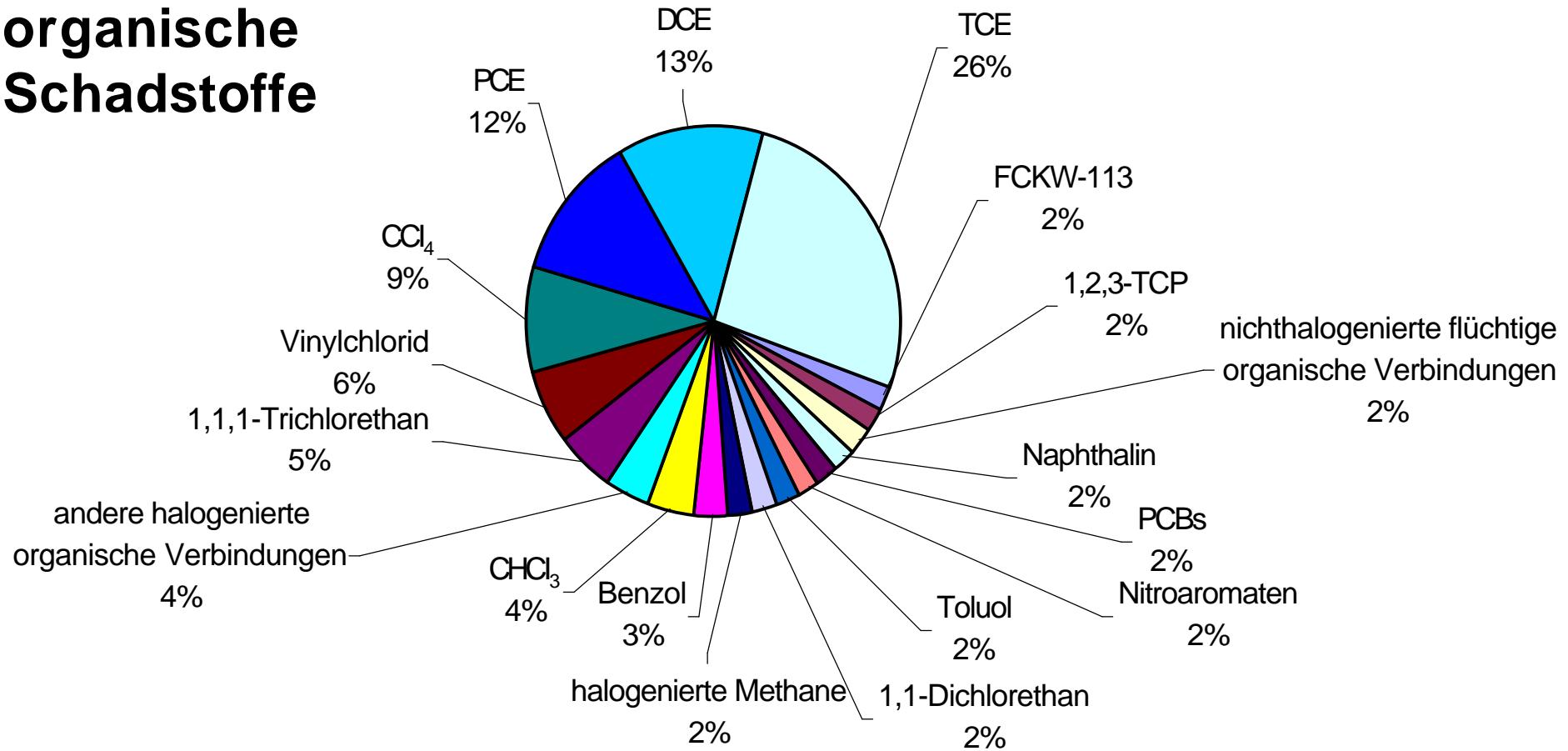
Materialien für die Anwendung in Reaktiven Wänden



Prozentangaben basieren auf insgesamt 124 Projekten (nach Scherer et al. (2000), *Critical Reviews in Environmental Science and Technology*, 30(3), 363-411)



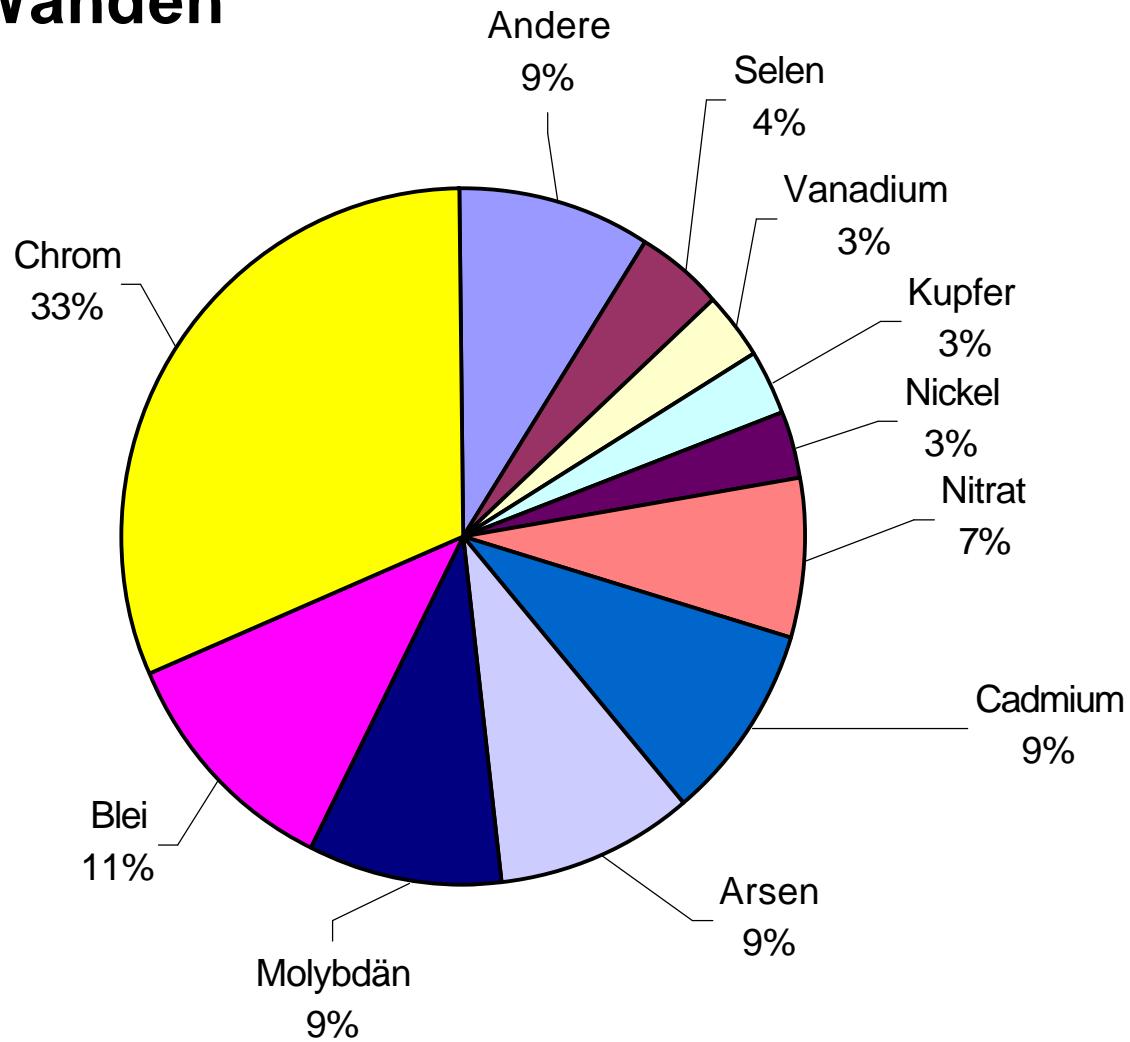
Mit Reaktiven Wänden behandelte organische Schadstoffe



Prozentangaben basieren auf insgesamt 124 Projekten (Scherer et al., 2000)



Mit Reaktiven Wänden behandelte anorganische Schadstoffe



Prozentangaben basieren auf insgesamt 124 Projekten (Scherer et al., 2000)



Reaktive Materialien für anorganische Grundwasserkontaminanten (1)

Material	Mechanismus	Kontaminante	Referenzen ¹
Eisenoxid-hydroxid	Sorption	U, Mo, Cr	Morrison, Spangler 1993, 1996 Morrison et al. 1995 Zachara et al. 1987
Torfmoos	Sorption	Cr, Cu, Zn, Ni, Cd, U, Mo	Christ et al. 1996 Gosset et al. 1986 Ho et al. 1995 McLellan, Rock 1987 Morrison, Spangler 1992 Sharma, Foster 1993
Modifizierte Zeolithe	Sorption	Pb, Cr, Se, Sulfat, Cd	Bowman et al. 1995 Haggerty, Bowman 1994 Kesraoui-Ouki et al. 1993 Lee et al. 1989 Li, Bowman 1997, 1998



Reaktive Materialien für anorganische Grundwasserkontaminanten (2)

Material	Mechanismus	Kontaminante	Referenzen ¹
Chitosan	Sorption	Hg, U, Cd, Pb, V, Ni, Mo, Ti, Se	Mitani et al. 1991
Podsol (spodic)	Sorption	As	Lindberg et al. 1997
Sägemehl, Braunkohle, Kohle	Sorption	Mo, U	Morrison, Spangler 1992
Titandioxid	Sorption	Mo, U	Morrison, Spangler 1992
Eisen(III)-chlorid mit Kalkstein	Sorption	U	Morrison, Spangler 1992



Reaktive Materialien für anorganische Grundwasserkontaminanten (3)

Material	Mechanismus	Kontaminante	Referenzen ¹
Eisen(III)-nitrat, Eisen(III)-sulfat	Sorption	Mo	Morrison, Spangler 1992
Hydroxyapatit Natürl. Apatit	Fällung	Pb	Ma et al. 1993, 1994, 1994, 1995
Eisen(III)-sulfat, Calciumchlorid, Bariumchlorid	Fällung	Mo, U	Morrison, Spangler 1992
Ca-hydroxid, Flugasche	Fällung	U	Morrison, Spangler 1992
Kalkstein	Fällung	Acid Mine Drainage (AMD)	Hedin et al. 1994 Turner, McCoy 1990



Reaktive Materialien für anorganische Grundwasserkontaminanten (4)

Nullwertiges Eisen	Chemische Reduktion	Cr, U, Tc, Nitrat, Nitrit, Mo, Ag, Sulfat, Hg	http://cgr.ese.ogi.edu/ironrefs (Dr. Paul Tratnyek, Oregon Graduate)
Eisen-Mineralien	Chemische Reduktion	Nitrat, Chromat	Hansen et al. 1996 Peterson et al. 1997
Nullwertiges Eisen	Erniedrigung Redoxpotential, Metallfällung	AMD (saure Grubenwässer)	Shelp et al. 1995
Organisches Material	Mikrobielle Sulfatreduktion u. Sulfidfällung	AMD	Benner et al. 1997
Organisches Material	Mikrobielle Nitratreduktion	Nitrat	Robertson, Cherry 1995 Robertson et al. 1991



Reaktive Materialien für organische Grundwasserkontaminanten (1)

Material	Mechanismus	Kontaminante	Referenzen ¹
Nullwertiges Eisen	Chemische Reduktion	Chloraliphäne, DDT, Nitroarom. einige Pestizide, Azofarbstoffe	http://cgr.ese.ogi.edu/ironrefs (Dr. Paul Tratnyek, Oregon Graduate)
Bimetallisches Eisen	Chemische Reduktion	Chlorierte Aliphäne, PCB	Grittini et al. 1995 Liang et al. 1997 Muftikan et al. 1995 Orth et al. 1998
Mg, Sn, Zn	Chemische Reduktion	Chlorierte Aliphäne	Arnold, Roberts 1998 Fennelly, Roberts 1998 Warren et al. 1995 Boronina 1995, 1998 Song et al. 1999 Su, Puls 1999



Reaktive Materialien für organische Grundwasserkontaminanten (2)

Material	Mechanismus	Kontaminante	Referenzen ¹
Eisen-Minerale (Oxide, Hydroxide, Sulphide)	Chemische Reduktion	Nitroaromaten chlorierte Aliphäten	Kriegman-King, Reinhard 1991, 1992, 1994 Butler, Hayes 1998 Haderlein, Pecher 1998 Sivavec et al. 1997 Klausen et al. 1995
Sauerstoff- oder Nitrat- freisetzende Stoffe	Mikrobieller Abbau	BTEX	Bianchi-Mosquera et al. 1994 Borden et al. 1997 Kao, Borden 1997
Mikroorganis- men „resting state“	Mikrobieller Cometabolis- mus	Chlorierte Aliphäten	Duba et al. 1996 Taylor et al. 1993



Reaktive Materialien für organische Grundwasserkontaminanten (3)

Material	Mechanis-mus	Kontaminante	Referenzen ¹
Tensid-modifizierte Böden	Sorption	Unpolare org. Schadstoffe	Burris, Antworth 1992 Lee et al. 1989 Wagner et al. 1994
Tensid-modifizierte Tone	Sorption	Unpolare org. Schadstoffe	Smith, Galan 1995 Smith, Jaffe 1994 Smith 1990
Tensid-modifizierte Zeolithe	Sorption	Unpolare org. Schadstoffe	Bowman et al. 1995
Kohle, Aktivkohle, Torf, Sägemehl	Sorption	Benzol	Rael et al. 1995



Reaktive Materialien für Grundwasserkontaminanten

¹ Referenzen siehe:

Scherer, M.M.; Richter, S.; Valentine, R.L.; Alvarez, P.J.J. (2000), „Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean Up“, Critical Reviews in Environmental Science and Technology, 30, 363-411.



Halbwertszeiten Eisen (1)

Schadstoffe	Reines Eisen $t_{1/2}$ (h)	Kommerzielles Eisen ^(m) $t_{1/2}$ (h)
Methan Tetrachlormethan Chloroform Bromoform	0.02^(a), 0.003^(g), 0.023⁽ⁱ⁾ 1.49^(a), 0.73^(g) 0.041^(a)	0.31-0.85^(b) 4.8^(b)
Ethan Hexachlorethan 1,1,2,2-Tetrachlorethan 1,1,1,2-Tetrachlorethan 1,1,1-Trichlorethan 1,1-Dichlorethan	0.13^(a) 0.053^(a) 0.049^(a) 0.065^(a), 1.4^(h) NA	NA NA NA 1.7-4.1^(b) NA
Ethen Tetrachlorethen Trichlorethen 1,1-Dichlorethen <i>trans</i> -1,2-Dichlorethen <i>cis</i> -1,2-Dichlorethen Vinylchlorid	0.28^(a), 5.2^(h) 0.67^(a), 7.3-9.7^(g), 0.68^(J) 5.5^(a), 2.8^(h) 6.4^(a) 19.7^(a) 12.6^(a)	2.1-10.8^(h), 3.2^(e) 1.1-4.6^(b), 2.4^(e), 2.8^(f) 37.4^(e), 15.2^(f) 4.9^(b), 6.9^(e), 7.6^(f) 10.8-33.9^(b), 47.6^(e) 10.8-12.3^(b), 4.7^(e)



Halbwertszeiten Eisen (2)

Schadstoffe	Reines Eisen $t_{1/2}$ (h)	Kommerzielles Eisen ^(m) $t_{1/2}$ (h)
Andere organische Stoffe		
1,1,2-Trichlortrifluorethan (Freon113)	1.02 ^(b)	NA
1,2,3-Trichlorpropan	NA	24,0 ^(c)
1,2-Dichlorpropan	NA	4,5 ^(c)
1,3-Dichlorpropan	NA	2,2 ^(c)
1,2-Dibrom-3-chlorpropan	NA	0,72 ^(b)
1,2-Dibromoethan	NA	1.5-6.5 ^(b)
<i>n</i> -Nitrosodimethylamin (NDMA)	1.83 ^(b)	NA
Nitrobenzol	0.008 ^(d)	NA
Anorganische Stoffe		
Chrom ^{(k)(l)} , Nickel ^(l)	NA	NA
Uran ^(l)	NA	NA
Nitrat ^(l)	NA	NA
Kein sichtlicher Abbau		
Dichlormethan ^{(a)(g)(h)}	NA	NA
1,4-Dichlorbenzol ^(h)	NA	NA
1,2-Dichlorethan ^(b)	NA	NA
Chlormethan ^(b)	NA	NA



Halbwertszeiten Eisen (3)

- | | |
|-----------------------------------|--|
| (a) Gillham und O`Hannsin (1994) | (i) Lipczynska-Kochany et al. (1994) |
| (b) ETI (1997) | (j) Orth und Gillham (1995) |
| (c) Focht (1994) | (k) Blowes et al. (1997) |
| (d) Agrawal und Tratnyek (1994) | (l) WSRC (1999) |
| (e) Sivavec und Horney (1995) | (m) Die Halbwertzeiten in dieser Tabelle dienen nur zur prinzipiellen Demonstration/Veranschaulichung. Die Halbwertzeiten für den Schadstoffabbau können veränderlich sein in Abhängigkeit der Eisensorte und der speziellen Grundwasserchemie am jeweiligen Standort. |
| (f) Mackenzie et al. (1995) | |
| (g) Matheson und Tratnyek (1994) | |
| (h) Schreiber und Reinhard (1994) | |
- NA = Nicht erhältlich

Quelle/Literatur siehe: Gavaskar, A.; Gupta, N.; Sass, B.; Janosy, R.; Hicks, J. (2000), Final Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation, Battelle, Columbus, Ohio;
<http://www.estcp.com/documents/techdocs/index.cfm>



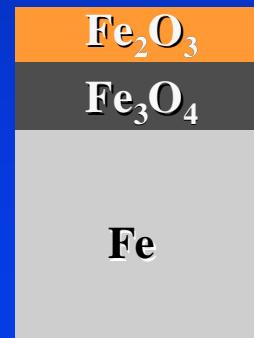
- **Most applications use granular zero-valent iron (ZVI) to treat chlorinated solvents**
 - Primarily TCE / PCE
 - Chemistry and kinetics well established
- **ZVI can also treat metals, radionuclides**
 - Hex-Chrome demonstrated extensively
- **ZVI treatment driven by iron corrosion reactions**
 - Lowers Redox potential, generates hydrogen
 - Friendly to dechlorinating bacteria
- **Not applicable to fuels, BTEX**
- **Over 30 full-scale systems in place**
- **Current focus is on documenting long-term performance**



Eisen / LCKW: Gillham et al. 2001

Commercial-Grade Connelly Iron

- Scrap metal (steel, cast iron)
- High temperature kilns
- Thick oxide film: double-layer structure
 - inner conducting Fe_3O_4 (magnetite)
 - outer passivating Fe_2O_3 (hematite, maghemite)



Factors in the Long-term Performance of Granular Iron PRBs

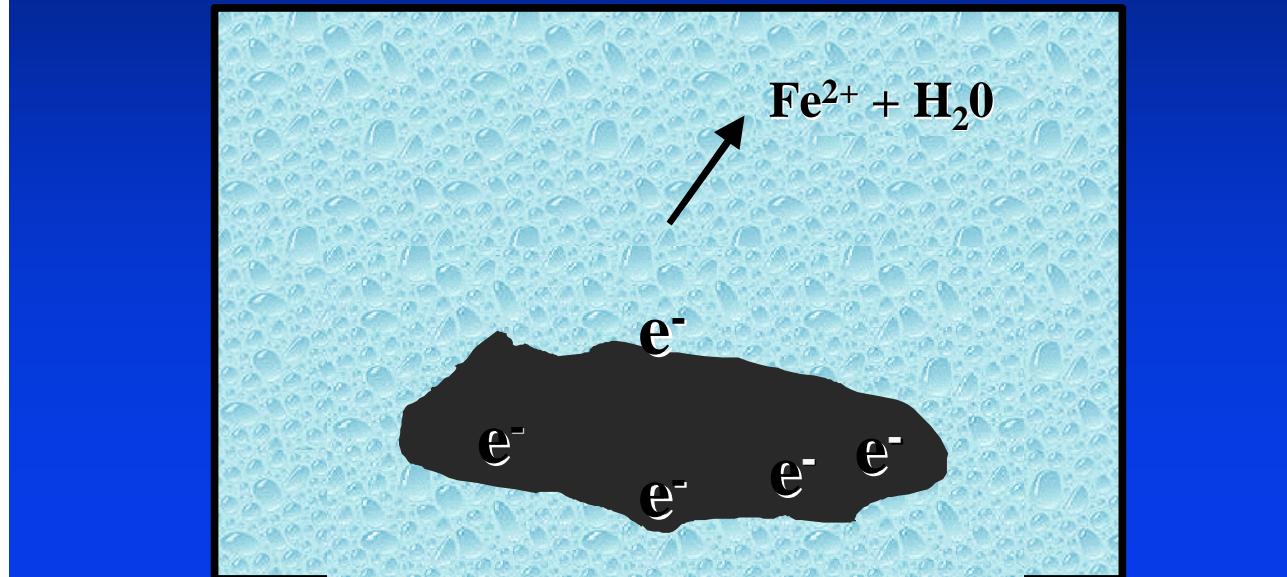
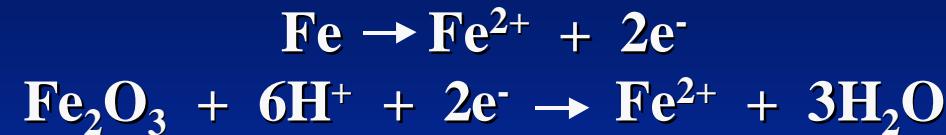
Robert W. Gillham, Kaylene Ritter
Yousheng Zhang, Marek Odziemkowski

