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EVALUATION OF SWELLING AND RE-SWELLING OF PREFORMED PARTICLE GELS (PPG) WHEN EXPOSED TO CO_2

by

SUJAY SURESH

A THESIS

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Approved by

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ABSTRACT

Long term water/gas flooding induces high permeability channels in reservoirs. Reservoir heterogeneity becomes the most prominent challenge faced in mature oil fields. Gel treatment has been a proven solution to counter the problem of reservoir heterogeneity, to provide in-depth treatment and improve the sweep efficiency for reservoirs. Preformed particle gels (PPGs) were developed as an alternative to in-situ gels as they preferentially penetrate and shutoff high permeability zones, leaving the low permeability zones undamaged. These gels have been predominantly used in water flooding projects, but have not been employed in carbon dioxide (CO_2) flooding projects. CO_2 Resistant Gel (CRG) is a novel PPG synthesized in Missouri S&T for better performance when exposed to CO_2. The objective is to present results from a pilot study to analyze the stability of commercially available PPGs and CRGs when exposed to CO_2 at varying pressures. The PPGs and CRGs were swollen in distilled water and solutions with salt concentrations of 0.25%, 1.0% and 10.0% NaCl. The swollen gels were placed in vessels designed in our labs, pressurized to 500 psi, 1100 psi, 1900 psi and 2500 psi and exposed to a temperature of 65 deg C for 1, 3 and 5 days. Dehydration, swelling ratio and gel strength of PPG and CRG after exposure to CO_2 have been reported. The gels were also analyzed using IR spectroscopy to investigate any chemical changes on exposure to CO_2 and studied under a Scanning Electron Microscope (SEM) to check for any vivid changes in gel network post exposure to CO_2. Results from both gels have been compared and it is seen that CRG performs better than commercially available PPG when exposed to CO_2. This static study paves way to understanding how the gel would perform under CO_2 before testing it under dynamic conditions.

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1. INTRODUCTION

1.1. STATEMENT AND SIGNIFICANCE

Secondary and tertiary recovery mechanisms are employed in the industry to extract oil and gas from a reservoir once the natural drive or primary recovery mechanisms withdraw. Primary recovery mechanisms account for only about 10 percent of the original oil in place recovered and secondary mechanisms account for 20 to 40 percent of the same. Initially, water flooding, a secondary recovery process, was initiated for pressure support after years of pressure depletion due to production (Hermansen et al. 1997, 2000). Fig 1.1 below shows the oil rate response in a field to water flooding.

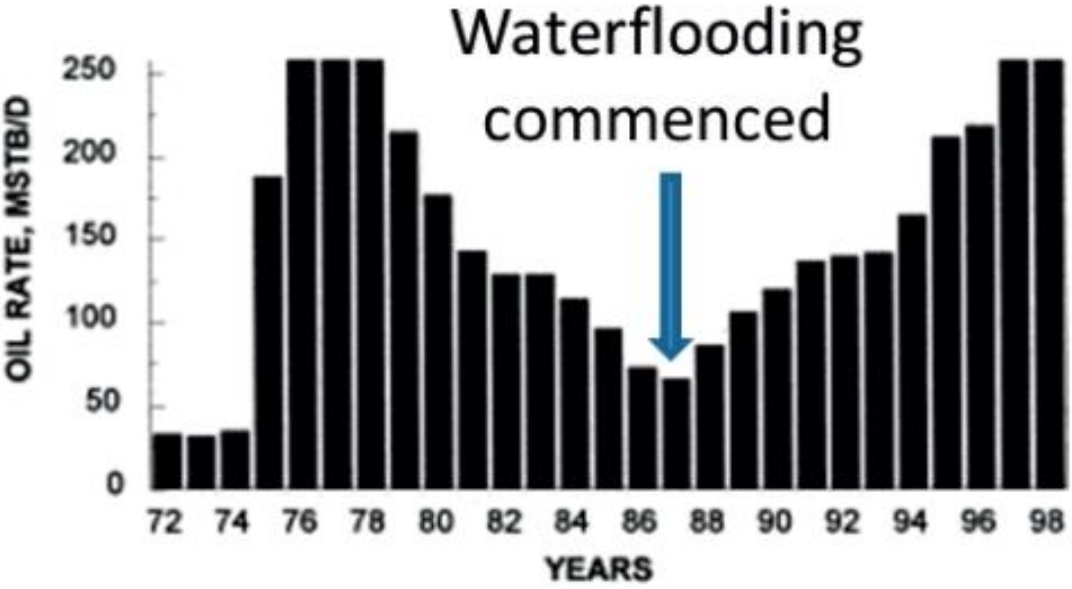

Fig 1.1.Oil production rate response to water flooding in the Ekofisk field
(Hermansen et al, 2000, Brattekås B., 2014)

Two-thirds of the oil in place left behind in reservoirs after primary and secondary recovery processes have been reported to be stranded oil (Bai, B., 2008; Kuuskraa, V.A. et al., 2006). A representation of this statement is seen in Fig 1.2. Enhanced oil recovery comes into play at this point to maximize the oil recovery.

EOR can be broadly classified into microbial process, chemical process, thermal process or gas injection process (Roger et al., 2003). Even at low oil prices, gas injection has proved to be a cost-effective method (Bai, B., 2008). The recovery efficiency of primary and secondary recovery processes is only 33%. EOR has the potential to produce up to 688 billion barrels of oil by 2030 according to the USA Department of Energy. Fig 1.2 shows the Primary/secondary recovery techniques' ability to produce oil.

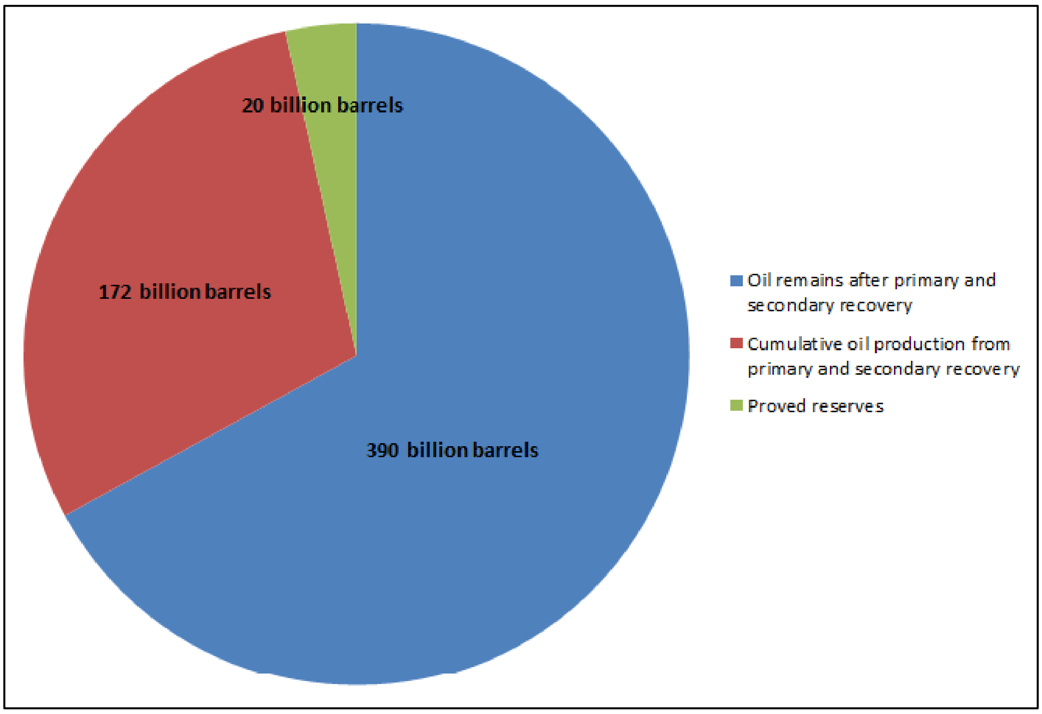

Fig 1.2.Primary/secondary recovery techniques' ability to produce oil (Godec, M. et al., 2011)

One of the main reasons why primary and secondary recovery mechanisms cannot retrieve most of the hydrocarbons from a reservoir is reservoir heterogeneity. One of the primary reservoir conformance problems is water channeling, which is also caused by reservoir heterogeneity, and it leads to fractures and streaks with high permeability. This in turn leads to high permeability contrast ratios in the reservoir which causes early water breakthrough during water flooding. Unwanted water production adversely affects well economics because of water-disposal costs, environmental issues, and reduced hydrocarbon production. In heterogeneous reservoirs, water floods may yield poor vertical sweep efficiencies. Due to this, water injected bypasses oil rich zones and large amounts of oil remain trapped in un-swept zones.

Conformance can be defined as the management and alteration of water and gas flows using the appropriate reservoir understanding to optimize hydrocarbon production (Soliman et al., 1999). Gel treatment, one of the widely used conformance control technologies, has been a proved solution to counter the problem of reservoir heterogeneity (Seright and Liang, 1995). It provides in-depth treatment and improves the sweep efficiency for reservoirs (Bai, B., 2008). This is a very cost effective chemical method to restrict the injection fluid from sweeping the already swept zones and redirect them towards the un-swept areas of the reservoir.

Polymer gels can be applied to production wells with excessive water or gas flow and to injection wells with poor injection profiles. There are two types of gels widely used- in-situ gels and preformed particle gels (PPG). Preformed particle gels (PPGs) were developed as an alternative to in-situ gels as they preferentially penetrate and shutoff high permeability zones, leaving the low permeability zones undamaged (Suresh S. et al., 2016). Thus, PPGs have been employed widely to improve the heterogeneity of mature reservoirs and improve the oil recovery.

PPG has been successfully employed in several water flooding projects and their properties have been reported for over a decade now.

1.2. OBJECTIVES

1. The main objective of this thesis is to present results from a pilot study to analyze the stability of commercially available PPGs and CRGs when exposed to CO_2 at varying pressures.
2. The three main points of discussion and grounds of comparison are the dehydration, re-swelling ratio and gel strength of both gels when exposed to CO_2.
3. Dehydration of both gels are analyzed as a function of the pressure of CO_2 which they are exposed to, the concentration of salt in the solution that the gels are swollen in before exposure to CO_2 and the time period for which the gels are exposed to CO_2.
4. This thesis also includes an investigation of the gel network and chemical properties of the gels on exposure to CO_2. A scanning electron microscope is used to

study the gel network and Fourier Transform Infrared Spectroscopy (FTIR) is used to investigate chemical changes.

1.3. SCOPE OF THIS WORK

The experiments in this work are to study the behavior of two of these polymer crosslinked gels and understand their behavior when exposed to CO_2. The study paves way to understanding how stable these gels will be when swollen in different salt concentrations and exposed to varied pressures of CO_2. Fig 1.3 below shows the scope of evaluation for the work.

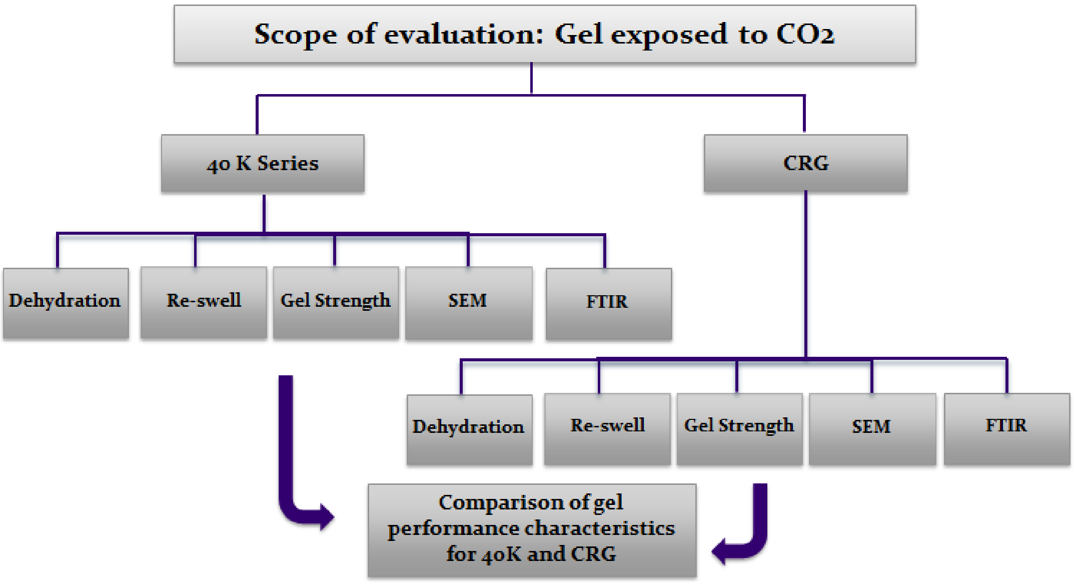

Fig 1.3.Scope of evaluation

2. LITERATURE REVIEW

2.1. EXCESS WATER PRODUCTION PROBLEM

Sydansk, Robert D. et al, 2011 refer to the unnecessary water production in reservoirs as bad water production. Unnecessary water production usually involves the flow of water and oil via separate flow paths to the producing interval of the wellbore (Sydansk, Robert D. et al, 2011). Excess water produced in wells due to coning from an underlying aquifer or from early water breakthrough in the water flooding process are examples for its causes.

Owing to long term water flooding, the problem of excess water production has become the primary challenge for oil field operators (Bai et al., 2008). For each barrel of oil, about three barrels of water is produced.

Excess water produced includes injection water, condensed water, formation water and a small amount of chemicals used for treatment. The water causes a threat to the environment and waste water disposal is an additional task in hand for oil companies.

Excess water production at a well site causes operational problems which include corrosion and scale formation in the tubing and flowline, environmental hazards, an increased load on fluid handling due to water lifting and handling costs, and most importantly, reduction in the economic life of a well. The amount of water produced varies between 10 and 20 barrels for every barrel of crude oil produced in mature fields (Veil, J.A. et al., 2004). Conformance control is the term coined to encounter this problem extensively.

2.2. AN INTRODUCTION TO CONFORMANCE CONTROL & GEL TREATMENT

Conformance control treatments contribute to the recovery of hydrocarbons in a reservoir successfully. According to Sydansk and Romero-Zerôn, 2011 conformance control treatments impact recovery in the following manner:

- Oil recovery increases
- They improve the sweep efficiency
- Oil recovery rates accelerate
- They reduce the environmental liabilities (by producing less H_2S containing water, less saline water etc.)

- They also reduce the oil recovery expenses. This is because when conformance control techniques are in place, the need to recycle drive fluids is reduced and this also lowers the operational and disposal costs

To encounter reservoir heterogeneity and direct injected fluids to the lower permeability zones which are un-swept, placement of gels have been reported to be a successful technique by several researchers (Seright and Martin 1991, Seright and Liang 1994, Seright 1995b, 1997, Tweidt et al. 1997, Seright et al. 1998, Portwood 1999, Sydansk and Southwell 2000, Seright et al. 2001a, 2001b, Bai B. et al 2004a, 2004b, Portwood 2005, Rousseau et al. 2005, Alhajeri et al. 2006, Willhite and Pancake 2008, Spildo et al. 2009, Stavland et al. 2011).

Excess water production and low oil recovery become more severe in mature oil fields which can be catered to reservoir heterogeneity. Gel treatment helps correct reservoir heterogeneity.

Not only does gel treatment help correct heterogeneity, but it also counters excess water production (Suresh S. et al. 2016). In Fig 2.1, the problem of fracture channeling during water flooding has been illustrated. This problem has been successfully treated using polymer gels.

Over the years, gel treatments have been proven to be a cost effective conformance control method. They have been successfully employed to block/reduce water/gas production from higher permeability zones, fractures, channels and fracture-like channels. They have been deployed for both injection and production wells. They effectively act as a plugging agent and aid in correcting the reservoir heterogeneity and reducing excess water production (Seright & Liang, 1994; Liang et al., 1992).

The use of gels as a blocking agent is cost effective and one of the best choices to mitigate channeling through super-K streaks and fractures. Gel placement, when done appropriately, increases the sweep efficiency, thereby increasing the oil recovery.

Gels are injected into a formation and placed in high permeability zones to act as plugging/blocking agents (Imqam A. et al. 2015a, 2015b). This helps maximize oil recovery during water flooding, allowing the injected water to sweep the earlier un-swept low permeability zones (Bai B. et al. 2013, Imqam A. 2014, Suresh S. et al. 2016).

Gels used are mainly comprised of polymer and cross-linker. Apart from these two primary components, they are also made up of certain other additives. They can be broadly classified as in-situ gels and preformed particle gels. Fig 2.1 shows the problem of fracture channeling during water flooding has been illustrated.

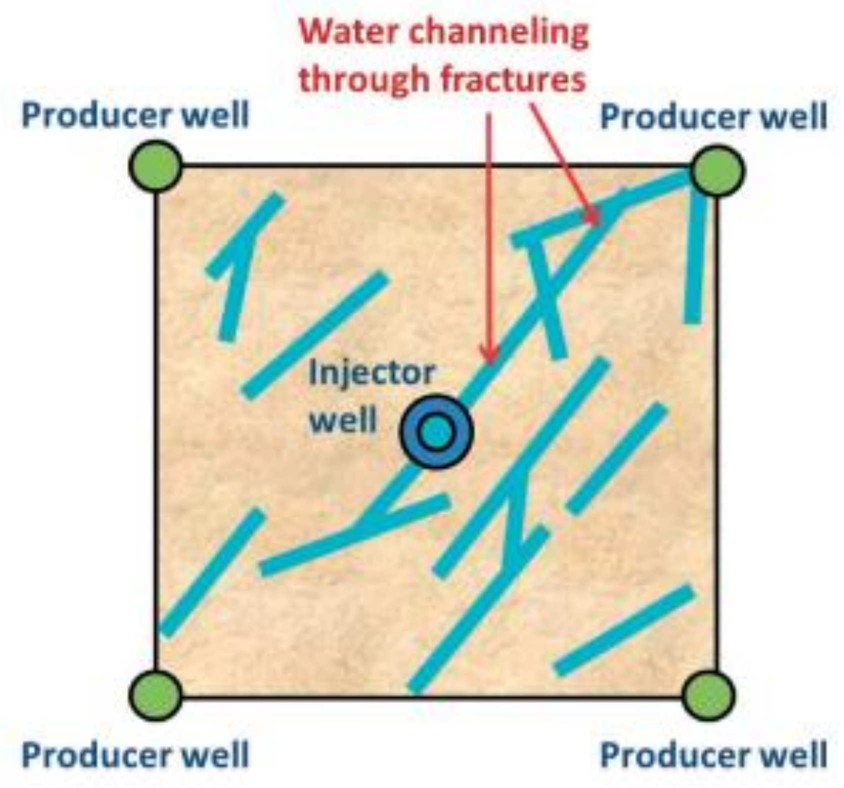

Fig 2.1.Fracture channeling during water flooding (Sydansk and Romero-Zerôn 2011, Brattekas B., 2014)

2.2.1. In-situ Gels. In-situ gels are traditional gels which have been widely employed for conformance control techniques in the industry. Polymer and cross-linker are mixed at surface facilities and injected as a gelant into the formation. The gelation process occurs in the reservoir and the rate of gelation depends upon the reservoir temperature, pressure and other conditions (Sydansk and Moore, 1992).

2.2.2. Preformed Particle Gels (PPG). PPGs were developed as an alternative to traditional in-situ gels to overcome certain distinct deficits like change of gelant compositions or chromatographic fractionation, dilution by formation water, uncertainties of gelling due to shear degradation and lack of gelation time control.

(Suresh S. et al. 2016). In contrast to in-situ gels, PPGs do not penetrate un-swept low permeability oil zones and only block zones with higher permeability. This improves the reservoir's sweep efficiency and maximizes oil production from zones left un-swept during water flooding.

