

DEPARTMENT OF ENERGY Environmental Management Los Alamos Field Office (EM-LA) Los Alamos, New Mexico 87544

Mr. John E. Kieling Bureau Chief Hazardous Waste Bureau New Mexico Environment Department 2905 Rodeo Park Drive East, Building 1 Santa Fe, NM 87505-6303



JAN 3 1 2019

Dear Mr. Kieling:

Subject: Submittal of the Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon

Enclosed please find two hard copies with electronic files of the "Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon." This report reflects discussions in pre-submittal meetings held with the New Mexico Environment Department on December 12 and 18, 2018. In those meetings, the results from the Fall 2018 tests at R-42 and R-28 and the approach for inclusion of those results into this report were discussed and agreed upon.

If you have any questions, please contact Danny Katzman at (505) 309-1371 (danny.katzman@em-la.doe.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Arturo Q. Duran Compliance and Permitting Manager Environmental Management Los Alamos Field Office

Enclosures:

1. Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon (EM2019-0011)

cc (letter with enclosure[s]): D. Katzman, N3B S. White, N3B C. Rodriguez, EM-LA

cc (letter with electronic enclosure[s]): L. King, EPA Region 6, Dallas, TX R. Martinez, San Ildefonso Pueblo, NM D. Chavarria, Santa Clara Pueblo, NM S. Pullen, NMED S. Yanicak, NMED emla.docs@em.doe.gov N3B Records Public Reading Room (EPRR) PRS Website

cc (letter emailed without enclosure[s]): E. Evered, N3B F. Johns, N3B J. Legare, N3B F. Lockhart, N3B G. Morgan, N3B B. Robinson, N3B B. Willis, N3B A. Duran, EM-LA D. Nickless, EM-LA D. Rhodes, EM-LA

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January 2019 EM2019-0011

# Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon



Newport News Nuclear BWXT – Los Alamos, LLC (N3B), under the U.S. Department of Energy Office of Environmental Management Contract No. 89303318CEM000007 (the Los Alamos Legacy Cleanup Contract), has prepared this document pursuant to the Compliance Order on Consent, signed June 24, 2016. The Compliance Order on Consent contains requirements for the investigation and cleanup, including corrective action, of contamination at Los Alamos National Laboratory. The U.S. government has rights to use, reproduce, and distribute this document. The public may copy and use this document without charge, provided that this notice and any statement of authorship are reproduced on all copies.

## Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon

January 2019

Responsible program	director:			
Bruce Robinson	BARK	Program Director	Water Program	1/23/2019
Printed Name	Signature	Title	Organization	Date
Responsible N3B rep	resentative:			
Erich Evered	AGO. I Nel	Program Manager	N3B Environmental Remediation Program	1/23/2019
Printed Name	Signature	Title	Organization	Date
Responsible DOE EN	I-LA representative:			
Arturo Q. Duran	Hause for	Compliance and Permitting Manager	Office of Quality and Regulatory Compliance	1/31/2019

Printed Name

Signature

Title

Organization Date

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#### Attachment

Attachment 1 Data Associated with the "Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon" (on CD included with this document)

### 1.0 INTRODUCTION

This fifth quarterly report presents results of two pilot-scale amendment tests conducted to evaluate feasibility for in situ treatment of hexavalent chromium [Cr(VI)] in the regional aquifer. The study is being conducted in accordance with the "Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon" (LANL 2017, 602505) as approved by the New Mexico Environment Department (NMED) (2017, 602546). The deployments occurred at regional groundwater monitoring wells R-42 and R-28. Sodium dithionite was injected into R-42 in late August 2017 and molasses was injected into R-28 in early September 2017 (Figure 1.0-1). The objectives of the tests are to evaluate (1) the ability of the amendments to reduce dissolved-phase Cr(VI) to insoluble and immobile trivalent chromium [Cr(III)] in the regional aquifer, (2) the longevity of the treatments in keeping Cr(VI) concentrations low (i.e., reduction capacity), (3) any adverse geochemical effects and their persistence, and (4) any adverse hydrological impacts of the treatments on hydraulic properties of the aquifer.

