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Shudai Peng

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OVERVIEW OF CO_2 LEAKAGE PROBLEMS AND SEALANTS FOR CO_2 LEAKAGE REMEDIATION

by

SHUDAI PENG

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Approved by

Baojun Bai, Advisor
Mingzhen Wei
Ralph E. Flori, Jr.

ABSTRACT

Excessive Carbon Dioxide (CO_2) emission has become a serious issue and caused lots of environmental problems. Carbon Capture and Storage (CCS) program has been developed to reduce the CO_2 content in the atmosphere. CO_2 storage has been targeted mainly on depleted oil or gas reservoirs and deep saline aquifers. However, leakage could occur through wellbores, cap rocks, formation faults, and fractures during and after CO_2 injection. To minimize the risk, different types of sealants have been investigated to prevent CO_2 leaks. The aim of this thesis is to provide a comprehensive review of the materials which could be used as CO_2 sealants. Based on the difference of materials components, this research has classified the sealants into seven types, including cements, geopolymers, foams, gel systems, resin systems, biofilm barriers, and nanoparticles. For each type of sealants, its chemical components, physical properties, stabilities, impact factors, applied environments, advantages and limitations were summarized. The most commonly used sealant for CO_2 leakage control from wellbore is still cement, and the aluminate-calcium based cement has the best properties. It is very challenging to seal the fractures and faults, far from wellbore due to the difficulty to deliver plugging materials into the in-depth of a reservoir. The thermo-stability is also a great challenge for most materials and should be evaluated under supercritical CO_2 condition.

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1.1. PROBLEMS CAUSED BY CO_2

Excessive emission of carbon may cause lots of environmental problems and the worst one is the ‘Greenhouse Effect’. This phenomenon has happened mainly because excess CO_2 had been produced and discharged.

1.1.1. Excessive CO_2 Emission. Figure 1.1 shows the global CO_2 emission from the year 1980 to 2016, the CO_2 emission was kept increasing in the past twenty-six years. The ‘Greenhouse Effect’ is the source of the global warming which has caused the increase of plant diseases and insect pests, the rising of sea level, climate anomalies and extraordinary weathers, harming for human's health.

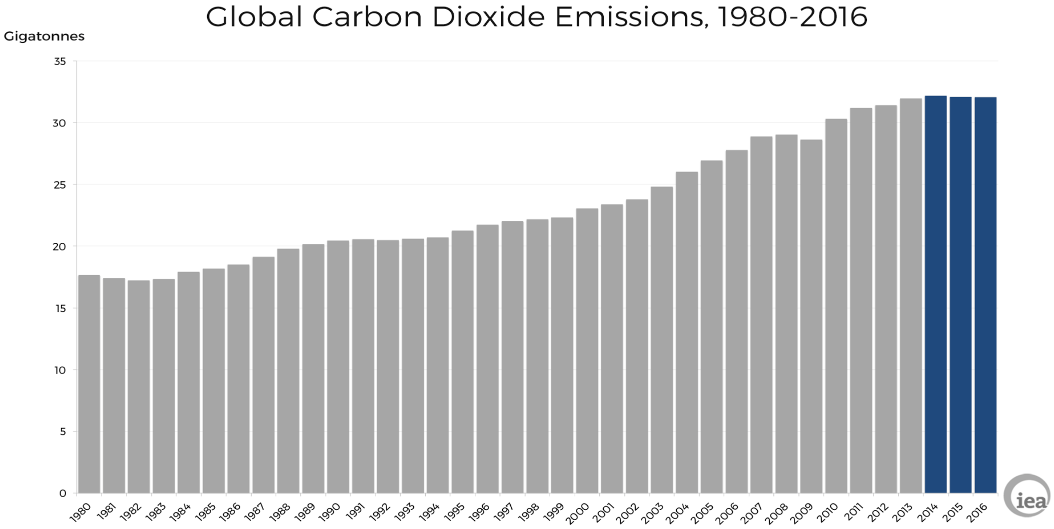


Figure 1.1. Global CO_2 emission from the year 1980 to 2016 (IEA, 2017)

1.1.2. CO_2 Sources. The CO_2 in the atmosphere has come from both natural sources and human-created (anthropogenic) sources.

CO_2 in the atmosphere mainly come from natural sources. Among all the natural sources, compared to other natural and human-created sources, oceans provide the largest volume of CO_2. Other sources of natural CO_2 include animal and plant respiration, decomposition of organic matter, forest fires, and emissions from volcanic eruptions. There are also naturally occurring CO_2 deposits found in rock layers within the Earth's crust that could serve as CO_2 sources (NETL).

Subsurface CO_2 leakage is also one of the largest natural CO_2 sources. The subsurface CO_2 exists mainly because of two reasons. The first reason is carbon produced by the buried material such as animals and plants' bodies. The second reason is injecting carbon to improve oil recovery as an EOR method. So far, CO_2 flooding has become one of the most widely used EOR methods.

Anthropogenic CO_2 also includes many sources such as subsurface CO_2 leakage, burning of fossil fuel, human breathing and so on. Among all these sources, electricity production has caused the largest CO_2 emission. Figure 1.2 shows the percentage of each kind of human-made CO_2 source.

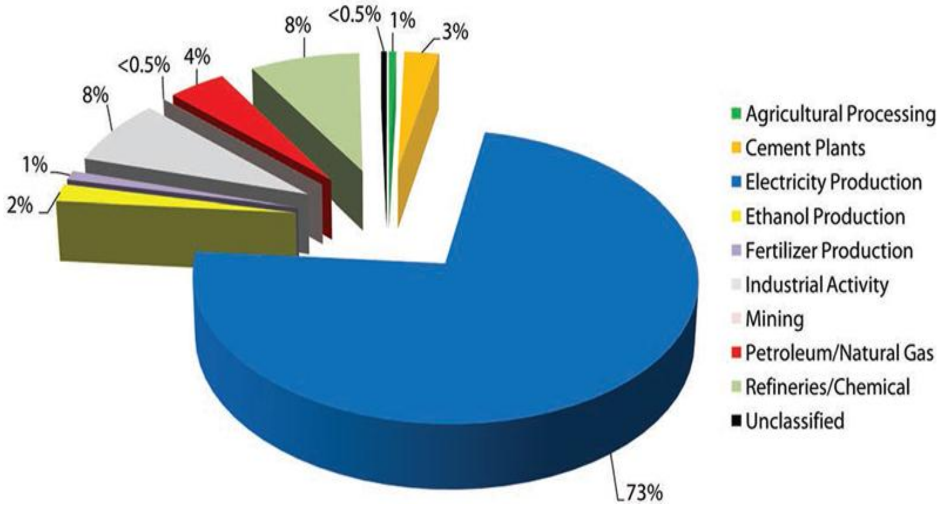


Figure 1.2. Anthropogenic CO_2 sources (NETL)

1.2. CO_2 CAPTURE AND STORAGE (CCS)

Superfluous CO_2 in the atmosphere has caused many problems. Hence that, the carbon dioxide capture project had been made and improved to solve these problems.

1.2.1. CCS Project. The CO_2 Capture and Storage (CCS) is an international partnership between the main energy companies, working alongside specialists from industry, technology providers and academia, to advance technologies and improve operational approaches to help make Carbon Capture and Storage (CCS) a viable option for CO_2 mitigation in the oil and gas industry. The CCS are renewing every year, which provides new carbon capture and storage strategies, policies, and laboratory and field tests reports.

1.2.2. CO_2 Storage Sites & Trapping Mechanisms. Saline aquifers and depleted oil/gas fields are the most commonly used CO_2 storage sites as Figure 1.3 shows. Therefore, CO_2 leakages always happen to these kinds of reservoirs. Table 1.1 illustrates the CO_2 trapping mechanisms of depleted oil and gas fields and saline aquifers. The storage sites favorable conditions have shown in Table 1.2.

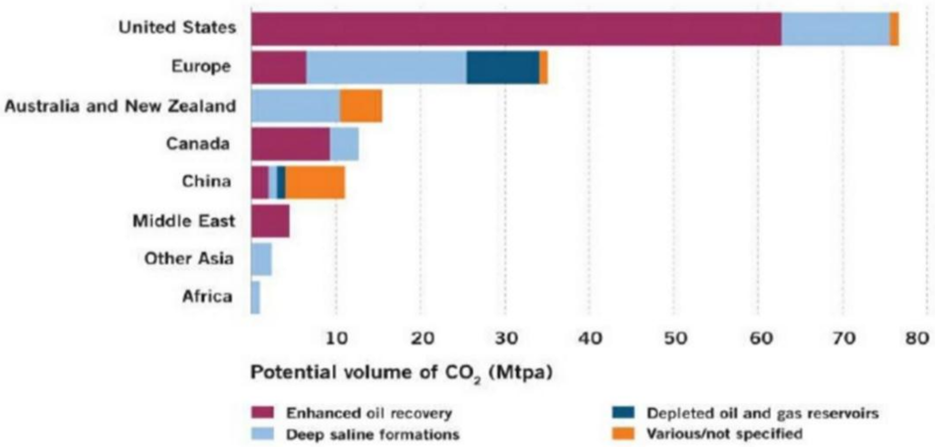


Figure 1.3. CO_2 geological storage sites locations and their potentials
(Global CCS Institute Members Meeting, 2012)

1) Depleted oil and gas fields.

The depleted oil and gas field are usually suitable places for storing CO_2 as they have integrated cap rock and relatively closed structures. In these types of storage sites, CO_2 will be successfully stored in these structures as these places are confined. The depleted fields also have the advantages of well known, easy to monitor. Based on the reasons above, the depleted fields could provide excellent chances of CO_2 leakage remediation.

2) Saline aquifers

The saline aquifers have become ideal storage places for CO_2 because the saline aquifers are wide spreading and have a large volume of space. Furthermore, the brine in saline aquifers can improve the solubility of CO_2.

Table 1.1. Geological CO_2 trapping mechanisms

Trapping Mechanism	CO_2 Trapping Phase	Description of Mechanism
Hydrodynamic	Supercritical Fluid	Undissolved CO_2 is trapped by overlying low-permeability caprock; CO_2 will be gradually dispersed
Residual	Gas Phase	CO_2 rises through water-saturated rock and displacing water from the pore space; the whole rock volume retains a residual saturation of CO_2
Solubility	Dissolved Liquid Phase	CO_2 is dissolved in the formation brine water; a major trapping mechanism
Mineral	Reacted Solid Phase	Dissolved CO_2 reacts with Ca, Fe, or Mg based mineral to form carbonate precipitates; not subject to leakage
Static Traps	Depend on underground conditions	CO_2 is simply trapped by low permeability formation layers, faults, and other geological structures

Table 1.2. CCS site characterization criteria (Based on IEA report, 2009)

Parameters	CCS site characterization criteria	
	Unfavorable	Favorable
Depth, m	<750-800	>800, <2500m
Geothermal Regime, degC/km	Gradients >35 degC/km and/or high surface	Gradients <35 degC/km and low surface temperature
Temperature, ℃	<35℃	>35℃
Formation Pressure, MPa	<7.5MPa	>7.5MPa
Formation Thickness, m	<20m	>20m
Caprock Thickness, m	10m	10m
Porosity, %	<10%	>10%
Permeability, md	<20md	>20md
Salinity, mg/L	7,113 – 120,000	
Formation Lithology	Aquifer or Reservoir: Sandstone & Carbonate, Seal: Shale	

2. OVERVIEW OF CO_2 LEAKAGE PROBLEMS

2.1. CO_2 LEAKAGE PROBLEMS

CO_2 leakage is a serious issue in the CCS projects, so it is important to understand CO_2 leakage reasons, pathways, and sealing methods.

2.1.1. Classification of CO_2 Leakage Pathways and Mechanisms. For the subsurface CO_2 storage, permanent containment of CO_2 has become one of the pivotal issues in CO_2 geological storage implementation process. The existence of a low-permeability cap rock is viewed as a significant element for a safe containment of CO_2 in the target storage formation; thus, any potential pathway is of major concern since it may allow buoyant CO_2 to migrate along and reach an overlying formation or be emitted at the surface, potentially impacting freshwater resources or sensitive stakes at the surface, respectively (J.-C. Manceaua et al, 2014). Figure 2.1 shows the potential CO_2 leakage pathways.

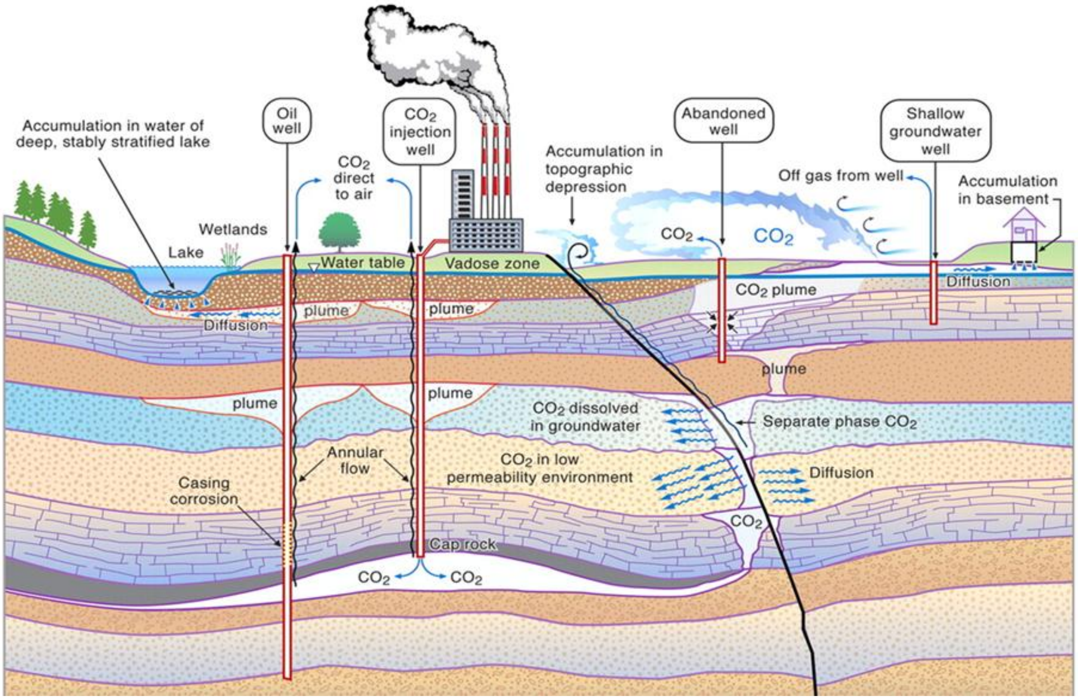


Figure 2.1. CO_2 Potential leakage pathways (Saptharishi, P. & Makwana, M, 2011)

Based on the research of Espie (2005), the main CO_2 leakage mechanisms include:

1) Wellbore failure

2) Bypassing of trap (spillage, aquifer migration)

3) Seal structure failure (capillary failure, faults, and fractures)

Based on the leakage channels and mechanisms, undesired CO_2 migration out of the geological storage formations shall be divided into two different types of pathways, geological leakage pathways and engineering (human-created) leakage pathways. These two types of pathways can also be classified into several distinct leakage pathways, which will be introduced in next part.

