

INVESTIGATIONS OF SUBSURFACE MINERAL PRECIPITATION
REACTIONS ASSOCIATED WITH
BRINE INJECTION

by
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Hydrology).

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ABSTRACT

Brines are injected into the subsurface every day for a variety of reasons including enhanced oil recovery, hydraulic fracturing, carbon sequestration, and wastewater disposal. Mixing of these injected brines with brines in injection formations in the subsurface can drive mineral precipitation, which can alter the porosity and permeability of the injection formation, and thus the ability to continue to inject fluid into or pump fluid out of the formation. The potential of mineral precipitation to damage a formation, makes the understanding of brine interaction in the subsurface incredibly important for energy development in the United States.

For oil and gas production brine injection occurs for two reasons: hydraulic fracturing and the disposal of water produced alongside hydrocarbons (produced water). Hydraulic fracturing requires 2-11 million gallons of water per well, and more 55% of wells in the United States are in drought affect areas. Continued development of wells increases the demand for water resources, and alternative sources of non-potable water for hydraulic fracturing would reduce demand on fresh water resources. For each barrel of oil produced it's estimated that 7 barrels of water are produced. In the United States 14-21 billion barrels of water are produced every year. 92% of this produced water is injected into the subsurface, with 71% for enhanced oil recovery and 21% for disposal in injection wells. Treatment of produced water to reduce precipitation has the potential to increase the lifetime of disposal wells.

Oil and gas activity in Texas creates 35% of the produced water in the United States and Texas has 12,000 wastewater disposal wells. The Permian Basin in Texas is one of the most productive oil basins in the United States, and is located in a high water stress region due to prolonged drought and water demands from diverse sources. This dissertation uses data from the Permian Basin to evaluate the potential for mineral precipitation in subsurface formations driven

by injection and mixing of brines of differing compositions in numerical simulations derived from general conceptual models of hydraulic fracturing and produced water disposal.

In the first manuscript in this dissertation batch and reactive transport models are used to investigate brines as an alternative water source for hydraulic fracturing from a mineral precipitation perspective. Injection rate, represented by injection volume and injection time vary widely by well and operator; geologic formations vary widely in porosity and permeability, and the effects of these variations on mineral precipitation in disposal wells are unknown. In the second manuscript, reactive transport simulations investigate the effects of porosity, permeability, injection time, and injection volume on mineral precipitation volumes caused by brine mixing in the subsurface. Produced water management is one of the biggest challenges associated with oil and gas development, and 21% of produced water in the United States is managed using disposal wells. This costs between \$0.05-\$2.65 per barrel, and can add significantly to the cost of production. Increasing the lifetime of these wells through the understanding of how to reduce mineral precipitation could lower costs. In the third manuscript in this dissertation, reactive transport simulations investigate how reduction in ion concentrations could increase the lifetime of disposal wells. Results from this dissertation provide insight into the effects of brine mixing in the subsurface and how variations can effect mineral precipitation.

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CHAPTER 1

INTRODUCTION

Brines are injected into the subsurface every day for a variety of reasons including enhanced oil recovery, carbon sequestration, hydraulic fracturing, and wastewater disposal. In many cases brine injection is related to energy production. In enhanced oil recovery (EOR), brine is injected into a geologic formation to increase oil production. Water alternating gas is the most common EOR recovery method in the United States (Manrique et al., 2007), where brine and CO₂ are injected in rotation. Oil recovery success from EOR is correlated with brine salinity (Zhang et al., 2007), with sea water having the potential to reduce formation permeability by up to 20% through mineral precipitation (Mahmoud & Gadallah, 2013) reducing recovery potential. Similarly, brines are injected into the subsurface during geologic carbon sequestration when the water alternating gas method of injecting supercritical CO₂ into the subsurface is used. If the brine has a high sulfate content mineral precipitation can occur (Mohamed & Nasr-El-Din, 2011) reducing storage potential of the formation. Hydraulic fracturing is the process of using high pressure fluid to fracture rock, increasing the porosity and permeability of a reservoir. In hydraulic fracturing, water chemistry is tailored to each formation from freshwater to prevent the mineral precipitation reactions from reducing desired gains in permeability. Each unconventional horizontal well uses 2-11 million gallons of water, much of that for hydraulic fracturing, and with the rising costs of fresh water, natural brines are being considered as an alternative (Vengosh et al., 2014) and the effects of brine mixing and mineral precipitation on formation porosity are under investigation (Marsac & Navarre-Sitchler, in prep a). Possibly the most common form of brine injection is wastewater injection, for example water produced with oil and gas injected into the ground for disposal due to the high salinity. This disposal method

frequently uses wells that are no longer productive, classed as EPA class II disposal wells. In this dissertation brine injection as a practice is investigated, and of the 4 occurrences discussed here hydraulic fracturing and wastewater disposal are individually addressed.

Hydraulic fracturing requires large volumes of fresh water, and frequently occurs in areas of drought, with approximately 47% of wells in the United States occurring in areas of high or extreme water stress (Freyman, 2014). An alternative to freshwater for hydraulic fracturing is brackish or saline groundwater (Vengosh, 2014). Brackish water from the Debolt Formation is currently used for hydraulic fracturing in the Horn River Basin in British Columbia, Canada (Rivard et al., 2014), and since 2010, increasing amounts of brackish water are utilized for oil and gas operations in the state of Texas (Nicot et al., 2012). Currently, the upper limit of TDS for fracking fluid is considered 25,000 ppm (Vengosh et al., 2014) but new development in friction reducers (Hallock et al., 2013) and other technologies are pushing this limit toward higher TDS (Nicot et al., 2012).

A portion of water injected in to the subsurface for hydraulic fracturing is recovered mixed with natural brines during well completion, this produced water is very high in TDS and must be disposed of along with water produced during production over the life of the well (Clark & Veil, 2009). On average, seven to nine barrels of water are produced with every barrel of oil (EPA, 2000; Veil et al., 2004), a ratio that increases over the life of a well (Clark & Veil, 2009). A global average of 220 million barrels of produced water per day associated with oil and gas activities (Khatib & Verbeek, 2003), of which US onshore wells produce an estimated 38 to 57 million barrels of produced water per day (API, 1988; API, 2000; Veil et al., 2004). Managing this produced water is one of the biggest challenges associated with oil and gas development (Shaffer et al., 2013).

Approximately 92% of produced water in the United States is managed by injection into subsurface geologic formations (API, 2000). Injection is divided into 2 categories: injection for enhanced oil recovery which represents ~71% of produced water management, and injection into disposal wells at ~21% of produced water management (API, 2000). Disposal of produced water can be expensive, with use of disposal wells costing between \$0.05-\$2.65 per barrel of water (Fakhru'l-Razi et al., 2009). With each barrel of oil comes multiple barrels of produced water, thus, disposal costs can add significantly to the cost of oil. Formations are chosen for disposal wells that are not hydrologically connected to future sources of drinking water or producing formations (Rubinstein & Mahani, 2015). Operators must also consider chemical compatibility between the produced water and formation water (Clark & Veil, 2009), as the chemistry of produced water varies widely depending on location (Rubinstein & Mahani, 2015). Chemical reactions between the two waters can result in mineral precipitation, blocking permeability and reducing the effectiveness and lifetime of the disposal well.

Whenever brine is injected into the subsurface, one potential concern is mixing with native formation brines and induction of mineral precipitation (Mohamed et al., 2011; Messer et al., 1978; Mahmoud & Gadallah, 2013). If brines are used for hydraulic fracturing, mineral precipitation could negate some of the effects of the fracturing, filling porosity and reducing permeability. With produced water disposal, mineral precipitation can cause increased formation pressures, reducing the possible injection rate of the produced water (Messer et al., 1978) and eventually causing the well to be sealed due to lack of injectivity. In both cases, it is possible that even small volumes of precipitation (less than 1% of total porosity filled) can reduce permeability near a well, and it is important to understand how variation in the system can affect mineral precipitation

Geologic formations vary widely with regards to porosity and permeability based on rock type, formation scenario, and location. While we understand that precipitation is a concern in brine mixing scenarios, we don't understand how this natural variation in the subsurface could affect mineral precipitation. In addition to geologic variability, variation in injection volumes and injection time could have large impacts on precipitation. These parameters can vary for many reasons, such as the purpose of the injection, the well, and the operator.

The studies in this dissertation focus on the Permian Basin, a 194,000 sq km area located in west Texas and southeastern New Mexico (Railroad Commission of Texas, 2018). Overall Texas produces 35% of the produced water in the United States (Clark & Veil, 2009) and has approximately 12,000 disposal wells (McCurdy, 2011). Thus, I chose the Permian Basin as the source of data for the three manuscripts contained in this dissertation. The Permian Basin is one of the most important and well-developed oil and gas basins in the United States (Chaudhary et al., 2016) Hydraulically fractured wells and produced water volumes in the Permian Basin have increased significantly over the last 15 years due to increased economic viability of fractured wells (Metcalf & Coronado, 2011). Current production of > 2 million barrels of oil per day (Railroad Commission of Texas, 2018) from 32 oil plays (Dutton et al., 2005) is expected to continue to increase, with over 70,000 well permits issued in the last 10 years (Railroad Commission of Texas, 2018). For each well, water use averages 5.7 million liters (Freyman, 2014), thus, water needs already high in the Permian Basin are also expected to increase. In fact, it is estimated that in 2020, 49 billion liters of water will be used in the Permian Basin alone for oil and gas development (Freyman, 2014). Additionally, a study published in 2014 placed 87% of oil and gas wells within the Permian Basin in areas of high or extreme water stress (Freyman, 2014) with projections placing the Water Supply Sustainability Risk Index in the Permian Basin

in the Extreme category when precipitation and water use changes with climate change are considered (Roy et al., 2019).

With the Permian Basin as an example, it is clear that managing water, both resources for production and as a waste product, is an important part of continued development of energy resources in the United States. Current approaches to address both reduction of freshwater usage and management of produced water involve the injection of brines into the subsurface with the potential for brine mixing and geochemical reactions that are currently not well understood. Understanding potential mineral precipitation induced by the mixing of brines of varying chemistries will help us evaluate brine use and disposal across the energy sector. In this dissertation, three studies are completed related to subsurface brine mixing and the subsequent mineral precipitation using reactive transport modeling. The first manuscript applies batch and reactive transport models to evaluate brine usage for hydraulic fracturing in replacement of fresh water with respect to mineral precipitation. The second manuscript examines how variation in porosity, permeability, injection rate and injection time can affect mineral precipitation from brine interaction using suites of reactive transport models. The third manuscript elucidates how changes in concentrations of ions affects total injection time before mineral precipitation causes the well to close using reactive transport models.

CHAPTER 2

GEOCHEMICAL MODELING INVESTIGATIONS OF BRINES AS A FRESH WATER ALTERNATIVE FOR HYDRAULIC FRACTURING

Abstract

Hydraulic fracturing uses 2-11 million gallons of water per oil and gas well, and over 55% of wells in the US are in drought affected area. As oil and gas development continues to increase, fresh water prices and demand increase with it, leading to a need for alternative sources of water for hydraulic fracturing. Natural brines have been used as an alternative, but only to a total dissolved solids (TDS) of < 25,000 ppm. Concerns regarding the use of high TDS brine include the potential for mineral precipitation induced by the mixing of injected brine with the formation water. This mineral precipitation could occlude porosity and reduce permeability, damaging the formation for extraction purposes. The Permian Basin was selected for study as it is one of the most productive oil basins in the US and has high TDS natural formation waters. A database of brine chemistry was generated, and from this synthetic waters representing the range of chemistry in the Permian Basin were defined. An equilibrium batch model was created for each water, specifically looking at the mineral precipitation induced by mixing the water with a median water representing formation water. These models informed reactive transport models which give insight into precipitation in a subsurface formation. Each model had an initial starting porosity of 20%. The minimum porosity in the model after injection of a 65,000 ppm TDS water was 19.8%, for a 99,000 ppm TDS water was 15%, and for a 157,000 ppm TDS water was 2.3%. These results have important implications for the understanding of using brines for hydraulic fracturing.

2.1 Introduction

Freshwater is the main source of water for oil and gas exploration in the United States, and has been since drilling began. As drilling operations expand and more wells are drilled, more freshwater is needed. Since 2004, natural gas production in the United States has increased by more than 30% due to an increase in hydraulic fracturing (Vengosh et al., 2014) to meet domestic energy needs. More than 55% of hydraulically fractured wells in North America are drilled in drought affected areas (Freyman, 2014), and over-extraction of water for hydraulic fracturing is identified as a top risk to water resources in the US (Vengosh, 2014). Hydraulic fracturing, used in the United States since 1947 (King, 2012), increases the porosity and permeability of production formations by injecting fluids until pressures are high enough to fracture the rock in-situ. Freshwater is often used for hydraulic fracturing, but acquisition of freshwater and disposal of produced fluids is a large portion of the cost of drilling and developing wells (Boschee, 2014). Each unconventional horizontal well uses 2-11 million gallons of water (Vengosh et al., 2014); thus, alternative sources of water for oil and gas purposes are paramount to reduce concerns of limited water resources. Alternatives to freshwater for hydraulic fracturing have the potential to lead to economic savings, better community relations, and predicable water supply for oil and gas production.

An alternative to freshwater for oil and gas operations is brackish or saline groundwater (Vengosh, 2014). Brackish water from the Debolt Formation is currently used for hydraulic fracturing in the Horn River Basin in British Columbia, Canada (Rivard et al., 2014), and since 2010, increasing amounts of brackish water are utilized for oil and gas operations in the state of Texas (Nicot et al., 2012). Currently, the upper limit of TDS for fracking fluid is considered

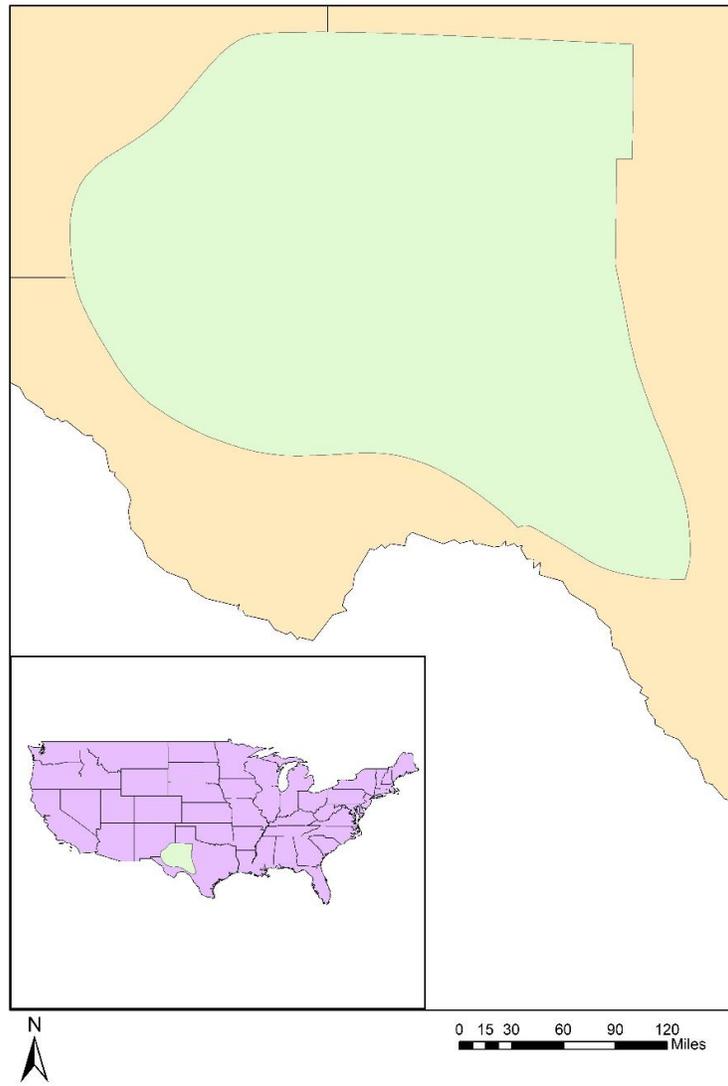


Figure 2.1 Location map of the Permian Basin

25,000 ppm (Vengosh et al., 2014) but new development in friction reducers (Hallock et al., 2013) and other technologies are pushing this limit toward higher TDS (Nicot et al., 2012). A possible consequence of using natural brines with high TDS (over 25,000 ppm) is precipitation in the production formation due to the mixing of injected water with formation water of different chemistry. Precipitation in the production formation can occlude pore space leading to a reduction in permeability and damaging the production formation, making it a concern associated with using natural brines for oil and gas purposes.

The Permian Basin in Texas, USA (Figure 1), is currently one of the most productive oil basins in the US (U.S Energy Information Administration, 2018) and has produced over 30 billion barrels of oil through the year 2000 from 1,339 known reservoirs (Dutton et al., 2004). More recently, production from the Permian Basin averaged ~ 1.7 million barrels per day in 2017 (Railroad Commission of Texas, 2018). Production is increasing, with over 70,000 well permits issued in the last 10 years (Railroad Commission of Texas, 2018). For each well, water use averages 1.5 million gallons (Freyman, 2014) hence the Permian Basin has high volume water needs that will continue to grow. In fact, it is estimated that in 2020 13 billion gallons of water will be used in the Permian Basin for oil and gas development (Freyman, 2014). Furthermore, a study published in 2014 placed 87% of oil and gas wells within the Permian Basin in areas of high or extreme water stress (Freyman, 2014). The combination of water usage for oil and gas operations and drought have previously caused competition for water resources leading to conflict between oil and gas companies and rural communities (Nicot and Scanlon, 2012; Vengosh et al., 2014). Water stress is only expected to increase with the combination of drought potential increasing as climate changes (Freyman, 2014) and continued development with

181,344 oil and gas wells on schedule as of January, 2018 (Railroad Commission of Texas, 2018).

