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## Coating a self-healing underground tank for safe storage of CO<sub>2</sub> in chalk reservoirs

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### Abstract

In the recent assessment report from the Intergovernmental Panel on Climate Change (IPCC), Carbon Capture and Storage (CCS) is mentioned as a promising way to mitigate climate change. There is currently intense interest in CCS related research. Beside the potential of underground CO<sub>2</sub> storage, there are certain challenges such as CO<sub>2</sub> capture, transport, storage safety, and so on, need to be addressed. One of the critical challenges with CO<sub>2</sub> storage in underground reservoirs is the potential for leakage back to the atmospheric environment. The North Sea chalk is mainly composed of calcite (CaCO<sub>3</sub>), for which the solubility in water is strongly enhanced by carbonation. Therefore, there is a dynamic reaction between CaCO<sub>3</sub> and CO<sub>2</sub> in aqueous solutions, which implies the importance of rock-fluid chemistry. Given the chemical reaction and other risks of leakage, a proposed solution is to introduce a smart coating layer which is able to block the leaking pathways, stop the leakage and the associated reactions. This research aims to synthesize a smart self-coating polymer which would be activated by Ca<sup>2+</sup> in the presence of water, chalk, and CO<sub>2</sub>. In this purpose, two functional groups and two polymer chains were selected. Four species of polymers were prepared and were characterized by FTIR. Two of them showed promising results, in terms of surface coating, stability, solubility, strong binding to chalk surface and self-aggregation in presence of Ca<sup>2+</sup>. The polymer, Poly(allylamine)-Nitrilotriacetic acid (PAA-NTA), showed specific properties that met the requirements as described earlier. Therefore, PAA-NTA was used for dynamic screening by employing CO<sub>2</sub> bubbles experiment. This polymer was able to stop the reaction between CO<sub>2</sub> and chalk successfully. The thickness of coating layers was between 100 nm to 1 μm, according to SEM analyses. In addition to that, statistical analysis of the elemental information confirms the potential of PAA-NTA in binding with the chalk surface. It was crucial to test the blocking potential of the synthesized polymer in real reservoir conditions, so a CO<sub>2</sub> core flooding experiment was designed. In this experiment first, an outcrop Stevns Klint core sample was saturated with formation brine to equilibrate the chalk surface with a representative brine. Then polymer was injected into the core to flush out formation water and saturate the core. After that, pure supercritical CO<sub>2</sub> at P=130 bar and T=70 °C was injected. It was observed that supercritical CO<sub>2</sub> sweeps almost all fluids (polymer) and no significant blockage was observed. However, in the next step, polymer and CO<sub>2</sub> were simultaneously injected into the core to make sure that there is enough amount of both polymer and CO<sub>2</sub> available in the rock pore space. During this step a significant continuous blockage was observed. In order to evaluate the core condition compared to the first round of pure supercritical CO<sub>2</sub> flooding, a second round was employed afterward. The second round of pure supercritical CO<sub>2</sub> injection showed a massive blockage (permeability reduction/differential pressure increase) compared to the first round. These results clearly support the potential of PAA-NTA on stopping the chalk dissolution in presence of CO<sub>2</sub>.

*Keywords:* Underground CO<sub>2</sub> storage; Polymer; Self-healing; Coreflooding

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## 1. Introduction

Recently, global warming as one of the contemporary climate changes is influencing Earth's weather patterns with increased risk of extreme events. The current changes are rapid compared to known previous events in Earth's history [1]. The main cause is the emission of greenhouse gases, mostly carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). In order to avoid the worst impacts of global warming and subsequent climate changes, the global limit of the average warming of the atmosphere was set to < 2 °C, and preferably < 1.5 °C (UNFCCC, 2015). In the recent assessment report from the Intergovernmental Panel on Climate Change (IPCC), carbon capture and underground storage (CCUS) is mentioned as a promising way to mitigate climate change. The cheapest storage approaches with large capacity cost roughly \$7-\$30 per ton of CO<sub>2</sub> sequestered and range from the injection of supercritical CO<sub>2</sub> into subsurface sedimentary formations to in-situ carbon mineralization [2]. Thereby, there is currently intense interest in the research into CCUS.

