DBS&A
Daniel B. Stephens & Associates, Inc.

Memorandum

To: Travis Hurst, CRC **Date:** November 2, 2022

From: Chris Wolf, P.G. and Beth Salvas, P.G.

Subject: CTV III Geochemical Modeling

1. Introduction

For a proposed carbon sequestration project CTV III, CRC has requested that Daniel B. Stephens & Associates, Inc. (DBS&A) perform geochemical modeling to help understand chemical reactions during carbon dioxide (CO_2) storage. Information used to perform the modeling described in this memorandum was provided by CRC.

Geochemical modeling was conducted to evaluate the compatibility of the injectate with groundwater and rocks comprising the Injection Zone and Confining Zone. The intent of the modeling is to identify the major potential reactions that may affect injection or containment (U.S. EPA, 2013).

Geochemical modeling using the PHREEQC (pH-REdox-Equilibrium) software was used to calculate the behavior of minerals and changes in aqueous chemistry and mineralogy based on chemical equilibrium conditions (Parkhurst and Appelo, 2013).

This technical memorandum describes the site conditions and modeling results for CTV III site (Tables 1 through 7).

Based on the geochemical equilibrium modeling, the injection of carbon dioxide at the CTV III site does not cause significant reactions that will affect the injection or containment of the gas.

2. Geochemistry for CTV III Storage Project

While rocks are buried in the earth's crust, chemical reactions between the rocks and groundwater are termed diagenesis, which involves the dissolution of minerals into groundwater and precipitation of minerals from solution. Reactions are driven by fluid movement, temperature, and pressure changes due to burial depth and compaction. Over time, minerals and cements may dissolve and form new minerals. Important reactions that typically occur in clastic sedimentary rocks include the following:

- Precipitation and dissolution of cements and authigenic minerals consisting of various minerals including quartz, clays, potassium feldspar (K-feldspar), plagioclase feldspar, siderite, gypsum, and pyrite
- Dissolution of feldspars, quartz, lithic fragments
- Formation of feldspar and quartz overgrowths
- Precipitation of illite, kaolinite and other clays

2.1 Injection Zone Fluid Geochemistry

Data from water samples collected in the Injection Zone in CTV III (Table 1) were used for the geochemical modeling because they included a complete suite of major ions and pH. With a total dissolved solids (TDS) concentration of 13,899 parts per million (ppm), the groundwater is considered brackish.

The net charge of a water sample may be calculated using the results for the cation and anion data. Because water has a net neutral charge, the sum of the cation and anion charges should be zero. Variations due to sampling and analyses often cause the calculated value to vary and a value within 5 percent of neutral is considered a “good” balance. The charge balance for the sample was calculated in PHREEQC at 5.3 percent. The charge balance was subsequently corrected in the models by allowing PHREEQC to alter the sulfate (SO_4) concentration to maintain the charge balance.

2.2 Injection Zone and Upper Confining Zone Mineralogy

Mineralogy was evaluated using x-ray diffraction (XRD) to determine the bulk and clay mineralogy of core samples.

At CTV III, mineralogy of the Injection Zone is dominated by quartz and feldspars, with variable clay mineral content ranging from about 15 to 30 percent (Table 2). The Upper Confining Zone is dominated by 25 to 35 percent clay minerals, with approximately equal amounts of quartz and feldspar (about 30 percent each).

2.3 Injectate Chemistry

For the geochemical modeling, two scenarios of different chemical compositions for the carbon dioxide injectate were developed (Table 3). The chemistry for Scenario 1 and Scenario 2 was modeled at CTV III.

3. Equilibrium Geochemical Modeling

When modeling groundwater geochemistry, the water chemistry, gas chemistry, and mineralogy are used to constrain the model because mineral solubility controls the concentrations of a mineral's elemental components in groundwater (Appelo and Postma, 2005). Mineral dissolution-precipitation reactions directly impact the aqueous chemistry. In general, as minerals dissolve the elemental concentrations in groundwater increase, and when minerals precipitate the elemental concentrations in groundwater decrease. Chemical equilibrium indicates that congruent reactions will appear balanced between reactants and products, with no apparent change in the chemical system.