Department of Earth Sciences
University of Waterloo
Waterloo, ON, N2L 3G1



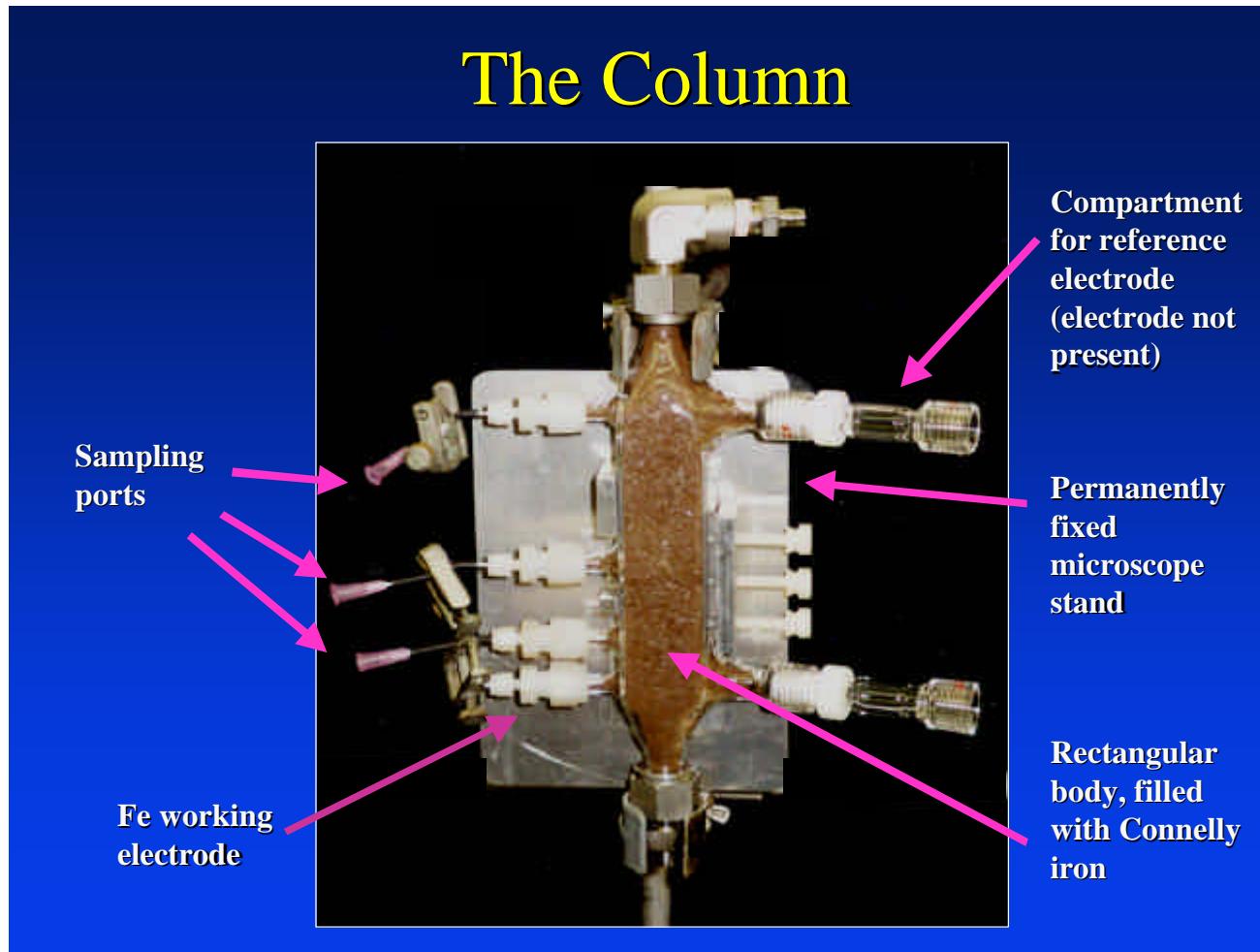
Eisen / LCKW: Gillham et al. 2001

Autoreduction Reaction



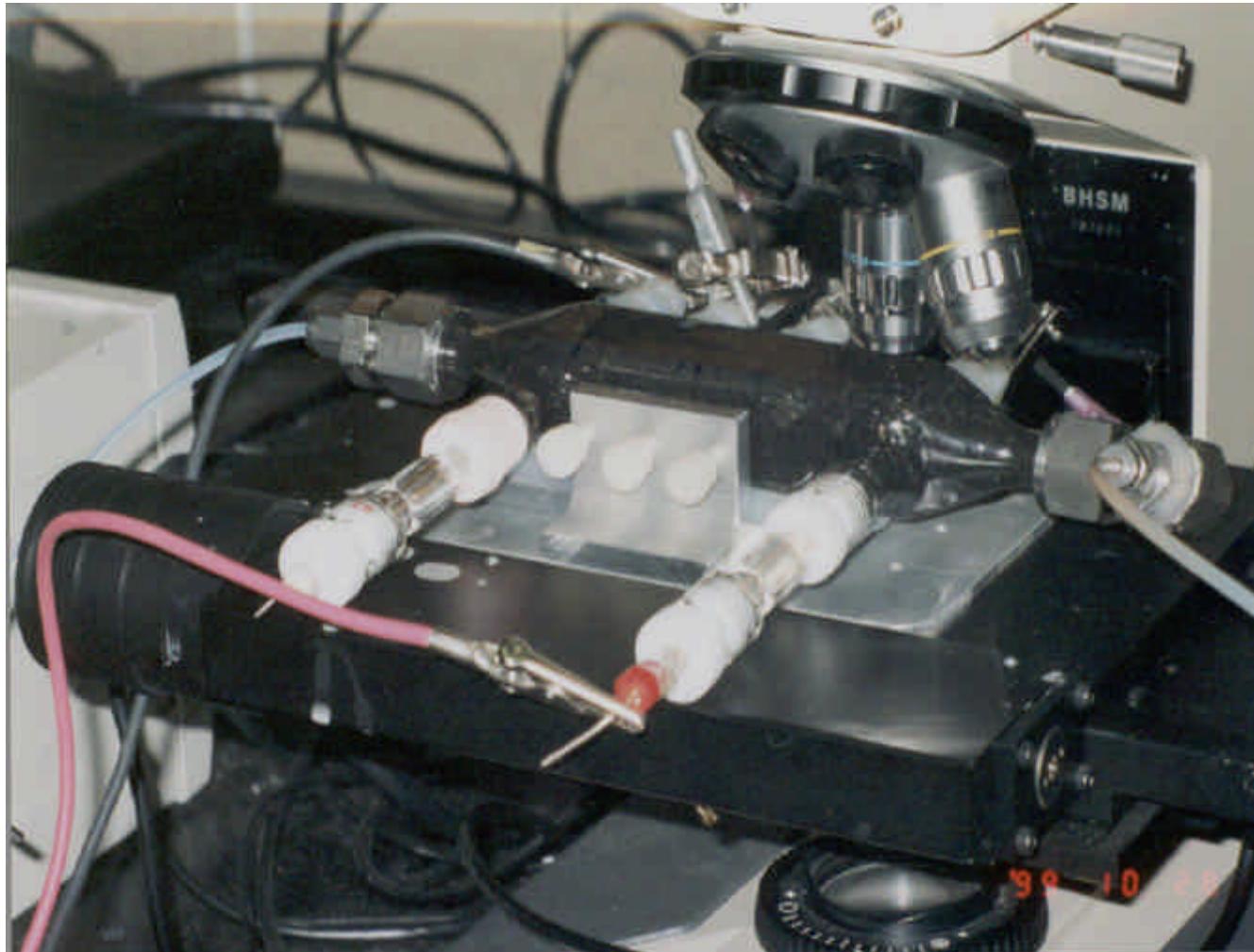


Eisen / LCKW: Gillham et al. 2001



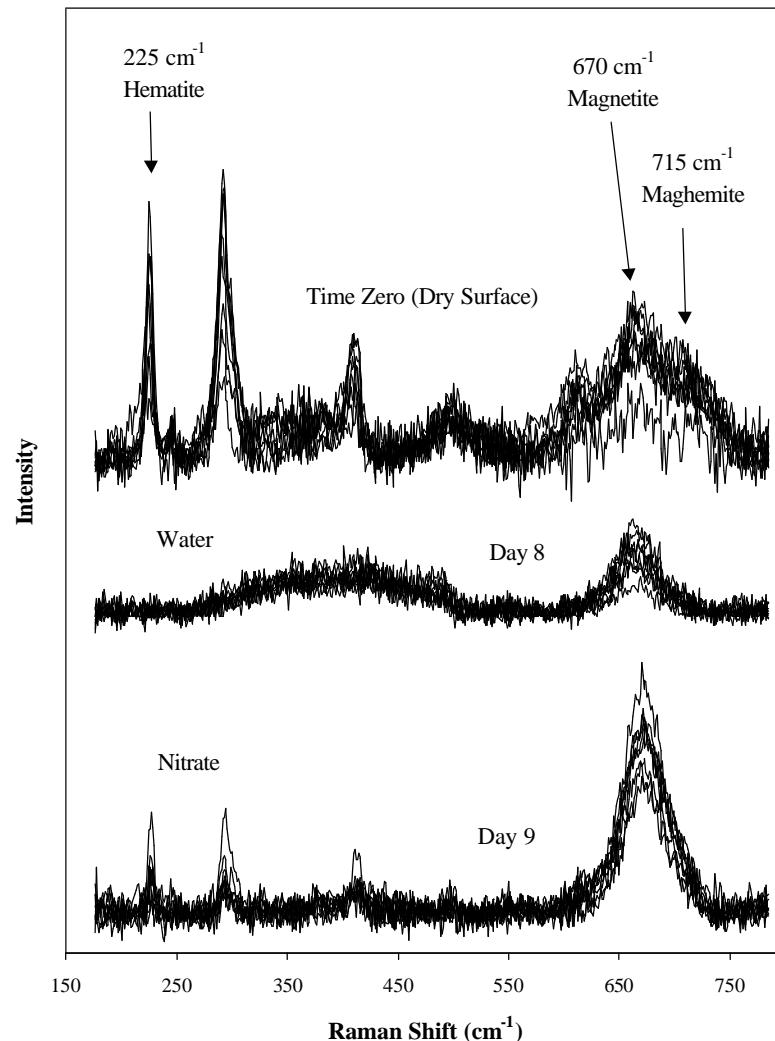


Eisen / LCKW: Gillham et al. 2001





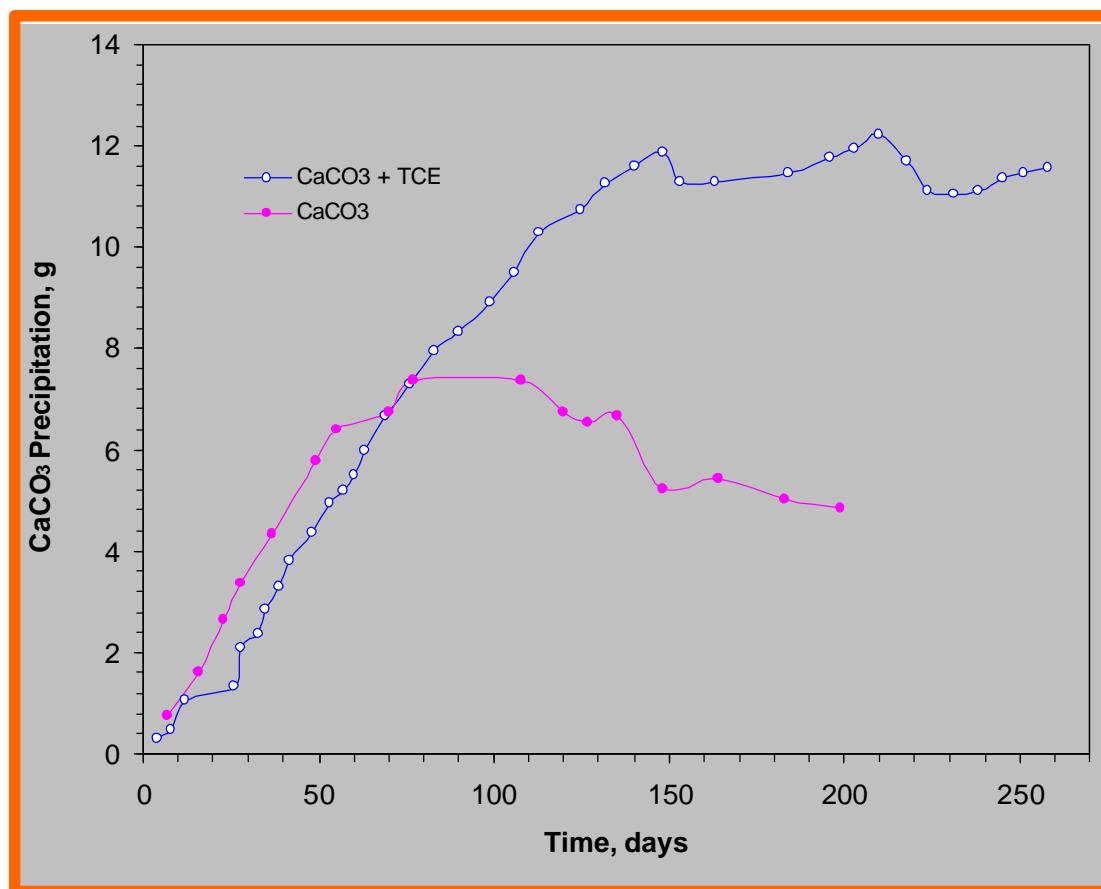
Eisen / LCKW: Gillham et al. 2001



- Rapid autoreduction of Fe_2O_3 in presence of water and TCE solution
- Persistent degradation of TCE
- Fe_2O_3 unstable in TCE solution
- Minor amount of nitrate reduction ($\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$ at equilibrium)
- Minor TCE reduction in presence of nitrate (Fe_2O_3 passivation)



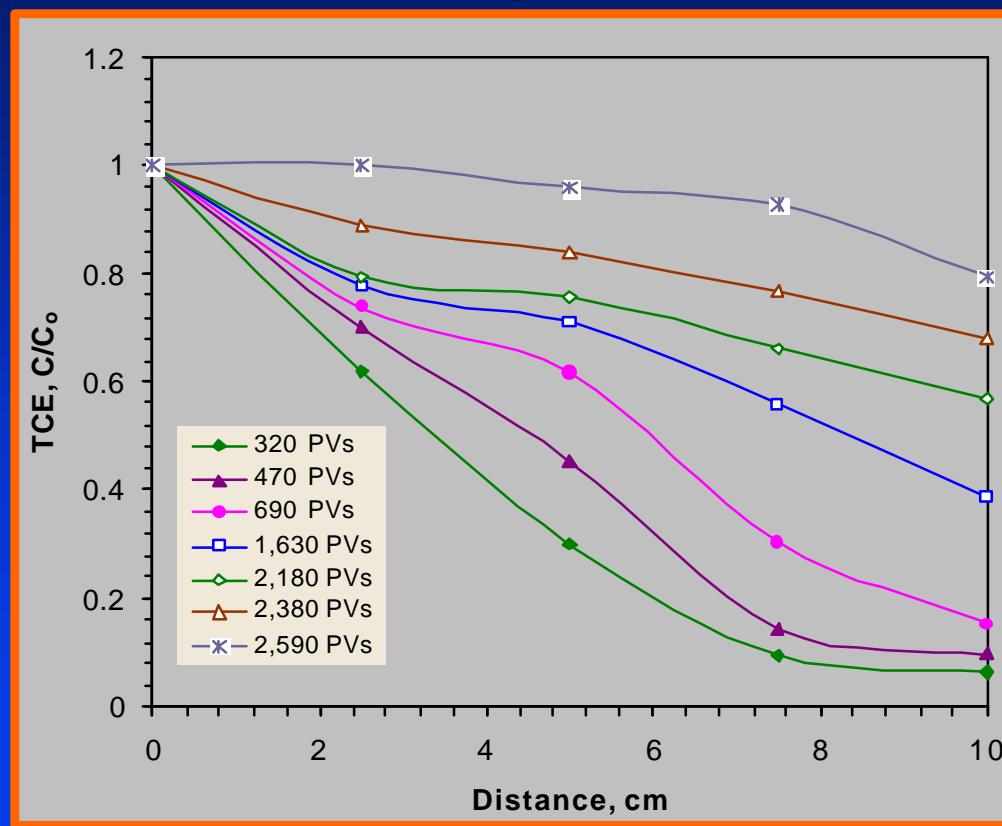
Eisen / LCKW: Gillham et al. 2001





Eisen / LCKW: Gillham et al. 2001

TCE Profiles Along the Iron Column (300 ppm CaCO₃ + 10 ppm TCE)





Eisen / LCKW: Gillham et al. 2001

Implications

CaCO_3 accumulates to 0.1 g/cm³ of iron

Assume:

- 100 mg/L decline in HCO_3^-
- porosity of geologic formation -- 0.33
- groundwater velocity of 10 cm/day

*Precipitate front will advance at
a rate of 1.3 cm/yr*



Eisen / LCKW: Gillham et al. 2001

Conclusions

1. Iron persists for long periods of time in 100% iron PRBs.
2. Persistence may be an important issue if the iron is highly dispersed or highly reactive.
3. Autoreduction of oxides is an essential process in performance of commercial iron.
4. Other oxidants such as nitrate may interfere with the autoreduction process.



Eisen / LCKW: Gillham et al. 2001

Conclusions (cont.)

5. Calcium carbonate precipitates form as a progressing front.
6. Precipitates do not cause a major decline in hydraulic conductivity.
7. Precipitates cause reduction in degradation rates.



Eisen / LCKW: Landis et al. 2001

An Examination of
Zero-Valent Iron
Sources used in
Permeable Reactive
Barriers

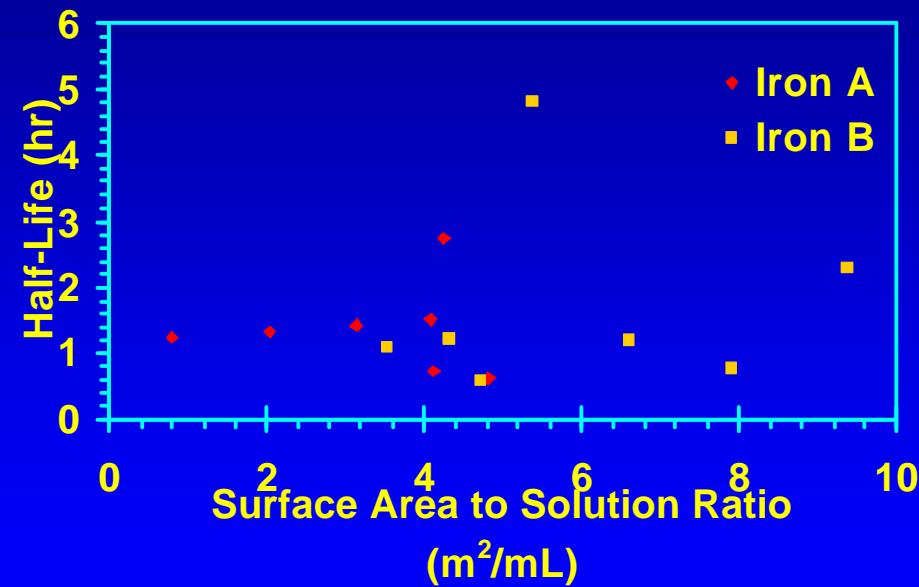
Dr. Richard Landis
– E.I. DuPont de
Nemours Co.

Dr. Robert Gillham,
Dr. Eric Reardon,
Randy Fagan
– University of
Waterloo

Robert Focht, John
Vogan – EnviroMetal

Presented at:
2001 International
Containment &
Remediation
Technology Conference
Orlando, Florida

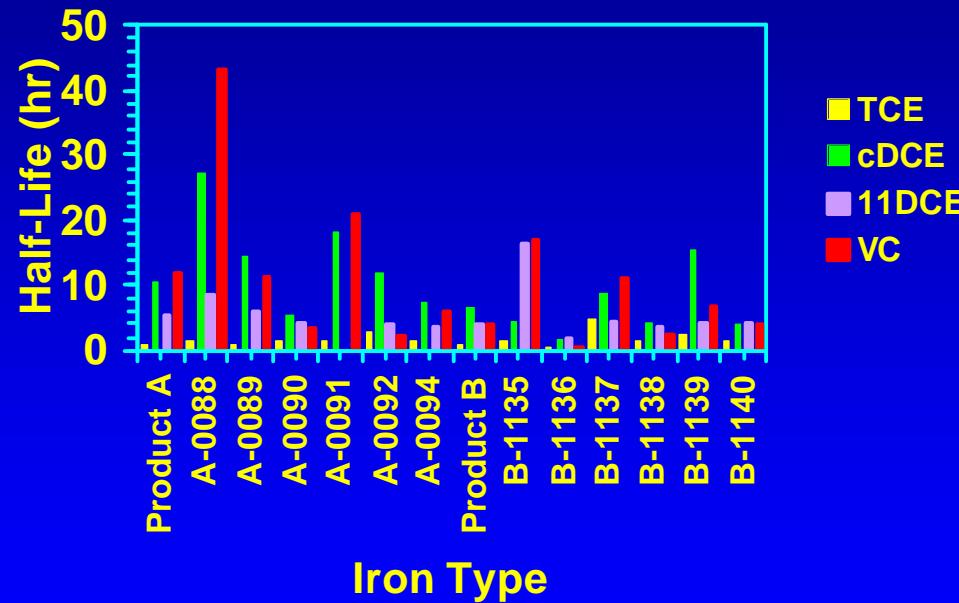
Degradation Rate vs Surface Area





Eisen / LCKW: Landis et al. 2001

Observed Degradation Rates





Summary of Progress to Date:

- Little correlation of BET surface area to degradation rates
- Gross elemental composition of feedstocks of both commercial sources appears similar
- “historical” differences in rates between sources confirmed in recent samples

Eisen /
LCKW:
Landis
et al.
2001

Future Work:

- Correlation between reactivity and carbon structure, trace metal content?
- Alternative measures of “reactive” surface area?
- Influence of milling procedures on reactivity?
- Water corrosion rate?



Eisen / LCKW: Sass et al. 2001

Geochemical Investigation of Three Permeable Reactive Barriers to Assess Impact of Precipitation on Performance and Longevity

Bruce Sass, Arun Gavaskar, Woong-Sang Yoon,
Neeraj Gupta, Eric Drescher

Battelle Memorial Institute, Columbus, OH

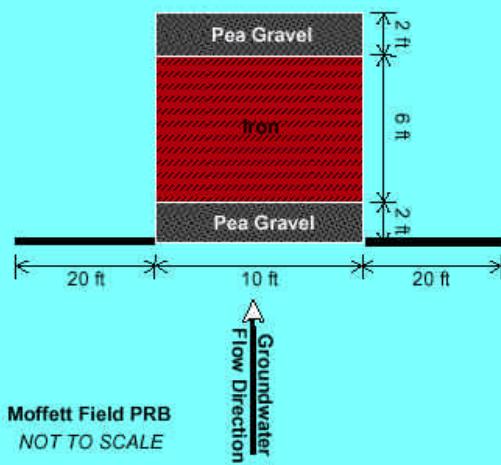
Charles Reeter

Naval Facilities Engineering Service Center, Port
Hueneme, CA

2001 International Containment & Remediation Technology Conference and Exhibition
Radisson Orlando Hotel, Orlando, Florida, USA
12 June 2001

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Moffett Federal Airfield, California



- Funnel & gate design pilot-scale system
- Constructed in April 1996
- Peerless iron (75 tons)
- Poured concrete base above thin aquitard at 22 ft bgs.
- Cored in Dec. 1997 and May 2001



Eisen / LCKW: Moffett: Standort (Mai 2000)





Eisen / LCKW: Moffett

Geochemistry - Preliminary Findings

- Groundwater chemical analysis indicates that the loss of inorganics in the reactive cell is substantial.
- Geochemical modeling provides insight into reactions that *might* be occurring.
- Analyses of core samples indicate that the mass of precipitate build-up is much less than would be expected based on groundwater data.
- Accelerated column tests help assess barrier longevity.

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7



Eisen / LCKW: Moffett

Average Change in Species Concentrations within Moffett Field Barrier Concentration in mg/L

	Na	K	Mg	Ca	HCO ₃	Cl	NO ₃	SO ₄
Influent	35.5	2.1	66.9	165	412	42.2	2.0	333
Effluent	29.1	1.4	1.0	10.4	62	39.1	0.0	18.0
Change	6.4	0.7	65.9	155	350	3.1	2.0	315
% Change	18%	34%	98%	94%	85%	7%	100%	95%

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10



Eisen / LCKW: Moffett

Long-Term Column Tests

- Two column experiments to investigate TCE degradation rates
- Master Builder iron used in “Lowry” column and Peerless iron used in “Moffett” column
- Groundwater collected from upgradient wells at Lowry AFB and Moffett Field
- Over 1000 pore volumes used in each column



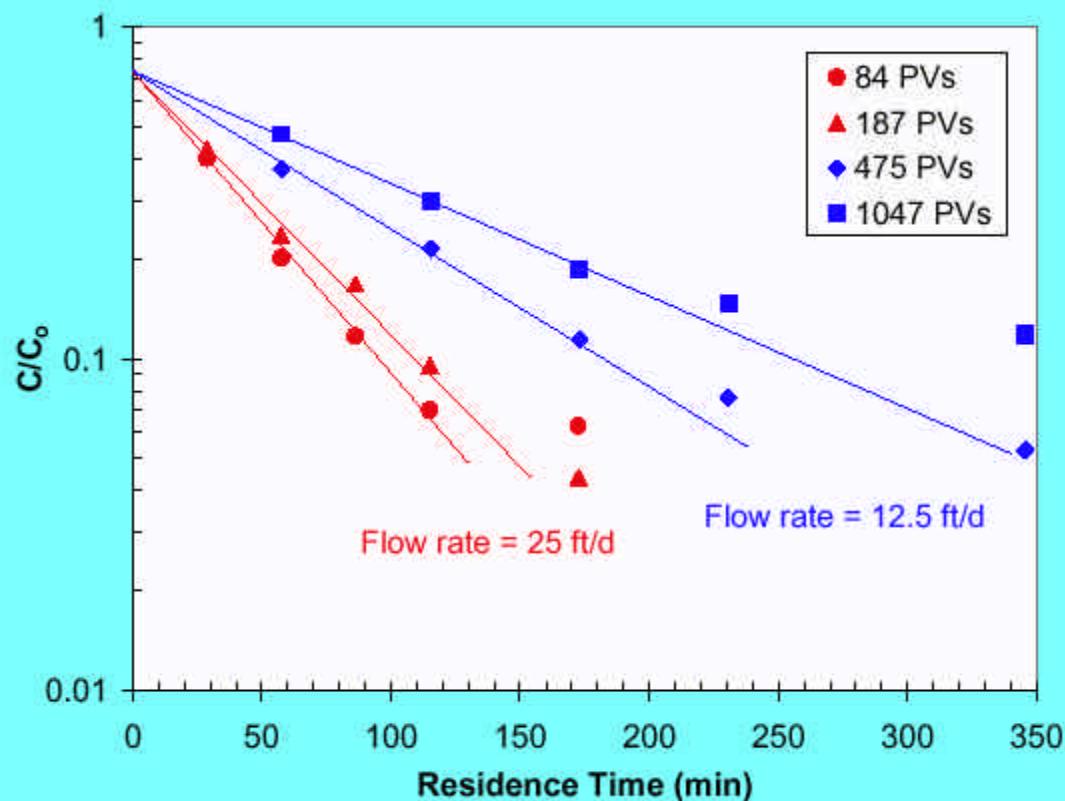
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14



Eisen / LCKW: Moffett

Moffett Field Column Test Results TCE Degradation Profiles



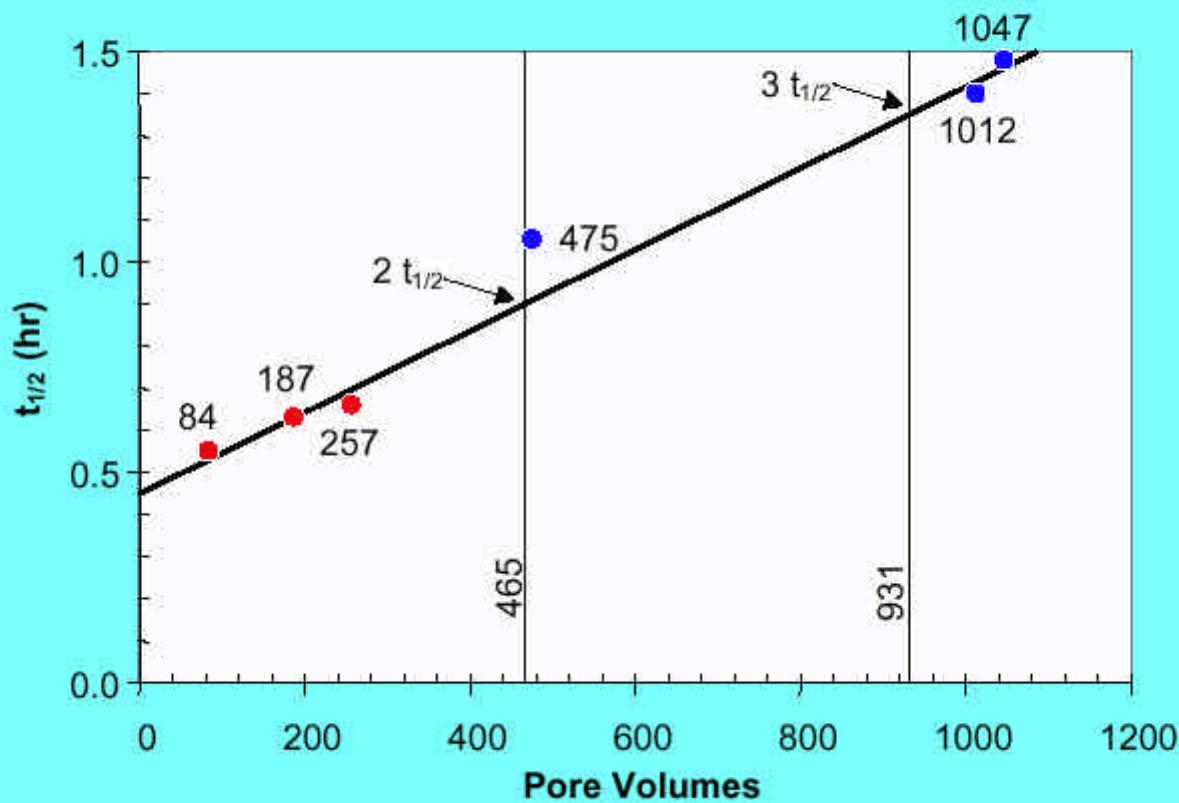
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16



Eisen / LCKW: Moffett

Moffett Field Column Test Results Change in TCE Half-Life with Age of Iron



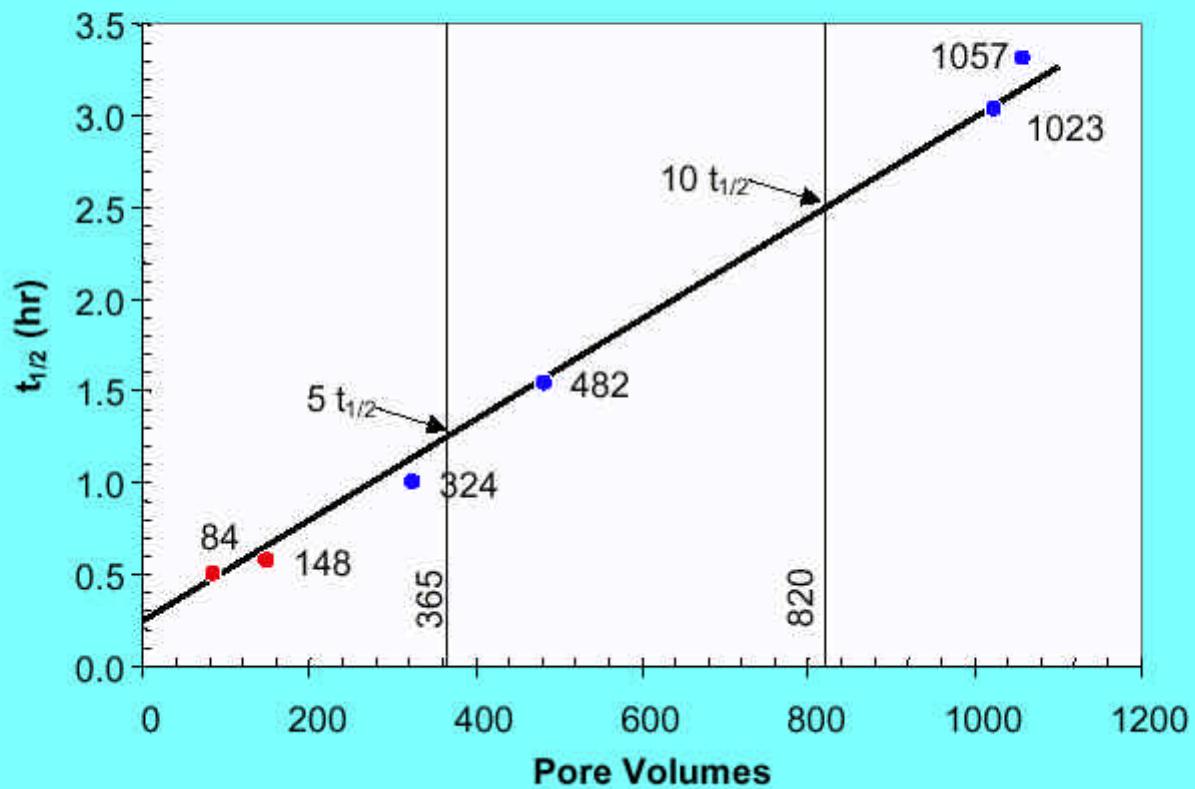
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17



Eisen / LCKW: Moffett

Lowry AFB Column Test Results Change in TCE Half-Life with Age of Iron



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19



Moffett: Modellierung, Yabusaki et al. 2001

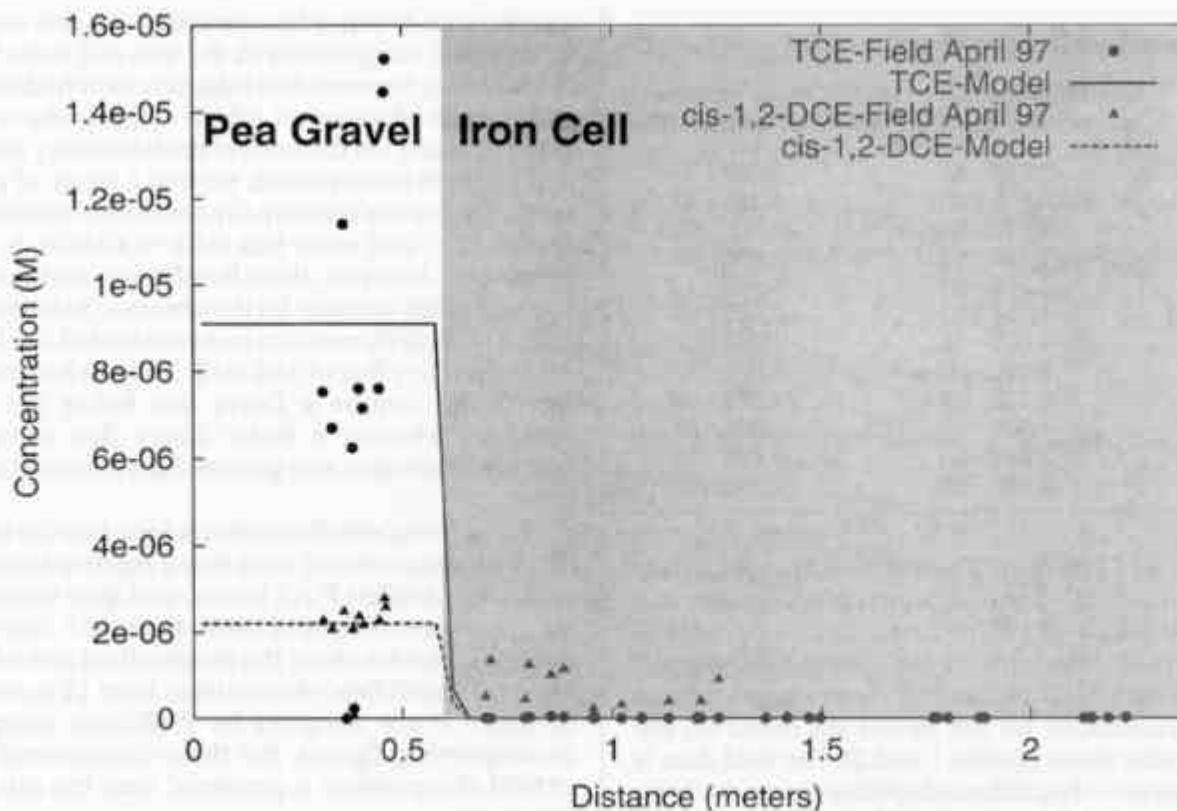
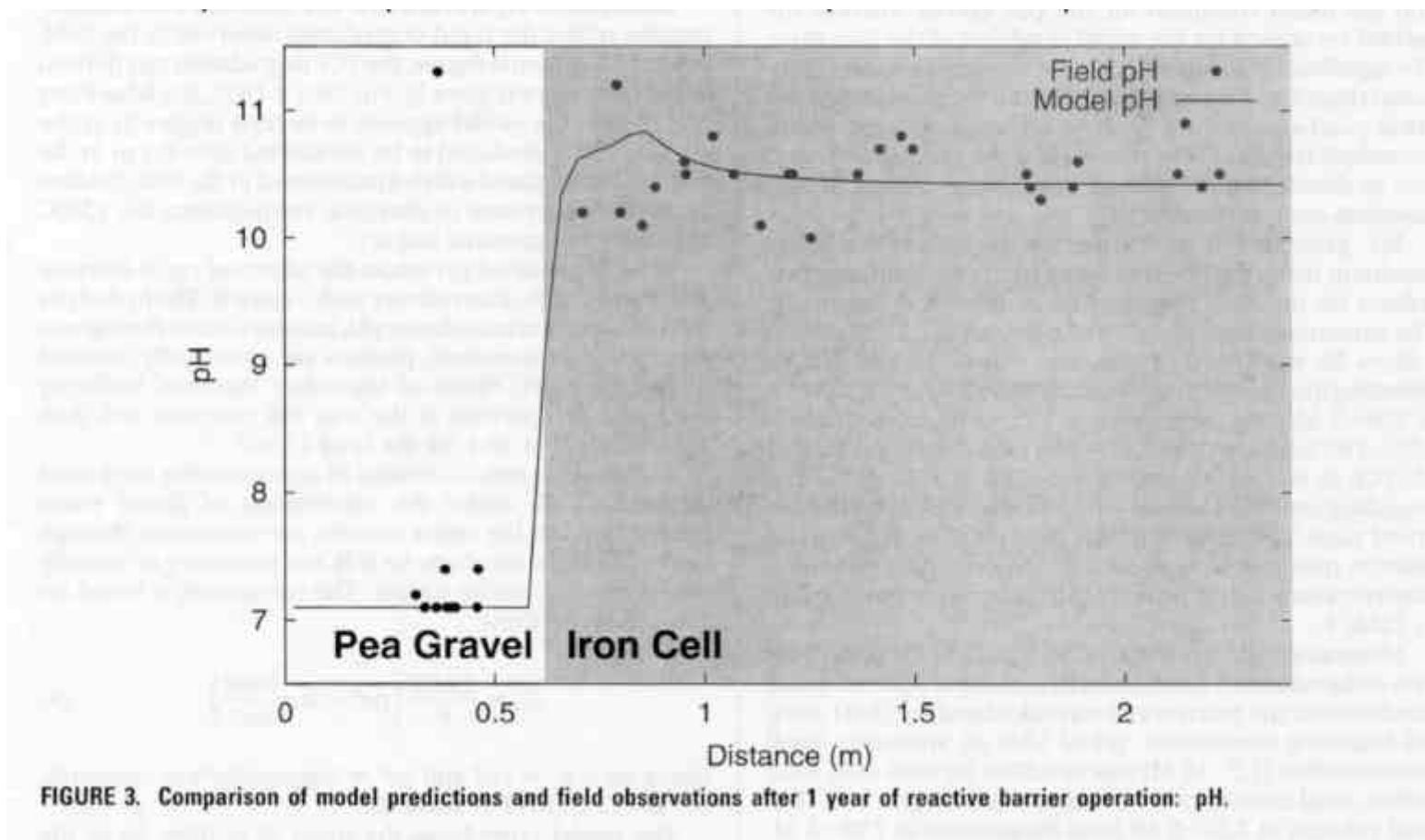


FIGURE 2. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: TCE and cis-1,2-DCE.

