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NMED Hazardous Waste Bureau

Environmental Management
Los Alamos Field Office
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Date: June 2, 2022
Refer To: N3B-2022-0212

Mr. Rick Shean
Bureau Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6313

Subject: Submittal of Evolution of Geochemical and Hydrologic Conditions in Monitoring Well R-42

Dear Mr. Shean:

Enclosed please find two hard copies with electronic files of the "Evolution of Geochemical and Hydrologic Conditions in Monitoring Well R-42." In a December 1, 2021, letter to the U.S. Department of Energy (DOE) Environmental Management Los Alamos Field Office (EM-LA), the New Mexico Environment Department (NMED) requested that DOE "submit a report to NMED by June 2, 2022 either documenting successful rehabilitation of R-42 or proposing a schedule for drilling a replacement well for R-42." The enclosed report satisfies this request by documenting successful rehabilitation of R-42 via a thorough review of the criteria identified in NMED letters dated December 1, 2021, and April 28, 2021.

If you have questions, please contact Christian Maupin at (505) 695-4281 (christian.maupin@em-la.doe.gov) or Cheryl Rodriguez at (505) 414-0450 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Troy Thomson
Program Manager
Environmental Remediation
N3B-Los Alamos

Sincerely,

ARTURO DURAN
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Arturo Q. Duran
Office of Quality and Regulatory Compliance
U.S. Department of Energy
Environmental Management
Los Alamos Field Office

Enclosure(s): Two hard copies with electronic files –
Evolution of Geochemical and Hydrologic Conditions in Monitoring Well R-42
(EM2022-0297)

cc (letter and enclosure[s] emailed):
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June 2022
EM2022-0297

Evolution of Geochemical and Hydrologic Conditions in Monitoring Well R-42

N3B Los Alamos

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1.0 BACKGROUND AND INTRODUCTION

In late August 2017, sodium dithionite was deployed in monitoring well R-42 (located at Los Alamos National Laboratory [LANL]) to evaluate in situ chemical reduction of hexavalent chromium [Cr(VI)] as a potential remedial action in the chromium plume area. Before the dithionite deployment, R-42 had the highest Cr(VI) concentration of any monitoring well in the chromium plume area (about 700 µg/L, with concentrations sometimes exceeding 1000 µg/L, from 2010 to 2013). The sodium dithionite (henceforth referred to simply as dithionite) deployment was successful in demonstrating reduction of Cr(VI), with little indication of a rebound in Cr(VI) concentrations in R-42 through the end of 2019. Details of the deployments and subsequent observations in R-42 through 2019 are documented in a series of eight quarterly progress reports, with the last being produced in June 2020 (LANL 2018a, 2018b; N3B 2018a, 2018b, 2019a, 2019b, 2019c, 2020).

In November and December 2020, R-42 was rehabilitated/redeveloped in an attempt to determine whether the continued observation of reducing conditions [and very low Cr(VI) concentrations] was a consequence of permeability reduction close to the well. The redevelopment resulted in a significant increase in the specific capacity of the well (pumping flow rate divided by water level drawdown). Also, an increasing trend in Cr(VI) concentrations became apparent in early 2021, suggesting that the 2020 redevelopment may have improved flow communication with the surrounding aquifer that accelerated the reoxidation of reducing conditions in the immediate vicinity of the well. These observations were made during a series of sampling events conducted roughly every 2 weeks from mid-January 2021 through early April 2021.

In August and September 2021, R-42 was pumped nearly continuously, withdrawing approximately 104,000 gal., to draw in prevailing oxidizing aquifer water in an attempt to exhaust local reducing conditions. The goal was to restore the well to pre-amendment geochemical conditions so that water samples from R-42 are representative of local aquifer geochemical conditions, especially Cr(VI) concentrations. The results from the extended purge were documented in an October 2021 report (N3B 2021).

Following the extended purge, R-42 was sampled approximately monthly from October 2021 through April 2022 to monitor the continuing evolution of geochemical conditions in R-42. At the end of each sampling event, the specific capacity was measured to determine whether permeability changes were occurring in the immediate vicinity of the well and to compare the specific capacity to conditions before dithionite injection. In late April and early May 2022, a borehole dilution tracer test was conducted in R-42 to estimate the ambient groundwater flow rate in the immediate vicinity of the well, which could be compared with a borehole dilution tracer test flow rate estimate from 2014.

This report summarizes the results from these activities and describes the geochemical and hydrologic changes that have occurred in R-42 since before the dithionite injection. It constitutes a response to a request from the New Mexico Environment Department (NMED) that "DOE must submit a report to NMED by June 2, 2022, either documenting successful rehabilitation of R-42 or proposing a schedule for drilling a replacement well for R-42" (NMED 2021a). The criteria that NMED specified for successful rehabilitation (NMED 2021a, 2021b) are discussed in the next section of this report, and the activities undertaken by the U.S. Department of Energy (DOE) to address these criteria are described in sections 3 and 4. Conclusions and recommendations are provided in section 5.

2.0 WELL REHABILITATION EVALUATION CRITERIA

NMED has requested both geochemical and hydrologic data for evaluating the ability of R-42 to provide representative samples for monitoring purposes. The geochemical criteria for rehabilitation, as DOE currently understands them, are listed in Table A-1 of Appendix A of this report. Table A-1 also provides recently measured values of all the geochemical parameters, as well as comments and historical observations, which are discussed further in section 3 of this report.

NMED provided the following hydraulic testing criteria to evaluate R-42 in two separate letters to DOE (NMED 2021a, 2021b):

- Repeat of the aquifer performance test conducted on June 17, 2013, at well R-42, for a minimum of 24 hr at a constant extraction rate of 9 gal. per minute (gpm), for comparison with the previous test results, including both hydraulic and water quality responses
- Spinner logging to verify that flow has been restored along the entire screen length
- Submittal of video-logging pre-redevelopment conditions
- Assessing flow velocity changes via dilution tracer tests; pre- and post-dilution tracer test results must be within 10% of pre-amendment results
- Pumping the entire screen length until field parameters stabilize to pre-amendment values and turbidity is below 5 nephelometric turbidity units (NTU) (this is addressed in this report as a geochemical criterion)
- Video-logging post-redevelopment conditions
- Post-redevelopment well discharge rate within 10 percent of pre-amendment well discharge rate (This is taken to be a specific capacity comparison.)

DOE considers all of these criteria to have been addressed except the first two, which required testing that could not be performed to NMED specifications.

- The 24-hr aquifer performance test at 9 gpm (the approximate rate in the 2013 long-term aquifer test) was not conducted because of long-term changes in water levels. When R-42 was redeveloped and reconfigured in November–December 2020, the water table in the well was about a foot below the top of the filter pack and about 4 ft above the top of the well screen, so an aquifer test at 9 gpm would have drawn the water level several feet down into the screened interval, creating inconsistent conditions for comparison with the 2013 aquifer test when the water level was approximately 6 ft higher and remained above the screened interval. Based on the water level at the time of the 2020 redevelopment relative to the top of the well screen, a 3–4 gpm pump was installed in R-42 as part of the reconfiguration, as this represented the maximum flow rate that could be pumped while still keeping the well screen submerged. It was also the maximum pumping rate for all sampling and purging that had been conducted in R-42 since just before the dithionite injection.
- Spinner logging in R-42 was not performed because (1) there were no previous spinner logs in R-42 for comparison, and (2) the flow rates needed for good spinner data would have resulted in drawdowns several feet into the well screen, thus negating the ability to evaluate whether flow has been restored “along the entire screen length.” Also, flow along the entire screen length would not necessarily be expected because of heterogeneity in geologic layer hydraulic conductivity.

In the following two sections of this report, geochemical and hydrologic conditions in R-42 are discussed, with attention given to the NMED criteria for successful rehabilitation. Section 5 of this report presents conclusions and a recommended path forward for R-42.

3.0 GEOCHEMISTRY IN R-42

Results of geochemistry measurements associated with the extended purging of R-42, including two samples collected in October 2021 after the extended purge was completed, were presented in a report provided to NMED at the end of October 2021 (N3B 2021). Several of these results are provided in this report for reference, and additional results are provided for samples collected approximately monthly from November 2021 through April 2022.

Table 1 summarizes the new sampling events, including the field parameters measured at each sample collection time (pH, temperature, specific conductance, dissolved oxygen [DO], turbidity, and oxidation-reduction potential [ORP]). Field parameters were measured onsite using a YSI, Inc., multiprobe system. One of the new sampling events (January 12, 2022) involved a purge of 12 casing volumes (CVs, where each CV is 46.2 gal.), with samples collected after 1, 3, 6, 9, and 12 CVs. This sampling event was intended to assess whether geochemical conditions at successively further distances into the aquifer and away from the wellbore were different from those after a customary 3-CV purge. Two other sampling events involved 6-CV purges (November 23, 2021, and March 15, 2021), with samples collected only after 6 CVs during the November 23, 2021, event and after 3 and 6 CVs during the March 15, 2021, event. These events matched the purge volumes for samples collected on October 5, 2021, and October 10, 2021, soon after the end of the extended purge. All other sampling events involved collecting a single set of samples after a 3-CV purge, which is the customary volume for Interim Facility-Wide Groundwater Monitoring Plan (IFGMP) sampling. However, sampling for dissolved organic carbon (DOC), which had not been done since March 2019, was performed during the April 12, 2021, sampling event, after 4 CVs were purged. The full suite of analytical results from the sampling events is available in the Locus Environmental Information Management (EIM) and Intellus databases that are accessible online.