Understanding mineral precipitation caused by the mixing of brines of varying chemistries will help to evaluate the possible complications of using brines from non-producing formations and regions in the Permian Basin for hydraulic fracturing. Previous studies have used geochemical models to investigate the interaction between hydraulic fracturing fluid and shales (Lu et al., 2016; Marcon et al., 2017). Specifically, the changes that could occur to produced water chemistry and rock properties over time were investigated experimentally in conjunction with geochemical modeling, precipitation was predicted and the differences between model and experimental results is thought to be due to lack of organics in the models (Lu et al., 2016). Marcon et al. (2017) found that while models could generally predict major aqueous ion trends, batch models did not accurately represent the decreasing available reactive surface area. Geochemical models are used here to identify potential mineral precipitation reactions that result when natural brines with TDS > 65,000 are mixed with formation waters from producing areas within the Permian Basin. As part of this study, we compiled all publically available water chemistry data in 2016 for the Permian Basin to create a representative database for geochemical modeling. Here we use the software packages Geochemist's Workbench (batch models) and PFLOTRAN (reactive transport models) to simulate mixing and injection to evaluate changes in porosity resulting from mineral precipitation. Two equilibrium batch models are created in Geochemist's Workbench; mixing models allow for exploration of endpoint chemistry for all possible ratios of the two waters, while titration models allow for examination of the reactions as waters reach equilibrium. These simple equilibrium models allow for large numbers of waters to be investigated. Results from equilibrium models are used to constrain reactive transport models

(RTMs) of brine injection that incorporate mineral kinetics and spatial distribution of mineral precipitation.

2.2 Methods

2.2.1 Database

Water chemistry data was collected from four sources: Texas Water Development Board (TWDB, 2015), USGS Produced Water Database (Blondes et al., 2016), National Water Information System (USGS, 2015), and National Carbon Sequestration Database (NETL, 2015). This data was used to create a database of water chemistry in the Permian Basin (Table 2.1). Data was collected within the boundaries of the Permian Basin as defined by the Bureau of Economic Geology (Bureau of Economic Geology, 2016). Data from these sources was reduced by pH, depth, charge balance, TDS and geologic unit data. Multiple sources contained repeated data points and these duplicates were identified and removed. The pH of selected data is limited to 4.5 to 9. Selected data must have a depth greater than 0 to ensure only groundwater data is considered. Only data with charge balance of +/- 5% and with TDS > 10,000 was included to ensure analytical accuracy and prevent inclusion of data that might be considered an underground source of drinking water (Title 40, Code of Federal Regulations, Section 144.3 C.F.R. §40-144.3). Many data entries contained geologic unit information in the form of industry vernacular instead of official geologic unit names. These were researched and replaced with geologic unit names if possible, and the data points were not selected if no information could be found to clarify the vernacular label. Data with geologic unit information were selected to allow for comparison within units across the Permian Basin, and to ensure locational accuracy within the Permian Basin. Geologic units with more than 50 data points were included in the final database to calculate representative statistics.

To expand the relevance of the results of this study to the Permian Basin as a whole and to other areas where the formation water chemistry is similar, 27 synthetic waters (Table 2.2) were created to represent the variation of water within the basin, instead of simply grouping water by geologic unit. This also allows the results of this study to be applied to other basins that have waters with similar chemical characteristics. Three main chemical characteristics define these 27 synthetic model waters: TDS, $\text{Cl}^-/\text{SO}_4^{2-}$, and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios. For each of these parameters the low (25th percentile), medium (50th percentile) and high (75th percentile) values were calculated. Concentrations of ions not associated with a ratio were kept constant for each TDS, which is mainly controlled by Na^+ and Cl^- concentrations. Nomenclature for water types is as follows: T for TDS followed by an L for low, M for medium, or H for high. This continues for Ca as Ca/Mg and Cl as Cl/SO₄. For example, the first water in Table 2.2 is coded as TLCaLCIL, this has low TDS, low Ca/Mg, and low Cl/SO₄. In contrast, TMCaLCIH is a water with medium TDS, low Ca/Mg, and high Cl/SO₄ ratios.

2.2.2 Equilibrium Batch Models

Geochemist's Workbench (Bethke, 2007; version 11.0.5) was used to create batch mixing and titration models of the reaction of each of the 27 synthetic waters with one median water (Table 2.2). The median water represents the median of the waters in the Permian Basin database of each major ion and pH, and allows for the comparison of precipitation and minerals created by each of the 27 synthetic waters. Mixing models represent the reaction of the synthetic and median waters in increasing fractions of a liter. Each step is independent of the previous and contains no memory, running from 100% of water A to 100% of water B in one hundred steps. In contrast, titration models represent the adding of 1 liter of each synthetic water to one liter of the

Table 2.1 Excerpt of the Permian Basin Groundwater Chemistry Database

ID	Formation	Ca (ppm)	Mg (ppm)	Ca/Mg	Na (ppm)	K (ppm)	HCO₃ (ppm)	Cl (ppm)	SO₄ (ppm)	Cl/SO₄	pH	TDS (ppm)
35758	GRAYBURG	2476	1047	2.37	12204	375	222	51584	1030	50.08	6.32	42089
35759	GLORIETA	3089	940	3.29	25878		195	46376	919	50.47	7.89	81046
35766	WOLFCAMP	11360	4680	2.43	42976		1319	141045	4962	28.43	5.55	150927
35767	DEVONIAN	1171	643	1.82	13328		130	31749	440	72.16	7.81	39793
35771	GRAYBURG	538	996	0.54	6375	36	205	48483	970	49.98	7.18	21159
35772	GRAYBURG	704	1000	0.70	9159	75	207	48600	974	49.90	7.45	28588
35775	DEVONIAN	6723	696	9.66	24748		143	35513	519	68.43	7.12	91411
35778	GLORIETA	2360	887	2.66	26467		185	45011	863	52.15	7.33	76824
35779	SAN ANDRES	1233	1151	1.07	3753	790	248	55700	1200	46.42	6.51	15632
35780	SAN ANDRES	21	1106	0.02	4132	547	240	53873	1119	48.17	7.58	12822
35781	SAN ANDRES	372	1119	0.33	2826	553	242	54275	1139	47.65	6.85	11131
35786	ELLENBURGER	8718	852	10.23	37602		176	43157	796	54.22	6.50	128024
35793	WOLFCAMP	2060	3836	0.54	36092		1108	130548	4097	31.86	8.30	101003
35803	SAN ANDRES	11690	1486	7.87	74654		388	78400	2000	39.20	6.21	244413
35817	GRAYBURG	3193	1086	2.94	55972	470	234	52713	1076	49.01	6.75	169315
35829	WOLFCAMP	1380	3810	0.36	20946		1097	130340	4046	32.21	7.08	60946
35833	GRAYBURG	284	972	0.29	5726		200	47399	944	50.21	8.24	17260
35834	GRAYBURG	453	990	0.46	3917		203	48154	963	50.03	6.80	14072
35840	GRAYBURG	9576	1103	8.68	4376	530	239	53722	1105	48.61	6.83	61135

Table 2.2 Synthetic waters derived from the Permian Basin groundwater chemistry database

Name	Ca/Mg	Cl/SO4	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	HCO ₃ (ppm)	Cl (ppm)	SO ₄ (ppm)	pH	TDS (ppm)
TLCaLCIL	1.97	32.96	2028	1028	21544	282	156	38416	1165	6.43	64660
TLCaLCIM	1.97	42.58	2028	1028	21544	282	156	38673	908	6.43	64660
TLCaLCIH	1.97	62.34	2028	1028	21544	282	156	38956	625	6.43	64660
TLCaMCIL	3.21	32.96	2330	727	21544	282	156	38416	1165	6.43	64660
TLCaMCIM	3.21	42.58	2330	727	21544	282	156	38673	908	6.43	64660
TLCaMCIH	3.21	62.34	2330	727	21544	282	156	38956	625	6.43	64660
TLCaHCIL	7.26	32.96	2687	370	21544	282	156	38416	1165	6.43	64660
TLCaHCIM	7.26	42.58	2687	370	21544	282	156	38673	908	6.43	64660
TLCaHCIH	7.26	62.34	2687	370	21544	282	156	38956	625	6.43	64660
TMCaLCIL	1.97	32.96	3299	1672	31425	499	264	59483	1805	6.895	98486
TMCaLCIM	1.97	42.58	3299	1672	31425	499	264	59881	1406	6.895	98486
TMCaLCIH	1.97	62.34	3299	1672	31425	499	264	60320	968	6.895	98486
TMCaMCIL	3.21	32.96	3789	1182	31425	499	264	59483	1805	6.895	98486
TMCaMCIM	3.21	42.58	3789	1182	31425	499	264	59881	1406	6.895	98486
TMCaMCIH	3.21	62.34	3789	1182	31425	499	264	60320	968	6.895	98486
TMCaHCIL	7.26	32.96	4369	601	31425	499	264	59483	1805	6.895	98486
TMCaHCIM	7.26	42.58	4369	601	31425	499	264	59881	1406	6.895	98486
TMCaHCIH	7.26	62.34	4369	601	31425	499	264	60320	968	6.895	98486
THCaLCIL	1.97	32.96	6860	3478	47155	930	616	95267	2890	7.4	157317
THCaLCIM	1.97	42.58	6860	3478	47155	930	616	95905	2252	7.4	157317
THCaLCIH	1.97	62.34	6860	3478	47155	930	616	96607	1550	7.4	157317
THCaMCIL	3.21	32.96	7880	2458	47155	930	616	95267	2890	7.4	157317
THCaMCIM	3.21	42.58	7880	2458	47155	930	616	95905	2252	7.4	157317
THCaMCIH	3.21	62.34	7880	2458	47155	930	616	96607	1550	7.4	157317

Table 2.2 continued

THCaHCIL	7.26	32.96	9087	1251	47155	930	616	95267	2890	7.4	157317
THCaHCIM	7.26	42.58	9087	1251	47155	930	616	95905	2252	7.4	157317
THCaHCIH	7.26	62.34	9087	1251	47155	930	616	96607	1550	7.4	157317
Median Water			3721	1250	31425	499	264	59886	1401	6.895	98445

median water in steps. Each step contains memory of the last, with steps running from 1 liter of water A to 1 liter of water A mixed with 1 liter of water B, creating a maximum ratio of 1:1 (the same as a mixing model with 50% A and 50% B in a total volume of 1 liter). Both types of models create a simple conceptual model of natural brine water used for fracking mixing with highly saline formation water, with no interaction with the formation rock itself. Here we only consider interactions between the inorganic ions and do not consider organic compounds or additives due to limitations in available data. More than 90% of the data points within the Permian Basin database had an ionic strength >1 ; therefore, the Pitzer activity model in Geochemist's Workbench was used to calculate activity coefficients by using the PhreeqPitz database (thermo_phrqpitz.tdat) distributed with the software (Appelo, 2015). A temperature of 70°C was used for all reactions, representing the average well depth within the database of 5800 ft and an average geothermal gradient in the Permian Basin (Ruppel et al., 2005). Both a mixing and titration model were run for each synthetic water in combination with the median water.

2.2.3 Reactive Transport Models

PFLOTTRAN, a multiphase, multicomponent reactive transport model (RTM) code (Mills et al., 2007), was used to model the injection of brine into porous media containing formation water. The simulation was performed on a structured grid with 1 km width in the x-direction and 600 m in the z-direction (Figure 2). Grid cells were 10 m in the x direction and 6 m in the z direction. The y direction is 1 m in width and contains one cell. The model contains quartz with a porosity of 20% and properties of fine sand (Fetter, 2008). Three simulations were performed with varying composition of injection water; these three waters produced the most precipitation from each the high, medium, and low TDS class in batch models chosen (TLCaHCIL,

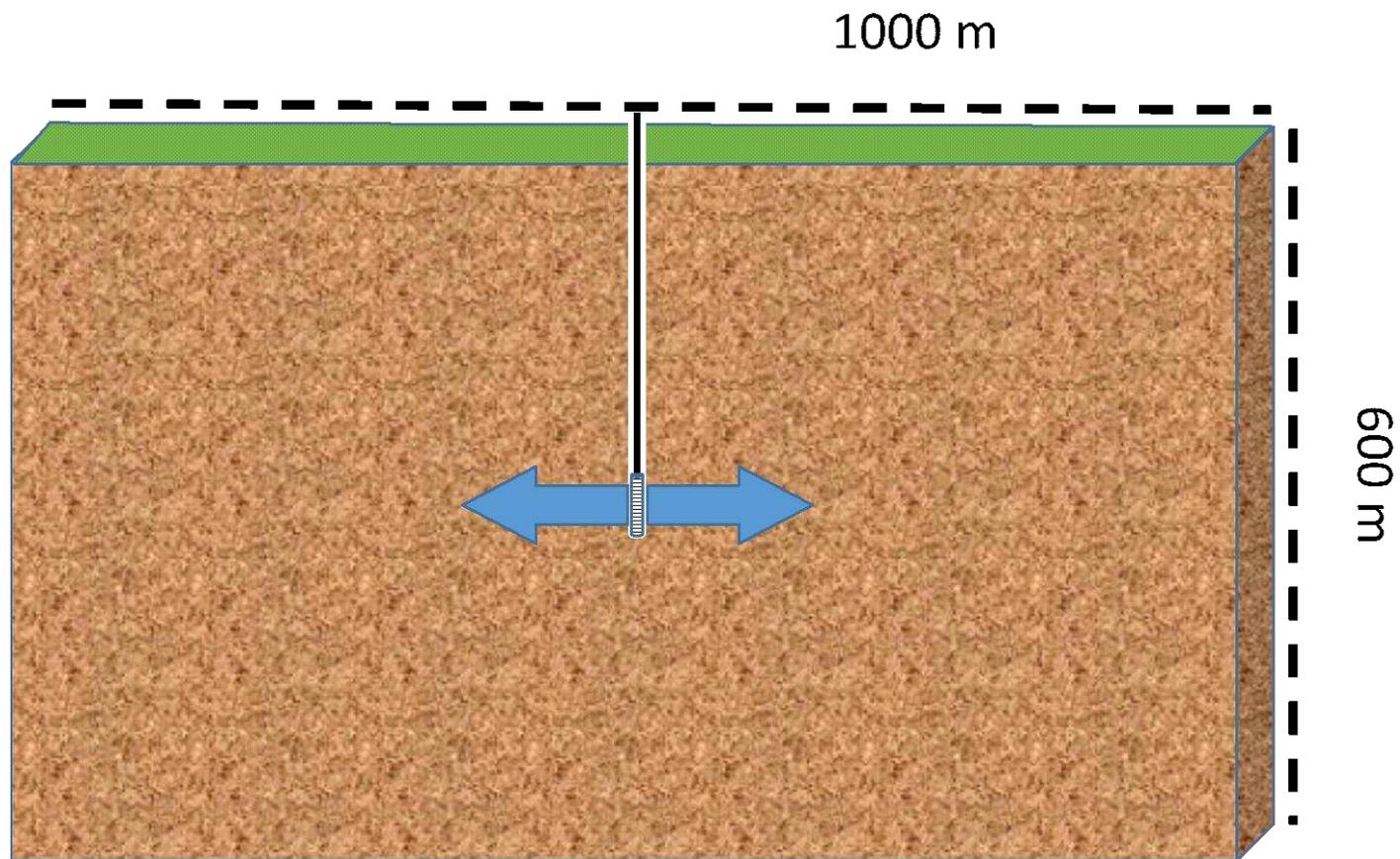


Figure 2.2 Conceptual model of the homogenous RTM model

TMCaHCIL, THCaHCIL). Waters with high Ca/Mg and low Cl/SO₄ were injected into a 10 m x 1 m x 6 m zone in the middle of the model at a depth of 300 m to investigate mineral precipitation from mixing of injection and formation waters. The top and bottom of the model are no flow boundaries, while all other boundaries mimic the model matrix.

Two million gallons of water were injected into each model over a period of ten days, representative of injection volumes (Vengosh et al., 2014) and well completion times (Boschee, 2014) for unconventional wells in the US. Injection starts after 1 day and ends on day 11. After injection no additional water is added or removed. Pressure gradients within the model are initially defined as hydrostatic, as injection increases pressure around the well water flows away from the injection region. Total simulation time for each model was 15 years. Quartz (Palandri & Kharaka, 2004; Tester et al., 1994), calcite (Palandri & Kharaka, 2004; Plummer et al., 1978), dolomite (Palandri & Kharaka, 2004; Busenberg & Plummer, 1982) and anhydrite (Palandri & Kharaka, 2004) were allowed to precipitate according to kinetic rate laws with the reaction rate calculated by equation 2.1 as implemented in PFLOTRAN (Lichtner et al., 2013).

$$I_m = -a_m(\sum_l k_{ml}(T)P_{ml}) \left| 1 - (K_m Q_m)^{1/\sigma_m} \right|^{\beta_m} \text{sign}(1 - K_m Q_m) \quad (2.1)$$

Where I_m in equation 2.1 is reaction rate (mol m⁻²s⁻¹), T is the temperature of the reaction in Kelvin, summation over l represents the parallel reaction mechanisms, K_m is the equilibrium constant (unitless), σ_m is Temkin's constant the average stoichiometric coefficient of the reaction (default is 1, unitless), β_m is the affinity power (default is 1, unitless), a_m is the specific mineral surface area (m²m⁻³), Q_m is the ion activity product (unitless), k_{ml} is a rate constant (mol m⁻²s⁻¹), and P_{ml} is a prefactor for the parallel reaction (m/K) (Lichtner et al., 2013).

