

Review of ASR Project at Terry Ranch Greeley, Colorado

Prepared for
City of Greeley, Colorado

Prepared by



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1. Introduction

As part of their water planning efforts for the future, the City of Greeley, Colorado (the City) plans to implement an aquifer storage and recovery (ASR) program, and is evaluating a potential project at Terry Ranch. ASR involves recharging and storing water in an aquifer for later use, and ASR wells are used to both inject and extract the water. The City plans to use surface water that has been treated at the Bellvue water treatment plant (WTP) as the recharge source water, and to store in and recover from the Upper Laramie Aquifer at Terry Ranch (Figure 1). The City is currently evaluating the feasibility of the Terry Ranch ASR project.

At the request of the City, Daniel B. Stephens & Associates, Inc. (DBS&A) has reviewed technical information related to the hydrogeology of the Upper Laramie Aquifer and geochemistry of the native groundwater, recharge source water, and mixing of these waters. For the review, DBS&A received data and reports from Leonard Rice Engineers, Inc. (LRE) of Denver, Colorado. This review has two components: (1) a peer review of the hydrogeologic and geochemical data and (2) an independent geochemical evaluation of recovered water during ASR operations, emphasizing uranium behavior.

2. ASR Description

ASR is a straightforward concept that uses an aquifer to store water that will be recovered for use at a later time (NGWA, 2014). At Terry Ranch, treated surface water (or recharge source water) would be stored in the Upper Laramie Aquifer. Water would be injected into the aquifer using ASR well(s); the water would be stored there for a period of time, and then recovered using the same well(s) or multiple wells.

During recharge, injection rates are controlled to maintain a water level that will exert enough pressure to drive water through the well screen into the aquifer (Figure 2). The recharge source water displaces the groundwater away from the well, and a stored water zone develops around the ASR well (NGWA, 2014; Pyne, 2005). This stored water will mostly be composed of the recharge source water, so the water quality will be similar to the recharge source water. A mixed zone of groundwater and recharge source water forms between the stored water and the native groundwater (Figure 2). The storage zone increases in volume during recharge and decreases in

volume during extraction. ASR operations can be implemented to manage the storage zone of water so that the recovered water quality is similar to the recharge source water quality.

The geology of the aquifer system is important to understanding the aquifer architecture. The rocks or sediments in the aquifer will have relatively high permeability and thickness that can transmit reasonable volumes of water to wells. The rocks or sediments that are in contact with the top and bottom of the aquifer may form boundaries or aquitards, which have lower permeability relative to the aquifer and confine groundwater in the aquifer unit. During ASR, an aquitard helps maintain and keep the storage zone in place.

ASR wells may be designed differently than typical water supply wells. In areas with layered aquifer systems like Terry Ranch, well screens may be installed that target thick intervals of sandstone or fractured rock with relatively high permeability. Wells with a deeper initial depth to water allow for a greater water column to develop in the well during injection, giving additional injection head to move water into the aquifer.

3. ASR Investigation Guidelines

Detailed planning, investigation, and execution are key factors for the successful implementation of all water projects, including ASR projects, because they involve complex natural systems and large capital investments for water treatment, transmission, and wells. To ensure success of ASR projects, several guidance documents and a textbook on ASR have been published that describe project evaluation, implementation, and operation (ASCE/EWRI, 2020; AWWA, 2015; NGWA, 2014; Pyne, 2005).

Considering the evaluation of hydrogeology and geochemistry, these ASR guidance documents provide similar investigation approaches. Adequate characterization during the initial investigation provides important information for making decisions about project implementation and success. Determining the variation of a natural system requires performing on-site investigations, using standard industry methods to determine the physical conditions at the site, and performing pilot testing using the same recharge source water and techniques to be employed during ASR project operations.

The hydrogeology and geochemistry are typically evaluated during the initial investigation, with evaluation criteria focusing on recharge source water quality, hydrogeologic suitability, and effects on water quality during ASR (ASCE/EWRI, 2020; AWWA, 2015; NGWA, 2014; Pyne, 2005).

The conceptual design of the ASR project should evolve in an iterative manner as data collection and analysis proceed.

3.1 Hydrogeology

For an ASR project, the hydrogeologic suitability needs to be understood before design decisions are made. Key design factors include production and injections rates of ASR wells, hydraulic response of the aquifer, and whether the aquifer is confined or unconfined. Aquifer characteristics that need to be determined include the following:

- Rock type(s)
- Depth and thickness of aquifer unit(s)
- Permeability
- Depth to water
- Aquifer type: confined or unconfined
- Production capacity
- Injection capacity

3.2 Geochemistry

For geochemistry characterization during ASR investigations, groundwater and recharge source water chemistry needs to be analyzed to determine compatibility of various mixtures of the two waters, and whether the waters will meet applicable water quality standards. A mixture of water will be stored in the aquifer, and may react with the rocks in the aquifer. This water-rock interaction may impact the chemistry of the stored water by dissolving or leaching material from the aquifer sediments or precipitating deposits onto the aquifer sediments. Material leached from the aquifer sediments may increase element concentrations in the stored water, potentially causing water quality standards to be exceeded. Waters that are not compatible may cause minerals to precipitate that may clog up the aquifer porosity and reduce the aquifer permeability, limiting injection and recovery capacities. Geochemical parameters and methods for the characterization include the following:

- Groundwater and recharge source water
 - ◊ Major ion and trace element concentrations
 - ◊ Alkalinity
 - ◊ Total dissolved solids (TDS)

- ◇ pH
- ◇ Temperature
- ◇ Dissolved oxygen
- ◇ Oxidation/reduction potential (ORP, Eh)
- ◇ Water compatibility
- Aquifer sediments collected during drilling
 - ◇ Lithology
 - ◇ Mineralogy
 - ◇ Major and trace element concentrations
 - ◇ Leachability of elements

These hydrogeologic and geochemical data are used to develop a conceptual model of the physical and chemical framework of the ASR project, and are important components of the project design. The data are used to determine design parameters such as injection rates, storage capacity of the aquifer, and water quality of the recovered water.

4. Terry Ranch ASR Project Review

The City is performing their due diligence regarding the proposed ASR project at Terry Ranch. Investigation and analyses began during summer 2020 and continued to February 2021. LRE evaluated the hydrogeology and geochemistry at Terry Ranch in support of the ASR investigation. DBS&A has also completed a peer review of the hydrogeologic and geochemical data, and a geochemical evaluation for the recovered water, as discussed below.

Documents detailing the hydrogeological and geochemical analyses were reviewed include the following:

- As-built well construction diagram for Terry Ranch City of Greeley Well EB-1 (LRE, 2020a)
- Borehole data and well construction information for Terry Ranch City of Greeley Wells WWR-1, WWR-4, EB-1, and EB-2 (LRE, 2020b)
- Memorandum regarding response to issues raised about the Terry Ranch Project (LRE, 2020c)

- Draft technical memorandum regarding Terry Ranch aquifer test analysis and well yield estimates (LRE, 2020d)
- Draft technical memorandum regarding Terry Ranch aquifer zonal sampling and analysis results (LRE, 2020e)
- *[Draft] 24hr and 72hr pilot cycle testing field parameters collected* (LRE, 2020e)
- Technical memorandum regarding Terry Ranch aquifer geochemical analysis, modeling, and ASR pilot testing (LRE, 2021)

4.1 Hydrogeology

At Terry Ranch, hydrogeologic investigations have focused on the geology, geophysics, and hydrology of the Laramie Formation. The on-site data were collected from existing wells (WWR) and new wells (EB) installed for the investigation (Figure 1).

Geologic data were reviewed from existing studies and evaluations performed at wells at Terry Ranch. The geologic formation of interest is the Cretaceous Laramie Formation, which is about 1,500 feet thick and hosts the regional aquifer proposed for use in this ASR project (LRE, 2020a and 2020b). The Laramie Formation is a series of sandstones and shales, which were deposited in a near-shore marine environment. The sediments that compose the Laramie Formation were eroded from rocks in the nearby mountains, including uranium-bearing granite rocks (USGS, 2014). The Laramie Formation is part of a sequence of sedimentary rocks extending throughout the Denver Basin that tend to increase in thickness to the north (Figures 3 and 4). The lithology and thickness of the Laramie Formation were confirmed during the drilling and testing of exploratory borings EB-1 and EB-2 (Figures 3 and 4).

Mineralogy was determined using x-ray diffraction (XRD) on composite samples of drill cuttings from EB-1 and EB-2 (Hazen, 2020). The sediments are typical of arkosic and subarkosic sandstones, with quartz and feldspar (K-spar and plagioclase) grains having the greatest abundance. Clay mineralogy is dominated by smectite when present.

The regional aquifer includes the Upper Laramie Aquifer and Lower Laramie Aquitard. The current studies have defined three parts of the Upper Laramie Aquifer including the upper aquifer, aquitard, and lower aquifer (Figure 2). The aquifer system is about 1,000 feet in thickness extending from 100 feet below ground surface (feet bgs) to 1,100 feet bgs (Figures 3 and 4). The Lower Laramie Aquitard is about 500 feet thick, and separates the Upper Laramie Aquifer from the Fox Hills Sandstone (Figures 3 and 4).

Borehole geophysical methods were used to identify the lithology of the Upper Laramie Aquifer and the Lower Laramie Aquitard (Figure 5). For on-site wells, gamma and resistivity logs help distinguish the lithology of the two units, particularly when interpreted together. In materials with a relatively greater permeability, the electric resistivity log tends to increase and the gamma log decreases. In lower permeability materials like clay or shale, the gamma log tends to increase and the electric resistivity log decreases. In Figure 5, Well EB-2 demonstrates this relationship between the Upper Laramie Aquifer (greater resistivity and lower gamma) and the Lower Laramie Aquitard (greater gamma and lower resistivity).

During the testing at wells EB-1 and EB-2, hydrogeologic investigation included direct measurements of the physical characteristics of the Upper Laramie Aquifer using well testing, aquifer tests, and hydrophysical techniques (LRE, 2020b, 2020d, and 2020e).

Well testing included measuring depth to water and flow rates. The depth to water (measured in feet bgs) appears to be deeper in the northern portion of the site (LRE, 2020d). The existing WWR wells were not designed as ASR wells, but they provide a good indication of potential ASR well yields and drawdown during pumping, and their flow rates ranged from 174 to 600 gallons per minute (gpm) (LRE, 2020d). Based on Table 5 in LRE, 2020d, the predicted specific capacity [flow rate (Q)/drawdown (s)] ranges from 0.4 to 1.4 gpm per foot of drawdown (gpm/ft).

Aquifer parameters were measured using hydrophysical techniques and aquifer testing. The hydrophysical tests measured permeability as hydraulic conductivity in feet per day (ft/d) and identified ambient flow zones in the aquifer that helped to delineate the upper and lower aquifers and differentiate the lower permeability aquitard (Figures 2 and 6). During aquifer testing, the permeability measured as aquifer transmissivity varies from 102 to 480 square feet per day (ft²/d) (LRE, 2020d), which is a reasonable range for implementing ASR (ASCE/EWRI, 2020). There was good agreement between the different methods used to calculate transmissivity (LRE, 2020d).

4.2 Geochemistry

At Terry Ranch, geochemical investigations have focused on water chemistry of the groundwater in the Upper Laramie Aquifer and potential reactions between the groundwater, recharge source water and aquifer sediments (LRE, 2021). The on-site data were collected from existing wells (WWR) and new wells (EB) installed for the investigation (Figures 1 and 7).

Water chemistry was characterized in the field and laboratory for groundwater and recharge source water from the Bellvue WTP. Field parameters were measured at the wellhead, including

electrical conductivity (EC), temperature (T), pH, oxidation/reduction potential (ORP or Eh), and dissolved oxygen (DO). Laboratory analyses were used to determine element composition, TDS, and water type. Additional laboratory tests included water compatibility and leaching tests using recharge source water and aquifer sediments. Geochemical modeling was performed to determine saturation indices, the potential for well or aquifer clogging due to mineral precipitation, and dissolved element speciation.

