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In-Situ Treatment for Hexavalent Chromium Using ISCR Enhanced Bioremediation in Saturated Clay Soils Results in No Further Action

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Overview

- Site History and Background
- Treatment Evaluation
- Chromium Geochemistry
- Pilot Test Treatment
- Full-Scale Remedy
- Conclusions

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Site History and Background

- **Site Background**
  - Midwestern Chrome Plating facility
- **Historical Land Use**
  - In operations for decades
  - Release of chromium [Cr(VI)] in shallow aquifer
  - Adjacent residential neighborhood

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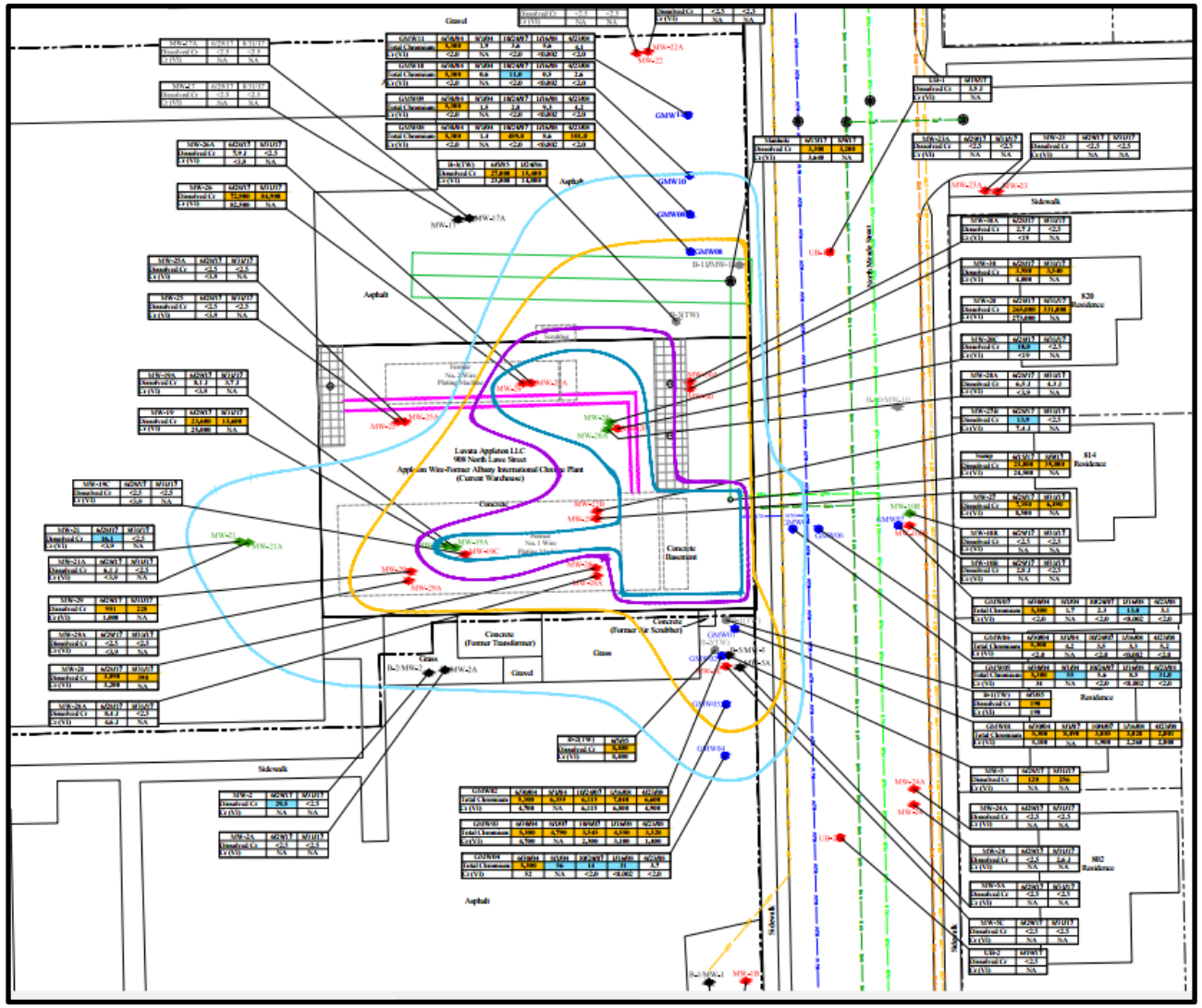
Site History and Background

