



**Application of PHREEQC for Evaluating  
Precipitation of Reactive Phases During  
Injection of Treated Effluent Water at Well  
KAFB-7, Kirtland Air Force Base,  
Albuquerque, New Mexico**

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## Abstract

An extensive petroleum hydrocarbon plume present in the regional aquifer has resulted from several decades of releases of jet fuel and aviation gasoline from the Bulk Fuels Facility at Kirtland Air Force Base (KAFB) in Albuquerque, New Mexico. Contaminated groundwater containing dissolved 1,2-dibromoethane, a lead scavenger present in aviation gasoline, is pumped to the surface at three operating extraction wells and treated using granular activated carbon. Treated effluent is stored in tanks prior to proposed injection at supply well KAFB-7 located on KAFB. Equilibrium geochemical calculations were performed using the computer program PHREEQC to quantify potential precipitation of calcite, amorphous  $\text{SiO}_2$ , and amorphous  $\text{Fe}(\text{OH})_3$  during injection of treated effluent at well KAFB-7. Treated effluent and KAFB groundwater are in very close equilibrium with calcite, having saturation indices very near or within  $0 \pm 0.050$  (at equilibrium,  $\text{SI} = 0$  for solid phases). These two waters are very similar in their major ion chemistries, which are represented by a calcium-sodium-bicarbonate-sulfate composition. Results of the PHREEQC simulations suggest that between 0.116 and 2.727 kg calcite/day will potentially precipitate, assuming 576,000 gallons of treated effluent are injected at well KAFB-7 on a daily basis. Amorphous silica and amorphous  $\text{Fe}(\text{OH})_3$  are expected to dissolve and should not form any precipitates on the KAFB-7 well screen under modeled geochemical conditions. Extensive precipitation of pyrolusite and barite are not likely based on PHREEQC modeling results with concentrations of dissolved manganese and barium in the  $\mu\text{g}/\text{kg}$  or  $\mu\text{g}/\text{L}$  range. Inspection of the KAFB-7 well screen on a regular basis using a down-hole video camera is strongly recommended to thoroughly evaluate potential precipitation of calcite during the proposed 120-day pilot injection test.

## 1 Purpose and Scope

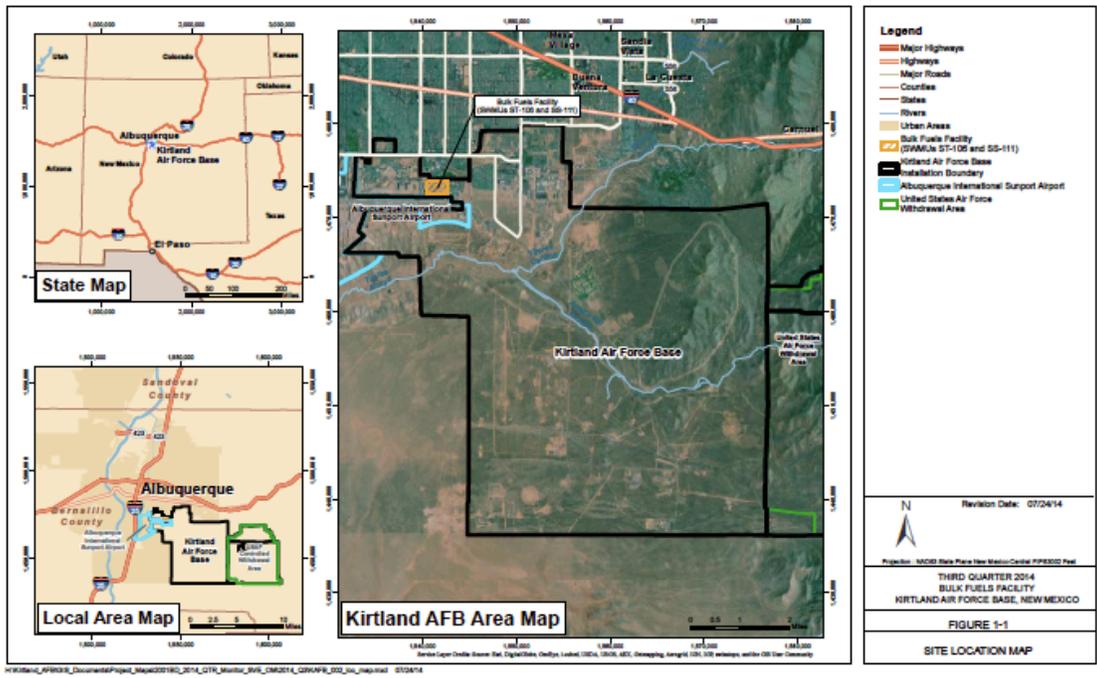
An extensive petroleum hydrocarbon contamination plume present in the regional aquifer has resulted from several decades of releases of jet fuel (JP-4 and JP-8) and aviation gasoline from the Bulk Fuels Facility (BFF) at Kirtland Air Force Base (KAFB) located in Albuquerque, New Mexico (Figure 1) (CBI 2015). Contaminated groundwater containing dissolved 1,2-dibromoethane (EDB); a lead scavenger present in aviation gasoline, is pumped to the surface at three operating extraction wells and treated using granular activated carbon (GAC). Treated effluent is stored in tanks prior to proposed injection at supply well KAFB-7 located on KAFB. Precipitation of calcite, amorphous silica, and other reactive minerals during injection and mixing of groundwater and treated effluent needs to be addressed to quantitatively evaluate potential clogging of the KAFB-7 well screen that may impact hydraulic properties to the well.