The first quarterly report, issued at the end of January 2018 (LANL 2018, 602862), provided details of how the amendments were deployed and of the pumping and sampling strategies in each of the test wells, as well as the geochemistry data from the tests, through the end of calendar year 2017. The second quarterly report (LANL 2018, 603031) provided (1) an update of the geochemistry data from the two amendments tests, (2) the results of a borehole dilution tracer test that was conducted in R-42 in January 2018 to estimate the post-amendment ambient groundwater flow velocity through the R-42 screened interval, and (3) an analysis of pre- and post-amendment drawdown data from both R-42 and R-28 to evaluate the effects of the amendments on near-well hydraulic conductivity. The third and fourth quarterly reports (N3B 2018, 700032; N3B 2018, 700108) provided an update of the geochemistry data from the two amendments tests.

This fifth quarterly report provides updated plots of geochemistry data from R-42 and R-28 that include results from additional samples collected during late September and through December 2018. Historical context is provided in order to support discussion of data obtained during the most recent pilot period (previous reports provide additional discussion related to corresponding pilot time periods). This report also includes data collected during semicontinuous pumping conducted at both wells during late October and into early November 2018. Pumping was conducted to effectively draw water samples from further outside of the wellbore into the amendments' radius of influence (ROI) and also towards the ambient aquifer. Well level changes were measured during the recent pumping and a discussion of the well drawdown and recovery will be provided in the next quarterly report.

All of the new geochemistry data associated with these samples are included in Attachment 1 (on CD included with this document, plotted along with previously reported data).

#### 2.0 UPDATE OF AMENDMENT TEST GEOCHEMISTRY RESULTS

#### 2.1 Sodium Dithionite at R-42

Figure 2.1-1 shows an updated plot of the concentration trends of selected dissolved cations and metals, including chromium, measured in samples collected from R-42 as a function of time. Operational timelines are also provided in Figure 2.1-1 (and in subsequent R-42 Figures 2.1-2 through 2.1-7) as black vertical dashed lines. The approximate timeline for injection batches are plotted near the left-most of the vertical dashed lines presented on each figure. The other vertical dashed lines shown to the right indicate subsequent dates when operational activities were conducted. Operational activities to the right of the amendment injection included the start of continuous pumping of R-42 in August 2017, and then the subsequent transition in September 2017 to pumping 5 days/wk (8 hr/day) from the well. This pumping

was stopped in October 2017. Biweekly 50-gal. purges were initiated after a dilution tracer test was conducted in January 2018, as described in the second quarterly report (LANL 2018, 603031). Following the dilution tracer test, each sampling event involved an approximate 50-gal. purge and did not include injections or water circulation. From October 22 and until November 2, 2018, an extended semicontinuous purge and sampling event was conducted at approximately 3 gpm (2.9 gpm) for 170 hr during the period. This R-42 3-gpm purge and sampling event was conducted to obtain samples representing groundwater further into the aquifer than is likely achieved during the 50-gal. purges. The results will be used to update the pumping and sampling approach accordingly.

As Figure 2.1-1 shows, there was a period that lacked purging/sampling that occurred from April 19 to June 13, 2018. This sampling hiatus is a result of the transition of environmental work conducted by the U.S. Department of Energy Environmental Management Los Alamos Field Office's contractor Los Alamos National Security, LLC (LANS) to Newport News Nuclear BWXT – Los Alamos, LLC (N3B) beginning on April 30, 2018.

Figures 2.1-2 through 2.1-7 provide the same vertical timelines and descriptions depicting operations as in Figure 2.1-1. Figures either show the full amendment period as in Figure 2.1-1, or the figures show a focused period that depicts only the most recent several weeks of data. For example, Figure 2.1-2 provides a subset of the more comprehensive data shown in Figure 2.1-1 by providing a timescale of only the more recent data starting in October 2018. Figure 2.1-2 also focuses only upon a subset of the analytes shown in Figure 2.1-1 (i.e., iron, manganese, and arsenic). Figure 2.1-3 focuses on sodium and sulfate for the full amendment period.

Figure 2.1-4 shows concentration trends for some of the other elements of interest, including arsenic and selenium over the full amendment period.

Figure 2.1-5 shows concentration trends for selected anions over the full period. Figure 2.1-6 focuses upon a subset of recent data for nitrate and nitrite only. Figure 2.1-7 focuses on recent bromide data.

Figures 2.1-8, 2.1-9, and 2.1-10 provide conceptual plan views of the well bore and developments on the well bore surroundings over the history of the well following the amendment injection.

