



# Deployment of Silica Gels for Improved CO2 Containment and Risk Mitigation.

Never Stand Still

Engineering

Petroleum Engineering

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## **Acknowledgement and Disclaimer**

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## EXECUTIVE SUMMARY

Long-term sequestration of carbon dioxide requires robust and effective caprock barriers and wellbore seals to prevent vertical migration of carbonated brines or supercritical carbon dioxide from the storage reservoir. Moreover, Australian legislation governing carbon dioxide storage places strict limitations on the horizontal migration of the carbon dioxide plume. Therefore, large-scale deployment of Carbon Capture and Storage in Australia requires effective methods for inhibiting carbon transport vertically and horizontally, for risk mitigation and as a rapid response in the event of inadvertent leakage.

Silica gels have the potential to produce inexpensive, effective, non-toxic barriers to flow in subsurface reservoirs. Silica gels are produced from silica sols, which are low cost by-products of geothermal power production. Deployed initially in the sol form, the gelation of silica sol may be triggered by lowering the pH. Gelation times depend on pH and sol concentration, which allows the gel timing to be adjustable at the surface to suit specific subsurface operations. This gives silica gels the potential to be strategically deployed to seal leakage pathways, create flow barriers and provide regional (horizontal and vertical) isolation.

The objective of this project is to develop strategies for the deployment of silica gels in carbon dioxide storage operations. This preliminary study considers the use of silica sols in the near wellbore region to reduce leakage risk or in response to active leaks in fractures in and around wellbore cements. This is achieved by studying the ability of silica gels to plug cement fractures after exposure to carbon dioxide rich brine and super-critical carbon dioxide, as well as the effects of brine and cement chemistry on the gelation times of silica sols.

When placed in contact with super-critical carbon dioxide and carbon dioxide rich brines, cements undergo a series of reactions that result in the creation of reaction fronts. These reaction fronts propagate into the cement body producing a series of reaction zones in their wake. These zones have a distinct chemistry and material properties (in particular porosity and permeability) compared to un-reacted cements. Thus, studies were conducted to see whether the formation or performance of the sol gels would be affected in the presence of these reaction zones.

Interactions between reacted cement and sol gels were studied by first preparing Portland Cement slabs that were cured for several weeks, before being cored and polished to produce a series of cylindrical cement cores. Fractures were produced in these cores, either by inducing tensile fractures or by cutting the samples along the length of each cylinder. The fractured samples were then either put aside to serve as unreacted samples, or reacted with carbonated brines, super critical CO<sub>2</sub> or hydrogen chloride solutions. In this manner, a series of fracture surfaces were created that had a range of different chemical properties and extents of reaction.

The cement samples were also scanned using X-Ray Computed Tomography prior to and following reaction with the different solutions to determine the extent of reaction. Sol gels were introduced into the fractured cement samples and allowed to set. The permeability of the samples was measured before and after the introduction of the sols to judge their ability to inhibit flow in the fractures. In some cases, the sample permeability was also measured under different levels of confinement to judge the sol gel's ability to withstand changing stress conditions. Samples were also scanned following the introduction of the silica sols to judge the extent of the deposition of the sol gels. Significant reductions in permeability were observed in all of the fractured samples and the sol gels retained their ability to prevent flow

despite changing stress conditions. However, upon examination of the XRCT images, it was clear that the sol gels did not evenly distribute across the fracture surfaces in all samples. This we believe is related to the effect of calcium ions on the gelation time, an effect that was considered in greater detail in the sol gelation experimental studies.

The silica sols will mix and react with the in-situ brines as they are introduced into the subsurface. This can change the gelation time or prevent the sol gel from forming entirely. In addition, in order to provide effective long-term barriers to flow, the sol gels must retain their integrity over long periods of exposure to the resident fluids. Thus two sets of experiments were conducted to investigate the potential role of brine chemistry on the gelation time and the long-term integrity of sol gels.

The first set of gelation experiments examined how gelation times were affected by the addition of brines of varying composition. Silica sol precursors were prepared and mixed with solutions of varying concentrations of NaCl, CaCl<sub>2</sub> and HCl as well as combinations of each. These studies highlighted the role that CaCl<sub>2</sub> has in increasing the gelation rate. This is important not only because Ca<sup>2+</sup> ions are prevalent in some brines – particularly deeper bittern brines and also carbonate formations – but also in brines reacted with wellbore cements. This increase in the reaction rate caused by the Ca<sup>2+</sup> ions appears likely the reason for the uneven distribution of sol gel observed in some of the cement fractures.

The second set of gelation experiments considered how the gels were affected by long-term exposure to brines of varying compositions. In particular sol-gels can shrink and crack after only a few days left exposed to the air. Hence it was wondered what would happen to the samples if exposed to brines of high salinity, due to differences in osmotic potential. Sol gel samples were prepared and set in small sections of PVC pipe, before being exposed to solutions of different composition (salinity and pH) and held under observation for 45 days. After the period, any changes in the samples were noted, and the samples were then drained and allowed to dry for a further 15 days.

The study showed that even very salty (2M NaCl) brines were insufficient to cause shrinking of the sol gels. Indeed, in a few cases the sol gels were observed to swell as a result of exposure to the brine. Conversely, drying resulted in shrinking in all samples, and the production of thin crystals in a couple of cases.

Through these studies we have considered the ability of sol-gels to provide effective barriers to carbonated brines and super-critical CO<sub>2</sub> in the subsurface. The results of this work indicate that sol gels can provide effective barriers to fluid flow under a range of operating conditions. However, care should be taken in selecting these gels, particularly when in contact with high concentrations of calcium (and other aqueous species with high ionic charges) as this can dramatically increase the gelation rate, which may affect their deployment.

## LAY SUMMARY

Long-term underground storage of carbon dioxide requires effective barriers to prevent leaks from the storage reservoir. Moreover, Australian laws place strict restrictions on the horizontal movement of carbon dioxide stored in the subsurface. Therefore, large-scale deployment of Carbon Capture and Storage in Australia requires effective methods to inhibit movement of carbon dioxide, for risk mitigation and as a rapid response in the event of inadvertent leaks.

Silica gels have the potential to produce inexpensive, effective, non-toxic barriers to flow in subsurface reservoirs. Silica gels are produced from silica sols, which are low cost by-products of geothermal power production. Deployed initially in the sol form, the gelation times can be adjusted at the surface to suit specific underground operations. This gives silica gels the potential to be deployed to seal leakage pathways, create flow barriers and isolate sections of the subsurface.

The objective of this project is to develop strategies for deployment of silica gels in carbon dioxide storage operations. This preliminary study considers the use of silica sols in the near wellbore region to reduce leakage risk or in response to active leaks in fractures in and around wellbore cements. This is achieved by studying the ability of silica gels to plug cement fractures after reactions with brine and super-critical carbon dioxide, as well as the effects of brine and cement chemistry on the gelation times of silica sols.

The results from the study show that silica sols can provide effective barriers to flow. They also demonstrate that sol gels are able to withstand extended exposure to salty and acidic brines. However, the study also reveals that the speed of gelation increases rapidly when high concentrations of calcium ions are present. Therefore, care should be taken to understand the underground water chemistry when using these gels to manipulate flow in the subsurface.

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### **ABBREVIATIONS**

CAC	Converging Active Contours method
CCS	Carbon Capture and Storage
SAOS	Small Amplitude Oscillatory Shear Test
scCO <sub>2</sub>	Super Critical Carbon Dioxide
XRCT	X-Ray Computed Tomography



## **INTRODUCTION**

Long-term sequestration of carbon dioxide requires robust and effective caprock barriers and wellbore seals to prevent vertical migration of carbonated brines or supercritical CO<sub>2</sub> from the storage reservoir. Moreover, Australian legislation governing CO<sub>2</sub> storage places strict limitations on the horizontal migration of the CO<sub>2</sub> plume. Large-scale deployment of CCS in Australia requires effective methods for inhibiting carbon transport vertically and horizontally, for risk mitigation and as a rapid response in the event of inadvertent leakage.

Oil and gas wellbores provide an obvious conduit for transmission of super critical CO<sub>2</sub> and carbonated brines from deep storage reservoirs to other subsurface strata and possibly even the atmosphere (Carroll et al 2016). While correct plugging and abandonment procedures can seal these wells, over time, reactions between the cement and the acid brine or super critical CO<sub>2</sub> can result in the formation of new leakage pathways (Kutchko et al 2007). This project seeks to reduce these risks by investigating the potential for colloidal silica gels to serve as an effective barrier to the leakage of carbonated brines and supercritical CO<sub>2</sub>.

There are several potential advantages to using silica gels. The silica sols from which the gels are formed are a non-toxic natural bi-product of geothermal operations. Silica gels i) have excellent sealing functionalities in harsh environments; ii) are relatively chemically inert; and iii) are easy to make with little or no operational difficulties i.e. pumpability depending on the desired formulation and durability. Silica gels can also be deployed from the formation up to the surface with little environmental risk (Hunt et al 2013).

If successful, this technology could provide a mitigation strategy to reduce the risks associated with long term CO<sub>2</sub> storage, or a rapid response to prevent leakage. Importantly, by reducing the risk of leakage, silica gels have the potential to reduce the costs of CO<sub>2</sub> sequestration even if not deployed, as the technology has the potential to lower insurance costs associated with long-term sequestration sites, by reducing the associated hazard of adverse events.

This preliminary study considers the use of silica sols in the near wellbore region to reduce leakage risk or in response to active leaks. This is achieved by studying the ability of silica gels to plug cement fractures after exposure to brine and CO<sub>2</sub> (so called “live brine”), as well as the effects of brine and chemistry on the gelation times of silica sols.

