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Using "Stacked Fractures" to Increase Oxidant Loading to Subsurface for VOC and 1,4-Dioxane Treatment

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Agenda

- Site Description
- Technology Overview
- Pre-Pilot Activities
- Pilot Planning and Implementation
- Post-Fracturing Investigation
- Performance Monitoring
- Troubleshooting
- Summary

Site Description

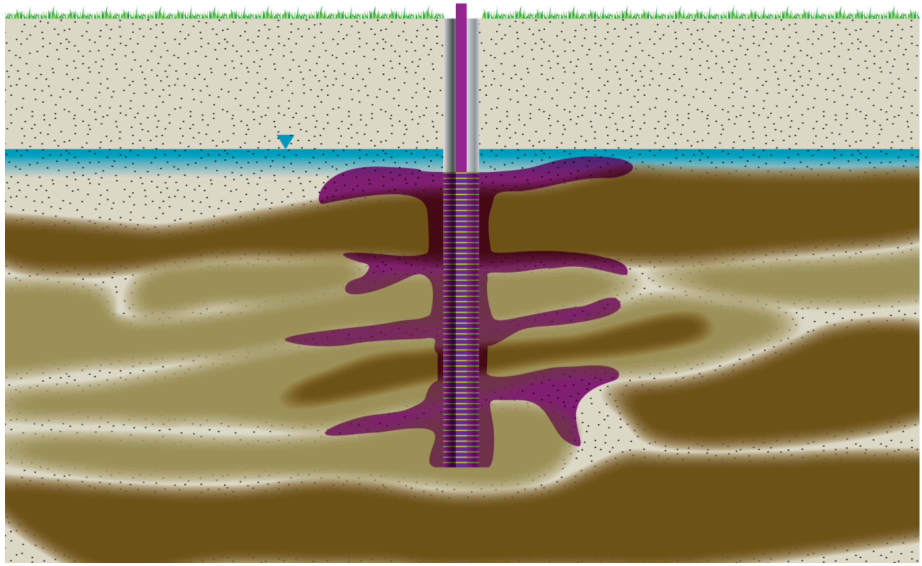
- Historical releases of VOCs and 1,4-dioxane
  - 1,4-dioxane up to 1,000 µg/L
  - PCE up to 5,000 µg/L
- Paleochannel impacts (water user)
  - 1,4-dioxane GW standard is 0.35 µg/L
- Previous AS/SVE (1990's) and ISCO (2000's)
- Hydrogeological challenges in source area
  - Target interval ~40-55' below ground
- FFS: RAOs, technology screening, and preferred alternative
  - Slow-release ISCO via fracturing
  - Treat source material before paleochannels

Why Slow-Release ISCO / Fracturing?

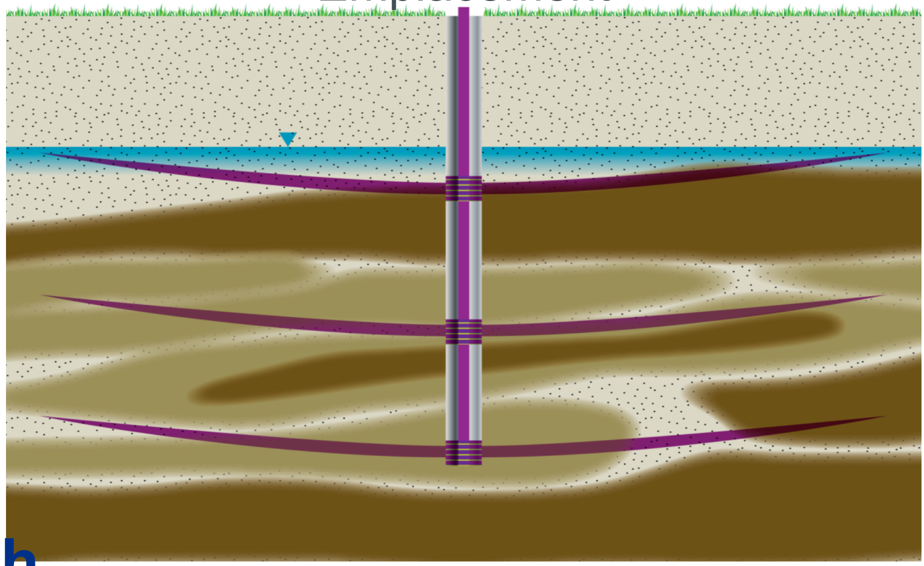
- ISCO can treat CVOCs and 1,4-dioxane
  - ISCO (modified Fenton's) destroyed contaminants previously
    - Rebound consistently observed (9 injection events)
  - In situ biological treatment of 1,4-dioxane is limited to date
  - Other options (thermal, extraction & treatment) cost prohibitive
  - Persulfate oxidant needs to be activated

- Fracturing has multiple benefits
  - DPT friendly application
  - Deliver oxidant (and pH activator) to low permeability units
  - Can "focus" treatment in individual depth intervals
  - Use of solid persulfate with hydrated lime – both will slowly release to aquifer
  - Allows for long-term treatment in one application (1-2 years)
  - Treatment in fewer points due to large treatment radius (15-25 feet)

