Identification of Natural Attenuation Mechanisms of Hexavalent Chromium in Groundwater through Geochemical and Matrix Diffusion Evaluations

Michael Lamar, P.E.

Bioremediation and Sustainable Environmental Technologies

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Site Summary

- History
  - Former ammunition site with chromic acid cleaning
  - Chromic acid discharged to unlined settling lagoons
  - Lagoon material removed (overburden only)
- Cr^{6+} concentrations
  - > 10,000 µg/L beneath and immediately downgradient of former lagoon
  - Elevated Cr^{6+} concentrations NW and S/SW of former lagoon
    - Up to 1,000 µg/L outside lagoon
    - Plume migration not generally downgradient flow direction
  - Up to 3,000 mg/kg in discrete limestone samples beneath former lagoon

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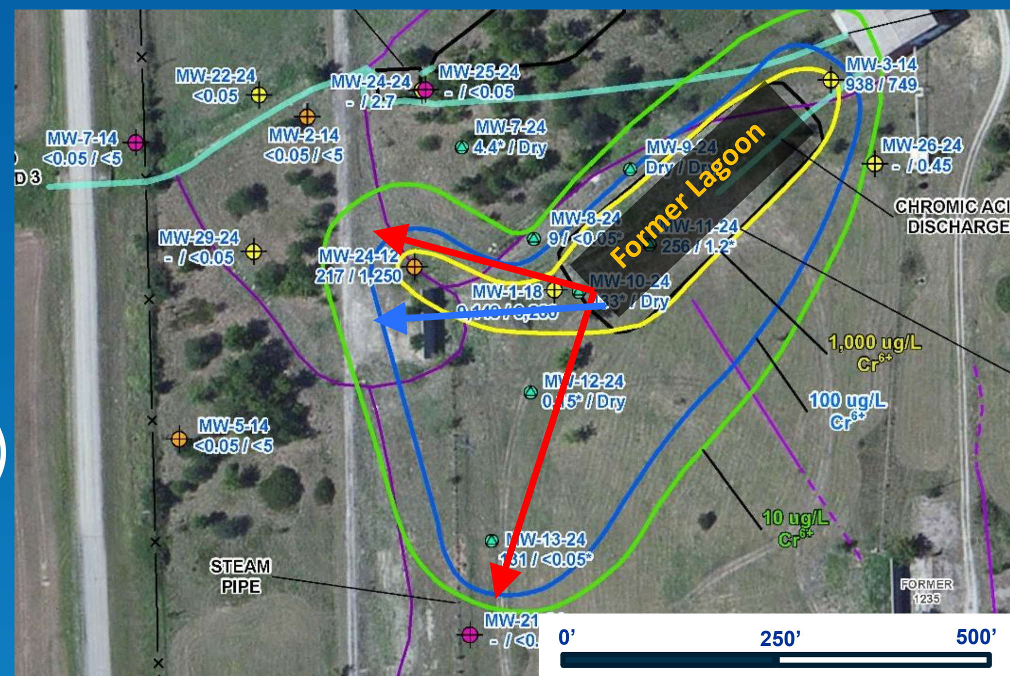
Site Summary, cont.

- Lithology (beneath lagoon)
  - Overburden - 0 – 4 ft bgs
  - Weathered limestone - 4-9 ft bgs
  - Competent limestone - 9-13 ft bgs
  - Weathered shale – 13-15 ft bgs
  - Competent shale – 15 – 35 ft bgs
  - Limestone pinches out to west
- Contaminant Plume (red arrow)
  - NW from lagoon
  - S/SW from lagoon
- GW flow direction (blue arrow)
  - Generally west
  - Low GW velocity



Observed Cr^{6+} concentration plume

Project Objective

- **Objective –** Identify natural attenuation mechanisms for hexavalent chromium (Cr^{6+}) in weathered/fractured limestone and shale
- **Methods –** Build a robust conceptual site model using:
  - Geophysical survey, core sampling, discrete interval well sampling
  - Electron microprobe (EMP)
  - X-ray diffraction (XRD)
  - Leachate testing
  - Metagenomics (biological reduction)
  - Modeling using PHREEQC (1D transport)
  - Bedrock matrix diffusion (not discussed)

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Geophysics / Core / Discrete GW Sampling Results

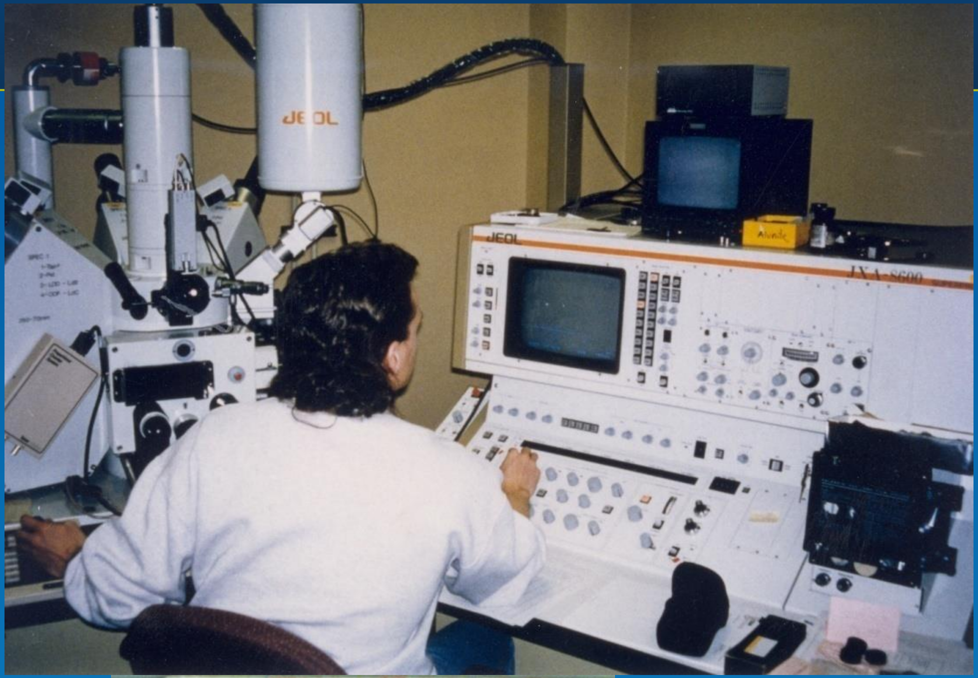
Above – precipitates on core
Below – fractured core