Surface areas for anhydrite were not found in the literature, therefore values for gypsum (Jeschke et al., 2001) were used in the model. Temperature was set to 70°C based on average well depth in the database and the Permian Basin geothermal gradient (Ruppell et al., 2005).

Table 2.3 Rate constants and surface areas used in numerical models

Mineral	Rate Constant (moles m⁻²s⁻¹)	Surface Area (m²m⁻³)
Quartz	6.61x10 ⁻¹³ , ¹	47700 ¹
Dolomite	1.55 x10 ⁻⁰⁶ , ²	200900 ²
Calcite	2.95 x10 ⁻⁰⁸ , ³	26150 ³
Anhydrite	6.46 x10 ⁻⁰⁴ , ⁴	17820 ⁵

¹Tester et. al (1994), ²Busenburg and Plummer (1982),

³Plummer et al. (1978), ⁴Palandri & Kharaka (2004) ,

⁵Jeschke et al. (2001)

2.3 Results

2.3.1 Mixing Models

In all mixing models, minerals precipitated when an injection water was mixed with average Permian Basin water (Figure 2.3 and Table 2.4). Precipitated minerals include calcite, anhydrite, and dolomite depending on the composition of the injection water. Injection waters with high TDS, high Ca/Mg, and low Cl/SO₄ produced the highest precipitate volume (THCaHCIL, Table 2.2); with a maximum mineral volume precipitated of 1.82 cm³ per liter of water. Porosity filled (Table 2.4) is a measure we use to determine how successful a model is, and it allows for the comparison of results between different models. Batch models (mixing and titration) have 100% porosity, as these models are all water with no matrix rock; whereas RTM have a set porosity and matrix. To calculate porosity filled we use the following equation:

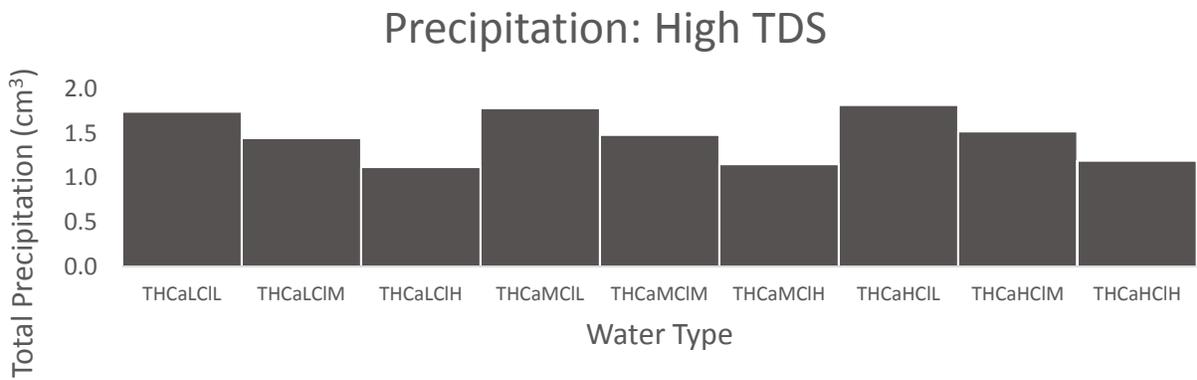
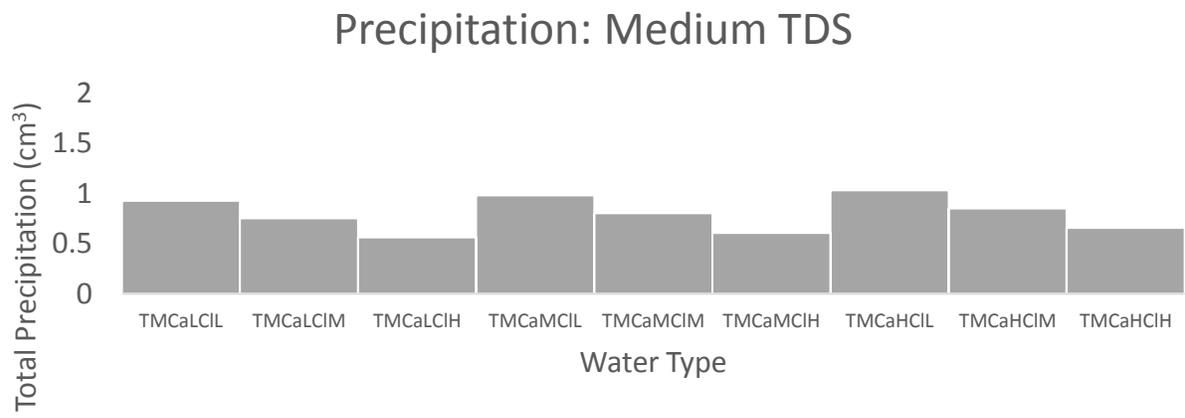
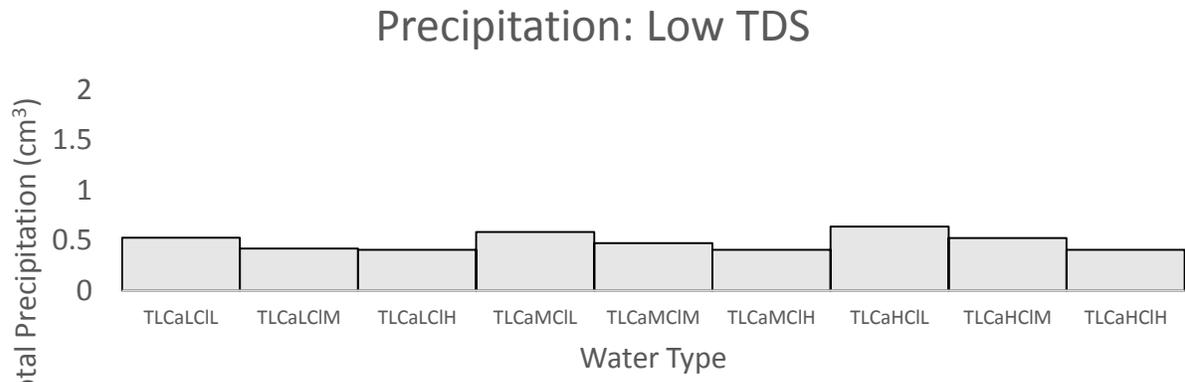


Figure 2.3 Volume of precipitated minerals per liter of water after mixing a specified water type with a median water for the Permian Basin. Graphs are separated into low TDS, medium TDS and high TDS.

$$P_F = \frac{M_V}{P_{TV}} \chi 100 \quad (2.2)$$

Where P_F is the porosity filled, M_V is the mineral volume that precipitated, and P_{TV} is the total available porosity, where M_V and P_{TV} have the same units.

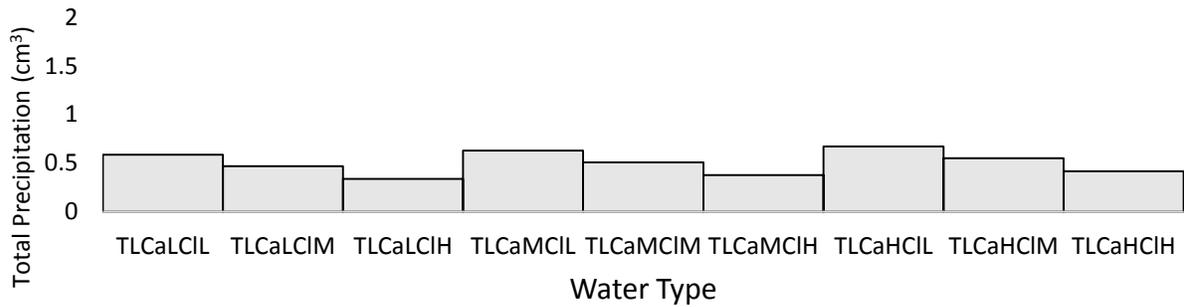
Table 2.4 Mixing model results for high TDS waters

Name	Precipitation (cm³)	Porosity Filled (%)
THCaLCIL	1.74	0.17
THCaLCIM	1.44	0.14
THCaLCIH	1.12	0.11
THCaMCIL	1.78	0.18
THCaMCIM	1.48	0.15
THCaMCIH	1.15	0.11
THCaHCIL	1.82	0.18
THCaHCIM	1.52	0.15
THCaHCIH	1.19	0.12

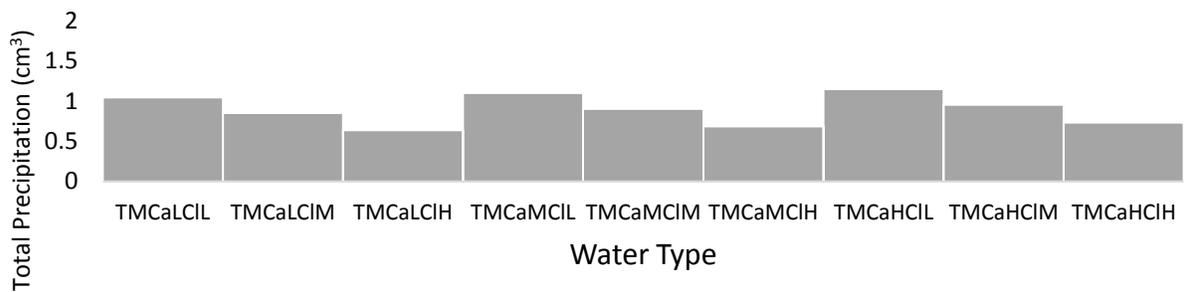
2.3.2 Titration Models

Mineral precipitation occurred in all titration models where each of 27 injection waters were mixed with a median Permian Basin water (Figure 2.4, Table 2.5). The synthetic water that created the most precipitation had high TDS, high Ca/Mg and low Cl/SO₄ (THCaHCIL). Minerals precipitated include dolomite and anhydrite depending on the model; with a maximum volume precipitated of 0.93 cm³ per liter of water (2L total in each model), lower than the batch model volumes precipitated. Lower Cl/SO₄ ratios led to increased precipitation compared to high Cl/SO₄ ratios of the same TDS class. Higher Ca/Mg ratios led to increased precipitation compared to low Ca/Mg ratios of the same TDS class.

Precipitation: Low TDS



Precipitation: Medium TDS



Precipitation: High TDS

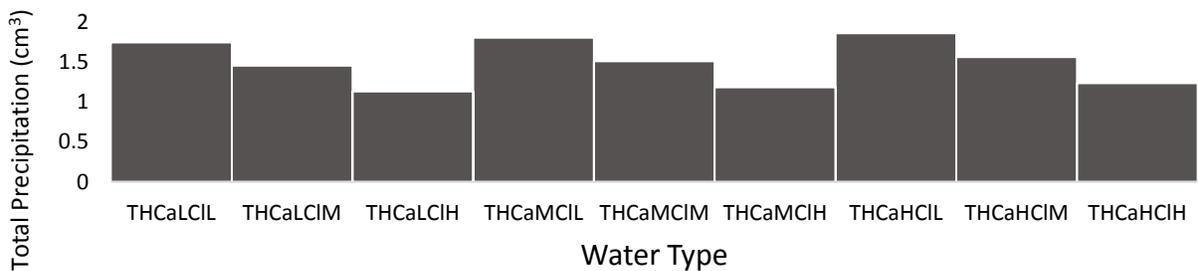


Figure 2.4 Mineral volume precipitated in titration models per 2 liters of water (1 liter of injection fluid titrated into 1 liter of median Permian Basin water). Graphs are separated into low TDS, medium TDS and high TDS.

Table 2.5 Titration model results for high TDS waters

Water ID	Precipitation (cm3)	Porosity Filled (%)
THCaLCIL	0.87	0.087
THCaLCIM	0.73	0.073
THCaLCIH	0.57	0.057
THCaMCIL	0.90	0.090
THCaMCIM	0.75	0.075
THCaMCIH	0.59	0.059
THCaHCIL	0.93	0.093
THCaHCIM	0.78	0.078
THCaHCIH	0.62	0.062

2.3.3 Reactive transport models of brine injection

While batch and titration models will predict volumes and phases of minerals precipitated, distribution of porosity around an injection point is important for evaluating the decrease in porosity varies with injection fluid composition. Porosity reaches a minimum of 2.3% for water THCaHCIL, 15% for water TMCaHCIL, and 19.8% for water TLCaHCIL. After 15 years, the minimum porosity in the THCaHCIL model rebounds slightly. Minimum porosity for TMCaHCIL and TLCaHCIL models remains constant after 15 years.

After injection ends, precipitation stops and precipitation volume remains constant through the runtime. In all three models, precipitation occurs in the zone where the injection water and formation water first mix in the injection region. Precipitation remains concentrated around the injection zone throughout the runtime.

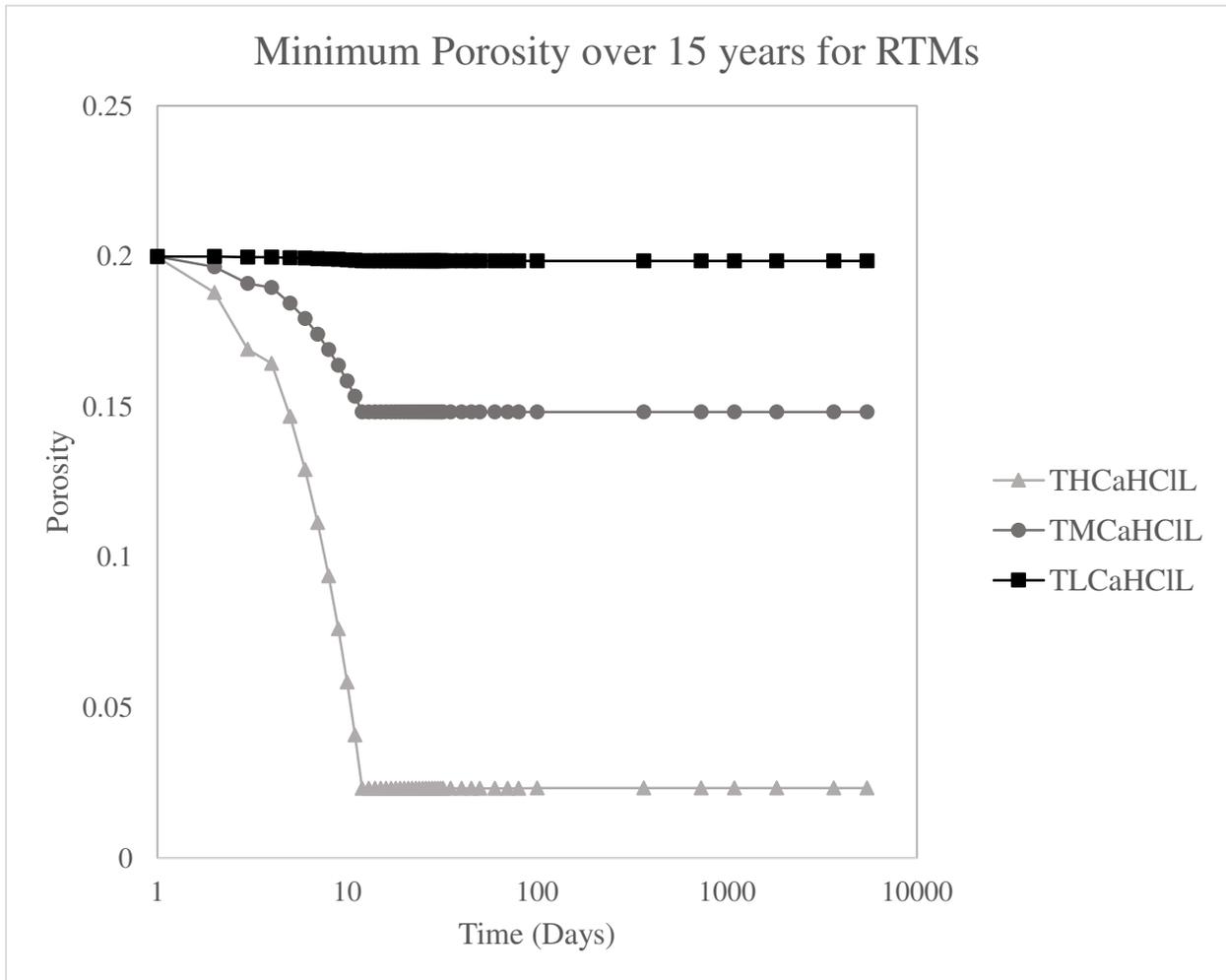


Figure 2.5 Graphs of the minimum porosity present in each model time step over the 15 year run time. Three modeled waters are investigated: High TDS, High Ca/Mg, and low Cl/SO4; Medium TDS, High Ca/Mg, and low Cl/SO4; and Low TDS, High Ca/Mg, and low Cl/SO4.

2.4 Discussion

2.4.1 Mineral Uncertainty

While dolomite is thermodynamically favored to precipitate based on the water chemistry and thermodynamic data, it is possible that dolomite will not be the dominant carbonate mineral to precipitate over the short time scales represented in the simulations. While a temperature of 70°C is favorable for dolomite precipitation (Warren, 2000), some of the brines have high Ca/Mg ratios which may not favor dolomite precipitation (Warren, 2000). Additional models were performed where dolomite was not allowed to precipitate. In these models calcite precipitated, also leading to reductions in porosity, with small differences in overall precipitation volume. Precipitation volumes from batch simulations where dolomite was suppressed compared to those where dolomite was not suppressed were <1% different for 21 out of the 27 total scenarios simulated (Table 5). Of the six water with >1% difference, the maximum volume difference of 2.1% (1.24 cm³ with dolomite compared to 1.26 cm³ with dolomite suppressed) was simulated for injection water THCaHCIH. Difference in precipitation volume >1% was also simulated for THCaHCIL (1.35% difference; 1.86 cm³ with dolomite compared to 1.88 cm³ with dolomite suppressed). This water was used as the injection water in the large scale RTMs in PFLOTTRAN. While research suggests that the precipitation of dolomite under these conditions is expected in the field, the simulation results suggest that even if dolomite does not precipitate calcite will precipitate still leading to reduced porosity of similar amounts.