At EB-1, ASR pilot testing consisted of two cycle tests: a 1-day cycle test and a 3-day cycle test. A known volume of recharge source water was injected into Well EB-1 followed by extraction (LRE, 2021). During extraction, field parameters were measured, and laboratory samples were collected.

Field parameter measurements provide information on the general conditions of the water, which impact the behavior of dissolved elements in solution and their interaction with aquifer sediments. The measurements provide the following:

- EC correlates with TDS.
- pH indicates if the water is acidic (<7) or alkaline (>7).
- ORP measures the relative dominance of oxidized versus reduced species in solution (Clark, 2015).
- DO provides the concentration of oxygen in the water.

Based on ORP and DO measurements, both the groundwater and recharge source water are oxidizing, with positive ORP readings and DO measured in all samples. All the water samples are alkaline.

The concentrations for dissolved elements were determined by an analytical laboratory. TDS concentration was 64 milligrams per liter (mg/L) in water from the Bellvue WTP, and ranged from 243 to 283 mg/L in groundwater of the Upper Laramie Aquifer (LRE, 2021).

At Terry Ranch, uranium concentrations in groundwater vary across the site, and some values exceed the U.S. Environmental Protection Agency (EPA) maximum contaminant level (MCL) and the Colorado Department of Public Health and Environment Regulation 41 (Reg 41) water quality standards. The treated surface water had no detectable uranium concentration.

Some concentrations of uranium and manganese in groundwater exceed water quality standards (e.g., Colorado Reg 41 standard and EPA MCL). Uranium concentrations have water

quality standards of 16.8 micrograms per liter ($\mu\text{g/L}$) (Reg 41) and 30 $\mu\text{g/L}$ (MCL), and the groundwater concentrations ranged from about 13 to 42 $\mu\text{g/L}$. Manganese concentration ranged from 1.4 to 66 $\mu\text{g/L}$, with a standard of 50 $\mu\text{g/L}$ (Reg 41 standard and federal secondary drinking water standard).

Water type is determined using the concentrations of major ions. The groundwater and recharge source water for the proposed project are considered calcium-bicarbonate (Ca-HCO_3) water types (LRE, 2021). Because the water major ion chemistry is similar for both waters, this indicates general compatibility.

Water compatibility was also determined by the analytical laboratory (Core, 2020; LRE, 2021). Groundwater and recharge source water were combined at five different mixing ratios and the mixtures were monitored for 21 days. Color, clarity, precipitation, reactivity, and pH were monitored. During testing, all the samples remained clear with no indication of precipitation, and pH was maintained from 8.1 to 8.4. The waters appear to be compatible.

Laboratory tests were conducted on composite samples of drill cuttings from EB-1 and EB-2 to determine if leaching is likely to occur during ASR operations. The drill cutting samples were crushed, and the recharge source water was used as a leaching solution. Two types of tests were completed: static and flow-through experiments (LRE, 2021). During both experiments, multiple water samples were collected over the days that the experiment was performed. Initially, uranium and arsenic concentrations were elevated above the Reg 41 standards and MCLs, and the concentrations decreased by the end of testing (LRE, 2021). The data may not be representative of conditions during ASR operations because the drill cutting samples may have contained drilling mud and were crushed prior to leaching, potentially enhancing the leachability of elements.

To understand potential chemical reactions that may occur during ASR operations, geochemical modeling was performed using the U.S. Geological Survey (USGS) model PHREEQ, which is a geochemical thermodynamic equilibrium model. The modeling used field parameter values and dissolved element concentrations as input. Calculations determined saturation indices and speciation (LRE, 2021).

The saturation index (SI) is a measure of the likelihood of a mineral to dissolve into groundwater or precipitate from groundwater. In groundwater, dissolved constituents interact with the aquifer sediments, and at chemical equilibrium the dissolved concentration of many elements is maintained by the dissolution and precipitation of mineral phase, which contains the element.

For example, dissolved fluoride concentrations may be controlled by the dissolution and precipitation of the mineral fluorite (CaF_2). SI values are interpreted as follows:

- Positive (+) values: oversaturated/mineral precipitates
- Zero (0) value: mineral at chemical equilibrium
- Negative (–) values: undersaturated/mineral dissolves

SI values were calculated for various mixtures of groundwater and recharge source water (LRE, 2021). Oversaturated minerals included calcite, dolomite, gibbsite, and goethite, so these minerals are likely to precipitate from groundwater. Undersaturated minerals include barite, gypsum, and halite, so if the mineral were present in the aquifer, it might dissolve.

SI values were calculated for minerals that contain uranium (uraninite), manganese (pyrolusite), and arsenic (arsenopyrite). The SI values for uraninite and arsenopyrite were undersaturated, indicating that they could dissolve if present in the aquifer, but the pH and Eh conditions in the aquifer are not favorable for these minerals to be present (LRE, 2021). SI values for pyrolusite were oversaturated and undersaturated, indicating that manganese could precipitate from some of the water mixtures.

Saturation indices were used to evaluate the potential for clogging of the aquifer or well screen during ASR operations. The most likely minerals that could precipitate are calcium carbonate (aragonite) or iron oxides (ferrihydrite). Calculations indicate that clogging is not expected to be an issue (LRE, 2021).

Element speciation is an important consideration for how the element reacts in solution and whether it will react with mineral surfaces in the aquifer. Speciation describes all the stable ions and complexes in the aqueous phase (dissolved in solution). For example, calcium may be present as the ion (Ca^{2+}) or dissolved complexes like CaCO_3 , CaSO_4 , CaHCO_3^- , or CaF^+ . The species that form are controlled by the pH and Eh conditions. A diagram is often used to show the speciation relative to pH and Eh, and helps illustrate whether an element is likely to be soluble and dissolved in groundwater (Figure 8). In the Eh-pH diagram, blue fields indicate that the element is soluble, and the dominant dissolved form is labeled. Stable mineral phases are shown in the brown fields.

In alkaline water that is oxidizing, uranium (VI) will form a uranyl complex (UO_2^{++}) that bonds with carbonate ions, forming uranyl carbonates with increasing pH (Figure 8). Terry Ranch

groundwater and Bellvue WTP (recharge source water) samples plot in the blue uranyl carbonate fields, indicating that uranium is soluble and tends to exist as complexes in solution (Figure 8).

4.3 Review Conclusions

The hydrogeological and geochemical investigations performed for the proposed project have adequately characterized the physical and chemical characteristics of the Upper Laramie Aquifer at Terry Ranch.

The Upper Laramie Aquifer is a good candidate for ASR because of the aquifer hydraulics and response during ASR, including the following:

- Laramie Formation sandstones have suitable permeability.
- Flow rates tested up to 600 gpm.
- Aquifer tests and cycle tests demonstrate aquifer hydraulics will support ASR.

The water chemistry appears favorable for the ASR project with high quality for both the treated surface (recharge source) water and groundwater:

- Waters are chemically compatible, so no adverse reactions are likely to occur due to mixing during ASR.
- Dissolved uranium naturally occurs in the groundwater.
- Both waters have similar pH and oxidizing potentials that control uranium behavior in water.
- Uranium should not leach from the aquifer during ASR operations.
- Uranium concentrations in stored and recovered water are not expected to exceed background concentrations.
- Uranium concentrations in the recovered water may be controlled through ASR operations or conventional water treatment techniques.

5. Evaluation of Uranium Geochemistry

DBS&A performed an evaluation of the aqueous geochemistry related to the proposed Terry Ranch ASR project. The analysis focused on the inorganic aqueous geochemistry of groundwater in the Upper Laramie Aquifer, particularly the behavior of uranium, including the

chemistry of mixing the groundwater with the recharge source water and the potential reactivity of aquifer sediments with the stored water. A detailed report on the geochemical modeling is provided as Appendix A.

Using the geochemical PHREEQC (Parkhurst and Appelo, 2013), batch equilibrium modeling is an appropriate initial approach for evaluating mineral stability and adsorption processes anticipated to occur during ASR operations at Terry Ranch.

5.1 Groundwater Mixing

The Bellvue WTP recharge source water and groundwater represented by Well EB-1 were mixed in PHREEQC to determine uranium concentrations for the recovered water (Table 1). Mixing calculations indicate that mixtures containing 40 percent or more of the recharge source water are expected to have uranium concentrations of 15.88 µg/L or less.

Table 1. Dissolved Uranium Concentrations Calculated by PHREEQC due to Mixing, Terry Ranch ASR

| | Bellvue WTP/Well EB-1 | | | | |
|----------------|-----------------------|-------|-------|-------|-------|
| Mixture (%) | 20/80 | 40/60 | 50/50 | 60/40 | 80/20 |
| Uranium (µg/L) | 21.14 | 15.88 | 13.25 | 10.62 | 5.35 |

µg/L = microgram per liter

5.2 Equilibrium Modeling

Based on results of batch-equilibrium simulations using the computer program PHREEQC, groundwater at Well EB-1 is in equilibrium with pyrolusite, oversaturated with calcite and ferrihydrite, and undersaturated with CaMoO₄, K-jarosite, rhodocrosite, schoepite, and uraninite. The Bellvue WTP injectate is in equilibrium with calcite, oversaturated with pyrolusite and ferrihydrite, and undersaturated with CaMoO₄, dolomite (ordered, disordered), K-jarosite, rhodocrosite, schoepite, and uraninite.

The presence of these uranium minerals in the Upper Laramie Aquifer is unlikely, based on the low measured concentrations of total and dissolved uranium in the aquifer and their instability in the Upper Laramie Aquifer. A hypothetical simulation was modeled in PHREEQC in which carnotite was set in equilibrium with the Upper Laramie Aquifer groundwater at Well WWR-1. To achieve chemical equilibrium, which could be encountered in an ore deposit, the

concentration of dissolved uranium was calculated at 6.67 mg/L. This calculated concentration greatly exceeds measured dissolved concentrations of uranium, which are less than 50 µg/L in the Upper Laramie Aquifer groundwater at Terry Ranch.

5.3 Uranium Speciation

Based on PHREEQC speciation simulations for groundwater at Well EB-1, natural dissolved uranium (U^{6+}) is stable as soluble ternary complexes of uranium(VI) carbonate ($Ca_2UO_2(CO_3)_3^0$) and carbonato ($CaUO_2(CO_3)_3^{2-}$) species. Such anionic aqueous complexes are weak adsorbates that do not significantly accumulate on solid surfaces, including iron coatings on aquifer sediments [hydrous ferric oxides (HFOs)] under the circumneutral pH to basic conditions (Langmuir, 1997) characteristic of the Upper Laramie Aquifer groundwater at Terry Ranch.

The recharge source water and native groundwater are oxic, and oxidation/reduction (redox) reactions enhancing dissolution of redox-sensitive minerals are not anticipated to occur during proposed ASR operations at Terry Ranch. Controls on the dissolved concentrations of uranium are likely desorption of uranium (VI) from iron coatings (HFOs) and clay minerals in the aquifer sandstones and groundwater in the absence of known uranium minerals. Surface complexation of UO_2^{2+} onto HFO, with Well EB-1 groundwater equilibrated with the HFO surface at pH 9.12, is minimal based on PHREEQC simulations. Concentrations of natural dissolved uranium are not expected to exceed groundwater background values during proposed ASR operations at Terry Ranch.