- Fractures in competent limestone had low Cr^{6+} concentrations
- Limestone-shale interface had elevated Cr^{6+} concentrations
- Flow tests (HPFM) during geophysics indicate low flow rates in existing fractures
- Unknown precipitate found in areas with highest observed Cr^{6+} concentrations (as high as 40 mg/L)
- Cr^{6+} in shale very low – highly reduced

Back diffusion likely not a primary factor in groundwater Cr^{6+} concentrations. New focus is precipitate material.

Electron Microprobe (EMP)

- Can view samples at 300,000X magnification
- Can analyze particles as small as 2 µm in diameter
- Can determine the forms (mineralogy) of Cr, and other metals
- Cr oxidation state (+3 vs +6) can be determined by the stoichiometry if the phase is not hydrated and the oxidation state of iron can be assumed.



EMP Results – Precipitate Analysis

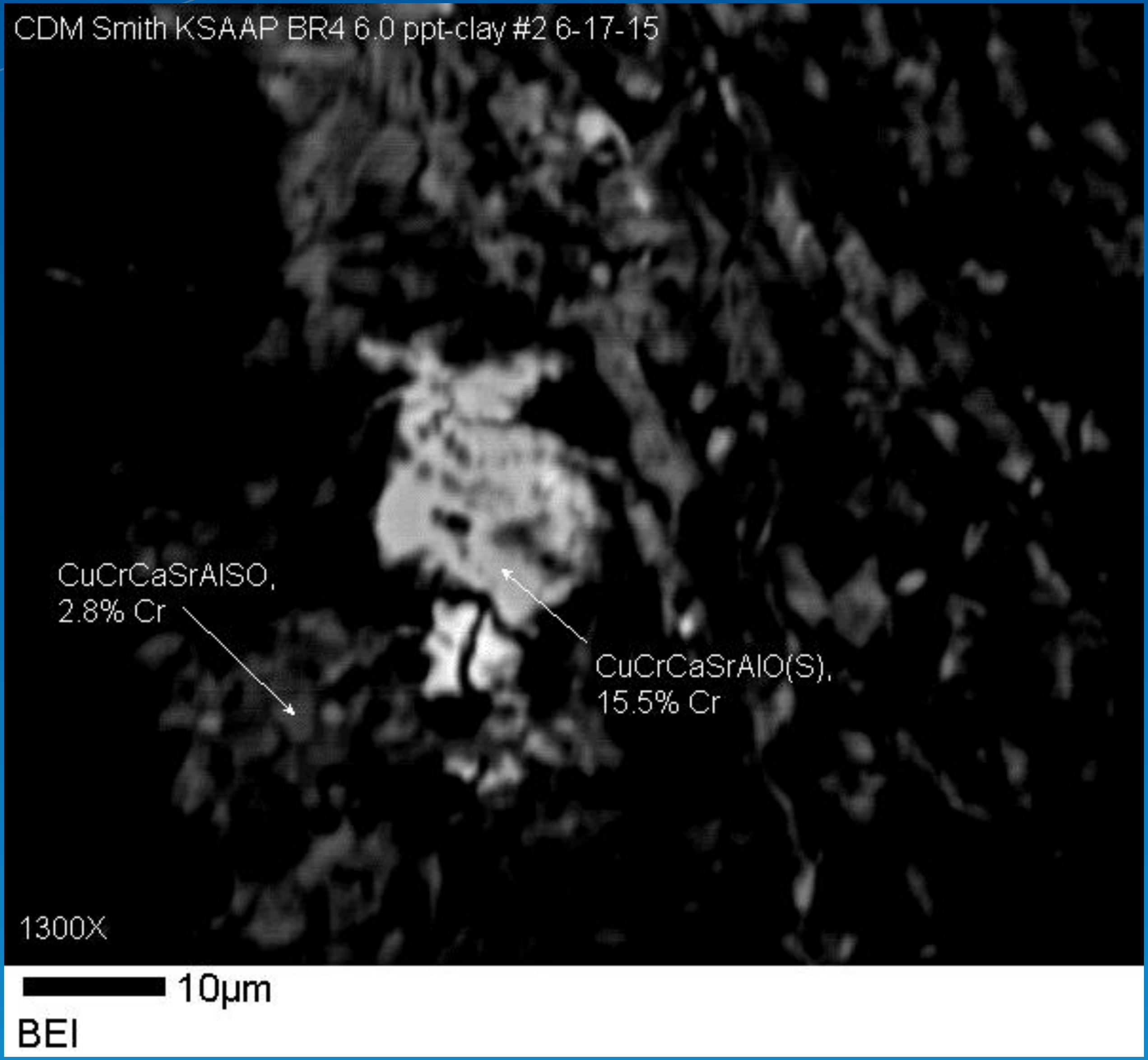
$CuCrO_4$

Hexavalent Chromium

Red = Cr
Blue = Si
Pink = O

Cu-Cr Silicate

Hexavalent or Trivalent Chromium



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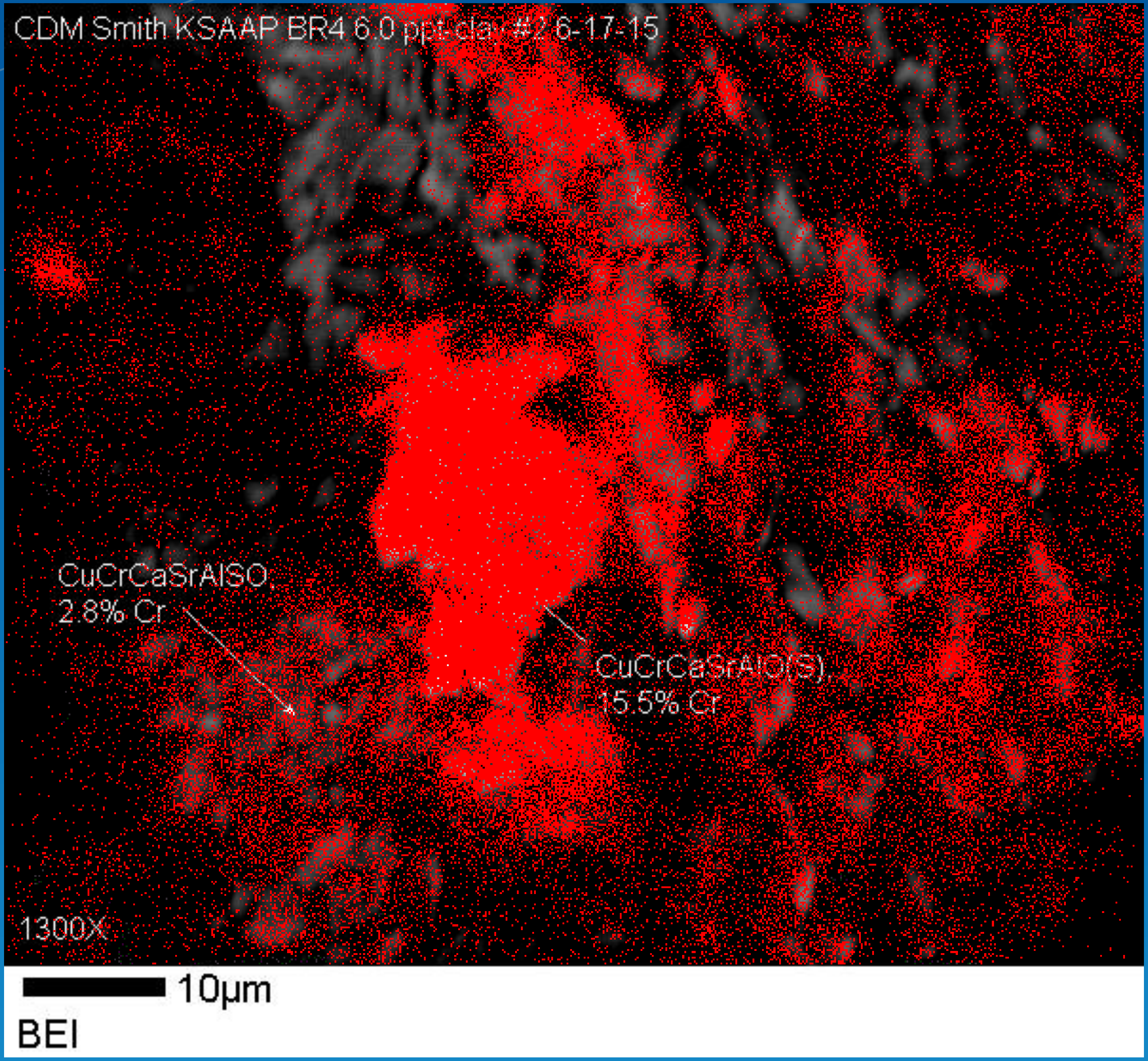

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Hexavalent or Trivalent Chromium