2.1.2. Geological Leakage Pathways. Geological leakage pathways indicate CO_2 is leaking through genetic pathways, and have no connection with human activities. Figure 2.2 shows several geological leakage pathways. Geologically stored CO_2 leaks through geological trails including several different ways:

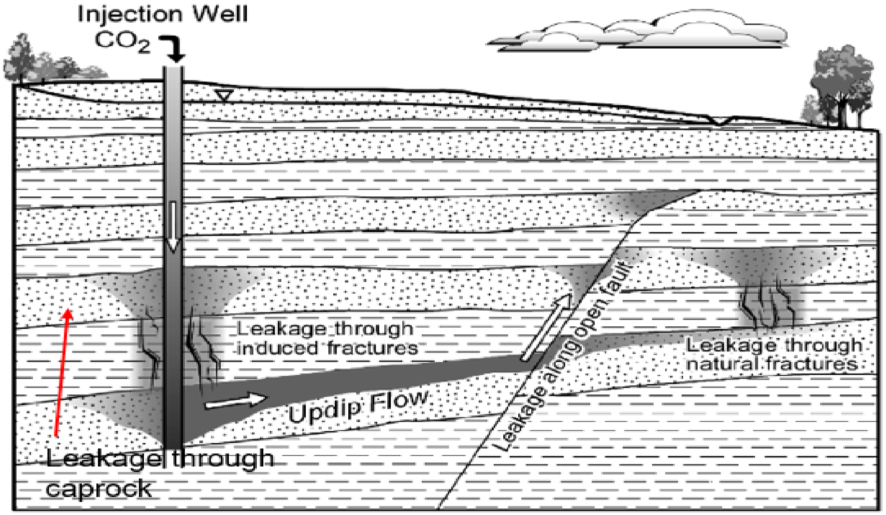


Figure 2.2. Geological CO_2 leakage pathways
(Based on Stefan Bachu & Michael A. Celia, 2009)

2.1.2.1. CO_2 leaks across cap rock. CO_2 leaks through cap rock may happen because of several reasons. The first one is that CO_2 can migrate through fissures in the cap rock. The second reason is when the formation permeability and pressure are excessively high, CO_2 could leak across the cap rock by itself due to the high formation permeability and pressure. According to these two reasons, abandoned oil and gas fields can be desired storage sites as they already have cap rocks which have high-level integrity and longtime stability. One thing to pay attention is that abandoned oil and gas fields are not entirely safe places for CO_2 storage. Development and production may degrade oil and gas field cap rocks with the stress threshold highly dependent on reservoir conditions (Zoback and Zinke, 2002). Injecting CO_2 into the depleted reservoir will lead to the re-pressurization of formation structure, and induce fissures forming as CO_2 leakage pathway.

2.1.2.2. CO_2 leaks through natural faults and fractures. CO_2 may leak across natural fractures and faults. These fractures and faults may form by geological activities such as earthquake and stratum movement, or loading and unloading of overburden.

2.1.2.3. Unconfined lateral migration. One important CO_2 leakage pathway is the potential for lateral migration of CO_2 in “open-system” saline formations (J.-C. Manceaua et al., 2014). Before the CO_2 is trapped and immobilized in storage sites, the buoyant carbon dioxide gravitates towards to flow up dip, mainly along surrounding rock layers or cap rock. Furthermore, the formation brine contains dissolved CO_2 which will flow together with the brine, and follow the direction of brine migration. This migration process may cause longer time when compared with the CO_2 leak across formation rock directly.

2.1.2.4. Volcanic and tectonic activities induced CO_2 leakage. Recent volcanism, tectonic uplift, seismic activity and other processes are showing impacts on CO_2 storage sites integrality. According to IEA greenhouse gas report (2007), a large amount of CO_2 was leaked from areas where volcanic activities are frequent. Previous researchers have approved that these areas are not suitable for permanent CO_2 storage.

2.1.3. Engineering Leakage Pathways. Human activities will also create engineering leakage pathways which are also called human-created leakage paths, and there are five basic types of engineering leakage pathways:

2.1.3.1. CO_2 leaks through abandoned wells. Depleted oil or gas fields where could be turned into CO_2 storage sites usually have abandoned wellbores. Figure 2.3. shows the CO_2 leaks through wellbore. To prevent CO_2 leakage, these wells that were drilled for decades should be located and properly sealed. For the storage operator, information of some open wells such as location and depth may not clear. Some wells which have not reached the storage depth may also become CO_2 leakage pathways as the leaked CO_2 could penetrate across the overlaying layers. (Gunter, et al., 1998).

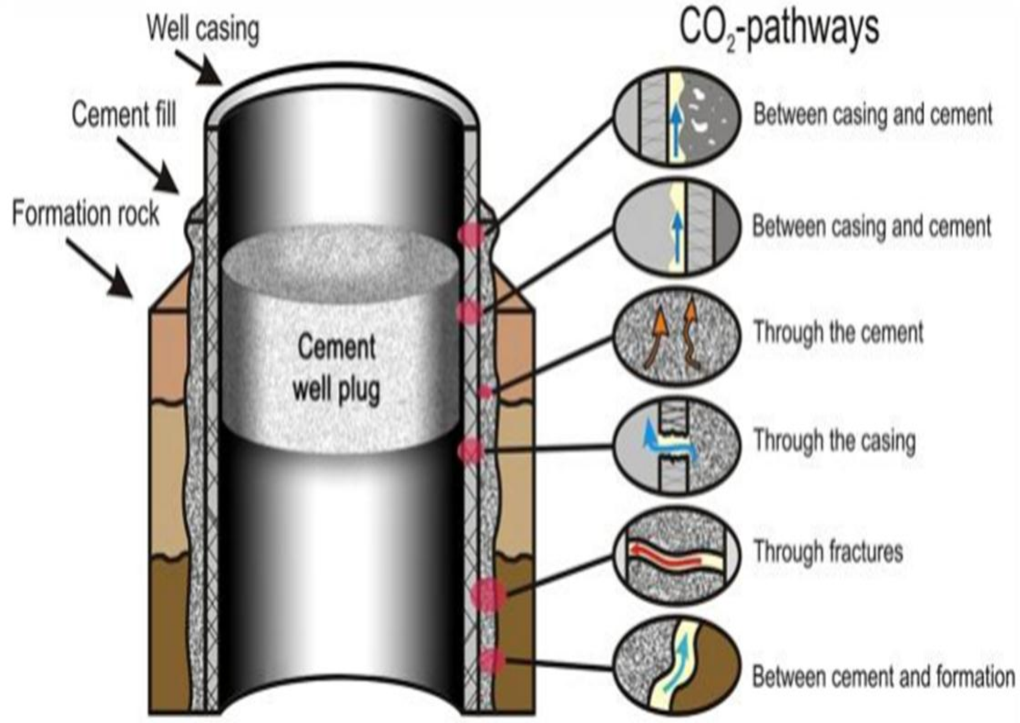


Figure 2.3. Abandoned well leakage pathways (Nordbotten and Celia, 2011)

2.1.3.2. CO_2 leaks due to injection operations. Many reasons such as inappropriate operational procedures, corrosion, and equipment malfunction may cause CO_2 leakage during injection process. CO_2 leakage could happen at all parts of the transportation and injection systems such as CO_2 transport pipeline, distribution manifold, and lines, wellhead, and tubing, casing, downhole packer assembly within the well.

2.1.3.3. CO_2 leaks through injection-induced fractures and faults. When large quantities of injection materials such as CO_2, water, and gels are injected underground, it may induce fractures and faults. According to the generated mechanisms, the fractures can be divided into shear and hydraulic fractures. These man-created fractures and faults may also cause the leak of CO_2. The risks resulting from injection-induced fractures and faults include:

1) Sheared injection wells and casing

2) Instability holes in well drilling process

3) CO_2 leakage along new or reactivated fault planes

4) Ground uplift/subsidence and earthquakes induced by injection

2.1.3.4. CO_2 leakage due to storage reservoir overfill. Misestimation of storage site structure may lead to overestimated of storage capacity, resulting in the over injection of CO_2. CO_2 leakage bypassing the surrounding rock happened at St. Johns Dome in Arizona where was one of the natural analogs. The reason of why the leakage happened was not because damaged cap rock, but rather because the naturally generated CO_2 overfilled its structural storage containment capacity. Gas leakage caused by overfill occurred within the Illinois Basin where was a gas storage zone.

2.1.3.5. CO_2 leakage due to post-storage disruption. After the CO_2 was injected and sealed effectively in the storage site, future human engineering activities such as future petroleum exploration, drilling new wells and mining operations may be harmful to the CO_2 storage area, disrupt the geological storage and cause CO_2 leakage.

2.1.4. Leakage Control Workflow. The carbon dioxide leakage control is also an important part of the CCS. The workflow of controlling carbon leakage shows below (Figure 2.4). The carbon leakage control processes are repeatable, which means we can repeat these steps until get satisfying assessment results.

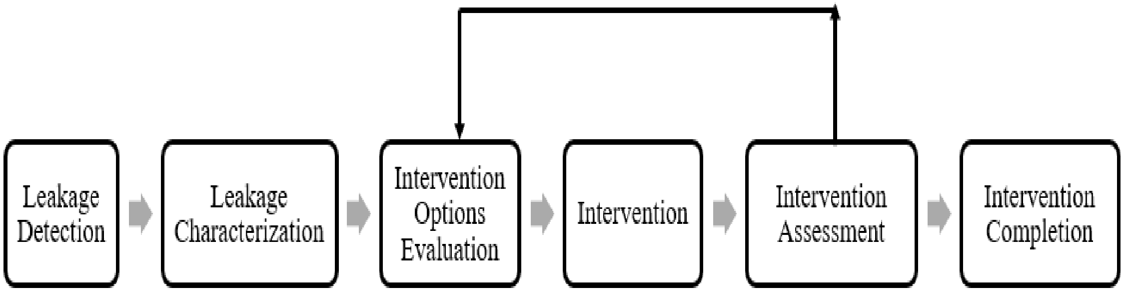


Figure 2.4. Workflow for CO_2 leakage intervention

2.2. CO_2 LEAKAGE DETECTION AND MONITORING

During the CO_2 capture and storage processes, CO_2 could leak through the wellbores, fractures, faults and because the reason of molecular diffusion, CO_2 may also overflow from the storage sites and cap rocks. The aims of detection and monitoring are preventing and mitigating subsurface CO_2 leak into the atmosphere, ground, oceans and fresh water aquifers. The detection and monitoring targets include integrity tests for the storage sites and cap rocks, analyzing CO_2 distribution, migration and storage conditions, finding possible leakage pathways and adopting remediation measures. According to the working principles, the detection and monitoring methods can be divided into geophysical and geochemical methods.

2.2.1. Geophysical Methods. Geophysical methods contain seismic methods, electrical monitoring, and pressure monitoring.

2.2.1.1. Seismic monitoring. Seismic methods are the most widely used methods in leakage detection and monitoring processes. The Seismic methods are sensitive to changes in saturation and pressure in areas above a container seal or in and around leak paths. The primary four seismic methods are:

1) 4D Time-lapse seismic monitoring

This method uses a surface source to create seismic waves. This approach can detect a small quantity of CO_2 flow in a larger area. The CCS project at Sleipner shows that 4D seismic method can monitor CO_2 moving conditions in thick saline aquifers. The limitation is that 4D seismic has a low vertical resolution, about 2 to 5 meters. The accuracy of monitoring mainly depends on CO_2 assemble properties, formation flow properties, and pressure. The monitoring results are not good when the CO_2 saturation is low, and the reservoir is not thick enough.

2) Cross-well seismic

This method puts the source and detectors in the nearby wells so that it can avoid the absorption of surface ground to the high-frequency signal. Therefore, this method has high resolution and can demonstrate the small volume of CO_2 leakage. Besides, CO_2 plume can be shown explicitly by using this approach according to a field test in the Firo saline aquifer, Texas.

3) Vertical Seismic Profiling (VSP)

The VSP method uses surface source and sets detectors in wellbores, so the VSP method has the advantages of a changeable cover area and higher resolution compared with surface seismic methods. This process can also help to provide an early warning for potential CO_2 leakage as it has vast and changeable cover area.

4) Micro-seismic

Micro-seismic employs surface or downhole detectors to monitor the micro-earthquakes which were induced by CO_2 injection operations. This method helps to evaluate the probability of conductivity fractures forming and shows CO_2 migration in small fractures.

2.2.1.2. Electrical monitoring. These methods mainly use the electrical ways to test the application area, then collect and analyze the data.

1) Gravimetrical test

This method checks the formation gravity change due to the change of substance distribution to assess the density and distribution of formation rock and flow. This technology contains surface and downhole models. The surface model can perform low-density CO_2 assemble in lower depth layers while it has a low vertical resolution. The downhole model can monitor near wellbore CO_2 migration. These two models are usually combined to use.