- **Site Conceptual Model**
  - Widespread and radial plume
  - Concs range widely: 250 ppb to >300 ppm
- **Site Challenges**
  - Limited access due to existing infrastructure
  - Low permeability (low K)
  - Wide range of impacts



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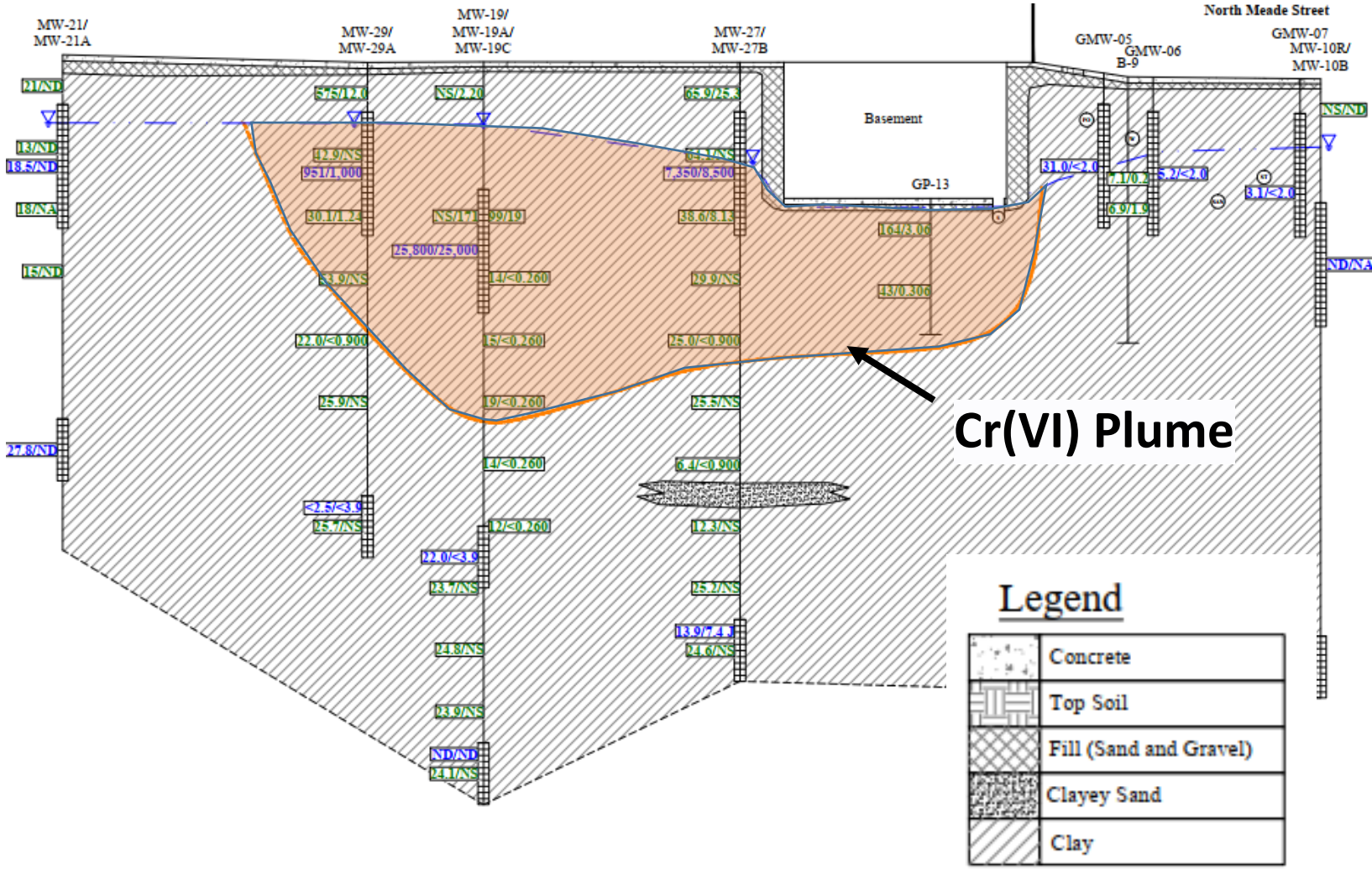
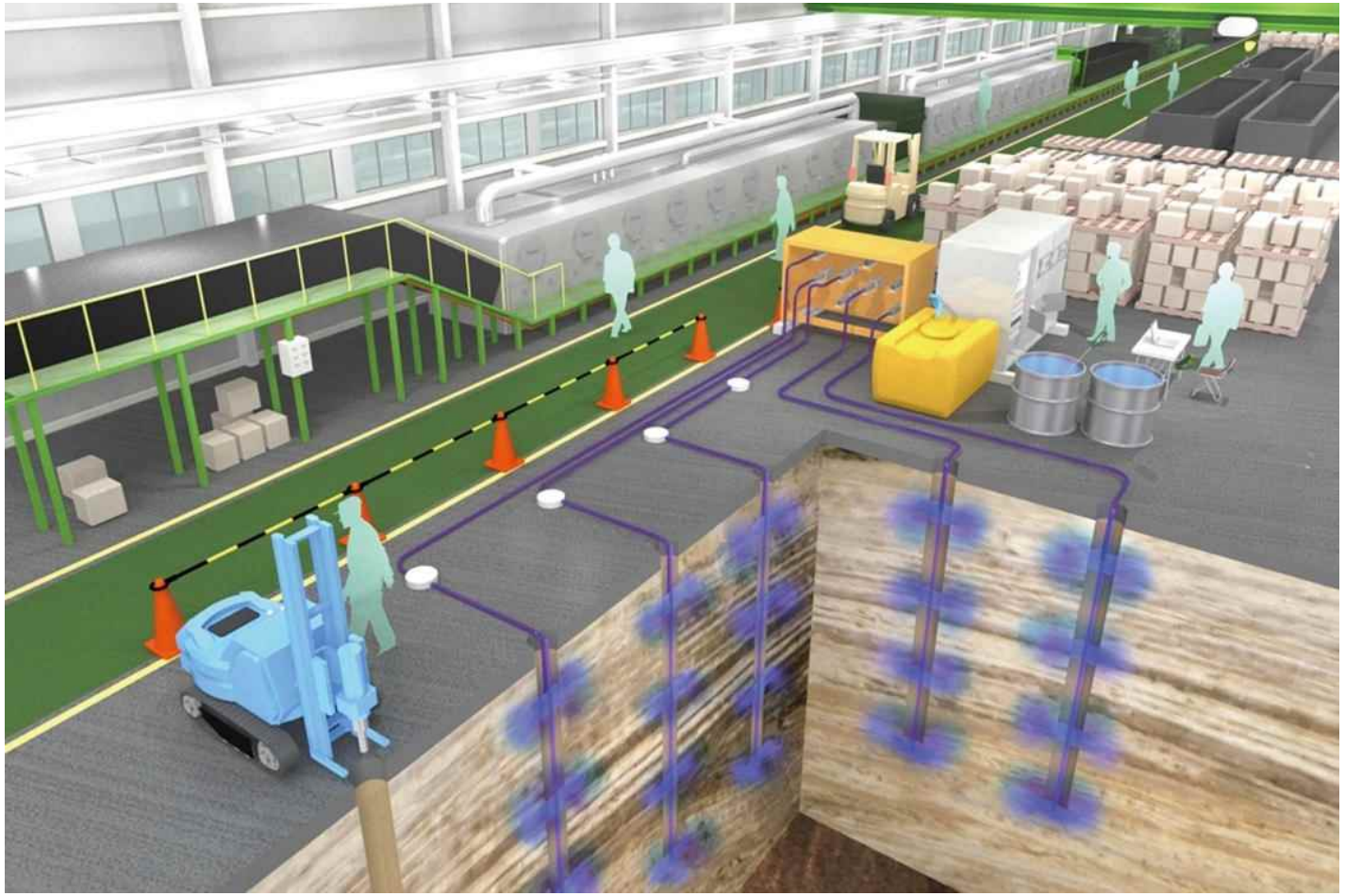
Site History and Background

