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The use of polymer-gel solutions for CO₂ flow diversion and mobility control within storage sites

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Abstract

This paper presents a study on the use of polymer-gel technology as an option to remediate non-conformal flow behaviour of CO₂ within the storage reservoir. Several polymer-gels with crosslinkers were tested. The rheology, gelation and working times of these polymer-gels at various concentrations were characterised under different temperatures representative of CO₂ storage reservoirs. Laboratory core flooding experiments were then carried out on high permeability core samples to test the suitability of polymer-gel solution for flow through and containment of CO₂ in porous media. The core samples saturated with brine were subjected to polymer-gel injection. Core sample permeability for CO₂ was then measured and the change in CO₂ permeability of the sample before and after polymer-gel injection was noted. Reservoir simulations for different scenarios of flow diversion were carried out using the permeability reduction results from the laboratory work on a realistic reservoir model with faults and high permeability channel structures.

Keywords: CO₂ storage; leakage remediation; polymer-gel; permeability.

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1. Introduction

In comparison to other likely storage sites, such as the depleted hydrocarbon fields, knowledge on the geological and petrophysical properties of saline aquifers is extremely limited. Hence, a considerable degree of uncertainty in the conformance of CO_2 flow in the subsurface in comparison to that estimated by theoretical/numerical computations is expected. This uncertainty may lead to undesired and unpredicted preferential flow of CO_2 into parts of the host reservoir, or leakage into shallower formations. To alleviate this, measures to achieve flow diversion may be implemented, such as: i) localised reduction in permeability by, e.g. the injection of gels or foams, or by immobilising the CO_2 in the pore space, ii) change of injection strategy, or iii) localised injection of brine creating a competitive fluid movement.

Crosslinked hydrolysed polymer-gel injection is used in petroleum industry to improve conformity of fluid flow in the reservoir, remediate leakage around wells and also used in conjunction with enhanced oil recovery at various temperature and pressure conditions [1-7]. Water-based gels are known as highly elastic semi-solids with high water content, trapped in the three-dimensional polymer structure of the gel [8]. Polyacrylamide (PAM) is the main crosslinked polymer used mostly by the industry [9, 10]. The use of biopolymers is more challenging as compared to the synthetic polymers due to chemical degradation at higher temperatures, causing loss of mechanical strength [11]. Most of polymer-gel systems are based on crosslinking of polymers with a heavy metal ion. The most common heavy metal ion used is Cr^{3+}. In a previous study [12], chromium acetate was used as a crosslinker. However, in view of its toxicity and related environmental concerns [8, 13], its application in reservoir conformance and CO_2 leakage remediation is considered to be limited. In the present study, chromium has been replaced by zirconium which is thought more environmental friendly.

This paper presents the research conducted to investigate the processes by which the use of polymer-gel injection reduces permeability of reservoir rocks to CO_2. The objectives were to: i) determine the rheological properties of various gel systems; ii) to assess the effectiveness of polymer-gels in permeability reduction via a series of core flooding experiments; and iii) to perform reservoir simulations for different scenarios in which CO_2 plume diversion can be assessed.

2. Characterisation of the bulk polymer-gel system

A range of polymer compounds were studied: two high molecular weight polyacrylamide-based polymers (AN1506 and AN907PG) and two partially hydrolysed polyacrylamides (AO22 and SB15) provided by SNF Floerger; a polysaccharide based xanthan gum, a low molecular weight partially hydrolysed polyacrylamide and a high molecular weight polyacrylamide supplied by Sigma Aldrich. All polymer compounds were tested with the new water-based zirconium chelate crosslinker. Table 1 outlines the properties of the polymer solutions prepared.

Table 1: Properties of polymers tested.

