Biogeochemical Remediation of the Chromium Plume in the Regional Aquifer, Los Alamos, New Mexico

Ground Water Quality Bureau
April 6, 2022

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Topics of Interest

• Source(s) of Chromium

• Chromium Distributions in the Regional Aquifer

• Remediation of Chromate at Wells R-28 and R-42 and Regional Aquifer System Response.
  • sodium dithionite/sodium sulfite injection at well R-42
  • molasses injection at well R-28
  • CrEX-3
  • pump and treat

• Summary

• Path Forward
Photograph of the Jemez Mountains and Pajarito Plateau (view to the west with past industrial sources of chromium(VI) discharges)

- TA-03 Source (31,000 to 72,000 kg [68,200 to 158,400 lbs.] Cr(VI) released from 1956 to 1972)
- TA-2 Source (decommissioned)
- TA-48 Source
- Sandia Canyon wetland
Potassium dichromate used to control corrosion in power plant cooling towers.

158,400 lbs. released to Sandia Canyon between 1956-1972 as potassium dichromate.

Migration from perched aquifer(s) to regional aquifer formed multiple sources.

Discovered in regional aquifer in December 2005.

NMED regulates total dissolved chromium in groundwater at 50 parts per billion (ppb).

Plume is 1 mile long / half mile wide. Thickness is uncertain.

Nature & Extent remains uncertain – in Campaign Approach along with Interim Measures.

Interim Measures - mid 2018 along Pueblo de San Ildefonso boundary.
Units of Measurement

- Parts per million (ppm), 1 ppm is analogous to one second in 0.0317 years or 11.57 days.
- Parts per million is equivalent to milligrams/liter (mg/L) in most waters, excluding seawater and brines.
- Parts per billion (ppb), 1 ppb is analogous to one second in 31.69 years.
- Parts per billion is equivalent to micrograms/liter (µg/L) in most waters, excluding seawater and brines.
- Milligrams/kilogram (mg/kg) of a chemical present in a solid is equivalent to ppm.
**Sodium Dithionite (Na$_2$S$_2$O$_4$) Injection at R-42 on August 24-25, 2017**

Injection of 9,000 gallons of raw R-42 water containing 350 kg of sodium dithionite (Na$_2$S$_2$O$_4$) and 245 kg of sodium sulfite (Na$_2$SO$_3$) to buffer the solution. 1,000 gallons of potable water were injected after the amendment, reacted for three days, and removed by pumping R-42.

**Molasses Injection at R-28 on September 9, 2017**

Injection of 30,000 gallons of raw R-28 water with 3.3 weight percent of molasses (33 g/kg). 1,500 gallons of potable water, containing 10 vol% ethanol, were injected after the molasses. No additional pumping immediately followed to remove molasses.

Observation wells near R-28 and R-42 are lacking to monitor migration of amendments.
Concentrations of Dissolved Chromium (Cr) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)

- Sodium dithionite/sodium sulfite injection (08/17) followed by pumping to October 16, 2017
- Migration of upgradient groundwater to R-42 during pumping
- Groundwater background for chromium = 7.48 ppb (µg/L) at 95th upper tolerance limit
- Baseline concentration Cr = 721 ppb (µg/L) on August 7, 2017
- NM groundwater std for Cr = 50 ppb (µg/L)
- Method detection limit (MDL)
- Reduction of Cr(VI) to Cr(III) with precipitation of amorphous Cr(OH)₃ with dissolved Cr concentrations typically below 3 ppb (µg/L)

Concentrations of Dissolved Chromium Versus Time at Regional Aquifer Well R-42
Summary of Groundwater Remediation at R-42

- Chromate has been reduced to chromium(III) at regional well R-42 by injection of sodium dithionite and sodium sulfite between 2017 and 2021.

- Chromium concentrations at R-42 typically exceed 600 ppb ($\mu$g/L) in early 2022. The well is generally providing chemical data representative of pre-amendment conditions.

- The volume of remediated groundwater and aquifer material is not known with certainty in the absence of observation wells near R-42.