This report presents results of equilibrium geochemical modeling simulating chemical reactions occurring during injecting treated effluent water at well KAFB-7. The computer program PHREEQC (**PH** **RE**dox **EQ**uilibrium **C** programming language), version 2.18.00, (Parkhurst and Appelo 1999) is used to perform batch equilibrium simulations consisting of mixing GAC-treated effluent with KAFB-7 groundwater at various mass ratios or fractions. Equilibrium geochemical modeling provides a viable approach in evaluating aqueous speciation of treated effluent, regional aquifer groundwater at KAFB-7, and mixed compositions and also quantifying key precipitation reactions that include mass transfer of specific reactive minerals such as calcite, amorphous SiO<sub>2</sub>, and amorphous Fe(OH)<sub>3</sub> taking place during precipitation and dissolution.

## 2 Background Site Conditions and Groundwater Contamination

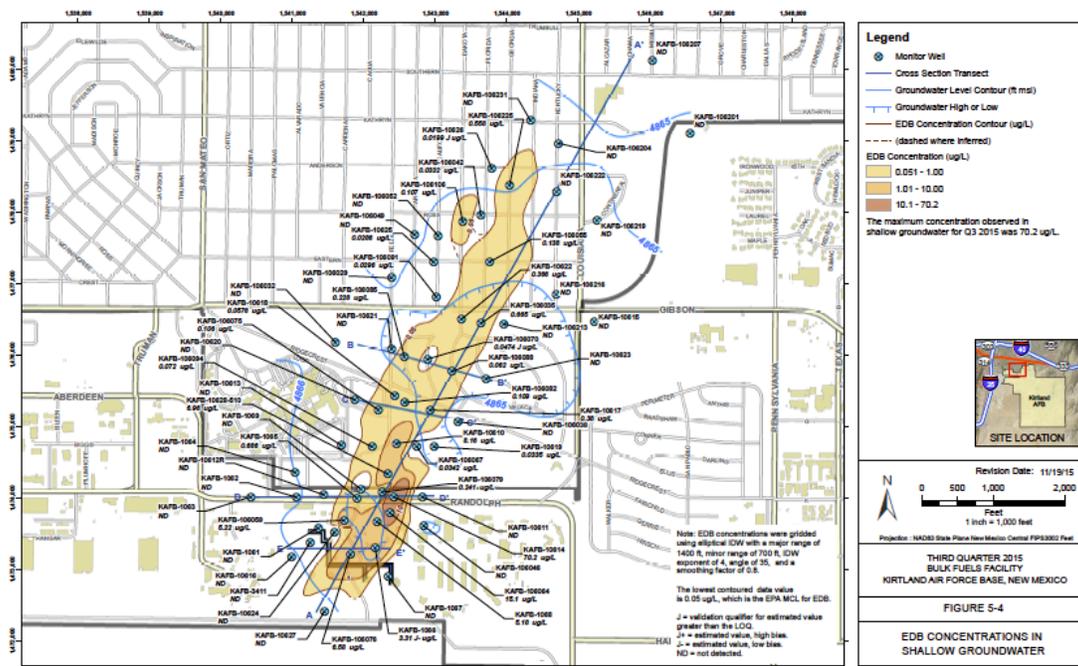
Jet fuel and aviation gasoline have migrated through the vadose zone to the regional aquifer beneath and in the vicinity of the BFF. Key contaminants of concern in the dissolved phase of the petroleum hydrocarbon plume mostly include EDB, benzene, toluene, ethylbenzene, and xylene isomers (BTEX) with some detections of naphthalene, and other aromatic and aliphatic petroleum hydrocarbons. The vadose zone is approximately 480 feet thick beneath KAFB, consisting of unconsolidated sediments derived from alluvial debris and ancestral sediments of the Rio Grande. The Sierra Ladrones Formation is approximately 3,000 feet thick and is the host sediments for the unconfined regional aquifer occurring generally east of the present-day Rio Grande in the Albuquerque area (Plummer et al. 2004). Petroleum hydrocarbons consisting of light non-aqueous phase liquid (LNAPL), vapor phase, adsorbed phase, and dissolved porewater phase are heterogeneously distributed throughout the vadose zone beneath the BFF. Over 750,000 gallons of jet fuel and aviation gasoline have been removed from the source area at the BFF since 2003. The dissolved hydrocarbons were first detected in the regional water table in 2001.

**Figure 1. Location Map of Kirtland Air Force Base (KAFB), Albuquerque, New Mexico (CB&I 2015). (Well KAFB-7 is located southeast the Bulk Fuel Facility within KAFB.)**



The LNAPL had migrated radially from the point(s) of entry at the regional water table and moved along the water table. There has been no measureable LNAPL on the regional water since 2013. The dissolved portion of the EDB plume for the third quarter of 2015 extends several thousands of feet north-northeast of the KAFB facility boundary as shown in Figure 2. 1,2-Dibromoethane is the primary contaminant of concern present in the dissolved phase, having an aqueous solubility of 4,321 mg/L (Falta 2004). This mobile chemical has migrated the greatest extent of all of the contaminants present in jet fuel and aviation gasoline, possibly along discreet preferred flow paths in the regional aquifer. Concentrations of EDB range from the nanogram per liter (ng/L) to microgram per liter ( $\mu\text{g/L}$ ) range in contaminated groundwater. The EPA and State of New Mexico drinking water standard for EDB is 50  $\mu\text{g/L}$  or parts per billion. Reduction of an unknown fraction of EDB to ethene under anaerobic conditions, within and adjacent to the past LNAPL area, is likely taking place. This is based on elevated above baseline concentrations of dissolved bromide (CB&I 2015), a dissociation product of EDB, measured in groundwater samples. Results of site-specific microcosm studies and pilot scale testing are planned for in the near future and will likely provide valuable information on *in situ* biodegradation of EDB in the regional aquifer.

