

SALT PRECIPITATION AND CEMENT DEGRADATION DURING CO₂ STORAGE: A BRIEF REVIEW

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Abstract: CO₂ emission has increased significantly in the past 50 years and it has become a real threat to the environment. One of the alternatives to decrease CO₂ emission is storage it into aquifer or depleted oil reservoirs. During CO₂ injection into reservoirs, industries have faced numerous problems. The main problems mentioned in the literature are salt precipitation and cement degradation. In this paper, we propose a methodology to select the most relevant works related to the previous mentioned problems. Afterwards, we prepare a brief literature review including the main physical mechanisms, phenomena, and finds regarding to salt precipitation and cement degradation. Finally, we conclude the paper showing the potential technological opportunities to be developed.

Keywords: CCS; CO₂ leakage; formation damage; well cement.

PRECIPITAÇÃO DE SAIS E DEGRADAÇÃO DE CIMENTO DURANTE A ESTOCAGEM DE CO₂: UMA BREVE REVISÃO

Resumo: As emissões de CO₂ vêm crescendo significativamente nos últimos 50 anos, tornando-se uma ameaça real ao meio ambiente. Uma das alternativas para diminuir a emissão de CO₂ é seu armazenamento em aquíferos ou reservatórios depletados. Durante a injeção de CO₂, as indústrias têm enfrentado inúmeros problemas. Os principais problemas mencionados na literatura são a precipitação de sais e a degradação de cimento. Neste artigo, propõe-se uma metodologia para selecionar os trabalhos mais relevantes e, em seguida, prepara-se uma sucinta revisão da literatura incluindo os principais mecanismos físicos, fenômenos, e descobertas relacionadas à precipitação de sais e degradação de cimento. Portanto, este trabalho procura apontar as potenciais oportunidades tecnológicas a serem desenvolvidas nesta abordagem.

Palavras-chave: CCS; Vazamento de CO₂; dano à formação; cimentação de poços.

1. INTRODUCTION

In the last few decades the emission of carbon dioxide (CO₂) has increased significantly around all over the world [1]. CO₂ is emitted from different sources as power plants, oil refineries, hydrogen, iron, cement and other industrial plants [2], besides of industrial emissions, individual anthropogenic emission of CO₂ from vehicles, residential gas consumption, collective transportation have contributed largely for increasing concentration level of disposal CO₂ in the environment [1]. The amount of CO₂ emission has become a problem of this century, and one of the alternatives to mitigate it is replacing the current energy sources to renewed energy ones [3]. However, this is not a feasible alternative at least for the next decades [3].

Another option to decrease the excess of CO₂ present in the atmosphere is CO₂ capture and storage (CCS) [4,5]. There are several technologies in development to capture CO₂ from air (artificial tree), from power plants and different industries utilizing different methods such as absorption, adsorption, membranes and cryogenics processes [6]. Most of these processes are very expensive, nevertheless CO₂ captured by these processes can be used to recycle CO₂ and produce new products that aggregate values and can be sold transforming such technologies economically feasible [7]. Whilst the aforementioned processes do not become practicable, many companies, mainly oil companies have used their own technologies to store CO₂ in aquifer or depleted oil reservoirs, to recover additional oil using CO₂ as a tertiary recovery method [8], or in case of unconventional scenarios, as shales gas in USA, CO₂ has been used as a working fluid to efficiently fracture the reservoir [9], or in Brazil's pre-salt fields, where the content of CO₂ can reach up to 44%, the produced CO₂ is directed reinjected into the same reservoir to solve simultaneously two problems, CO₂ releasing to atmosphere and enhanced oil recovery (EOR) [10]. Despite the oil industries have been using CO₂ injection for more than 20 years, they are still facing different challenges [11].

