



Department for
Business, Energy
& Industrial Strategy

Primary Store Geochemical Model & Report

Key Knowledge Document

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Foreword

The Net Zero Teesside (NZT) project in association with the Northern Endurance Partnership project (NEP) intend to facilitate decarbonisation of the Humber and Teesside industrial clusters during the mid-2020s. Both projects will look to take a Final Investment Decision (FID) in early 2023, with first CO₂ capture and injection anticipated in 2026.

The projects address widely accepted strategic national priorities – most notably to secure green recovery and drive new jobs and economic growth. The Committee on Climate Change (CCC) identified both gas power with Carbon Capture, Utilisation and Storage (CCUS) and hydrogen production using natural gas with CCUS as critical to the UK's decarbonisation strategy. Gas power with CCUS has been independently estimated to reduce the overall UK power system cost to consumers by £19bn by 2050 (compared to alternative options such as energy storage).

Net Zero Teesside Onshore Generation & Capture

NZT Onshore Generation & Capture (G&C) is led by bp and leverages world class expertise from ENI, Equinor, and TotalEnergies. The project is anchored by a world first flexible gas power plant with CCUS which will compliment rather than compete with renewables. It aims to capture ~2 million tonnes of CO₂ annually from 2026, decarbonising 750MW of flexible power and delivering on the Chancellor's pledge in the 2020 Budget to "support the construction of the UK's first CCUS power plant." The project consists of a newbuild Combined Cycle Gas Turbine (CCGT) and Capture Plant, with associated dehydration and compression for entry to the Transportation & Storage (T&S) system.

Northern Endurance Partnership Onshore/Offshore Transportation & Storage

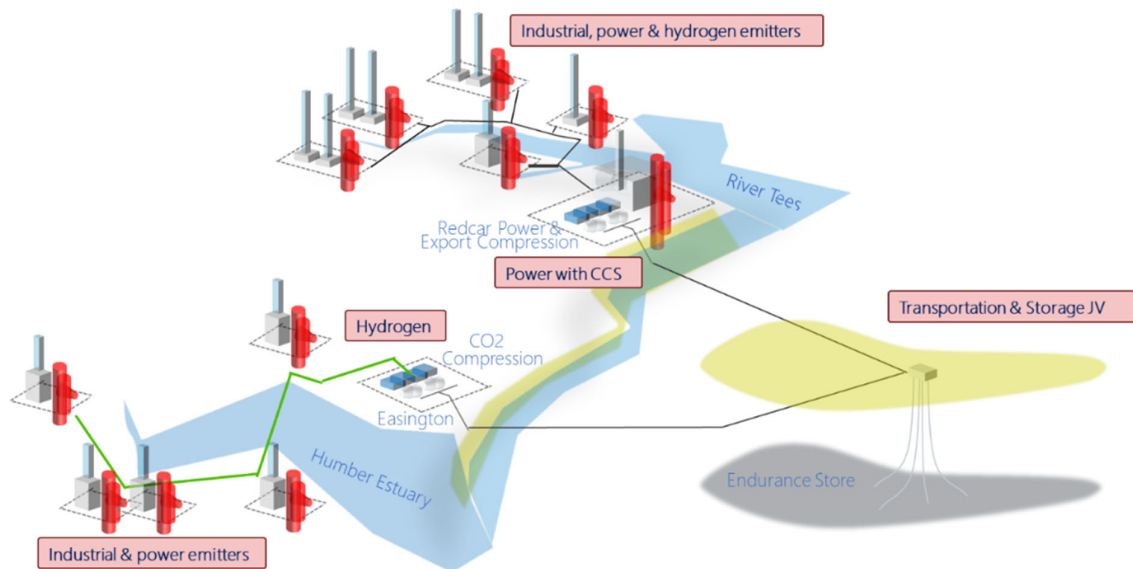
The NEP brings together world-class organisations with the shared goal of decarbonising two of the UK's largest industrial clusters: the Humber (through the Zero Carbon Humber (ZCH) project), and Teesside (through the NZT project). NEP T&S includes the G&C partners plus Shell, along with National Grid, who provide valuable expertise on the gathering network as the current UK onshore pipeline transmission system operator.

The Onshore element of NEP will enable a reduction of Teesside's emissions by one third through partnership with industrial stakeholders, showcasing a broad range of decarbonisation technologies which underpin the UK's Clean Growth strategy and kickstarting a new market for CCUS. This includes a new gathering pipeline network across Teesside to collect CO₂ from industrial stakeholders towards an industrial Booster Compression system, to condition and compress the CO₂ to Offshore pipeline entry specification.

Offshore, the NEP project objective is to deliver technical and commercial solutions required to implement innovative First-of-a-Kind (FOAK) offshore low-carbon CCUS infrastructure in the UK, connecting the Humber and Teesside Industrial Clusters to the Endurance CO₂ Store in the Southern North Sea (SNS). This includes CO₂ pipelines connecting from Humber and Teesside compression/pumping systems to a common subsea manifold and well injection site

at Endurance, allowing CO₂ emissions from both clusters to be transported and stored. The NEP project meets the CCC's recommendation and HM Government's Ten Point Plan for at least two clusters storing up to 10 million tonnes per annum (Mtpa) of CO₂ by 2030.

TEESSIDE (NZT)



HUMBERSIDE (ZHC)

NEP

The project initially evaluated two offshore CO₂ stores in the SNS: 'Endurance', a saline aquifer formation structural trap, and 'Hewett', a depleted gas field. The storage capacity requirement was for either store to accept 6+ Mtpa CO₂ continuously for 25 years. The result of this assessment after maturation of both options, led to Endurance being selected as the primary store for the project. This recommendation is based on the following key conclusions:

- The storage capacity of Endurance is 3 to 4 times greater than that of Hewett
- The development base cost for Endurance is estimated to be 30 to 50% less than Hewett
- CO₂ injection into a saline aquifer is a worldwide proven concept, whilst no benchmarking is currently available for injection in a depleted gas field in which Joule-Thompson cooling effect has to be managed via an expensive surface CO₂ heating solution.

Following selection of Endurance as the primary store, screening of additional stores has been initiated to replace Hewett by other candidates. Development scenarios incorporating these additional stores will be assessed as an alternative to the sole Endurance development.

Executive Summary

Geochemical simulation, combined with a reservoir physics, can be used to simulate the subsurface physical and chemical processes relevant to the storage of CO₂ and hence reduce the inherent uncertainty and risks. The overall stability and equilibrium state of the subsurface can be described within a broad spectrum of geochemical simulation techniques, the basis for which is a conceptual geochemical model of a given system. In this study, the system of interest is the Bunter Sandstone Formation in the Endurance structure, the potential subsurface store of supercritical CO₂ injection as part of the Net Zero Teesside CCUS project.

Two geochemical simulation packages, PHREEQC and Geochemist's Workbench (GWB) were used, together with a custom conceptual model, to define the subsurface system and make predictions about its response to the injection of CO₂. The results indicate that the injection of supercritical CO₂ into the Endurance structure is unlikely to have a net negative impact on either the reservoir or the clay or halite seals, with very low risk of damage from chemical processes.

The dissolution of CO₂ into the brine causes the pH to drop, but this drop is mitigated (buffered) by interaction with carbonate minerals. Total CO₂ solubility is limited by the presence of buffering minerals but is broadly in line with, if slightly lower than, typical values for saline brines of ~1 mol%. Mineral interactions with the acidic brine are not substantial enough to lead to significant formation or clastic seal damage.

In the near-wellbore region, near complete vaporisation of brine by dry CO₂ due to mutual solubility effects means that there will be no basis for any chemical reactions to occur and the risk of sanding through cement dissolution is extremely limited. At the reservoir/seal interface, the presence of clay minerals has little to no effect on the likelihood of mineral dissolution and so the clastic seal integrity will not be impacted. If the acidic reservoir brine were to reach the clay/halite interface, some dissolution of the halite into the undersaturated brine is predicted. However, this would become quickly saturated, forming a boundary layer beyond which no more halite is dissolved. Thus, the risk to halite integrity is also limited.

Near well-bore geochemical processes were also studied via a fully coupled reactive transport simulation using GEM™. The model investigated the potential for injectivity loss caused by near-wellbore dry-out and halite precipitation and tested mitigation schemes by periodic fresh-water flushing.

The results indicate that a drying front propagates into the reservoir at high injection rates, where it causes modest porosity and permeability loss, but has negligible effect on injectivity. However, at low injection rates a moving drying front does not develop. Capillary-induced brine back-flow causes massive localised halite precipitation in the very near-wellbore region, resulting in catastrophic injectivity loss. The injection rate threshold between these regimes is ~30 mmscfd (~0.6 MTPA), although this threshold rate is extremely sensitive to brine relative permeability and capillary pressure.

Periodic flushing with fresh water can entirely prevent halite precipitation and injectivity loss. The effectiveness of this mitigation is insensitive to the details of the flushing schedule, so it is a flexible technique that can be optimised based on operational and/or cost criteria.

1.0 Introduction

The purpose of this document is to summarize the work program completed on geochemical aspects of the integrated subsurface description of the Endurance store. This follows previous studies such as those completed as part of the White Rose project. Early analysis of previous studies highlighted a number of key areas to further advance understanding, which were drawn together and used in the development of geochemical models used to test subsurface uncertainties and assess risk.

Subsurface storage risks can be broadly classified as those relating to containment, capacity, injectivity and monitorability, with those covered by this document focussing on containment and injectivity. Key areas to advance geochemical understanding to assess containment and injectivity uncertainties and risks at the Endurance store were identified as:

CO₂ and brine interactions within the reservoir and within the two key sealing formations, the Röt Clay and the Röt Halite, and any impact on containment integrity.

