Potential for In Situ Treatment of Cyanide in Groundwater by Iron Addition

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Problem

- Iron cyanide complexes are obstinately uncooperative
- Very stable in groundwater and resists "destruction"
- Conventional pump and ex situ treatment is expensive



Typical Groundwater Remedy:

\$ Pump groundwater

\$ Ex situ treat in engineered treatment plant

\$ Dispose treatment residuals



Typical Groundwater Remedy:

\$ Very active management

\$ Well proven, reliable but expensive

\$ Ex. Cost \$25 million to treat 200 gpm
for 30 years



Potential In Situ Remedy:

- Create &/or stabilize iron cyanide minerals within aquifer
- Reduce solubility of iron cyanide complexes
- Reduce Total and WAD CN concentrations in groundwater



Potential In Situ +/-

+ May be passive or low management+ Cost fraction of ex situ treatment

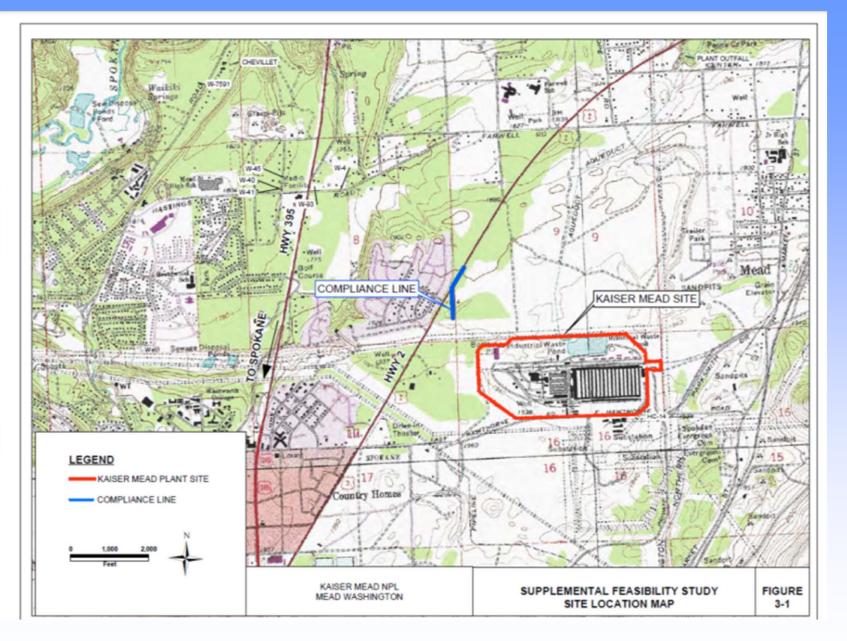
- No full scale or long term field tests, so
- Long term reliability is unproven



Case Study: Kaiser Mead, WA Groundwater Cyanide Plume









Natural Cyanide Sources

Numerous including:

- Biological all plants, many microbes, even few arthropods.
- Forest Fires
- Lightning
- Carbonaceous meteorite impacts



Industrial Cyanide Sources

Numerous including:

adhesives, electroplating, cement stabilizer, fire retardant, herbicides, pesticides, pharmaceuticals, & **hydrometallurgy**