PPGs are manufactured at surface facilities and injected into the reservoir. They range from 10µm-millimeters in size which is much larger in comparison to Bright Water (<1µm), Microgels (1-10µm) and pH sensitive polymers (µm), all used to improve oil recovery in mature oil fields. Apart from size, these blocking agents have varied swelling ratios as well. High permeability streaks/channels and induced fractures are often extensively present in mature reservoirs.

PPGs being in millimeter size ranges preferentially enter high permeability channels/conduits and fractures thereby minimizing gel penetration into low permeability matrixes. Fig 2.2 and Fig 2.3 are a representation of the gel injection profile into a formation having low permeability (K_L) and high permeability (K_h) zones. The orange zones in the figures are the gel injected zones. It can be seen in Fig 2.3 that the mm sized PPGs injected do not penetrate deep into the low permeability zones and thus leave them undamaged.

Fig 2.2.Polymer Flooding, In-situ gel

Fig 2.3.PPG treatment (mm sized)

PPGs are dried crosslinked polyacrylamide powder, super-absorbent in nature and swell 30-200 times their original size when they come in contact with water or brine. (Bai et al. 2007, Imqam A. et al. 2015, Suresh S. et al. 2016). The swollen PPG is capable of forming a gel pack after placement in a fracture. The permeability of the gel pack can be controlled by varying the particle size and gel strength (Imqam et al. 2014, 2015a, 2015b, 2015c). PPGs swell when in contact with water/brine and this can be seen in Fig 2.4 and Fig 2.5 below. This quantifies the fact that PPG is a super absorbent polymer.

Fig 2.4.PPG before swelling

Fig 2.5.PPG after swelling

Millimeter-Sized PPGs have been applied to over 5000 wells in water floods and polymer floods in China (Bai et al. 2013). They are mainly used in reservoirs with fracture-like channels and fractures having permeability in the range of Darcies. The advantages of PPGs are listed below:

- PPGs resist temperatures up to 120^oC (250^oF) (Bai et al., 2013).
- PPGs preferentially penetrate higher permeability zones due to their large size (in mm) and thus do not damage the oil rich zones (Suresh S., 2016).
- The strength and size for PPGs can be controlled as they are manufactured on surface facilities. They are environment friendly and are not sensitive to reservoir minerals (Bai et al., 2004).
- Unlike in-situ gels, PPGs are injected at the well site as a single component. This reduces the operational and labor costs.
- To adjust and design PPGs for better results, real-time monitoring data can be used.
- In-situ gels are often sensitive to the salinity, multivalent cations and H_2S in produced water (Chauveteau et al. 2003; Bai et al. 2007a & 2007b), whereas PPGs can be prepared at the surface using the produced water at the site without affecting their stability.
- Several of their properties have been reported over the years (Li, Y. et al. 1999, Bai, B. et al. 2004a, 2004b,2010, Bai, B.,2008, Zhang et al., 2010, Elsharafi et al., 2013, Imqam, A. et al., 2014, Suresh, S. et al. 2016).

2.3. CO_2 FLOODING

Lambert et al. reported that CO_2 flooding was commercially applied for enhanced oil recovery for the first time in Texas in the 1970’s. This is not new to the industry; in the Permian Basin, West Texas and Eastern New Mexico, CO_2 flooding has been a prominent tertiary recovery process for about 30 years (since the mid – 1980s) (Perera, M. S. et al, 2016).

CO_2 flooding has been in use for over four decades now at the Permian basin (Although most of the CO_2 used was naturally sourced from New Mexico and Colorado) (Logan et al., 2007) and around the world. But, when taking a look at the world outside of the United States, CO_2 EOR has only been used over the last 10 years (Perera, M. S. et al, 2016).

Depending on various reservoir conditions like pressure, temperature and the composition of crude oil, CO_2 floods can be immiscible or miscible. They are also widely used for WAG (Water Alternating Gas) operations.

2.3.1. Advantages Of CO_2 Flooding. Reducing post-water flood residual oil saturation is the main objective of a miscible CO_2 flood (Bank et al. 2007). Usage of CO_2 over other gases in enhanced oil recovery is most favorable. This is because of its properties at typical reservoir conditions. At lower reservoir pressures, CO_2 tends to be miscible with oil in a reservoir (Holm, L. W., 1986) and at higher pressures and temperatures; it maintains a higher viscosity than other miscible gases (Lambert et al. 1996). Fig 2.6 shows the change in viscosity and density of CO_2 as a function of pressure and temperature.

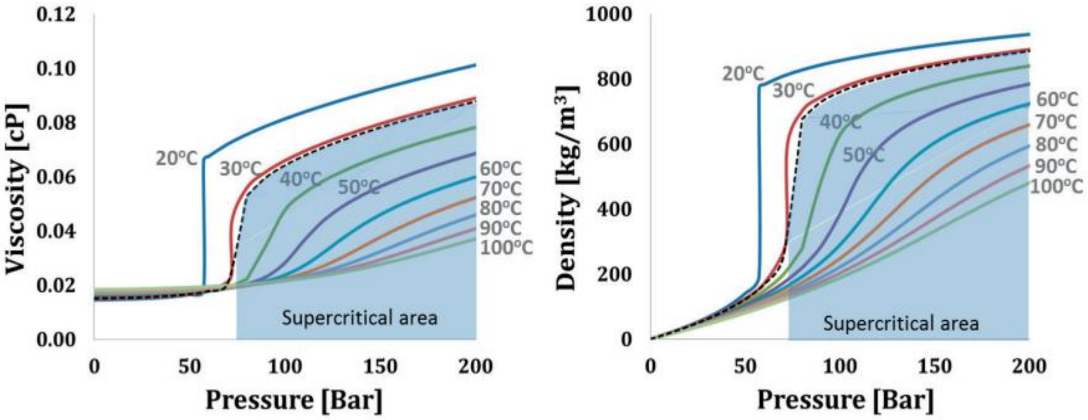

Fig 2.6.Change in viscosity (left) and density (density) of CO_2 as a function of pressure and temperature (Lemmon et al., 2014, Brattekas B., 2014)

When two or more substances mixed in all proportions form a single homogeneous phase, the phenomenon is called miscibility (Holm, L. W., 1986). CO_2 and other miscible gases when injected into a reservoir are only miscible with oil above a certain pressure. Thisis referred to as the minimum miscibility pressure (MMP). The MMP varies with factors like reservoir temperature, crude oil composition and injected gas composition (Yuan et al. 2005). The MMP for CO_2 is much lower compared to other gases and this is also one of the biggest advantages.

In CO_2-EOR flooding, the interfacial tension between the gas and oil diminishes after a series of mass transfers between the two and they appear as one phase (Ghomian et al. 2008). Bank et al. 2007 state the advantages of CO_2 flooding by categorizing its recovery mechanism as decreased oil viscosity and oil swelling in the reservoir, which occurs when CO_2 and reservoir oil mix, extraction of lighter hydrocarbons into the gas phase, and an additional viscous pressure in the drive fluid.

Thus, CO_2 EOR has several advantages over water flooding and coupling this tertiary recovery process along with gel treatment could maximize the oil recovery (Kulkarni, M.M. et al., 2003, Kuuskraa, V.A. et al., 2006, Godec, M. et al. 2011, Imqam, A., 2015b, Perera, M. S. et al., 2011a, 2011b, 2012, 2016, Godec, M. et al. 2011, Ranathunga, A.S. et al., 2014).

2.3.2. Statistics For CO_2 Flooding Today. CO_2 enhanced oil recovery (EOR) is the second largest tertiary recovery process in the world after thermal processes (Perera, M. S.et al, 2016 and Kulkarni, M.M., 2003). It contributes about 5% of the domestic oil production in the USA, which is likely to double by 2020 (Enick and Olsen 2012, Kuuskraa and Wallace 2014).

CO_2 EOR has several advantages over water flooding and this was reported as early as 1982 as discussed earlier (Holm, L. W., 1982). Thus, coupling this tertiary recovery process along with gel treatment could maximize the oil recovery.

Reducing emissions from greenhouse gases has been a primary concern for quite some time, and that, combined with the objective of reducing dependence on foreign energy sources has made carbon dioxide (CO_2) enhanced oil recovery (EOR) one amongst the front runners to help enhance hydrocarbon extraction.

According to reports published, in 2008 over 250,000 barrels per day (bpd) of incremental oil produced internationally came from about a 100 CO_2 EOR projects in the United States (Perera, M. S. et al, 2016). 153 miscible CO_2 floods were carried out in 2010, and 139 of them were in the USA (Al-adasani et al. 2012).

According to the Annual Energy Outlook published in 2016, in the lower 48 states of United States, onshore crude oil production using CO_2 EOR will increase from 0.3 Mbbl/day in 2015 to 0.7 Mbbl/day in 2040 as oil prices will rise and affordable sources of CO_2 will become available (EIA - Annual Energy Outlook, 2016). Keeping all these in mind, it is essential to extend conformance control to CO2 flooding projects and optimize our operations to maximize oil recovery.

2.3.3. Conformance Control Using Gels For CO_2 Flooding. Just like in water flooding, CO_2 flows preferentially through the easiest paths in the reservoir when injected. This results in early breakthrough of gas during injection, leaving oil trapped in un-swept zones (Jarrell, P.M. et al, 2002). In 2008, Vargas-Vasquez and Romero-Zerón reported that successful gel treatments direct CO_2 from high permeability zones towards lower permeability zones.

Gel treatments have been predominantly used for water flooding projects as a conformance agent, but, field applications and laboratory experiments have been performed to divert CO_2 (Martin and Kovarik, 1987; Martin and Kovarik, 1988; Seright, 1995; Hughes, Friedmann, Johnson, Hild, Wilson, and Davies, 1999; Karaoguz, Topguder, Lane, Kalfa, and Celebioglu, 2007; Pipes and Schoeling, 2014).

Hydrolyzed polyacrylamide (HPAM) with Cr(III) Acetate is the most employed gel system in the oil industry. Vargas-Vasquez and Romero-Zerón, 2008 and Vargas-Vasquez et al., 2009 reported that these gels are more resistant to acidic conditions than other gels like borate cross-linked guar which are limited to certain pH conditions.

Karaoguz et al, 2007 and Topguder, 2010 reported several field applications of Cr(III) Acetate cross-linked PAM gels in the Bati Raman field in southeastern Turkey. Reservoir heterogeneity and unfavorable mobility ratios between injected CO_2 and heavy oil was a major problem. However, application of gels for conformance control improved the sweep efficiency and increased oil recovery by 12%.

Experiments have been performed to analyze effectiveness of gel treatment to divert CO_2. However, no laboratory studies have been carried out yet to try and understand the behavior of gels when exposed to CO_2.

3. EXPERIMENTAL DESCRIPTION

3.1. EXPERIMENTAL SETUP

To conduct this experiment successfully, high pressure vessels were fabricated. A detailed list of all materials and apparatus used are presented below:

3.1.1. Materials Used. Commercially available PPG - 40K series gel, CRG, brine solutions and industrial grade CO_2 are the materials used for this study.

3.1.1.1. Commercially available Preformed Particle gel (PPG). 20-30 mesh size of 40K Series superabsorbent polymer gel (Potassium salt of crosslinked polyacrylic acid/polyacrylamide copolymer) were employed.

3.1.1.2. CO_2 Resistant Gel (CRG). 20-30 mesh of CO_2 Resistant Gel (CRG), synthesized in Missouri University of Science & Technology, Rolla were used for the experiments.

3.1.1.3. Brine concentration. 4 different solutions of brine were used for the experiments: concentrations of 0.00% NaCl (distilled water), 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution.

3.1.2. High Pressure Vessels. High pressure vessels designed and assembled at our laboratory are capable of withstanding up to 4000 psi of pressure. Gels were placed inside these vessels and they were pressurized with CO_2 up to desired pressures.

Fig 3.1 below is a representation of the high pressure vessel designed for our experiment. Every component used has a pressure rating of up to 4000psi. The middle piece has outer threads on both ends and the top and bottom pieces have threads on the inside to enable the assembling of the three pieces.

A quartz sight glass was permanently machined on to the bottom piece. The initial design did not include this sight glass. When gel was exposed to CO_2 on our trial experiments, the gel expelled water and reduced in weight when exposed to varying pressures. To ensure visual manifestation of the loss of water, this sight glass was included. Removable meshes (Stainless steel type, 30x30mm size) were tightly fit into the bottom piece as seen in the figure. A removable mesh was also placed at the top end of the middle piece. A pressure gauge and a valve were fixed to the top piece as seen below.

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The valve is used to inject CO_2 into the vessel. The gauge provides easy monitoring for the pressure in the vessel. Fig 3.1 below is a representation of the high pressure vessel designed for our experiment.

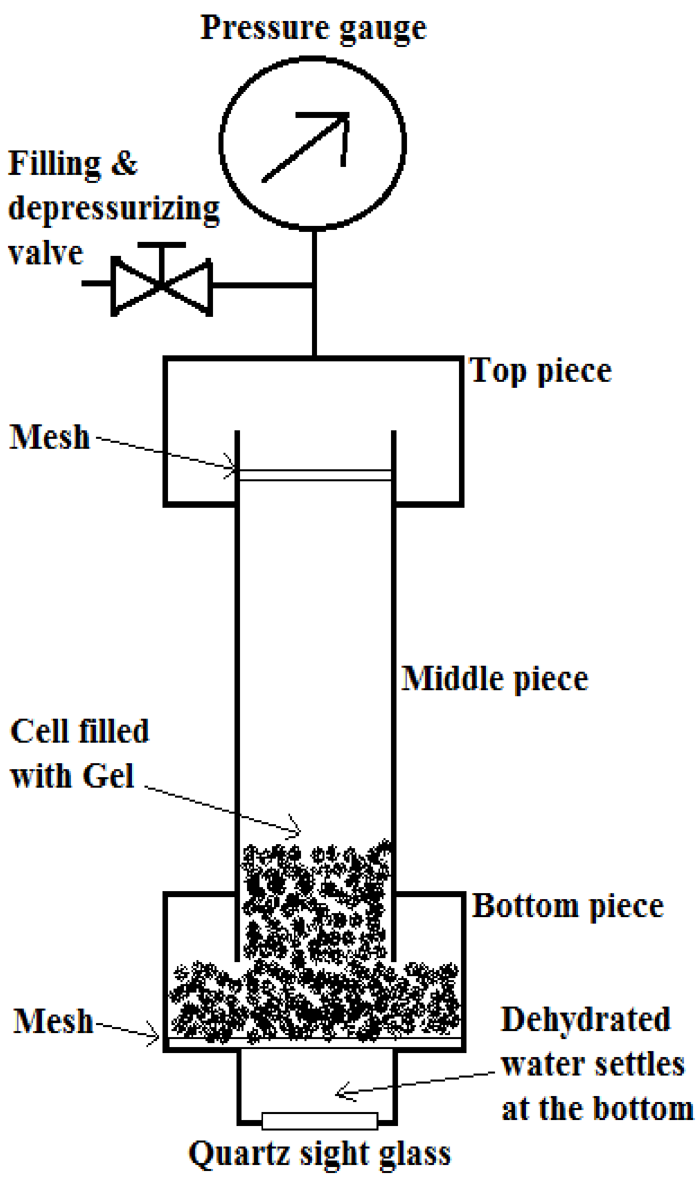

Fig 3.1.Sketch for high pressure vessel designed for the experiment

Fig 3.2 is a picture of the vessels machined in the laboratory as per the design shown in Fig 3.1 above.

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Fig 3.2.High pressure vessels

3.1.3. Assembling High Pressure Vessels. Both ends of the middle piece were threaded with Teflon tape with about ten turns. Following this, a layer of high vacuum grease was applied before the pieces were tightly threaded together on a bench vise in the workshop.

On initial trials, the vessels did not hold up to 2500 psi of CO_2 and leakage was found from the two threaded regions holding the three pieces together.

After facing several hurdles in being able to contain the gas pressurized in the vessel, using ten turns of Teflon tape and high vacuum grease proved to be a successful technique in containing the gas.

3.1.4. Pressurizing The Vessels. Apparatus was set up as seen in Fig 3.3 to pressurize the high pressure vessels. Industrial grade cylinder of CO_2 compressed to about 350 psi was used.

`

As a pilot study, it was decided not to expose the gels placed in the vessel to very high pressures in one go but rather increase the pressure slowly so that they did not extrude through the mesh at the bottom of our vessels. Fig 3.3 shows the apparatus used to pressurize the High Pressure Vessels.

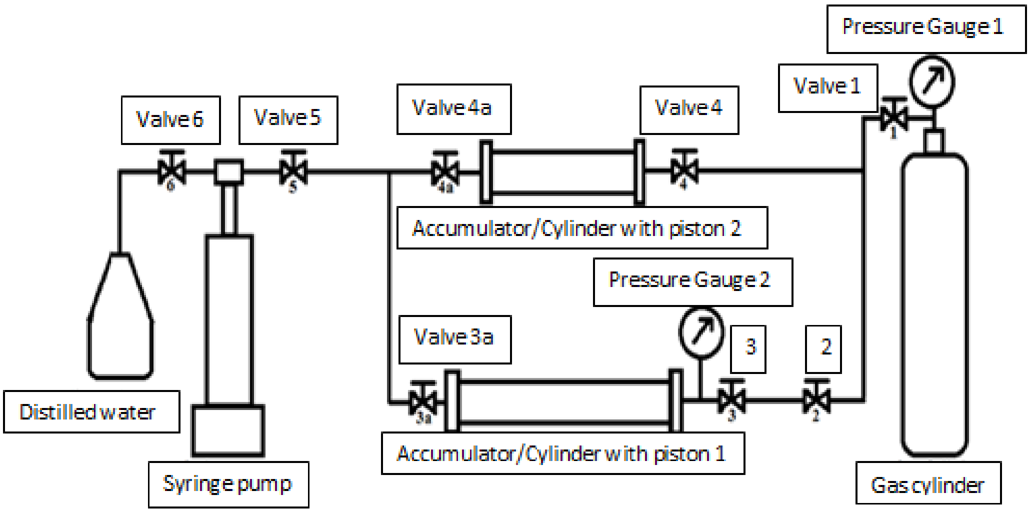

Fig 3.3.Apparatus to pressurize high pressure vessels

In order to compress the gas further for our experiments, 2 accumulators and a syringe pump as seen above in Fig 3.3 were used. The procedure to pressurize the vessels is as follows: Initially, with all valves open, the accumulators are filled with CO2 and valve 1 is shut.

1. Valve 3a and valve 4 are then closed. The syringe pump is now run to pressurize the gas in Accumulator 2.
2. As the piston reaches the right end of the cylinder, valve 4 is open and this increases the pressure in the system.
3. The pressure in accumulator 1 rises now and this can be seen in pressure gauge 2. Valve 3 is then closed to store the pressurized gas. For example, if the pressure in the system seen in gauge 2 is 350 psi before this cycle, it would be around 400 psi after this cycle of compression.
4. This cycle of accumulating pressure in Accumulator 1 by pressurizing the gas in Accumulator 2 is continued until the desired pressure is built up.

`

5. Once the gas is stored at desired pressure in Accumulator 1, the connection between valve 2 and valve 3 are carefully opened and the line is connected to the filling valve of the high pressure vessel.
6. Lastly, the discharge valve 3 of the accumulator and the filling valve are slowly opened and the vessel is pressurized as needed.