Mechanisms that control halite precipitation within the reservoir following the injection of CO₂ and its impact to injectivity, and mitigation effectiveness by periodic fresh-water flushing.

These were investigated via two discrete geochemical modelling and simulation studies.

Part A: Geochemical Modelling

2.0 Background

Water is ubiquitous in subsurface sedimentary accumulations of the type typically considered for long-term CO₂ storage. Its composition is dependent on a wide range of factors, but is generally deemed to be in equilibrium with other components of the system, e.g. rock, hydrocarbons, etc. Any disturbance of the subsurface system, such as the injection of CO₂, will affect this equilibrium and lead to a series of reactions which may have wide-reaching consequences.

CO₂ is readily soluble in water, depending on its salinity and, if not buffered, will cause a drop in pH. This in turn will affect the relative solubility of minerals in the system and may lead to dissolution or precipitation, which will have an impact on the flow properties of the rock. Furthermore, interaction of low pH brine with soluble minerals may cause damage to the seal

rock increasing the risk of gas leakage. Conversely, near-well reservoir rock properties may be improved and redistribution of mineral components may improve seal retention properties.

Geochemical modelling is the process used to simulate the potential interactions outlined above. It can take into account a number of different system components, conditions and transitions, e.g. brine composition and salinity, formation mineralogy, gas composition, presence of hydrocarbons, temperature and pressure changes, mineral dissolution and precipitation, ion exchange, fluid mixing and many others.

Combined with deep understanding of the reservoir physics (flow dynamics), geochemical modelling can be used to predict the subsurface impact of CO₂ injection, and highlight any potential associated risks.

2.1 Aims

A detailed understanding of the combined chemical and physical interactions occurring as a result of CO₂ injection reduces the uncertainty associated with formation and seal integrity. Insight from geochemical modelling into the potential reactions can inform predictions relating to near-wellbore sanding, formation damage, injectivity problems and seal damage.

Geochemical modelling will also allow prediction of the likely composition of any potential produced water, which will support decisions related to its treatment and/or disposal.

The aim of this study is to provide an illustrative example of a typical geochemical workflow, focussed on the Northern Endurance Partnership. The proposed injection of supercritical CO₂ into the Endurance structure in the Southern North Sea is evaluated using conceptual and geochemical modelling and specific areas of risk and uncertainty are addressed.

3.0 Geochemical Modelling and Interpretation

The geochemical modelling process aims to provide an insight into those subsurface interactions which could impact the efficacy and efficiency of the carbon storage process. The process employs software using empirical system data to construct a range of scenarios to make inferences about the overall stability of the system. The results can inform the decision-making process at many stages of project development.

These aspects of the subsurface can be described within a broad spectrum of geochemical simulation techniques. In the case of homogeneous reactions and some heterogeneous reactions, an equilibrium, saturation model can be applied. For more advanced evaluations, kinetic rate laws, reaction path and mineral stability models and reactive transport simulations can be used. The basis for a simulation is a conceptual geochemical model of a given system that can be subjected to either or both forward and inverse modelling processes.

3.1 Endurance Conceptual Model

3.1.1 Purpose

Geochemical predictions should be made and viewed in light of the reservoir physics, which will dominate in subsurface processes and control the extent and style of chemical reactivity.

The bulk of the geochemical modelling focusses on batch calculations; a conceptual model can help combine these into a comprehensive view of the dynamic subsurface.

3.1.2 Endurance Model

The conceptual model for Endurance was constructed based on the main points of geochemical uncertainty and risk (**Figure 1**). Initial scenarios for testing uncertainties are posed in **Table 1**. They are arranged by depth of the formation being tested.

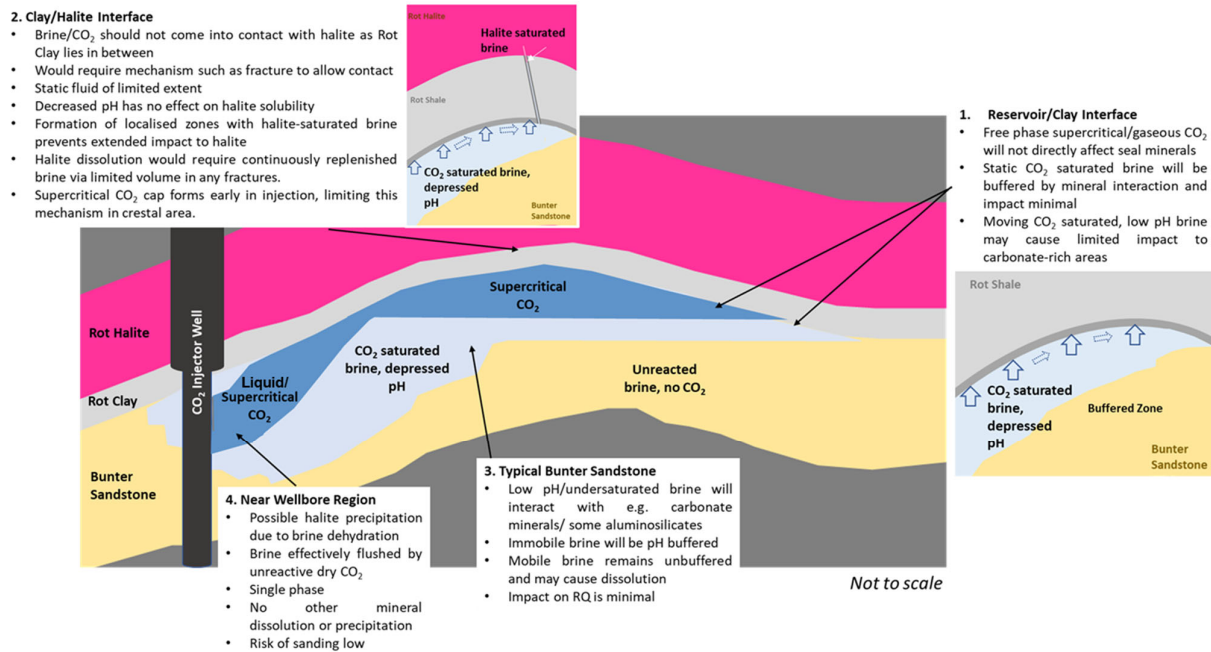


Figure 1 - Conceptual model of CO₂ injection into Endurance, illustrating the most important locations for possible geochemical processes.

Assumptions: a. CO₂ is added to the system at the base of the growing plume as per planned development, limiting contact of low pH brine with base seal; b. If CO₂ were added at the top of the plume, static fluids would become mobile and instances/rates of reaction would increase.

Table 1 – Scenarios for testing geochemical uncertainties

Brine	Mineral Set	Scenario Uncertainty
4589.37ft Brine	Base Röt Halite seal XRD Plug 20	If brine/CO2 breached the Röt Clay, what reactions could occur at the Röt Clay/Halite interface? Will Röt Halite be chemically eroded? If so, on what time scale?
	Base Röt Halite anhydrite layer seal XRD Plug 34	If brine/CO2 breached the Röt Clay, what reactions could occur if it contacts an anhydrite-rich section as opposed to halite-rich? Will anhydrite be chemically eroded? If so, on what time scale?
	Upper Röt Clay anhydrite-rich seal XRD Plug 56	If the lower Röt Clay is breached by chemical erosion/reaction, what reactions could occur in the Upper Röt anhydrite-rich claystone layers? Is the process inhibited due to the formation of products?
	Mid Röt Clay seal XRD Plug 76	What reactions could occur in more carbonate-rich mid Röt Clay? Is the process inhibited due to the formation of products?
	Base Röt Clay seal XRD Plug 84	What reactions could occur at the reservoir/seal interface? Will Röt Clay be chemically eroded? If so, on what time scale?
4634 ft Brine	Anhydrite-rich Bunter reservoir XRD Plug 86	How will CO2 react with anhydrite-rich Bunter Sst? On what timescale?
	Bunter reservoir carbonate-rich	How will CO2 react with carbonate-rich Bunter Sst? If it is eroded, on what timescale?

	layer XRD Plug 139	
4722 ft Brine	Bunter reservoir higher quartz XRD Plug 219	How will CO2 react with quartz-rich Bunter Sst? On what timescale?
	Bunter reservoir higher clay XRD Plug 269	How will CO2 react with the clay-rich Bunter Sst? On what timescale?
	Typical Bunter reservoir XRD Plug 343	How will CO2 react with typical Bunter Sst? On what timescale?
5167.5 ft Brine	Deeper Bunter reservoir XRD Plug 573	How will CO2 react with deep, clay-rich Bunter Sst? On what timescale?

3.2 Data

The data used in the geochemical modelling was obtained from the White Rose project, generated by National Grid as part of the earlier potential CO2 storage project (White Rose, 2016). The brine analysis was carried out by Expro in Hampshire in 2013 and is considered to be of high quality. Reservoir conditions used in the modelling are: pressure = 142 bar and temperature = 56°C.