With the lowest estimate of 1000 Gt of CO<sub>2</sub> storage capacity, CCUS is promising, however, there are still many challenges, such as CO<sub>2</sub> capture, transport, storage safety, injectivity and corrosion particularly for carbonate reservoirs. Probabilistic modeling of risks associated with leakage suggests that 98% of the CO<sub>2</sub> will be retained in 10,000 years with small risks [2,3]. However, this possibility of leakage needs to be mitigated. Major risks associated with the storage of CO<sub>2</sub> in underground sandstone pore space include leakage from wellbores or non-sealed fractures in the caprock, pressure build-up in the reservoir that could result in caprock hydraulic fracturing, and contamination of drinking water [2]. When considering storage in the spent North Sea chalk reservoirs, there are specific challenges due to the rock-fluid chemistry and the potential for dissolution because calcium carbonate (CaCO<sub>3</sub>) in the sediment is the main component of the North Sea Chalk reservoir. The solubility can increase significantly due to the formation of carbonated water.

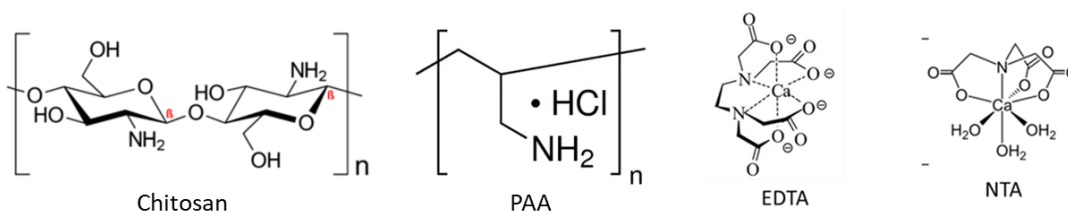
Building barriers between CO<sub>2</sub> and CaCO<sub>3</sub> is a promising and potentially robust solution to stop CaCO<sub>3</sub> dissolution. Layers of coating on the surface of CaCO<sub>3</sub> can stop CO<sub>2</sub> from coming into contact with CaCO<sub>3</sub> and prevent dissolution. A suggested improvement is a mobile polymer based smart material which is self-healing and mobile. When the smart material comes into contact with the chalk interface, Ca<sup>2+</sup> ions will bind chemically with the material and form a rigid hydrogel which is impenetrable to water and CO<sub>2</sub> [4]. In addition, this rigid hydrogel will potentially be able to block leaking channels in the chalk. Furthermore, the smart material can also bind at the chalk interface, because the functional groups form strong bonds with a Ca<sup>2+</sup> ion [5]. Following the deposition of the hydrogel, there is no contact between CO<sub>2</sub> or carbonated water and the chalk, which results in halting the dissolution process.

In the present work, we have selected two functional groups (EDTA and NTA) and two polymer chains (chitosan and PAA), in total four polymer candidates to test the formation of a barrier between CO<sub>2</sub> and chalk. These four polymers were screened for the ability to form a hydrogel and also for their solubility in water which is a requirement for injection into the reservoir. The binding properties with chalk for the chosen polymer was tested in a batch experiment with CO<sub>2</sub> and subsequently in a core flooding setup at reservoir conditions. In these experiments the polymer is injected in varying sequences with CO<sub>2</sub> and high pressure and temperature corresponding to the reservoir to test the performance of the polymer as a protecting agent for the chalk.