In the following sections, we outline the aims and objectives of this project, then describe the methods used to test the ability of the sol gels to form effective barriers to flow in fractured cements. Next we provide the results from these tests and offer a discussion of how these results extend our existing understanding of these materials. Finally, we outline the conclusions of the report and describe additional work required for the next steps in this project.

## **PROJECT AIM, OBJECTIVES, MILESTONES AND PERFORMANCE MEASURES**

The objective of this preliminary investigation is to study the feasibility of deploying silica sols in fractured wellbore cement to mitigate carbon-dioxide leakage. The behavior of these gels was studied under a range of different circumstances – examining their ability to seal cement fractures: both unaltered and after undergoing extensive reaction, the effects on the gelation time and strength after mixing with brines of different compositions, and examining

the effects of long-term exposure of the sol gels to fluids with a range of salinities and acidities. The milestones associated with achieving this objective are summarized in Table 1.

Table 1 : Project milestone summary

Milestone ID	Milestone Title	Status (%)	Relevance to project and achievement
M1	Prepare sample cores	100%	Samples were prepared from cured Portland cement that was cored and polished to form cylindrical samples. The samples were then fractured or saw-cut and prepared for testing.
M2	Scan Unreacted cores	100%	Sample cores were scanned before reaction to provide a baseline from which the extent of reaction could be determined.
M3	Sample reactions	100%	Samples were reacted with super critical CO <sub>2</sub> , carbonated brines and hydrochloric acid to create reaction zones along the fracture surfaces.
M4	Scans of reacted cores	100%	XRCT images were taken of reacted cement cores. These images allow the extent of reaction to be determined.
M5	Permeability measurements of plugged cores	100%	The permeability of plugged cores was measured to determine the ability of the silica sol gels to prevent flow. These tests demonstrated the ability of the silica sol gel to provide an effective barrier to flow in cement fractures.
M6	Scans of plugged cores	100%	XRCT scans were taken to evaluate the extent of deposition of the gel along the sample cores.
M7	Gelation Study	100%	Gelation studies were conducted examining the effect of brines of different compositions on the gelation times and gel integrity.
M8	Submit final report	100%	Present report.

## METHODOLOGY

The experimental study includes three main stages a) prepare the cement plugs and make silica sol recipe and fracture the cement samples, b) X-ray micro computed tomography of the samples before and after exposure to live brine/ScCO<sub>2</sub> to investigate the dissolution and precipitation effect of the chemical reactions and c) permeability and leak-off measurement to assess the performance of the silica gel in sealing the fracture in the cement samples.

### a) Sample Preparation (Milestone M1)

#### *Preparation of Cement samples*

In order to prepare the cement samples, two standard 20kg British cement bags were used. Each 20kg bag of cement was mixed with 10 liters of water as per product instructions on water-cement ratio. Cement and water were transferred to an iron mixing bucket with approximately 15-liter volume. An industrial hand-held blender was used to ensure that cement was properly mixed and no dry cement powder remained on the bottom of the mixing container. Approximately 8 minutes of blending was performed to secure maximum exposure and mixture of cement with water. After blending, an industrial hand-held vibrator was additionally used in the slurry to drive out residual bubbles created in the blending process. The vibration lasted approximately 2 minutes. As the mixing bucket can only handle 20 kg of cement and its product slurry, the mixing process was repeated twice. Slurry produced after blending was immediately transported into standard 6-gallon chemical storage buckets. A total of two full buckets of slurry were prepared. The chemical storage buckets have a sealable lid which is capable of preventing moisture from escaping cement body during the

curing process, which is a major concern of premature healing and potential mechanical damage to the cement.

Slurry with chemical storage buckets were then transported into a controlled-temperature room. The temperature in the room was set at approximately 40 degree Celsius, while air convection between inside and outside of the room was prevented during curing time to make the moisture content stable. The slurry sealed in chemical storage buckets were stored uninterrupted in the stable-temperature room for over 30 days to ensure that cement samples reach their maximum strength. In the next step, a variable-rotational-speed drilling bench (Figure.1) was used to core the samples with required sizes. Samples with 0.5-inch (1.25 cm) diameter and 1-inch (2.5 cm) length were then cored and their end surfaces were polished to ensure proper contact during testing.



Figure. 1 Equipment used to prepare the cement samples: a) coring and b) cutting machines.

After coring some of the samples were saw-cut into two pieces to produce an artificial opening. Additional cores underwent further processing to simulate more realistic fracture geometry. These tensile fractures were created along the middle of the samples using the ‘Brazilian test’ method (Massoumi et al, 2018). To induce the tensile fracture in the samples, a pair of grooves with approximate depth of 0.5 mm was made along the length of the sample. A pair of stainless-steel rods with a diameter of 1 mm was then placed firmly in the grooves, and stress was applied by a loading frame on the rods to create the fractures in the samples (Figure. 2). The samples were then wrapped by heat shrinks for further testing.

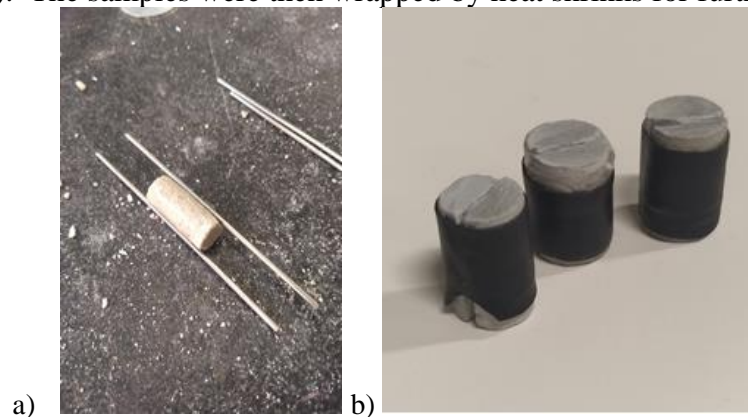


Figure 2. a) Method for forming the tensile fractures and b) fractured samples wrapped in heat shrinks

### *Silica Sol Prepared for Injection*

The properties of the colloidal silica gel can be modified with changing the recipe containing sodium chloride and hydrochloric acid (Hunt et al 2013). Given proper ingredient proportion and mixing order, colloidal silica gel mixture can set in target location and reaches the required mechanical strength. The colloidal silica SOL used in this study was a LUDOX® SM colloidal silica by Sigma-Aldrich with composition of 30 wt% SiO<sub>2</sub> with pH of 9.5-10.3@25°C. The hydrochloric acid was UNIVAR® HYDROCHLORIC ACID 32% AR with 31.5 w/w% HCl content. The HCl solution is diluted with deionized water to 1 N and stored in confined glass bottle for further use. The sodium chloride was a Chem-supply® Sodium Chloride AR. NaCl solid was mixed with deionized water to make 2.5 N solution and stored in confined glass bottle for further use. The blending process was conducted inside 50ml volume plastic Petri dish (Figure. 3).

The order of mixing was first assessed to investigate whether it can affect the silica gel formation. Results indicated that ingredients input order should always be colloidal silica sol – deionized water – HCl solution and finally NaCl solution. With consistent 20°C reaction temperature and 1 min blending time along with fixed ingredient mixing order, further attempts were carried out to explore a proper proportion of all ingredients to reach the maximum gel strength. Several trial & error attempts led to a ratio of 6 volumetric units of original colloidal silica sol, 3 volumetric unit of deionized water, 1 volumetric unit of 1 M HCl solution and 1 volumetric unit of 2.5 M NaCl solution to reach the highest gel strength.

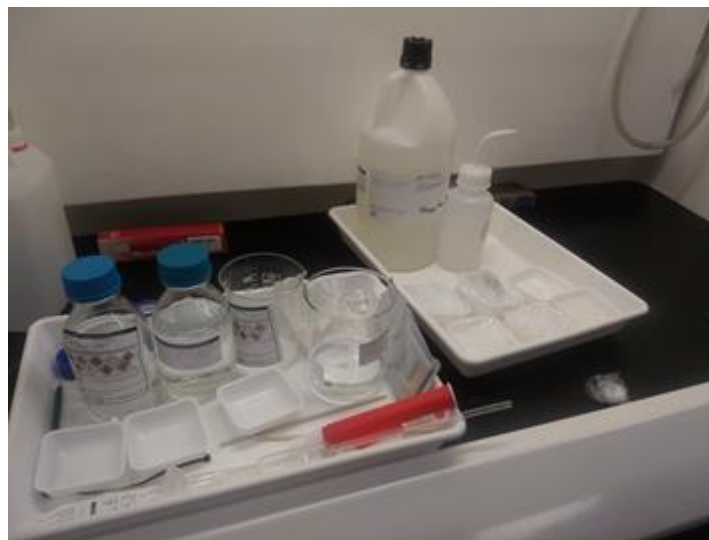


Figure. 3 Ingredients used in sol gel preparation

### **b) X-ray micro computed tomography (Milestones M2, M4, M6)**

The micro CT scanning was performed twice on each sample: one before exposure to live brine/ScCO<sub>2</sub> and one after exposure. The reason for the scans was to investigate the effect of fluid exposure on fracture in the cement and cement body itself. The CT scanning was performed in CT facility, Tyree Energy Technology Building, UNSW Sydney. The micro-CT system is a high resolution helical micro-CT scanner. Instrument specifications and imaging parameters are provided in Sheppard et al. (2004). In this technique, the sample is exposed to a polychromatic beam, which is attenuated as it passes through the sample. The attenuated radiations are received by an array of detectors and transferred to a computer to reconstruct a 3D multiphase gray-scale image (tomogram). Each data point in the tomogram (voxel) represents the effective X-ray attenuation coefficient which is a function of density and

atomic number of the material. The obtained image resolution was  $\sim 10.0 \mu\text{m}$ . To characterize the gray-scale image of the sample, the image is segmented using the converging active contours (CAC) method (Sheppard et al., 2004). In this method two threshold values are set based on a layer-by-layer inspection of the 3D tomogram. Data points with gray-scale values higher than the upper threshold are labelled as solid and the values below the lower threshold are labelled as void. The values between the upper and lower thresholds (undecided regions) are set using the image gray-scale value gradient at boundary regions. CAC then simultaneously grows the boundaries of the solid and void regions toward each other until all boundaries converge (Schlüter et al., 2014). CAC was applied to all images to segment them into (i) fracture phase and (ii) solid phase (Figure 4).