|	AN1506	AN907PG	AO22	SB15	Xanthan	HPAM-LMW	PAM-HMW
Polymer type	Poly-acrylamide-based	Poly-acrylamide-based	Poly-acrylamide-based	Poly-acrylamide-based	Poly-saccharide	Poly-acrylamide-based	Poly-acrylamide-based
Molecular weight	High molecular weight	High molecular weight	Medium molecular weight	Medium molecular weight	High molecular weight	Low molecular weight	High molecular weight
Form	Powder	Powder	Partially hydrolysed	Partially hydrolysed	Powder	Partially hydrolysed	Powder
Concentrations Prepared [%]	0.05 0.5 0.1 1 0.25 5	0.05 0.5 0.1 1 0.25 5	0.25 4.1 6	0.25 4.1 6	0.25 0.3 0.5	0.25 10	0.25 5
Base solution	0.5%wt NaCl in deionised water						
Temperature [°C]	22 - 60						
Crosslinker	Tyzor 217: water-based zirconium chelate (Zr^+ content: 5.4%), supplied by SNF Floerger (Manufactured by Dorf Ketal)						
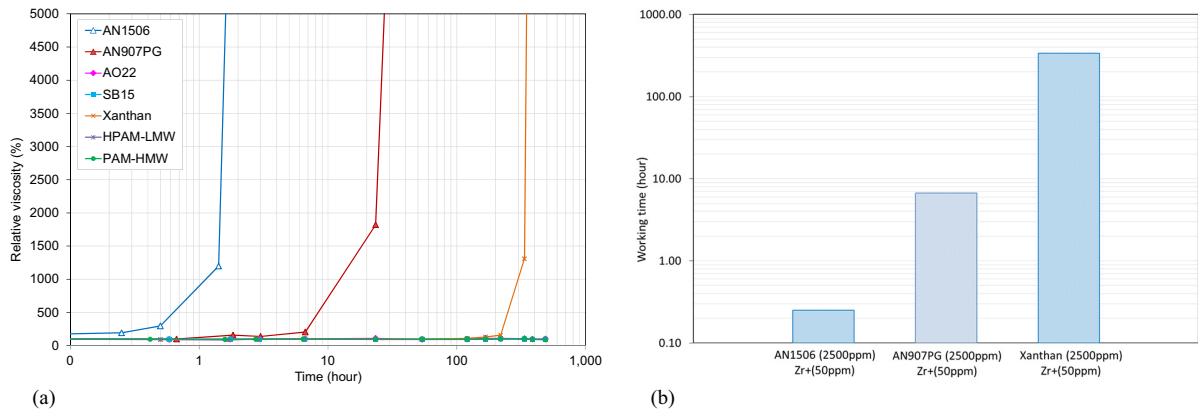
Fig 1. (a) Viscosity evolution over time for different polymer-gel solutions; (b) comparison of the working time for AN1506, AN907PG and xanthan gum at polymer and crosslinker concentrations of 2,500ppm and 50ppm, respectively.

The first experimental step was to study the rheological properties of polymer-gel systems. This included changes in initial viscosity (μ_0) of the polymer solutions over a period of time. A threshold ratio of $\mu/\mu_0 \leq 200\%$ was set to identify their working time, i.e. the time period required for the injection of polymer solution into the target reservoir formation [12]. Gelation process and working time were investigated for a range of polymer and crosslinker concentrations at various temperatures. Polymer-gel solutions were prepared using 0.5%wt NaCl in deionised water. For powdered polymers (AN1506 and AN907PG, Xanthan and PAM-HMW), stock solutions of high concentrations were prepared in 0.5%wt NaCl and were diluted to desired concentration by adding 0.5%wt NaCl before each test. Samples of similar concentrations were prepared and their viscosity changes after adding Zr^+ were monitored over a period of time. The results are presented in Fig. 1.

The results in Fig 1a show that AN1506 and AN907PG were crosslinked by Zr^+, and produced strong gels within approximately 1.5h and 28h, respectively. Xanthan gum also produced gel after significantly longer period of time compared to AN1506 and AN907PG, i.e. 480h (20 days). Hence, xanthan gum provided a longer working time (Fig. 1b). Other polymers, i.e. AO22, SB15, HPAM-LMW and PAM-HMW did not produce gel even at much higher concentrations (up to 10%) and higher temperatures (up to 60°C).

In the next step, AN1506 was selected for further investigation to study the effect of polymer and crosslinker concentrations on the gelation process and working time. This polymer was chosen because it underwent gelation, for a range of different concentrations (500ppm-2000pm), unlike AN907PG. Two sets of experiments were carried out with a range of AN1506 and Zr^+ concentrations. The results are presented in Fig. 2a to 2d.

In general, higher concentrations of polymer resulted in faster gelation (Fig. 2a) and the production of stronger gels. For samples with low polymer concentrations (<500ppm), only partial gelation was observed and the produced gel was found to be weak and uneven.

The amount of crosslinker added to the solution was also found to be influential in the gelation process and working time. However, it was observed that the effect of crosslinker concentration does not follow a similar trend as the polymer concentration. Higher concentrations of crosslinker may prevent or hinder the gelation process significantly. This phenomenon is mainly related to the coiling effect of crosslinker ions on the polymer chains and eventually resulting in the precipitation of polymer molecules [14]. Therefore, the amount of crosslinker has to be within an optimum range. In order to achieve this, the ratio of polymer to crosslinker (*P/X*) has to be taken into account when designing a polymer solution. The *P/X* ratios that were considered in this work ranged between 1 and 166. It was generally observed that polymer solutions with *P/X* between 1 and 10 did not undergo gelation, whereas, polymer solutions with *P/X* greater than 10 were found to be more likely to undergo gelation.