Cr(VI) concentrations (measured as total chromium) in R-42 decreased to below the New Mexico groundwater standard of 0.05 mg/L soon after the dithionite deployment and have remained well below this level. Since the beginning of 2018, chromium concentrations have remained at levels below 0.01 mg/L (Figure 2.1-1), which suggests that the aquifer in the vicinity of R-42 maintains sufficiently reducing conditions in all cases to reduce and immobilize Cr(VI). The pH before, during, and following the recent 3-gpm purge is approximately 7.0 standard units. This value remains significantly lower than pre-deployment values that were near 8.0. The persistence of these lower pH values is indicative of a continued influence from geochemical reactions following the dithionite deployment.

Concentrations of dissolved iron have persisted at elevated levels over the better part of the past year and at concentrations approximately a thousand times higher than the pre-amendment level (i.e., 10 mg/L versus 0.01 mg/L). There was a period in late 2017 when iron was lower, probably since the well was not as extensively purged as during other periods, potentially because of iron oxidation in the well bore. Following a slow but steady decline in dissolved iron over the past year during which a 50-gal. purge sampling method was employed, the recent 3-gpm pumping purge prompted an increase in the iron concentration from approximately 10 to 15 mg/L (Figures 2.1-1 and 2.1-2). This level also held steady for the sample taken 6 wk after this purge. The rise in concentration during the 3-gpm purge suggests that pumping drew water from further away from the well and also from areas where the amendment's ROI remains more prominently reducing (Figure 2.1-10).

Manganese and arsenic trends are shown in Figures 2.1-2 and 2.1-4. The trends correlate with that of iron. Both manganese and arsenic exhibited elevated levels shortly after injections that have been slowly diminishing over the past year. Concentrations of both have remained well above pre-amendment levels, indicating persistent reducing conditions (i.e., the pre-amendment level is approximately 0.001 mg/L for both). Manganese levels, which increased from 3 to 4 mg/L during the 3-gpm purge, fell back to below the pre-purge levels 6 wk after the purge. Arsenic levels rose from 0.002 to 0.010 mg/L during the 3-gpm purge and then to 0.016 mg/L for the post-purge sample. Similar to the trends in iron, the increases in manganese and arsenic levels also suggest that the purge drew upon aquifer environments that were more highly reduced than the near-borehole water that was sampled previously under the 50-gal. purges.

Figures 2.1-1, 2.1-3, and 2.1-5 present the sodium and sulfate trends. The amendment, containing sodium dithionite and sodium sulfite (and to a lesser extent sodium bromide), was the origin of the elevated sodium. These reagents also provided the sulfur that acted as the primary sulfur source that produced sulfate through oxidation reactions. Sulfate has been the most prominent anion measured in R-42 since the amendments. Sodium has helped to ionically balance sulfate (i.e., maintain charge balance) in samples following the time of the amendment. Sodium has most likely acted as an accompanying ion to sulfur species during the amendment test (i.e., accompanied sulfate and other more reduced sulfur species such as sulfite) and can be considered as a tracer to the sulfur species. Sulfate and sodium levels initially spiked upwards following amendment deployment and then subsequently trended downwards (Figures 2.1-1 and 2.1-5). At first, during post-amendment pumping, the sulfate and sodium levels fell rapidly, and then during later phases the levels decreased more slowly as they began approaching pre-amendment levels. Before the recent 3-gpm extended purge event, the diminished sulfate and sodium levels had fallen to levels approximately double their historical concentrations (from June 2016, before a local test that involved a sodium addition). The data from the 3-gpm purge resulted in increased levels of both, possibly drawing concentrations of these now soluble species from downgradient (i.e., the migration area as shown in Figure 2.1-10). It is also possible that sodium and sulfate were present in low permeability zones near the well that the 50-gal, purges were accessing. Following peaking of levels during the 3-gpm purge, sulfate and sodium levels began to decrease, suggesting that the pumping also began reaching further out towards aquifer-influenced regions where concentrations of both are lower.