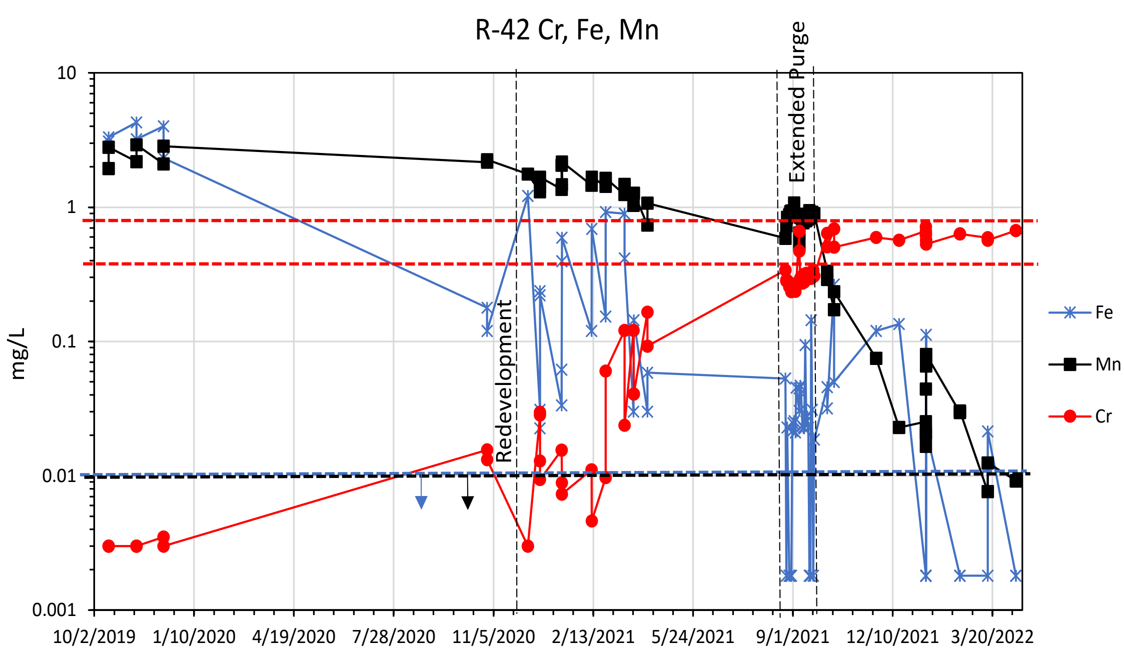
Table 1
Summary of Sampling Events from November 2021 to April 2022, Including Field Parameters Measured Each Time Samples Were Collected

Date	Casing Volumes*	pH	Temp (^{o}C)	Specific Conductance (µS/cm)	Dissolved O_2 (mg/L)	Turbidity (NTU)	ORP (mV vs Ag/AgCl)
11/23/2021	6	7.52	20.3	513	4.39	29.4	217.9
12/16/2021	3	7.55	20.3	516	4.07	9.94	240.3
1/12/2022	1	7.63	19.8	639	4.53	4.4	176.9
1/12/2022	3	7.63	20.6	650	4.71	2.52	221.5
1/12/2022	6	7.6	20.8	651	4.59	1.92	247.1
1/12/2022	9	7.58	20.7	650	4.5	1.8	251.2
1/12/2022	12	7.57	20.7	649	4.46	1.36	243.7
2/15/2022	3	7.56	20.6	506	4.96	1.74	211.5
3/15/2022	3	7.51	20.5	527	3.71	0.92	192.4
3/15/2022	6	7.49	20.6	526	3.95	0.78	221.8
4/12/2022	3	7.51	19.7	532	4.43	0.88	238.2
4/12/2022	4	7.5	20.2	531	4.72	1.44	246.9

* One casing volume = 46.2 gal.

Table A-1 in Appendix A provides a summary of recent solute and field parameter values relative to the NMED target criteria for successful rehabilitation, as DOE currently understands them. Almost all parameters have achieved the NMED target criteria or are currently very close to achieving them (sometimes just meeting and sometimes just missing in different sampling events). The only exception is DO, which has consistently been below the NMED target criterion of > 6.0 mg/L. Ferrous iron and sulfide have not been measured because the measurements required field Hach kits that were unavailable at the time of sampling. However, total iron in filtered samples has recently been measured below the ferrous iron criterion, and there were no odor indications of sulfide, which can be detected at very low concentrations by smell. New Hach kits will be available for planned May or June 2022 sampling events to determine if these parameters are indeed meeting their respective criteria.

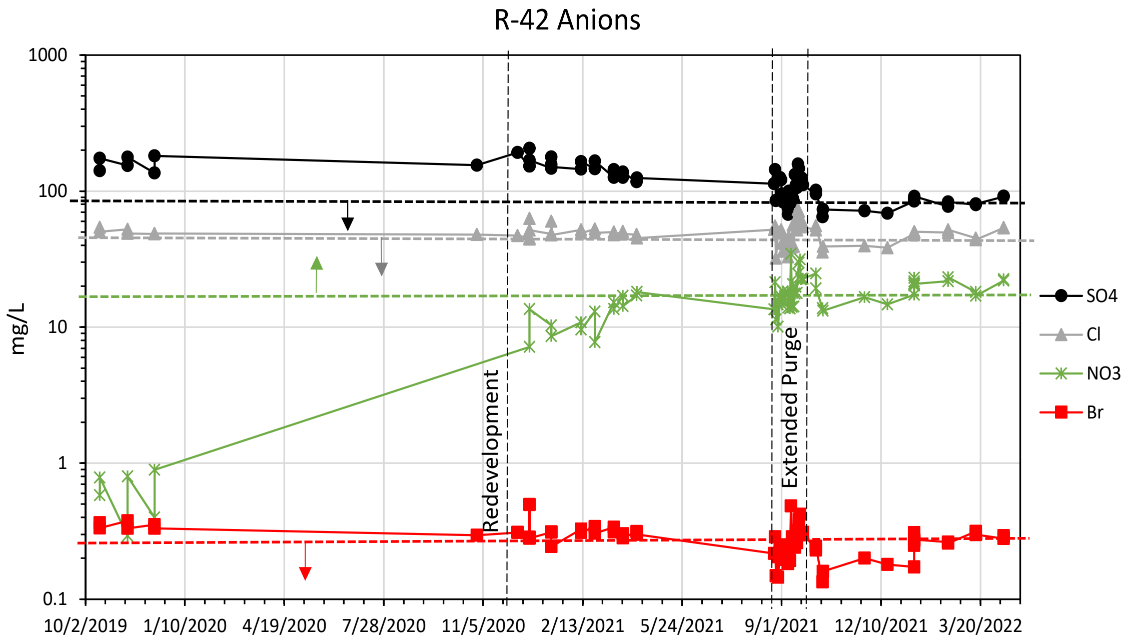
Plots of recent trends of some of the key parameters that were significantly perturbed by the dithionite injection, starting just before the 2020 redevelopment of R-42, are provided in Figures 1, 2, and 3. In each figure, the NMED criteria are plotted as horizontal dashed lines, with upward arrows indicating a lower bound target and downward arrows indicating an upper bound target [for Cr(VI) and pH, the target is a range indicated by two dashed lines]. The targets are generally consistent with pre-dithionite concentrations in R-42. Figure 1 shows trends for total (filtered) chromium, iron, and manganese, the analytes most significantly impacted by the dithionite injection.



Notes: Horizontal dashed lines represent NMED target criteria for rehabilitation for the parameter with the same colored symbols. Downward arrows indicate an upper-bound target (iron and manganese targets coincide). Chromium target range is indicated by the two red dashed lines.

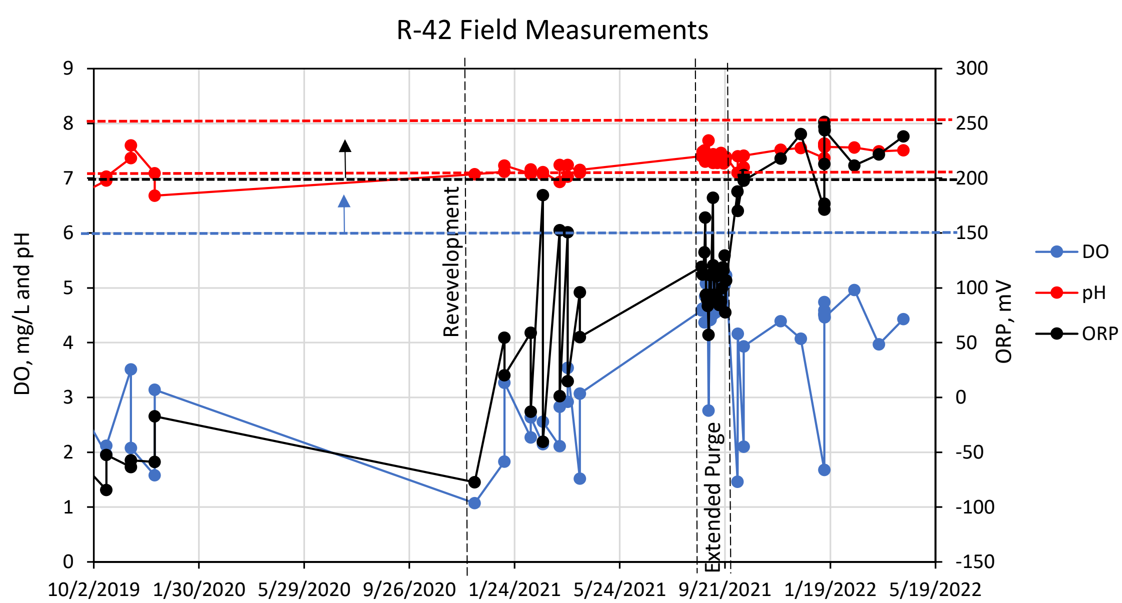
Figure 1 Concentration trends of iron, manganese, and chromium in R-42 from October 2019 to April 2022

Figure 2 shows trends for key anions, including sulfate (SO_4), a degradation product of dithionite and an oxidation product of sulfides and other reduced-sulfur phases that were deposited in the aquifer after the dithionite injection. Also shown in Figure 2 are nitrate (NO_3), a redox-sensitive anion that decreased significantly after the dithionite injection; bromide (Br), a conservative anion that was injected with the dithionite as a nonreactive tracer; and chloride (Cl), a conservative anion that was relatively unperturbed by the dithionite injection and should serve as a good marker for whether the chemistry of water flowing through R-42 has changed significantly over time independent of the dithionite injection.



Notes: Horizontal dashed lines represent NMED target criteria for rehabilitation for the parameter with the same colored symbols. Upward arrows indicate a lower-bound target and downward arrows indicate an upper-bound target. Nitrate is plotted as nitrate ion; some values in EIM and Intellus are reported as "Nitrate-Nitrite as N". N values are multiplied by 4.42 to obtain nitrate.

Figure 2 Concentration trends of selected anions in R-42 from October 2019 to April 2022

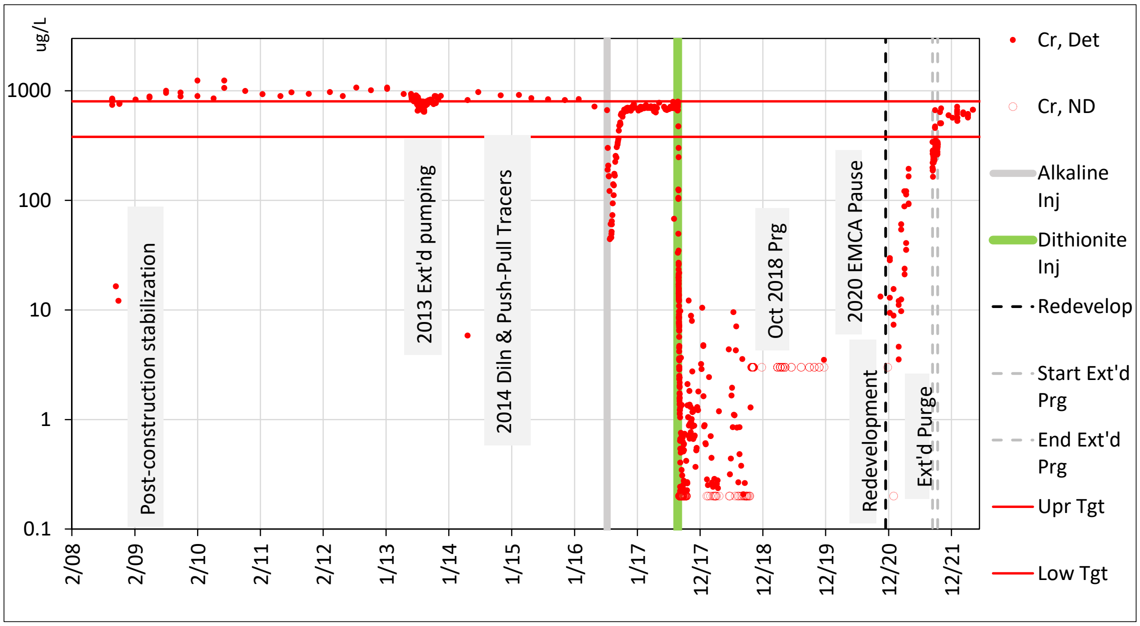


Notes: Horizontal dashed lines represent NMED target criteria for rehabilitation for the parameter with the same colored symbols. Upward arrows indicate a lower-bound target. pH target is a range indicated by the two red dashed lines.