Liquid Injection



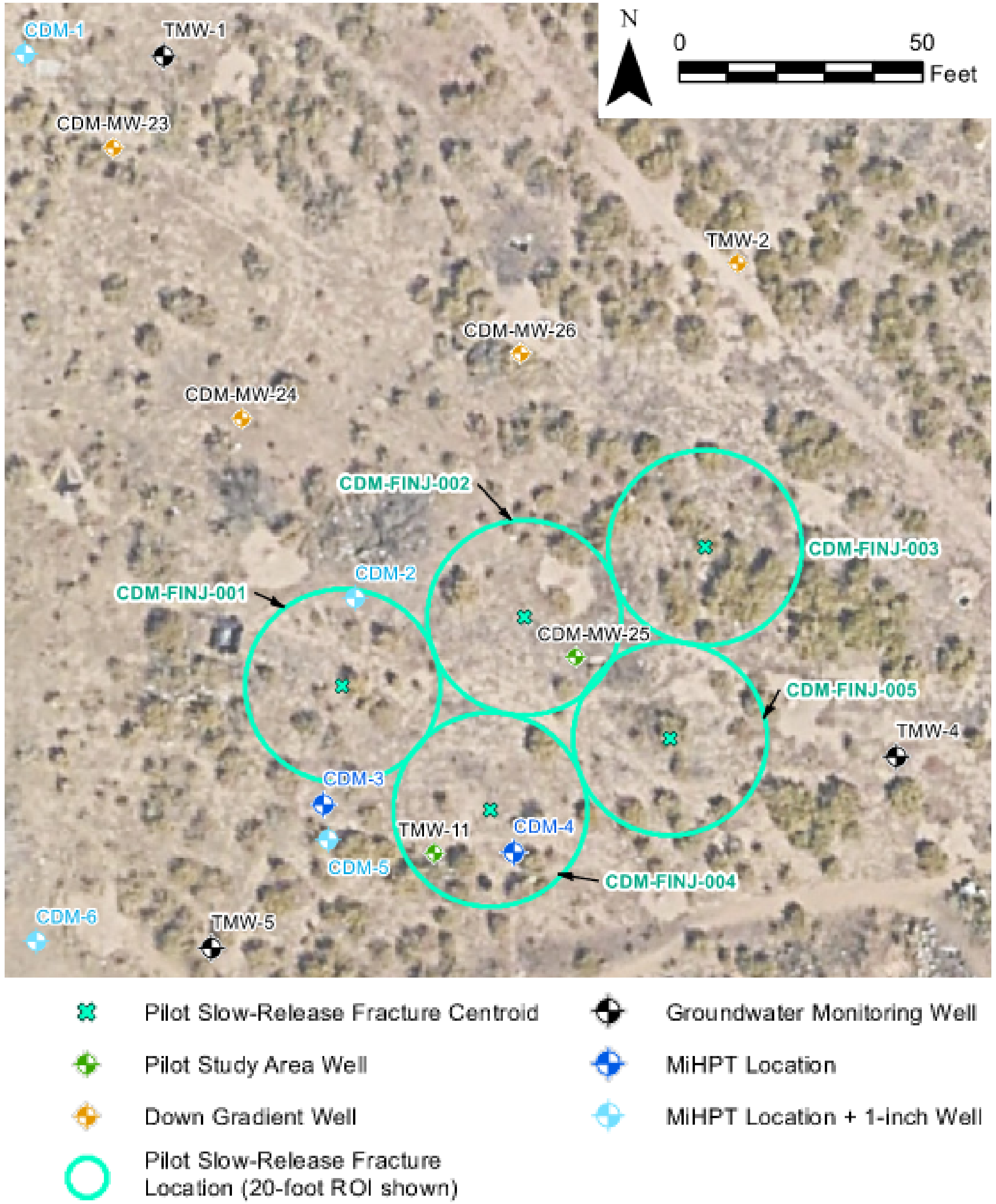
Fracturing – Solid Phase Emplacement



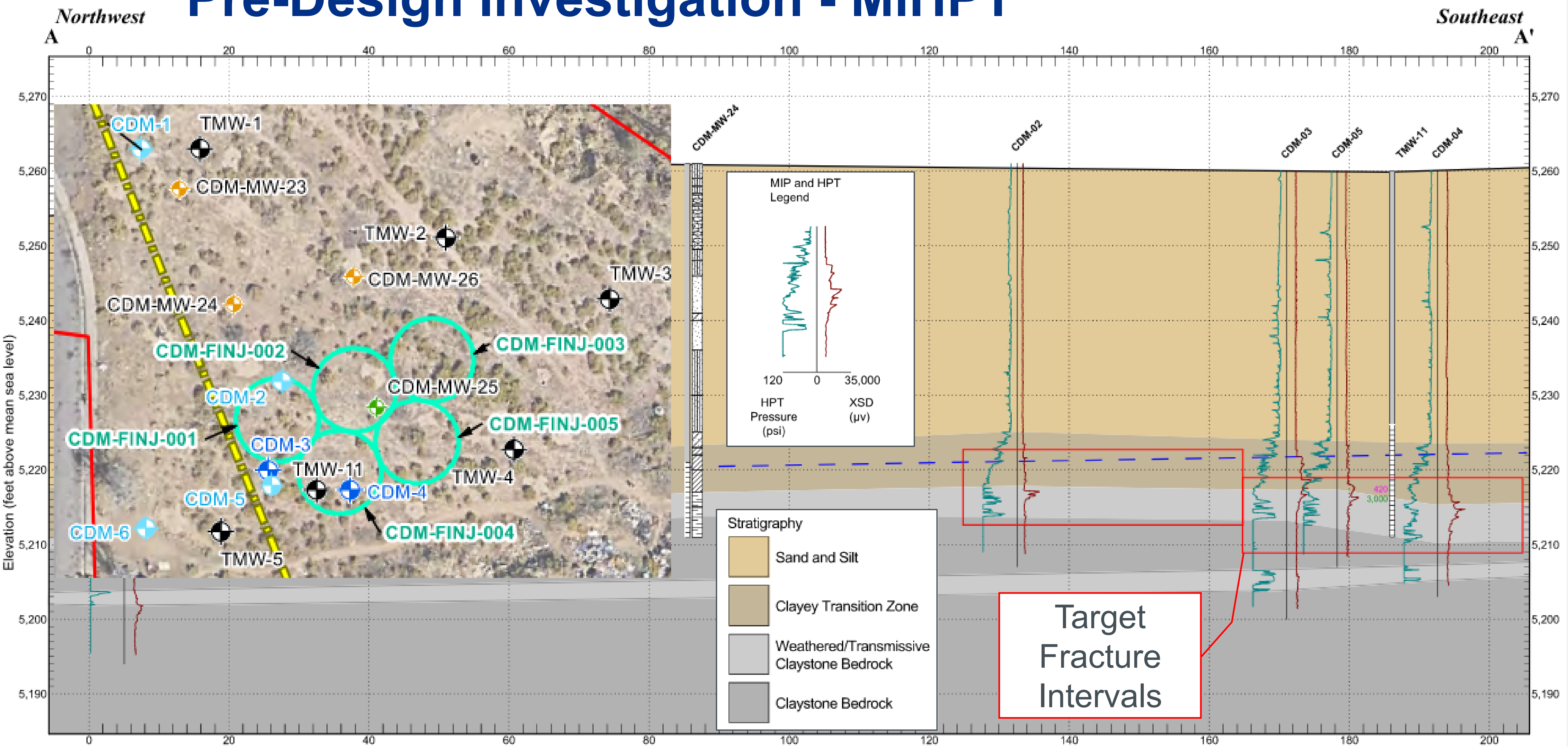
Pilot study recommended to evaluate this approach

Pre-Pilot Characterization

- MiHPT investigation (light blue / blue labels)
  - Target vertical treatment intervals (based on PID/XSD)
  - HPT to understand vertical conductivity changes
  - Electrical conductivity for baseline (to compare to post-pilot)
- Temporary Monitoring Wells (light blue labels)
  - Based on MiHPT results
  - Used to delineate 1,4-dioxane (and VOC) in groundwater
- New Permanent Monitoring Wells
  - 4 in pilot study area
  - 1 downgradient for plume delineation
- Soil oxidant demand and pH buffer capacity test
  - Collected soil from CDM-MW-23
  - Collected water from TMW-7 (not shown – south of figure)