The PHREEQC model was used to evaluate potential changes to mineralogy and aqueous composition in the subsurface due to CO_2 injection. The mineral, gas, and aqueous phases were assumed to be in chemical equilibrium.

Based on the available injectate gas compositions, the ideal gas law and Raoult's Law were used to calculate the gas composition in moles. The pressure of 207.5 atmospheres (atm) at CTV III was used to calculate the partial pressures of the injectate components.

A reservoir temperature of 66°C was used for CTV III.

3.1 Geochemical Database

For reactions involving water and minerals, the equilibrium relationship between products and reactant activities (concentrations) can be calculated using known values for parameters like Gibb's energy found in thermodynamic databases (Zhu and Anderson, 2002). Thermodynamic values for these calculations are compiled in databases from several entities, including the U.S. Geological Survey (USGS) and Lawrence Livermore National Laboratory. A database developed at the Lawrence Livermore National Laboratory (LLNL.dat) was used for this evaluation. The LLNL.dat database includes a temperature range for the thermodynamic data provided from 0 to 300°C. This database is appropriate for the groundwater concentrations, pressure, and temperature used in the modeled scenarios.

When modeling saline waters, the Pitzer database (Parkhurst and Appelo, 2013) is often used, but it has thermodynamic data for a limited number of minerals including calcite, dolomite, gypsum, and quartz. The Injection Zone and Upper Confining Zone are predominantly composed of minerals that are not included in the Pitzer database, so the LLNL.dat database was used because it also includes smectite, illite, pyrite, and the minerals listed in Table 2.

For the injection gases, methane is included in the database as a gas and aqueous phase, but ethane is not included as a gas phase. The ethane gas portion of the injection chemistry was not modeled. The mass fractions were normalized excluding the ethane.

3.2 Saturation Indices

Saturation indices (SIs) were calculated that represent whether a particular mineral (e.g., calcite or gypsum) is in chemical equilibrium with the groundwater. SI calculations are used to predict if a mineral is likely to precipitate or dissolve in the groundwater, and if these reactions change the concentrations of dissolved elements.

Chemical equilibrium was assumed for the reactions in the model. Equilibrium modeling sets the saturation indices to a zero (0) value for a given mineral. Minerals used in the modeling scenarios are based on those detected using XRD and their relative abundances. The assumption of chemical equilibrium allows dissolution and precipitation reactions to be quantified in the model.

The formula for calculating saturation indices (SI) is as follows:

$$SI = \frac{IAP}{K_{sp}} \quad (1)$$

where *SI* = saturation index
IAP = ion activity product
K_{sp} = solubility product

Using gypsum as an example (Clark, 2015), the ion activity product of gypsum (IAP_{gypsum}) is the product of the activity (a, activity is approximately equal to concentration in dilute solutions) of calcium (Ca) and sulfate (SO_4):

$$IAP = a_{Ca^{2+}} \times a_{{SO_4}^{2-}} \quad (2)$$

The solubility product, K_{sp}, is an indication of the relative solubility of a mineral in water. A value less than zero (<0) indicates that the mineral will dissolve and contribute ions to solution and may result in a relatively high activity or concentration. A value greater than zero (>0) indicates that the mineral has a low solubility, may precipitate from solution, and will not contribute many ions to the solution. For the mineral gypsum, the K_{sp} based on the dissociation reaction of gypsum in water is calculated as follows:

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$K_{sp} = \frac{a_{Ca^{2+}} + a_{SO_4{}^{2-}} + a_{H_2O}}{a_{gypsum}} = 10^{-4.60} \quad (3)$$

Interpreting the results of the SI calculation is straightforward:

- SI > 0 indicates that mineral is supersaturated in solution and may precipitate onto aquifer matrix or pore space.
- SI = 0 indicates that mineral is at chemical equilibrium with the water.
- SI < 0 indicates that mineral is undersaturated in solution and may dissolve from aquifer matrix.

Due to potential systematic errors introduced during sampling and analysis, results within the range of ±0.5 of zero are typically considered in or near chemical equilibrium.

4. Geochemical Model Input

To construct the equilibrium models in PHREEQC, site specific data was used as input including water chemistry, mineralogy, temperature, and pressure.

Data include the water chemistry for the Injection Zone at both sites (Table 1) that were entered as received in ppm for elemental concentrations and standard units for pH.