- NMED is requiring DOE to investigate nature and extent of iron and manganese released to groundwater from sodium dithionite injection at R-42.
Groundwater in the regional aquifer is oxic, having measurable dissolved oxygen typically ranging from 5 to 8 ppm (mg/L).

Groundwater in the regional aquifer has pH values typically ranging from 7.5 to 8.5.

Microbes consist of aerobic, anaerobic, and facultative bacteria, which switch back and forth between aerobic and anaerobic populations.

Diverse populations of aerobic, anaerobic, and facultative bacteria occur in groundwater in the regional aquifer and are also attached to aquifer solids as biofilms.
- Aerobic bacteria biosynthesize dissolved oxygen for cell growth.

- Anaerobic bacteria, in the absence of dissolved oxygen, biosynthesize nitrate, manganese, chromium, iron, sulfur, and inorganic and organic carbon for cell growth.

- Anaerobic bacteria are stimulated by consuming organic carbon and utilizing other redox-sensitive chemicals (nitrogen, manganese, iron, and sulfur) in the absence of dissolved oxygen.
**Sodium Dithionite (Na₂S₂O₄) Injection at R-42 on August 24-25, 2017**
Injection of 9,000 gallons of raw R-42 water containing 350 kg of sodium dithionite (Na₂S₂O₄) and 245 kg of sodium sulfite (Na₂SO₃) to buffer the solution. 1,000 gallons of potable water were injected after the amendment, reacted for three days, and removed by pumping R-42.

**Molasses Injection at R-28 on September 9, 2017**
Injection of 30,000 gallons of raw R-28 water with 3.3 weight percent of molasses (33 g/kg). 1,500 gallons of potable water, containing 10 vol% ethanol, were injected after the molasses. No additional pumping immediately followed to remove molasses.
Molasses is a viscous product resulting from refining sugar cane or sugar beets into complex sugars (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}).

### Generic Composition of Sugar Cane Molasses

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/kg, ppm) [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Soluble Solids</td>
<td>219,000 [21.9]</td>
</tr>
<tr>
<td>Reducing Sugars</td>
<td>178,000 [17.8]</td>
</tr>
<tr>
<td>Total Sugars</td>
<td>499,000 [49.9]</td>
</tr>
<tr>
<td>Sucrose</td>
<td>321,000 [32.1]</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
</tr>
<tr>
<td>Energy</td>
<td>12,130 kilojoules/kg (2,899 kilocalories/kg)</td>
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</tbody>
</table>

parts per million is ppm, kilogram is kg
<table>
<thead>
<tr>
<th>Acid</th>
<th>Concentration (mg/kg, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>2,000</td>
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<tr>
<td>Aconitic</td>
<td>8,000</td>
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<tr>
<td>Formic</td>
<td>1,000</td>
</tr>
<tr>
<td>Glutamic</td>
<td>34,000</td>
</tr>
<tr>
<td>Lactic</td>
<td>500</td>
</tr>
</tbody>
</table>

parts per million is ppm, kilogram is kg
Groundwater Chemistry (pre injection of molasses)
Concentrations of contaminants such as chromium (Cr), nitrate (NO₃), sulfate (SO₄) exceed groundwater background.

Aerobic Respiration (biosynthesis of dissolved oxygen)

R-28 Biochemical Evolution

Nitrate Reduction
Mn(IV) and Cr(VI) Reduction
Fe(III) and U(VI) Reduction
S(VI) Reduction

Time Scale:
hours - days
years

Post Injection of Molasses

Groundwater Chemistry (post injection of molasses)
Above baseline concentrations of iron (Fe), manganese (Mn), total organic carbon (TOC), organic nitrogen, total carbonate alkalinity, and total dissolved solids (TDS) with acidic pH.

Concentrations of contaminants such as chromium (Cr), nitrate (NO₃), uranium (U) are within groundwater background.

Generation of hydrogen sulfide and methane and biomass with residual molasses and other forms of dissolved and suspended organic matter produce biofouling.

