

REDOX CHEMISTRY OF AQUIFER SYSTEMS IN THE PRESENCE OF RESIDUAL DRILLING FLUIDS

BY

**PATRICK LONGMIRE¹, MICHAEL DALE²,
KIM GRANZOW¹, AND STEPHEN YANICAK¹**

¹DEPARTMENT OF ENERGY - OVERSIGHT BUREAU

²HAZARDOUS WASTE BUREAU

NEW MEXICO ENVIRONMENT DEPARTMENT

1183 Diamond Dr., Suite B

Los Alamos, New Mexico 87544

Email: patrick.longmire@state.nm.us

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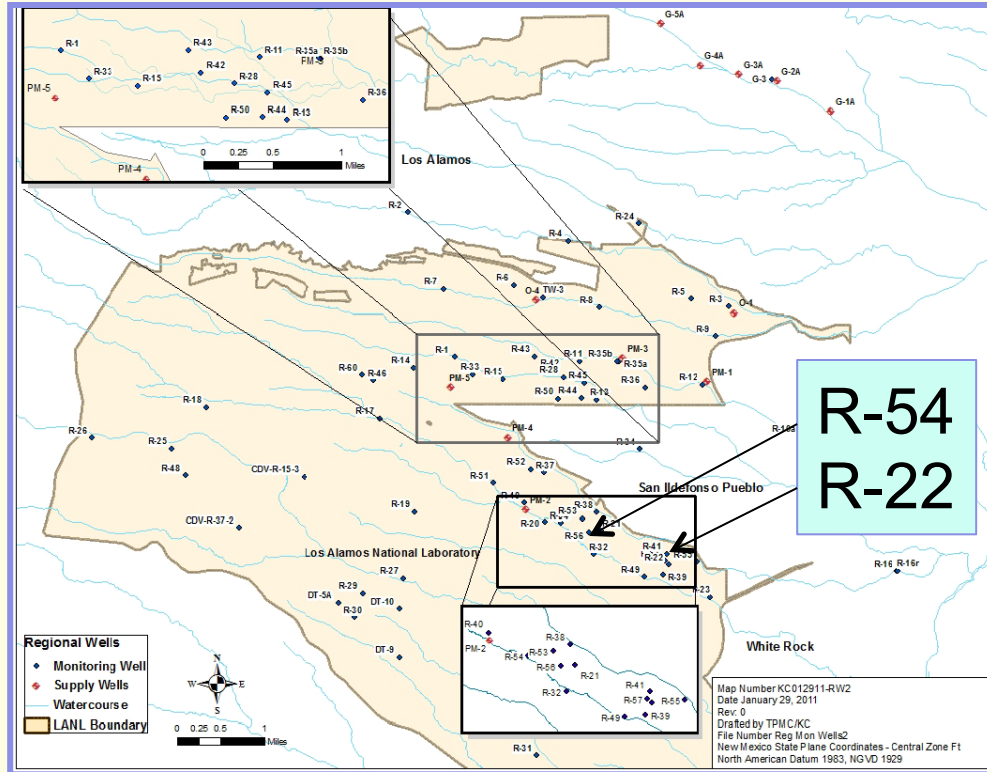
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REDOX CHEMISTRY OF AQUIFER SYSTEMS IN THE PRESENCE OF RESIDUAL DRILLING FLUIDS

- I. Introduction**
- II. Types of Drilling Fluids**
- III. Background Solute Concentrations**
- IV. Residual Drilling Fluid Impacts**
- V. Well Rehabilitation**
- VI. Summary and Conclusions**

Map Showing Monitoring Well Locations at Los Alamos National Laboratory (LANL), New Mexico



A total of 67 regional aquifer monitoring wells have been drilled at LANL since 1997. This includes 35 single screen and 32 multiscreen wells.

The regional aquifer monitoring wells exceed 300 meters in depth and are constructed of stainless steel.

Los Alamos National Laboratory

LANL Hydrostratigraphy and Reactive Solids

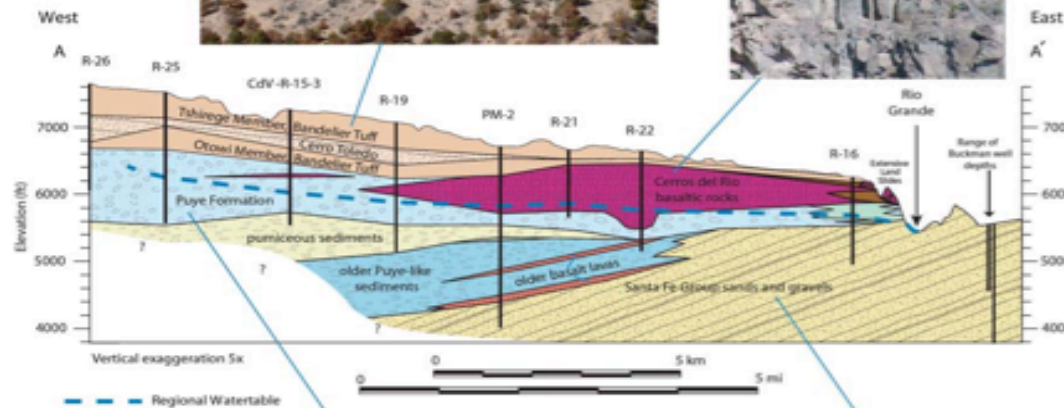
clay minerals,
 $\text{Fe}(\text{OH})_3$, zeolites

Perched Zones

Perched Zones and
Regional Aquifer

MnO_2 , clay minerals,
 $\text{Fe}(\text{OH})_3$, calcite

Well R-22, Screen 1
Well R-54, Screen 1
(Cerros del Rio basalt)



clay minerals,
 $\text{Fe}(\text{OH})_3$

Perched Zones and
Regional Aquifer

MnO_2 , clay minerals,
 $\text{Fe}(\text{OH})_3$, calcite

Regional Aquifer

Mean Background Concentrations of Redox-Sensitive Solutes and Eh for the Regional Aquifer, Los Alamos, New Mexico (NMED, 2013)

Analyte	¹ mM or ² μM	¹ mg/L or ² μg/L
ClO ₄	² 2.73e-03	² 0.27
DO	¹ 0.19	¹ 5.93
NO ₃ -NO ₂ (N)	¹ 0.03	¹ 0.44
Mn	² 0.03	² 1.82
Cr	² 0.06	² 3.12
Fe	² 0.20	² 0.27
Total CO ₃ Alkalinity	¹ 1.23	¹ 61.4
U	² 1.81e-03	² 0.43
SO ₄	¹ 0.03	¹ 2.95
Eh	Not Applicable	401 (mV)

Note: Nitrate-nitrite (412 analyses), sulfate (407 analyses), total carbonate alkalinity (409 analyses), DO (399 measurements), and Eh (367 measurements) provided by LANL. Analytical results for metals (102) provided by NMED. Mean pH = 7.84.

Typical Sequence of Drilling Fluid Use, Los Alamos National Laboratory, New Mexico