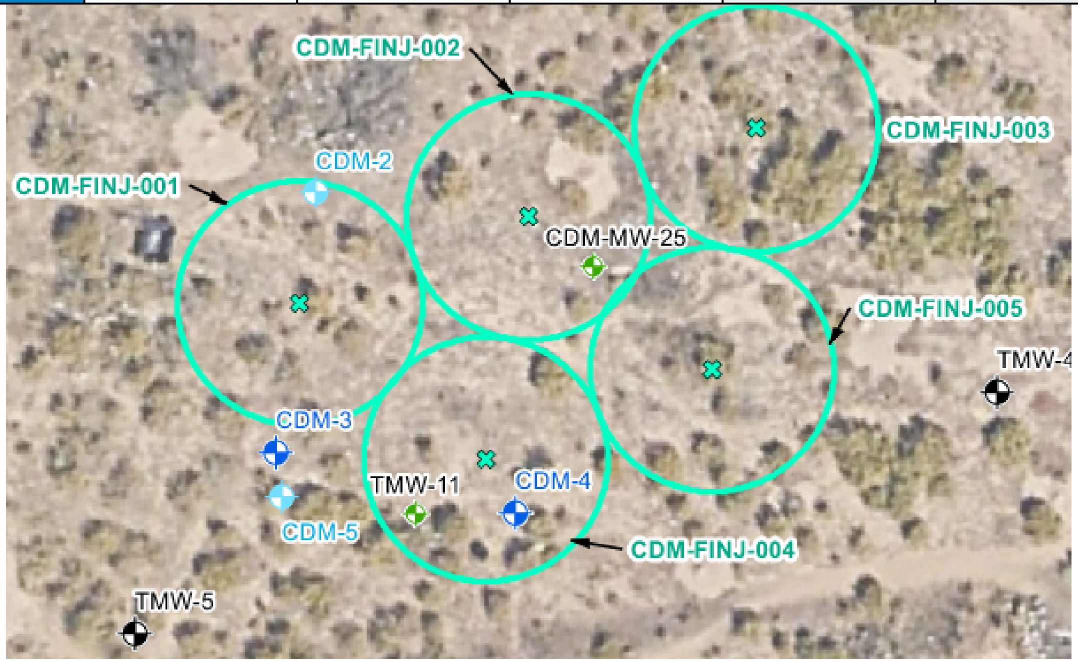
Pre-Design Investigation - MiHPT



Pilot Implementation – Design

- 5 fracture locations
- Target 20-ft radius
- 4 vertical intervals / location
  - Intervals optimized based on MiHPT
- 1,100 lb persulfate (KP) / 500 lb hydrated lime (HL) per frac
- Highly viscous slurry – toothpaste consistency
- 8 intervals “stacked” (doubled treatment in same interval)
  - Performed to increase KP/HL mass in intervals

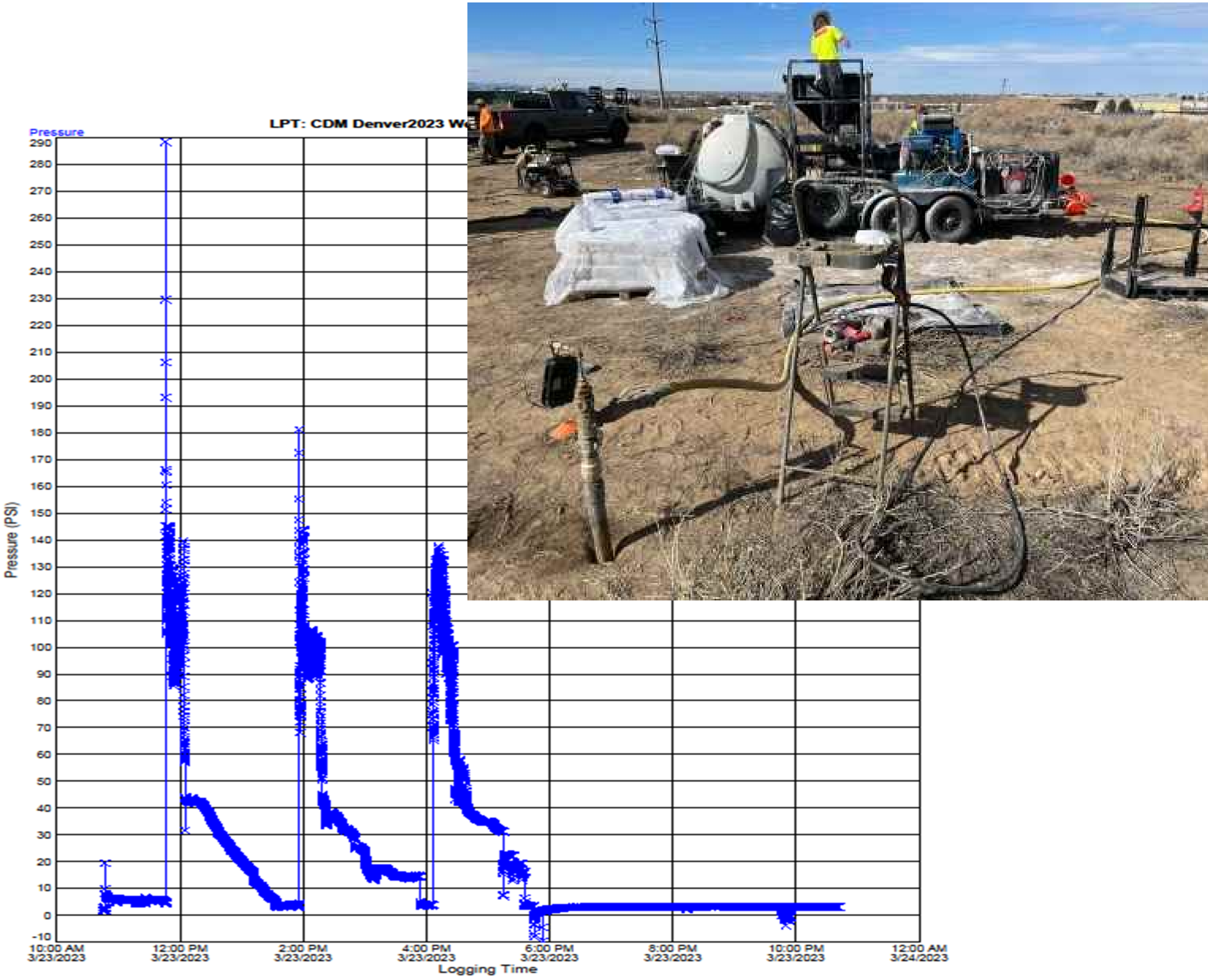
Fracture / Injection ID	CDM-FINJ-001	CDM-FINJ-002	CDM-FINJ-003	CDM-FINJ-004	CDM-FINJ-005
38-41 ft bgs	X	X	X		
40-43 ft bgs				X	X
41-44 ft bgs	X	X	X		
43-46 ft bgs				X	X
44-47 ft bgs Stacked	X X	X X	X X		
46-49 ft bgs Stacked				X X	X X
47-50 ft bgs Stacked	X X	X X	X X		
49-52 ft bgs				X	X



Pilot Implementation – Performance Summary

- "Notching" performed prior to fracturing
- All 28 fractures successfully performed
  - Stacked fractures all performed without incident
- Max pressures ranged from 100 – 280 psi
  - No surfacing occurred
- 30,856 lb KP and 14,000 lb HL added
- 7,300 gallons injected (180 – 300 gallons per interval)
- Injections lasted 15 to 40 minutes