Table 1 provides a list of physicochemical properties of EDB, 1,2-dichloroethane (1,2-DCA), and benzene relevant to environmental investigations conducted at KAFB and other petroleum hydrocarbon-contaminated sites. The rate of transport



**Figure 2. Concentrations of 1,2-Dibromoethane (EDB) Beneath the Regional Water Table, Kirtland Air Force Base (KAFB), Albuquerque, New Mexico (CB&I 2015).**

**Table 1. Transport Properties of 1,2-Dichloroethane (EDB), Benzene, and 1,2-Dichloroethane (1,2-DCA) (modified from Falta 2004).**

Property	EDB	Benzene	1,2-DCA
Molecular Weight (g/mol)	187.86	78.11	98.96
Aqueous Solubility (mg /L)	4,321	1,750	8,520
Vapor Pressure (kPa)	1.47	8.00	8.10
Organic Carbon Partition Coefficient, KOC (mL/g)	44.0	83.0	14.0
Henry's Constant (dimensionless)	0.029	0.220	0.050
Groundwater Retardation Coefficient, $f_{oc} = 0.001$	1.17	1.31	1.05
Gas Phase Retardation Coefficient, $f_{oc} = 0.001$	46.9	8.20	23.1

<sup>a</sup>Montgomery 1979; <sup>b</sup>Bedient et al. 1999; <sup>c</sup>Charbeneau 2000; <sup>d</sup>bulk density = 1.50 g/cm<sup>3</sup>, porosity = 0.4; and <sup>e</sup>water saturation = 0.50.

of an organic contaminant in groundwater is directly correlated with its aqueous solubility. Organic compounds with lower aqueous solubility migrate at slower rates in groundwater compared to higher soluble organic compounds. Aqueous solubilities of EDB, benzene, and 1,2-DCA are 4,321 mg/L, 1,750 mg/L, and 8,520 mg/L, respectively (Falta, 2004). 1,2-Dichloroethane is expected to migrate at a faster rate in groundwater compared to EDB and benzene, based on its higher aqueous solubility. Hydrophobic or water disliking organic compounds adsorb onto mineral surfaces and solid organic matter to a greater extent than hydrophilic (water liking) organic compounds (Wiedemeier et al. 1999). Organic carbon partition coefficients ( $K_{OC}$ ) for EDB, benzene, and 1,2-DCA are 44.0 L/kg, 83.0 L/kg, and 14.0 L/kg, respectively (Falta, 2004). Adsorption or partitioning of benzene onto solid surfaces occurs to a higher extent compared to EDB and 1,2-DCA. Falta (2004) reports dimensionless Henry's law constants for EDB, benzene, and 1,2-DCA as 0.029, 0.220 and 0.050, respectively. Benzene will volatilize to a greater extent than EDB during air sparging and soil vapor extraction, whereas EDB and 1,2-DCA having lower Henry's law constants and higher aqueous solubility partition more into groundwater and soil pore water.

Three groundwater extraction wells (KAFB-106228, KAFB-106233, KAFB-106234) are actively pumping and treating EDB-contaminated groundwater. The first extraction well, KAFB-106228 started pumping on June 30, 2015. The three extraction wells are located within the dissolved EDB portion of the groundwater plume north-northeast of BFF. EDB is removed from contaminated groundwater through adsorption and/or partitioning onto GAC, which has a high specific surface area in excess of 500 meters<sup>2</sup>/gram. Concentrations of EDB in treated effluent are typically less than analytical detection (0.01 µg/L) using EPA method 8011 (US EPA 2014). Treated water is stored in tanks prior to gravity injection at well KAFB-7. It is anticipated that the treated water will be injected up to a rate of 400 gallons per minute (576,000 gallons per day) at KAFB-7 during a 120-day pilot study anticipated to start in early 2016. Approximately 19.4 million gallons of groundwater have been extracted, treated, and stored in closed tanks. Approximately 8.590 g (8,590 mg) of EDB have been removed from groundwater treatment system as of early January 2016. Mixing of the injected water with native groundwater at well KAFB-7, however, may result in precipitation of several reactive minerals, including calcite, amorphous SiO<sub>2</sub>, and amorphous Fe(OH)<sub>3</sub>. Potential clogging of the well screen at KAFB-7 can affect hydraulic properties of this injection well resulting from precipitation of one or more of these reactive phases.

### **3 Geochemical Modeling**

A detailed understanding of diverse geochemical processes taking place before, during, and after injecting EDB-treated effluent water into groundwater at well KAFB-7 is essential for critically evaluating aqueous speciation and precipitation of reactive minerals and amorphous solids. The computer program PHREEQC is capable of performing diverse low-temperature geochemical calculations relevant to environmental investigations. Zhu and Anderson (2002) provide many

examples of PHREEQC applied to environmental investigations. The following description of PHREEQC is taken from Parkhurst and Appelo (1999).