## 2. Methods and results

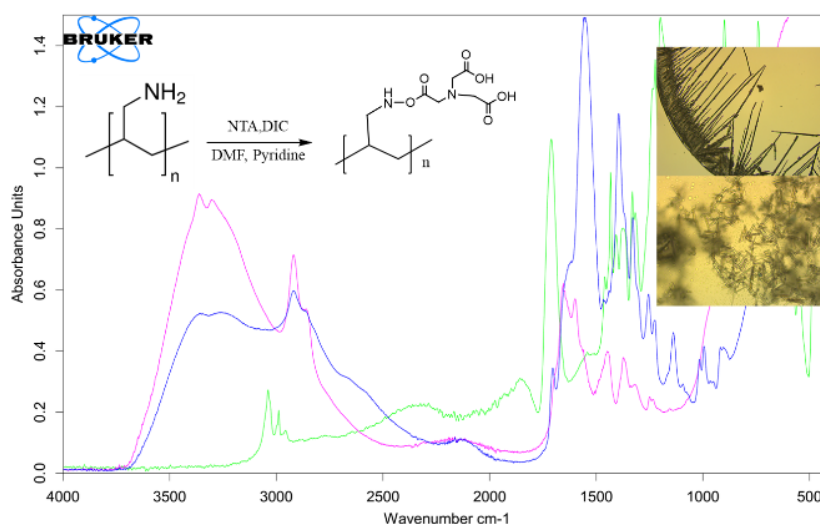
### 2.1. Screening of polymers

In the beginning, two polymer chain candidates and two functional groups were chosen, giving a total of four polymer candidates. The two polymer chains were Chitosan and Polyallylamine (PAA). Chitosan is a linear polysaccharide which is derived from crustaceans and widely used as a seed treatment and biopesticide in agriculture, a fining agent for winemaking, bandages to reduce bleeding and as an antibacterial agent. It is environmentally friendly and is known to form gels with solvents. PAA is a water-soluble cationic polymer with primary amino groups (free base types) for chemical reactions. PAA is able to modify surfaces and provide cationic character allowing the user to selectively attract negatively charged functional groups to the coated surface or the dissolved water-soluble cationic polymers. So PAA has a broad range of applications in the polymer industry and research. EDTA and NTA both show strong binding properties to Ca<sup>2+</sup> ions. They were both possible candidates for the modification groups for the polymer. However, the chemical structure of these chelate compounds was different (see Figure 1). There are six binding points in the EDTA-Ca<sup>2+</sup> chelate compound and Ca<sup>2+</sup> is packed inside. As for the NTA-Ca<sup>2+</sup> compound, there are three to four binding points, and the other positions can chelate with other molecules or another NTA molecule.



**Figure 1:** The chemical structure Chitosan and PAA and of the chelates EDTA and NTA

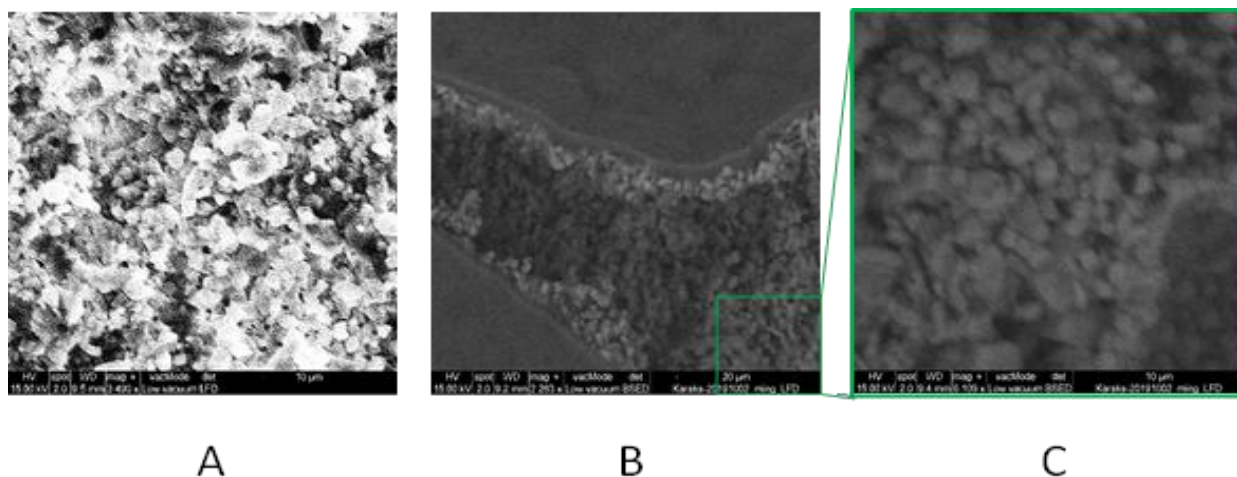
The focus of further testing was on these four polymers: chitosan-EDTA, chitosan-NTA, PAA-EDTA, and PAA-NTA. All of these combinations were tested in batch experiments with chalk to see if had the required binding and emulsification properties. The initial tests of the polymers showed that Chitosan is hard to dissolve in water therefore would be difficult to inject into the reservoir on a large scale. PAA shows high solubility in water and some solvents including ethanol, DMF, pyridine and liquid CO<sub>2</sub> and therefore PAA was chosen as more suitable in this project. The screening experiments for binding of the chelating agents showed that NTA did bind strongly with the chalk surface, but EDTA did not; NTA showed self-healing property, but EDTA did not (see Figure 7). Thereby, NTA would be the functional group for modification of the polymers, and PAA-NTA the chosen polymer/functional group combination.