Drilling Phase

Mud Rotary-

**Drilling Fluid (Bentonite, Soda Ash, Water);
Polymer Additives (EZ-MUD®); and**

Air Rotary-

**Water; Surfactant (QUIK-FOAM, AQF-2);
Injected Polymer Additives (EZ-MUD®); and
Casing Lubricants (TORKease)**

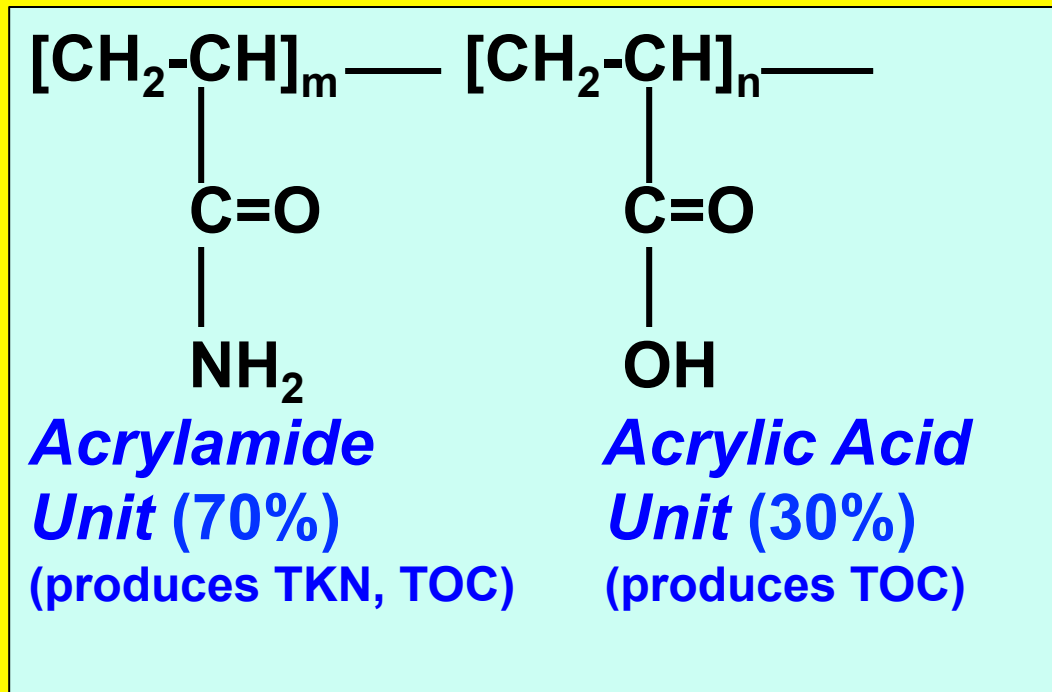
Well Construction Phase

**Annular Fill, Water, Portland Cement, Bentonite Chips
or Pellets, Polymer (EZ-MUD®)**

Well Development-Rehabilitation Phase

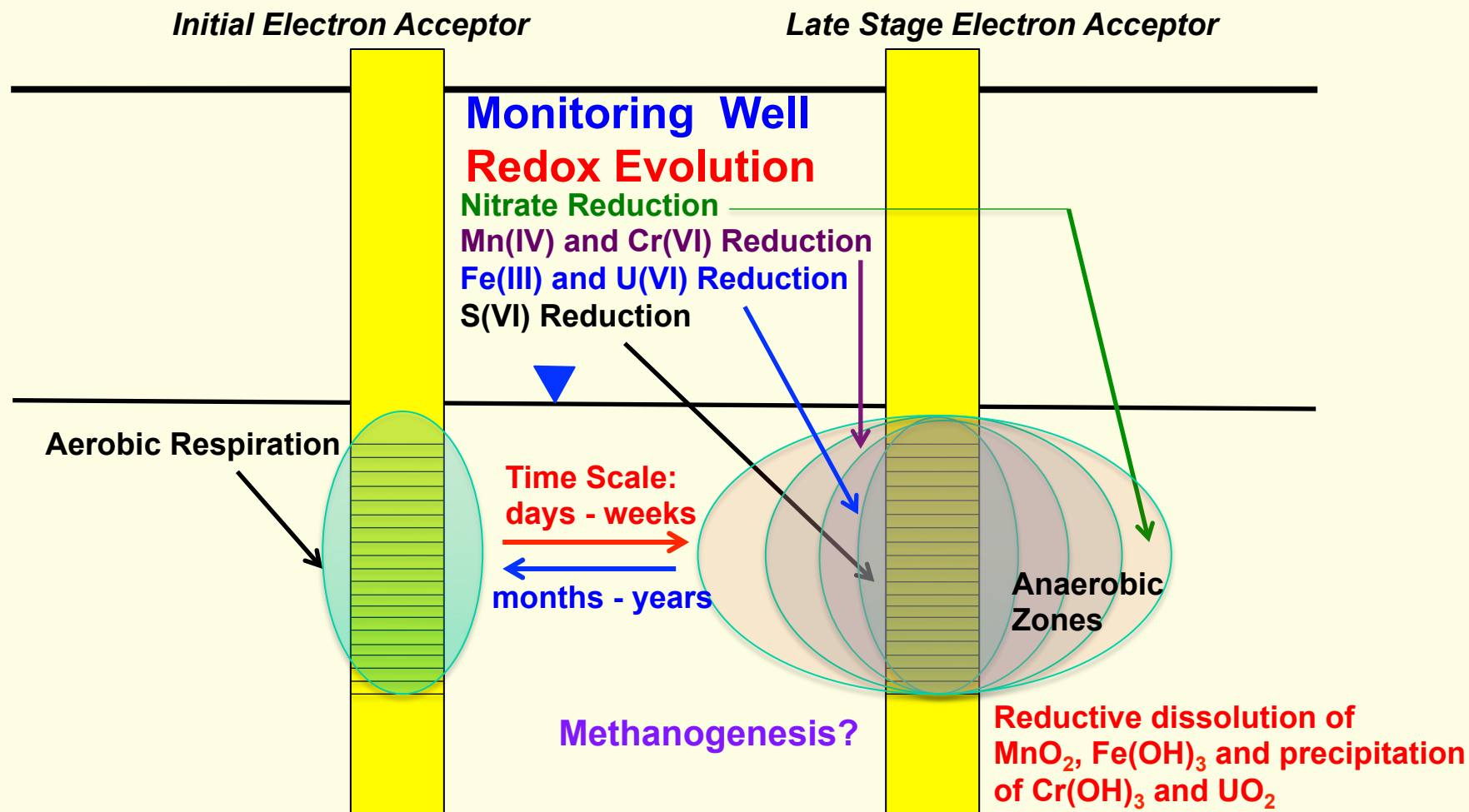
**Formation Water, Physical Methods, KOH, H₃PO₄,
Sodium Acid Pyrophosphate (SAPP)**

Chemistry of Polyacrylamide-Polyacrylate Copolymer (EZMUD®) (Longmire, 2002)



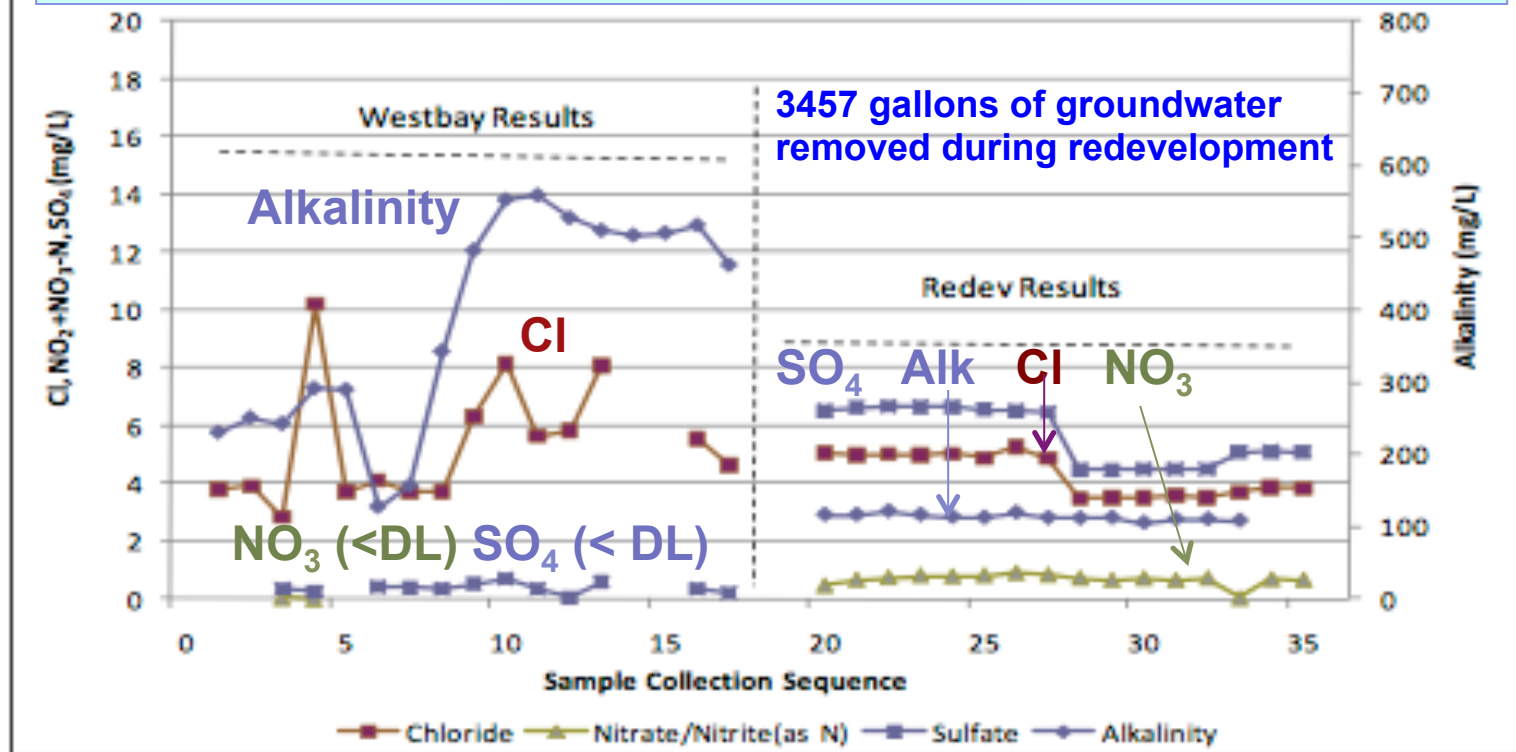
Final Oxidation Products: Ammonia, TKN, and Carbonate Alkalinity
Molecular Weight: 4 to 6 million atomic mass units

Conceptual Model of Electron Acceptor Zones Surrounding a Monitoring Well Containing Residual Organic Drilling Fluids



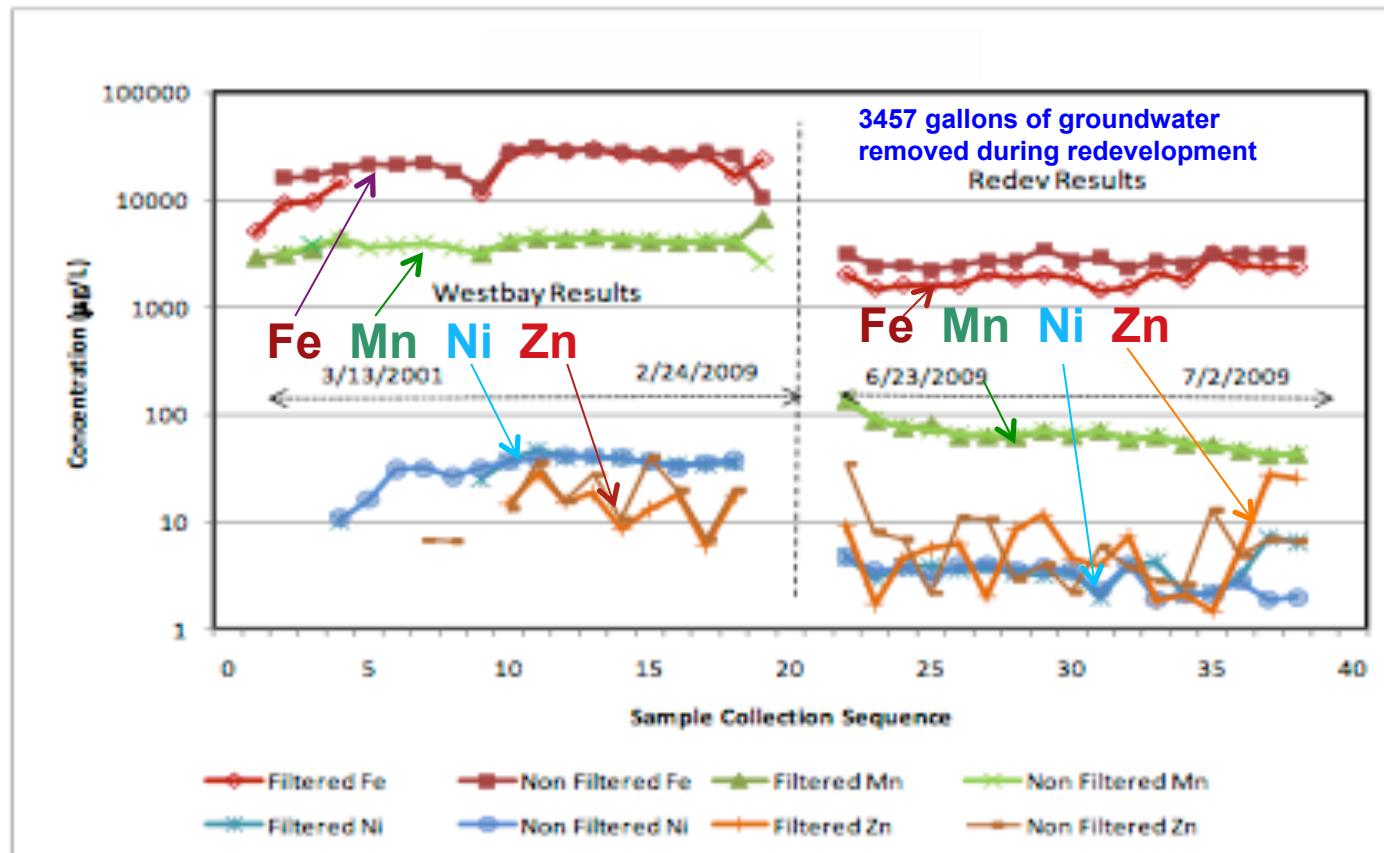
Concentrations of Dissolved Anions at Regional Aquifer Well R-22, Screen 1, From 2001 to 2008 (Longmire, 2002; LANL, 2009)

Non-Impacted Groundwater: Alkalinity, 61 – 68 mgCaCO₃/L; Cl, 2.21 – 3.71 mg/L; NO₃, 0.49 – 0.61 mg/L; and SO₄, 2.53 – 3.21. Well R-57, Screen 1



Note: Total carbonate alkalinity (CO₃²⁻+HCO₃⁻), chloride (Cl⁻), sulfate (SO₄²⁻), nitrite+nitrate (as N) (NO₂⁻+NO₃⁻-N) during characterization sampling using Westbay equipment (March 2001–September 2008) and during redevelopment (June and July 2009).