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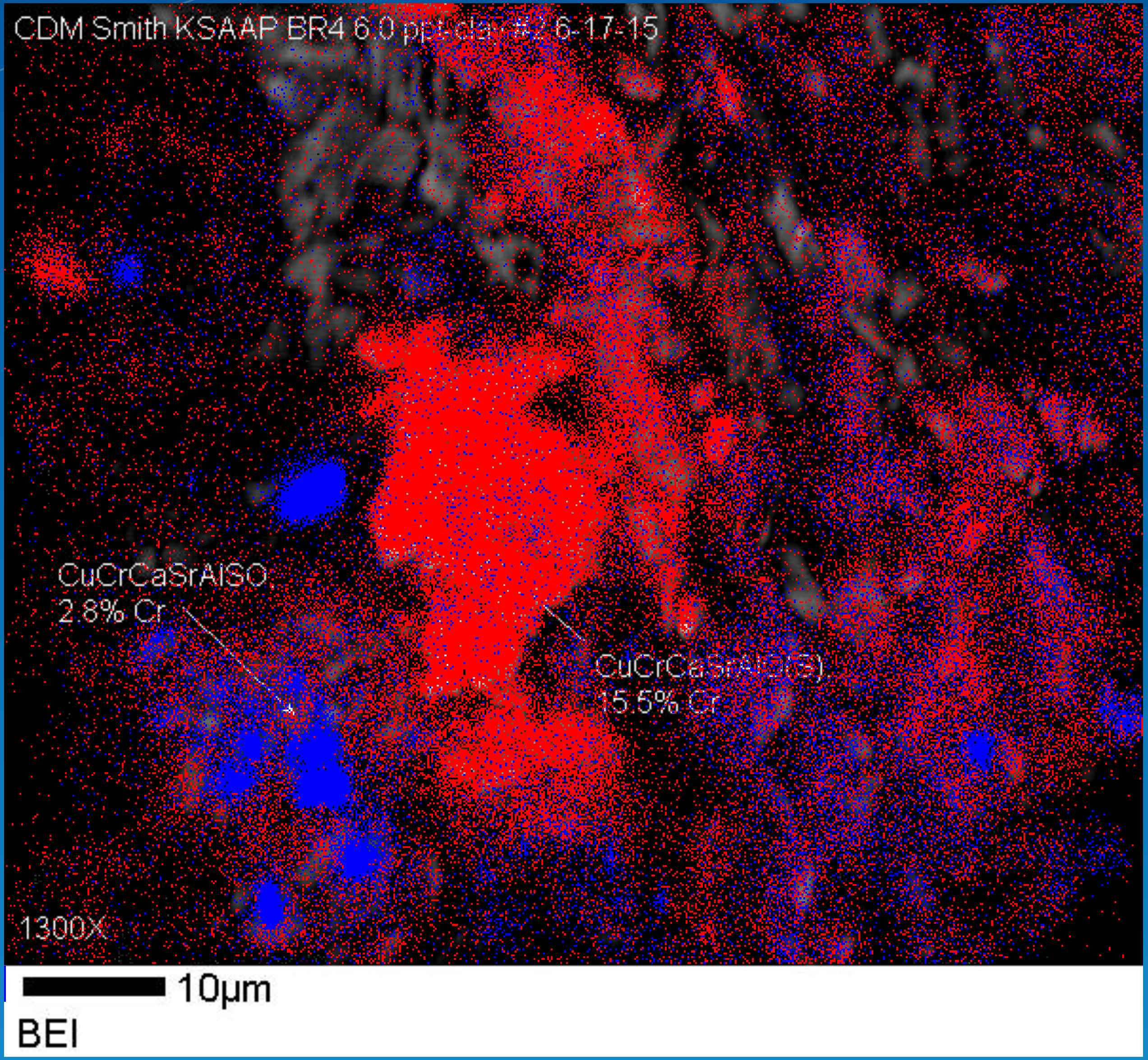

