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Method for Identification of Types and Amounts of Salts that may Precipitate due to Brine Dry Out and Application to UK Southern North Sea Candidate CO_2 Stores

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Abstract

Resident formation water vaporization in the near well zone may pose challenges for carbon dioxide (CO_2) storage operations. If dry CO_2 is injected into a reservoir, the brine in the very near well zone will evaporate into the CO_2 stream, leaving behind precipitated salts. This paper introduces a simple thermodynamic scale prediction approach to quickly identify salts that could precipitate at an injection site and subsequently lead to loss of injectivity and escalate the cost of capture operations. With this method, operators can forecast likely flow assurance related injectivity issues prior to injection of CO_2 and plan their injection schemes and mitigation strategies, if necessary.

To conduct this study, formation water compositions were obtained from the literature for various formations worldwide, and compiled into a spreadsheet. The work of Talman et al. (2019) was used as a baseline for precipitation calculations as it clearly identified salt precipitation at an active CO_2 injection site – the Aquistore project in Saskatchewan, Canada – which has salinity greater than 300,000 mg/L. The analysis of the compiled data was divided into two parts.

- Part 1 focused on demonstration, previous and operational carbon sequestration projects worldwide.
- Part 2 focused on fields in the UK Southern North Sea. The existence of gas fields in the UK Southern North Sea near major regions of CO_2 emission and the presence of this mature gas province with many fields close to cessation of production makes it a desirable candidate for CO_2 storage. With some fields in this region suspected to be connected and communicating, attempt was made to infer possible connectivity/compartmentalization between fields by evaluating the available salinity of formation waters compiled from literature and annotating on the North Sea Transition Authority Offshore interactive map for further studies.

In contrast to the literature that only addresses NaCl precipitation in formation waters having salinities of > 300,000 mg/L, this work shows that various other salts may also co-precipitate alongside halite, addressing brines with salinities greater than 100,000 mg/L. However, most of the salts that are likely to precipitate are highly soluble in water, so treatment with fresher brines will be sufficient to remove them, and scale dissolver chemicals should not be required. In the UK Southern North Sea fields, although NaCl remains the most dominant salt, $MgCl_2$ and $CaCl_2$ may also co-precipitate.

Introduction

''If we look at the history of industrialization, societies generally started by dumping waste products into the environment, be it sewage, slag, industrial waste, sulphur dioxide and so on. Once the negative consequences of the release were understood society then moved to stop the practice and became prepared to pay the price. This is the challenge that society needs to face with carbon dioxide (CO_2)'' (Tucker, 2018). The Intergovernmental Panel on Climate Change (IPCC) and International Energy Agency (IEA) both identify Carbon Capture and Storage (CCS) as a key technology to stabilizing greenhouse gas concentration in the atmosphere and achieving the net zero target. The yearly emission of CO_2 on Earth is around 36 Gt (100 Mt daily) of which about 45 Mt per annum is the collective capacity of the 35 commercial CCUS facilities in operation as reported in the 2022 World Energy Outlook by the International Energy Agency. As recognized at the 28th Conference of the Parties to the UN Framework Convention on Climate Change, global greenhouse gas emissions need to reduce by 43% by 2030 if the 2050 net-zero target is to be achieved. However, despite the resolution of the 2015 Paris Agreement to keep the rise in mean global temperature to well below 2°C (3.6°F) above pre-industrial levels, and preferably limit the increase to 1.5°C, the level of CO_2 in the atmosphere continues to rise. In December 2023, researchers involved in the Global Carbon Project highlighted that greenhouse emissions in 2023 increased by 1.1% and 1.5% relative to 2022 and pre-pandemic levels respectively.

The IEA estimates that 1.2 Gt and 6.2 Gt of CO_2 needs to be captured yearly by 2023 and 2050, respectively, with about ten commercial facilities commissioned monthly from 2022 till 2030. The graph (**Fig. 1**) below which is from Mauna Loa Observatory in Hawaii, USA, shows the need to act fast.

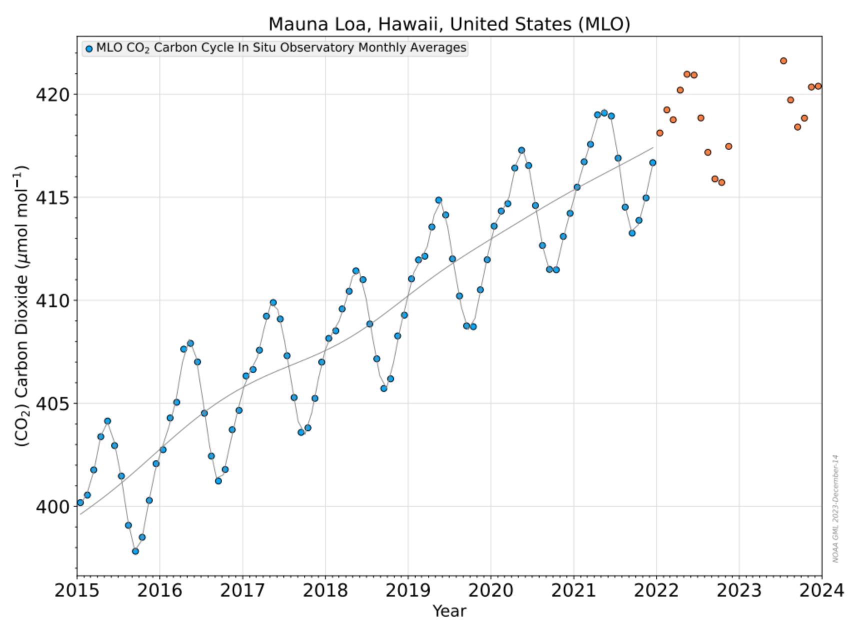

Fig. 1 - CO_2 Concentration Measurement (Earth Systems Research Laboratories – Global Monitoring Laboratory; accessed 14th December 2023)

CCS technology however requires a storage site that needs to be certified fit for injection of CO_2. **Fig. 2** below shows the pillars/questions that must be satisfied for a site to be considered geologically safe for injection.