2) Electrical test

Electromagnetic wave method utilizes the spread of electric or magnetic wave to image the change of underground electrical resistivity and conductivity. The detectors can be set on the surface or in wellbores. The electromagnetic wave method has been used in the US to monitor CO_2 movement in EOR processes.

The Electrical Resistance Tomography (ERT) uses the changes of underground electrical resistivity caused by CO_2 injection to monitor the CO_2 distribution and migration, including surface and cross-well tests. The cross-well tests can be used with seismic methods to lower the uncertainty of the assessments for the monitoring. The ETR can help to detect CO_2 leakage to the surface, however, due to the variable components underground, and it’s hard to use this technology.

3) Well logging

The standard well logging includes electrical resistivity, neutron, acoustic wave, gamma, density, natural potential, temperature and cement bond tests. These technologies can provide information of CO_2 saturation, monitoring CO_2 leakage through the wellbore and lower the uncertainty of the seismic assessments.

4) Ground potential

Fluid flow in porous media coupling with the ground potential, so tracking the changes of ground potential can help to monitor CO_2 migration in porous media. The advantages of this method are easy to use and lower cost than other monitoring methods.

2.2.1.3. Pressure monitoring. This method is monitoring pressure data collected from the injection and monitoring wells. The advantage is pressure response in the subsurface propagate quickly, so it is useful for the early detection of leaks. The main analyzing methods include:

1) Pressure transient data indicating CO2 breakthrough.

2) Pressure anomalies indicating leakage are detectable in the presence of measurement error and spatial heterogeneity.

3) Considers the signal-to-noise ratio of pressure anomaly data compared to background noise which provides an effective means for detecting when a leak exists (Sun et al.).

2.2.2. Geochemical Methods. Geochemical methods include well flow chemistry analyzes, tracer tests, solid air analyzes, and atmospheric monitoring.

2.2.2.1. Well flow chemistry analyzes. Analyzing well flow chemistry properties will help to understand the underground CO_2 movement, dissolution, and reaction with other fluid. It takes the small cost to get subsurface CO_2 distribution and other particular types of data. This technique is entirely useful in reservoir CO_2 storage process, and the test area can be vast because there are a large number of wells which could be used.

2.2.2.2. Tracer tests. Tracer is made by micro solid particle, dissolved gas, and liquid. Injected tracer could move with CO_2 to monitoring CO_2 migration. Tracer is useful in finding CO_2 flow pathways, monitoring CO_2 migration, estimating CO_2 flow rate and volume in the oilfield.

2.2.2.3. Solid air analyzes. This technology provides a good way to monitor near surface CO_2 leakage. The CO_2 leakage will lead to the change of ground components, so this method can help to find deep CO_2 migration and predict CO_2 migration pathways

2.2.2.4. Atmospheric monitoring. CO_2 leaks from the storage sites may cause the changing of CO_2 flux and concentration. By using Eddy covariance method and CO_2 detectors, it is easy to detect CO_2 leakage. However, because the effects of complex pathways and wind, there will be errors in estimating CO_2 leakage volume.

A portable infrared CO_2 detector is a good choice as it has low detection limit, easy to use, can be performed continuously, and can find CO_2 concentration increasing on time. It is suitable for point detection.

2.2.3. Underground Simulation Technology. The underground simulation is one of the major component of CO_2 storage monitoring. The simulation work and field monitoring should supplement each other to optimize the monitoring. In the past ten years, CO_2 storage simulation technology has been improved a lot, mainly including CO_2 migration, flow properties, and final disposal condition.

2.3. REMEDIATION OPTIONS FOR CO_2 LEAKAGE

According to the leakage workflow that has been mentioned in Section 2.1.4, when CO_2 leakage accrues, leakage detection and monitoring should be done immediately. The second step is to report the geological structures, production or injection history, and other information. Then we can make a remediation plan based on the monitoring results and leakage area information.

The remediation operations should be corresponding with the leakage pathways and mechanisms. Four types of coping strategies have been made to remediate the CO_2 leakage (Modified from Benson and Hepple, 2005).

1) For leakage through cap rock

- Use lower injection rate and more injection wells to lower injection pressure;
- Eliminate formation fluid in the storage site to lower the formation pressure;
- Build a hydraulic barrier (N_2, brine, or other fluid which does not increase cap rock permeability) to increase the leakage site overlying pressure;
- Use extraction wells near the leakage area to cut off the leakage;

• Shutoff the injection and remove the excess CO_2 out of storage site, then reinject it into another applicable storage zone.

2) For leakage through fractures and faults.

• Storage site CO_2 injection must be stopped at once.

• Start the leakage detection, use geophysical and geochemical methods to check formation area, and employ well logging for questionable well checking.

• Study the geology of the area where surround the CO_2 storage site, and find out which area could be an accumulative place for the leaked CO_2. Put all the collected information together.

• Analyze the comprehensive information, then drill wells to recover and locate CO_2 movement in formation. After that, use some methods to remediate CO_2 leakage by setting plugs, producing barriers, and lowering storage site pressure.

• The leakage control operation should not only stop the leak of CO_2 but also reset the problem storage area to reduce future leakage.

3) For leakage due to lack of well integrity.

• Wellhead and welltree maintenance

• Tubing repair

• Packer replacement

• Casing repair (Patching casing, squeezing cementing, swaging)

• Plug and abandon (For wells which cannot be fixed)

a) Planning
b) Well killing
c) Pull out the completion equipment and tubing
d) Apply well logging to evaluate well conditions
e) Reservoir and potential cross-flow plugging
f) Take out intermediate well casing then set additional plugs
g) Set top plug
h) Remove the surface casing upper part, conductor, and wellhead

4) For leakage due to well blowout.

• Heavy mud fluid needs to be injected into well casing to kill the well; some other technics could also be used to abandon or remediate the blow-out well.

- If the blow-out well is not easy to approach, drill another injection well nearby to intercept the subsurface casing and pump heavy mud could also help to shutoff the well blow-out (Hepple, R. P., & Benson, S. M., 2005).

2.4. CO_2 LEAKAGE SEALANT TYPES

Sealants play a major role in reducing CO_2 leakage process. The sealant materials should have these following characteristics:

1) Sealants for CO_2 leakage control usually work under relatively low pH conditions (3-6), so enough chemical stabilities are essential, for example, sealants for CO_2 leakage should have acid resistance ability, thermal stability and no harm to the matrix of the rock formation

2) Pressure is an important factor which can influence sealant performance. Therefore, sealants need appropriate mechanical properties to tolerate high pressures.

3) Some other properties such as high-temperature stability, longer-term stability, cost-effective, high sealant integrity and environmental friendly are also significant for sealants.

Researchers have studied many sealants for remediating and mitigating carbon leakage. The commonly used sealants such as cement, geopolymers, foams, gel systems, nanoparticles, and biofilms barriers have been studied. The main part of this thesis will describe each kind of sealants, including their composition, flow properties, mechanic strength, factors which impact on sealants performance, applied area, field applications, advantages, limitations, and some other features according to their unique characteristics.

3. CO_2 LEAKAGE CONTROL SEALANTS

3.1. CEMENT

Cements are the most important types of sealants for remediating CO_2 leakage through wellbores.

3.1.1. Cement Types and Usages. According to different compositions, cements can be defined as Portland cement and Non-Portland cement. The Portland cement was used to know as ordinary Portland cement made by adding gypsum into the clinker. So far, the Portland cement is still the most widely used cement in the world. The non-Portland cements are high resistance, sustainable cements with the addition of property improvement materials. Figure 3.1 shows the cement classifications for CO_2 leakage remediation operations. The most widely used types of cement for well integrity include Portland Cement Class G, Aluminate Cement, Sulfate-Aluminate cement, and Phosphate-Aluminate Cement.

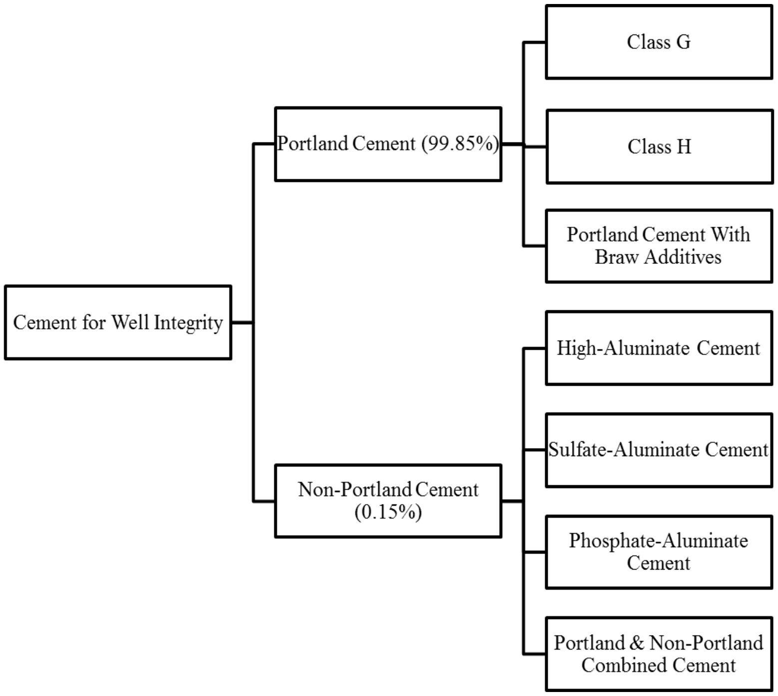


Figure 3.1. Cement classifications for CO_2 leakage remediation operations

The two Tables (3.1, 3.2) show the difference of components and properties between other types of cement and Portland Class G cement. The difference occurs because CO_2 and $Ca(OH)_2$ could react easily, which could cause the loss of cement material and lead to the leakage of CO_2 through wellbore. When comparing to the others, Portland cement has more $Ca(OH)_2$, and lower acid-resistance.

Table 3.1. Main chemical composition of raw cement materials by weight

Cement Types/ Materials	**Portland Class G Cement**	**Aluminate Cement**	**Sulfate-Aluminate Cement**	**Phosphate-Aluminate Cement**
CaO	62-67	32-44	36-45	35-46
SiO_2	20-24	3-15	3-12	5-10
Al_2O_3	4-7	33-60	28-40	30-45
Fe_2O_3	5-6	1-15	1-3	1-15
P_2O_5	-	-	-	10-15
MgO	5			4
$K_2O + N_2O$				
SO_3			8-15	
TiO_2+MnO_2			-	

Table 3.2. Different physical properties of various cements

Cement Types Properties	Portland Class G Cement	Aluminate Cement	Sulfate-Aluminate Cement	Phosphate-Aluminate Cement
t_i, min	> 45	> 30	8-60	Variable
t_f, min	< 390	< 360	10-90	Variable
Specific Surface Area, m^2/kg	≥ 300	≥ 300	350-400	≥ 300
3 Days Compressive strength, MPa	22-37	30-50	42-72	Variable
28 Days Compressive strength, MPa	42.5-72.5	85	45-75	Variable
***t_i - Initial Setting Time *t_f - Final Setting Time *Compressive strength was tested in no-corrosion conditions**				

3.1.2. Cement Corrosion Mechanisms. CO_2 usually reduce the well cement plugging performance through two ways: chemical eluviation and carbonization contraction. Chemical eluviation indicates the reactions between CO_2 and $Ca(OH)_2$, these reactions cause the loss of cement materials such as C-S-H and $Ca(OH)_2$ (Equation 1 to 5); therefore, the cementing properties will decrease.

$CO_2 + H_2O \rightarrow H_2CO_3$ (1)

$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3$ (2)

$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$ (3)

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + H_2O$ (4)

$\text{C-S-H} + \text{H2CO3} \rightarrow \text{CaCO3} + \text{Amorphous Silica}$ (5)

When the cement raw materials hydrolyzing temperature is less than 80 ℃, hydrolyzed cement materials will react and form a type of swelling agent which named as AFt, and the process is shown in the Equation 6.

$C_3A + Ca(OH)_2 + CaSO_4 \bullet 2H_2O \rightarrow \text{AFt (Swelling Agent)}$ (6)

The reaction between CO_2 and $Ca(OH)_2$ will consume $Ca(OH)_2$, and thus, reduce the forming of AFt. This process causes the destruction of cement structure and leads to the shrinkage of cement volume.

3.1.3. Factors Impacting Cement Properties and Improvement Methods. According to the corrosion mechanism, researchers found out that reducing the percentage of CaO could help to improve cement CO_2-resistance ability, so the non-Portland cement and compounded cement were developed. Besides the cement types, some other parameters of cements such as permeability, water-cement ratio, and with or without additives also have influence on cement acid-resistance level. In addition to the cement chemical compositions, many other external parameters also affect the cement CO_2-resistance, including corrosion time, temperature, CO_2 partial pressure, CO_2 phase, formation fluid ions types and percentages.

3.1.3.1. Corrosion time. Zhu (2006) used Portland cement class G to find the relationship between CO_2 corrosion time and cement compressive strength. The experiment was performed under 120 °C, and the CO_2 partial pressure was 1.5MPa. As shown in Figure 3.2, the cement compressive strength was decreased with the increase of CO_2 curing time.

3.1.3.2. Corrosion temperature. Zhu (2006) used Portland class G cement with different additives to test the relationship of corrosion temperature versus compressive strength and corrosion depth. Figure 3.3 shows the results of Zhu (2006)'s research and illustrates that high temperature will intensify CO_2 corrosion.