In order to model the geochemistry of the clay minerals identified by XRD, an aluminum concentration was calculated in PHREEQC by equilibrating the provided water chemistry with the aluminosilicate clay mineral, smectite. The modeled aqueous concentration was used in subsequent modeling at 0.073 ppm for CTV III. These concentrations are reasonable for a sandstone aquifer at the neutral pH values.

For input into PHREEQC, the mineralogy in Table 2 were converted to moles per liter (mol/L) using porosity and bulk density values as follows:

- Injection Zone at CTV III, rock density of 2.65 kilograms per liter (kg/L) and porosity of 27 percent
- Upper Confining Zone at CTV III, rock density of 2.23 kg/L and porosity of 29 percent

The converted values for mineralogy that were input into PHREEQC are in shown Table 4.

Average temperature provided for the Injection Zone is 66 C at CTV III with an average pore volume pressure of 207.5 atm. The amount of carbon dioxide in 1 liter of gas at 207.5 atm and 66°C based on ideal gas law (PV = nRT) is 7.5 moles.

5. Geochemical Modeling Results and Discussion

Model results showing the changes in mineralogy designated as equilibrium phases in PHREEQC are presented for CTV III in Table 5 for the Injection Zone and in Table 6 for the Upper Confining Zone. Model results are presented in Table 7 for CTV III for the water chemistry based on the equilibrium phases. The modeling steps were as follows:

- Injection Zone: Use the Injection Zone groundwater sample and equilibrate with each selected mineralogy data set for the Injection Zone and carbon dioxide at given reservoir pressures.
- Upper Confining Zone: Use the model results for Injection Zone and equilibrate with the Upper Confining Zone mineralogy data set and carbon dioxide at final reservoir pressure.

Equilibrium geochemical modeling of the injection of carbon dioxide indicate that changes in mineralogy and aqueous chemistry are likely to occur, but overall, both geologic units are composed dominantly of silicate minerals such as quartz and feldspar that are not expected to be highly reactive during carbon dioxide sequestration. More reactive minerals like calcite and dolomite are present in relatively smaller amounts compared to the silicate minerals.

Although the model indicates that minerals will dissolve and precipitate, the net change in mass is minimal. Based on the molar mass, there is a small increase of less than 2 percent in the Injection Zone and a small increase of less than 1.5 percent in the Upper Confining Unit. These changes indicate mineral precipitation is occurring during injection. The amount of porosity in the Injection Zone and Upper Confining Zone is not expected to be significantly impacted by mineral dissolution and precipitation reactions during carbon dioxide sequestration.

The TDS concentration is predicted to increase due as dissolved aqueous species increase from the injection gases dissolving into the groundwater.

Based on the modeling, the following reactions are expected to occur:

- Dissolution of feldspars and calcite and the precipitation of quartz and siderite.
- Smectite and/or kaolinite dissolution resulting in the precipitation of illite.
- Chlorite (chamosite) when initially present is not stable, and dissolves releasing iron, aluminum and silica to solution.
- Anorthite when initially present is not stable, and dissolves releasing sodium, calcium, aluminum and silica to solution, likely contributing to calcite and clay mineral formation.
- Albite tends to be a stable feldspar mineral.
- Pyrite tends to dissolve releasing iron and sulfate to solution.

For both geologic units, the formation of carbonates like calcite, dolomite, or siderite was predicted to occur in several model scenarios. The formation of carbonate minerals can be an important mechanism to remove and immobilize carbon dioxide from solution through incorporation in the mineral phase.

The CO_2 gas in the injectate will form carbonate minerals, dissolve into solution, or remain in a gas phase.

Based on the equilibrium modeling, the aqueous chemistry results are provided in Table 7. Results indicate the following:

- Carbon dioxide will dissolve into solution and is included in the total inorganic carbon (TIC), which also includes bicarbonate and carbonate species. Results indicate that when carbon dioxide is dissolved in solution, the following dissolved species will occur as the following ions and complexes: carbon dioxide, bicarbonate, sodium bicarbonate, calcium bicarbonate, and magnesium bicarbonate.
- The pH values were around 6.5 in CTV III.
- The pe varied between oxidizing and reducing conditions for the various model runs.
- The calcium in solution includes the following ions and complexes: calcium, calcium bicarbonate, and calcium sulfate complex.