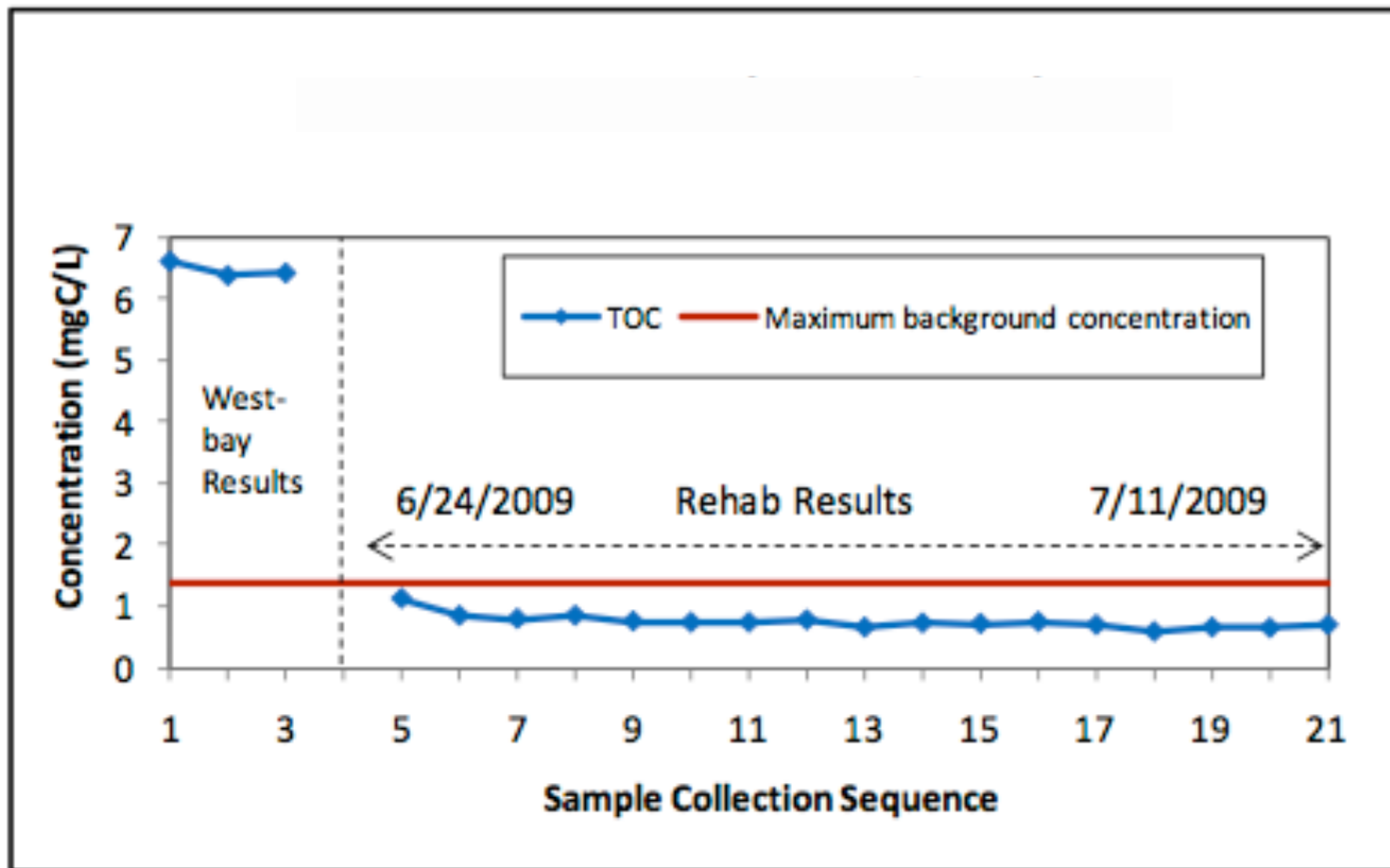
Concentrations of Dissolved Metals at Regional Aquifer Well R-22, Screen 1, From 2001 to 2008 (Longmire, 2002; LANL, 2009)



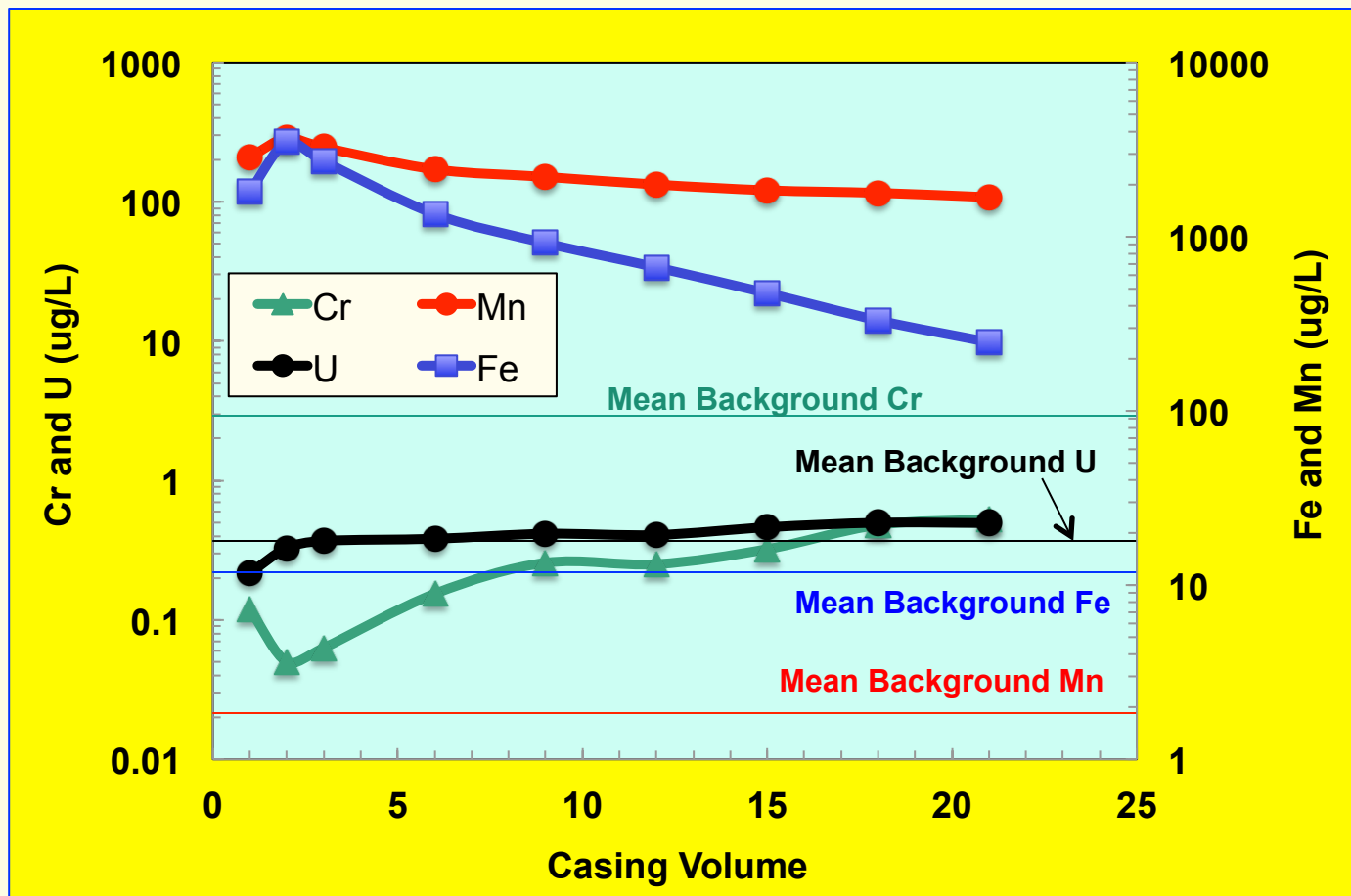
Note: Dissolved (filtered) and total (nonfiltered) concentrations of iron (Fe), manganese (Mn), nickel (Ni), and zinc (Zn) during characterization sampling using Westbay equipment (March 2001–September 2008) and during redevelopment (June and July 2009).

Non-Impacted Groundwater: Fe, $<10 \mu\text{g/L}$; Mn, 17.9 – 44.2 $\mu\text{g/L}$; Ni, 1.06 – 1.20 $\mu\text{g/L}$; and Zn, 4.2 – 6.48 $\mu\text{g/L}$. Well R-57, Screen 1

Concentrations of Total Organic Carbon at Regional Aquifer Well R-22, Screen 1 (Longmire, 2002; LANL, 2009)

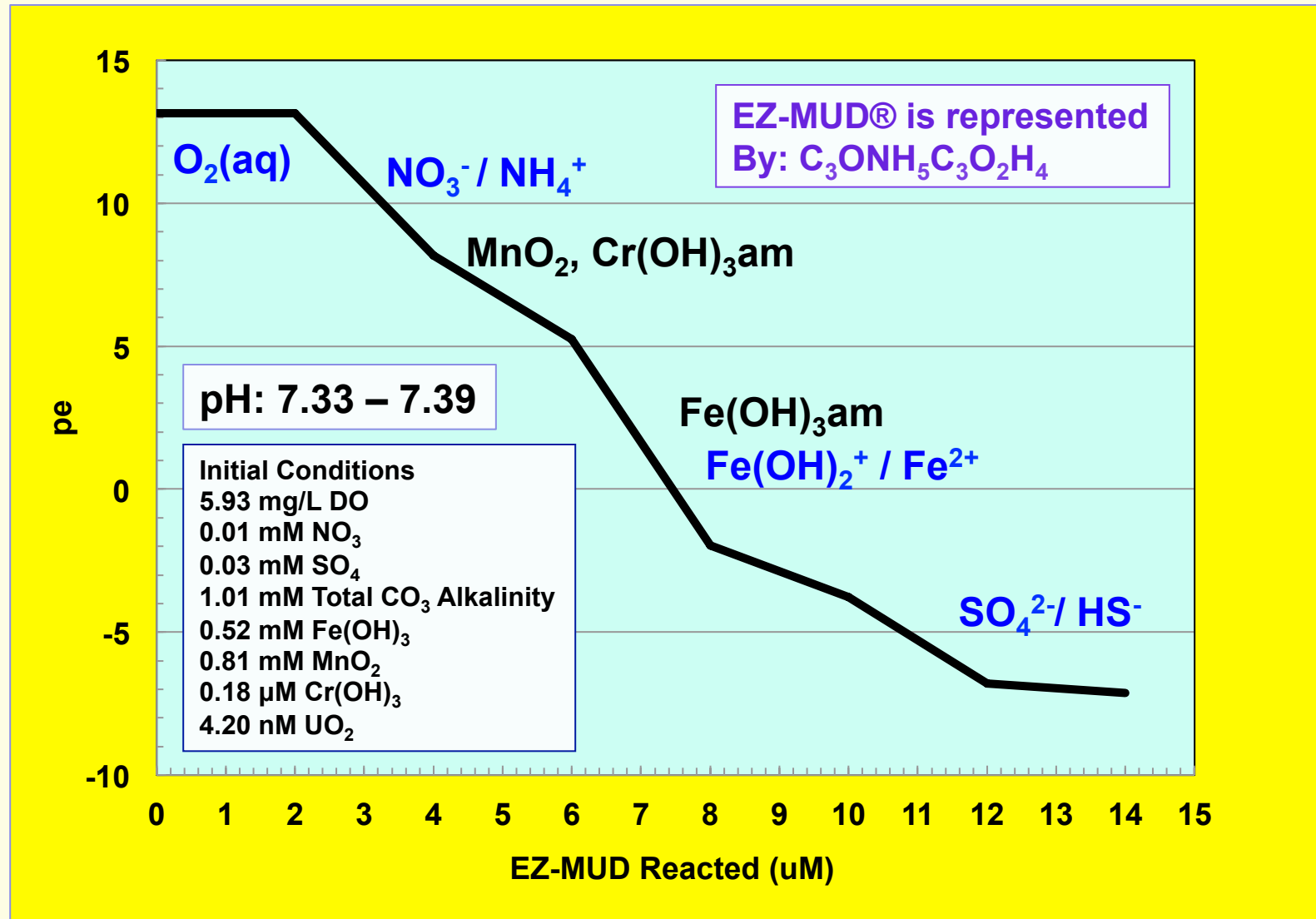


Concentrations of Dissolved Chromium, Iron, Manganese, and Uranium at Regional Aquifer Well R-54, Screen 1 (11/02/2011)