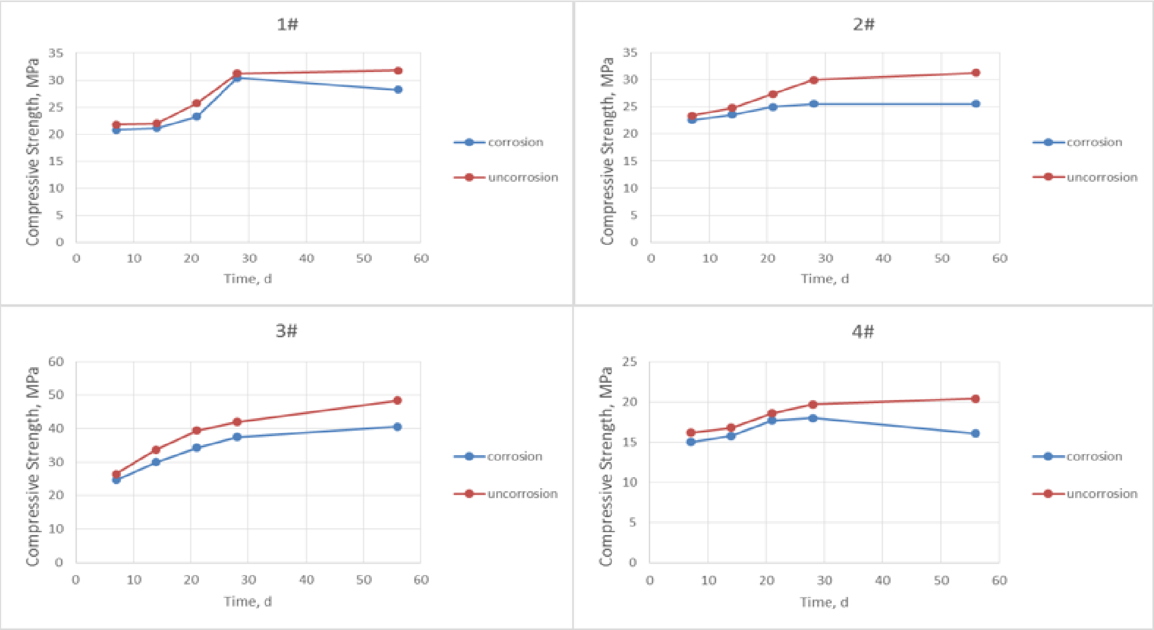


Figure 3.2. Relationships between CO_2 corrosion time and cement compressive strength (Data source: Zhu, 2006)

3.1.3.3. CO_2 partial pressure. The increase of CO_2 partial pressure will increase the CO_2 solubility in the water, and lead to the growth of water acidity. Through this way, the increase of CO_2 partial pressure accelerates the corrosion process of cement. Zhu (2006)'s results support this theory and are shown in Figure 3.4.

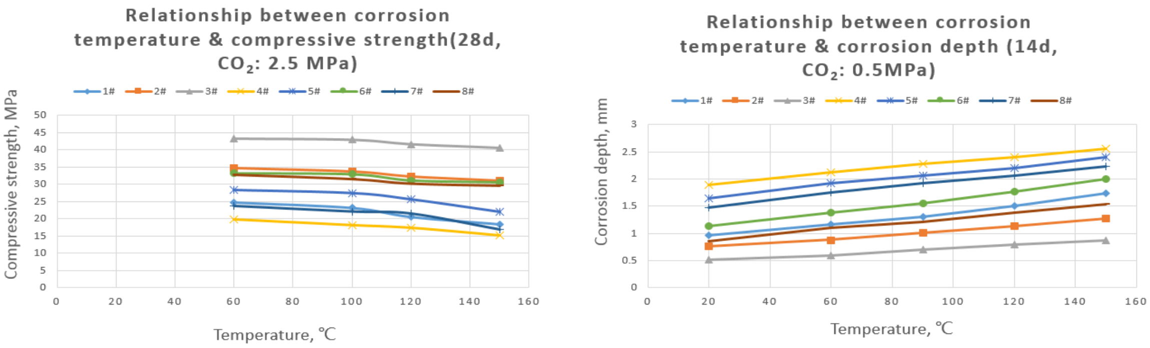


Figure 3.3. Relationship of corrosion temperature versus compressive strength and corrosion depth (Data source: Zhu, 2006)

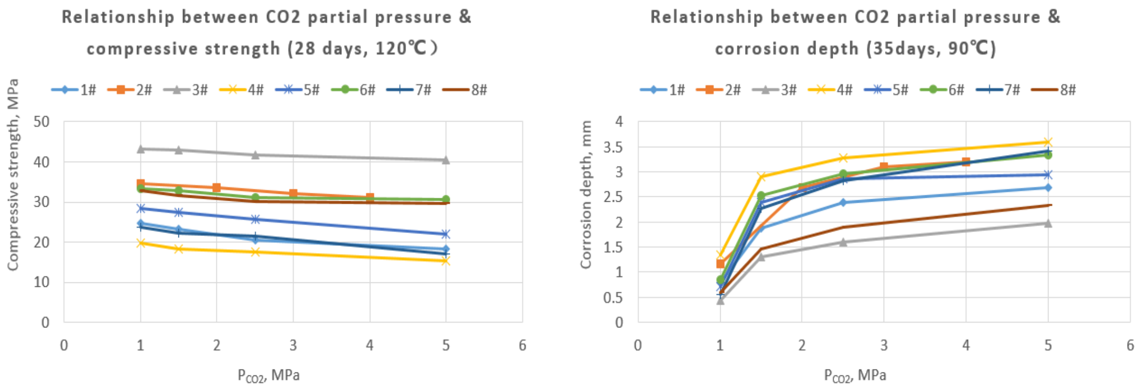


Figure 3.4. Relationship of CO_2 partial pressure versus compressive strength and corrosion depth (Data source: Zhu, 2006)

3.1.3.4. CO_2 phase. Different CO_2 phases show different corrosion velocities to cement. In wellbore condition, CO_2 usually stay as a gas solution or supercritical phase. The supercritical CO_2 corrosion depends on CO_2 diffusion velocity, the corrosion process likely happens in the atmosphere, and the $CaCO_3$ equally distributed at the corrosion part, as there is no continuous water phase to transport the formed $CaCO_3$. However, because CO_2 solution can't distribute as equally as SC-CO_2, and has continuous water phase, the CO_2 solution will react with cement materials and form $CaCO_3$ shield in some area, so the corrosion velocity is fast at the beginning, then it will become slow. Figure 3.5 (Bu, et al., 2010) shows the corrosion differnece between CO_2 solution and supercritial CO_2.

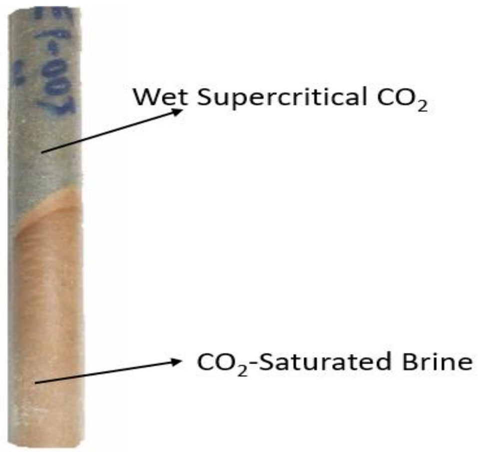


Figure 3.5. The cement exposed to different phases of CO_2 (Bu et al., 2010)

3.1.3.5. Improvement methods. To promote the cement CO_2-resistance performance, firstly, the design of cement pore size distribution should be optimized to improve cement compressive strength and reduce cement permeability (Table 3.3, 3.4).

Table 3.3. Cement pore size distribution (Fu Ying, 2014)

Cement Type	Pore Size Distribution			
	MAX	10%	50%	90%
Portland Class G	90	-	<53	<21
Micro-fine Cement	16	<3	<5.6	<10
Unit: μm				

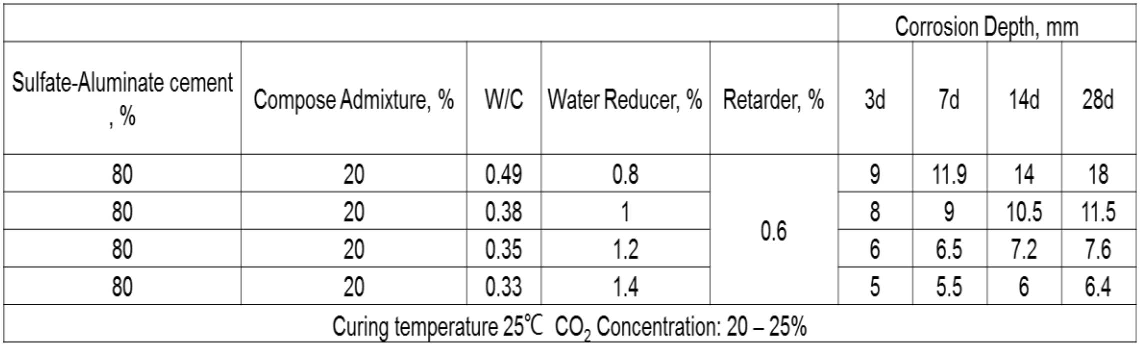
Table 3.4. Portland cement and micro-fine cement ratio impacting cement properties at 110 °C, and curing for 24 hours (Fu Ying, 2014)

Portland Class G : Micro-fine cement	Initial Consistence, Bc	24h Compressive Strength, MPa
10：0	12	15.6
9: 1	13.5	16.2
8：2	14	17
7：3	15	18.3
6：4	16	20
5：5	17.5	21.8
4：6	21	Too thick to test
3：7	23.5	Too thick to test

Secondly, the excessive water-cement ratio will increase cement porosity and reduce cement compaction, so adjusting water-cement ratio can help to improve cement properties. Zhang et al. (2008)'s research proved this theory (Table 3.5). However, a smaller water-cement ratio may not mean better properties. If the cement is too thick, the injectability of cement will be reduced. Each kind of cement has its proper water-cement ratio; the water-cement ratio should be adjusted according to real conditions.

Finally, using additives is good for enhancing cement CO_2-resistance. Table 3.6 shows the information of commonly used additives which mainly aim to improve cement density, compressive strength, and chemical stability. Through these ways, additives help cement get better CO_2-resistance ability. When choosing cement additives, some requirement should be noticed. Additives should be selected according to different conditions; additives should not harm to cement properties (abuse, has adverse reactions with cement materials); additives should be environment-friendly; additives should be cost-effective.

Table 3.5. Water-cement ratio affecting cement CO_2 resistance ability (Zhang et al, 2008)



					Corrosion Depth, mm			
Sulfate-Aluminate cement , %	Compose Admixture, %	W/C	Water Reducer, %	Retarder, %	3d	7d	14d	28d
80	20	0.49	0.8	0.6	9	11.9	14	18
80	20	0.38	1		8	9	10.5	11.5
80	20	0.35	1.2		6	6.5	7.2	7.6
80	20	0.33	1.4		5	5.5	6	6.4
Curing temperature 25℃ CO_2 Concentration: 20 – 25%								

As an example, sodium aluminate is an inorganic substance. It can react with CO_2 and then forms sediment. CO_2 dissolution could produce carbon acid in water. The react between sodium aluminate and carbon acid will form aluminate hydroxide precipitate (Equation 7) (Shen, Z., & Wang, G. T., 1997). According to the mechanism above, sodium aluminate is a good candidate for being cement additive.

$$NaAl(OH)_4 + CO_2 \rightarrow Al(OH)_4 \downarrow + NaHCO_3 \qquad (7)$$

Almost all the well integrity and abandonment operations currently use cements mainly. It is estimated that about 99.85% of the total (16,438) of all CO_2 EOR wells used Portland cement for CO_2 zonal isolation (Sweatman, R.E et al., 2009).

3.1.4 Advantages and limitations. Table 3.7 lists the advantages and limitations of each type of cement.

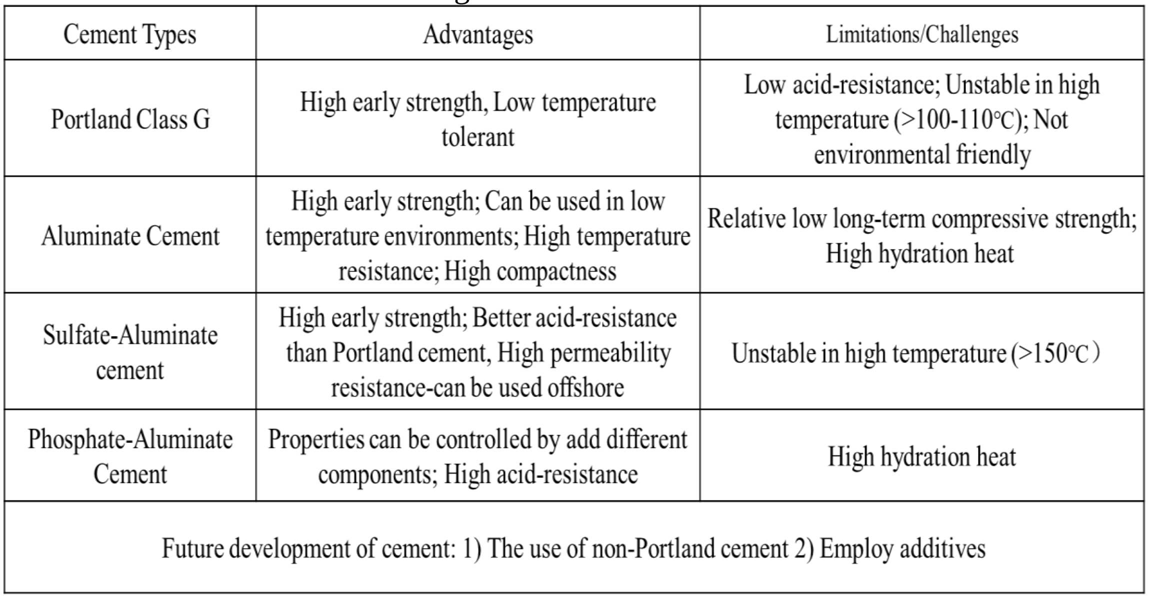
Table 3.6. Commonly used additives for improving cement properties

Additive Type	**Commonly Materials**	**Mechanism**	**Purpose**
Accelerator	Inorganic Salts, Oxalic Acid	Chang the solubility of cementing materials	Accelerate hydration process, improve cements' early strengths
Retarder	Lignosulfonate, Low Molecular Weight Cellulose	Adsorb on particle surface, and delay the forming of cement structure	Extend setting time, maintain cement plasticity for longer time
Dispersant	Calcium Lignosulfonate, Water-soluble Melamine Resin, Aldehyde Ketone Condensation Compounds	Lubrication	Lower cement slurry consistence, improve mobility, accelerate cementing process
Reinforcer	Swelling Agent, Gel, Latex	Swelling or optimize pore size distribution	Improve cement acid-resistance and some other properties
Defoamer	Silicone Oil, OP Emulgator	Reduce the partial surface tension of foam, cause the breaking of foam	Reduce the foam forming in cement mixing process, improve cement strength and compactness
Fluid Loss Additive	Bentonite, Modified Cellulose, Resin, Latex	Reduce permeability of cement filter cake, increase fluid-phase viscosity	Reduce fluid loss and gas channeling, improve cement tenacity
Lightening Admixture	Fly, Ash, Micro-silicon, Cenosphere	Add low density materials	Reduce cement density
Weighting Admixture	$Fe_2O_{3,}$ $BaSO_4$, Mn_2O_4	Add high density materials	Increase cement density
Micro-silicon (Diameter 0.1-0.2µm)/Silicon	SiO_2	Reduce cement density, Particle size distribution optimization, form C-S-H with $Ca(OH)_2$	Improve cement compactness and compressive strength, increase high temperature tolerant

Table 3.6. Commonly used additives for improving cement properties (cont.)