The final step of the polymer characterisation was to investigate the effect of reservoir temperature on the gelation process and working time. The results presented in Fig. 3 show a comparison between the gelation time (4a) and working time (4b) of similar compounds at 22°C and 60°C. The working time is significantly reduced at elevated

temperatures and, therefore, lower concentrations of polymer and crosslinker may be used in order to maintain a reasonable working time for leakage remediation in deeper storage sites.
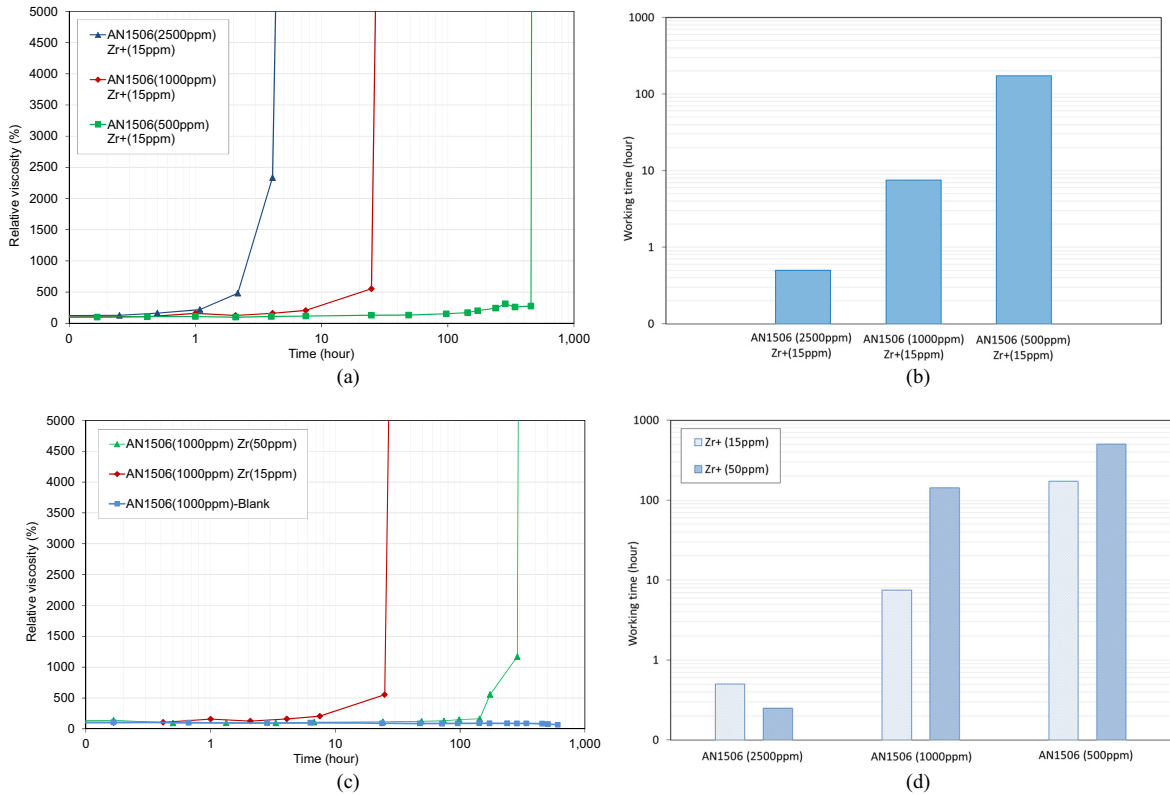

Fig 2. (a) Viscosity evolution of polymer-gel solutions at different concentrations; (b) the effect of polymer concentration on working time of the two polymers tested; (c) Viscosity evolution of polymer-gel solutions at different concentrations; (d) the effect of polymer and crosslinker concentrations on working time of the two polymers tested.
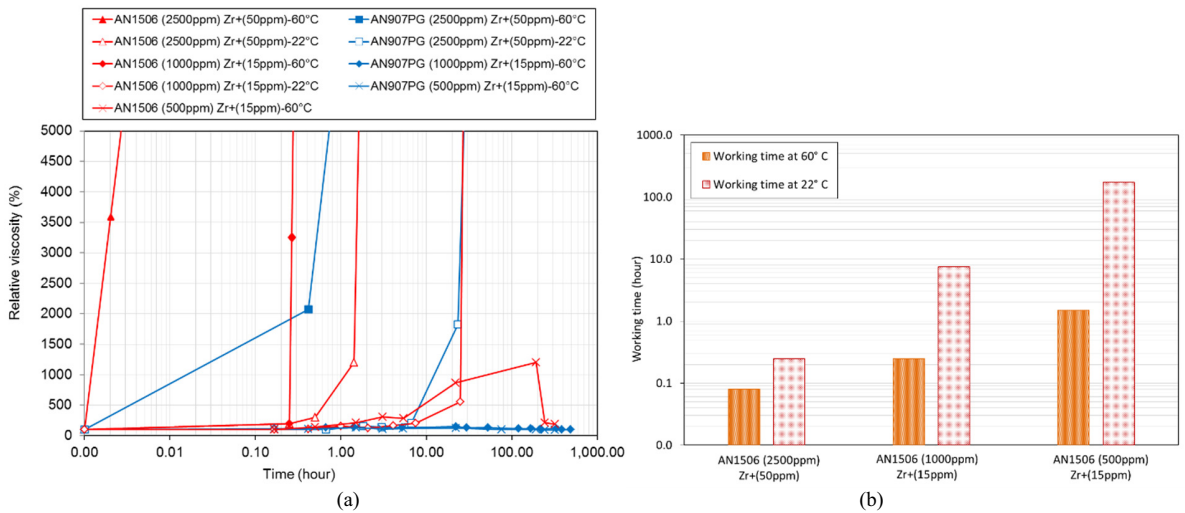

