In Situ Chemical Reduction (ISCR)

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Richard A. Brown, Ph.D.; Maureen Leahy, Ph.D.

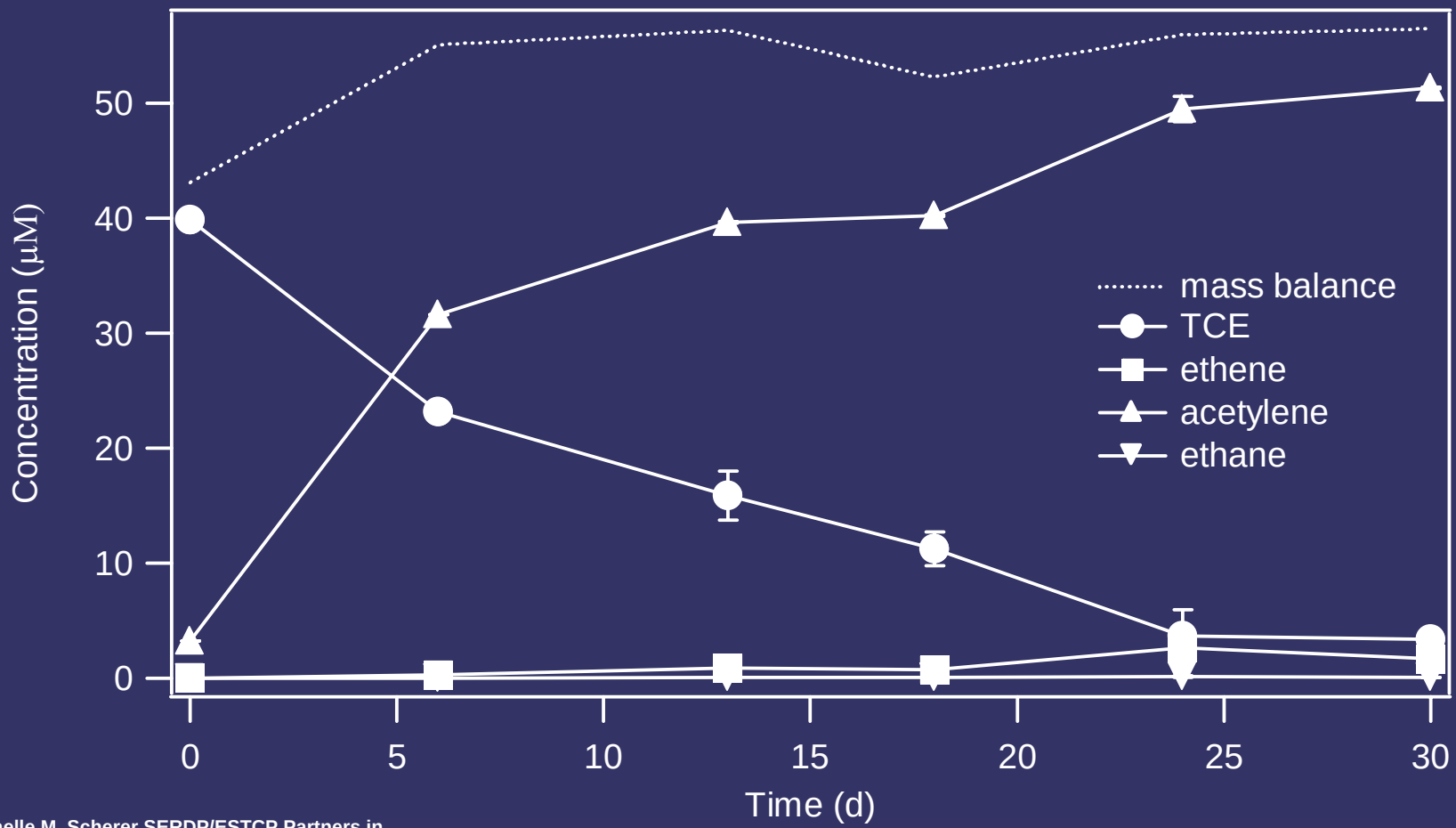
The Four Pillars of ISCR

1. **Abiotic processes are frequently based on reduced metals**
2. **Abiotic pathways are different than biological pathways**
3. **Abiotic process are surface catalyzed**
4. **Abiotic processes can be enhanced by chemical reductants or biological reduction**

