

Geochemical Considerations and Remediation of Cyanide at Complex Sites Using Batch and Flow Experiments

Alex Kugler ^a, Mariah Doughman ^a, Andy Plymale ^a, Rachel Anguish ^a, Aidan Henson ^a, Jenna Schroeder ^a, Nancy Escobedo ^a, Melissa Dieguez ^a, Leah Thompson ^a, Jacqueline Hager ^a, Mark Carlson ^b, Sarah Saslow ^a, Rob Mackley ^a

^a Pacific Northwest National Laboratory
^b Oregon State University

Introduction

Groundwater contamination presents unique remediation challenges. At remediation sites, cyanide may be present as free, weak-acid dissociable, and metal-complexed species, which each exhibit distinctly different subsurface mobility, recalcitrance, and treatment interactions. Understanding treatment technology performance for cyanide under site specific challenges is essential to select viable remediation solutions.

This work aims to address two Hanford relevant concerns, 1) what commercially available *ex situ* treatments would be able to remove ferrocyanide from groundwater and 2) which proposed subsurface treatment technologies, if any, may mobilize cyanide.

Methods

Lab-scale batch and/or column tests were performed to evaluate the effect of a suite of remediation technologies in simulated Hanford groundwater (SGW) on different cyanide species. A key aim of these experiments was to evaluate the potential for candidate DV-1 treatment technologies to generate free cyanide from potentially comingled complexed cyanide in columns at ~14 °C.

Batch experiments targeting the removal of ferrocyanide (1.5 g/L and 10.5 g/L) using ion exchange (IX) resins, and common adsorbents in SGW were also performed to evaluate *ex situ* treatment options.

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Experimental Design

Table 1. IX resins and adsorbents used in ferrocyanide *ex situ* treatment testing.

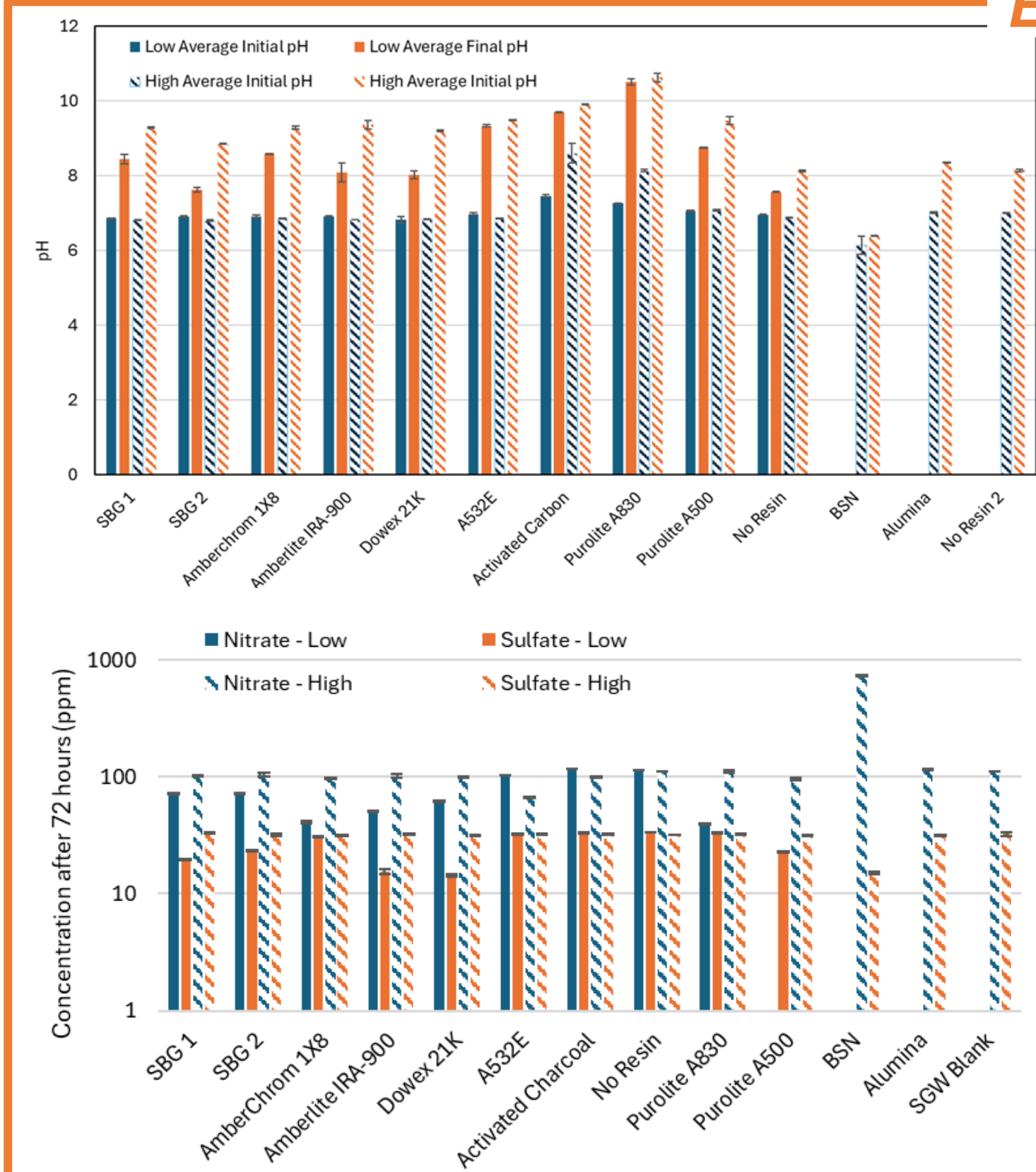
Strong Base Resins	Type/Structure	Manufacturer
SBG 1	I, Gel	ResinTech, Inc.
SBG 2	II, Gel	ResinTech, Inc.
Amberchrom 1X8	I, Gel	DuPont
Amerlite IRA-9000	I, Macroreticular	DuPont
Purolite A500	I, Macroporous	Purolite
Dowex 21K	I, Gel	DuPont
A532E	I, Gel	Purolite
Weak Base Resin	Type	Manufacturer
Purolite A830	Weak base, Macroporous	Purolite
Adsorbents	Type	Manufacturer
Activated charcoal	Granular	Sigma-Aldrich
Bismuth subnitrate	Powder	Sigma-Aldrich
Alumina	Powder	Sigma-Aldrich

