Response to the "Approval with Direction for the Well R-12 Rehabilitation and Conversion Summary Report, Los Alamos National Laboratory, EPA ID No: NM0890010515, HWB-LANL-GROUNDWATER-MISC," Dated December 21, 2007

INTRODUCTION

To facilitate review of this response, the New Mexico Environment Department's (NMED's) comments are included verbatim (italicized), as presented in the approval with direction. Los Alamos National Laboratory's (LANL's or the Laboratory's) responses follow each NMED comment.

COMMENTS

NMED Comment

1. Elimination of Disqualified Indicators for Well Screen Analysis

To use the methodology developed in the Well Screen Analysis Report (Revision 2) for well screen analysis, one must assume that the perched intermediate and regional groundwater is not significantly influenced by anthropogenic organics, or relevant ions and metals that have been identified as indicators. In other words, these indicators have values comparable to background levels in groundwater. This assumption is necessary because the methodology is dependent on the comparison of six categories of indicator values to their background levels to identify whether or not a well screen is capable of providing data representative of the formation water.

In the case when formation water has been affected by anthropogenic organics, however, a sequence of microbial metabolism may occur in groundwater because the lack of an organic substrate is usually the limiting factor that restricts microbial activities in perched intermediate and regional groundwater beneath the facility. The consequence of microbial metabolism in groundwater will result in a reduction in dissolved oxygen, nitrate, sulfate and redox potential in formation water, as well as production of ferrous iron, dissolved manganese, carbon dioxide and methane. As long as anthropogenic organics are present in perched intermediate or regional groundwater, the assumption that the groundwater can still maintain background levels of the indicators may become invalid. Consequently, many geochemical species and parameters may no longer be useful as indicators for well screen analysis dependent on the sequence of microbial metabolism that occurs in the groundwater.

Based on the source information and the geochemical and hydrologic analyses, the Report provides strong evidence that the perched intermediate groundwater has been affected by organic carbon, nitrate and uranium. Possible sources include groundwater recharge that contains organics from ash generated during the May 2000 Cerro Grande fire, treated sewage effluent from Sandia, Los Alamos, and/or Pueblo Canyons, and contaminants released to Los Alamos Canyon. The Report also indicates that the elevated concentrations of ferrous iron and dissolved manganese above background levels are likely attributable to microbial reductive dissolution of iron oxyhydroxide and manganese dioxide that have taken place in the groundwater outside the zone affected by drilling fluids. Two blank samples collected by rinsing sampling equipment and pipes also show increased total iron and manganese close to their respective background levels in the perched intermediate groundwater. As a result of the organically induced microbial metabolism, it can also be reasonably *assumed that concentrations of dissolved oxygen in the groundwater can be reduced below the background level because bacteria prefer using molecular oxygen as an energy source, to nitrate, iron oxyhydroxides and manganese dioxides. Either the decrease in concentrations of the redox-sensitive species (such as dissolved oxygen and nitrate) or the increase in concentrations of dissolved iron and manganese can cause reduction of redox potential in intermediate groundwater below the background level.*

The concentration changes of many geochemical indicators triggered by the increased organic carbon in the groundwater are very similar to those that occurred in the zone surrounding a well screen where microbial metabolism is induced and sustained by the presence of residual drilling fluids. Apparently, these parameters, including total organic carbon, dissolved oxygen, nitrate, ferrous iron, dissolved manganese, uranium, and redox potential, provided misleading information vis à vis analysis of R-12 well screens, as well as evaluation of contamination in the perched intermediate groundwater. Therefore, they are not useful indicators to evaluate whether R-12 screens are able to yield samples representative of the formation water and must be removed from the indicator list when performing the screen analysis of R-12.

LANL Response

1. Two points are relevant in response to this comment. First, the statement above ("*The concentration changes of many geochemical indicators triggered by the increased organic carbon in the groundwater are very similar to those that occurred in the zone surrounding a well screen where microbial metabolism is induced and sustained by the presence of residual drilling fluids.*") is correct. The well screen analysis accounts for conditions that can be attributed to predrilling or site conditions, including contamination from various sources, and excludes them from the analysis (Table B-2 and section 2.7.4). As discussed in sections 2.7.3 and 2.7.4, however, the elevated total organic carbon (TOC) in the 2007 pumped samples is attributed primarily to the presence of residual drilling fluids because of its decreased concentration during pumping. For this reason, TOC is not attributed primarily to site conditions and is retained for the well screen analysis, although contributions from the Cerro Grande fire may be a minor cause of the elevated concentration of TOC.

   Second, as noted in section 2.7.3 and Table B-2, nitrate and uranium were already not included in the well screen analysis performed for the original version of this report because of their attribution to site contamination. Dissolved oxygen and noncorrected redox potential (oxygen-reduction potential [ORP]) are qualitative parameters that are used with other analytes to determine whether reducing conditions are present. They are retained as such in the well screen analysis. We agree that iron and manganese should be removed from the analysis because of site conditions caused by the corroded discharge pipe and have revised the well screen analysis accordingly (section 2.7.4 and Tables B-1 and B-2).

NMED Comment

2. Evaluation of New Approaches for Well Screen Analysis

The limitation of the developed methodology for well screen analysis, as pointed out in Comment 1, suggests the need for additional approaches to evaluate well screens when the groundwater is significantly contaminated by anthropogenic chemicals. The new minerals possibly formed in the drilling fluid-impacted zone is one of the issues that could potentially pose a long-term threat to sample quality by adsorption of and/or reaction with potential contaminants of concern. Only limited information is available about these potentially newly formed minerals.