Reduced Iron Minerals Active in Dechlorination

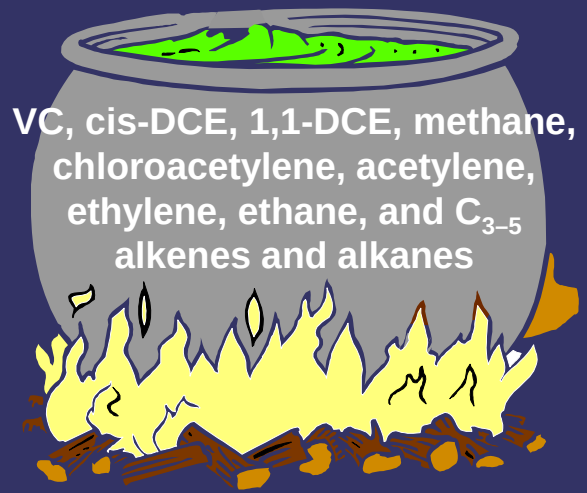
- Pyrite FeS,
- Marcasite FeS_2
- Green Rust $[Fe^{2+}_6Fe^{3+}_2(OH)_{18}\cdot 4(H_2O)]$
- Magnetite $Fe^{3+}_2Fe^{2+}O_4$
- Siderite $FeCO_3$
- Artificially Created
  - Steel Slag amended with Fe^{+2}
  - Cement amended with Fe^{+2}
  - Minerals treated with reductants

Reduction of TCE by FeS

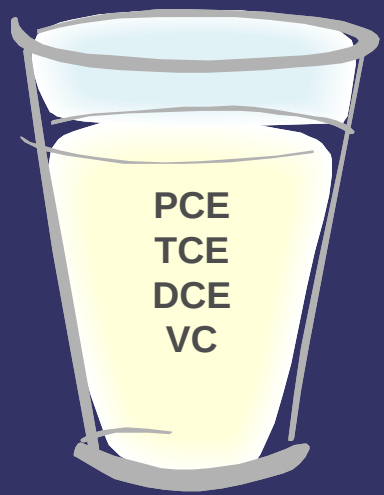


Michelle M. Scherer SERDP/ESTCP Partners in Environmental Technology Technical Symposium & Workshop December 2005