Additive Type	**Commonly Materials**	**Mechanism**	**Purpose**
Fly Ash/Slag	SiO_2, Al_2O_3, Fe_2O_3	React with $Ca(OH)_2$ and form hydraulic gelation compounds	Improve cement compressive strength and durability
Swelling Agent	Al_2O_3, CaO, $CaSO_4$, MgO	Materials swelling during hydration process	Reduce cement shrink and porosity, improve cement compactness
Organic Polymer	Butyl-benzene latex, Resin Polymer (epoxy resin)	Seal the pores in cement, form organic film on cement surface	Improve cement acid-resistance, reduce cement porosity and permeability
Stabilizer	Inorganic Salt	Cooperate with other additives	Improve additives effects and cement properties

Table 3.7. Advantages and limitations of cement sealants



Cement Types	Advantages	Limitations/Challenges
Portland Class G	High early strength, Low temperature tolerant	Low acid-resistance; Unstable in high temperature (>100-110℃); Not environmental friendly
Aluminate Cement	High early strength; Can be used in low temperature environments; High temperature resistance; High compactness	Relative low long-term compressive strength; High hydration heat
Sulfate-Aluminate cement	High early strength; Better acid-resistance than Portland cement, High permeability resistance-can be used offshore	Unstable in high temperature (>150℃)
Phosphate-Aluminate Cement	Properties can be controlled by add different components; High acid-resistance	High hydration heat
Future development of cement: 1) The use of non-Portland cement 2) Employ additives		

An ideal cement system should be chemically resistant to CO_2 and acid brines, have low permeability, mechanical properties that can withstand production operations. The cement needs to have a certain flexibility to adapt its structure to surrounding environments. Additionally, the mechanical properties need to be maintained for long-term in CO_2 environment. It would be better that the cement or one of its components could swell upon when contacting with CO_2 to eventually repair physical failures (fractures, micro-annulus) that may occur under specific downhole conditions (Daou, F et al., 2014)

3.2. GEOPOLYMER

Geopolymer is a type of amorphous alumina-silicate cementitious material. It can block CO_2 by forming crosslinked geopolymer structures through the geopolymerization process.

3.2.1. Geopolymer Introduction. In this section, geopolymer types and the difference between geopolymer and Portland cement will be introduced.

3.2.1.1. Geopolymer types. Geopolymers include three classifications of inorganic polymers which depend on the ratio of Si/Al in their structures. Based on the ratio of Si/Al and materials types, geopolymer can be divided into eight types (Davidovits, J., 2005), and Figure 3.6 shows the chemical structure of different kinds of geopolymer.

1. Kaolinite / Hydrosodalite based geopolymer, poly(sialate), Si: Al = 1:1;
2. Metakaolin MK-750 based geopolymer, poly(sialate-siloxo), Si: Al = 2:1;
3. Calcium based geopolymer, (Ca, K, Na)–sialate, Si: Al = 1, 2, 3;
4. Rock-based geopolymer, poly(sialate-multisiloxo), 1 < Si: Al < 5;
5. Silica-based geopolymer, sialate link, and siloxo link in poly(siloxonate)，Si: Al > 5;
6. *Fly ash based Geopolymer, Si: Al = 1, 2;
7. Phosphate based geopolymer;
8. Organic-mineral geopolymer.

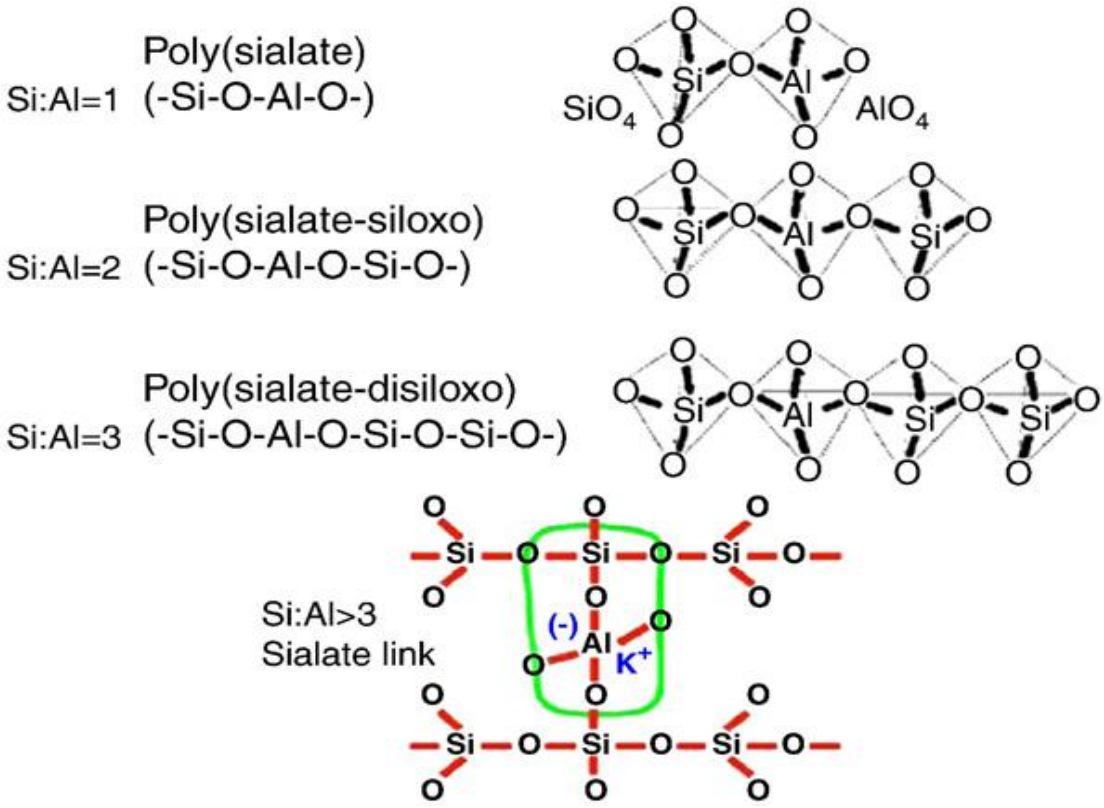


Figure 3.6. Chemical designation of geopolymers (Li, C et al, 2010)

Geopolymers are mainly used to produce geopolymer cements and geopolymer resin systems. This part will focus on geopolymer cements. Geopolymer cement is a new type of material which could replace traditional Portland cement for isolating CO_2 at near wellbore area, and well leakage control.

Figure 3.7 demonstrates the components of various types of geopolymer cement. An alumina silicate based material, a user-friendly alkaline reagent (sodium or potassium soluble silicates with a molar ratio (MR) SiO_2: M_2O between 1.45 to 1.85, M being Na or K, and safety problems may happen during geopolymer cement production if the ratio of SiO_2: M_2O is less than 1.45 which means not user-friendly) and water are required for creating geopolymer cement. Room temperature hardening relies on the addition of calcium cations, essentially iron blast furnace slag (Davidovits, J., 2005). Among all these types of geopolymer cement, fly ash based geopolymer cement is the most widely studied.

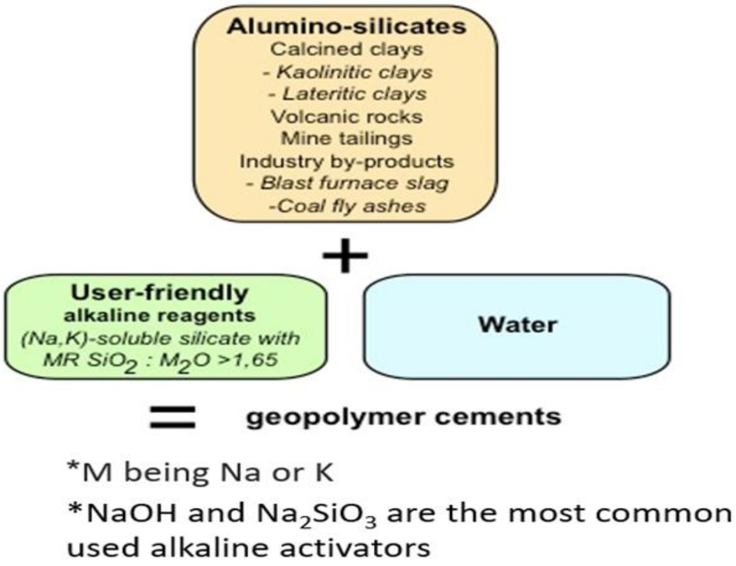


Figure 3.7. Geopolymer cement components (Based on Davidovits, J., 2005)

3.2.1.2. Difference between geopolymer and ordinary Portland cement. The setting process of geopolymer (GP) is different from the ordinary Portland cement (OPC) systme. As Figure 3.8 shows, geopolymer cement can form a corsslinked network and improve GP's compressive strength and acid-resistance ability, and these will be further introduced in the advantages and limitations part.

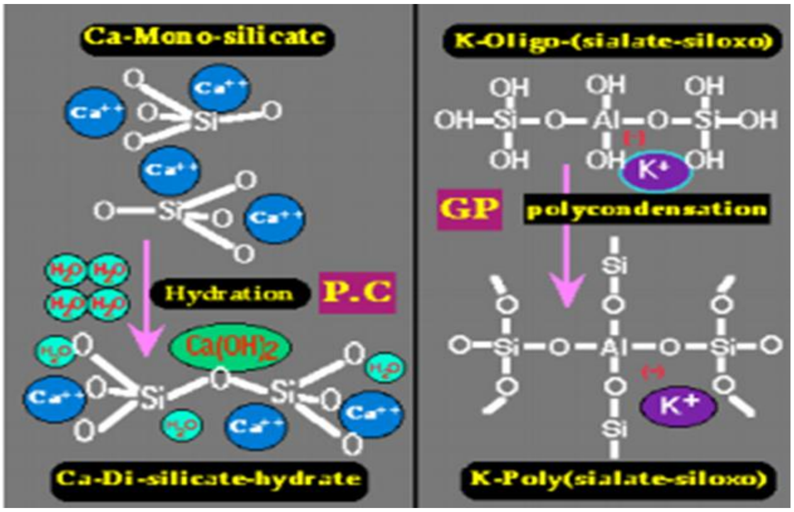


Figure 3.8. Setting differences between OPC and GP (Davidovits. J., 2013)

The chemical composition difference of geopolymer and Portland has been shown in Table 3.8. Geopolymer cement contains more SiO_2 and Al_2O_3 than ordinary Portland cement. These two types of constituents are not easy to react with CO_2, which means geopolymer cement has better acid-resistance than ordinary Portland cement.

Table 3.8. Components differences between fly ash based GP and OPC
(Data Source: Wallah, S et al., 2006, Al Bakri, A. M et al., 2012, Thokchom, S et al., 2009, Sugumaran, M., 2015)

Constituents	Percentage (wt, %)	
	GP	OPC
	Fly Ash Class F	
SiO_2	48-56	20-24
Al_2O_3	23-35	4-7
Fe_2O_3	3-15	5-6
CaO	0-8	62-67
MgO	0.2-1.4	5
K_2O	0.7-0.85	
SO_3	0.2-0.5	
AL/FLY ASH, W/C	0.3-0.5	0.4-0.46

*AL – Alkaline Liquid, $Na_2O + SiO_2$ 36%-38% by mass

The ranges of compressive strength and setting time of geopolymer are wide because many factors have shown impacts on these two properties. The impact factors for geopolymer will be introduced in next part.

3.2.2. Factors Impacting Geopolymer Performance. Many factors will influence the geopolymer performance (setting time, compressive). This section focuses on geopolymer setting time and compressive strength.

3.2.2.1. Setting time (fly ash based geopolymer as example). The initial or/and final setting time of fly ash based geopolymer depends on curing temperature, water to solid (W/S) ratio, and alkaline/fly ash ratio (contains Si/Al ratio and Na/Al ratio).

Ahmer used fly ash based geopolymer to test how these parameters affect geopolymer final setting time. The fly ash contains Al_2O_3 - 43.25%, SiO_2 -20.58%, Fe_2O_3 - 12.41%, and CaO - 11.11%. AR grade NaOH and Na_2SiO_3 (SiO_2 - 37.79% and Na_2O -

16.36%). Figure 3.9 demonstrates the relationships between each parameter and geopolymer final setting time.