Fig 3. Effect of temperature on polymer-gel solutions: (a) viscosity evolution; (b) working time.

3. Core flooding experiments using polymer gel solutions

Core flooding experiments were carried out using two high permeability core samples to assess the applicability of the polymer-gel system in remediating the non-conformal flow of CO_2 within the reservoir. The porosity of the samples was measured using a pre-calibrated Boyle's law pycnometer. Single phase N_2 and CO_2 permeabilities of the sandstone core samples were measured in a Hassler-type core holder. Fig. 4 presents the experimental set up used for the core flooding tests and the Hassler-type core holder, which was used to apply a constant confining stress of 2.75 MPa during the experiments. . Table 2 presents the experimental conditions and summary of the core characterisation results for samples used in this study.

1: precision pump
2: continuous flow pump
3: flow controlled line
4: constant pressure line
5: cleaning line
6: inlet pressure transducer
7: outlet pressure transducer
8: confinement pressure transducer
9: back pressure valve
10: collecting beaker
11: Hassler cell with core
12: pressure confinement line
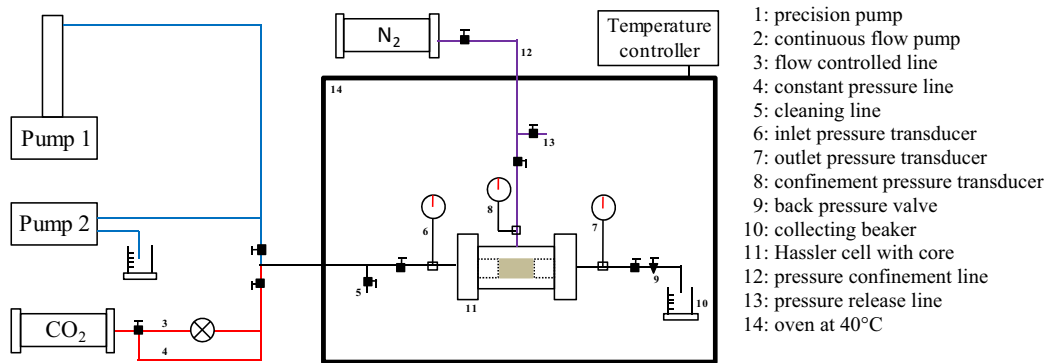13: pressure release line
14: oven at 40°C

Fig. 4. Laboratory setup for the core flooding experiments.

Table 2. Summary of the core characterisation and experimental conditions used to assess the impact of polymer flooding on CO_2 permeability.

Parameter	Sample A (Guiting carbonate)	Sample B (Doddington sandstone)
Porosity	0.30	0.15
Permeability to N_2 [mD]	1,011.93	763.66
Permeability to CO_2 [mD]	670.25	578.78
Salinity of brine [%]	3	3
Polymer and Zr^+ concentrations [ppm]	1,000; 15	1,000; 50
Polymer-gel injection rate [mL/min]	1	1
Pore volume of polymer injected	2.5	1.5

The following procedure was implemented during the core-flooding experiments:
- Core samples were subjected to vacuum for 24 hours.
- Porosity and density of the samples were measured using helium.
- Permeability of the core samples to N_2 and CO_2 were measured under a range of gas injection pressures, up to ~0.38MPa and at ~2.75MPa confining pressure.
- Based on the results presented in the previous sections, a polymer-gel solution with AN1506 (1000ppm) and Zr^+ (15ppm) was prepared in 0.5%wt NaCl base solution. Considering the results of the polymer characterisation carried out, the working time for this solution was expected to be around 7 to 8 hours and the gelation time approximately 24 hours.
- Core samples were saturated with brine (3% NaCl)
- Polymer was injected using an ISCO syringe pump. Polymer solution was injected at a constant rate until about 2-2.5 pore volumes (PV) of polymer solution was injected.