3.2. EXPERIMENTAL PROCEDURE

A detailed description of the procedure from preparing the gels for the experiment to assessing gel performance characteristics are described below:

3.2.1. Preparing PPG, Swelling Ratio Measurement. A step by step procedure to prepare the samples and measure swelling ratio is as below:

1. Dry PPG (40K series & CRG) is weighed on a weighing scale. The weight is always noted up to 4 decimal places.
2. PPG used for all experiments are initially swollen in their respective solvent (DW, 0.25% NaCl solution of brine, 1.00% NaCl solution of brine and 10.00% NaCl solution of brine) for 5 hours.
3. After 5 hours, the PPG and the solvent are poured on to a fine mesh. The sample is kept covered at room temperature (around 23 deg C) for exactly 24 hours.
4. After 24 hours, the gel is collected and carefully weighed. The swelling ratio/swelling capacity [6] of the gel is now measured as:

Swelling ratio = (Weight of PPG after swelling – Weight of dry PPG) / Weight of dry PPG)

3.2.2. Placing PPG In High Pressure Vessels. For each experiment around 50 gm of swollen sample was used. For our experiments, the vessels were pressurized to 500 psi (CO_2 in gas phase below supercritical conditions), 1100 psi (CO_2 phase close to supercritical conditions – wherein it would exist partially as gas and partially as a supercritical fluid), 1900 psi and 2500 psi (2 varying pressures above supercritical conditions of CO_2 wherein it would exist as a supercritical fluid) at 65 deg C. This apparatus was set up at room temperature (around 23 deg C). To account for the increase in pressure with increasing temperature, the vessels were pressurized to around 500 psi, 850 psi, 1250 psi and 1500 psi respectively at room temperature.

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Once pressurized, the vessels were placed vertically in an oven heated to 65 deg C. Their pressures rise to the required testing pressures (pressure for a constant volume of gas increases with increasing temperature).

The vessels were periodically checked for any excess pressure which was relieved in the first one hour of placement in the oven. PPG swollen in 4 different solutions at 4 different pressures for 1 day, 3 days and 5 days were placed in the vessels.

3.3. GEL PERFORMANCE CHARACTERISTICS BEFORE AND AFTER EXPOSURE TO CO_2

A detailed procedure to analyze dehydration, re-swell ratio, gel strength, chemical shift and study the gel network of gels are presented.

3.3.1. Dehydration. Dehydration gives a measure of the liquid retaining capacity of the gel. The swollen gel when exposed to CO_2 loses some amount of solvent. The objective of studying the dehydration of PPG on exposure to CO_2 is to check if it expels the same amount of solvent when exposed to varied pressures of CO_2. A step by step procedure to measure the dehydration is presented below:

1. Vessels placed in the oven with swollen PPG are removed from the oven after the stipulated period of time (1 day/ 3 days/ 5 days) and allowed to cool down for an hour at room temperature.
2. The filling/depressurizing valve is opened very slowly to release the CO_2.
3. The vessel is then held on a bench vise in the workshop and the bottom piece is disassembled. The gel is carefully collected on a fine mesh.
4. Next, the top piece is disassembled and every particle of the gel (to the best of our capability) is collected.
5. The gel is then weighed on the same weighing scale. The dehydration is now measured by weight as:

$$\textit{Dehydration} = \textit{Weight of PPG placed in the cylinder} - \textit{Weight of PPG after exposure to } CO_2$$

The free water released by the gel on exposure to CO_2 is collected in the bottom piece below the mesh. This water is visible from the quartz sight glass when the vessels were kept inside the oven.

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3.3.2. Re-swell Ratio. The reason for measuring the Re-swell ratio is to check if PPG swells the same number of times before and after exposure to CO_2. Results led to further investigation of the change in properties after the gel is exposed to CO_2. A step by step procedure to measure the re-swell ratio is presented below:

1. Samples collected after dehydration are placed on an aluminum foil and kept in the oven at 65 deg C for 96 hours. The gel dries up at this temperature as the water absorbed vaporizes over 96 hours.
2. A small amount of this dry gel is collected and weighed.
3. This new sample is once again immersed in the original solvent (DW/0.25% NaCl solution/ 1.0% NaCl solution/10.0% NaCl solution) for five hours so it can re-swell. (For example, gel sample which is originally swollen in 1.0% NaCl solution, exposed to CO_2 and then dried in an oven is re-swollen in the same 1.0% NaCl solution).
4. The salt solution is poured out and refilled every half an hour. (Note that the PPG being re-swollen in this step has some salt trapped in it. This sample was previously swollen in brine and exposed to CO_2. On reheating in an oven, only the water vaporizes. Thus, replacing solvent periodically at this stage ensures that the salt content in the sample comes into equilibrium with the salt content of the solution).
5. After 5 hours, the swollen sample is placed on a mesh and left covered for 24 hours for the extra solvent to drain at room temperature (around 23 deg C).
6. Then, the gel is carefully collected and weighed. Now, the re-swell ratio is measured as:

$$\textit{Re-swell ratio} = (\textit{Weight of } CO_2 \textit{ exposed PPG after swelling} - \textit{Weight of dry } CO_2 \textit{ exposed PPG}) / \textit{Weight of dry } CO_2 \textit{ exposed PPG}$$

3.3.3. Gel Strength. The gel strength of PPG is measured for samples before and after exposure to CO_2. The measurement of G’ in Pa is intended to mainly check if the gel degrades in the presence of CO_2. If the gel strength reduces, it could indicate degradation or loss of polymer/cross-linker.

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It is also done to check if the gel strength varies with the amount of time the gel is exposed to CO_2. The method used to measure the gel strength of preformed particle gels is in accordance to Muhammed, F. A. et al, 2014.

G' (elastic/storage modulus) is measured at 1 Hz and a 1mm gap between the surface and the rotating plate. The gel strength of all the 1 day samples are measured using a HAAKE MARS Modular Advanced Rheometer System as seen in Fig 3.4.

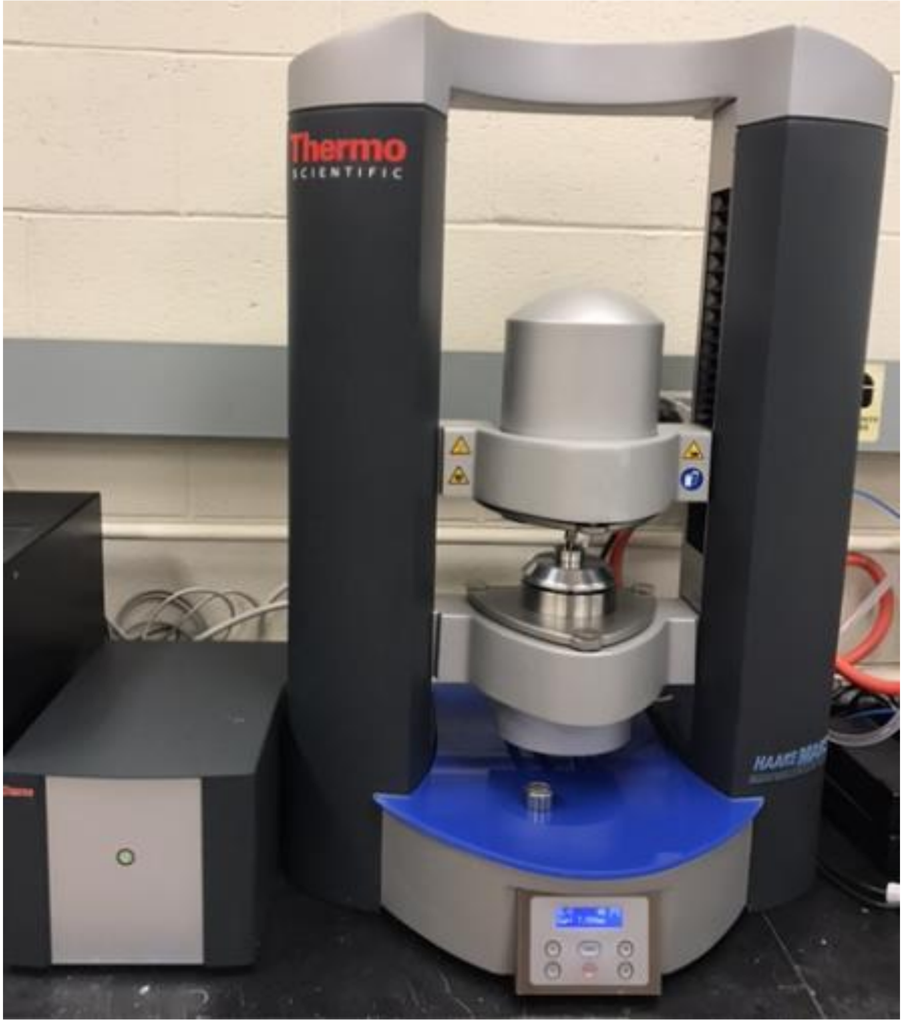

Fig 3.4.HAAKE MARS Modular Advanced Rheometer System

3.3.4. Scanning Electron Microscope (SEM). This is a type of electron microscope which focusses a beam of electrons on the sample and produces an image containing information regarding the sample's surface topography. PPG before and

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after exposure to CO_2 are studied under an SEM. This is to check if there are any noticeable differences on the gel's surface topography on exposure to CO_2.

The gel samples are prepared before being analyzed under an SEM. The procedure for preparing the samples is as follows:

1. Place 4-5 particles of gel in a test tube. Ensure the particles are separated from each other. Place the test tube in a freezer for up to 12 hours. In order to save time, the test tubes can also be placed in an ice box and exposed to liquid nitrogen to freeze the samples quickly.
2. Next, these samples are freeze dried for up to 16 hours so that the water in the sample can be sucked out.
3. The samples are carefully sliced and sputter-coated with a Gold-Palladium coating. A HUMMER VI Sputter Coater as seen in Fig 3.5 is used for this.
4. Now the samples are analyzed under a 4700 FESEM. The SEM used is as seen in Fig 3.6.

Fig 3.5.HUMMER VI Sputter Coater

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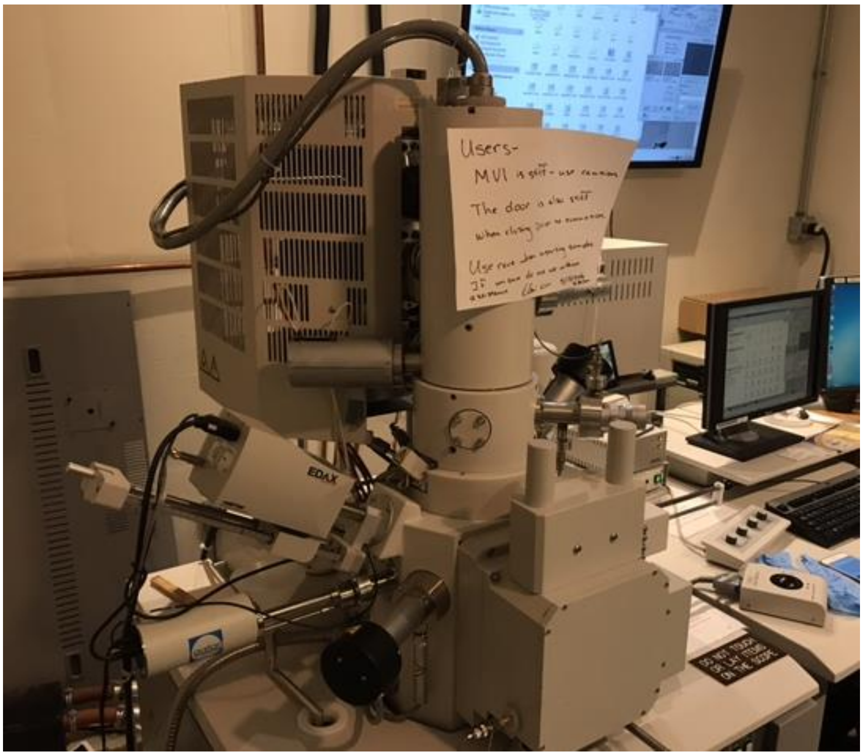

Fig 3.6.4700 FESEM used for analysis

3.3.5. Fourier Transform Infrared Spectroscopy (FTIR). This technique obtains the infrared spectrum of absorption or emission of a solid, liquid or gas. A beam containing many frequencies of light shines on the sample and the amount of that beam absorbed by the sample is measured. Different elements absorb at different wavelengths. Studying PPG samples before and after exposure to CO_2 by this IR spectroscopy method allows us to view any changes in the chemistry of the gel. The procedure to prepare the samples for this analysis is as follows:

1. Samples to be analyzed are placed in test tubes (up to about 20% of the test tube).
2. The test tubes are placed in an oven heated to 65 deg C for about 24 hours.
3. About 1/8th inch of sample is taken on a micro spatula ground to powder. It is mixed with 0.5 teaspoon of prepared KBr pellet.
4. This sample is now placed on a pellet press as seen in Fig 3.7 and pressed up to 7000 psi.
5. Once the sample is pressed, it is analyzed in a Nexus Nicoler FTIR. The equipment used is as in Fig 3.8.

Fig 3.7.Pellet press assembly

Fig 3.8.Nexus Nicoler FTIR equipment

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4. RESULTS ANALYSIS AND DISCUSIONS PART I

4.1. COMMERCIALLY AVAILABLE PPG, 40K SERIES GEL

The gel used for the experiments is a potassium salt of crosslinked polyacrylic acid/polyacrylamide copolymer. It is one of the HPAM variants used in the oil industry which is commercially available.

4.1.1. Dehydration. The gel, when exposed to CO_2, shows dehydration over varying pressures of CO_2. The amount of dehydration also varies with the amount of time the gel is exposed to CO_2. The dehydration is not extremely high owing to the increase in pressure, but it is noticeable.

Around 50 grams of sample measured up to 4 decimal places placed inside the high pressure cylinders reduces in weight as the water in the swollen gel is expelled on exposure to CO_2 and drains to the bottom of the cylinder. The weight loss percentage for each case is calculated as:

Weight loss % = (Weight lost by swollen PPG after exposure to CO_2/Weight of swollen PPG placed in the vessels prior exposure to CO_2) x 100

As discussed before, PPG is swollen in 4 different solutions: DW, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution. For the gel swollen in each of the mentioned solutions, 16 sets of experiments are performed at 4 different pressures of 500 psi, 1100 psi, 1900 psi and 2500 psi at 65 deg C for 1 day, 3 days and 5 days.

Note that the results presented indicate the percentage of weight loss on exposure to CO_2. Higher percentage of weight loss on exposure to CO_2 indicates higher dehydration.

Fig 4.1 shows the weight loss percentage for 40K series gel swollen in distilled water and exposed to CO_2.

From the figure, it is seen that the amount of water expelled by the gel is directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for.

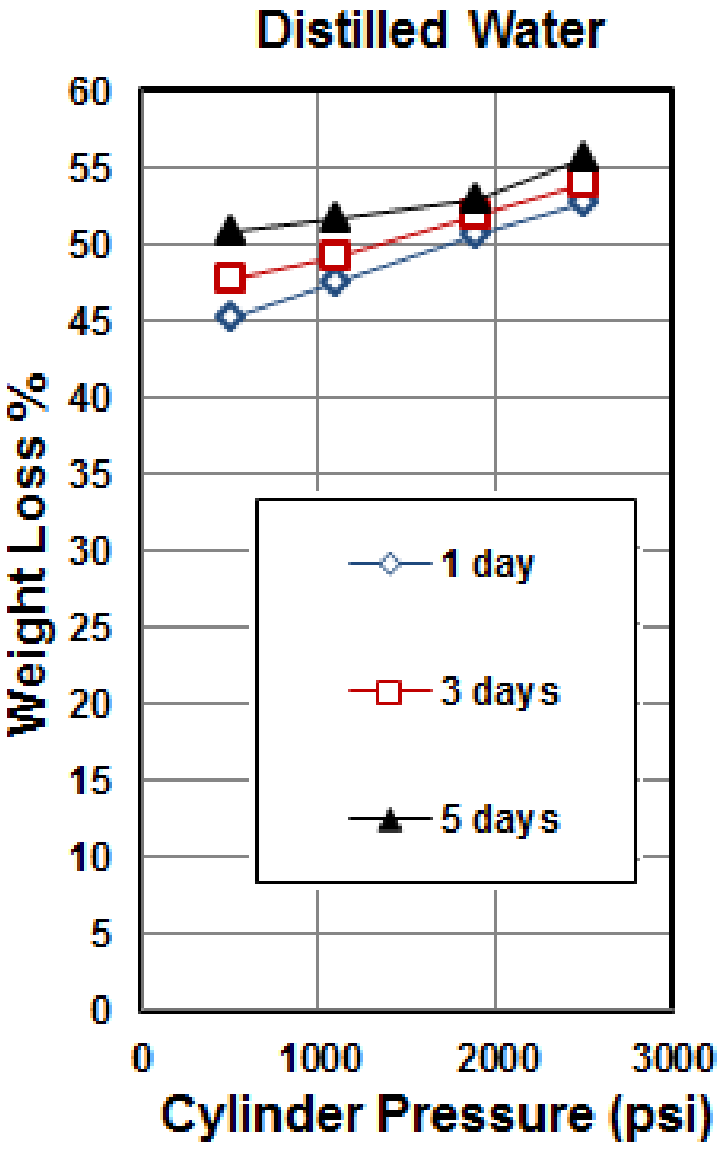


Fig 4.1.Dehydration for 40 K gel swollen in distilled water when exposed to CO_2

The weight lost due to dehydration is very high for 40K gels swollen in DW. The gels lose between 45.241% and 55.469% of water absorbed on exposure to the gas from experiments. This is not a preferable phenomenon.

After the first few experiments, weight loss on exposure to gel was noticed and the design of the vessel was altered. The sight glass was incorporated on the bottom piece to visually ensure the water expulsion. The results for the weight loss percentage for each of the experiments are recorded in Table 4.1.

Fig 4.2 shows the weight loss percentage for 40K series gel swollen in 0.25% NaCl solution and exposed to CO_2. From the figure, it is seen that the amount of water expelled by the gel is again directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for. The weight lost due to dehydration is relatively lower in this case when compared to PPG swollen in DW.

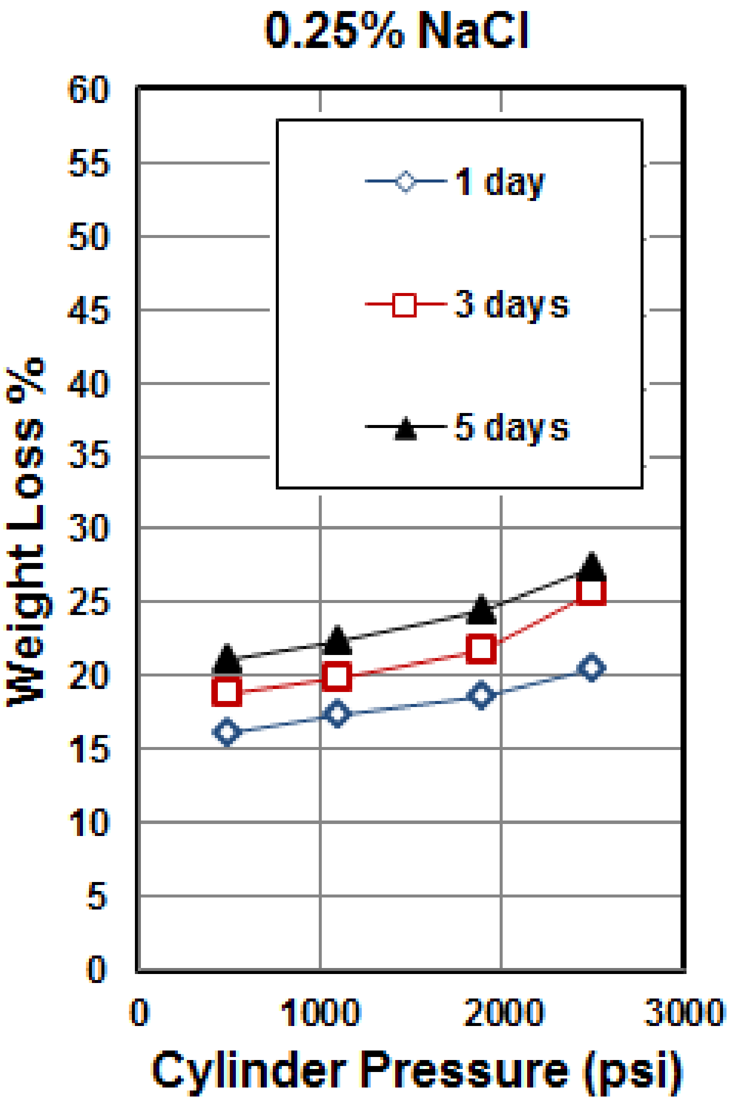


Fig 4.2.Dehydration for 40 K gel swollen in 0.25% NaCl Solution when exposed to CO_2

The gels lose between 16.21% and 27.47% of water absorbed on exposure to the gas from experiments. The loss in weight is again not preferable, but it is seen that the performance of this gel when swollen in salt solution and exposed to CO2 is better when compared to the previous case. The results for the weight loss percentage for each of the experiments are recorded in Table 4.2. Table 4.1 shows recorded values for dehydration measurement of samples swollen in distilled water.