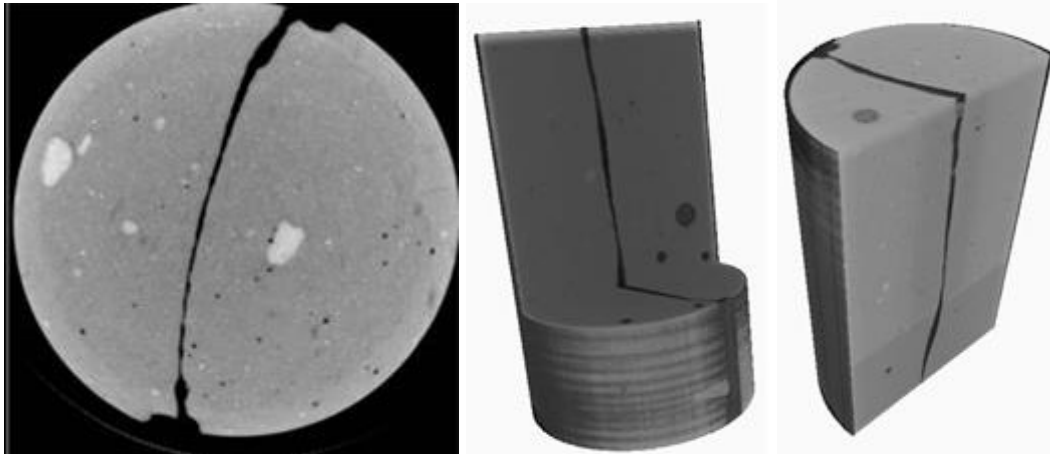


Figure. 4 Micro CT tomography image sampled from the test bodies

### c) Experimental procedure (Milestones M3, M5, M7)

*Sample/ (CO<sub>2</sub>/brine) live brine, super critical CO<sub>2</sub> and HCl exposure (Milestone M3)*

Samples were reacted with both live (i.e. carbonated) brine, super critical CO<sub>2</sub> and HCl. A core-flooding apparatus was employed to react cement samples with super-critical carbon dioxide (scCO<sub>2</sub>). The experiment was performed in three steps: I) measuring the permeability of the sample before being reacted with sc-CO<sub>2</sub> II) Reacting the sample with sc-CO<sub>2</sub> III) measuring the permeability of the sample after flooding. The injected sc-CO<sub>2</sub> flows through the fracture path. The conductivity of the fracture depends on the aperture size which in turn depends on the amount of confining pressure. A confining pressure of 24 MPa was selected in all steps to ensure that the fracture width is the same throughout the experiment.

Moreover, live brine (i.e. carbonated brine) was made using the synthetic brine recipe and CO<sub>2</sub> pressure suggested by CI Walsh et al (2014b). The details are shown in Table 2. The CO<sub>2</sub> pressure of 3.0 MPa was applied in a litter of brine hosting the cement samples to trigger the reaction between the live brine and cement samples. The samples were exposed to live brine in the chemical reactor set at 60 °C for 4 weeks.

Additional samples were also reacted with hydrochloric acid to generate fractures with extensive reaction zones more indicative of longer-term exposure to carbonated brines. In these samples, the faces of the cement fractures were immersed in 1M HCl solution for a period of 3-4 days.

Table 2. Composition of the brine solution employed in the study

Reagent-grade salt	mole·kg H <sub>2</sub> O <sup>-1</sup>
NaCl	1.01
NaHCO <sub>3</sub>	0.00792
Na <sub>2</sub> SO <sub>4</sub>	0.0369
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.0353
MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.0159

*Permeability measurement and leak-off test (Milestone M5)*

The permeability of the fractured samples was measured using steady state method (Roshan et al, 2015) with water before placing the silica sol into cement fractures. After placing the gel when it was set in the fracture (so called leak-off test), the CO<sub>2</sub> pressure was applied on a step manner on the upstream side of the samples. The confining pressure for the leak-off tests was consistently 100 psi higher than injection pressure. Initial permeability tests in the other hand were performed at constant 200 psi confinement. The confinement pressure for all the permeability tests were delivered via ENERPAC®P391 manual pressure generator, combined with the test cell (Figure 5); while the injection of deionized water for initial permeability measurements was delivered by VINDUM PUMP®VP-3.5K-HC. Both injection pressure and confinement pressure can be read with help of gauges installed on the instruments. The permeability is calculated with original Darcy's law given as:

$$k = \frac{Q \times \mu \times L}{A \times dP}$$

Where Q is the flowrate in ml/s,

K is the permeability in Darcy,

A is area in square centimetres,

dP is the change in pressure in psi,

μ is the fluid viscosity in centipoise,

L is the length of the cylinder in centimetres.

It is noted that the downstream side of the cell was open to atmosphere. After measuring the permeability of the wrapped sample, the silica sol was injected to the sample and held for an hour. The samples were then taken out of the cell and placed in the silica sol prepared with the previously explained recipe. The samples stayed submerged in the silica sol for one day before they were cut out for the leak-off testing (Figure 5).

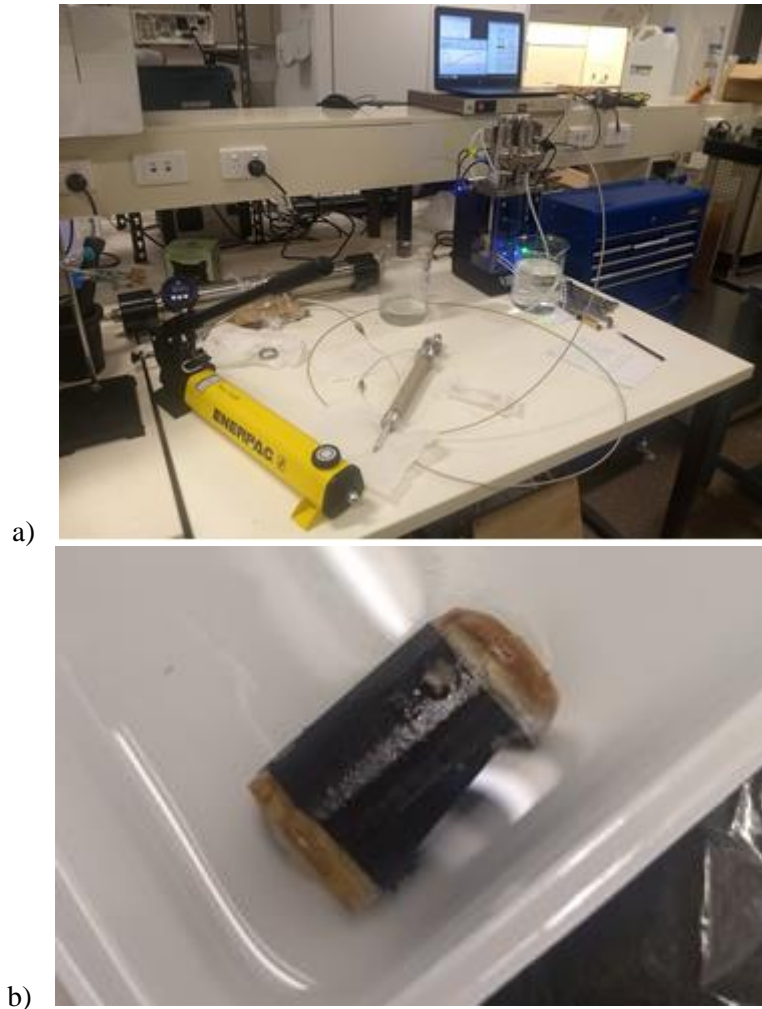


Figure. 5 Setup (a) used for permeability and leak-off tests and (b) a fractured cement sample submerged in silica sol

*Brine/Silica gel interaction (Milestone M7)*

During injection in the subsurface, there is ample opportunity for the silica sol to be exposed to and mix with in situ brines. This has the potential to alter the gelation time or prevent gelation altogether. In addition, silica gels successfully formed in the subsurface will likely experience long exposure to salty and acidic brines – potentially affecting their ability to seal fractures in the long term. Therefore, two sets of experiments were conducted: the first evaluated to what extent the gelation times would be affected by changes to the brine composition, while the second considered what effect long term exposure to brines of different pH and salinity might have on the gels.

*\*Gelation experiments (Milestone M7)*

The effect of brine composition on gelation time was tested by considering the relationship between time and silica concentration, NaCl concentration, HCl concentration, and Ca concentration.

Gelation is the process by which the particles in a colloidal sol are linked together in branched chains that fill the whole volume of sol so that there is no increase in the concentration of silica in any macroscopic region in the medium. Instead, the overall medium becomes viscous and then is solidified by a coherent network of particles that retains the

liquid by capillary action. Small amplitude oscillatory shear (SAOS) testing is ideal for tracking the structural build-up in such a gel. During the SAOS test, a sample is subjected to a continuous sinusoidal excitation of either a fixed deformation or a fixed shear stress. The response (either shear stress or deformation, respectively) of the material to the excitation can be measured and can be used to evaluate the gelation time of the material. When the applied excitation is very low, the test can be a non-destructive technique since the material remains in the elastic range during testing.