“PHREEQC is based on an ion-association aqueous model that performs (1) aqueous speciation and mineral saturation index calculations; (2) batch-reaction and one-dimensional (1-D) transport calculations involving reversible reactions, including aqueous, mineral-solid phase (amorphous), gas, solid-solution, surface complexation of adsorbates onto HFO, ion-exchange, and irreversible reactions including specified mole transfers of reactants, kinetically-controlled reactions, mixing of solutions, and temperature changes; and (3) inverse modeling that finds sets of mineral and gas mole transfers that account for differences in compositions between waters, within specified compositional uncertainty limits.”

Geochemical calculations including solute speciation, mineral stability, mixing reactions, and mass transfer of reactive solids were evaluated using PHREEQC. The EQ3/6 thermodynamic database contained in PHREEQC was used during the simulations, having the most extensive reactions for major ions, trace elements, silica, and other inorganic solutes. Precise and accurate analytical results for filtered water samples are required as input to PHREEQC to produce meaningful and relevant simulations for evaluating geochemical processes occurring in aquifer systems. Meaningful modeling results using PHREEQC and other geochemical computer codes strongly depend on charge balance errors for chemical analyses performed on filtered samples being less than  $\pm 5$  percent.

The purpose for conducting geochemical simulations described in this report is to quantify complex multiphase (solid, aqueous, and gas) reactions occurring during mixing of KAFB-7 groundwater with treated effluent including:

- Speciation of iron(II, III), manganese(II), and sulfur(VI)
- Stability of calcite, amorphous  $\text{SiO}_2$ , and amorphous  $\text{Fe}(\text{OH})_3$ .

Adsorption/desorption processes involving trace elements are not included in the model simulations because the mass of ferrihydrite or hydrous ferric oxide (HFO) has not been measured in sediment or core samples at well KAFB-7.

### **3.1 Summary of Water Chemistry for Well KAFB-7 and Treated Effluent**

Table 2 provides a summary of analytical results for dissolved major ions and selected trace elements for well KAFB-7 (CB&I 2015), which are used as input to the PHREEQC simulations. Regional aquifer groundwater sampled from well KAFB-7 consists of a mixed ionic composition dominated by calcium, sodium, and bicarbonate (reported as total carbonate alkalinity). The solute charge balance error for chemical analyses performed on this groundwater sample is excellent, having a value of -0.94 percent. Groundwater is moderately oxidizing having a concentration of dissolved oxygen (DO) of 5.0 mg/L and a field oxidation-reduction potential (ORP) of +281 millivolts (mV). A HORIBA ORP-Ag/AgCl electrode containing a filling solution of 3.33 molar KCl was used during

sampling. A correction factor of +192 mV, corresponding to a groundwater temperature of 19.23 °C, was added to the ORP measurement to calculate an Eh value of +473 mV.

**Table 2. Groundwater Chemistry of the Regional Aquifer at Well KAFB-7 (Analytical results provided by CB&I) (Sampled on October 15, 2015).**

Analyte	Millimoles/Liter	Milligrams/Liter (except as noted)
Calcium	1.03	41.1
Magnesium	0.26	6.33
Sodium	0.93	21.3
Potassium	0.05	1.96
Chloride	0.27	9.61
Sulfate	0.28	27.1
Total Carbonate Alkalinity	2.46 as bicarbonate (150 mg/L as HCO <sub>3</sub> <sup>-</sup> )	123
Silica	0.93	26.1
Iron	8.95e-04	0.050, U
Manganese	2.31e-05	0.00127
DOC	0.06	0.69
Aluminum	3.71e-03	0.100, U
Arsenic	1.62e-05	0.00121
Barium	8.30e-04	0.114
Nitrate-Nitrite(N)	0.32	4.45
Strontium	3.0e-03	0.267
Temperature (°C)	Not applicable	19.23
pH	Not applicable	7.64
ORP (mV), Eh (mV)	Not applicable	+281, +473
DO	0.16	5.0
Charge Balance (%)	Not applicable	-0.94

Total dissolved concentration of iron is less than 0.050 mg/L (non-detect and noted as a “U” value), suggesting that reduction of dissolved iron(III) to iron(II) has not taken place in the regional aquifer at well KAFB-7. Results of speciation calculations using PHREEQC show that total dissolved iron is stable in the +III oxidation state at well KAFB-7. Concentration of nitrate plus nitrite(N) is 4.45 mg/L confirming the occurrence of a nitrate plume at well KAFB-7. Nitrate commonly dominates over nitrite in most aquifer systems under strongly oxidizing and circumneutral pH conditions (Langmuir 1997). The dissolved concentration of aluminum is less than 0.100 mg/L, which is the instrument analytical detection limit using EPA method 6010 (inductively coupled argon plasma-optical emission spectroscopy). The concentration of dissolved organic carbon (DOC) is 0.69 mg C/L, which probably is representative of baseline conditions in the regional aquifer not impacted by the jet fuel-aviation gasoline plume. Dissolved organic carbon, however, may be a component of the nitrate plume at well KAFB-7.