- The upstream and downstream valves were shut and the sample saturated with polymer-gel solution was left gel for a period of time (at least 24 hours) to account for the gelation time.
- CO_2 was injected at constant pressure (~0.38MPa) into the core sample to measure post-polymer-gel injection CO_2 permeability and the effectiveness of the polymer-gel system.

In general, polymer injection at a constant rate was found to be challenging for both samples A and B. In the case of sample B, which had a lower initial permeability, pressure build-up at the inlet became more frequent after the first PV injection. The polymer injection method was therefore set to constant pressure. As a result, the injection rate was very slow and a time period of 5 to 6 hours was required for the injection of ~2.5PV of polymer-gel solution into the sample.

Fig. 5 shows that as a result of polymer-gel injection with concentrations of 1,000ppm AN1506 and 15ppm Zr^+, substantial permeability reduction was observed for both Samples A and B. In the case of Sample A, initial CO_2 permeability of 670mD was reduced to 1mD, representing a 99.85% reduction (Fig 5). For the case of Sample B even greater reduction (over 99.99%) in permeability was achieved using a similar polymer-gel system.

The range of permeability reduction values were then used for the purpose of assessing the effectiveness of polymer-gel injection in CO_2 flow diversion using numerical modelling.
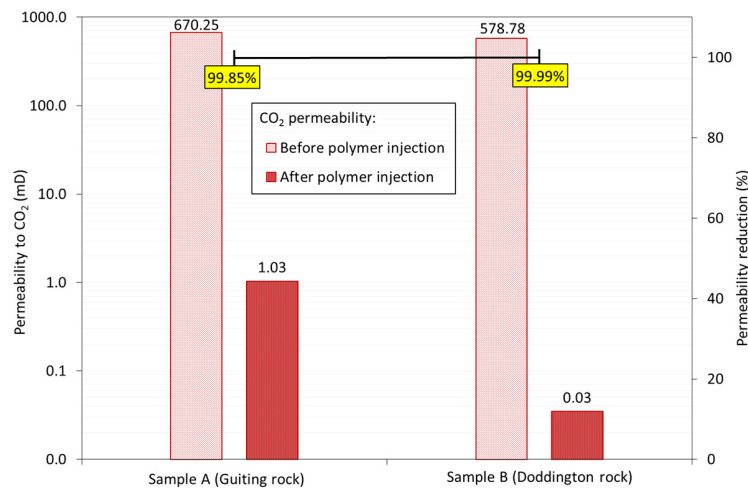

Fig. 5. Effect of polymer-gel treatment in reducing permeability for CO_2 in Guiting carbonate and Doddington sandstone, at 22°C.

4. Numerical simulation of polymer-gel injection

A numerical reservoir model was set up to study the mobility control of CO_2 plume using polymer-gel injection within a heterogeneous saline aquifer and test the diversion of its flow away from a sub-seismic fault. The structural model used in this study represents a saline aquifer with a broad and considerably dipping anticlinal structure (Fig. 6), where the containment of CO_2 is envisaged. The model grid spans an area of 36km×10km and includes five major sealing faults. The grid broadly comprises of three layers, namely: (1) a reservoir layer with an average thickness of 240m and resolution of 200m×200m×4m; (2) a caprock (seal) layer with an average thickness of 225m and resolution of 200m×200m×225m; and (3) a shallow aquifer layer with an average thickness of 175m and resolution of 200m×200m×175m. The depth of the model ranges between -1,087m and -3,471m.