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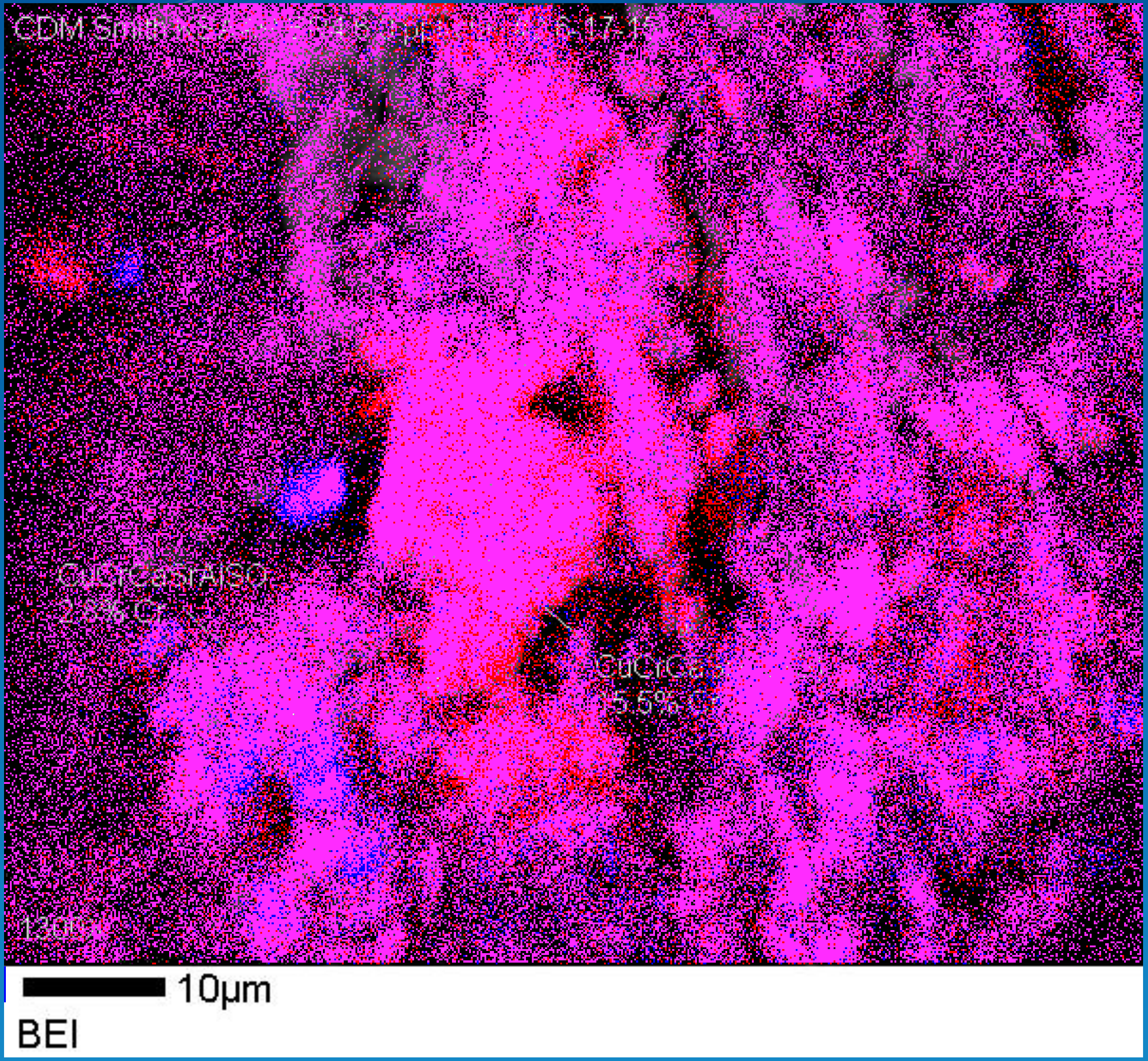
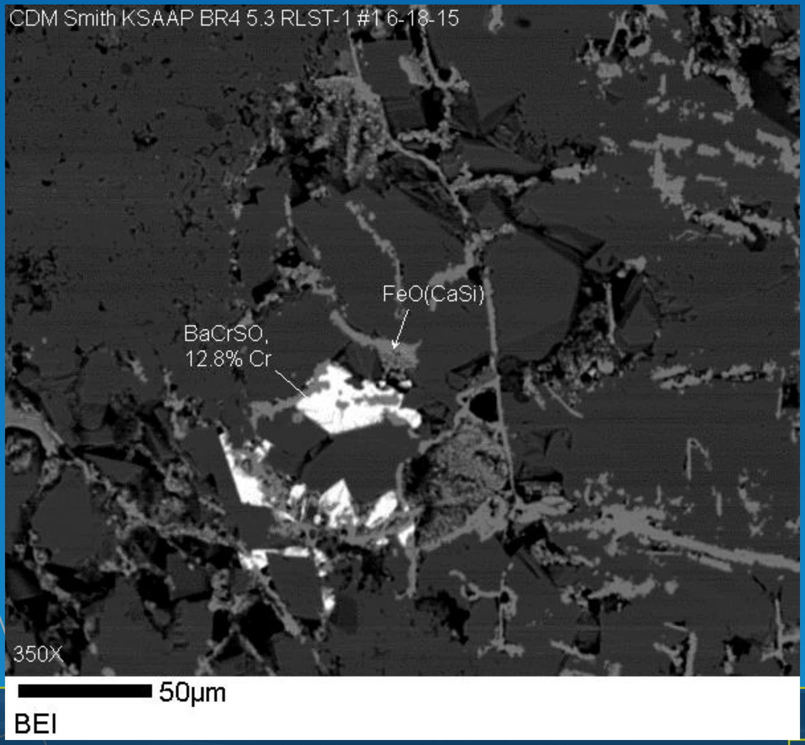


EMP Results – Precipitate Analysis

- Cr-Substituted Barite
- Hexavalent chromium
- Pure barium chromate (BaCrO4) contains 29% Cr