Based on the geochemical equilibrium modeling, the injection of carbon dioxide at the CTV III site does not cause significant reactions that will affect the injection or containment of the gas.

References

Appelo, C.A.J. and D. Postma. 2005. *Geochemistry, groundwater and pollutio*n. Second edition. Balkema, Rotterdam.

Clark, I. 2015. *Groundwater geochemistry and isotopes.* First edition. CRC Press. https://doi.org/10.1201/b18347.

Parkhurst, D.L. and C.A.J. Appelo. 2013. *Description of input and examples for PHREEQC version 3: A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations (No. 6-A43)*. U.S. Geological Survey.

U.S. Environmental Protection Agency (U.S. EPA). 2013. *Geologic sequestration of carbon dioxide underground injection control (UIC) program Class VI well site characterization guidance*. EPA 816-R-13-004. Available at <https://www.epa.gov/uic/final-class-vi-guidance-documents>.

Zhu, C., G. Anderson, and D.S. Burden. 2002. *Environmental applications of geochemical modelin*g. Cambridge University Press.

Tables

Table 1. Baseline Geochemistry, CTV III Reservoir Formation

Analyte	Concentration (ppm[a]) at Injection Zone Brine Well
Bicarbonate	1,448.5
Calcium	61.5
Chloride	6,867.2
Magnesium	8.9
Potassium	75
pH (s.u.)	8.32
Silica	12.8
Sodium	5,053.6
Sulfate	294.9
Total dissolved solids	13,889.4

[a] Unless otherwise noted
ppm = Parts per million
s.u. = Standard units

Table 2. Mineralogy for Upper Confining Zone, Injection Zone, and Lower Confining Zone

Well	Zone	Depth (feet)	Mineralogical Content (%)														
			Quartz	Plagioclase	Andesine	Albite	K-Feldspar	Oligoclase	Calcite	Dolomite	Glauconite	Pyrite	Kaolinite	Chlorite	Illite and Mica	Smectite	Total Clay
Well 1	Upper Confining Zone	4,442.5	26.0	0.0	11.0	14.0	17.0	0.0	1.0	0.0	0.0	0.0	5.0	3.0	0.0	0.0	31.0
		4,454.5	30.0	0.0	6.0	8.0	15.0	15.0	0.0	0.0	0.0	0.0	2.0	6.0	0.0	0.0	26.0
Well 2		4,476.5	30.0	0.0	6.0	13.0	18.0	4.0	0.0	0.0	0.0	0.0	5.0	9.0	0.0	0.0	29.0
		4,480.5	26.0	0.0	10.0	13.0	20.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0	0.0	0.0	31.0
		4,498.5	34.0	0.0	13.0	13.0	19.0	0.0	0.0	0.0	0.0	0.0	1.0	2.0	0.0	0.0	21.0
		4,500.5	28.0	0.0	0.0	0.0	19.0	19.0	0.0	0.0	0.0	0.0	0.0	12.0	0.0	0.0	34.0
Well 3		4,425.5	35.0	25.0	0.0	0.0	15.0	0.0	0.0	0.0	0.0	0.0	5.0	5.0	5.0	10.0	25.0
Well 4		4,622.0	42.2	18.7	0.0	0.0	10.7	0.0	0.0	0.0	0.0	0.6	9.4	3.4	4.5	0.0	27.8
Well 5		4,905.0	34.9	20.7	0.0	0.0	10.2	0.0	0.7	0.0	0.0	1.1	15.2	5.8	5.8	0.0	32.3
	Injection Zone	7,098.0	41.1	17.6	0.0	0.0	9.7	0.0	0.0	0.0	0.0	0.5	25.3	3.4	1.3	0.0	31.2
Well 6		6,987.0	35.0	0.0	8.0	10.0	17.0	0.0	0.0	0.0	3.0	0.0	10.0	4.0	0.0	0.0	27.0
		6,991.0	39.0	0.0	7.0	11.0	19.0	7.0	0.0	0.0	1.0	0.0	3.0	2.0	0.0	0.0	16.0
		7,000.0	28.0	0.0	13.0	13.0	17.0	0.0	0.0	0.0	2.0	0.0	10.0	4.0	0.0	0.0	27.0
		7,006.0	28.0	0.0	8.0	8.0	15.0	14.0	0.0	0.0	2.0	0.0	8.0	6.0	0.0	0.0	25.0
	Lower Confining Zone	8,828.0	23.0	—	9.0	12.0	9.0	0.0	3.0	0.0	0.0	1.0	12.0	5.0	—	—	43.0
		8,830.0	30.0	17.0	—	—	11.0	—	0.0	0.0	—	4.0	3.4	14.4	6.1	14.1	38.0
		8,909.0	20.0	—	10.0	10.0	13.0	0.0	0.0	0.0	2.0	2.0	5.0	3.0	—	—	43.0
		8,937.0	20.0	—	5.0	7.0	8.0	0.0	0.0	0.0	0.0	2.0	14.0	6.0	—	—	58.0
		8,939.0	24.0	18.0	—	—	11.0	—	1.0	0.0	—	3.0	3.0	15.5	7.7	16.8	43.0
		8,940.0	23.0	—	15.0	14.0	12.0	0.0	0.0	0.0	0.0	0.0	4.0	5.0	—	—	36.0
		8,942.0	23.0	—	6.0	9.0	10.0	0.0	0.0	0.0	0.0	2.0	12.0	5.0	—	—	50.0
		9,439.0	20.0	—	7.0	7.0	9.0	0.0	0.0	0.0	0.0	1.0	0.0	5.0	—	—	56.0
		9,441.0	21.0	—	9.0	10.0	12.0	0.0	2.0	0.0	0.0	3.0	0.0	0.0	—	—	43.0