- **Site Hydrogeology**
  - Glacial geology
    - Low K clays with interbedded sand
  - Shallow water table (~5 ft bgs)
  - Oxic geochemistry (150 to 200 mV ORP)
  - Impacts >20 ft. bgs



Treatment Evaluation

- **Treatment Needs**
  - Effective in low K and inside building
  - Address range of concs
  - Immediate and long-term treatment
- **Treatment Evaluation**
  - Pump and Treat? X
  - Excavation? X
  - In-Situ Metals Immobilization? ✓
    - In-Situ treatment within existing infrastructure



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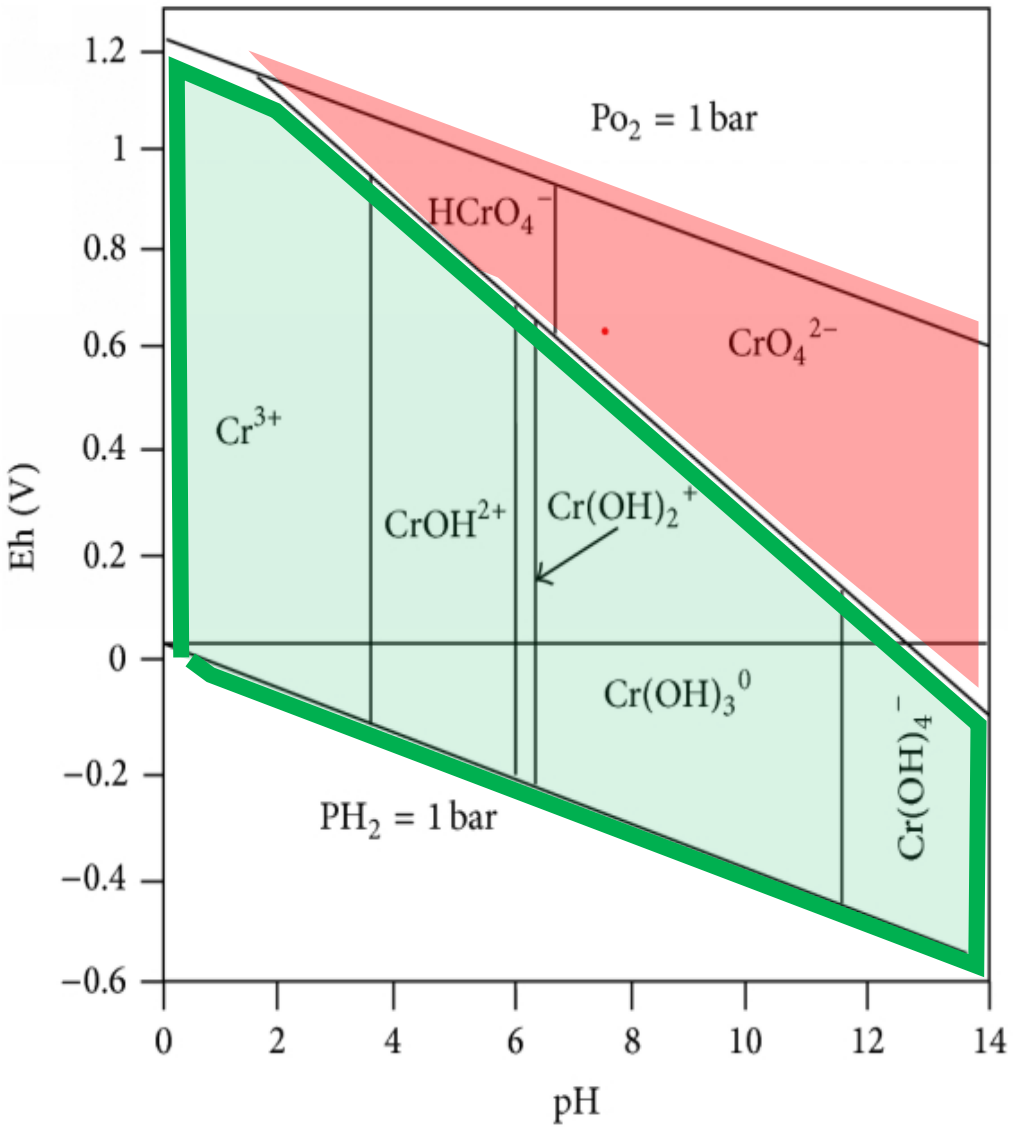
Chromium Geochemistry