Table 3 provides analytical results for major ions and trace elements in treated effluent sample KAFB-106228 EFF (CB&I 2015), which is also used as input to the PHREEQC simulations. This water sample has a calcium-sodium-sulfate-bicarbonate composition. The charge balance error for the sample is -0.04 percent. KAFB-106228 EFF is oxidizing with a DO concentration of 4.29 mg/L and a field ORP value of +115 mV. A correction factor of +195 mV, corresponding to a groundwater temperature of 21.03°C, was added to the ORP measurement to calculate an Eh value of +310 mV. The GAC-treated effluent sample is not as strongly oxidizing as compared to the KAFB-7 sample, which is consistent with it having been recently collected from the GAC unit.

The total dissolved concentration of iron is 0.0131 mg/L and is qualified as a “J” value, indicating that the concentration of this solute is above the instrument detection limit but below the quantitation limit using EPA method 6010 (Table 3). Results of speciation calculations using PHREEQC show that total dissolved iron is stable in the +III oxidation state for sample KAFB-106228 EFF. The concentration of DOC is 2.60 mg C/L, which probably consists of soluble organic carbon present in contaminated groundwater and hydrophilic organic carbon compounds desorbed from the GAC. Concentration of nitrate plus nitrite(N) is 0.20 mg/L, which is much less than that measured in the KAFB-7 sample (Table 2). The dissolved concentration of aluminum is less than 0.025 mg/L, which is the instrument analytical detection limit using EPA method 6010.

## **3.2 Results of PHREEQC Simulations Under Equilibrium Conditions**

### **3.2.1 Speciation of Iron, Manganese, and Sulfur**

When determining if precipitation of reactive minerals is likely to occur, speciation of major and trace solutes, pH, and redox control precipitation/dissolution and adsorption/desorption occurring in pristine and contaminated aquifer systems. Mineral dissolution occurring within the petroleum hydrocarbon plume at KAFB produces significant changes in solute speciation during biodegradation and

subsequent oxidation of BTEX and aromatic and aliphatic compounds. Reductive dissolution of redox-sensitive solid phases, including ferrihydrite and manganese dioxide, takes place during biodegradation of jet fuel and aviation gasoline in the

**Table 3. Water Chemistry for Sample KAFB-106228 EFF (analytical results provided by CB&I 2015). (Sampled on September 8, 2015).**

Analyte	Millimoles/Liter	Milligrams/Liter (except as noted)
Calcium	0.95	38.1
Magnesium	0.22	5.36
Sodium	1.04	24.0
Potassium	0.06	2.16
Chloride	0.39	14.0
Sulfate	0.39	37.0
Total Carbonate Alkalinity	2.26 as bicarbonate (138 mg/L as HCO <sub>3</sub> <sup>-</sup> )	113
Silica	0.94	26.4
Iron	2.35e-04	0.0131, J
Manganese	29.90e-06	5.44e-04
DOC	0.22	2.6 J
Aluminum	9.27e-04	0.025, U
Arsenic	1.30e-05	9.73e-04
Barium	1.01e-03	0.139
Nitrate-Nitrite(N)	0.01	0.2
Strontium	3.07e-03	0.269
Temperature (°C)	Not applicable	21.03
pH	Not applicable	7.77
ORP (mV), Eh (mV)	Not applicable	+115, +310
DO	0.13	4.29
Charge Balance (%)	Not applicable	-0.04

subsurface. Precipitation of these two solids during injection of treated effluent at well KAFB-7 is also dependent on aqueous speciation of dissolved iron and manganese, pH, and redox under oxidizing conditions. The dominant dissolved species for iron, manganese, and sulfur at well KAFB-7 include the following aqueous complexes at pH 7.64 and Eh +473 mV (pe = 8.156) (Table 1):

Iron(III),  $\text{Fe}(\text{OH})_3^0$  (log molality = -6.075),

Manganese(II),  $\text{Mn}^{2+}$  (log molality = -7.701), and

Sulfur(VI),  $\text{SO}_4^{2-}$  (log molality = -3.596).

Sulfate is the dominant sulfur species and dissolved sulfide is not present in groundwater at well KAFB-7 and GAC-treated effluent under strongly oxidizing conditions. The calculated ionic strength of the groundwater sample collected at well KAFB-7 is 4.981e-03 moles of solutes/kg  $\text{H}_2\text{O}$  (molal). The nitrogen(V) species  $\text{NO}_3^-$  is calculated by PHREEQC to dominate under oxidizing conditions at well KAFB-7.

The parameter pe is defined as  $-\log_{10}[\text{e}^-]$ , which is related to Eh by:

$$\text{pe} = \text{Eh}(\text{volts})(n)(F)/2.303(R)(T) \quad (\text{Langmuir 1997})$$

where,

n = number of electrons,

F (Faraday constant) = 23.061kcal/volt g equivalent,

R (gas constant) = 1.987e-03 kcal/mole, and

T = temperature (Kelvin).

pe = Eh(volts)/0.05916 at 25°C (Langmuir 1997).

pe was calculated from corrected Eh measurements provided by CB&I and used as input to the PHREEQC simulations.

