Response to the "Direction for Further Action at Well R-20 Rehabilitation and Conversion Summary Report, Los Alamos National Laboratory, EPA ID No: NM0890010515, HWB-LANL-GROUNDWATER-MISC," Dated February 11, 2008

INTRODUCTION

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

NMED Comment

1. **Analysis of Increased Iron Concentrations Using Geochemical Models**

   In the Conclusion Section of the Report, the Permittees attribute the increases in dissolved iron concentrations measured from Screens 1 and 2 of R-20 during the December 2007 sampling events to three potential conditions. They are: (1) reductive dissolution of iron minerals that are naturally present as components of the local geologic materials; (2) oxidation of iron sulfides that have been accumulated in the vicinity of the well screens due to drilling fluid impacts; and (3) presence of reduced groundwater in the regional aquifer outside the zones impacted by drilling fluids. Although all three conditions could potentially cause increases in dissolved iron concentrations in groundwater, the site-specific data help eliminate the possibility that the first and third potential occurrences are major factors in raising dissolved iron concentrations in groundwater.

   Both reductive dissolution of iron minerals and development of reduced groundwater in the regional aquifer would most likely be caused by the presence of organics including residual drilling fluids. However, total organic carbon (TOC) concentrations measured during the 2007 sampling events are all close to the groundwater background level and passed the criteria established for well screen analysis, as shown in Tables B-1a and B-1b of the Report. In the absence of organic [carbon] as a driving force, reductive dissolution of iron minerals could not be sustained, and the continuous increases in dissolved iron concentrations in groundwater (as shown in Figure 2.6-6 of the Report) should not be observed.

   Furthermore, if the increases in dissolved iron concentrations were due to reductive dissolution of iron minerals or reduced conditions of the formation water, other lines of supporting evidence, such as reduced nitrate concentrations and elevated manganese concentrations, should be observed as a result of the sequence of redox reactions. As documented in the Well Screen Analysis Report, Revision 2, iron reduction occurs as one of a sequence of redox reactions after nitrate reduction and manganese reduction. This case is not supported by the data obtained from screens 1 and 2 of R-20 during the 2007 sampling events because both nitrate and manganese concentrations remained close to their respective background levels and passed the criteria established for the well screen analysis (Table B-1b of the Report).

   The possibility that the formation water is directly contaminated by ferrous or dissolved iron is also very low. Ferrous iron, if present in groundwater outside the drilling fluid impact zones, will react with dissolved oxygen (DO) in groundwater since the site-specific conditions (including temperature and pH) favor such a reaction. In terms of dissolved iron and DO concentrations, the formation water should reach an equilibrium condition because of the relatively long residence (reaction) time. As a *result, the formation water should maintain a concentration pattern over time that displays an inverse relationship between ferrous iron concentrations in groundwater and DO levels. As shown in Figure 2.6-1, 2.6-2 and 2.6-6, however, the accelerating increases in dissolved iron concentrations during the 2007 sampling events are coupled with steady increases in DO concentrations rather than decreases. These data indicate nonequilibrium conditions for dissolved iron and DO in groundwater, suggesting that the dissolved iron is less likely to come from the formation water outside the drilling fluid impacted zones.*

In appears that oxidation of iron sulfides may be causing the increases in dissolved iron concentrations in groundwater, if contamination of water samples by introduced iron is not an issue. During the 2007 sampling events, the extended pumping likely drew fresh formation water into the two screens of R-20. Once the fresh water passed through the drilling fluid impact zones, iron sulfides as new minerals, that accumulated in the vicinity of Screens 1 and 2, may react with DO in groundwater resulting in the increases in dissolved iron and the decreases in DO in groundwater. The observation (in Screen 2 of R-20) of elevated concentrations of sulfate, the other potential product of oxidizing iron sulfides, also supports the likelihood of the occurrence of oxidation of iron sulfides.

To better understand the geochemical reactions that have occurred in the vicinity of Screens 1 and 2 of R-20 , the Permittees must conduct a geochemical modeling analysis of the data collected during the Westbay (before 2006), the July 2006 and the December 2007 sampling events. The geochemical modeling analysis of these data must focus on understanding the reasons for the increases in concentrations of dissolved iron and sulfate during the December 2007 sampling event. The geochemical modeling analysis must investigate the possibility that iron sulfides are oxidized by DO and other potential oxidants under natural groundwater conditions, and identify the limiting factors that could restrict natural oxidation of iron sulfides. These modeling efforts will be useful to develop a rehabilitation strategy to minimize the potential influence of the newly-formed reactive minerals on the quality of water samples collected from well R-20.