Figure 3 Field measurements of pH, DO, and ORP in R-42 from the fall of 2019 to April 2022

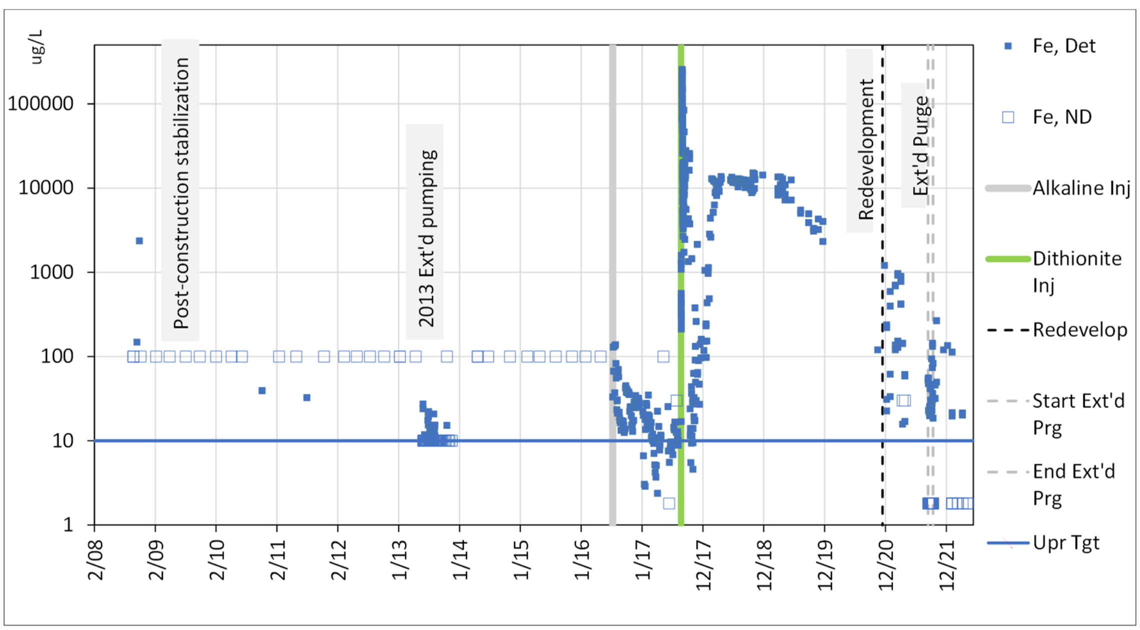
Figure 3 shows DO, pH, and ORP, all of which were significantly depressed by the dithionite injection.

Figures 4, 5, and 6 show longer-term trends for chromium, iron, and manganese in R-42 (since well installation). These figures provide perspective on the pre-dithionite concentrations of these constituents and how much they were perturbed by the dithionite. Similar plots for many constituents, including field parameters, are provided in Appendix A as Attachment A-1 (on CD included with this document).



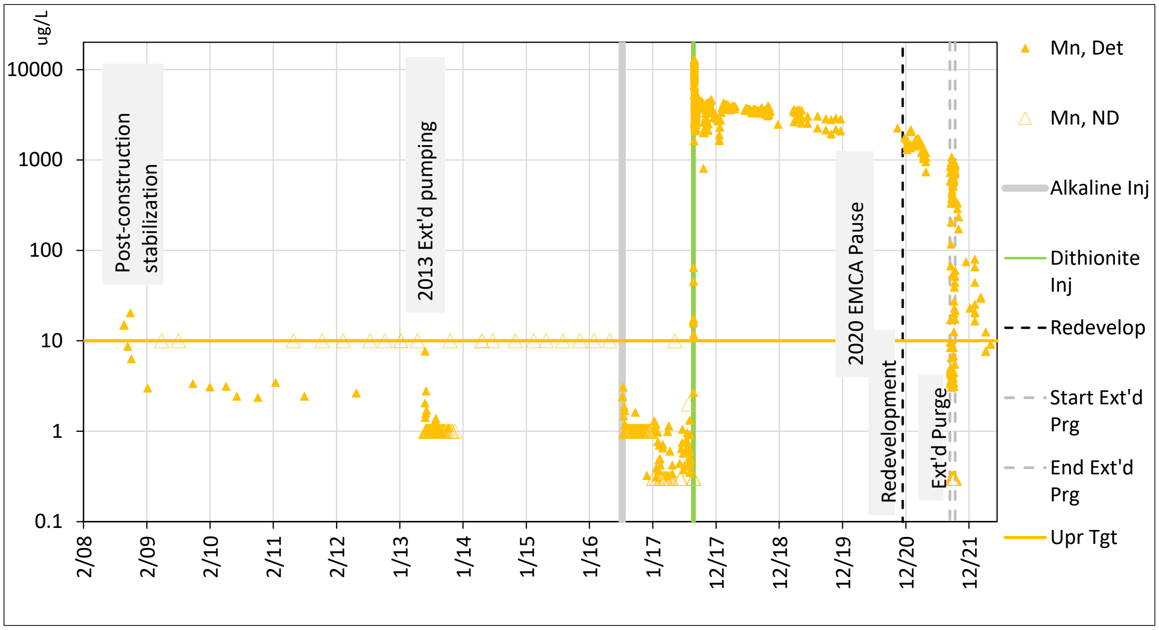
Notes: Diln = dilution; Ext'd = extended; Prg = purge.

Figure 4 **Chromium concentration trend in R-42 (log scale) since well installation, with annotations indicating significant events**



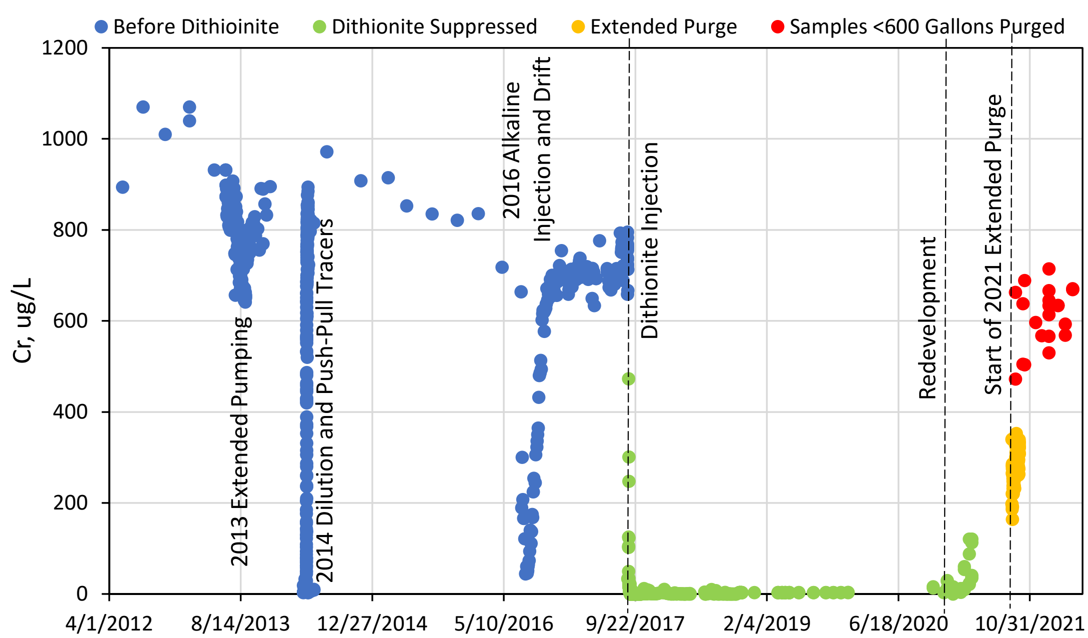
Notes: Ext'd = extended; Prg = purge.

Figure 5 **Iron concentration trend in R-42 (log scale) since well installation, with annotations indicating significant events**



Notes: Ext'd = extended; Prg = purge.

Figure 6 Manganese concentration trend in R-42 (log scale) since well installation, with annotations indicating significant events



Notes: Red symbols indicate samples collected during or after the 2021 extended purge after less than 600 gal. pumped, corresponding to IFGMP protocols.

Figure 7 Long-term chromium concentration trend in R-42 (linear scale)

Figure 7 shows a plot of chromium concentrations since 2012, using a linear concentration scale rather than the logarithmic scale used in the other figures. This allows pre-dithionite trends to be more readily identified than in Figure 4, and it also facilitates a qualitative evaluation of restoration of chromium concentrations to pre-dithionite levels. All of the red data points in Figure 7 correspond to samples taken after less than 600 gal. purged, either after the 2021 extended purge or after an intentional pumping interruption of about 3 days during the extended purge, which was conducted to see how geochemical conditions would rebound after a short interruption. These points correspond to samples collected in accordance with IFGMP purging protocols for monitoring wells that are not sampled during or immediately after an extended period of pumping. Thus, the red points represent the concentrations that would be reported since September 2021 if R-42 were part of the IFGMP (with the exception of two data points on January 12, 2022, that were from samples collected before three CVs had been purged).

As mentioned above, only DO remains as a geochemical parameter that is not meeting the NMED target criterion at R-42. However, essentially all of the redox-sensitive parameters that might be dependent on DO concentrations (e.g., chromium, iron, manganese, selenium, arsenic, uranium, nitrate, sulfate) would be predicted to be in the same oxidation state at the current DO concentrations of around 4 mg/L as at the NMED criterion of >6 mg/L. Both 4 mg/L and 6 mg/L DO are considered highly oxidizing thermodynamically, and there are no species that DOE is aware of in the regional aquifer that would be expected to change oxidation state between these two values.