The dominant species for iron, manganese, and sulfur in effluent sample KAFB-106228 EFF include the following aqueous complexes at pH 7.77 and Eh +310 mV (pe = 5.307) (Table 2):

Iron(III),  $\text{Fe}(\text{OH})_3^0$  ( $\log_{10}$  molality = -6.653),

Manganese(II),  $\text{Mn}^{2+}$  ( $\log_{10}$  molality = -8.086), and

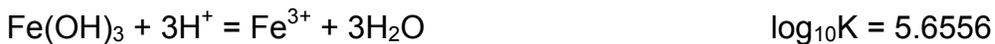
Sulfur(VI),  $\text{SO}_4^{2-}$  ( $\log_{10}$  molality = -3.457).

The calculated ionic strength of sample KAFB-106228 EFF is 4.809e-03 molal. The nitrogen(V) species  $\text{NO}_3^-$  also dominates according to PHREEQC output under oxidizing conditions characteristic of groundwater at well KAFB-7.

### 3.2.2 Stability of Solid Phases

Reversible precipitation and dissolution of reactive minerals considered to be present in both the regional aquifer at well KAFB-7 and GAC-treated effluent under equilibrium conditions are quantified by determining saturation index (SI) values for solid phases. The SI is a thermodynamic measure of the degree of saturation (equilibrium), oversaturation (precipitation), or undersaturation (dissolution) of a solid phase in water ( $SI = \log_{10}[\text{solute activity product}]/[\text{solubility product}]$ ); at equilibrium  $SI = 0 \pm 0.05$ ) (Langmuir 1997).

Dissolution reactions for calcite, amorphous  $\text{SiO}_2$ , and amorphous  $\text{Fe}(\text{OH})_3$  and their  $\log_{10}$ dissociation constants listed in the LLNL thermodynamic database contained in PHREEQC are provided below.



The dissolution product of amorphous  $\text{SiO}_2$  is dissolved silica in the form of aqueous  $\text{SiO}_2$ , but in nature, silicic acid ( $\text{Si}(\text{OH})_4^0$ ) is the stable form below pH 9.71 at 25°C (Langmuir 1997). Dissolution of  $\text{Fe}(\text{OH})_3$  is controlled as a direct function of pH and indirectly by redox according to the above reaction. Dissolved concentrations of iron(II) species and redox will also influence solubility of amorphous  $\text{Fe}(\text{OH})_3$ . The dissociation constant for this amorphous solid represents a precipitated form of amorphous  $\text{Fe}(\text{OH})_3$  that has “aged.”

Table 4 presents results of selected SI calculations performed using well KAFB-7 groundwater and GAC-treated effluent. Groundwater at well KAFB-7 is in equilibrium with  $\text{Fe}(\text{OH})_3(\text{am})$  and very closely approaching equilibrium with calcite. Calcite is a component of the Sierra Ladrões Formation containing detrital material derived from the Madera Limestone. This solid phase is a reactive mineral that typically is in equilibrium with groundwater controlling dissolved concentrations or activities of calcium and bicarbonate and pH. Groundwater sampled from well KAFB-7 is oversaturated with barite, chalcedony, and pyrolusite and under equilibrium conditions, these minerals/solid phases are expected to precipitate. The regional aquifer groundwater, however, is undersaturated with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), amorphous silica ( $\text{SiO}_2$ ), and strontianite ( $\text{SrCO}_3$ ) and these minerals are expected to be unstable and undergo dissolution to a varying degree. Dissolved concentrations of silica are most likely controlled by dissolution/precipitation of amorphous silica, even though KAFB-7 groundwater is slightly undersaturated with this solid phase. The calculated partial pressure of  $\text{CO}_2$  is  $10^{-2.50}$  bar and is typical of most aquifer systems.

Results of PHREEQC calculations show that sample KAFB-106228 EFF is in equilibrium with calcite (Table 4). This water sample is oversaturated with barite, chalcedony, and pyrolusite and is undersaturated with amorphous  $\text{Fe}(\text{OH})_3$ , gypsum, amorphous silica, and strontianite. Dissolved concentrations of silica are

most likely controlled by dissolution of amorphous silica, even though the effluent is slightly undersaturated with this solid phase. The calculated partial pressure of CO<sub>2</sub> is 10<sup>-2.66</sup> bar, which is also typical of aquifer systems. This value is higher than the partial pressure of CO<sub>2</sub> under atmospheric conditions (CO<sub>2</sub>(g) = 10<sup>-3.5</sup> bar). Treated effluent is stored in closed tanks and CO<sub>2</sub> gas dissolved in the water has not equilibrated with the atmosphere.

**Table 4. Results of Saturation Index Calculations Using PHREEQC**

Solid Phase/Gas	Well KAFB-7	Sample KAFB-106228 EFF
Barite (BaSO <sub>4</sub> )	0.16	0.36
Calcite (CaCO <sub>3</sub> )	-0.06	0.02
Chalcedony (SiO <sub>2</sub> )	1.04	0.47
CO <sub>2</sub> (g)	-2.50	-2.66
Fe(OH) <sub>3</sub> (am)	-0.01	-0.49
Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)	-2.34	-2.23
Pyrolusite (MnO <sub>2</sub> )	7.01	6.85
SiO <sub>2</sub> (am)	-0.55	-0.57
Strontianite (SrCO <sub>3</sub> )	-0.36	-0.25

Pyrolusite was not included as one of the reactive minerals because groundwater and treated effluent are not in equilibrium with this solid. While these solutions are strongly oversaturated with pyrolusite (Table 4) and this mineral is expected to precipitate from solution, the mass of pyrolusite that precipitates is small compared to calcite, based on measured concentrations of dissolved manganese of less than 2 µg/L (Tables 2 and 3). Masses of pyrolusite expected to precipitate from KAFB-7 groundwater and treated effluent under equilibrium conditions are 2.312e-08 molal (0.002 mg MnO<sub>2</sub>/kg H<sub>2</sub>O) and 9.905e-09 molal (0.0009 MnO<sub>2</sub>/kg H<sub>2</sub>O), respectively.

