

Colloidal release in high temperature porous media with oversaturated fines during supercritical CO₂ transport

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ABSTRACT

This paper presents the impacts of supercritical CO₂ transport in high temperature porous media with oversaturated fines. The latter phenomenon (indicates oversaturated fines) is in which the lift force of the fine particle over pore surface is greater than the gravitational and electrostatic forces combined, where the fines are released from the pore surfaces and transport along with the permeating fluid as colloidal-suspension flow. During transport, the fines are captured in the pore-throats and thereby deteriorating the permeability and decreasing fluid recovery as well. Therefore, three sets of coreflood tests have been conducted to examine the fines mobilization in porous media during supercritical CO₂ transport and the results have been compared with the results obtained from the subcritical CO₂ flow. Produced suspension-colloids have been sent for microstructural analysis and its outcomes, supported the experimental results. Statistical modelling and literature data were employed and compared for model validation, which revealed high agreement.

Credit author statement

B. Kanimozhi: Experimental Setup and Work, Model Prediction, Calculation, S. Mahalingam: Experimental Setup and Work, and Supervision, Venkat Pranesh: Experimental Design and Work, Data Analysis, Wrote the Manuscript, R. Kesavakumar: Statistical Modelling and Supervision, S. Senthil: Experimental Setup and Work, SEM Interpretation, S. Ravikumar: Sandstone Rock Core and Clay Minerals Characterization, Shanthi Pradeep: SEM Interpretation and Sample Physical Properties Examination, Sandhya Senthil: Data Evaluation, Calculation and Analysis, Raji Murugan: Data Evaluation, Calculation and Analysis

1. Introduction

The phenomenon of colloidal-suspension flows and fines migration in porous materials is a common and frequent event in the petroleum, chemical, geothermal, agricultural, metallurgical, and water resource industries. Specifically, during the process of oil and gas recovery, water production from aquifers, thermal energy extraction and storage, waste

management, microfiltration, crop irrigation, mineral processing etc., (Malgaresi et al., 2020, 2019; Zhang et al., 2019; Shahverdi et al., 2018; You et al., 2014; Ramaswamy and Raghavan, 2011; Sen and Khilar, 2006; Orts et al., 2000). But, this paper emphasizes on the applications to oil and gas recovery and aquifers during CO₂ injection. Because, for the past 3 decades the CO₂ the most notorious greenhouse gas has been employed in the oil and gas fields to mobilize the subsurface reservoir fluids and recovery as well (Pranesh, 2016). Additionally, solid fine particles are naturally present in the porous media. Mostly, these fines are clay and crystalline minerals, such as kaolinite, illite, montmorillonite, smectite, quartz, etc. Even solid fines may occur in the porous rocks due to the erosion of rock matrix and also, there is a bacterial growth in the reservoir rocks (Kanimozhi et al., 2019a; Wennberg et al., 1996). Actually, fines in the porous medium under supercritical CO₂ flow detaches from the pore surface and transport along with the permeating fluid, which is reported both in laboratory and field case studies (Pearce et al., 2019; Xie et al., 2017). Fig. 1 presents the schematic diagram of fines behaviour and colloidal release during supercritical CO₂ flow in the porous media. Usually, fines attached on the rock

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surface are under the governance of the four forces, namely, gravity, electrostatics, lift, and drag. Former two forces keep the fine particle over the rock surface and the latter two forces detach from the rock surface (Zeinijahromi et al., 2016). Generally, fines have a size of order 1 μm (Raha et al., 2007). Commonly, a fine particle over a pore surface is held by a torque balance criterion, as mentioned by the below equation (Yang et al., 2016; You et al., 2016):

$$\frac{\partial(\phi c + \sigma_s + \sigma_a)}{\partial t} + U \frac{\partial c}{\partial x} = 0 \quad (1)$$

where, $\sigma_s + \sigma_a$ = Concentrations of attached and strained fines, U = Darcy velocity, c = Volumetric concentration of suspended particles, t = time, ϕ = Porosity and, x = Distance

Suspended fines in the CO_2 transport in porous media damages the permeability. Actually, fines are held over the rock surface under mechanical torque as mentioned by Zeinijahromi et al. (2016). Under external fluid flow in porous media, when the attaching torque exceeds the attaching torque, the fines tend to remain strongly over the pore surface and also known as undersaturated fines. When this phenomenon occurs in the reverse order it is called as oversaturated fines (Chequer and Bedrikovetsky, 2019). To understand this behaviour in a simple way, following explanation is given.

If the lift and drag forces are greater than gravitational and electrostatic forces then it is called oversaturated fines. This is the condition for fines detachment and migration. This can be mathematically represented below:

$$(F_l + F_d) > (F_g + F_e) = \text{Oversaturated Fines} \quad (2)$$

If the gravitational and electrostatic forces are greater than lift and drag forces then it is called undersaturated fines. This is the condition for fines attachment and retention. This can be mathematically represented below:

$$(F_l + F_d) < (F_g + F_e) = \text{Undersaturated Fines} \quad (3)$$

where,

F_l = Lift Force, F_d = Drag Force, F_g = Gravitational Force, and, F_e = Electrostatic Force

The permeability is declined under the condition of oversaturated fines. These are characterized by pore-throat capture, plugging, clogging, binding (clustering), and bridging. Where the fluid transport in the pore channel has been completely restricted. This phenomenon is shown

schematically in Fig. 1 during supercritical CO_2 transport in porous media with oversaturated fines. Additionally, temperature plays a key role in detaching the fines from the pore surface. Higher temperature reduces the electrostatic forces that hold the fines to the pore surface (You et al., 2016) and as a result, the fines are liberated and migrate in the porous interspace. At a certain point, they are captured in the pore-throat and constitute to permeability decline and fluid flow impairment.