A high precision rheometer was used for the rheological test, during which the temperature of the sol solution was maintained at a constant 20 °C. The rheometer consists of concentric cylinders with the inner and outer diameters of 26.661 and 28.913 mm respectively, and a gap width of 2.252 mm. The inner and outer surfaces in contact with paste samples are roughened to reduce wall slip. The gap between the two cylinders is small, thus a constant shear rate could be assumed across the testing samples.

Two types of oscillatory shear tests were conducted to evaluate the structural build-up of sol gels by the SAOS tests: oscillatory stress sweep and oscillatory time sweep. The oscillatory shear tests involve two important testing parameters, i.e. strain amplitude and frequency. The strain is defined as  $\gamma = \frac{R\Omega}{w}$  where  $R$  is the inner cylinder diameter (m),  $\Omega$  is the angle of displacement (rad) and  $w$  is the gap between the inner and outer cylinder.

The Oscillation Stress Sweep is first of all used to determine a material's linear visco-elastic range, which is to say that the measurement parameters are set in this manner that stress and strain amplitude have a linear relationship which can be described by the following equation:

$$\sigma = C \times \gamma$$

A more practical way to identify the linear visco-elastic range is to look for the region where the material functions as e.g.  $G'$  and  $G''$  are independent of the stress / strain value.

Oscillatory time sweeps were used to investigate the evolution of rheological properties due to structural changes. In this test procedure, the amplitude and frequency were kept constant. The  $G'$  and loss modulus ( $G''$ ) were measured every 10 s. The loss factor ( $\tan\delta$ ) is the ratio between the  $G''$  and  $G'$ . The intersection of  $G''$  and  $G'$  (i.e. when the loss factor is one) marks the time of gelation.

The following figure (Figure 6) shows storage module profile versus shear stress at the constant frequency of 1 Hz for the silica sol prior to gelation. As can be seen, the storage module seems to be quite independent of shear stress for a wide range of 1 to 100 Pa. Therefore, for measuring the gelation time through the oscillatory time sweep test each point in this interval can be selected.



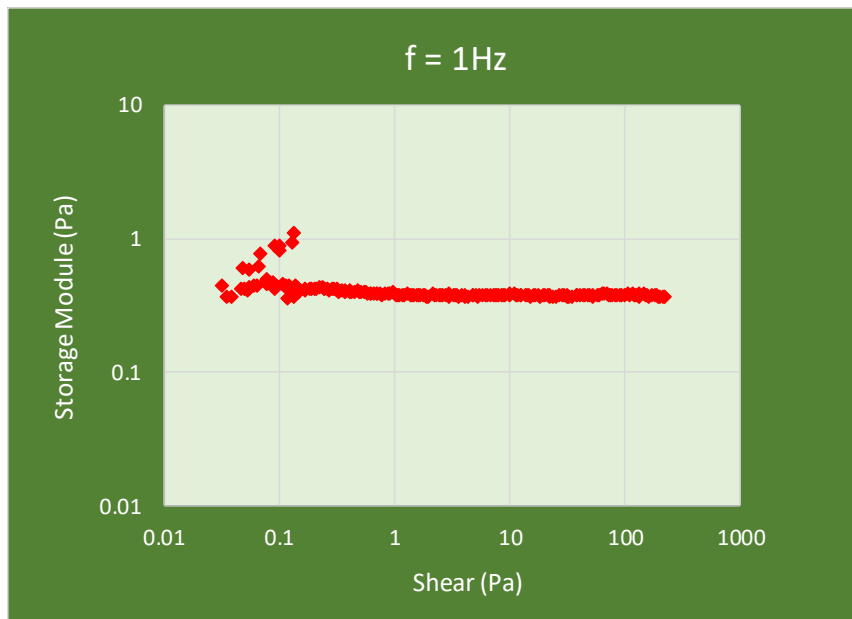


Figure 6. Storage modulus ( $G'$ ) profile versus shear rate at the frequency of 1 Hz.

For the oscillatory time sweep tests, frequency and shear stress were set equal to 1 Hz and 1 Pa which are in the linear viscoelastic region of the sol.

As subsurface brines have a complex chemical composition, a series of rheological tests were conducted isolating and examining the effect of varying concentrations of NaCl, SiO<sub>2</sub>, pH and CaCl<sub>2</sub> on the gelation times, as well as studies that considered combinations of each. The results of these tests are reported later in this document.

*\*Silica-Gel Brine Exposure (Milestone M7)*

Drying of the sol-gels results in a loss of the liquid held by capillary action. This causes shrinking and embrittlement of the gel and can lead to fractures. In the subsurface drying is unlikely, however, it raises a question as to whether the high osmotic potential of saline brines might have a similar effect on the sol gels – resulting in a loss of integrity over time. Accordingly, a series of tests were conducted where silica gel samples were prepared in short PVC cylinders and placed in beakers containing brines covering a range of salinities and pHs. The samples were left immersed in the brines for 45 days and monitored periodically for signs of structural changes. At the end of the 45 days all samples were examined, any changes recorded and the brine removed. The samples were then dried for the next two weeks to compare the effects of exposure to the brines with exposure to the atmosphere. Time-lapse images of three of the samples were also recorded at regular intervals over the entire 45-day period (Figure 7).

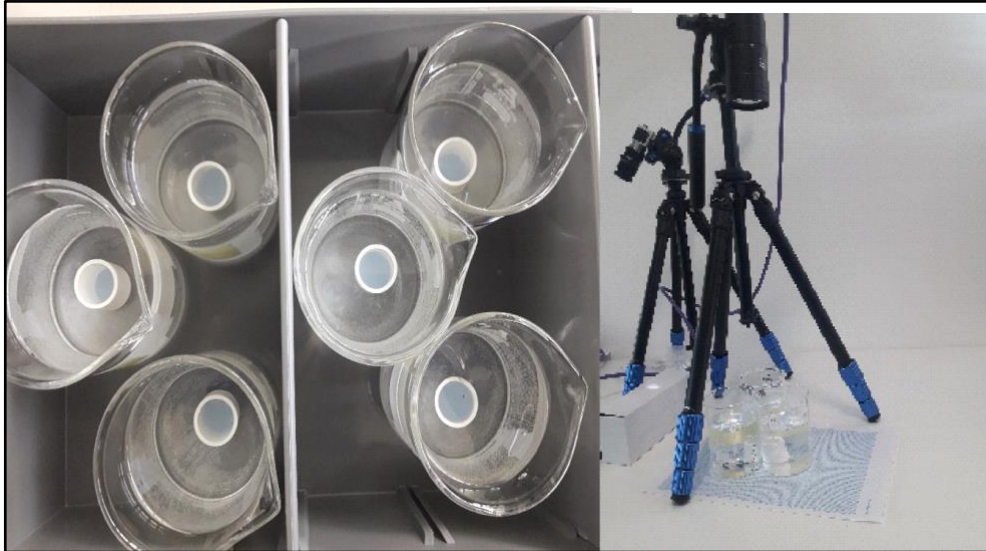


Figure 7. Samples prepared to study the durability of silica gel in different environments, left: samples placed in a tray, covered with a plastic and kept for 45 days at room temperature, right: three of the samples placed under a camera for more closer observation of the changes

## RESULTS

### a) Effect of live brine/ $\text{ScCO}_2$ exposure on fractured cement

To assess the effect of live brine on fracture and body of the cement, the ct scans of the cement samples from before and after live brine exposure were analysed. Figure 8 shows the segmented fracture of the cement sample F before and after exposure to the live brine. The difference between the segmented images and tomograph from middle of the samples is additionally shown in Figure 9 for the analysis.

It is known that cement is altered to aragonite, calcite, and amorphous silica by the  $\text{CO}_2$ -rich brines. It can be seen from Figure 8 that some part of the fracture was enlarged when exposed to live brine due to calcium being dissolved. The saturated calcium brine was further precipitated in the fracture leaving residues that has closed some part of the fracture (Figure 8). The dissolution was ultimately limited by diffusion at the cement-solution interface in the fracture. The deeper the live brine diffuses into the fracture, the larger precipitation was occurred. The majority of the residues are supposed to be aragonite, calcite, and residual anhydrous  $\text{Ca}_2\text{SiO}_3$ . It is also very interesting to observe that the diffusion of live brine into the uniform cement body is very heterogeneous raising the question as to what other mechanisms control the diffusion of live brine.