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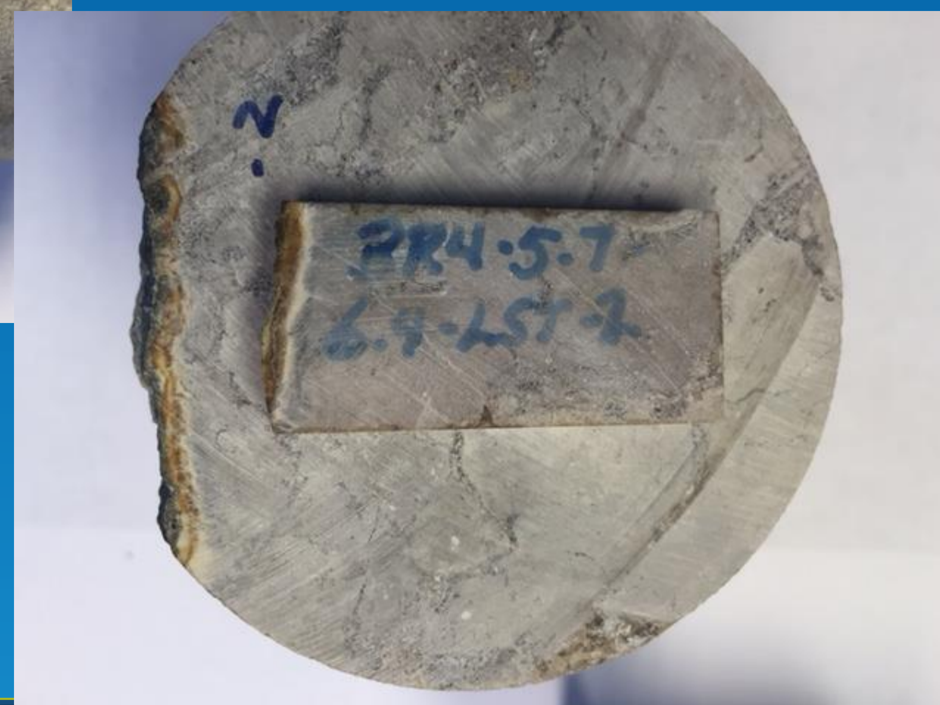
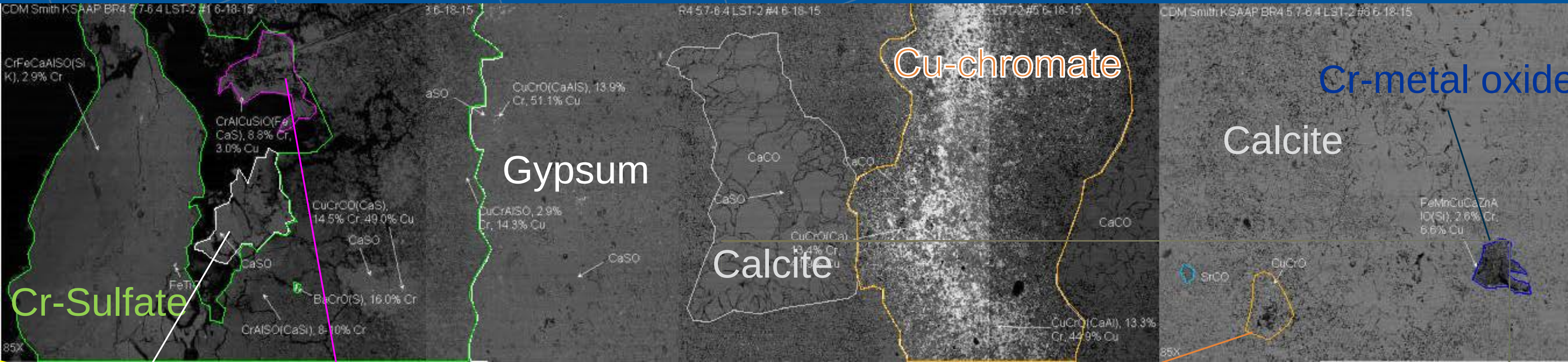
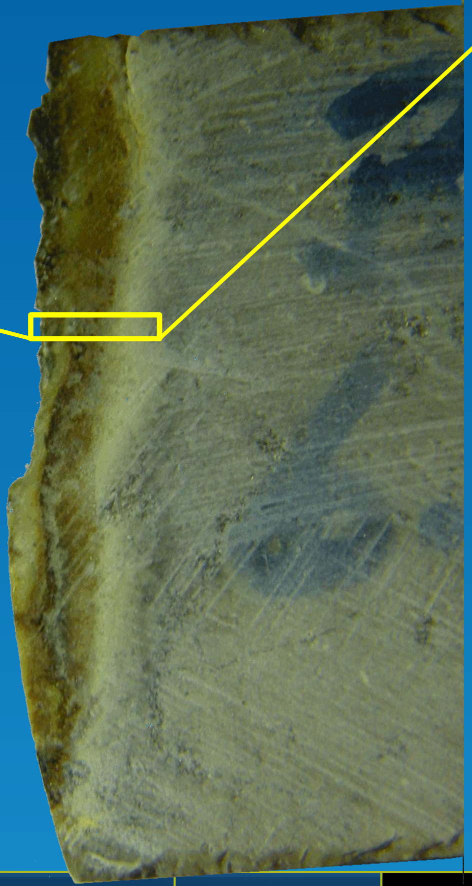
Precipitate Sample Thin Section







Thin sections show how chromium precipitates formed on limestone surface

Summary of EMP Results

Beneath former lagoon

- Secondary precipitates: copper chromate (6 to 13% Cr), barium chromate (2 to 22% Cr), Al-Cr silicates (6 to 20% Cr)
- Layers of precipitates including chromium compounds and gypsum in highly weathered material
- matrix chromium: Cr substituted jarosite (6 to 12% Cr); Cr substituted iron oxides (0.09 to 0.14 % Cr)

Outside of lagoon

- Could not find or identify Cr phases in matrix limestone
- Secondary precipitates: FeCr oxyhydroxide (10-12% , Cr^{3+})
- Shale: mainly iron sulfide with Cr (1%), some barium chromate (18% Cr)

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Solubility and XRD Confirm EMP Findings

- Solubility of copper chromate matches observed groundwater concentrations
  - Lab solubility tests on basic copper chromate (reagent grade)
    - 170 to 259 mg/L Cr^{6+} (depending upon pH)
    - PHREEQC Modeled $\log(K_{sp}) = 11.48$
  - Lab tests on secondary precipitate from site precipitate sample using site groundwater (no chromium)
    - 22.7 to 245 mg/L Cr^{6+} (depending on liquid to solid ratio)
- X-Ray diffraction (XRD) test results confirmed the presence of basic copper chromate and other minerals (hashemite, ferrihydrite) found in EMP