Figures 2.1-5 and 2.1-6 illustrate the long-term and recent trends for both nitrate and nitrite. The nitrate has been depressed below pre-deployment levels since the end of the post-amendment purges, indicating a continued reduced state in the R-42 samples from October 2017 to mid-October 2018. With the exception of a single outlying data point, nitrite was not detected during this period. As shown in Figure 2.1-6, upon the start of the recent 3-gpm purge, nitrite appeared while nitrate nearly disappeared. The nitrate-to-nitrite flip appears to represent a shift that was close to stoichiometric in regard to nitrogen. In the recent sample, 6 wk after the end of the 3-gpm purge, both nitrate and nitrite were found to be nondetect (which indicates a reducing environment). The combined nitrate/nitrite nitrogen has been significantly lower than the pre-amendment nitrogen (i.e., approximately 20 mg/L of nitrate) since the end of the amendment purge and through the most recent sample collections. Both the initial shift from nitrate to nitrite during the 3-gpm purge and the even lower combined nitrate/nitrite concentrations (i.e., nondetect) following the purge indicate that the purge accessed more reducing ROI conditions than were previously accessed under conditions when the 50-gal. purge approach more likely represented primarily gradient-driven flow through the well.

Figures 2.1-5 and 2.1-7 show long-term and recent trends for bromide. Bromide originated from the co-deployed amendment tracer (i.e., sodium bromide). The bromide was predominantly captured during the initial post-amendment months when continuous pumping was conducted. Bromide levels steadily trailed off until August 2018, when the concentration essentially reached pre-deployment levels of approximately 0.2 mg/L, indicating a return of ambient groundwater conditions with respect to

conservative ions. Like sodium and other analytes previously described, bromide recognized a modest increase in concentration during the recent 3-gpm purge. The concentration held relatively stable in the sample following the purge. Although the increase in bromide was modest (from approximately 0.22 to 0.45 mg/L), the increase indicates that the 3-gpm purge effectively reached further into ROI and also into downstream migration zones (Figure 2.1-10), or into low permeability zones adjacent to the well that the 50-gal. purges did not access.

Concentrations of other constituents were also affected by the 3-gpm pumping. Before the pumping, calcium, magnesium, and potassium all had approximated pre-deployment levels and were not greatly affected by the purge, indicating an ambient aquifer influence both before and during the period. Chloride levels fell to mid-2016 levels indicating that the pumping assisted in reaching further aquifer influence.

The 3-gpm purge suggests that ROI region(s) in the R-42 vicinity are still exhibiting reducing conditions. The dissolved oxygen and oxidation-reduction potential field measurements also remained low, indicative of reducing conditions. Breakthrough or near-breakthrough of ambient levels for species that are not susceptible to reducing ROI conditions is evident for calcium, magnesium, and chloride.

Concentrations of other elements or ions not shown in Figures 2.1-1 through 2.1-7 can be found in Attachment 1 (on CD included with this document).

### 2.2 Molasses at R-28

Figure 2.2-1 shows an updated plot of the concentration trends of selected dissolved cations and metals, including chromium, measured in samples collected from R-28 as a function of time. Operational timelines are also provided in Figure 2.2-1 (and in subsequent R-28 Figures 2.2-2 through 2.2-7) as black vertical dashed lines. The approximate timeline for injection batches are plotted near the left-most of the vertical dashed lines presented on each figure. The other vertical dashed lines shown to the right indicate subsequent dates when operational activities were conducted. Chronologically, following the amendment injection, these operational activities included the start of "no net pumping," a 1000-gal. purge sample, and a transition to 50-gal. purge sampling. Finally, from October 22 and until November 2, 2018, an extended semicontinuous purge and sampling event was conducted at approximately 2.6 gpm (for 170 hr during the period). As Figure 2.2-1 shows, no purging/sampling occurred from April 19 to June 13, 2018. This gap in sampling is a result of the transition of environmental work from LANS to N3B.

Figures 2.2-2 through 2.2-7 show the full amendment period, as in Figure 2.2-1. Some figures focus only upon limited water quality parameters.

Figure 2.2-2 focuses on chromium, pH, and total organic carbon (TOC). Following the injection, chromium concentrations increased to greater than 0.5 mg/L, potentially associated with small-scale leaching of the stainless-steel well screen. Following the 1000-gal. purge in November 2017, chromium concentrations declined from approximately 0.15 mg/L following the purge to approximately 0.065 mg/L in April 2018. During this period, pH was low (less than 5.5, with two exceptions) mainly because of production of organic acids from fermentation. (Organic acids levels are assumed to correspond with the measure of the TOC, which remained elevated, at approximately 1000 mg/L in April 2018). The data indicate that the persistence of Cr(III) produced from reduction of Cr(VI) in groundwater was caused by the increased solubility of Cr(III) minerals at the observed pH levels and potentially additional complexation by organic acids. The pH data was not collected from April through the purge event in October 2018. During this period, as TOC (and organic acids) declined, reaching a minimum of 102 mg/L on September 17, 2018, this decline is believed a probable factor that supported chromium concentrations to decrease to below the New Mexico groundwater standard of 0.05 mg/L during mid-July 2018. The chromium concentration has remained below the standard since that time. During the 2.6-gpm purge, chromium concentrations fell further and to the lowest levels yet observed (approximately 0.01 mg/L), while pH increased to above 5.5.