5.4 Uranium Behavior during ASR Operations

In the Upper Laramie Aquifer, geochemical conditions defined by measurements of pH and Eh control uranium behavior in groundwater. In the alkaline and oxidizing groundwater, uranium (VI) will form soluble uranyl carbonate complexes with a net negative charge, which do not tend to be adsorbed to reactive surfaces like iron coatings or clays. At the pH values observed, these iron coatings and clays have a net negative surface charge, so they do not adsorb the anionic uranium complexes. Uranium is not significantly retained in the Upper Laramie Aquifer.

Geochemical conditions are favorable for the proposed ASR project, and uranium concentrations are not expected to exceed background concentrations or applicable water quality standards. Due to the similar chemical nature of the recharge source water and groundwater, the waters are expected to form a compatible mixture. When water is stored in the aquifer at Terry Ranch, uranium is not expected to desorb from the aquifer sediments into

the stored water, so the uranium concentration of the extracted water will reflect dilution of groundwater by the recharge source water. Mixtures containing 20 percent or more of the recharge source water are expected to meet the applicable MCLs, and mixtures containing 40 percent or more recharge source water are expected to meet Colorado Reg 41 standards (Table 1).

6. Recommendations

DBS&A recommends that hydrogeologic and geochemical analyses continue as the Terry Ranch ASR project's planning and design phases proceed, including the following:

- Continuing to monitor water levels on a quarterly basis
- Collecting water quality samples from select wells on a routine basis

We further recommend that future testing include the following:

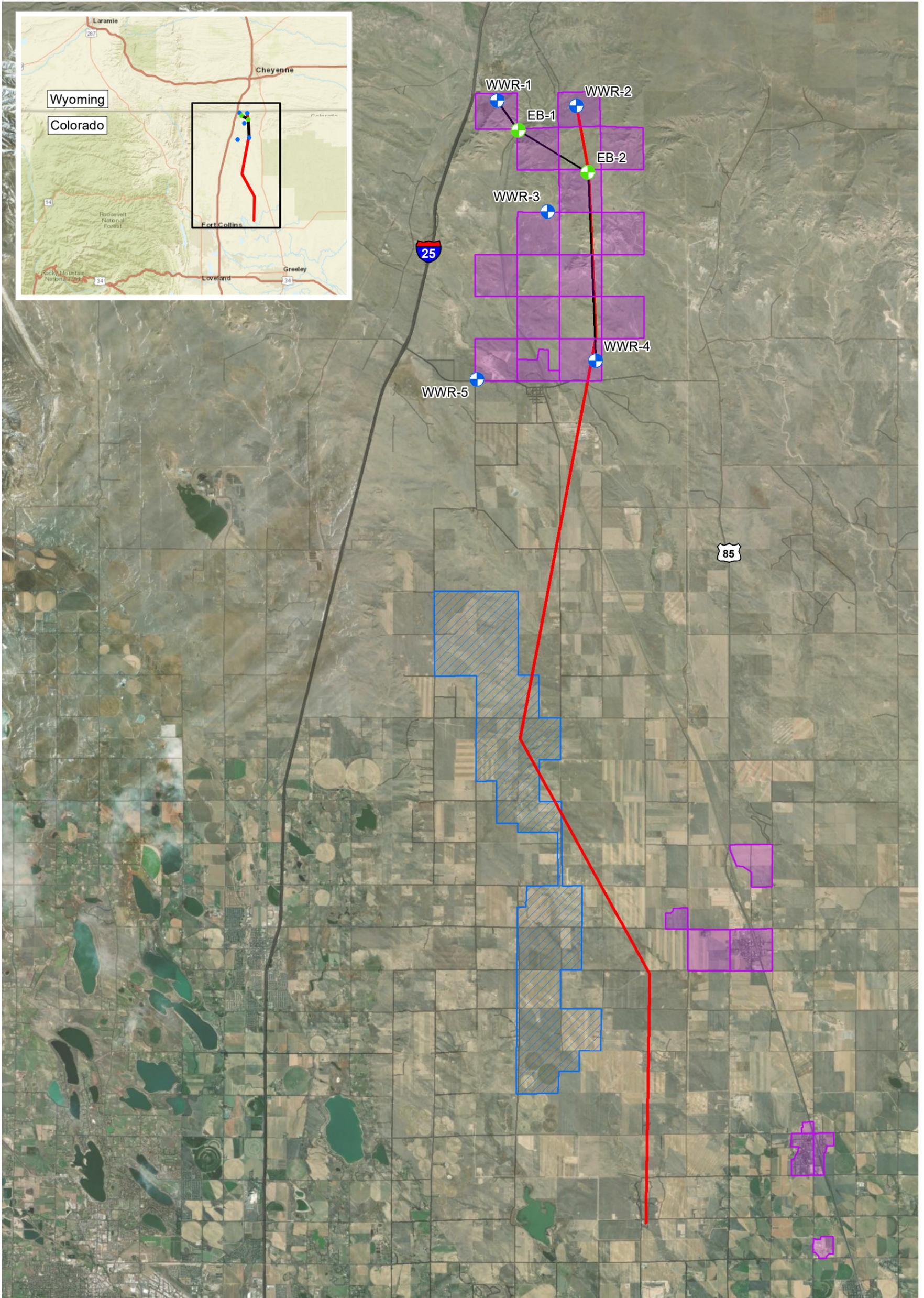
- Design, drill, construct, develop, and test an ASR well based on the analyses performed to date, in a location within the northern portion of Terry Ranch to maximize aquifer thickness and depth to water.
- Install piezometers near the ASR well to collect additional hydraulic data for calculating aquifer parameters.
- Collect rock core samples during drilling and analyze the samples.
- Determine the aquifer interval within the Upper Laramie Aquifer to use for ASR operations.
- When recharge source water is available in sufficient volume, conduct additional ASR pilot testing at the project's design capacity.

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Figures



Base image source: Maxar, Vivid 2017-2019 composite



0 6,000 12,000 Feet



Explanation

- Proposed boundary
- Terry Ranch
- East-west cross section
- North-south cross section
- Road



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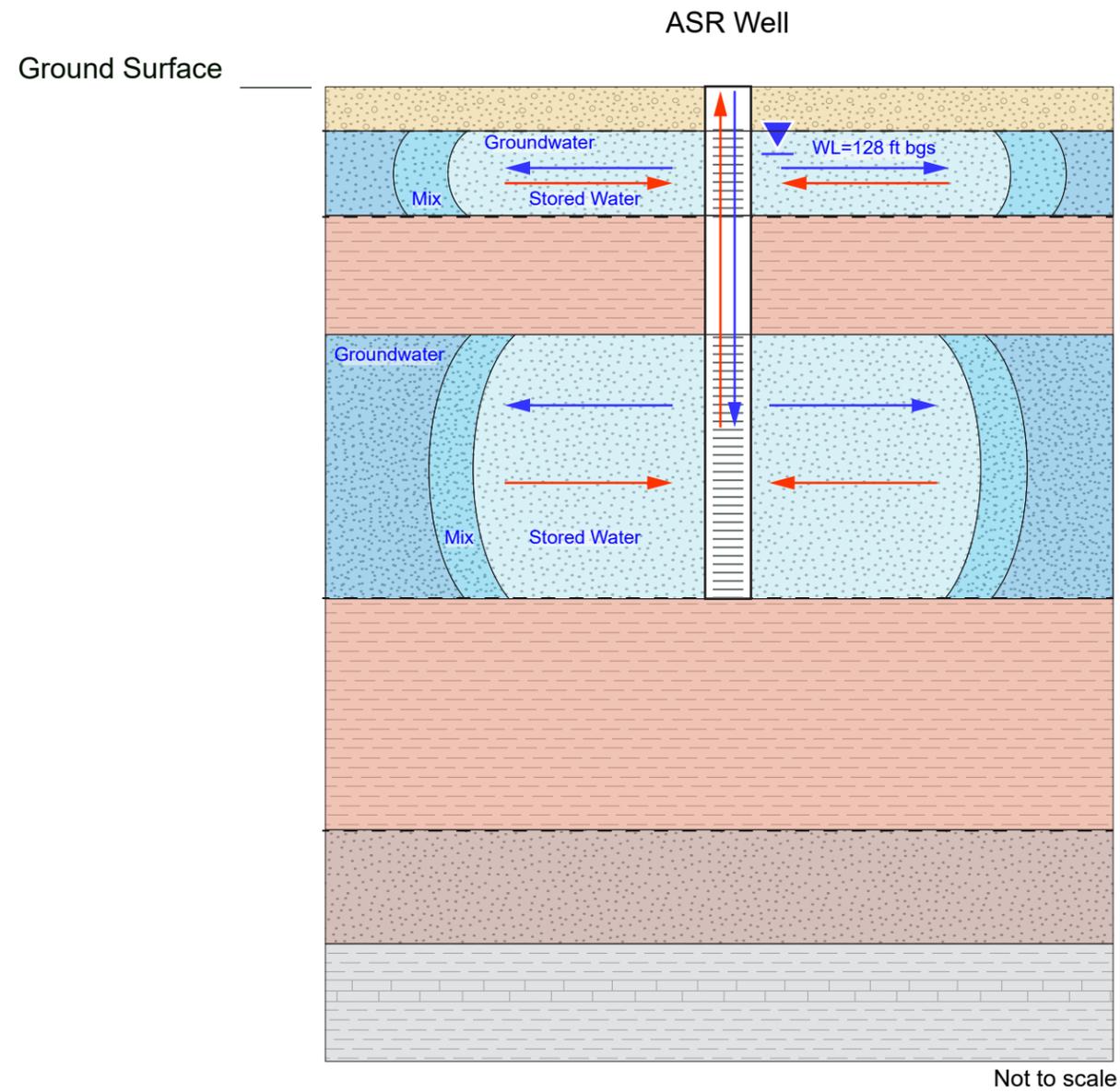
ASR PROJECT REVIEW
GREELEY, COLORADO
Site Map

Figure 1

S:\Projects\B20.1393_Greenley_CO_Geochemistry\VR_Drawings\All\Updated_Template\F02_Conceptual ASR Terry Ranch.ai

| Geology | Regional Aquifer | Terry Ranch Hydrogeology | Depth (ft bgs) |
|-----------------------|------------------------|--------------------------|----------------|
| White River Formation | | | 0 |
| | | Upper Aquifer | 100 |
| | | Aquitard | 200 |
| | Upper Laramie Aquifer | | 400 |
| | | Lower Aquifer | 600 |
| Laramie Formation | | | 800 |
| | Lower Laramie Aquitard | | 1,000 |
| | | Aquitard | 1,200 |
| | | | 1,400 |
| Fox Hills Sandstone | | | 1,600 |
| | | | 1,800 |
| Pierre Shale | | | 2,000 |

Notes:
 ft bgs = feet below ground surface
 ASR = aquifer storage and recovery
 SWL = static water level
 Conceptual model based on hydrogeology and testing at well EB-1