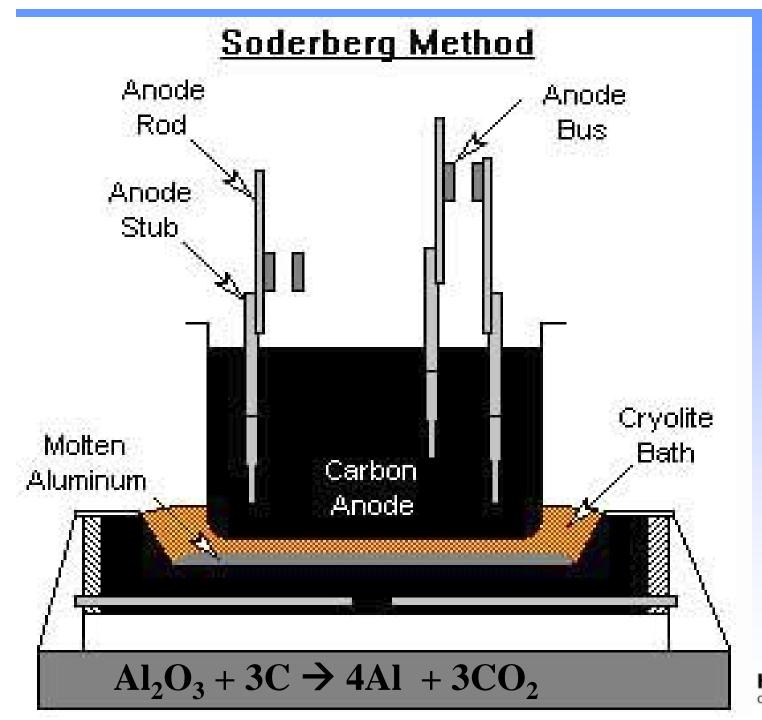


Incidental Cyanide Sources

Numerous as produced during thermal processing of carbonaceous materials:

- Coking and coal gasification,
- Municipal waste sludge incineration
- Alumina reduction





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SPL Leachate Characteristics			
Alkaline	pH 9 to 12		
Fluoride	1,000 to 8,000 mg/L		
Total Cyanide	200 to 4,000 mg/L		
Ferricyanide	200 to 4,000 mg/L		
WAD and Free CN	0 to 20 mg/L		

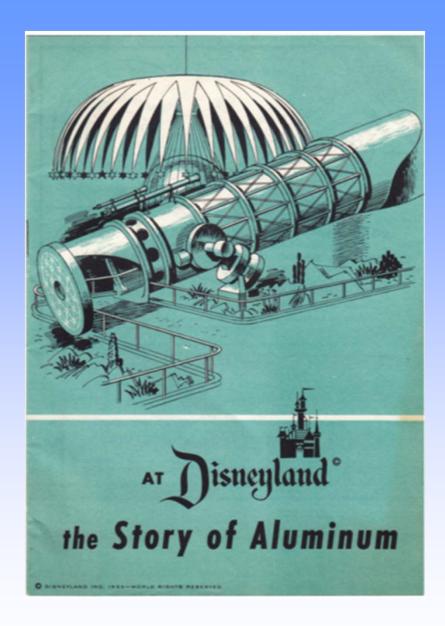


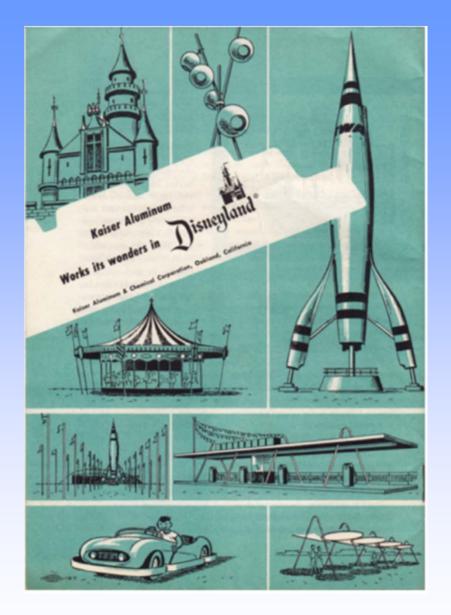
Kaiser Mead Operational Timeline:

1942

Alumina reduction facility built by ALCOA for US government - High quality Al used to build airplanes









Operational Timeline:

1946 ALCOA forced by US to divest due to fear of Al monopoly

1946 – 2000 Operated by Kaiser

2004 Kaiser bankruptcy & Consent Decree to resolve CERCLA liability



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On Site / Webcast Auction	2111 E Hawthorne Road Mead (Spokane), Washington, 99021 Map/Directions	USD	Click Here	Related	Sales	
Date & Time	Inspection / Preview Tuesday May 1st (9am-4pm) Or by Appointment Contact: tracym©newmillcapital.com			2.0	Onsite & Webcast Auction - Imperial Valley Cheese Wednesday May 7, 2014 El Centro, CA - Imperial Valley Cheese Swiss & Muenster Production & Packaging Facili Details	
Wed. May 2nd. & Thurs May 3rd.				1		
Start Time 9am (PST)						
Buyer's Premium 15% Onsite and 18% Online Buyer's Will Apply to All Sales in Addition to Applicable Local and State Sales Tax			P	Real Estate Available - Imperial Valley Cheese El Centro, CA - Real Estate For Sale - 30,000 SqFt Dairy Products Manufacturing Plant. Details		
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Remediation Timeline:

- 1978 CN and F found in drinking water wells
- 1983 Placed on CERCLA NPL list
- 1983 2000 Interim remedial actions
- 2000 Final Cleanup Action Plan Selected



Remediation Timeline 2002 Corrective Actions implemented – (source control only)

2012 Performance Evaluation concludes groundwater cleanup standards not met

2014 Draft Supplemental Feasibility Study



Aqueous Forms of Cyanide

"Free Cyanide"

$HCN_{gas} \leftrightarrow CN_{aq} + H^+ pK_a = 9.24$

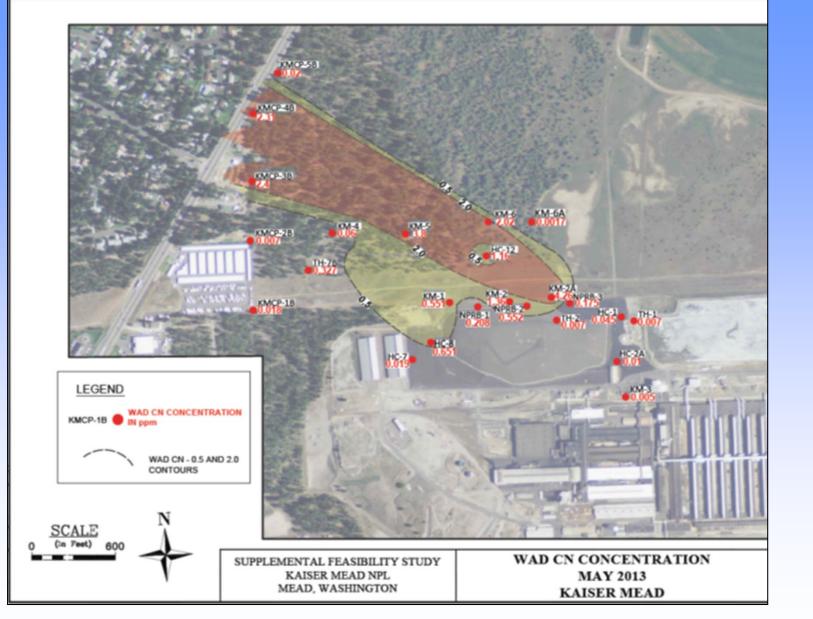


WAD Cyanide Analytical Form

"weak acid dissociable" = HCN gas released by weak acid digestion (pH 4.5 to 6)

• WAD = free CN + weak metal complexes (e.g. Ag, Cd, Cu, Zn)





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Total Cyanide Analytical Form

= HCN released by strong acid digestion (pH < 2)