3.2.1 Mineralogy

Table 2 - XRD data for core samples collected through the Endurance seal and reservoir formation (from White Rose, 2016).

plug	Depth (ft)		Illite/Smectite	Illite+Mica	Kaolinite	Chlorite	Quartz	K Feldspar	Plagioclase	Calcite	Dolomite	Siderite	Magnesite	Halite	Anhydrite	Pyrite	Hematite	Total
20	4551.00	Röt Halite	0.0	0.0	0.0	0.0	TR	0.0	0.0	0.0	0.0	0.0	0.0	99.7	0.3	0.0	0.0	100.0
34	4565.15		0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	1.4	28.0	70.1	0.0	0.0	100.0
56	4586.90	Röt Clay	0.0	23.6	0.0	4.2	11.5	TR	1.9	0.0	14.8	0.0	0.0	0.0	43.2	0.0	0.8	100.0
76	4607.55		0.0	36.8	0.0	3.2	20.9	TR	4.8	0.0	27.2	0.0	0.0	0.0	5.5	0.0	1.6	100.0
84	4615.00		0.0	35.2	0.0	2.4	31.1	2.2	2.3	0.0	18.5	0.0	0.0	2.5	4.0	0.0	1.8	100.0
86	4616.90		0.0	TR	0.0	TR	62.7	5.9	2.1	0.0	1.3	0.0	0.0	1.9	26.0	0.0	TR	99.9
139	4670.00	L3	0.0	5.0	TR	0.7	15.3	0.7	1.6	62.8	4.2	0.0	0.0	0.0	8.7	0.0	1.1	100.0
170	4701.00	L2	0.0	3.3	0.0	0.8	66.4	7.1	6.3	0.3	3.9	0.0	0.0	7.1	4.3	0.0	0.4	99.9
219	4749.95		0.0	3.9	TR	0.6	75.0	4.9	5.6	0.0	6.8	0.0	0.0	2.6	0.0	0.0	0.6	100.0
269	4800.10		0.0	13.1	TR	2.1	56.2	4.2	11.8	0.0	4.3	0.0	0.0	2.8	2.9	0.0	2.6	100.0
343	4874.00		0.0	9.5	TR	2.1	64.4	4.4	10.8	0.0	1.4	0.0	0.0	3.6	2.0	0.0	1.9	100.0
399	4929.95		0.0	7.9	TR	1.2	63.1	6.1	8.8	6.1	1.3	0.0	0.0	3.2	1.5	0.0	0.7	99.9
459	4990.00		0.0	7.3	TR	1.5	67.2	4.6	8.0	4.4	1.3	0.0	0.0	2.8	2.0	0.0	1.1	100.0
521	5052.20	L1	0.0	5.0	TR	0.8	69.8	7.1	8.2	TR	1.9	0.0	0.0	5.2	1.3	0.0	0.7	100.0
573	5104.00		0.0	12.1	0.0	0.8	63.5	4.0	10.6	3.8	1.0	0.0	0.0	2.4	1.1	0.0	0.9	100.0

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3.2.2 Brine

The formation water in Endurance is very high salinity (~ 250,000 mg/kg TDS, **Table 3**) and the detailed chemical analysis carried out originally by Expro suggests that it also contains unusually elevated concentrations of metals and heavy metals (**Table 4**). pH values measured immediately after extraction from the pressurised vessels are low, as expected for a highly saline brine with low bicarbonate content in the absence of abundant carbonate minerals.

Table 3 - Major brine characteristics from three MDT (1.04, 1.09 and 1.13), one separator (2.1) and one DST (2.14) samples (White Rose, 2016).

	units	L1a	L2a	L3b		Röt Clay
Sample Reference		1.04	1.09	1.13	2.1	2.14
Sampling Point / Depth	ft	5167.5	4722	4634	Separator Water Line	4589.37
Physicochemical Parameters						
pH immediate @ 20.7 ± 1.2°C Initial		6.20	5.25	5.34	-	4.55
Resistivity @ 20°C	ohm.m	0.0461	0.0466	0.047	0.0466	0.0465
Density @ 20.00 ± 0.08°C	kg/L	1.1958	1.1881	1.1868	1.1976	1.1976
TDS - Measured @ 0.2 µm - By Mass	mg/kg	256146	247659	247730	259680	258925

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Table 4 - Detailed chemical analysis of 5 Endurance brine samples collected at various depths. The composition of sample 1.09 was used for the bulk of the geochemical modelling.

ADS Reference	ADS 80379	ADS 80381	ADS 80382	ADS 80553	ADS 80573
Field / Well Reference	CCS Project / 42/25d-3				
Sample Reference	1.04	1.09	1.13	2.10	2.14
Sampling Point / Depth	5167.5 ft MD	4722.0 ft MD	4634.0 ft MD	Separator Water Line	4589.37 ft MDBRT
Anionic Species (soluble) (mg/kg)					
Chloride	154146	148780	148164	155600	155405
Fluoride *	0.15	0.12	0.10	0.13	0.14
Sulphate	296	359	385	360	364
Bromide	473	460	444	438	470
Nitrate	< 4	< 4	< 4	< 4	< 4
Iodide	< 4	< 4	< 4	< 4	< 4
Phosphate	< 20	< 20	< 20	< 20	< 20
Total Carbonate (as Bicarbonate) Immediate	38	37	43	-	39
Delay After flash (min)	11	7	8	-	9
Total Carbonate (as Bicarbonate) Subsequent	51	43	34	19	41
Delay After flash (min)	6526	6465	6430	-	4785
Formate	< 2	< 2	< 2	< 2	< 2
Acetate	< 2	< 2	< 2	< 2	< 2
Propionate	< 3	< 3	< 3	< 3	< 3
Butyrate	< 4	< 4	< 4	< 4	< 4
iso-Valerate	< 4	< 4	< 4	< 4	< 4
Cl:Br	326	323	334	355	331
Cationic Species (soluble) (mg/kg)					
Lithium	7.9	8.0	7.6	8.4	8.5
Barium	2	1	1	1	1
Strontium	108	111	103	117	116
Calcium	8858	8610	8037	8985	9129
Magnesium	2543	3014	3192	3138	3103
Sodium	85512	79664	79953	83763	84792
Potassium	1400	1469	1483	1553	1525
Iron	< 1	< 1	< 1	2	1
Copper	3.9	1.7	1.3	1.0	1.7
Zinc	7.8	8.5	7.9	8.9	8.8
Manganese	2.6	1.6	1.5	1.7	1.7
Aluminium	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
Ammonium •	< 10	< 10	< 10	< 10	< 10
Lead	1.1	1.3	1.4	1.4	1.5
Chromium	0.3	0.4	0.4	0.7	0.7
Nickel	< 0.2	1.8	1.6	< 0.2	0.4
Cadmium	0.2	0.2	0.2	0.1	0.2
Cobalt	0.15	0.16	0.16	0.09	0.08
Silver	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
Elements / Neutral Species (soluble) (mg/kg)					
Vanadium	0.07	0.07	0.08	0.07	0.06
Arsenic	1.2	1.3	1.5	2.1	2.4
Boron	9	10	9	10	10
Phosphorus	< 6	< 6	< 6	< 6	< 6
Silicon	3	3	3	4	4
Sulphur	83	102	107	101	100
Cationic Species (total) (mg/kg)					
Total Barium	2	2	1	2	1
Total Iron	< 1	1	< 1	3	1
Mercury (µg/kg)					
Soluble Mercury	0.4	0.2	0.2	0.3	< 0.2
Total Mercury	0.3	0.2	0.2	0.3	< 0.2
Total Cl ⁻ equivalent (mg/kg)	154597	149271	148670	156071	155906
Total Na ⁺ equivalent (mg/kg)	101403	96204	96174	101021	102133
Total NaCl equivalent (mg/kg)	255999	245474	244845	257092	258039
Cation/Anion Balance	101.15%	99.39%	99.76%	99.82%	101.02%
Cation/Anion Bias	1.15%	-0.61%	-0.24%	-0.18%	1.02%

3.3 Software

Two separate software packages were used to conduct the geochemical modelling: PHREEQC and Geochemist's Workbench (GWB). The most important features of each package are outlined below.

3.3.1 PHREEQC

- Freeware originating from the USGS.
- Designed to perform a wide variety of aqueous geochemical calculations including: equilibrium speciation, saturation, batch reaction kinetic rate and 1D reactive transport model capability, with capacity for forward and inverse modelling, including isotope fractionation and surface complexation.
- A number of options are available to model non-ideal solute and gas behaviour. These include the Debye-Hückel/B-dot, specific ion interaction theory and the Pitzer virial formulation.
- The Peng-Robinson equation of state (EoS) used to calculate the non-ideal gas density, vapour pressure, vapour-liquid equilibrium and thermodynamic variables of supercritical fluids.
- Henry's law is used for gas solubility calculations in water as a function of partial pressure/fugacity.
- PHREEQC has limited graphical capability and cannot perform 2D reactive transport modelling.
- PHREEQC is an equilibrium saturation model that can be used as a pre-processor to condition data for use in coupled flow and reactive transport simulators to facilitate prediction of dynamic subsurface processes.
- The code also provides for modelling aspects of mutual solubility dry-out using the brine evaporation function and pseudo dual-phase scenarios can be captured for supercritical fluids using the gas saturation limits implicit within the programme

3.3.2 Geochemist's Workbench (GWB)

- Licenced set of tools for manipulating chemical reactions, calculating stability diagrams and equilibrium states and reactive transport modelling.
- The primary advantage in using the range of integrated GWB modules is the ease with which the input and outputs from the different tools can be integrated.
- The Geochemist's Spread Sheet (GSS) module provides for creating a library of analysis results from which multiple simulations can be run simultaneously. In addition, the GSS allows rapid calculation of species activities, gas fugacities, mineral saturation states and many more parameters, without the need to run individual simulations for each sample and post-process the output.

- Critically, GWB is a powerful tool for generating illustrative diagrams, balancing reaction and calculating solution and mineral stability parameters, using a range of activity models for a broad spectrum of brine salinities. The reaction path, phase diagram and data overlay functions provide for a powerful set of data analysis tools to establish the state of equilibrium between hosted fluids and the aquifer/reservoir-aquitard/seal mineral media.
- Currently, GWB is limited in its treatment of gas solubility, having no saturation limit. PHREEQC should be used as a pre-processor for this reason when maximum solubility of a gas for a given solution composition is required.
- The GWB package includes the flexibility to specify a similar range of solubility models (B-dot, Pitzer etc), and also allows for the use of the PHREEQC database for direct comparison of results. Three equation of state model options are included in GWB, a choice of fluid density calculation methods and the ability to specify media properties such as porosity, permeability, heat capacity and bulk volume.