When the Si/Al ratio is low, the geopolymerization reaction process is short as there is little amount of silica available for the reaction, and geopolymerization takes less time to complete its major portion of dissolution reaction resulting in the lower setting time of geopolymer. However, the higher amount of silica also decreases the geopolymer formation due to very fast compaction.

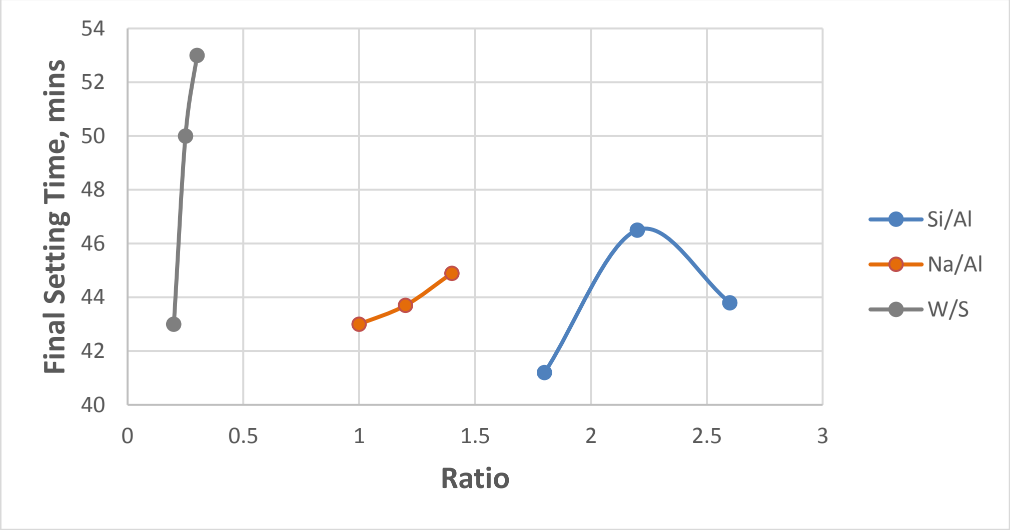


Figure 3.9. Effect of parameters on final setting time (Data: Ahmer Ali Siyala, 2015)

Increasing the Na/Al ratio causes higher dissolution of fly ash releasing more silica and alumina and less calcium in the solution which causes enhancement in geopolymerization or gel formation and the reaction takes more time to complete the early stage reaction, therefore, increase of setting time. Water takes part in the dissolution of aluminosilicate and polycondensation of geopolymers. Small water to soilid ratio will lead to the insufficiency dissolution of fly ash and reduce setting time. Increasing w/s ratio causes more fly ash dissolution, then takes more time for reaction, through this way, geopolymer setting time is increased. Higher temperature accelerates the geopolymerization reaction, and reduces the final setting time. The setting time of geopolymer could be handled up to 120 minutes without any sign of setting for curing temperature ranging from 65 to 80 °C (Rangan, B. V. et al, 2005).

Figure 3.10 lists the overall effect of parameters on geopolymer final setting time. Si/Al ratio plays the most important role while temperature has the lowest impact on final setting time.

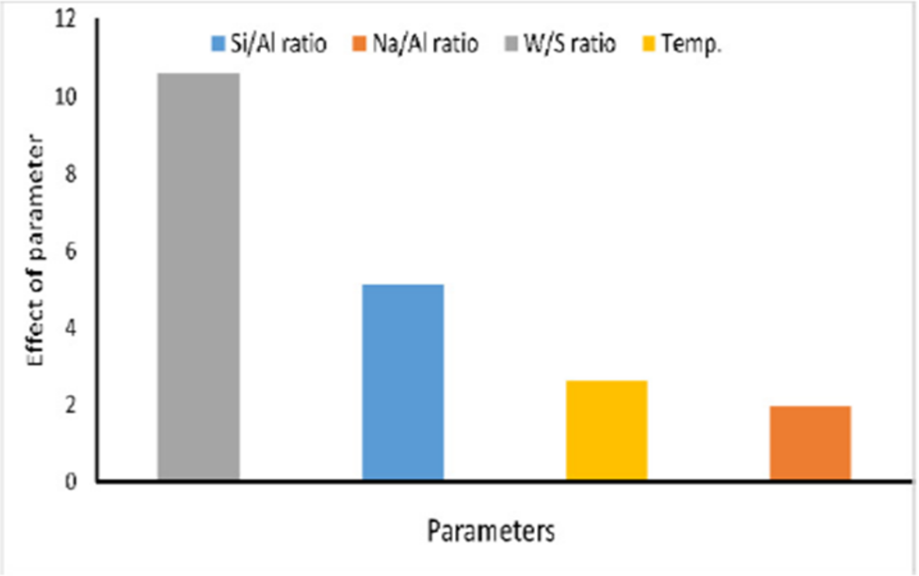


Figure 3.10. Overall effect of parameters on final setting time (Ahmer Ali Siyala, 2015)

3.2.2.2. Compressive strength (fly ash based geopolymer as example). High temperature may not help to improve geopolymer compressive strength because higher curing temperature (this test cured at 70 to 90 °C for 24 hours) causes the loss of moisture which is very important for the developing of geopolymer structure. Suitable curing time (geopolymer was curied for 24 hours at 70 °C in Ahmer’s research) helps to increase geopolymer compressive strength. If the curing time is longer than 24 hours, the compressive strengrh of geopolymer will be reduced because overlong curing causes the breakdown of the gel structure of the geopolymer matrix (Van Jaarsveld, Van Deventer & Lukey, 2002). Figure 3.11 demonstrates the realationship between geopolymer compressive strength and curing temperature.

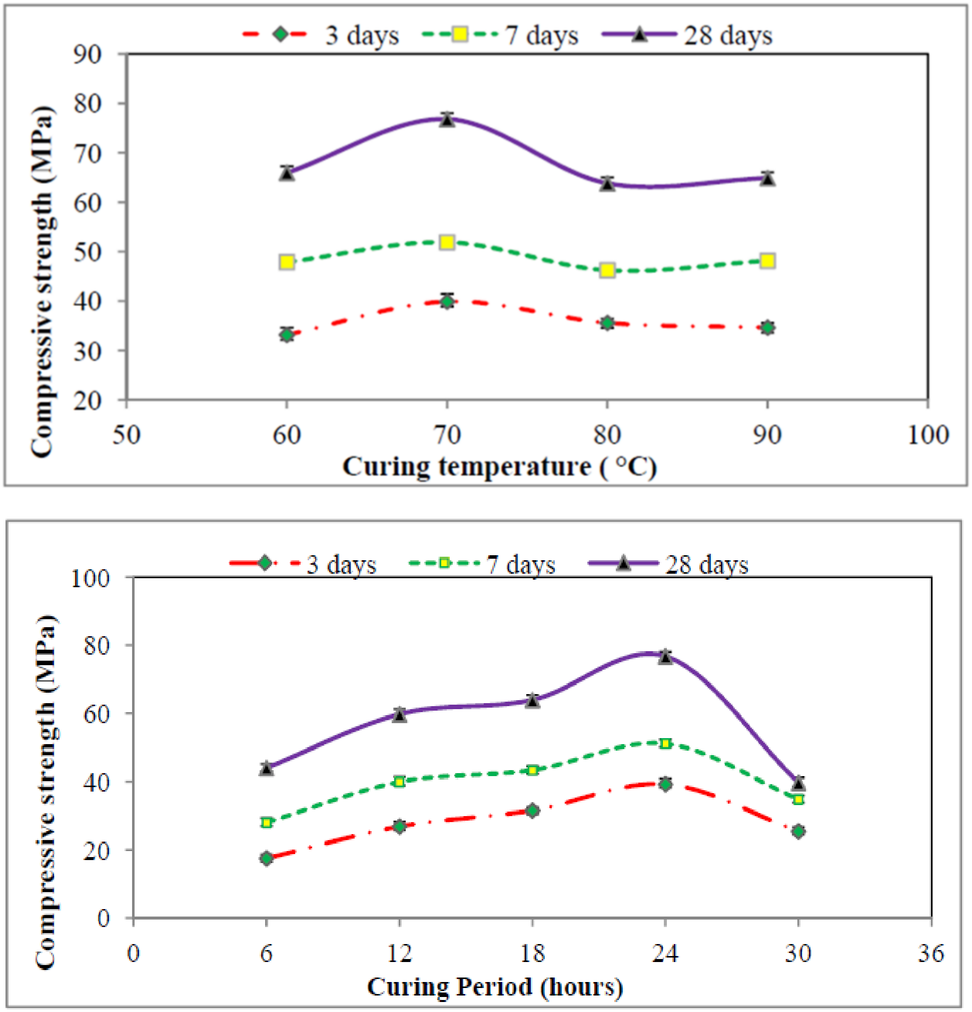


Figure 3.11. Curing temperature & curing time affecting geopolymer compressive strength (Omar A. Abdulkareem & Mahyuddin Ramli, 2015)

Na_2SiO_3/NaOH ratio shows an impact on geopolymer compressive strength. High NaOH content, which means the low Na_2SiO_3/NaOH ratio is good for the dissolution of SiO_2 and Al_2O_3 in the geopolymer production processes, and that is why low Na_2SiO_3/NaOH ratio (0.8-1.2) provides high compressive strength. However, when the Na_2SiO_3/NaOH ratio is very small, indicating less Na_2SiO_3, the content of SiO_2 is insufficient, and the lack of SiO_2 resulted in the reduced compressive strength of geopolymer. The effect of this parameter on geopolymer is shown in Figure 3.12.

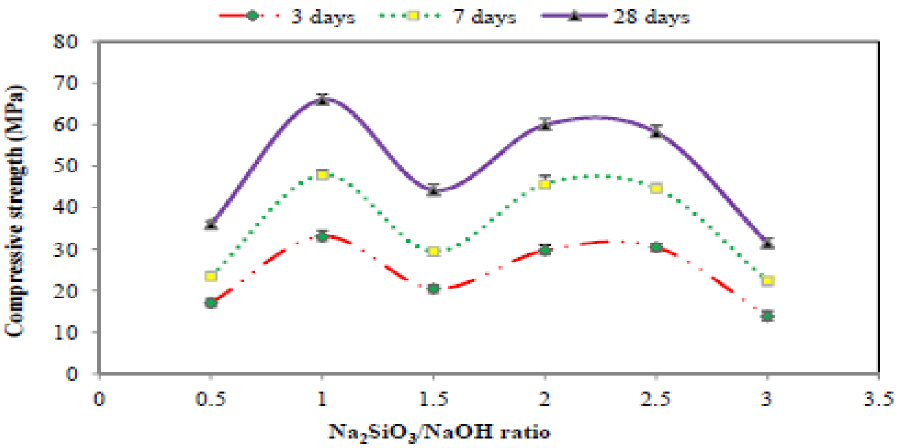


Figure 3.12. Effect of different Na_2SiO_3/NaOH mass ratios on the compressive strength development of geopolymers (Omar A. Abdulkareem & Mahyuddin Ramli, 2015)

Alkaline/fly ash ratio was found to have a significant influence on the compressive strength of geopolymer. The increase of alkaline/fly ash ratio could increase the water content, causing high dissolution of SiO_2 and Al_2O_3 species at the dissolution–hydrolysis stage and more hydrolyzed ions are available to the hydrolysis-polycondensation stage, which finally resulted in high geopolymerization rate and high strength geopolymer (Zhang et al., 2009). The effect of this parameter on geopolymer has been shown in Figure 3.13. This test cured the geopolymer at room temperature for 24 hours, which is the reason of why its compressive strength at seven days was less than the experiments above.

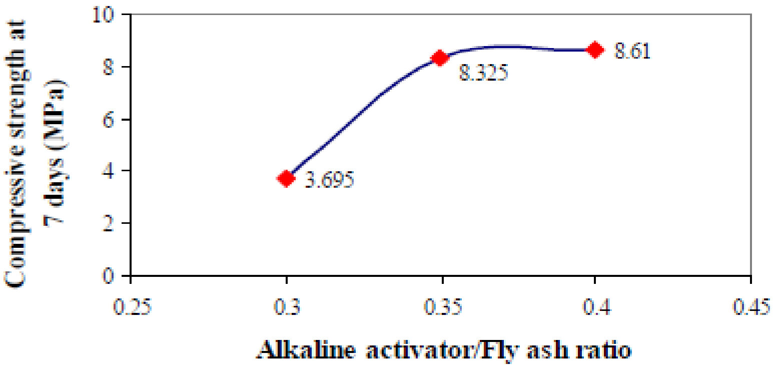
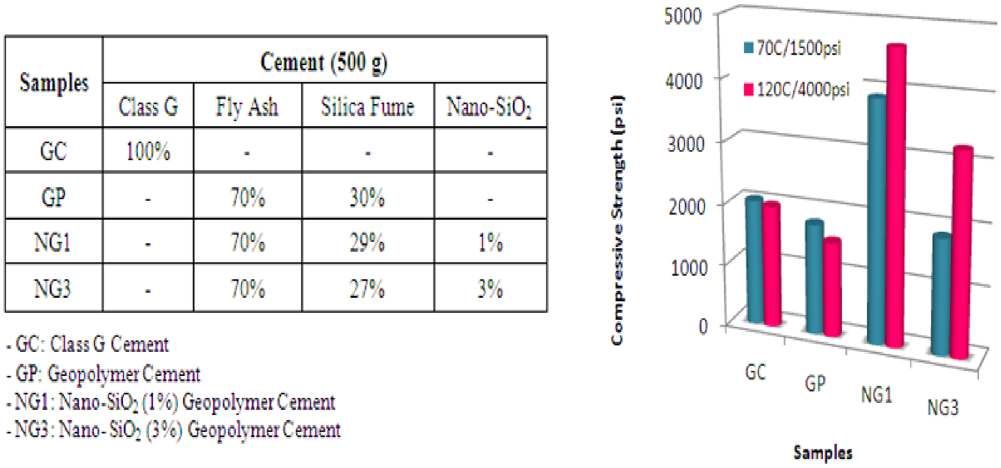


Figure 3.13. Alkaline activator/fly ash ratio affecting the compressive strength of fly ash-based geopolymer (Al Bakri, M., Mohd, A. et al, 2012)

Alkaline activator types can also influence compressive strength. The compressive strength of the K-containing geopolymers is higher than the Na counterparts because Na-containing pastes are more viscous and harder to mix. To reach the same compressive strength level, the amount of Na-solution must be increased by 50% as compared to the K-solution, which means that the Na-based geopolymers are less user-friendly than the K-based geopolymers (Davidovits, J., 2011 & Fan, F. 2014)

Additives could help to promote geopolymer properties. From Figure 3.14, we can find that adding nano-silica into fly ash based geopolymer could help to improve cement compressive strength. The reason is that nano-silica can improve cement compactedness, and thus increase geopolymer compressive strength at high-pressure and high-temperature conditions.