Groundwater and treated effluent are slightly oversaturated with barite. KAFB-7 groundwater and treated effluent have SI values for barite equal to 0.16 and 0.36, respectively (Table 4). Masses of barite expected to precipitate from KAFB-7 groundwater and treated effluent under equilibrium conditions are 2.532e-07 molal (0.0591 mg BaSO<sub>4</sub>/kg H<sub>2</sub>O) and 5.735e-07 molal (0.1339 BaSO<sub>4</sub>/kg H<sub>2</sub>O), respectively.

### 3.2.3 Results of Mixing Calculations

Geochemical modeling was performed using PHREEQC to quantify masses of calcite, amorphous  $\text{SiO}_2$ , and amorphous  $\text{Fe}(\text{OH})_3$  that may potentially precipitate during mixing of treated effluent (sample KAFB-106228 EFF) with groundwater (sample KAFB-7) at various ratios. These three reactive phases are at equilibrium or closely approach equilibrium with GAC-treated effluent and KAFB-7 groundwater according to PHREEQC simulations. Fractions of KAFB-7 groundwater mixed with effluent range from 0.9 to 0.1 corresponding to fractions of GAC-treated effluent ranging from 0.1 to 0.9. The solutions were set in equilibrium with calcite, amorphous silica, and amorphous  $\text{Fe}(\text{OH})_3$  to quantify the mass of each solid phase that potentially precipitates or dissolves during mixing. Dissolved concentrations of iron were set at values reported by the analytical laboratory, which provides an upper bound for the concentration of dissolved iron and the maximum mass of amorphous  $\text{Fe}(\text{OH})_3$  that potentially precipitates or dissolves. The pe values of treated effluent and KAFB-7 groundwater are controlled by the dissolved oxygen/water ( $\text{O}_2/\text{H}_2\text{O}$ ) redox couple to maximize the redox state of these two waters and enhance precipitation/dissolution of amorphous  $\text{Fe}(\text{OH})_3$ . It is very likely, however, that redox conditions in groundwater and treated effluent are controlled by mixed redox couples that include  $\text{O}_2(\text{aq})/\text{H}_2\text{O}$ ,  $\text{MnO}_2/\text{Mn}^{2+}$ , and  $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ , based on redox studies conducted on aquifer systems (Langmuir 1997). This condition does not affect solubility and mass transfer calculations for calcite and amorphous  $\text{SiO}_2$ , as their solubility is independent of redox under circumneutral pH conditions.

Results of solution mixing calculations using PHREEQC are provided in Table 5, consisting of precipitated or dissolved masses of calcite, amorphous  $\text{Fe}(\text{OH})_3$ , and amorphous  $\text{SiO}_2$ . Positive values of mass transfer for solids indicate precipitation and negative values indicate dissolution. Calcite is expected to precipitate in all mixed solutions of treated effluent with KAFB-7. Amorphous  $\text{Fe}(\text{OH})_3$  and amorphous  $\text{SiO}_2$  are expected to dissolve in all mixed solutions and should not form precipitates on the KAFB-7 well screen under modeled geochemical conditions.

Table 6 provides masses of calcite precipitating in units of mg solid/kg solvent ( $\text{H}_2\text{O}$ ) during mixing. At a mixing ratio of 50 percent KAFB-7 to 50 percent treated effluent, 0.649 mg calcite/kg water is expected to precipitate under equilibrium conditions. Assuming that 400 gallons per minute (576,000 gallons per day) of treated effluent are injected at well KAFB-7 with a mixing ratio of 50 percent effluent to 50 percent groundwater, approximately 1,415 grams (1.415 kg) of calcite are expected to precipitate per day. Details of this calculation are provided below.

3.785 L = 1 gallon of water; 1 kg water = 1 L water with a density =  $1.00 \text{ g/cm}^3$ ,  
(3.785 kg/gallon)(576,000 gallons) = 2,180,160 kg water.

Mass of calcite:  $(0.649 \text{ mg/kg})(2,180,160 \text{ kg water}) = 1,414,924 \text{ mg calcite}$ ,  $(1,414,924 \text{ mg})(0.001 \text{ g/mg}) = 1,415 \text{ g calcite/day}$  or  $1.415 \text{ kg calcite/day}$ . Assuming that the pilot study operates for four months (120 days), and using the stated mixing ratio of 50 percent treated effluent to 50 percent KAFB-7 groundwater from above, approximately 170 kg of calcite are anticipated to precipitate from groundwater.