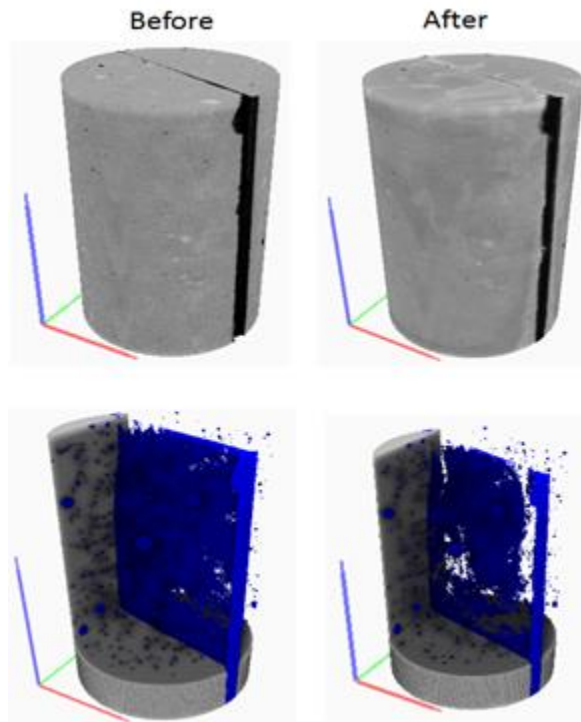


Figure 8. The segmented fracture from one of the samples (sample F) showing the fracture before exposure to live brine (left) and after exposure (right)

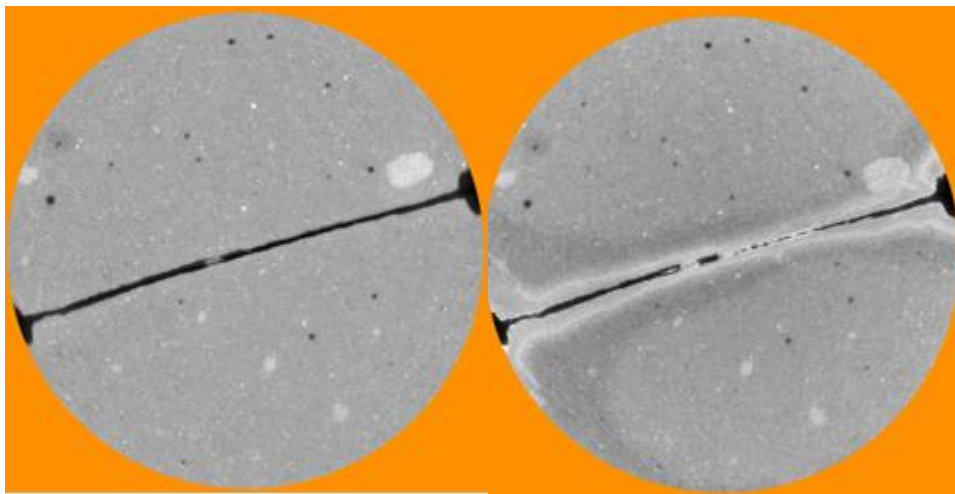


Figure 9. Tomograph showing the precipitation and/or dissolution of minerals by live brine exposure in the fracture for sample F.

In addition to carbonated brines, the cement samples were also reacted with super-critical carbon dioxide. These samples showed little change despite the exposure. This is in line with other experiments (Kutchko et al 2008) which show significantly greater signs of chemical alteration in cements exposed to carbonated brines as opposed to dry super-critical carbon dioxide. It is also evident that the permeability of the fractured cement was not affected by exposing the cement sample to super-critical carbon dioxide.

### b) Ability of Silica gel to seal cement fractures

All pre-gel permeability values of six samples were presented in Table 2 and can give a reference for comparison with samples after blockage by the gel.

Table 3. Permeability of fractured cement samples before placing the gel in the fractures

Sample	Permeability (Darcy)
A	30.1
B	20.0
C	30.4
D	30.7
E	17.7
F	21.8

The result of leak-off tests is presented in Figure 10. It is noted that the results of five samples are only presented as the gel in one sample was damaged during handling preventing it from high pressure resistance. As can be seen from this figure, the silica gel withstands the upstream CO<sub>2</sub> pressure as high as 500 psi without any leak at the confinement 100 psi higher than injection pressure for each step. No gas flow was observed at the downstream side of the cell for any test step. This proves that the silica gel is a very good sealing material to block the fractures formed in cement structure at low cost and environmentally friendly way. We also noticed that the higher the confinement, the higher inlet pressure can be applied to the samples. It is intuitive in the sense that it compresses the gel and it can take further load, however it is interesting to see that such external confinement/load does not damage the gel structure meaning that the gel has excellent elastic properties.

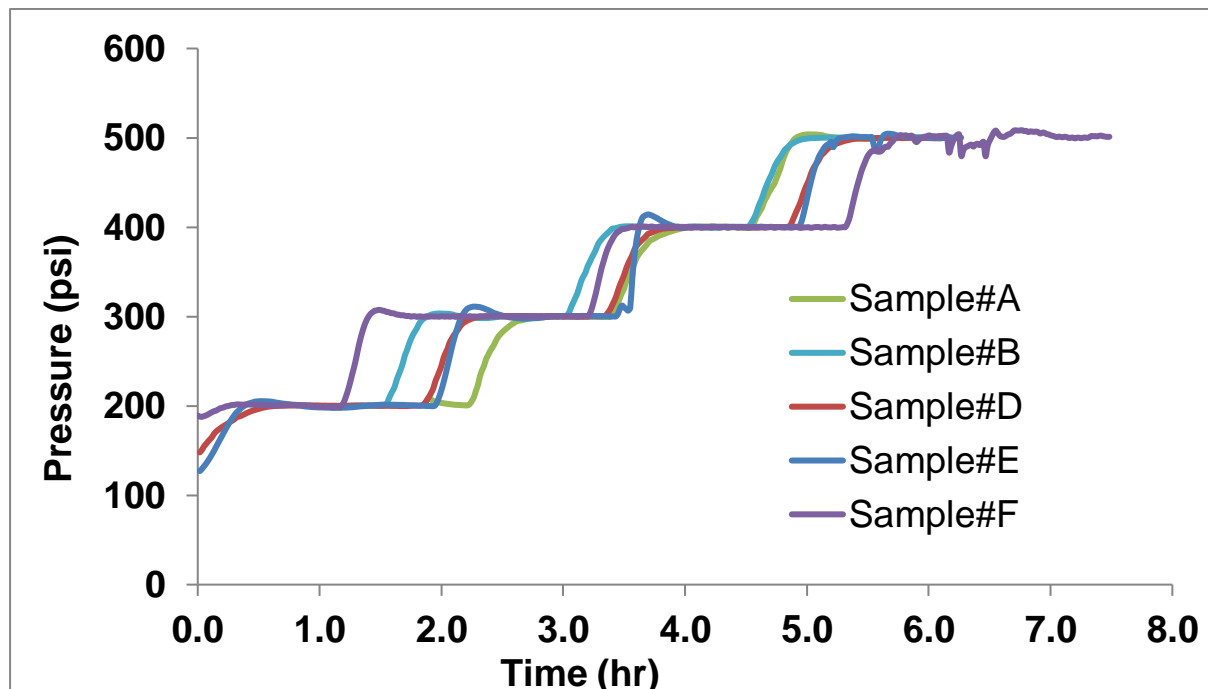


Figure. 10 Pressure (y axis, in psi) vs Test time (x axis, in hh/mm/ss) profiles during leak-off tests of all test bodies.

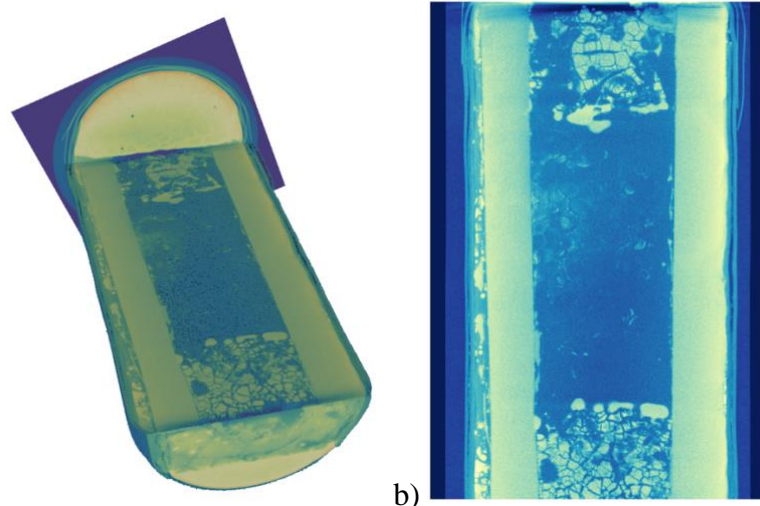


Figure. 11 XRCT reconstruction of gel in a saw-cut sample exposed to HCl: a) cutaway view of showing the location of the image on the right; b) distribution of the gel within the sample. In this sample, the gel has only penetrated a short distance into either end of the core before setting.

However, one unexpected result of this study was the effect of the cement chemistry on the gelation time. While it was originally speculated that the alkaline cement might prevent gelation, this was not observed in any of the samples examined. Indeed in some cases, it appears that gelation times were reduced as a result of the effect of the cement chemistry. This is illustrated in Figure 11, which shows the distribution of gel within a saw-cut cement sample. In this sample, the silica sol has gelled quite rapidly sealing the ends of the sample, but not covering the center. The role of chemistry on sol gelation is investigated in greater depth in the following section.

### c) Effect of brine composition on sol gelation

Rheological studies were carried out to determine the effect of different fluid compositions on the gelation time of the silica sol. These studies considered the relationship between gelation time and silica concentration, NaCl concentration, HCl concentration, and Ca concentration.

#### *Effect of silica concentration*

The effect of  $\text{SiO}_2$  concentration on gelation time is shown in Figure 12. From the five samples prepared, the sample with the silica concentration of 2.02 M did not gel. At silica concentration of 2.69 M the gelation time recorded to be 7500 seconds. By increasing the silica concentration to 3.03 the gelation time decreased to 2120 seconds. The gelation time continued to drop but by smaller increments as the silica concentration was increased to 3.37 M and then to 3.7 M.