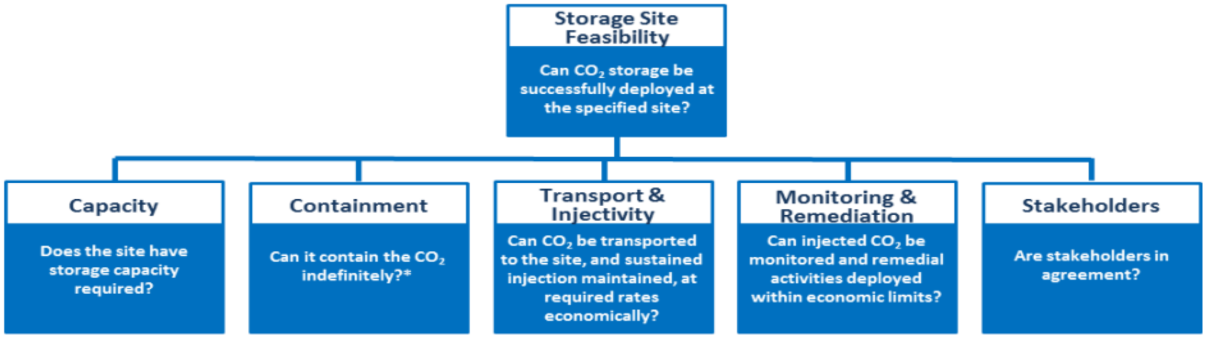

Fig. 2 - Pillars of Carbon Capture and Storage (Tucker, 2022)

Once the storage site has been demonstrated to have the required capacity, the next thing is to establish that the capacity to store can be accessed, and that sustained injection can be maintained at required rates economically throughout the injection period. The total mass of CO_2 that can be injected will decrease if there is a restriction to the accessible volume of the system if there is a risk of cap rock failure or if there is salt precipitation.

Theory and Methods

The phenomenon of salt precipitation has been described by Cui et al. (2023) as a combination of gas-liquid seepage and mineral crystallization. When CO_2 is injected into a saline aquifer, the CO_2 displaces the resident brine, increasing the molar fraction of water in CO_2 stream, and then water evaporates into the CO_2 stream which increases brine salinity. The complete evaporation of irreducible water causes a dry out zone. CO_2 solubility in brine increases with increasing pressure and decreases with increasing temperature and salinity. Eqs. 1 and 2 below illustrate the chemical reactions that give rise to changes in pH when CO_2 dissolves in the aqueous phase:

$$CO_{2(aq)} + H_2O = H^+ + HCO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Changes in pH can accompany mineral dissolution or precipitation reactions, but this paper concentrates on precipitation not due to changes in the composition other than the increases in concentrations of all components as the aqueous solvent evaporates.

Three flow zones, namely (i) single-phase brine, (ii) CO_2-Water two phase and (iii) single-phase CO_2 form during CO_2 injection operations. **Fig. 3** is a visualization of the three regions of flow that develop in a reservoir during CO_2 injection:

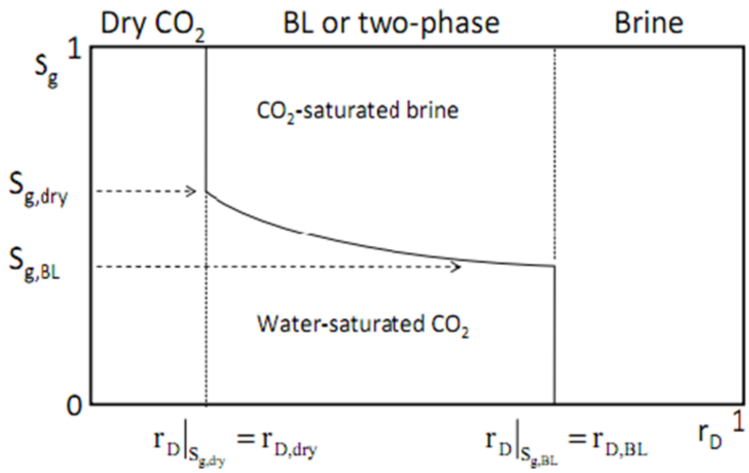

Fig. 3 - Zones that develop during CO_2 injection. (Burton et al., 2008)

At the point where the concentrations of dissolved salts in the brine exceed their solubility limits, the salts begin to precipitate and build up over time leading to blocked pore throats and reduced injectivity. Talman et al. (2019) reported that in the case of Aquistore, deposition of salt occurred when the well was shut in, aquifer brine re-entered the well, brine evaporated into CO_2 and then the thermodynamic condition in the well changed. **Fig. 4** below shows the process of salt precipitation using a wellbore image from Aquistore.

