From flask to field: Lessons for transferring remediation technology to nuclear waste sites

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Environmental Management
safety ✧ performance ✧ cleanup ✧ closure

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Quick overview:

Office of Groundwater and Soil Remediation

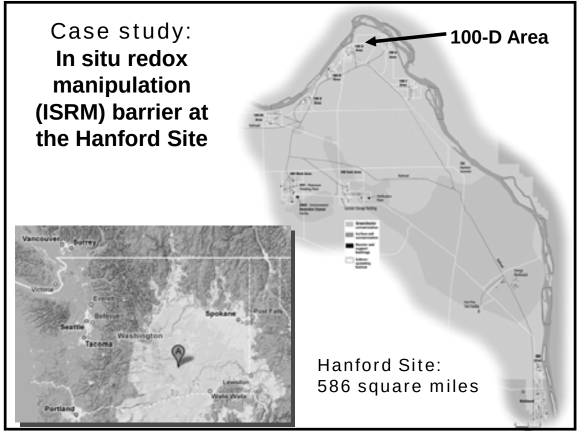
Engineering & Technology EM-20
(Mark Gilbertson, Deputy Assistant Secretary)

- **Groundwater & Soil Remediation EM-22** — Dr. Vince Adams, Director
- **Waste Processing**
- **D&D and Facility Engineering**

Groundwater and Soil Remediation Program

- 60 sites in 22 states
- 200 contaminated plumes
- contaminated soils
- 300 remedies in place

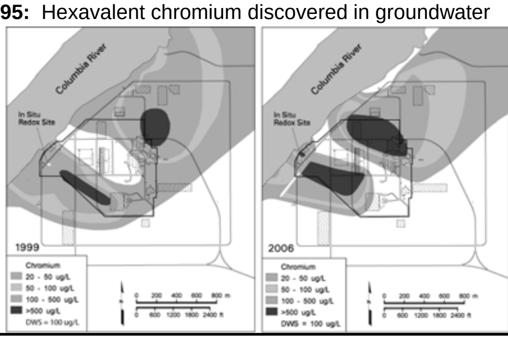
Case study:
In situ redox manipulation (ISRM) barrier at the Hanford Site



Contamination at the 100-D Area

1944-1967: Plutonium production
- sodium dichromate used as a corrosion inhibitor in cooling water

1995: Hexavalent chromium discovered in groundwater

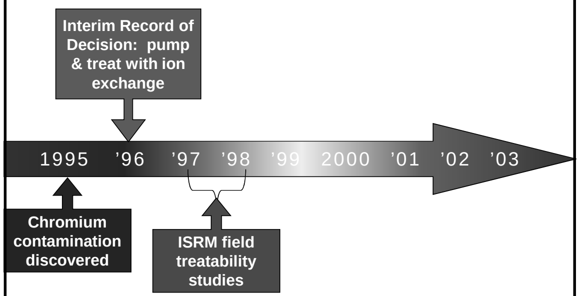


Remediation timeline at 100-D Area

Interim Record of Decision: pump & treat with ion exchange

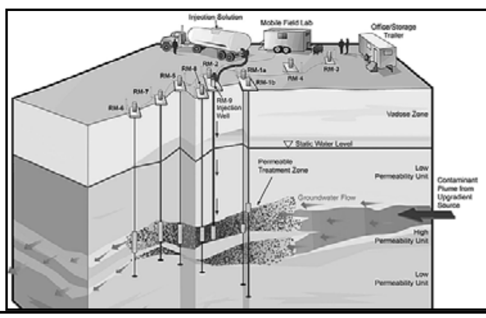
1995 '96 '97 '98 '99 2000 '01 '02 '03

Chromium contamination discovered



ISRM treatability studies

- Strongly-reducing chemicals are injected into the subsurface, creating a permeable reactive zone
- Redox-sensitive species are transformed (chromium, other metals & radionuclides)



Chromium treatment via ISRM

- Inject reductant solution (sodium dithionite)
- Dithionite reduces natural iron(III) to iron(II)
- Iron(II) provides primary reduction capacity for transforming **hexavalent chromium to trivalent chromium**, Cr(VI) → Cr(III)

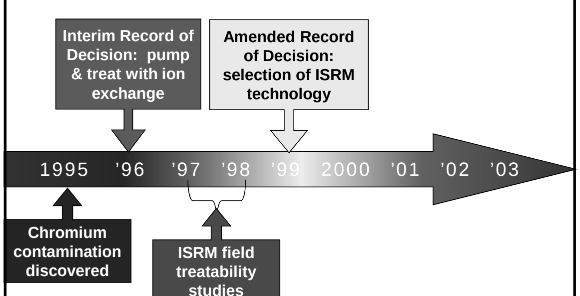
trivalent chromium:
- less soluble
- less mobile
- less toxic