2.4.2 Batch models compared to reactive transport simulations

The main difference between the results of the batch models and reactive transport simulations is the change in porosity. For the water THCaHCIL, the batch mixing model predicted a maximum decrease in porosity of 0.18%. The RTM predicted a maximum decrease

Table 2.6 Dolomite suppression vs precipitation in titration models

Name	Precipitation (cm³)	Precipitation Dolomite Suppressed (cm³)	Percent Difference (%)
TLCaLCIL	0.54	0.54	0.75
TLCaLCIM	0.43	0.43	0.88
TLCaLCIH	0.31	0.31	1.10
TLCaMCIL	0.58	0.58	0.33
TLCaMCIM	0.47	0.47	0.34
TLCaMCIH	0.35	0.35	0.40
TLCaHCIL	0.63	0.63	-0.16
TLCaHCIM	0.51	0.51	-0.23
TLCaHCIH	0.39	0.39	-0.39
TMCaLCIL	0.93	0.93	0.30
TMCaLCIM	0.76	0.75	0.30
TMCaLCIH	0.56	0.56	0.32
TMCaMCIL	0.98	0.98	-0.06
TMCaMCIM	0.80	0.81	-0.12
TMCaMCIH	0.61	0.61	-0.26
TMCaHCIL	1.03	1.04	-0.48
TMCaHCIM	0.85	0.86	-0.66
TMCaHCIH	0.66	0.66	-0.93
THCaLCIL	1.74	1.76	-0.63
THCaLCIM	1.45	1.46	-0.76
THCaLCIH	1.13	1.14	-1.15
THCaMCIL	1.80	1.82	-0.94
THCaMCIM	1.51	1.53	-1.19
THCaMCIH	1.18	1.20	-1.60
THCaHCIL	1.86	1.88	-1.35
THCaHCIM	1.56	1.59	-1.67
THCaHCIH	1.24	1.26	-2.11

in porosity of 88.5%. The discrepancy between the two types of model may be related to two things: (1) batch models run to equilibrium, while RTMs are kinetically controlled; and (2) spatial dimensions and limited porosity are considered in an RTM grid, and not present in batch models. In the RTMs, all precipitation is concentrated in the injection zone cell, while the rest of the domain retains the original porosity. RTMs and batch models may predict similar total volumes of precipitation, with batch models predicting a decrease of 0.18% and RTMs predicting an overall porosity decrease of 0.029%. However, batch models only have one cell, while RTMs have 10,000 cells, and RTMs predict the concentration of precipitation in one cell. While batch models indicate that high TDS waters would be appropriate for oil and gas purposes, RTMs show that the concentration of precipitation reduces the porosity, and thus permeability, of the formation. It is also important to note that the RTM contains a matrix of quartz (considered non-reactive) while the batch models contain only water-water interactions with no matrix.

In future modeling of brine mixing focused on precipitation, batch models are useful for running large numbers of simulations to make decisions about where to focus study with RTMs. RTMs take significantly more computational time and resources and are more complex to build, but are necessary to place the geochemical reactions in the context of a porous formation. In injection scenarios the distribution of mineral precipitation is critical to the permeability of the formation. Due to the localized effects of brine injection, we recommend small grid sizes for RTMs. This can allow for more refined grids, or for significantly reduced model run times which will allow for the exploration of multiple water chemistries with the same computing time cost.

2.5 Conclusions

Batch models of the reaction between synthetic formation and injection waters indicate that using brines for oil and gas purposes would create a minimal amount of precipitation, filling less than 0.2% of available pore space with 75th percentile TDS brines within the Permian Basin. Both types of batch models concluded the same synthetic water caused the most precipitation, a water with high TDS, high Ca/Mg and low Cl/SO₄ (THCaHCIL). This is consistent with the minerals precipitated: anhydrite (CaSO₄), and dolomite (CaMg(CO₃)₂). The higher the TDS of the water, the more likely it is that precipitation will occur; a high Ca/Mg creates increased calcium, a component of both precipitated minerals; and a low Cl/SO₄ creates increased SO₄, a component of anhydrite.

The RTMs were created with the water that caused the highest amount of mineral precipitation in batch models from each TDS class. The RTM results do not support the conclusions of batch models, with porosity decreasing by up to 88.5% within the grid over 15 years of observation. While total porosity throughout the models may be similar, in RTMs precipitation concentrates in the injection zone, damaging the pay formation. The small porosity changes occurring in batch models indicate that for high TDS waters mineral precipitation is not a concern. However, the addition of kinetics and space in RTMs paints a different picture, with high TDS waters causing a problematic filling of porosity. RTMs suggest that in waters with medium and low TDS mineral precipitation due to water mixing is not a major concern for hydraulic fracturing with brines within the Permian Basin.

The modeling outlined here provides the beginnings of studying brines as freshwater alternatives for oil and gas uses, an important undertaking in drought-affected producing areas. However, further study is needed to investigate brine usage with more complex heterogeneous

reactive transport models and experimental approaches to validate the model results presented here.

CHAPTER 3

REACTIVE TRANSPORT SIMULATIONS OF INJECTED BRINE MIXING

Abstract

Brine injection is prevalent in energy production in the United States, where it is used for a range of purposes including enhanced oil recovery, hydraulic fracturing, carbon sequestration, and wastewater water disposal. For every 1 barrel of oil produced in the United States 7 barrels of water are produced, and wastewater injection is common for disposal of water produced with oil and gas. During injection this produced brine mixes with formation water in the subsurface, and this can cause mineral precipitation reactions. Mineral precipitation occludes porosity and can lead to the eventual abandonment of a disposal well. Injection rate, represented by injection volume and injection time vary widely by well and operator; geologic formations vary widely in porosity and permeability, and the effects of these variations on mineral precipitation in disposal wells are unknown. Texas contains over 12,000 wastewater disposal wells, making the Permian Basin an excellent location to investigate these affects. Twenty-five reactive transport simulations were created to discover how variations in porosity and permeability affect mineral precipitation. Initial porosity had no effect on precipitation, while permeability had a minimal effect. Twenty-five additional simulations were created to investigate injection time and volume. The longer the injection time the more mineral precipitation occurred, and the more volume the more precipitation occurred; indicating that faster rates are desirable. These results have important implications for how variation in formations and disposal affect wastewater disposal.

3.1 Introduction

Brine injection is incredibly common in the United States. In many cases this brine injection is related to energy production; such as enhanced oil recovery, hydraulic fracturing,

carbon sequestration, and wastewater disposal. In enhanced oil recovery (EOR), brine is injected into the formation to increase oil production. Water alternating gas is the most common EOR recovery method in the United States (Manrique et al., 2007), where brine and CO₂ are injected in rotation. Oil recovery success is based on brine salinity (Zhang et al., 2007), with sea water having the potential to reduce formation permeability by up to 20% through mineral precipitation (Mahmoud & Gadallah, 2013) reducing recovery potential. Brines are injected into the subsurface during carbon sequestration when the water alternating gas method is used. If the brine has a high sulfate content, mineral precipitation can occur (Mohamed & Nasr-El-Din, 2011) damaging the storage formation. In hydraulic fracturing, water chemistry is tailored to each formation to prevent the mineral precipitation reactions from reducing gains in permeability, but with the rising costs of fresh water brines are being considered as an alternative (Vengosh et al., 2014) and the effects of brine mixing and mineral precipitation on formation porosity are being investigated (Marsac & Navarre-Sitchler, in prep a). Possibly the most common form of brine injection is wastewater injection, for example from oil and gas production and geothermal energy. In the United States, for every barrel of oil produced, an average of 7 barrels of water is produced (Lee et al., 2002), much of which is disposed through deep well injection. For example, approximately 95% of the produced water in Texas fields is disposed of through deep well injection (Veil et al., 2004).

When brines are injected into the subsurface for disposal, chemical interactions between injected brines and native formation waters have the potential to induce mineral precipitation, possibly reducing porosity and permeability of the formation (Mohamed et al., 2011; Messer et al., 1978; Mahmoud & Gadallah, 2013, Marsac and Navarre-Sitchler, in prep a). This decreased porosity and permeability can lead to declining production and eventual abandonment of oil and gas wells (Van Dorp et al., 2009; Kleinitz et al., 2001) and decreased efficacy of disposal wells

(Messer et al., 1978). Brine injection is a necessary step in the production of energy; therefore, understanding potential chemical interactions between injected and formation fluids and subsequent mineral precipitation in the subsurface is an important part of maintaining formation integrity and to increasing the efficiency of energy development in the United States.

One of the most productive oil and gas basins in the US, Permian Basin, TX (Chaudhary et al., 2016) produced an average 1.7 million barrels of oil per day in 2017 (Railroad Commission, 2018). To support this production there are 7,000 fields, with over 6,000 drilling permits issued in 2018 (Railroad Commission, 2018). Brine injection for hydraulic fracturing is also a potential mechanism to reduce freshwater use in the Permian Basin (Vengosh et al., 2014; Marsac & Navarre-Sitchler, in prep a). The hydraulic fracturing process uses between 2 and 6 million gallons of water per well, and 87% of oil and gas wells drilled in the Permian Basin are in areas of high or extreme water stress (Freyman, 2014), creating this need for an alternative to fresh water. At this time, low TDS brines are used in the Permian Basin for hydraulic fracturing, but the current upper limit of TDS for fracking fluid is considered to be 25,000 ppm (Vengosh et al., 2014). However, development in new technologies is pushing the boundary (Nicot et al., 2012), allowing for the consideration of hydraulic fracturing with brines of TDS > 65,000 ppm, though the geochemical implications of high TDS brine injection are still under investigation (e.g. Marsac & Navarre-Sitchler, in prep a).

In wastewater disposal, mineral precipitation can cause increased pressures, reducing the possible injection rate of produced water (Messer et al., 1978) and eventually causing the well to be sealed. If brines are used for hydraulic fracturing, mineral precipitation could negate some of the effects of the fracturing, filling porosity and reducing permeability. In a previous study based on brine chemistry in the Permian Basin, Marsac and Navarre-Sitchler (in prep a) identified

dolomite, calcite, and anhydrite as the suite of minerals predicted to precipitate when natural brines of different chemistry are injected into the subsurface using Permian Basin brine compositions to constrain numerical simulations.

Geologic formations vary widely with regards to porosity and permeability based on rock type, formation scenario, and location. While previous work indicates that precipitation is a concern in brine mixing scenarios (Mahmoud & Gadallah, 2013; Marsac & Navarre-Sitchler, in prep a; Mohamed & Nasr-El-Din, 2011) placing the precipitation in the context of variability in geologic formations is a necessary next step. Results from previous models (Marsac & Navarre-Sitchler, in prep a) show that even small amounts of overall precipitation (less than 1% total model porosity filled) can be concentrated around the injection zone, highlighting the potential implications of brine injection on the ability to inject brine or remove oil from a formation. Additional evaluation of brine injection into different rock types with a variety of porosities and permeabilities will provide insight into the problem of mineral precipitation with brine injection in natural systems.

In addition to geologic variability, variation in injection volumes and injection time could control the volumes and spatial distributions of precipitation. Injection parameters can vary for many reasons, such as the purpose of the injection, the well, and the operator. Maximum mineral precipitation occurs when precipitation reactions are allowed to reach equilibrium (Bethke, 2007) indicating that injection time is an important factor. Brine injection volumes impact mineral precipitation due to reactant concentration replenishment continuing to drive the precipitation reaction.

Here we evaluate two suites of brine mixing simulations, the first suite tests how natural variations in geologic formations, specifically porosity and permeability, affect predicted mineral

volumes. The second suite of simulations evaluates how injection parameters, specifically injection volume and injection time, can affect mineral precipitation volume. These simulations collectively address questions regarding how sensitive brine mixing scenarios are to parameter variation. Ultimately, the simulations provide preliminary insight into how injection can be managed to reduce the impacts of mineral precipitation during brine injection.

3.2 Methods

Simulations were performed using the software package PFLOTRAN, a massively parallel, multiphase, multicomponent reactive transport code (Mills et al., 2007). Each model has a structured 100 m x 100 m x 100 m grid, with variable grid cell sizes, allowing for 1 m³ grid cells around the injection zone and 1000 m³ grid cells on the outer regions of the grid. There are 28 cells in the x direction, 20 cells in the y direction, and 20 cells in the z direction. Every model has the same injection zone, a 31.25 m³ region in the middle of the model grid (Figure 3.1), and a run time of 3 years. Each model initializes for 1 day, with injection starting at the end of day 1 and injection time varying by model (Table 3.2). Pressure is initially hydrostatic, with the only flow in the formation induced by pressure changes associated with injection. The top and bottom of each model is a no flow boundary, while the north, south, east, and west boundaries have the same conditions as the matrix.

The suite of simulations all have the same chemistries, including the formation water and the injection water. Water chemistries were derived from a Permian Basin groundwater database (Marsac & Navarre-Sitchler, in prep a), where data was compiled from four sources: Texas Water Development Board (TWDB, 2015), USGS Produced Water Database (Blondes et al., 2016), National Water Information System (USGS, 2015), and National Carbon Sequestration Database (NETL, 2015). The formation water chemistry represents a median of all Permian Basin

groundwaters, and has a TDS of 99,000 ppm. The injection water chemistry has a medium TDS, high Ca/Mg ratio, and a low Cl/SO₄ ratio and a TDS of 101,000 ppm. The temperature of each model is 70°C to represent average well depth in the Permian Basin. Each model has a quartz matrix with minimal amounts of calcite, dolomite and anhydrite to allow for precipitation of these minerals (Table 3.1).

Reaction rate is calculated by equation 3.1 as implemented in PFLOTRAN (Lichtner et al., 2013).

$$I_m = -a_m(\sum_l k_{ml}(T)P_{ml}) \left| 1 - (K_m Q_m)^{1/\sigma_m} \right|^{\beta_m} \text{sign}(1 - K_m Q_m) \quad (\text{Equation 3.1})$$

Where I_m in equation 3.1 is reaction rate (mol m⁻²s⁻¹), T is the temperature of the reaction in Kelvin, summation over l represents the parallel reaction mechanisms, K_m is the equilibrium constant (unitless), σ_m is Temkin's constant the average stoichiometric coefficient of the reaction (default is 1, unitless), β_m is the affinity power (default is 1, unitless), a_m is the specific mineral surface area (m²m⁻³), Q_m is the ion activity product (unitless), k_{ml} is a rate constant (mol m⁻²s⁻¹), and P_{ml} is a prefactor for the parallel reaction (m/K) (Lichtner et al., 2013).

We chose 4 parameters for study: porosity, permeability, injection volume, and injection time. Each of these parameters were chosen to evaluate the ability to optimize brine injection with respect to limiting mineral precipitation. Porosity and permeability vary based on location, geologic formation, and rock type; making these important parameters for insight into how formation variability impacts mineral precipitation. Injection volume and injection time vary based on well, operator, and why injection is occurring. These parameters are crucial to understanding how industry variation can effect mineral precipitation.