Gravelle et al. (2011), made an experimental analysis and colloidal release modelling in porous media. The authors initially studied the solid particle production in the sandstone storage sites and subsequently, conducted colloidal release and fines detachment experiments by reducing the ionic strength of the permeating water. Their modelling results indicated that water flow in the porous medium drastically released the colloidal particles in the porous medium and additionally, new solid particles are produced from the erosion of the rock matrix. Furthermore, You et al. (2015), investigated the temperature effects on the particle mobilization in porous media. The authors conducted laboratory based mathematical modelling to study this phenomenon. Their modelling results revealed that fines are highly susceptible for detachment and migration under higher temperatures and actually, this phenomenon was experienced in the geothermal reservoirs. They emphasized that fines are attached over the rock surface under the torque balance between drag and electrostatic forces. But, under increasing reservoir rock temperature the electrostatic forces get weakened and consequently, the fines are detached and migrated in the pore channel. In addition, attached particle size distribution can be determined by the maximum retention function that is fine release capacity.

Also, Zhang et al. (2020), studied the fines migration effects on the wettability of sandstone rocks and its mineral components during CO_2 injection in aquifers. Actually, the authors investigate the CO_2 -brine wettability of minerals and sandstones. They stated that in general five types of minerals are existing in the sandstone rocks, such as quartz, kaolinite, chlorite, microcline, and Muscovite. Contact angle (wettability) test and SEM-EDS tests have also been performed. It was observed from their modelling that the wettability of sandstone was not affected by temperature and pressures. But, clay mineral fines wettability are affected by the fluid chemistry and temperature to some extent and moreover, microstructural images indicated that surface changes in kaolinite, chlorite, and muscovite under the regime of CO_2 -saturated brine.

Fig. 2 shows the single system heat transfer model for colloidal

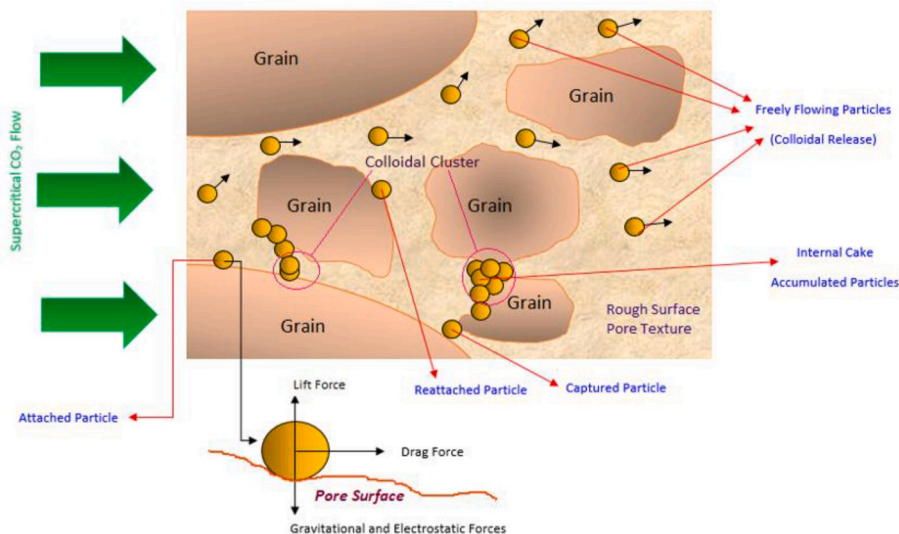


Fig. 1. Schematic diagram indicating colloidal release in porous media during CO_2 Flow.

release in porous media during carbon dioxide transport. It can be seen from the figure that the external fluid source supercritical CO₂ (q_g) carries heat during transport in the porous medium and emit heat to the pore surfaces and this process is called supercritical heat transfer (Q_1). Then huge amount of heat is stored (Q_2) in the pore surface, which act as a source of heat sink. Now the porous medium, which acting as a heat engine produces high degree of heat release and this due to the external fluid invasion on pore surface, which holds the heat (heat conduction) releases the heat to the porous interspace, also known as heat rejection. Then, the overall equation can be written as follows:

$$W_R = q_g + Q_2 \quad (4)$$

where, W_R is the work done due to radiation for liberating or detaching the fines from the pore surface, q_g is the mass flow rate of supercritical CO₂ and Q_2 is the heat rejection from the pore surface. Overall, equation (4) can be considered as the mass transfer term for fines migration in porous media during CO₂ flow.

Pranesh and Ravikumar (2019), performed thermodynamic modelling to porous media as a function of fines migration during water flow. Initially, the authors made an analytical model for heat transfer, conduction, and rejection in porous media. Their analytical modelling outcomes gave an explanation to the fines pore surface detachment and the migration hypothesis under increasing porous medium temperature. In Fig. 3, the authors have given an analytical solution for the non-linear variation of pore wall thermal conductivity with taking fines into an account. Under the assumption of a single capillary tube of porous media model, there are three thermal excitation levels due to continuous heat flow in porous media (Q). Thermal excitation levels 1 and 3 will be higher because it is close to the pore surface and L is the pore surface roughness or texture, which also contribute in the temperature rise. Fines will be detached, suspends, migrate, and re-attach within this thermal regime. Actually, t_1 and t_2 are the temperatures maintained at two ends of the pore wall and $+\beta$ and $-\beta$ are the formation damage coefficient with respect to non-linear temperature. Here the pore surface heat conduction variation plays a crucial role in detaching the fines from the pore surface. Their condition is mentioned below:

$$K = K_i(1 + \beta t) \quad (5)$$

Where, K is the thermal conductivity of the pore wall, K_i initial pore wall with varying thermal conductivity, β is the coefficient of formation damage, and t is time.

There are frequent reports on fines migration in porous media during CO₂ flow. For instance.