**Figure 2:** Preparation of PAA-NTA and characterization by FTIR. NTA (green), PAA (pink), PAA-NTA (blue).

For the preparation of PAA-NTA a mixture of DMF/pyridine/water/NaOH was used to dissolve it and the products were measured by FTIR (see Figure 2). It showed strong absorption bands of C=O and NH in the IR. PAA-NTA aggregated during the reaction and formed gel with a light yellow colour. This gel could be dissolved by 0.1 M NaOH. In the end, the final clear yellow solution was stable and could be used for the flooding experiment.

A PAA-NTA coated chalk sample was measured by SEM in order to investigate the coating effects of the polymer. In the picture Figure 3B, we can see the coating layers. It can also be seen that the coating was only located at the surface, not deep inside the rock, in layers of 1 μm or less. There were many cracks on the coating layers because the chalk had to be dried before measurement. The reason that the PAA-NTA doesn't penetrate into the rock, could be evidence of the self-healing of PAA-NTA polymers. This has been investigated further in the CO<sub>2</sub> flooding experiment.

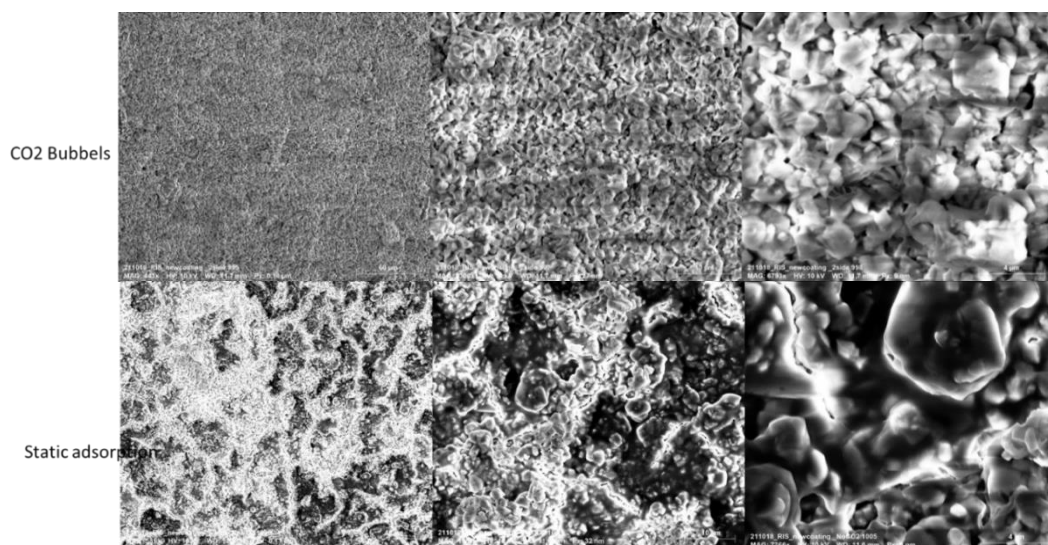


**Figure 3:** SEM image of chalk surface. A) chalk without coating; B) chalk with coating PAA-NTA; C) Magnification of the coated area

## 2.2. Static adsorption and dynamic adsorption

Experiments to test the adsorption process of the polymer on chalk thin sections were performed under both dynamic and static conditions. It is crucial to include both adsorption processes when we study the underground CO<sub>2</sub> storage, since in practice, dynamic adsorption is occurring during the injection/leakage phase, while static adsorption is playing role during long-term storage. The dynamic tests were carried out on six similar small thin sections, which were put into three groups. The first group was blank and was just kept in the same solvent (water) as the other groups. The second group was in contact with CO<sub>2</sub> bubbles in the vial, in addition to water solvent and the chalk without coating polymers. The hot CO<sub>2</sub> bubbles were flowing continuously in the chamber. The chalk coated with PAA-NTA was in the third group, and the reaction conditions were the same as in the second group. Reactions for all the groups were continued for 48 hours. After that, a small thin section from each group was taken out with a tweezer and washed with water, and dried with air for 2-5 minutes. Then the samples were immobilized on the support and coated around 20 nm with carbon. Then the samples were analyzed with SEM (Figure 4). In order to test static adsorption conditions two pieces of similar small thin sections were put in the vials with same amount of solvent. The static adsorption sample was kept for 48 hours at static condition. As can be seen in figure 4, we obtained different surface topologies after coating by performing the CO<sub>2</sub> bubbles experiments. It suggests that static and dynamic adsorption could influence the coating process differently. The coating layer was thinner in the dynamic adsorption experiment. The big pores changed to small ones. Even micron-size pores had been filled polymers in the static adsorption sample.