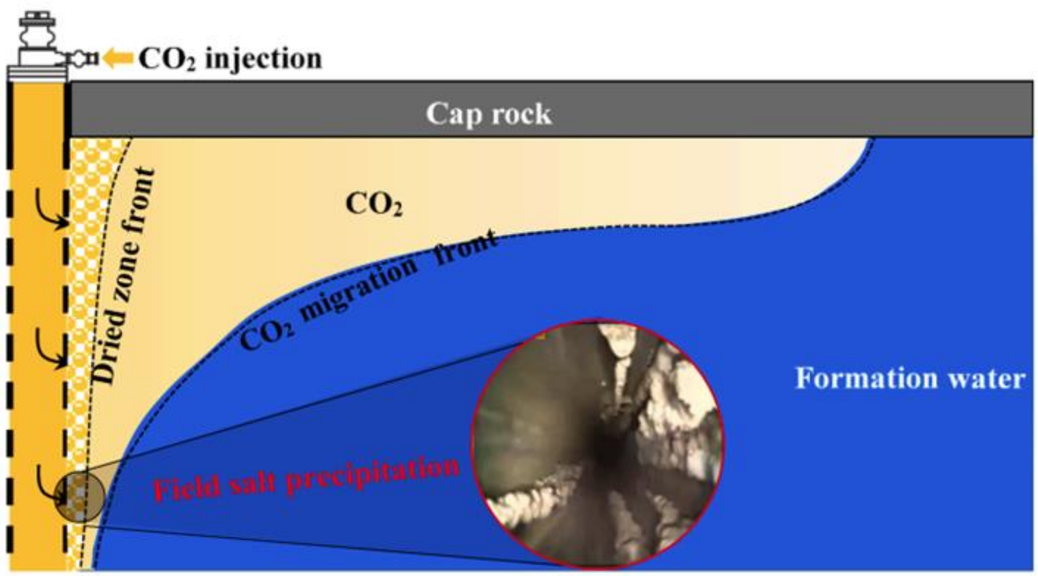

Fig. 4 - Salt precipitation near wellbore during CO_2 injection into saline aquifers (Cui et al., 2023)

With regards to the question of salt precipitation being only a near-well phenomenon or not, several authors have tried to answer this question. The possibility of salt precipitation being a faraway phenomenon was reported by Roels et al. (2014) while the answer of near-well phenomenon was also presented by Van Dorp et al. (2009) and Kleinitz et al. (2001). However, Miri and Hellevang (2016) attempted to put this confusion to rest by relating the location of precipitation to drying regimes (diffusive or capillary). They also made it known that although chemical and physical processes govern salt precipitation, the former has more contribution. A schematic showing the physical processes is seen in **Fig. 5** below:

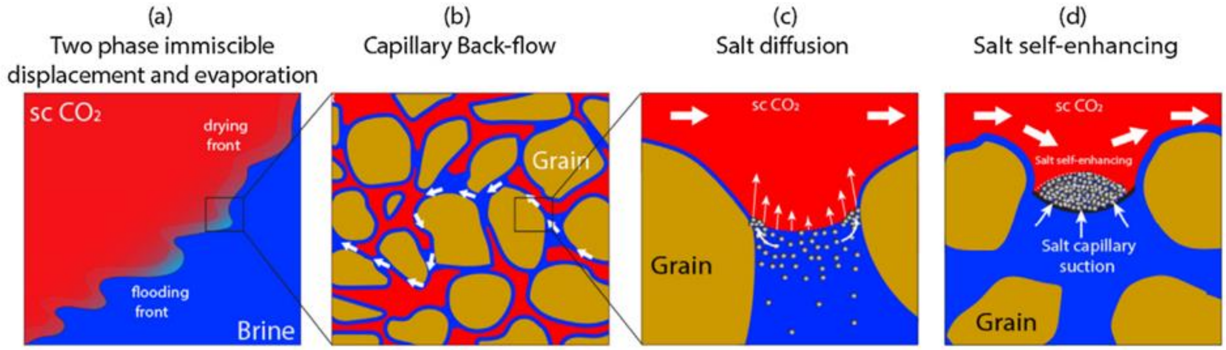

Fig. 5 - Physical processes contributing to salt precipitation (Miri and Hellevang, 2016)

Methodology

For this study, Microsoft Excel was used to compile the required data from literature and perform the necessary calculations. The knowledge of basic chemistry was also essential. The simple flowchart below (**Fig. 6**) shows the step-by-step process adopted to arrive at the desired solution.