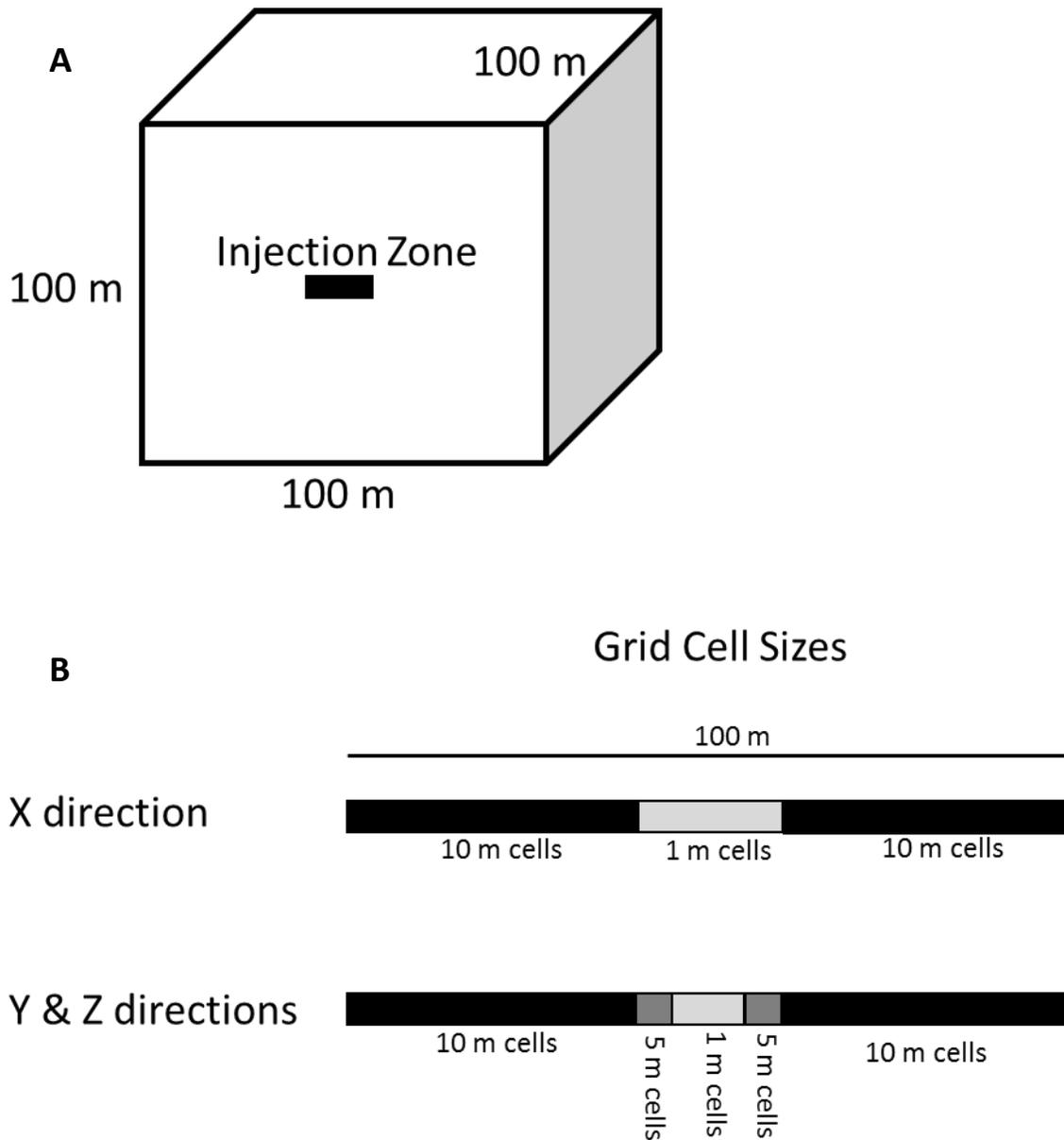


Figure 3.1: A) 3-D reactive transport model setup, with injection zone in the center. B) X direction and Y/Z direction grid cell sizes are shown, with 28 cells in the x direction, 4 10 m cells, 20 1 m cells, and 4 10 m cells; 20 cells in the y direction, 4 10 m cells, 1 5 m cell, 10 1 m cells, 1 5 m cell, and 4 10 m cells; and 20 cells in the z direction, 4 10 m cells, 1 5 m cell, 10 1 m cells, 1 5 m cell, and 4 10 m cells

Table 3.1 Rate constants and surface areas used in numerical models

Mineral	Rate Constant (moles m⁻²s⁻¹)	Surface Area (m²m⁻³)
Quartz	6.61x10 ⁻¹³ , ¹	47700 ¹
Dolomite	1.55 x10 ⁻⁰⁶ , ²	200900 ²
Calcite	2.95 x10 ⁻⁰⁸ , ³	26150 ³
Anhydrite	6.46 x10 ⁻⁰⁴ , ⁴	17820 ⁵

¹Tester et. al (1994), ²Busenburg and Plummer (1982),

³Plummer et al. (1978), ⁴Palandri & Kharaka (2004) ,

⁵Jeschke et al. (2001)

Table 3.2 Simulation Parameters

<u>Porosity (%)</u>	<u>Permeability (m²)</u>	<u>Time (days)</u>	<u>Total Volume (liters)</u>
6.5	7.5 x 10 ⁻¹⁵	4	189,250
11.5	7.5 x 10 ⁻¹⁴	7	378,500
16.5	7.5 x 10 ⁻¹³	10	757,000
21.5	7.5 x 10 ⁻¹²	13	1,514,000
26.5	7.5 x 10 ⁻¹¹	16	2,271,000

The first suite of models systematically varies porosity and permeability to investigate controls on mineral precipitation. The base model has a permeability of 7.5x10⁻¹³ m² and a porosity of 16.5%. From this base model, permeability was varied by 2 orders of magnitude above and below 7.5x10⁻¹³ m² (Table 3.2), for models at permeabilities of 7.5x10⁻¹¹ m², 7.5x10⁻¹² m², 7.5x10⁻¹³ m², 7.5x10⁻¹⁴ m², and 7.5x10⁻¹⁵ m². From the base model porosity was varied by 5% twice above and below the starting value of 16.5% (Table 3.2), for models at porosities of 6.5%, 11.5%, 16.5%, 21.5%, and 26.5%. Every combination of these 5 porosity and 5 permeability values was modeled. Each model had 757,000 liters of water injected over 10 days.

The second suite of models systematically varies the injection rate and total injection volume to investigate how industry injection parameters affect mineral precipitation. To represent rate, the amount of days over which injection occurs was varied. The base model has an injection time of 10 days. Total time was varied in three day increments, with models for 4, 7, 10, 13 and 16 days. (Table 3.2). For hydraulic fracturing, while 2-6 million gallons of water are used per well, each well is divided into a number of segments, and each segment only receives a portion of the hydraulic fracturing fluid. We have chosen 10 segments as our representative value, where each model represents only one segment and 1/10 of the total water volume that would be injected. The median injection volume is 757,000 liters, with 10 segments for a total volume of 7,570,000 liters or 2 million gallons. For our total injections values we chose 1,892,500 liters; 3,785,000 liters; 7,570,000 liters; 15,140,000 liters; and 22,710,000 liters (Table 3.2). Each model had a permeability of $7.5 \times 10^{-13} \text{ m}^2$ and a porosity of 16.5%.

3.3 Results

3.3.1 Porosity & Permeability

Twenty-five simulations were performed to test all combinations of porosity and permeability values in Table 3.2. Values in Table 3.3 represent the maximum porosity decrease in each model which occurs around the injection zone, making it an important area for well lifetime.

Table 3.3 Absolute Change in Percent Porosity from Porosity-Permeability Simulations

		Permeability				
		7.5×10^{-15}	7.5×10^{-14}	7.5×10^{-13}	7.5×10^{-12}	7.5×10^{-11}
Porosity	6.5%	6.5%	6.5%	6.5%	6.5%	6.5%
	11.5%	9.4%	10.5%	10.6%	10.7%	10.7%
	16.5%	9.4%	10.5%	10.6%	10.7%	10.7%
	21.5%	9.4%	10.5%	10.6%	10.7%	10.7%
	26.5%	9.4%	10.5%	10.6%	10.7%	10.7%

These results indicate that initial porosity does not control the total volume of precipitation during the injection period. Initial permeability does lead to some small variation in mineral precipitation volume in the simulations, with less precipitation in models with lower initial permeabilities. All models that started with 6.5% porosity reached zero percent porosity at day 8 of the model run, during the active injection period. At this point the model was stopped because no additional injection is possible. PFLOTRAN does not take into consideration geomechanical processes such as the alteration of the formation due to the pressure of continued injection at low porosities, so a porosity of zero is not a realistic result. However, it is used as an endpoint for the purpose of comparing models in the study. It is important to note that the starting porosity for 6.5% porosity models is lower than the total precipitation that occurs in all other models.

3.3.2 Injection Volume & Rate

Twenty-five models were run to test all combinations of injection volume and injection time values in Figure 1. Values in Table 3.4 represent the maximum porosity decrease in each model which occurs around the injection zone, making it an important area for continued injection. Variations in both injection rate and injection time generate varying volumes of mineral precipitation (Table 3.4). Increases in injection time, which also represent decreases in injection rate, increase the total amount of precipitation (Figure 3.2). This also means that the higher the volume of injected water, the greater the gains in precipitation are as the injection time is increased (Figure 3.2). For example, there is a 2.3% absolute change in percent porosity between 189,250 liters over 4 days (3.5%) compared to the same volume over 16 days (5.8%), compared to a 9.6% absolute change in percent porosity between 2,271,000 liters over 4 days (6.9%) compared to 2,271,000 liters over 16 days (16.5%). Increases in injection volume cause increases in

precipitation, furthermore in these same models, the higher the injection time, the greater the gains in precipitation are as injection volume

Table 3.4 Absolute Change in Percent Porosity from Injection Time-Injection Volume

		Days				
		4	7	10	13	16
Volume	189250	3.5%	4.5%	5.1%	5.5%	5.8%
	378500	4.6%	6.5%	7.8%	8.7%	9.5%
	757000	5.6%	8.4%	10.6%	12.4%	13.9%
	1514000	6.5%	10.1%	13.3%	16%	16.5%
	2271000	6.9%	11%	14.6%	16.5%	16.5%

is increased (Figure 3.3). Precipitation volume, or porosity decrease, is positively correlated to both injection time (where injection volume is held constant) and injection volume (where injection time is held constant) (Figure 3.3). However, differences in injection time generate more differences in decreased porosity than injection volume. For example, absolute change in percent porosity is 3.4% higher when 2,271,000 liters is injected over 4 days compared to 189,250 liters injected over 4 days; but, when the same volumes are injected over 16 days there is a difference in decreased porosity of 10.7%.

Three injection rate - injection time models resulted in porosity = 0% at some location in the model domain. For 13 days of injection and an injection volume of 2,271,000 liters, the model reached 0% porosity on day 13, the last day of the injection period. For 16 days of injection and an injection volume of 1,514,000 liters the model reached 0% porosity on day 16, the last day of the injection period. For 16 days of injection and an injection volume of 2,271,000 liters the model reached 0% porosity on day 13, 3 days before the end of the injection period. It is important to

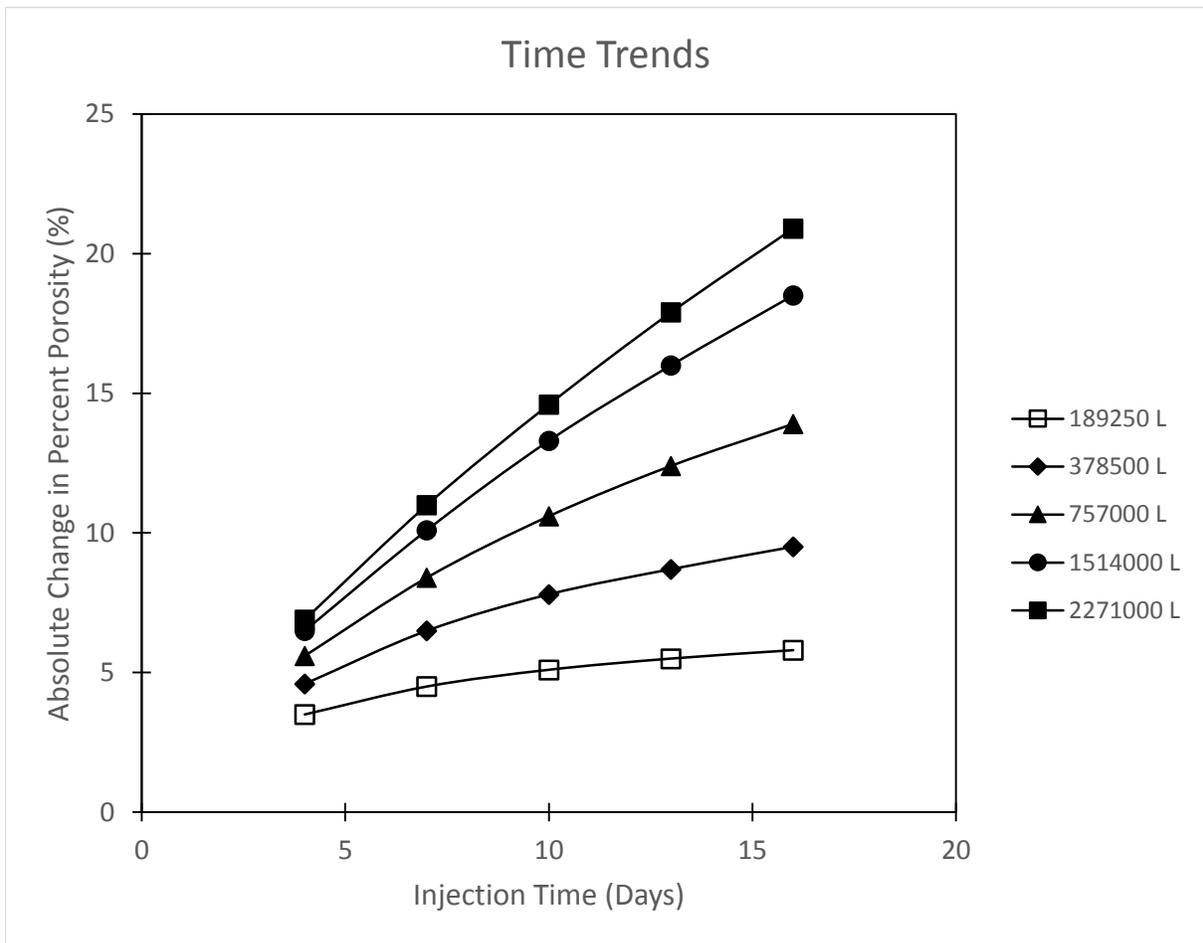


Figure 3.2: Precipitation volume trends over models with the same injection volume, but different injection times.

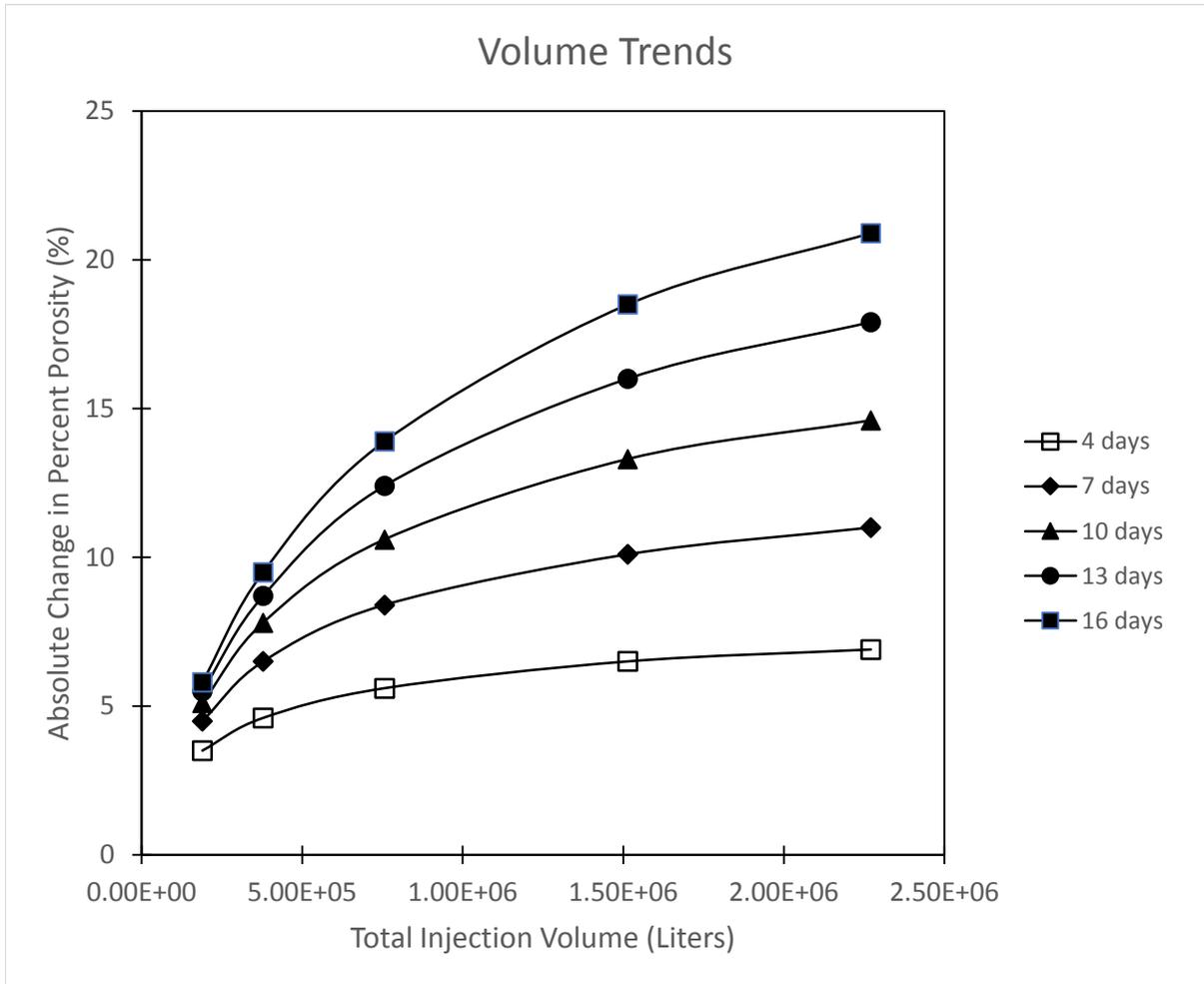


Figure 3.3 Precipitation volume trends over models with the same injection time, but different injection volumes.

note that after the injection period ends, porosity stabilizes and does not change over the rest of the 3 year model run time.

3.4 Discussion

Results from the suite of simulations indicate that injecting wastewater at a faster rate would significantly lengthen the lifetime of the well from a porosity standpoint. However, high-volume waste water disposal wells are thought to have caused the increase of earthquakes in Oklahoma (Keranen et al., 2014; McGarr and Barbour, 2017; Weingarten et al., 2015). Specifically, three earthquakes over a magnitude 5 occurred in Oklahoma in 2016, one of which was the largest ever recorded in Oklahoma at magnitude 5.8 (McGarr and Barbour, 2017). It is important to note that PFLOTTRAN does not include geomechanical processes and so cannot be used to draw conclusions on stress or strain accumulation due to injection. In our study the highest injection rate used is 567,750 liters/day. Whereas the high volume disposal wells that are thought to cause earthquakes are operating at a minimum injection rate of 47,691,000 liters/month, or about 1,589,700 liters/day (Weingarten et al., 2015), over twice the rate tested in this study. Here, we cover injection volumes of 189,250 liters to 2,271,000 liters, with higher injection rates and shorter injection times designed to represent hydraulic fracturing and disposal of brines associated with oil and gas production. However, the injection rate of brines varies greatly depending on the purpose of the injection. Lower injection rates and longer injection times are designed to capture this variation.