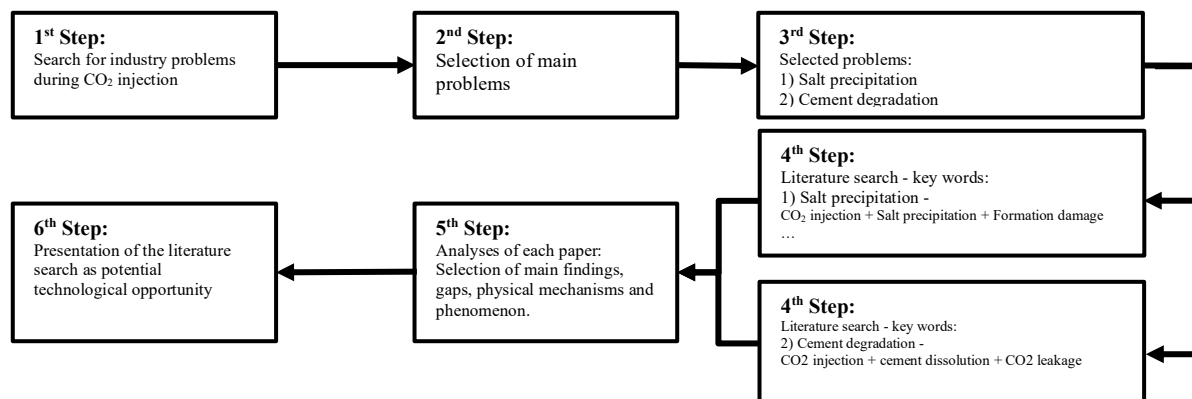
During CO₂ injection, CO₂ can react with well cement altering its porosity and permeability. The well cement degradation could cause CO₂ and reservoir fluids leakage [12]. Other common problem during CO₂ injection is salt precipitation and rock dissolution. In general, these processes occur due to CO₂ reaction with rock matrix, or due to CO₂ mass and heat exchanging with saline water [5,13–15].

In this paper we briefly address the main challenges during well cement degradation and salt precipitation during CO₂ storage. We also present the main chemical reaction equations and explain phenomenological mechanisms of cement degradation and salt precipitation based in a deep literature research.

2. METHODOLOGY

This paper presents a literature review of two main problems faced by petroleum companies during CO₂ injection into reservoirs – salt precipitation and cement degradation. Firstly, we searched at the literature for all problems involving CO₂ capture and storage (CCS) and we evaluate the technology readiness level of each problem. Then we chose the problems that industries are still trying to solve. Afterwards, we herein evaluate a great number of papers that have been published in the past 10 years. We make a critical analysis of each paper and present the available phenomenological explanations for the aforementioned problems. Fig. Figure 1 shows a block diagram of the research methodology.

Figure 1: Description of literature research.



3. RESULTS AND DISCUSSION

3.1. Salt precipitation

There are numerous papers that show evidences of salt precipitation during CO₂ injection into reservoir [5,16]. In general, CO₂ is injected into reservoir in supercritical thermodynamic conditions, when it meets the formation water occurs heat exchange and consequently water evaporation. The evaporated water is carried by CO₂ flux. This process dries out the saline water leading to a severe increased in salt concentration. When the salt exceeds its solubility, it occurs salt precipitation. The salt accumulate in the pore throat and reduce the reservoir permeability and porosity [5,17].

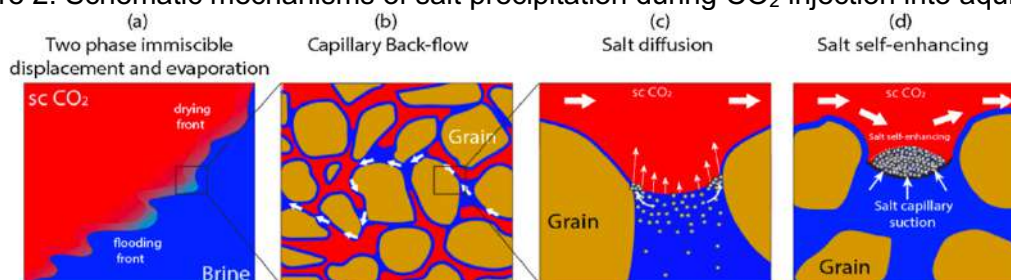
One of the first studies related to salt precipitation during supercritical CO₂ (scCO₂) injection was reported by [18]. They performed core flood experiments in Berea sandstone saturated with 25% NaCl brine and injected scCO₂ for 32 hours. It was observed a 60% permeability reduction due to salt precipitation and consequently injectivity decline. They also conducted numerical simulation studies and concluded that permeability impairment is also predicted due to substantial salt precipitation. In order to mitigate this phenomenon, the authors suggested fresh water pre-flushing prior to scCO₂ injection. This suggestion is doubtful, it is well know that injection of fresh water in sandstone reservoir can cause severe damage due to fines migration [19,20]. Other researchers also documented similar results utilizing different experimental methodologies and concluded that besides salinity, there other parameter that can direct affect the salt precipitation [13,14,21,22]. However, there are some researches claiming that in some conditions, water evaporation can increase the path of CO₂ into porous media. This point of view may increase the CO₂ relative permeability and improve injectivity [23,24]. On the contrary, other research group observed reduction of 50% of CO₂ relative permeability during salt precipitation [21]. Although numerous experimental investigations reported in the literature, there are still a lack of understanding of the physics and thermodynamic behavior inside the porous media.