Yabusaki, S.; Cantrell, K.; Sass, B.; Steefel, C. (2001),
Env. Sci. Tech., 35, 1493-1503

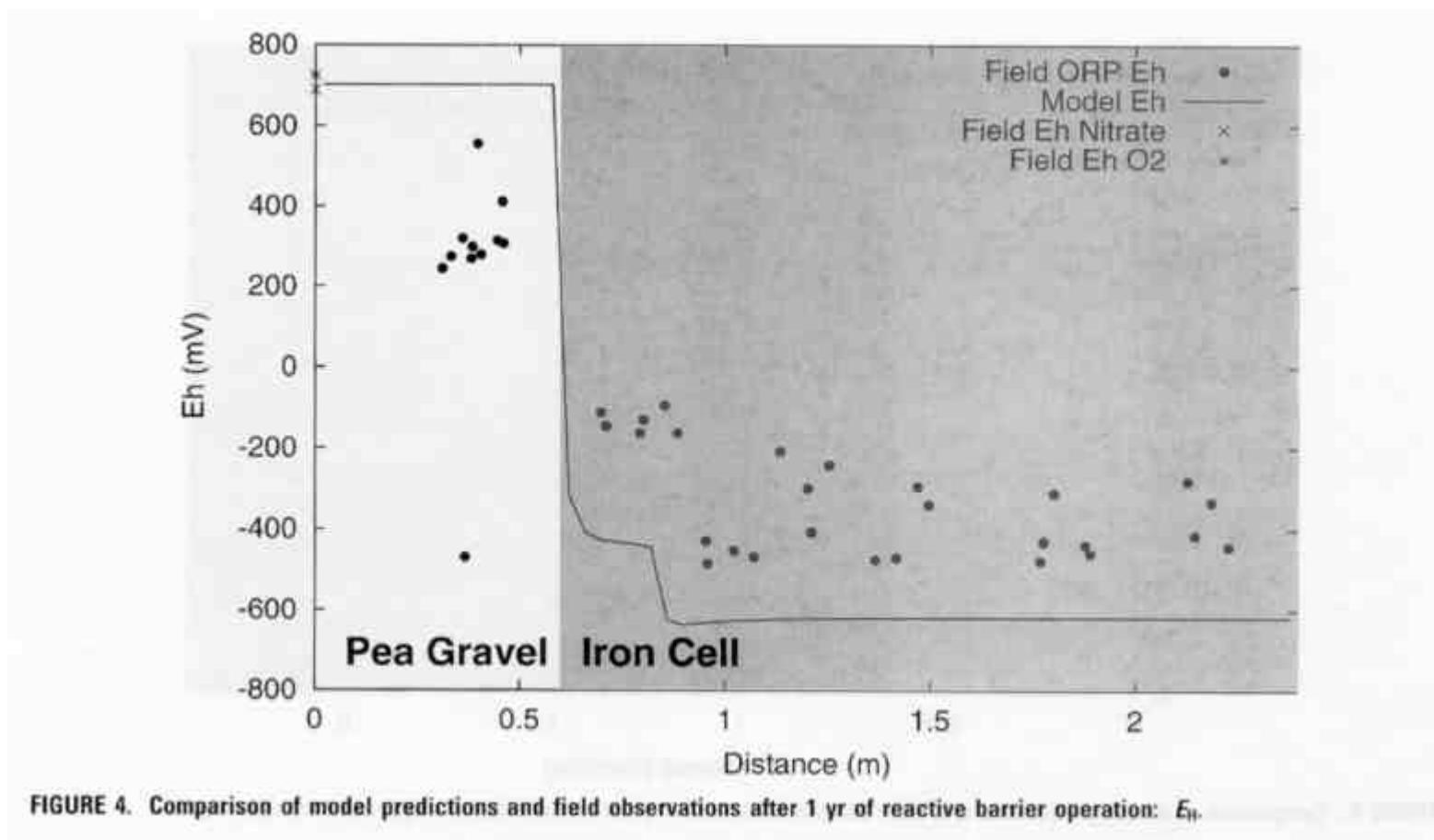


Moffett: Modellierung





Moffett: Modellierung





Moffett: Modellierung

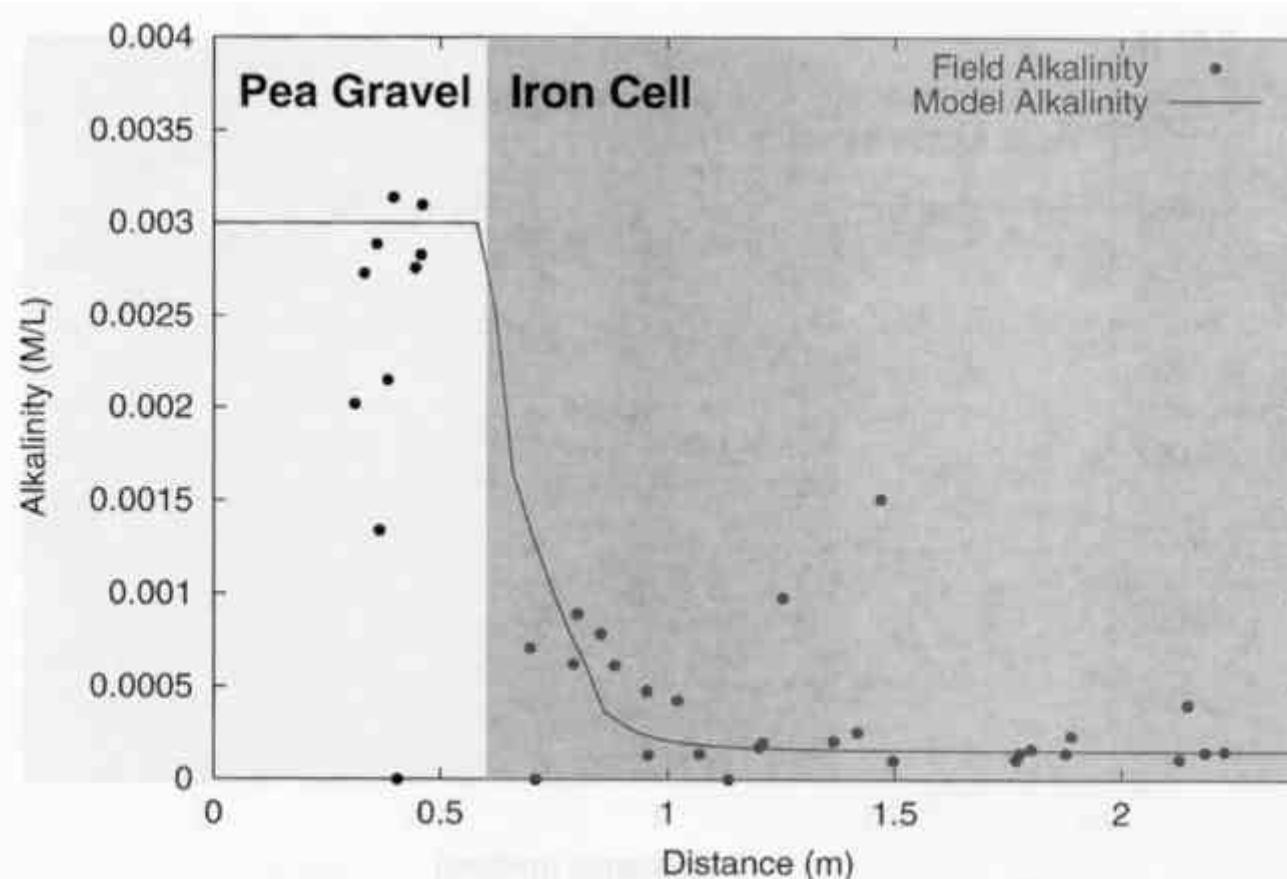


FIGURE 5. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: alkalinity (as CaCO_3).



Moffett: Modellierung

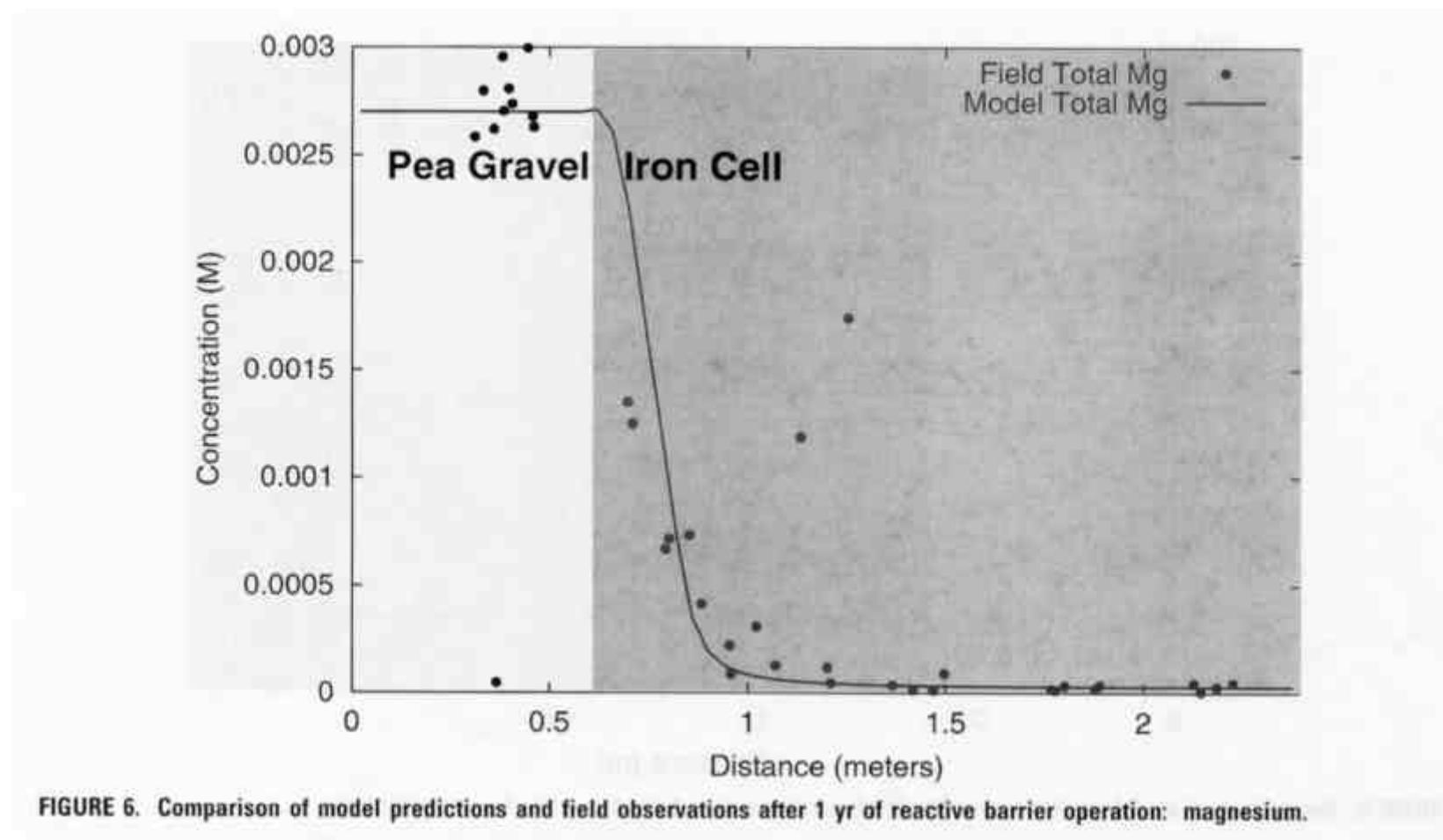


FIGURE 6. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: magnesium.



Moffett: Modellierung

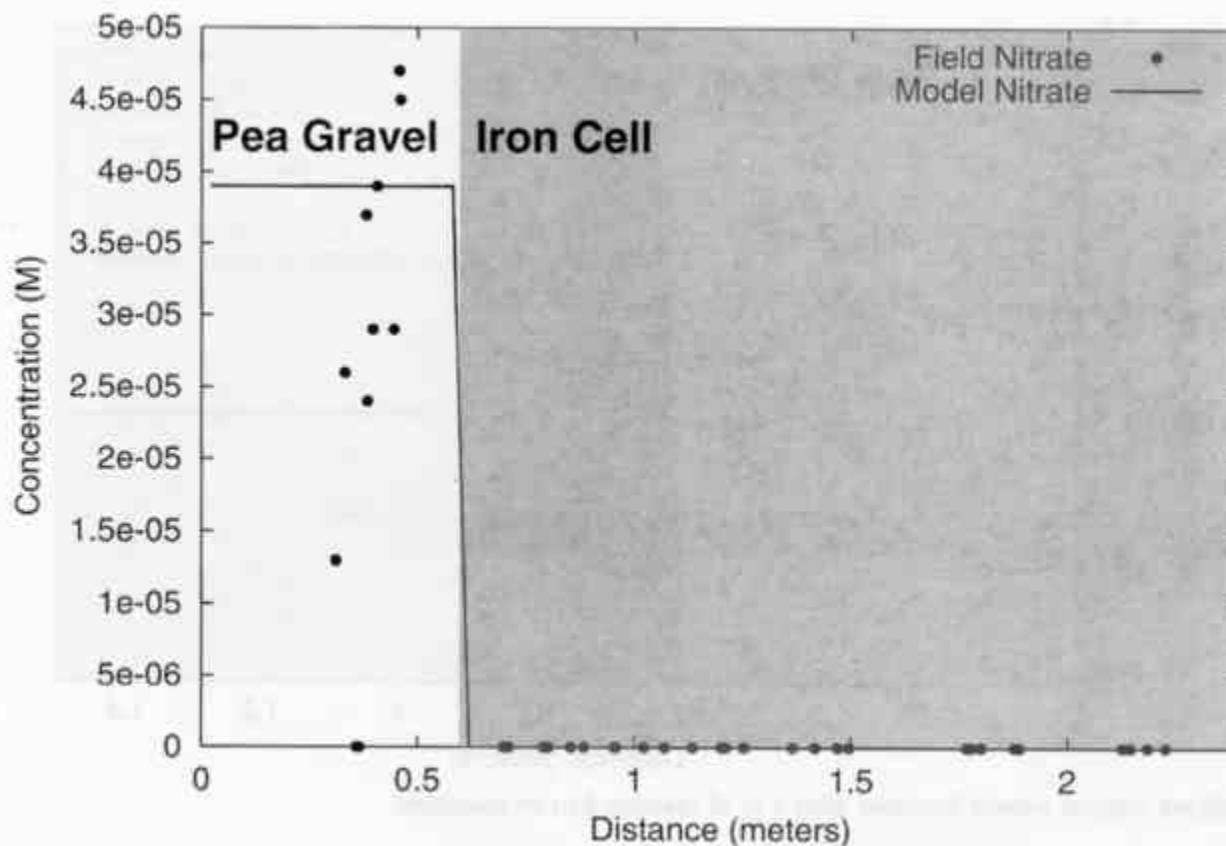


FIGURE 8. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: nitrate.



Moffett: Modellierung

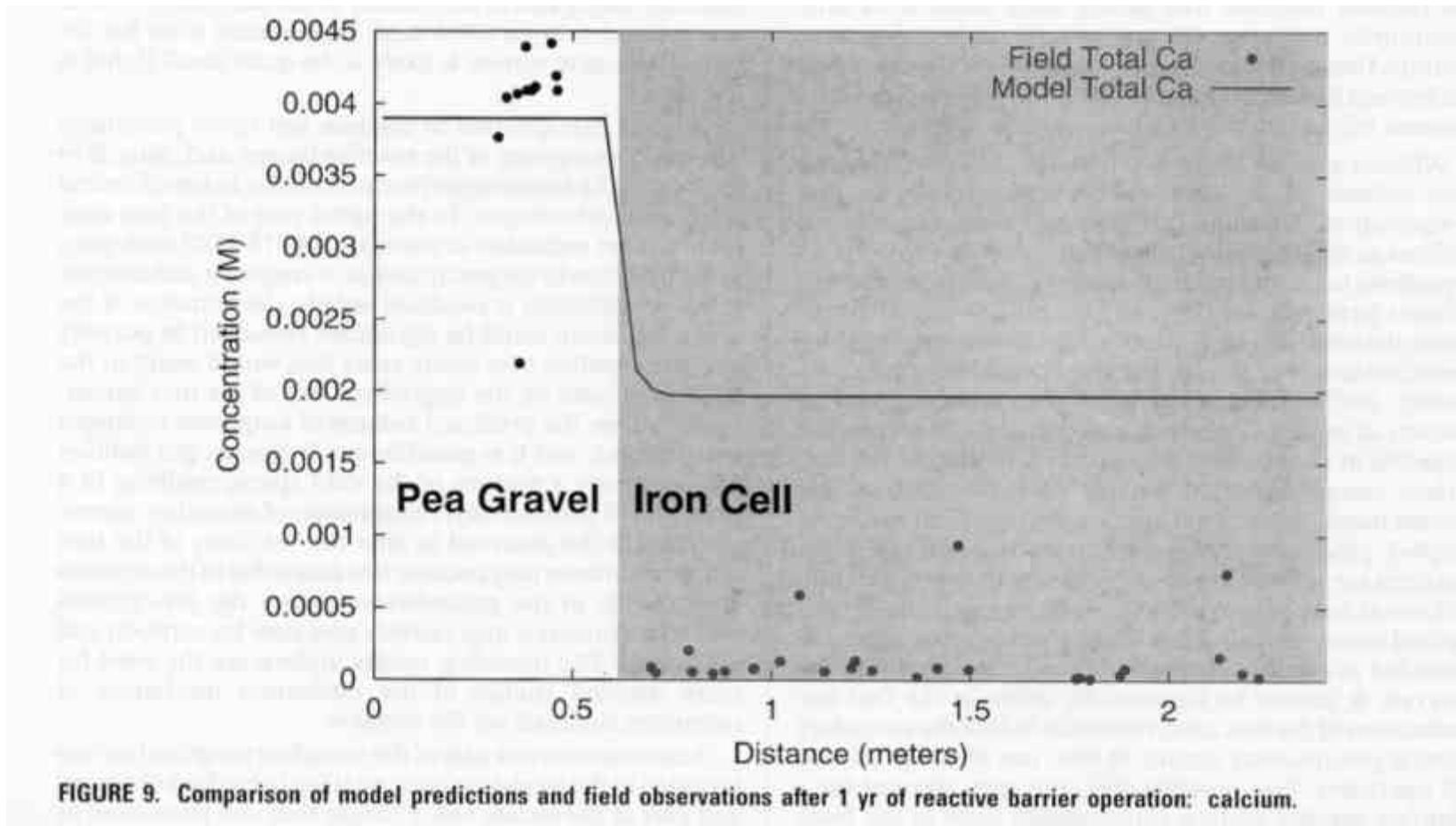


FIGURE 9. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: calcium.



Moffett: Modellierung

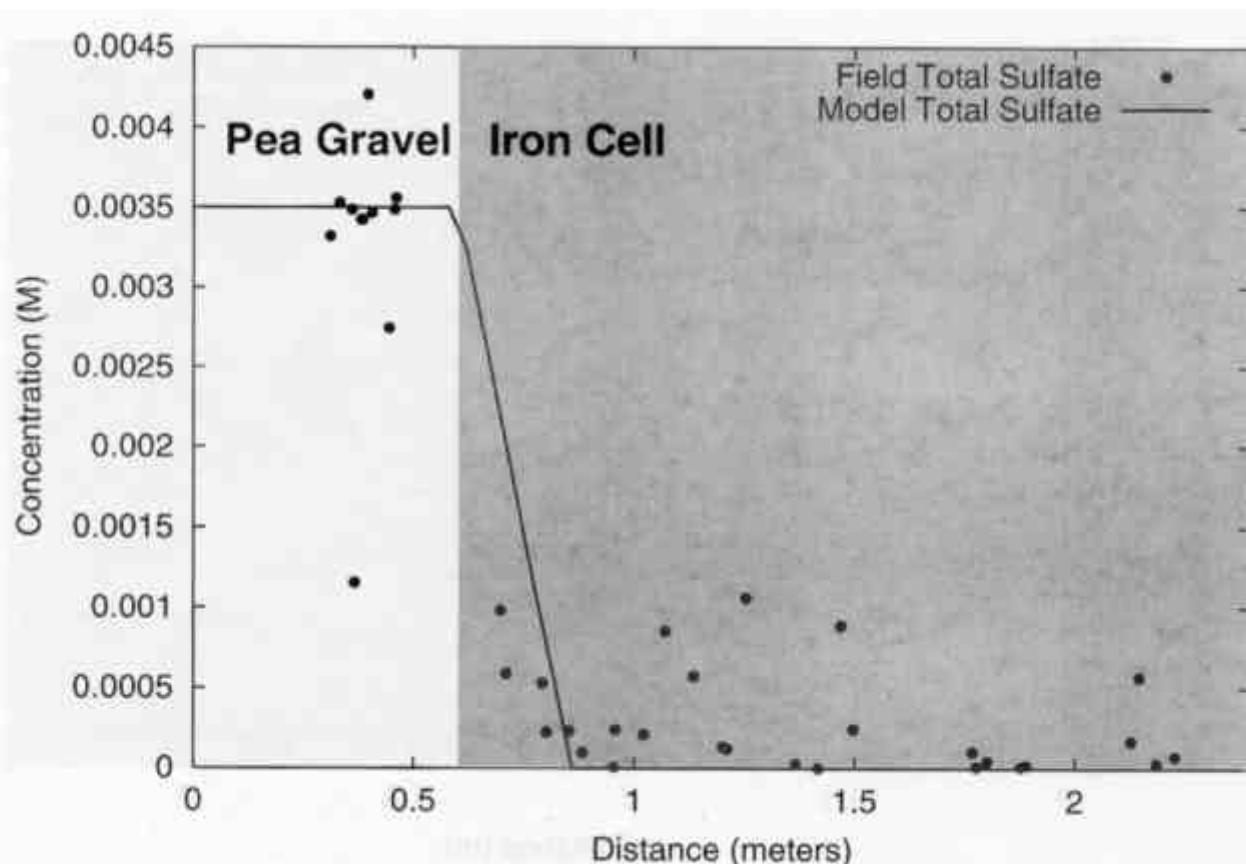


FIGURE 7. Comparison of model predictions and field observations after 1 yr of reactive barrier operation: sulfate.