Table 4.1.Dehydration for samples swollen in distilled water

Weight loss %			
Pressure (psi)	Samples swollen in Distilled Water		
	1day	3days	5days
500	45.241	47.723	50.873
1100	47.542	49.125	51.642
1900	50.529	51.748	52.910
2500	52.651	53.938	55.469

Table 4.2.Dehydration for samples swollen in 0.25% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 0.25% NaCl Solution		
	1day	3days	5days
500	16.21	18.89	21.21
1100	17.42	19.85	22.35
1900	18.65	21.68	24.37
2500	20.59	25.74	27.47

Fig 4.3 shows the weight loss percentage for 40K series gel swollen in 1.00% NaCl solution and exposed to CO_2. It is seen that the amount of water expelled by the gel is again directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for. This is illustrated in Fig 4.3.

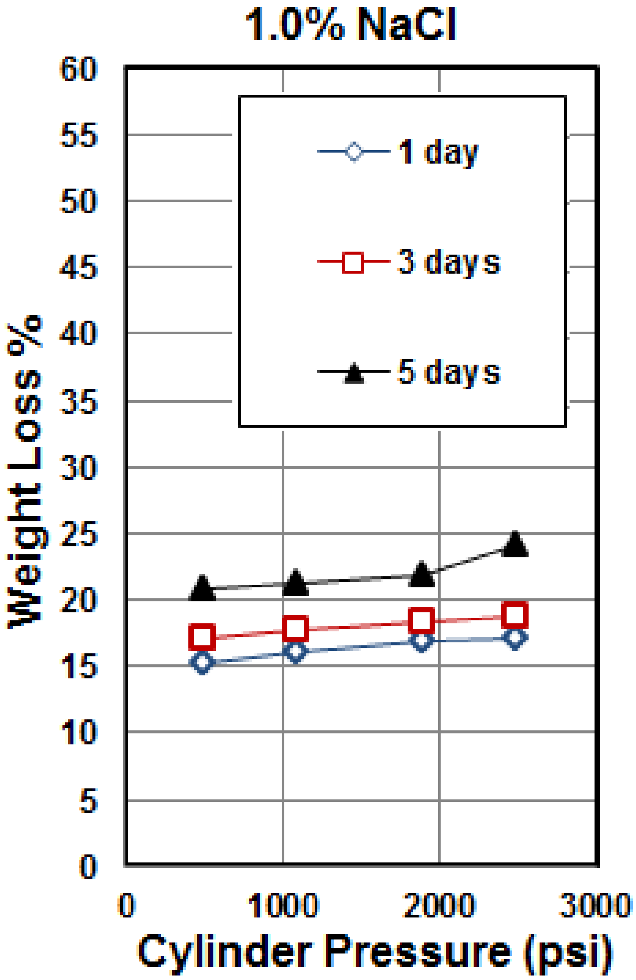


Fig 4.3.Dehydration for 40 K gel swollen in 1.00% NaCl Solution when exposed to CO_2

The weight lost due to dehydration is relatively lower in this case when compared to the last 2 cases. The gels lose between 15.257% and 24.157% of water absorbed on exposure to the gas from experiments.

The loss in weight is again not preferable, but it is seen that the performance of this gel when swollen in salt solution with an increased percentage of salt and exposed to CO_2 is better when compared to the previous two cases. The results for the weight loss percentage for each of the experiments are recorded in Table 4.3.

Fig shows the weight loss percentage for 40K series gel swollen in 10.00% NaCl solution and exposed to CO_2. In this last case as well, it is seen that the amount of water expelled by the gel is directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for. This is illustrated in Fig 4.4.

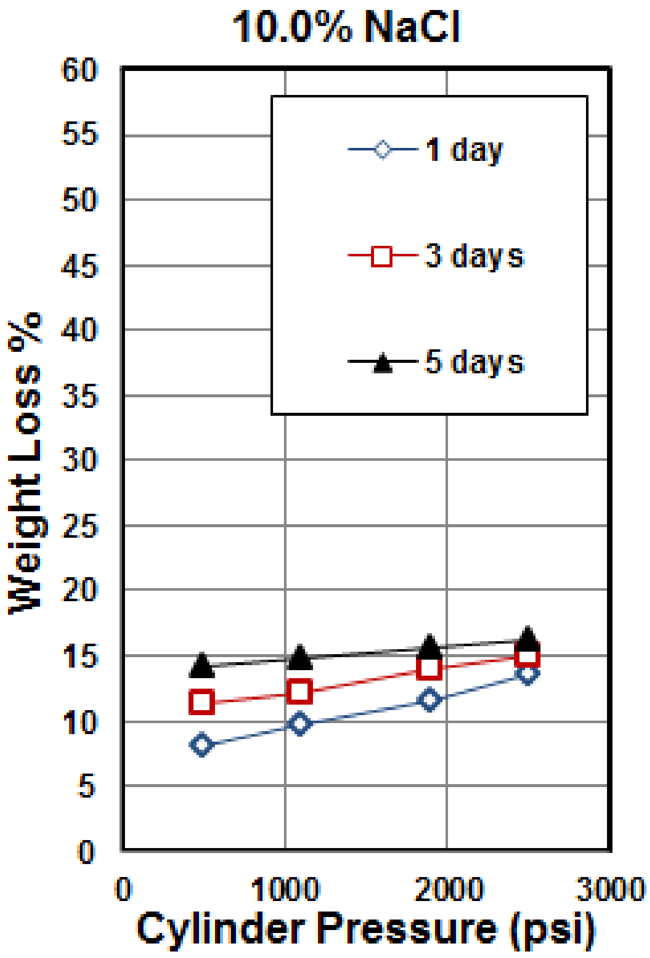


Fig 4.4.Dehydration for 40 K gel swollen in 10.00% NaCl Solution when exposed to CO_2

The weight lost due to dehydration is relatively lower in this case when compared to the last 3 cases. The gels lose between 8.10% and 16.25% of water absorbed on exposure to the gas from experiments.

The loss in weight is again not preferable, but it is seen that the performance of this gel when swollen in salt solution with a much more increased percentage of salt when exposed to CO_2 is better when compared to the previous three cases. The results for the weight loss percentage for each of the experiments are recorded in Table 4.4. Table 4.3 presents all the experimental values for dehydration measurement of samples swollen in 1.00% NaCl Solution.

Table 4.3.Dehydration for samples swollen in 1.00% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 1.00% NaCl solution		
	1day	3days	5days
500	15.257	17.157	20.862
1100	16.106	17.802	21.235
1900	17.001	18.381	21.972
2500	17.207	18.739	24.157

Table 4.4.Dehydration for samples swollen in 10.00% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 10.00% NaCl solution		
	1day	3days	5days
500	8.10	11.28	14.20
1100	9.75	12.20	14.72
1900	11.61	14.06	15.53
2500	13.50	15.01	16.25

The first observation made from the results is that the dehydration of 40K gel in presence of CO_2 reduces with increasing salt concentration. For example, the weight loss percentage of PPG swollen in DW and exposed to CO_2 pressurized to 2500 psi for 5 days is seen to be 55.469%. On the other hand the weight loss percentage of PPG swollen in 10.0% NaCl solution and exposed to CO_2 pressurized up to 2500 psi for 5 days is seen to be only 16.25%.

Secondly, it is noticed that the dehydration for each case increases with increasing pressure of CO_2 that the gel is exposed to. For example, the weight loss percentage for PPG swollen in 0.25% NaCl solution and exposed to CO_2 pressurized up to 500 psi for 5 days is seen to be 16.21%. The weight loss percentage increases to 17.42%, 18.65% and 20.59% when the pressure is increased to 1100 psi, 1900 psi and 2500 psi respectively.

Thirdly, the samples are exposed for 3 different time periods to check if the duration of exposure to CO_2 has any effect on the gel. This is seen to increase with increasing time of exposure to gas. For example, the weight loss percentage for PPG swollen in 1.0% NaCl solution and exposed to CO_2 pressurized up to 500 psi for 1 day is seen to be 15.257%. At the same pressure, the weight loss percentage increases to 17.157% and 20.862% when exposed for 3 days and 5 days respectively.

Table 4.5 below shows values for the dehydration measurement of samples swollen in 1.00% NaCl Solution exposed to CO2 for 20 days.

Table 4.5.Dehydration for samples swollen in 1.00% NaCl Solution exposed to CO_2 for 20 days

Samples swollen in 1.00% NaCl solution exposed to CO_2 for 20 days	
Pressure (psi)	Weight loss %
500	39.221
1100	40.134
1900	41.197
2500	45.608

In order to check if the gel further dehydrated on exposure to CO_2 for a longer period of time, the gels swollen in 1.0% NaCl solution and pressurized to 500 psi, 1100 psi, 1900 psi and 2500 psi were exposed to CO_2 for 20 days.

The results show further dehydration. The weight loss percentage was 39.221%, 40.134%, 41.197% and 45.608% respectively. Thus, we see that the gels continually expel the water they had absorbed on exposure to CO_2. The results are tabulated in Table 4.5.

4.1.2. Re-swell Ratio. The swelling capacity of the gel is noticed to be altered when exposed to CO_2 i.e. the number of times the dry PPG swells in a solution is reduced when it is exposed to CO_2. The percentage of reduction in swelling is also seen to vary with the salt concentration of solution the PPG is swollen in. The percentage of re-swell is calculated as:

*Re-swell % = (Number of times PPG swells after exposure to CO_2/ Number of times PPG swells before exposure to CO_2)] *100*

1 day and 5 day samples from PPG swollen in each of the salt concentrations are used for analyzing the re-swell ratio. Varying pressures do not affect the re-swell as suggested by results. Table 4.6, Table 4.7, Table 4.8 and Table 4.9 show the number of times the gel re-swells after exposure to CO_2.

Table 4.6.Number of times 40K re-swells in distilled water

Pressure (psi)	Distilled Water	
	1day	5days
500	153.469	154.133
1100	153.103	154.965
1900	152.760	155.663
2500	153.354	154.873
Average:	154.04	

Table 4.7.Number of times 40K re-swells in 0.25% NaCl solution

Pressure (psi)	0.25% NaCl solution	
	1day	5days
500	32.387	31.704
1100	31.985	32.102
1900	31.698	31.362
2500	32.007	33.155
Average:	32.05	

Table 4.8.Number of times 40K re-swells in 1.00% NaCl solution

Pressure (psi)	1.00% NaCl solution	
	1day	5days
500	17.605	17.324
1100	17.238	17.629
1900	17.540	18.006
2500	17.152	17.026
Average:	17.44	

Table 4.9.Number of times 40K re-swells in 10.00% NaCl solution

Pressure (psi)	10.0% NaCl solution	
	1day	5days
500	9.191	9.323
1100	8.959	9.465
1900	8.531	9.875
2500	9.201	9.135
Average:	9.21	

The number of times PPG swells in solution is reduced on exposure to CO_2. Fig 4.5 illustrates this phenomenon. The blue dots are indicative of the number of times dry PPG swells in DW, 0.25% NaCl solution, 1.00% NaCl solution and 10.00% NaCl solution. The red dots show the reduced number after exposure to CO_2.

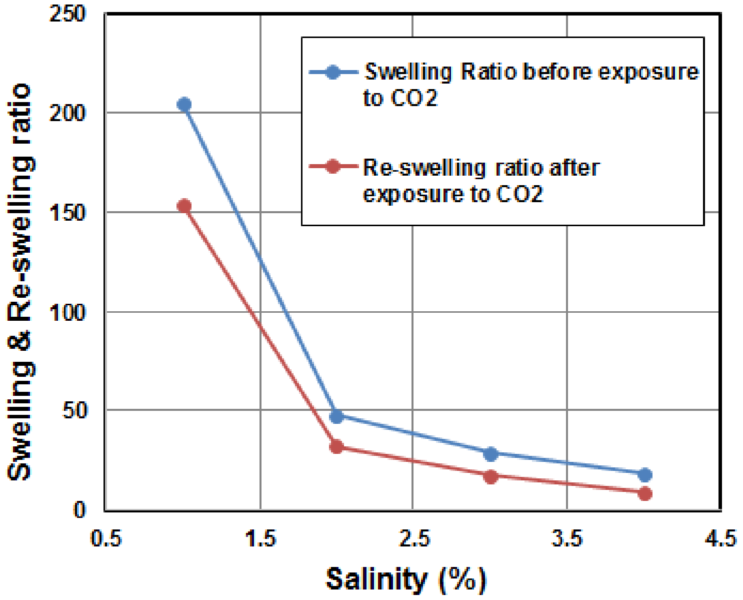


Fig 4.5.Comparison of swelling ratio before and after exposure to CO_2 for 40K

The data for the number of times that gel swells before exposure to CO_2 and after are presented in Table 4.10. In every case the gel swells lesser after exposure to CO_2 (re-swell) than it did before.

Table 4.10.Comparison of the number of times PPG swells in respective solution before and after CO_2

	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
	Number of times PPG swells			
Before CO_2	205	47.69	28.82	18.69
After CO_2	154.04	32.05	17.44	9.21

In order to simplify and present the data, an average of the 1 day and 5 day samples have been used. From the results, PPG swollen in DW, 0.25% NaCl, 1.0% NaCl and 10.0% NaCl solutions when exposed to CO_2 at pressures varying from 500 psi – 2500 psi will swell 154.04, 32.05, 17.44 and 9.21 times respectively. Table 4.11 shows the swelling ratio for 40K after exposure to CO2 compared to swelling ratio before exposure.

Table 4.11.Swelling ratio for 40K after exposure to CO_2 compared to swelling ratio before exposure

% Re-swell				
Pressure (psi)	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
500	75.025	67.195	60.645	49.520
1100	75.127	67.095	60.958	49.028
1900	75.225	66.115	61.669	49.225
2500	75.18	68.315	59.295	49.035
Average:	75.14	67.18	60.64	49.20

Salinity of the solution affects re-swell of the gel. Fig 4.6 shows the percentage Re-swell for PPG swollen in different solutions.

With increasing salinity, the re-swelling capacity of PPG is also seen to reduce. Giving an example, it can be seen that PPG swollen in DW and exposed to CO_2 swells 75.14% of what it did before it was exposed to CO_2. But, PPG swollen in 10% solution and exposed to CO_2 only swells about 49.20% of what it did before it was exposed to CO_2.

The percentage re-swell for each case is tabulated in Table 4.11. Averages of the 1 day and 5 day values have been taken into account at each pressure.

Re-swell is not affected by increasing pressures of CO_2. Also, it is noticed that the number of days for which PPG is exposed to CO_2 does not have a significant impact on this phenomenon. But, salinity of solvent in which PPG is swollen in does have a drastic impact on the re-swell. The re-swell ratio is only affected by the salinity. These results probed a deeper investigation. Fig 4.6 shows the percentage Re-swell for PPG swollen in different solutions.

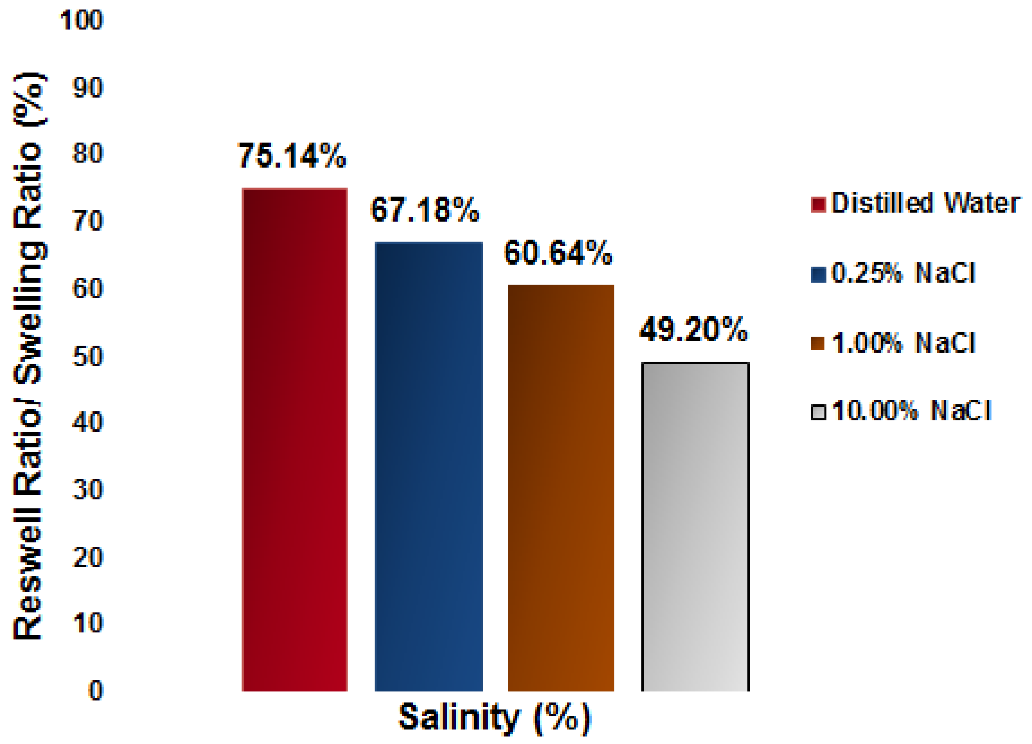


Fig 4.6.% swelling ratio for 40K after exposure to CO_2 compared to swelling ratio before exposure (Data in Table)

4.1.3. Gel Strength. All the samples were analyzed at frequencies ranging from 0.1 Hz to 10 Hz and all of them were observed to be giving steady G' readings at a frequency of 1 Hz. Following that the G' was measured for all the 1 day samples. Their average was taken for each case (graphical representation of the values in Fig 4.7).

The G' values for PPG swollen in DW, 0.25% NaCl, 1.0% NaCl and 10.0% NaCl at 500 psi, 1100 psi, 1900 and 2500 psi for 1 day were measured.

Similar to the Re-swell percentage, pressure did not seem to have any effect on the gel strength as well. Thus, an average of all the values for G' measured were taken for PPG swollen in solutions of different salt concentrations.

The G’ values for PPG swollen in DW, 0.25% NaCl, 1.0% NaCl and 10.0% NaCl at 500 psi, 1100 psi, 1900 and 2500 psi for 1 day were measured.