Not to scale

Explanation

Flow direction

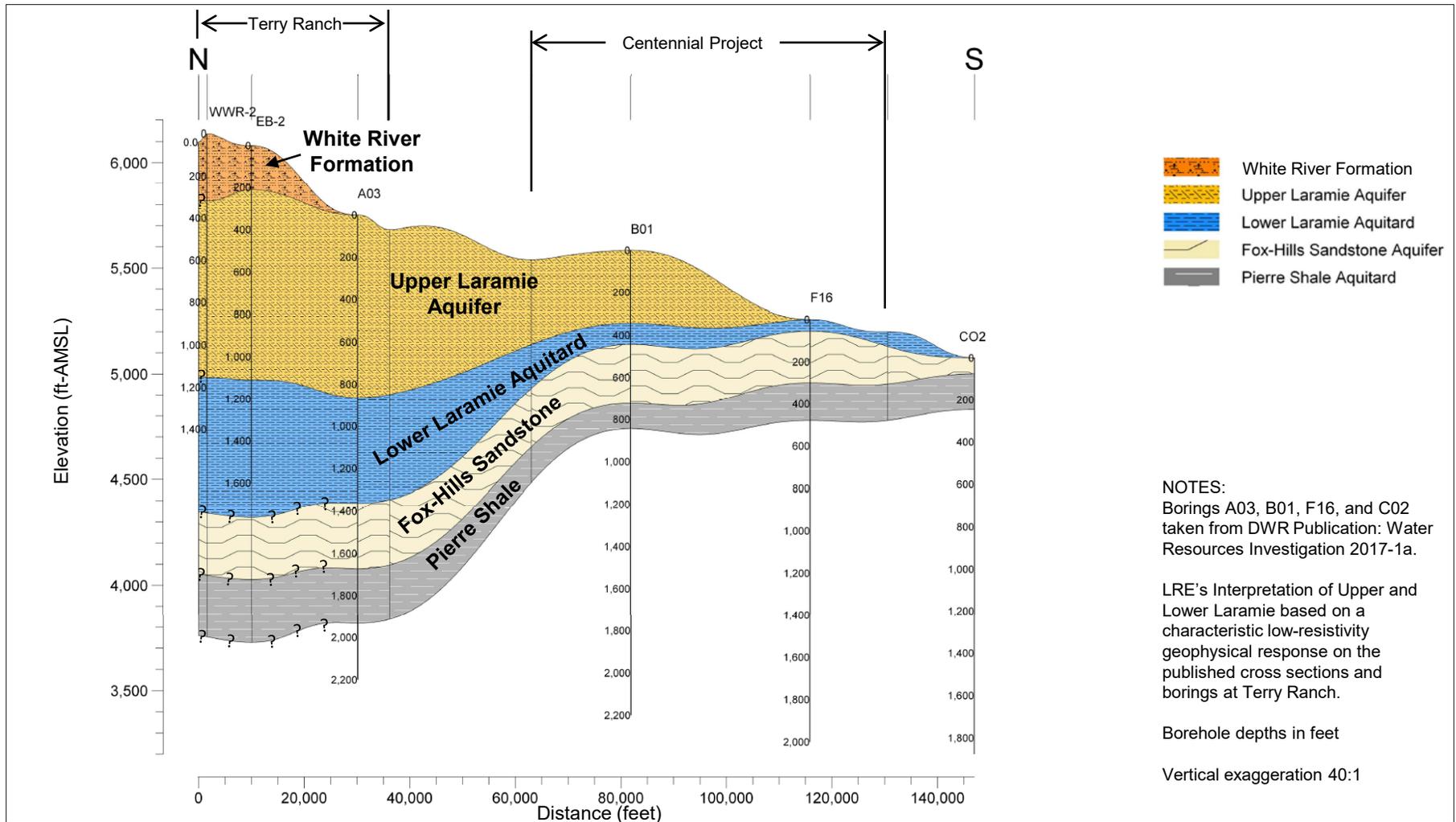
Injection ← (blue arrow)

Extraction → (red arrow)

ASR well screen



ASR PROJECT REVIEW
 GREELEY, COLORADO
**Conceptual ASR Project at
 Terry Ranch**



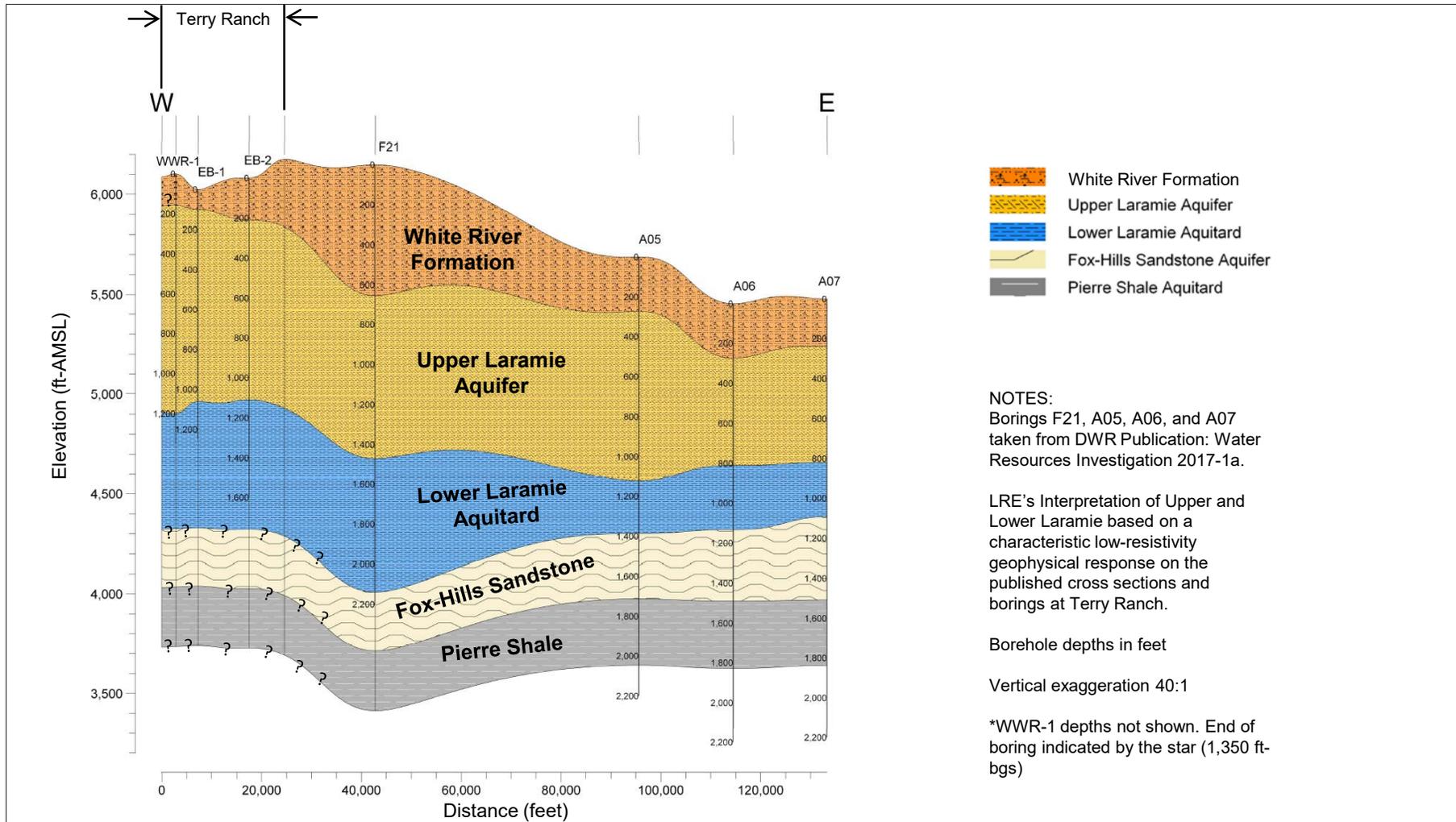
Source: Leonard Rice Engineers, Inc. (LRE Water) December 11, 2020

ASR PROJECT REVIEW
 GREELEY, COLORADO
North-South Cross Section
Terry Ranch to Centennial Project

Figure 3



DBS&A
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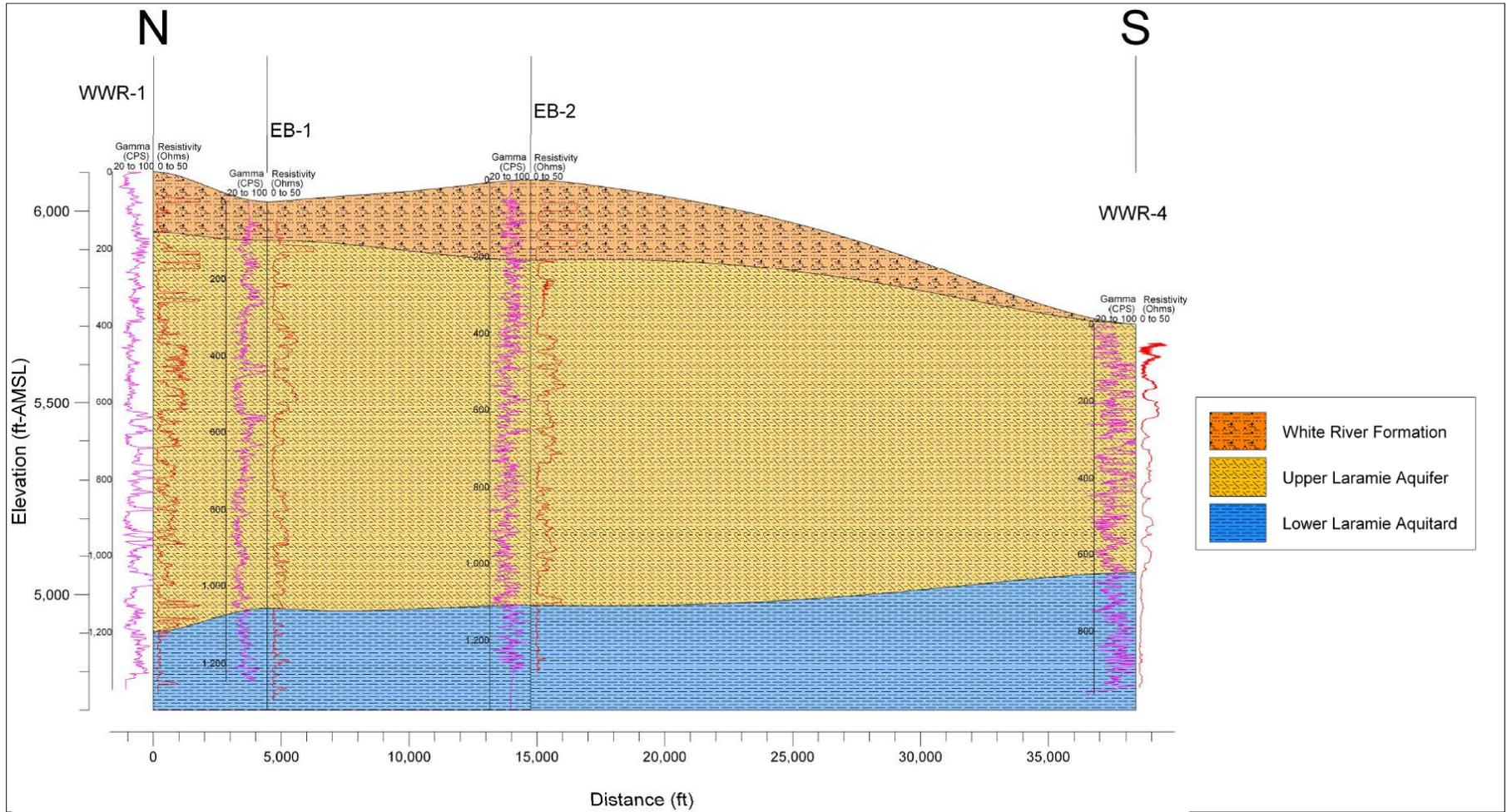
Source: Leonard Rice Engineers, Inc. (LRE Water) December 8, 2020

ASR PROJECT REVIEW
 GREELEY, COLORADO
East-West Cross Section
Terry Ranch to Centennial Project