Eisen / LCKW: Ultraschall, Geiger et al. 2001

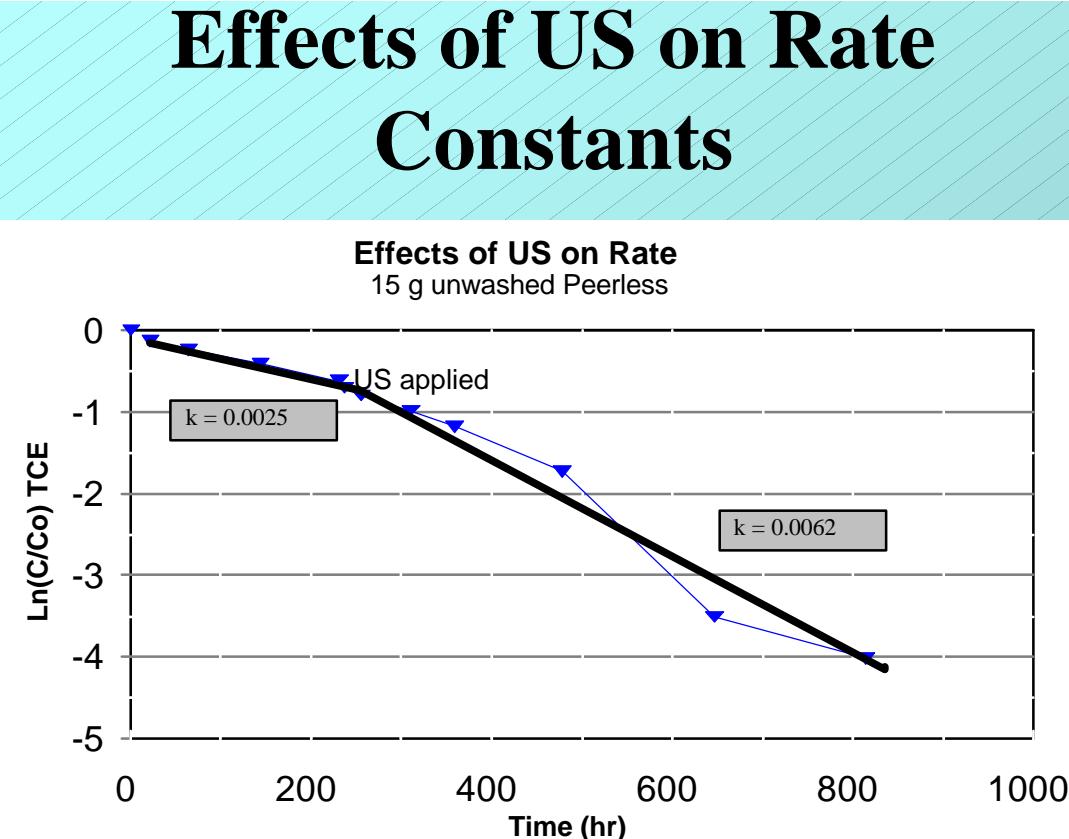
The Use of
Ultrasound to
Restore the
Dehalogenation
Activity of Iron in
Permeable
Reactive Barriers

*Cherie L. Geiger¹,
Christian A. Clausen¹,
Debra R. Reinhart²,
Aamod. Sonawane¹,
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Jacqueline Quinn³*

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Chemistry, UCF,

²Department of Civil
and Environmental
Engineering, UCF,

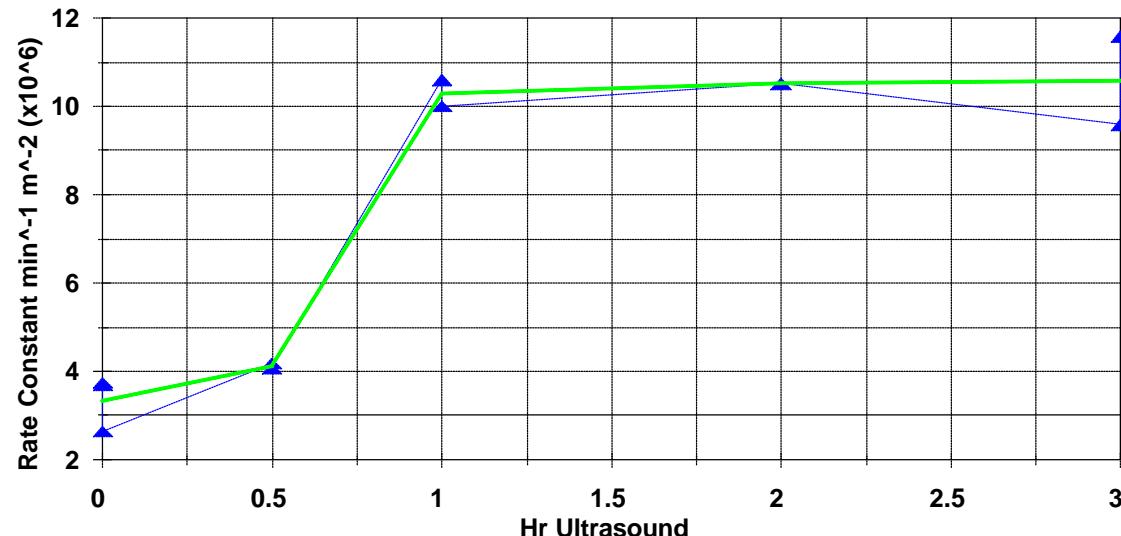
³ NASA, Kennedy
Space Center, FL





Eisen / LCKW: Ultraschall

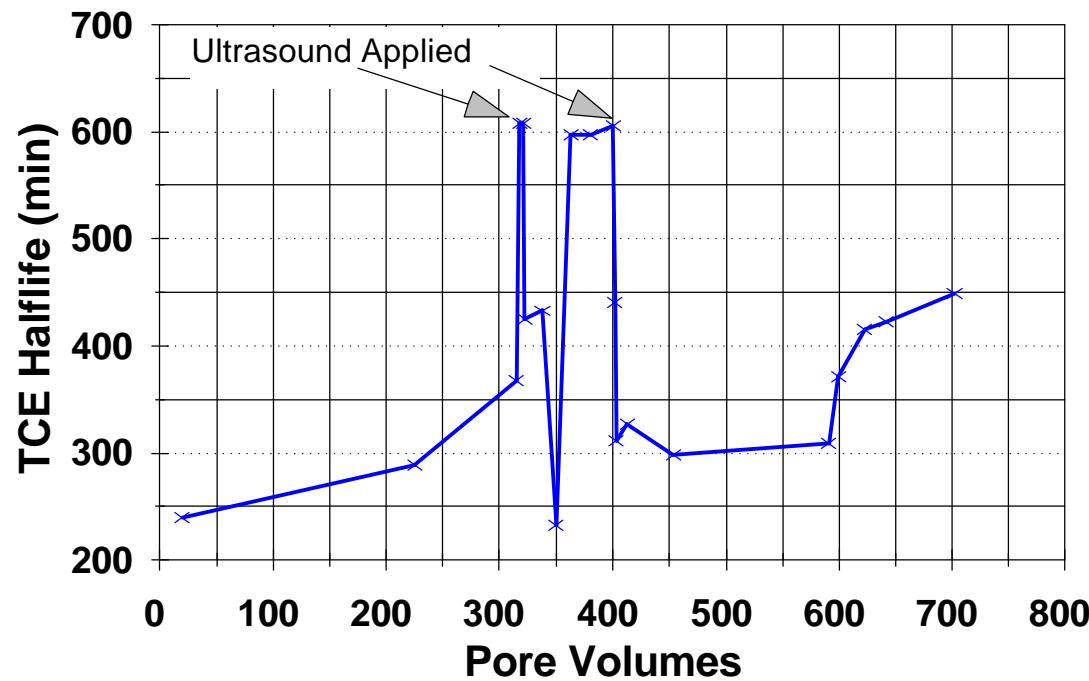
Impact of Time of US Use on Rate Constants





Column Studies Using Ultrasound

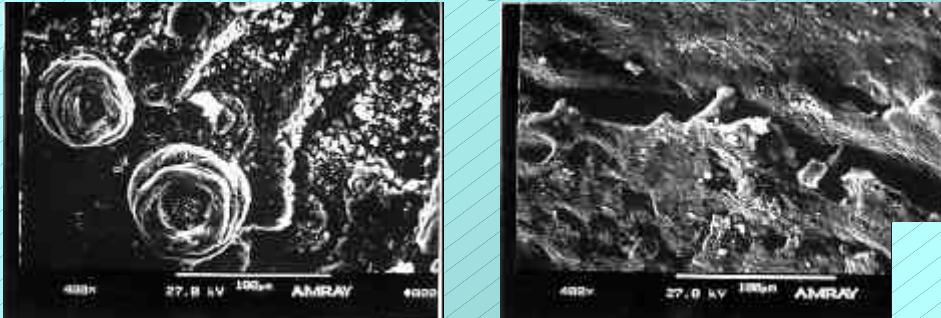
**Ultrasound Effect on TCE Halflife
Column Studies**





Eisen / LCKW: Ultraschall Geiger et al. 2001

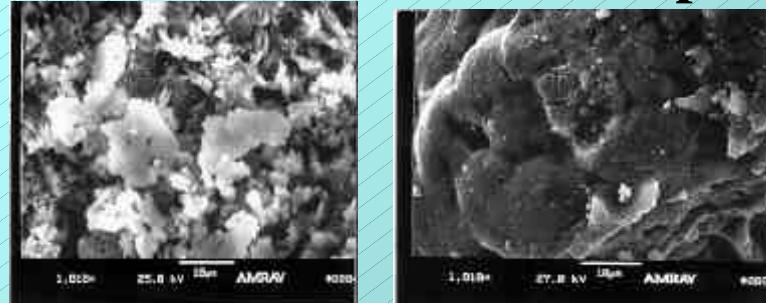
Oxidized Filings - US Impact



- Various structures on surface: filaments, platelets (L)
- Sonication removes structures, cracks smooth surface (R)



Oxidized 100-Mesh - US Impact



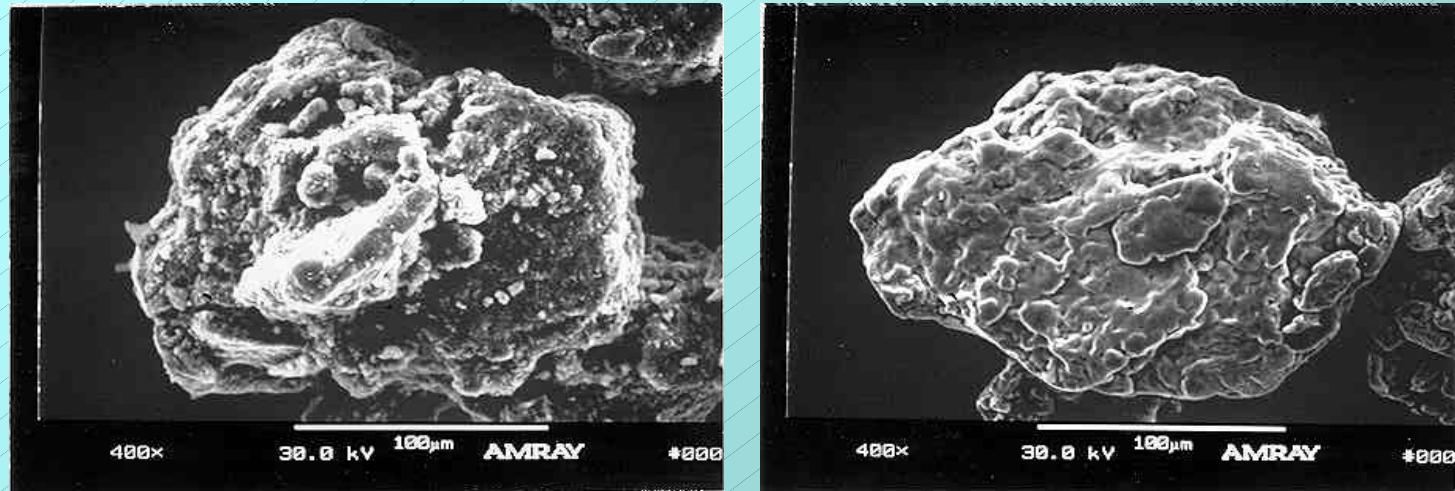
- Platelet-type structures, underlying surface obscured (L)
- Sonication removes platelets, cracks smooth surface (R)





Eisen / LCKW: Ultraschall

GW Soaked Filings - US Impact

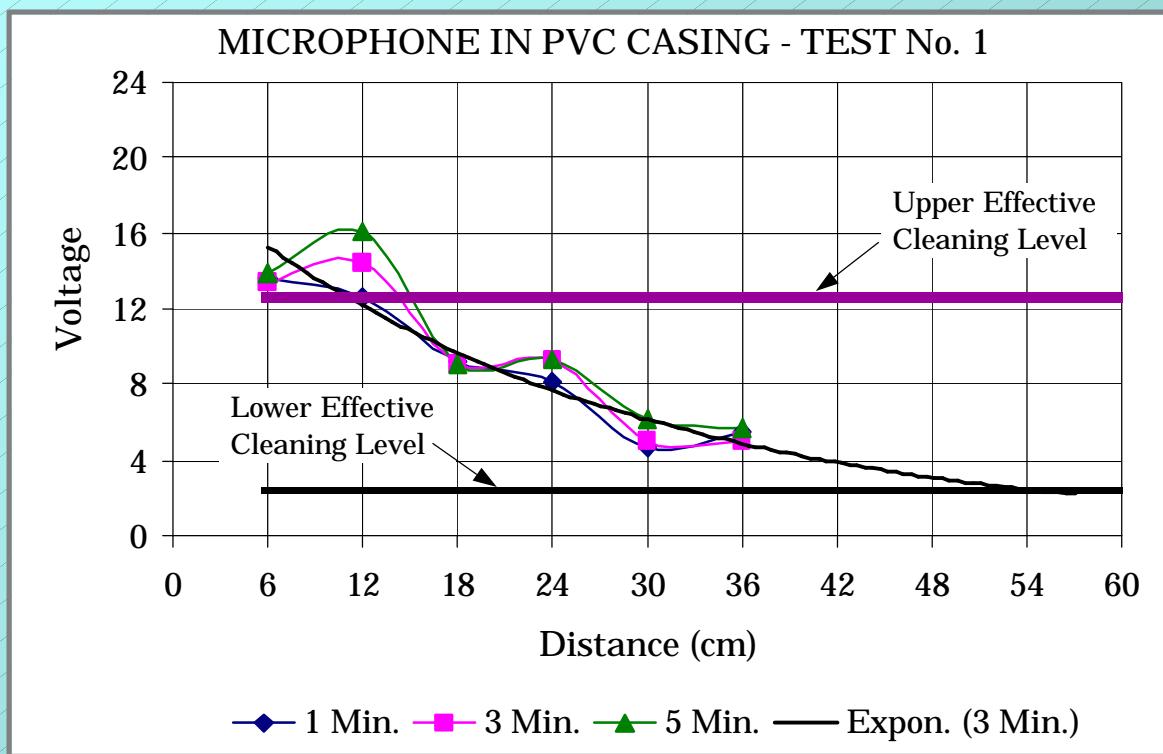


- Obvious debris after several months in groundwater (L)
- After sonication, surface looks similar to acid-washed material (R)



Eisen / LCKW: Ultraschall

Extrapolated Data for PVC Casing 1000W at 57% Output



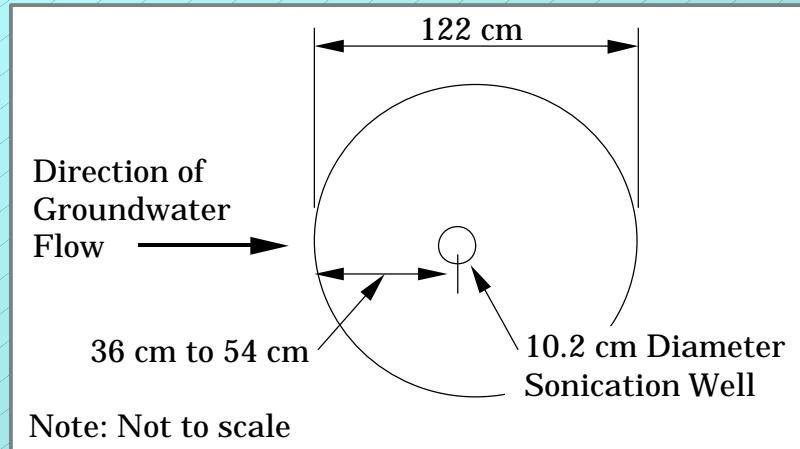
1





Eisen / LCKW: Geiger et al. 2001

Field Implementation of Ultrasonic Unit



- Locate sonication well between 36-cm and 54-cm from front edge of field borehole
- Install 10.2 cm (4 in.) diameter well



1



Eisen / LCKW: Geiger et al. 2001

Analysis of Field Application

- Core samples are taken before and after ultrasound application
- Samples are removed within 54-cm of well
- Samples are stored under N₂ and returned to UCF laboratory
- In inert atmosphere glovebox, iron is separated from matrix (if necessary), weighed and used in zero-headspace vial kinetic experiments





Eisen / LCKW: Ultraschall

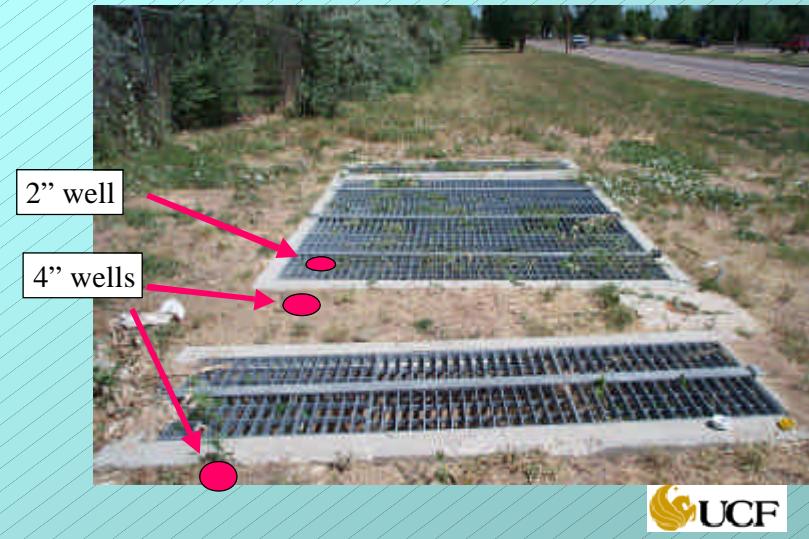
KSC Field Sonication Results Variables: Time and US Frequency

Relative Depth	30 min at 40 kHz	90 min at 40 kHz	30 min at 25 kHz	90 min at 25 kHz
<u>Percentage Improvement of Half-Life Compared to Unsonicated Samples</u>				
Shallow 7-12 ft.	24	41	58	67
Intermediate 13-18 ft.	22	28	41	66
Deep 18-26 ft.	21	33	45	59





Second Field Site



Eisen / LCKW: Ultraschall, Geiger et al.

Two four-inch wells were installed to accommodate the 25 kHz transducer





Eisen / LCKW: Ultraschall, Geiger et al. 2001

40 kHz
transducer fits
in existing
2-inch well





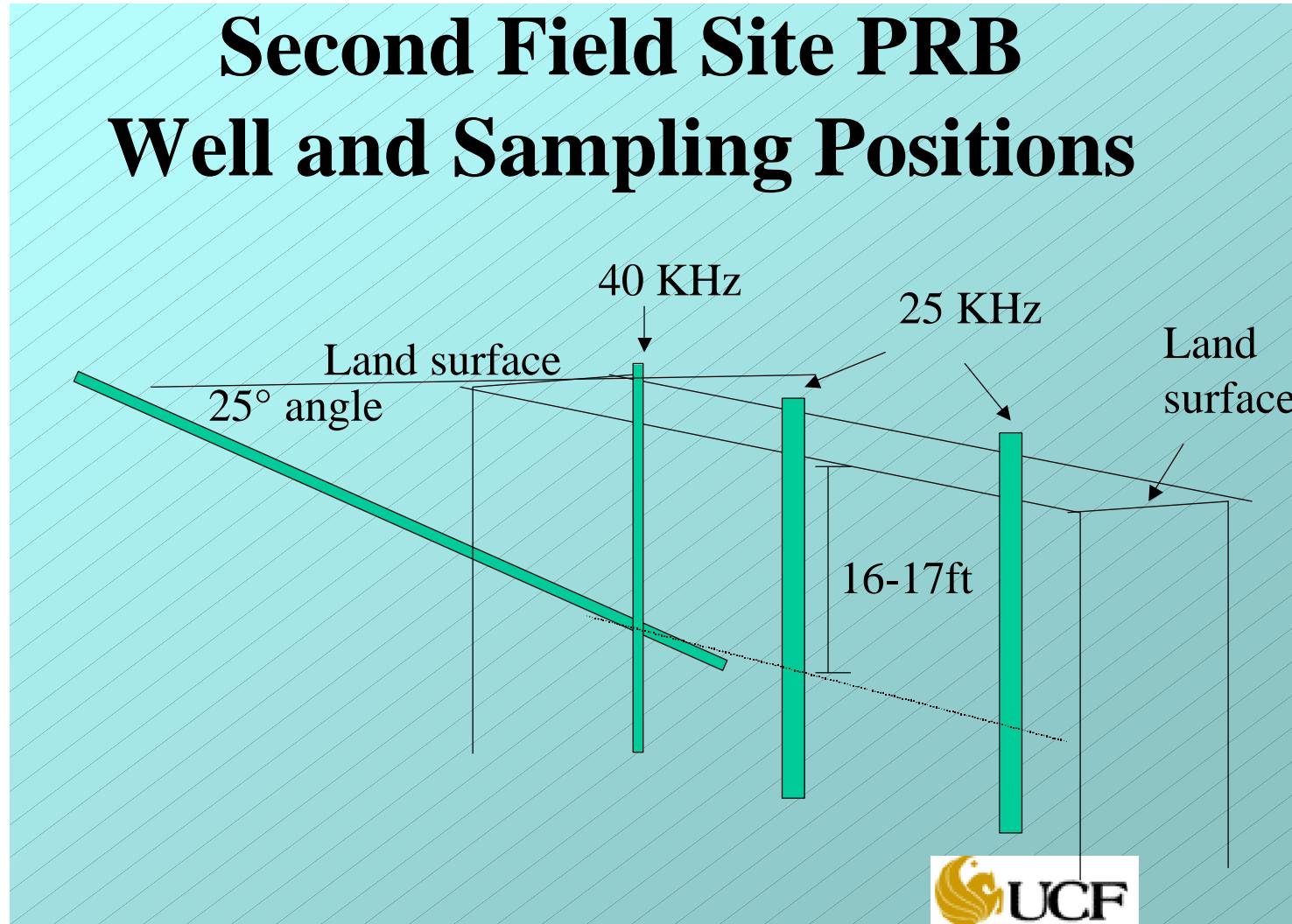
Eisen / LCKW: Ultraschall, Geiger et al. 2001

25 kHz
transducer
requires four-
inch well:
radiates over
longer area per
time





Eisen / LCKW: Ultraschall





Eisen / LCKW: Ultraschall

- Der TCE-Abbau durch Eisen in Grundwasser erzeugt verschiedene Ausfällungen durch anorganische Verbindungen auf der Eisenoberfläche, die den TCE-Abbau reduzieren.
- Die Anwendung von Ultraschall kann Ausfällungen etc. beseitigen und die Aktivität des Eisens verbessern.
- Durch die Ultraschallanwendung zeigen sich keine Veränderungen in der Grundwasser-Chemie; eine Trübung verstärkt sich nur vorübergehend (24 h).
- Der Prozess ist mobil einsetzbar, er erfordert wenig Ausrüstung, technischen Aufwand sowie Personal und erzeugt nur geringe Kosten.



Eisen / LCKW: Ultraschall, alte Publikationen

September, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 2709–2710 (1985) 2709

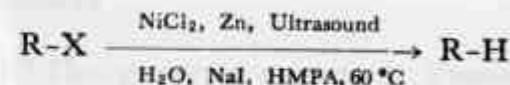
Ultrasounds in Synthetic Reactions. III. Reduction of Organic Halides with Nickel(II) Chloride-Zinc-Water¹⁾

Junzo YAMASHITA,* Yoshio INOUE, Takashi KONDO, and Harukichi HASHIMOTO
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki-Aoba, Sendai 980
(Received March 29, 1985)

Synopsis. The reductive dehalogenation of aryl chlorides as well as other organic halides was facilitated with nickel(II) chloride-zinc-water in hexamethylphosphoric triamide irradiated with ultrasound.

There are a number of methods for the reduction of alkyl or aryl halides using transition metals.²⁾ But aryl chlorides are rather resistant to the reduction. It is known that low valent nickel complexes *in situ* generated from nickel(II) salt-zinc powder-trifluoromethylbenzene irradiated with ultrasound.

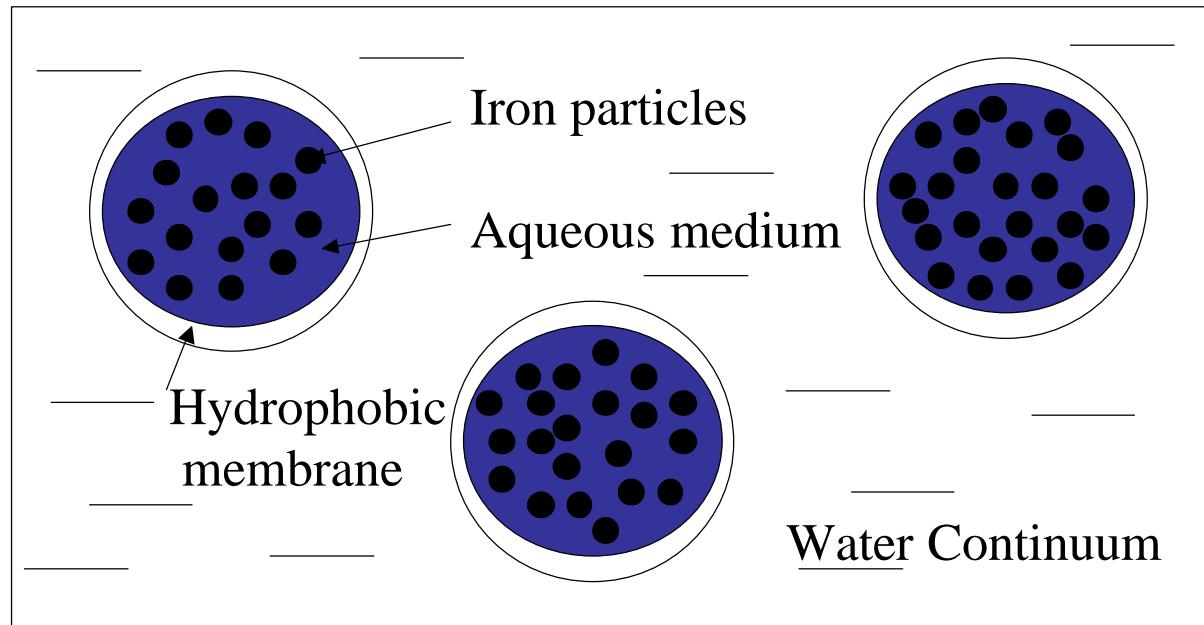
HMPA at 60 °C under ultrasound-irradiation.



Several reaction parameters were examined and the results are shown in Table 1. The ease of reduction of halobenzenes decreased in the order: iodobenzene>bromobenzene>chlorobenzene(runs 1,2, and 4), which is consistent with the proposed oxidation-



Eisen / LCKW: Nanoeisen, Geiger et al. 2001



Nanoscale iron particles contained in emulsion micelle

NANOSCALE AND MICROSCALE IRON EMULSIONS FOR TREATING DNAPL

Cherie L. Geiger¹, Christian A. Clausen¹, Debra R. Reinhart², Kathleen Brooks¹, Jacqueline Quinn³ and David Major⁴

¹Department of Chemistry and ²Department of Civil and Environmental Engineering, University of Central Florida, 4000 Central Florida Blvd. Orlando, FL, ³NASA, Kennedy Space Center, Kennedy Space Center, FL, 32899;

⁴GeoSyntec Consultants, Inc., 160 Research Lane, Guelph, Ontario, Canada, N1G5B2



Eisen / LCKW: Nanoeisen, Geiger et al. 2001



**Micrograph of a nano-iron emulsion dispersed in water Mag= 1000X.
The composition of the emulsion is 38.7% corn oil, 42.4% water,
10.5% iron and 8.4% surfactant.**



Eisen / LCKW: Nanoeisen

Emulsion	Nano Iron (wt%)	Corn Oil (wt%)	Water (wt%)	Surfactant (wt%)
Blend #1	9.21	42.39	46.08	2.30
Blend #2	9.00	41.44	45.04	4.50
Blend #3	8.44	38.82	42.19	10.55
Blend #4	13.13	20.13	65.65	1.09
Blend #5	13.45	61.88	22.42	2.24
Blend #6	17.74	21.76	59.12	1.38



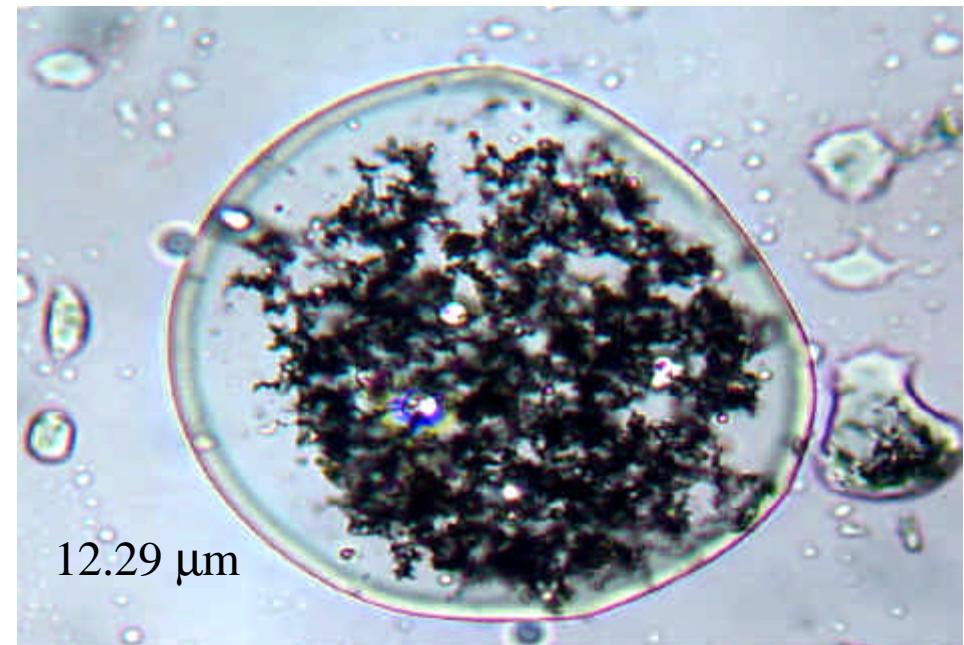
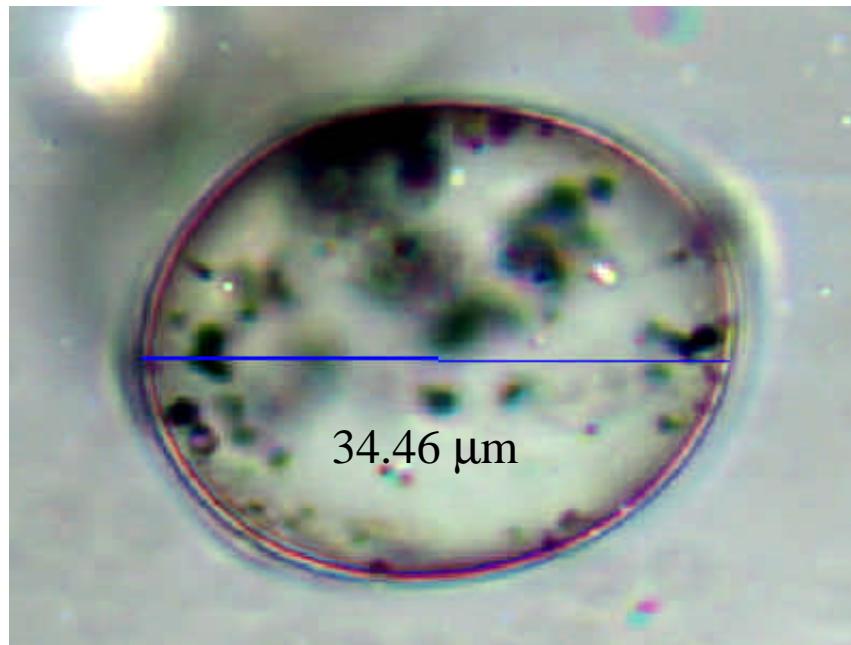
Eisen / LCKW: Nanoeisen