= WAD CN + strong CN complexes

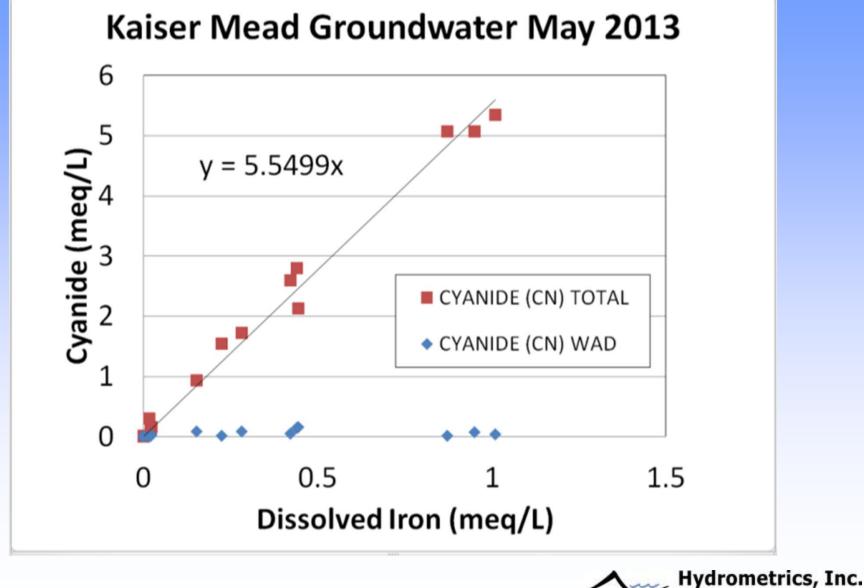


Strong Cyanide Complexes

 Notably Iron and mixed Fe-metal-CN (ex. Fe(CN)₆⁴⁻; KFe(CN)₆³⁻)