TOC concentration increased with a concentration of 332 mg/L at the end of the purge. The data indicate a different geochemical environment in the aquifer adjacent to R-28 compared with the area in the aquifer further into the ROI. Near the well, chromium persisted likely under more strongly fermentative conditions where lower pH and more fully consumed TOC were observed. Samples collected from the extended purge are more representative of the reducing conditions that have been established within the ROI. In the aquifer further from the well, a higher pH and more residual TOC indicate a lower amount of fermentation, resulting in a higher pH range in which Cr(III) is less soluble and also potentially lowering the amount of organic acids available for complexing Cr(III). These chromium results indicate the longevity of the Cr(VI)-reducing conditions generated by the injected molasses.

Figure 2.2-3 focuses on the iron and manganese data. Dissolved iron and manganese were initially generated after the molasses injection. Following a general decline over the subsequent test period, both iron and manganese levels have remained elevated throughout the test and recently remain at about three orders of magnitude higher than pre-amendment levels. Both iron and manganese levels were observed to rise, prompted by the beginning of the 2.6-gpm extended purge. These increases indicate that the pumping reached further out into the ROI. Also, subsequent decreases in iron and manganese concentrations during the purge suggest that the extended purge reached further from the well. Similar to chromium, the December 2018 sampling set that followed the end of the purge appeared to maintain the concentrations of both iron and manganese levels seen at the end of the purge.

Figure 2.2-4 shows concentration trends for some of the other elements of interest, including arsenic and selenium. Arsenic has demonstrated a slow and steady decline since February 2018. The 2.6-gpm purge accelerated the rate of decline in arsenic levels, which fell from 0.007 to 0.004 mg/L. With one exception at 0.014 mg/L in June 2018, selenium has remained nondetect since March 2015. Although nickel levels fell overall throughout the period, the purge drew higher nickel levels temporarily. The sample following the purge exhibited falling nickel levels with the lowest nickel concentration value to date.

Figure 2.2-5 shows concentration trends for selected anions. Chloride concentrations generally fell throughout the test period, starting from elevated concentrations above 1000 mg/L in the molasses amendment and approaching historical background levels in the most recent sample set. The 2.6-gpm purge accelerated the rate of decline, indicating that the pumping pulled water from portions of the aquifer outside of the ROI.

Figures 2.2-5 and 2.2-6 illustrate bromide, sulfate, and TOC trends. Sodium bromide is the tracer that was introduced with molasses. Sulfate may come from either of two potential sources: (1) from the ambient aquifer water that contains approximately 60 mg/L or (2) from the molasses amendment itself, which contained approximately 1000 mg/L of organic sulfur that may be converted to sulfate by microbes or oxidation. The TOC represents molasses and/or ethanol and metabolic reaction products from each, such as organic acids (as described previously in this section). The levels of all three (i.e., TOC, bromide, and sulfate) were elevated following the molasses deployment and ethanol chase. Both the bromide and sulfate levels decreased following the ethanol chase (and then rebounded to an extent), TOC levels rose slightly following the addition of the ethanol. TOC, bromide, and sulfate levels generally fell over the subsequent period as upgradient water flowed through the well and purges were conducted. Sulfate levels fell to below pre-amendment concentrations in July 2018, indicating action of sulfate-reducing bacteria. The concentrations of TOC, bromide, and sulfate increased during the recent 2.6-gpm purge. Concentrations of bromide and sulfate rose initially during the purge, indicating conditions were not as strongly sulfate reducing within the ROI. The levels then fell during subsequent pumping. The lower bromide level is indicative that the pumping may have been reaching further out and towards the edge of the ROI. Following the purge, the sulfate level fell back to its low pre-purge level. TOC levels also rose initially during the extended purge, indicating less microbial consumption and, more specifically, in conjunction with the pH data, indicating less fermentation. Its slight fall during the subsequent purge is also indicative of reaching

further out towards the edge of the ROI. Following the purge, the bromide maintained its low level and both TOC and sulfate exhibited further decrease (likely because of further microbial degradation).