The geological model in the reservoir layer is represented by a fluvial-channel system, typically containing braided sandstone channels and interbedded floodplain deposits (the inter-channel region) of mudstone or siltstone. The channel layout parameters implemented in the model to represent the fluvial-channel system are given in Table 3. The values of the petrophysical properties used in the static geological model attribution (Table 4) are based on the Late Triassic Fruholmen Formation in the Hammerfest Basin, in the southern Barents Sea [15], which is located
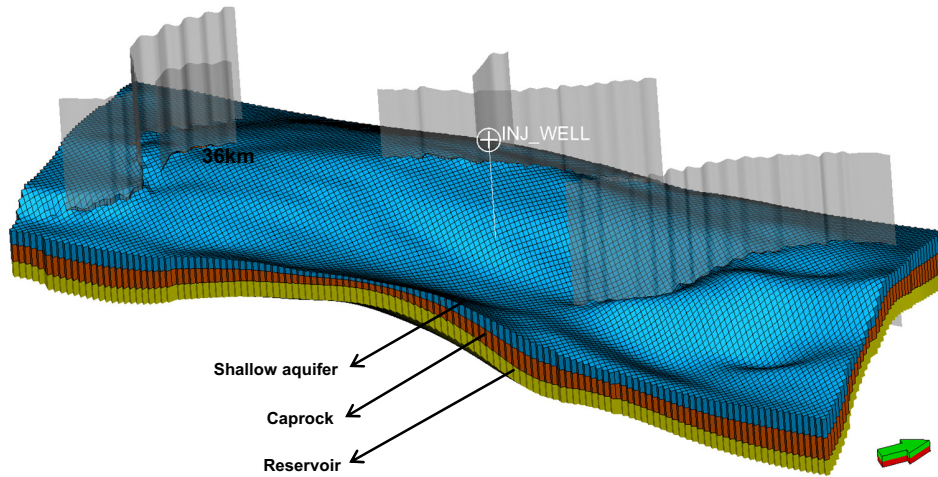
Fig. 6. The structural model of the numerical saline aquifer (36km×10km) containing five major faults and three stratigraphic layers - (1) reservoir layer; (2) caprock (seal) layer; (3) shallow aquifer layer.

Table 3. Channel layout parameters used in the reservoir layer of the geological model.

	Min	Mean	Max
Amplitude [m]	400	500	600
Wavelength [m]	14,000	15,000	16,000
Width [m]	1,400	1,500	1,600
Thickness [m]	4	8	12

Table 4. Petrophysical properties used in the geological model.

Petrophysical properties		Channels	Inter-channel region	Caprock	Shallow aquifer
Porosity	Min; Mean; Max	0.1; 0.18; 0.25	0; 0.1; 0.25	0.01	0.05; 0.15; 0.25
	Standard deviation	0.05	0.05	0	0.05
Horizontal Permeability [mD] *	Min; Mean; Max	125; 3,000; 7,000	0.1; 10; 100	0.0001	100; 3,000; 5,000
	Standard deviation	2,000	40	0	1,000
NTG	Min; Mean; Max	0.6; 0.9; 1	0; 0.2; 0.5	0.01	0.6; 0.9; 1