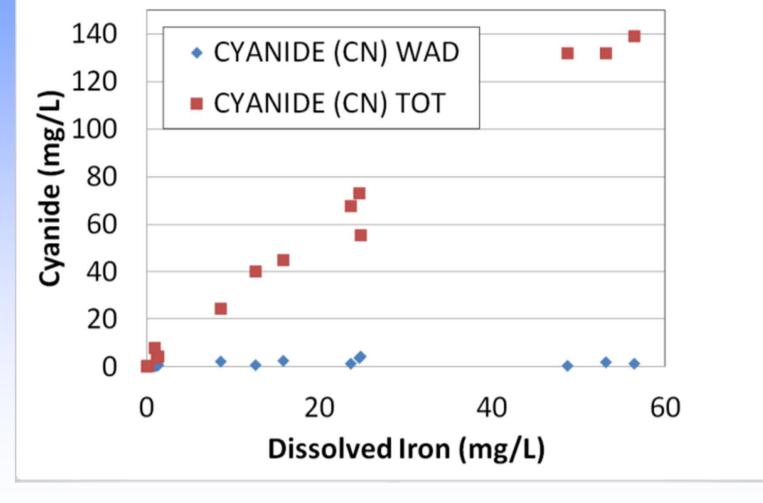
• But also Co, Pt, Au, Pd



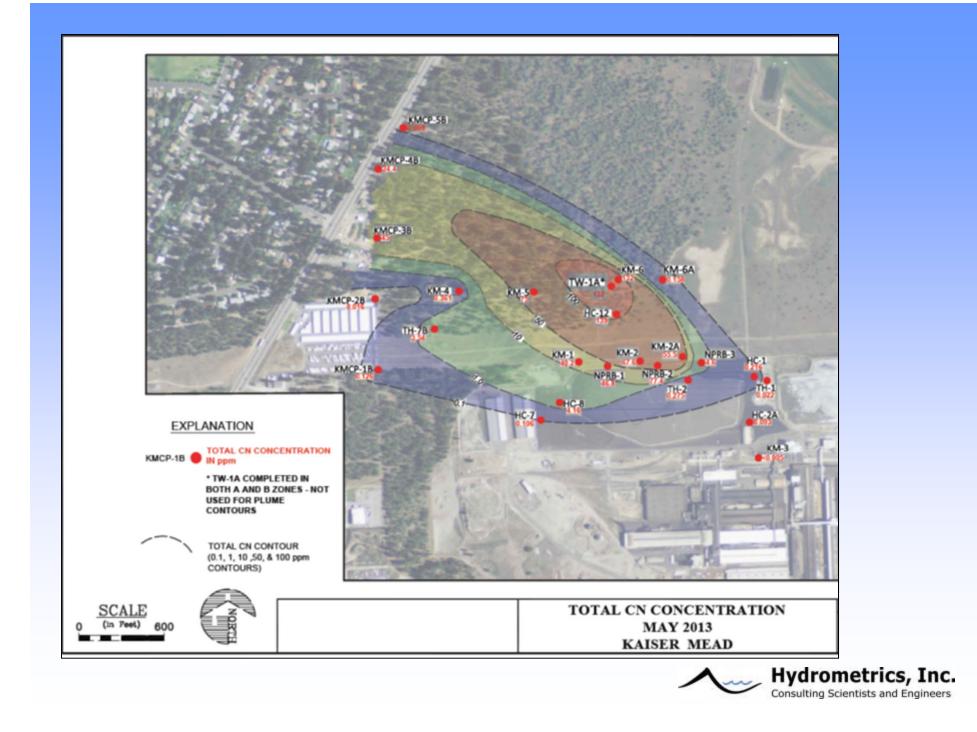


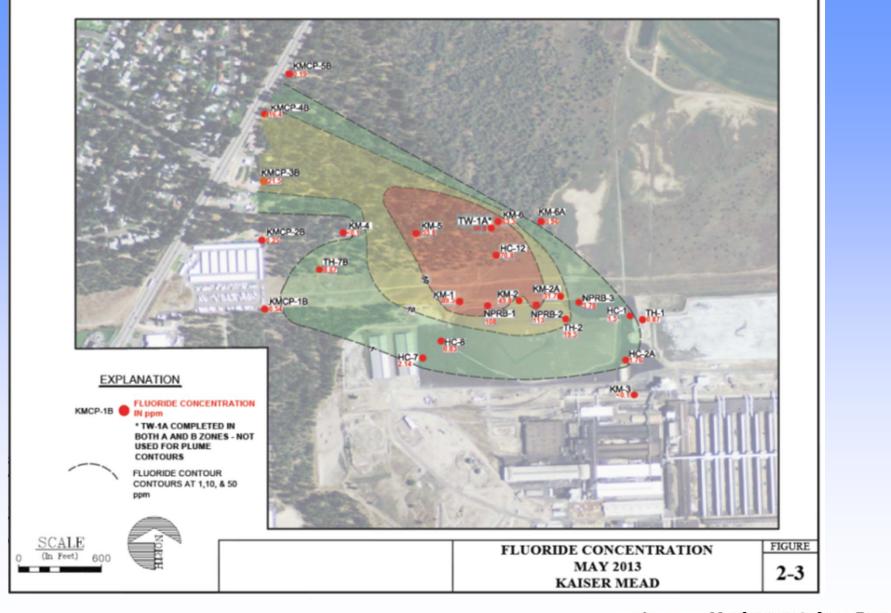
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Kaiser Mead Groundwater May 2013

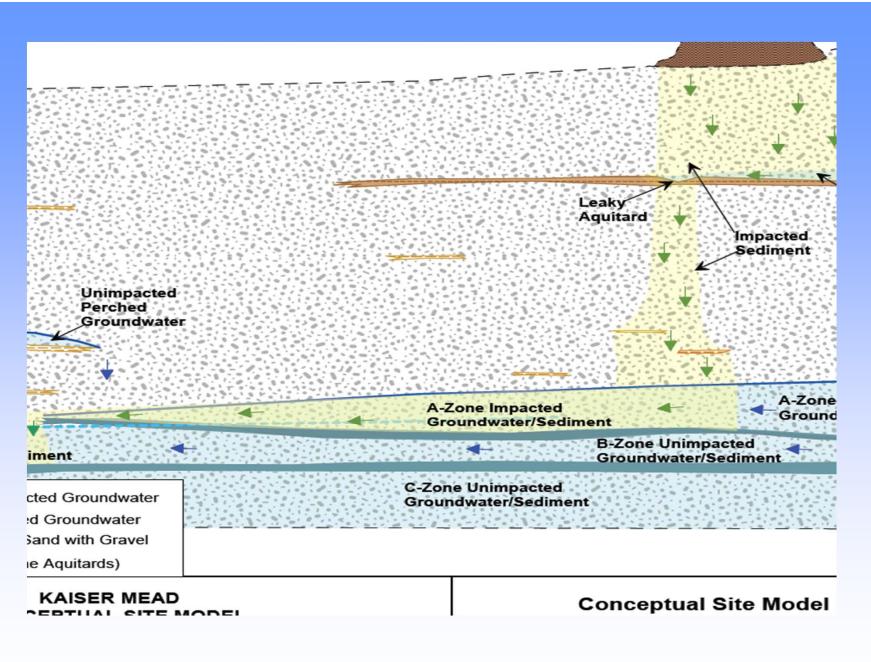








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Interest In In Situ:

- Desire for lower cost option than P&T
- Evidence of secondary source of F & CN in vadose zone &/or aquifer suggest conditions may be right to further stabilize CN & F minerals within aquifer



	CONDITIONS	RESULTS
Ghosh et al (1999)	Batch and column testing of PRB with ZVI	60 to 80 percent total cyanide removal
Wildeman et al (2006)	Testing of SRBRs with ZVI	ZVI alone did not remove CN but promoted biological removal
Peale et al (2008)	Bench and pilot- scale testing of PRB with carbon source and ZVI.	WAD CN reduced from 1 to 0.01 mg/L.

In Situ Concept

- Create &/or stabilize iron cyanide minerals within aquifer
- Reduce solubility of iron cyanide complexes
- Reduce Total, WAD and Free CN concentrations in groundwater



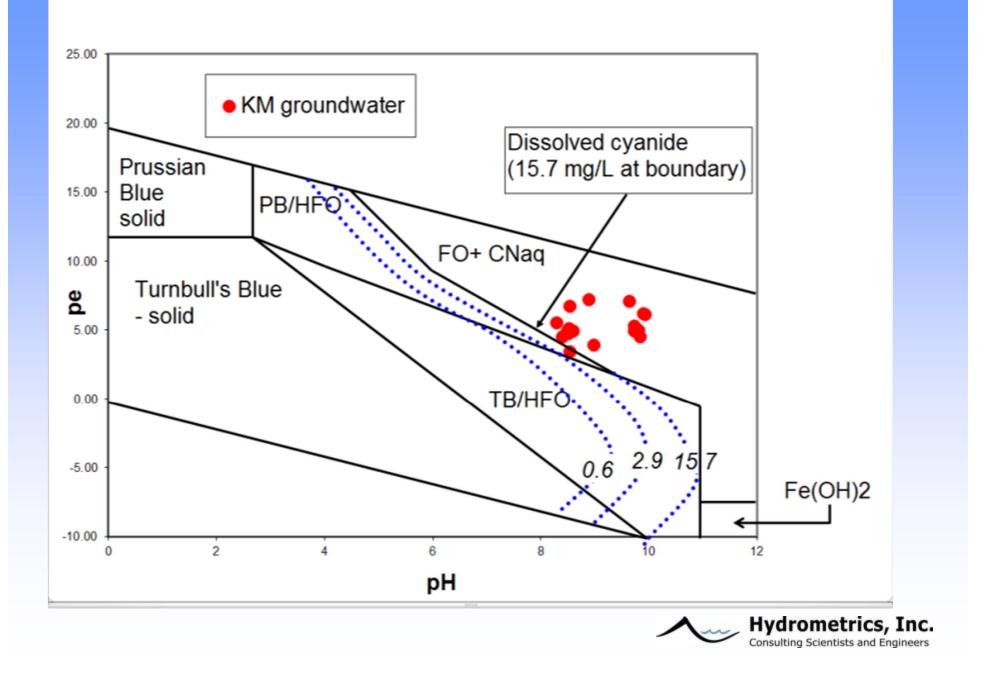
Iron Cyanide Minerals

• Prussian Blue : $Fe_4(Fe(CN)_6)_3$

Acidic oxidizing conditions

- Turnbull's Blue: $Fe_3(Fe(CN)_6)_2$
 - Neutral to alkaline reducing conditions
- Solid Solutions
 - Turnbull's Blue\Ferric Hydroxide (Fe(OH)₃)
 - Prussian Blue\Ferric Hydroxide