Table 2 provides a redox ladder (Eh where reduced and oxidized species have equal abundance) for several redox-sensitive elements/species of interest generated using the PHREEQC geochemical model (Parkhurst and Appelo, 1999), assuming recent R-42 water chemistry at a pH of 7.5. The table shows that the transition Eh values for all species of interest are lower than the Eh associated with DO levels of 4 mg/L and 6 mg/L (which have trivial difference in Eh). The only transition that would be predicted to occur at an Eh greater than those listed for the two DO concentrations is for ClO_4^- being reduced to a lower oxidation state of Cl, which is predicted to occur at a DO that significantly exceeds the solubility of DO (and the Eh is much greater than that for 6 mg/L DO). The fact that ClO_4^- has been persistent throughout much of the chromium study area indicates that any transition to a lower Cl oxidation state must have significant kinetic limitations.

Table 2
Redox Ladder for Various Elements/Species in R-42 Water

Element	Most Abundant Species at Transition	Eh, V
O_2, 6 mg/L	NA	0.795
O_2, 4 mg/L	NA	0.792
N	NO_3^- / N_2	0.682
Mn	$MnO_2(s)$ / Mn^{2+}	0.567
Cr	$CrO_4^=$ / $Cr(OH)_3(s)$	0.504
Se	$SeO_4^=$ / $HSeO_3^-$	0.437
Fe	$Fe(OH)_3(s)$ / Fe	0.061
As	$HAsO_4^=$ / H_3AsO_3	-0.053
U	$Ca_2UO_2(CO_3)_3$ / $U(OH)_5^-$	-0.106
S	$SO_4^=$ / HS-	-0.249

Notes: Eh values correspond to equal abundance of reduced and oxidized species, as predicted by PHREEQC at a pH of 7.5. Calculations for all elements except N were done using the minteq.v4 database, with appropriate additions to account for uranyl ternary carbonate complexes. Calculations for N were done using the PHREEQC database.

Suspended solids were collected on a 1.2-µm silver filter during the February 15, 2022, sampling event to attempt to characterize the colloidal material causing elevated turbidity in R-42. X-ray diffraction (XRD) analyses of these solids did not identify any crystalline phases, but iron was qualitatively identified as a significant component of the solids. During the April 12, 2021, sampling event, both 0.45-µm filtered and unfiltered groundwater samples were collected for cation and metal analyses, and these samples confirmed (by difference) that iron was the predominant cationic/metallic element in the suspended material that did not pass through the filter. Other elements had only minor differences between filtered and unfiltered samples, and these differences may not be statistically significant. The constituents that may have been affected by filtration are presented in Table 3.

Table 3
Analytical Results for Unfiltered and Filtered Samples from the April 12, 2022, R-42 Sampling Event for Parameters that Appear to Show a Difference Depending on Filtration

	Fe	Cr	Mn	As	V
Unfiltered	0.293	0.748	0.0113	0.00118	0.0274
Unfiltered	0.146	0.693	0.0099	0.00106	0.0285
Filtered	0	0.669	0.0092	0.000834	0.0250
Filtered	0	0.671	0.0091	0.000881	0.0255

Notes: Units are mg/L. All samples were collected at the same time (~3 CV), with duplicates for both unfiltered and filtered samples.

These results suggest that the suspended solids that are generating turbidity in groundwater in R-42 are predominantly ferric iron solids that may have minor amounts of associated trivalent chromium [Cr(III)] and perhaps manganese, arsenic, and vanadium (the apparent association of all of these minor constituents is based on differences between concentrations measured in unfiltered and filtered samples). These solids were likely created when aqueous or sorbed ferrous iron [Fe(II), generated from the dithionite injection] re-oxidized to ferric oxide [Fe(III)] when oxidizing groundwater flowed back into the dithionite reaction zone. Almost all of this Fe(III) would have initially precipitated as colloidal material because of the exceedingly low solubility of Fe(III) at the pH of the R-42 groundwater. Such colloidal material would likely not have an ordered crystalline structure, which is consistent with the lack of a crystalline phase signature in the XRD spectra of the filtered solids collected on February 15, 2022. The colloidal material might also contain small amounts of Cr(III) because aqueous Cr(VI) would be expected to be one of the oxidants reoxidizing Fe(II) to Fe(III). This reoxidation would have likely resulted in some coprecipitation of Fe(III) and Cr(III), which are known to form solid solutions because of their electronic similarity. The speculative associations of manganese, arsenic, and vanadium with the suspended material might be attributed to sorption to the ferric iron, although some coprecipitation with ferric iron cannot be ruled out.

4.0 HYDROLOGIC CONDITIONS IN THE VICINITY OF R-42

Hydrologic conditions in the vicinity of R-42 were evaluated by measuring specific capacity at the end of each sampling event from November 2021 to April 2022, and also by conducting a borehole dilution tracer test from April 25 to May 9, 2022. Additionally, pre- and post-redevelopment video logs were taken in R-42 (on DVD in Attachment 1 included with this document). Specific capacity measurements were compared with previous measurements taken from just before the dithionite injection through the end of the 2021 extended purge to determine whether the recovery of specific capacity following the 2020 redevelopment had persisted. The estimate of natural groundwater flow rate passing through the R-42 well screen obtained from the borehole dilution tracer test was compared with a flow rate estimate obtained in a 2014 borehole dilution tracer test, which was 3 yr before the dithionite injection.

4.1 Pre- and Post-Redevelopment Video Logs

Video log surveys were conducted in R-42 before and after the redevelopment activities that took place from November 16 to December 9, 2020. The pre- and post-redevelopment video logs were run on November 16 and December 10, 2020, respectively. The video logs are included as Attachment 1 (on DVD included with this document). Observations from the video log conducted before the 2020 redevelopment show mostly minor accumulations of material resting in some of the screen slots, primarily in the upper and lower sections of each 10-ft section of the approximately 20-ft screen interval. The composition of the material is not known, but it does not have the characteristics of significant biological growth. In the post-redevelopment video log, this material is almost completely absent, and the well screen looks clean and free of any type of material in the slots. As with the log collected before redevelopment, there is no indication of organic material in the well screen.

4.2 Specific Capacity Estimates

Specific capacity is generally used to estimate yield for public water supply or industrial wells (Risser 2010). At R-42, however, it is used as a qualitative measure of near-well permeability, given the limited pumping time periods and the uncertainty associated with flowmeter measurements at low flow rates. To this end, DOE's main criterion for measuring specific capacity as an indicator of near-well permeability is that the water level stabilizes and is no longer noticeably decreasing, or any small decreasing trend can be attributed to normal barometric fluctuations. Water levels routinely fluctuate by as much as half a foot over 24-hr periods due to normal barometric effects, and these fluctuations can be even greater when weather systems cause major air pressure changes.

Figure 8 shows the specific capacity of R-42 measured at various times, from before the dithionite injection until the last sampling event in April 2022. While the dithionite injection clearly decreased specific capacity, the 2020 redevelopment restored specific capacity to pre-dithionite levels or higher. Recent specific capacity estimates have had considerable scatter, which is likely associated with the uncertainty in measuring the low flow rates during sampling. There also appeared to be a slight decrease in the specific capacity estimate during the 2021 extended purge, although this decrease was followed by higher specific capacity measurements during subsequent sampling events. During these subsequent sampling events, all but one of the six specific-capacity measurements were greater than the specific capacity measured immediately before the dithionite injection.

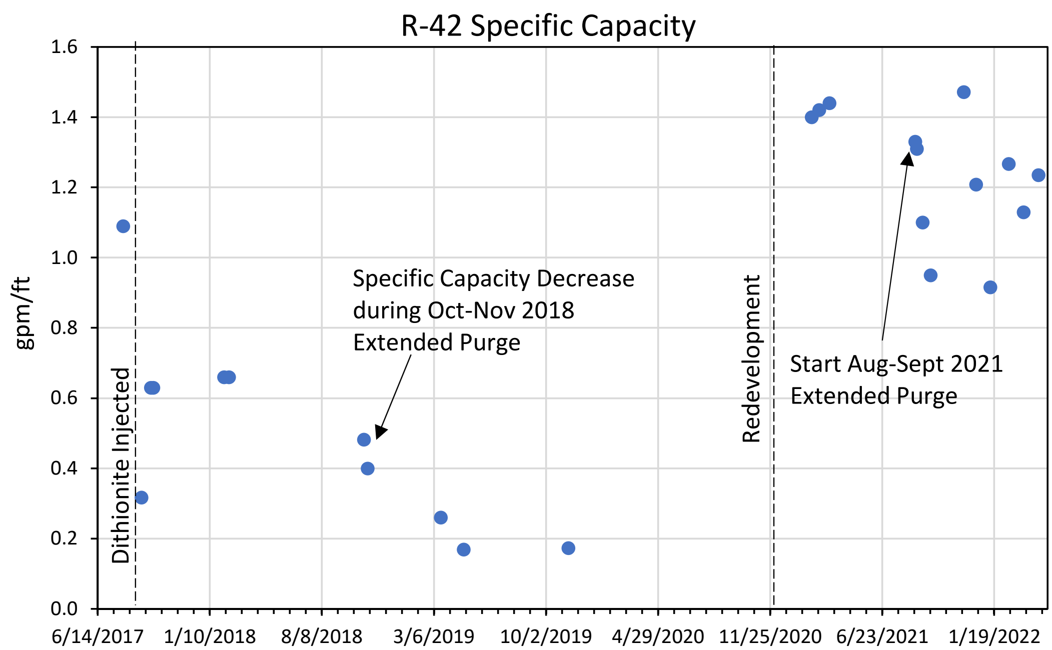
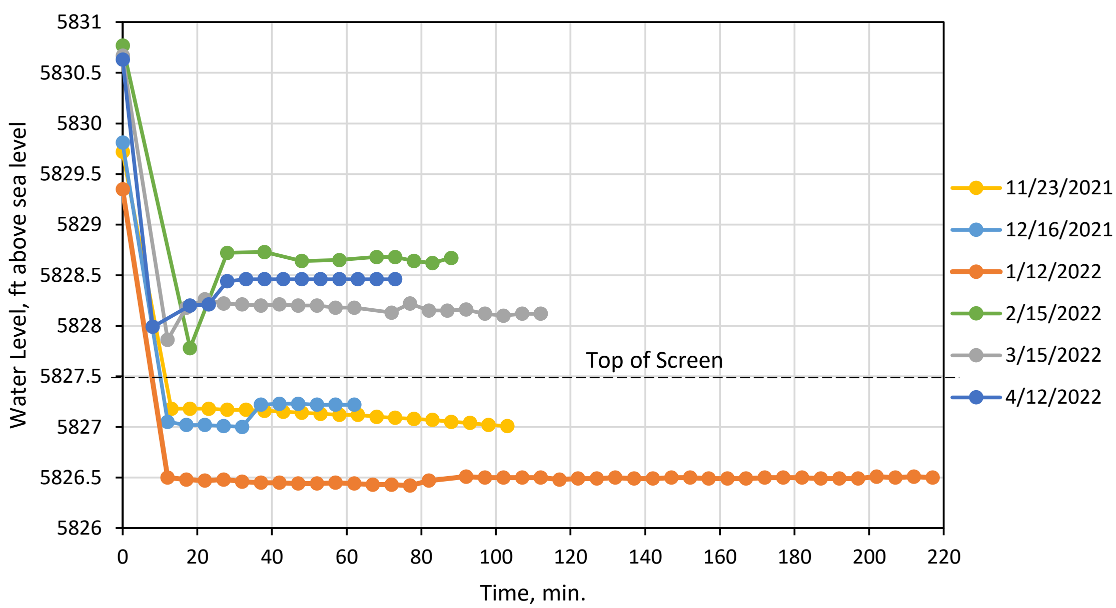


Figure 8 **Estimated specific capacities of R-42 at various times from before the dithionite deployment to April 2022**



Note: Top of R-42 screen is 5827.5 ft above sea level. Recorded pumping rates ranged from 2.6 to 3.5 gpm, with initial rates sometimes being higher than final stabilized rates used for specific capacity estimates.