— = Not detected

Table 3. Estimated Compositions for Carbon Dioxide Injectate

Gas	Mass Fraction
Injectate Scenario 1	
Carbon dioxide	0.99352
Nitrogen	0.00644
Hydrogen Sulfide	0.00001
Sulfur Dioxide	0.00003
Total	1.00
Injectate Scenario 2	
Carbon dioxide	0.9995
Methane	0.0004
Hydrogen Sulfide	0.0001
Total	1.00

Table 4. Mineralogy Input for PHREEQC Selected for Upper Confining Zone and Injection Zone

PHREEQC Mineral	Chemical Formula	Molar Mass (g/mol)	Input			
			Upper Confining Zone		Injection Zone	
			%	mol/L	%	mol/L
Quartz	SiO_2	60.08	35	31.81	35	41.74
Albite (for plagioclase)	$NaAlSi_3O_8$	263.02	25	5.19	0	4.90
K-Feldspar	$KAlSi_3O_8$	278.33	15	2.94	17	4.38
Celadonite (for glauconite)	$K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2$	429	0	0.00	3	0.50
Kaolinite	$Al_2Si_2O_5(OH)_4$	258.16	5	1.06	10	2.78
Chamosite-7A	$Fe_2Al_2SiO_5(OH)_4$	664.18	5	0.41	4	0.43
Illite	$K_{0.6}Mg_{0.25}Al_{1.8}Al_{0.5}Si_{3.5}O_{10}(OH)_2$	389.34	5	0.70	0	1.20
Smectite-low-Fe-Mg	$Ca_{.02}Na_{.15}K_{.2}Fe^{++}{}_{.29}Fe^{+++}{}_{.16}Mg_{.9}Al_{1.25}Si_{3.75}H_2O$	549.07	10	0.99	0	0.85

Upper Confining Zone = 4,425 feet
Injection Zone = 6,987 feet
g/mol = Grams per mole
mol/L = Moles per liter

Table 5. Mineralogical Changes Based on Equilibrium Geochemical Modeling with Scenario 1 Injectate Chemistry