The most acceptable phenomenological mechanisms of salt precipitation during scCO₂ injection into reservoir available in the literature is defended by [15,24,25], constated via microscopic visualizations experiments by [16], and clearly described by [5]. According to [5], there are 5 distinguished physical mechanisms leading to salt precipitation, as shown in Fig. Figure 2.

The first mechanism is the *two-phase displacement* where scCO₂ drives the formation water way from the injector well. This mechanism regards the viscous forces and mobility of each phase. Simultaneously to the first mechanism there are instantaneous *water evaporation*, this water steam is carried by the scCO₂ flux and this

phenomenon is called the second mechanism. The third mechanism occurs due to *capillary effects*, after the exposed by scCO_2 , the porous media still has a film of formation water around the rock grains, by capillary effects, the saline water in front of this region is driven backwards to positions where water has dried out. This effect is shown in Figure 2b, where the water flow direction is opposite to the scCO_2 flow. The third mechanism is responsible to bring back salt and concentrate even more region closer to the injector well, decreasing the well injectivity. The fourth mechanism refers to *salt diffusion* way to the dried-out front (Fig. Figure 2c). The fifth mechanism is called salt self-enhancing and occurs due to capillary effects that drive the salt to the scCO_2 -water interface (Fig. Figure 2d).

Figure 2: Schematic mechanisms of salt precipitation during CO_2 injection into aquifer [5].

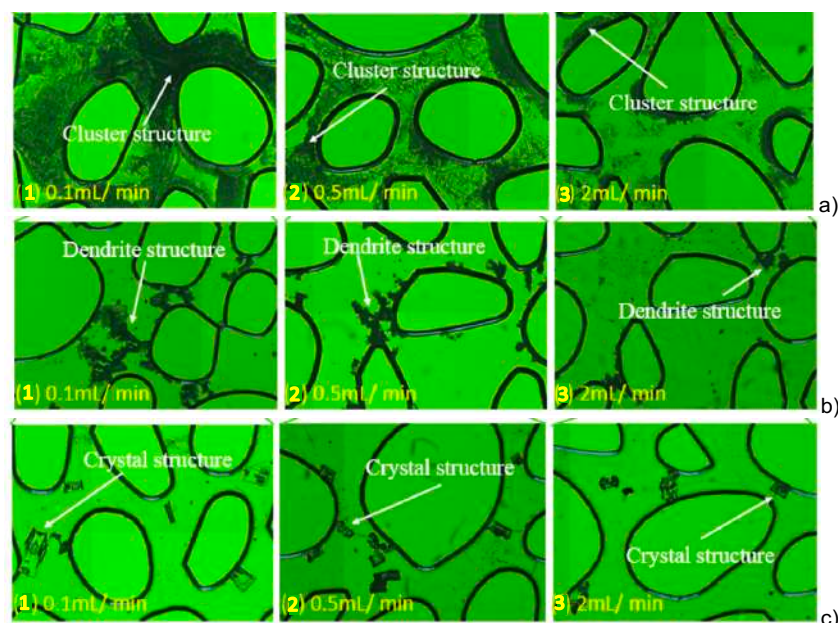


The evidences of most of the described mechanisms suggested by [5], it was experimentally visualized by [16] as shown in Fig. Figure 3. In agreement with [5], experiments conducted by [16] have shown that there are parameters that can interfere directly to salt precipitation, as scCO_2 flow rate and rock wettability (Fig. Figure 3).