3.4 Model Limitations

The PHREEQC (pH redox equilibrium) code is primarily an equilibrium-speciation-saturation simulator. It does have capacity for an integrated treatment of forward and inverse modelling, surface complexation, kinetic rate laws and 1D reactive transport, but the limited capacity to capture spatial relationships in 2D and 3D restricts interpretation of where reactions of interest are most likely to occur in the subsurface system. PHREEQC is most powerful when used as a pre-processor in conjunction with coupled fluid flow and reactivity simulators, to form a realistic prediction of subsurface processes. The latter do not provide for all the possible reactions in a given system, whereas the only limitation for geochemical simulators such as PHREEQC is the input database of thermodynamic data. Coupled fluid and reactive transport simulators such as CMG's GEM™ use similar geochemical databases, but require a supervised approach, specifying the reactions of interest.

It is also important to note that thermodynamic reactions follow the path to an equilibrium state without taking kinetics or geology into account unless explicitly included. This means that any model will predict what should happen, but not necessarily what will happen. Understanding which predicted reactions are the most likely to occur in reality requires experience in conceptual geochemical modelling and a good understanding of the specific geological system. In general, thermodynamic data is collected for pure phases and mineral stoichiometry influences the saturation state calculations, e.g. clay and cyclo-silicate phases with complex stoichiometry and large unit cells will typically show much higher saturation indices than simple minerals such as quartz. If the latter were to be represented as Si_2O_4 instead of SiO_2 , the saturation state would be doubled. For this reason, the analyst must have knowledge of the respective mineral paragenesis to correctly interpret the simulator outputs.

3.4.1 Database Options

Software tools such as PHREEQC and GWB rely on empirical data contained in one of a number of different databases as the basis for their calculations. The information in these databases is of varying quality consistency of data is a key aspect e.g. calorimetry conducted for phases in 1980 may not be consistent with methods applied for other phases in 1990 and combination of these values in the same database can produce inconsistent results. Additionally, there are different activity/fugacity models used in combination with the thermodynamic databases to feed methods of speciation. The options available are typically hard-coded to the database to make predictions of species activity and gas fugacity for a given solution composition.

The assumptions and limitations for each of the activity models must be considered when interpreting the outcomes of a simulation (Bethke, 2008). The selection of which is the most appropriate activity model to use is made easier with experience, but for solutions with an ionic strength <0.7 (mean ocean water ~ 0.64) the Debye-Hückel or B-dot equation is applicable (e.g. PHREEQC, LLNL, Minteq databases). The databases associated with the Debye-Hückel equation and its extended forms are generally more comprehensive in their treatment of both aqueous complexes and mineral phases when compared with formulations for hypersaline brines. The Pitzer virial equations are commonly used for more saline brines (ionic strength >0.7), designed to calculate activity coefficients for electrolyte brines (e.g. Pitzer, HMW databases). Unfortunately, this is a salt model and doesn't include aluminosilicates. Furthermore, the data contained in the Pitzer model was gathered at 25°C and has limited applicability to higher temperature systems. The database files for both PHREEQC and GWB are in raw text formats and can easily be edited. The GWB software includes an editing tool to assist with maintaining correct syntax (TEdit).

3.5 Workflow and Results

3.5.1 Definition of the System

To best define a composition as complex as the Endurance brine, the most appropriate database to use with PHREEQC is the Lawrence Livermore National Library (LLNL) thermodynamic database. This database is common to both PHREEQC and GWB and was converted from the latter format for use in PHREEQC. The database is comprehensive and there are limits on temperature range, but data for the aqueous species and mineral phases of interest is considered consistent. The database also makes use of three activity models. Unfortunately, LLNL does not use an appropriate thermodynamic model to accurately account for the effect of the extreme salinity, so comparisons were also made using the Pitzer database.

3.5.2 Calculating Mineral Saturation and Brine Component Speciation Using PHREEQC

A number of basic initial steps must be completed in PHREEQC to use as the basis of further modelling. These steps will:

- Generate predicted brine compositions which can be used to compare with measured data to establish the presence of any systematic analytical error or identify any potential additional processes that have affected the analysis (ion balance and ion balance error).
- Help identify the dominant mineral assemblage and establish whether the water composition reflects what has been reported about the reservoir mineralogy, i.e. with which minerals the brine appears to be in equilibrium (the equilibrium assemblage).

The brine composition, density and pH are specified at reservoir temperature (pressure cannot be defined directly for the solution initial conditions, but addition of a gas phase facilitates input of a pressure value). The software calculates the equilibrium composition of the brine and predicts which minerals are either supersaturated and should precipitate (Saturation Index [SI] >0), undersaturated and should dissolve (SI <0), or in equilibrium leading to a stable system (SI = 0) (See Annex A for example PHREEQC input and output files).

Once established, the most appropriate mineral assemblage is included in the PHREEQC model to allow the minerals to buffer the composition and pH of the brine. This method assumes an effective unlimited supply of each mineral and predicts that the system will come to equilibrium, which will not necessarily be the case. No attempt is made to define relative or finite amounts of specific minerals, since the nature of the reactive surface area of the pore space remains unknown.

Owing to the uncertainty in the model created by the extremely high salinity brine, calibration of the results within PHREEQC are carried out using two methods:

- The same model is run with a 10x or 100x dilute version of brine.
- The model is re-run, excluding certain components, using the Pitzer database (more appropriate for high salinity, but far more limited in thermodynamic data)

For the purposes of this study, a single, representative brine composition was selected and used – an MDT sample collected from 4722 ft depth.

3.5.2 Initial Results

The results of the initial steps are presented in **Table 5**. In all cases, the minerals predicted to be closest to saturation are a reasonable reflection of the mineralogical data. The most important minerals for affecting brine composition are carbonates and halite – aluminosilicates play a minimal role. Buffered pH values for the LLNL and Pitzer databases are slightly lower than measured. This may reflect the speed with which pH can increase once the pressure in a storage vessel is released and brine comes into contact with the atmosphere.

Table 5 - Results of initial stages of PHREEQC modelling.

Model	#	Database	Brine depth (ft)	Brine Type	Equilibrium mineral assemblage	pH	Ionic strength	Dissolved CO2 (mol/kg)
Basic equilibrium	1	LLNL	4722	Original	n/a	5.212	3.49	0.000972
	2	PITZER	4722	Original	n/a	5.252	4.54	0.001368
Including CO2	3	LLNL	4722	Original	Calcite Dolomite Halite Quartz	4.451	6.80	0.7397
	4	PITZER	4722	Dilute	n/a	3.086*		1.103
	5	LLNL	4722	Dilute	Calcite Dolomite Halite Quartz	4.618	5.80**	0.866
	6	PITZER	4722	Original	Barite Calcite Dolomite Halite Quartz	3.933	6.73	0.4019
<p>* very low pH due to lack of buffering mineral assemblage in the presence of CO2-saturated brine, model created for direct comparison with GWB</p> <p>** elevated ionic strength due to halite dissolving into undersaturated brine from mineral assemblage and increasing salt concentration</p>								

3.5.4 CO2 Solubility and System Stability

The addition of CO2 to the system must be modelled in the context of the conceptual model. Using PHREEQC, calculating the solubility of CO2 in a given brine, at given conditions, is an iterative process. CO2 is modelled as a separate gas phase using the GAS_PHASE keyword and the CO2 partial pressure is sequentially increased until the point of gas saturation. The model assumes all CO2 is dissolved in the brine until maximum solubility, which can be recognised as the point at which the first pseudo supercritical CO2 phase separates from the aqueous matrix dictated by the Peng-Robinson EoS. The ultimate solubility will be determined by the system temperature, system pressure, gas partial pressure, brine salinity and composition and interaction with minerals.

3.5.5 Results of Adding CO2

The presence of CO2 causes the brine pH to drop (**Table 5, Figure 2**). In an unbuffered system (e.g. Model 4) this drop is significant. The presence of carbonate minerals will buffer the pH through dissolution and precipitation and the pH drop will be less severe (e.g. Models 3, 5 and 6). The total CO2 solubility is limited by the presence of buffering minerals but is broadly in line with, if slightly lower than, typical values for saline brine of ~1 mol%. CO2 solubility is higher in less saline brine (e.g. Models 4 and 5).