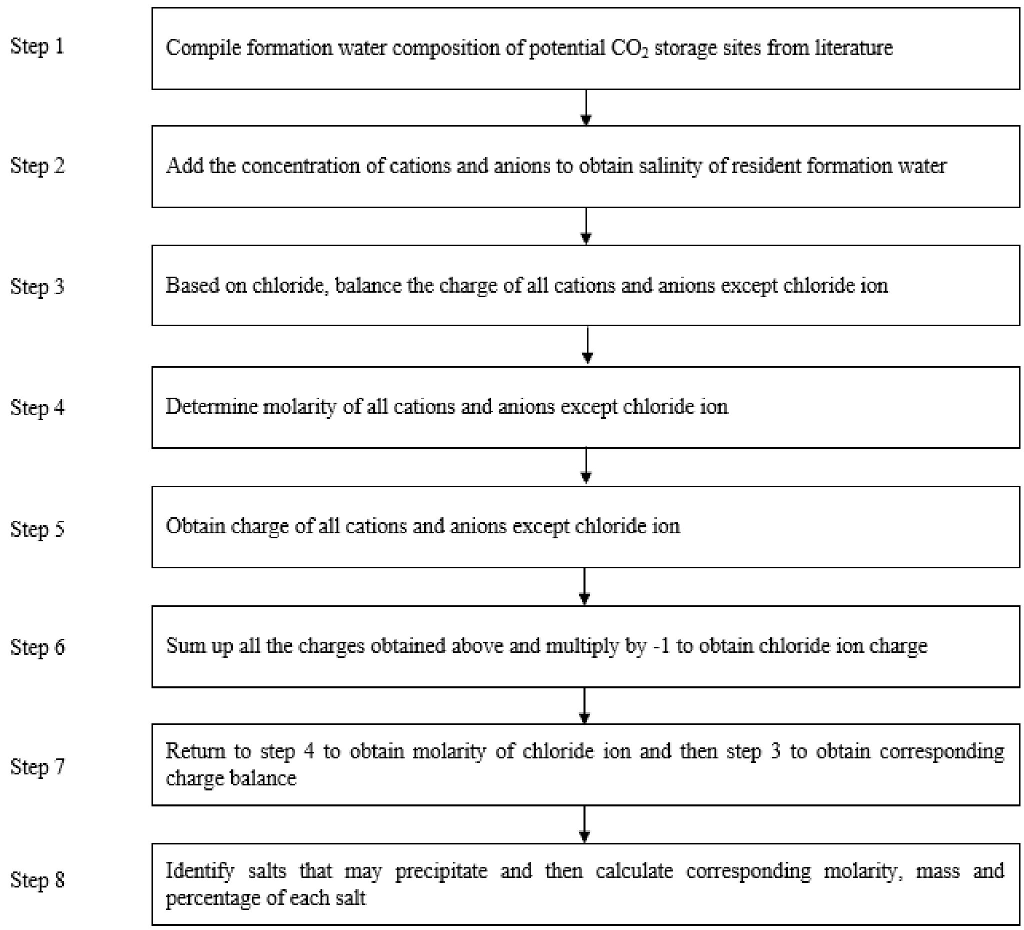

Fig. 6 - Flowchart showing step-by-step process.

Results

Overview

This project focused on identifying salts that could precipitate during CO_2 injection as well as solvents to remove these salts. To achieve this, the pre-injection formation water compositions of demonstration, previous and operational carbon sequestration projects, as well as potential CO_2 injection sites, were obtained from literature. The analysis of the compiled data was then divided into two parts. The first part was based on demonstration, previous and operational carbon sequestration projects around the world while the second part focused on fields in the UK Southern North Sea.

Demonstration, Previous and Operational Carbon Sequestration Projects

First, carbon sequestration projects around the world were identified, classified based on the type of storage site and then resident brine composition were compiled. This can be seen in **Table 1 - 3** below. The Teapot Dome has the lowest salinity brine considered and Aquistore has the highest salinity brine considered in terms of total dissolved solids (TDS). The work of Talman et al. (2019) was used as a baseline for precipitate calculation as it clearly observed salt precipitation at an active CO_2 injection – Aquistore – which has salinity greater than 300,000 mg/L.

Table 1- Formation Water Composition of CCS Projects in Saline Aquifer

		Concentration of Ions (mg/L)												
Type of Storage		Saline Aquifer												
Project name		Sleipner[a]	Sleipner[b]	Sleipner[c]	Snovhit	Gorgon	Decatur	Aquistore	Ketzin[d]	Ketzin[e]	Ketzin[f]	Ketzin[g]	Teapot Dome
Location		Norwegian North Sea			Barent Sea, Norwegian Coast	Barent Island, Australia	Illinois Basin, USA	Saskatchewan, Canada	Central Germany				Wyoming, USA
Storage Formation		Utsira			Tubåen	Dupuy	Mount Simon	Deadwood	Stuttgart				Tensleep
References		Czernichowski et al. (1999)			Trémosa et al. (2014)	IEAGHG (2012)	De Silva et al. (2005	Talman et al. (2019)	Hilke et al. (2010)				IEAGHG (2012)
	Na^+	9,138	8,307	10,392	56,418	7,400	36,708	87,700	87,400	90,400	88,400	90,400	842
	K^+	24,081	29,578	208	496	8,250	1,212	4,960	412	297	294	282	90
	Ca^{2+}	237	215	426	4,628	34	14,188	32,500	2,092	2,059	2,133	2,090	368
	Mg^{2+}	400	345	630	477	22	2,479	1,700	814	835	852	842	34
	Cl^-	47,612	49,317	18,482	96,418	11,771	90,348	203,000	134,000	139,000	136,000	139,000	1,070
	SO_4^{2-}	113	144	n.d	210	669	n/a	150	3,893	3,676	3,638	3,744	
	HCO_3^-	262	311	707	482	6,822	n/a	50	88	57	56	58.7	148
TDS (mg/L)		81,843	88,217	30,845	159,129	34,968	144,935	330,060	228,699	236,324	231,373	236,417	2,552

[a&b] Data from BGS surface analysis of drilling mud contaminated pore water from the Utsira Formation in the Sleipner field cores at 1085.1m and 1085.9m respectively

[c] Data from surface analysis of uncontaminated pore water samples from the Utsira formation in the Osberg field