	Mineralogical Content (mol/L)					
Mineral	Initial	Final	Delta	Initial	Final	Delta
Pressure (atm)	*207.5*			*207.5*		
Sample	*Injection Zone at 6,987 feet*			*Confining Zone at 4,425 feet*		
Albite	4.90	3.35	–1.56	5.19	5.21	0.02
Anhydrite	0	0	0	0	0	0
CO_2(g)	7.38	5.38	–2.00	7.38	7.41	0.03
Calcite	0	0	0	0	0	0
Chamosite-7A	0.50	0.79	0.29	0	0.18	0.18
Dolomite	0.43	0.40	–0.03	0.411	0.413	0.002
H2S(g)	0	0.002	0.002	0	0.0001	0.0001
Illite	0.00008	0	–0.00008	0.00008	0	–0.00008
K-Feldspar	1.20	0	–1.20	0.70	0	–0.70
Kaolinite	2.94	3.369	0.43	2.94	3.18	0.24
N_2(g)	2.78	4.603	1.83	1.06	1.64	0.59
Pyrite	0.0750	0.0749	–0.0001	0.075	0.075	1.517×10^{-6}
Quartz	0	0	0	0	0	0
SO_2(g)	41.74	44.55	2.811	31.8	31.6	–0.21
Siderite	0.0002	0	–0.0002	0.0002	0	0.00
Smectite-low-Fe-Mg	0.85	0.84	–0.01	0.99	0.99	–0.01

Negative (–) delta value indicates that mineral or gas dissolves into solution, while positive (+) delta value indicates that mineral precipitates from solution.
mol/L = Moles per liter
atm = Atmospheres

Table 6. Mineralogical Changes Based on Equilibrium Geochemical Modeling with Scenario 2 Injectate Chemistry

	Mineralogical Content (mol/L)					
Mineral	Initial	Final	Delta	Initial	Final	Delta
Pressure (atm)	*207.5*			*207.5*		
Sample	*Injection Zone at 6,987 feet*			*Confining Zone at 4,425 feet*		
Albite	4.9	3.42	–1.48	5.19	5.29	0.10
CH_4(g)	0.008	0	–0.008	0.008	0	–0.008
CO_2(g)	7.45	5.45	–2.00	7.45	7.48	0.03
Calcite	0	0	0	0	0	0
Celadonite	0.50	1.18	0.68	0	0.572	0.572
Chamosite-7A	0.43	0.50	0.07	0.41	0.51	0.10
Dolomite	0	0.011	0.011	0	0.009	0.009
H_2S(g)	0.001	0	–0.001	0.001	0	–0.001
Illite	1.20	0	–1.20	0.70	0	–0.70
K-Feldspar	2.94	3.07	0.13	2.94	2.88	–0.06
Kaolinite	2.78	4.70	1.92	1.06	1.74	0.68
Pyrite	0	0	0	0	0	0
Quartz	41.74	45.04	3.30	31.81	32.09	0.28
Smectite-low-Fe-Mg	0.85	0.40	–0.45	0.99	0.54	–0.45

Negative (–) delta value indicates that mineral or gas dissolves into solution, while positive (+) delta value indicates that mineral precipitates from solution.
mol/L = Moles per liter
atm = Atmospheres

Table 7. Modeled Equilibrium Aqueous Concentrations with Scenario 1 and Scenario 2 Injectates

Constituent	Concentration (mg/L [a])			
Injection Chemistry	*Scenario 1*		*Scenario 2*	
Geologic Zone	*Injection Zone at 6,987 feet*	*Confining Zone at 4,425 feet*	*Injection Zone at 6,987 feet*	*Confining Zone at 4,425 feet*
Pressure (atm)	*207.5*	*207.5*	*207.5*	*207.5*
Al^{3+}	0.002	0.002	0.002	0.002
TIC	123,749	122,162	122,955	120,515
Ca^{2+}	0	0	0	0
Cl^{-}	6,962	6,962	6,962	6,962
Fe^{2+}	3,458	3,419	3,440	3,382
K^{+}	198	196	197	194
Mg^{2+}	391	387	390	384
N_2	6.9	6.8	—	—
Na^{+}	40,876	40,416	40,669	39,980
SO_4^{2-}	111	133	179.92	276
SiO_2	36	35	35	35
TDS (sum)	175,788	173,717	174,829	171,728
pH (s.u.)	6.55	6.54	6.55	6.55
pe (unitless)	0.012	0.013	0.013	0.013

[a] Unless otherwise noted
mg/L = Milligrams per liter
atm = Atmospheres
TDS = Total dissolved solids
s.u. = Standard units