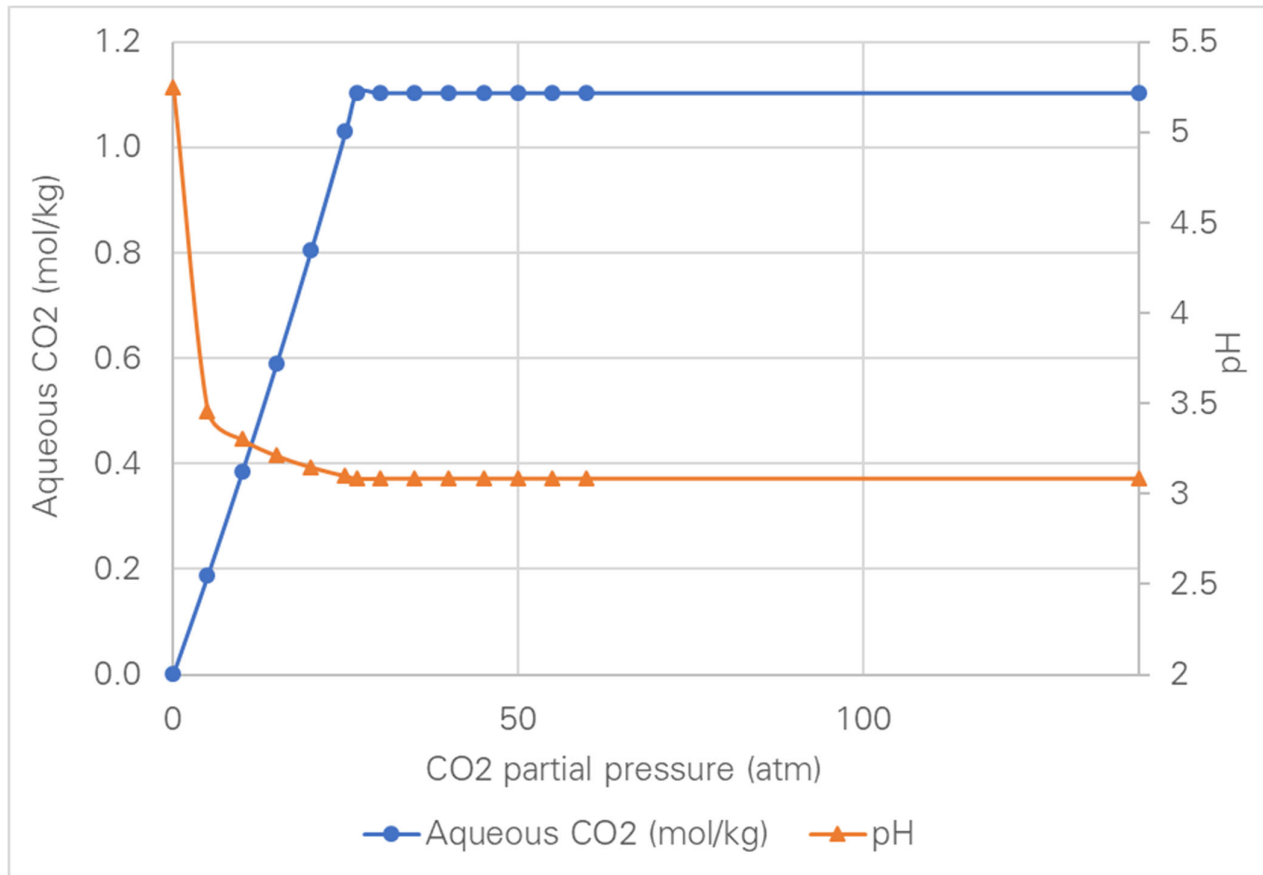


Figure 2 - Illustrating the pH drop and CO2 solubility limit in an unbuffered, dilute version of the Endurance brine (Model 4).

Table 6 indicates the effect on the reservoir mineralogy when a Typical Endurance brine is saturated with CO₂. Quartz, the most abundant mineral, is unaffected by the drop in pH and small amounts of calcite and dolomite will dissolve and precipitate respectively. The largest impact by far is on the halite, which is predicted to dissolve in large quantities. However, this is caused by the severe undersaturation of the brine with respect to halite, rather than the pH change.

Table 6 - Mineralogical response to decreasing pH caused by CO₂ injection (Model 3 and 6).

Database	Moles in assemblage					
	Phase	SI	Initial	Final	Delta	Mineral behaviour
LLNL	Calcite	0	10	9.693	-0.3068	Dissolve
	Dolomite	0	10	10.11	0.11	Precipitate
	Halite	-0.1	10	0	-10	Dissolve
	Quartz	0	10	10	0	n/a
PITZER	Barite	0	10	10	0	n/a
	Calcite	0	10	9.989	-0.1082	Dissolve
	Dolomite	0	10	10.0001	0.000909	Precipitate
	Halite	-0	10	7.836	-2.164	Dissolve
	Quartz	0	10	10	0	n/a

This part of the modelling process is extremely useful, together with the conceptual model, in addressing the specific questions raised in **Table 1**:

What impact will dissolved CO₂ have on the reservoir/seal interface?

Adding Illite to the mineral assemblage, to represent the clay minerals of the seal, has no effect on pH or dissolved CO₂. Illite is unaffected by the presence of the low-pH brine, any dolomite present may dissolve in places, but this will be limited and is only likely to be significant if the brine at the seal interface is continuously replenished (location 1 on conceptual model shown in **Figure 1**)

What impact will dissolved CO₂ have on the seal clay/halite interface?

A CO₂-saturated brine, equilibrated with clay minerals and carbonates, is nevertheless still undersaturated with respect to halite (as mentioned above). This brine will therefore dissolve any halite present until saturation (equilibrium has been reached). However, in a static system, initial reaction will create a stable halite-saturated boundary layer, following which no further damage to the halite will occur (location 2 on conceptual model shown in **Figure 1**). If CO₂ were added at the top of the plume, static fluids would become mobile and may lead to enhanced dissolution of the halite. This is not planned for development of Endurance where CO₂ will be injected downdip of the crest.

What impact would the presence of anhydrite have on seal stability?

The addition of anhydrite to the seal mineral assemblage has a negligible impact. Tiny amounts of anhydrite are predicted to dissolve, however the extent of the anhydrite-rich zone is limited and, as described in the conceptual model, the dynamic flow required for continuous dissolution is very unlikely. Any unexpected anhydrite-enriched zones may experience some initial enhanced dissolution but would quickly form a saturated boundary layer as described (for halite) above.

3.5.6 Results Calibration with GWB

Calibration was carried out to determine whether GWB and PHREEQC produce comparable results given the same input parameters. Unfortunately, during the calibration process, it was discovered (and confirmed by the software provider) that GWB does not apply a saturation limit for gases (**Figure 3**), meaning it cannot be used to predict maximum CO₂ solubility. Inputs to GWB for gases must first be constrained with PHREEQC.

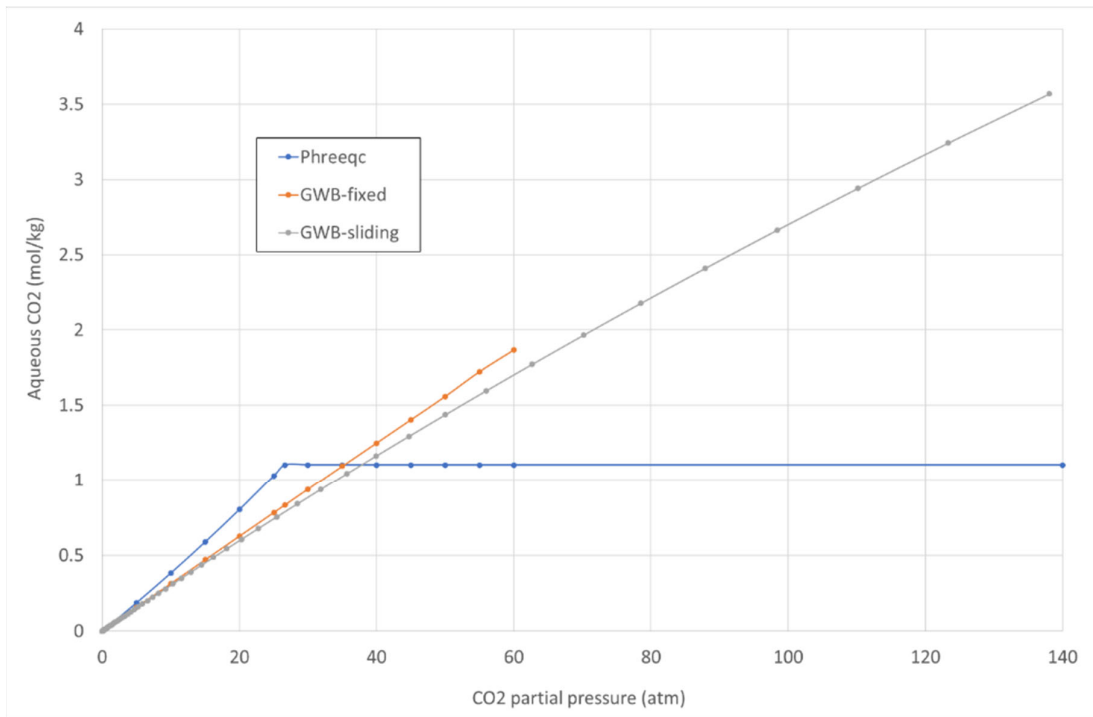


Figure 3 - Results from comparing difference versions of model 4 (table) using PHREEQC and GWB.

Nevertheless, some comparisons can be made and models 1, 2, 3, 4 and 6 from **Table 5** were reproduced using GWB. In those cases where CO₂ partial pressures were required (Models 3 and 6), these were generated using PHREEQC. The default Thermo.dat database was used and is an abridged version of the LLNL database used in PHREEQC. This provided consistency between the databases used by the different simulators. The calibration process was further constrained by the inability of GWB to use the Pitzer database at temperatures exceeding 25°C.

Table 7 shows the results of using GWB to run repeats of PHREEQC models for calibration purposes. Model 4 was included to test the capacity of GWB to effectively model gases and was modelled in GWB using two methods: (1) adding a fixed amount of CO₂ to the brine, and (2) gradually increasing CO₂ saturation in the brine up to max solubility using a sliding fugacity path. The results and comparison with PHREEQC are shown in **Figure 3**.

Table 7 - Results of GWB calibration of models previously used in PHREEQC.

Model	#	Database	Brine depth (ft)	Brine Type	Equilibrium mineral assemblage	pH	Ionic strength	Dissolved CO ₂ (mol/kg)
Basic equilibrium	1	Thermo	4722	Original	n/a	5.25*	4.935	0.0005969
	2	PITZER	4722	Original	n/a	5.25*	5.97	0.0006075
Including CO ₂	3	Thermo	4722	Original	Calcite Dolomite Halite Quartz	5.247	9.873	0.6873
	6	PITZER	4722	Original	Calcite Dolomite Halite	5.182	6.146	0.3773
* pH as originally input. GWB will not recalculate pH in a basic equilibrium model.								