- **In-Situ Metals Immobilization**
  - **Starts with fundamental geochemistry**
- **Chromium Geochemistry**
  - Hexavalent – CrO_4^{-2}
  - Trivalent – Cr(OH)
- **Eh-pH Diagram**
- **Cr(IV) compounds are not stable under normal environmental conditions**
- **Once Cr(III) hydroxide is formed it remains stable**



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How to Treat Hex Chrome?

- **How to Treat Hex Chrome?**
  - Simple Treatment = Provide Electrons
    - In-Situ Chemical Reduction (ISCR) and Enhanced Anaerobic Bioremediation
  - Recall Eh-pH diagram – once formed Cr (III) is stable precipitate under most conditions
- Treatment Chemistry Example

$$CrO_4^{-2} + 1.5\ Fe^0 + 5H_3O^+ \rightarrow Cr(OH)_3 + 1.5\ Fe^{+2} + 6H_2O$$

Cr^{+6} Cr^{+3}

*With excess iron, chromium can also form trivalent mixed iron chromium hydroxides $Fe_xCr_{1-x}(OH)_3$

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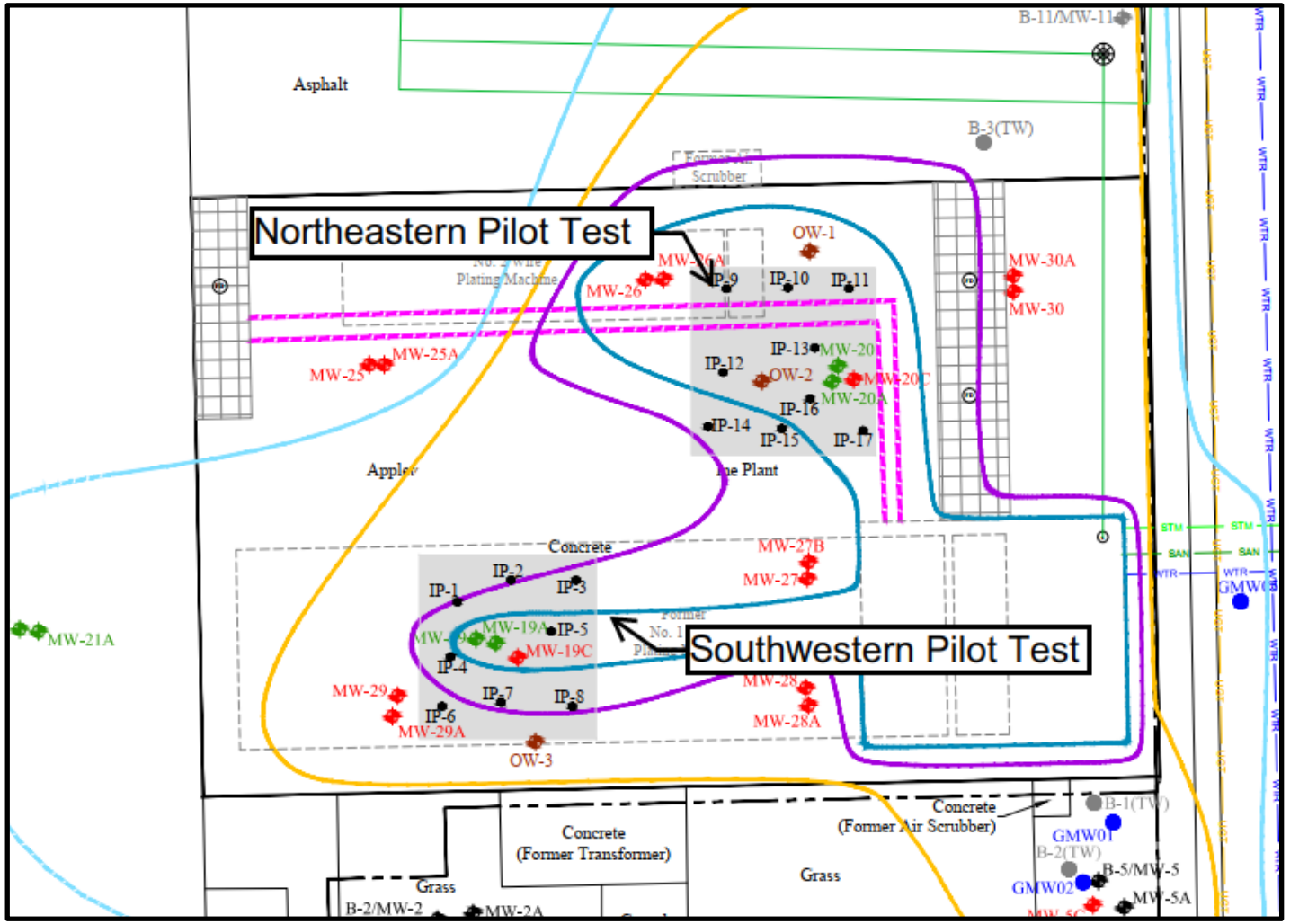
Pilot Test Treatment

- **Pilot Test Objectives**
  - Demonstrate aquifer can accept fluids via in-situ injections
  - Determine optimal ISCR and Anaerobic Bio combination
- **Scope of Work**
  - <u>Southwestern Pilot</u>:
    - ISCR via viscous microscale ZVI slurry
  - <u>Northeastern Pilot</u>:
    - Anaerobic bio using colloidal, emulsified electron donor
    - ISCR via Divalent Iron (DVI)