Initial porosity of the disposal formation had no effect on total precipitation occurring in models (Table 3.3); while variations in permeability created a 1.3% absolute difference in percent porosity from the largest to the smallest values. The only exception to this is the 6.5% porosity models, where initial porosity is lower than the total porosity change in other models. However,

these models have a similar linear decrease in porosity to all other models, and we do not observe that the low porosity is having an effect on precipitation. These model results indicate that the porosity and permeability of the formation will have little effect on the precipitation created by brine injection. Whether a high porosity, high permeability sand; or a low porosity, low permeability shale; these models demonstrate that within the parameters of the simulations we predict the precipitation volume from the injection of brine will have little variation. These results demonstrate that these models are applicable across a wide range of geologic formations.

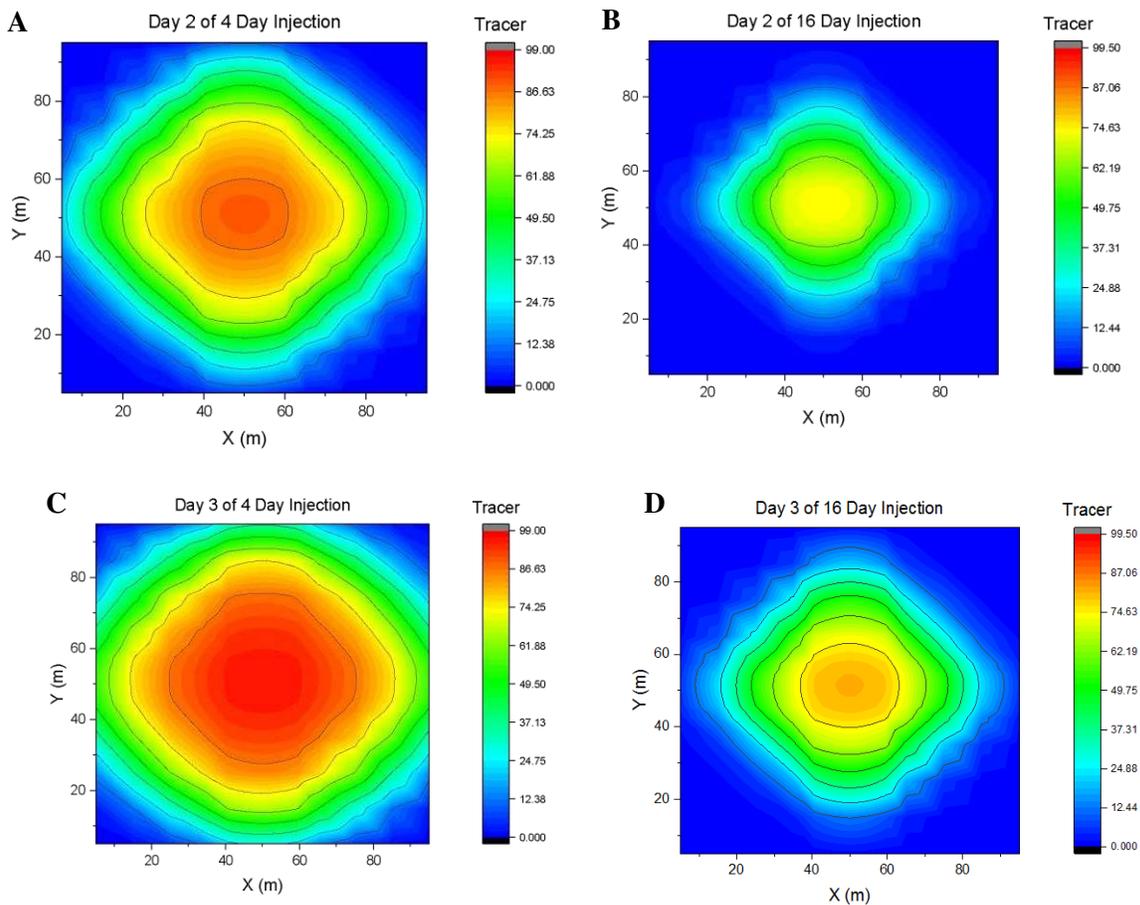


Figure 3.4 Graphs of tracer and calcium concentration in 4 day and 16 day models with 2,271,000 liters of injection. A and B show the tracer concentration of day 2 of the 4 day and 16 day models respectively. C and D show the tracer concentration of day 3 of the 4 day 16 models respectively.

One of the main trends revealed in the results of the injection volume and injection time suite of models is that when the same volume of water is injected over more days, higher volumes of precipitation occur. As the injection rate increases the mixing between the injection water and formation water decreases because the amount of time the waters have to mix decreases. This lack of mixing leads to lower amounts of precipitation. Figures 3.4A and 3.4B compare day 2 of the 4 day and 16 day mixing models respectively. Comparing the two, we can see that it appears that the 4 day model has more total area of mixing than the 16 day model. However, Figures 3.4C and 3.4D compare the next day in the model, and for the 4 day model there was a significant growth in the effect of the injection, with water being quickly pushed out. For the 16 day model, the injection water has not moved as far, giving it more time to mix and react with the formation water. We believe that the increased mixing time, created by the lower injection rate, is what is causing the higher amounts of precipitation.

3.5 Conclusions

Here we created 50 reactive transport simulations to test how the mineral precipitation caused by brine mixing changes with geologic and industry variation, specifically with porosity, permeability, injection time and injection volume. Initial porosity and permeability varied between 6.5% - 26.5% and $7.5 \times 10^{-15} \text{ m}^2$ and $7.5 \times 10^{-11} \text{ m}^2$, respectively, and were found to have little to no effect on the total precipitation volume in PFLOTTRAN models. The highest permeability model generated a 1.3% higher absolute decrease in percent porosity than the lowest permeability model. This indicates that for brine injection models in PFLOTTRAN, only one set of porosity and permeability values need to be tested to represent a wide range of rock types.

Injection time and injection volume were found to have pronounced effects on total mineral precipitation volumes. Injection time was varied from 4 to 16 days, and had a considerable effect on total precipitation volume, with longer injection times causing up to 16% more absolute change in percent porosity than shorter injection times. We propose the cause of this increase in precipitation is high injection rates decreasing the amount of time the two waters can mix. Injection volume was varied from 189,250 liters to 2,271,000 liters, and had a considerable effect on total precipitation volume, with larger injection volumes causing up to 15.1% greater decrease in porosity than smaller injection volumes.

In this paper we address the effects that physical traits such as porosity, permeability, injection time, and injection volume had on precipitation during brine mixing. Moving forward, lab experiments are needed to verify the results found in these models. While this study provides valuable insight into understudied brine effects on the subsurface from physical traits, testing needs to be done on chemistry, with further study needed to quantify how brine chemistry may affect the longevity of wastewater disposal wells.

CHAPTER 4

EXTENDING THE LONGEVITY OF PRODUCED WATER DISPOSAL WELLS: EVALUATION USING REACTIVE TRANSPORT SIMULATION

Abstract

Produced water management is one of the biggest challenges associated with oil and gas development, with 21% of produced water in the United States managed using disposal wells. Produced water disposal costs between \$0.05-\$2.65 per barrel for injection, and with an average of 7 to 9 barrels of water produced for every barrel of oil it can add significantly to the cost of production. Texas contains 12,000 produced water disposal wells and 35% of all produced water in the United States is produced by oil and gas wells in Texas, making the Permian Basin an important location to study. Disposing of produced water through injection causes the mixing of the produced water with the formation water, this interaction can lead to mineral precipitation. Precipitation can occlude porosity and eventually lead to the abandonment of the well, making the investigation on which ions induce the highest volumes of mineral important to understanding how to treat produced water. Reactive transport modeling was used to investigate the effect of specific ion reduction in total possible injection time for a disposal well. Three simulations are created of a 25%, 50%, and 75% reduced concentration of each Ca^{2+} , Mg^{2+} , HCO_3^- , and SO_4^{2-} , and compared to the control results. Bicarbonate reduction increased the lifetime of the well the most, with a 75% reduction leading to over 4,000 years in gained injection time. Calcium reduction was also very successful, with an almost 14 year gain in injection time with a 75% reduction. These results can be used to inform targeted treatment of produced water to extend the lifetime of disposal wells.

4.1 Introduction

A global average of 220 million barrels of water is produced every day from oil and gas activities (Khatib & Verbeek, 2003). It is estimated that United States onshore wells generate 14 to 21 billion barrels of produced water every year (API, 1988; API, 2000; Veil et al., 2004), with an average ratio of 7 to 9 barrels of water for every 1 barrel of oil produced (EPA, 2000; Veil et al., 2004). As wells age, the ratio of water to oil produced rises (Clark & Veil, 2009), creating a growing problem of produced water in the United States.

Produced water management is one of the biggest challenges associated with oil and gas development (Shaffer et al., 2013). 92% of produced water in the United States is managed of using injection (API, 2000). Injection is divided into 2 categories: injection for enhanced oil recovery which represents 71% of produced water management, and injection into disposal wells at 21% of produced water management (API, 2000). Disposal of produced water can be expensive, with use of disposal wells costing between \$0.05-\$2.65 per barrel (Fakhru'l-Razi et al., 2009). With each barrel of oil causing multiple barrels of produced water, disposal costs can add significantly to the cost of oil.

There are various issues to consider when planning an injection well. Formations are chosen for disposal wells that are not hydrologically connected to future sources of drinking water or producing formations to limit the potential impact of injection on water resources (Rubinstein & Mahani, 2015). Operators also consider optimization of chemical compatibility between the produced water and formation water (Clark & Veil, 2009), as the brine chemistry and chemistry of produced water can vary depending on location (Engle et al., 2016; Hanor, 1994; Land, 1987; Lowenstein et al., 2003; Rubinstein & Mahani, 2015). Chemistry of the formation and disposed waters control potential chemical reactions between the two waters that can result in mineral

precipitation, blocking permeability and reducing the effectiveness and lifetime of the disposal well.

One way to manage chemical interactions between produced water and formation water is to treat the produced water prior to well disposal to ensure chemical compatibility between waters. Produced water starts with chemistry of flowback water, which is a mix of hydraulic fracturing fluid and formation water returning to the surface, but as the well ages produced water is dominated by formation water that is co-produced with oil (King, 2012). Treatment of produced water is comprised of a number of different processes, a review of which is outside the scope of this paper, but in general treatment starts with the removal of solids and organic compounds using a combination of filtration, separation, flocculation, and bioreactors (Fakhru'l-Razi et al., 2009). After the removal of solids and organic compounds, total dissolved solids (TDS) is evaluated and treated as needed using water desalination methods for produced water that include: mechanical vapor compression, membrane distillation, and forward osmosis (Shaffer et al., 2013) with new methods such as electrodialysis being developed (Sirivedhin et al., 2004). Variation in the desalination method can change the efficiency of the removal of specific ions (Sirivedhin et al., 2004). A small volume of mineral precipitation can cause a well to plug in brine injection scenarios (Marsac & Navarre-Sitchler, In prep a), making the investigation on which ions induce the highest volumes of mineral important to understanding how to treat produced water.

The Permian Basin is a 75,000 sq mile area located in west Texas and southeastern New Mexico (Railroad Commission of Texas, 2018). It contains 32 oil plays (Dutton et al., 2005), with over 2 million barrels of oil produced per day (Railroad Commission of Texas, 2018). This is only expected to increase with over 5,000 drilling permits issued between January and July of 2018 (Railroad Commission of Texas, 2018), and as of September 2018 3,722 wells are drilled but

uncompleted (U.S Energy Information Administration, 2018). Texas produces 35% of all the produced water in the United States (Clark & Veil, 2009) and has approximately 12,000 disposal wells (McCurdy, 2011), making this an important location to study produced water disposal wells.

Here we use reactive transport models to study how produced water chemistry affects mineral precipitation in disposal wells in the Permian Basin. We draw on a database of brine groundwater in the Permian Basin (Marsac & Navarre-Sitchler, In prep a) to simulate the inorganic composition of potential produced water. The database allows us to estimate an average Permian Basin brine as a control water, and vary the concentration of ions to simulate how produced water chemistry affects the lifetime of disposal wells. These simulations will allow us to make recommendations for treatment of produced water that will minimize mineral precipitation.

4.2 Methods

Thirteen reactive transport models were constructed to evaluate the impact of removal of specific ions on the longevity of an injection well. Over time mineral precipitation clogs pores around the injection zone and reduces porosity to zero, preventing further disposal of produced water. We chose four ions common in produced water and varied the concentrations to evaluate the efficacy of treating produced water on mitigating mineral precipitation: Ca, Mg, SO₄ and HCO₃. These ions are the constituents of the three minerals found to precipitate in chemically similar waters: dolomite (CaMg(CO₃)₂), anhydrite (CaSO₄) and calcite (CaCO₃) (Marsac & Sitchler, *In Prep*). One reactive transport model represents a control or baseline simulation, a water developed from a database of groundwater in the Permian Basin (Marsac & Sitchler, *In Prep*) that represents the 25th percentile of TDS (total dissolved solids) in the Permian Basin, with a high Ca/Mg ratio and low Cl/SO₄ ratio. TDS of water produced in the Permian Basin varies from 20,000 ppm to 300,000 ppm (Boschee, 2014); the control water has a TDS of approximately 65,000 ppm.

This water created the most mineral precipitation in its TDS class in previous geochemical models (Marsac & Sitchler, *In Prep*), and was thus chosen for this study's investigation into mineral precipitation. For each ion chosen, three models were created as a variation from the control water with reduction of the ion concentration by 25%, 50%, and 75% (Table 4.1) and ran until porosity reached 0%. Thus, each model had a different run time based on the results. It is important to note that the simulations did not include feedback between reduction in porosity and potential geomechanical processes related to continued injection at low porosity. Stress and strain accumulation are not calculated, thus an end point of 0% porosity is a hypothetical end point meant only for comparison between the models as injection rates would likely need to be modulated based on geomechanical evaluation of a given injection formation. Extension of the models presented here into a geochemical framework that accounts for the reduction in porosity due to precipitation is a logical next step but outside the scope of the work presented here. For all models formation water chemistry is the same, representing the median water from our Permian Basin groundwater database.

All models are simulated in PFLOTRAN, a massively parallel, multiphase, multicomponent reactive transport code (Mills et al., 2007) and performed on Blue Waters, a petascale supercomputer located at the National Center for Supercomputing Applications and the University of Illinois Urbana-Champaign. Each model consists of a 100 m x 100 m x 100 m grid with 28 cells of variable size in each the x, y, and z direction. The variable grid allows for smaller cells near the injection zone, and larger cells farther away, to capture precipitation behavior right at the injection zone (Marsac & Navarre-Sitchler, *In prep a*; Marsac & Navarre-Sitchler, *in prep b*). Each axis, moving from 0 to 100 m, contains 4 cells of width 10 m, 20 cells of width 1 m, and 4 cells at 10 m, allowing for detailed 1 m³ grid cells in the center and large 1000 m³ cells on the

outside. The injection zone is 5 m³ with dimensions of 5 m x 1 m x 1 m, mimicking a horizontal disposal well. Initial porosity is 16.5%, and the matrix is quartz (83.2%) with 0.1% calcite, 0.1% dolomite and 0.1% anhydrite (Table 4.2). All models are simulated at 70°C, representing average depth and geothermal gradient in the Permian Basin (Ruppel et al., 2005). Injection occurs at a rate of 75,700 liters/day until porosity reaches 0%. Pressure in the models is initially hydrostatic, with injection as the only driver for groundwater flow. The top and bottom of the model are no flow boundaries, while the north, south, east and west faces have the same properties as the matrix, allowing water to leave the model.

Reaction rate is calculated by equation 4.1 as implemented in PFLOTRAN (Lichtner et al., 2013):

$$I_m = -a_m(\sum_l k_{ml}(T)P_{ml}) \left| 1 - (K_m Q_m)^{1/\sigma_m} \right|^{\beta_m} \text{sign}(1 - K_m Q_m) \quad (\text{Equation 4.1})$$

Where I_m in equation 4.1 is reaction rate (mol m⁻²s⁻¹), T is the temperature of the reaction in Kelvin, summation over l represents the parallel reaction mechanisms, K_m is the equilibrium constant (unitless), σ_m is Temkin's constant the average stoichiometric coefficient of the reaction (default is 1, unitless), β_m is the affinity power (default is 1, unitless), a_m is the specific mineral surface area (m²m⁻³), Q_m is the ion activity product (unitless), k_{ml} is a rate constant (mol m⁻²s⁻¹), and P_{ml} is a prefactor for the parallel reaction (m/K) (Lichtner et al., 2013).