Emulsion Type	Day 1	Day 2	Day 3	Day 7	Day 12
Surfactant A Blend #4	DL	6.15	8.91	19.32	38.06
Surfactant A Blend #5	DL	2.38	2.49	5.47	13.08
Surfactant B Blend #4	DL	4.03	6.21	10.29	14.69
Surfactant C Blend #4	DL	3.04	4.82	6.21	9.87
Surfactant C Blend #5	DL	7.04	9.92	28.94	33.88
Control	DL	DL	DL	DL	0.21

Ethen-Entwicklung [ppm] in 5 ml-Headspace-Vials; DL = detection limit



Eisen / LCKW: Nanoeisen



Links: Nano-Eisen-Emulsion dispergiert in Wasser, rechts: Nanoemulsion



Eisen / LCKW, Nanoeisen: Wang, Zhang 1997

Synthesizing
Nanoscale Iron
Particles for
Rapid and
Complete
Dechlorination
of TCE and
PCBs

Wang, C.B.;
Zhang, W.-X.
(1997)

Env. Sci. Tech.
31(7), 2154-2156

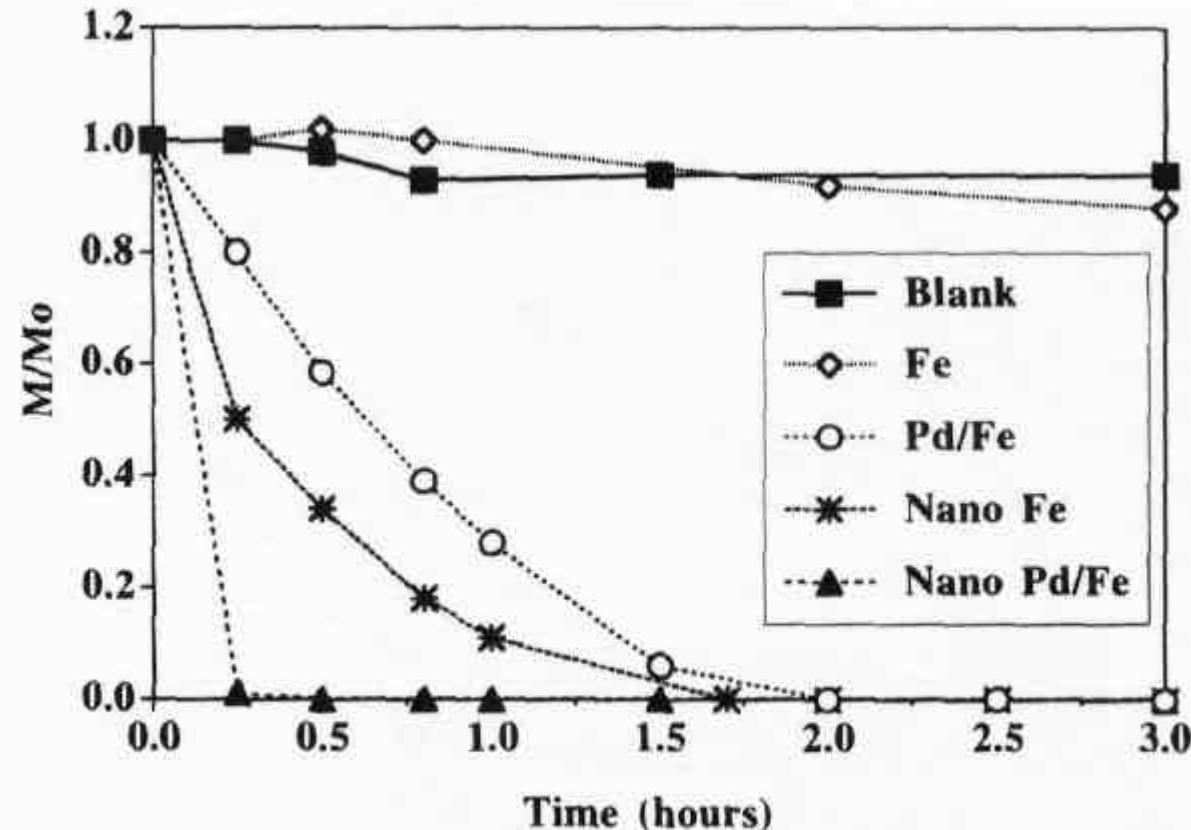


FIGURE 2. Reactions of TCE with commercial Fe powders (Fe), Pd-modified commercial Fe powders (Pd/Fe), nanoscale Fe particles (Nano Fe), and nanoscale Pd/Fe particles (nano Pd/Fe). Initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL.



Eisen / LCKW, Nanoeisen: Wang, Zhang 1997

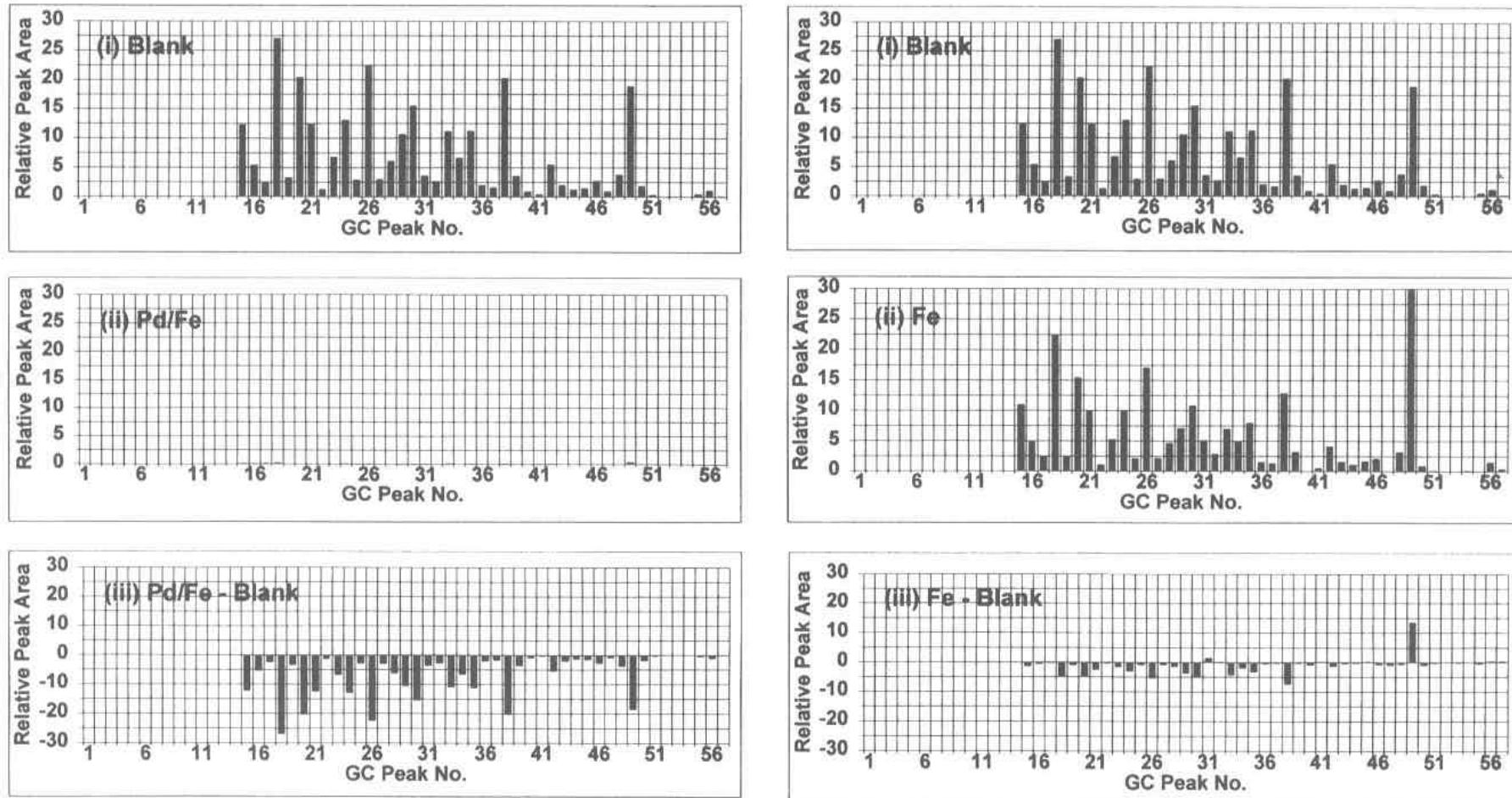


FIGURE 3. Changes in GC relative peak areas of an Aroclor 1254 solution in 17 h with (a) nanoscale Pd/Fe particles and (b) nanoscale Fe particles. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (iii) were the difference between (ii) and (i) and represented the net degradation. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL.



Nanoeisen: Xu, Zhang 2000

Subcolloidal
Fe/Ag Particles for
Reductive
Dehalogenation of
Chlorinated
Bzenes

Xu, Y.X.;
Zhang, W.-X.
(2000)

Industrial and
Engineering
Chemistry
Research 39(7),
2238-2244

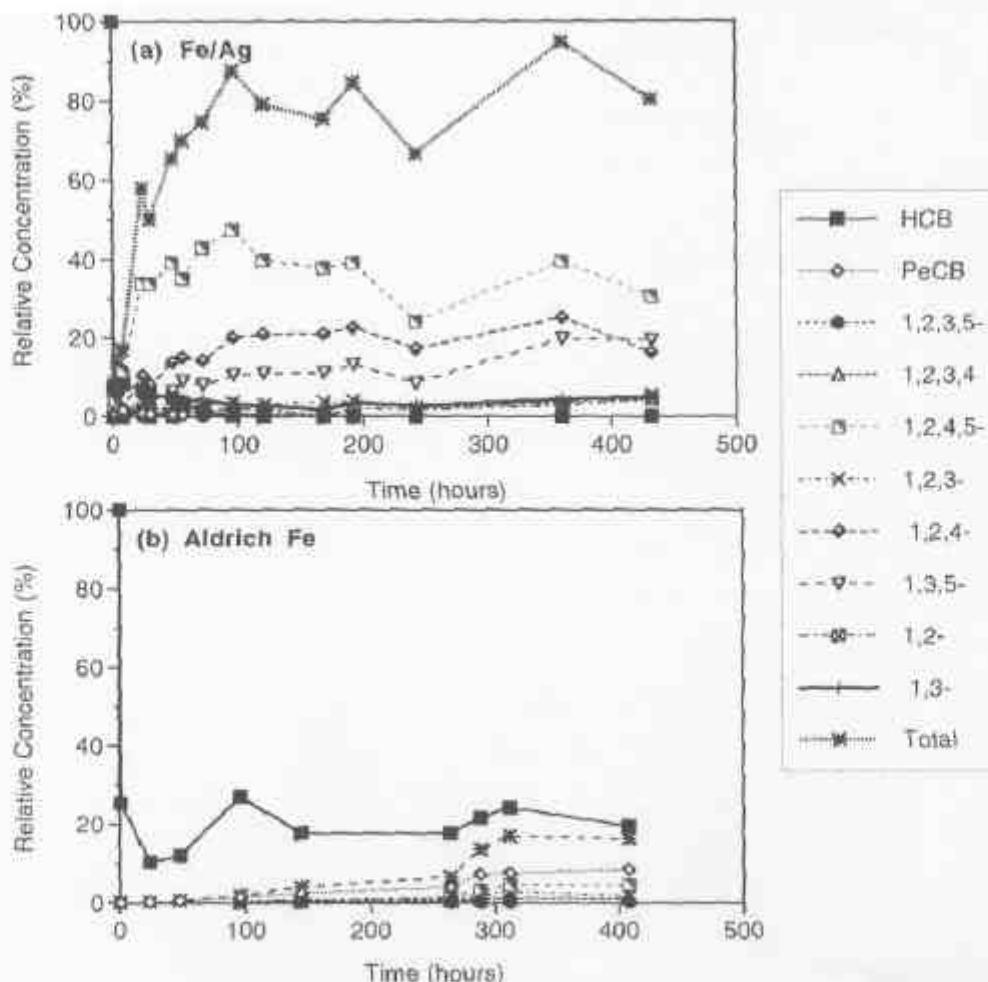


Figure 3. Transformation of HCB with (a) subcolloidal Fe/Ag particles and (b) Aldrich Fe particles (10 μm). Initial HCB concentration was 4 mg/L. Metal particle loading was 0.5 g/20 mL for the Fe/Ag and 5 g/20 mL for the Aldrich iron. Concentrations are normalized to the initial HCB concentration. The total in the figure refers to the sum of all daughter products in solution.



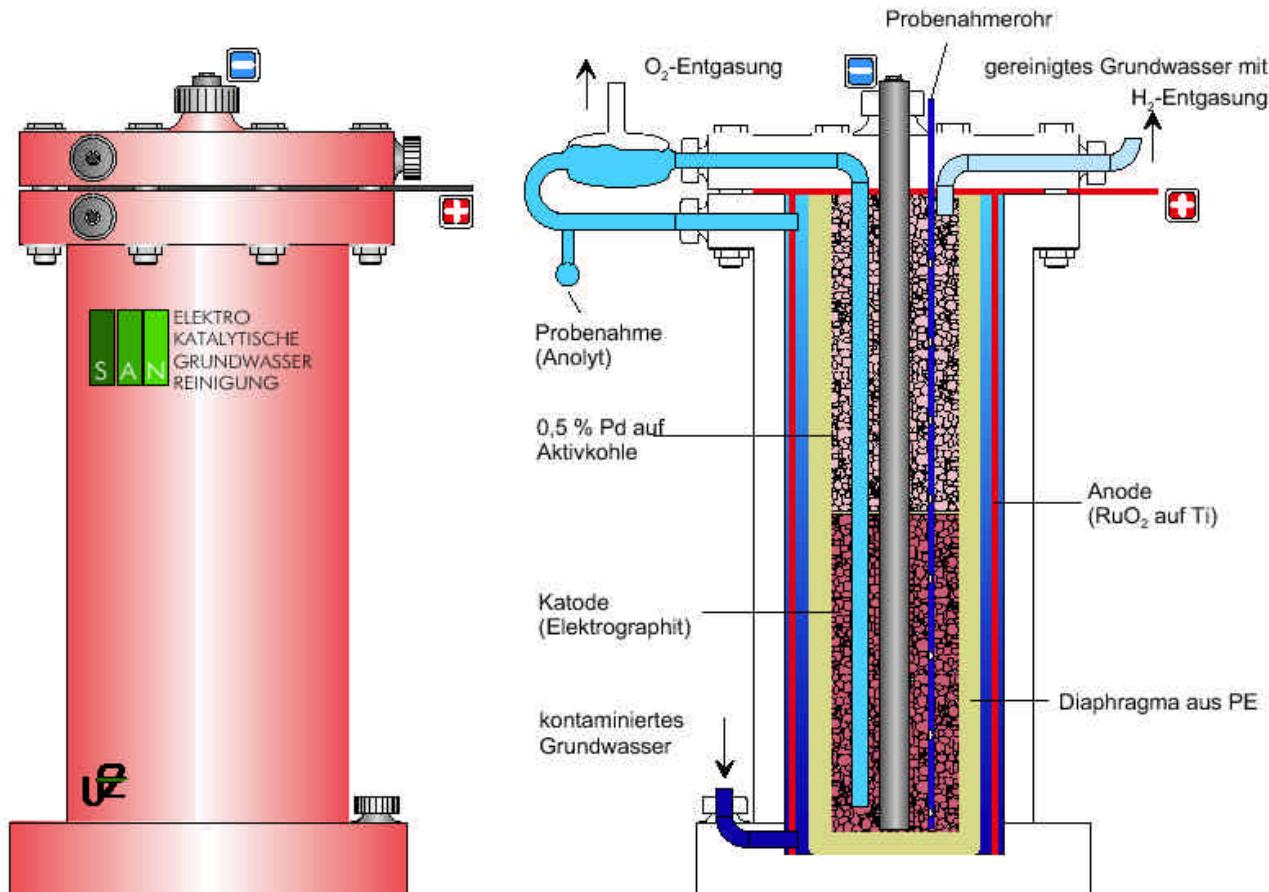
Metalle / CKW: Pd, Mackenzie et al. 2000

**Dechlorination of
Chlorohydrocarbons in
Groundwater Using
Novel Membrane-
Supported Pd Catalysts**

**Mackenzie, K.; Koehler,
R.; Weiss, H.; Kopinke,
F.-D. (2000)**

In: Wickramanayake, G.B.;
Gavaskar, A.; Chen, A.S.C.
(Ed.) Chemical Oxidation
and Reactive Barriers, The
Second International
Conference on Remediation
of Chlorinated and
Recalcitrant Compounds,
Monterey, California, May
22-25, 2000, vol. C2-6, 331-
338

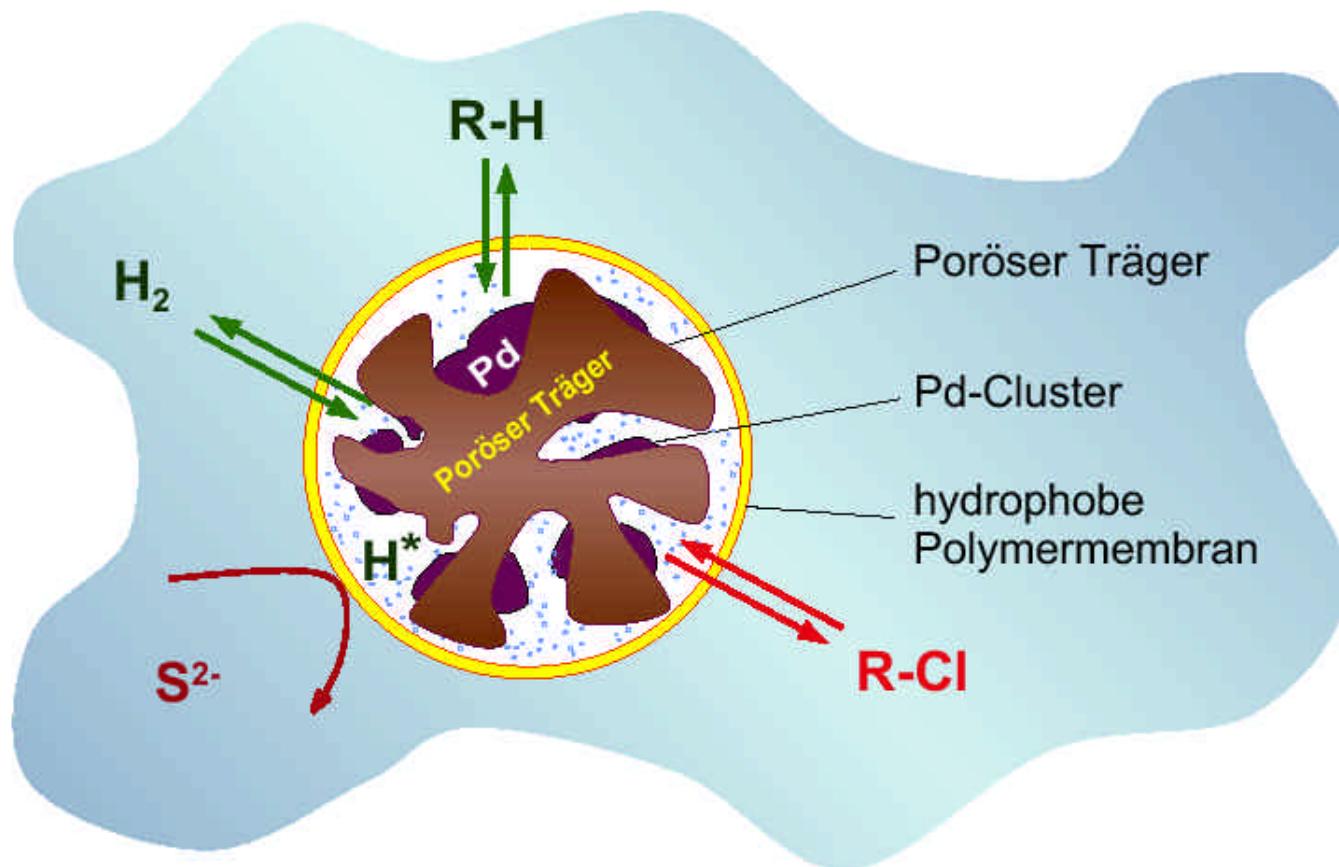
Elektrokatalysereaktor für die "Mobile Testeinheit" Bitterfeld





Metalle / CKW: Pd, Mackenzie et al. 2000

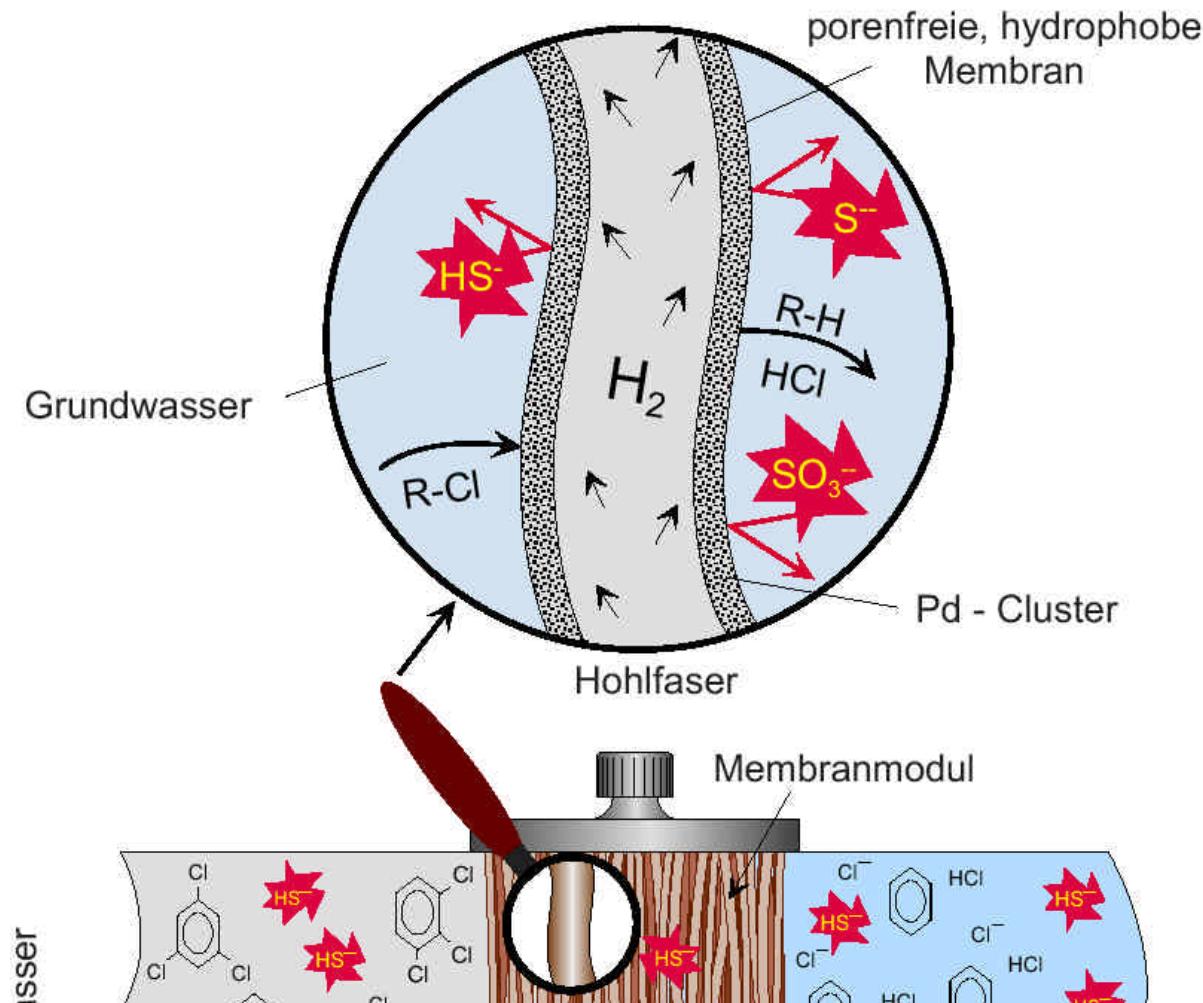
Palladium-Trägerkatalysator mit Membranhülle





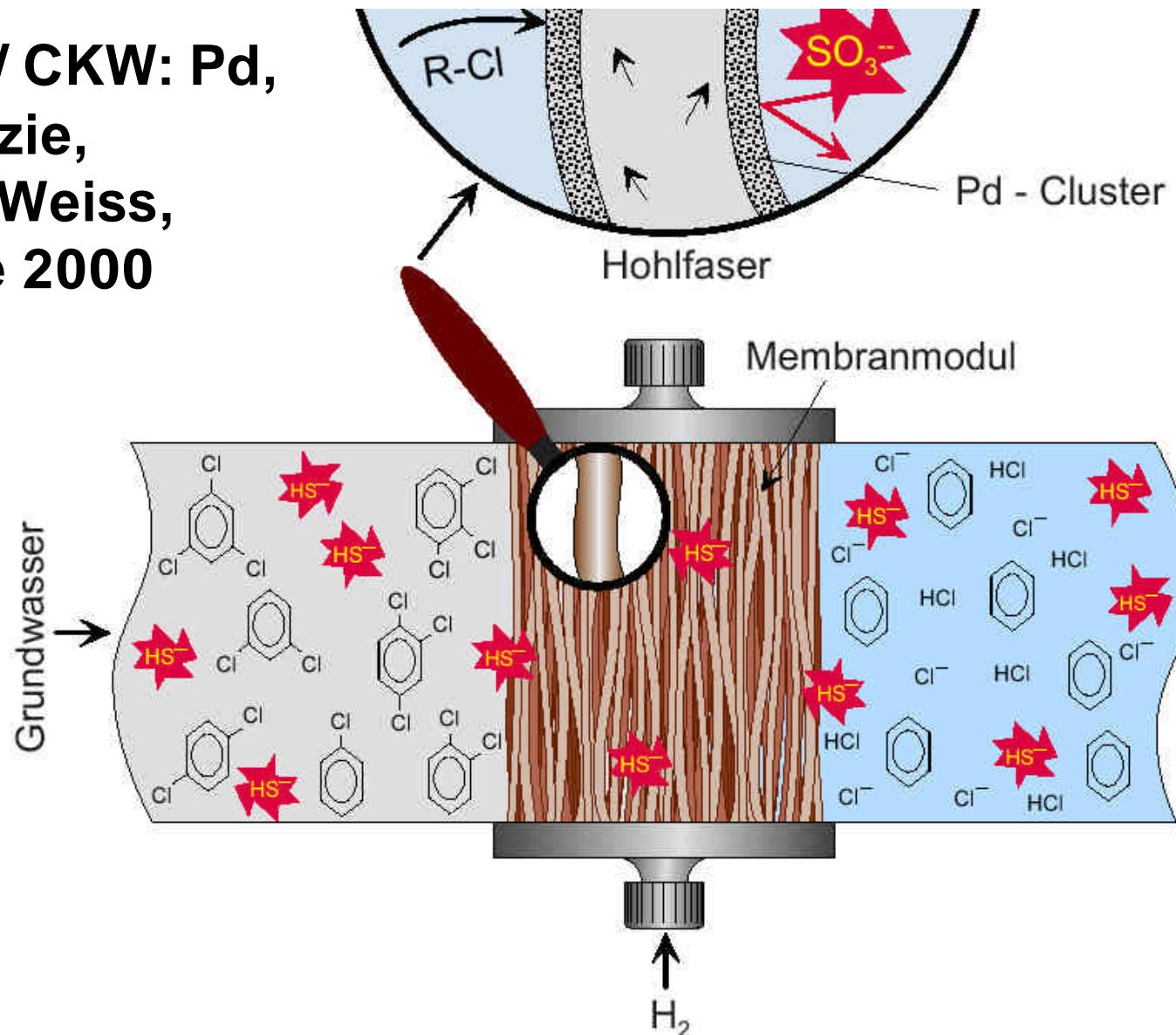
**Metalle /
CKW: Pd,
Mackenzie
et al. 2000**