Figure 2.2-7 illustrates the nitrate and nitrite trends during the test progression. Nitrate has been reduced below pre-deployment levels since deployment of the molasses. Nitrite exhibited an initial spike following molasses deployment, followed by a depression subsequent to the ethanol chase. Following a partial rebound in September 2017, the nitrite has been generally decreasing. More recently, since about July 2017, both nitrite and nitrate have been decreasing more visibly, as shown in Figure 2.2-7. The levels of both nitrate and nitrite fell to nondetect during the 2.6-gpm extended purge event and also remained nondetect after the last sample collected in December 2018. This may indicate that the nitrogen sources in the molasses were consumed by microbes and that any nitrogen contribution from the aquifer was also consumed, or that more electrons in the reducing water are going to denitrification versus fermentation and sulfate reduction compared with the condition of the near-well environment before purging.

In addition to the nutrient indicators (i.e., sulfate, nitrate, and nitrite), phosphate has also followed a similar pattern. Following the 2.6-gpm purge, levels of sulfate, nitrate/nitrite (nondetect), phosphate, and TOC in the samples all reached low levels.

Concentrations of some other constituents shown in Figures 2.2-1, 2.2-4, and 2.2-5 were also affected by the 2.6-gpm pumping. Pumping drew potassium down and closer to pre-deployment levels (potassium was a significant amendment constituent). Silica was drawn down slightly and to its pre-deployment levels. Calcium, which was near its pre-deployment level before the 2.6-gpm purge, did not significantly change with the purge, suggesting it is not being affected by the conditions in the ROI.

Concentrations of other elements or ions not shown in the figures can be found in Attachment 1 (on CD included with this document).

#### 3.0 DISCUSSION AND RECOMMENDATIONS

Results to date illustrate that both dithionite and molasses can support chromium reduction and removal from groundwater over long periods of time. Results from the Fall 2018 extended purge events at R-42 and R-28 were more representative of the general conditions that are currently present in the full ROI around these two wells.

As discussed above, the dithionite amendment test at R-42 still requires more time to determine Cr(VI) reduction capacity imparted to the aquifer in the ROI. Chromium has not yet begun to break through into R-42. The 3-gpm purge demonstrated that the surrounding ROI that was reached through pumping and capture of groundwater in the more reduced zones showed increases in concentrations of other species, such as iron, manganese, and nitrite. The purge also appeared to pull water influenced by the aquifer in terms of the chloride, which is not reactive to reduction in the ROI. The 3-gpm purge pulled from further beyond the radius of the well than the 50-gal. purges did and minimized any potential effects from atmospheric oxygen in the well. Pumping appeared to reach further into ROI zones with conditions that remain reducing.

The molasses amendment test at R-28 will similarly require more time to determine reduction capacity and to confirm and analyze recent and ongoing changes in the aquifer biogeochemistry. Following the initial purges, the amendment has exhibited conditions that have treated chromium below the ambient level of 0.5 mg/L. Chromium was linked to pH conditions and did not become treated to the New Mexico standard level (0.05 mg/L) until mid-2018 when pH had rebounded up to approximately 5.5. Since that time and as the pH has further increased, the dissolved chromium continued to decrease and is recently at its lowest achieved levels of around 0.01 mg/L. The pH has not yet returned to pre-deployment levels.

Iron and manganese levels and other indicators such as dissolved oxygen and oxidation-reduction potential indicate the persistence of reducing conditions amenable to reducing Cr(VI). The recent 2.6-gpm extended purge was indicative of reaching out into the molasses ROI and also appears to capture some influence outside of the ROI.

The results of the extended purge presented in this report indicate that favorably reducing and varying geochemical conditions remain present in the aquifer surrounding R-42 and R-28. The path forward is to conduct a purge and sampling protocol that is expected to provide data that will facilitate further assessment of conditions in the aquifer and possibly help accelerate completion of the present study phase (Phase 1). The data from the extended purge continue to show concentrations of byproduct constituents (e.g., sulfate, iron, manganese) that do not allow direct land application of produced water via the land application discharge permit (DP-1793). Therefore, continuous pumping for the Phase 1 test at R-42 and R-28 creates significant logistics challenges, especially during winter months. Effective immediately, sampling will occur on a biweekly basis and apply time-series sampling over a purge volume of approximately 1000 gal. Samples will be collected at approximately 50 gal., 350 gal., 700 gal., and 1000 gal. At pumping rates of approximately 3 gpm and 2.6 gpm at R-42 and R-28, respectively, the sampling can be conducted within an 8-hr work day. Samples will be analyzed for metals, anions, and TOC. Field parameters will be collected for each sample in the time series.