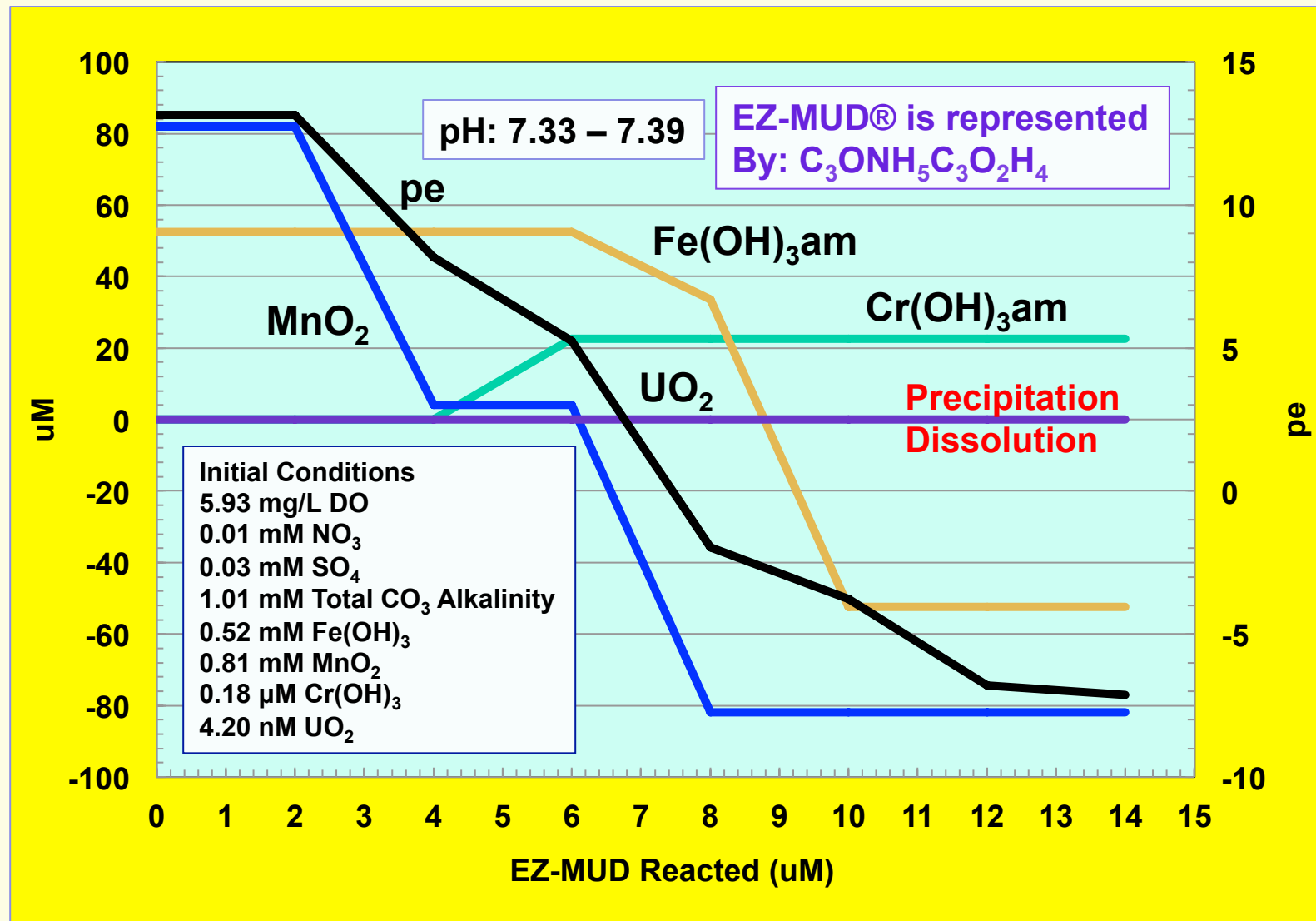


Well R-54 was drilled using an air rotary method with AQF-2 (surfactant). Hammer oil leaked into regional groundwater creating anaerobic conditions, initiating multiple redox reactions over time. R-54, screen 1 is completed in basaltic sediments of the Cerros del Rio basalt.

Results of Calculated Redox Titration Curve (25°C) Using PHREEQC for the Mean Regional Aquifer Composition Reacting with EZ-MUD®



Results of Mass Transfer Calculations (25°C) Using PHREEQC for the Mean Regional Aquifer Composition Reacting with EZ-MUD®



Summary of Impacted Monitoring Wells Completed in the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Impacted Well Screens	Original Completion	Primary Residual Drilling Fluids	Rehabilitated	Conversion	Representative Samples
Regional Aquifer Screens					
CdV-R-15-3 (S4 to S6)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S4)	Yes
CdV-R-37-2 (S2 to S4)	No-purge Westbay	EZ-MUD, QUIK-FOAM	Yes	Single Screen Pump (S2)	No
R-5 (S3 & S4) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-7 S3	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-8 (S1 & S2)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-14 (S1 & S2)	No-purge Westbay	QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S1)	Yes
R-16 (S2 to S4)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Dual Screen Pump (S2 & S4)	Yes (S2) & No (S4)
R-19 (S3 to S7)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-20 (S1 to S3) [CP]	No-purge Westbay	QUIK-FOAM, Bentonite Mud	Yes	Dual Screen Pump (S1 & S2)	No
R-22 (S1 to S5) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	Yes	No	Unknown
R-25 (S5 to S9) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-31 (S2 to S5)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-32 (S1 to S3)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S1)	Yes
R-33 (S1 & S2)	Low-Flow Barcad	EZ-MUD, QUIK-FOAM	Yes	Dual Screen Pump (S1 & S2)	Yes
R-54 S1 [CP?]	Dual Screen Baski	Hammer Oil	No	No	No
R-61 S1 & S2 [CP]	Dual Screen Baski	Hammer Oil	Yes	No	No
[CP] - Contamination Present					

Key Findings

Nine of 16 screens (56%) of multiscreen wells have undergone rehabilitation.

Five of 16 screens (31%) of multiscreen wells provide representative samples.

Five of 16 screens (31%) of multiscreen wells are in a contaminant plume.

Eleven of 110 screens (67 wells) contain residual drilling fluids (10%).

Summary of Impacted Monitoring Wells Completed in the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Impacted Well Screens	Original Completion	Primary Residual Drilling Fluids	Rehab Attempted	Conversion	Representative Samples
Regional Aquifer Screens					
CdV-R-15-3 (S4 to S6)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S4)	Yes
CdV-R-37-2 (S2 to S4)	No-purge Westbay	EZ-MUD, QUIK-FOAM	Yes	Single Screen Pump (S2)	No
R-5 (S3 & S4) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-7 S3	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-8 (S1 & S2)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-14 (S1 & S2)	No-purge Westbay	QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S1)	Yes
R-16 (S2 to S4)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Dual Screen Pump (S2 & S4)	Yes (S2) & No (S4)
R-19 (S3 to S7)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-20 (S1 to S3) [CP]	No-purge Westbay	QUIK-FOAM, Bentonite Mud	Yes	Dual Screen Pump (S1 & S2)	No
R-22 (S1 to S5) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	Yes	No	Unknown
R-25 (S5 to S9) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-31 (S2 to S5)	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-32 (S1 to S3)	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump (S1)	Yes
R-33 (S1 & S2)	Low-Flow Barcad	EZ-MUD, QUIK-FOAM	Yes	Dual Screen Pump (S1 & S2)	Yes
R-54 S1 [CP?]	Dual Screen Baski	Hammer Oil	No	No	No
R-61 S1 & S2 [CP]	Dual Screen Baski	Hammer Oil	Yes	No	No

[CP] -Within Contaminant Plume

Key Findings

Nine of 16 screens (56%) of multiscreen wells have undergone rehabilitation.

Five of 16 screens (31%) of multiscreen wells provide representative samples.

Five of 16 screens (31%) of multiscreen wells are in a contaminant plume.

Eleven of 110 screens (67 wells) contain residual drilling fluids (10%).

Summary and Conclusions

- **Complete removal of residual drilling fluids from monitoring wells is essential in obtaining long-term, representative groundwater samples needed for geochemical and risk analysis.**
- **Success of well rehabilitation depends on site-specific hydraulic properties of each saturated zone; type, mass, and reactivity of residual drilling fluid; and method and duration of well development.**
- **Approximately 31% of multiscreen monitoring wells have been successfully remediated.**

Summary and Conclusions

- Reduction of DO , NO_3^- , CrO_4^{2-} , SO_4^{2-} , and $\text{UO}_2(\text{CO}_3)_2^{2-}$ has been observed at multiscreen monitoring wells containing residual organic drilling fluids.
- Reductive dissolution of MnO_2 , FeOOH , and/or $\text{Fe}(\text{OH})_3$ and reductive precipitation of $\text{Cr}(\text{OH})_3$ and UO_2 most likely have taken place under natural and contaminated conditions.
- Dissolution of calcium carbonate (calcite) most likely has occurred during oxidation of residual organic drilling fluids under elevated partial pressure of CO_2 gas.
- Desorption of trace elements (Ni, Zn) from FeOOH and/or $\text{Fe}(\text{OH})_3$ most likely has occurred during reductive dissolution of these adsorbents.