Pilot implementation successful



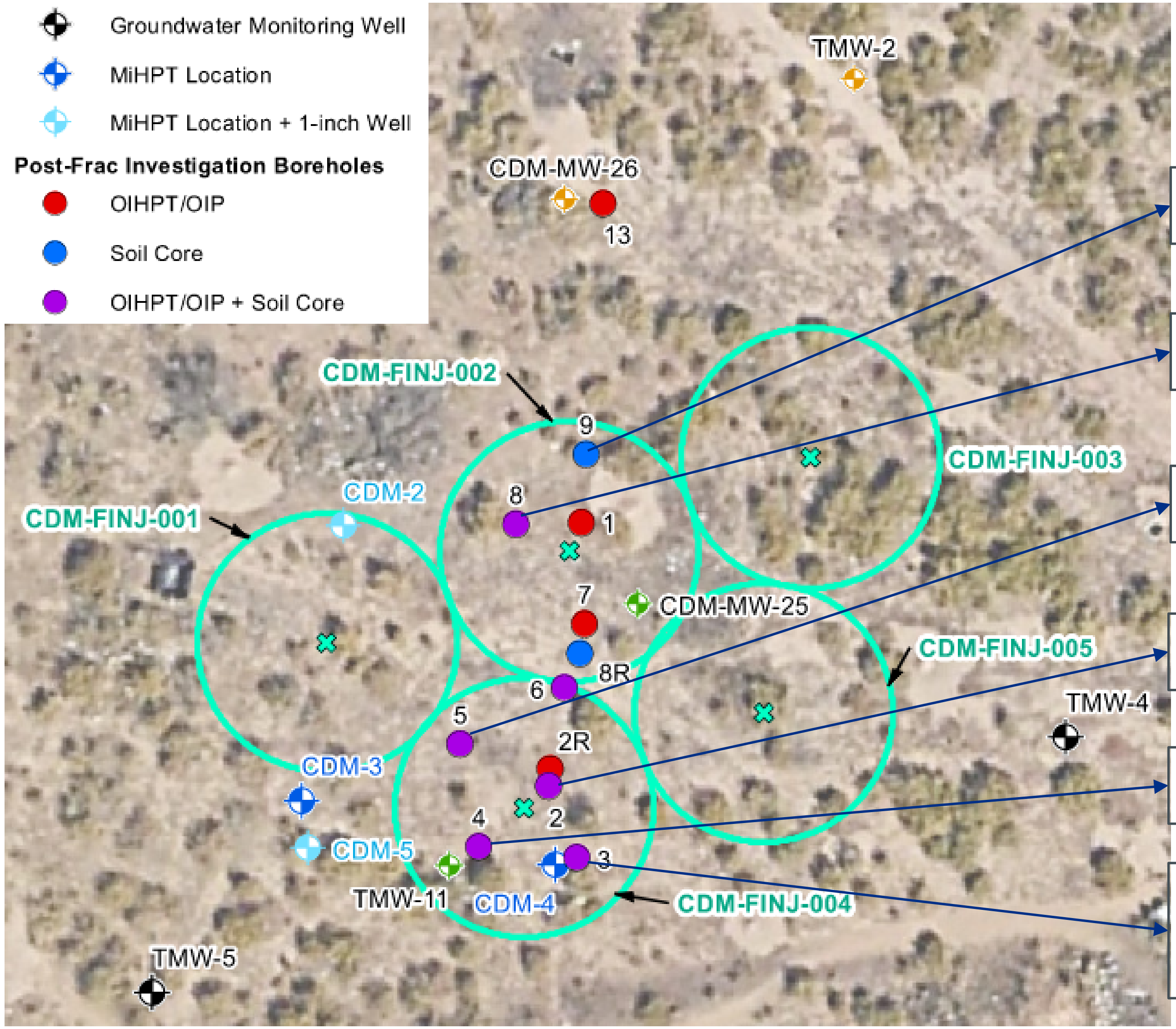
Pressure curves from 3 fracture intervals

Post-Fracturing Investigation Tools

- Soil Sampling and soil pH measurement
  - Visual inspection of soil core → identification of fracture locations
  - Field pH test → confirmation of slurry distribution (pH ~ 12)
- High Resolution Tools
  - Optical Interface Profiler (OIP)
    - Photos using visible light → visual identification of amendment slurry
  - Hydraulic Profiling Tool (HPT)
    - Inject water, measure pressure → relative hydraulic conductivity measurement to identify permeability improvements
  - Electrical Conductivity (EC) probe
    - Clear change in conductivity (grain size, salts) → identification of slurry

All done concurrently using DPT

Post-Fracturing Investigation – Soil Results



Fractures identified in 6 of soil 8 investigation locations

#9 – 16’ from FINJ-002 (5mm @ 48’ bgs)

#8 – 12’ from FINJ-002 (10mm @ 39’ bgs)

#5 – 16’ from FINJ-004 (3mm @ 48’ bgs)

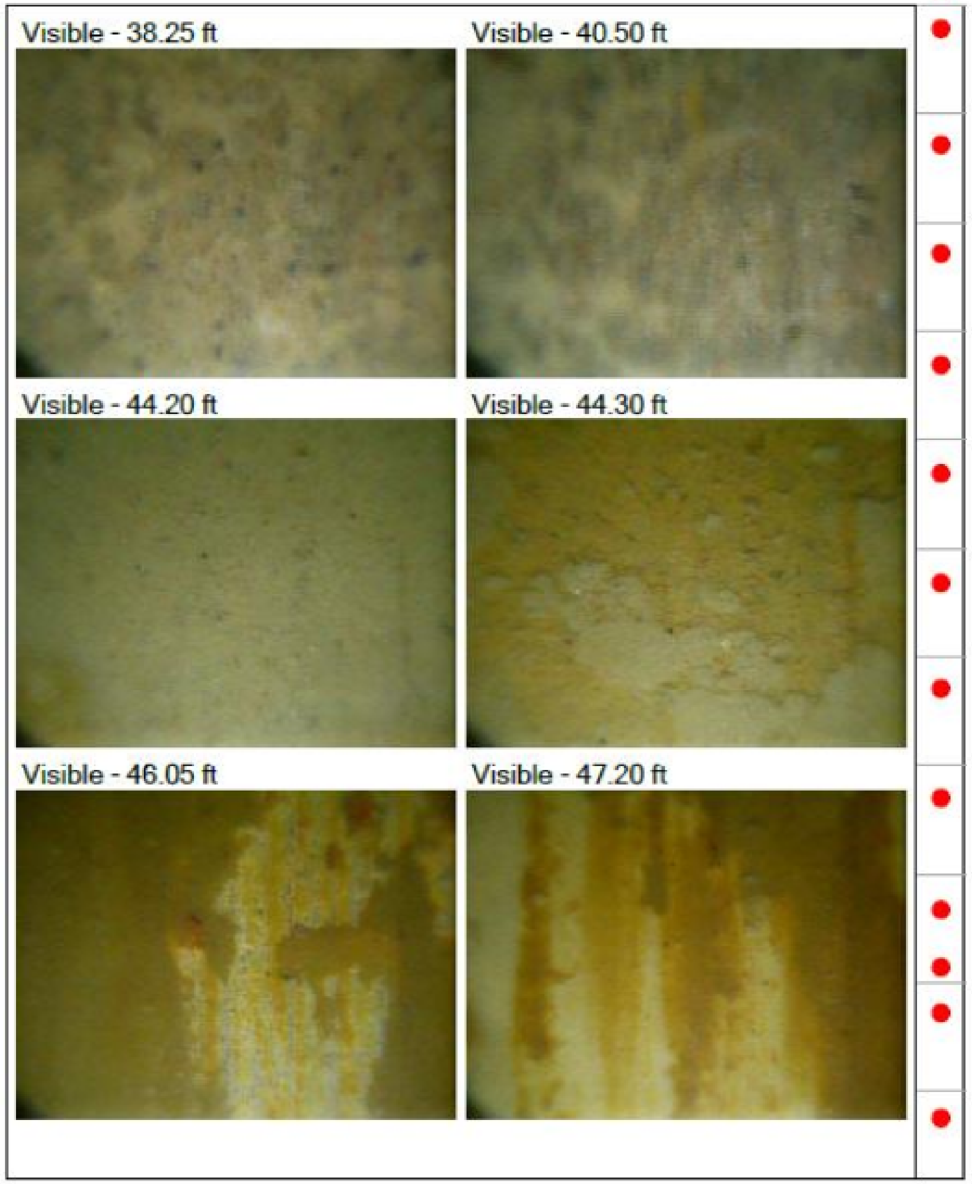
#2 – 4’ from FINJ-004 (5mm @ 50’ bgs)