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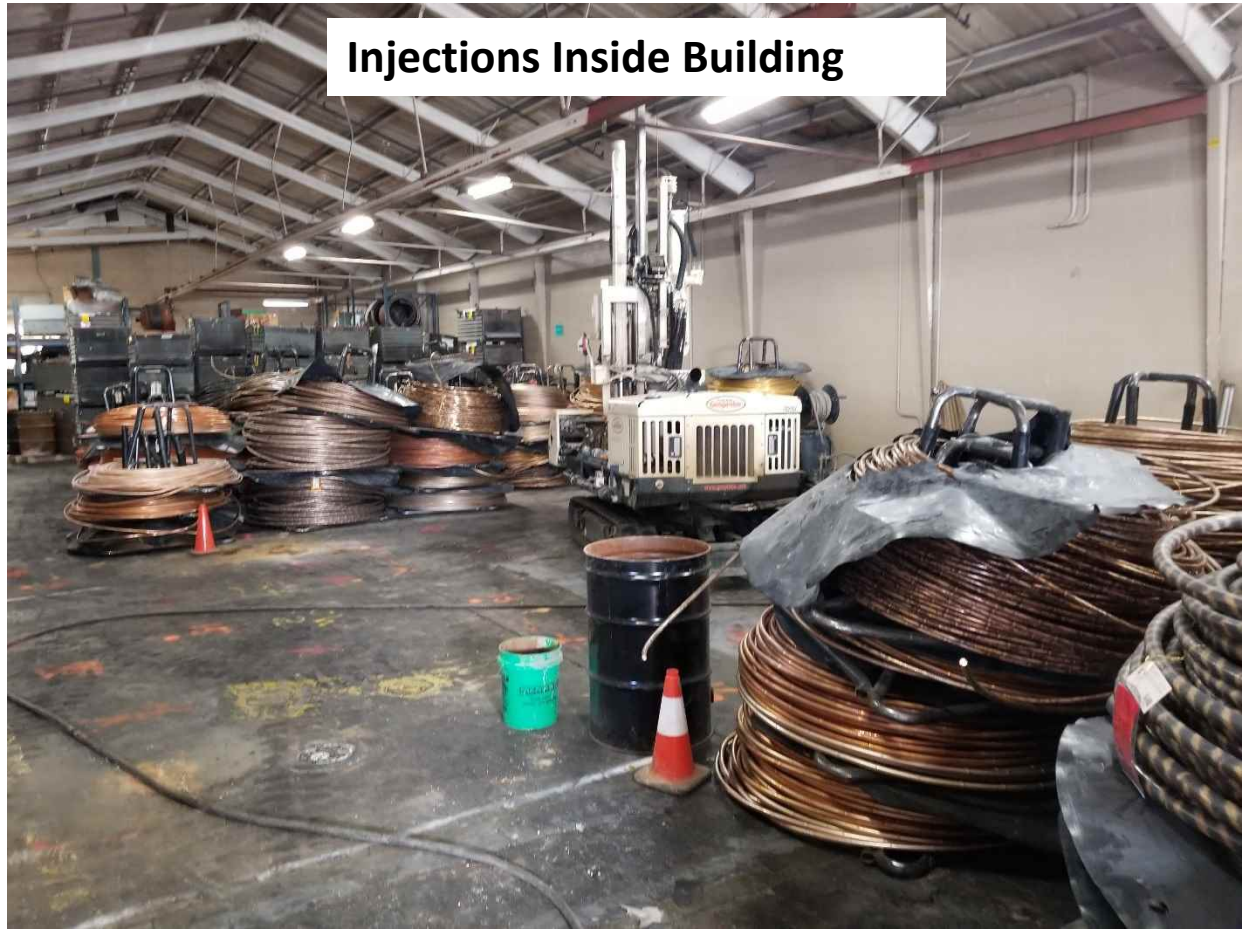
Pilot Test Treatment



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Pilot Test Treatment

- **Southwestern Pilot Test**
  - As anticipated, ISCR effective for treatment
  - Immediate reductions within 3 months
  - *Total hex chrome reduction of ~19 mg/L*

Monitoring Well Identification	Screen Interval	Remediaion Status	Sample Date	Dissolved Metals		
				Chromium	Manganese	Iron
Reporting Units				µg/L	µg/L	µg/L
MW-19/19R		Pre	4/23/18	18,900	<11.3	<155
		Post Pilot Test	7/16/18	172	948	22,400
		Post Pilot Test	8/20/18	97.6	1640	88,200
		Post Pilot Test	1/21/2019*	16.1	608	12,200

- **Northeastern Pilot Test**
  - Anaerobic bioremediation effective for treatment
  - Immediate reductions within 3 months
  - <u>Total hex chrome reduction of ~117 mg/L</u>

Monitoring Well Identification	Screen Interval	Remediaion Status	Sample Date	Dissolved Metals		
				Chromium	Manganese	Iron
Reporting Units				µg/L	µg/L	µg/L
MW-20/20R		Pre	04/23/18	296,000	<11.3	<155
		Post Pilot Test	07/16/18	161,000	99.1	929 J
		Post Pilot Test	08/20/18	174,000	73.1	156
		Post Pilot Test	1/21/2019	179,000	37.1	<35.4