Supplemental Material

Analytical Methods

Major Ions

Ion chromatography, titration, and inductively coupled plasma-optical emission spectroscopy

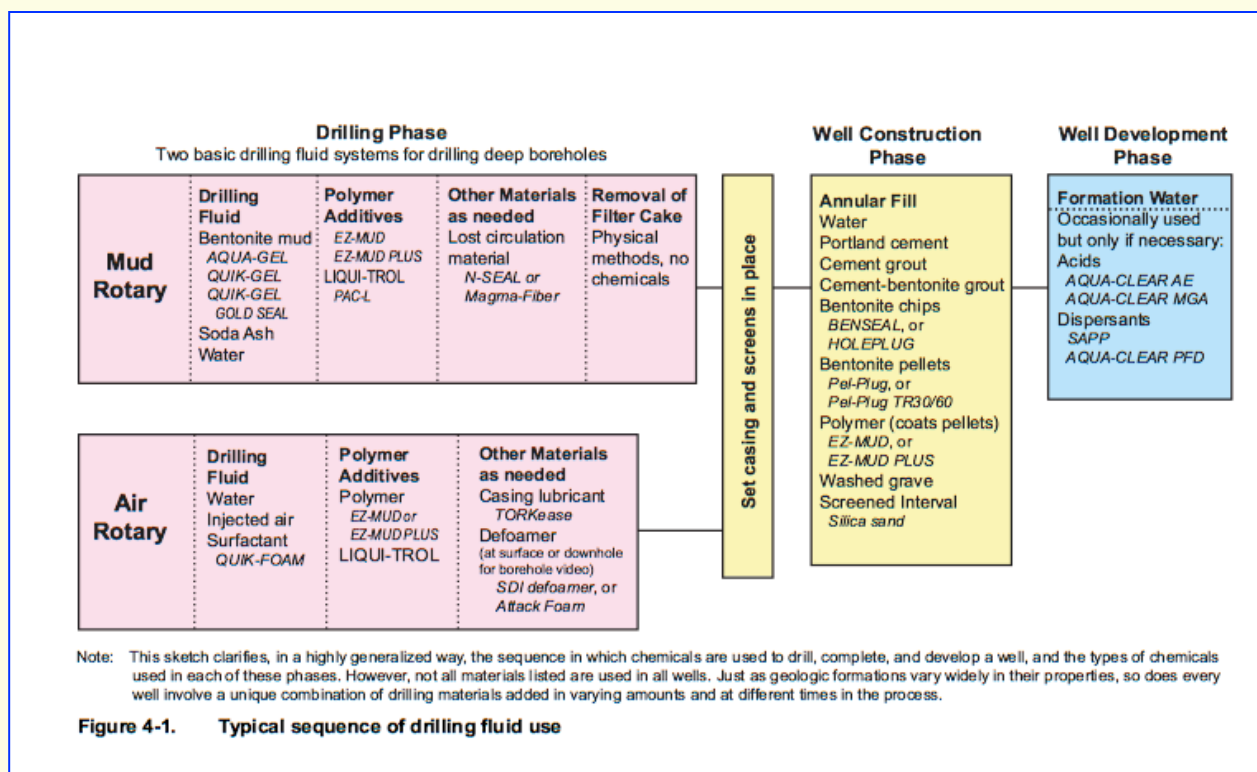
Trace Elements

Inductively coupled plasma-optical emission spectroscopy and (high resolution) inductively coupled plasma-mass spectrometry

Field Parameters

Dissolved oxygen, pH, ORP, temperature, specific conductance, and turbidity

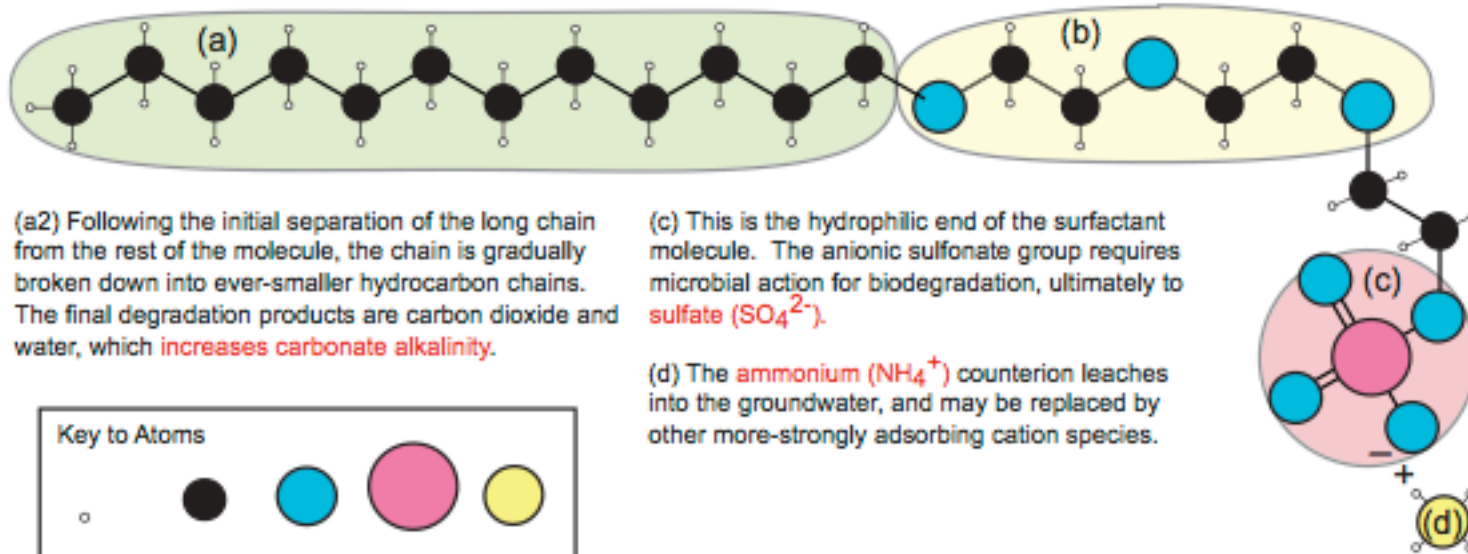
Typical Sequence of Drilling Fluid Use, Los Alamos National Laboratory, New Mexico (LANL, 2007)



Chemistry of an Anionic Surfactant (QUIK-FOAM®) (LANL, 2007)

(a1) This long hydrocarbon chain is the uncharged hydrophobic end of the surfactant molecule. The first stage of biodegradation probably involves detachment of this chain by hydrolysis. This process requires microbial activity to break the first carbon-carbon bond.

(b) The central ethylene oxide portion of the molecule, once detached from the long-chain hydrocarbon and sulfonate groups, biodegrades first into alcohols. Its ultimate breakdown products are carbon dioxide and water, thereby increasing carbonate alkalinity.



Note: An example of an alcohol ethoxy sulfate (AES) is sodium laureth sulfate. The structure and biodegradation mechanisms for the surfactant in QUIK-FOAM are expected to be similar to those depicted for this widely-studied AES. In the molecule sketched above, ammonium has been substituted for sodium as the counterion, to more closely parallel the QUIK-FOAM surfactant's composition.

CHEMISTRY OF ANIONIC SURFACTANTS

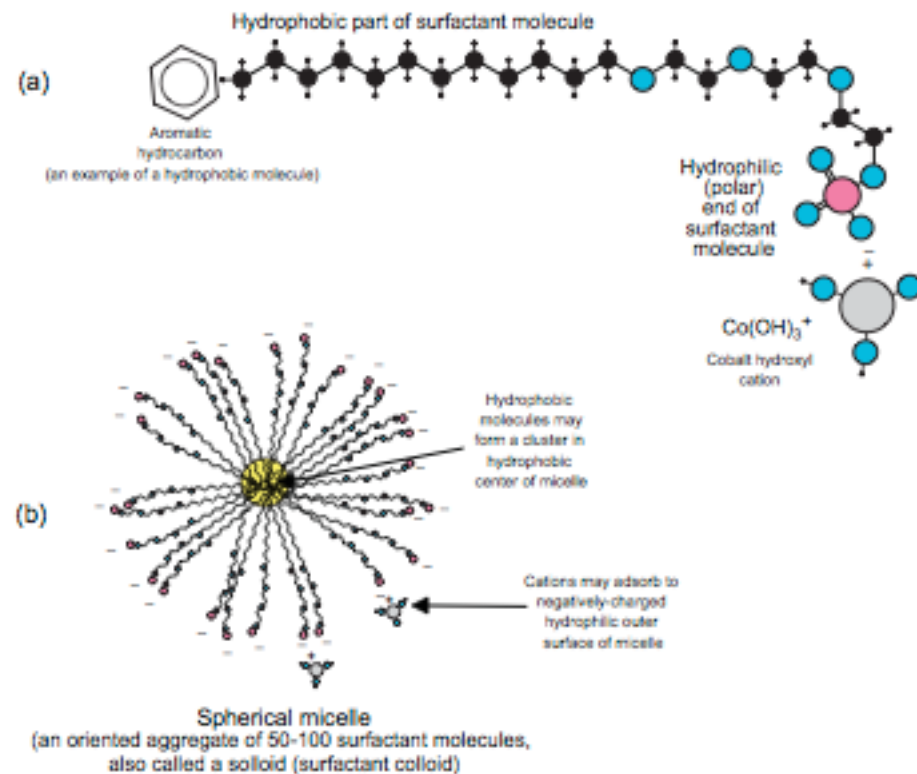
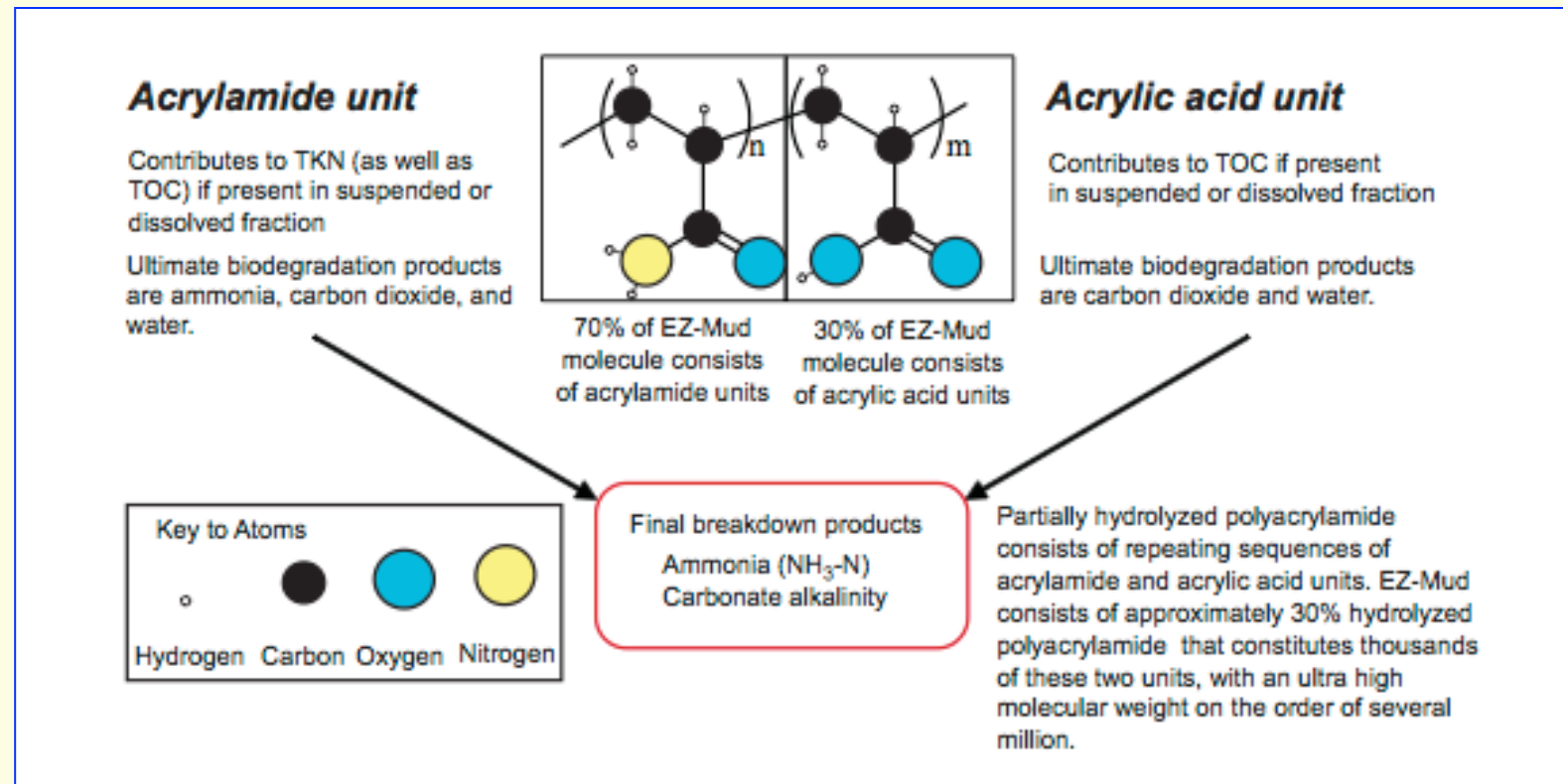