In general, GWB predicts slightly higher pH values than PHREEQC for brine in the presence of CO₂. The dissolved CO₂ concentrations are comparable due to the initial data being generated in PHREEQC. The default EoS in GWB is the Tsonopoulos formulation that may account for the minor differences in the results.

3.6 Understanding Produced Water Geochemistry

The development plan for the Northern Endurance Partnership includes the option to produce water from the Endurance structure (Bunter Sandstone Formation) as part of the pressure management process. This water production will occur relatively late on in project life but plans for its discharge or treatment and disposal need to be in place early to ensure regulatory compliance.

It can be assumed that the produced brine will have a composition broadly similar to that analysed in 2013. However, while the earliest brine produced may not have interacted with CO₂ at all, over time the produced water is likely to become more and more saturated with CO₂, with a consequently adjusted composition.

3.6.1 Speciation of High-hazard Brine Components

As previously highlighted, the Endurance brine is unusually concentrated in transition and heavy metals, many of which are toxic to marine life. In some cases, the degree of toxicity is linked to the nature of the species in solution, which will vary according to brine composition. For example, zinc (Zn), can be present in a range of dissolved complexes (ZnCl₄²⁻, ZnCl₂, ZnCl⁺, ZnCl₃⁻, Zn²⁺, ZnHCO₃⁺, ZnSO₄), but geochemical modelling indicates that the species ZnCl₄²⁻ is two orders of magnitude more concentrated in the Endurance brine than any other Zn species.

Brine discharge modelling has previously highlighted the six brine components considered to be the most significant contaminants. These components are: arsenic (As), zinc (Zn), copper (Cu), chromium (Cr), lead (Pb) and cadmium (Cd). The results from previously described models were used to identify the distribution of species (speciation) of these components in the Endurance brine. The results can be seen in **Figure 4** and will be compared with new speciation analysis to refine the modelling process. In time, this simulation output will be used to highlight those specific dissolved species which are mostly to cause damage to marine life.

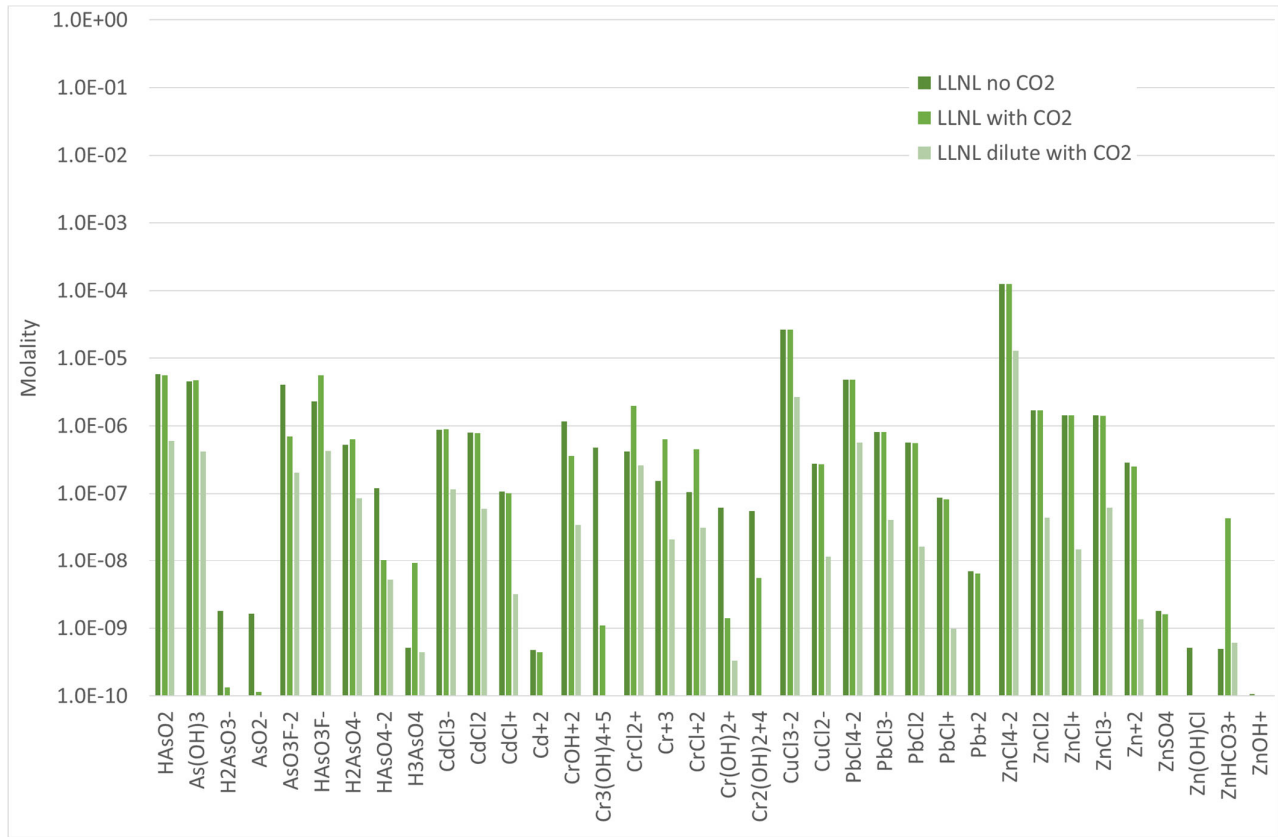


Figure 4 - Distribution of high hazard brine components in a typical Endurance brine.

4.0 Conclusions

Geochemical simulation, in conjunction with the conceptual modelling, indicates that the injection of supercritical CO2 into the Endurance field (Bunter sandstone reservoir) is unlikely to have a net negative impact on either the reservoir formation or the seal.

The dissolution of CO2 into the brine will cause a drop in pH. This process will be buffered by the presence of carbonate minerals. The buffering process will cause small amounts of mineral dissolution or precipitation, but not enough to cause significant formation damage.

In the near-wellbore region, the almost complete vaporisation of brine by dry CO2 due to mutual solubility effects means that there will be no basis for any chemical reactions to occur and the risk of sanding through cement dissolution is extremely limited.

At the reservoir/seal interface, the presence of clay minerals has little to no effect on the likelihood of mineral dissolution and so the seal integrity will not be impacted. If the acidic reservoir brine were to reach the seal/halite interface, e.g. through mechanically induced fractures, some dissolution of the halite into the undersaturated brine is predicted. However, in the most likely scenario, the brine adjacent to the halite would quickly become saturated,

forming a boundary layer beyond which no more halite is dissolved. Thus, the risk to halite integrity is also limited.

The modelling process can also be used to predict the distribution of toxic/hazardous species in any produced water, which will impact decisions relating to relating to its treatment, disposal or discharge.

5.0 References

White Rose, 2016. K40: Subsurface geoscience and production chemistry reports. Capture Power Limited, 300pp.,
[https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/531045/K40 Subsurface Geoscience and Production Chemistry.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/531045/K40_Subsurface_Geoscience_and_Production_Chemistry.pdf)

Bethke, C.M., 2008. Geochemical and Biogeochemical Reaction Modeling, Cambridge University Press, 2nd edition, 542pp.

Annex A

Example PHREEQC Input file

```

DATABASE c:\phreeqc\database\LLNL.dat
SOLUTION 1 #Endurance Water B 4722
units    mg/kgw
pH       5.25
temp     56
density  1.1881
Cl       148780
F        0.12
S(6)    359
Br       460
Alkalinity 37 as HCO3
Li       8
Ba       1
Sr       111
Ca       8610
Mg       3014
Na       79664
K        1469
Fe       1
Cu       1.7
Zn       8.5
Mn       1.6
Al       0.00001
Pb       1.3
Cr       0.4
Ni       1.8
Cd       0.2
As       1.3
B        10
Si       3
S(-2)   0.104
EQUILIBRIUM_PHASES
Quartz      0
Halite      0
Calcite     0
Dolomite   0
Anhydrite  0
Illite     0
GAS_PHASE 1
  -fixed_pressure
  -pressure 142
  -volume 1
  -temperature 56
CO2(g)     34
END

```

Part B: Coupled Reactive Transport Geochemical Simulation

6.0 Near-Wellbore GEM™ Modelling for Endurance

6.1 Introduction

Injectivity loss caused by near-wellbore dry-out and halite precipitation has been identified as a key risk to the NZT/NEP project. The project proposal is to inject dry CO₂ into the hypersaline (~250,000 ppm%w) aquifer. Therefore, vaporization of the brine into the CO₂ phase (and dissolution of the CO₂ into the brine) and halite precipitation will occur.

CMG's GEM™ reservoir simulator was used to model the coupled transport, mutual solubility and geochemical effects in the near-wellbore region surrounding the injector. The model was intended to provide mechanistic insight into the phenomenon, assess the effect of uncertainty, and test mitigation schemes (brine flushing). It is a continuum model and therefore has the obvious shortcoming in that processes are not modelled at the pore-scale, e.g. the distribution of halite precipitation within an individual pore is not captured.

6.2 Model

The model is axis-symmetric (**Figure 5**) and in most cases the reservoir properties are uniform. Limited layer-cake heterogeneity is introduced in some cases.