Copper chromate precipitates control groundwater concentration

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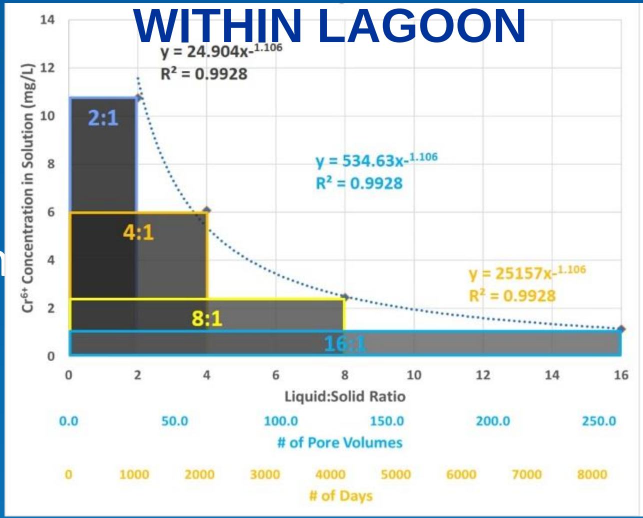
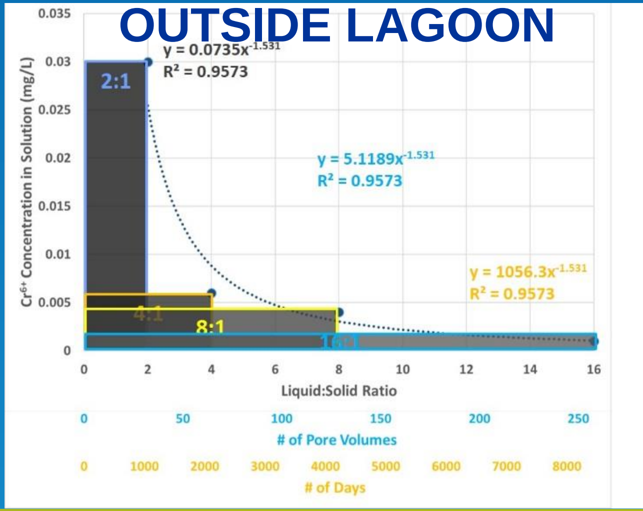
Geochemistry – Groundwater Leaching Tests

- Leaching tests were performed to understand Cr^{6+} release mechanisms into groundwater
  - Better understand the fate and transport of Cr^{6+} in the groundwater and solid matrices
- Results show:
  - Source material is present in bulk samples both within and downgradient of former lagoon
  - Cr^{6+} concentrations as high as 350 µg/L and 2,500 µg/L may be present in groundwater in contact with the chromate precipitates downgradient of lagoon
  - > 100 µg/L Cr^{6+} plume likely to remain > 200 years

Cr6+ is controlled by a soluble phase





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Metagenomics

- Comprehensive evaluation can identify and quantify microbial populations key to reducing hexavalent chromium
- Results indicate both aerobic and anaerobic bacteria are present to support biological reduction of hexavalent chromium
  - Under observed aerobic conditions
    - Pseudonomads present – able to aerobically reduce Cr^{6+}
    - High populations of iron-reducing bacteria present under aerobic conditions – these may compete with abiotic Cr^{6+} reduction
  - Under observed anaerobic conditions
    - Diverse population of bacteria present capable of reducing Cr^{6+}
    - However, under anaerobic conditions, geochemical conditions alone should result in Cr^{6+} to Cr^{3+}

Bacterial population likely assisting in Cr^{6+} reduction

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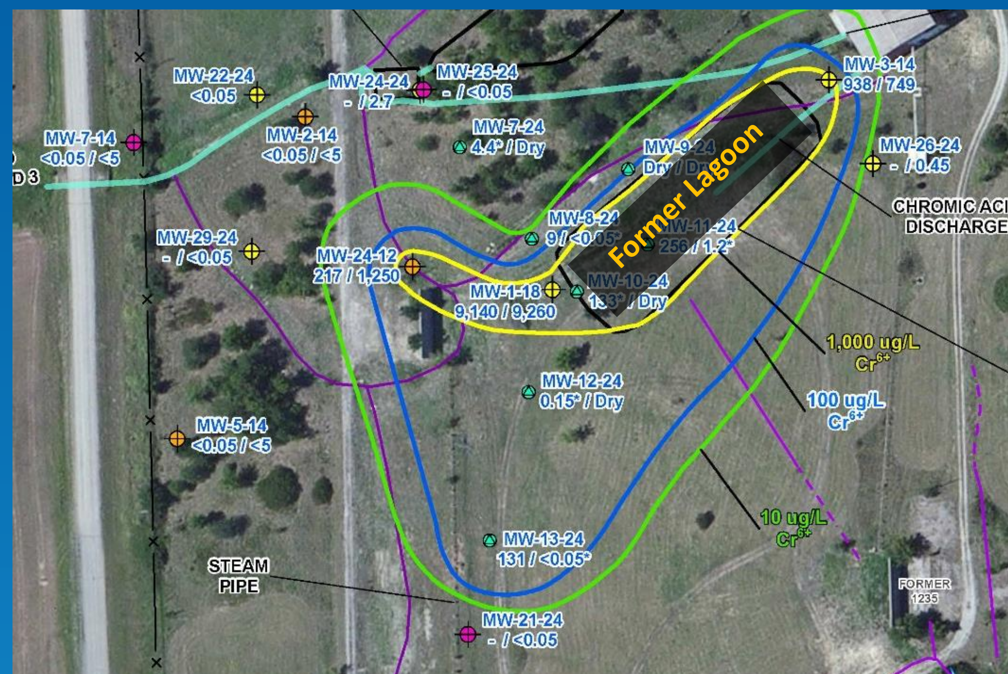
Geochemical Modeling

- PHREEQC model used to compare field results with anticipated equilibrium concentrations
- Field concentrations generally lower than anticipated based on solubility
  - This is likely due to dilution from mixing with vertical intervals that do not have precipitates (10-ft screened wells)
  - Discrete vertical zones with precipitates had concentrations approaching solubility (0.5-ft screened CMT interval)
- Model shows – again – that soluble phase controls groundwater Cr^{6+} concentration

1-D Modeling

- 1-D transport model developed based on PHREEQC results
  - 1-D results do **not** match current conditions
  - Groundwater mounding during lagoon operation likely caused impacted groundwater to flow radially from lagoon
  - Plume migration occurred south via density driven flow in limestone-shale interface and weathered limestone