Similar to the Re-swell percentage, pressure did not seem to have any effect on the gel strength as well. Thus, an average of all the values for G’ measured were taken for PPG swollen in solutions of different salt concentrations. Fig 4.7 shows the gel strength of PPG before and after exposure to CO_2 in each case.

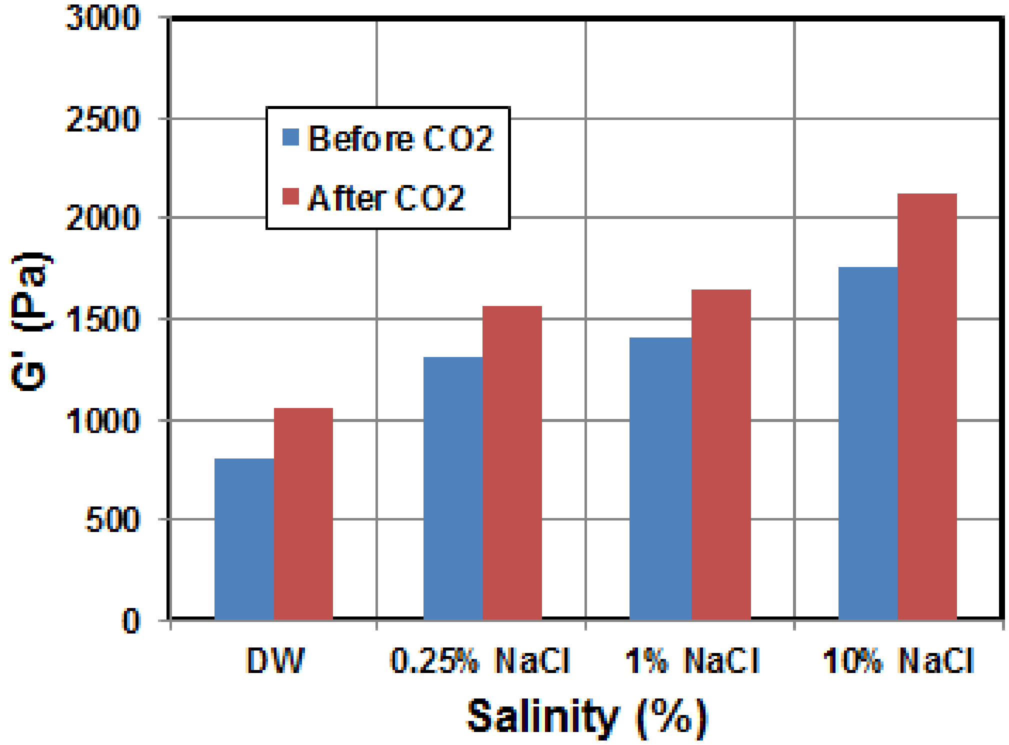


Fig 4.7.Gel strength of PPG before and after exposure to CO_2 in each case

Table 4.11 shows the G’ values for PPG swollen in DI, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution before and after exposure to CO_2. The gel strength does not change much when exposed to varied pressures and time. Thus, an average of the values has been presented.

The gel strength was measured mainly to check if the gel had degraded in presence of CO_2. But, the G’(Pa) was seen to increase after exposure to CO_2 for PPG swollen in different solutions. This result clearly indicates that gel had not degraded.

If there was any degradation and loss of polymer or cross-linker from the structure, we would expect the G’ to be lesser than before.

As seen, the gel strength of PPG increases with the increasing salt concentration of the solution it is swollen in. Also, on exposure to CO_2, the gel strength is seen to increase. Further discussion and investigation was carried out to analyze the results obtained and reason our findings. Table 4.12 shows the gel strength of PPG before and after exposure to CO_2.

Table 4.12.Gel strength of PPG before and after exposure to CO_2

G’ (Pa)				
	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
Before CO_2	804.786	1308.571	1405.714	1761.429
After CO_2	1063.368	1567.046	1651.857	2121.952

4.1.4. Scanning Electron Microscope (SEM). Gels swollen in 0.25% NaCl solution before and after exposure are studied under an SEM. The samples used were exposed to 2500 psi for 5 days.

The large pore spaces are where water existed. The crosslinked polymer readily absorbed water in here to swell. On zooming in at 10μm, loosely spaced clusters of salt are seen.

Fig 4.8 and 4.9 show SEM results for 40K Series gel swollen in 0.25% NaCl solution before exposure to CO_2 at 100μm and 10μm respectively.

Fig 4.10 and Fig 4.11 show pictures of the same gel after being exposed to CO_2. As seen in Fig 4.10 and Fig 4.11, and comparing them to the gel structure before exposure to CO_2, the pore spaces are smaller and tighter. This is because the NaCl has increased much more here, reducing pore space for water. Thus, the crosslinked polymer now absorbs lesser water from the solution and swells lesser. Also, looking into the SEM picture at 10μm, the salt clusters here look much tighter and closely spaced, further reducing the capacity of the gel to absorb water.

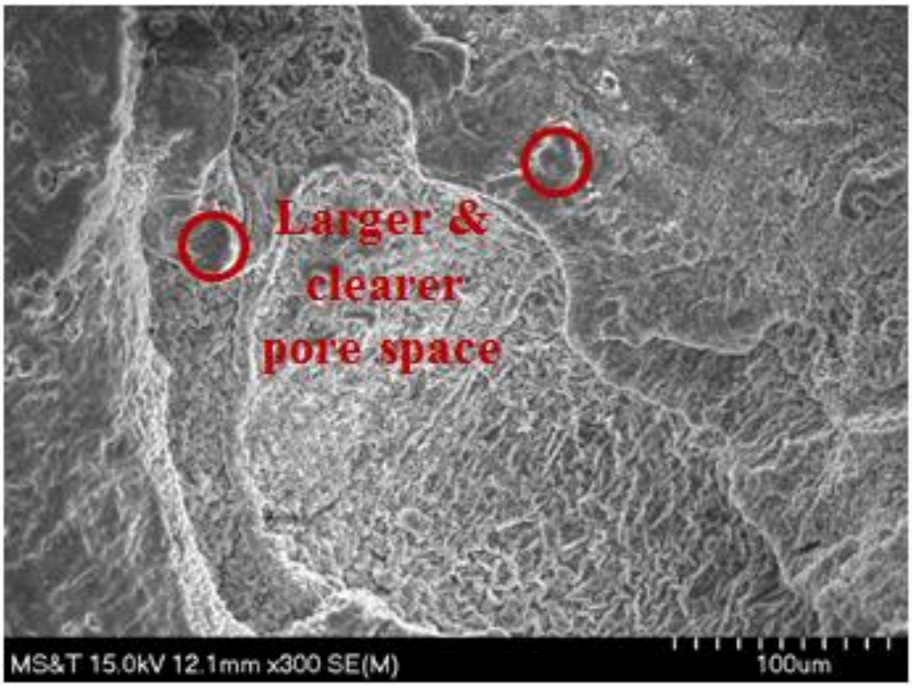


Fig 4.8.SEM results for 40K Series gel swollen in 0.25% NaCl solution before exposure to CO_2 at 100μm

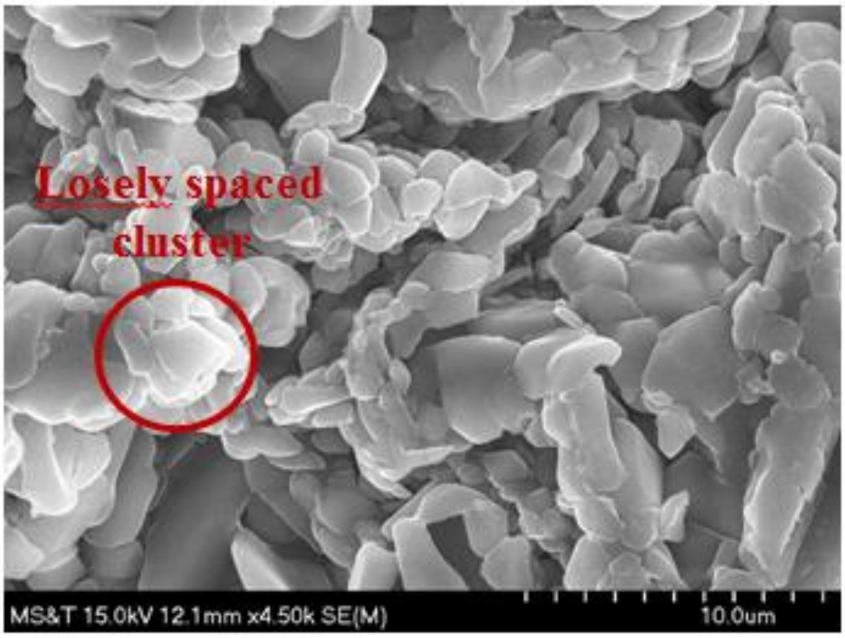


Fig 4.9.SEM results for 40K Series gel swollen in 0.25% NaCl solution before exposure to CO_2 at 10μm

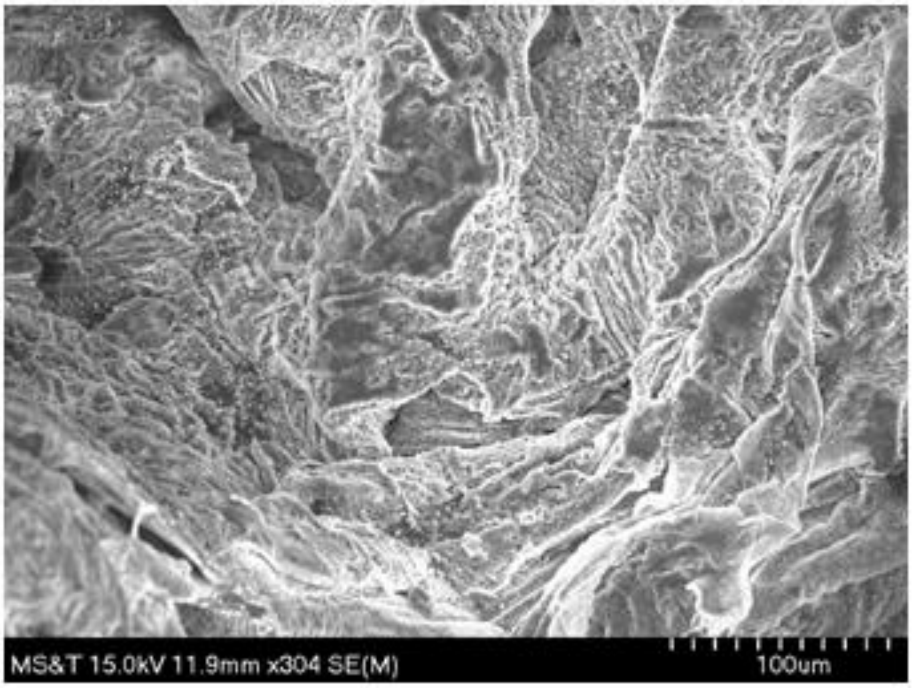


Fig 4.10.SEM results for 40K Series gel swollen in 0.25% NaCl solution after exposure to CO_2 at 100µm

Fig 4.11.SEM results for 40K Series gel swollen in 0.25% NaCl solution after exposure to CO_2 at 10 µm

However, it is to be noted that this gel was re-swollen after exposure to CO_2. That being said, the gel already had some NaCl trapped in it. Replenishing the solution it was re-swollen in should have brought the NaCl content in PPG in equilibrium with the solution, theoretically speaking.

Two arguments can be presented after analyzing these results. It is either the increased salt content that has led to a tighter structure or it is the CO_2 that has led to shrinkage and a tightly held structure.

Also, from the pictures it can be concluded that there are no vivid structural differences in the PPG structure before and after exposure to CO_2. They only seem to get tighter after exposure to CO_2.

This could also be due to the increased salt content. Due to uncertainties, it was decided to check if CO_2 altered the structures chemistry. An FTIR test was conducted on the samples.

4.1.5. Fourier Transform Infrared Spectroscopy (FTIR). Fig 4.12 shows the IR spectrum for PPG swollen in 0.25% NaCl solution before exposure to CO_2. This particular sample was exposed to CO_2 at 2500 psi at a temperature of 65 deg C for 5 days.

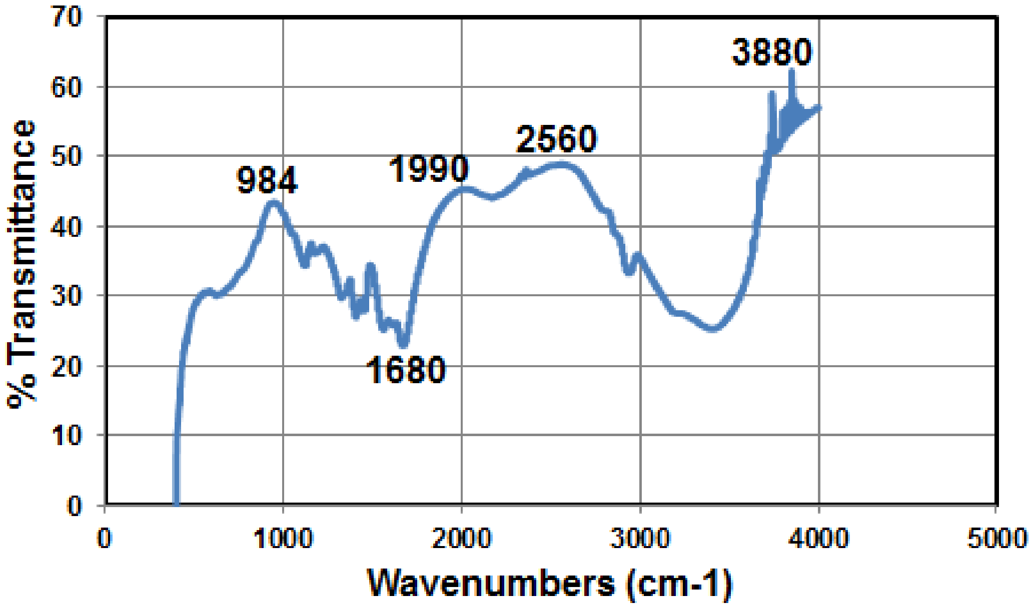


Fig 4.12.FTIR results for 40K Series gel swollen in 0.25% NaCl solution before exposure to CO_2

Fig 4.13 shows the IR spectrum for PPG swollen in 0.25% NaCl solution after exposure to CO_2.

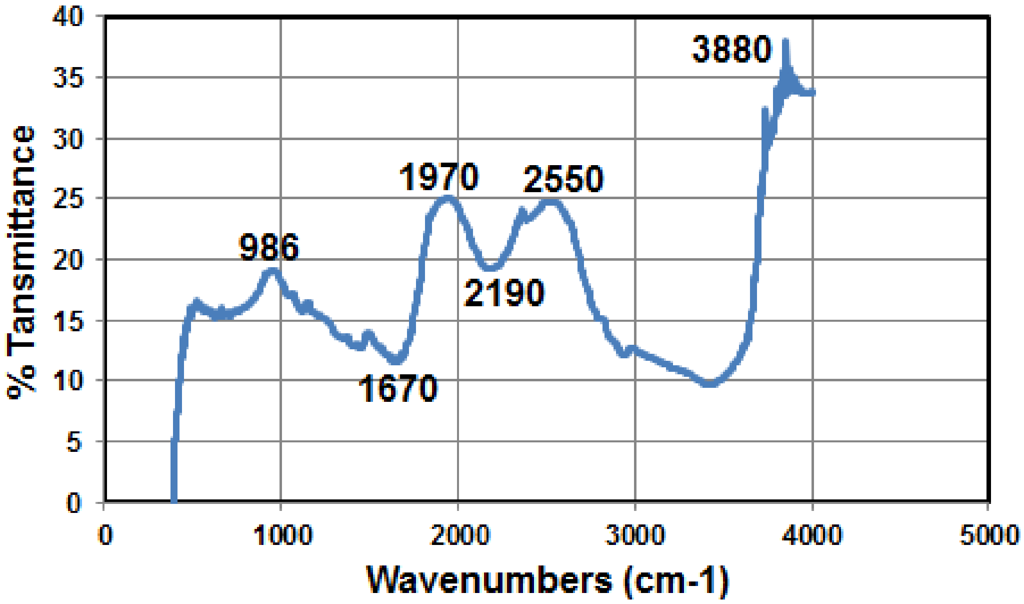


Fig 4.13.FTIR results for 40K Series gel swollen in 0.25% NaCl solution after exposure to CO_2

Comparing the IR absorption bands for this PPG sample before and after exposure to CO_2, it can be seen that the IR absorption band at 2190 cm^{-1} is very predominant after the gel has been exposed to CO_2. The other IR absorption bands are in the same range. This was seen in gels swollen in 1.0% NaCl and 10.0% NaCl solutions as well.

4.1.6. Further Investigations. In order to try and find out why the gel was expelling water further investigations were conducted.

4.1.6.1. Gels exposed to nitrogen. On finding that 40K Series gels exposed to CO_2 dehydrate, it was decided to expose the gels to nitrogen and check for dehydration. It was decided to run tests with nitrogen because it is an inert gas unless exposed toextreme conditions. nitrogen remains an inert gas under the conditions that these samples are tested in. Nitrogen had no effect whatsoever on the gel. PPG swollen in DI, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution was exposed to nitrogen at 500 psi for 1 day, 3 days and 5 days at 65 deg C. In all cases, the gel was found to be completely stable and did not show any dehydration. The results led us to believe that the acidic nature of the gas was responsible for the instability or that CO_2 was reacting with the PPG structure and changing its chemistry.

4.1.6.2. Check to see if pH was responsible for dehydration and reduction in swelling ratio on exposure to CO_2. In order to check for the effects of pH alteration on this gel, solutions of different pH (0.5, 2.0, 3.0 and 3.5) prepared with concentrated hydrochloric acid and distilled water were used. The gels were first swollen in their respective solutions and their swelling ratio was measured as discussed before. Please note that the solution the gels were swollen in were flushed every half an hour and replenished for up to 5 hours; as explained by Imqam, A. et al., 2016.

Following this, the gels were placed in an oven at 65 deg C for 96 hours as explained under the procedure of re-swell. These dried gels were now re-swollen in their respective solutions (same solution pH as before). The solution used for re-swell was also flushed every half an hour for up to 5 hours.

The reason for replenishing the solution was to ensure that the pH of PPG is in equilibrium with the solution in time. (This gel has a pH value of 5.0-6.0 [24] as manufactured).

Table 4.13 shows results for the swelling ratio, re-swell ratio and the re-swell percentage.

Table 4.13.Effect of pH on Re-swell

Solution pH in which PPG was swollen	0.5	2.0	3.0	3.5
Swelling Ratio	5.956	31.237	117.190	238.920
Re-swell ratio	2.111	12.029	57.160	163.350
Re-swell %	35.44 %	38.47 %	48.78 %	68.37 %

As seen, the re-swell capacity of the gel deteriorates as the pH reduces/acidity increases.

The results clearly indicate that pH has a profound effect on reducing the re-swelling capacity of this gel. The solubility of CO_2 increases with increasing pressure (Henry, W., 1803). In 2015, Laurent Truche et al. reported that the pH of water-NaCl-CO_2 solutions varied with the change in NaCl concentrations (Laurent Truche et al., 2016). Based on the varying pH values measured for their sample solutions, these ranges of pH were decided to be tested on PPG.

4.1.6.3. Chemical analysis of dehydrated water. After checking for any degradation from gel strength and checking for any changes in the chemical structure of the gel post exposure to CO_2, it was decided to analyze the free water collected at the bottom of the vessel.

The objective for this test was to try and reconfirm that no polymer/cross-linker was expelled by the gel when exposed to gas. Fig 4.14 shows pictures of chemical analysis of the dehydrated water.