LANL Response

1. The report attributed the increases in dissolved iron concentrations measured from screens 1 and 2 of R-20 during the December 2007 sampling events to three potential conditions: (1) reductive dissolution of naturally occurring iron minerals in local aquifer materials, (2) oxidation of iron sulfides that have been accumulated near the well screens due to drilling fluid impacts, and (3) presence of reduced groundwater in the regional aquifer outside the zones impacted by drilling fluids. The collection of additional samples in March 2008, accompanied by geochemical modeling, indicates that none of the three hypotheses were correct. The additional samples were collected through a stainless-steel pipe and filtered through three different filter sizes. These results indicated an absence of colloidal iron and iron concentrations that are representative of the regional aquifer. The results were corroborated by geochemical modeling. The analytical results are discussed in section 4.1, and the modeling is discussed in section 4.2 of the revised report. These results indicate that the mild-steel pipe used to collect samples in November and December 2007 was responsible for the high iron concentrations in those samples. Henceforth, well rehabilitation activities will use a stainless-steel discharge pipe in place of a mild-steel pipe whenever possible.

NMED Comment

2. ***Rehabilitation of R-20 by Using an Oxygen Release Compound***

   As discussed in Comment 1, iron sulfides are likely present in the vicinity of Screens 1and 2 of R-20. The newly formed minerals are reactive with certain potential contaminants of concern, and therefore may lead to contaminant concentrations measured in water samples that are lower than those present in the formation water. It appears that the mechanical development procedures that have been used for rehabilitating R-20 may not be as effective as necessary to remove these reactive minerals. The geochemical data suggest that natural oxidation may be a promising method for restoring the formation mineralogy or deactivating the newly formed minerals. Natural oxidation, however, may be too slow to rehabilitate R-20 to timely meet the groundwater monitoring requirements at Technical Area (TA) 54.

   The addition of oxygen to groundwater is an economical process to enhance clean up [of] groundwater contamination and restore groundwater to aerobic conditions. A variety of oxygen release compounds that are able to steadily release oxygen to groundwater are available commercially. In terms of R-20, the increased dissolved iron concentrations appear to limit the ability of Screens 1 and 2 to provide reliable data for monitoring certain contaminants of concern (such as volatile organic compounds) identified at TA-54. To expedite restoration of the geologic formation or deactivation of the newly formed minerals in the vicinity of the well screens, the Permittees must develop a method for use of oxygen release compounds (such as hydrogen peroxide) as an enhanced rehabilitation technique. An increase in DO concentrations in groundwater surrounding the well screens will enhance the processes for oxidation of not only iron sulfides, but also any residual organic drilling fluids. The Permittees must propose and implement a technique to further rehabilitate both Screens 1 and 2 of R-20 to minimize potential influence of the reactive minerals on the quality of water samples.

LANL Response

2. In a letter to NMED (LANL 2008, 101640), the Laboratory stated that the use of hydrogen peroxide to achieve oxidation in well R-20 would be feasible if the procedure were carefully designed and executed. The Laboratory also proposed collection of additional samples and performance of geochemical modeling before deciding to use chemicals in the well. At a meeting held on April 15, 2008, the Laboratory showed analytical results of samples collected in March 2008 that were collected through a stainless-steel pipe and filtered through three different filter sizes. These results indicated an absence of colloidal iron and showed iron concentrations that are representative of the regional aquifer. The results were corroborated by geochemical modeling. The analytical results are discussed in section 4.1, and the modeling is discussed in section 4.2 of the revised report. Based on these results, NMED, Laboratory, and the U.S. Department of Energy mutually decided that it was unnecessary to apply chemical rehabilitation methods at the well.

NMED Comment

3. ***Installation of Sampling System***

   Following completion of rehabilitating Screens 1 and 2 of R-20 using an oxygen release compound, the Permittees must install the proposed sampling system and collect water samples to evaluate performance of the rehabilitation.

LANL Response

3. The permanent Baski-fabricated dual-pump sampling system was installed between May 20 and May 22, 2008. Its installation is described in section 2.6 of the revised report.

REFERENCE

LANL (Los Alamos National Laboratory) March 1, 2008. "Submittal of the Response to the Direction for Further Action at Well R-20 Rehabilitation and Conversion Summary Report," Los Alamos National Laboratory letter (EP2008-0104) to J.P. Bearzi (NMED-HWB) from S.G. Stiger (EP Associate Director) and D. Gregory (DOE-LASO), Los Alamos, New Mexico. (LANL 2008, 101640)