Proof of Concept Testing





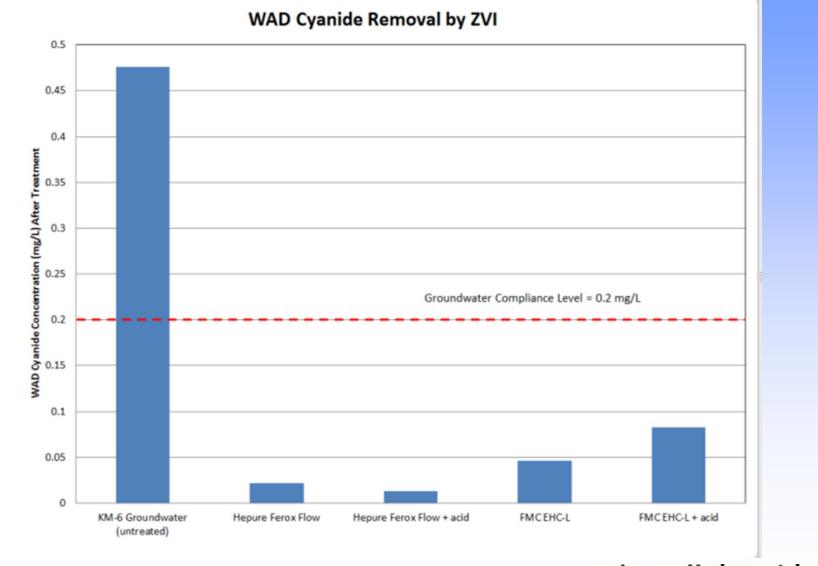
Two Reagents

Hepure Technologies: -FeroxTM Flow brand ZVI

FMC Environmental Solutions: -EHC-L emulsified ZVI with carbon and nutrients

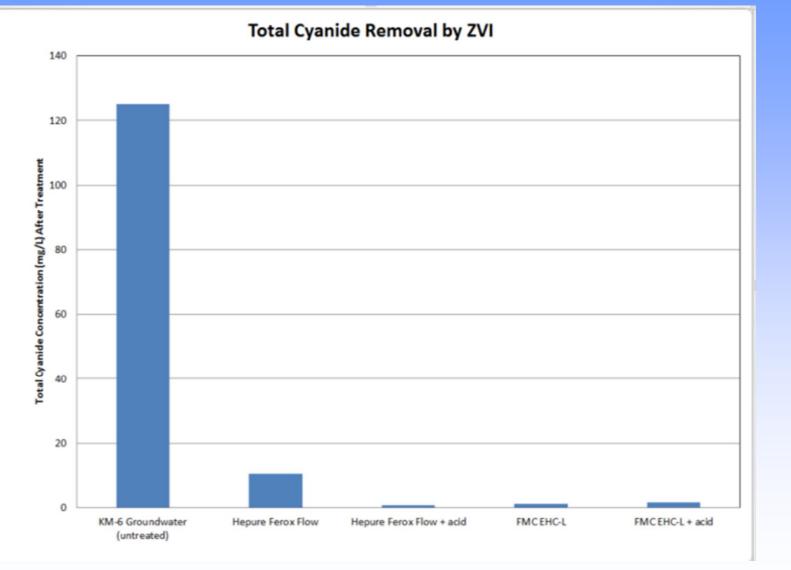


Results



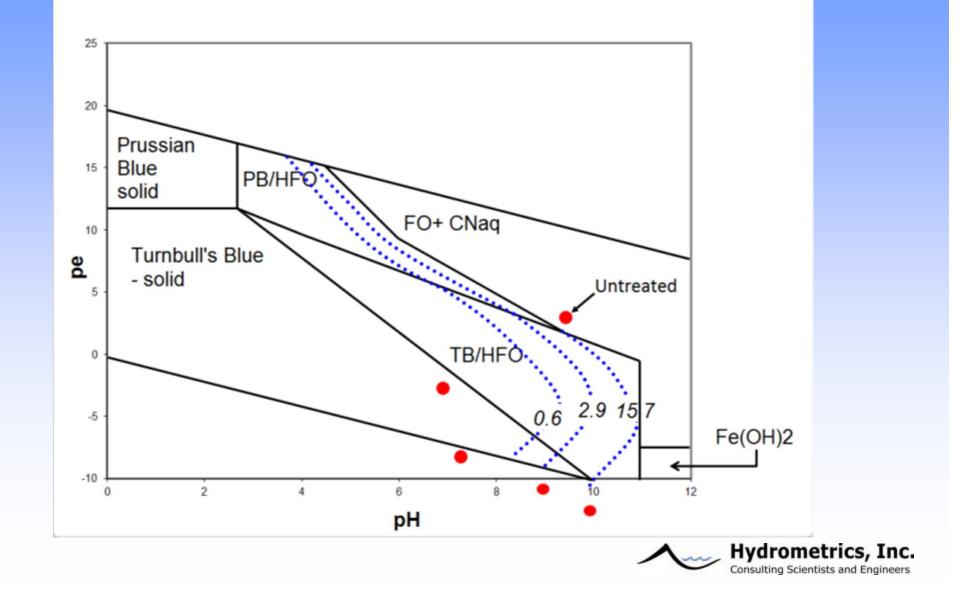
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Results