Figure 4



DBS&A
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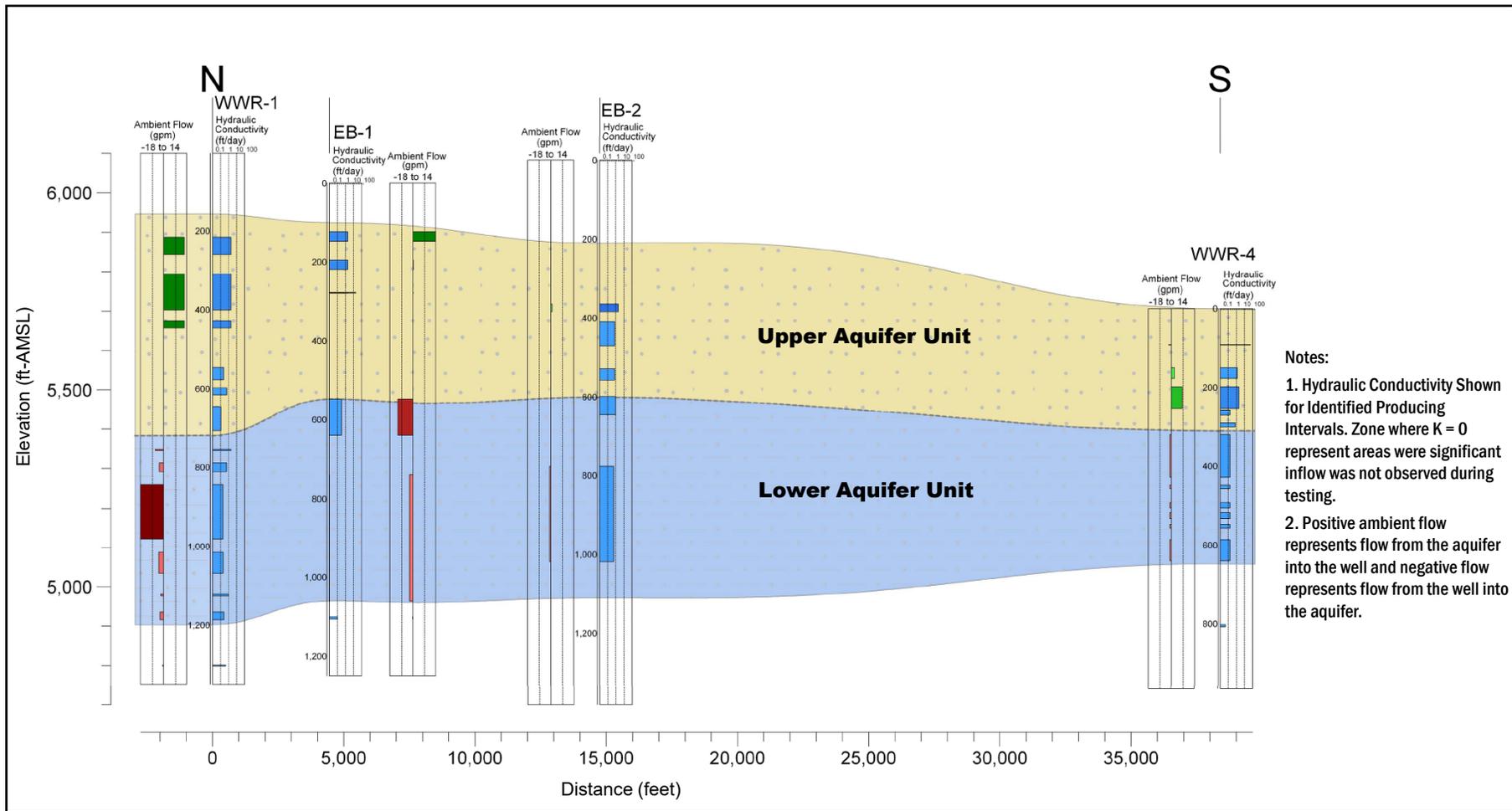
Source: Leonard Rice Engineers, Inc. (LRE Water) December 8, 2020

ASR PROJECT REVIEW
GREELEY, COLORADO
**Stratigraphy with Resistivity and
Gamma Response**
Terry Ranch to Centennial Project

Figure 5



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Notes:

1. Hydraulic Conductivity Shown for Identified Producing Intervals. Zone where $K = 0$ represent areas where significant inflow was not observed during testing.
2. Positive ambient flow represents flow from the aquifer into the well and negative flow represents flow from the well into the aquifer.

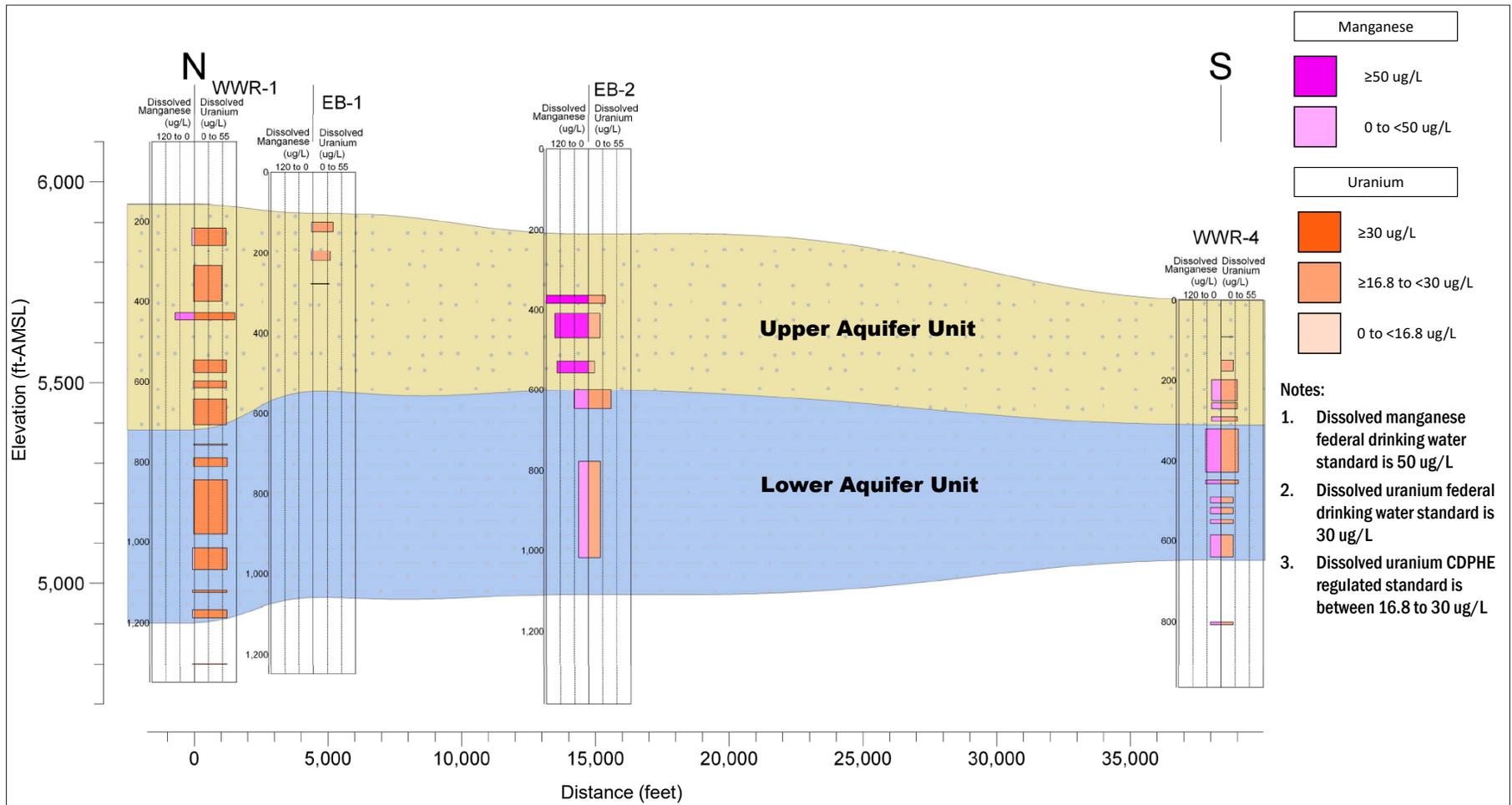
Source: Leonard Rice Engineers, Inc. (LRE Water) December 8, 2020

Figure 6



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ASR PROJECT REVIEW
 GREELEY, COLORADO
Ambient Flow and Hydraulic Conductivity
Terry Ranch to Centennial Project



Source: Leonard Rice Engineers, Inc. (LRE Water) December 8, 2020

ASR PROJECT REVIEW
 GREELEY, COLORADO
**Zonal Sampling Results for
 Manganese and Uranium
 Terry Ranch to Centennial Project**

Figure 7



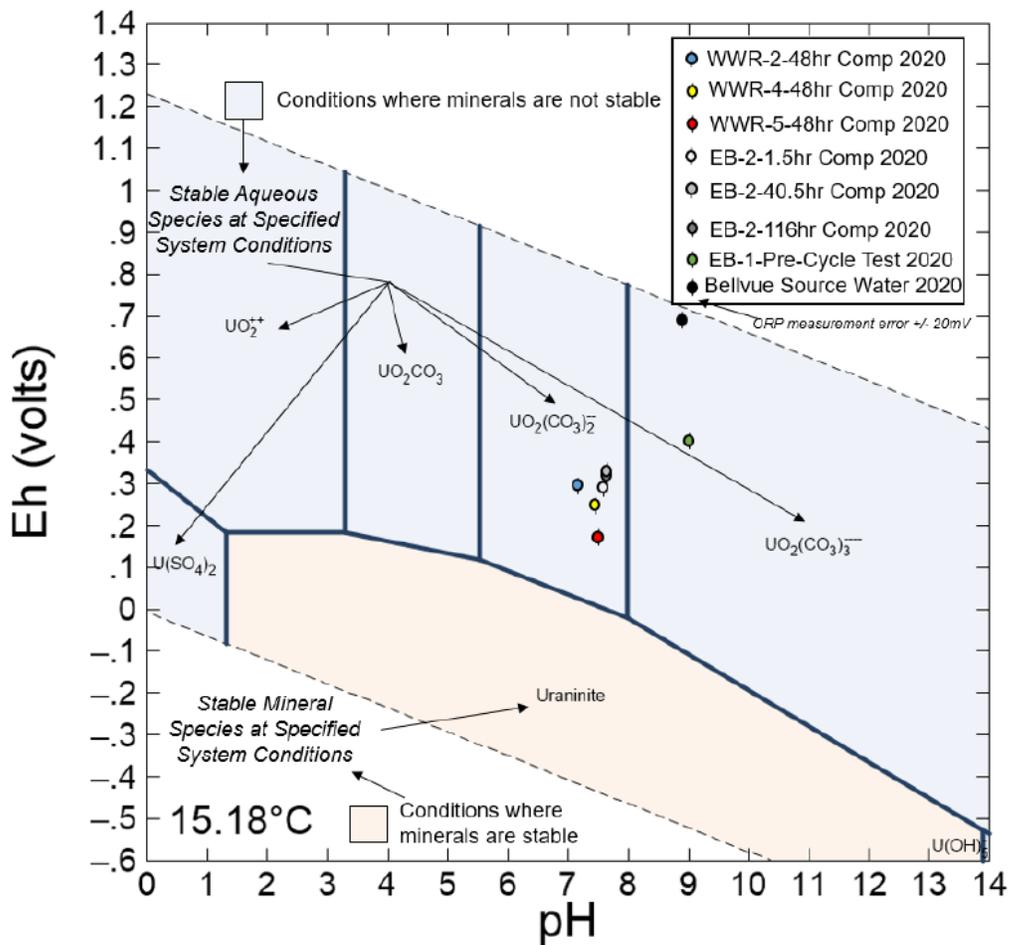


Diagram $UO_2(CO_3)_2$, $T = 15.18^\circ C$, $P = 1.013 \text{ bars}$, $a[\text{HCO}_3^-] = 10^{-2.614}$, $a[\text{H}_2\text{O}] = 10^{-2.476}$, $a[\text{SO}_4^{2-}] = 10^{-3.812}$, $a[\text{SiO}_2(\text{aq})] = 10^{-3.47}$, Suppressed: Cofinite

Source: LRE, 2021

Appendix A
Batch-Equilibrium
Modeling Report

**Batch-Equilibrium Modeling of Upper Laramie Aquifer
Groundwater, Terry Ranch, Weld County, Colorado**

**Patrick Longmire, Ph.D.
Principal Aqueous Geochemist**

Environmental Geochemistry, LLC

January 24, 2021

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Batch-Equilibrium Modeling of Upper Laramie Aquifer Groundwater, Terry Ranch, Weld County, Northern Colorado

Patrick Longmire, Ph.D.,

Principal Aqueous Geochemist

Environmental Geochemistry, LLC

January 24, 2021

Abstract

Quantifying geochemical processes occurring during groundwater mixing using geochemical modeling is an important component in evaluating viability of aquifer storage and recovery (ASR). Results of geochemical modeling, using the computer program PHREEQC (Parkhurst and Appelo 2013), are presented for the proposed ASR site at Terry Ranch, northern Colorado. Oxidation-reduction, aqueous speciation, adsorption/desorption, and mineral precipitation/dissolution control geochemical interactions occurring during mixing of the Bellvue Water Treatment Plant (WTP) injectate and native Upper Laramie Aquifer groundwater reacting with the aquifer matrix. Substantial groundwater mixing is expected to occur during proposed ASR operations at Terry Ranch based on favorable hydraulic properties of the Upper Laramie Aquifer with an estimated transmissivity of 273 feet²/day (LRE 2020d). Natural uranium is an important solute in the Upper Laramie Aquifer at Terry Ranch with concentrations exceeding the federal standard of 30 micrograms/liter (µg/L) and the Colorado Regulation 41 standard 16.8 µg/L.