Mahalingam et al. (2019), analysed the kaolinite fines migration in porous limestone media during subcritical CO₂ transport. The authors

conducted coreflood experiments to examine this fines migration in the porous carbonate rocks under subcritical conditions. It was revealed from their experimental results that even under subcritical carbon dioxide transport conditions a huge mass transfer of fines has occurred. Additionally, there is a high degree of enthalpy release, abnormal pressure levels in the rock and most importantly, drastic decline of the porous limestone permeability. It should be noted that fines migration is a serious problem even under subcritical conditions. Moreover, Othman et al. (2018), studied the fines migration in sandstone rocks during supercritical CO₂ injection. The authors conducted an experimental and analytical investigation to characterize the fines migration and permeability impairment in the porous sandstone rock during CO₂ transport under supercritical conditions. The main outcomes of the author's research is that there are a migration of quartz, clay (fines), and cement that have decreased the permeability of the sandstone. The microstructural and analytical tests revealed that many pores has been blocked due to instantaneous cement precipitation and entrapment of fines. Furthermore, Sokama-Neuyam et al. (2017), examined the impacts of fines mobilization during CO₂ injection in sandstone cores. Initially, the authors emphasized that CO₂-brine-rock reactions can instigate the fines mobilization in the porous sandstone core. CO₂ injection in the rock potentially lift the fines from the pore surface and migrate in the porous interspace and ultimately, plug the pore-channels, which finally leads to permeability deterioration. Importantly, petrophysical characteristics of the rock and hydrodynamic forces play a vital role in triggering this formation damage and in addition, mineral dissolution and salt precipitation also lead to this phenomenon under CO₂ presence. On the whole, the ultimate objective of this investigation is to estimate and quantify the colloidal-suspension flow in the high temperature porous medium and subsequent, permeability damage and fluid flow decline due to oversaturated fines during supercritical CO₂ transport. Additionally, to examine the fine structure and propose a mechanism that caused the porous material permeability to deteriorate under CO₂ influx.

2. Materials and methods

This section presents the materials and methods that were employed in this paper. Actually, Three sets of coreflood flow test were performed at the temperatures 120 °C (Subcritical, Sb-C), 220 °C (Supercritical, Sc-C), and 240 °C (Supercritical, Sc-C). Actually, the supercritical carbon dioxide flow performance and its impact on porous sandstone core permeability at a higher reservoir temperature was compared with the performance of the subcritical flow.

2.1. Sample preparation

Fig. 4 a) shows the typical photograph of kaolinite clay under 200 mesh size and 4 b) shows the microstructural images of the kaolinite fines under 400 nm magnification. Actually, kaolinite fines were taken in this investigation since this type of fine is abundant and predominant in aquifers, petroleum, and geothermal reservoirs (Wu et al., 2012; Liu et al., 2017). For this purpose, a sandstone core with 35 wt% kaolinite clay content was taken for the tests and the core is having 8.5 cm diameter and a length of 30 cm. The sandstone core is having a porosity of 27% and 200 mD of permeability. This core is exclusively customized for this experimental investigation and this sandstone was procured from a wholesale mineral supplier. The origin of this sandstone rock is from Cauvery Basin, Tamil Nadu, India.

2.2. Coreflood setup

Fig. 5 shows a schematic diagram of the coreflood test setup. It can be seen from the figure that the sandstone core is placed in a stainless steel cylindrical core holder and in turn placed inside the oven. The oven is attached with a thermocouple and three pressure gauges (for measuring

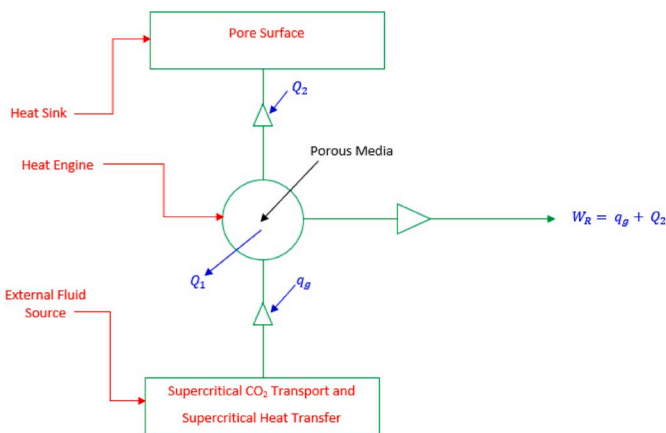


Fig. 2. Single system heat transfer model for colloidal release in porous media due to CO₂ Flow.

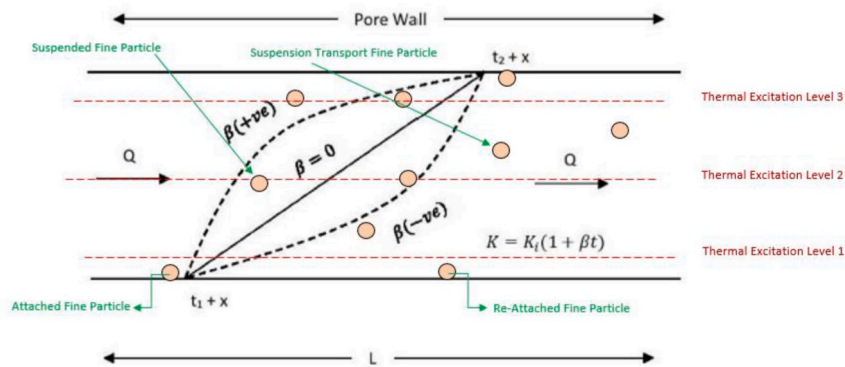


Fig. 3. Non-linear variation of porous wall thermal conductivity and excitation level profile (Pranesh and Ravikumar 2019).

literatures Kanimozhi et al. (2019b) and Mahalingam et al. (2019).

2.3. Coreflood test procedure

The procedure of this coreflood test is mentioned in the below points:

- Firstly, CO₂ cylinder is opened and carbon dioxide gas of 25 kg mass at subcritical condition is injected in the porous sandstone rock core. Subsequently, the mobilized kaolinite fines-gas suspension (adsorbed on the fines) is collected in the effluent collector tank.
- This same procedure is repeated for the other two sets of rock core temperature by supercritical CO₂.
- Then, samples in the effluent were dried and sent to microstructural tests for examining the kaolinite fine particle structures that has potentially blocked/damaged the permeability of the porous sandstone rock core and gas mobilization decrease as well.
- Furthermore, statistical modelling was performed along with a literature data for model validation.