#4 – 12’ from FINJ-004 (3mm @ 48’ bgs)

#3 – 8’ from FINJ-004
(1mm @ 37’ and 3mm @ 48’ bgs)

Post-Fracturing Investigation – OIP Results

- White mass identified in multiple vertical intervals and initially thought to be white oxidant slurry
- Observed thicknesses (> 20 mm) much higher than fracture thicknesses
- OIP results did not match with visual observations in soil samples
- Background Location 13 showed white mass in multiple intervals
- OIP RESULTS NOT USED



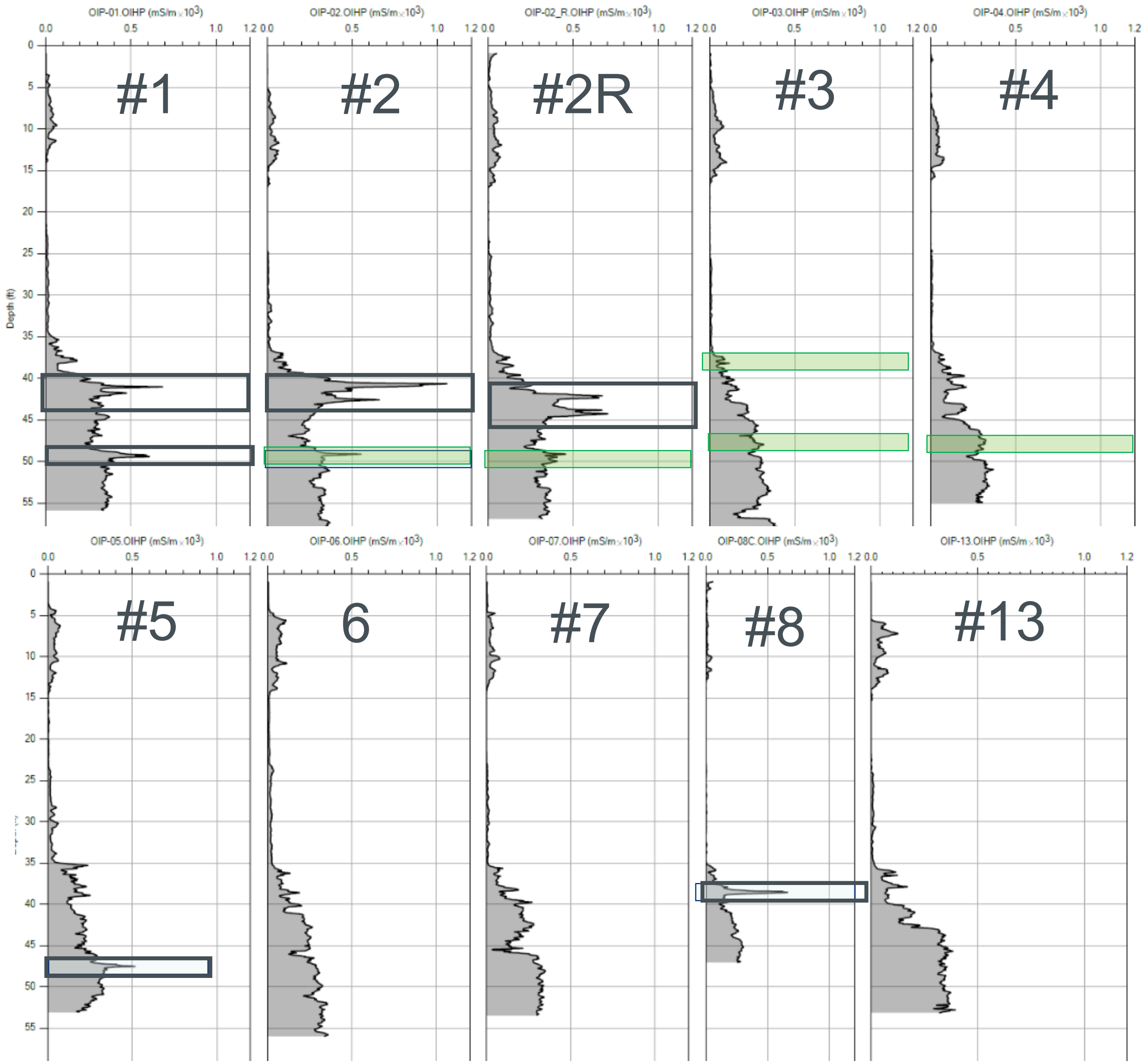
Location 5

Post-Fracturing Investigation - EC Results

- Significant EC spikes corresponded with some visual soil confirmations
  - #2, #5, #8
- EC spikes in #1, #2/2R not identified in soil cores may indicate fractures