Products Formed

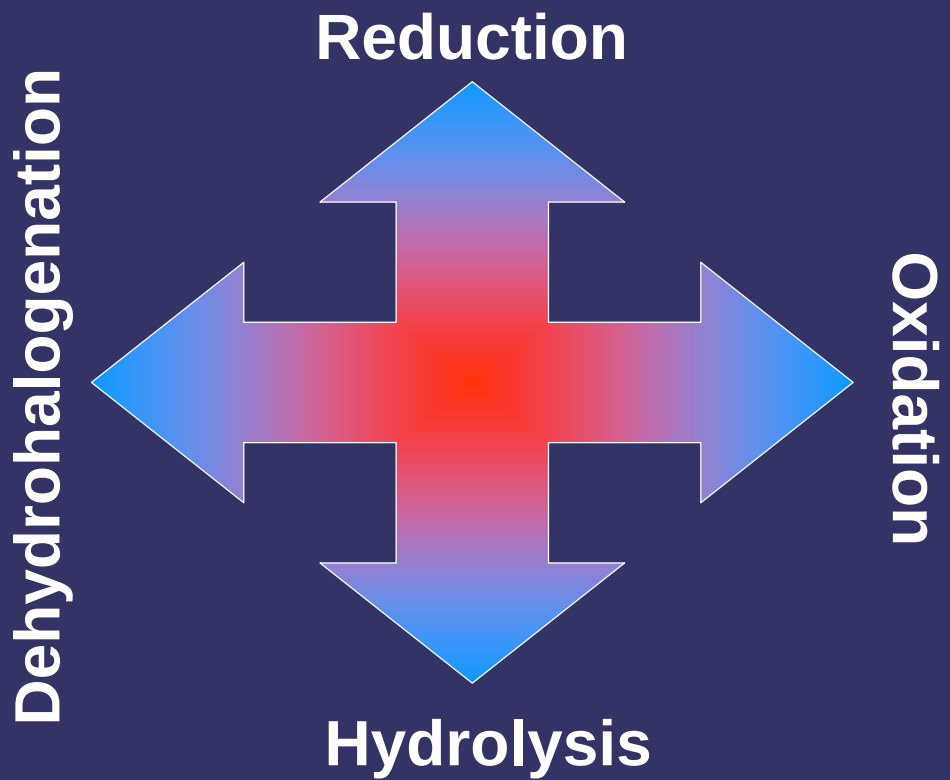


Abiotic

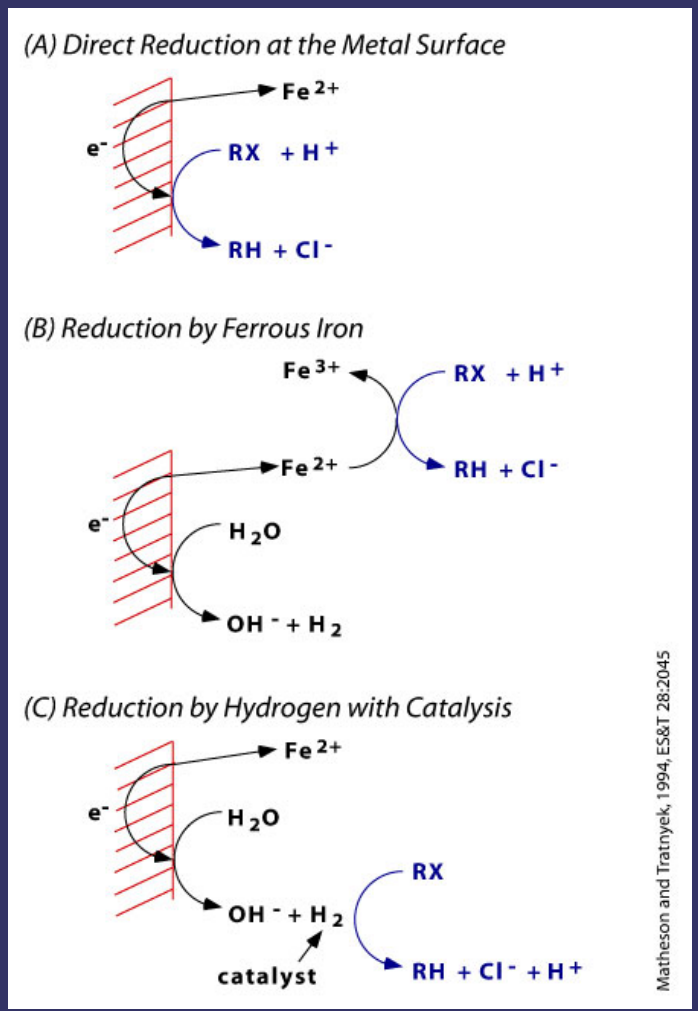


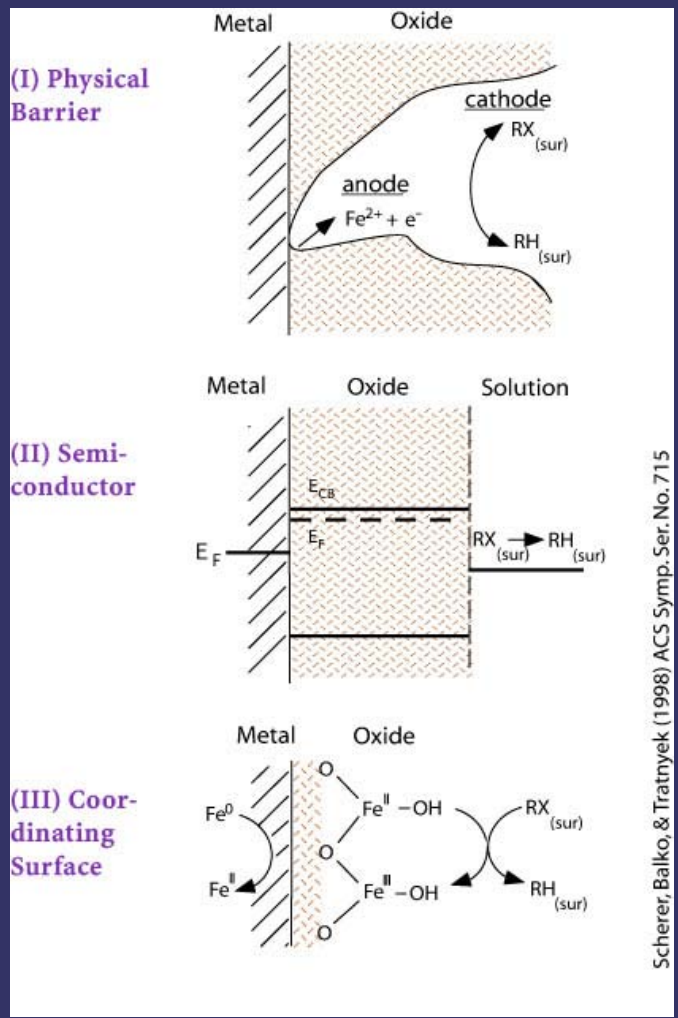
Biotic

Abiotic Pathways



Surface Catalysis





ERM

Enhancing Abiotic Reactions

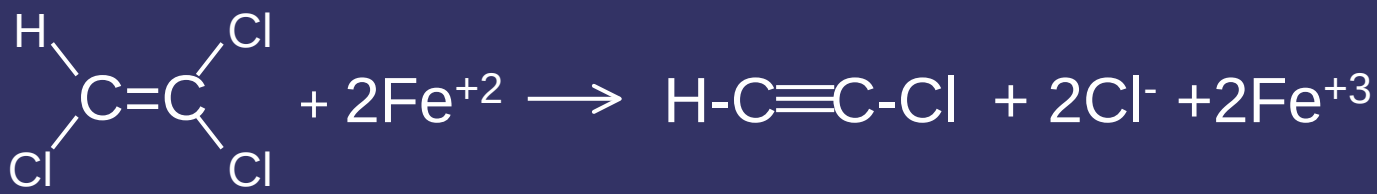
- **Chemical Enhancements**
  - Increasing reduced iron – ISRM
  - Enhancing Reactivity
- **Biological Enhancements**
  - Synergy
  - Biogenic reduced minerals (FeS)