As the scCO_2 flow rate increases, the deposition of salt precipitation decreases. This is explained by drag force that exceeds the attached forces on salt crystals. The rock wettability also plays an important role in salt precipitation, hydrophilic surface (Fig. Figure 3a) contributes much more salt crystal deposition than neutral surface (Fig. Figure 3b) and hydrophobic rock surface (Fig. Figure 3c) [16].

Despite of solids phenomenological and physical finds, it is necessary to understand better the thermodynamic behavior of salt precipitation to mitigate it.

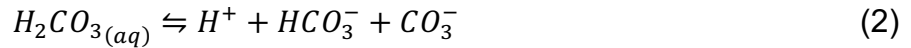
Figure 3: Salt precipitation at 3 different scCO_2 flow rate conditions (1) 0.1; (2) 0.5; and (3) 2 mL/min; at different rock wettability scenarios a) hydrophilic; b) neutral; c) hydrophobic [16].



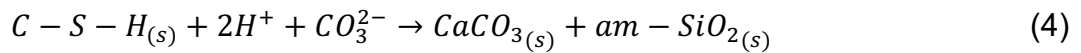
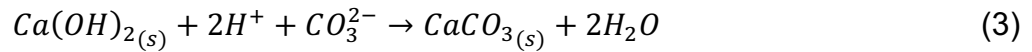
3.2. Cement degradation

The connection between the surface and the reservoir is the drilled well, where it is sealed by cementation between the well casing and the reservoir formation to stabilize the well wall. Usually the cement has very low permeability and prevent the scaping of any fluids from the reservoir. However, in the last few years, wells have shown leakage problems during CO₂ injection or even after the well has been cemented and abandoned [12,26].

These problems are mainly caused when scCO₂ meets the saline water in the reservoir and dissolves into aqueous phase, generating carbonic acid leading to a severe lowering of pH as describe by the following chemical reaction [12,27]. In general, the cement used in the injector wells has pH between 12 and 14 [12,27], therefore, if the cement is exposed to a low pH environment, as the one created by CO₂ dissolved in formation water (Eqs. 1 and 2).



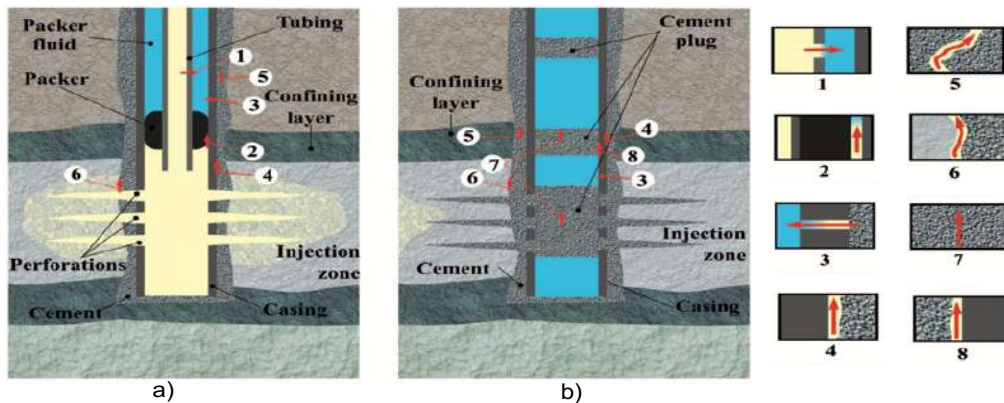
The cement suffers dissolution reactions as described by reaction equations 3 and 4 (cement carbonation) [12,27].



where $Ca(OH)_{2(s)}$ is the actually the cement phase, $C - S - H_{(s)}$ is calcium silicate hydrate, which is the biding phase of cement past, and $am - SiO_{2(s)}$ is amorphous silica gel [4,12]. Eqs. 1 – 4 are the main reaction equations that describe cement degradation.