Reductive dissolution of MnO₂, Fe(OH)₃ and precipitation of Cr(OH)₃ and UO₂
Concentrations of Dissolved Chromium (Cr) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

Concentrations of Dissolved Chromium Versus Time at Regional Aquifer Well R-28

During corrosion of stainless steel well casing, chromium(III) reacts with dissolved organic carbon, which initially limited precipitation of chromium hydroxide under acidic pH conditions.

Tracer (sulfonate/deuterium) injection (9/16)

1000 gallon purge (11/20/17)

Corrosion of stainless steel well casing by organic acids establishing acidic pH conditions and release of metals to groundwater.

baseline condition Cr = 295 ppb (µg/L) on Sept. 3, 2017

method detection limit (MDL) Cr MDL (3 ppb or 3 µg/L)

NM groundwater std for Cr = 50 ppb (µg/L)

groundwater background for chromium = 7.48 ppb (µg/L) at 95th upper tolerance limit.
Concentrations of Total Organic Carbon Versus Time at Regional Aquifer Well R-28

Concentrations of Total Organic Carbon (TOC) ppm (mgC/L) over time at Regional Aquifer Well R-28. Key events:

- Molasses breakdown/oxidation by in situ microbes
- Tracer (sulfonate/deuterium) injection (9/16)
- Molasses injection (9/9/17)
- Groundwater background for total organic carbon = 1.08 ppm (mg/L) 95th percentile upper tolerance limit
- 1000 gallon purge (11/20/17)
Concentrations of Total Organic Carbon and Total Carbonate Alkalinity Versus Time at Regional Aquifer Well R-28

- **molasses breakdown/oxidation by in situ microbes**
- oxidation of TOC by in situ microbes produces total carbonate alkalinity
- groundwater background for total organic carbon = 1.08 ppm (mg/L) 95th percentile upper tolerance limit
- oxidation of molasses to carbonate alkalinity under oxic conditions
  \[ O_2 + CH_2O + \text{microbes} \rightarrow CO_2 \text{gas} + H_2O \]
- Variable concentrations of total carbonate alkalinity were measured during pumping
- groundwater background for dissolved total carbonate alkalinity = 72.9 mg CaCO_3/L upper tolerance limit at 95th percentile
Dissolved Oxygen Versus Times at Chromium Extraction Wells

Suppressed dissolved oxygen at extraction well CrEX-3 is influenced by reducing R-28 groundwater mixing with downgradient oxidizing groundwater near CrEX-3.

Molasses injection at R-28 (9/9/17)
Elevated dissolved manganese at extraction well CrEX-3 is influenced by R-28 groundwater mixing with downgradient groundwater near CrEX-3.
Elevated dissolved manganese occurs at CrEX-3 after mixing with groundwater sourced from R-28. Dissolved manganese is mobile in the regional aquifer after injection of molasses at R-28.

Groundwater background for dissolved manganese = 12.1 ppb (µg/L) at 95th percentile
At regional well R-28, chromate has been reduced to chromium(III) by oxidation of reactive organic carbon (molasses) during consumption by *in situ* bacteria (aerobic, anaerobic, and facultative).

Oxidation and consumption of molasses by *in situ* bacteria initially produced organic acids that decreased groundwater pH as low as 4.6. This caused corrosion of stainless-steel well casing with secondary release of chromium, iron, manganese, other metals to groundwater.

Residual organic matter/biomass and biofilms have created reactive biogeochemical conditions that render R-28 useless in providing representative geochemical and hydraulic data and information. The well will be replaced by a new well (R-76) in 2022 - 2023.

Molasses injection at R-28 indirectly impacted extraction well CrEX-3 by mobilizing iron, manganese, dissolved organic carbon, and other chemicals.
Path Forward

- NMED and DOE concur that R-28 does not provide technically defensible groundwater monitoring data and information. A replacement well (R-76) will be drilled in 2022 - 2023.