Based on batch-equilibrium simulations using the computer program PHREEQC (Parkhurst and Appelo 2013), the native Upper Laramie Aquifer groundwater at monitoring well EB-1 is in equilibrium with pyrolusite; is oversaturated with calcite, dolomite (ordered, disordered), ferrihydrite, and pyrolusite; and is undersaturated with CaMoO₄, fluorite, gypsum, K-jarosite, rhodocrosite, schoepite, and uraninite. The Bellvue WTP injectate is in equilibrium with calcite; is oversaturated with ferrihydrite and pyrolusite; and is undersaturated with CaMoO₄, dolomite (ordered and disordered), fluorite, gypsum, K-jarosite, rhodocrosite, schoepite, and uraninite based on PHREEQC simulations. Precipitation of uranium(IV, VI) minerals, such as carnotite, coffinite, haiweeite, schoepite, tyuyamunite, and uraninite, is unlikely due to mineral instability and insufficient concentrations of dissolved natural uranium that are less than 50 µg/L in the native Upper Laramie Aquifer at Terry Ranch. Ternary calcium uranyl carbonate complexes are excellent tracers to assess groundwater mixing of the oxic Bellvue WTP injectate with oxic native groundwater in the Upper Laramie Aquifer. It is likely that desorption of uranium(VI) from hydrous ferric oxide (HFO) and clay minerals controls dissolved concentrations of uranium in the native Upper Laramie Aquifer. Surface complexation of UO₂²⁺ onto HFO, with well EB-1 groundwater equilibrated with the HFO surface at pH 9.12, is minimal based on PHREEQC simulations. Concentrations of natural dissolved uranium are not expected to exceed groundwater background during the proposed ASR operations at Terry Ranch.

1.0 Introduction

The City of Greeley, Colorado has contracted with Leonard Rice Engineers, Inc. (LRE) to assess the production potential and aquifer storage and recovery (ASR) feasibility of the Upper Laramie Aquifer underlying the Terry Ranch in Weld County, northern Colorado. Daniel B. Stephens & Associates, Inc. (DBS&A) was contracted by the City of Greeley to perform geochemical

modeling to evaluate the fate and transport of natural uranium occurring in the native Upper Laramie Aquifer groundwater prior to implementing ASR operations at Terry Ranch. Numerous groundwater samples were collected by LRE from five production wells, including WWR-1, WWR-2, WWR-3, WWR-4, and WWR-5, and two temporary monitoring wells (EB-1 and EB-2) for robust chemical, radiological, and biological analyses to characterize the groundwater quality in the Upper Laramie Aquifer at Terry Ranch as part of the ASR assessment (LRE 2021a). Figure 1 shows the locations of the five production wells and two temporary monitoring wells. Groundwater samples and surface-water samples were collected as part of the ASR assessment consisting of: (1) 24- and 48-hour composite, (2) depth-specific, (3) packer test, (4) Bellvue Water Treatment Plant (WTP) injectate, and (5) pilot treatment test. The production and monitoring wells are completed in the upper and lower units of the Laramie Aquifer with the upper unit recommended for ASR based on suitable hydraulic properties, including hydraulic conductivity and transmissivity. Surface-water samples were collected by LRE from the Bellvue WTP as part of the pilot treatment test conducted at Terry Ranch (LRE 2021a).

Geochemical reactions, including mineral precipitation/dissolution and adsorption/desorption, are anticipated to occur as the Bellvue WTP injectate mixes with native groundwater during ASR, which potentially reacts with aquifer solids in the Upper Laramie Aquifer. Natural uranium, gross alpha activity, and manganese are constituents of concern in groundwater at Terry Ranch. Natural uranium occurs in the Upper Laramie Aquifer at production well WWR-1 with total concentrations ranging from 39.5 to 43.0 micrograms/liter ($\mu\text{g/L}$), which exceed the federal primary maximum concentration level (MCL) of 30 $\mu\text{g/L}$ and the State of Colorado, Regulation 41 health-based limit of 16.8 $\mu\text{g/L}$. Total concentrations of natural uranium are 21.2 $\mu\text{g/L}$ and 22.2 $\mu\text{g/L}$ in two groundwater samples collected from 340 feet below ground surface (bgs) at well EB-1 (LRE 2020e). Total concentrations of manganese were calculated by LRE (2020e) to range from 50.9 $\mu\text{g/L}$ to 72.7 $\mu\text{g/L}$ at well EB-2 in depth-specific samples, which exceed the federal secondary MCL of 50 $\mu\text{g/L}$. Gross alpha activity ranged from 16.9 to 31 pCi/L in groundwater samples collected from the five production wells (LRE 2020e) and exceed the federal and Colorado standard of 15 pCi/L. Gross alpha activity measured in groundwater samples collected from the Upper Laramie Aquifer results from decay of natural isotopes of uranium, including uranium-238, -235, and -234 associated with aquifer solids.

The purpose of this report is to evaluate geochemical interactions that are anticipated to occur during mixing of the Bellvue WTP injectate with native Laramie Formation groundwater during ASR operation at Terry Ranch. Batch-equilibrium simulations using the computer program PHREEQC (Parkhurst and Appelo 2013) were conducted to quantify potential geochemical reactions occurring during mixing of the Bellvue WTP injectate with native Upper Laramie Aquifer groundwater, which potentially reacts with aquifer solids. Geochemical components of interest include solute speciation, mineral stability, and adsorption/desorption of uranium and other adsorbates associated with hydrous ferric oxide (HFO) during groundwater mixing. Hydrous ferric oxide is a very common adsorbent that ubiquitously occurs in oxidizing aquifers worldwide (Langmuir 1997). The input files for computer simulations include groundwater chemistry data collected by LRE (2021a) for the Bellvue WTP injectate and at production well WWR-1 and monitoring well EB-1 prior to a 24-hour cycle test conducted in December 2020.

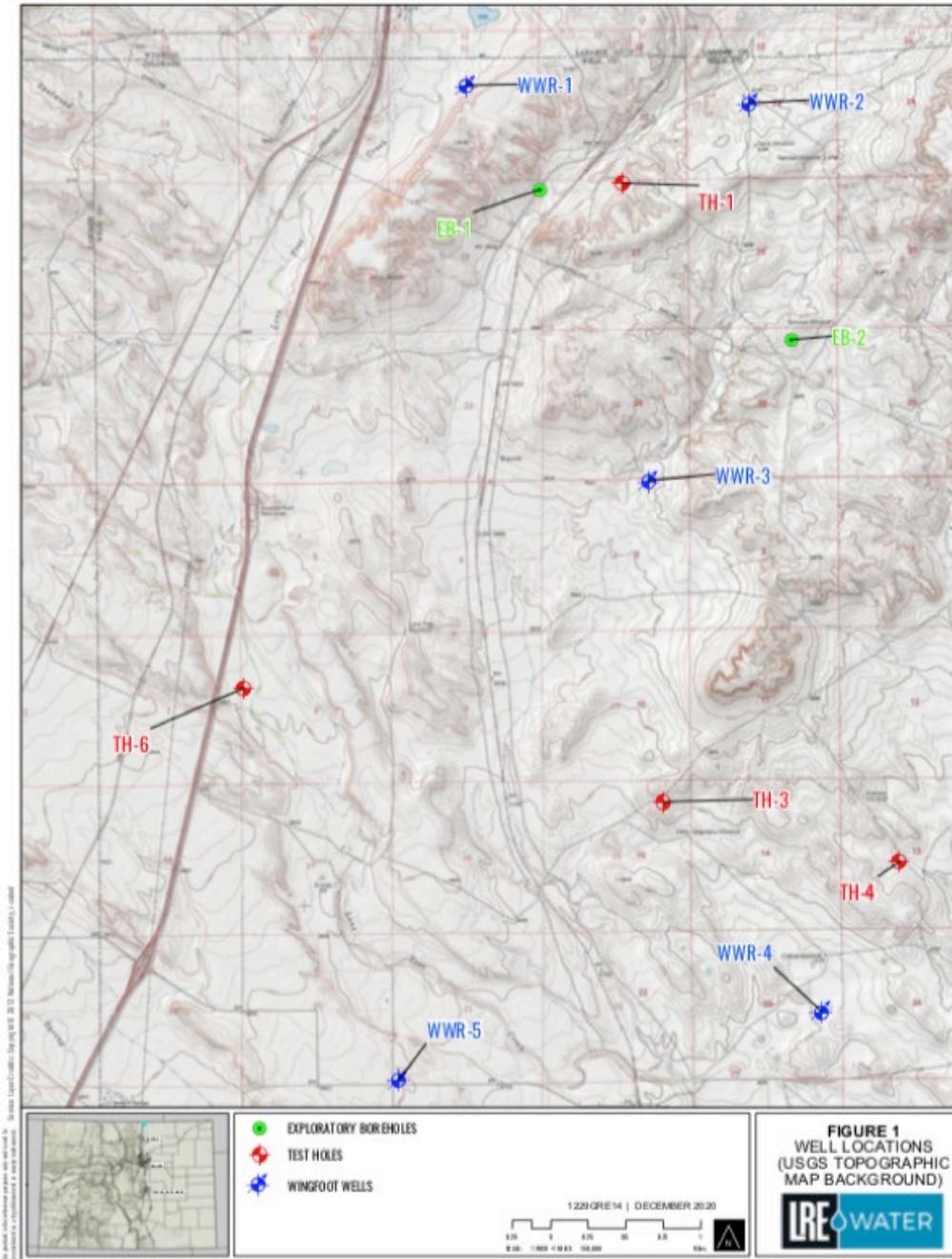


Figure 1. Well location map, Terry Ranch, northern Colorado (source: LRE 2021b).