Please note that the points c) and d) are not associated with coreflood test and they are separately executed in field emission scanning electron microscope (FESEM) and statistical package for social science (SPSS).

2.4. Pressure analysis

Fig. 6 presents the pressure decline with respect to increasing pore volume injection. Actually, Yang et al. (2019), stated that from laboratory coreflood pressure measurements helps to measure and characterize the intensities of fines concentration, permeability, and fluid recovery decline in the porous media.

Moreover, it can be seen from Fig. 6 that there are no signs of abnormal pressure growth and fluctuation. Under super and subcritical flow conditions, the pressure tends to plummet heavily for gradual increase of PVI. In between stages, the pressure drop for the subcritical case was noted to be lesser than the supercritical CO₂ case and this is highly attributed to the surface roughness and retained colloids as mentioned clearly in the previous section. Then, during the following pore volume injections the pressure decreases sharply during Sc-C state and stabilizes during the later stages of the PVI. Hence, increasing porous medium temperature and supercritical heat transfer in porous media generates higher fines concentration that eventually migrates and plug the pore-throat areas across the sandstone core. Decrease of pressure across the porous rock core contributes to the fluid transport loss and injected fluid decline as well. Because, during pressure deterioration in the porous rocks there will be no energy to mobilize the reservoir fluids and injected fluids in the porous interspace (Pranesh et al., 2018).

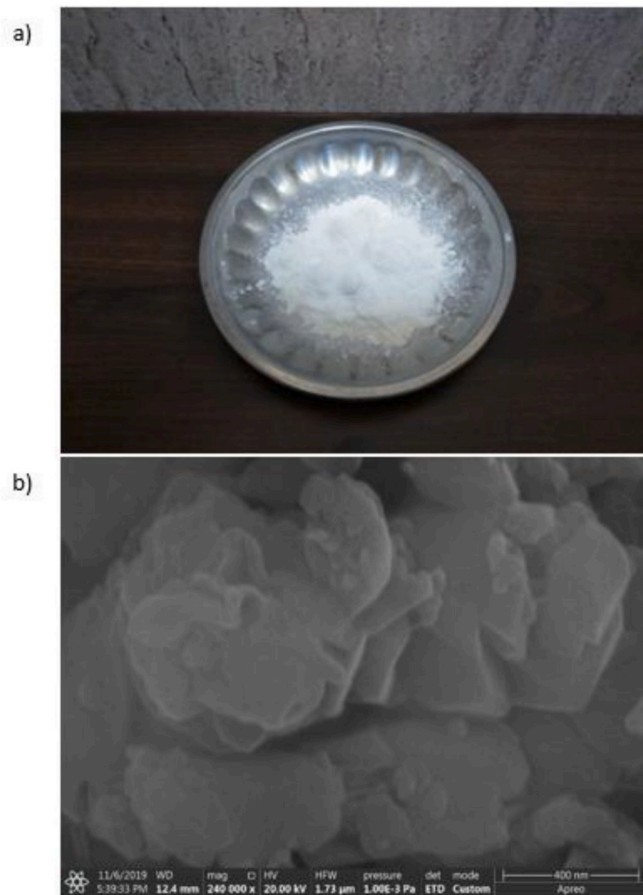


Fig. 4. a) Typical kaolinite clay photograph under 200 mesh size, b) A microstructural image of the kaolinite fines under 400 nm magnification.

the pressure difference across the core). One pressure gauge is connected to the inlet and outlet flow lines of the core centre and another two are connected to the inlet and outlet flow lines of the core. One side of the core holder has provisions for pneumatic piston pump (for pressure exertion) and suspension flow. On this same side CO₂ cylinder is attached and overall these components are connected to the core oven system. Other side of the core oven apparatus has the provision (exit line) for effluent tank (for collecting the suspension-colloids). The flow lines are provided with ball valves and the whole core-oven thermal system is connected to the data acquisition system and subsequently, connected to the computer. This coreflood setup design was employed and executed based on the suggestions and methodology given the

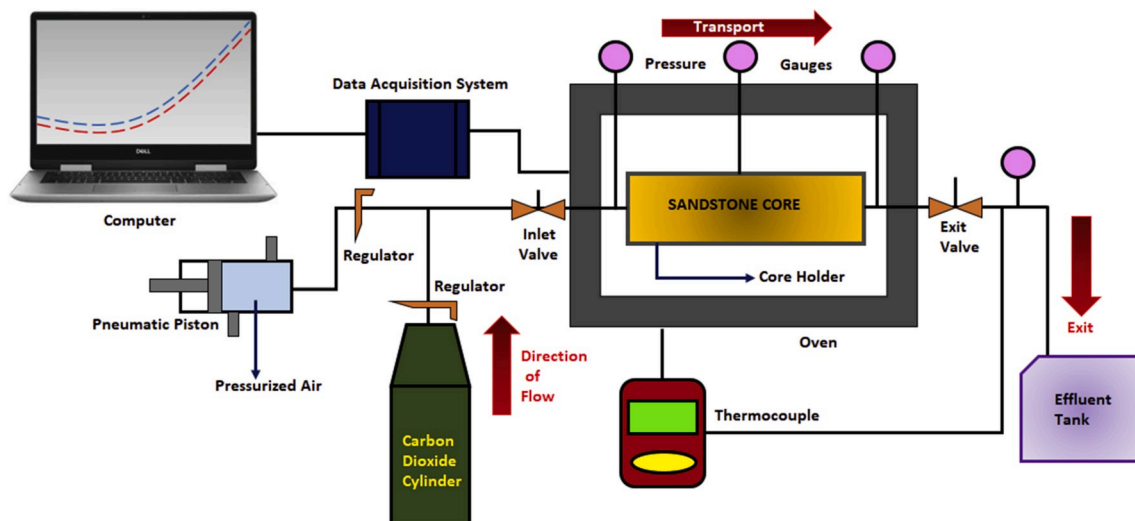


Fig. 5. Experimental setup.