The CO₂ leakage can occur by different mechanisms [12,26]. During CO₂ injection in active well, the piping pressure is very high, and it can cause corrosion on pipeline/tubing as shown in Fig. Figure 4, #1. Due to high pressure, it is possible leakage throughout the packer (Fig. Figure 4, #2). Another possible leakage can occur throughout the cracking at the cement case (Fig. Figure 4, #3), however it is not common. The leakages described by Fig. Figure 4, #4 – #8 are characterized by the previous reactions equations and it is mainly due to cement degradation/dissolution [26].

Figure 4: Possible CO₂ leakage mechanisms in a) activity CO₂ injector well and b) abandoned well [26].



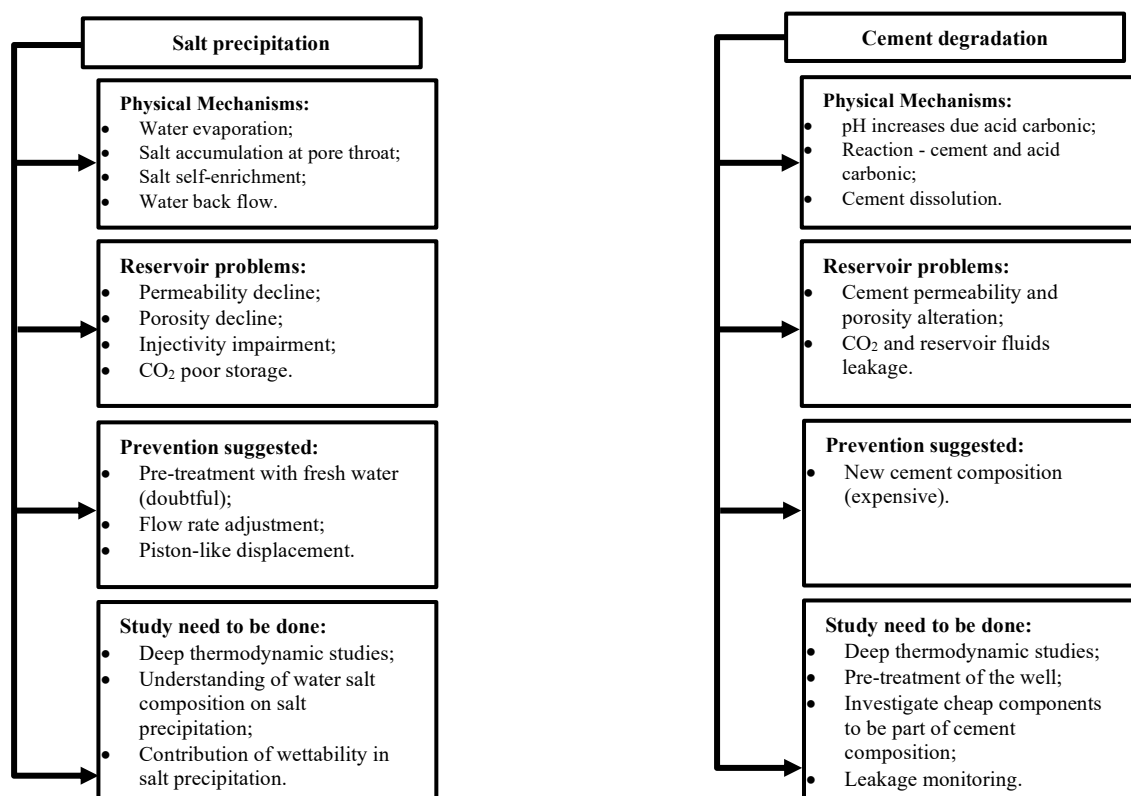
There are many researches in development to study the parameters and conditions that most affect the aforementioned leakage mechanisms [12,28]. Some researchers are trying to develop a more resistance cement and even to utilize nanotechnology to improve the cement composition [4], while others are studying different scenarios and realizing study cases to better understand what is really leading to cement degradation [29,30].

Despite all studies in progress, there is still a lack of researches that intent to study deeply the thermodynamic behavior of scCO₂-brine to avoid the cement degradation or even to improve the cement composition based on thermodynamic analyses.