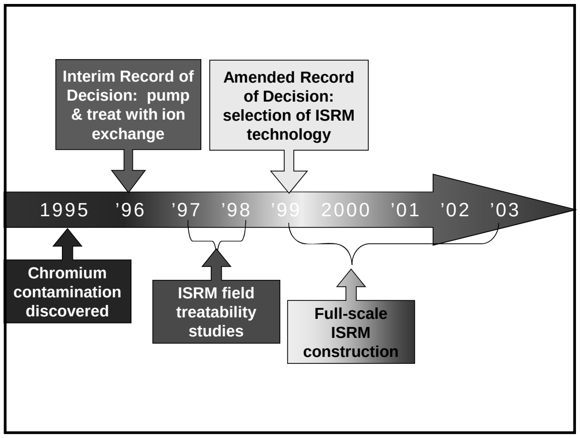
Treatability studies performed

- Laboratory comparisons of reducing agents
- Dithionite injection-withdrawal experiments
  - small scale
  - field scale (5 wells)
- Bromide tracer experiment
  - before and after dithionite injection at the treatability test wells

Conclusions from treatability studies

- Hexavalent chromium was successfully converted
- Extensive iron reduction was observed in sediment cores
- Natural iron was expected to be adequate
- **Barrier was predicted to remain effective for approximately 20 years**

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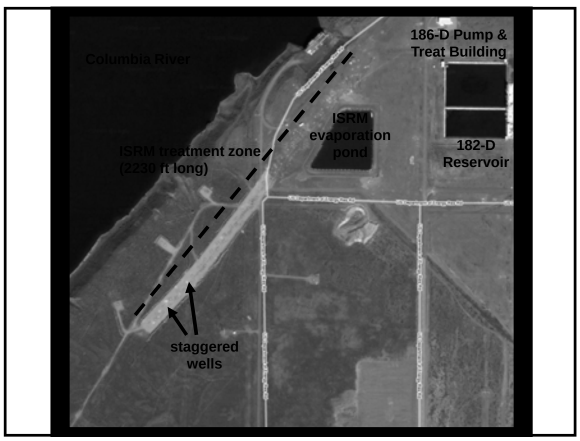
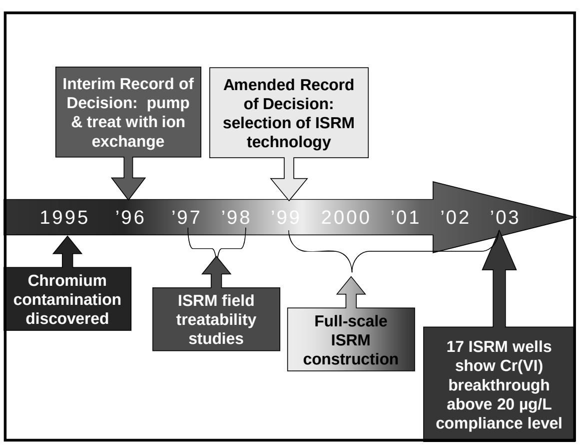
ISRM field treatability studies
Full-scale ISRM construction


Columbia River
186-D Pump & Treat Building
ISRM evaporation pond
182-D Reservoir
ISRM treatment zone (2230 ft long)
staggered wells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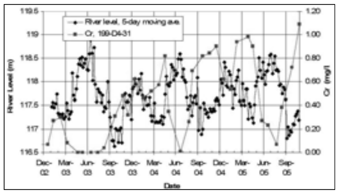
Full-scale ISRM construction
17 ISRM wells show Cr(VI) breakthrough above 20 µg/L compliance level

Hypothesized causes of ISRM failure

- **Physical heterogeneity**
  - **preferential flow paths**
    - high-permeability channels identified in about half of 25 tested wells; channels may be laterally continuous near water table
    - preferential flow worsened by leaking 182-D Reservoir
  - **fluctuating water table**
    - net regional flow is towards Columbia River, but reversal occurs at high river stage

Chromium concentration and Columbia River level observed over time at one well



Szecody, J. E. et al.. 2005. Effect of geochemical and physical heterogeneity on the Hanford 100D Area in situ redox manipulation barrier longevity. Pacific Northwest National Laboratory report to Dept. of Energy, PNNL-15499.

ISRM failure, continued

- **Chemical heterogeneity**
  - **influx of oxidants such as dissolved oxygen, nitrate**
    - not adequately considered in design calculations
  - **inadequate naturally-occurring iron**
    - reductive capacity lost, especially in high-permeability zones
    - decreases both the *rate* and *extent* of chromium transformation

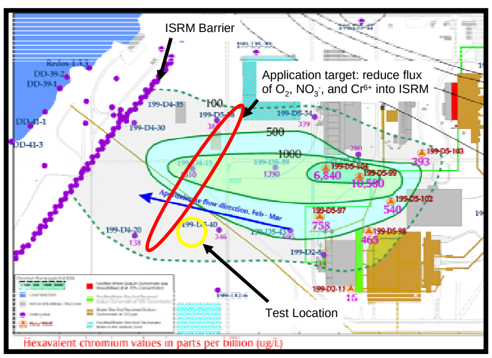
Recommendations of a 2004 technical assistance team