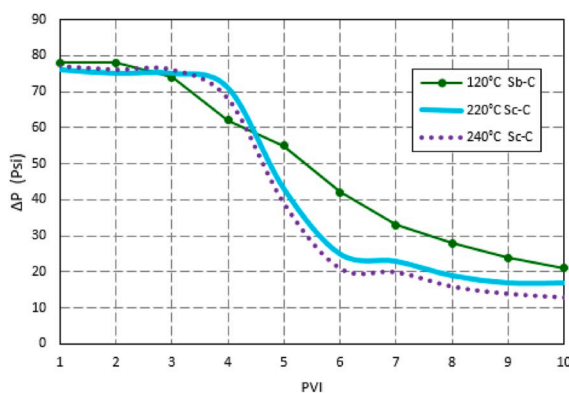


Fig. 6. Pressure deterioration with respect to increasing pore volume injection.

3. Results and discussions

3.1. Gas saturation

Fig. 7 presents the gas saturation increase with respect to increasing time. In fact, gas saturation was measured by counter current imbibition (CCI) technique (McPhee et al., 2015). During CO₂ injection in the

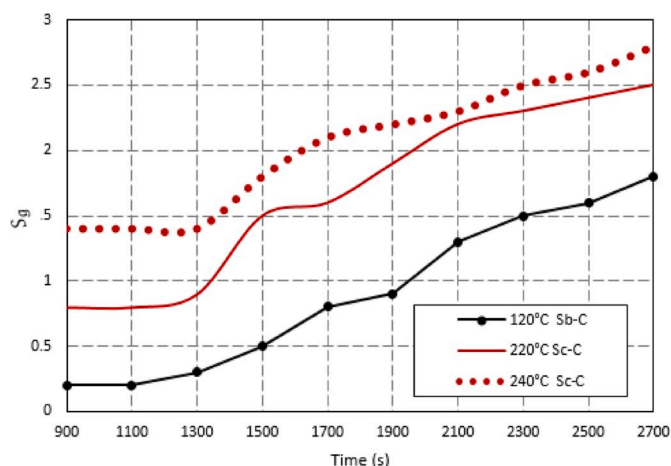


Fig. 7. Variation of gas saturation with respect to increasing time.

porous sandstone rock core, the supercritical fluid is being saturated in the core and this is detected by flow sensor, where the data were fed in the data acquisition system/software to record weight changes as a function of time. The change in the weight of the rock core indicates the weight of the CO₂. In general, the mobility ratio between the reservoir oil and injected fluid phase is an essential characteristic in the determination of sweep efficiency and oil recovery in porous sandstone rocks (Molnes et al., 2016). It can be seen from Fig. 7 that the carbon dioxide gas saturation exhibited a linear rise in the porous sandstone material for increasing injection time and these were observed under both supercritical and subcritical CO₂ flow conditions. However, the intensity of saturation was found to be higher in supercritical than in subcritical condition. Nevertheless, the subcritical case also indicated an increasing level of gas saturation in the porous media. Even, during the subcritical flow conditions the fines will be excited and detached from the pore surfaces (Mahalingam et al., 2019) and also, the porous medium temperature plays a significant role in enhancing the injecting fluid saturation in the porous media (Kanimozhi et al. 2019a,b). It should be noted that under all three cases the gas saturation was almost stabilized during the initial stages of injection. This is attributed to reservoir heterogeneity and feasible cross flow between low and high permeable zones, which affects the CO₂ transport in the porous media (Al-Bayati et al., 2019).

3.2. Enthalpy release

Fig. 8 presents the enthalpy release increase with respect to increasing injection time. Enthalpy release measurement method can be found in the appendix. Generally, the enthalpy release in porous media is associated with heat rejection from the porous rock surface, reservoir fluid phase heat transfer, and also, fluid phase change heat transfer (Pranesh and Ravikumar 2019; Kanimozhi et al., 2018). Furthermore, in high temperature porous media there will be a large production of entropy due to high mass transfer of in-situ fines (Kanimozhi et al., 2019a). Fines are easily detached under elevating porous rock temperature due to the decreasing strength of the detaching torque (Chequer and Bedrikovetsky, 2019; You et al., 2014; Schembre and Kovscek, 2005). Additionally, the fluid flow and behaviour, temperature, and thermal conductivity of porous media may dictate the enthalpy rate in the porous media (He et al., 2019; Narasimhan, 2013). It can be seen from Fig. 8 that under supercritical CO₂ flow condition the enthalpy levels were soaring linearly, but the subcritical CO₂ flow the enthalpy release showed a gradual and sluggish growth. Typically, the CO₂ transport in a porous medium under subcritical conditions cannot liberate tremendous

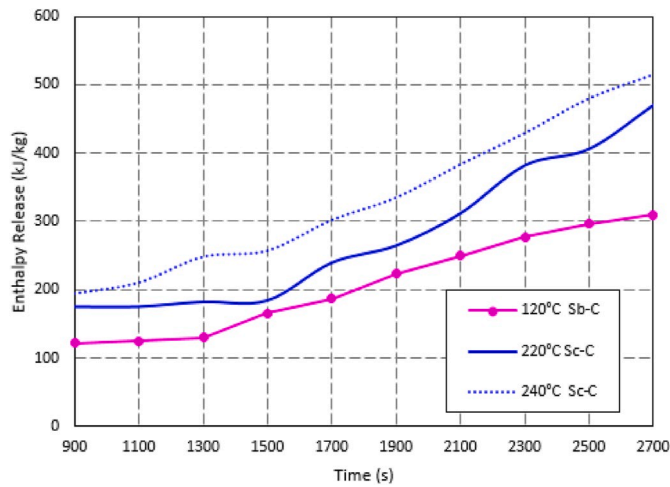


Fig. 8. Variation of enthalpy release with respect to increasing time.

heat or high degree of heat transfer due to pressure volatility across the porous rock (Mahalingam et al., 2019). In this case, also, the enthalpy release rates at all three scenarios indicated a slight stabilization and this is also due to the explanation given in the previous section (Al-Bayati et al., 2019).