In Situ Redox Manipulation

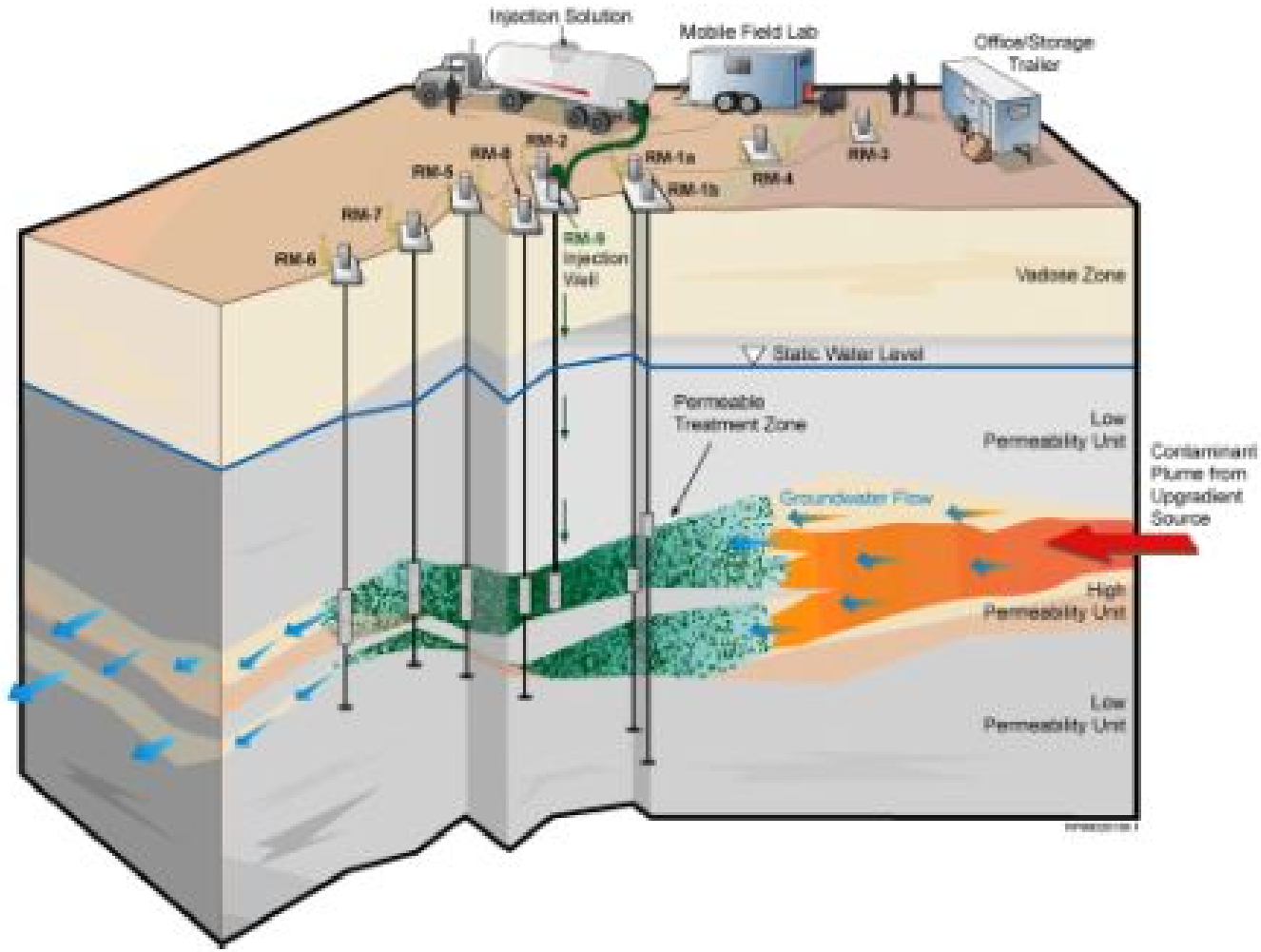
Iron Chemistry:

$6Fe^{+3} + S_2O_4^{=} + 4H_2O \rightarrow 6Fe^{+2} + 2SO_4^{=} + 8H^{+}$

Dechlorination:



In Situ Redox Manipulation



Reduced Minerals can be Biogenic

Iron Reduction

$3Fe_2O_3 + 2e^- + 2H^+ \rightarrow 2Fe_3O_4 + H_2O$

Sulfate Reduction

$SO_4^= + 8H^+ + 8e^- \rightarrow S^= + 4H_2O$

$4Fe_2O_3 + 9S^= + 16H^+ \rightarrow 8FeS + SO_4^= + 8H_2O$

Conclusions

- **Reduced iron minerals can effectively degrade chlorinated solvents including chloroethenes (PCE, TCE), chloroethanes (TCA, DCA) and chloromethanes (carbon tetrachloride),**
- **Reduced iron minerals react by generally the same pathways as ZVI to dechlorinate chlorinated solvents.**
- **A number of iron minerals such as pyrites, green rust (mixed Fe (II) and Fe (III) oxides and hydroxides), and magnetite are active reductants,**
- **Oxidized iron minerals can be reduced *in situ* by the application of a chemical reductant or by biological reduction generating active reduction zones.**

Combinations with ISCR

- **Spatially**
  - ISCO→ISCR
  - BRD→ISCR
  - Thermal→ISCR
  - BRD→ISCR→MNA
  - ISCR→MNA
  - ZVI→ISCR→MNA
- **Temporally**
  - ISCO (Persulfate)→ISCR
  - BRD→ISCO
  - AS/SVE→ISCR

BRD = Biological Reductive Dechlorination

"If you only knew the power of the Dark Side!"