	Standard deviation	0.05	0.05	0	0.05

*vertical permeability = 0.1 × horizontal permeability

at depths similar to those considered in this study. The property attributions were generated using Sequential Gaussian Simulation (SGS) in order to represent the variability in the distribution of these values. Example realisations of the porosity and horizontal permeability distributions for the top reservoir layer are illustrated in Fig. 7.

In order to setup a scenario wherein CO_2 leakage occurs and test subsequent leakage remediation by flow diversion of the plume using polymer-gel injection, a sub-seismic fault was introduced in the model (by grid refinement) at a distance of 1km away from the injection well (INJ_WELL), located at the flank of the anticline (Fig. 8a). The fault has a lateral dimension of 800m×2m and assumed to be non-sealing, with a uniform vertical permeability of 10,000mD spanning the reservoir and the caprock thickness (approximately 450m). A compositional flow model was then setup using Schlumberger's ECLIPSE 300 (E300) software based on a quasi-isothermal, multi-phase and multi-component algorithm, enabled by the CO2STORE option which considers mutual solubilities of CO_2 and brine.
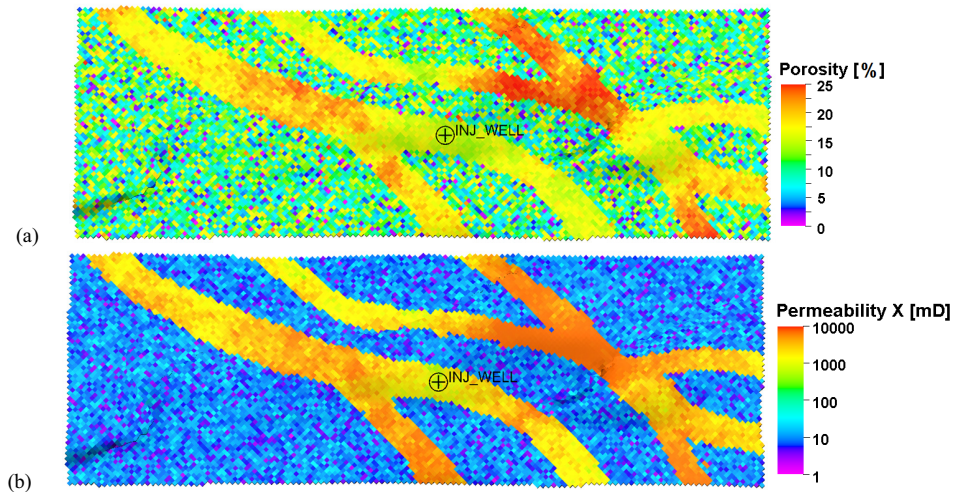
Fig. 7. Example realisations of petrophysical properties distribution for the top layer of the reservoir: (a) Porosity; (b) Horizontal permeability.
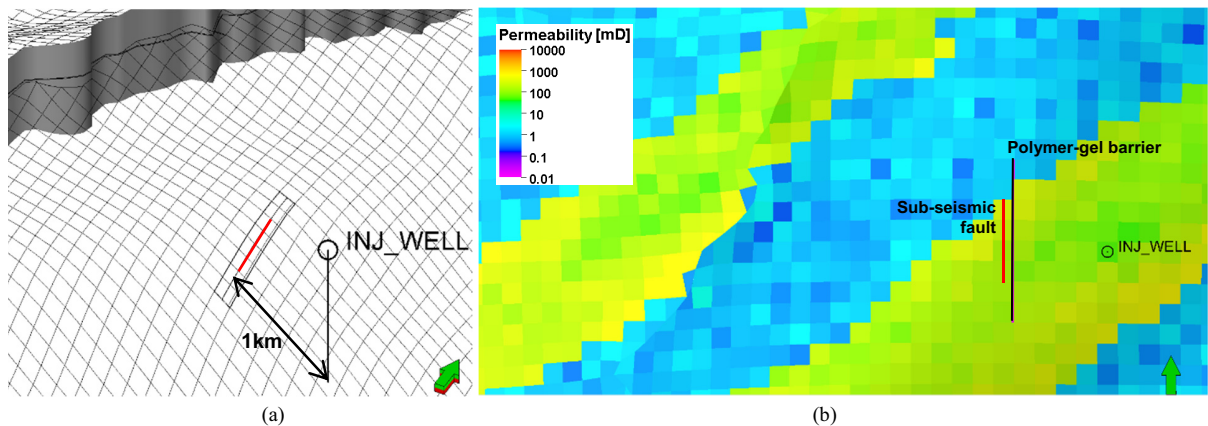