Samples	Cement (500 g)			
	Class G	Fly Ash	Silica Fume	Nano-SiO$_2$
GC	100%	-	-	-
GP	-	70%	30%	-
NG1	-	70%	29%	1%
NG3	-	70%	27%	3%

- GC: Class G Cement
- GP: Geopolymer Cement
- NG1: Nano-SiO$_2$ (1%) Geopolymer Cement
- NG3: Nano- SiO$_2$ (3%) Geopolymer Cement

Figure 3.14. Cements compressive strength under different conditions
(Based on Ridha, S., & Yerikania, U., 2015)

3.2.3. Advantages and Limitations. Geopolymer has the benefit of relatively high-temperature resistance. Nasvi (2012) made the test which compared the difference of uni-axial compressive strength between fly ash based geopolymer and Portland cement class G at different temperatures. The result of the test is shown in Figure 3.15, and it illustrates geopolymer has better performance than Portland cement at high-temperature (Larger than 37°C). At room temperature, geopolymer’s compressive strength was reduced and lower than Portland cement. As the geopolymer has relatively high-temperature stability, it could work at high-pressure and high-temperature conditions.

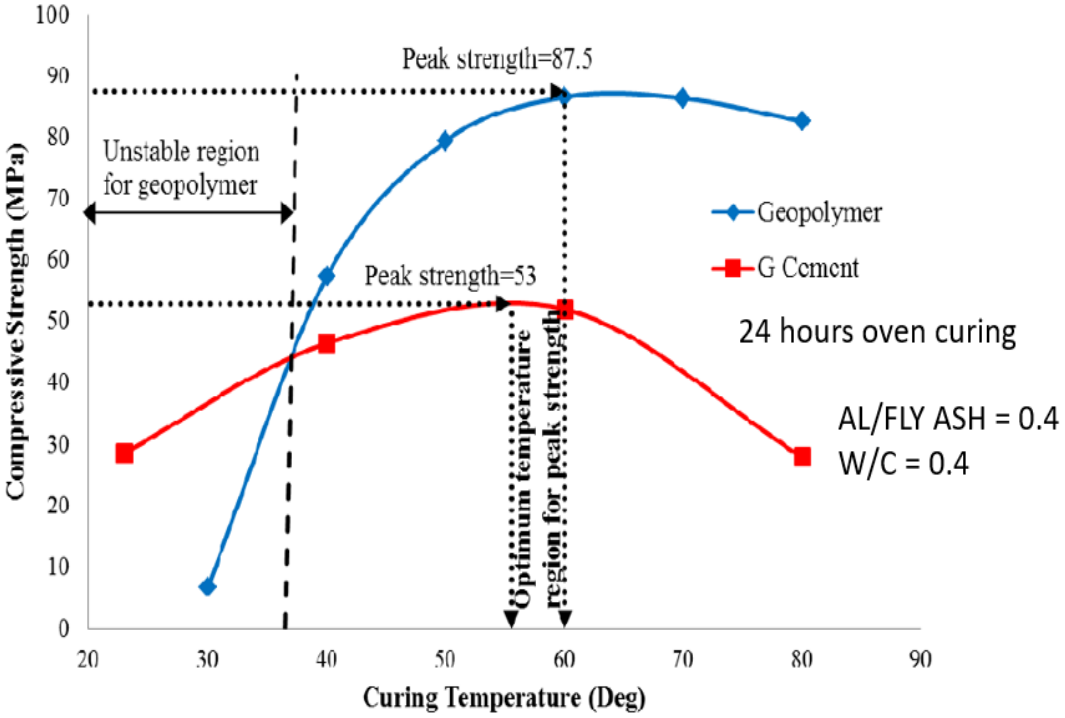


Figure 3.15. The variation of uni-axial compressive strength of Portland G cement and geopolymer under varying curing temperatures (Nasvi, M.C.M. et al., 2012)

Geopolymer has higher acid-resistance than Portland cement and some other materials. Davidovits (2003) tested the breakup percentage of different materials in the acid environment (5% acid solution, ambient condition) and found out geopolymer had the lowest breakup percentage compared with other materials (Figure 3.16).

Geopolymer cement has very low shrinkage. Davidovits (2013) mentioned that the shrinkage of rock based geopolymer cement during setting is less than 0.05%. Hardjito (2004) proved that the drying shrinkage of fly ash based geopolymer cement was extremely small.

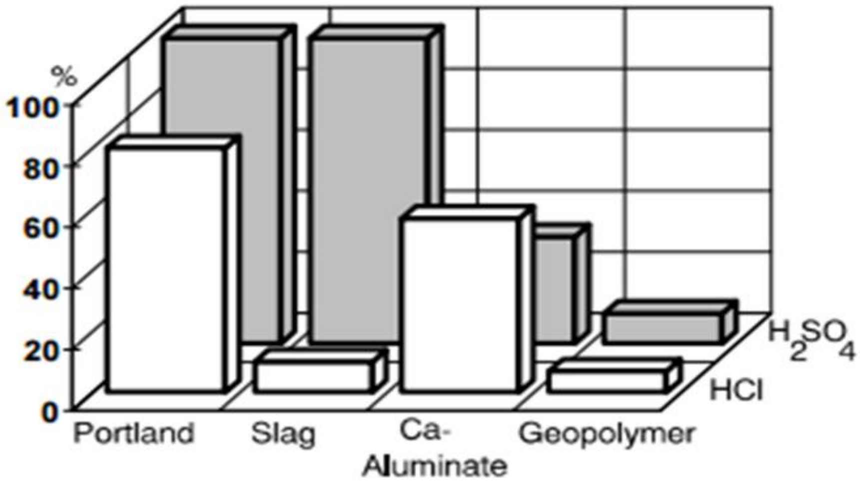
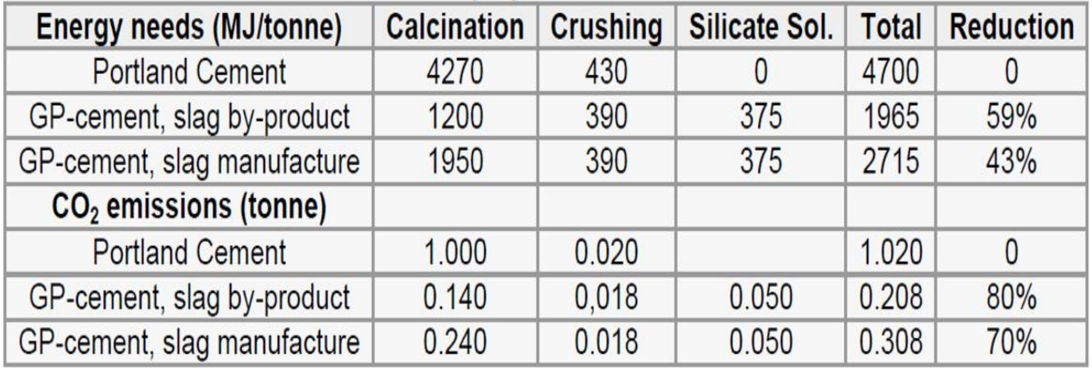


Figure 3.16. Different materials break up percentages in acid environment (Davidovits, 1994)

Table 3.9 lists the energy needs and CO2 emissions difference when making one ton of geopolymer and Portland cement. Compared with Portland cement, geopolymer has lower CO_2 emission while making processes and costs less energy. The goal of CCS is to reduce the CO_2 emission, so the environmental friendly property of sealant is very important.

Table 3.9. Energy needs and CO_2 emissions difference between create one ton of rock-based geopolymer cement and Portland cement (Joseph Davidovits, 2013)



Energy needs (MJ/tonne)	Calcination	Crushing	Silicate Sol.	Total	Reduction
Portland Cement	4270	430	0	4700	0
GP-cement, slag by-product	1200	390	375	1965	59%
GP-cement, slag manufacture	1950	390	375	2715	43%
CO_2 emissions (tonne)					
Portland Cement	1.000	0.020		1.020	0
GP-cement, slag by-product	0.140	0,018	0.050	0.208	80%
GP-cement, slag manufacture	0.240	0.018	0.050	0.308	70%

The limitations include: 1) Geopolymer cement requires special handling needs and is extremely difficult to create. It needs to use chemical materials, for example, the sodium hydroxide, which has negative effect on human health; 2) Because the dangers in geopolymer cement creating processes, so it is sold only as a pre-cast or pre-mix material ; 3) The sensitive geopolymerization process is easy to be affected by temperature, so that the geopolymer cement requires a curing process, which means it need to be cured at elevated temperature under a correctly regulated temperature range (Hardjito et al. 2004; Lloyd and Rangan 2009).

3.3. FOAMS

The foam could be another potential CO_2 leakage remediation material. Foam is a gas-liquid mixture where the liquid containing the surfactant forms a continuum wetting the rock whereas a part or all of the gas is made discontinuous by thin liquid films called lamellae (Talebian et al., 2013).

3.3.1. Foams as CO_2 Leakage Sealants. In the CO_2 flooding operation, supercritical CO_2 is injected with surfactant solution to form CO_2 foam. When CO_2 is leaking from the deep formation, CO_2 is in supercritical phase because of the formation temperature and pressure, and can directly react with forming agents.

The foam could reduce CO_2 mobility in porous media through the ways which are listed below. Foam contributes to decrease the CO_2 movement; it is a type of material which will reduce CO_2 leakage speed, and provides more time for further leakage remediation operations.

1) The foam could help exceed the pressure drop to drive bubbles at a constant velocity exceed that of an equivalent volume of liquid, and thus the effective viscosity of CO_2 phase increases.

2) The movement of surfactant induces surface tension gradient that slow bubble motion, and thus increases the effective viscosity.

3) Wetting phase liquid caused gas phase trapping (Middle-sized pores) (Figure 3.17).

4) The foam could alleviate the gravity segregation, shifts competition between viscous and gravity forces (Figure 3.18). The left part shows overriding happens when

CO_2 (blue) is injected into a water flooded core containing residual oil (red) and brine water (yellow); the right shows foam is injected with CO_2, and CO_2 overriding is reduced.

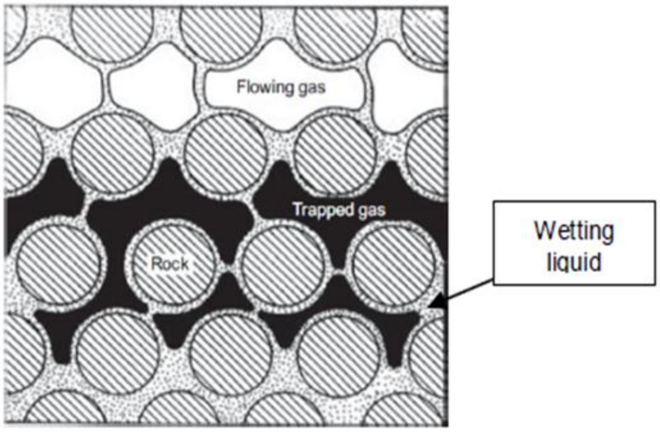


Figure 3.17. Foam trapping gas in porous media (Radke and Gillis, 1990)

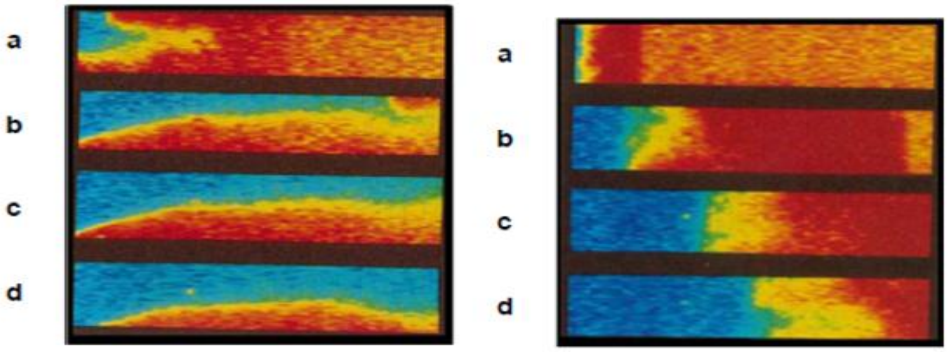


Figure 3.18. Foam reduced CO_2 overriding
(Wellington, S. L., & Vinegar, H. J., 1985)

3.3.2. Factors Impacting Foam Performance. We can use the foam half-life time, volume, weight, and resistance factor to evaluate foam performance. Many factors can affect the foam performance such as surfactant types, surfactant concentration, CO_2 phases, formation permeability, temperature, pressure, salinity, formation fluid ions, and pH.

Surfactant types and concentration can influence the foam stability. Based on ions properties, the surfactant can be defined as nonionic, cationic, anionic, and amphoteric. Seyed Amir Farzaneh, Mehran Sohrabi (2014) conducted experiments and proved that anionic foaming agents could form foams with higher stability. The results also demonstrated that the surfactant with smaller carbon number usually has higher foam stability. Based on the research of Boonyasuwat, S. et al. (2009), an adoptable foaming agent should have carbon number larger than ten. However, surfactants which have too long carbon chains are also unbefitting forming agents as they have relatively lower solubility. Figure 3.19 shows that the surfactant solution concentration increasing will improve the foam half-life time. However, after reached a particular concentration, foam stability decreases with increasing surfactant concentration.