2.0 Water Chemistry of Bellvue Water Treatment Plant (WTP) Injectate and Native Upper Laramie Aquifer Groundwater, Terry Ranch, Northern Colorado

Table 1 provides analytical results for water samples, including the Bellvue WTP injectate and native Upper Laramie Aquifer groundwater collected by LRE (2021a) on December 4, 2020 prior to a 24-hour cycle test conducted at monitoring well EB-1. Native Upper Laramie Aquifer groundwater has higher concentrations of major ions and total dissolved solids (TDS) compared to the injectate, which has experienced water-rock interactions occurring over tens of thousands of years compared to treated surface water. The native Upper Laramie Aquifer

groundwater and Bellvue WTP injectate are characterized by calcium-sodium-bicarbonate solutions. The Bellvue WTP injectate and well EB-1 groundwater sampled on December 4, 2020 have speciated charge balances of -1.95 and -1.65 percent, respectively, calculated by the computer program PHREEQC (Parkhurst and Appelo 2013). Oxidation-reduction potential (ORP, Eh) was measured during sampling (LRE 2020a) and pe (-log₁₀ activity of electron) values were calculated for the Bellvue WTP injectate and well EB-1 groundwater samples, which are moderately to strongly oxidizing (Table 1). A non-detect concentration of total dissolved arsenic of 0.3 µg/L for the Bellvue WTP injectate (Table 1) is one-half of the analytical detection limit (0.6 µg/L) using inductively coupled plasma-mass spectrometry (ICP-MS) at Colorado Analytical.

Table 1. Dissolved major ion and trace element chemistry of Bellvue Water Treatment Plant (WTP) injectate and native Upper Laramie Aquifer groundwater prior to 24-hour cycle test conducted in December 2020 at Terry Ranch, northern Colorado (LRE 2021a).

| Analyte (mg/L) | Bellvue WTP Injectate | Native Upper Laramie Aquifer Groundwater |
|--|-----------------------|--|
| Total carbonate alkalinity (mgCaCO ₃ /L) | 45.8 | 172.6 |
| Calcium (mg/L) | 14.3 | 41.8 |
| Magnesium (mg/L) | 2.77 | 5.82 |
| Sodium (mg/L) | 8 | 30.1 |
| Potassium (mg/L) | 1.1 | 7.3 |
| Chloride (mg/L) | 4.72 | 3.37 |
| Fluoride (mg/L) | 0.64 | 0.27 |
| Nitrate as N (mg/L) | 0.05 | 0.96 |
| Sulfate (mg/L) | 13.7 | 27.1 |
| Arsenic (µg/L) | 0.6, U | 6 |
| Copper (µg/L) | 5.5 | 1.5 |
| Iron (µg/L) | 88 | 253 |
| Lead (µg/L) | 0.3 | 0.4 |
| Manganese (µg/L) | 4 | 3.4 |
| Molybdenum (µg/L) | 0.6 | 2.3 |
| Uranium (µg/L) | 0.2, U | 26.4 |
| Total organic carbon (mgC/L) | 2.1 | 0.5, U |
| Total dissolved solids (mg/L) | 69 | 312 |
| pH (standard units) | 8.67 | 9.12 |
| ORP (mV) | +518.9 | +192.6 |
| Eh (mV), (calculated from an YSI 9626904 pH/ORP module, 3.5 M KCl) | +733.9 | +405.6 |
| pe (-log ₁₀ activity of electron) | +13.0383 | +7.1478 |
| Temperature (C) | 10.5 | 12.8 |
| Speciated charge balance (percent) ¹ | -1.95 | -1.65 |

U result was below the method detection limit.

Total organic carbon (TOC) and total carbonate alkalinity are from non-filtered samples.

Colorado Analytical performed inorganic and TOC analyses (LRE 2021a).

¹Speciated charged calculated balance performed by P. Longmire, using PHREEQC, on January 22, 2021.

3.0 PHREEQC

Geochemical-thermodynamic computer programs are used as one of several quantitative tools, along with groundwater analytical results and hydrogeological, mineralogical, and geophysical data and information, as part of conducting site characterization and remediation investigations. Analytical results from groundwater samples collected by LRE (2021a) at well EB-1 on December 4, 2020 serve as input to the model simulations. Batch equilibrium-geochemical modeling was

performed using the computer program PHREEQC (**pH-REdox-EQ**uilibria-**C++** computer language)-Version 3 (Parkhurst and Appelo 2013). Chemical kinetics are not included as part of the PHREEQC simulations; however, reactive minerals reaching equilibrium over short periods of time in groundwater systems are evaluated. Minteq.v4.dat is the chemical thermodynamic database used in the geochemical simulations because it contains recently compiled and critically reviewed speciation and solubility data for aqueous and solid phases of uranium(IV, VI) (Grenthe et al. 1992).

Thermodynamic databases may contain systematic errors associated with experimental studies that hinder accuracy and internal consistency. Critical evaluation of thermodynamic data for major ions, radionuclides, and metals/trace elements, including arsenic, chromium, and uranium, however, have been conducted by the U. S. Geological Survey, universities, and research institutions over the past three decades. Such efforts improve the meaningfulness and relevance of geochemical models and their application to environmental investigations. Solute speciation, mineral saturation indices, and adsorption calculations for calcium, sulfate, and uranium were carried out using PHREEQC. Transport of uranium(VI) in groundwater is controlled by redox and pH conditions, solution composition, especially total carbonate alkalinity and dissolved calcium, and the presence of adsorbents, including ferric (oxy)hydroxide, solid organic matter, and clay minerals with large surface areas (smectite) (Langmuir 1997).

3.1 Solute Speciation Calculations

Results of uranium speciation calculations for the Bellvue WTP injectate and native Upper Laramie Aquifer groundwater samples at well EB-1 are provided in Table 2. Based on PHREEQC simulations, dissolved uranium is stable as soluble ternary complexes of uranium(VI) carbonate (neutral charge) and carbonato (anion) species. Such anionic aqueous complexes are weak adsorbates that do not significantly accumulate on solid surfaces under circumneutral to basic pH conditions (Langmuir 1997). Formation constants for dissolved ternary calcium-uranyl carbonate complexes provided by Dong and Brooks (2006) were added to the PHREEQC input files using Minteq.v4.dat database. Specifically, these ternary uranyl complexes do not significantly adsorb on HFO and other solids because of steric hindrance and net-negative surface charge present on adsorbents under circumneutral to basic pH conditions.

Table 2. Results of PHREEQC speciation calculations for Bellvue Water Treatment Plant (WTP) injectate and well EB-1 groundwater samples collected on December 4, 2020, Terry Ranch, Colorado (Source of data for calculations: LRE 2020).

| Bellvue WTP Injectate | | | | |
|---|-----------------|---|-----------------|-------------------|
| Solute | Molality | Speciated Form | Molality | Percentage |
| U(VI) | 4.202E-10 | $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ | 2.301E-10 | 54.76 |
| | | $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ | 1.788E-10 | 42.55 |
| | | $\text{UO}_2(\text{CO}_3)_3^{4-}$ | 8.989E-12 | 2.14 |
| Well EB-1 Groundwater, Upper Laramie Aquifer | | | | |
| Solute | Molality | Speciated Form | Molality | Percentage |
| U(VI) | 1.109E-07 | $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ | 6.772E-08 | 61.06 |
| | | $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ | 4.225E-08 | 38.10 |
| | | $\text{UO}_2(\text{CO}_3)_3^{4-}$ | 9.503E-10 | 0.86 |

Table 3 presents PHREEQC results of calculated concentrations of dissolved uranium produced from mixing ratios of Bellvue WTP injectate to native Upper Laramie Aquifer groundwater equal to 20, 40, 50, 60, and 80 percent. The initial concentrations of dissolved uranium in Bellvue WTP

injectate and well EB-1 groundwater are less than analytical detection (0.4 µg/L) and 26.4 µg/L, respectively (Table 1). Dissolved concentrations of uranium are less than the federal standard of 30 µg/L and decrease below the Colorado Regulation 41 of 16.8 µg/L during groundwater mixing and are below the Colorado standard with mixing ratios of Bellvue WTP injectate to native Upper Laramie Aquifer groundwater that are 40 and higher.

Table 3. Calculated concentrations of dissolved uranium using PHREEQC for different mixing ratios of Bellvue Water Treatment Plant (WTP) injectate and well EB-1 groundwater, Terry Ranch, northern Colorado (Source of data for calculations: LRE 2021a).

| | Bellvue WTP Injectate/well EB Groundwater (%) |
|---|---|---|---|---|---|
| | 20 | 40 | 50 | 60 | 80 |
| Dissolved concentration of uranium calculated by PHREEQC | | | | | |
| Uranium (µg/L) | 21.14 | 15.88 | 13.25 | 10.62 | 5.35 |

3.2 Mineral Saturation Index Calculations

Results of saturation index calculations are provided in Table 4. Reactive minerals and amorphous solids precipitate from solution when the reaction half-time of a given phase is shorter than groundwater residence time, allowing equilibrium to be reached within minutes, hours, days, or months (Langmuir 1997, Drever 1988). Several classes of reactive minerals and amorphous solids include alkaline earth carbonates and sulfates, metal oxides-hydroxides, amorphous silicates, and metal (oxy)hydroxides. Non-reactive minerals (feldspars, amphiboles, and pyroxenes) may take thousands of years to precipitate, require elevated temperatures, and generally do not control solution compositions or influence contaminant migration in most aquifer systems. Non-reactive minerals include most high temperature and pressure silicates. The saturation index (SI) is defined as (Langmuir 1997):

$$SI = \log_{10}[(\text{ion activity product})/(\text{solubility product})].$$

Equilibrium between a given amorphous solid and mineral and aqueous solution is reached when SI equals 0 ± 0.05 and forward (precipitation) and reverse (dissolution) reaction rates are equal; oversaturation occurs when SI is greater than zero and precipitation of a solid takes place; and undersaturation occurs when SI is negative and dissolution of a solid is expected (Langmuir 1997). Groundwater at well EB-1 is in equilibrium with pyrolusite; is oversaturated with calcite, dolomite (ordered, disordered), and ferrihydrite; and is undersaturated with CaMoO_4 , fluorite, gypsum, K-jarosite, rhodochrosite, schoepite, and uraninite according to PHREEQC simulations (Table 4). The Bellvue WTP injectate is in equilibrium with calcite; is oversaturated with ferrihydrite and pyrolusite; and is undersaturated with CaMoO_4 , dolomite (ordered, disordered), fluorite, gypsum, K-jarosite, rhodochrosite, schoepite, and uraninite.

Presence of the above uranium minerals in the Upper Laramie Aquifer is unlikely, based on measured low concentrations of total and dissolved uranium in the aquifer and their instability in the oxic Upper Laramie Aquifer. For example, results of a PHREEQC simulation in which carnotite, a common uranyl mineral found in sedimentary uranium roll front deposits (Langmuir 1997), is set in equilibrium with the Laramie Aquifer groundwater at production well WWR-1 requires 6.67 mg/L of dissolved uranium. This calculated concentration greatly exceeds

measured dissolved concentrations of uranium that are less than 50 µg/L in the Upper Laramie Aquifer groundwater at Terry Ranch.