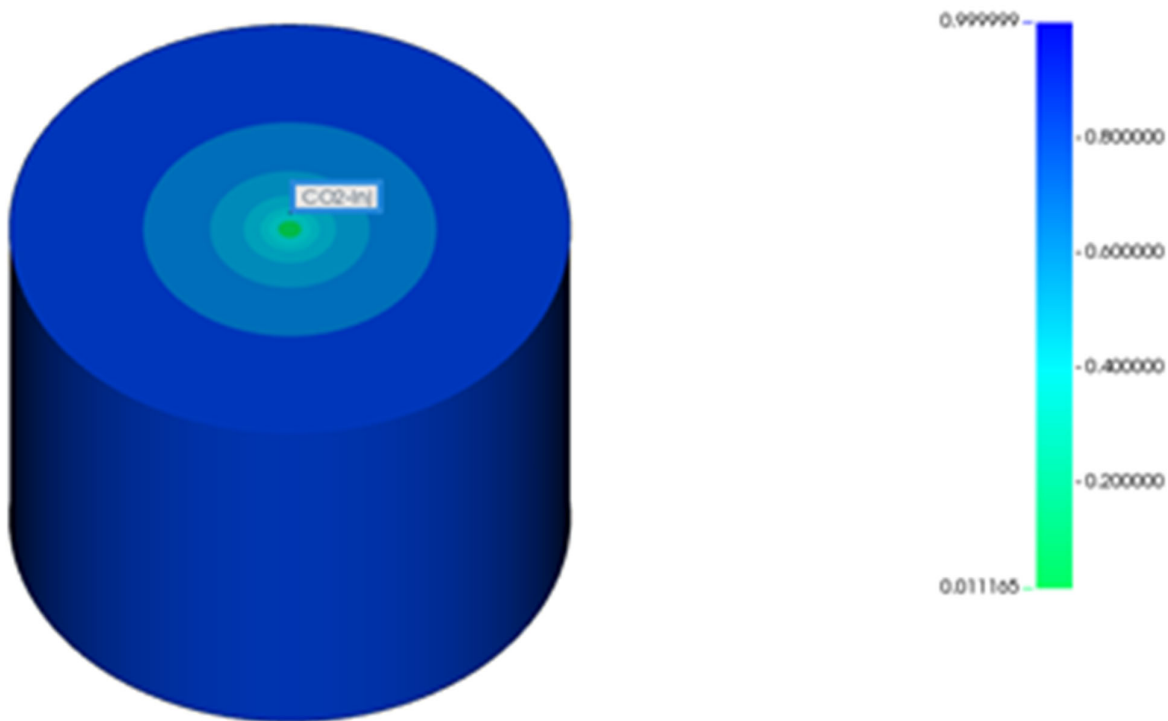


Figure 5 - Near wellbore mechanistic model for Endurance in GEM™.

GEM™ allows for the inclusion of a water component in the Equation of State (EoS) and therefore deals with brine vaporisation rigorously. CO₂ solubility is calculated with a salinity-dependent form of Henry's law.

For simplicity the brine only contains Na⁺ and Cl⁻ ions. Precipitation occurs instantaneously when the brine reaches threshold activity product (no transport of supersaturated fluid). The precipitated halite immediately becomes immobile and reduces local porosity according to the pore space it occupies (no transport of solids). The corresponding permeability reduction is calculated from the Kozeny–Carman relationship.

The model parameters are based on Endurance properties:

- i. Radius x height = 1600 x 200 ft
- ii. Nr x Nz = 110 x 1
- iii. Cell size (Δr) = 1 ft at wellbore, geometrically increasing in far field
- iv. Pressure = 2000 psi
- v. Bottom hole temperature (BHT) = 15°C
- vi. Porosity (Φ) = 0.2
- vii. Permeability K_x = 300 mD
- viii. Relative permeability – Corey:
 - Base-case: $S_{wr} = 10\%$, $N_w = 4$, $N_g = 2.5$, $k_{rg}(S_{wrg}) = 0.7$
 - Downside: $S_{wr} = 10\%$, $N_w = 6$, $N_g = 3.5$, $k_{rg}(S_{wrg}) = 0.7$
 - Upside: $S_{wr} = 10\%$, $N_w = 3$, $N_g = 1.8$, $k_{rg}(S_{wrg}) = 0.9$
- ix. Maximum capillary pressure = 573 psi
- x. Salinity = 5.7 mol/kgw = 250,000 ppm%w

6.3 Results

6.3.1 Dry-out and Precipitation Mechanisms

The behaviour of the model with continuous injection for a duration of 2 years was investigated across a range of rates: 1 – 100 mmscfd (0.02 – 1.93 MTPA). **Figure 6** shows the resulting radial profiles of S_w (water saturation) and permeability reduction factor for $Q_{gas} = 10$ and 50 mmscfd. Each line corresponds to a time instant since the beginning of injection (value of cumulative injection); the lines get darker as time increases.

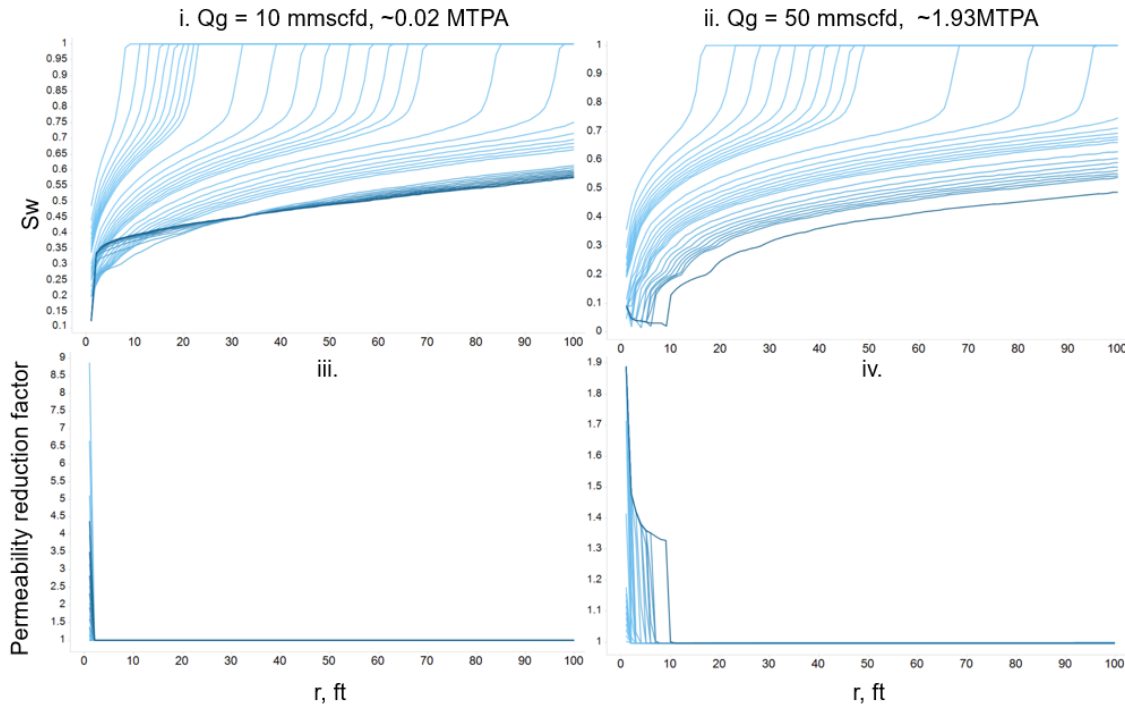


Figure 6 - Sw and permeability reduction factor profiles for Qg = 10 and 50mmscfd (darker colour - later time).

In both cases, the standard immiscible displacement front travels radially outwards from the wellbore into the reservoir and causes a rapid drop in Sw which reaches r = 100 ft after a few days. The water saturation in the immediate vicinity of the near-wellbore is then further reduced by vaporisation. This low-saturation region sets up a capillary pressure gradient which acts to suck brine from the reservoir towards the wellbore. In the high-rate case (**Figure 5** and **Figure 6**) the outwards pressure gradient in the CO2 phase is large enough to overcome the capillary suction and a moving drying front also propagates into the reservoir. The halite precipitation is distributed behind this front and therefore the corresponding permeability reduction is modest. In the low-rate case (**Figure 5** and **Figure 6**), where the pressure gradient in the injected CO2 is lower, capillary-suction induces a back-flow of brine, which continuously supplies the near-wellbore region with brine from the reservoir. This brine is continuously vaporised by the incoming CO2, and therefore massive localised precipitation and permeability loss occur in the immediate vicinity of the wellbore.

Figure 7 shows the injectivity index as a function of cumulative injection for the high- and low-rate cases. In the high-rate case, with distributed precipitation, negligible effect is predicted on well performance and the injectivity index remains constant. In the low-rate case, the injectivity drops catastrophically soon after injection begins, and it is entirely lost after a throughput of 1 bnscf.

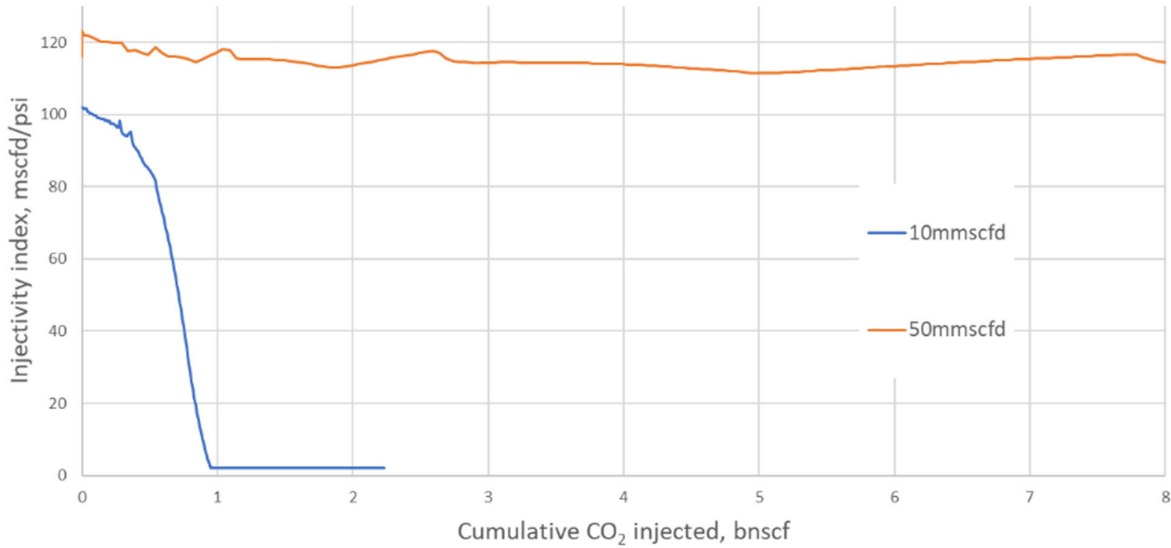


Figure 7 - Injectivity index for Q_g = 10 and 50 mmscfd.