A principle goal is to work towards a more continuous pumping and sampling approach that will move more groundwater pore volumes through each treatment zone to accelerate chromium breakthrough and provide a more quantitative estimate of chromium reduction capacity and longevity of byproduct generation.

### 4.0 REFERENCES AND MAP DATA SOURCES

#### 4.1 References

The following reference list includes documents cited in this report. Parenthetical information following each reference provides the author(s), publication date, and ERID, ESHID, or EMID. This information is also included in text citations. ERIDs were assigned by the Laboratory's Associate Directorate for Environmental Management (IDs through 599999); ESHIDs were assigned by the Laboratory's Associate Directorate for Environment, Safety, and Health (IDs 600000 through 699999); and EMIDs are assigned by N3B (IDs 700000 and above). IDs are used to locate documents in N3B's Records Management System and in the Master Reference Set. The NMED Hazardous Waste Bureau and N3B maintain copies of the Master Reference Set. The set ensures that NMED has the references to review documents. The set is updated when new references are cited in documents.

- LANL (Los Alamos National Laboratory), July 2017. "Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-17-25406, Los Alamos, New Mexico. (LANL 2017, 602505)
- LANL (Los Alamos National Laboratory), January 2018. "Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-18-20467, Los Alamos, New Mexico. (LANL 2018, 602862)
- LANL (Los Alamos National Laboratory), April 2018. "Second Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-18-23418, Los Alamos, New Mexico. (LANL 2018, 603031)

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#### 4.2 Map Data Sources

Hillshade; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\Data\HYP\LiDAR\2014\Bare\_Earth\BareEarth\_DEM\_Mosaic.gdb; 2014.

Unpaved roads; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder; \\slip\gis\GIS\Projects\14-Projects\14-0062\project\_data.gdb\digitized\_site\_features\digitized\_roads; 2017.

Drainage channel; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder; \\slip\gis\GIS\Projects\15-Projects\15-0080\project data.gdb\correct drainage; 2017.

Structures; Los Alamos National Laboratory, KSL Site Support Services, Planning, Locating and Mapping Section; 06 January 2004; as published 29 November 2010.

Paved Road Arcs; Los Alamos National Laboratory, FWO Site Support Services, Planning, Locating and Mapping Section; 06 January 2004; as published 29 November 2010.

Chromium plume > 50 ppb; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\13-Projects\13-0065\shp\chromium\_plume\_2.shp; 2018.

Regional groundwater contour May 2017, 4-ft interval; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\16-Projects\16-0027\project\_data.gdb\line\contour\_wl2017may\_2ft; 2017.

Regional groundwater contour November 2017, 2-ft interval; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\16-Projects\16-0027\project\_data.gdb\line\contour\_wl2017nov\_2ft; 2017.

Point features; As published; EIM data pull; 2017.

Technical Area Boundaries; Los Alamos National Laboratory, Site Planning & Project Initiation Group, Infrastructure Planning Office; September 2007; as published 13 August 2010.



Figure 1.0-1 The Cr(VI) plume showing locations of the R-42 dithionite test and the R-28 molasses test



Notes: The pre-test concentrations were approximately as follows: Na = 50-60 (16), Ca = 30 (55), K = 2, Mg = 12 (15), Fe = 0.01 (0.1), Mn = 0.001, Cr = 0.7. Values indicate levels immediately preceding 2017's amendment. Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample

Figure 2.1-1 Concentrations of selected cations and metals in R-42 dithionite test as a function of time

- Na, Det/Flt
- + Ca, Det/Flt
- 🛚 K, Det/Flt
- × K, ND
- Mg, Det/Flt
- ∦ Fe, Det/Flt
- Mn, Det/Flt
- Mn, ND
- Cr, Det/Flt
- o Cr, ND



Notes: The pre-test concentrations were approximately as follows: Na = 50–60 (16); Ca = 30 (55), K = 2, Mg = 12 (15), Fe = 0.01 (0.1), Mn = 0.001, Cr = 0.7. Values indicate levels immediately preceding 2017's amendment. Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample

Figure 2.1-2 Concentrations of iron, manganese, and arsenic in R-42 dithionite test as a function of time (recent)