[d] Water chemistry after 30.2m^3 of water was produced

[e] Water chemistry after 54.7m^3 of water was produced

[f] Water chemistry after 60.8m^3 of water was produced

[g] Water chemistry after 78.7m^3 of water was produced

Table 2 - Formation Water Composition of CO_2-EOR Projects

Concentration of Ions (mg/L)					
Type of Storage		CO_2-EOR			
Project name		Zama	Weyburn- Midale	Uthmaniyah	Uthmaniyah
Location		Northwestern Alberta, Canada	Saskatchewan, Canada	Eastern Province of Saudi Arabia	
Storage Formation		Keg River F	Midale Beds	Arab-D (Low Salinity)	Arab-D (High Salinity)
References		IEAGHG (2012)	Li et al. (2004)	Lindlof and Stoffer (1983)	
	Na^+	65,223	29,140	29,680	51,187
	K^+	314	454		
	Ca^{2+}	9,800	1,970	13,574	29,760
	Mg^{2+}	2,400	566	1,575	4,264
	Cl^-	100,000	52,640	73,861	143,285
	SO_4^{2-}	1,450	3,800	404	108
	HCO_3^-	810			
TDS (mg/L)		179,997	88,570	119,094	228,604

Table 3 - Formation Water Composition of CCS Projects in Depleted Reservoirs

Concentration of Ions (mg/L)				
Type of Storage		Depleted Reservoirs		
Project name		In Salah	Otway	Otway[h]
Location		Central Algeria	Victoria, Australia	
Storage Formation		Tournaisan (C10.2)	Paaratte	
References		Trémosa et al. (2014)	Vu et al. (2017)	Ennis-King et al. (2017)
	Na^+	35,500	563.3	342.2
	K^+	225	56.1	134.9
	Ca^{2+}	22,400	121.5	35.1
	Mg^{2+}	5,276	102.4	18.4
	Cl^-	110,250	181.3	270.5
	SO_4^{2-}	656	5.6	10.3
	HCO_3^-	178	1,996.3	
TDS (mg/L)		174,485	3,027	811.4

Project Ranking (Based on Salinity)

Table 4 - Project Ranking (Based on Salinity; with Aquistore as reference for percentage difference)

Ranking	Project Name	Salinity (mg/L)	Percentage Difference in Salinity (%)	Total Mass of Chloride Salts (g/L)	% NaCl
1	Aquistore	330,000	0.00	365.54	60.99
2	Ketzin	229,000 - 236,000	28.48	231.38 - 239.25	95.79 - 96.07
3	Uthmaniyah	119,000 - 229,000	30.61	137.80 - 274.79	47.35 - 54.75
4	Zama	180,000	45.45	219.23	75.63
5	In Salah	174,000	47.27	215.75	41.83
6	SnØvhit	159,000	51.82	164.43	87.22
7	Decatur	145,000	56.06	168.41	55.41
8	Weyburn - Midale	89,000	73.03	81.09	91.35
9	Sleipner	31,000 - 88,000	73.33	32.79 - 80.60	26.20 - 80.55
10	Gorgon	35,000	89.39	19.12	98.39
11	Otway	800 - 3,000	99.09	0.44 - 1.39	62.40 - 100
12	Teapot Dome	2,600	99.21	3.77	56.81

UK Southern North Sea Fields

The existence of the UK Southern North Sea near major regions of CO_2 emission in the United Kingdom and its presence as a mature gas province with many fields close to cessation of production makes it a desirable candidate for CO_2 sequestration. In this area, there are three geological ages that can be attributed to the reservoirs here namely the Carboniferous, Permian, and Triassic.

In this second part of the work, attempt was made to infer possible connectivity/compartmentalization between fields by evaluating the available formation water salinity compiled from literature, as the biggest concern in CO_2 sequestration is the loss of containment. Data for analysis was extracted from the Compendium of North Sea Oil and Gas fields by (Warren & Smalley (1994) and Compositional Variation of North Sea Formation Water by Warren et al. (1994). Again, the methodology of Talman et al. (2019) was used as a baseline for precipitate calculation. Pickerill field has the least brine considered and Clipper field has the highest brine considered in terms of total dissolved solids (TDS).