3.3. Fines concentration and permeability decline

This subsection presents the fines concentration increase with respect to pore volume injection (PVI) and porous rock permeability decline with respect to injection time. Fines concentration and permeability decline are directly proportional, because higher fines concentration decreases the permeability level in the porous rock (Kanimozhi et al., 2019b). Moreover, kaolinite content in the porous rocks gradually deteriorate the permeability (Russell et al., 2017). Literally, higher mass transfer coefficient of fines in porous media can be achieved with soaring temperature as this was reported in laboratory and field case studies (You et al., 2016, 2013). Actually, after the end of each coreflood test the kaolinite clay fines are collected in the effluent. This effluent was passed to dynamic light scattering (DLS Method) analysis to obtain the quantitative data of fines concentration.

It can be seen from Fig. 9 a) that increasing PVI produces higher rate of kaolinite fines concentration and it should be observed that under

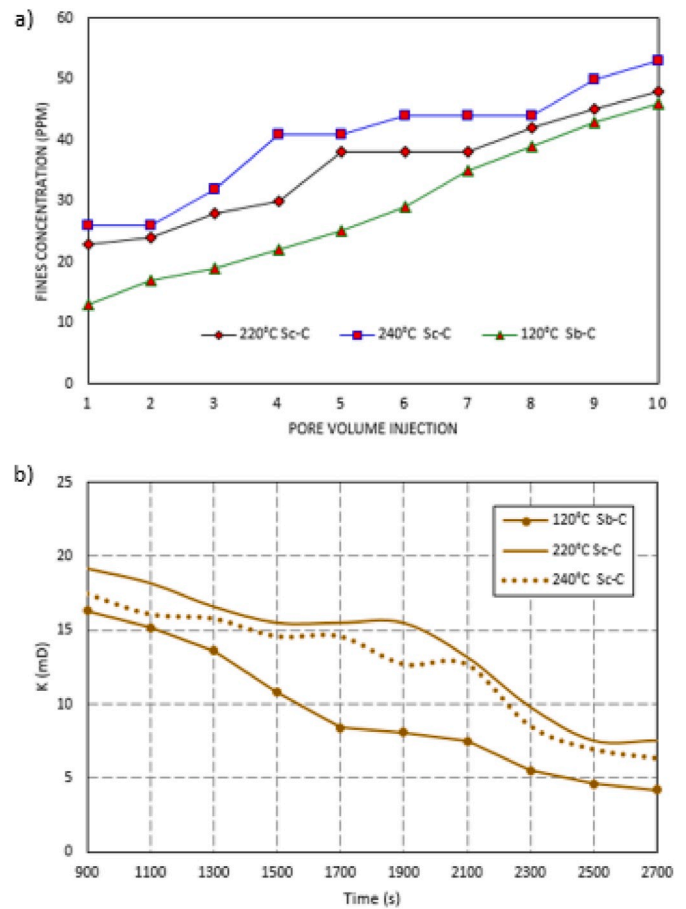


Fig. 9. a) Fines concentration increase with respect to increasing PVI, b) Permeability with respect to increasing time.

using the following formula:

$$\Delta k = \frac{A}{L} \left(\frac{\Delta q_o - \Delta q_i}{\Delta t} \right) - \beta U \quad (6)$$

where,

Δk = Change in permeability of a material, A = Area of the porous material, L = Length of the porous material, Δt = Change in time, Δq_o = Change of fluid flow from the porous material, Δq_i = Change of fluid flow to the porous material, β = Formation damage coefficient or fines retention in porous material, U = Fluid flow velocity in a porous material

supercritical CO₂ conditions the concentration of kaolinite fines underwent a stabilization. This was observed during initial and between stages of the PVI, but the subcritical CO₂ case indicated a gradual linear increase in the fines concentration. However, the kaolinite fines concentration under subcritical condition is lesser than the supercritical conditions and whatsoever, it should be taken into account that even subcritical CO₂ scenario produces a linear and high quantity of concentration of kaolinite fines. Subsequently, the permeability decline was observed for increasing time, shown in Fig. 9 b). The permeability decline is highly attributed to the pore-straining that is the capture of fines in the pore-throat are by size exclusion mechanism (Gomes et al., 2017; Bedrikovetsky, 2008). Actually, during the experiment the permeability values were quantified by a data acquisition system and PC software. Furthermore, permeability decline can also be calculated by

It can be seen from Fig. 9 b) that subcritical CO₂ flow conditions showed a high level of permeability decrease, when compared to supercritical conditions. This unusual behaviour could be due to re-attachment of fines on the pore surfaces and also, due to drift in the suspended phase, where the fine particle might have lost the momentum to mobilize in the porous media and therefore, get trapped between the rock teeth (also, known as colloid retention) or fabrics in other words roughness of the pore surface (Torkzaban and Bradford, 2016; Gu et al., 2016; Khanna, 2014; Kampel, 2007). Nevertheless, it should be taken into account that the porous sandstone permeability was greatly deteriorated under both super and subcritical cases. Table 1 shows the physical properties of the produced suspensions.

Table 1

Produced suspension physical properties.

Injection Parameter (PVI)	Temperature (°C)	Fluid Phase State	Electrical Conductivity (μS/cm)	Thermal Conductivity (W/m-K)	Zeta Potential (mV)
1	220 °C	Supercritical	194	2.1	+58
2	220 °C	Supercritical	196	2.3	+58
3	220 °C	Supercritical	205	2.6	+52
4	220 °C	Supercritical	210	3.5	+50
5	220 °C	Supercritical	213	4.1	+45
6	220 °C	Supercritical	226	4.5	+42
7	220 °C	Supercritical	235	5.2	+33
8	220 °C	Supercritical	237	5.2	+12
9	220 °C	Supercritical	244	5.5	+12
10	220 °C	Supercritical	246	5.7	+4
1	240 °C	Supercritical	202	2.4	+56
2	240 °C	Supercritical	214	2.4	+54
3	240 °C	Supercritical	228	2.4	+54
4	240 °C	Supercritical	236	3.3	+44
5	240 °C	Supercritical	240	4.2	+44
6	240 °C	Supercritical	248	4.8	+44
7	240 °C	Supercritical	250	4.8	+16
8	240 °C	Supercritical	253	5.4	+5
9	240 °C	Supercritical	255	5.9	+5
10	240 °C	Supercritical	264	6.2	+3
1	120 °C	Subcritical	146	1.4	+48
2	120 °C	Subcritical	159	1.5	+41
3	120 °C	Subcritical	165	1.8	+35
4	120 °C	Subcritical	173	2.2	+35
5	120 °C	Subcritical	185	2.6	+35
6	120 °C	Subcritical	190	2.9	+30
7	120 °C	Subcritical	195	3.6	+14
8	120 °C	Subcritical	206	3.8	+2
9	120 °C	Subcritical	217	4.4	+2
10	120 °C	Subcritical	223	5.1	+1