4.3 Results

4.3.1 Control Water

The control water had injection for 1070 days, or 2.9 years, before reaching 0% porosity. Anhydrite, dolomite and calcite precipitated, with dolomite and calcite being the dominate constituents (Figure 4.1). For the purposes of this study the specific mineral does not matter, we are solely concerned with total mineral volumes. Previously we conducted simulations

Table 4.1 Water chemistries used in each of the 13 reactive transport models

Water	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	HCO₃ (ppm)	Cl (ppm)	SO₄ (ppm)	pH	TDS (ppm)
Formation Water	3721	1250	31425	499	264	59886	1401	6.9	98508
Control	2687	370	21544	282	156	38416	1165	6.43	64660
25% Lower Ca	2015	370	21544	282	156	38416	1165	6.43	63988
50% Lower Ca	1343	370	21544	282	156	38416	1165	6.43	63316
75% Lower Ca	672	370	21544	282	156	38416	1165	6.43	62645
25% Lower SO ₄	2687	370	21544	282	156	38416	874	6.43	64369
50% Lower SO ₄	2687	370	21544	282	156	38416	583	6.43	64078
75% Lower SO ₄	2687	370	21544	282	156	38416	291	6.43	63787
25% Lower HCO ₃	2687	370	21544	282	117	38416	1165	6.43	64621
50% Lower HCO ₃	2687	370	21544	282	78	38416	1165	6.43	64582
75% Lower HCO ₃	2687	370	21544	282	39	38416	1165	6.43	64543
25% Lower Mg	2687	277	21544	282	156	38416	1165	6.43	64567
50% Lower Mg	2687	185	21544	282	156	38416	1165	6.43	64474
75% Lower Mg	2687	92	21544	282	156	38416	1165	6.43	64381

Table 4.2 Rate constants and surface areas used in numerical models

Mineral	Rate Constant (moles m ⁻² s ⁻¹)	Surface Area (m ² m ⁻³)
Quartz	6.61x10 ⁻¹³ , ¹	47700 ¹
Dolomite	1.55 x10 ⁻⁰⁶ , ²	200900 ²
Calcite	2.95 x10 ⁻⁰⁸ , ³	26150 ³
Anhydrite	6.46 x10 ⁻⁰⁴ , ⁴	17820 ⁵

¹Tester et. al (1994), ²Busenburg and Plummer (1982),
³Plummer et al. (1978), ⁴Palandri & Kharaka (2004) ,
⁵Jeschke et al. (2001)

to investigate how the presence or absence of dolomite would affect total mineral volume. We found that there was on average less than a 1% difference in mineral volume between the same model with and without dolomite (Marsac & Navarre-Sitchler, In prep a).

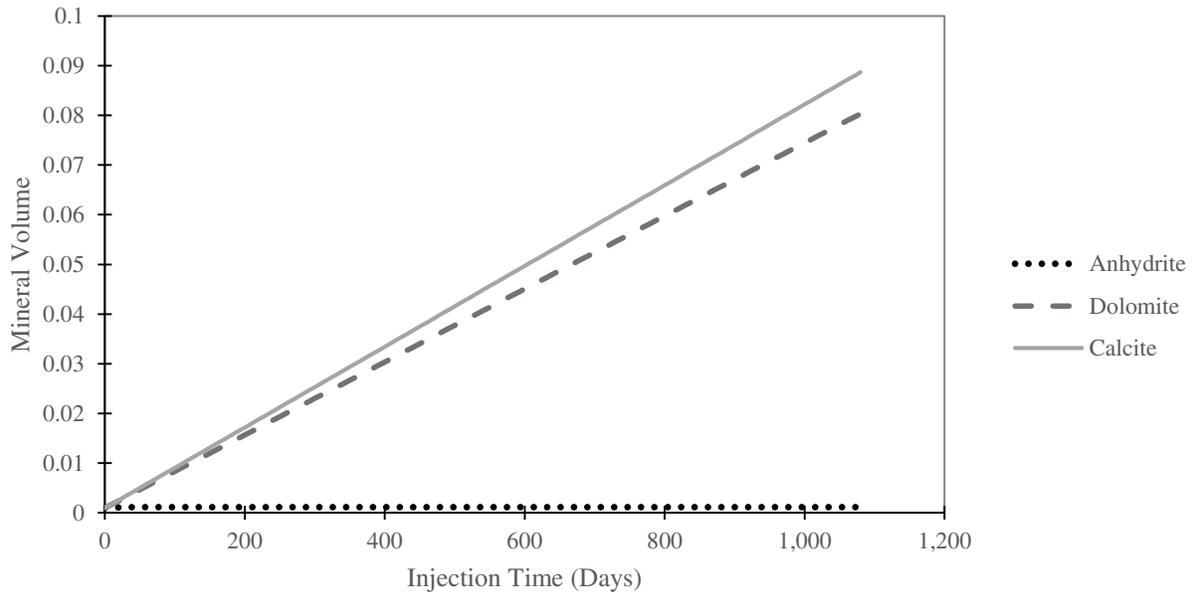


Figure 4.1 Graph of the control water and the minerals that are precipitating over the injection time. Most of the mineral volume is made up of calcite and dolomite. Anhydrite only makes up a minimal portion of the mineral volume, and its volume remains constant over time while calcite and dolomite continue to precipitate.

4.3.2 Calcium Reduction

Three models were simulated with calcium reduced by 25%, 50%, and 75% (Figure 4.2). The 25% reduction of calcium led to an increase in injection time of 580 days, for a total injection time of 1650 days. The 50% reduction of calcium led to an increase in injection time of 2120 days, for a total injection time of 3190 days. The 75% reduction of calcium led to an increase in injection time of 5110 days, for a total injection time of 6180 days or 16.9 years. The difference between the control and calcium reduction simulations are the volumes of calcite and dolomite precipitation. Calcite precipitation decreases while dolomite precipitation increases, but there is a decrease in total precipitation volume leading to an increase in injection time.

4.3.3 Magnesium Reduction

Three models were made to show the effect of magnesium reduction by 25%, 50%, and 75% (Figure 4.3). The reduction of magnesium by 25% led to an increase in injection time of 70 days, for a total injection time of 1140 days. The reduction of magnesium by 50% led to an increase in injection time of 170 days, for a total injection time of 1240 days. The reduction of magnesium by 75% led to an increase in injection time of 310 days or 0.85 years, for a total injection time of 1140 days. As magnesium is reduced, dolomite volume decreases, as it is the only precipitating mineral containing magnesium. The lack of dolomite frees up calcium which increases the total volume of calcite in reduced magnesium models compared to the control model. The volume of anhydrite precipitated is the same as the control model.

4.3.4 Sulfate Reduction

Sulfate reduction was represented by three reactive transport models with 25% reduction, 50% reduction, and 75% reduction in sulfate concentration from the control water (Figure 4.4). For a 25% reduction in sulfate, a 20 day decrease in injection time was observed, for a total

injection time of 1050 days. For a 50% reduction in sulfate, a 40 day decrease in injection time was observed, for a total injection time of 1030 days. For a 75% reduction in sulfate, a 50 day decrease in injection time was observed, for a total injection time of 1020 days. As sulfate concentration decreases, calcite volume increases creating the reduction in injection time.

4.3.5 Bicarbonate Reduction

Bicarbonate reduction was tested with three reactive transport models representing a 25% decrease, 50% decrease and 75% decrease in bicarbonate concentration from the control water (Figure 4.5). For a 25% reduction in bicarbonate, a 1190 day increase in injection time was observed, for a total injection time of 2260 days. For a 50% reduction in bicarbonate, a 7350 day increase in injection time was observed, for a total injection time of 8420 days, or about 23 years. For a 75% reduction in bicarbonate, we ran a model for 30,000 days or over 80 years, results showed a change in porosity of less than 0.3%. To run this model to completion on Blue Waters would take an estimated 30,000 node hours, and was deemed unnecessary due to the linear trend in porosity reduction. By extrapolating these results out over time, assuming a continued linear trend in precipitation, we expect that porosity would reach 0% after 1,747,830 days, or almost 4789 years of injection. Both calcite and dolomite contain bicarbonate, and these minerals dominate the precipitation volume (Figure 4.1). By reducing bicarbonate, calcite and dolomite mineral volumes are greatly reduced, leading to the immense gains in injection time.

4.4 Discussion

It is important to note that precipitation and porosity reduction is concentrated around the injection zone, thus preventing further injection is caused by only a small region of the model domain. The majority of the cells in the model maintain the original porosity of 16.5% (Figure 4.6). This indicates that very little mineral volume, compared to the volume effected by injection,

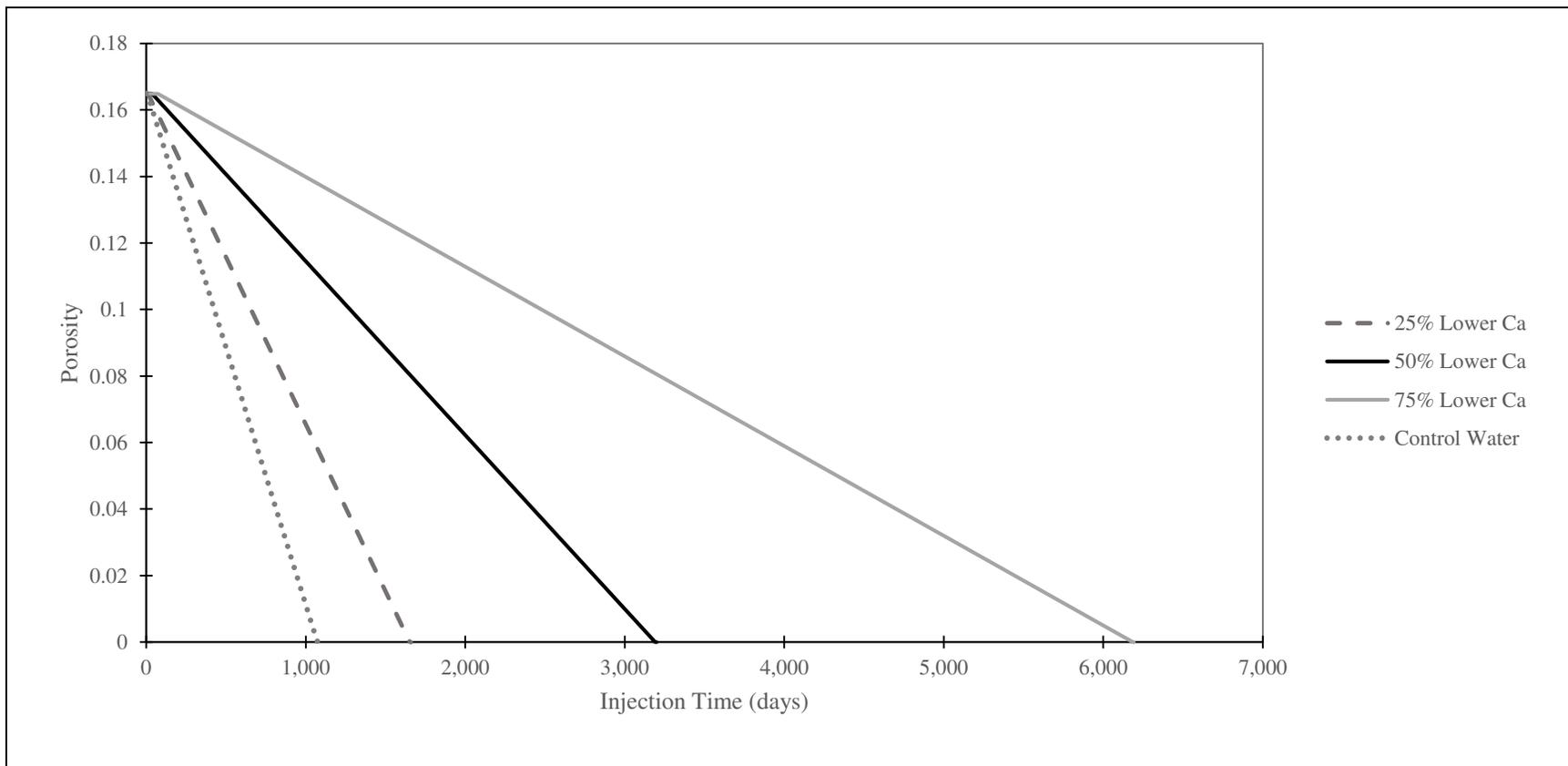


Figure 4.2 Porosity results of calcium reduction models compared to the control water. Injection time represents how long the injection occurs before porosity reaches zero. A 25%, 50%, and 75% reduction in calcium all increased injection time.

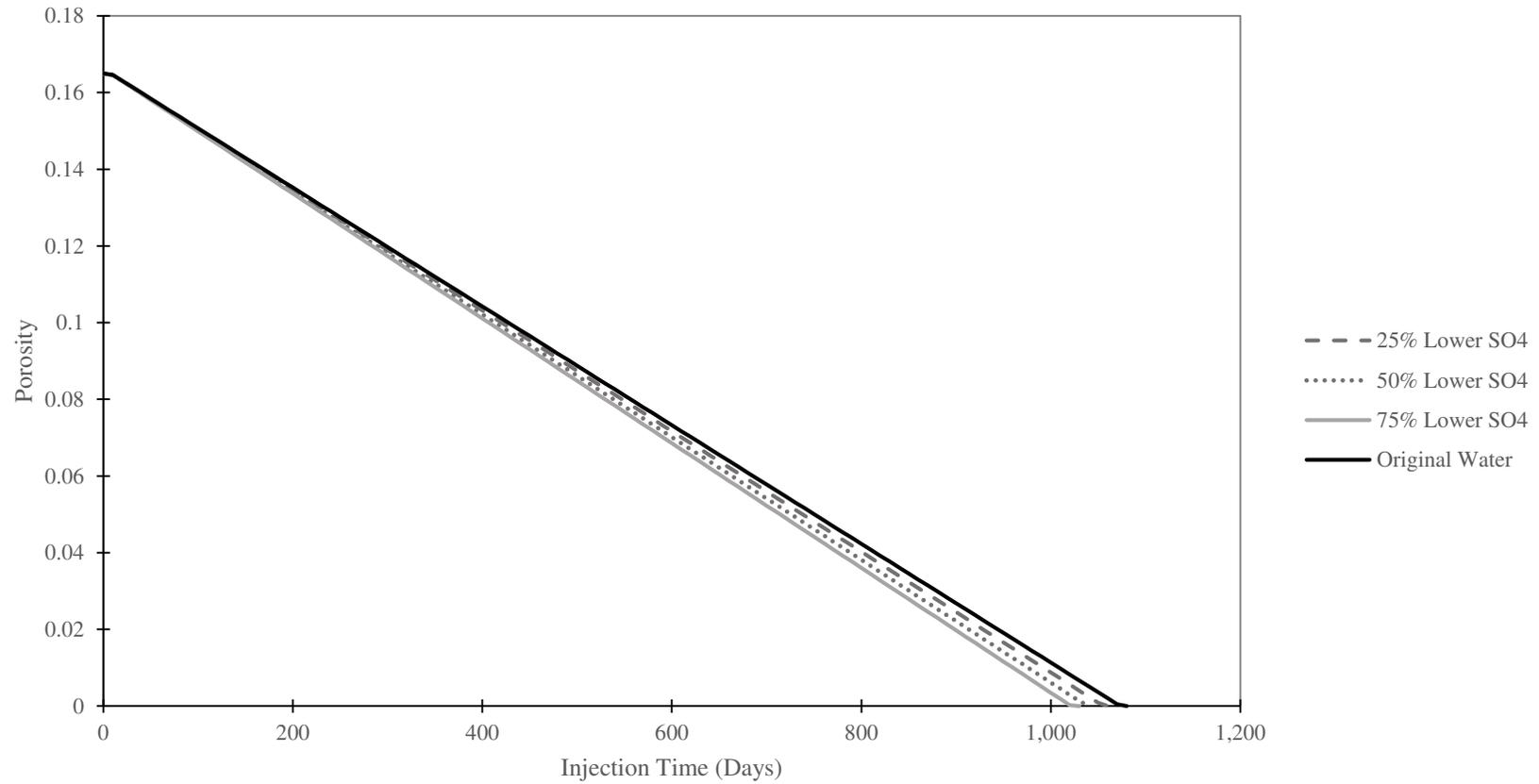


Figure 4.3 Mineral precipitation trends shown as porosity reduction over time for each of the magnesium reduction models, compared to the control water model. Each of the 25%, 50%, and 75% reductions of magnesium lead to increases in injection time over the control water.

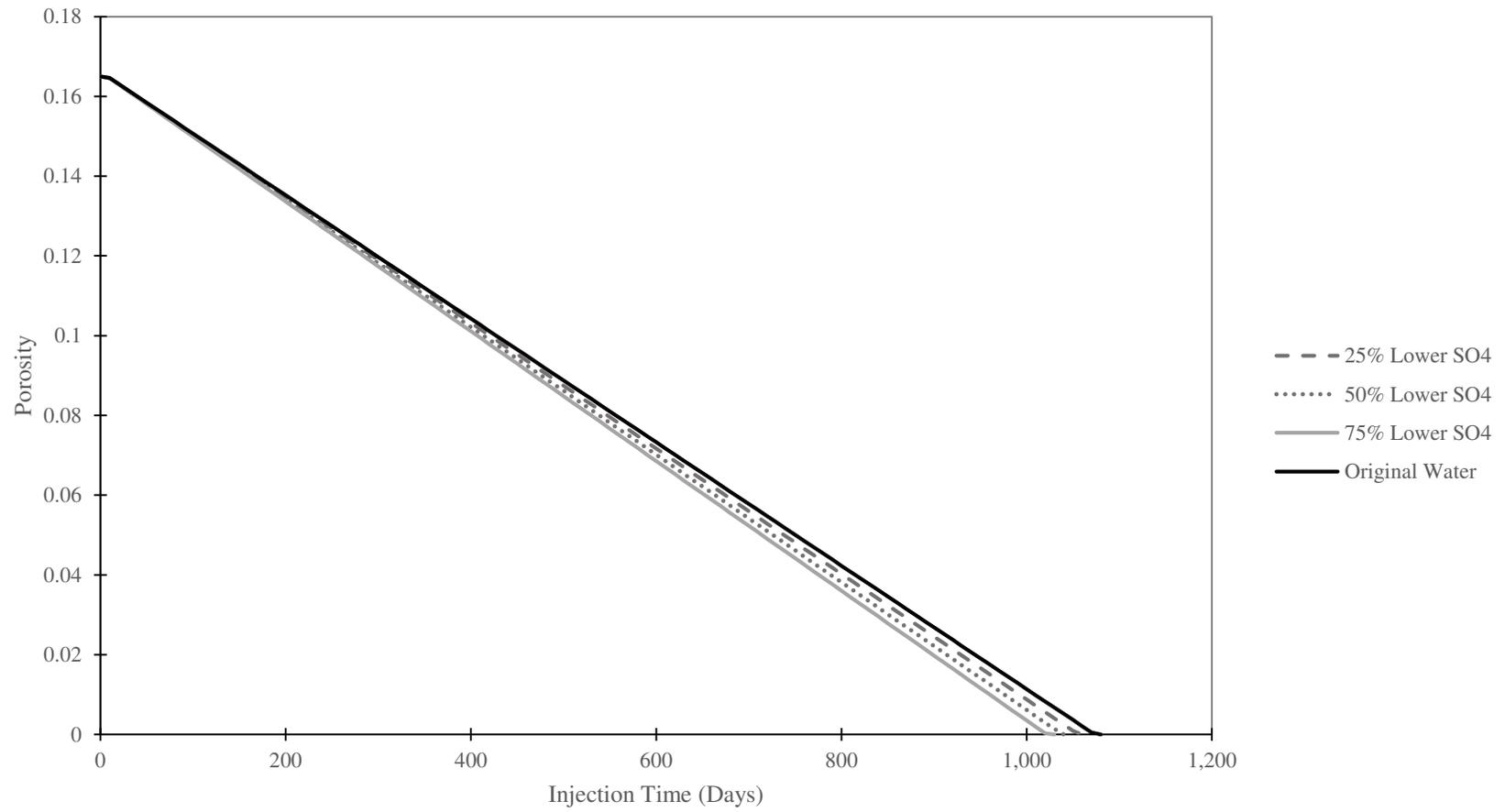


Figure 4.5 Results of bicarbonate reduction shown as trends in porosity over injection time. Each of the 25%, 50%, and 75% reductions in bicarbonate caused gains in injection time, however the gains are significantly higher compared to other ions.

can reduce the efficacy of a disposal well. Precipitation occurring directly around the injection well enforces the idea that mineral precipitation is of particular concern in produced disposal wells, and in any scenario where brine is being injected into the subsurface.