According to the results, it was exciting that PAA-NTA could coat the chalk successfully under both conditions.



**Figure 4 :** SEM images of the static adsorption and dynamic adsorption chalk samples.

### 2.3. First pure CO<sub>2</sub> flood

The first pure CO<sub>2</sub> flooding was conducted when the core was fully saturated with polymer. The differential pressure across the core plug and produced gas flow are shown in Figure 5. As it was mentioned before, the injection rate was constant equal to 1cc/hr. It was observed that there are several pressure jumps during CO<sub>2</sub> flooding, which can be interpreted as partial blockage and the creation of a new pathway. In addition, the CO<sub>2</sub> reached the core inlet around 0.5 PV (this is due to dead volume at the inlet section of the core flooding rig), and the breakthrough happened approximately at 1.5 PV, which shows that CO<sub>2</sub> had been swept all the pore space out of polymer.

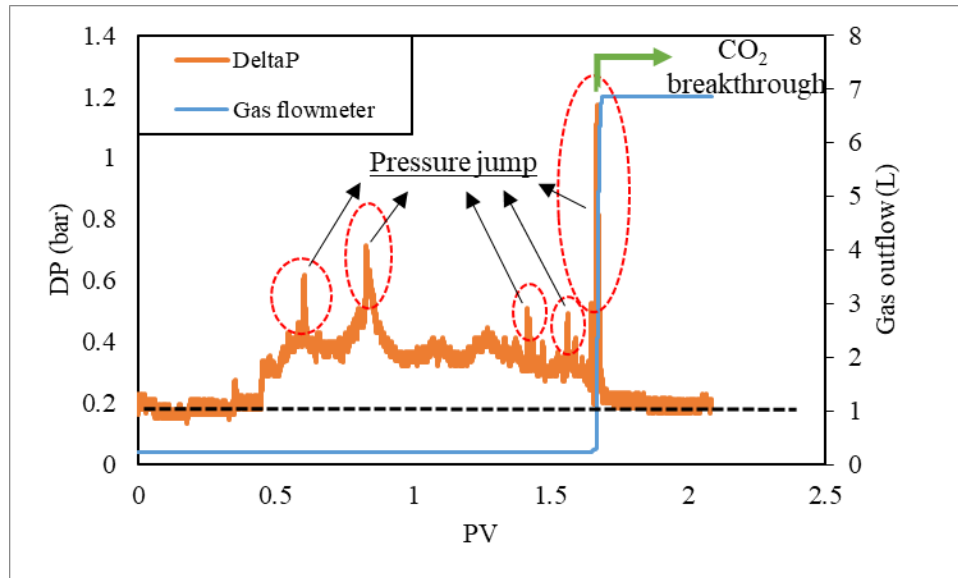


Figure 5: Differential pressure across the core and produced gas flow rate during pure CO<sub>2</sub> flood.

### 2.4. Co-injection of CO<sub>2</sub> and polymer

As observed from the previous section, almost all polymer was swept with CO<sub>2</sub> and probably there was not enough polymer in the core to coat the chalk. Therefore, co-injection of polymer and CO<sub>2</sub> insured us, that both CO<sub>2</sub> and polymer are available in the core. The differential pressure across the core plug and produced gas flow during co-injection of CO<sub>2</sub> and polymer were shown in Figure 6. It was observed that the breakthrough of the solution is almost after 1 PV, which again confirms that this mixed solution could be able to penetrate almost all the pore space. After the breakthrough, a continuous ascending trend in the differential pressure was observed, which suggests a continuous pore blockage in the core. However, like the first pure CO<sub>2</sub> flood step, DP jumps were observed which might be due to pore blockage and the creation of new pathways. The experiment was stopped after almost 6.5 PV since we ran out of polymer. At the end of this step, approximately 10 bar pressure deviation from the case of pure CO<sub>2</sub> injection was observed which can confirm the ability of the solution to block pore spaces. Furthermore, it was observed that the pressure increased after the breakthrough, which means that self-healing happened after the breakthrough. Compared to the variation of deltaP from the pure CO<sub>2</sub> experiment, Co-injection was larger due to the self-healing process.