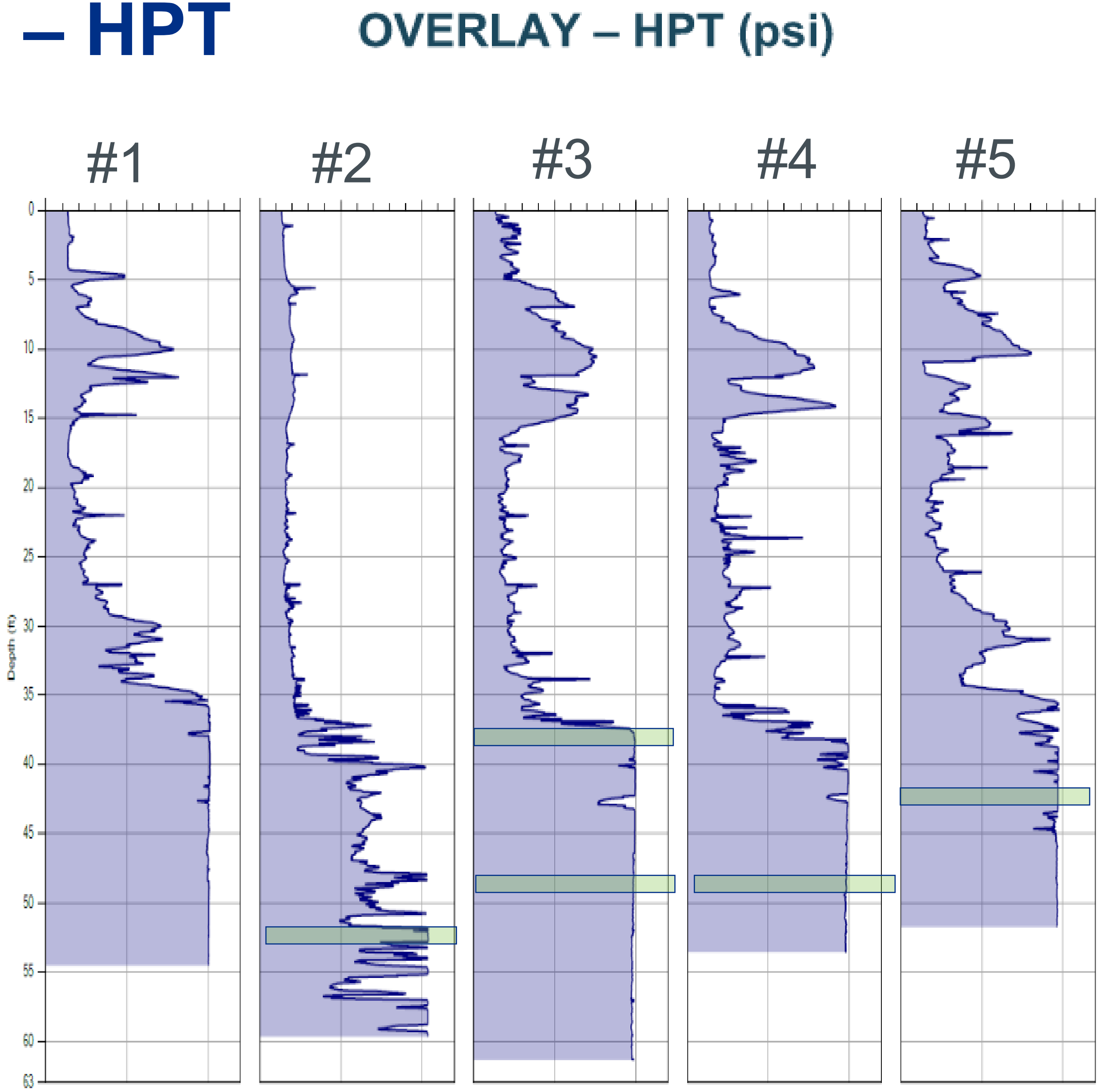
Note:
Green shading – soil confirmation of fractures
Dark outline – EC spikes

OVERLAY – EC (mS/m)



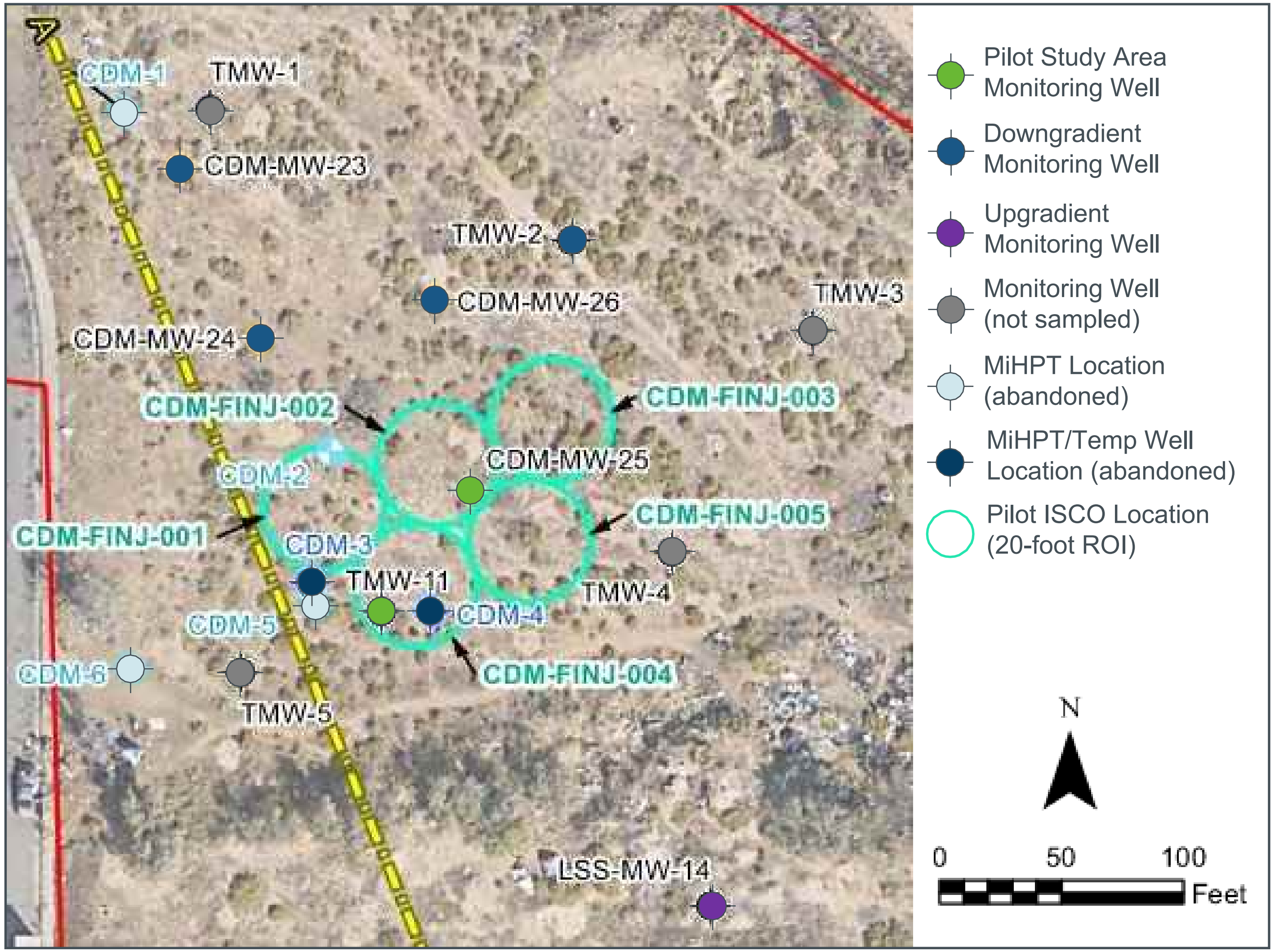
Post-Fracturing Investigation – HPT Results

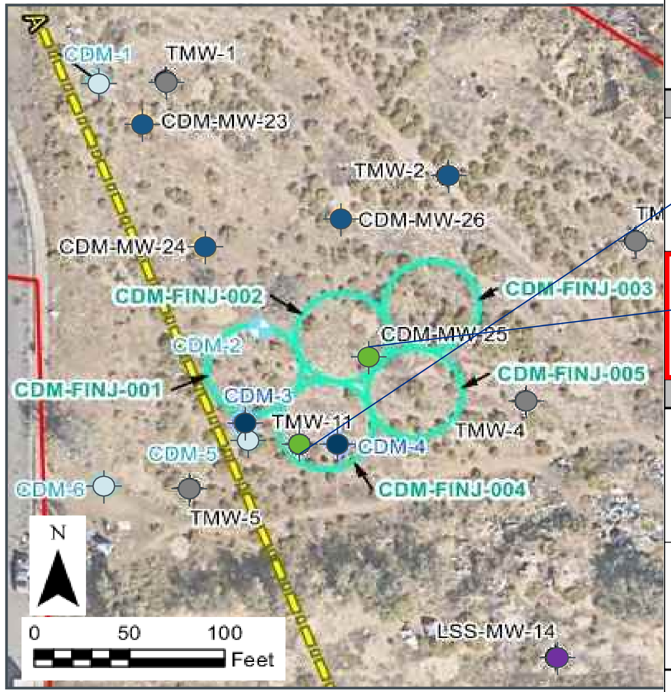
- No real correlation with HPT results and soil confirmations (green shaded intervals)
- HPT stopped because the injected water was smearing OIP
- Oxidant slurry was not expected to increase hydraulic conductivity



