Aqueous Chemistry of Chromium in an Oxidizing Aquifer System, Pajarito Plateau, New Mexico

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Abstract
Chromium (Cr) is a trace element of considerable interest to aqueous geochemists, environmental scientists and toxicologists due to high toxicity of Cr(VI). Cr(VI) is stable under oxidizing conditions, whereas Cr(III), dichromate, bichromate, and chromate, Cr(H) hydroxide precipitates under relatively reduced conditions, and equilibrium concentrations of Cr are typically less than 0.01 ppm (0.005 mg/L). In intermedial pH conditions, Potassium dichromate (31,000 to 72,000 ppm) was used as an anticorrosion agent at a cooling tower at Los Alamos National Laboratory (LANL) from 1956 to 1972 and discharged to a wastewater. Chromate has migrated approximately 290 meters through the vadose zone under anhydrous media flow conditions to reach the water table. The transport time for Cr(VI) migrating through the vadose zone downgradient from the main discharge source is estimated at 20 years. Flashy calcite concentrations of dissolved total Cr in the regional aquifer, mainly in the form of Cr(VI), range from 5,774 ppm to 6,624 ppm (0.003 to 0.005 mg/L), while concentrations of hematite in the aquifer reach 0.024 ppm (1.24 mg/L). First-order calculations suggest that Cr(VI) migration within the regional aquifer at LANL is approximately equal to the average advective groundwater flow-rates ranging from 25 to 50 m/year. Total dissolved concentrations of Cr show either steady-state or increasing trends at monitoring wells over time, suggesting that natural attenuation of Cr is not occurring to a significant extent. The Cr trends suggest that there are multiple entry points to the regional water table from more than one source. The regional aquifer is characterized by a calcium, sodium-bicarbonate composition and is oxidizing with respect to Fe and Mn. This aquifer contains measurements of dissolved oxidized oxygen ranging from 0.16 to 0.25 ppm (0.12 to 0.20 mg/L). Advective transport of Cr(VI) in the regional aquifer sediments is limited by adsorptions with small surface area minerals such as manganese(II) oxides competing oners, (sulfate and bicarbonate), and basic pH (3.6). Reduction of Cr(VI) to Cr(III) is limited by the scarcity of electron donors, including reactive Fe(II) phases, reductive organic carbon, and dissolved sulfate.

Chromium Release at Technical Area-03, Los Alamos National Laboratory

- Over 15 years of Cr(VI) releases from the TA-03 cooling tower.
- Between 21,000 and 72,000 kg of Cr(VI), with a mean of 54,000 kg, were released between 1956 and 1972 to Sandia Canyon.
- Most of the Cr(VI) released is from dissolution of potassium dichromate (K2Cr2O7).
- Approximately 1100 kg of Cr(VI) reached the regional aquifer (LANL 2012). This is based on estimates made prior to drilling of R-50 and R-62.

Water Table Map for the Regional Aquifer, Los Alamos National Laboratory, NM (LANL 2012)

Concentrations of Chromium in the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Calculated Rates of Chromium Transport in the Regional Aquifer, Los Alamos, NM

- Cr migration rate = groundwater-flow rate (feet/year)/R (73 feet/year)/R = 0.5 - 49 feet/year; (131 feet/year)/R = 0.5 - 83 feet/year; (164 feet/year)/R = 0.5 - 109 feet/year.

The most representative Cr transport rates must likely range from 83 to 109 feet/year in the regional aquifer of R-28. This range, based on extensive monitoring data provided by LANL (2012) and MACE and Cr trend analysis.

Redox Behavior of Chromium in Aquifer Environments

- Soluble chromium(III) is stable in the regional-aquifer system characterized by strongly oxidizing conditions with respect to Fe, Mn, and oxidized oxygen.
- Chromium is migrating at nearly the same rate of groundwater flow rate within the regional aquifer (Puuye Formations) and the Miocene (Mancos) micaceous sediments).
- Chromium mass, nature, and extent of chromium contamination in the vadose zone and regional aquifer is not completely known.
- Natural attenuation of chromium(III) is not an effective process taking place in the regional-aquifer system.
- Successful aquifer remediation of chromium in the regional aquifer requires complete understanding of:
  - Nature and extent of contamination and
  - Geochemical, biochemical, and hydrological characteristics.

Summary and Conclusions

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Photo of the Jemez Mountains and Pajarito Plateau (view from the west with industrial sources of chromium(VI) discharge)