Fig. 8. (a) The grid refinement representing the sub-seismic fault feature (800m×2m) and polymer-gel barrier (1600m×20m), located 1km away from the injection well; (b) Permeability attribution and position of the polymer-gel barrier between the injection well and the sub-seismic fault.

The simulation of CO_2 injection in the saline aquifer was carried out at a rate of 1Mt/year, for a period of 30 years comprising of: initial CO_2 injection; leakage detection and polymer-gel injection (remediation); and post-remediation CO_2 injection. The lower limit of leakage detection was assumed to be 5,000 tonnes of CO_2 in the shallow aquifer [16]. Once the leakage through the sub-seismic fault was detected, CO_2 injection was stopped for a period of nine months, during which polymer-gel injection in the reservoir layer is implemented. The polymer-gel barrier was assumed to have a region of influence with a dimension of 1,600m×20m×240m, at a distance of approximately 100m away from the fault towards the injection well, as shown in Fig. 8b. With the barrier in place, CO_2 injection was re-started for the remaining period of the simulation, representing the post-remediation period.

Different permeability reduction values at the location of the polymer-gel barrier were tested in the model, considering 2-5 orders of magnitude of reduction. The plume distributions at the end of the simulation period, as illustrated in Fig. 9, suggest that leakage through the fault continues during the post-remediation period when the barrier permeability is >0.1mD. For permeabilities below this value, the plume is diverted away from the fault. This is also shown by the cumulative leakage plot in Fig. 10 where the maximum simulated mass of CO_2 that could have leaked is ~94,000 tonnes.
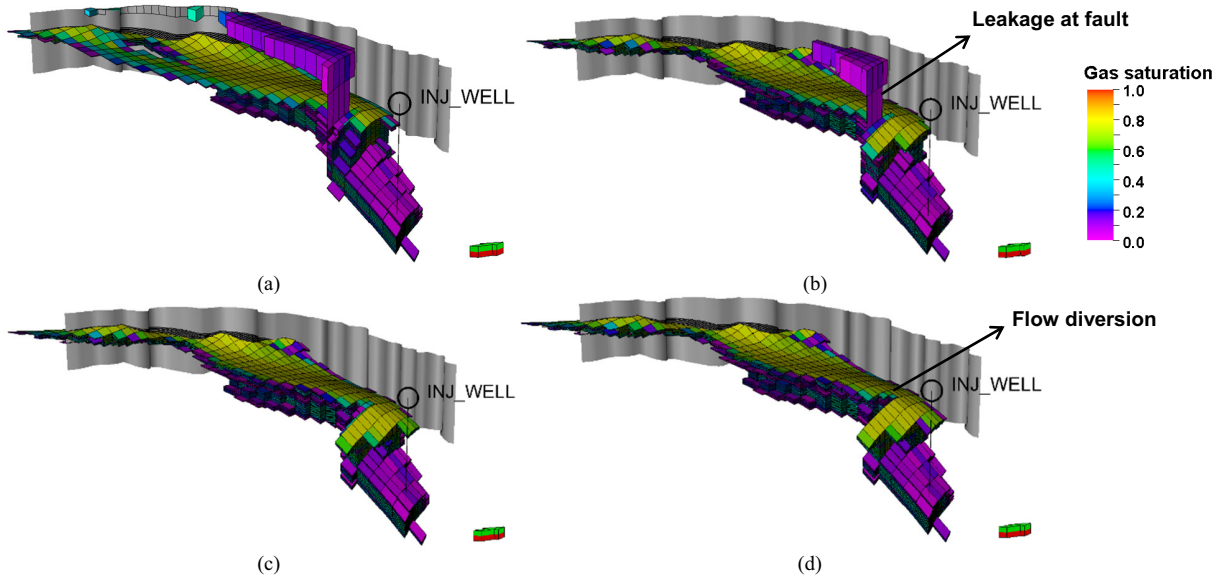
Fig. 9. Plume distribution at the end of the 30 year simulation period (year 2045) when the permeability of the polymer–gel barrier is: (a) 10mD; (b) 1mD; (c) 0.1 mD; (d) 0.01mD.
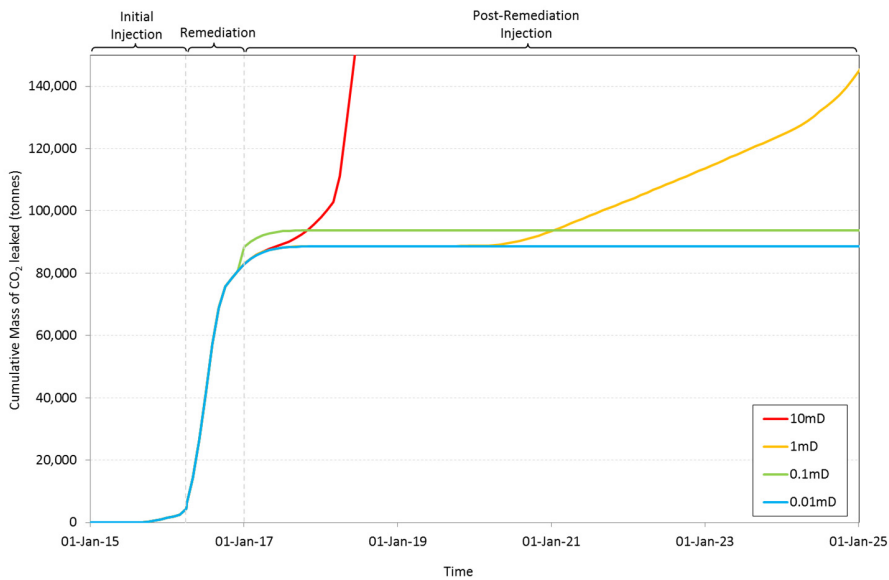

Fig. 10. Cumulative mass of CO_2 that could have leaked into the shallow aquifer for different cases of polymer-gel barrier permeabilities.

5. Conclusions

Parameters such as polymer type, molecular weight, polymer concentration, crosslinker concentration, ratio of polymer-to-crosslinker and temperature were found to be influential on the gelation process and working time of the polymer-gel solutions tested.

Laboratory experiments have shown that the gelation time for polyacrylamide-based polymer gel systems decreased with the increase in polymer concentration. Furthermore, for identical combination of polyacrylamide and Zr^+, the gelation time was found to decrease with increase in temperature.

Laboratory core-flooding experiments performed on high permeability cores saturated with 3% brine have shown a reduction of more than 99% in gas permeability at polymer concentrations of 1,000ppm, and Zr^+ concentration of 15ppm in 0.5%wt NaCl.

Based on the permeability reduction results obtained from laboratory experiments, a numerical model of a fluviatile saline aquifer was setup to assess the effectiveness of polymer-gel injection in diverting the flow of CO_2 plume away from a leaking sub-seismic fault. Modelling results obtained for a 30 year simulation period suggests that remediation is effective for barrier permeabilities ≤0.1mD. However, this is based on the current assumption of a large region of the reservoir influenced by polymer-gel injection. In the field, the barrier geometry achieved would depend on the injection well layout used, viscosity of the polymer injected, reservoir temperature, salinity, pH sensitivity of the effective viscosity of polymer-gel, and reservoir heterogeneity. Further modelling work being carried out involves scenario analysis and simulation of polymer/crosslinker solution injection in ECLIPSE 300 to assess the area of influence and the effectiveness of this remediation technique using different well layouts and reservoir conditions.

Acknowledgements

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