Figure 9. **Manually recorded water levels during each of the six R-42 sampling events from November 2021 to April 2022**

Figure 9 shows manually recorded drawdown curves during each of the six sampling events that occurred from November 2021 to April 2022. These curves are consistent with the early portion of other drawdown curves that have been recorded at R-42 over many years. Drawdown occurs very rapidly and typically stabilizes within a matter of minutes, especially at the lower pumping flow rates used for sampling (e.g., 2–3 gpm). Some of the sampling events initially involved pumping at slightly higher rates, followed by a decrease in flow rate. Drawdown recovered slightly when this occurred (e.g., December 16, 2021; February 15, 2022; March 15, 2022; and April 12, 2022). During three of the recent sampling events, the water level in R-42 dropped to within the upper foot of the screened interval.

Although there are uncertainties, and specific capacity as used here is a somewhat qualitative measure of permeability in the immediate vicinity of a well, the results shown in Figure 8 suggest that the 2020 R-42 redevelopment resulted in a recovery of near-well permeability to pre-dithionite injection levels. The results also indicate that the near-well permeability has remained at approximately these levels since December 2020.

4.3 Borehole Dilution Tracer Test

On April 25, 2022, a borehole dilution tracer test was initiated in R-42 by injecting a solution of approximately 10 mg/L of sodium 1,5-naphthalene disulfonate, dissolved in R-42 water, into a transducer access tube screened near the water table, while pumping water at the same rate or a slightly higher rate from below the screened interval. The procedure for conducting borehole dilution tracer tests has been previously described in section 2 of Attachment 1 of the 2018 “Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization” (Chromium Compendium) (LANL 2018c), so only a brief summary is provided here.

The matching of the injection and extraction flow rates (or a slightly higher extraction rate than injection rate) was intended to ensure that the tracer solution remained in the well casing and was not pushed into the filter pack or the formation during the injection. When the tracer solution returned to the surface via the pump discharge line and reached a stable concentration approximately equal to the injection concentration, the tracer injection was stopped and the withdrawal flow from the well was redirected into the injection tubing. This established a circulation system in which the tracer-bearing water was continuously cycled between the surface and the screened interval, with the tracer being forced to flow down the length of the screened interval inside the casing with each pass. The reinjection of all water pumped from the well (minus any small amount collected for samples) ensured that there was no net injection or withdrawal of water occurring. Under these conditions, the rate of decline in tracer concentration in the circulation loop can be related to the volumetric flow rate of the groundwater that is flowing naturally through the screened interval (Drost 1968, Ogilvi 1958). Mathematically,

$$\frac{d\ lnC}{dt} = -\frac{Q}{V} \qquad \textbf{Equation 1}$$

where C = tracer concentration

t = time, h

Q = volumetric flow rate, L/h

V = volume of circulation loop, L

Note that $\frac{d\ lnC}{dt}$ is the slope of a plot of *lnC* or *ln(C/Co)* versus *t*, where *Co* is the initial tracer concentration.

The volumetric flow rate Q, estimated by multiplying the known *V* by the slope of the *lnC* or *ln(C/Co)* versus *t* curve, can then be related to the specific discharge in the aquifer near the well (Palmer 1993), which in turn can be converted to a linear groundwater flow rate estimate by dividing the specific discharge by an assumed flow porosity. However, for the R-42 test, the goal was not to obtain an absolute estimate of a groundwater flow rate, but rather to see if the deduced flow rate through the screened interval was similar to the flow rate estimated from a 2014 borehole dilution tracer test conducted in R-42. If the deduced flow rates were similar, this would indicate that hydrologic conditions near R-42 in 2014, 3 yr before the dithionite injection, were similar to what they are now, nearly 5 yr after the dithionite injection.

The results of the 2014 borehole dilution tracer test are summarized in section 2 of Attachment 1 of the Chromium Compendium (LANL 2018c). The estimate of volumetric flow rate through the screened interval in R-42 in this test was about 3.5 L/hr.

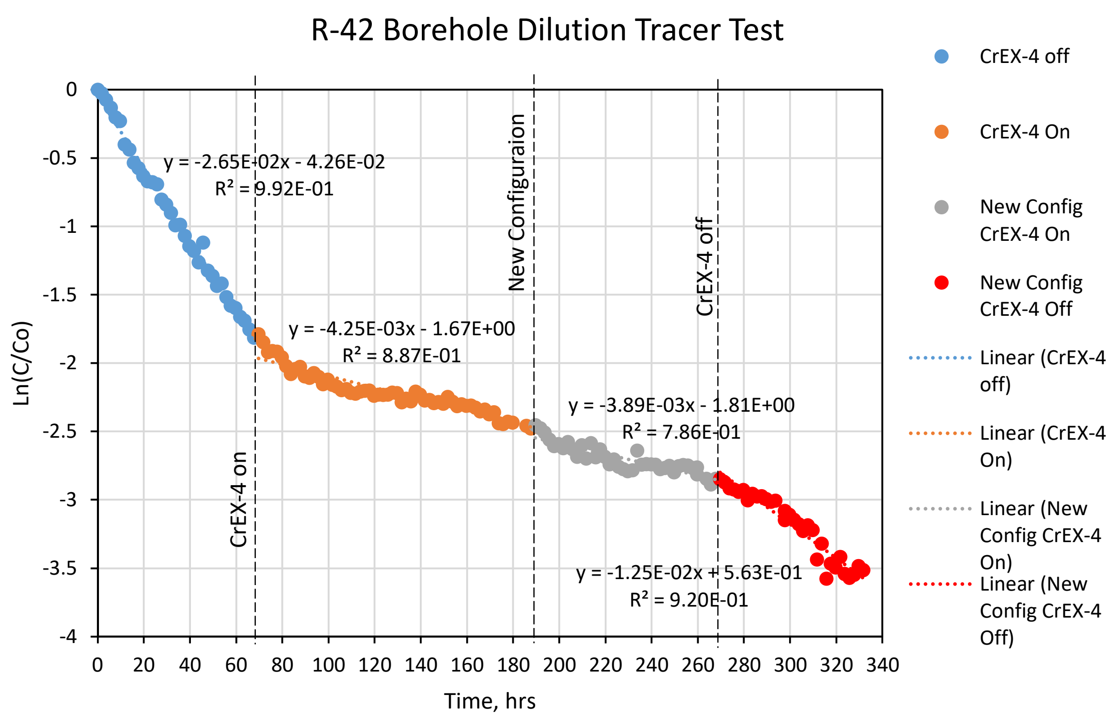
The sodium 1,5 naphthalene disulfonate (1,5-NDS) tracer used in the 2022 borehole dilution tracer test was the same tracer that was used in all previous borehole dilution tracer tests conducted within the chromium study area (LANL 2018c), including the 2014 test at R-42. This tracer is known to be nonreactive with well completion materials and aquifer sediments, and it has a very low detection limit (~1 μg/L).

Samples were collected from the circulation loop every 2 hr in 60-mL amber glass bottles (Qorpak) with Teflon-lined screw caps using an autosampler (ISCO Foxy 200) that was set up in a trailer next to the R-42 wellhead. The method of tracer analysis was high-performance liquid chromatography (HPLC) with fluorescence detection (excitation at ~225 nm wavelength and emission at ~330 nm), which has been used to analyze all naphthalene sulfonate tracers that have been deployed in the chromium study area. However, simple fluorescence spectrophotometry without HPLC to chromatographically separate the different naphthalene sulfonates was also used for many of the previous borehole dilution tracer tests.

CrEX-4 was turned off three days before the start of the tracer test, as CrEX-4 did not exist in 2014, and the intent was to match flow conditions that existed in 2014 to the extent possible. However, the other interim measure (IM) extraction and injection wells were kept in operation, with the exception of CrIN-1, which was shut off to balance the impact of turning off CrEX-4. This plan assumed that all IM wells, except CrEX-4, were far enough away from R-42 that a valid comparison with the 2014 test could be made with the other IM wells operating. R-42 had not exhibited water level responses to the operation of the other IM wells as it has to CrEX-4. CrEX-4 was to be turned on after a good tracer curve was established to opportunistically determine if it had any effect on the flow rate within the R-42 well screen.

For the purposes of interpreting the borehole dilution tracer test, the volume of the tracer circulation loop (V in equation 1) was estimated to be about 80 gal., or about 300 L. There is some uncertainty in this estimate because the transducer tube used as the return line in the circulation loop was not full of water (the return line was drawing a vacuum), so the water volume in this tube during circulation was not known exactly. However, the time for the tracer to return to the surface during tracer injection suggested a volume of about 80 gal. given the measured flow rate of just over 3 gpm. Based on the known dimensions of the well and the equipment configuration, the volume estimated to be circulating in the well casing (mostly within the screened interval) was about 25 gal., and the volume in the discharge tube to the surface was about 38 gal., so the volume in the transducer tube and in surface plumbing is estimated to be on the order of 15–20 gal. Note that the volume of the circulation loop in the 2014 test was about 210 gal. because a bigger downhole pump was in use then and the discharge pipe to the surface had a larger diameter than in 2022. Thus, if the flow rates sweeping the screened interval were the same at both times, the slope of the *ln(C/Co)* versus time curve in the 2022 test should be nearly 2.5 times greater than in the 2014 test.