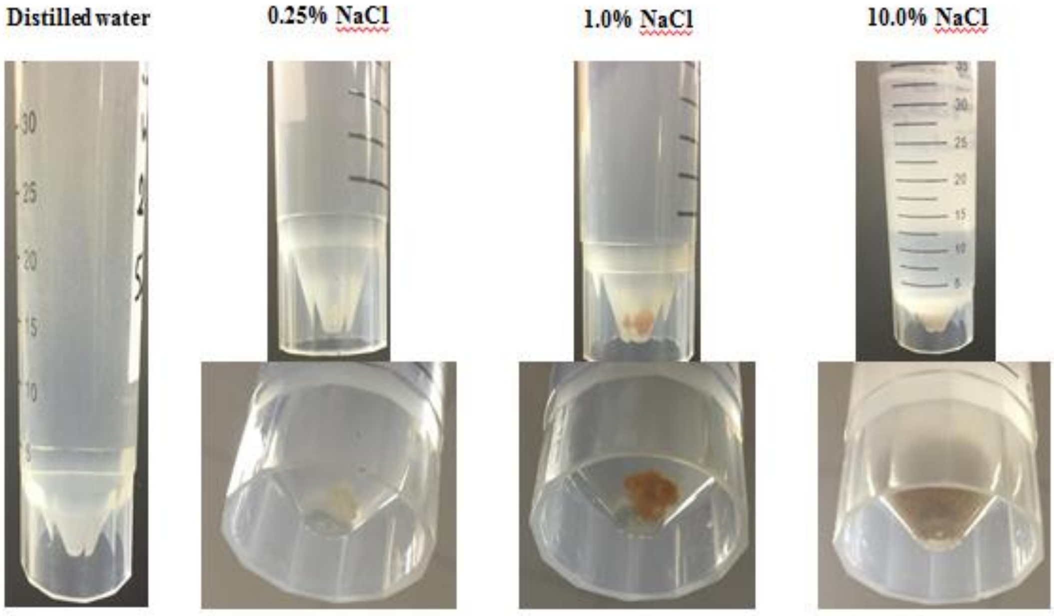


Fig 4.14.Chemical analysis of dehydrated water

Samples exposed to CO_2 at 2500 psi for 1 day have been used for this analysis. The free water collected from 40K gel swollen in DW, 0.25% NaCl solution, 1.00% NaCl solution and 10.00% NaCl solution are collected in test tubes. The test tube is topped up with acetone and the test tubes are heated at 40 deg C for half an hour. On shaking the tubes, dissolved substances are seen to separate out of clear solution and they settle down at the bottom of the test tube as seen in Fig 4.14.

For the free water collected from samples swollen in DW, no residue is found. But dissolved substances clearly phase out from free water collected in case of samples swollen in salt solutions. The amount of residue increases with the increasing salt solution.

The residue is separated from the clear solution using a fine mesh. This residue is mixed with DW to check if it dissolves completely in it. The residue did completely mix into DW and it can be concluded that it is the expelled salt.

4.1.6.4. Check for pH. Three attempts were made to check if the pH of the gel swollen in different salt concentrations exposed to CO_2 had different pH values. Unfortunately all the attempts failed. Following this step a literature review was conducted wherein it was discovered that a researcher, Laurent Truche et al. reported in 2015 that the pH of water-NaCl-CO_2 solutions varied with the change in NaCl concentrations. The effect of varying pH on the gels re-swell ratio was then tested as described before. The three attempts made to check for pH are as follows:

1. A pH strip was placed inside the high pressure vessel when the gels were placed inside and pressurized with CO_2. The pH strip was placed inside the bottom piece. The strip completely turned greyish in colour, not allowing the estimation of pH.
2. A digital pH meter was used to measure the pH. The gels before and after exposure to CO_2 were mixed in the solvent they were swollen in for the analysis. The results indicated different pH values for different amounts of gel sample size. Thus, this method was not an accurate measure of the pH.
3. Next, the samples before and after exposure to CO_2 were once again tested using a pH strip. This time, the strips were not placed inside the vessel, but single particles before and after exposure to CO2 were placed on the strip. The strip gave a standard measure of 3.5 for all samples. This method cannot be accurate because CO_2 which might have entered the gels structure will come

into equilibrium with atmosphere when the sample is exposed to the open. Thus, in conclusion, these three methods to test pH of gels before and after exposure to CO_2 can be considered as failed attempts.

5. RESULTS ANALYSIS AND DISCUSIONS PART II

5.1. CO_2 RESISTANT GEL (CRG)

CRG is a novel gel synthesized in Missouri S&T. It's composition is still confidential. Experiments have been performed on these gels to compare their performance characteristics to 40K series gel.

5.1.1. Dehydration. Just as for 40 K series gel, around 50 grams of sample, measured up to 4 decimal places, is placed inside the high pressure cylinders. It reduces in weight as the water in the swollen gel is expelled on exposure to CO_2 and drains to the bottom of the cylinder. The weight loss percentage for each case as before:

Weight loss % = (Weight lost by swollen PPG after exposure to CO_2*/Weight of swollen PPG placed in the vessels prior exposure to* CO_2*) x 100*

CRG is also swollen in 4 different solutions: DW, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution. For the gel swollen in each of the mentioned solutions, 12 sets of experiments are performed at 3 different pressures of 500 psi, 1100 psi and 1900 psi at 65 deg C for 1 day, 3 days and 5 days. Once again, please note that the results presented indicate the percentage of weight loss on exposure to CO_2. Higher percentage of weight loss on exposure to CO_2 indicates higher dehydration.

Fig 5.1 shows the weight loss percentage for 40K series gel swollen in distilled water and exposed to CO_2. From the figure it is seen that the amount of water expelled by the gel is directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for.

The weight lost due to dehydration is very low for CRG swollen in DW. The gels lose between 2.606% and 4.872% of water absorbed on exposure to the gas from experiments. Weight loss is definitely not a preferable phenomenon, but, the experiments indicate a very minimal loss in weight due to dehydration.

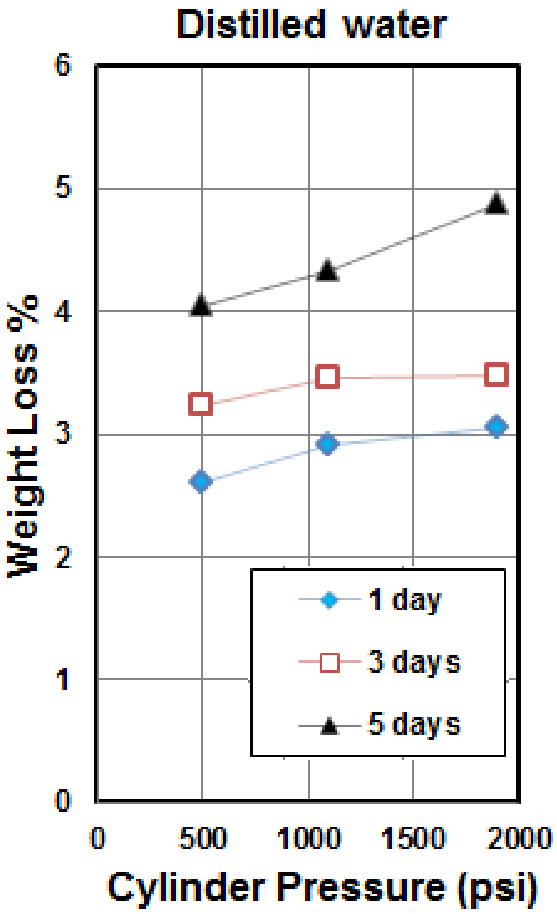


Fig 5.1.Dehydration for CRG swollen in distilled water when exposed to CO_2

The results for the weight loss percentage for each of the experiments are recorded in Table 5.1.

Table 5.1 Dehydration for samples swollen in distilled water

Weight loss %			
Pressure (psi)	Samples swollen in Distilled Water		
	1day	3days	5days
500	2.606	3.235	4.051
1100	2.904	3.459	4.321
1900	3.057	3.474	4.872

Fig 5.2 shows the weight loss percentage for CRG swollen in 0.25% NaCl solution and exposed to CO_2. From the figure it is seen that the amount of water expelled by the gel is again directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for. The weight lost due to dehydration is almost the same in this case when compared to CRG swollen in DW.

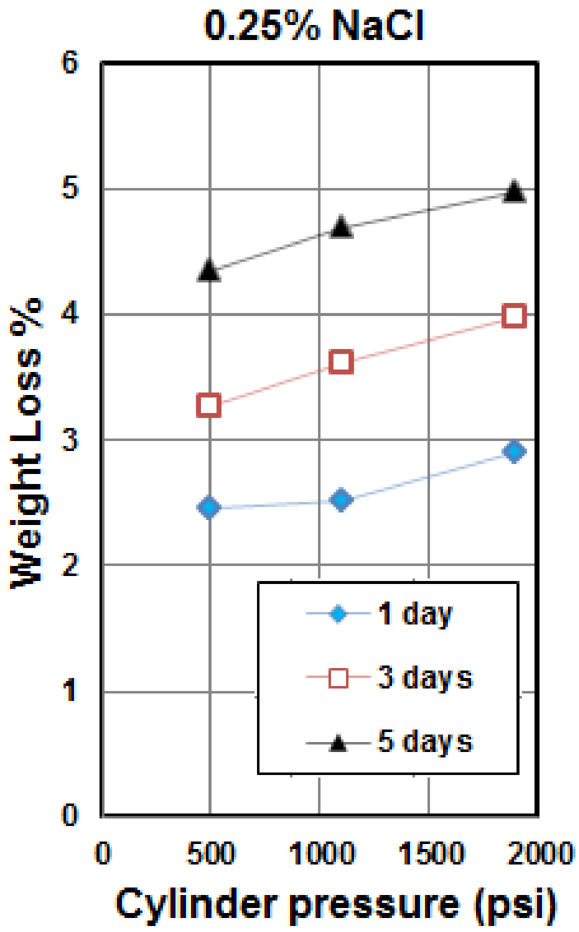


Fig 5.2.Dehydration for CRG swollen in 0.25% NaCl Solution when exposed to CO_2

The gels lose between 2.465% and 4.975% of water absorbed on exposure to the gas from experiments. The loss in weight is again not preferable, but it is seen that the performance of this gel when swollen in salt solution and exposed to CO_2 is almost similar to the previous case.

The results for the weight loss percentage for each of the experiments are recorded in Table 5.2.

Fig 5.3 shows the weight loss percentage for CRG swollen in 1.00% NaCl solution and exposed to CO_2. It is seen that the amount of water expelled by the gel is again directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for. This is illustrated in Fig 5.3.

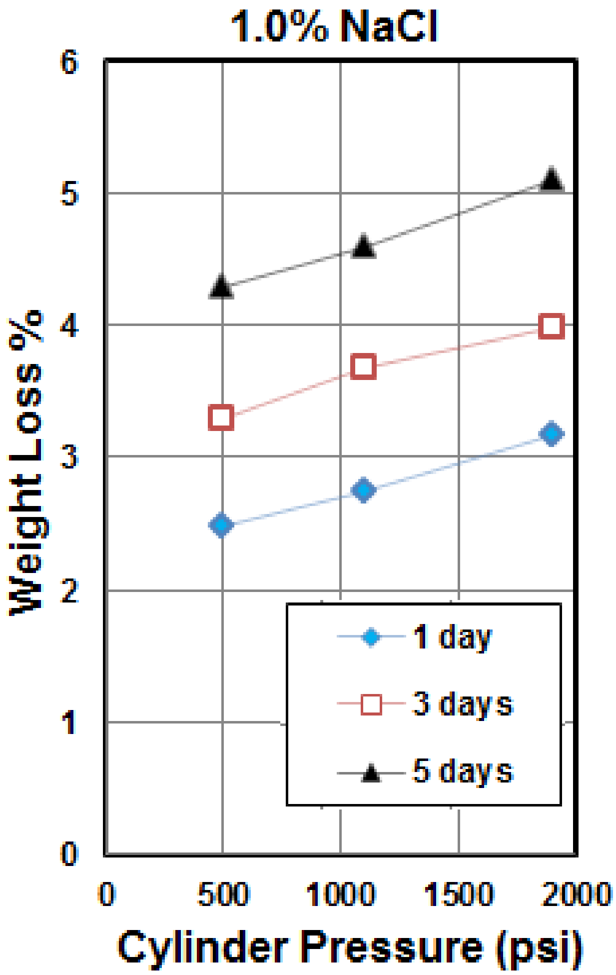


Fig 5.3.Dehydration for CRG swollen in 1.00% NaCl Solution when exposed to CO_2

The weight lost due to dehydration is again almost similar in this case when compared to the last 2 cases. The gels lose between 2.489% and 5.098% of water absorbed on exposure to the gas from experiments. The loss in weight is once again not preferable, but it is seen that the performance of this gel, when swollen in salt solution with an even more increased percentage of salt and exposed to CO_2, does not change much when compared to the previous two cases.

The results for the weight loss percentage for each of the experiments are recorded in Table 5.3. Table 5.2 shows the results recorded for the dehydration of CRG swollen in 0.25% NaCl solution.

Table 5.2.Dehydration for CRG swollen in 0.25% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 0.25% NaCl solution		
	1day	3days	5days
500	2.465	3.271	4.346
1100	2.522	3.618	4.689
1900	2.895	3.977	4.975

Table 5.3.Dehydration for CRG swollen in 1.00% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 1.00% NaCl solution		
	1day	3days	5days
500	2.489	3.295	4.291
1100	2.754	3.681	4.582
1900	3.161	3.992	5.098

Fig 5.4 shows the weight loss percentage for CRG swollen in 10.00% NaCl solution and exposed to CO_2.

In this last case as well, it is seen that the amount of water expelled by the gel is directly proportional to the increase in pressure and to the period of time that the gel is exposed to CO_2 for.

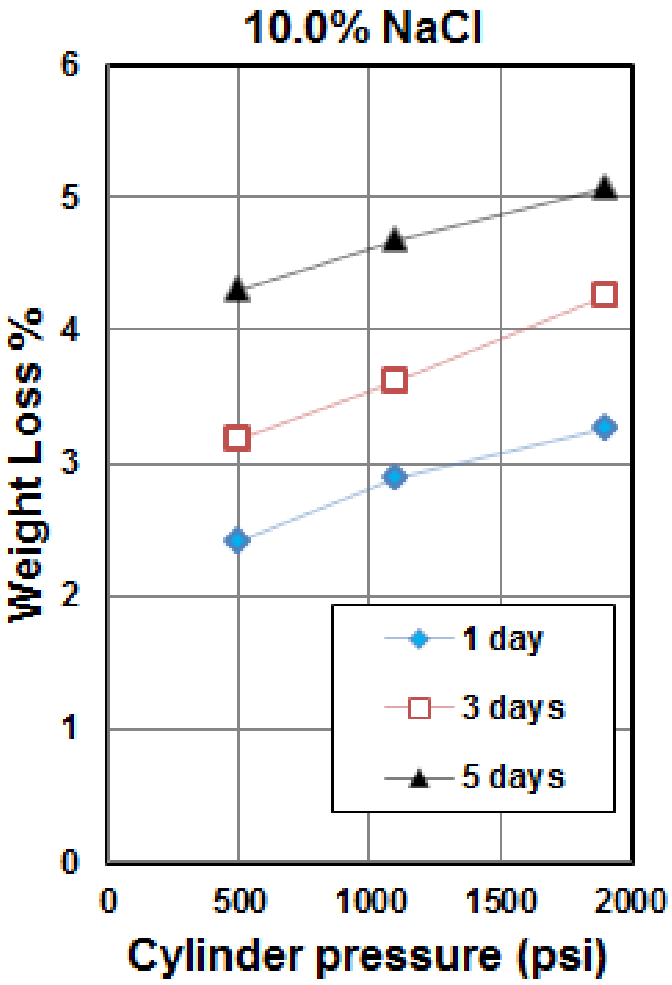


Fig 5.4.Dehydration for CRG swollen in 10.00% NaCl Solution when exposed to CO_2

The weight lost due to dehydration is once again almost same in this case when compared to the last 3 cases. The gels lose between 2.418% and 5.075% of water absorbed on exposure to the gas from experiments. The loss in weight is again not preferable, but it is seen that the performance of this gel, when swollen in salt solution with a much more increased percentage of salt when exposed to CO_2, is almost similar compared to the previous three cases.

The first observation made from the results is that the dehydration for CRG in presence of CO_2 is not affected too much by the salt concentration.

For example, the weight loss percentage of CRG swollen in DW and exposed to CO_2 pressurized to 1900 psi for 5 days is seen to be 4.872% and the weight loss percentage of CRG swollen in 10.0% NaCl solution and exposed to CO_2 pressurized up to 1900 psi for 5 days is seen to be 5.075%.

The results for the weight loss percentage for each of the experiments are recorded in Table 5.4.

Table 5.4.Dehydration for CRG swollen in 10.00% NaCl Solution

Weight loss %			
Pressure (psi)	Samples swollen in 10.00% NaCl solution		
	1day	3days	5days
500	2.418	3.188	4.299
1100	2.892	3.619	4.670
1900	3.261	4.255	5.075

Secondly, it is noticed that the dehydration for each case increases with increasing pressure of CO_2 that the gel is exposed to. But, this increase is not much. For example, the weight loss percentage for PPG swollen in 0.25% NaCl solution and exposed to CO_2 pressurized up to 500 psi for 5 days is seen to be 4.346%. The weight loss percentage increases to 4.689% and 4.975% when the pressure is increased to 1100 psi and 1900 psi respectively.

Thirdly, the samples are exposed for 3 different time periods to check if the duration of exposure to CO_2 has any effect on the gel. This is seen to increase with increasing time of exposure to gas. Once again, this increase is only to an order of around 1.0% weight loss increase per day, which is not very much. For example, the weight loss percentage for CRG swollen in 1.0% NaCl solution and exposed to CO_2

pressurized up to 500 psi for 1 day is seen to be 2.489%. At the same pressure, the weight loss percentage increases to 3.295% and 4.291% when exposed for 3 days and 5 days respectively.

5.1.2. Re-swell Ratio. The percentage of reduction in swelling is seen to vary with the salt concentration of solution the CRGG is swollen in. The percentage of re-swell is once again calculated as:

*Re-swell % = (Number of times PPG swells after exposure to CO_2/ Number of times PPG swells before exposure to CO_2)] *100*

1 day and 5 day samples from CRG swollen in each of the salt concentrations are used for analyzing the re-swell ratio. Varying pressures do not affect the re-swell as suggested by results. Table 5.5, Table 5.6, Table 5.7 and Table 5.8 show the number of times the gel re-swells after exposure to CO_2.

Table 5.5.Number of times CRG re-swells in distilled water

Pressure (psi)	Distilled Water	
	1day	5days
500	10.069	10.085
1100	10.032	10.006
1900	9.995	9.987
Average:	10.029	

Table 5.6.Number of times CRG re-swells in 0.25% NaCl solution

Pressure (psi)	Distilled Water	
	1day	5days
500	9.951	9.917
1100	9.860	9.912
1900	9.856	9.826
Average:	9.887	

Table 5.7.Number of times CRG re-swells in 1.00% NaCl solution

Pressure (psi)	Distilled Water	
	1day	5days
500	9.592	9.525
1100	9.578	9.505
1900	9.511	9.481
Average:	9.532	

Table 5.8.Number of times CRG re-swells in 10.00% NaCl solution

Pressure (psi)	Distilled Water	
	1day	5days
500	4.274	4.348
1100	4.311	4.268
1900	4.249	4.272
Average:	4.287	

The number of times CRG swells in solution reduces just like 40K series on exposure to CO_2, but the trend is very different. The blue dots are indicative of the number of times dry CRG swells in DW, 0.25% NaCl solution, 1.00% NaCl solution and 10.00% NaCl solution. The red dots show the reduced number after exposure to CO_2.