Groundwater Performance Monitoring

- Monitoring Events
  - Baseline
  - 1-month
  - 3-month
  - 6-month
- 7 monitoring wells
- Parameters
  - COCs: VOCs & 1,4-dioxane,
  - Oxidant distribution: Persulfate, potassium, DO, ORP, pH
  - Other: bromide, sulfate, chromium

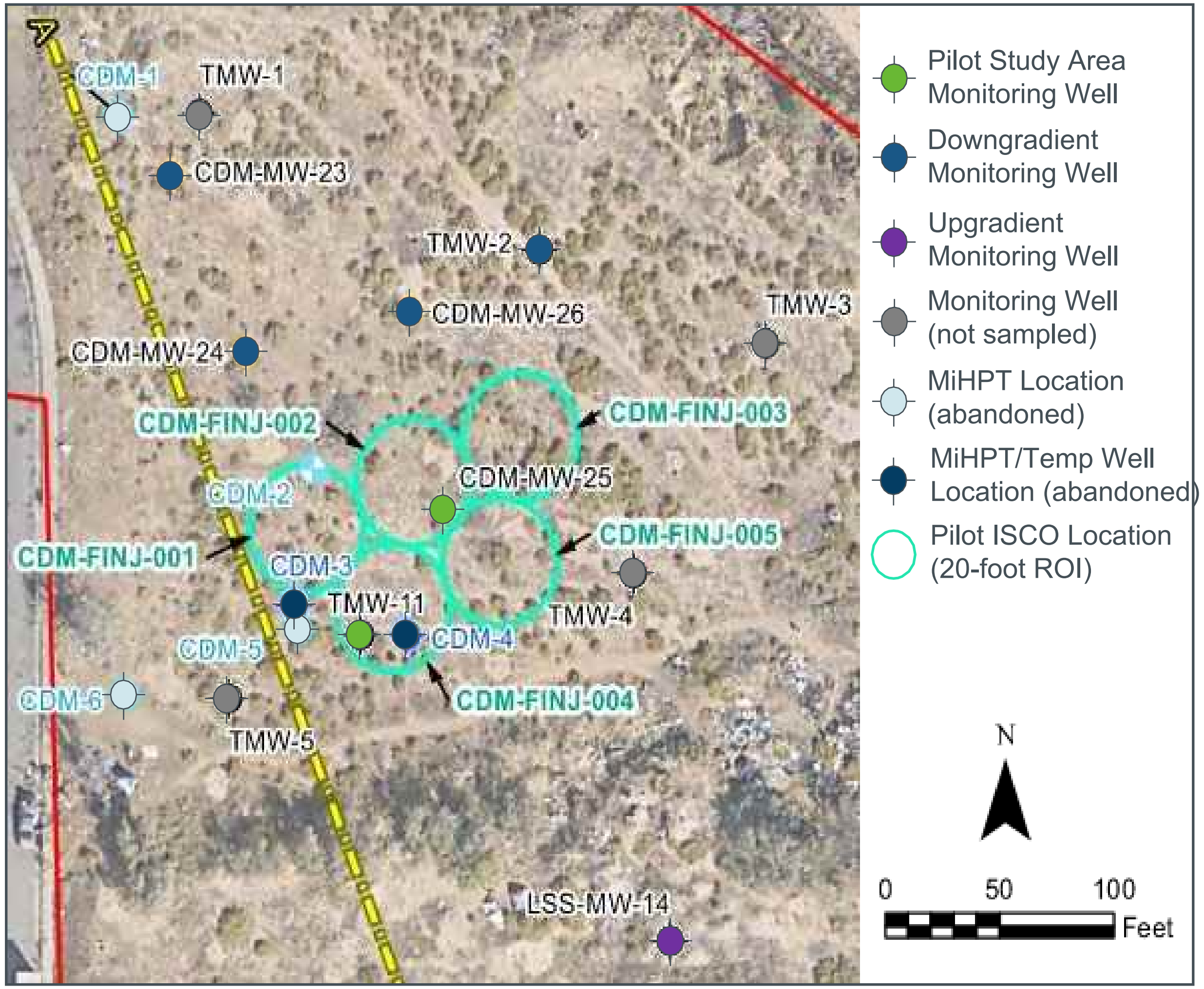




Well ID	Sample Event	Sample Date	Water Quality: Water Level	Temperature	Specific Conductance	Dissolved oxygen (DO)	pH	Oxidant Reduction Potentia	Turbidity	Analytical Parameters: Persulfate	1,4-Dioxane	Q	Tetrachloroethene (PCE)	Q	Bromide	Q	Sulfate	Q	Potassium	Q	Chromium	Q	Hexavalent Chromium	Q
		Units:	ft btoc	deg C	µS/cm	mg/L	PH	mV	NTU	mg/L	ug/L	Q	ug/L	Q	mg/L	Q	mg/L	Q	ug/L	Q	ug/L	Q	mg/L	Q
Upgradient Background Well																								
LSS-MW-14	Baseline	03/15/23	48.80	13.9	1,374	3.6	7.47	42	7.05	0	8.4		1,100		0.57	F1	220	F1	3,800		1.6	J	NS[3]	
	1-month	04/25/23	48.73	14.0	1,021	6.4	7.43	200	3.26	0	10		1,300		1.1		210		3,500		1.8	J	NS[3]	
	3-month	06/28/23	48.65	16.7	1,291	3.5	7.65	63	9.89	0.0-0.7	7.5		870	J+	0.5	U	210		3,800		3		NS[3]	
	6-month	10/03/23	48.51	15.3	1,272	5.8	7.4	33	30.7	1.4	21		990	D	0.5	U	190						NS[3]	
Pilot Study Area Wells																								
TMW-11	Baseline	03/15/23	40.7	12.5	2,108	4.4	7.17	176	NS[1]	NS[1]	69		3,000		0.81		520		NS[1]		NS[1]		NS[3]	
	1-month	04/26/23	40.71	10.4	43	11	7.13	278	NS[1]	2,020	75		1,100		NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
	3-month	06/28/23	40.72	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	770	97		1,300	J+	NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
	6-month	10/03/23	40.94	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	1.7	150		520	J	NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
CDM-MW-25	Baseline	03/15/23	40.79	14.1	2,301	4.3	7.27	105	1.56	0	110		3,500	J	0.74		470		4,400		0.89	J	NS[3]	
	1-month	04/25/23	41.26	11.7	6,051	37	7.35	393	NS[2]	4,990	48		1,200		0.5		210		1,200,000		81		NS[3]	
	3-month	06/27/23	41.68	19.9	3,977	18	7.36	368	1.29	4,790	110		1,600	J+	0.5	U	870		500,000		71		0.03	
	6-month	10/02/23	41.84	19.5	2,987	10	7.8	347	1.23	4,800	140		2,000		0.5	U	690						0.04	
Downgradient Monitoring																								
CDM-MW-23	Baseline	03/15/23	42.43	15.9	1,796	1.4	7.08	77	0.54	0	77		2,600		0.5		230		3,400		1.2	J	NS[3]	
	1-month	04/25/23	43.29	14.1	1,355	1.5	7.01	318	NS[2]	0	89		3,500		0.61		410		3,100		1.4	J	NS[3]	
	3-month	06/27/23	43.95	18	1,685	2.9	7.1	179	0.17	0	95		1,900	J+	0.24	J	220		3,300		1.3	J	NS[3]	
	6-month	10/02/23	44.28	26.9	1,492	4.0	7.06	136	0.02	0	140		1,200	D	0.5	U	210						NS[3]	
CDM-MW-24	Baseline	03/15/23	40.95	11.5	1,161	0.95	7.26	146	24	0.0-0.7	69		2,300		0.52		450		4,900		2.2		NS[3]	
	1-month	04/26/23	41.62	13.6	1,354	1.6	7.07	256	NS[2]	0.7	63		3,200		0.44	J	1200		4,100	J	2.2		NS[3]	
	3-month	06/27/23	42.53	16.9	1,646	1.5	7.26	243	19.7	0	60		2,500	J+	0.5	F1	200		4,100		1.9	J	0.02	U
	6-month	10/02/23	42.8	17.5	1,617	1.7	7.15	150	0.02	0	120	J	1,700	D	0.5	F1	200						0.02	U
CDM-MW-26	Baseline	03/15/23	41.45	14.1	2,343	2.0	7.22	101	0.02	0	94		440		0.72		450		5,000		0.75	J	NS[3]	
