In-Situ Gaseous Reduction of Cr(VI) in Vadose Zone Soils with H$_2$S Gas

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In-Situ Gaseous Reduction for Cr(VI) is a cost effective approach to address challenging vadose zone heavy metal impacts.

First applied in 1998 at the White Sands Missile Range as a cooperative DOE/DOD pilot study.

The approach has significant benefits including:
- Improved distribution through vadose zone soils as compared to liquid reductants
- Rapid reaction and treatment times
- Reduced potential for mobilizing Cr(VI) to groundwater

Significant drawbacks include safety considerations during implementation.
The Problem

- Cr(VI) mobilized by water percolating through the unsaturated zone
- Excavation difficult and costly at depth

How ISGR Works

- Reduction and immobilization of Cr(VI) or other redox-sensitive metals (maybe perchlorate?)
- Treatment with a low-concentration hydrogen sulfide (H₂S) gas mixture
- Oxidized metals are reduced and immobilized

Case Study - Site Background

- Aerospace Manufacturing Facility
  - 10 years of plating operations

- Release due to migration through slab joints and cracks, and breaches in spill collection system (upper right)

- Roof’s down spout drove Cr(VI) vadose zone impacts to ~40’ bgs (lower left). GW at 96’ bgs

- **Goal:** Remediation to residential standards
  - No deed restriction
  - Sale of property in less than 1 year
• Hexavalent Chromium and Cadmium
• Three impacted areas identified
• Slab D area: Cadmium impacts to 7 ft bgs
• Slab A/B area:
  • Cr(VI) impacts to 95 ft bgs
  • Above rSRLs to 45 ft bgs
  • No groundwater impacts
• Alternatives Evaluated:
  • Excavation
  • Immobilization
  • In-Situ Reduction
  • In-Situ Gaseous Reduction
• Shallow Excavation of impacts to 10’

• ISGR of deeper Cr(VI) impact above residential soil screening levels (30 mg/kg)

• All Cadmium impacts were within the top 7-feet of soil

• Deep Cr(VI) impacts constrained to a small area near the suspected release point.

• ISGR area backfilled with 1-foot of hydrated bentonite prior to backfill
Injection Design

• ISGR treatment interval from 10-45’ BGS

• Fast remediation timeline for sale of property, 1 year for:
  • Characterization
  • Work-plan development
  • Bench scale testing
  • Permitting
  • Full scale implementation
  • Reporting
  • No Further Action determination

• Focus on a safe, efficient, uniform distribution of H₂S gas in treatment interval
• Passed H2S gas through columns of homogenized soil

• Evaluated H2S concentrations and exposure duration

• Calculated mass H2S/mass soil treated

• Results
  • Recommended concentration of 400 ppm
  • Injected at 60 cfm
  • For 16 weeks of injection
200 ppm H2S Bench Study Results

Dashed lines indicate that analytical data for the 0-5cm core sample from the 1hr time point was compromised during shipping.

Soil Core Sample Location (From Column Influent):
- 0-5cm
- 5-10cm
- 10-15cm

200 ppm H2S Flow Through: Sampled at 1, 2.5, 3hr intervals
Ado Engineering Facility
Phoenix, AZ

August 14
Figure 2
400 ppm H2S Bench Study Results

![Graph showing C(V) Concentrations (mg/Kg) over time for different soil core sample locations: 0-5cm, 5-10cm, and 10-15cm. The graph indicates a significant decrease in concentration over time.](image-url)
Well Construction

- Triple nested injection well
  - Optimal control of vertical Injection
  - Maximize H₂S Distribution

- Extraction wells
  - Single wells screened from 10-45’ ft bgs
System Construction
Extraction / Injection System
Distribution System
Health and Safety

- H$_2$S Monitoring/Alarms
  - In gas cabinet (injection shutdown, extraction continues)
  - In ambient air (full shutdown)
  - In stack (full shutdown)
  - Autodialer to Fire Department and 24 hour alarm response team
  - Backup battery powered monitoring/alarms

- Placarding

- All cabinet work or alarm response in Level B
Alarm Situation

- Autodialer callout on a Sunday afternoon
  - $H_2S$ detected in Cabinet $>10$ ppm

- Fire department and designated project emergency personnel responded
  - Fire Department responders not adequately prepared for $H_2S$, notwithstanding extensive notifications

- Alarm in cabinet, but not ambient
  - Diagnosed as a loose rotameter connection
Results!

Extraction Well
Hydrogen Sulfide Concentrations

- EW-1
- EW-2
- EW-3
- EW-4
- EW-5
- EW-8

Hydrogen Sulfide Concentration (ppmv)


Preferential Flow Direction

1 2 3 4 5 6
Results!

• Samples collected after 8 weeks of injection

• Field screening of drill cuttings
  • Generally good reduction
  • Pockets of remaining low-level Cr(VI)
Results!

- Confirmation results ranged from ND (<0.04 mg/kg) to 140 mg/kg
- 95% UCL of post-remediation Cr(VI) = 16.34 mg/kg (30 mg/kg SRL)
- 98.8% reduction in overall Cr(VI)
- No Further Action obtained from ADEQ!
ISGR Cost

• ISGR treatment of ~410 cu. yards of soil ~$250,000
  • Approximately $650/yard
  • Includes:
    • Treatment Skid
    • Well Installation (7 sonic wells)
    • Permitting
    • Labor/monitoring
    • H₂S supply
    • Post-Treatment Characterization (2 borings)

• Unit cost would be reduced for larger-scale implementation
Excavation Cost

- Excavation of ~400 yards of shallow soil: ~$230,000
  - Includes:
    - Limited access excavation
    - Confirmation Sampling
    - Backfill
    - Re-poured slab
    - Transport and Disposal (80% RCRA hazardous)
• ISGR treatment achieved Cr(VI) remediation goals quickly and cost-effectively

• Non-detect results achieved for Cr(VI) throughout the majority of the treatment area

• Implementation is difficult, requiring close oversight and extensive H&S precautions

• Scaled up treatment of larger soil volumes will improve cost effectiveness, but will also pose additional H&S concerns with H$_2$S storage, management, and delivery
Questions?