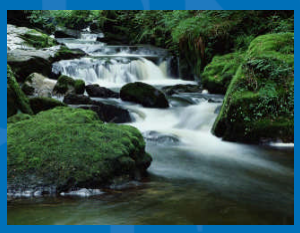
Chromium Chemistry in the Subsurface

Dr. Robert W. Puls



Office of Research and Development
National Risk Management Research Laboratory, Ground Water & Ecosystems Restoration Division, Ada, OK

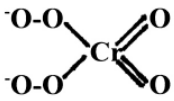
May 5, 2009

Chromium Use

- Leather tanneries
- Electroplating
  - –Hard-chrome plating for aircraft industry
- Pigments
- Printing inks
- Photographic films

1

Chromium Oxidation States



- Exists in oxidation states ranging from
  - – +6 to -2 but
  - –only the +6 and +3 states are commonly found in the environment
- Oxidized form, anionic, high mobility in subsurface
  - –Cr (VI) as $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCrO_4^-$
- Reduced form, cationic, low mobility in subsurface
  - –Cr (III) as Cr^{3+}, $CrOH^{2+}$, $CrOH^+$

2

Chromium Toxicity

- Cr (VI) is acutely toxic, mutagenic, carcinogenic
  - –MCL for total Cr is 0.1 mg/L in waters
  - –Ambient water quality criteria for aquatic life:
    - 0.016 mg/L, acute
    - 0.011 mg/L, chronic
- Cr (III) has low toxicity, and is an essential micronutrient

3

Average Soil Concentrations and Analysis

- Generally range from 5 to 100 mg/Kg total Cr
- Cr (VI) solid concentrations are not measured directly
  - –Must use extraction methods, e.g. EPA method 3060A, alkaline digestion
  - –Other methods also available

4

Aqueous Concentration Determinations

- Total Cr usually analyzed using ICP
- Cr (VI) analysis using diphenylcarbazide (colorimetric method, EPA 7199)
  - –Field test kits also available

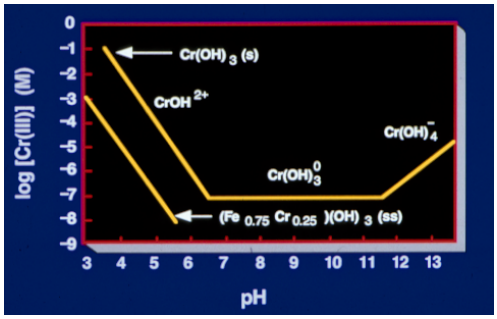
5

Chromium Speciation

- Speciation of Cr (VI) in water varies with pH and Cr (VI) concentration
- Speciation of Cr (III) in water varies with pH and solubility largely controlled by hydroxide minerals
  - Can form complexes with organic ligands, forming Cr (III) organic complexes

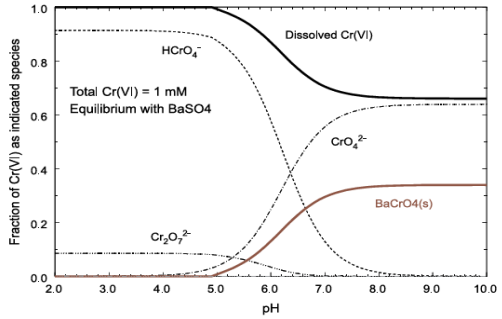
6

Solubility of Cr(III) and Dominant Aqueous Species



7

Distribution of Cr (VI) in Equilibrium with Barite



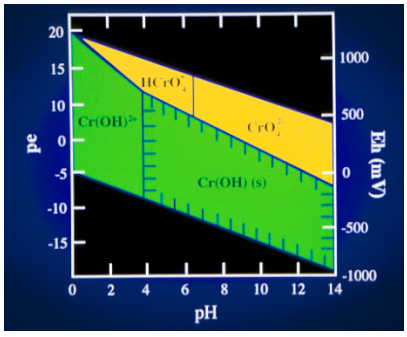
8

Adsorption of Cr in Subsurface

- Cr (III) adsorbs strongly for most pH ranges as soils and sediments generally possess net negatively charged surface sites (i.e. immobile, precipitation more likely)
- Cr (VI) adsorbs less strongly but does adsorb, especially to iron oxide/hydroxide surface sites at pH < 7
  - presence of competing anions (e.g. SO_4^{2-}, PO_4^{3-}) will reduce adsorption and promote mobility

9

Cr Eh-pH Diagram



10

Remediation Strategy

- Reduce oxidized Cr (VI) to Cr (III) and change from highly toxic, highly mobile form to almost non-toxic, immobile form
  - Reductants include ferrous iron, sulfide, organic materials, and other reductants

11

Soil Remediation: Minerals Capable of Providing Fe^{2+}, S^{2-} for Cr (VI) reduction

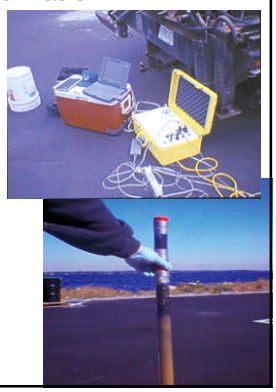
- Biotite
- Magnetite
- Iron Sulfides
- Nontronite

Also Soil Organic Matter can reduce Cr (VI), especially under slightly acidic conditions

12

Site Characterization

- **Ground Water Measurements**
  - **ph, Eh, DO, Specific Conductance, DOC, Alkalinity**
  - **Major cations (e.g. Ca, Mg, Na, K)**
  - **Major anions (e.g. sulfide/sulfate, nitrate/nitrite, phosphate,)**
  - **Mn, Fe**
- **Solid Phase Measurements**
  - **Mineralogy**
  - **Total metals**
  - **Extraction methods**
- **Geochemical modeling**