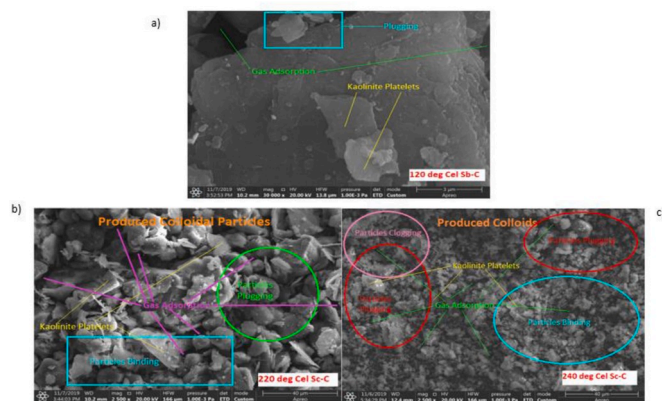


Fig. 10. Microstructural Image of the produced suspensions, a), 120 °C, b) 220 °C, c) 240 °C, for enlarged view of all these images the reader is advised to see the appendix.

3.4. Microstructural analysis

Fig. 10 shows the microstructural images of the produced colloids at the operating temperatures of 120 °C, 220 °C, and 240 °C. Actually, Field Emission Scanning Microscopy (FESEM) was employed to characterize the kaolinite fines structure between the sand grains. Moreover, Khilar and Fogler (1998), stated that fines morphology, structure and geometry can be characterized and determined only by the microstructural investigations. Also, this helps to quantify and predict the permeability damage in the porous formations (Civan, 2007). It can be seen from Fig. 10 a) that under 120 °C produced colloids there is a clear appearance of kaolinite fines with a platelet structure and geometry and plugging was also noted, and the black spots indicates the areas of gas adsorption over sand grain. It was reported that CO₂ flow in sandstone core and adsorption generates clay swelling and formation of electric double layers around the clay minerals and also, the decreased CO₂ slip

effects harm the permeability decline (De Silva et al., 2017). Furthermore, under 220 °C and 240 °C produced colloids there is an apparent display of kaolinite fines plugging, binding, and clogging.

The occurrence of plugging and binding is due to the formation of internal cake and pore-bridging between the rock grains or pore-throat. But, clogging also occurs near the pore-throat area, but its formation mechanism in the porous media is quite different. In general, fines clogging under suspension flow occurs in the porous media as a result of agglomeration and flocculation (Hu et al., 2013; Goldenberg et al., 1993). Additionally, pore clogging is a series consequence of simultaneous process from fines detachment by fluid transport through migration, trapping, and accumulation of fines at the pore-throats and eventually to pore clogging (Han et al., 2019). However, the clogging can be reduced by changing the fluid flow rates (Torkzaban et al., 2015). Moreover, sometimes, low flow rates results in deposition rate and sand texture clogging under the influences of physicochemical effects (Mesticou et al., 2016). Overall, in comprehensive view these factors have constituted in the increase of fines concentration and a permeability decline in the porous media as it was evident in Fig. 9a) and b).

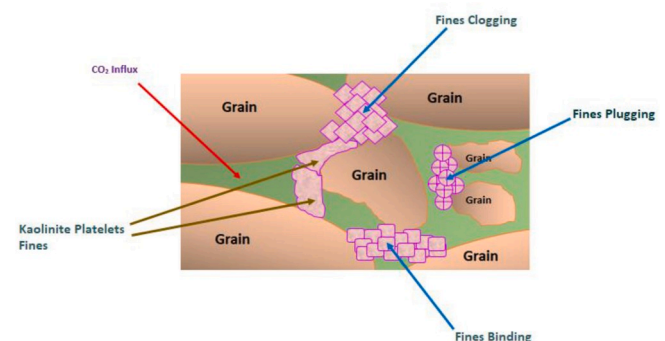


Fig. 11. Schematic diagram of pore-throat plugging, clogging, and binding by kaolinite fines under CO₂ saturation.

Therefore, it should be understood that colloidal release in the porous media is a function of fluid flow rate, temperature, and fluid chemistry, which ultimately impact the fluid permeability.

Fig. 11 shows the schematic diagram of fines behaviour near the pore-throats by different process. It can be seen from this figure that the kaolinite platelets fines obstruct the pore-throat by capturing between the rock grains and moreover, Chequer and Bedrikovetsky (2019), has given a schematic diagram and indication of kaolinite fine platelet that obstruct the pore-throat as they have observed during the coreflood and microstructural investigations. Additionally, in other zones the fines clogging, binding, and plugging was presented. Altogether, this has contributed in the permeability damage to the sandstone rock core under both supercritical and subcritical carbon dioxide transport. It should be observed from the microstructural study that during supercritical CO₂ transport only the fines underwent the phenomenon of clogging, binding, and plugging. Fines binding is also known as particle clustering, as schematically shown in Fig. 1. There is also a high possibility of the formation of fines clogging, binding, and plugging (FCBP) under subcritical conditions. The magnification of the Sb-C case is just 3 μm , but the supercritical cases were under the magnification of 40 μm . The FCBP detection is feasible under Sb-C conditions upon testing the samples at or above 40 μm scales. However, the main goal of this paper is only to characterize and present the kaolinite fines behaviour and subsequently, the permeability decline under Sc-C and Sb-C was taken merely for the comparison purpose.