- Regional aquifer well R-42 is currently being evaluated by NMED and DOE for providing reliable data and information representative of pre-injection of chemicals.

- Site-specific hydrogeological and geochemical conditions are not conducive for using biogeochemical amendments (sodium dithionite and molasses) to remediate the chromium plume at LANL. Pump and treat is the preferred remediation technology.

- Additional characterization on the nature and extent of the chromium plume (lateral and vertical) is required to successfully remediate the chromium plume in the regional aquifer.
Los Alamos National Laboratory and Surrounding Area, North Central New Mexico
Chromium Plume Detail – Coalesced Plumes

source of figure: DOE
Sodium Dithionite and Reaction Sequence for Iron and Chromium

A: $\text{Na}_2\text{S}_2\text{O}_4 = 2\text{Na}^+ + 2\text{SO}^{•-}_2$ (sodium dithionite dissociates to sodium cation and sulfoxyl radical)

B: $\text{SO}^{•-}_2 + \text{Fe}^{3+} + \text{H}_2\text{O} = \text{SO}_3^{2-} + \text{Fe}^{2+} + 2\text{H}^+$ (sulfoxyl radical oxidizes to sulfite and reduces ferric iron to ferrous iron; sulfite oxidizes to sulfate and produces acidic conditions)

C: $3\text{Fe}^{2+} + 5\text{H}^+ + \text{CrO}_4^{2-} = 3\text{Fe}^{3+} + \text{Cr(OH)}_3 + \text{H}_2\text{O}$ (ferrous iron reduces chromate to chromium[III])

Sulfur atoms are shown in yellow.
Sodium atoms are shown in purple.
Oxygen atoms are shown in red.
PHREEQC Batch Model of Chromium Reduction by Sodium Dithionite (Na$_2$S$_2$O$_4$) and Sodium Sulfite (Na$_2$SO$_3$) at Regional Aquifer Well R-42

Aquifer Solid Phases

Oxidizing Groundwater

\[ \text{CrO}_4^{2-} \quad \text{CrO}_4^{2-} \quad \text{CrO}_4^{2-} \]

\[ \text{Fe}_{\text{dissolved}} = 15 \text{ ppb} \]
\[ \text{Cr}_{\text{dissolved}} = 718 \text{ ppb} \]
\[ \text{pH} = 7.46 \]

\[ \text{Cr(OH)}_3_{\text{am}} (\text{solid}) \]

\[ \text{ppb} = \text{parts per billion} \]

Reduction of Cr(VI)

\[ \text{CrO}_4^{2-} \quad \text{CrO}_4^{2-} \quad \text{CrO}_4^{2-} \]

\[ \text{Cr(OH)}_2^+ \quad \text{Cr(OH)}_2^+ \]

\[ \text{pH} = 6.20 \]
\[ \text{Cr}_{\text{dissolved}} = 75.1 \text{ ppb} \]
\[ \text{Cr(OH)}_3_{\text{am}} = 643 \text{ ppb precipitates} \]

Na$_2$S$_2$O$_4$ (10,446 ppm) and Na$_2$SO$_3$ (7,563 ppm) (0.06 molal)

\[ \text{pH} = 7.44 \]
\[ \text{Cr}_{\text{dissolved}} = 1.0 \text{ ppb} \]
\[ \text{Cr(OH)}_3_{\text{am}} = 717 \text{ ppb precipitates} \]

Na$_2$S$_2$O$_4$ - Na$_2$SO$_3$ and NaHCO$_3$ (5,040 ppm) - Na$_2$CO$_3$ (6,359 ppm) (0.06 molal)

R-42 sampled May 6, 2016
Eh-pH Diagram for Part of the Cr-O-H System at 25°C and 1 Bar, Total Dissolved Cr = 10^{-4.74} Molal

A: \( \text{Na}_2\text{S}_2\text{O}_4 \rightarrow 2\text{Na}^+ + 2\text{SO}_2^- \cdot \)
\( \text{SO}_2^- \cdot + \text{Fe}^{3+} + \text{H}_2\text{O} = \text{SO}_3^{2-} + \text{Fe}^{2+} + 2\text{H}^+ \)