Table 5 - Formation Water Composition of Fields in the UK Southern North Sea

Project Name / Field	Proposed Storage Formation/Reservoir	Geological Age	Na^+	Ca^{2+}	Mg^{2+}	K^+	Cl^-	SO_4^{2-}	$HCO3^-$	TDS
Anglia	Rotliegendes	Permian	67840	21000	3410	1470	151940	505	145	246310
Anglia			65940	17000	4500	2400	147000	370		237210
Anglia			80261	12000	6800	2810	168625	700		271196
Anglia			77490	28300	3900	3100	184600	330		297720
Anglia			72350	22830	4240	2260	167250	240	9	269179
Barque	Leman Sandstone (Rotliegendes)	Permian	65500	15200	14500	2000	175480	840		273520
Cleeton	Rotliegendes	Permian	54250	18800	2100	887	121234	340		197611
Clipper*******	Rotliegendes	Permian	70450	239000	3500	2350	165240	565		481105
Esmond	Bunter	Triassic	104000	7100	2400		190000	380	24	303904
Forbes	Bunter	Triassic	112000	8380	1510	800	191000	2100	24	315814
Pickerill	Rotliegendes	Permian	70340	19560	280	1130	154910	265	4	246489
Pickerill			57064	15794	3447	557				76862
Pickerill			16247	29273	729	760				47009
Ravenspurn South********	Rotliegendes	Permian	66190	23380	2870	8310	161060	620		262430
Ravenspurn South			66100	26930	2850	4820	163100	470		264270
Ravenspurn North	Carboniferous	Carboniferous	69200	25500	3700	1500	142200	260		242360
Thames	Rotliegendes	Permian	73430	15510	4980	1660	156905	520	42	253047
Thames*********			86339	3758	3203		144382	6528	214	244424
Thames			70360	10860	3560	9020	145630	1500	70	241000
Thames			74980	14030	4680	1540	155630	515		251375
Thames*********			92298	1683	2443		148016	6124		250564
Welland	Rotliegendes	Permian	72650	14030	4760	1530	152300	425	67	245762
Welland			68520	11340	3390	1590	136970	520		222330
Indefatigable **********	Leman Sandstone (Rotliegendes)	Permian	77940	11822	4093		146763	461		241079
Corvette	Leman Sandstone (Rotliegendes)	Permian								0
Leman***********			75250	12770	2910		146830	570	21	238351
Leman***********			67470	10850	2380		138290	430	150	219570
Leman***********			77700	12100	2900		144000	600	230	237530
Leman***********			56620	12190	2330		117962	1391	6	190499
Leman***********			53350	8380	1780		101200	700	120	165530
Hyde************	Lower Leman Sandstone (Rotliegendes)	Permian	74500	20700	2580	1480	146000	430		245690
Hyde************	Lower Leman Sandstone (Rotliegendes)		72100	19900	2540	1425	146000	420		242385
Hyde************	Lower Leman Sandstone (Rotliegendes)		69900	20850	2560	1550	136996	390	47	232293
Amethyst (West and East)*************	Leman Sandstone (Rotliegendes)	Permian	61800	22000	2520	1230	149000	830	155	237535
Amethyst (West and East)	Leman Sandstone (Rotliegendes)		60100	18900	3060	1275	140750	0	100	224185
Amethyst (West and East)	Leman Sandstone (Rotliegendes)		65600	21500	2840	1330	147200	350	35	238855
Amethyst (West and East)	Leman Sandstone (Rotliegendes)		61500	20860	3610	1330	144090	355	64	231809
West Sole	Lower Leman Sandstone (Rotliegendes)	Permian	54850	20350	9280	2800	150310	1040		238630