Grundschema eines Membranreaktors





**Metalle / CKW: Pd,
Mackenzie,
Köhler, Weiss,
Kopinke 2000**





Metalle / CKW: Pd, Mackenzie, Köhler, Weiss, Kopinke 2000

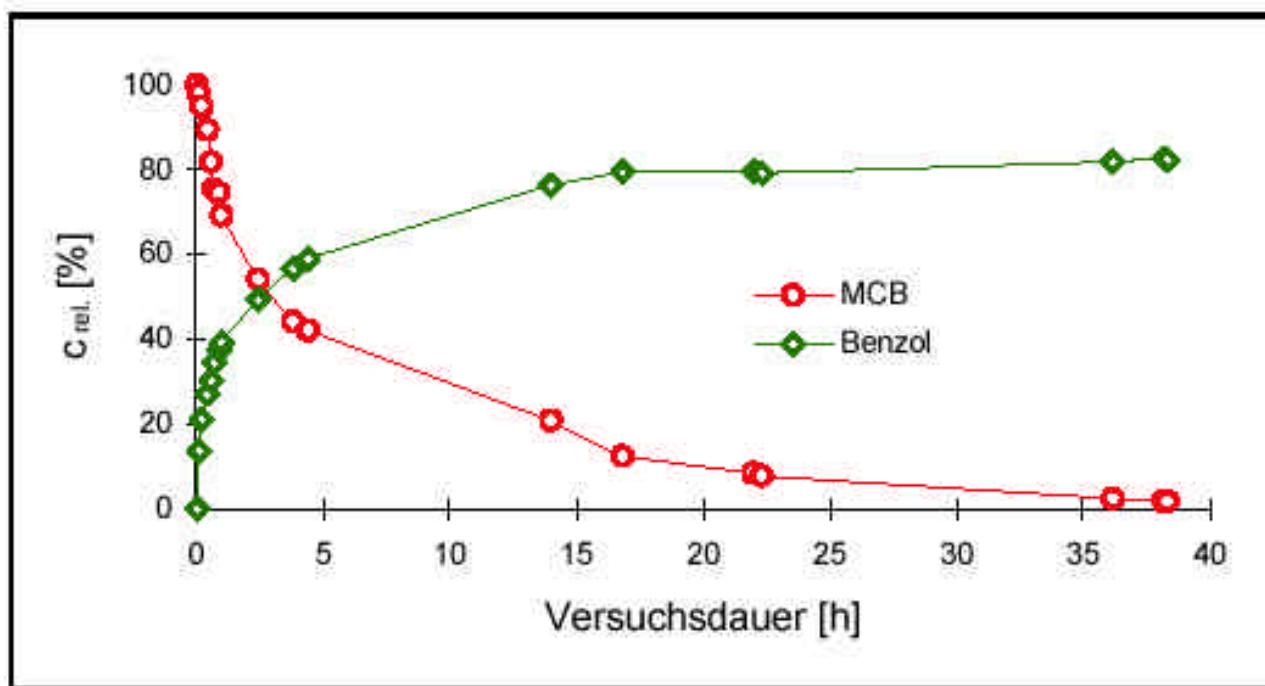


Abbildung 4.48: MCB-Reduktion an palladisiertem THOMAPLAST®-Silikonschlauch
(Schlauchabmessungen: $(1,8 \times 0,4 \times 1000)$ mm; ca. 0,7 Ma% Pd;
 $C_{0, MCB} = 3070 \text{ ppmv}$; $V_{H_2} = 2,35 \text{ l}$)



Schlauchmodul und
Tiefbrunnensäule
(UFZ Leipzig-Halle GmbH /
SAFIRA, Bitterfeld)



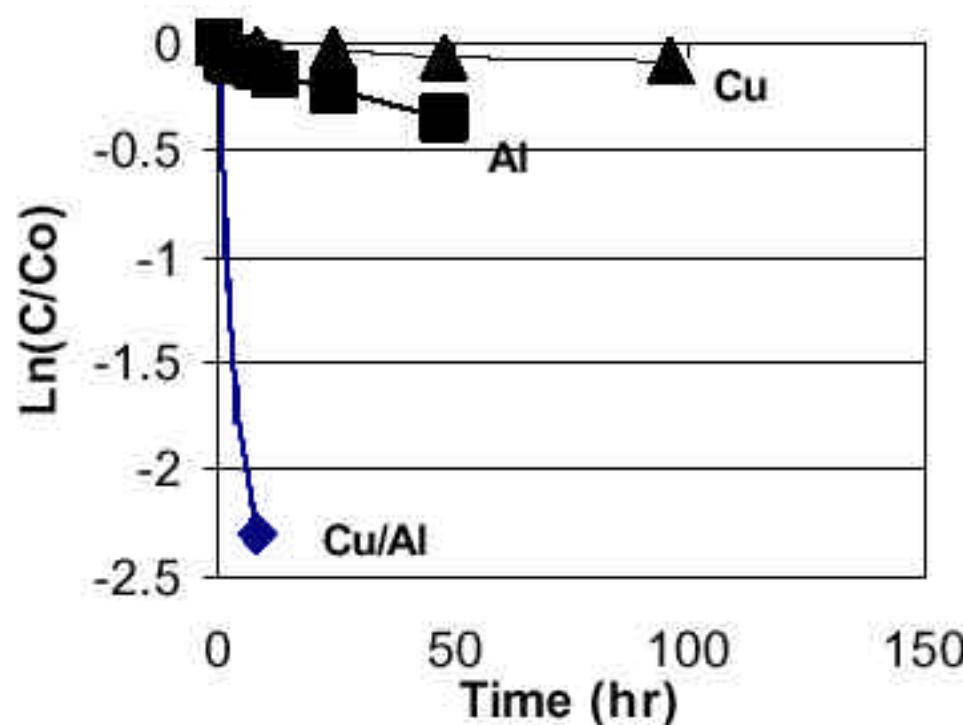


Metalle / CKW: Al/Cu, Lien and Zang 2001

Enhanced
Dehalogenation of
Halogenated
Methanes by
Bimetallic Cu/Al

Lien, H.-L.; Zhang,
W. (2001)

Presented at:
2001 International
Containment &
Remediation
Technology
Conference Orlando,
Florida



Degradation of carbon tetrachloride by bimetallic Cu/Al, Al, and Cu.



Metalle / CKW: Al/Cu, Lien and Zang 2001

Table 1. Product Distributions (mole %), observed first-order rate constants (K_{obs} , hr⁻¹) and bond strength (kJ/mole) [5] for halogenated methanes in reactions with Cu/Al

	K_{obs}	R^2	Products (mole %)	Bond strength
CCl ₄	0.582	0.985	CH ₄ (23), CHCl ₃ (<1)	287.9
CHCl ₃	0.324	0.994	CH ₄ (13), CH ₂ Cl ₂ (8)	320.5
CH ₂ Cl ₂	0.066	0.800	CH ₄ (14), CH ₃ Cl (16)	338.1
CHBr ₃	0.846	0.997	CH ₄ (35)	262.1

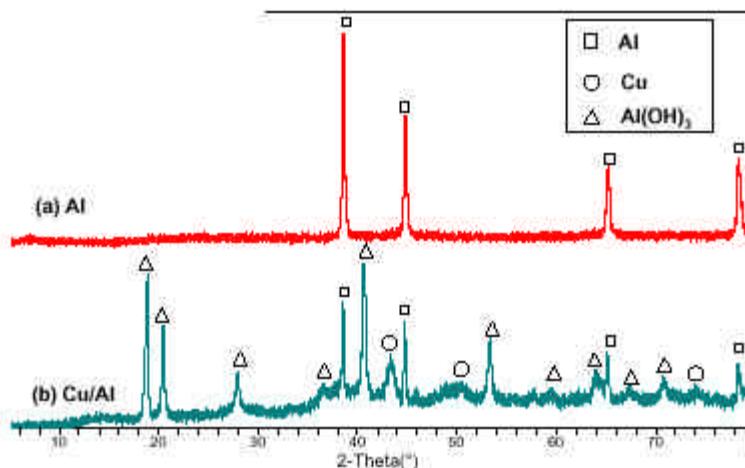


Figure 1. XRD patterns of Al and bimetallic Cu/Al.



Metalle / CKW: Zn, Schlimm, Heitz 1995

Development of a
Wastewater
Treatment Process:
Reductive
Dehalogenation of
Chlorinated
Hydrocarbons by
Metals

Schlimm, Ch.;
Heitz, E. (1996)

Environmental
Progress, 15, 38-47

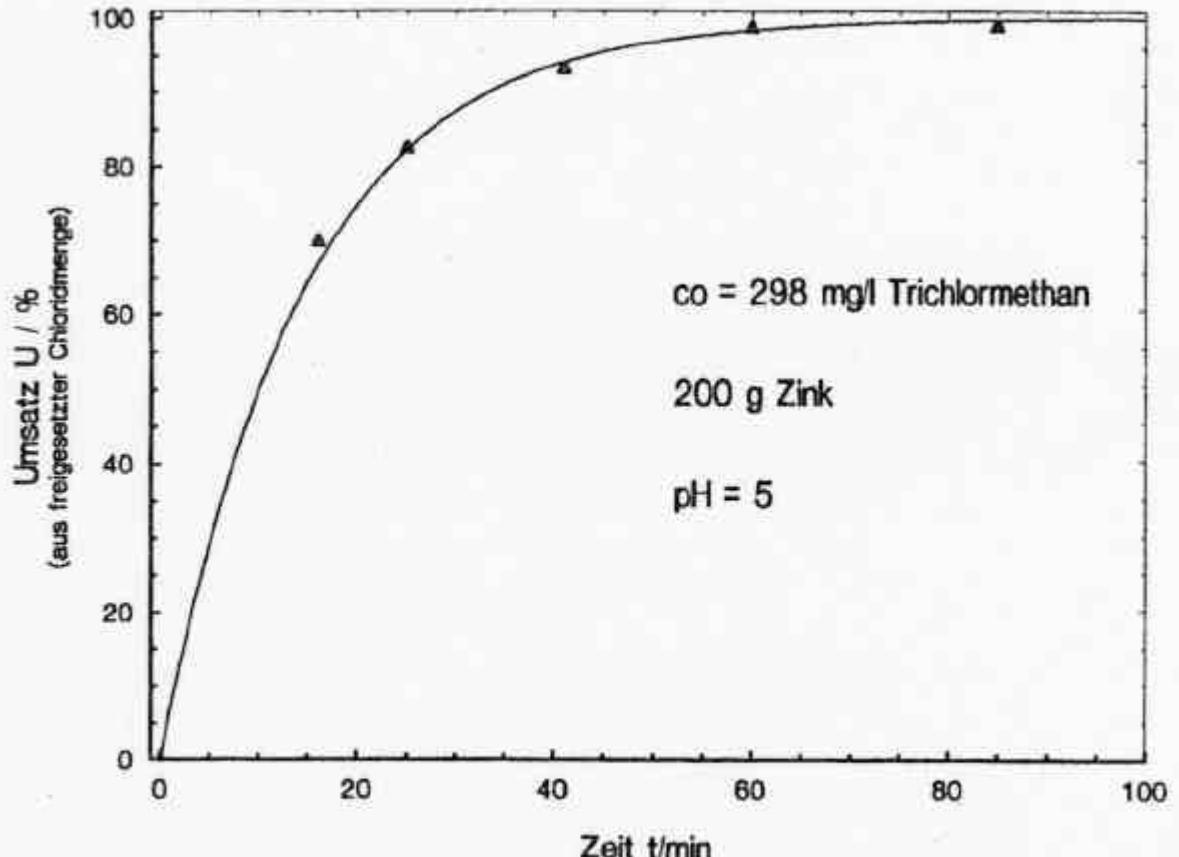


Abb. 6.2: Trichlormethanabbau mit 200 g Zink bei pH=5. Umsatz als Funktion der Zeit



Metalle / CKW: Zn, Schlimm, Heitz 1995

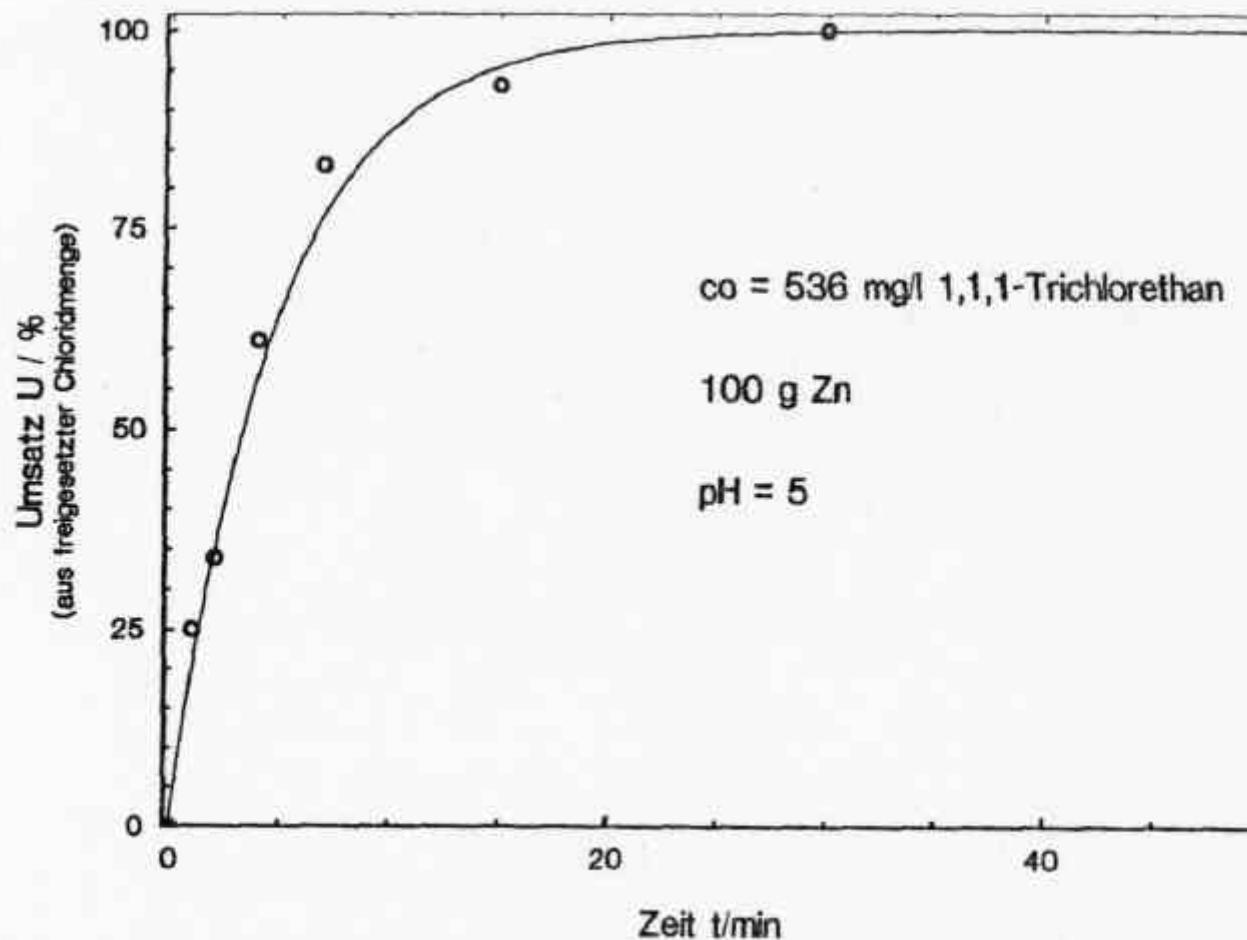


Abb. 6.3: TCA-Abbau mit 100 g Zink bei pH=5. Umsatz als Funktion der Zeit



Metalle / CKW: Al/Cu, Schlimm, Heitz 1995

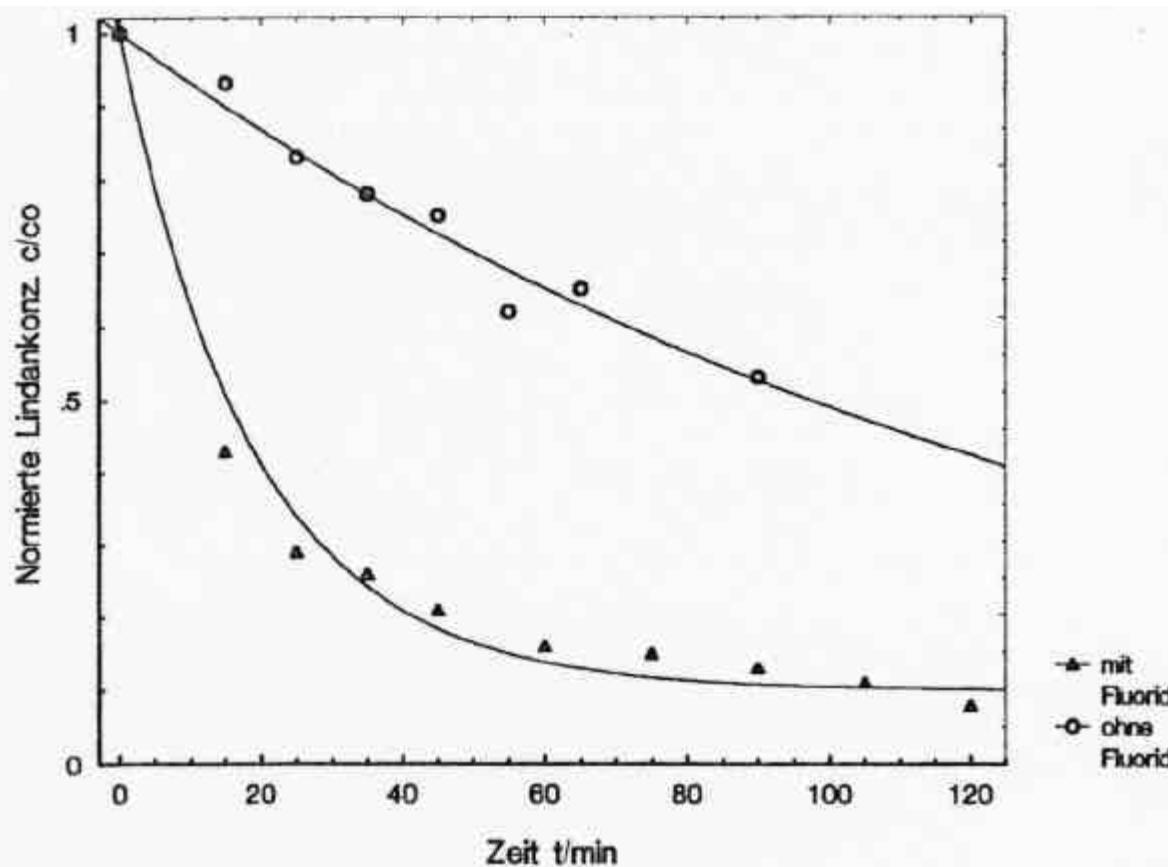


Abb. 5.6: Abbau von Lindan mit 100 g Al/Cu, $\dot{V} = 0,8 \text{ l/h}$; Einfluß des Fluoridzusatzes (0,1 mol/l).



Metalle / CKW: Mg/Cu, Schlimm, Heitz 1995

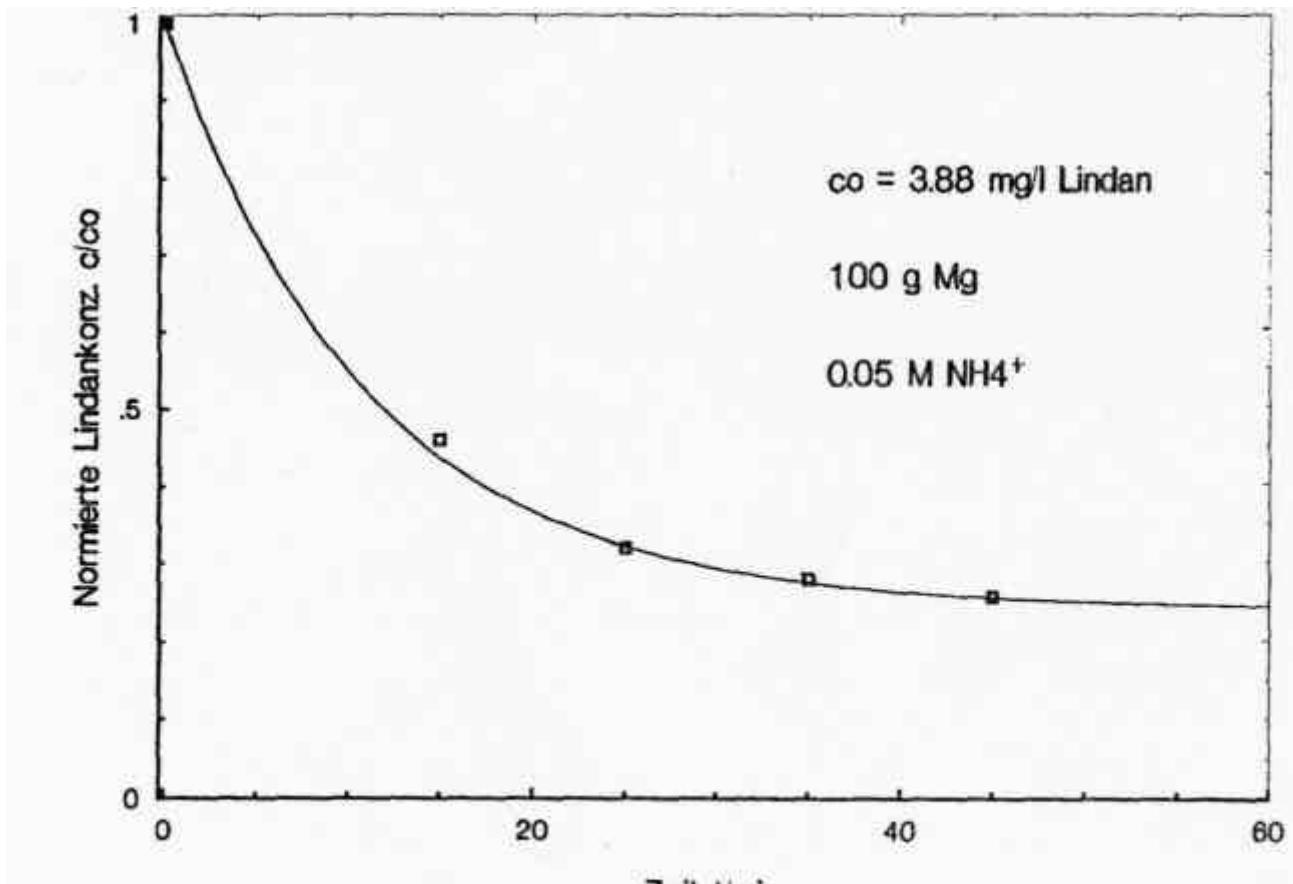


Abb. 5.7: Lindanabbau mit 100 g Mg/Cu; $\dot{V} = 0,8 \text{ l/h}$; Zusatz 0,05 mol/l NH_4^+ .



Metalle / CKW: Zn/Cu, Schlimm, Heitz 1995

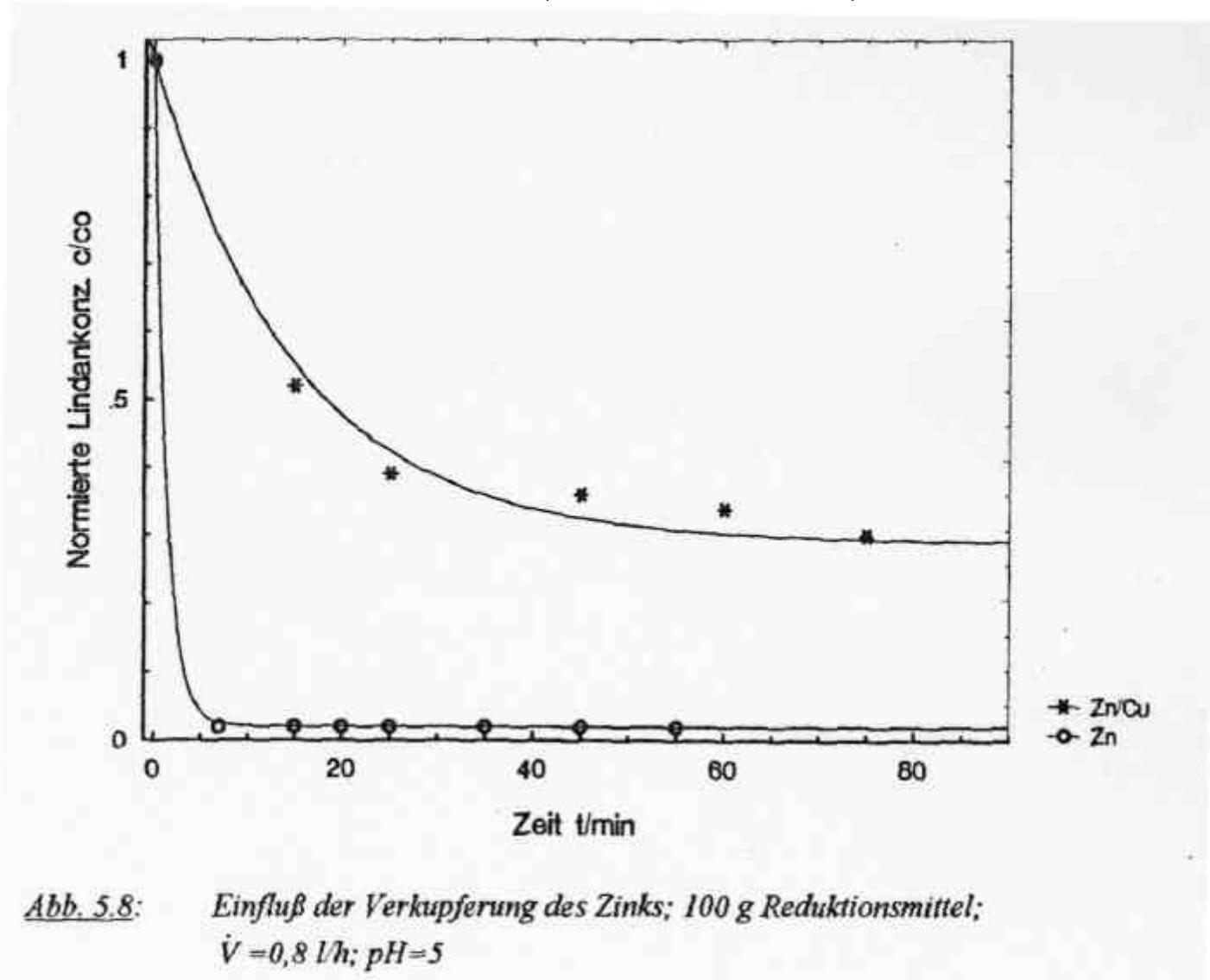
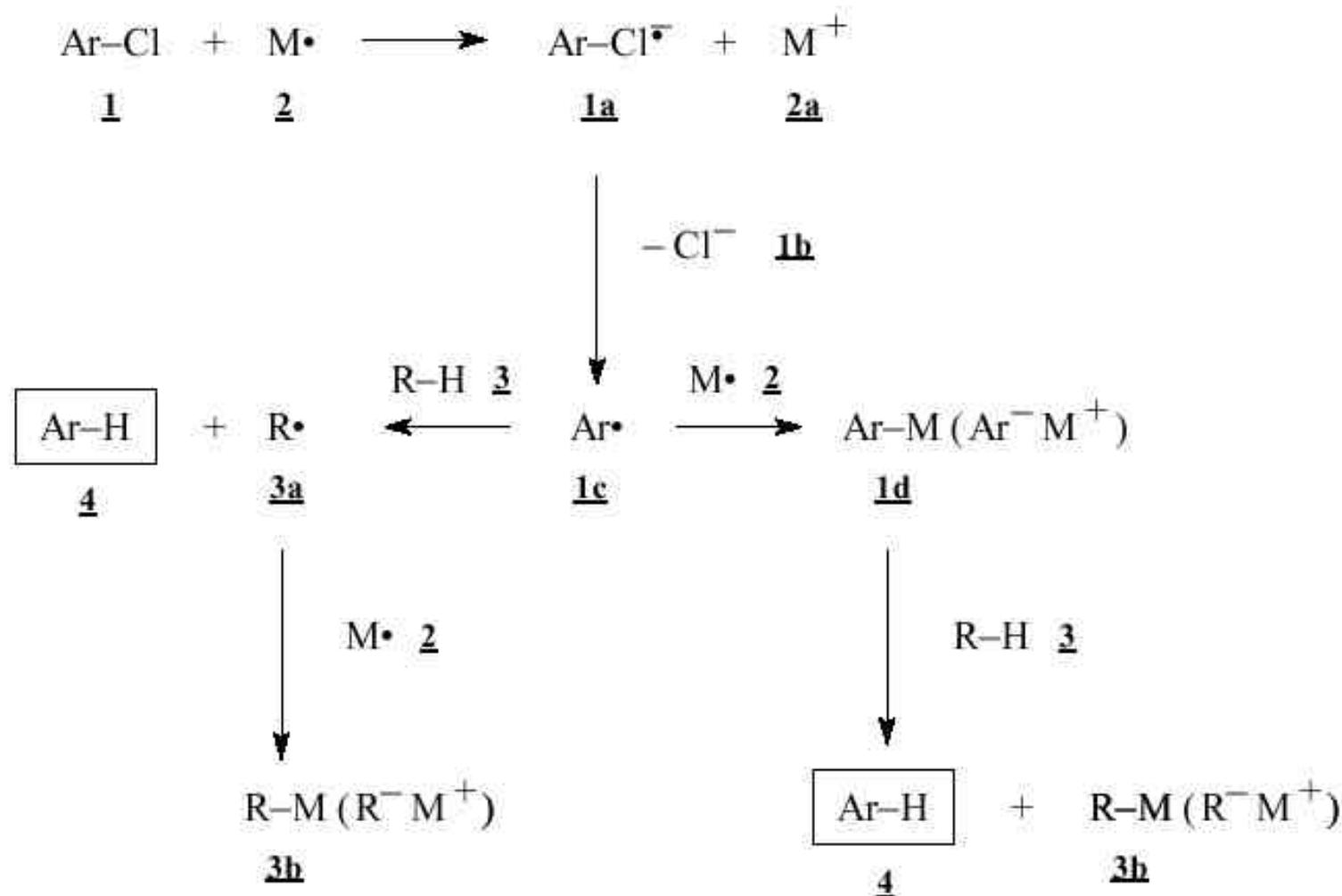