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Pilot Test Treatment

- **Pilot Test Takeaways**
  - **Anaerobic bioremediation treatment has greater removal than ZVI slurry (distribution)**
  - **DVI and ZVI slurry are not optimal reductants**
    - **DVI (Ferrous Iron) was fully consumed during pilot test**
    - **ZVI Slurry – less than ideal distribution**

	Microscale ZVI	Oil Emulsion/Soluble Iron
Reactivity	Good	Good
Delivery	**High pressures induce fractures**	Low viscosity and low-pressure injection
Persistence	Good	**Limited**
Ease of Use	**Requires high pressure pumps**	Good

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Full-Scale Remedy

- **Full Scale Optimization**
  - Leverage the same electron donor for full scale treatment
    - Excellent distribution within low K formation
  - Incorporate ZVI based ISCR
    - Boost treatment strength
  - <u>Optimize ZVI Amendment</u>
    - Use colloidal, sulfidated ZVI (S-MZVI)
    - Enhanced distribution, longevity and reactivity compared to slurry ZVI

Colloidal ZVI suspension

Low pressure sandbox demo

Commodity ZVI Slurry

Depiction of subsurface fractures

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Full-Scale Remedy

- **Full Scale Results**
  - 99% reduction achieved and maintained in all monitoring wells
  - Treatment effective across entire concentration spectrum
  - Treatment removal increased by ~150%
- **NFA Granted**
  - Regulators issued closure for hex chrome following full-scale remedy
    - PFAS investigation ongoing

Monitoring Well Identification	Screen Interval	Remediation Status	Sample Date	Dissolved Metals			Field Parameters					
				Chromium	Manganese	Iron	Temperature	pH	Specific Conductance	Oxidation Reduction Potential	Turbidity	Dissolved Oxygen
Reporting Units				µg/L	µg/L	µg/L	Celsius	S.U.	mS/cm	mV	NTU	mg/L
NR 140 Enforcement Standard (ES)				100	300	300*						
NR 140 Preventative Action Limit (PAL)				10	60	150*						
MW-20/20R	5.1 - 15.1	Pre	06/28/17	265,000	NA	NA	NA	NA	NA	NA	NA	NA
			08/31/17	331,000	NA	NA	NA	NA	NA	NA	NA	NA
			04/23/18	296,000	<11.3	<155	15.73	7.21	2.70	282	50.4	NA
		Post Pilot Test	07/16/18	161,000	99.1	929 J	20.33	7.10	2.73	78	47.8	8.76
			08/20/18	174,000	73.1	156	19.93	7.54	2.52	103	0.0	10.05
			01/21/19	179,000	37.1	<35.4	17.09	8.20	2.55	126	1.9	5.02
		Post Full-Scale	04/10/20	7.0	114	9,250	17.90	7.48	1.41	-114	149	1.47
			06/30/20	10.9	166	23,000	20.62	6.98	2.25	-102.7	934	1.01
			09/29/20	16.7	178	17,800	20.36	7.09	2.15	-78.4	57.8	0.69
DUP-1			09/29/20	22.8	179	17,200	NA	NA	NA	NA	NA	NA
MW-20R			12/29/20	<3.9	160	1,950	15.24	7.02	2.41	-81.9	235.4	4.09
			03/17/21	145	328	23,100	16.41	7.14	2.17	-51.2	59.96	2.58
			07/07/21	4.9 J	130	10,700	20.68	7.14	2.10	-80.6	36.16	4.60

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Conclusions

- **In-Situ Metals Immobilization for Cr(VI) is highly effective**
  - **Offers immediate and long-term treatment without site disruption**
- **Combining ISCR and Anaerobic Bioremediation is recommended**
  - **Leverage both treatment technologies when possible**
- **ISCR selection is key for optimization**
  - **ZVI based ISCR is recommended – greater strength and quicker transformation to trivalent chromium**
  - **Mobility, reactivity, longevity and overall treatment is enhanced with colloidal iron**

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Questions?

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