As seen, in the figure, CRG almost swells the same number of times before and after exposure to CO_2 for when it is swollen in DW, 0.25% NaCl solution and 1.00% NaCl solution and exposed to CO_2. However, the gel swells only about half the number of times before and after exposure to CO_2 for when it is swollen in 10.00% NaCl solution and exposed to CO_2. The data for the number of times that gel swells before exposure to CO_2 and after are presented in Table 5.9. Fig 5.5 represents the comparison of swelling ratio before and after exposure to CO_2 for CRG.

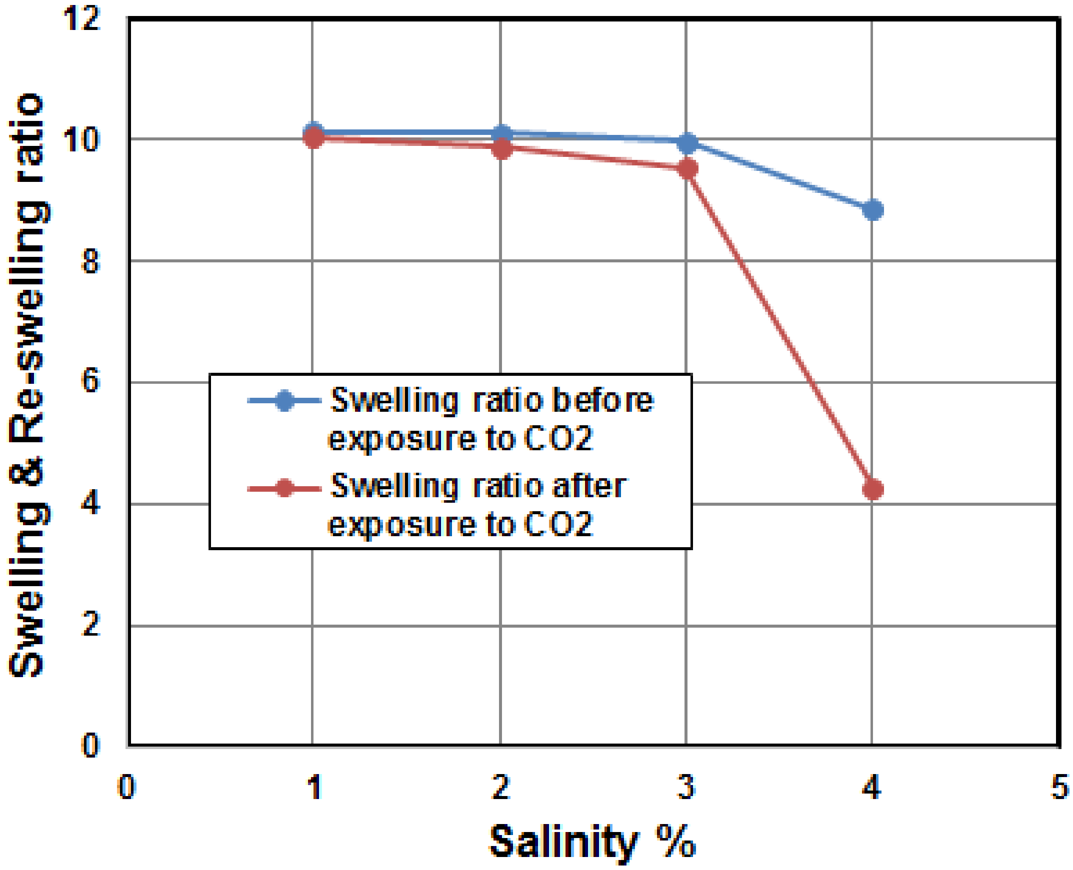


Fig 5.5.Comparison of swelling ratio before and after exposure to CO_2 for CRG

Table 5.9.Comparison of the number of times CRG swells in respective solution before and after CO_2

	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
	Number of times CRG swells			
Before CO_2	10.141	10.098	9.966	8.865
After CO_2	10.029	9.887	9.532	4.287

In order to simplify and present the data, an average of the 1 day and 5 day samples have been used. From the results, CRG swollen in DW, 0.25% NaCl, 1.0% NaCl and 10.0% NaCl solutions when exposed to CO_2 at pressures varying from 500 psi – 1900 psi will swell 10.029, 9.887, 9.532 and 4.287 times respectively.

High salinity of the solution alone is seen to affect the re-swell of gel. Fig 5.6 shows the % ee-swell for CRG swollen in different solutions.

With increasing salinity the re-swelling capacity of CRG does not reduce much until the salinity is as high as 10.00%. Giving an example, it can be seen that CRG swollen in DW and exposed to CO_2 swells 98.89% of what it did before it was exposed to CO_2. Also, CRG swollen in 0.25% NaCl and 1.00% NaCl solutions, exposed to CO_2 swells 97.91% and 95.64% respectively of what it did before it was exposed to CO_2. But, PPG swollen in 10% solution and exposed to CO_2 only swells about 48.36% of what it did before it was exposed to CO_2.

The percentage re-swell for each case is tabulated in Table 5.10 . Averages of the 1 day and 5 day values have been taken into account at each pressure.

In conclusion, re-swell is not affected by increasing pressures of CO_2. Also, it is noticed that the number of days for which PPG is exposed to CO_2 does not have a significant impact on this phenomenon. But, high salinity of solvent in which PPG is swollen in does have a drastic impact on the re-swell. The re-swell ratio for CRG is only affected by high salinity.

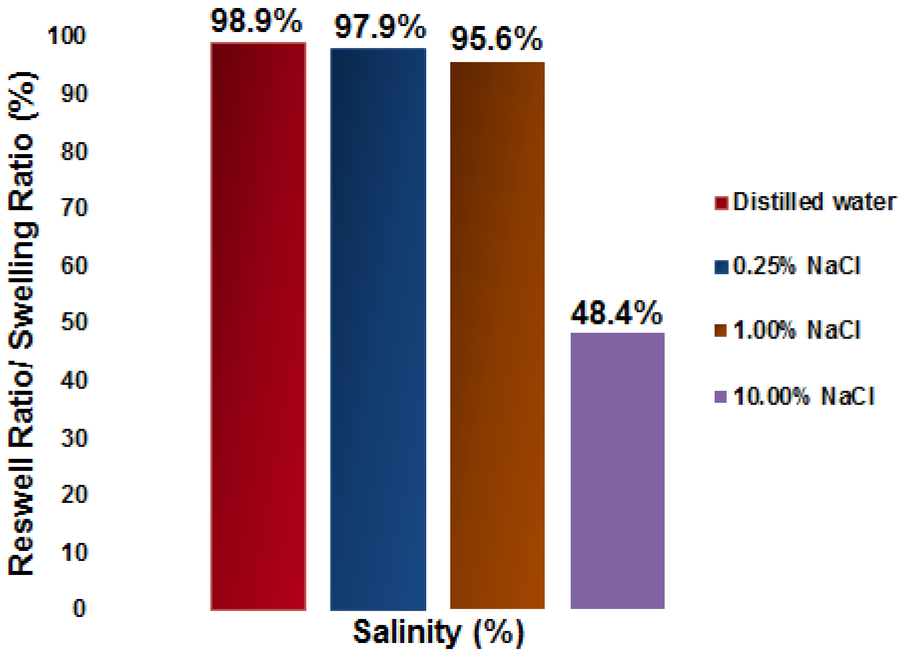


Fig 5.6.% swelling ratio for CRG after exposure to CO_2 compared to swelling ratio before exposure (Data in Table)

Table 5.10.Swelling ratio for CRG after exposure to CO_2 compared to swelling ratio before exposure

% Re-swell				
Pressure (psi)	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
500	99.37	98.38	95.91	48.63
1100	98.8	97.9	95.74	48.39
1900	98.52	97.45	95.28	48.06
Average:	98.89	97.91	95.64	48.36

5.1.3. Gel Strength. All the samples were analyzed at frequencies ranging from 0.1 Hz to 10 Hz and all of them were observed to be giving steady G' readings at a frequency of 1 Hz. Table 5.10 shows the G' values for CRG swollen in DI, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution before and after exposure to CO_2.

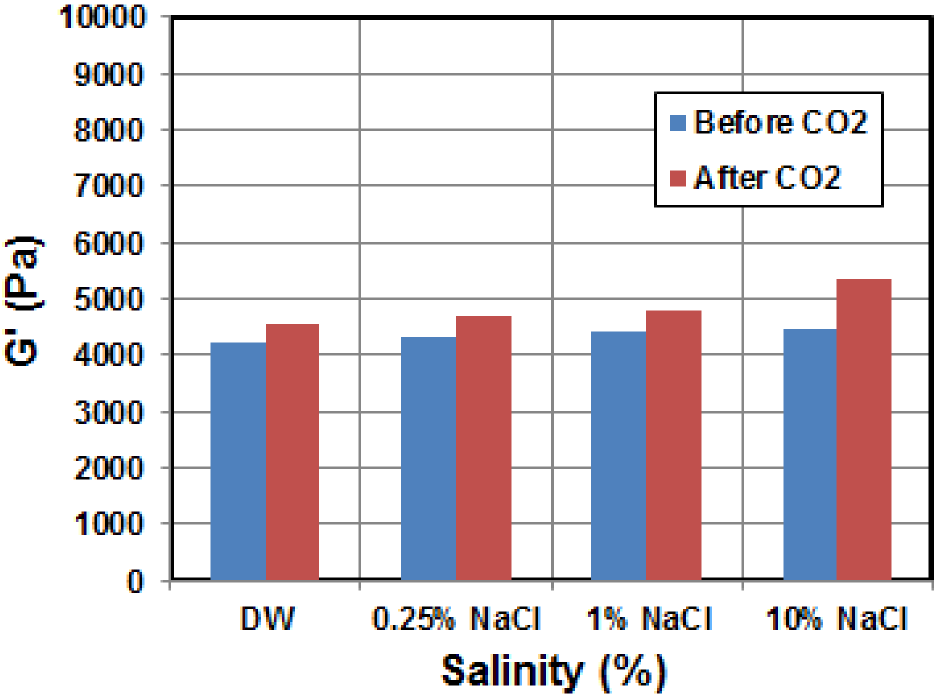


Fig 5.7.Gel strength of CRG before and after exposure to CO_2 in each case

Following that, the G' was measured for all the 1 day samples. Their average was taken for each case (graphical representation of the values in Fig). The G' values for CRG swollen in DW, 0.25% NaCl, 1.0% NaCl and 10.0% NaCl at 500 psi, 1100 psi and 1900 psi for 1 day were measured.

Similar to the Re-swell percentage, pressure did not seem to have any effect on the gel strength for CRG as well. Thus, an average of all the values for G' measured were taken for PPG swollen in solutions of different salt concentrations.

Table 5.11 shows the G' values for CRG swollen in DI, 0.25% NaCl solution, 1.0% NaCl solution and 10.0% NaCl solution before and after exposure to CO_2. The gel strength does not change much when exposed to varied pressures and time. Thus, an average of the values has been presented after exposure to CO_2.

Table 5.11.Gel strength of PPG before and after exposure to CO_2

G' (Pa)				
	Distilled Water	0.25% NaCl	1.0% NaCl	10.0% NaCl
Before CO_2	4210	4343	4409	4479
After CO_2	4566	4682	4765	5333

For CRG, the gel strength does not change much depending on the concentration of salt solution swollen in. Although, there is a slight increase in gel strength with increasing salt in the solution in which it swells. Also, on exposure to CO_2, the gel strength increases for every case, but the increase is not extremely high.

5.1.4. Scanning Electron Microscope (SEM). Gels swollen in 0.25% NaCl solution before and after exposure are studied under an SEM. The samples used were exposed to 1900 psi for 5 days. Fig 5.8 and Fig 5.9 show the gel network for sample which was not exposed to CO_2. Pictures seen are at 100µm and 10µm respectively. The gel network before exposure to CO_2 looks hazy.

From Fig 5.8 and Fig 5.9, the polymer and cross-linker networking is noticeable, but the network seems to exist in a premature stage. The pore spaces are where the brine exists, which cause the swelling. Fig 5.10 and Fig 5.11 are pictures of the same gel after being exposed to CO_2 at 100µm and 10µm respectively.

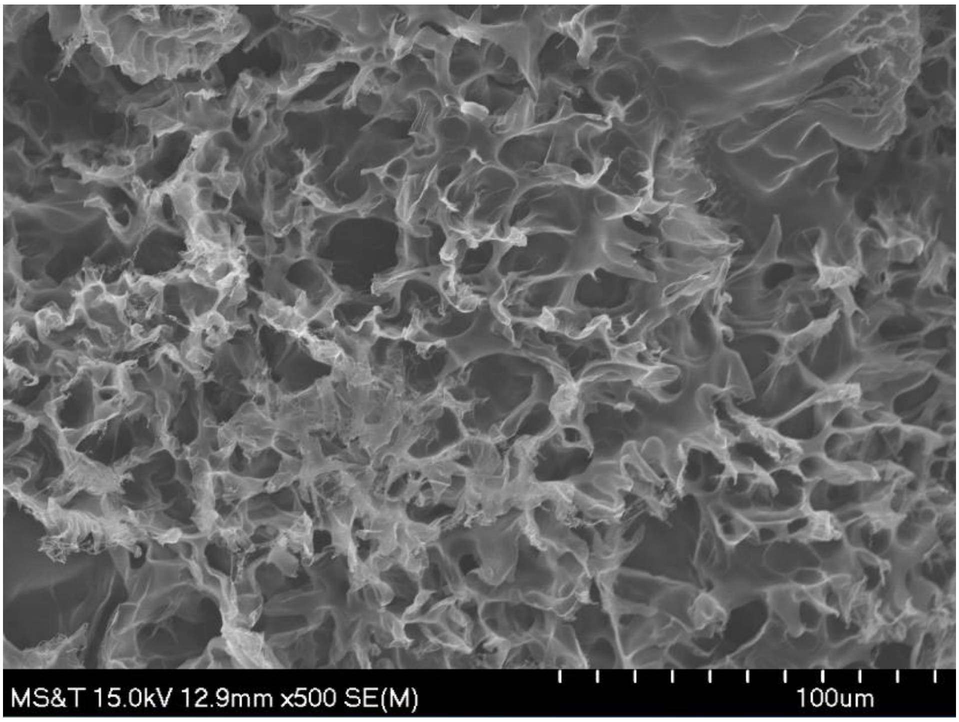


Fig 5.8.SEM results for CRG swollen in 0.25% NaCl solution before exposure to CO_2 at 100 μm

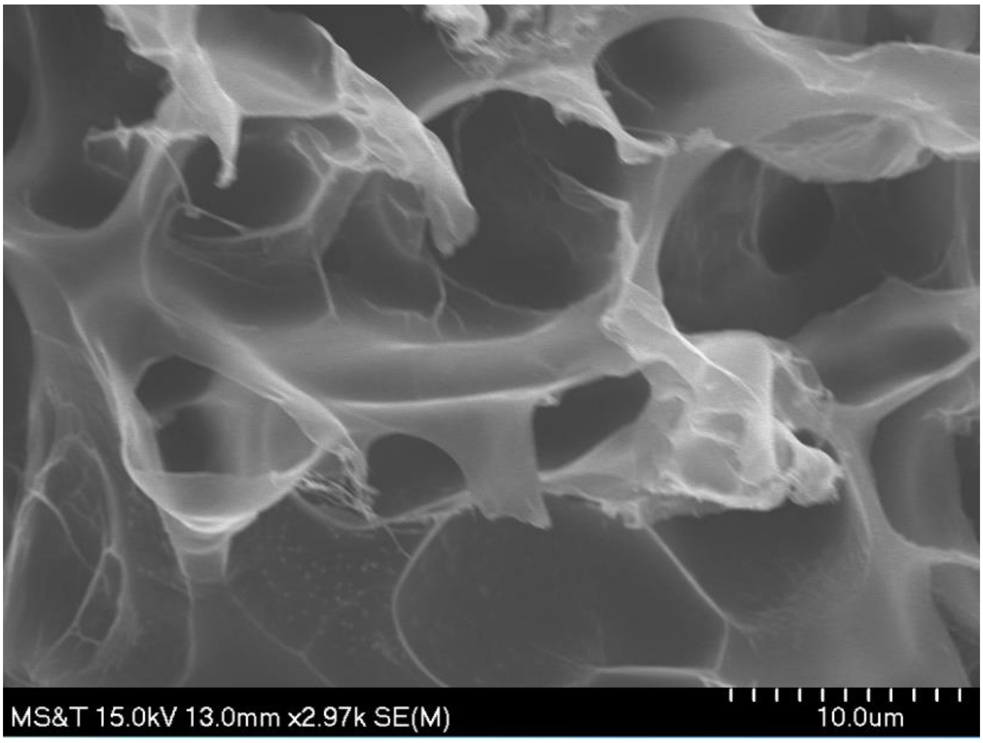


Fig 5.9.SEM results for CRG swollen in 0.25% NaCl solution before exposure to CO_2 at 10 μm

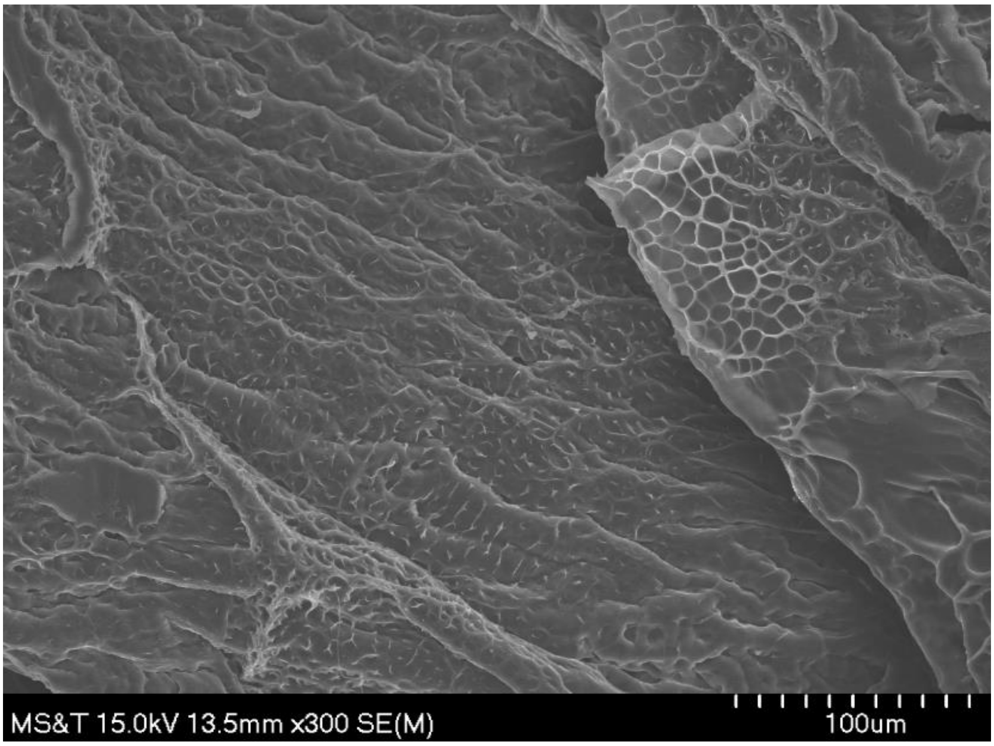


Fig 5.10.SEM results for CRG swollen in 0.25% NaCl solution after exposure to CO_2 at 100 μm

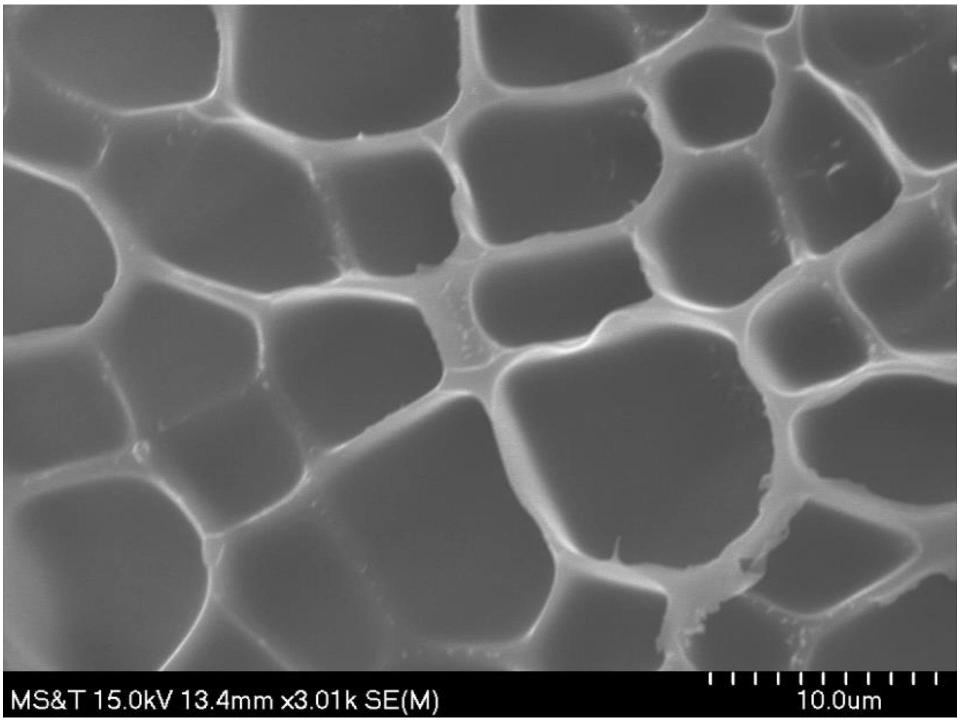


Fig 5.11.SEM results for CRG swollen in 0.25% NaCl solution after exposure to CO_2 at 10μ

As seen in Fig 5.10 and Fig 5.11 and comparing it to the gel network before exposure to CO_2, the polymer and cross-linker network does not seem to change post exposure.