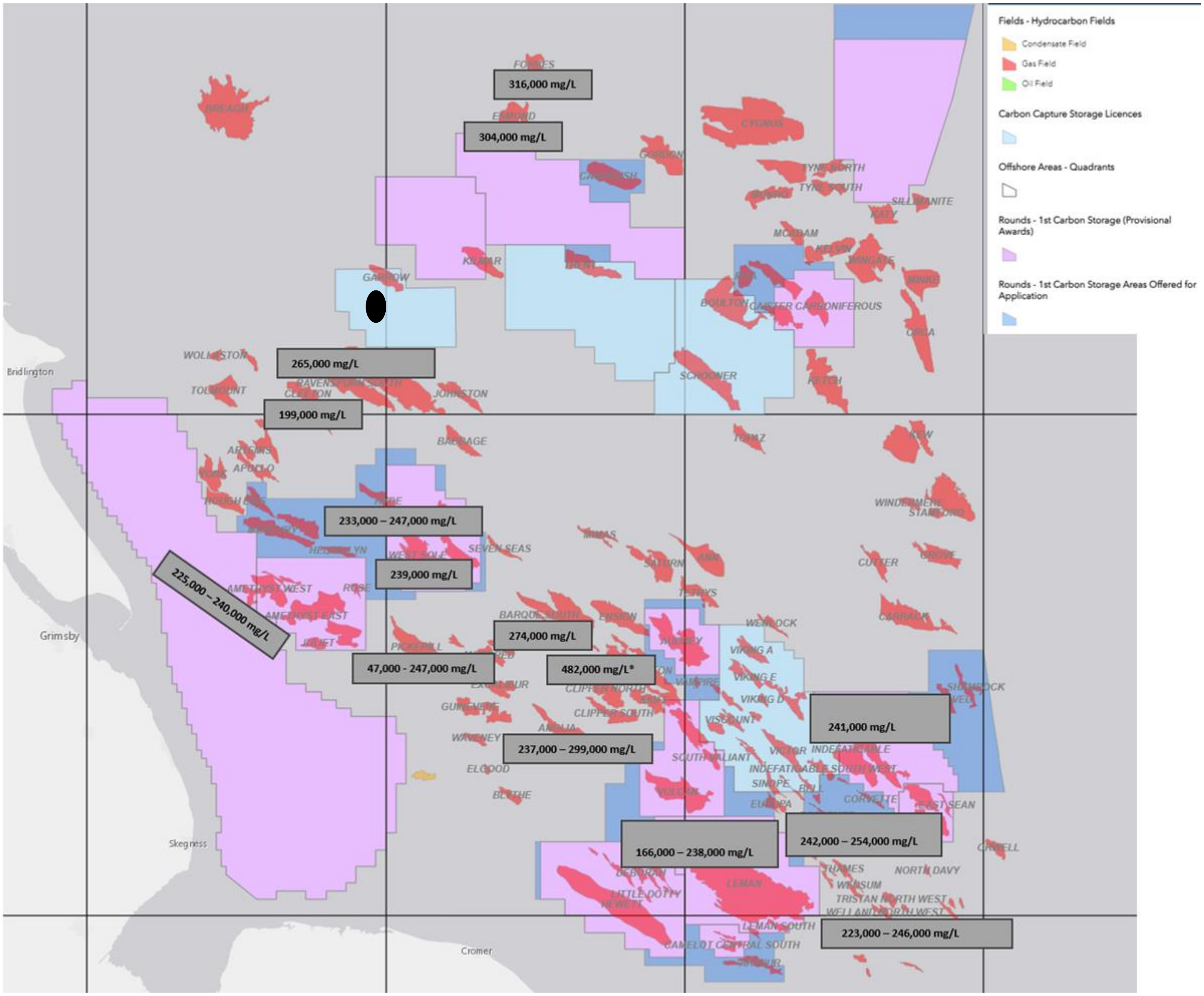

Fig. 7 - Map showing salinity in terms of total dissolved solids (TDS) for fields in the Southern North Sea (North Sea Transition Authority; accessed 10th August 2023)

Project Ranking (Based on Salinity)

Table 6 - Project Ranking (Based on Salinity, with Clipper as reference for percentage difference)

Ranking	Field	Salinity (mg/L)	Percentage Difference in Salinity (%)	Total Mass of Chloride Salts (g/L)	% NaCl
1	Clipper*	482,000	0.00	1088.65	16.45
2	Forbes	316,000	34.44	326.37	87.24
3	Esmond	304,000	36.93	309.89	85.31
4	Anglia	237,000 – 299,000	37.97	271.64 - 338.82	58.14 - 65.98
5	Barque	274,000	43.15	346.08	48.11
6	Ravenspurn South	265,000	45.02	292.93 - 302.86	56.18 - 58.08
7	Thames	242,000 – 254,000	47.30	249.81 - 287.53	64.92 - 90.50
8	Hyde	233,000 – 247,000	48.76	277.89 - 289.06	63.94 - 65.55
8	Pickerill	47,000 – 247,000	48.76	156.22 - 254.65	26.44 - 70.22
10	Welland	223,000 – 246,000	48.96	246.37 - 278.15	66.40 - 70.70
11	Indefatigable	241,000	50.00	275.03	72.04
12	Amethyst	225,000 – 240,000	50.21	250.01 - 271.34	59.00 - 61.46
13	West Sole	239,000	50.41	295.45	47.19
14	Leman	166,000 – 238,000	50.62	180.03 - 264.97	73.13 - 75.33
15	Cleeton	199,000	58.71	225.61	61.13

*Unusually high Ca concentration was reported making salinity very high and the analysis was reported not to charge balance Possibly typographical error ?

Discussion

In 2017, the UK Oil & Gas Authority conducted a salting study on fields in the Southern North Sea to quantify the impact of salt precipitation on production losses. According to the report, seven field operators participated in the study due to direct experience with or in anticipation of salt precipitation issues. Although the names of the fields studied were not available in the document, clues were, however, provided. Salting majorly affected wells in the Permian age fields, and then Carboniferous age fields, which typically have higher salt concentrations than Triassic and Permian fields. Based on the study and in addition to Leman field which is of Permian age and reported by Navarathna et al (2023) to have experienced salt precipitation, we believe all but field 2 and 3 could have similar issues. However, this needs to be confirmed.

Since Gluyas and Bagudu (2020) reported a salinity value of 250,000 ppm NaCl equivalent for Endurance CCS Bunter formation (black circle in **Fig. 7**) which is of Triassic age and Warren and Smalley (1994) reported water composition of Esmond and Forbes field of Bunter formation and also Triassic age to be 304,000mg/L and 316,000mg/L respectively, we believe these values can be used as benchmark for Bunter formation of other fields of Triassic age in the North Sea where data is unavailable.

Possible communication/compartmentalization between fields based on Salinity?

Several authors (de Jonge-Anderson and Underhill, 2022; Goffey et al., 2020; Underhill et al., 2023) have highlighted the subsurface geology issues that fields in the Southern North Sea face ranging from connectivity, small size, structural compartmentalization, low reservoir permeability etc; which makes it imperative to understand the fields in detail before selecting for CO_2 sequestration. For instance, the large variation in salinity recorded in Pickerill field as seen in **Table 6** above could be an attestation to its compartmentalization.

An in-depth look into the values of salinity and location of each field made it possible to speculate possible connected fields whose subsurface geology needs to be studied in greater detail before this inference can be confirmed. A list of these fields is given below:

1. Hyde and West Sole
2. Esmond and Forbes
3. Thames complex and Welland if Tristan Northwest has similar salinity.
4. Leman and Thames Complex (Thames, Yare, Bure and Wensum)]
5. Pickerill and Barque
6. Barque and Clipper if recorded Ca concentration for Clipper field is wrong.
7. Anglia and Clipper if recorded Ca concentration for Clipper field is wrong.

A list of unconnected fields based on formation water composition is given below:

1. Ravenspurn and Cleeton
2. Amethyst and West Sole/Hyde
3. Indefatigable and Leman/Thames Complex

Fig. below is a map of fields in the UK Southern North Sea with circle showing possible connected fields and the red X showing unconnected fields inferred only from available formation water composition.