The results of the borehole dilution tracer test are shown in Figure 10 as a plot of *ln(C/Co)* versus time. When the test was started with CrEX-4 off, the slope of the tracer curve (blue symbols in Figure 10) suggested a volumetric flow rate through the screened interval of about 8 L/hr, more than 2.5 times the flow rate in the 2014 tracer test. This high rate prompted an inquiry into the reconfiguration of the well after the 2020 redevelopment. This inquiry determined that during the 2020 recompletion, the 4.9-ft screen of the transducer tube that was used as part of the injection and circulation loop was placed into the upper 4.9 ft of the R-42 screened interval, with the top of both screens matching exactly. This was a deviation from the original plan to ensure that the transducer tube screen was fully submerged, and it is a nonideal configuration for a borehole dilution tracer test, as the flow out of the transducer tube directly into the screened interval of the main casing could potentially cause tracer to be artificially forced out through the screen, which could result in a faster decline in tracer concentration than would be observed if only the natural flow was sweeping tracer out of the screened interval. As long as the extraction and injection flows were balanced (by maintaining closed-loop circulation), any extra injection flow being forced out the screened interval would be compensated for by flow of tracer-free groundwater into the interval, thus causing artificially rapid dilution of the tracer. In 2014, a different transducer tube was in use, with a screened interval from approximately 427 to 427.5 ft bgs, with the bottom about 4 ft above the top of the casing screen and the top about 5 ft below the water table at the time.



Note: Equations of linear regression trendlines, showing slopes of different colored portions of the data, are indicated next to the data segments.

Figure 10 Natural log of normalized tracer concentrations *ln(C/Co)* versus time during the R-42 borehole dilution tracer test

Before the nonideal configuration was discovered, CrEX-4 was turned on after the test had run for about 68 hr, which was after a stable *ln(C/Co)* versus time slope had been established with CrEX-4 off. CrIN-1 was also turned on at this time. The orange symbols in Figure 10 are the data after CrEX-4 was turned on. Although the nonideal configuration was hypothesized to preclude a defensible quantitative assessment of the impact of CrEX-4, flows in the vicinity of R-42 were clearly affected by CrEX-4. The decrease in slope after turning CrEX-4 on would normally suggest a decrease in volumetric flow rate (by about a factor of 6), although the data are somewhat more scattered and the slope does not appear to be as constant as before CrEX-4 was turned on. However, the decrease in slope in this case could also be attributed to an increase in flow rate caused by turning CrEX-4 on, with the decreasing slope being the result of tracer that was artificially injected upgradient of R-42 (when CrEX-4 was off) flowing back into R-42 when CrEX-4 was turned on.

To reduce the possibility of artificial tracer injection, the circulation loop configuration was changed after the test had been run for about 190 hr, including the last 125 hr with CrEX-4 on. The return flow from the surface, which originally was routed into the transducer tube, was redirected to flow through a small opening in the wellhead plate where the electrical cable for the downhole pump penetrated the plate. This ensured that water returning to R-42 would be introduced at the water table above the screened interval in the main casing, rather than within the upper portion of the screened interval. Allowing water to cascade down approximately 930 ft of casing was not considered ideal, but this was the only way to achieve the desired configuration for a borehole dilution tracer test given the nonideal transducer screen placement. To ensure that only one variable was changed at a time, CrEX-4 was kept on.

The grey data points of Figure 10 are the data after the change in configuration with CrEX-4 on. It is apparent that the overall slope of the tracer decay curve with CrEX-4 on did not change significantly after the configuration change. It is also apparent that there was similar scatter in the data and short-term variability in the slope after the configuration change. This suggested that the nonideal configuration at the start of the test may have had only a minimal impact on the test results. The test was allowed to run with CrEX-4 on for about 75 hr after the configuration change, in part to allow some time for any tracer that might have been pushed upgradient during the early part of the test to flow past R-42 and no longer affect the tracer decay curve. Ideally, more time would have been allowed for the test to run in this configuration before turning CrEX-4 back off, but the threat posed by the Cerro Pelado fire prompted a decision to turn CrEX-4 off after 75 hr, approximately 265 hr after the start of the test. CrIN-1 was turned off at the same time to match the conditions during the first 68 hr of the test. The red data points of Figure 10 are the data after this change was made. They show that a fairly well-defined slope was established, which is significantly greater than the slope with CrEX-4 on, although it is less than half the slope during the first part of the test with CrEX-4 off (blue data points). The test was only run for about 65 hr in the new flow circulation configuration, with CrEX-4 off, before a mandatory field work stoppage due to the Cerro Pelado fire forced the termination of the test.

The volumetric flow rate estimated through the screened interval over the last 65 hr of the test, with CrEX-4 off, was about 1.13 gal./hr, or about 4.26 L/hr. This estimate assumes a circulation loop volume of 90 gal., or about 10 gal. larger than in the original, nonideal configuration. The increase in volume is based on the observation that, when the change in configuration was made, the water level in the well decreased starting about 2 min after the change (indicating that the return flow down the transducer tube was decreasing before the new return flow down the casing reached the water table), and then the water level started to recover about 7 min later (indicating that the flow down the casing reached the water table). From the timing of these events, and knowing roughly what the circulation flow rate was, it is estimated that there was about an additional 10 gal. in the circulation loop in the new configuration. (This estimate also included another 2 ft of casing length above the screened interval but below the water table that was circulating in the new configuration.) The uncertainty with this estimate is probably at least $\pm$10% given that the estimate in the original configuration was somewhat uncertain, and the uncertainty increased with the configuration change.

The volumetric flow rate estimate of 4.26 L/hr is about 20% higher than the estimate of 3.5 L/hr from the 2014 borehole dilution tracer test in R-42. If the uncertainty in the circulation loop volume estimate at the end of the test ranges from 80 to 100 gal., then the corresponding range of volumetric flow rate estimates would be 3.79 to 4.73 L/hr, with the lower end of the range being within ~8% of the 2014 flow rate estimate. Although the best estimate, and most of this range, exceeds the 10% criterion specified by NMED for agreement with the 2014 flow rate estimate (NMED 2021b), a higher flow rate in 2022 is not considered problematic because it suggests that the ambient groundwater flow rate in the vicinity of R-42 has increased since 2014, indicating that the permeability near the well is at least as high now as it was before the dithionite deployment. Note that the slope of the tracer curve appeared to be greater over the last ~40 hr of the test (a volumetric flow rate estimate of 5.08 L/hr) than over the entire 65-hr period when CrEX-4 was off at the end of the test, which may indicate a transition period after turning CrEX-4 off. This estimate represents a greater deviation from the NMED criterion, but it is in the direction of suggesting a further increase in permeability rather than a decrease.

While the flow rate estimate at the end of the 2022 borehole dilution tracer test might have been affected by tracer being artificially injected upgradient of R-42 during the early part of the test, the movement of such tracer through the well later in the test would only decrease the slope of the curve, and hence the flow rate estimate later in the test. Note that under ideal test conditions, there should never be any tracer upgradient of the well, so any tracer moving into the well from upgradient will decrease the slope, and once this tracer has all moved into the well or downgradient, the slope should stabilize at a steeper value. The slope at the end of the test (especially the last ~40 hr) was quite stable, suggesting that any influence of upgradient tracer was negligible by that time. The difference in the slopes between the earliest and latest portions of the test with CrEX-4 off (blue and red data points, respectively) suggest that the forced flow of tracer out of the screened interval during the early portion of the test was about 0.78 gal./hr or 2.95 L/hr. Thus, a total of about 150 gal. of tracer-bearing water could potentially have been forced out of the screened interval during the first 190 hr of the test when the nonideal circulation loop configuration was in use.

If this volume had been pushed out radially into a homogeneous, isotropic aquifer with a flow porosity of 0.2 (ignoring the higher porosity of the approximately 3-in.-thick filter pack around the screen, and assuming only the screen length was active, not the filter pack length), the radial injection distance would have been about 0.38 m if there were no ambient groundwater flow. However, the previous linear groundwater flow velocity estimate (specific capacity divided by a flow porosity of 0.2) in the vicinity of R-42 from the 2014 tracer test was about 0.14 m/day, which was in good agreement with later estimates from a 2014 push-drift-pull tracer test [section 3 of Attachment 1 of the Chromium Compendium (LANL 2018c)]. So, in 190 hr of artificially pushing tracer out of the screened interval, groundwater around the well would have moved downgradient about 1.1 m. For the deduced radial injection rate of 2.95 L/hr and a linear ambient groundwater flow rate of 0.14 m/day, a stagnation point would have occurred about 6 cm upgradient of the well (again ignoring the higher porosity of the filter pack, which would decrease the distance to the stagnation point). Even allowing for some uncertainty in this estimate, tracer would not be predicted to have moved upgradient more than about 10 cm from R-42. This upgradient tracer mass would flow back into the well, or downgradient of the well, less than a day after the circulation loop configuration was changed to eliminate artificial injection of tracer. Even if the ambient groundwater flow rate were about a factor of 3 lower when CrEX-4 was on, as the change in slope of the tracer decay curve in the latter part of the test would suggest, it would have taken only a little over 2 days to sweep the upgradient tracer into the well screen or downgradient. This suggests that the tracer curve obtained at the end of the test after CrEX-4 was turned off, which occurred about 75 hr after the circulation loop configuration change, should have been free of any artifacts from upgradient tracer.

While it appears that CrEX-4 pumping affected the tracer decay curve in the borehole dilution tracer test, quantifying this effect is confounded by the nonideal configuration at the start of the test. However, the inference from the differences in slopes of the tracer decay curve before and after turning CrEX-4 off after the circulation loop configuration had been modified suggests that the flow rate was about 3 times higher when CrEX-4 was off. Figure 11, which shows water levels in R-42 (uncorrected for barometric effects) superimposed on the tracer decay curve of Figure 10, offers no obvious insights into what may have caused the dramatic changes in the apparent flow rate through R-42 with CrEX-4 on or off. Water levels were recorded every minute during the tracer test. The water level measurements were much nosier in the original circulation loop configuration than in the modified configuration; apparently, the injection of water into the transducer tube caused much more fluctuation in water levels than the injection of water down the casing of the well. This observation lends further confidence to the results obtained after the circulation loop reconfiguration.