Abb. 5.8: Einfluß der Verkupferung des Zinks; 100 g Reduktionsmittel;
 $\dot{V} = 0,8 \text{ l/h}$; $pH = 5$



Metalle / CKW: Reduktive Dehalogenierung - Mechanismen



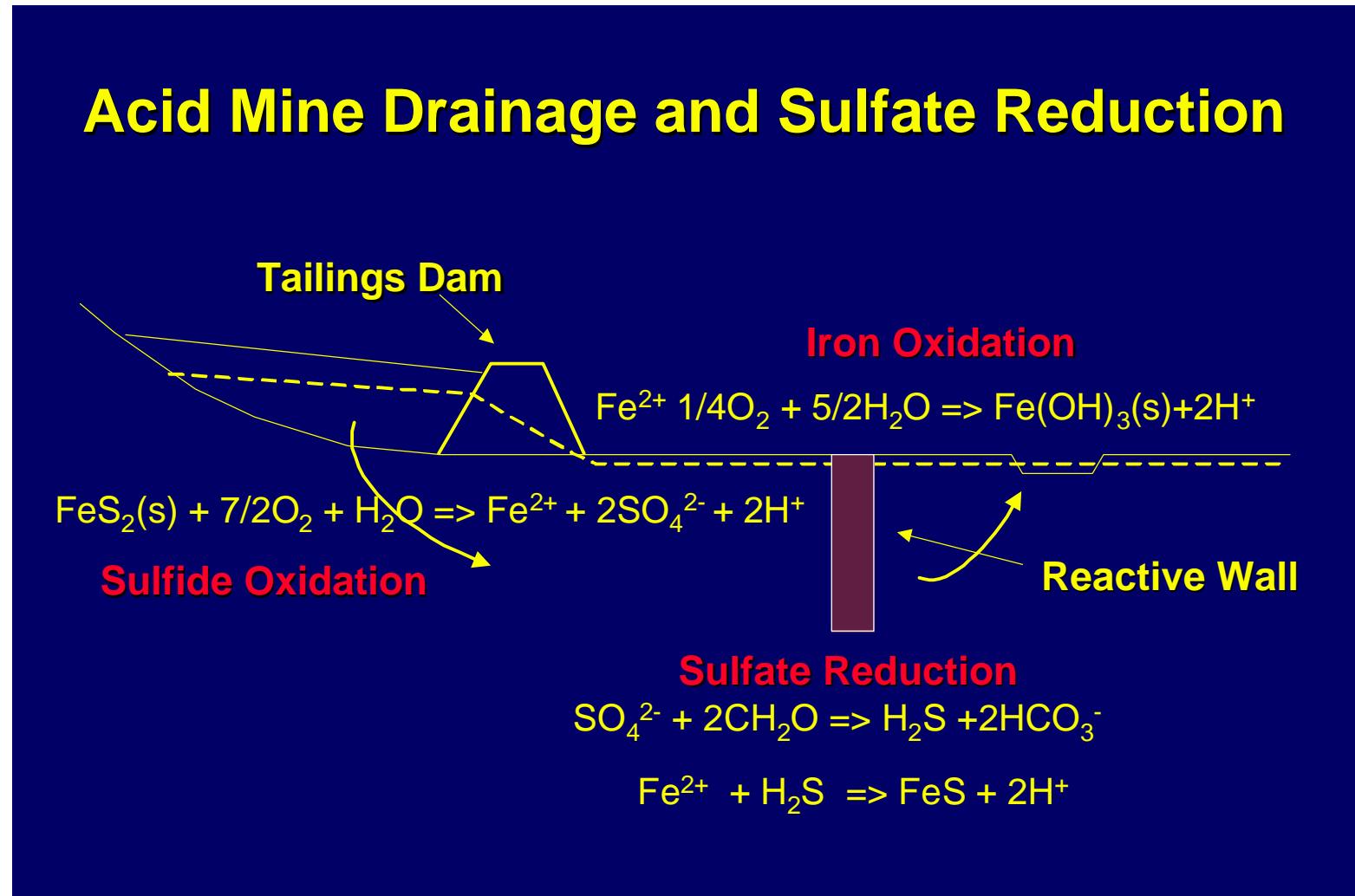


Kompost / Saures Grubenwasser : Smyth et al. 2001

In Situ
Treatment of
Acid Mine
Drainage in
Groundwater
Using
Permeable
Reactive
Materials

Smyth, D.J.A.;
Blowes, D.W.;
Benner, S.G.;
Hulshof, A.H.M.

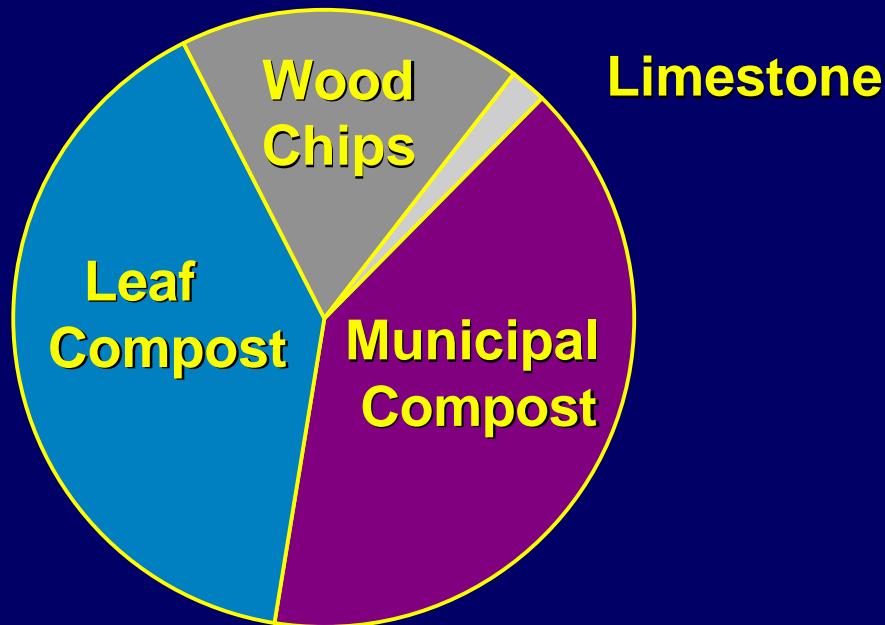
2001
International
Containment &
Remediation
Technology
Conference
Orlando,
Florida





Kompost / Saures Grubenwasser : Smyth et al. 2001

Reactive Mixture Composition for PRB





Kompost / Saures Grubenwasser : Smyth et al. 2001

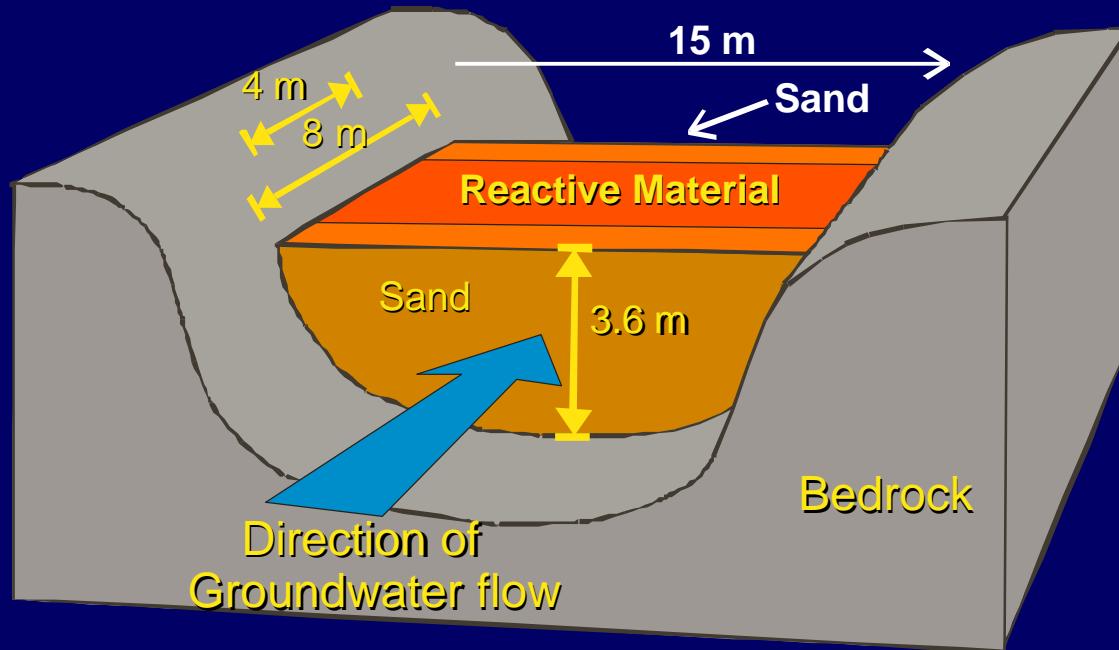
Nickel Rim Groundwater Plume

- Sulfate 2000- 4000 mg/L
- Iron 200-1200 mg/L
- pH slightly acidic (pH 6)
- Alkalinity 0-50 mg/L CaCO₃



Kompost / Grubenwasser: Smyth et al. 2001

Porous Reactive Wall Installation



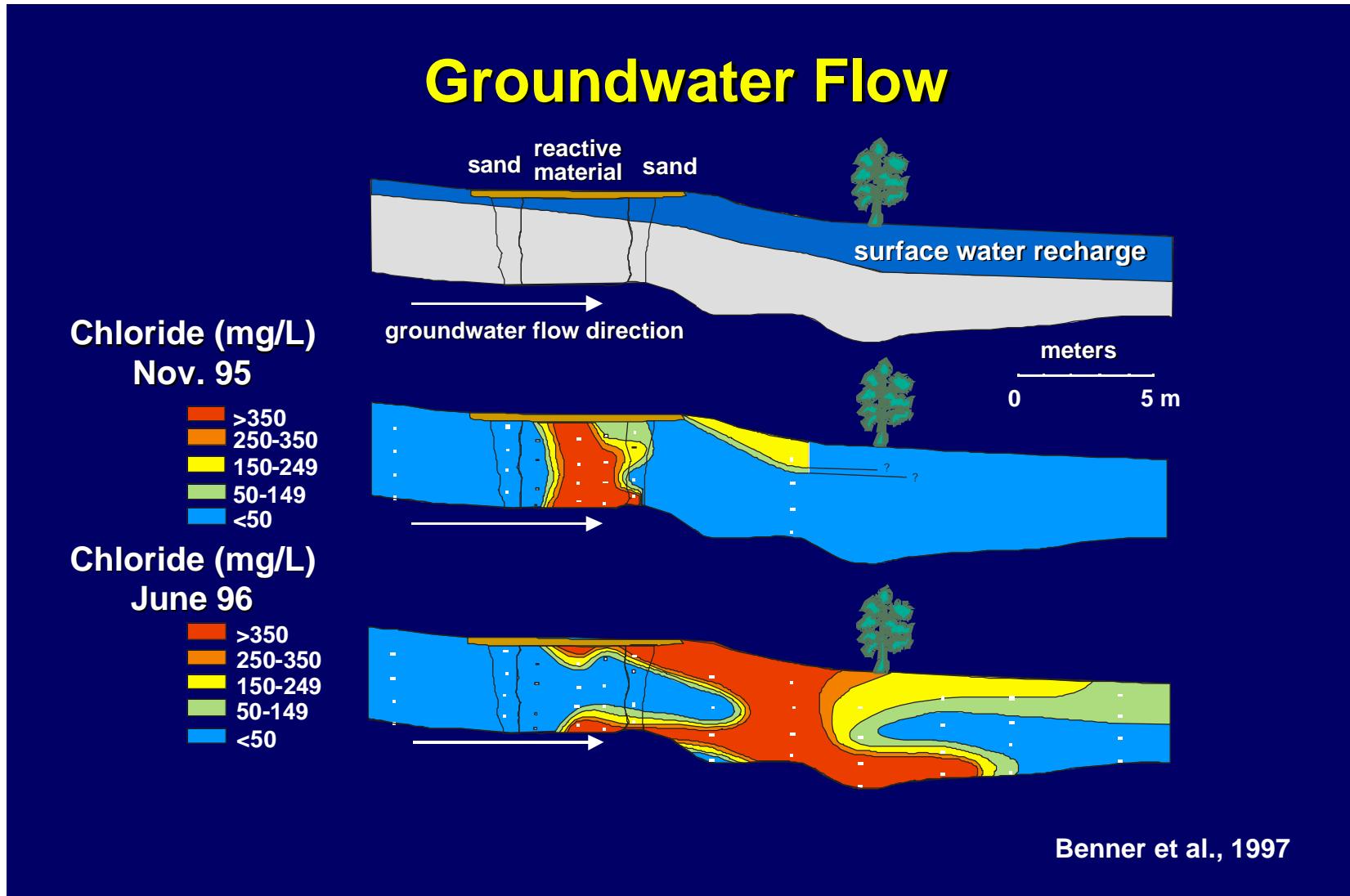


Kompost / Grubenwasser: Smyth et al. 2001



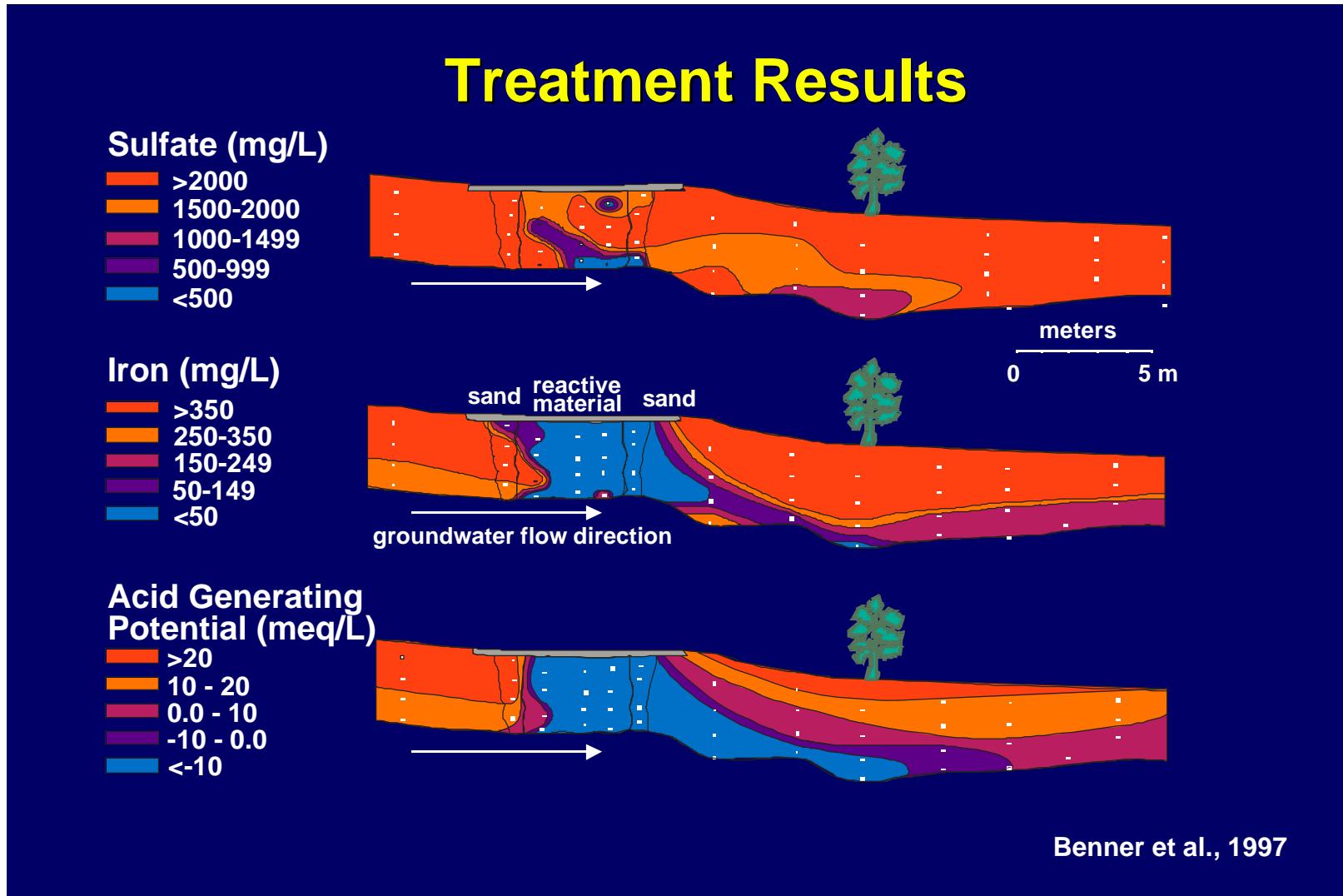


Kompost / Saures Grubenwasser : Smyth et al. 2001





Kompost / Saures Grubenwasser : Smyth et al. 2001





Smyth et al. 2001

Sulfate Reduction in PRB

- Decreasing sulfate concentrations
- Sulfate-reducing bacteria
- Dissolved sulfide present
- Isotopic enrichment of ^{34}S in remnant sulfate
- Iron monosulfides identified in cores



Smyth et al. 2001

Issues

- Heterogeneities in PRB
- Location of installation
- Longevity; decreasing reactivity with time
- Residence time of contaminated groundwater in PRB is critical to level of treatment achieved



Smyth et al. 2001

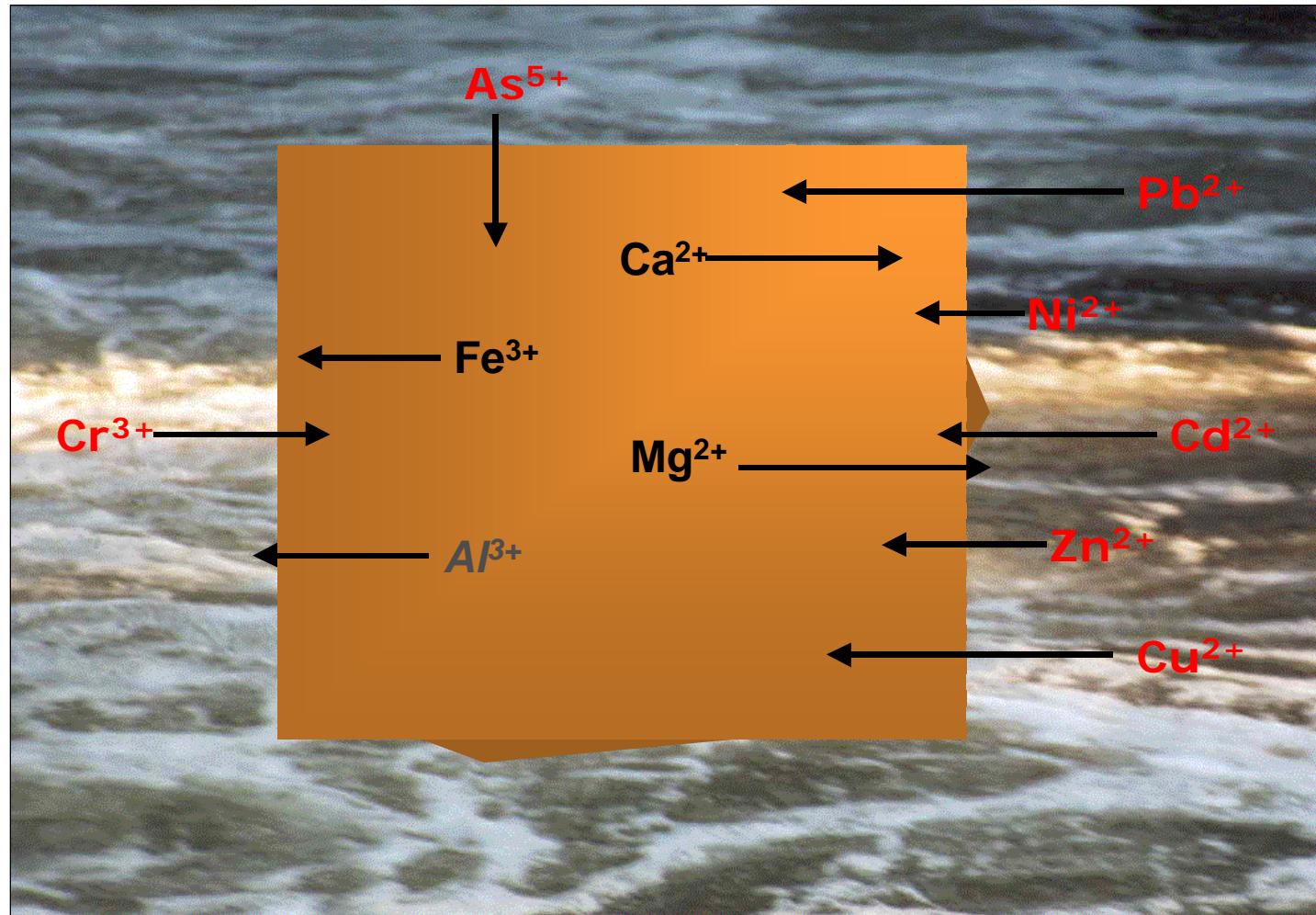
CONCLUSIONS

- Sulfate-reducing PRBs suitable for treating dissolved metals associated with AMD and sulfate-rich groundwater
- Field-scale demonstrations in progress
- Field evidence for the formation of iron and other metal sulfide minerals
- Conversion of water from net acid producing to net acid consuming



Sorbentien / Schwermetalle: Ecker 2001

Dr. Ecker GmbH
Wasserreinigungssysteme





Sorbentien / Schwermetalle: Ecker 2001

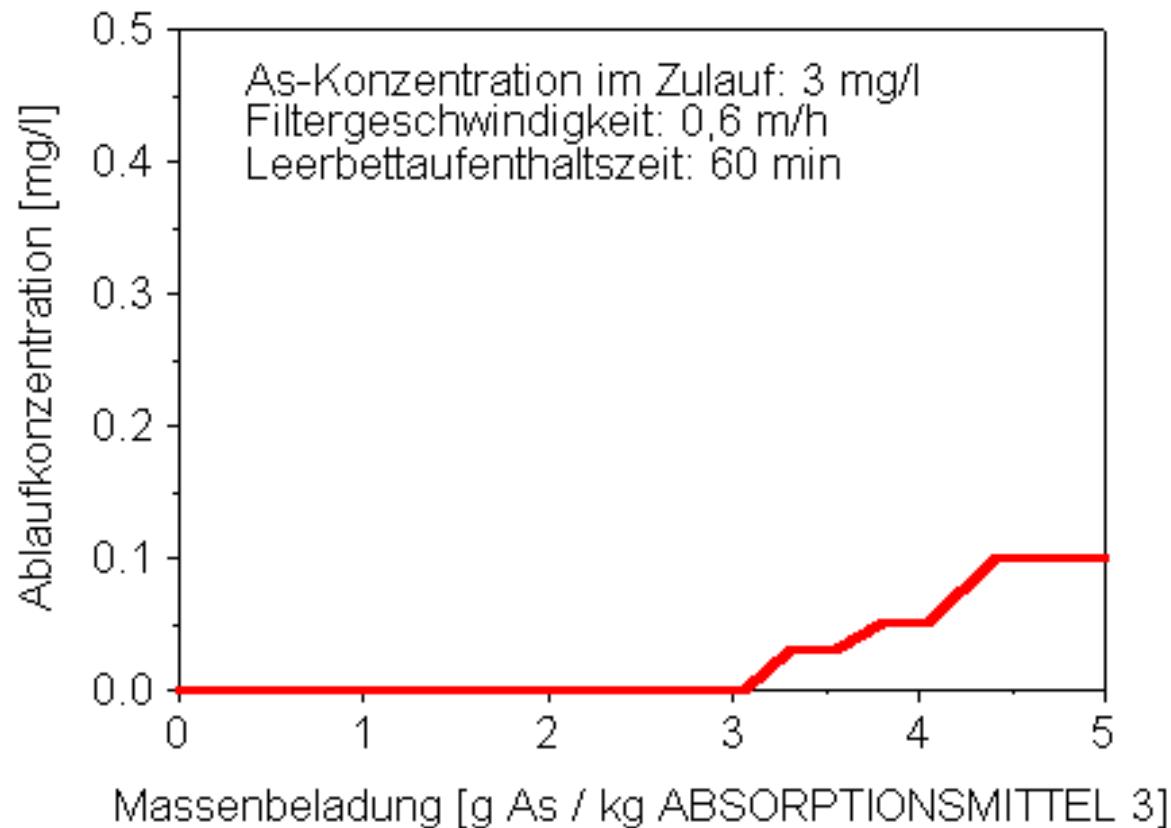


Charakterisierung von ABSORPTIONSMITTEL 3

Partikeldurchmesser:	0,3 - 5 mm
Schüttgewicht:	ca. 600 kg/m ³
sonstiges:	neigt nicht zum Verkeimen

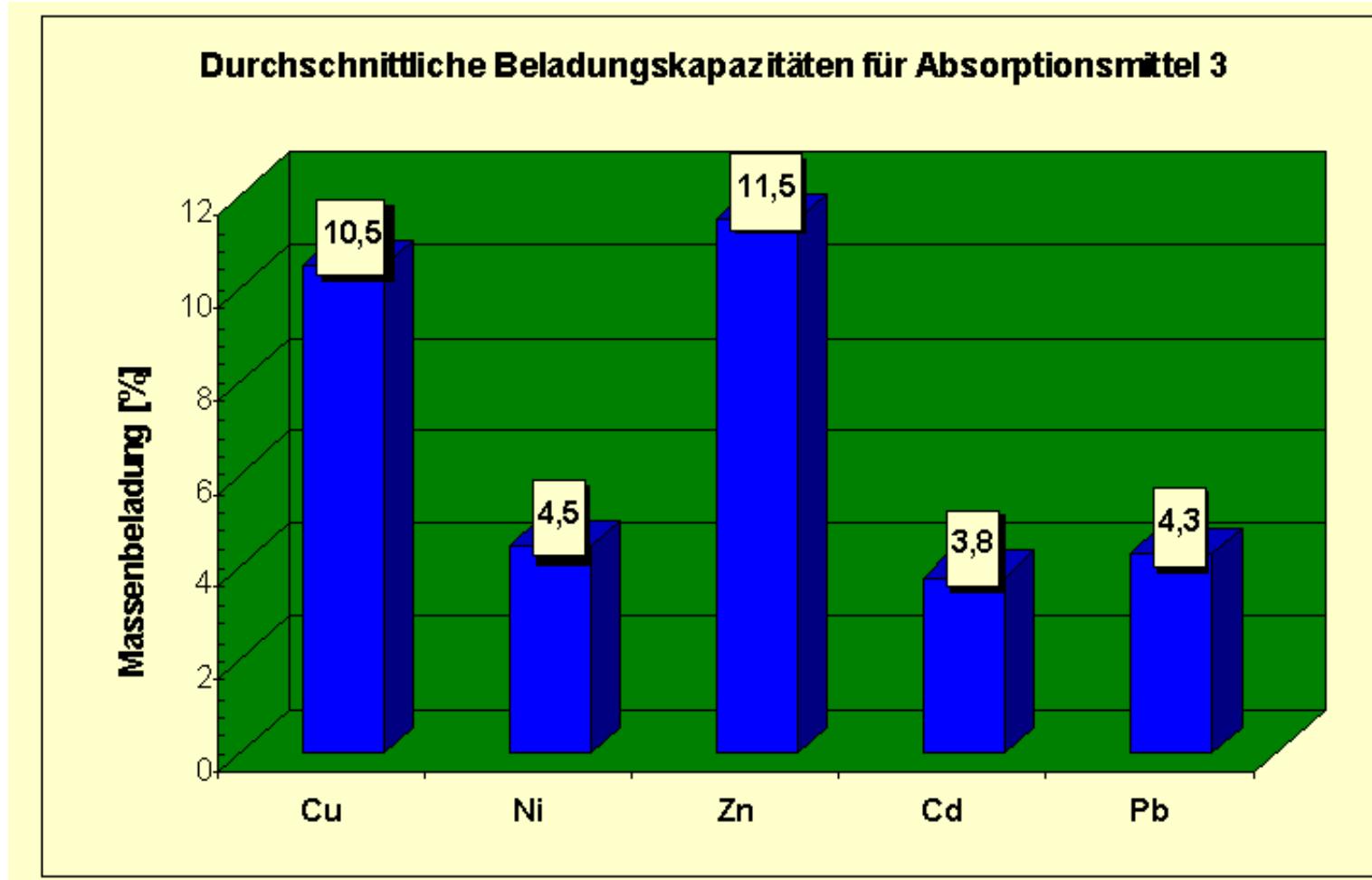


Sorbentien / Schwermetalle: Ecker 2001





Sorbentien / Schwermetalle: Ecker 2001





Mögliche Komponente des Absorptionsmittels 3: Tricalciumaluminat

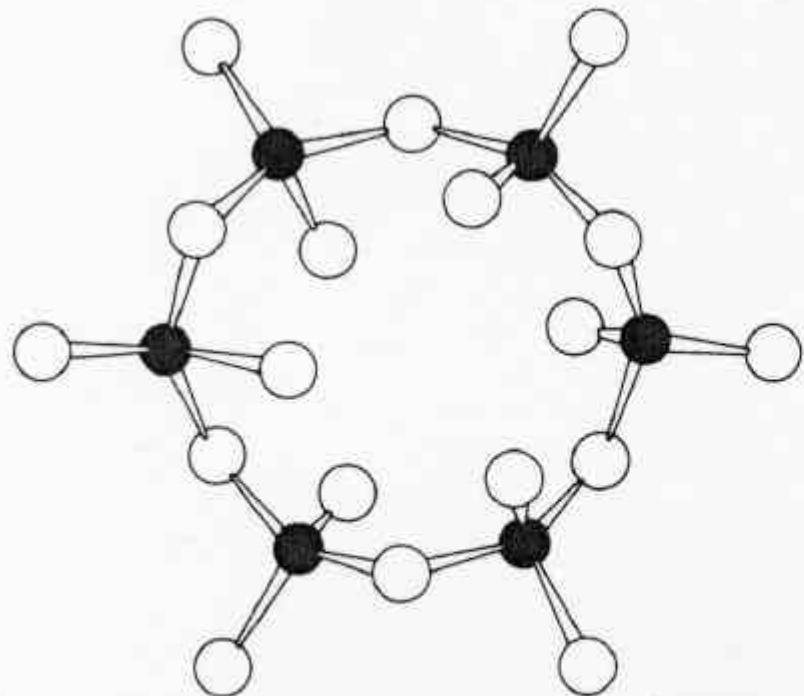


Abb. 7.18 Struktur der Einheit $[Al_6O_{18}]^7-$ im $Ca_3Al_2O_6$ (d. h. $Ca_9Al_6O_{18}$). Die Abstände $Al-O$ fallen durchweg in den Bereich 175 ± 2 pm