5.1.5. Fourier Transform Infrared Spectroscopy (FTIR). Fig 5.12 shows the IR spectrum for CRG swollen in 0.25% NaCl solution before exposure to CO2. This particular sample was exposed to CO2 at 2500 psi at a temperature of 65 deg C for 5 days.

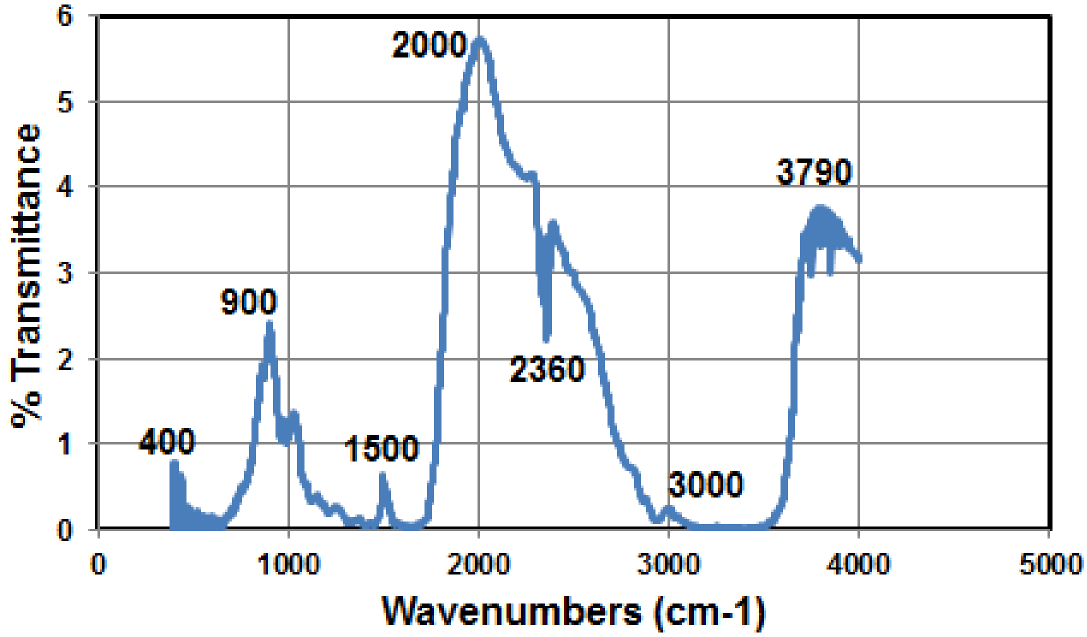


Fig 5.12.FTIR results for CRG swollen in 0.25% NaCl solution before exposure to CO_2

Fig 5.13 shows the IR spectrum for CRG swollen in 0.25% NaCl solution after exposure to CO_2.

Comparing the IR absorption bands for this CRG sample before and after exposure to CO_2, no different peak is noticed after exposure to gas. The IR absorption bands before and after exposure to CO_2 show peaks at wavenumbers in similar ranges. This was seen in gels swollen in 1.0% NaCl and 10.0% NaCl solutions as well.

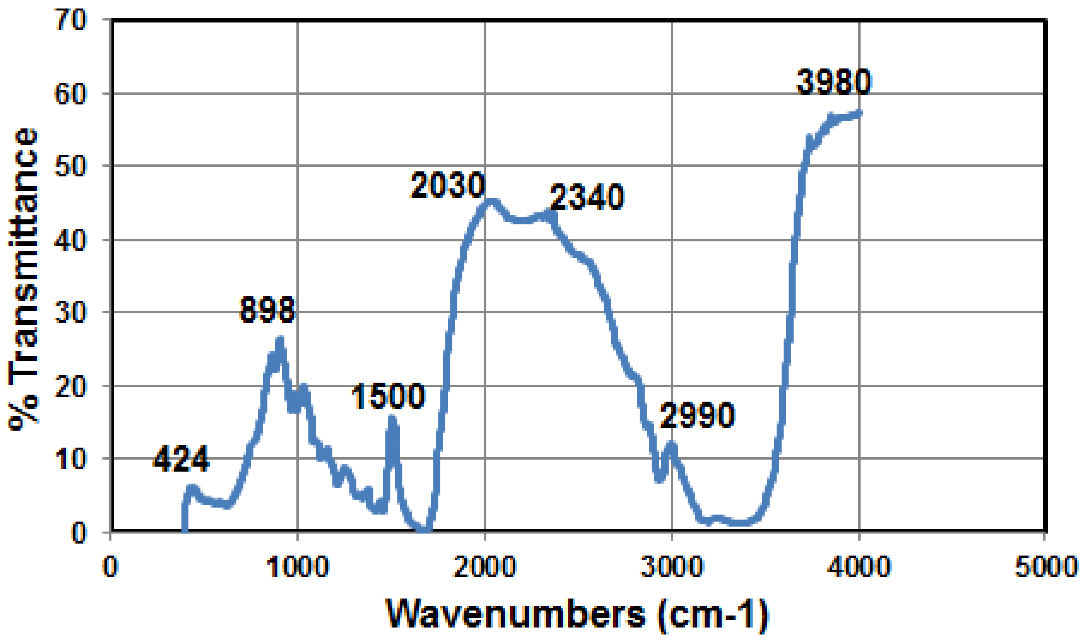


Fig 5.13.FTIR results for CRG swollen in 0.25% NaCl solution after exposure to CO_2

Results from FTIR suggest that there is no significant change in the chemistry of the gel on exposure to CO_2.

6. CONCLUSIONS AND RESEARCH BENEFITS

6.1. CONCLUSIONS

1. Compiling results from all the experiments performed and comparing the dehydration of 40K and CRG in presence of CO_2, it is seen that CRG is much more stable in presence of CO_2 than 40K gel. Fig 6.1 and Fig 6.2 below show the compiled results of dehydration for 40K and CRG respectively.

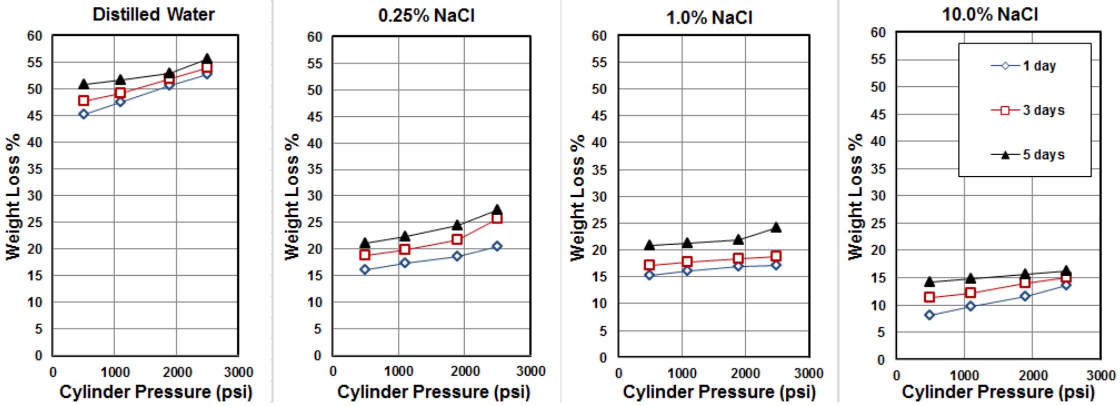


Fig 6.1.Compiled results for dehydration of 40K gel

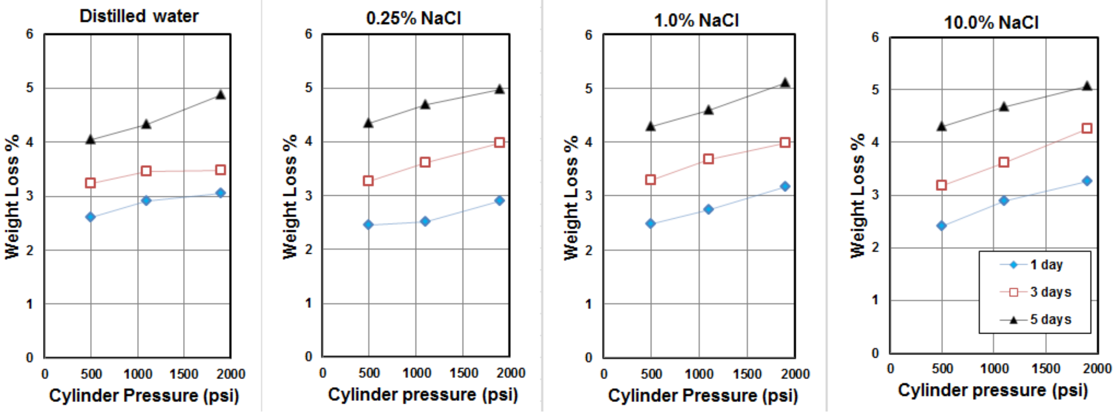


Fig 6.2.Compiled results of dehydration for CRG

As seen from the figures above, the percentage Dehydration for 40K series gel ranges between a minimum of 8.1% and a maximum of 55.5% from all the sets of experiments performed. On the other hand, for all the experiments done for CRG, the percentage Dehydration ranges between a minimum of 2.4% and a maximum of 5.1%.

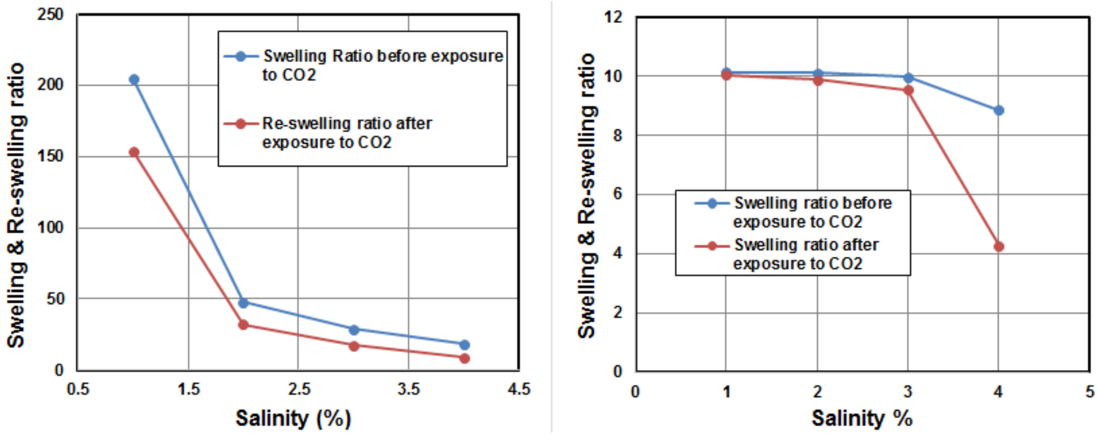
Analyzing dehydration as a function of CO_2 pressure that the gels are exposed to, both gels are seen to expel more water as the pressure increases. Although it can be said that as pressure increases, the dehydration does not profoundly increase. This conclusion applies to both 40K series gel and to CRG.

Analyzing dehydration as a function of salt solution swollen in 40K series gel shows better performance than when swollen in higher salt concentration and exposed to CO_2. In other words, 40K gel swollen in distilled water and exposed to CO_2 dehydrates much more than 40K series gel swollen in 10% NaCl solution and exposed to CO_2. For CRG, the concentration of salt in the solution in which it is swollen does not affect the dehydration. CRG swollen in distilled water and exposed to CO_2 dehydrates to almost the same extent as CRG swollen in 10% NaCl solution exposed to CO_2.

Lastly, analyzing dehydration as a function of time, it is seen that for both 40K series gel and for CRG the dehydration increases when exposed to CO_2 for longer periods of time.This comparison shows that 40K series gel swells much lesser when exposed to $CO_{2,}$ whereas exposure to CO_2 does not affect the re-swell as much.

40K series gel re-swells lesser number of times on exposure to CO_2 than before exposure to CO_2. These gels swollen in DW, 0.25% NaCl, 1.00% NaCl and 10.0% NaCl solutions re-swell to 75.14% (they swell 205 times before exposure to CO_2 and swell 154.04 times after exposure to CO_2) , 67.18% (they swell 47.69 times before exposure to CO_2 and swell 32.05 times after exposure to CO_2), 60.64% (they swell 28.82 times before exposure to CO_2 and swell 17.44 times after exposure to CO_2) and 49.2% (they swell 18.69 times before exposure to CO_2 and swell 9.21 times after exposure to CO_2) of their original state.

CRG re-swells almost the same number of times on exposure to CO_2 than before exposure to CO_2. These gels swollen in DW, 0.25% NaCl, 1.00% NaCl and 10.0% NaCl solutions re-swell to 98.89% (they swell 10.141 times before exposure to CO_2 and swell 10.029 times after exposure to CO_2) , 97.91% (they swell 10.098 times before exposure to CO_2 and swell 9.887 times after exposure to CO_2), 95.64% (they swell 9.966 times before exposure to CO_2 and swell 9.532 times after exposure to CO_2) and 48.36% (they swell 8.865 times before exposure to CO_2 and swell 4.287 times after exposure to CO_2) of their original state. The ability of CRG to re-swell on exposure to CO_2 is seen to be excellent up to salt concentrations of 1.0% NaCl, but at a higher salt concentration of 10.0% the re-swell capacity is drastically reduced. This is because salt occupies most of the pore space in the gel, not allowing solution water to be absorbed. Fig 6.3 shows the compiled results of Re-swell for 40K and CRG respectively.



Figs 6.3.Comparing re-swell of 40K gel (left) and CRG (right)

3. Firstly, the gel strength for CRG is much more than that of 40K series gel when swollen. 40K has gel strength of 805 Pa, 1309 Pa, 1406 Pa and 1761 Pa when swollen in DW, 0.25%, 1.0% and 10.0% NaCl solutions. On the other hand, CRG has gel strength of 4210 Pa, 4343 Pa, 4409 Pa and 4479 Pa when swollen in DW, 0.25%, 1.0% and 10.0% NaCl solutions.

After exposure to CO_2, the gel strength for 40K increases quite a lot. It increases to 1063 Pa, 1567 Pa, 1652 Pa and 2122 Pa. This is because the gel expels water and this dehydration makes the gel structure tighter increasing the gel strength. On the other hand, on exposure to CO_2, the strength for CRG increases to 4566 Pa, 4682 Pa, 4765 Pa and 5333 Pa. This increase in gel strength is also because of the expulsion of water in the gel. Fig 6.4 below is the compiled results for gel strength measured for 40K series gel and for CRG before and after exposure to CO_2.

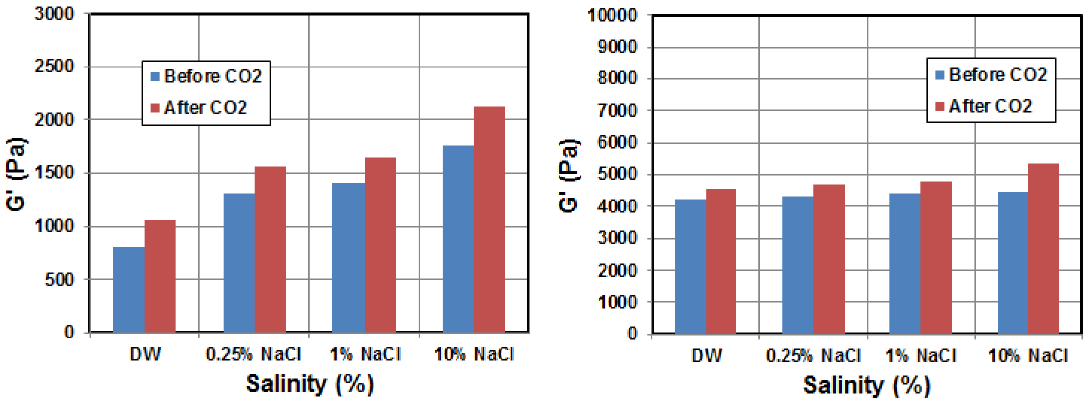


Fig 6.4.Comparing gel strength of 40K gel (left) and CRG (right)

Analyzing gel strength as a function of salt solution swollen in, the gel strength for 40K series gel is seen to increase quite a lot with increasing salt solution in which it is swollen. This is not the case for CRG. For CRG, though the gel strength does increase with increasing salt solution in which it is swollen, but, the order of increase is minimal.

4. Results from SEM show that for 40K series gel, there are no vivid structural differences in the PPG structure before and after exposure to CO_2. They only seem to get tighter after exposure to CO_2. This could also be due to the increased salt content. On the other hand, for CRG, the polymer and cross-linker network do not seem to change at all on exposure to CO_2.

5. Results from FTIR analysis show that gel chemistry changes after exposure to CO_2 for 40K series gel, but, does not change for CRG.

In conclusion, an overall study of the mentioned gel performance characteristics show that CRG is much more stable when exposed to CO_2 than commercially available 40K series gel.

6.2. RESEARCH BENEFITS

An understanding of how 40K series gel and CRG behave when exposed to CO_2 in static conditions has been presented in this research. From the results presented, it is to be noted that CO_2 causes dehydration of these cross-linked polymer gels. The goal while synthesizing gels to be used in CO_2 flooding projects should be to try and reduce dehydration. Also, this pilot study paves way for a detailed study of 40K series gel and CRG in dynamic conditions.

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VITA

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