While the majority of models testing the reduction of ion concentrations to decrease mineral precipitation were successful, some were not (Table 4.3). Here, success is defined as increased injection time, and the larger the gain in time the more successful the reduction of that particular ion is at increasing the longevity of produced water disposal wells. Magnesium reduction did increase injection time, but even reducing the magnesium concentration by 75% only gave an extra 310 days of injection. Magnesium is only a component of one of the three minerals that can precipitate in all models, dolomite (Figure 4.1).

The models that were the most successful reduced an ion that was present in at least two of the minerals present; calcite, dolomite, and anhydrite. Calcium is present in calcite, dolomite, and anhydrite; and even a 25% reduction in calcium concentration led to an increase of injection time of 580 days or over 1.5 years. This is almost twice as much increased injection time than a 75% reduction in magnesium. A 75% reduction in calcium led to an increase in injection of 5110 days, or 14 years. This is a significant gain in injection time, indicating that treatment of produced water for calcium is worth pursuing as a method to increase longevity of the produced water disposal wells.

Bicarbonate is needed in the formation calcite and dolomite, the two minerals dominating precipitation volumes in the control water model (Figure 4.1). Bicarbonate had the largest gain in injection time from a 25% reduction in concentration, with an increase in injection time by 1190 days or over 3 years. A 75% reduction in bicarbonate increases injection time by

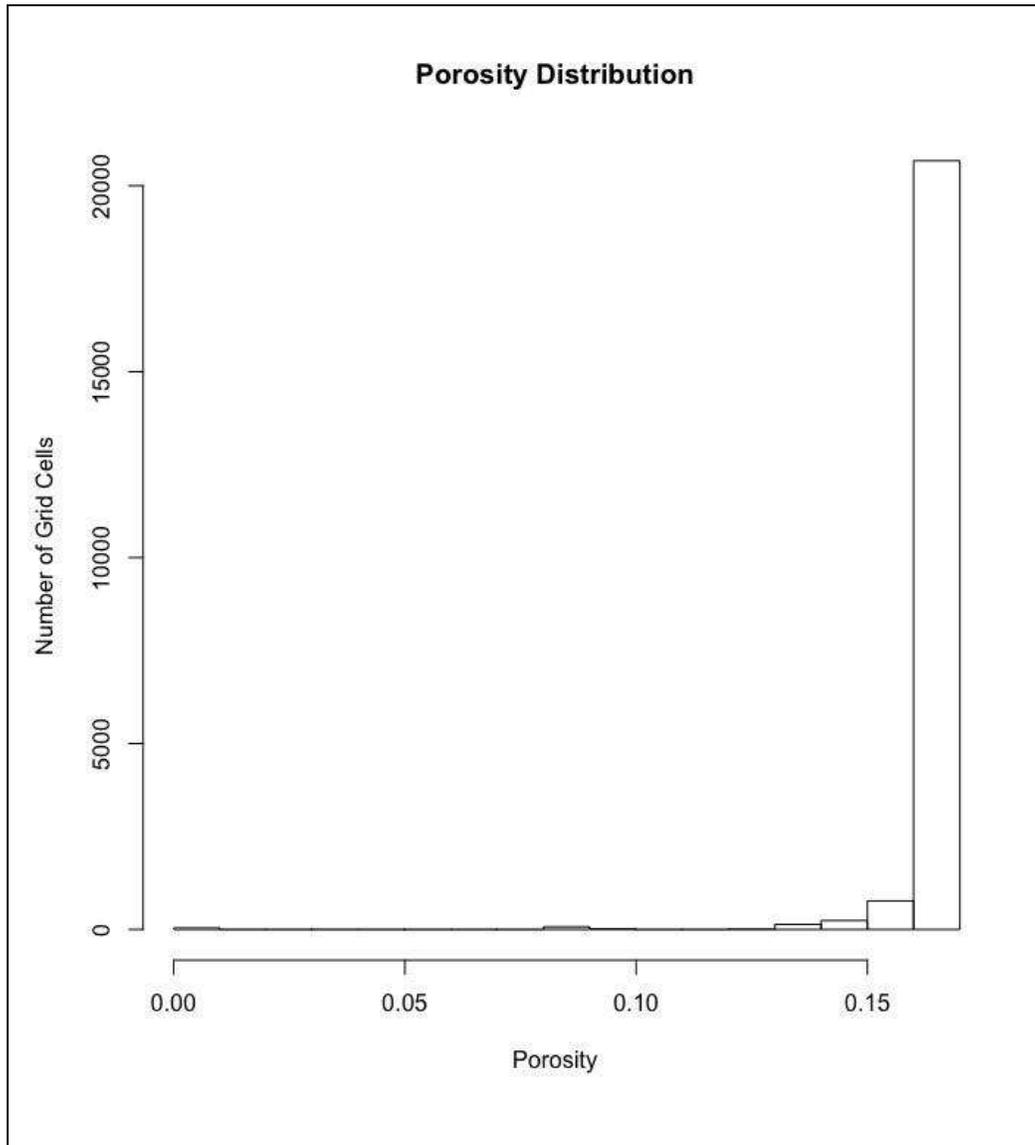


Figure 4.6 Histogram of porosity distribution in the control water model. The majority of cells maintain the original porosity of 16.5%, while injection is blocked by a small minority reaching 0% porosity.

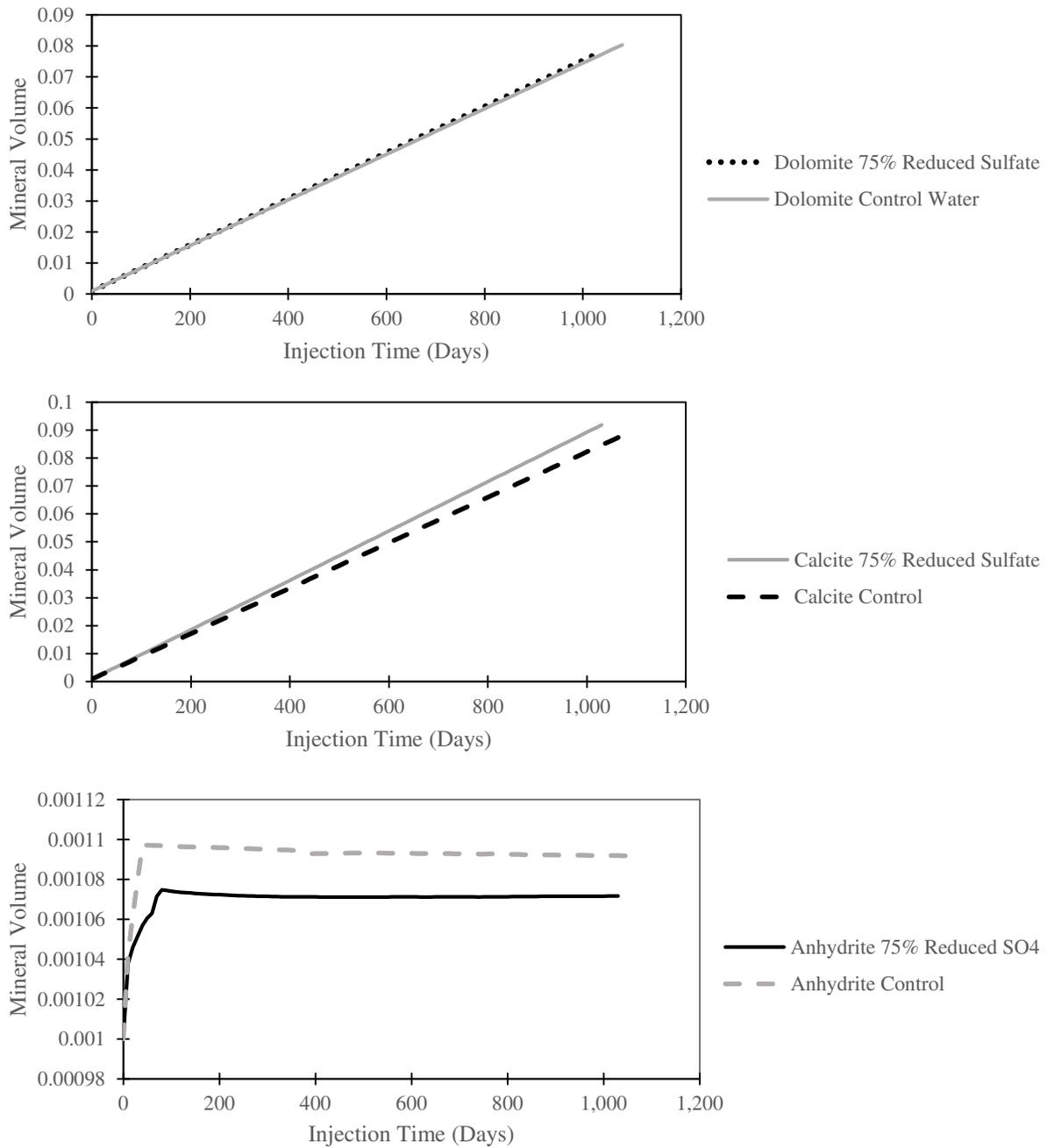


Figure 4.7 Graphs comparing the mineral volume over time for the control model and the 75% reduced sulfate model for each dolomite, calcite, and anhydrite. Dolomite concentration is similar in the control and reduced. Anhydrite volume lowers with reduced sulfate, but the total volume of anhydrite so low this doesn't have an appreciable effect on the model. Calcite volume is higher in the sulfate reduced model compared to the control, causing the decrease in injection time.

Table 4.2 Injection Time Results

<u>Water</u>	<u>Injection Time (Days)</u>	<u>Gained Injection Time (Days)</u>
Control (TLCaHCIL)	1070	
25% Lower Ca	1650	580
50% Lower Ca	3190	2120
75% Lower Ca	6180	5110
25% Lower SO ₄	1050	-20
50% Lower SO ₄	1030	-40
75% Lower SO ₄	1020	-50
25% Lower HCO ₃	2260	1190
50% Lower HCO ₃	8420	7350
75% Lower HCO ₃	1748900	1747830
25% Lower Mg	1140	70
50% Lower Mg	1240	170
75% Lower Mg	1380	310

1747830 days or almost 4800 years. These large increases in injection time indicate that treating produced water for bicarbonate is worth pursuing as a method for increasing the longevity of produced water disposal wells.

Sulfate is present only in anhydrite, which is the mineral contributing the least to total mineral volume (Figure 4.1). Reducing sulfate decreased the injection time, and we propose this is due to two factors: the first that anhydrite is a small component of the mineral volume, and the second that decreasing the sulfate concentration increases the availability of ions, specifically Ca, needed for the formation of the dominant minerals: calcite and dolomite. Anhydrite volume does decrease with a 75% reduction in sulfate (Figure 4.7), but only by 0.002%. While dolomite volume remains approximately the same over the 1020 day injection time of the 75% reduced sulfate model, calcite volume increases with a 75% reduction in sulfate by 0.23% (Figure 9). The

gain in volume of calcite is significantly more than the decrease in volume of anhydrite, accounting for the decreased injection time.

4.5 Conclusions

In this study we created 13 reactive transport models to test the how reducing the concentration of ions present in brine will reduce mineral precipitation and thus increase the total possible injection time. Calcite, dolomite, and anhydrite are the minerals that precipitate in our control model, so ions tested include: Ca, Mg, HCO_3 , and SO_4 . For each ion, 3 models are created of a 25%, 50%, and 75% reduction in ion concentration. Reduction of calcium, magnesium, and bicarbonate all create gains in injection time, but gains with magnesium reduction were minimal at 310 days with a 75% reduction. Calcium created significant gains in injection time with 5110 gained injection days with a 75% reduction, and bicarbonate created the largest gains in injection time with over 4000 years in injection time gained with a 75% reduction. Reduction of sulfate reduced injection time by 50 days for a 75% concentration reduction. While anhydrite volume is reduced, this decrease in injection time is caused by an increased volume of calcite.

These results indicate that treatment of calcium and bicarbonate in produced water should be pursued as a way to increase the longevity of produced water disposal wells, or in any well where brine is being injected into the subsurface. Further study is needed to investigate whether the proposed treatments are viable at the scale of an oil and gas operation.

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CHAPTER 5

CONCLUSIONS

This dissertation has covered three different studies, all with the common thread of investigating anthropogenic induced brine mixing driving mineral precipitation in the Permian Basin subsurface using reactive transport modeling. In Chapter 2, we investigated the mineral precipitation effects of using brines during hydraulic fracturing. First, we created a database of Permian Basin groundwater and used it to create batch models of brine mixing scenarios of chemistries with varying TDS, Ca, Mg, Na, and Cl. Batch model waters that create the highest volume of mineral precipitation are then used in reactive transport models that simulate the water injection associated with hydraulic fracturing. We found that while batch models indicated that mineral precipitation would be minimal, reactive transport models indicated that this small amount of precipitation concentrates in the area around the injection site greatly reducing porosity and damaging the formation.

In Chapter 3, we investigated how geologic formation variability and industry injection variation effect mineral precipitation associated with brine mixing. Two suites of 25 brine injection reactive transport models are developed, the first to test variation in porosity and permeability of the formation, and the second to test variation in injection volume and injection time. All models have the same water chemistry, porosity varies between 6.5%-26.5%, permeability varies between $7.5 \times 10^{-15} \text{ m}^2$ and $7.5 \times 10^{-11} \text{ m}^2$, injection time varies from 4 to 16 days, and injection volume varies from 50,000 gallons to 600,000 gallons. We found that initial porosity has no effect on mineral precipitation and initial permeability can cause mineral precipitation differences of 1.3%. Injection volume differences caused a 15.1% increase in

mineral precipitation and injection time differences caused a 16% increase in mineral precipitation.

In Chapter 4, we investigated how treatment of brines for specific ions could affect the longevity of wastewater disposal wells. The 4 ions we test are Ca, Mg, SO₄, and HCO₃. For each ion, a reactive transport model is made for a 25%, 50%, and 75% reduction in concentration. These models are allowed to run until porosity reached 0%. A 75% reduction in sulfate concentration reduces injection time by 50 days. While a 75% reduction of magnesium causes a 310 gain in injection time. Calcium and bicarbonate saw the largest gains in injection time, with 5110 days gained with a 75% reduction in calcium and over 4000 years gained with a 75% reduction in bicarbonate.

This dissertation provided many new takeaways for the field of brine mixing reactive transport models. Here we have learned that batch models do not predict reactive transport model results for porosity changes in precipitation scenarios. This is due to the variation in how space is treated in these models, with reactive transport models allowing the concentration of precipitation in critical areas of the model. Another important takeaway from this research is that initial porosity has no effect on mineral precipitation, which indicate that precipitation model results are applicable to formations over a large range of porosities. Permeability had a small effect on precipitation results, demonstrating that model results could be applied over a range of permeabilities with a small error.

This dissertation also provided new data for water supply and disposal for the energy sector. Here we found TDS limits to prevent detrimental mineral precipitation during hydraulic fracturing. Another important takeaway is that injection time and injection volume have a large effect on mineral precipitation volumes, with lower volumes over shorter times causing the

lowest amount of precipitation. Finally, in Chapter 4, we found that treating water for calcium or bicarbonate before using deep well disposal could greatly increase well longevity.

I hope this dissertation provides groundwork for moving forward in water management in the energy sector. Using freshwater for hydraulic fracturing should be abandoned, with brines becoming the new normal and more advanced treatment, geochemical modeling, and chemistry analysis used to ensure the safety of the formation. The demand and cost for water in an increasing dry environment will force this change, so it would be prudent for companies to begin research and implement change now. We have shown that injection time and volume matter, thus careful planning of well schedules and continued study on efficiency could lead to significantly less mineral precipitation, protecting the well integrity. Finally, we have shown that reducing specific ions can greatly reduce mineral precipitation, extending the lifetime of disposal wells. This can be used to inform wastewater treatment and where companies should spend money on research and development of treatment techniques.

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