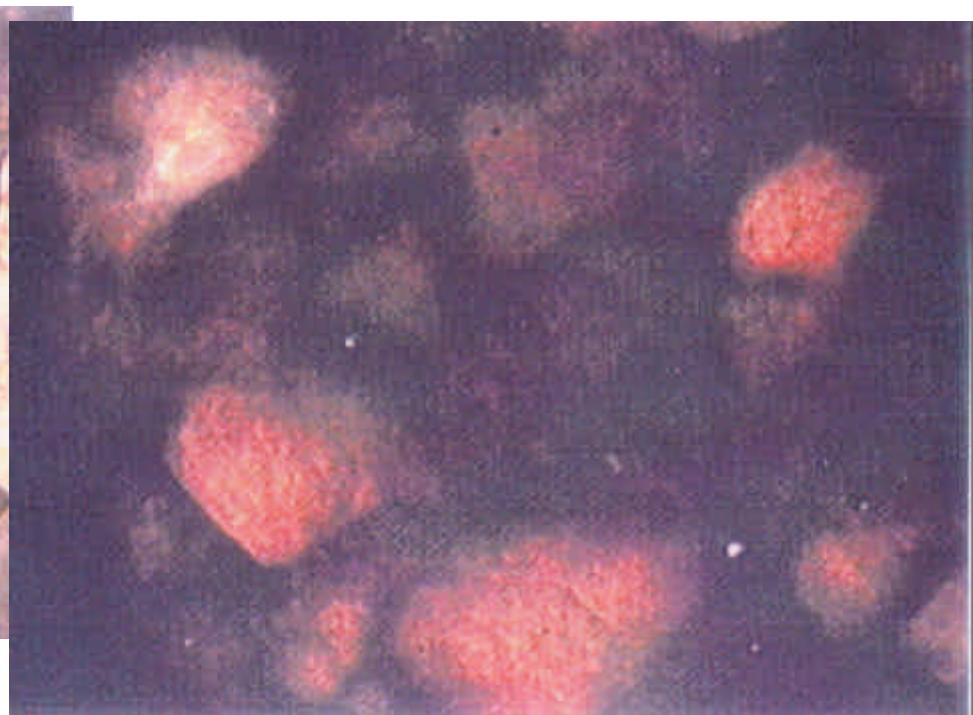


Huminstoffbarrieren / PAK und Schwermetalle:

Oeste, F.D. DE 4443828 A1 (1994)

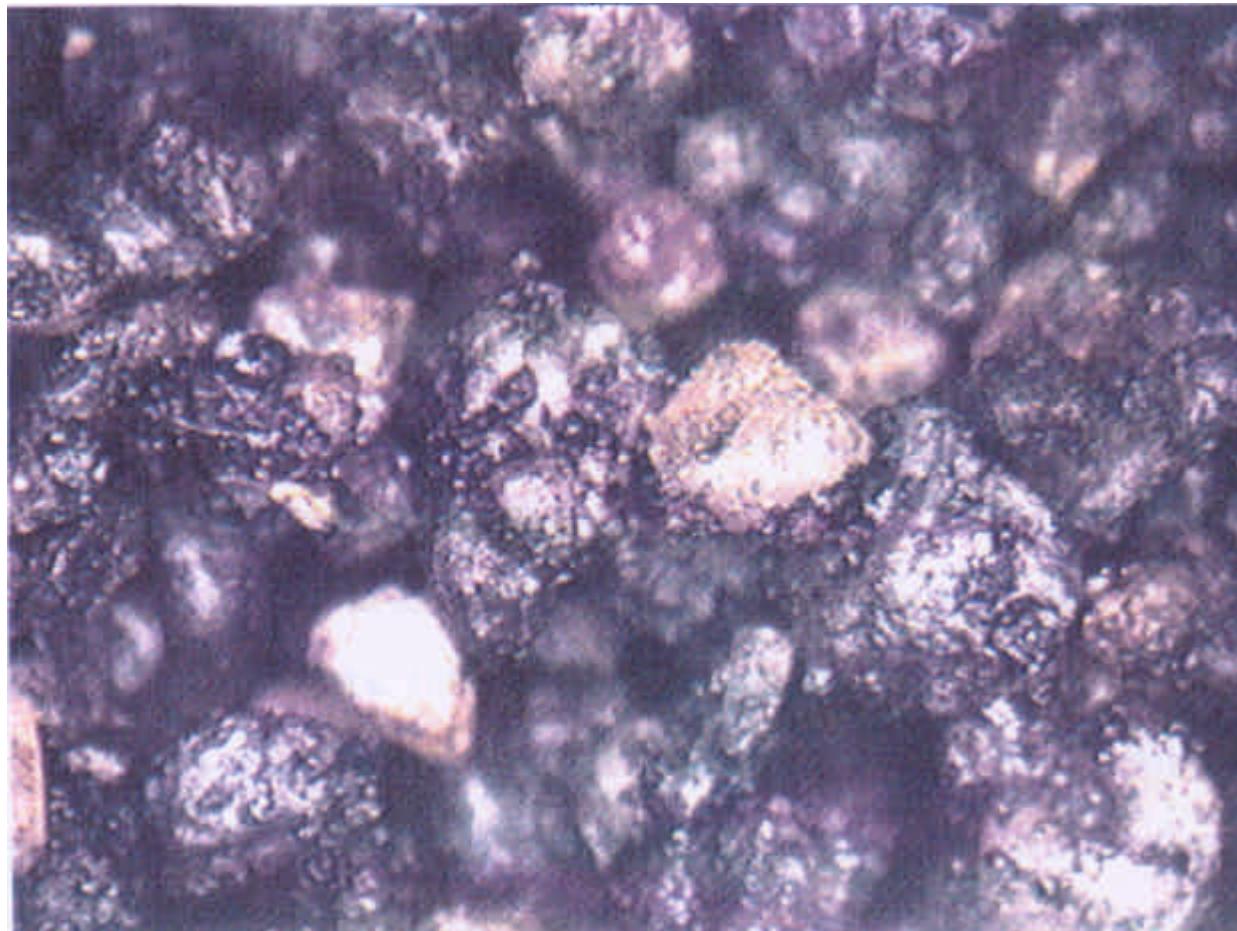
Colonna, M. (1995), „Barriere zur Altlastensicherung auf Basis von Huminstoffen“, Diplomarbeit, Märkische Fachhochschule Iserlohn

Balcke, G.U. (2000), „Anthropogene Huminstoffe als Sorbentien und Reagenzien zur Immobilisierung von organischen Schadstoffen in Grundwässern“, Dissertation Universität Leipzig



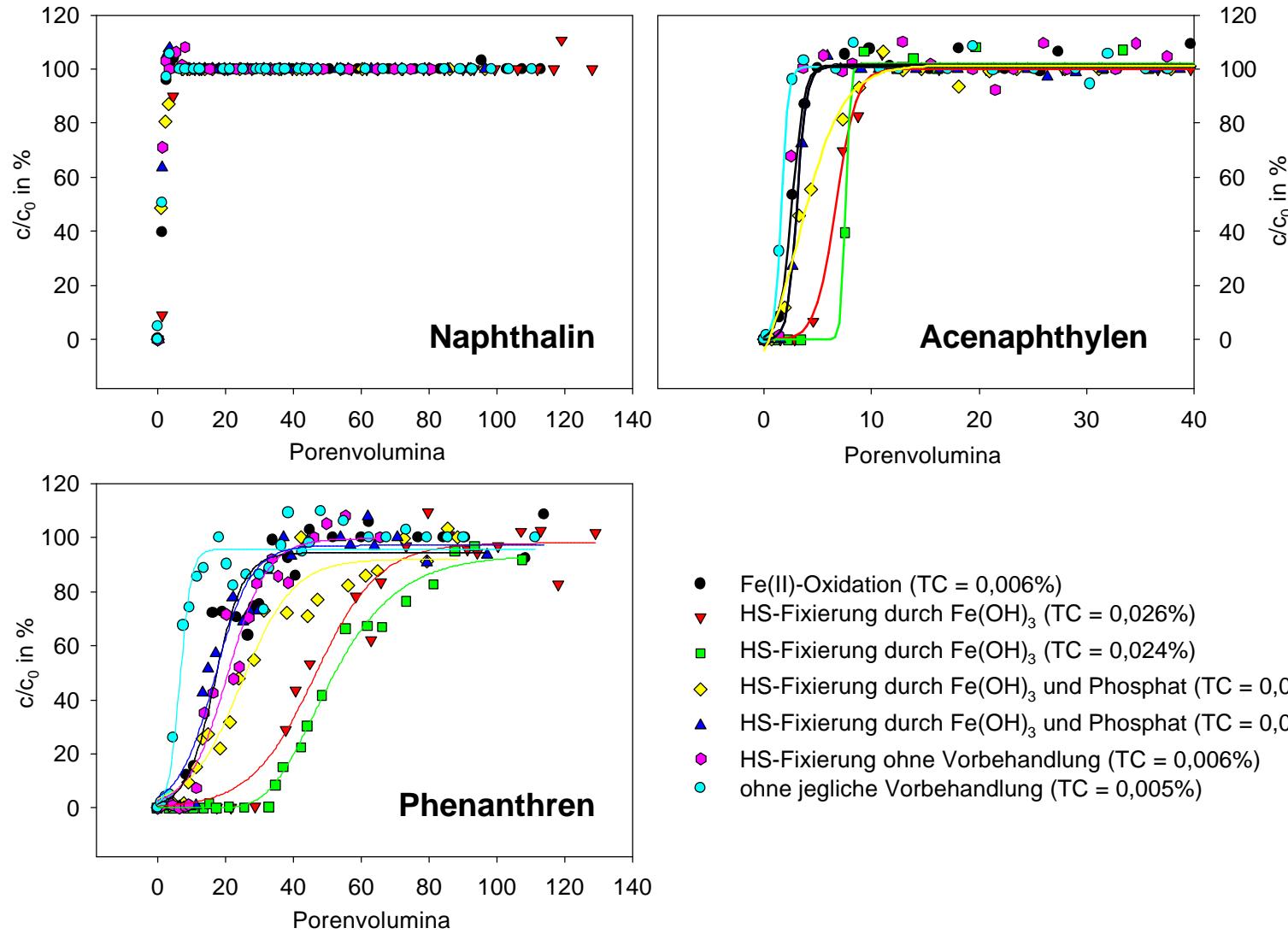


Huminstoffbarrieren: Oeste 1994





Huminstoffbarrieren / PAK: Balcke 2000





Adsorberpolymere / LCKW: Pilchowski 1999

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Tab. 1: Freundlich-Parameter und Δ -Werte der Adsorption von LCKW aus Wasser ohne und mit Huminstoffbelastung sowie von HS aus Wasser bei 25 °C.

Freundlich parameters and Δ -values of the adsorption of VCHC from water without (o.) and with (m.) humic substance as well as of HS from water at 25 °C.

Adsorbens	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	Dichlorethan		Trichlorethan		Trichlorethen		HS
			o. HS	m. HS	o. HS	m. HS	o. HS	m. HS	
WOFATIT EP 63	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	1.14	1.19	4.66	4.66	5.72	4.73	—
	n	—	0.60	0.52	0.66	0.73	0.76	0.59	—
	Δ	%	4.3	4.5	8.8	8.9	6.9	12.1	—
DOWEX XUS 43493	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	0.89	0.90	2.46	2.52	5.17	4.09	0.85
	n	—	0.76	0.72	0.65	0.65	0.95	0.89	0.25
	Δ	%	4.7	7.8	10.3	14.2	10.0	8.7	3.7
DOWEX XUS 43546	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	0.57	0.69	1.84	1.94	3.07	3.38	—
	n	—	0.69	0.66	0.67	0.64	0.71	0.77	—
	Δ	%	4.1	4.5	6.0	7.2	2.6	8.4	—
MACRONET MN 100	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	1.04	1.06	3.60	3.24	3.50	2.78	0.47
	n	—	0.65	0.65	0.97	0.78	0.78	0.68	0.83
	Δ	%	4.2	4.8	11.4	14.6	8.8	11.9	2.7
MACRONET MN 200	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	0.97	0.89	3.98	3.08	4.49	3.82	1.66
	n	—	0.72	0.74	0.76	0.52	0.95	0.83	0.26
	Δ	%	4.1	5.5	11.6	10.9	14.7	16.9	9.5
NORIT ROW	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	1.23	1.19	5.49	4.24	2.97	2.33	2.73
	n	—	0.65	0.66	0.82	0.72	0.50	0.44	1.0
	Δ	%	4.7	3.4	5.4	12.5	18.9	12.4	18.3
PRECOLITH BKK 3	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	1.25	1.18	6.42	5.02	5.32	4.02	2.93
	n	—	0.67	0.66	0.92	0.94	0.66	0.57	1.0
	Δ	%	4.8	2.8	7.9	6.7	4.6	19.0	16.0
HYDRAFFIN CG	K_F	mmol ⁽¹⁻ⁿ⁾ · L ⁿ /g	0.62	0.62	3.88	3.84	4.18	3.95	0.78
	n	—	0.98	0.86	1.0	1.0	0.85	0.84	0.99
	Δ	%	4.3	4.0	8.0	4.8	7.6	9.5	7.5



Adsorberpolymere / LCKW: Pilchowski 1999

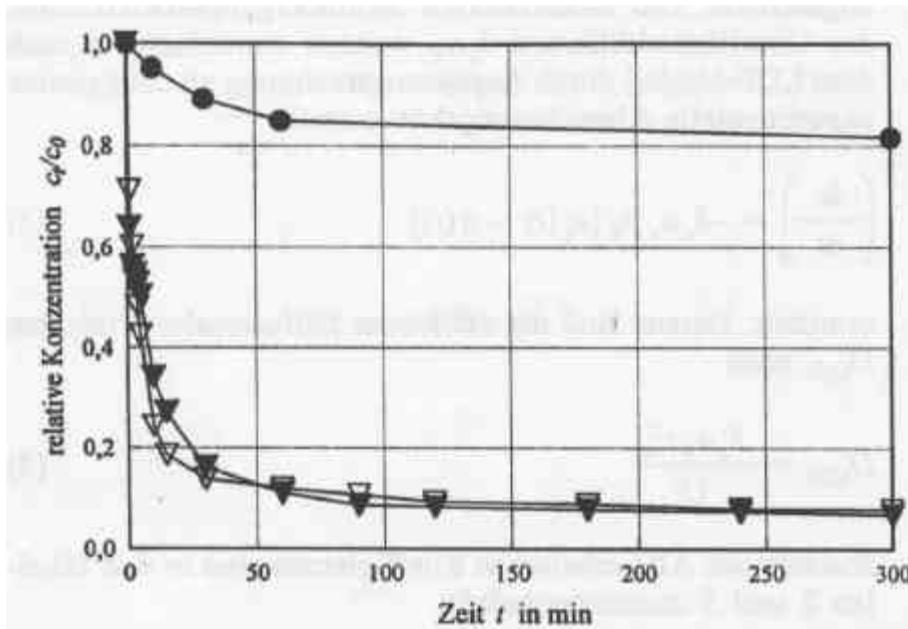


Bild 11: Konzentrations-Zeit-Kurven der Adsorption von TCA aus Wasser ohne und mit Huminstoffbelastung sowie von HS aus Wasser an MACRONET MN 200 bei 25 °C.

Concentration-time-curves of adsorption of trichloroethane from water without and with humic substance (HS) as well as of HS from water by MACRONET MN 200 at 25 °C.

▽ TCA ohne/without HS ▼ TCA mit/with HS . ● HS

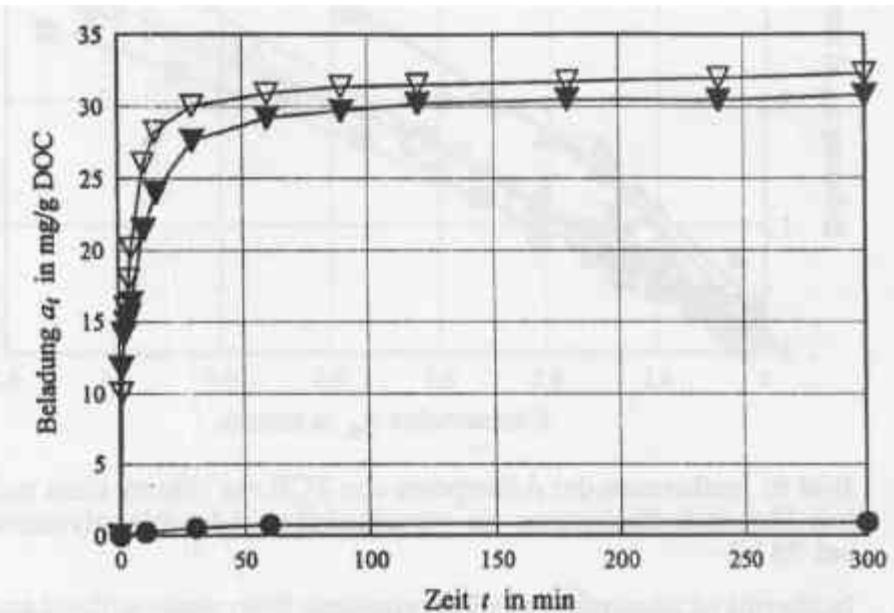


Bild 12: Beladungs-Zeit-Kurven der Adsorption von TCA aus Wasser ohne und mit Huminstoffbelastung sowie von HS aus Wasser an MACRONET MN 200 bei 25 °C.

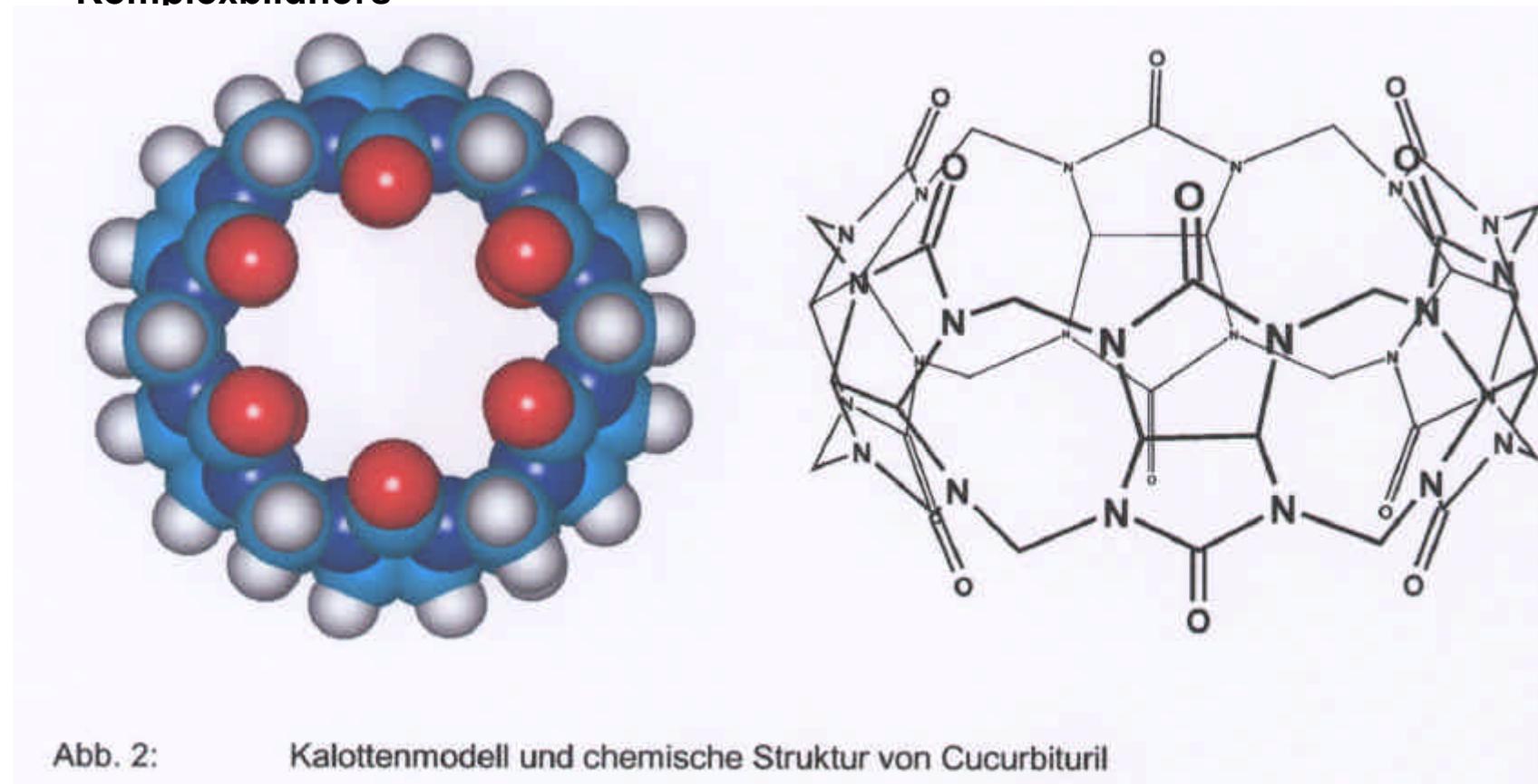
Loading-time-curves of trichloroethane from water without and with humic substance (HS) as well as of HS from water by MACRONET MN 200 at 25 °C.

▽ TCA ohne/without HS ▼ TCA mit/with HS . ● HS



Cucurbituril / Aromaten: Buschmann et al. 1999

Buschmann, H.-J.; Jansen, K.; Dantz, D.A., Schollmeyer, E. (1999),
BMBF-Forschungsvorhaben 02WT9730/1 „Entwicklung eines
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Grundwasser mit Hilfe eines makrozyklischen, regenerierbaren
Komplexbildners“





Cucurbituril / Aromaten: Buschmann et al. 1999

Tabelle 3: Abtrennung in Prozent (Fehler 5 %) verschiedener Aromaten, (Ausgangskonzentration 10 mg/l, -volumen 10 ml) durch Zugabe von 500 mg festem Cucurbituril aus Wasser.

Verbindung	prozentuale Abtrennung
Benzol	41
Toluol	73
Xylol	88
Naphtalin	87
Acenaphthen	44
Anthracen	71
Chlorbenzol	64
1,2-Dichlorbenzol	70
1,2,4-Trichlorbenzol	86
4-Chlorphenol	62
4-Nitrotoluol	68



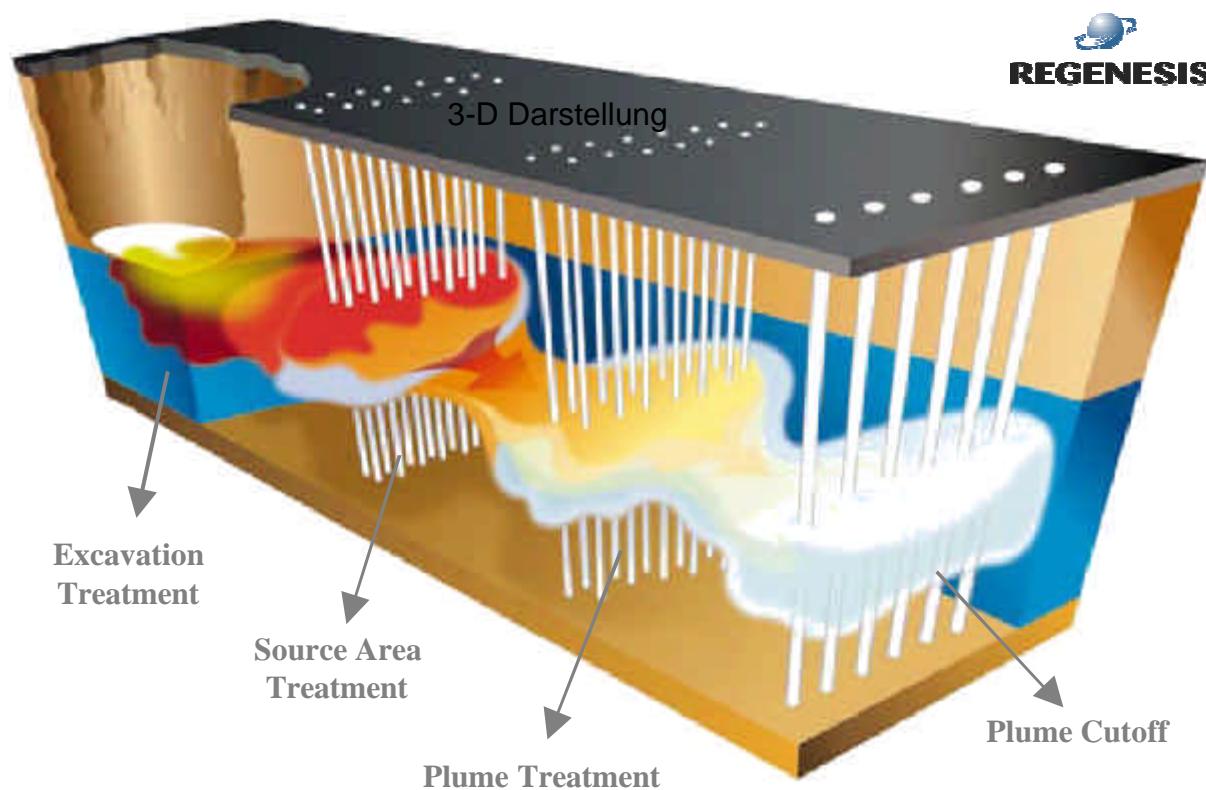
Cucurbituril / Aromaten: Buschmann et al. 1999

2,4-Diaminotoluol	95
2,4-Dinitrotoluol	75
2-Nitrophenol	78
2,6-Dichlor-4-nitroanilin	78
4-Nitroanilin	95



ORC und HRC / Organische Schadstoffe:

Regenesis, San Clemente, CA 92672-6244, U.S.A.
Envirosoft Dr. Raphael GmbH, Schwerte





ORC und HRC / Organische Schadstoffe: Regenesis, Envirosoft

Beschleunigung des aeroben Abbaus

Problem: Vielfach besteht im belasteten Grundwasser ein Mangel an Sauerstoff! Lösungsmöglichkeiten:

- 👉 Zufuhr über zuströmendes Grundwasser?
- 👉 Eintrag von (Luft-) Sauerstoff über Lanzen
- 👉 Sauerstofftransport über die Wasserphase
- 👉 Zufuhr von Sauerstoffträgern: Nitrat, Wasserstoffperoxid, etc. oder
- 👉 Oxygen Release Compound, **ORC**



Anwendung ORC & HRC

Im Grundwasser:

- 👉 Beschleunigung (vor allem aerober Prozesse)
- 👉 Steuerung und/oder
- 👉 Auslösung biologischer Schadstoffumsetzungen

Anwendung von ORC

- 👉 ORC wird direkt
 - 👉 ins Schadenszentrum oder
 - 👉 in die Schadstofffahne eingebracht
- 👉 ORC dient auch zur Errichtung biologisch aktiver Barrieren



ORC (OXYGEN Release Compound) ist ...

- 👉 eine spezielle Formulierung von Magnesiumperoxid (MgO_2), die nach Kontakt mit Wasser langsam gelösten Sauerstoff in hohen Konzentrationen freisetzt
- 👉 über Brunnen oder Bohrungen zu diesem Zweck ins Grundwasser eingebbracht wird,
- 👉 und dort die Mikroorganismen über 6-9 Monate mit Sauerstoff versorgt
- 👉 $MgO_2 + H_2O \Rightarrow 1/2 O_2 + Mg(OH)_2$



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