₩ Fe, Det/Flt

Mn, Det/Flt



Notes: The pre-test concentrations were approximately as follows: Na = 50-60 (16), SO4 = 80. Values indicate levels immediately preceding 2017's amendment. Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample

Figure 2.1-3 Concentrations sodium and sulfate in R-42 dithionite test as a function of time (recent)



Notes: The pre-test concentrations were approximately as follows: Si = 35, Fe = 0.01 (0.1), Mn = 0.001, Se = 0.002 (<0.005), As = 0.001 (0.002), Cr = ~0.7 (~1.0). Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample

Figure 2.1-4 Concentrations of selected constituents during R-42 dithionite test as a function of time

- Si, Det/Flt
- ₩ Fe, Det/Flt
- Fe, ND
- Mn, Det/Flt
- 🗆 Mn, ND
- Cr, Det/Flt
- o Cr, ND
- As, Det/Flt
- + As, ND
- ĭ Se, Det/Flt
- ×Se, ND



Notes: The pre-test concentrations were approximately as follows: Br = ~0.2, Cl = 50-60 (45), NO2 = <0.2, NO3 = 20 (25), SO4 = 80. Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample

Figure 2.1-5 Concentrations of anions in R-42 dithionite test as a function of time

Br, Det

A Cl, Det

NO2, Det

🔷 NO2, ND

¥ NO3, Det

X NO3 ND

• SO4, Det



Notes: The pre-test concentrations were approximately as follows: NO2 = <0.2, NO3 = 20 (25). Also, if different, historic values are included in parentheses. Values are in mg/L. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample Figure 2.1-6 Concentrations of nitrate and nitrite in R-42 dithionite test as a function of time (recent)



Notes: The pre-test concentrations were approximately as follows: values both immediately preceding 2017's amendment injection and also, if different, values for 2014/2015 are shown in mg/L: Br~0.2. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample

Figure 2.1-7 Concentrations of bromide in R-42 dithionite test as a function of time (recent)





Figure 2.1-8 Progressive snapshots of the conceptual R-42 plan view model: September 2017 (right after injection). Element and compound levels as mg/L.



Figure 2.1-9 Progressive snapshots of the conceptual R-42 plan view model: End September 2017 (right after 77,000-gal. purge)



Figure 2.1-10 Progressive snapshots of the conceptual R-42 plan view model: October 2018 (right before 3-gpm purge)



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: Na = 16, Ca = 47, K = 2, Mg = 12, Fe = 0.01–0.025, Mn = 0.001-0.005, Cr = 0.5. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample Figure 2.2-1 Concentrations of selected cations and metals in R-28 molasses test as a function of time



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: Na = 16, Ca = 47, K = 2, Mg = 12, Fe = 0.01-0.025, Mn = 0.001-0.005, Cr = 0.5. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample. Figure 2.2-2 Concentrations of chromium, pH, and TOC in R-28 molasses test as a function of time



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: Fe = 0.01-0.025, Mn = 0.001-0.005. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample.

Figure 2.2-3 Concentrations of iron and manganese in R-28 molasses test as a function of time

🗶 Fe, Det

Mn, Det



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: Si = 35, Fe = 0.01-0.025, Mn = 0.001-0.005, Cr = 0.5, Se = ND-0.01, As = 0.0005, Ni = 0.01-0.04. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample.

Figure 2.2-4 Concentrations of selected constituents during R-28 molasses test as a function of time



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: Br = 0.2, Cl = 45, NO2<0.01, NO3 = 19, SO4 = 60, PO4<0.01. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample.

Figure 2.2-5 Concentrations of anions in R-28 molasses test as a function of time

Br, Det
▲ Cl, Det
NO2, Det
$\times$ NO2, ND
<mark>≭</mark> NO3, Det
ж NO3, ND
• SO4, Det
• PO4, Det
○ PO4, ND



Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L Br = 0.2, SO4 = 60. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample.

Figure 2.2-6 Concentrations of bromide, sulfate, and TOC in R-28 molasses test as a function of time

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Notes: The pre-test concentrations were approximately as follows: values are shown in mg/L: NO2<0.01, NO3 = 19. Acronyms: Det = Detected, ND = Not Detected, FIt = Filtered Sample.

Figure 2.2-7 Concentrations of nitrate and nitrite in R-28 molasses test as a function of time

## **Attachment 1**

Data Associated with the "Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon" (on CD included with this document)