4. CHALLENGES AND NEXT STEPS

The brief studies regarding to *salt precipitation* and *cement degradation* have shown that there are a lot of points to be investigated and improved. Figure 6 shows a block diagram to illustrate the challenges relate to each topic and the next steps to prevent/mitigate these problems.

Figure 5: Challenges and next steps for major problems during CO₂ injection.



5. CONCLUSION

This paper aimed to select from contemporaneous literature the main problems regarding to CO₂ injection and storage into reservoirs. After an intensive literature search, it was found that *salt precipitation* and *cement degradation* were the main problems during CO₂ storage into reservoirs. Despite all physical mechanisms, finding, and suggestion to mitigate these problems, a deep thermodynamic understanding of both problems still needs to be done. Besides that, new experiments and understanding related to rock properties, formation water composition, new cement formulation and its economic feasibility need to be performed. Therefore, this paper

shows that there are still numerous problems to be solved during CO₂ injection and its also indicates ways to be followed to advance in this research area.

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5. REFERENCES

- ¹H. Ritchie, M. Roser, CO₂ and greenhouse gas emissions, Our World Data. (2017).
- ²J. Gale, Overview of CO₂ emission sources, potential, transport and geographical distribution of storage possibilities, in: IPCC Work. Carbon Dioxide Capture Storage, 2002: pp. 15–29.
- ³H. Ostovari, A. Sternberg, A. Bardow, Rock 'n' use of CO₂: carbon footprint of carbon capture and utilization by mineralization, Sustain. Energy Fuels. (2020).
- ⁴M. Tiong, R. Gholami, M.E. Rahman, Cement degradation in CO₂ storage sites: A review on potential applications of nanomaterials, J. Pet. Explor. Prod. Technol. 9 (2019) 329–340.
- ⁵R. Miri, H. Hellevang, Salt precipitation during CO₂ storage—A review, Int. J. Greenh. Gas Control. 51 (2016) 136–147.
- ⁶A. Al-Mamoori, A. Krishnamurthy, A.A. Rownaghi, F. Rezaei, Carbon capture and utilization update, Energy Technol. 5 (2017) 834–849.
- ⁷F.M. Stuardi, F. MacPherson, J. Leclaire, Integrated CO₂ capture and utilization: A priority research direction, Curr. Opin. Green Sustain. Chem. 16 (2019) 71–76.
- ⁸J.R. Sminchak, S. Mawalkar, N. Gupta, Large CO₂ Storage Volumes Result in Net Negative Emissions for Greenhouse Gas Life Cycle Analysis Based on Records from 22 Years of CO₂-Enhanced Oil Recovery Operations, Energy & Fuels. 34 (2020) 3566–3577.
- ⁹R.S. Middleton, J.W. Carey, R.P. Currier, J.D. Hyman, Q. Kang, S. Karra, J. Jiménez-Martínez, M.L. Porter, H.S. Viswanathan, Shale gas and non-aqueous fracturing fluids: Opportunities and challenges for supercritical CO₂, Appl. Energy. 147 (2015) 500–509.
- ¹⁰A.S. Carvalhal, G.M. Nunes Costa, S.A.B. Vieira de Melo, Simulation of Enhanced Oil Recovery in Pre-Salt Reservoirs: The Effect of High CO₂ Content on Low Salinity Water Alternating Gas Injection, SPE Reserv. Characterisation Simul. Conf. Exhib. (2019) 11.
- ¹¹Y. Li, P.G. Ranjith, M.S.A. Perera, Q. Yu, Residual water formation during the CO₂ storage process in deep saline aquifers and factors influencing it: A review, J. CO₂ Util. 20 (2017) 253–262.
- ¹²M. Bagheri, S.M. Shariatipour, E. Ganjian, A review of oil well cement alteration in CO₂-rich environments, Constr. Build. Mater. 186 (2018) 946–968.
- ¹³Y. Wang, T. Luce, C. Ishizawa, M. Shuck, K. Smith, H. Ott, M. Appel, Halite precipitation and permeability assessment during supercritical CO₂ core flood, in: Int. Symp. Soc. Core Anal. Halifax, 2010: pp. 4–7.
- ¹⁴G. Bacci, A. Korre, S. Durucan, Experimental investigation into salt precipitation during CO₂ injection in saline aquifers, Energy Procedia. 4 (2011) 4450–4456.
- ¹⁵Y. Peysson, L. André, M. Azaroual, Well injectivity during CO₂ storage operations in