Observed Cr^{6+} concentration plume

Natural Attenuation Summary

- Groundwater Cr^{6+} is solute controlled by precipitates, not diffusion controlled
  - Cr^{6+} plume will likely remain (> 200 years) unless precipitates are removed
- Cr^{6+} in shale attenuating under reduced conditions in presence of carbon
- Southern extent of plume not expanding
  - No southern gradient
  - Western gradient migrates to shale
- Northwestern extent of plume also not expanding
  - Also migrating into shale

Natural attenuation keeping plume stable. However, without precipitate removal elevated Cr^{6+} concentrations will remain > 200 years

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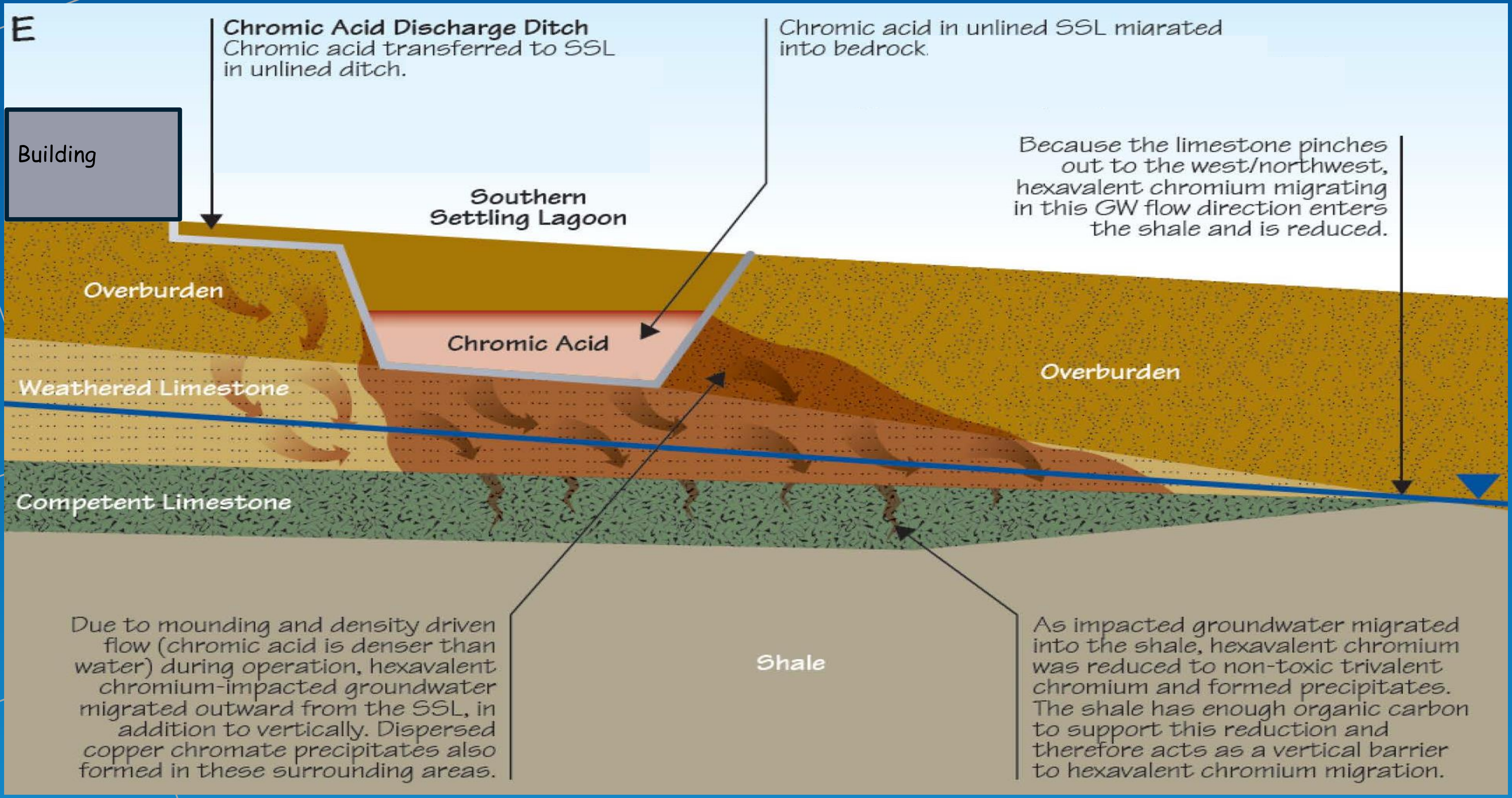
Revised CSM



E
Chromic Acid Discharge Ditch
Chromic acid transferred to SSL in unlined ditch.
Chromic acid in unlined SSL migrated into bedrock.
Building
Southern Settling Lagoon
Because the limestone pinches out to the west/northwest, hexavalent chromium migrating in this GW flow direction enters the shale and is reduced.
Overburden
Chromic Acid
Overburden
Weathered Limestone
Competent Limestone
Shale
Due to mounding and density driven flow (chromic acid is denser than water) during operation, hexavalent chromium-impacted groundwater migrated outward from the SSL, in addition to vertically. Dispersed copper chromate precipitates also formed in these surrounding areas.
As impacted groundwater migrated into the shale, hexavalent chromium was reduced to non-toxic trivalent chromium and formed precipitates. The shale has enough organic carbon to support this reduction and therefore acts as a vertical barrier to hexavalent chromium migration.

Thank you!

Any questions?

Contact Information

Michael Lamar

CDM Smith Inc.

Email: lamarmr@cdmsmith.com

Ph: 303-383-2461

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