3.5. Gas discharge rate

Fig. 12 presents the gas discharge rate decline with respect to increasing gas injection time. It can be seen from Fig. 12 that under Sc-C condition the decrease in the gas discharge rate was recorded for increasing injection time. But, the decline rate of gas discharge under Sb-C was observed to be higher than the Sc-C. It was demonstrated that CO₂ flow in porous media containing fines can undergo a surface reactions and deteriorate the permeability, which in turn barricade the space for fluid flow (Mahalingam et al., 2019). Additionally, increase and decrease of surface energy produced by the fines attachment and detachment influence the reservoir fluid recovery rate (Kanimozhi et al., 2019a). Furthermore, it was evident from the microstructural test that fines plugging, binding, and clogging has completely damaged the gas permeability in the porous sandstone rock core and most importantly, the kaolinite fine particle with platelet geometry has obstructed and strained the pore-throat regions, schematically indicated in Fig. 11, has blocked the CO₂ transport in the sandstone core. Moreover, surface roughness may dominate the slow mobilization of suspension in the porous media (Oliveira et al., 2014) and this also contribute in the permeability decline of the porous medium under increasing temperatures (Kanimozhi et al., 2019b).

3.6. Model validation

Fig. 13 presents the model validation, which was plotted between gas injection time and gas discharge rate. Already it was mentioned that high temperature porous media with oversaturated fines constitute to permeability deterioration and mainly, injectivity decline. For this purpose these two parameters were taken for the validation. The experimental model was tested against the multiple linear regression statistical model called SPSS (Statistical Package for Social Science) that shown good accord. Additionally, the experimental model was tested against the literature model, Mahalingam et al. (2019), gas discharge rate model. Moreover, the test results indicated good agreement. Although the gas discharge rate curves of Mahalingam et al. (2019) and experimental models were outlying, but the curves were decreasing linearly. Furthermore, the Mahalingam et al. (2019) was also an experimental data, but those are under subcritical CO₂ conditions. However, both supercritical and subcritical CO₂ cases exhibited

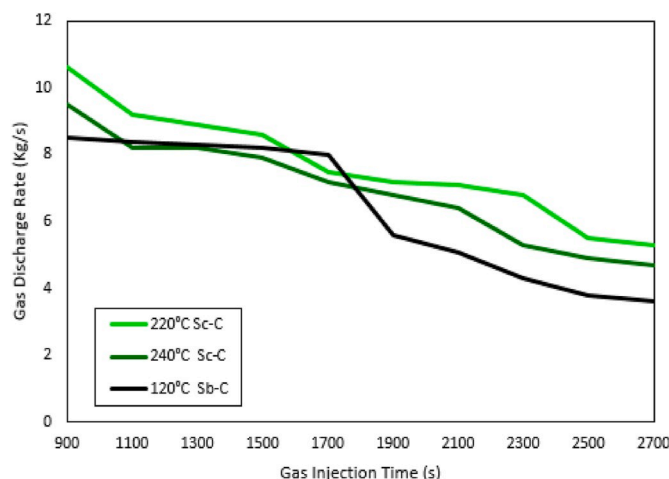


Fig. 12. Gas discharge rate decrease with respect to increasing injection time.

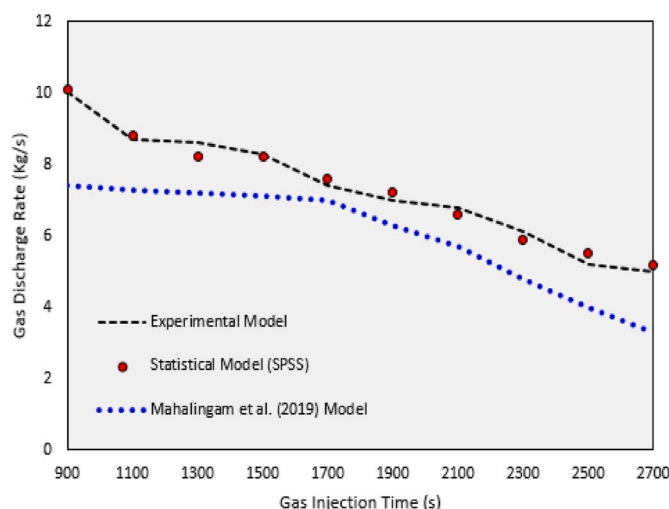


Fig. 13. Model validation.

declining curves. Overall, the entire model is validated successfully and it should be remembered that CO₂ under both conditions can detach the fines in the porous media and lead to pore-straining and permeability decline, which ultimately resulting in injectivity decline and reservoir fluid recovery as well.

4. Conclusions

Initially, both supercritical and subcritical CO₂ flow in high temperature porous media triggered the fines detachment from pore surface and yielded a high amount of produced colloids. It was primarily founded that the supercritical CO₂ flow impacts on fines migration is greater than the subcritical CO₂ flow with regards to temperature. On the basis of experimental investigation, microstructural tests, and statistical modelling results, the following conclusions can be established:

- First of all, there is a high level of CO₂ gas saturation in porous media during super and sub-critical flows. Consequently, the enthalpy release rate and concentration of fines in porous media has increased steadily. As a result the porous sandstone rock permeability has decreased drastically.
- The pressure in the porous sandstone media declined for increasing rate of pore volume injection and also, deterioration of the gas discharge rate was observed. Mainly this behaviour is attributed to

the fines plugging, clogging, and especially, due to the platelet geometry that obstructed the pore-throat of the porous media and ultimately, damaged the permeability.

- It was observed from the microstructural images that fines tend to have a platelet structure and the fines have undergone binding, plugging, and clogging. These are an essential properties of fine particles in order to barricade the pore-throat and decline the permeability of the porous materials.
- Furthermore, the experimental model was tested against the statistical and literature models, which showed good accord. On the whole, this paper has elucidated and demonstrated the importance of super and sub-critical CO₂ transport on the permeability of the porous media as a function of oversaturated fines and temperature.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2020.107345>.

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