In summary, halite precipitation at high CO₂ injection rate does not lead to injectivity loss even after significant throughput, but at low rate, halite precipitation causes complete injectivity loss very rapidly. A progressive transition between these two regimes occurs at an injection rate of ~30 mmscfd (~0.6 MTPA).

6.3.2 Uncertainty

The model was used to explore the effect of uncertainty in all parameters on the mechanisms of dry-out and precipitation: relative permeability, capillary pressure, permeability, salinity, BHT, porosity-permeability relationship.

The qualitative behaviour discussed above is insensitive to these uncertainties but the threshold injection rate between the two regimes is very sensitive to certain parameters. In general, any change that increases brine mobility will increase the threshold rate at which catastrophic injectivity loss occurs. For instance, the up- and down-side relative permeability move the threshold rate up and down by almost one order of magnitude respectively.

6.3.3 Mitigation – Periodic Brine Washing

If the brine in the near-wellbore region is replaced with fresh water no precipitation can occur until it has all been vaporized and the original hypersaline aquifer brine has back-flowed from the reservoir and encountered dry CO₂. Therefore, an obvious scheme to mitigate injectivity loss is to periodically inject slugs of fresh water into the wells.

The model was used to investigate the flushing schedule required. Slug sizes of 1000, 2000, and 4000 bbls were tested at intervals of 6 months, 1 year and 2 years respectively, to maintain a constant average fresh-water consumption of 2000 bbls/year.

Figure 8 compares the resulting injectivity indices with the continuous-injection (un-mitigated) case for a CO₂ injection rate of 10 mmscfd. In the case with no flushing, catastrophic injectivity

loss occurs as observed above. For each of the flushing schedules tested, catastrophic injectivity decline was prevented, and almost constant well performance was maintained for a cumulative CO₂ injection of more than 20 bscf.

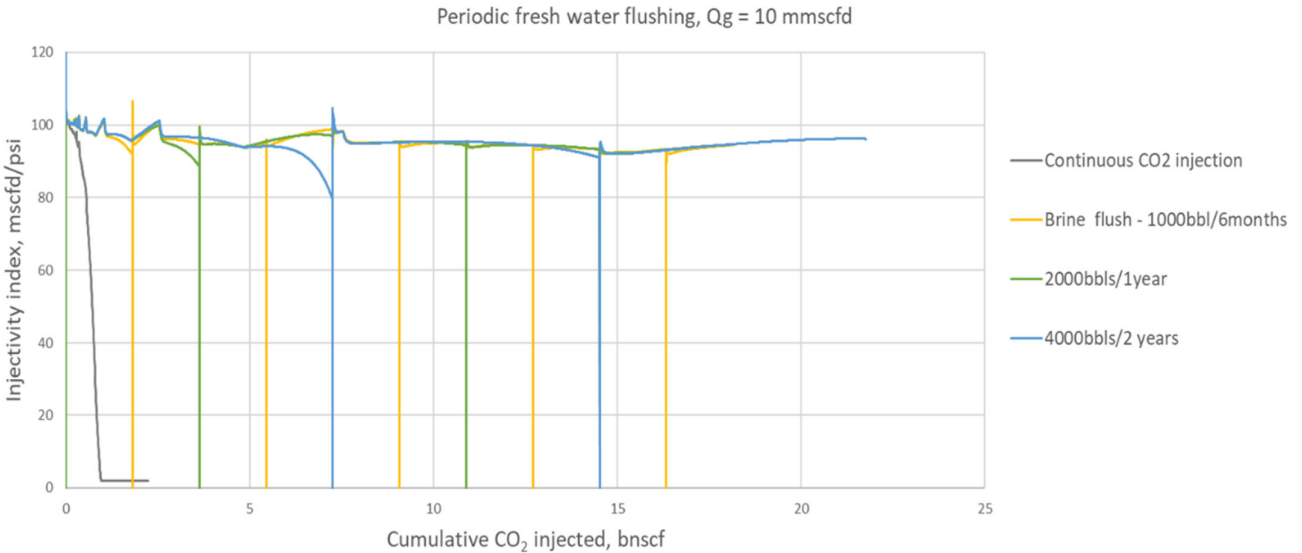


Figure 8 - Periodic freshwater flushing.

The effectiveness of this mitigation technique is not sensitive to the details of flushing schedule, if the average of 2000 bbls/year is maintained. This suggests that it is an operationally flexible procedure, and that the flushing schedule can be optimised based on operational and/or cost criteria. However, the effect of heterogeneity in the real reservoir could modify these results significantly. Similar mitigation can be achieved by flushing with low-salinity brines (compatibility with the aquifer brine ensured).

6.3.4 Heterogeneity

The model was extended to investigate a very simple layer-cake permeability distribution approximately representative of the Endurance reservoir formation. The original domain was divided into 20 layers. Horizontal permeability varied over 2 orders of magnitude, in the range 3 – 877 mD, such that the average was equal to that of the homogeneous model. Vertical permeability was 3 mD (uniform). The J-function formulation was used to scale the capillary pressure. All other parameters were unchanged from the homogeneous model.

Figure 9 shows the injectivity index of the layer-cake model and the corresponding homogenous model for Q_g = 10 mmscfd. Initially both models exhibit similar steep injectivity decline, but in the heterogenous case it does not collapse to zero. Instead, it stabilises and remains approximately constant at ~40 % of its original value. Halite precipitation turns out to mostly occur in the high-permeability layers as the former have a larger CO₂ throughput initially (and therefore a much larger volume of brine backflow and its associated halite precipitation). The lower-permeability intervals present less brine backflow leading to better preserved injectivity. An injectivity variation of this form may be in better agreement with field observations than the total loss of injectivity observed in the homogeneous case.

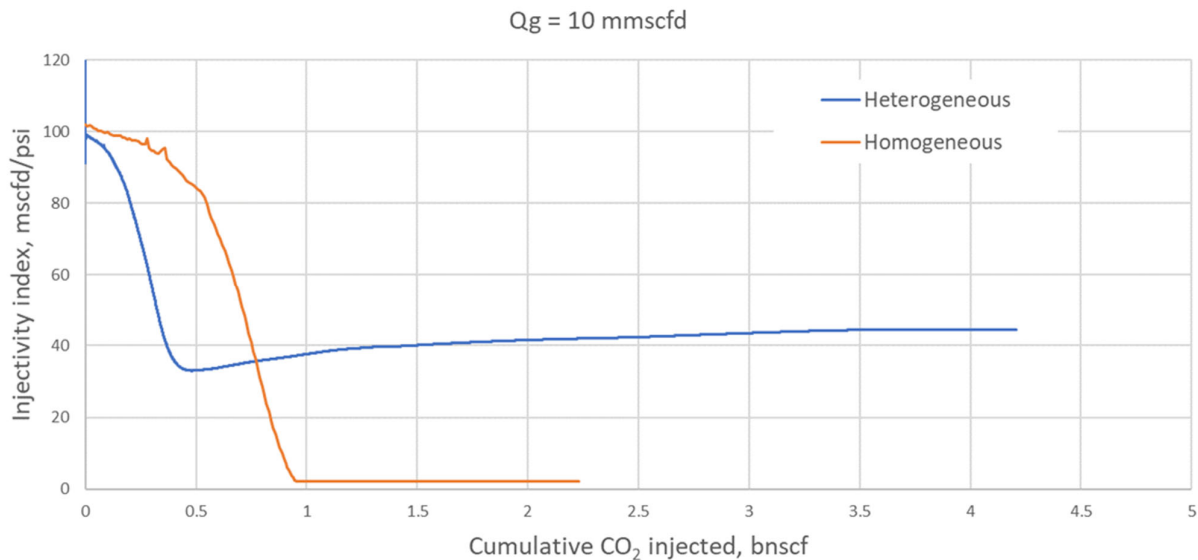


Figure 9 - Injectivity index for comparable homogeneous and heterogeneous cases.

6.4 Conclusions

A fully coupled transport, mutual-solubility, and geochemical near-wellbore model of CO₂ injection into the hypersaline Endurance aquifer has been constructed. It has been used to investigate the basic mechanisms that control halite precipitation, uncertainty, mitigation by periodic fresh-water flushing, and the effect of layer-cake heterogeneity. The following conclusions are obtained:

1. At high injection rate a drying front propagates into the reservoir, where it causes modest porosity and permeability loss, and has negligible effect on injectivity.
2. At low injection rate a moving drying front does not develop. Capillary-induced brine back-flow causes massive localised precipitation in the very near-wellbore region and catastrophic injectivity loss.
3. The injection rate threshold between these regimes is ~30 mmscfd (~0.6 MTPA).
4. This threshold rate is extremely sensitive to brine relative permeability and capillary pressure.
5. Periodic flushing with fresh water can entirely prevent halite precipitation and injectivity loss. The effectiveness of this mitigation is insensitive to the details of the flushing schedule, so it is a flexible technique that can be optimised based on operational and/or cost criteria.
6. Models with layer-cake permeability distributions exhibit less severe injectivity loss than the corresponding homogeneous cases and may be a better match to the injectivity decline observed in field data.

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