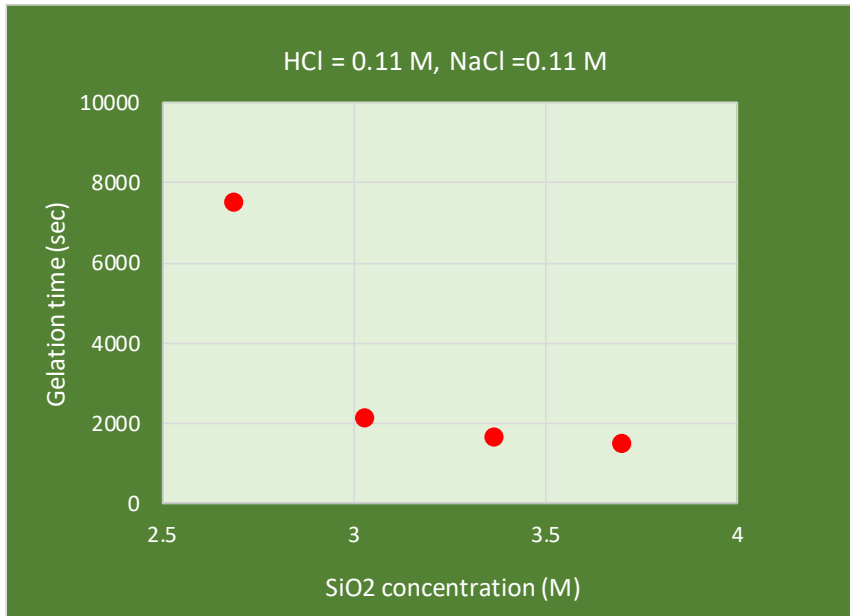


Figure 12. Gelation time profile versus SiO<sub>2</sub> concentration at constant NaCl and HCl concentration.

#### *Effect of NaCl concentration*

To study the effect of NaCl concentration on the gelation time, five silica solutions were prepared. In all of them, the silica and HCl concentration were kept constant at 3.37 M and 0.11 M, respectively. Figure 13 demonstrates gelation time profile of the samples versus NaCl concentration varying from 0 to 0.22 M. The gelation time dropped rapidly by increasing NaCl concentration to 0.11, however, the rate of decline becomes lessened as the NaCl concentration increases from 0.11 M to 0.22 M.

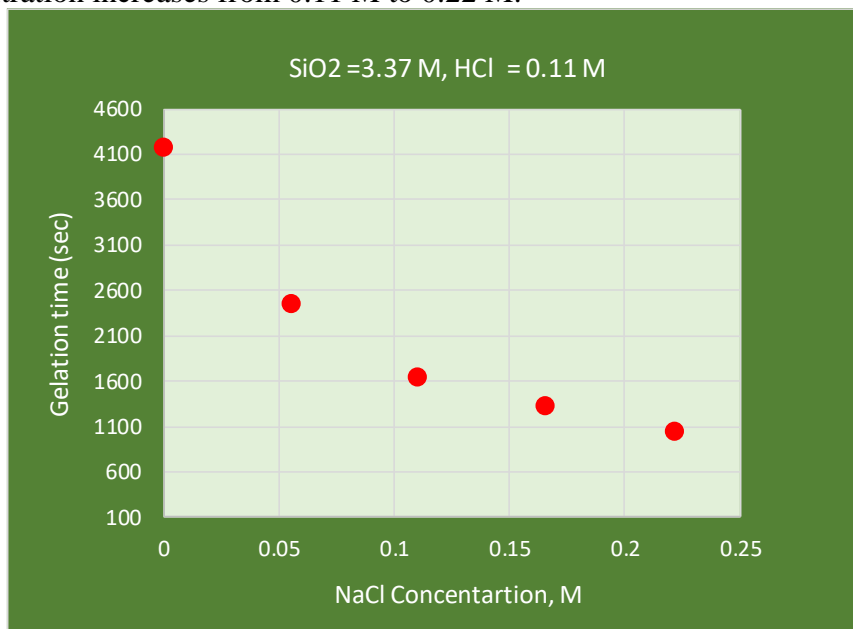


Figure 13. Gelation time profile versus NaCl concentration at constant SiO<sub>2</sub> and HCl concentration.

#### *Effect of HCl concentration*

Figure 14 shows the profile of gelation time variation versus HCl concentration. Eight samples were prepared with the same SiO<sub>2</sub> and NaCl concentration. The samples with HCl

concentration of 0.22 M, 0.16 M, and zero HCl never gelled. However, in all the remaining 5 samples the gelation time plummeted by increasing HCl concentration from 0.05 M to 0.15 M, hitting a low point of 1629 seconds. However, it grew rapidly when the concentration of HCl increased from 0.11 M to 0.15 M. It seems that in respect to the gelation time, there is an optimum value for HCl concentration and consequently pH of the solution.

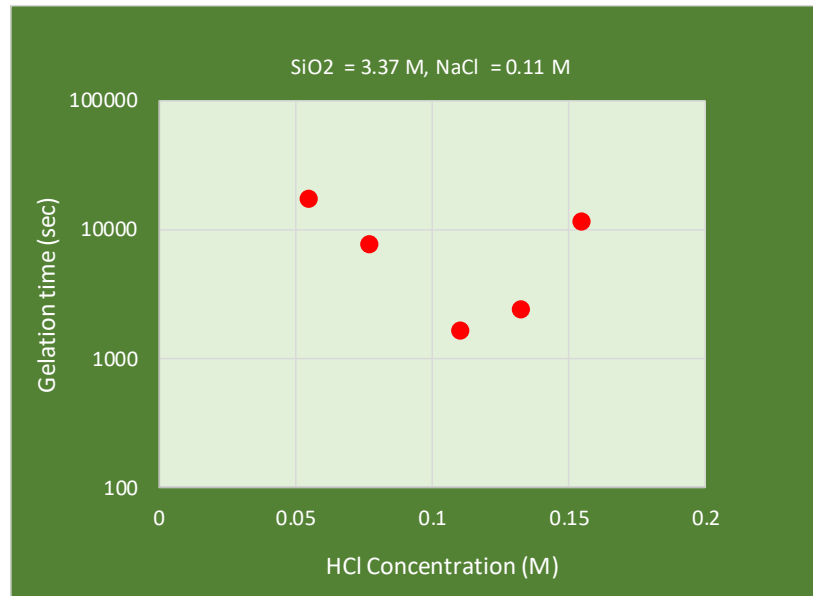


Figure 14. Gelation time profile versus HCl concentration at constant SiO<sub>2</sub> and NaCl concentration.

#### *CaCl<sub>2</sub> Concentration*

The effect of CaCl<sub>2</sub> on the gelation time was considered through three different measurements: I) the samples just contain SiO<sub>2</sub> and CaCl<sub>2</sub> II) the samples contain SiO<sub>2</sub>, HCl, and CaCl<sub>2</sub> and III) the samples contain SiO<sub>2</sub>, NaCl, HCl, and CaCl<sub>2</sub>.

##### I) SiO<sub>2</sub> + CaCl<sub>2</sub>

We prepared four samples of silica solution in all of which the silica concentration was constant at 3.37 M, but the CaCl<sub>2</sub> concentration varied from 0.002 M to 0.11 M. The most interesting results of these samples was that with CaCl<sub>2</sub> concentration of 0.002 M there was no gelation after 1 month, but with higher concentrations of 0.011, 0.055, and 0.11 M there was almost immediate gelation. Ca<sup>2+</sup> concentrations of 0.04-0.06 M were typical in carbonated brines exposed to Portland cement in a previous study (Walsh et al 2014a).

Table 4. Gelation time versus CaCl<sub>2</sub> concentration at fixed concentration of SiO<sub>2</sub> and absence of NaCl and HCl.

SiO <sub>2</sub> concentration, M	CaCl <sub>2</sub> concentration	Gelation time (seconds)
3.37	0.002	Never gelled
3.37	0.011	Immediate gelation
3.37	0.055	Immediate gelation
3.37	0.11	Immediate gelation

In the cases of immediate gelation, the gelation started at surface where the CaCl<sub>2</sub> was introduced to the sol. To show this more visually, in another experiment, we added a small amount of natural blue dye to the CaCl<sub>2</sub> before introducing it to the silica sol. As can be observed in Figure 15, the gel formed at the surface, leaving the sol at the bottom of the

container ungelled. The remaining sol gelled after a couple of hours but there existed some cavities in its structure.

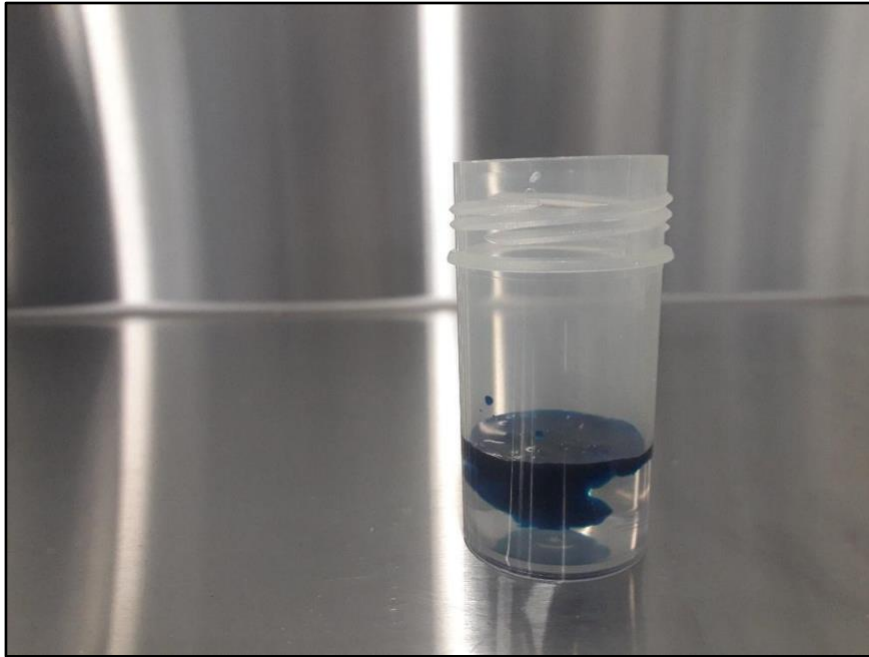


Figure 15. Evidence of immediate gelation when adding 0.11 M  $\text{CaCl}_2$  solution (blue coloured) to  $\text{SiO}_2$  solution.