Table 4. Results of gas and mineral-solid phase saturation indices calculated by PHREEQC for Bellvue Water Treatment Plant (WTP) injectate and Well EB-1 groundwater, Terry Ranch, northern Colorado (Source of data for calculations: LRE 2021a).

| | Bellvue WTP Injectate | Well EB-1 Groundwater |
|--|-----------------------|-----------------------|
| Phase | Saturation Index | Saturation Index |
| Calcite (CaCO ₃) | -0.01 | +1.34 |
| CaMoO ₄ | -3.90 | -3.00 |
| CO ₂ gas | -4.03 | -3.96 |
| Dolomite (CaMg(CO ₃) ₂) (disordered) | -1.21 | +1.42 |
| Dolomite (CaMg(CO ₃) ₂) (ordered) | -0.60 | +2.02 |
| Ferrihydrite (Fe(OH) ₃) | +3.01 | +3.28 |
| Fluorite (CaF ₂) | -1.97 | -2.40 |
| Gypsum (CaSO ₄ ·2H ₂ O) | -2.88 | -2.30 |
| K-Jarosite (KFe ₃ SO ₄ (OH) ₆) | -4.27 | -3.71 |
| Pyrolusite (MnO ₂) | +9.62 | -0.02 |
| Rhodochrosite (MnCO ₃) | -1.63 | -0.72 |
| Schoepite (UO ₂ (OH) ₂ ·H ₂ O) | -7.83 | -7.93 |
| Uraninite (UO ₂) | -30.33 | -19.72 |

Table 5 presents results of mixing calculations using PHREEQC to evaluate SI values for calcite and pyrolusite at different mixing ratios of Bellvue WTP injectate to native Upper Laramie Aquifer groundwater equal to 20, 40, 50, 60, and 80 percent. The mixed groundwater remains oversaturated with both minerals and precipitation is expected to occur in the Upper Laramie Aquifer during ASR. Calcite becomes less oversaturated with increasing percentages of Bellvue WTP injectate, which causes more calcite to precipitate from groundwater during mixing. Additional precipitation of calcite should not decrease the effective porosity and transmissivity of the Upper Laramie Aquifer during ASR because this mineral is an accessory component of the aquifer matrix.

Table 5. Saturation indices for calcite and pyrolusite calculated by PHREEQC at different mixing ratios of Bellvue Water Treatment Plant (WTP) injectate and well EB-1 groundwater, Terry Ranch, northern Colorado (Source of data for calculations: LRE 2021a).

| | Bellvue WTP Injectate/well EB Groundwater (%) |
|-------------------------|---|---|---|---|---|
| | 20 | 40 | 50 | 60 | 80 |
| Saturation Index | | | | | |
| Calcite | +1.22 | +1.08 | +0.99 | +0.88 | +0.59 |
| Pyrolusite | +9.87 | +9.85 | +9.84 | +9.84 | +9.86 |

3.3 Adsorption (Surface Complexation) Calculations

Adsorption is considered to be the only viable geochemical process that controls dissolved concentrations of uranium in oxic groundwater at well EB-1. PHREEQC is used to quantify adsorption processes, including surface complexation with HFO, based on the diffuse double layer model discussed in detail by Langmuir (1997). This phase commonly occurs in soils,

sediments, and aquifer systems worldwide and is an important adsorbent for numerous cations and anions. One millimole concentration of HFO (0.089 g HFO) is assumed for the PHREEQC simulations discussed below. This adsorbent provides active negative- and positive-charged binding sites for cations and anions, respectively, under varying pH conditions, temperature, and solution composition. This amount of adsorbent provides a substantial concentration of binding sites for metal adsorption, especially for cations under circumneutral pH conditions, however anion adsorption significantly decreases under basic pH conditions characteristic of well EB-1. Adsorption calculations using PHREEQC do not include adsorption or partitioning of uranyl cation onto solid organic matter and clay minerals such as gibbsite, kaolinite, and smectite.

The specific surface area of HFO is 600 meters²/gram solid (Langmuir 1997). Hydrous ferric oxide has 0.005 mol/mol iron of high energy or strong sites (Hfo_sOH) and 0.2 mol/mol iron of low energy or weak sites (Hfo_wOH) (Langmuir 1997). Surface charge on HFO changes from a net-positive charge to a net-negative charge with increasing pH, which enhances adsorption of cations at higher or more basic pH values. Intrinsic adsorption constants for bicarbonate and carbonate (Ilnl database) and uranium (VI) (Langmuir 1997) were added to the minteq.v4.dat database to quantify adsorption of these anions onto HFO by making the PHREEQC simulations more realistic and applicable to site conditions at well EB-1. Intrinsic adsorption constants for bicarbonate, carbonate, and uranium(VI) with HFO are provided below:



Table 6 provides results of the surface complexation calculations for well EB-1 groundwater at pH 9.12, using PHREEQC and analytical results shown in Table 1. One millimole of HFO (0.089 g), which is equilibrated with well EB-1 groundwater, contains 5.0E-06 moles of strong binding sites and 2.0E-04 moles of weak binding sites with the concentration of weak adsorption sites exceeding the number of strong sites. Results of the PHREEQC simulation show that Pb²⁺ and Ca²⁺ dominate adsorption onto strong sites that significantly limits other cations from adsorbing onto HFO, including uranyl cation (UO₂²⁺). Magnesium and arsenic(V) dominate adsorption onto weak sites present on HFO and limits adsorption of anions.

Moles of uranyl cation (6.023E-23 and 2.517E-13) present on strong and weak adsorption sites, respectively, are many orders of magnitude lower than those for lead (3.108E-6 and 1.577E-07) and calcium (1.498E-06 and 2.380E-05) (Table 6). Approximately 1.50E-05 mg of Pb²⁺ adsorbs onto 1 millimole HFO (strong sites) corresponding to a mole fraction equal to 0.622. Magnesium dominates adsorption on weak sites at 1.024E-04 moles (0.0042 mg) with a mole fraction of 0.512. Competition of adsorption sites between dissolved lead, calcium, magnesium, and arsenic(V) and uranyl cation (UO₂²⁺) present on HFO results in poor adsorption of uranyl on Upper Laramie Aquifer sediments at well EB-1.

A PHREEQC simulation was performed with equilibrating the surface of HFO (0.089 g) with well EB-1 groundwater and mixing 20 percent this groundwater with 80 percent Bellvue WTP injectate. Initial water chemistries for the two solutions are provided in Table 1. The mixed

solution contains a calculated dissolved concentration of uranium of 5.35 µg/L using PHREEQC (Table 3). An insignificant amount of uranium (4.159E-12 moles, 1.747E-08 µg), represented as the surface complex Hfo_wOUO_2^+ , adsorbs onto weak sites of the HFO surface equilibrated with the mixed solution containing 5.35 µg/L of dissolved uranium at pH 8.99. This simulation supports the high mobility of uranium(VI) at well EB-1 and oxic groundwater flowing through the Upper Laramie Aquifer at Terry Ranch. During increasing mixing of Bellvue WTP injectate with well EB-1 groundwater, dissolved concentrations of uranium decrease (Table 3) and there are no surface sites present on HFO to release or desorb additional concentrations of uranium to groundwater. This is consistent with analytical results for uranium showing an initial decrease in uranium concentrations with mixed groundwater consisting entirely on Bellvue WTP injectate (LRE Waterf 2020). Dissolved concentrations of uranium steadily increase to pre-injection values as increasing percentages of native Upper Laramie Aquifer groundwater are extracted during 24- and 48-hour cycle tests conducted at well EB-1 (LRE Waterf 2020, LRE 2021a).

Table 6. Results of PHREEQC surface complexation calculations for groundwater samples collected at well EB-1 on December 4, 2020, Terry Ranch, northern Colorado. Concentration of HFO equals one millimole (0.089 g HFO) equilibrated with well EB-1 groundwater, pH = 9.12. (Source of data for calculations: LRE 2021a).

| Surface Species-Strong Sites | Moles or Molality | Mole Fraction | Percentage |
|------------------------------|-------------------|---------------|------------|
| Hfo_sOHPb^{2+} | 3.108E-06 | 0.622 | 62.2 |
| Hfo_sOCa^{2+} | 1.498E-07 | 0.300 | 30.0 |
| Hfo_sOCu^+ | 3.343E-07 | 0.067 | 6.7 |
| Hfo_sOHAsO_4^{3-} | 3.453E-08 | 0.007 | 0.7 |
| Hfo_sO^- | 1.301E-08 | 0.003 | 0.3 |
| Hfo_sOH | 1.199E-08 | 0.002 | 0.2 |
| Hfo_sOH_2^+ | 2.522E-10 | 5.044E-04 | 0.05 |
| Hfo_sOHSO_4^{2-} | 6.716E-12 | 1.343E-06 | 1.343E-04 |
| Hfo_sOHUO_2^{2+} | 6.023E-23 | 1.205E-17 | 1.205E-15 |
| Surface Species-Weak Sites | Moles or Molality | Mole Fraction | Percentage |
| Hfo_wOMg^+ | 1.024E-04 | 0.512 | 51.2 |
| Hfo_wOHAsO_4^{3-} | 3.923E-05 | 0.196 | 19.6 |
| Hfo_wCa^+ | 2.380E-05 | 0.119 | 11.9 |
| Hfo_wO^- | 1.478E-05 | 0.074 | 7.4 |
| Hfo_wOH | 1.362E-05 | 0.068 | 6.8 |
| Hfo_wCO_3 | 3.315E-06 | 0.017 | 1.7 |
| Hfo_wOCu^+ | 1.948E-06 | 0.010 | 1.0 |
| Hfo_wHCO_3 | 4.119E-07 | 0.002 | 0.2 |
| Hfo_wOH_2^+ | 2.873E-07 | 0.001 | 0.1 |
| Hfo_wOUO_2^+ | 2.517E-13 | 1.258E-09 | 1.258E-07 |

4.0 Summary and Conclusions

Geochemical-thermodynamic computer programs, such as PHREEQC, are used as one of several quantitative tools, along with groundwater analytical results and hydrogeological, mineralogical, and geophysical data and information for conducting site characterization and ASR feasibility investigations. Batch equilibrium modeling is an appropriate initial approach to evaluate mineral stability and adsorption processes anticipated to occur at the proposed ASR site at Terry Ranch, Weld County, northern Colorado.

Based on PHREEQC speciation simulations, natural dissolved uranium present in the native Upper Laramie Aquifer at well EB-1 is stable as soluble ternary complexes of uranium(VI) carbonate ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$) and carbonate ($\text{CaUO}_2(\text{CO}_3)_3^{2-}$) species. Such anionic aqueous complexes are weak adsorbates that do not significantly accumulate on solid surfaces, including HFO, under circumneutral pH to basic conditions (Langmuir 1997) characteristic of the Upper Laramie Aquifer groundwater at Terry Ranch.

Based on results of batch-equilibrium simulations using the computer program PHREEQC, groundwater at well EB-1 is in equilibrium with pyrolusite; is oversaturated with calcite and ferrihydrite; and is undersaturated with CaMoO_4 , K-jarosite, rhodocrosite, schoepite, and uraninite. The Bellvue WTP injectate is in equilibrium with calcite; is oversaturated with pyrolusite and ferrihydrite; and is undersaturated with CaMoO_4 , dolomite (ordered, disordered), K-jarosite, rhodocrosite, schoepite, and uraninite.

Presence of the above uranium minerals in the Upper Laramie Aquifer is unlikely, based on measured low concentrations of total and dissolved uranium in the aquifer and their instability in the Upper Laramie Aquifer. For example, results of a PHREEQC simulation in which carnotite is set in equilibrium with the Laramie Aquifer groundwater at production well WWR-1 requires 6.67 mg/L of dissolved uranium. This calculated concentration greatly exceeds measured dissolved concentrations of uranium that are less than 50 $\mu\text{g/L}$ in the Laramie Aquifer groundwater at Terry Ranch.

Dissolved ternary calcium uranyl carbonate complexes are excellent tracers to quantitatively assess groundwater mixing of the Bellvue WTP injectate with native Upper Laramie Aquifer groundwater. The Bellvue WTP injectate and native groundwater are oxic and oxidation-reduction reactions enhancing dissolution of redox-sensitive minerals is not anticipated to occur during proposed ASR operations at Terry Ranch. It is likely that desorption of uranium(VI) from HFO and clay minerals controls dissolved concentrations of uranium in the native Upper Laramie Aquifer groundwater in the absence of known uranium minerals. Surface complexation of UO_2^{2+} onto HFO, with well EB-1 groundwater equilibrated with the HFO surface at pH 9.12, is minimal based on PHREEQC simulations. Concentrations of natural dissolved uranium are not expected to exceed groundwater background during proposed ASR operations at Terry Ranch.

5.0 References

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