Figure 4-12 Schematics of potential interactions between anionic surfactants and constituents in groundwater: (a) interactions with hydrophobic and hydrophilic ends of a surfactant molecule, and (b) interactions with a surfactant micelle

Chemistry of Polyacrylamide-Polyacrylate Copolymer (EZMUD®) (Longmire, 2002; LANL, 2007)



Summary of Monitoring Wells Completed in Perched-Intermediate Zones, Los Alamos National Laboratory, New Mexico

Impacted Well Screens	Original Completion	Primary Residual Drilling Fluids	Rehabilitated	Conversion	Representative Samples
Intermediate Aquifer Screens					
R-5 S2 [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-9i (S1 & S2) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-12 (S1 & S2) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	Yes	Dual Screen Pump (S1 & S2)	No
R-19 S2	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-25 (S1 to S4) [CP]	No-purge Westbay	EZ-MUD, QUIK-FOAM	No	No	No
R-26 S1	No-purge Westbay	EZ-MUD, QUIK-FOAM, Bentonite Mud	Yes	Single Screen Pump	Yes
R-40i [CP]	Single Screen	QUIK-FOAM	No	No	No
R-55i [CP]	Single Screen	Hammer Oil	No	No	No

[CP] - Contamination Present

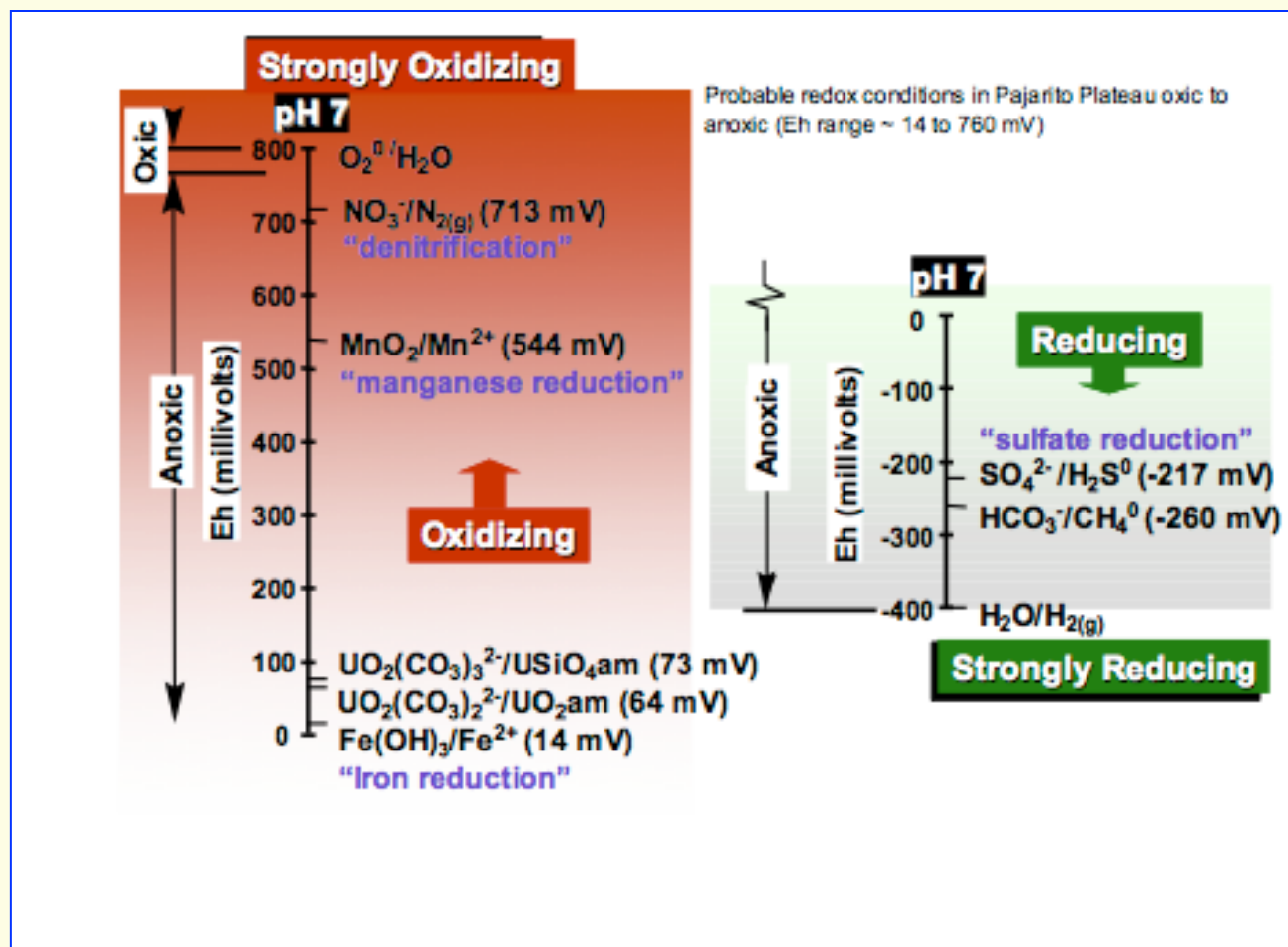
Key Findings

Two of 8 screens (25%) of multiscreen wells have undergone rehabilitation.

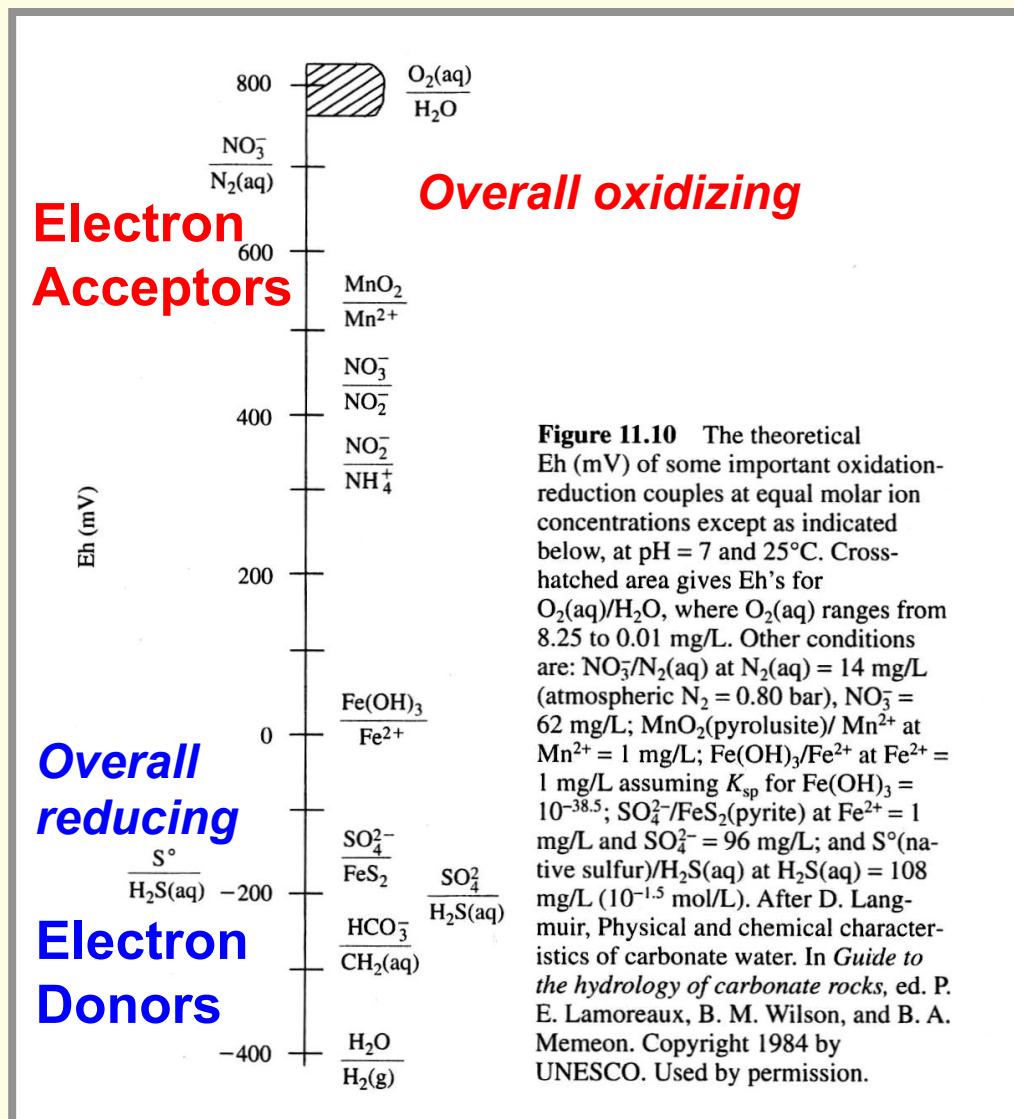
One of 8 screens (12%) of multiscreen wells provide representative samples.

Six of 8 screens (75%) of multiscreen wells are in a contaminant plume.