## II) $\text{SiO}_2 + \text{HCl} + \text{CaCl}_2$

Five samples with the same  $\text{SiO}_2$  and  $\text{HCl}$  concentration were prepared to study the effect of  $\text{CaCl}_2$  on the gelation time in the presence of  $\text{HCl}$ . Overall, the presence of  $\text{HCl}$  delayed the gelation time compared to the case where only  $\text{CaCl}_2$  was added to the silica sol. At  $\text{CaCl}_2$  concentration of 0.002 M, the gelation time was 8658 seconds. The gelation time dropped rapidly when we increased the  $\text{CaCl}_2$  concentration to 0.005 M and then to 0.01 M. The gelation time keeps decreasing but more slowly as the  $\text{CaCl}_2$  concentration is increased to 0.05 M and 0.11 M.

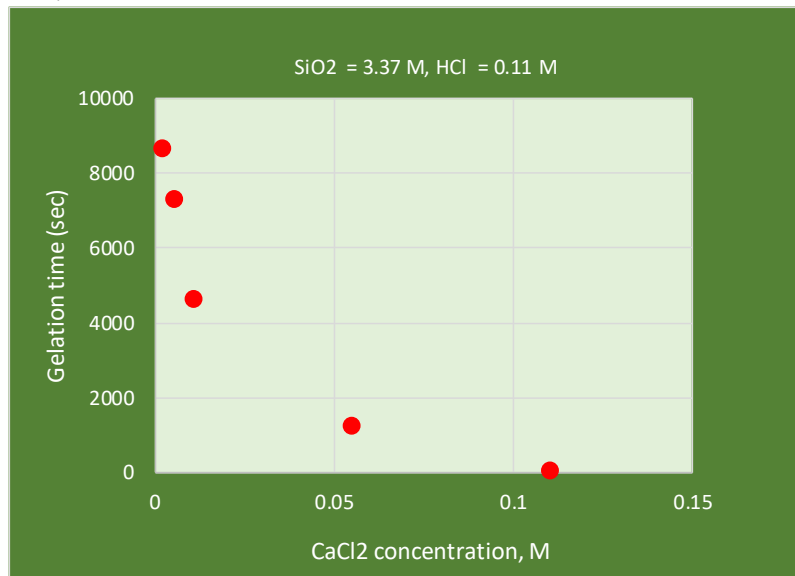


Figure 16. Gelation time profile versus  $\text{CaCl}_2$  concentration at constant  $\text{SiO}_2$  and  $\text{HCl}$  concentration.



### III) $\text{SiO}_2 + \text{NaCl} + \text{HCl} + \text{CaCl}_2$

To investigate the effect of  $\text{CaCl}_2$  on the gelation time when both  $\text{NaCl}$  and  $\text{HCl}$  are available in the system, five samples with constant  $\text{SiO}_2$ ,  $\text{HCl}$ , and  $\text{NaCl}$  concentration were prepared. The variation of gelation time versus  $\text{CaCl}_2$  concentration is similar to the previous examples. However, the most significant difference is that the presence of  $\text{NaCl}$  decreases the gelation time significantly.

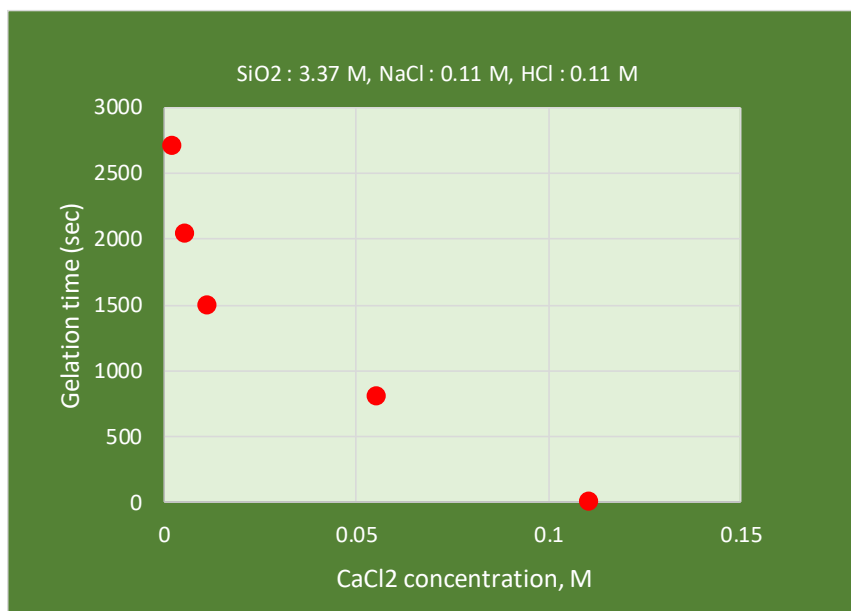


Figure 17. Gelation time profile versus  $\text{CaCl}_2$  concentration at constant  $\text{SiO}_2$ ,  $\text{NaCl}$ , and  $\text{HCl}$  concentration.

These results are significant as an initial concern of the study was whether the silica sol would gel in the presence of cement. Acid is typically used to trigger gelation, and it was postulated that this could be countered by contact with the cement. However, these studies suggest that gelation times will actually decrease due to the  $\text{Ca}^{2+}$  ions in solution. The higher ionic strength of the aqueous  $\text{Ca}^{2+}$  destabilizes the silica sol, causing it to gel faster than would otherwise be expected. In some cases, this results in extremely rapid gelation, which may at first appear to exclude the use of silica sols gels for some applications. However, if required, longer gelation times can be achieved by adjusting the pH or by including additives such as aluminate which have been shown to increase gelation time.

#### d) Effect of Brine Exposure on silica gel.

To investigate the chemical stability of the silica gel over time, 10 samples of silica sol with  $\text{SiO}_2$ ,  $\text{NaCl}$ , and  $\text{HCl}$  concentration of 3.37 M, 0.11 M, and 0.11 M, respectively were prepared. After 2 hours when the gelation process completed, we placed the samples in 10 different environments for 45 days. A summary of the samples and our observations after 45 days are presented in Table 5. Samples 2B, 3B and the Ref samples were recorded by a time-lapse camera during the 45 days to more closely observe any changes. After this time, the samples were removed from the solution and exposed to the air for 14 days. All samples except for the 3 that were recorded were kept covered to prevent evaporation. The water level in the 3 recorded samples was maintained by adding de-ionized water at regular intervals.

Little change was observed in the gels over 45 days. Several samples experienced some minor swelling, and in a few cases some material appeared either as sediment or as a wispy cloud attached to the top of the cylinders. However, in all cases the gel plugs remained intact without any obvious degradation. This is a stark contrast to the behaviour of the gels on drying, all shrank considerably to approximately half their original diameter. Three of the samples – those exposed to higher acidity brines prior to drying – produced white brittle fibres, which emerged from both the top and bottom of the containers.

These results indicate that although the silica sol gels may shrink considerably when exposed to air, the gels are largely unaffected by contact with even highly saline brines. This also mirrors our experience in the laboratory, where sol gels will start to shrink within a few days of exposure to the air, but last many months without change in sealed sample jars.

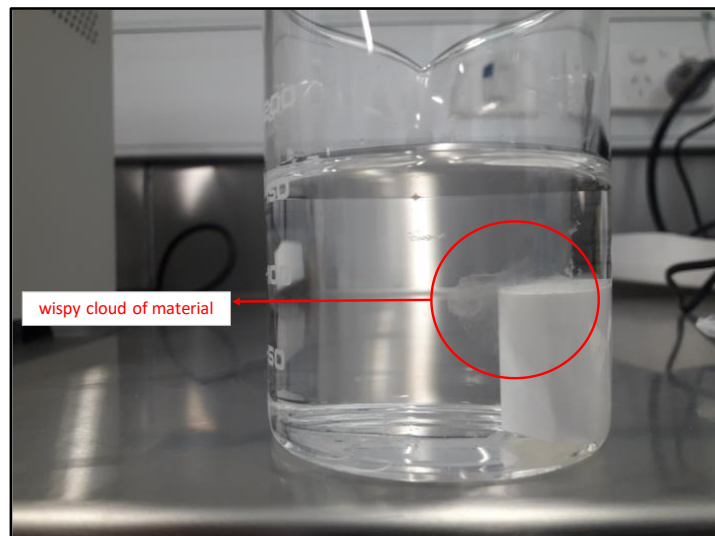


Figure 18. Example of “cloud” of material formed on top of Sample 2 following prolonged exposure to NaCl brine.