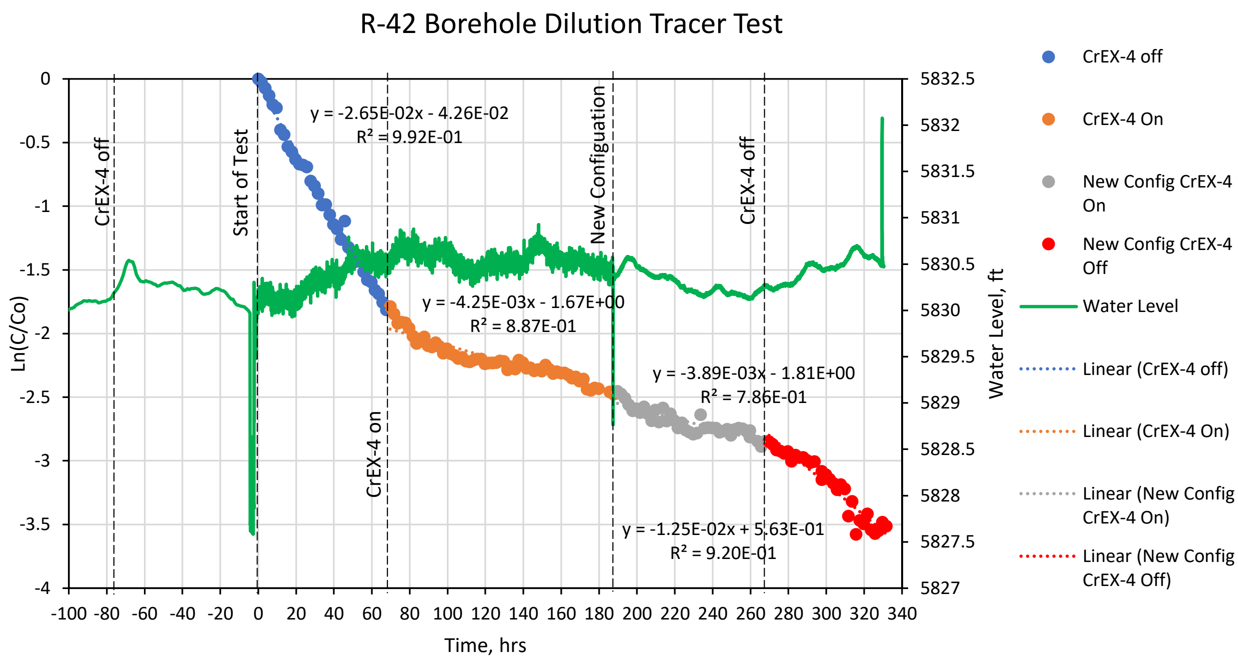


Figure 11 **R-42 water levels (uncorrected for barometric effects) superimposed on natural log tracer concentrations during the R-42 borehole dilution tracer test**

The relatively good agreement that was obtained between the volumetric flow rate estimates from the 2014 borehole dilution tracer test and the end of the 2022 test might be considered somewhat surprising given that water levels have dropped approximately 8 ft between 2014 and 2022, and the IM extraction and injection wells were nonexistent in 2014. Figure 12 shows a water level record in R-42 since it was installed, with vertical dashed lines indicating the times of the two borehole dilution tracer tests. Besides changes in flow rates that might occur because of the overall water level decline (which could change boundary conditions and hydraulic gradients for flow through the screened interval), seasonal pumping impacts from Los Alamos County supply well pumping may also occur (which could cause different vertical components to flow at different times of the year). Figure 12 shows that the 2014 test, conducted during the first week of April, was right at the peak of a water level cycle, just before supply wells were turned on for the season. The 2022 test, which was started on April 25, was conducted just after water levels had begun to drop from seasonal supply well pumping. Thus, it would not have been surprising to see a different flow rate estimate in 2022 than in 2014 even if permeability near the well was unchanged. Conversely, if the permeability did change, this might not necessarily result in flow rate changes through the R-42 screened interval because of the differences in hydrologic conditions at the times of the two borehole dilution tracer tests. However, regardless of whether or not permeability near R-42 changed, the fact that the volumetric flow rate estimate through the screened interval is higher in 2022 (with CrEX-4 off) than in 2014 suggests that the geochemical observations in R-42 are reflecting conditions in the surrounding aquifer at least as well as they did in 2014. Thus, the 2022 test results provide confidence that geochemical observations in R-42 are not being significantly affected by any permeability reduction near the well caused by the dithionite deployment.

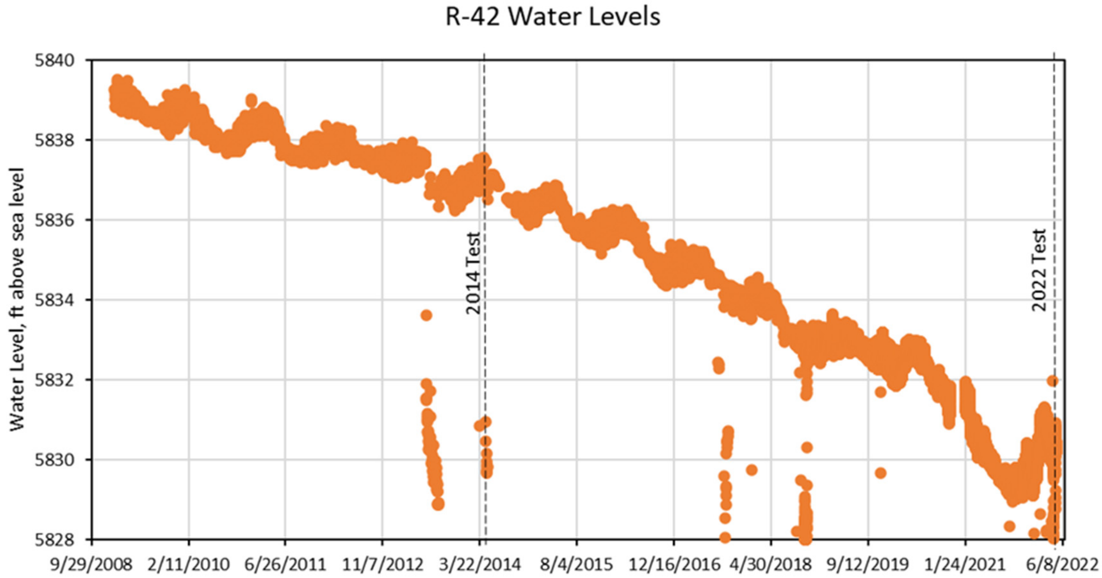


Figure 12 R-42 water level record since well installation, with vertical dashed lines showing times of the two borehole dilution tracer tests

5.0 CONCLUSIONS AND RECOMMENDATIONS

The geochemical trends in R-42 indicate that both the 2020 redevelopment and the 2021 extended purge were highly beneficial in exhausting the reduction capacity induced by the 2017 dithionite deployment and in restoring R-42 to pre-amendment geochemical conditions. All of NMED's target criteria for geochemical restoration have been effectively met as of April 2022, with the exception of field-measured DO, which is currently at about 4 mg/L versus the NMED criterion of >6 mg/L. However, DO concentrations of 4 mg/L and 6 mg/L are both considered highly oxidizing thermodynamically, and there are no species that DOE is aware of in the regional aquifer that would be expected to change oxidation state between these two DO levels (see Table 2). Hence, DOE considers a DO concentration of 4 mg/L to be sufficient to alleviate concerns about other geochemical parameters being adversely affected. Chromium concentrations in 2022 sampling events have been consistently measured at concentrations close to their pre-dithionite levels and have consistently fallen between the lower and upper limits specified by NMED as a target range for geochemical restoration. Iron and manganese concentrations have similarly achieved NMED target levels in recent sampling. Also, sodium and sulfate, the two predominant constituents in the dithionite injection (the latter being a reaction product, not an injected constituent), have returned to pre-dithionite levels (Figures A-7 and 2 [and A-8], respectively, and Table A-1 in Appendix A).

Since the 2020 redevelopment of R-42, the specific capacity of the well during sampling or purging events has been consistently near or above specific capacity estimates before the 2017 dithionite deployment. Video logs of R-42 before and after the 2020 redevelopment, included as Attachment 1 to this report, indicate that the redevelopment improved hydraulic communication between the inside and outside of the well. A borehole dilution tracer test conducted in R-42 from April 25 to May 9, 2022, yielded a volumetric groundwater flow rate estimate through the screened interval when CrEX-4 was turned off that was ~20% higher than an estimate obtained from a 2014 borehole dilution tracer test, before any IM wells existed.

While it is not possible to say how much of the improvement in hydraulic conditions in R-42 can be attributed to the 2020 redevelopment versus natural processes that may have occurred anyway, these results collectively provide confidence that geochemical observations in R-42 reflect conditions in the surrounding aquifer without being affected by permeability reduction near the well.

The results presented in this report demonstrate that R-42 has been rehabilitated as a monitoring well that will provide representative geochemical data. Accordingly, DOE recommends that R-42 be reinstated into the IFGMP. Water chemistry data will be monitored to evaluate any temporal changes in geochemical conditions. If observations suggest a reversion to conditions consistent with adverse impacts from the dithionite deployment, the suitability of R-42 for continued monitoring will be discussed and re-evaluated with NMED.

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Appendix A

Summary of Recent Laboratory and Field Parameter Values Relative to New Mexico Environment Department Target Criteria for Successful Rehabilitation and Additional Figures and Data

Table A-1
Summary of Recent Laboratory and Field Parameter Values Relative to New Mexico Environment Department Target Criteria for Successful Rehabilitation

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Laboratory Parameters				
Alkalinity, total carbonate	55–100 mg/L as HCO_3	Primarily within target bounds after 2021 redevelopment. Exceeded only a few times since Aug 2021. Achieved targets since Feb 2022.	The 2016 alkaline injection likely precipitated divalent carbonate solids. The 2021 rehabilitation/redevelopment likely accessed persisting carbonate-rich zone. Concentration fluctuations observed during purge events such as Oct 2018 and 2021 extended purges. At least the 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-38
Aluminum	<1 µg/L, nondetect	Achieved target (nondetections).	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-11
Ammonium-N	<0.1 mg/L	Achieved target.		A-45
Antimony	<1.0 µg/L, nondetect	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout.	A-12
Arsenic	<2.0 µg/L	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout. Concentrations lowered following 2021 rehabilitation.	A-13
Barium	<100 µg/L	Achieved target.		A-33
Beryllium	<1.0 µg/L, nondetect	Achieved target.		A-14
Boron	<50 µg/L	Achieved target.		A-46
Bromide	<0.25 mg/L	Straddling target following 2021 extended purge (~0.2 to 0.3 µg/L)	Injected as a tracer with 2017 dithionite. Br followed similar trends as Na and sulfate following the dithionite injection. While Br was already nearing the target, it fell even closer to the target after the 2021 redevelopment.	2, A-37
Cadmium	<0.30 µg/L, nondetect	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-15

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Calcium	<55 mg/L	Approximated target after Jan 2022.	Calcium likely precipitated during both the 2016 alkaline injection (as a carbonate) and the 2017 dithionite (as a sulfate). Approximated target for a majority of the history since early 2018. Concentration fluctuations observed during purge events such as the Oct 2018 and 2021 extended purges. Apparently these purges access richer zone(s) that are not significant water sources when the well is not being purged.	A-34
Cesium	<1 µg/L, nondetect	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-16
Chloride	<45 mg/L	Approximated target (recent results <20% above target).	Cl has been fairly steady at ~50 mg/L following the Oct 2018 purge. This value is between and close to values that both preceded the alkaline Injection (high 40's of mg/L) and those before the dithionite injection (low 50s of mg/L).	2, A-39
Chromium	breakthrough 380–800 µg/L, if reduced chromium as Cr(III), <3 µg/L	Achieved target range (since Oct 2021).	The dithionite significantly suppressed chromium concentrations after the 2017 injection and until the 2021 rehabilitation/redevelopment. The 2021 redevelopment achieved the first observable and demonstrated a significant restoration towards target rehabilitation values. Similar restorative trending restarted with the 2021 extended purge achieving the NMED Target range. A planned 3-day pumping interruption during the 2021 purge resulted in sampling of higher concentrations; The first sample collected (on 9/7/2021, after 50 gal. of pumping) had a Cr(VI) concentration of 663 µg/L, which was essentially the same as pre-dithionite concentrations circa 700 µg/L.	1, 4, A-1
Cobalt	<1 µg/L, nondetect	Achieved target since Sept 2021.	Concentrations lowered following 2021 extended purge.	A-17
Copper	< 0.8 µg/L, nondetect	Achieved target since Nov 2021.	Concentrations lowered following 2021 extended purge.	A-18
Dissolved organic carbon	<1.0 mgC/L	See TOC[c]. Similar to TOC since dithionite injection.		A-48