Selected Redox Couples (at pH7 and 25C) for the Pajarito Plateau and Surrounding Areas, New Mexico

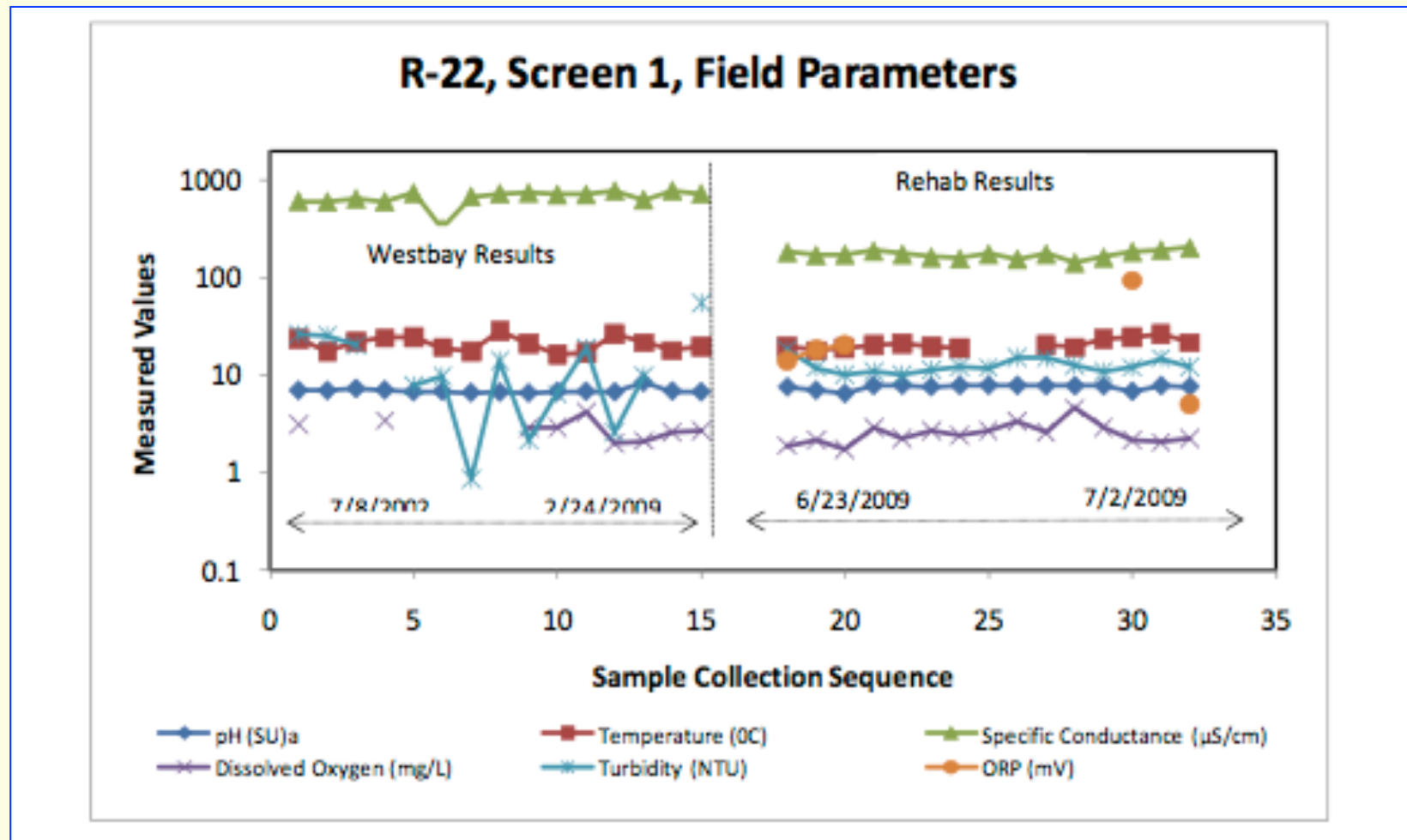


Redox Reaction Sequences and Redox Ladder in Natural Systems

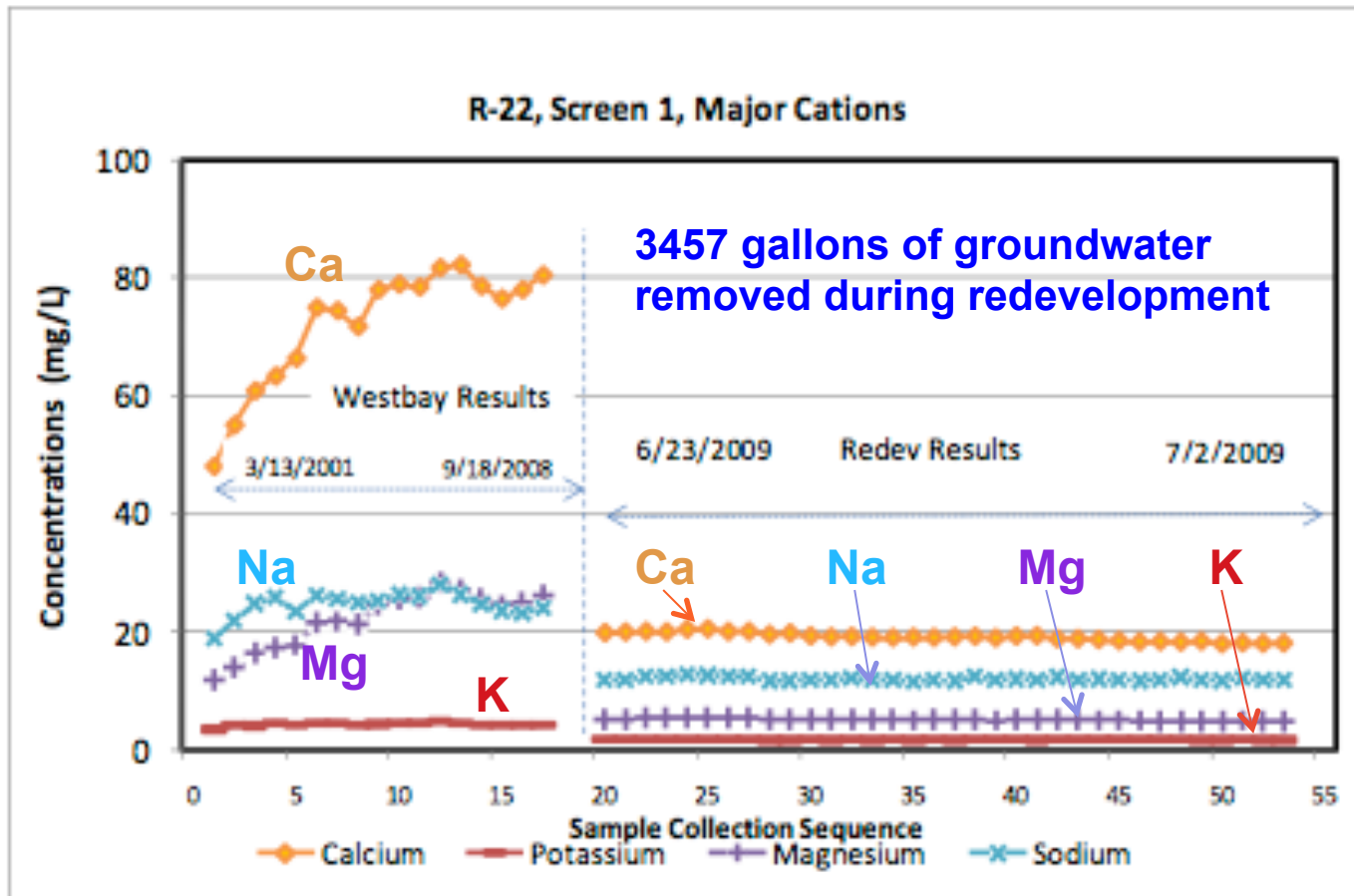


The above figure shows the Eh value at pH 7 and 25°C for important redox couples in natural waters under specified conditions (Langmuir, 1997). Langmuir D., 1997, Aqueous Environmental Geochemistry, Prentice Hall, New Jersey, 600 p.

Field Parameters at Regional Aquifer Well R-22, Screen 1 (LANL, 2009)

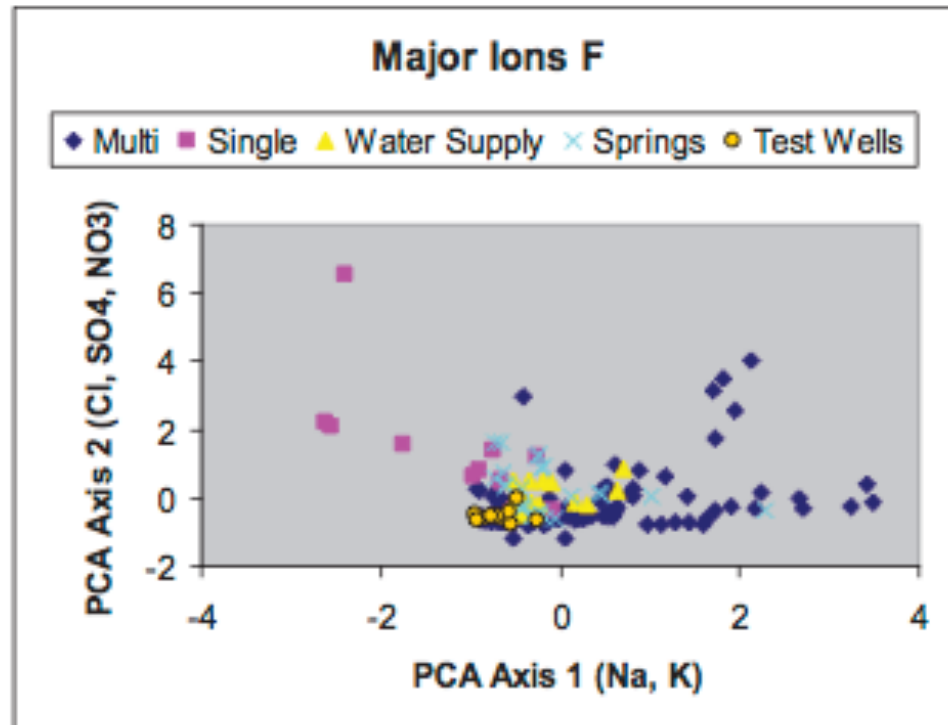


Concentrations of Dissolved Cations at Regional Aquifer Well R-22, Screen 1 From 2001 to 2009 (LANL, 2009)



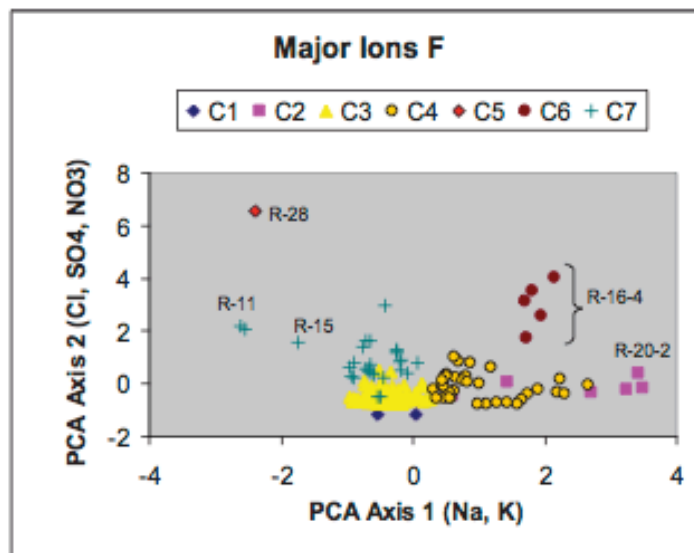
Note: Calcium (Ca^{2+}), potassium (K^+), sodium (Na^+), and magnesium (Mg^{2+}) concentrations during characterization sampling using Westbay equipment (March 2001–September 2008) and during redevelopment (June and July 2009).