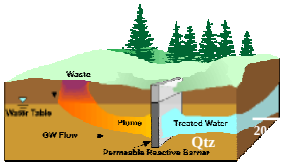
13

Site Characterization

- **Ground Water Sampling**
  - **How were the samples collected**
  - **Were they filtered? What was the turbidity?**
  - **How preserved?**
- **Solid samples**
  - **How were the samples collected?**
  - **How preserved and stored?**
  - **When extracted and**
  - **analyzed?**

14

Ground Water Remediation: Permeable Reactive Barriers

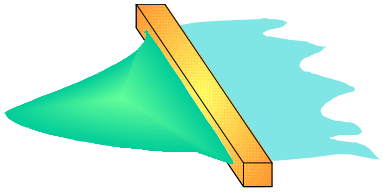


A passive in situ treatment system that uses reactive media emplaced in the saturated subsurface to intercept a contaminated ground water plume to degrade or immobilize contaminants in place

15

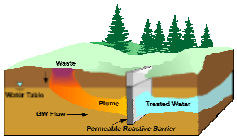
Goal = Passive Remediation System

- The plume enters under the natural gradient
- The entire plume is captured by the system
- Regulatory concentration goals are achieved at point of compliance



16

Permeable Reactive Barriers



- Remediation of Metals—Issues
  - Immobilization Mechanisms & Reversibility
    - Adsorption-Desorption
    - Precipitation-Dissolution
  - Toxicity

17

Chromate Reduction By Zero-Valent Iron

$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$

$Fe^{2+} + CrO_4^{2-} + 4H_2O \rightarrow (Fe_x, Cr_{1-x})(OH)_3 + 5OH^-$

Conversion of toxic, mobile Cr (VI) to less toxic, immobile Cr (III)

18

Zero Valent Iron PRB

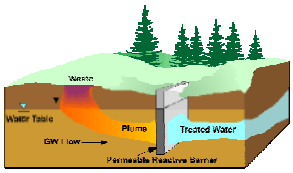
Elizabeth City, NC

Cr and TCE
Pilot-scale installed 1994
Full scale in 1996
150 ft length, 2 ft wide, 25 ft deep
Trencher
13 years of monitoring

19

20

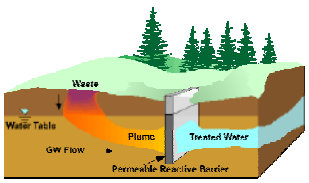
PRB Cost –Effectiveness



- **Up front capital costs comparable to pump-and-treat surface methods**
- **O&M significantly less = greatly reduced overall costs**
- **USCG site, NC; savings of over $5M over 13 yr vs. P&T**

21

PRB Long-Term Performance

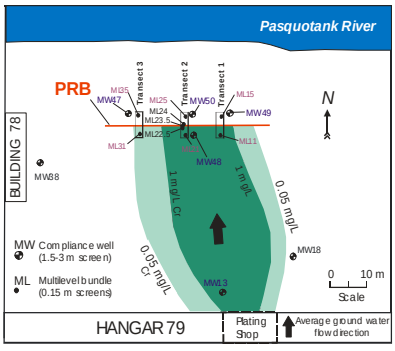


- Consistent immobilization of contaminants over 13 yr
- Cr easier to address than most contaminants
- Projected lifetime for most sites >10 yr

22

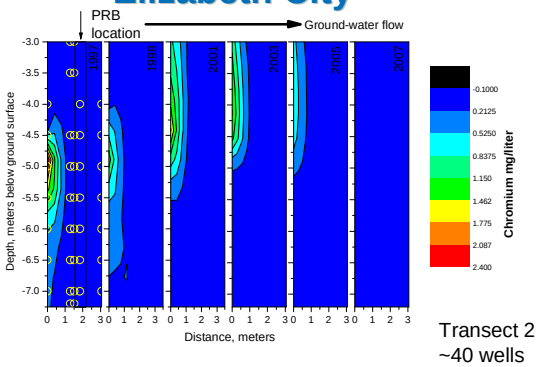
Elizabeth City – Site Map

1996 plume



23

Chromium – Elizabeth City



Transect 2
~40 wells

24

Cr Treatment with FE^0

25

Macalloy Corporation Superfund Site Region 4

PRB for Cr (VI)

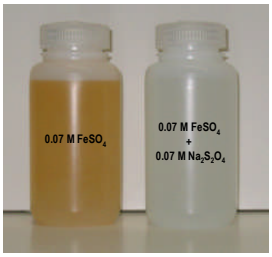
- **Novel in-house reductant technology developed to treat solid and dissolved phase Cr(VI) *in situ* (patented by Kerr Lab)**
- **Implemented in fall 2004 to protect coastal area**
- **Expected to save over $1 million relative to alternative technologies considered**
- **Expected to accelerate clean-up of Cr(VI) groundwater plume 5-fold**

26

Sodium Dithionite and Fe II Injections to create a permeable reactive barrier system in place

- Accomplished via injection through wells
- Enables deep emplacement

27



- In the absence of sodium dithionite, Fe(II) rapidly oxidizes and precipitates out as $Fe(OH)_3$
- Sodium dithionite acts as anti-oxidant allowing for stabilization and persistence of reactive Fe(II) in subsurface

28

SUMMARY

- Cr (VI) is carcinogenic and a threat to human and ecological health
- There are adequate and acceptable methods to characterize and assess Cr contaminated sites
- Cr chemistry in the environment is well understood
- There are documented methods to address Cr contamination in soils and ground water

29