Table 2. DV-1 technologies studied in batch and column for cyanide mobility.

DV-1 Technology	Treatment Constituents
Deionized Water (DI)	
Gas Bio (Ethane)	C ₂ H ₆ injection, with N ₂
Simulated Perched Water (SPW)	
Liq Bio (Molasses)	Molasses, 0.625 g/L
Simulated Groundwater (SGW)	
Calcium Citrate Phosphate (CCP)	35 mmol/L total PO ₄
Bismuth Subnitrate (BSN)	1.5 wt.% bismuth subnitrate in sediments
Tin Apatite (Sn(II)-PO ₄)	3.0 wt.% tin apatite in sediments
Sulfur Modified Iron (SMI)	0.7 wt.% in sediments for SMI followed by 35 mmol/L total PO ₄
Calcium Polysulfide (CPS)	0.725 vol.% in solution
Polyphosphate (Poly-PO ₄)	35 mmol/L total PO ₄

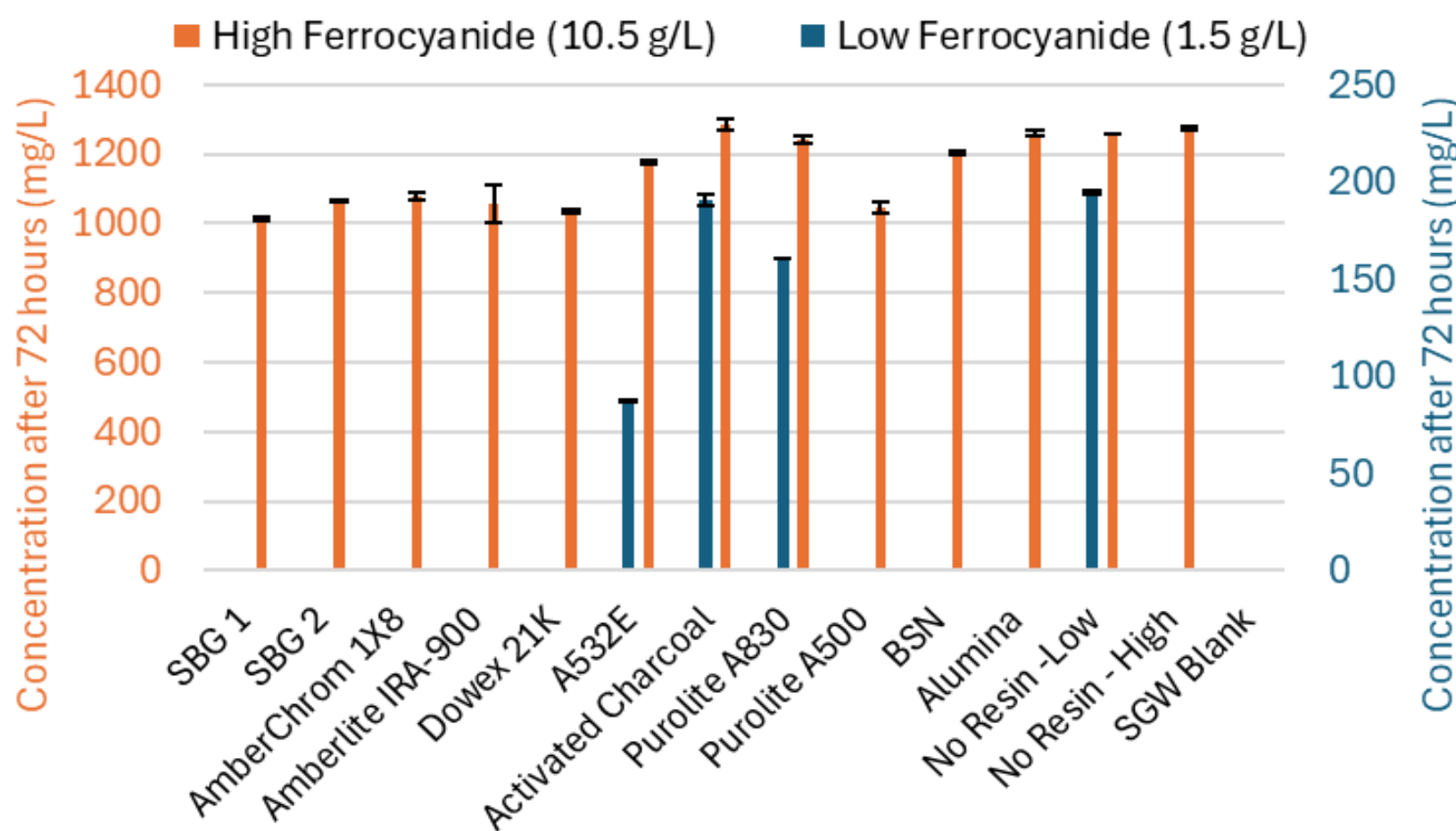
*Controls without a treatment technology were run for all solutions with sediment

Results



Ex Situ Treatment

The pH increases immediately upon adding most treatment technologies to SGW with the change in pH increasing with increasing ferrocyanide concentration.



Nitrate and sulfate competed for uptake at the lower concentration of ferrocyanide but when saturated, little not no competitive anion uptake occurred.

Low (1.5 g/L) ferrocyanide samples showed that most IX resins took up all the ferrocyanide, except for A532E, A830 and the activated charcoal. This test demonstrated that at high, but possible, influent concentrations these resins would be highly competitive. To further demonstrate loading differences, a much higher concentration, 10.5 g/L ferrocyanide, was used. This test revealed an overall grouping of the materials, with A500 showing the highest uptake, with the other strong base resins performing moderately well. The ion exchange resin alternatives, BSN, alumina, and activated charcoal were not effective.

These experiments demonstrate that ferrocyanide is readily taken up by various anion exchange resins in SGW; however, there is potential for interference from nitrate and co-contaminants (e.g., TcO₄⁻), which may require further investigation.

DV-1 Cyanide Mobility

Batch experiments (data not shown) were used to examine the effects of DV-1 technologies on ferricyanide, ferrocyanide, and potassium cyanide. Little to no significant generation of free cyanide was documented. Three technologies, BSN, SMI, and Sn(II)-PO₄ were selected for 1-D column leach studies after incubation with the technology for 90 days with ferrocyanide addition. Column leach studies highlighted that 1) some of the ferrocyanide remains sorbed to the sediments, 2) that little not free cyanide is produced, 3) that BSN causes a pH drop in the first few pore volumes, and 5) that BSN and SMI show considerable sorption of the ferrocyanide with very little leaching over time. **These experiments demonstrate that while ferrocyanide and other cyanide species may interact with sediments, and the technologies, minimal free cyanide is generated.**