Results of Principal Component Analysis Conducted on Major Ion Solutes, LANL, New Mexico (LANL, 2007)



Tight grouping of test well, water supply and springs samples. Most single-screen wells consistent with these "baseline" stations. A few single-screen wells show elevated nitrate concentrations, which do not appear to be drilling related.

Results of Principal Component Analysis Conducted on Major Ion Solutes, LANL, New Mexico (LANL, 2007)



Interpretation:

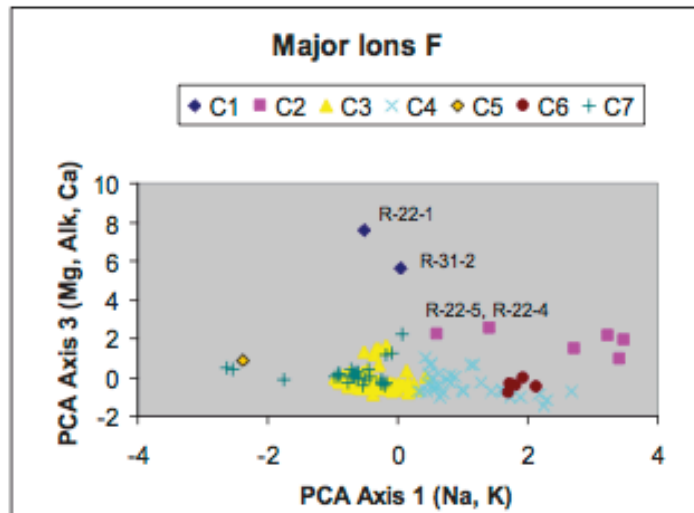
C3 = Consistent with White Rock Canyon springs or existing wells

C7 = Possible or slight impacts

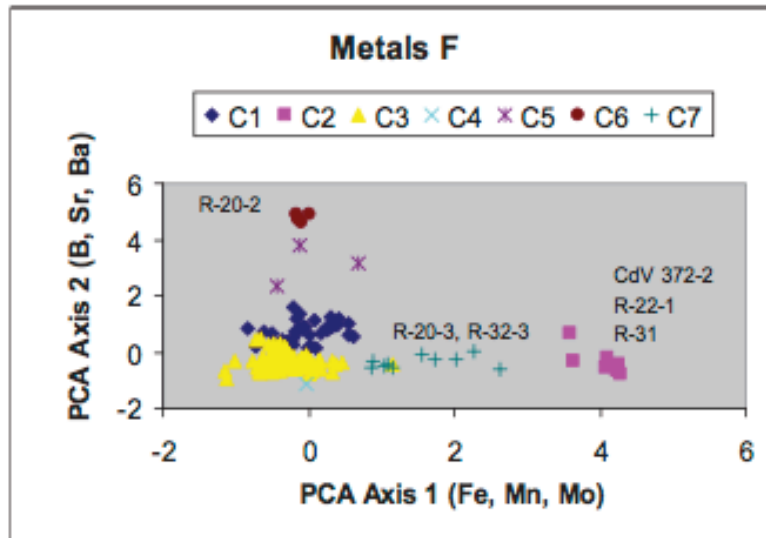
C4 = Moderate impacts

C1, C2, C5, C6 = Significant impacts

R-11 and R-15 show elevated NO₃ concentrations which do not appear to be drilling related. C7 appears to reflect natural chemical variability within aquifer, rather than drilling impacts.



Results of Principal Component Analysis Conducted on Trace Solutes, LANL, New Mexico (LANL, 2007)



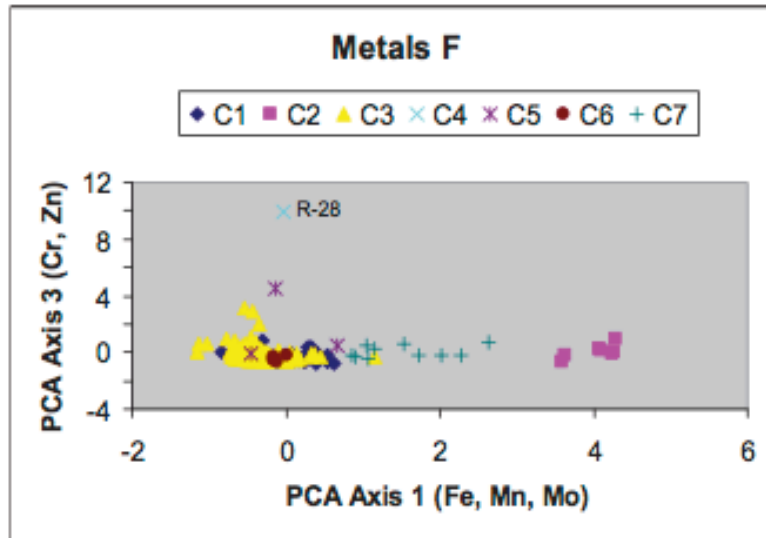
Interpretation:

C3 = Consistent with White Rock Canyon springs or existing water-supply wells

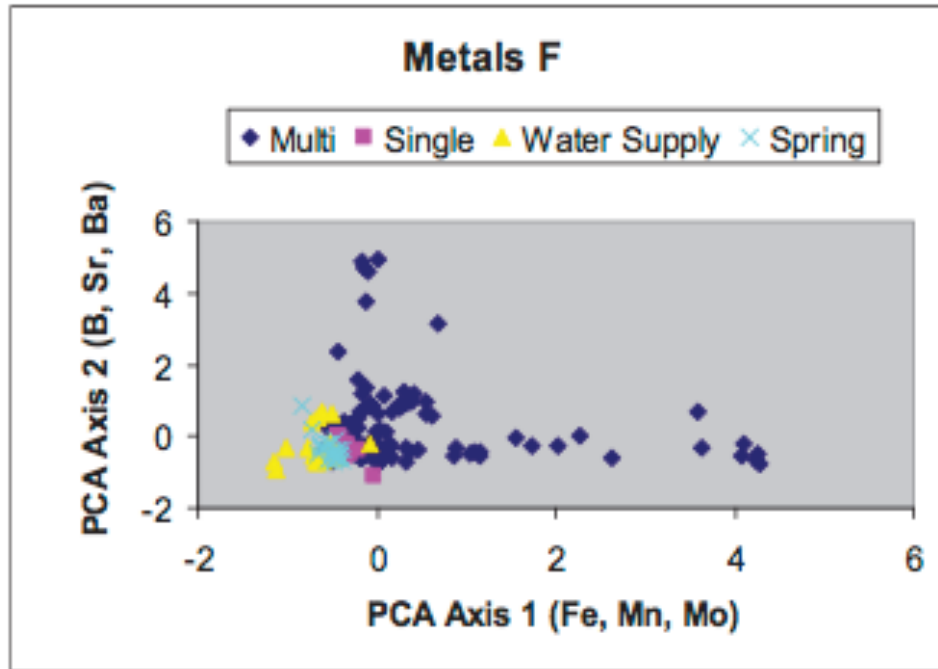
C1 = Possible to slight impacts

C5, C7 = Moderate impacts

C2, C4, C6 = Significant impacts















Results of Principal Component Analysis Conducted on Trace Solutes, LANL, New Mexico (LANL, 2007)



Water supply wells consistent with springs, indicating minimal or no residual drilling impacts. Many single-screen wells consistent with springs and water-supply wells.

Photographs of Sulfate-reducing Bacteria Tests for Regional Aquifer Well R-61 (LANL, 2013)

R-61 Sulfate Reducing Bacteria	Screen 1			Screen 2		
	Day 1	Day 12	Day 15	Day 1	Day 12	Day 15
May-12	No Test Done			No Test Done		
Nov-12						
Feb-13						

Results of Biological Activity Reaction Tests for Regional Aquifer Well R-61 (LANL, 2013)

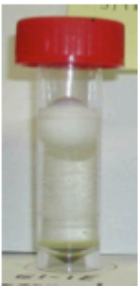
















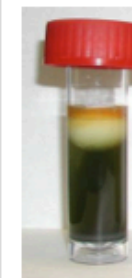
Well screen	Test Start Date ^a	Purge Volume	Field Parameters at Time of BART Sample Collection					Aggressivity of Bacterial Populations ^b		
			Field pH	Sp Cond (µS/cm)	DO (mg/L)	ORP (mV)	Turbidity (NTU)	Iron-Related Bacteria (IRB-BART)	Slime-forming Bacteria (SLYM-BART)	Sulfate Reducing Bacteria (SRB-BART)
R-61 S1	5/12/12	DP + 1CV	7.0	157	<1	-42	4	Moderate (Lag = 3 days)	Moderate (Lag = 4 days)	—
	11/15/12	DP + 1CV	6.5	177	4	216	10	Moderate (Lag ~ 3 days)	Moderate (Lag ~ 3 days)	Not aggressive (Lag = 11 days)
	2/11/13	DP + 1CV	6.7	156	5	-66	12	Moderate (Lag = 3 days)	Moderate (Lag = 5 days)	Not aggressive (Lag = 11 days)
R-61 S2	5/12/12	DP + 1CV	6.8	220	<1	-78	1	Moderate (Lag = 3 days)	Moderate (Lag = 3 days)	—
	11/15/12	DP + 1CV	6.4	192	1	-90	15	Moderate (Lag ~ 3 days)	Moderate (Lag ~ 3 days)	Not aggressive (Lag = 13 days)
	2/12/13	DP + 1CV	6.4	213	1	-127	9	Moderate (Lag = 3 days)	Moderate (Lag = 4 days)	Not aggressive (Lag = 13 days)

Abbreviations: CV = casing volume, DO = dissolved oxygen, DP = drop pipe, Lag = time lag, NTU = nephelometric turbidity unit, ORP = oxidation-reduction potential, S1 = screen 1, S2 = screen 2, Sp Cond = specific conductance

^a Tests were started on the same day that the sample was collected, with the exception of the samples collected for R-61 S1 and R-61 S2 in May 2012. These samples were collected on 5/9/12 and delivered to the analytical laboratory to start the BART tests on 5/12/12.

^b Threshold values used to estimate aggressivity for these samples are based on those presented in DBI (2004). Different bacterial populations show characteristic reaction sequences within the various types of tests. The significance or level of aggressivity for each type of bacteria is determined by the reaction type first observed, length of time between the start of the test and the occurrence of the first reaction (time lag), and the sequence and type of subsequent reactions that develop. Threshold time lags shown in this table are for the specific types of reactions observed in the tests summarized in and may not be applicable to tests conducted on other samples. A control sample consisting of sterilized de-ionized water was included in all tests.

Photographs of Iron-related Bacteria Tests for Regional Aquifer Well R-61 (LANL, 2013)

R-61 Iron related Bacteria	Screen 1			Screen 2		
	Day 1	Day 6	Day 10	Day 1	Day 6	Day 10
May-12						
Nov-12						
Feb-13						

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