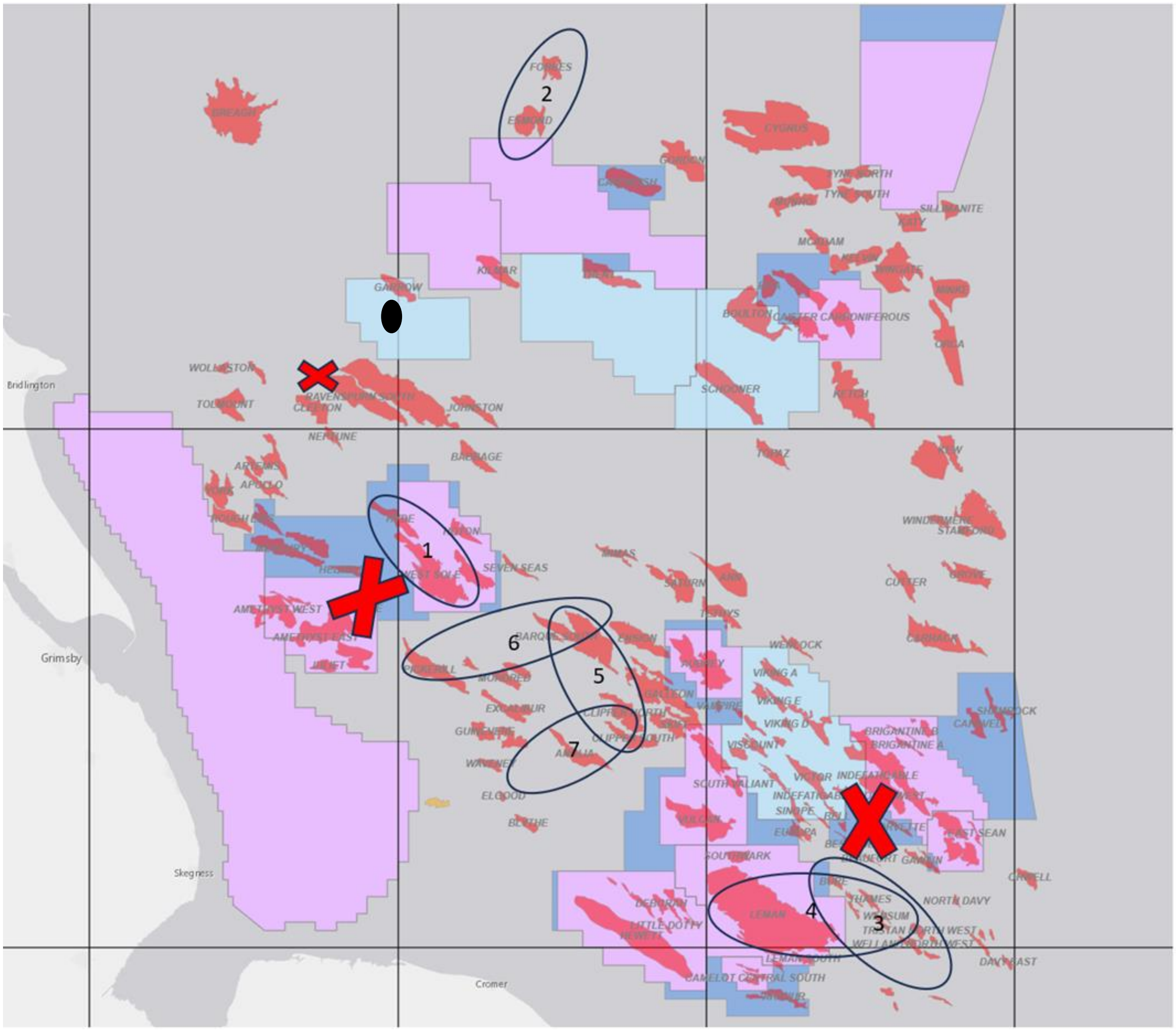

Fig. 8 - Map showing possible connected and unconnected fields in the UK Southern North Sea based on salinity (North Sea Transition Authority; accessed 10th August 2023).

Conclusions

Several attempts have been made to try to understand halite precipitation i.e., NaCl, and since Na and Cl tend to be the most abundant ions in formation waters, this makes sense. Halite can be removed by wash water treatments, precisely because NaCl is highly soluble in water. However, there will be other components in the brines, meaning other salts will precipitate alongside halite. Some of these other salts may have much lower solubilities, and so, unlike halite, may not be removed by wash water treatments, but require more aggressive dissolver treatments. This work focused on salt precipitation – a challenge that might reduce injectivity; the third pillar as highlighted in Fig. 2 that needs to be in place. By identifying salts prone to precipitation, operators can better plan CO_2 injection schemes to mitigate injectivity issues.

The type of salts that can precipitate during CO_2 injection have been identified for a variety of sequestration projects and fields using resident formation water composition obtained from literature. This work now makes it possible for potential carbon sequestration operators to quickly have an idea of the mass of salt per litre of water to expect prior to injection of CO_2 and plan their injection schemes to avoid escalated project cost.

By calculating the concentration of precipitates, several conclusions can be drawn from the analysis. These conclusions are stated as follows:

- Generally, salt precipitation is a concern regardless of the magnitude of salinity. However, it can be a major concern when salinity is greater than 100,000mg/L.
- Most of the salts that are likely to precipitate are highly soluble in water so treatment with fresh water should be sufficient just like in gas wells. A pre-emptive solution could be displacing formation water with slug of fresh water before injecting CO_2.
- Although NaCl remains the most dominant salt in the Southern North Sea, $MgCl_2$ and $CaCl_2$ should not be ignored. If the water composition of the fields in the Southern North Sea are correct, lot of research will be needed to understand formation behaviour to optimize the freshwater treatment and reducing the long-term effect of precipitation.

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