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Fluoride	0.2 – 0.4 mg/L	Slightly above upper range for Jan, Feb, and Apr 2022 (~0.5–0.6 mg/L). Achieved target range for 6 CV[d] in Mar 2022. Concentration may be falling towards target (since Dec 2022).	Fluoride was elevated following the 2016 alkaline injection. Fluoride fell into the target range during the Oct 2018 purge. The 2022 rehabilitation likely accessed a zone with remaining elevated fluoride.	A-40
Hardness	125 – 170 mg/L	See Ca, Mg, Ba, Sr, and alkalinity		
Iron (total dissolved)	<10 µg/L, nondetect	Achieved target range: Sometimes during the 2021 extended purge and often during the more-normal sampling since Jan 2021. Jan 2022: 3 CV and 6 CV achieved target. Concentration rose to ~112 at 9 CV (although back down to ~20 µg/L at 12 CV). 02/2022: Achieved target at 3 CV. 03/2022: ~20 µg/L at 3 CV and 6 CV. 04/2022: Achieved target at 3 CV. Continuing future downtrending appears likely.	Downtrending towards target rehabilitation values occurred during the pumpout following the dithionite injection (on a log basis, Appendix A figure). While concentration remained elevated and stable during 2018 and into 2019 pumping/sampling, a downtrend started again in early 2019 (following and possibly prompted by an Oct 2018 purge and several subsequent 350- and 1000-gal. purges). The 2021 redevelopment and 2021 extended purge accessed some relatively higher concentrations while performing these purging and rehabilitation actions. Similar to other chemical trends (e.g., manganese, NO_2, and some other metals), this seems to demonstrate a difference in water sources that R-42 can access. In contrast with normal sampling (i.e., sampling following only ~3-CV purges), extensive pumping seems to access some region that remains affected by dithionite reducing conditions. Subsequent sampling (with briefer purging) achieved a further restorative downtrend achieving NMED targets.	1, A-3
Ferrous iron	<10 µg/L, nondetect	By extension of "iron (total dissolved)" results, achieved target range: Sometimes during the 2021 extended purge and often during the more-normal sampling since Jan 2021.		

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Lead	<0.30 µg/L, nondetect	Achieved target (nondetection) after Sep 2021.	2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-19
Lithium	<40 µg/L	Likely falling towards the target following the 2021 extended purge.	Concentration fluctuations during significant purging such as the 2013, post-dithionite pumping, and 2021 extended purges.	A-31
Magnesium	<15 mg/L	Approximated upper target at between ~14 and 17 mg/L after Nov 2021 .	Similar trends as calcium.	A-35
Manganese	<10 µg/L	Achieved target range during last 2 sampling rounds. It seems that the 2021 extended purge helped exhaust sources of manganese near the well. Downtrending appears to continue.	Consistent downtrending towards target rehabilitation values occurred during the pumpout following the dithionite injection. While slowing, consistent downtrending continued during 2018 and 2019 pumping/sampling. The 2021 redevelopment accelerated the restorative downtrending. After a brief hiatus, the 2021 extended purge initially accessed low concentrations that then generally increased through continued purging. This was similar to other chemical trends (e.g., iron & NO2). Concentration fluctuations observed during purge events such as the Oct 2018 and 2021 extended purges. Apparently these purges temporarily access zones that are not significant water source(s) when the well is not being purged. In contrast with normal sampling (i.e., sampling following ~3 CVs), extensive pumping seems to access regions that remain affected by dithionite reducing conditions. Subsequent sampling (with briefer purging) achieved a further-restorative downtrend closely approximating NMED targets.	1, A-2
Mercury	<0.07 µg/L	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout.	A-20
Molybdenum	<1 µg/L, nondetect	Achieved target.	Concentrations lowered following 2021 extended purge.	A-21
Nickel	<30 µg/L	Achieved target.	Likely dithionite-induced and significant removal during subsequent pumpout. Concentrations lowered following 2021 extended purge.	A-22
Nitrate-N	>4.0 mg/L	Achieved target.	Likely has uptrended since early 2019 (following the Oct 2018 purge and several subsequent 350 & 1000 gal. purges).	2, A-9

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Nitrite-N	<0.01 mg/L, nondetect	Achieved target range: Sometimes during the 2021 extended purge and essentially during the first 6 of 12 CVs in Jan 2021. Straddled target in Feb 2021's 3 CV sampling. Achieved target during sampling since Mar 2021.	Consistent downtrending towards target rehabilitation values occurred following the 2017 dithionite injection and likely until the 2021 extended purge. In contrast with normal sampling (following ~3 CV purges), extensive pumping (including Jan 2021's 12 CV) seems to access regions that remain affected by dithionite reducing conditions. Subsequent sampling (with briefer purging) achieved a further-restorative downtrend closely approximating NMED targets.	A-10
Oxalate	<0.01 mg/L, nondetect	Achieved target.		A-41
Perchlorate	>1.0 µg/L	Achieved or approximated target.		A-42
Phosphorus	<0.01 mg/L, nondetect	Achieved target.		A-43
Potassium	<3.0 mg/L	Achieved target.		A-32
Rhenium	<0.1 µg/L, nondetect	Achieved target.		
Selenium	<2.5 µg/L, nondetect	Achieving/straddling target (including nondetections) after Jan 2022.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-23
Silica (SiO_2)	80 mg/L	Achieved or straddled lower target range starting in 2022.		A-44
Silver	<1.5 µg/L (GGRL DL)	Achieved target.		A-24
Sodium	<17 mg/L	Approximated target after 2021 extended purge (at between ~15 and 19 mg/L.)	Originated directly from dithionite. Significant removal during subsequent pumpout. Falling concentrations may have stabilized following the Oct 2018 extended purge until the 2020 rehabilitation. Concentrations were significantly lowered during the 2020 rehabilitation.	A-7
Strontium	<200 µg/L	Straddling target since Jan 2022.	Similar trends as calcium.	A-36
Sulfate	<85 mg/L	Straddling target since Dec 2021.	Similar trends as sodium.	2, A-8

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Sulfide	<0.01 mg/L, nondetect	No odor observed.		
Thallium	<0.60 µg/L, nondetect	Achieved target starting Aug 2021.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-25
Tin	<1 µg/L, nondetect	Achieved target starting Jan 2022.		A-26
Titanium	<2 µg/L, nondetect	Achieved target starting Sept 2021.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged.	A-27
Total dissolved solids	<400 mg/L	Achieved target in Apr 2022 (not taken in preceding months).	TDS[e] trended similarly as sodium and sulfate. After increasing during the dithionite injection, it was reduced by the subsequent pumpout. Its falling concentration steadied out during the EMCA[f] pause. Concentration fell further during the 2021 extended purge and likely has steadied out near the target value since then. (Note that specific conductivity and an estimated summation of major ions was used to supplement TDS trends)	A-47
Total Kjeldahl nitrogen	<0.10 mg/L, nondetect (GEL, offsite laboratory)	Likely achieving target (Apr 2022 results were nondetect at ~0.145 and 0.179 mg/L).		A-45
Total organic carbon	<1.0 mgC/L	Straddled target since Jan 2022. Higher values as Jan 2022's 12-CV purge proceeded and in Apr 2022.		A-48
Uranium	>0.5 µg/L	Achieved target starting Nov 2021.	Likely alkaline injection-induced and significant removal during subsequent pumpout. 2021 rehabilitation appears to have achieved concentration values in-line with projected pre-alkaline historical trend.	A-28
Vanadium	>3 µg/L	Achieved target starting Dec 2021.		A-29
Zinc	< 5.2 µg/L (GGRL DL)	Achieved target starting Oct 2021.	Likely dithionite-induced and significant removal during subsequent pumpout. 2021 extended purge appeared to access a richer zone that is not a significant source when the well is not being purged. Concentrations lowered following 2021 extended purge.	A-30

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Field Parameters				
Color	Nondetect	Achieved within 3 CV: - Jan 2022 cleared up by ~1 CV, - Feb 2022 Green tint cleared up by ~1.5 CV, - Mar 2022 slight yellow tint cleared up by ~2 CV, - Apr 2022 yellow-brown tint cleared up by ~1.5 CV)		
Dissolved oxygen, mg/L	>6.0 mg/L	Still below target. The 2021 extended purge achieved the highest consistent DO[g] since the dithionite injection. The recent trend for each sampling event starting in Dec 2021 entailed DO starting at ~2 mg/L and then rising to ~4-5 mg/L through the pumping of a few CVs.		3, A-4
Odor	Nondetect	Achieved after the 2021 extended purge. (Note that "organic odor" was observed during early purging in Nov 2021 and an "earthy odor" in Jan 2022 prior to ~ 1 CV).		A-47
pH	7.1–8.0	Achieved after 2021 extended purge		3, A-6
Specific conductance, µS/cm	<500 µS/cm	Achieved target during and after 2021 extended purge (excluding a few anomalous readings)		A-47

Solutes (dissolved)	NMED[a] Rehabilitation Target	Status after Rehabilitation, Redevelopment, and 2021 Purging	Comments and Historical Observations	Associated Figures[b]
Turbidity, NTU	<2.0	Achieved starting in Feb 2022 within 3 CVs. (Jan 2022 achieved target at ~6 CV)	Higher turbidities occurred following the 2021 extended purge possibly due to material loosened and accessed during rehabilitation, redevelopment, and purging.	A-49
Uncorrected ORP, mV	>+200 mV	Achieved starting Jan 2022 (by ~2 to 4 CVs).		3, A-5

[a] NMED = New Mexico Environment Department.

[b] See Attachment A-1 for Figures A-1 through A-49.

[c] TOC = Total organic carbon.

[d] CV = Casing volume.

[e] TDS = Total dissolved solids.

[f] EMCA = Essential mission critical activities.

[g] DO = Dissolved oxygen.

Attachment A-1

Additional Figures and Data
(on CD included with this document)

Attachment 1

Video Logs of R-42 Before and After 2020 Redevelopment
(on DVD included with this document)