Based on the geochemical data obtained from perched intermediate and regional groundwater samples, certain sulfide minerals, especially iron sulfides (such as pyrite), are likely important new minerals formed in the drilling fluid-impacted zones. These minerals are reactive with many potential contaminants of concern, potentially reducing the detected concentrations relative to the actual concentrations present in the formation water for certain contaminants of concern that are sensitive to redox reaction and adsorption. These minerals can be easily formed by reactions between iron oxyhydrides (sic) that are present in the geologic formations beneath the Pajarito plateau, and sulfide produced from microbial reduction of sulfate. Sulfate is a widespread and native component of the common redox reaction that is triggered by sulfate-reducing bacteria and often observed in drilling fluid-impacted zones once groundwater becomes anaerobic during microbial digestion of residual drilling fluids.

Theoretically, the newly formed iron sulfides could have an isotopic depletion of $^{34}S/^{32}S$ *in comparison to the original formation materials because of isotope fractionation, especially kinetic fractionation that may have occurred in drilling-fluid impacted zones. The Permittees must therefore assess the feasibility of using stable sulfur isotopes to distinguish newly precipitated minerals from the formation materials and estimate the volume of precipitates. Quantifying the newly formed minerals will help in evaluation of the potential impacts of these minerals on water sample quality.*

LANL Response

2. The Laboratory agrees that a comparison study would be useful of the native mineralogy of the aquifer and altered mineralogy resulting from the presence of residual drilling fluids. If it is possible to conduct such a study in the field rather than using simulations, sulfur isotopes would be instructive. A field study will involve penetration of well casing that will render useless the entire well and not just the screened interval. When a decision is made to plug and abandon a well that was drilled with fluids, we will investigate the possibility of penetrating the casing and collecting mineral samples that can be analyzed in a variety of ways, including isotopically.

NMED Comment

3. Other Comments

3a. Redevelopment of Screen 1 was conducted by jetting and pumping separately (not simultaneously), as reported in Section 2.3 of the Report. This procedure is a deviation from the procedure (jetting while simultaneous pumping) documented in the NMED-approved Work Plan for R-Well Rehabilitation and Replacement (Revision 2). It is generally accepted that jetting with water accompanied by simultaneous air-lift pumping is a good practice to prevent clogging of the formation. Please explain the discrepancy.

LANL Response

3a. As indicated in section 2.3 of the revised report, during the high velocity jetting process, all three screens in R-12 were open. Because of the substantially lower head in screen 3 and the high capacity of this zone, downward flux within the well carried formation water from screens 1 and 2, along with the potable jetting water, into screen 3 throughout the process, such that the composite static water level in the open well was located just above screen 3. This effect was hydraulically equivalent to pumping screen 1 at its maximum capacity but without the use of a submersible pump. Thus, high velocity jetting and pumping (by gravity) occurred simultaneously to maximize the development effect on screen 1 and, therefore, there was no deviation from the proposed plan. Passive pumping of screen 1, via gravity flow into the well, occurred throughout the jetting process.

NMED Comment

3b. In Section 2.7.2, the Report attributes gas bubbles observed during several redox potential (ORP) measurements to unreliable readings. An alternative explanation is that the bubbles are attributable to carbon dioxide and/or methane produced during digestion of residual drilling fluids or anthropogenic organics. This may be true when the ORP reading indicates anaerobic conditions in the measured groundwater (such as -232 millivolts). The increase in alkalinity observed from screen 1 of R-12 also supports the alternative explanation. The Permittees must analyze the ORP readings while gas bubbles are observed to confirm the explanation. In addition, the Permittees should consider adding methane as a routine analyte to further evaluate this possibility.

LANL Response

3b. With respect to the observation of gas bubbles observed during several ORP measurements, it may be possible to analyze the readings while gas bubbles are observed when pumped samples are collected. (Note that this is not possible in wells where the Westbay sampling system is installed.) Section 2.7.2 of the report states that the qualitative ORP readings show a reliable trend overall, with the exception of a few readings, and this has been verified in field notebooks. With respect to the recommendation to analyze for methane, the "Well Screen Analysis Report, Revision 2" (LANL 2007, 096330) referred to previous analyses for methane during a number of sampling events, all of which produced nondetects. Methane is not stable in the presence of sulfate that was detected above 20 mg/L in all groundwater samples analyzed as part of this investigation. Total sulfide concentrations were less than detection (0.009 ppm) and it is very unlikely that methane gas would be stable in the absence of sulfide. The groundwater at R-12 screen 1 is too oxidizing for sulfide to be stable based on detectable sulfate and noncorrected ORP readings. The Laboratory sees no reason to analyze routinely for methane for this reason and also because sulfate is detected in the majority of samples. Methane is stable only under sulfate-reducing conditions, so it should not be present when sulfate is detected.

NMED Comment

3c. According to the Report, an active sampling system to collect samples from screens 1 and 2 has not been installed in R-12. The Permittees must complete installation of the sampling system by January 15, 2008.

LANL Response

3c. As stated in sections 2.0 and 2.6 of the revised report, completion of installation of the dedicated sampling system at R-12 took place on December 13, 2007.

REFERENCE

LANL (Los Alamos National Laboratory), May 2007. "Well Screen Analysis Report, Revision 2," Los Alamos National Laboratory document LA-UR-07-2852, Los Alamos, New Mexico. (LANL 2007, 096330)