- deep saline aquifers—Part 1: Experimental investigation of drying effects, salt precipitation and capillary forces, *Int. J. Greenh. Gas Control*. 22 (2014) 291–300.
- ¹⁶D. He, P. Jiang, R. Xu, Pore-Scale Experimental Investigation of the Effect of Supercritical CO₂ Injection Rate and Surface Wettability on Salt Precipitation, *Environ. Sci. Technol.* 53 (2019) 14744–14751.
- ¹⁷J. Jeddizahed, B. Rostami, Experimental investigation of injectivity alteration due to salt precipitation during CO₂ sequestration in saline aquifers, *Adv. Water Resour.* 96 (2016) 23–33.
- ¹⁸N. Muller, R. Qi, E. Mackie, K. Pruess, M.J. Blunt, CO₂ injection impairment due to halite precipitation, *Energy Procedia*. 1 (2009) 3507–3514.
- ¹⁹T. Russell, D. Pham, M.T. Neishaboor, A. Badalyan, A. Behr, L. Genolet, P. Kowollik, A. Zeinijahromi, P. Bedrikovetsky, Effects of kaolinite in rocks on fines migration, *J. Nat. Gas Sci. Eng.* 45 (2017) 243–255.
- ²⁰L. Chequer, A. Vaz, P. Bedrikovetsky, Injectivity decline during low-salinity waterflooding due to fines migration, *J. Pet. Sci. Eng.* 165 (2018) 1054–1072.
- ²¹Y. Wang, E. Mackie, J. Rohan, T. Luce, R. Knabe, M. Appel, Experimental study on halite precipitation during CO₂ sequestration, in: *Int. Symp. Soc. Core Anal. Held Noordwijk, Netherlands, 2009*: pp. 27–30.
- ²²H. Ott, K. de Kloe, M. van Bakel, F. Vos, A. van Pelt, P. Legerstee, A. Bauer, K. Eide, A. van der Linden, S. Berg, Core-flood experiment for transport of reactive fluids in rocks, *Rev. Sci. Instrum.* 83 (2012) 84501.
- ²³H. Ott, M. Andrew, J. Snippe, M.J. Blunt, Microscale solute transport and precipitation in complex rock during drying, *Geophys. Res. Lett.* 41 (2014) 8369–8376.
- ²⁴H. Ott, S.M. Roels, K. De Kloe, Salt precipitation due to supercritical gas injection: I. Capillary-driven flow in unimodal sandstone, *Int. J. Greenh. Gas Control*. 43 (2015) 247–255.
- ²⁵Y. Peysson, Permeability alteration induced by drying of brines in porous media, *Eur. Phys. J. Appl. Phys.* 60 (2012) 24206.
- ²⁶N. Gaurina-Međimurec, B. Pašić, Design and mechanical integrity of CO₂ injection wells, *Rud. Zb.* 23 (2011) 1–8.
- ²⁷B.G. Kutchko, B.R. Strazisar, D.A. Dzombak, G. V Lowry, N. Thaulow, Degradation of well cement by CO₂ under geologic sequestration conditions, *Environ. Sci. Technol.* 41 (2007) 4787–4792.
- ²⁸O. Omosebi, H. Maheshwari, R. Ahmed, S. Shah, S. Osisanya, S. Hassani, G. DeBruijn, W. Cornell, D. Simon, Degradation of well cement in HPHT acidic environment: Effects of CO₂ concentration and pressure, *Cem. Concr. Compos.* 74 (2016) 54–70.
- ²⁹V. Barlet-Gouédard, G. Rimmelé, O. Porcherie, N. Quisel, J. Desroches, A solution against well cement degradation under CO₂ geological storage environment, *Int. J. Greenh. Gas Control*. 3 (2009) 206–216.
- ³⁰C. Teodoriu, O. Bello, A review of cement testing apparatus and methods under CO₂ environment and their impact on well integrity prediction—Where do we stand?, *J. Pet. Sci. Eng.* 187 (2020) 106736.