- Characterize the aquifer more extensively
- Develop an improved conceptual model
- Drain the nearby reservoir
- Employ techniques to mend the barrier

Mending the ISRM barrier

- **Discontinue dithionite use**
  - does not reduce chromium directly
  - long-term effectiveness is limited by iron(II) availability, especially in preferential pathways
- **Amend ISRM chemically and/or biologically with:**
  - **calcium polysulfide** (*directly* transforms chromium)
  - **organic substrates**
  - **micro- or nano-scale iron** injected within preferential pathways
    - do not use soluble iron: problems with aquifer cementation & lowered permeability at some sites

ISRM amendment using biostimulation



From: Fruchter, J.S., Truex, M. J., and Vermeul, V. R. "100-D Area Biostimulation Treatability Test". Status report, July 2008.

Two biostimulation approaches being tested upgradient of the barrier

- **injection of soluble substrate (molasses)**
  - increased microbial biomass stimulates iron reduction, consumption of oxygen & nitrate
  - substrate can be replenished as needed
- **injection of immiscible substrate (vegetable oil)**
  - oil dissolves and is biodegraded more slowly than a soluble substrate
  - substrate can be replenished as needed

Molasses injection

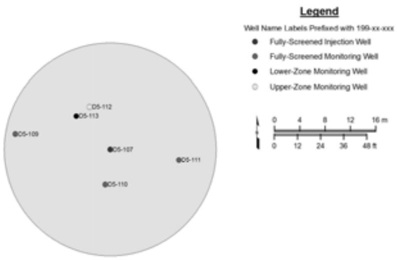


Figure from: Truex et al., "Hanford 100-D Area Biostimulation Soluble Substrate Field Test: Interim Data Summary for the Substrate Injection and Process Monitoring Phases of the Field Test." Report #17619, Pacific Northwest National Laboratory, June 2008.

- **Performance monitoring:**
  - geophysical surveys
  - substrate distribution
  - microbial community profiles & decay
  - chromium isotope analysis
- **Reducing conditions maintained in test cell for 9 months**
- **Chromate concentrations generally less than 30% of upgradient levels during this time**

Conclusions and lessons learned

- **Site heterogeneity can strongly influence remediation system performance**
  - majority of ISRM wells performed acceptably
  - "failing" wells were observed adjacent to functioning wells
- **Impacts may not be observed or predicted from laboratory and field demonstrations**
  - short duration, limited spatial extent
- **Economical methods for improved subsurface characterization are needed**
  - physical, geochemical, biological

- **Effects of existing infrastructure, site features, and seasonal variability should not be overlooked**
  - large leaking reservoir near ISRM barrier
  - presence of oxidants
    - predicted barrier lifespan decreases from 20 years to 10 years when 60 mg/L nitrate plume is considered
  - river level (flow direction, flow rate)
- **Combined remedies may be more effective than single remediation strategies**
  - e.g., inexpensive "pretreatment" biostimulation zone to protect and extend ISRM capacity
- **Use non-proprietary reagents and easily-rejuvenated systems to minimize costs**

Upcoming DOE-sponsored technical forum

Attenuation of metals and radionuclides in the subsurface

June 6-8, 2009, University of South Carolina

Long-term remediation research needs (basic and applied science, commercialization, application)

- conceptual model development
- reagent delivery
- characterizing heterogeneity
- biogeochemical processes
- fate & transport in complex systems
- remedial performance monitoring & sustainability

Backup slides

Groundwater and Soil Remediation
Technical Needs

	Common needs across DOE complex	Strategic initiatives
Sampling & Characterization Technology	➢Low-cost field characterization & monitoring techniques acceptable to regulators ➢Characterization in and around piping/storm drains	**Improved Sampling & Characterization Strategies**
Modeling	➢Improved conceptual models and incorporation of science into modeling ➢Fate & transport models that account for unique subsurface characteristics and reactive processes	**Advanced Predictive Capabilities**
In Situ Technology	➢Costs-effective techniques during remedial action and post-closure ➢Monitored natural attenuation (MNA)	**Enhanced Remediation Methods**
Long-Term Monitoring	➢Low-cost monitoring tools to reduce lifecycle costs ➢Long-term monitoring for MNA and barrier performance	**Enhanced Long-Term Monitoring Strategies**

Long-term stewardship

- **Established to meet post-closure obligations**
  - Sites with future missions transfer to other agencies:
    - SC, NNSA, or NE
  - DOE sites without future mission transfer to DOE Legacy Management (LM)
- **Transition process primary DOE orders**
  - 430.1B Real Property and Asset Management
- **LM – high-performing organization**

Hanford plumes illustrate scope of long-term monitoring needs