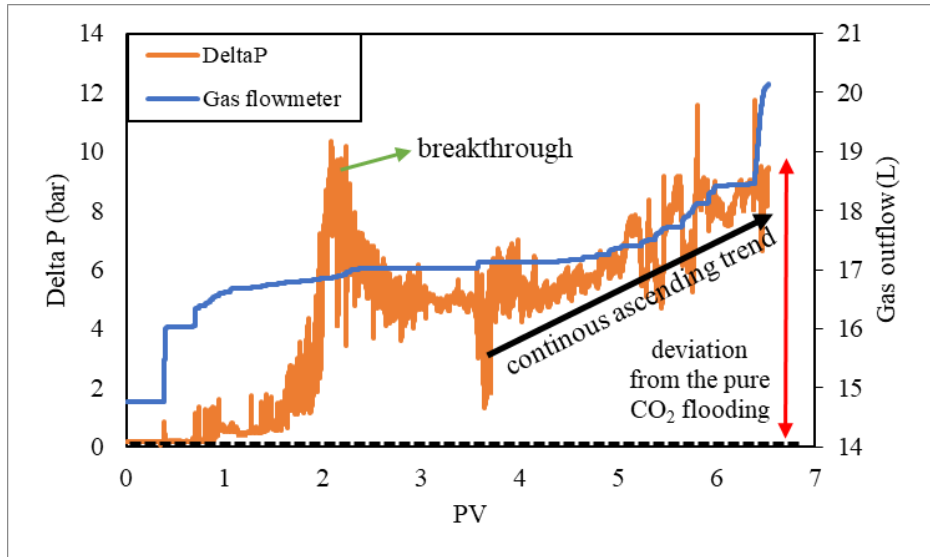


Figure 6: Differential pressure across the core and produced gas flow rate during co-injection of CO<sub>2</sub> and polymer.

2.5. Second pure CO<sub>2</sub> flood

After co-injection of polymer and CO<sub>2</sub>, again pure CO<sub>2</sub> was injected. This was done in order to compare the results with the first pure CO<sub>2</sub> flood step and confirm the pore blockage in the core sample. Figure 7 shows the differential pressure across the core and produced CO<sub>2</sub> during this second pure CO<sub>2</sub> flood step. First of all, the breakthrough time has been decreased way less than 1 PV, which suggests that some pore throats have been blocked and there is no access to the whole pore space. Also, there are fewer pressure jumps this time. We can speculate that almost all small pores were blocked during the previous step and only the larger pores are available for the flow, which was the same results as what we got from the adsorption experiment. In beginning, there were new channels around 0.4 PV, but they healed immediately. But after the main breakthrough after 0.5 PV, the self-healing process was weak due to not enough available polymer.

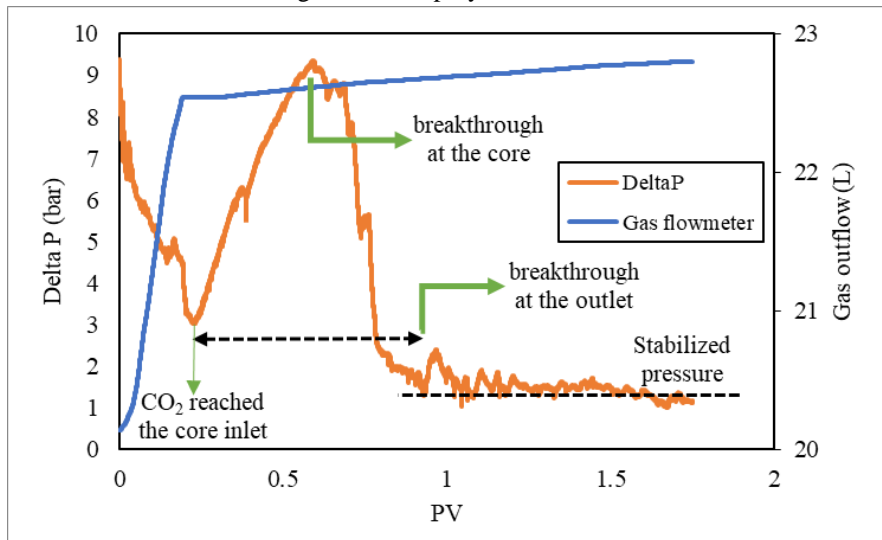


Figure 7: Differential pressure across the core and produced gas flow rate during second pure CO<sub>2</sub> flood.