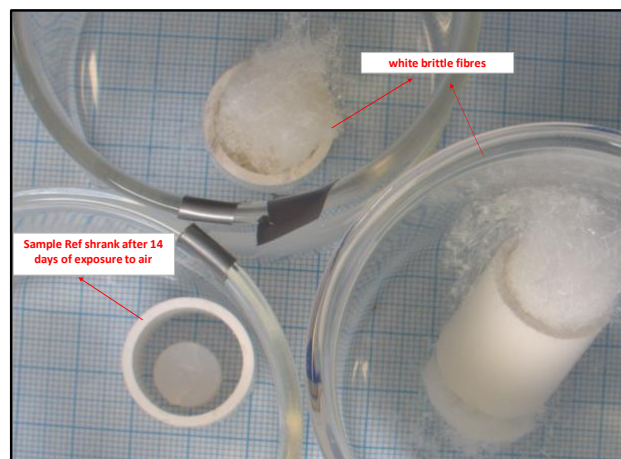


Figure 19. The reference sample (Sample Ref) shrank after 14 days of exposure to air (bottom left), white brittle fibres formed at the top and bottom of Samples 2B and 3B.

Table 5. A summary of the samples name, salinity and pH of the environment, and observations during the chemical stability tests of silica gel.

Sample No.	Salinity (NaCl M)	pH	Observations (after 45 days)	Observations on drying (14 days exposure to air)
Ref	0	6.45	<ul style="list-style-type: none"> <li>Some precipitation observed on glass as a result of evaporation of water</li> <li>Cloudy residue on surface of water</li> <li>Some white sediment at bottom</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably, transparent glass-like appearance, some cracking observed, hard with slightly sticky exterior</li> </ul>
1	0.5	6.45	<ul style="list-style-type: none"> <li>Some sediment at bottom of beaker</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
2	1	6.45	<ul style="list-style-type: none"> <li>"Wispy" cloud of material at top of sample</li> <li>Gel swelled</li> <li>Some mold as black spots in the gel</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
3	2	6.45	<ul style="list-style-type: none"> <li>Gel swelled</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
1A	0.5	2.13	<ul style="list-style-type: none"> <li>Very small amount of sediment at bottom</li> <li>Gel swelled</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
2A	1	2	<ul style="list-style-type: none"> <li>Small amount of sediment</li> <li>Gel swelled</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
3A	2	1.8	<ul style="list-style-type: none"> <li>Some swelling observed</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably</li> </ul>
1B	0.5	1.8	<ul style="list-style-type: none"> <li>some sediment</li> <li>some floating material</li> <li>Gel swelled (observed above level of PVC cylinder and emerged below)</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably over, white brittle fibres formed from both top and bottom of sample several days after drying commenced</li> </ul>
2B	1	1.7	<ul style="list-style-type: none"> <li>Some white sediment at bottom</li> <li>Some minor precipitation observed on glass as a result of evaporation of water</li> <li>Gel swelled (observed above level of PVC cylinder)</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably over, white brittle fibres formed from both top and bottom of sample several days after drying commenced</li> </ul>
3B	2	1.5	<ul style="list-style-type: none"> <li>Some white sediment at bottom</li> <li>Some minor precipitation observed on glass as a result of evaporation of water</li> <li>Gel swelled (observed above level of PVC cylinder)</li> </ul>	<ul style="list-style-type: none"> <li>Sample shrank considerably over 10 days; white brittle fibres formed several days after drying commenced</li> </ul>

## DISCUSSION

The research conducted under this project represents a preliminary investigation into the feasibility of deploying silica sol gels to inhibiting flow in fractured wellbore cement in sequestration operations. The cement can be the initial cement used behind the casing in the wellbore or the cement used to plug the wellbore for abandonment purposes.

Silica sols are non-toxic and relatively inexpensive materials that may be caused to gel by changing their chemical composition. As such they have the potential to be used to prevent or inhibit carbon-dioxide leaks from CO<sub>2</sub> storage operations, whether in the form of supercritical CO<sub>2</sub> or carbonated brine.

We have modelled fractures in a wellbore environment by exposing cement samples to supercritical CO<sub>2</sub> and carbonated brine. In addition, we have also considered unreacted samples, as well as samples exposed to hydrochloric acid to simulate more extensive degradation of the cement. The permeability of these samples was measured before and after being plugged with silica sol gels. The results of the permeability studies demonstrate that sol gels are able to successfully plug open cement fractures and that the resulting seals are robust despite significant changes in the fracture stress. This is important as carbon-sequestration environments are likely to experience changes to the in-situ stress conditions during injection and storage. Moreover, the sol-gel plugs were able to provide effective barriers preventing the flow of both brine and carbon-dioxide. No flow was recorded in the samples (zero permeability) with the inlet CO<sub>2</sub> pressures up to 500 psi and effective stress of 100 psi i.e. confining stress was 100 psi lower than inlet pressure. As the confining stress increases, the ability of the plugged sample to withstand higher pressure is also enhanced and higher inlet pressure of CO<sub>2</sub> can be applied without any leak.

Importantly, however, the XRCT scans in some of the plugged samples show that the gels formed sooner than anticipated and failed to cover the entire fracture. This was an unexpected result as it was originally thought that the opposite might be true, namely that the lower acidity of the cement-exposed brine might inhibit or prevent gel formation. However, the subsequent studies into the gelation rate demonstrate that this is counteracted by the presence of calcium ions in the aqueous solution, which accelerates the formation of the sol-gel. Indeed, in certain cases we were able to induce gelation in the sols without modifying their initial chemistry using the calcium ions from the cement alone. It should be noted that the faster gelation times should not be taken as indicative for all sol-gels. It is anticipated that the gel times can be extended either by modifying the base recipe used for these experiments or through the addition of aluminate which has been shown elsewhere to extend gel times. Nevertheless, these results do highlight the importance of accounting for the aqueous geochemistry when deploying the gels.

It is not enough that the gels reduce the fracture permeability – they must also be able to maintain their integrity under subsurface conditions. Our study into the effects of brine exposure on silica gels indicates that the gels are relatively insensitive to prolonged exposure to brines of even quite high salinity (2M) and acidities (<2 pH). For reference, carbonated brines regarded as typical for the Weyburn-Midale CO<sub>2</sub> sequestration project have a salinity of 1M with a pH of 3.95-4.6 (Smith et al 2013, Walsh et al 2014a). Despite the more extreme conditions considered in the present study, no shrinkage was observed in any of the samples, which suggests that the gels are unlikely to lose their ability to plug the fracture over long

periods of time. This is in stark contrast with the samples when exposed to the open atmosphere.

From the operational perspective, the injectivity of sol is relatively straight forward as the gel viscosity is very low. The placement of the sol can be also controlled by managing the gelation time i.e. as soon as the sol is in place, it should start gelling. The important part of the field -scale deployment lies in the design of the gel recipe in respect to the ionic solution exposure (already exist in the wellbore from the formation or other parts of the operation).

Additional work therefore remains to be done to properly understand the deposition of the gels in real world environments. Specifically, we recommend that future research examines gelation within individual fractures and fracture networks to better understand how these processes may be controlled in actual fracture geometries. Moreover, given the sensitivity of the gelation time to the aqueous chemistry, we also recommend that future studies be conducted that examine the degree of mixing between the sol gel and the in-situ brines in these environments to better predict the evolution of the injected sol-gels.

## **CONCLUSION**

A comprehensive study was performed to assess the ability of silica gel to block fractures in cement samples. By conducting an extensive set of experiments, we were able to investigate in particular a) the effect of live brine on dissolution/precipitation of the fracture and cement matrix as a result of exposure to live brine, b) the effect of brine chemistry on the properties of the silica gel and c) the effectiveness of the silica gel to seal the fracture in cement samples.

Our results show the robustness of the silica gel to seal the fractures in cement samples. This is a significant finding as such gel can be used for any engineered barrier dealing with underground porous formations. For example, sol gels can be used to prevent flow in fractured cement, or other porous-fractured systems, it can be used for well abandonment in coal seam gas reservoirs from around the borehole all the way up to the surface (or where fracture gradient of the formation is met), it can be used to block water passage in mines and elsewhere.

## **RECOMMENDATIONS**

The present study has focused on the ability for sol gels to plug fractures in cements. Nevertheless, how best to deploy these gels remains an open question. In particular our study has shown that the presence of calcium in the in situ brine can significantly accelerate the gelation process. In this case, it may be best to adapt the sol composition to the particular type of fracture or brine chemistry. Likewise, while we have shown that sol-gels can successfully block small fractures under laboratory conditions, it is a different matter to deploy them successfully in the field. We do not recommend a full field test at this stage, but instead suggest that the next study should consider the ability for these gels to operate in larger-scale block tests, more closely approximating real wellbore geometries. Additional work should also be conducted to develop numerical models to simulate the deposition of these gels to better plan for their deployment.

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## **APPENDIX**

### **Conference Presentations**

S. Hatami, S. Walsh, T. Hughes, H. Roshan, The performance of Silica Gels as a barrier to CO<sub>2</sub> leakage in wellbore cements and the near wellbore environment, CO<sub>2</sub>CRC CCUS Symposium 2019  
S Hatami, S Walsh, T Hughes, H Roshan, 2019, Deployment of Silica Gels to prevent CO<sub>2</sub> leakage, AGU Fall Meeting

### **Staff Involved in the Project**

Dr. Hamid Roshan

Dr. Stuart Walsh

Dr. Thomas Hughes

Mr. Sobhan Hatami (PhD candidate, Monash)

Mr. Hongyi Sun (Masters Student, UNSW)

Mr. Hongyi Sun obtained a Masters in Petroleum Engineering qualification in part due to work conducted under this project.

## **SIGN OFF**

I, the undersigned, being a person duly authorised by the Grantee, certify that:

- (a) the above information is true and complete;
- (b) the expenditure of the Funding received to date has been used solely on the Project; and
- (c) there is no matter or circumstances of which I am aware that would constitute a breach by the Grantee or, if applicable the End Recipient and Subcontractors', of any term of the Funding Deed.

Signature:



Position: Senior Lecturer

Name: Hamid Roshan

Date: 18/02/2020