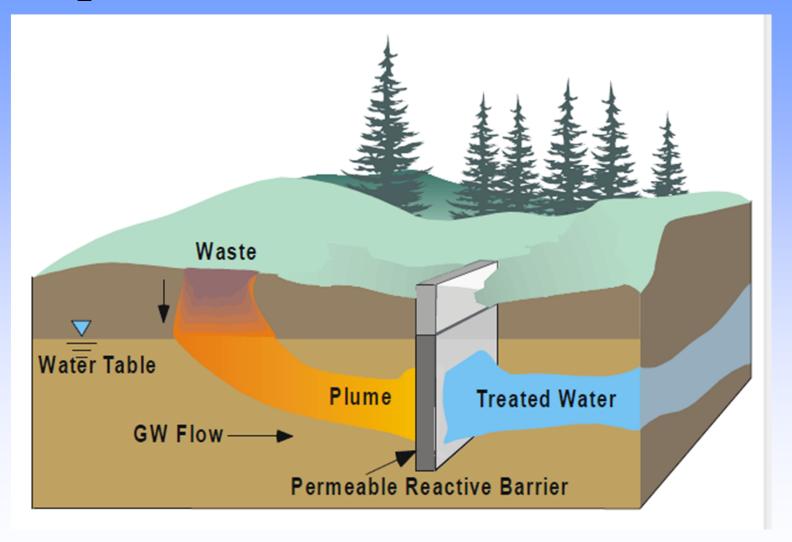




Results



Implementation





Installation - Excavation





Installation - Trenching

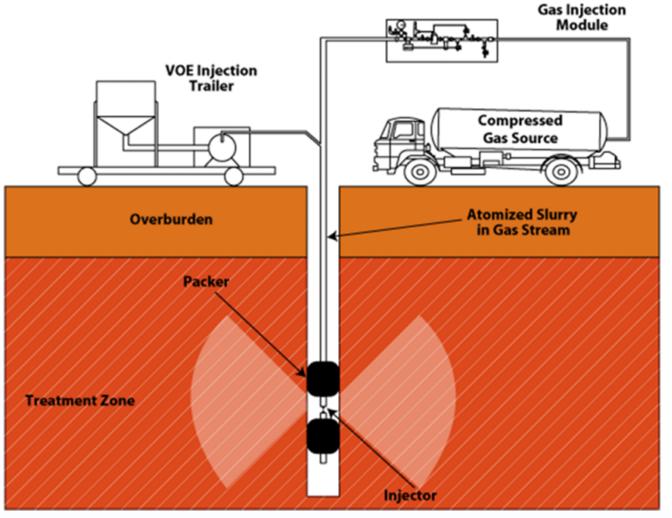




Installation – Auger Mixing



Hydraulic Fracturing





Status of In Situ Treatment at Kaiser Mead:

- Concept is proven
- Rough cost approx. 20% of ex situ
- Uncertainties



Uncertainties

- No operating full scale systems
- Difficulty/cost of installation
- Hard to reverse/decommission once installed



Uncertainties

- Long term reliability and effectiveness:
 - -Aquifer plugging
 - -Reagent consumption
 - -Noxious byproducts
 - -Stability of cyanide minerals



Potential Best Fit for Sites:

- Total cyanide/iron cyanide complexes are particular concern
- Secondary CN source in subsurface
- Shallow aquifer



Potential Best Fit for Sites:

- Desire passive or semi-passive
- Desire minimal surface facilities
- Non-destruction of CN is OK



END