B: \( 2\text{H}_2\text{O} + \text{CrOH}^{2+} = \text{Cr(OH)}_3^0 + 2\text{H}^+ \)
\( \text{Cr(OH)}_3^0 \rightarrow \text{Cr(OH)}_3(\text{am}) \)

\( 3\text{Fe}^{2+} + 5\text{H}^+ + \text{CrO}_4^{2-} = 3\text{Fe}^{3+} + \text{Cr(OH)}_3 + \text{H}_2\text{O} \)
pH Versus Activity of Cr(III) at 25C and 1 Bar (Palmer and Wittbrodt 1991)

Sources of thermochemical data: Rai et al. 1987 and Sass and Rai 1987
Concentrations of Dissolved Chromium Versus Time at Regional Aquifer Well R-42 (source of data: DOE)

- Sodium dithionite/sodium sulfite injection (8/17)
- Reduction of Cr(VI) to Cr(III) with precipitation of Cr(OH)₃
- Migration of upgradient groundwater to R-42 during pumping
- NM groundwater standard for chromium = 0.05 ppm (mg/L)
- Carbonate injection (7/16)
Concentrations of Dissolved Iron Versus Time at Regional Aquifer Well R-42 (source of data: DOE)

- Concentrations of dissolved iron were monitored over time at Regional Aquifer Well R-42.
- Data includes carbonate injection on 7/16 and sodium dithionite/sodium sulfite injection on 8/17, followed by pumping to October 16, 2017.
- Reduction of Fe(III) to Fe(II) with dissolution of Fe(OH)$_3$ or "rust" present as a solid in the regional aquifer.
- Groundwater background for dissolved iron is 53.8 ppb (µg/L) at the 95th percentile.
- The New Mexico groundwater standard for Fe is 1,000 ppb (µg/L).

The graph shows a significant decrease in iron concentrations post-injection and pumping.
Concentrations of Dissolved Manganese (Mn) Versus Time at Regional Aquifer Well R-42

- Concentrations of dissolved manganese versus time at Regional Aquifer Well R-42.
- Sodium dithionite/sodium sulfite injection followed by (8/17) pumping to October 16, 2017.
- Carbonate injection (7/16).
- Reduction of Mn(IV) to Mn(II) with dissolution of MnO₂ present as a solid in the regional aquifer.
- Pumping of R-42.
- Groundwater background for dissolved manganese = 12.1 ppb (µg/L) at 95th percentile.
- NM groundwater standard for Mn = 200 ppb (µg/L).
- Method detection limit (MDL).

Concentrations of dissolved manganese (Mn) versus time at Regional Aquifer Well R-42 (source of data: DOE).
Concentrations of Dissolved Sulfate \((SO_4)\) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)

Baseline condition:
- \(SO_4 = 75\) ppm (mg/L) on August 7, 2017

Groundwater background for dissolved sulfate = 4.59 ppm (mg/L) 95\(^{th}\) percentile, upper tolerance limit

NM groundwater std for \(SO_4 = 600\) ppm (mg/L)

Carbonate injection (7/16)

Sodium dithionite/sodium sulfite injection (8/17) followed by pumping to October 16, 2017

Dissociation and oxidation of sodium dithionite and sodium sulfite to sulfate and reduction to hydrogen sulfide

Excess sulfate due to oxidation of sulfide minerals
Molasses is a viscous product resulting from refining sugarcane or sugar beets into complex sugars ($C_{12}H_{22}O_{11}$).

 Sucrose (very simple model for molasses)

Carbon atoms are shown in black.  
Hydrogen atoms are shown in white.  
Oxygen atoms are shown in red.
Molasses is a viscous product resulting from refining sugarcane or sugar beets into complex sugars \(\text{C}_{12}\text{H}_{22}\text{O}_{11}\). 