**Table 5. Results of PHREEQC Simulations Quantifying Stability of Selected Minerals and Amorphous Solids During Mixing of KAFB-7 Groundwater and GAC-Treated Effluent.**

Mixing Ratio (KAFB-7/Treated Effluent)	pH	pe	Calcite (mMolal)	Fe(OH)3(am) (mMolal)	SiO2(am) (mMolal)
1 (100% KAFB-7, 0% effluent)	7.66	13.305	-0.06646	-1.90e-05	-1.100
0.9	7.72	13.229	0.01250	-5.894e-05	-1.109
0.8	7.72	13.212	0.01099	-1.060e-04	-1.118
0.7	7.72	13.194	0.009846	-1.535e-04	-1.126
0.6	7.73	13.177	0.007986	-2.013e-04	-1.134
0.5	7.73	13.159	0.006489	-2.497e-04	-1.142
0.4	7.73	13.141	0.004996	-2.984e-04	-1.151
0.3	7.74	13.123	0.003505	-3.475e-04	-1.159
0.2	7.74	13.106	0.002018	-3.969e-04	-1.167
0.1	7.74	13.088	0.0005339	-4.468e-04	-1.176
0 (0% KAFB-7, 100% effluent)	7.76	13.052	0.02096	-4.938e-04	-1.186

Note: Positive and negative values indicate precipitation and dissolution, respectively.

The mass of calcite anticipated to precipitate from solution at a mixing ratio of well KAFB-7 groundwater to treated effluent equal to 0.9 to 0.1 is provided below.

Mass of calcite:  $(1.251 \text{ mg/kg})(2,180,160 \text{ kg water}) = 2,727,380 \text{ mg calcite}$ ,  $(2,727,380 \text{ mg})(0.001 \text{ g/mg}) = 2,727 \text{ g calcite/day}$  or  $2.727 \text{ kg calcite/day}$ . Assuming that the pilot study operates for four months (120 days), approximately 327 kg of calcite are anticipated to precipitate from groundwater at a mixing ratio of well KAFB-7 groundwater to treated effluent equal to 0.9 to 0.1.

The mass of calcite anticipated to precipitate from solution at a mixing ratio of well KAFB-7 groundwater to treated effluent equal to 0.1 to 0.9 is provided below.

Mass of calcite:  $(0.053 \text{ mg/kg})(2,180,160 \text{ kg water}) = 115,548 \text{ mg calcite}$ ,  $(115,548 \text{ mg})(0.001 \text{ g/mg}) = 116 \text{ g calcite/day}$  or  $0.116 \text{ kg calcite/day}$ . Assuming that the pilot study operates for four months (120 days), approximately 14 kg of

calcite are anticipated to precipitate from groundwater at a mixing ratio of well KAFB-7 groundwater to treated effluent equal to 0.1 to 0.9.

**Table 6. Results of PHREEQC Simulations Quantifying Mass Transfer of Selected Minerals and Amorphous Solids During Mixing of KAFB-7 Groundwater and GAC-Treated Effluent.**

Mixing-Ratio (KAFB-7/ Treated Effluent)	pH	pe	Calcite (mMolal)	Calcite (mg/kg)
1 (100% KAFB-7, 0% effluent)	7.66	13.305	-0.06646	6.652 (dissolved)
0.9	7.72	13.229	0.01250	1.251
0.8	7.72	13.212	0.01099	1.10
0.7	7.72	13.194	0.009846	0.985
0.6	7.73	13.177	0.007986	0.799
0.5	7.73	13.159	0.006489	0.649
0.4	7.73	13.141	0.004996	0.50
0.3	7.74	13.123	0.003505	0.351
0.2	7.74	13.106	0.002018	0.202
0.1	7.74	13.088	0.0005339	0.053
0 (0% KAFB-7, 100% effluent)	7.76	13.052	0.02096	2.098

Note: Positive and negative values indicate precipitation and dissolution, respectively.

#### 4 Summary and Conclusions

Equilibrium geochemical calculations were performed using the computer program PHREEQC to quantify potential precipitation of calcite, amorphous SiO<sub>2</sub>, and amorphous Fe(OH)<sub>3</sub> during injection of GAC-treated effluent at well KAFB-7. Calcite is the most important reactive phase that very closely approaches equilibrium with groundwater and is a constituent of the Madera Limestone, which is a component of the Sierra Ladrones Formation. Kinetic processes do not need to be considered for the PHREEQC simulations involving these three reactive solids. Treated effluent and KAFB groundwater are in close equilibrium with respect to calcite, having SI values near or within  $0 \pm 0.050$ . The two waters are very similar in their major ion chemistries, which are represented by a calcium-sodium-bicarbonate composition with pH values of 7.64 and 7.77 for well KAFB-7 groundwater and treated effluent, respectively.

Results of the PHREEQC simulations suggest that between 0.116 and 2.727 kg calcite/day will potentially precipitate, assuming 576,000 gallons of treated effluent are injected on a daily basis. The lower value represents a mixing ratio of KAFB-7 groundwater to treated effluent equal to 0.1 to 0.9, and the upper value

represents a mixing ratio of KAFB-7 groundwater to treated effluent equal to 0.9 to 0.1. At equal masses of mixing, 1.415 kg calcite/day is expected to precipitate. Amorphous silica and amorphous  $\text{Fe}(\text{OH})_3$  are expected to dissolve and should not form precipitates on the KAFB-7 well screen under modeled geochemical conditions. Excessive amounts of precipitation of pyrolusite and barite are not likely based on PHREEQC modeling results and low concentrations of dissolved manganese and barium ( $\mu\text{g}/\text{kg}$  or  $\mu\text{g}/\text{L}$  range) measured in the water samples. Visual inspection of the KAFB well screen on a regular basis is strongly recommended to evaluate precipitation of calcite during the 120-day pilot injection test anticipated starting in early 2016.

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