	1-month	04/25/23	41.88	15.1	1,687	1.2	7.17	192	NS[2]	0	71	J	3,500		5.7		210		4,200		0.6	J	NS[3]	
	3-month	06/27/23	42.21	17.3	2,102	1.1	7.23	271	1.11	0.07	100		2,500	J+	0.57		370		4,600		0.76	J	0.02	U
	6-month	10/02/23	42.52	14.9	2,096	0.6	7.19	215	3.55	0	120		3,100		0.5	U	360						0.02	U
TMW-2	Baseline	03/16/23	40.33	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	120		660		NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
	1-month	04/26/23	40.43	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	140		NS[1]		NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
	3-month	6/28/2023	42.64	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	100		NS[2]		NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	
	6-month	10/3/2023	42.08	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	NS[1]	120		NS[2]		NS[1]		NS[1]		NS[1]		NS[1]		NS[3]	

Groundwater Monitoring Results

- Pilot study area – TMW-11
  - ↓ PCE (3,000 to 520 µg/L)
  - ↑ DO and ORP
  - ↙↗ Persulfate (ND to 1.7 mg/L)
- Pilot study area – CDM-MW-25
  - ↖↘ PCE (3,500 to 2,000 µg/L)
  - ↙↗ 1,4-dioxane (110 to 140 µg/L)
  - ↑ DO (supersaturated) and ORP
  - ↑ Persulfate (ND to 4,800 mg/L)
  - ↑ Potassium (0.004 to 500 g/L)
  - ↑ Total chromium (0.9 to 71 µg/L)

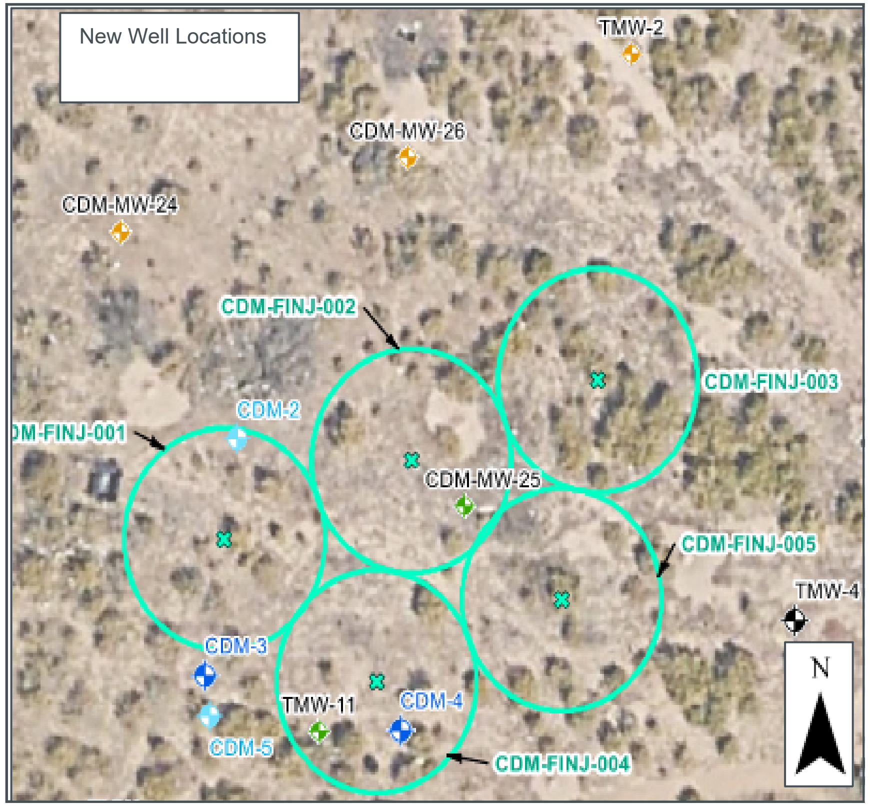


GW Performance Summary (through 6 months)

- Low recharge / limited analysis from TMW wells
- No apparent impacts outside treatment area after 6 months
- Impacts in both treatment area wells (TMW-11 and CDM-MW-25)
  - High persulfate – but 75% below saturation (appx. 20 g/L)
  - High potassium (CDM-MW-25)
  - DO and ORP increased sharply
  - PCE and 1,4-dioxane decreased by 50% in CDM-MW-25 (but has recently increased)
  - PCE decreased over 80% to 520 µg/L in TMW-11, 1,4-dioxane increased slightly to 140 µg/L
  - Elevated chromium in CDM-MW-25 (likely local phenomenon)
    - Downgradient chromium monitoring – no elevated chromium to date

Pilot Monitoring - Troubleshooting

- Likely causes for limited results to date
  - Oxidant loading and/or pH activator
  - Limited/uneven vertical and/or lateral distribution of treatment material
  - Monitoring well location(s)
  - GW velocity
- Optimized monitoring required
  - Install new wells near injection points and immediately downgradient
    - Log boreholes and ID for potential white / high pH intervals
  - Collect vertically discrete data from wells (ORP, pH, conductance)
  - If necessary -
    - Re-evaluate SOD/pH buffer capacity
    - Treatability column study
    - Dye tracer study to GW velocity



Summary

- High viscosity oxidant slurry successfully injected to low permeability groundwater
  - Mixing potassium permanganate and hydrated lime successful
- “Stacking” fractures can increase treatment loading to locations
- Electrical conductivity was an effective marker for fracture ID, OIP and HPT were not
- Existing wells were not reliable monitoring points
- More robust monitoring network required for evaluation
- Design parameters may need to be based on data collection from multiple locations

Questions?

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