**Generic Inorganic Composition**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/kg, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>2,050</td>
</tr>
<tr>
<td>Iron</td>
<td>47.2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2,420</td>
</tr>
<tr>
<td>Manganese</td>
<td>15.3</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>310</td>
</tr>
<tr>
<td>Potassium</td>
<td>14,640</td>
</tr>
<tr>
<td>Sodium</td>
<td>370</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.9</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>219,000 (21.9 wt. %)</td>
</tr>
</tbody>
</table>

parts per million is ppm, kilogram is kg
pH Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

- **basic pH (25°C)**
- **neutral pH (25°C)**
- **acidic pH (25°C)**

**Acidic Conditions**: During the oxidation and breakdown of molasses, low-molecular weight organic acids are produced, establishing acidic pH conditions.

**Corrosion**: Corrosion of stainless steel well casing by organic acids.

**Events**:
- **molasses injection (9/9/17)**
- **1000 gallon purge (11/17)**
Concentrations of Dissolved Iron (Fe) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

Concentrations of Dissolved Iron Versus Time at Regional Aquifer Well R-28

- Corrosion of stainless steel well casing with molasses consumption by *in situ* microbes with additional ferric hydroxide and iron oxide dissolution producing high concentrations of dissolved iron.

- Tracer (sulfonate/deuterium) injection (9/16)

- Molasses injection (9/9/17)

- 1000 gallon purge (11/17)

Groundwater background for dissolved iron = 53.8 ppb (µg/L) at 95th percentile.
Concentrations of Dissolved Manganese (Mn) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

The graph shows the concentrations of dissolved manganese (Mn) versus time at Regional Aquifer Well R-28. The data is from DOE.

Key points:
- Concentrations range from 0 to 45,000 ppb (µg/L).
- Key events:
  - Corrosion of stainless steel well casing with additional manganese dioxide dissolution producing high concentrations of dissolved manganese.
  - Molasses injection (9/9/17).
  - 1000 gallon purge (11/17).
- Groundwater background for dissolved manganese = 12.1 ppb (µg/L) at 95th percentile.
- Method detection limit (MDL) for Mn = 200 ppb (µg/L).
- NM groundwater standard for Mn.

Date range from 12-27-2014 to 03-15-2023.
Concentrations of Dissolved Potassium Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

molasses provides additional potassium and sulfate to groundwater, which changed the groundwater from a calcium-sodium-bicarbonate to a potassium-calcium-sulfate composition during 2017 - 2018.
Concentrations of Dissolved Sulfate Versus Time at Regional Aquifer Well R-28 (source of data: DOE)

- Molasses provides additional sulfate to groundwater with some sulfur species reducing to hydrogen sulfide.
- Tracer (sulfonate/deuterium) injection (9/16).
- Molasses injection (9/9/17).
- Baseline condition $SO_4 = 62$ ppm (mg/L) on Sept. 3, 2017.
- NM groundwater std for $SO_4 = 600$ ppm (mg/L).
- Groundwater background for dissolved sulfate = 4.59 ppm (mg/L) upper tolerance limit at 95th percentile.
- 1000 gallon purge (11/17).
Elevated total carbonate alkalinity at extraction well CrEX-3 is influenced by R-28 groundwater mixing with downgradient groundwater near CrEX-3. Molasses oxidizes to total carbonate alkalinity during biosynthesis by bacteria.
Dissolved Chloride Versus Times at Chromium Extraction Wells

Date

Cl (ppm, mg/L)

Dissolved Chloride Versus Time at Chromium Extraction Wells

- CrEX-1
- CrEX-2
- CrEX-3
- CrEX-4
- CrEX-5

molasses injection at R-28 (9/9/17)
Dissolved Manganese Concentration Versus Time at Extraction Well CrEX-3

Dissolved Manganese Concentrations at Extraction Well CrEX-3

- molasses injection at R-28 (9/9/17)
- well development

Date:
- 12-27-2014
- 05-10-2016
- 09-22-2017
- 02-04-2019
- 06-18-2020
- 10-31-2021
- 03-15-2023