## 2.6. Comparison of DP for different injection steps

Figure 8 shows the comparison of DP for different injection steps. The PV for co-injection of CO<sub>2</sub> and polymer has been multiplied by 1/3 in order to have a better visual insight. The increasing DP trend when polymer and CO<sub>2</sub> had been injected at the same time clearly shows the main blockage period. On the other hand, the second pure CO<sub>2</sub> flooding step showed a drastic change in DP compared to the first CO<sub>2</sub> injection step. The stabilized pressure for the second pure CO<sub>2</sub> injection was approximately more than 5 times higher than the first pure CO<sub>2</sub> flooding step. In addition to that, the significant reduction in the breakthrough time for the second pure CO<sub>2</sub> flood rather than the first CO<sub>2</sub> flood clearly indicates the pore blockage and inaccessible pore spaces, confirming the observations seen in the SEM images of thin sections.

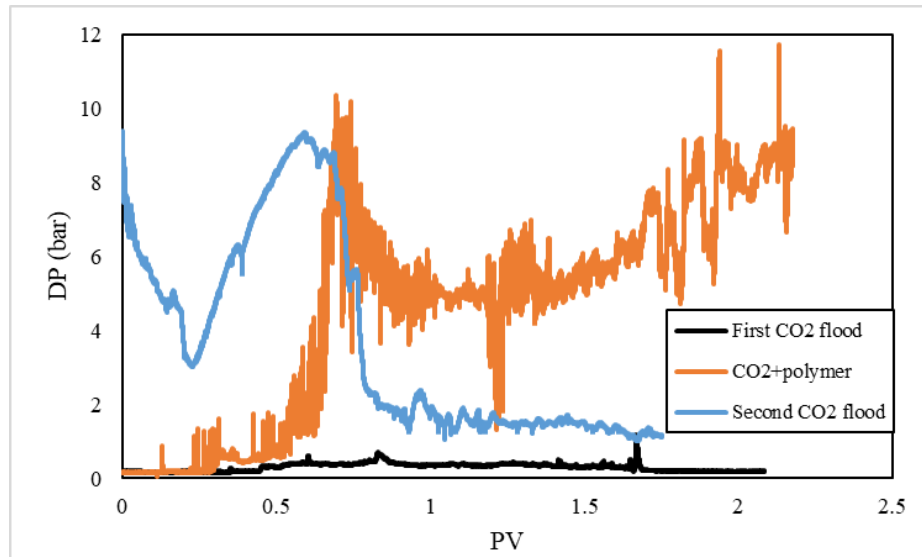


Figure 8: Comparison of differential pressure across the core during different injection steps.

## 2.7. Self-healing in elution polymers

It was quite interesting that we could see the self-healing polymer directly (see Figure 9). The elution fractions were collected when performing the experiment, so there were self-aggregated polymers after the second pure CO<sub>2</sub> flood experiment. These large polymer gels had to be formed after elution because they could not go through the core. This shows PAA-NTA had the self-healing ability directly.



Figure 9: PAA-NTA self-aggregation in core flood eluents.

## 3. Conclusions and Futures

In this study we have investigated the potential of injectable functional polymers for limiting the dissolution of chalk or carbonates during CO<sub>2</sub> injection and storage at reservoir conditions. The tested polymer, PAA-NTA, showed specific properties that met the requirement of stability, solubility, strong binding on chalk, and self-aggregation when coming into contact with Ca<sup>2+</sup> ions. It was also stable under reservoir conditions at high pressure and temperature. Batch test indicated that the polymer could self-heal the CO<sub>2</sub> containing reservoir if leaking occurs as the polymer aggregates at surfaces. Both the SEM images of thin sections subjected to static and dynamic



polymer exposure and the core flooding experiment where water and polymer were co-injected indicated that the fine pore space is blocked by the polymer and hence that the available surface area for reaction is significantly reduced.

This new recipe could reduce the risks associated with injecting CO<sub>2</sub> into chemically active reservoir rocks. Further work should include X-ray CT imaging to reveal insights into how the polymer influences the CO<sub>2</sub> flow in the pores and show if the PAA-NTA is able to permeate the pore space or exclusively aggregates at the surface.

### **Acknowledgements**

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