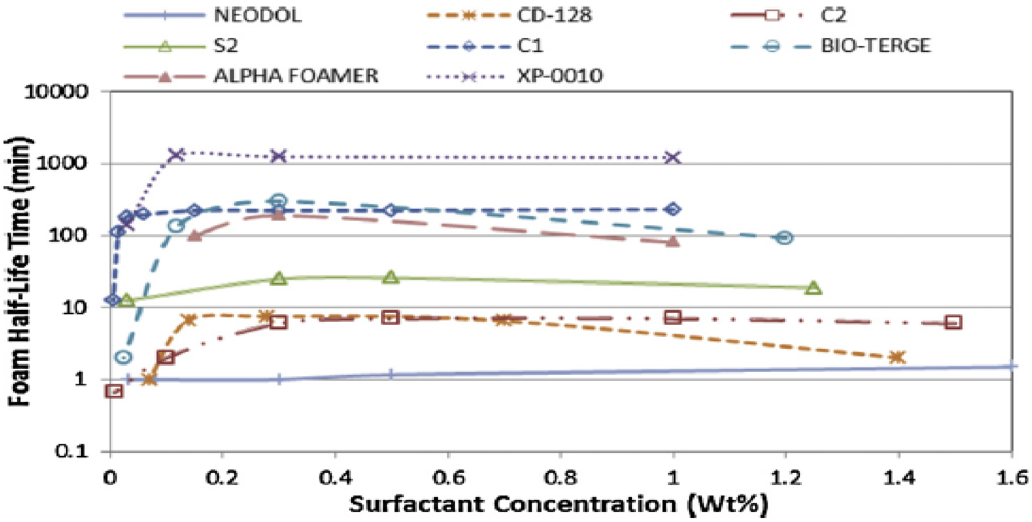


Figure 3.19. Various surfactant types and concentrations affecting on foam half-life time (Seyed Amir Farzaneh, Mehran Sohrabi, 2014)

The impact of CO_2 phase on foam performance has been proved, and the results are shown in Table 3.10 (Zhang et al., 2014). Zhang (2014) used 1.5 wt% anionic surfactant and 100,000mg/L brine water, CO_2 could form foam in each phase. However, the foam turns to be like emulsion and has longer half-life time with the increase of CO_2 density (Table 3.10). This table also illustrates that high temperature can reduce foam properties, because high-temperature causes foam evaporation, reduces foam viscosity, and increases the drainage rate, and finally accelerates foam collapse.

Table 3.10. CO_2 generated foams performance at different CO_2 phases (Zhang. Y, et al., 2014)

Phase of CO_2	Temperature /℃	Pressure /MPa	Density of CO_2 / $g{\cdot}cm^{-3}$	Foam volume / mL	Half life
Gas phase	60	0.5	0.0081	56.5	29.1 min
Liquid phase	30	10	0.7224	348.5	>24 h
Supercritical phase	60	10	0.2927	282.6	114.4 min

CO_2 foam has larger flow resistance in the high permeability zone rather than low permeability zone (Zhou, G. H., et al., 2006). This means that foam has better performance in high permeability zones. Table 3.11 shows the foam performance at different permeability conditions.

Table 3.11. CO_2 foam blocking and mobility control ability of N-NP-15c-H measured at different permeabilities (Zhang. Y., et al, 2014)

No.	Temperature /℃	Permeability /10^{-3} μ m^2	Resistance factor	No.	Temperature / ℃	Permeability /10^{-3}μ m^2	Resistance factor
1	40	18.83	24.5	6	70	445.69	362.0
2	40	47.75	82.8	7	100	14.46	13.3
3	40	445.69	536.3	8	100	43.13	29.7
4	70	16.11	18.2	9	100	445.69	207.0
5	70	47.75	67.9				

Pressure could affect foam bubble size and interfacial tension (IFT). However, the impact of pressure is complexly and depends on different types of foam (Liu, Y, et al., 2005). At most conditions, the ionic surfactant foam half-life time and volume increase with pressure growth. However, nonionic foam volume increase while foam half-life time decrease with increasing pressure. Low pH could reduce foam volume, while increasing the surfactant concentration may help balance the effect of low pH. Salinity impact on foam behavior depends on foam types. With the growth of surfactant foaming agent concentration, the pH and salinity influences are reduced (Liu, Y. et al., 2005).

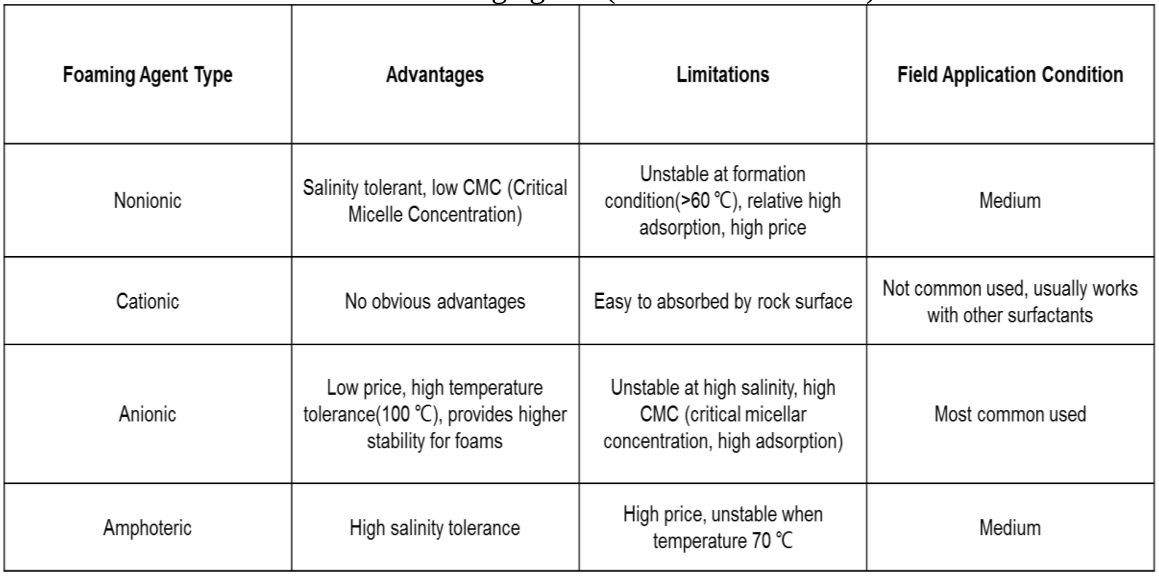
Foam flow rate also has the relationship with foam performance. Di Mo et al. (2014) conducted core tests using foam which contains 5000 ppm nano-silica and the foam quality was 20%. The results showed that, the foam mobility decreases and resistance factor increases when flow rates increase.

Sang et al. (2017) conducted experiments to prove that the increase of ions concentration helps generate more CO$_2$ foam, and the generated foam was more stable compared to the small ions concentration condition. The results also demonstrated that bivalent ions such as Ca^{2+} had the more significant effect on CO$_2$ foam stability and generation.

3.3.3. Advantages and Limitations. Foam viscosity is much lower than cement and geopolymer so that it can penetrate into the in-depth of a reservoir. However, foam cannot provide good blocking to fractures and fracture-like channels.

The advantages and limitations of foams with are listed in Table 3.12 below.

Table 3.12. Advantages, limitations, and field application conditions of foams with different foaming agents (Based on Petrowiki)



Foaming Agent Type	Advantages	Limitations	Field Application Condition
Nonionic	Salinity tolerant, low CMC (Critical Micelle Concentration)	Unstable at formation condition(>60 ℃), relative high adsorption, high price	Medium
Cationic	No obvious advantages	Easy to absorbed by rock surface	Not common used, usually works with other surfactants
Anionic	Low price, high temperature tolerance(100 ℃), provides higher stability for foams	Unstable at high salinity, high CMC (critical micellar concentration, high adsorption)	Most common used
Amphoteric	High salinity tolerance	High price, unstable when temperature 70 ℃	Medium

3.4. GEL SYSTEMS

Gel systems have been widely used in CO_2 EOR flooding as conformance control agents. Gel systems can seal the high permeability zones, control the profile of CO_2, and improve the CO_2 sweep efficiency. Researchers have studied gel systems for CO_2 leakage control. Figure 3.20 shows the classifications of conformance control gel systems.

3.4.1. Organic Crosslinked Polymer (OCP) System. In these gel systems, organic polymer gels are the most widely applied for CO2 leakage control, especially the organic crosslinked polymer gel (OCP). Usually, the base polymer of this system is a copolymer of acrylamide and t-butyl acrylate (PAtBA). An organic crosslinker is a material based on polyethyleneimine (PEI). The amine groups on PEI react with the amide (and probably with the ester groups) to form an amide linkage (Vasquez et al., 2010). Figure 3.21 shows the OCP system general crosslinking mechanism (X = O, N; R = $C(CH_3)_3$, $C(CH_3)_2$, NH_2, CH_2SO_3H, $N(CH_3)_2$).

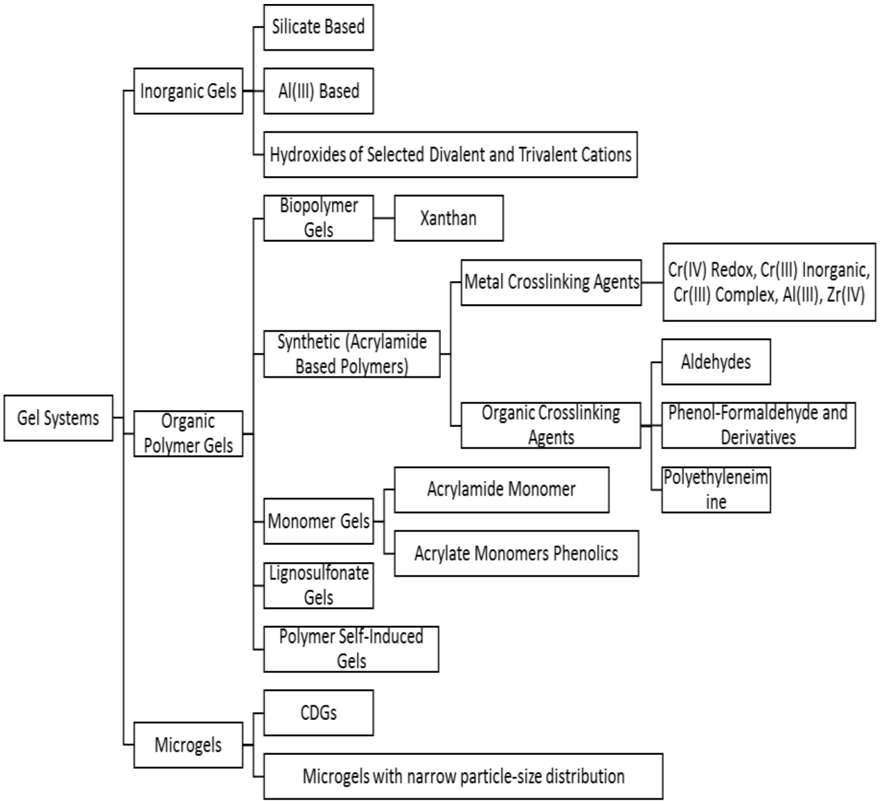


Figure 3.20. Classification of gels based on chemical composition (Based on Petrowiki)

The OCP systems have been successfully applied to sandstone, carbonate, and shale formations which need conformance treatment (Vasquez et al., 2010). Table 3.13 describes some types of OCP systems and some of their properties.

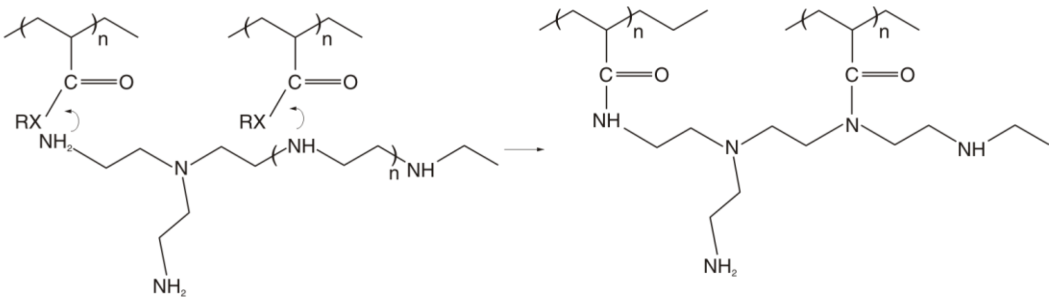


Figure 3.21. OCP system general crosslinking mechanism (Vasquez, J. E. et al, 2010)

Table 3.13. Some types of OCP systems and their properties

OCP system			Apply condition ranges				Reference
Base material	Crosslinker	Others	Temperature, °C	Viscosity (before/after gelation), cp	Optimum pH	Formation pressure, MPa	
PAM	PEI	-	16 – 60	30/30,000	Neutral or weak-alkaline	> 17.93	Aird, T. H. (2014), Vasquez, J. E. et al (2010), Bach et al (2001)
PAtBA	PEI	-	49 – 127				
PAtBA	PEI	Water-soluble carbonate retarder	127 – 177				
PAM	Phenol-Formaldehyde	-	60 – 140	8.9-89/Not mentioned	8 – 9	-	Albonico, P. et al (1995)
PAtBA	PEI	Fluid-loss control additives and non-cement particulates	4 – 204	20-30/Not mentioned	Neutral or weak-alkaline	> 17.93	Vasquez, J., & Curtice, R. (2015)
High-molecule-weight (8~15 million Dalton) partially hydrolyzed polyacrylamide, PHPA	PEI	Non-ionic surfactant	Could reach 107.2	20/10,000	-	-	Crespo, F. et al (2014)

3.4.2. HPAM/PAM Crosslinked with Metal Agents. HPAM based polymer could also help reduce CO_2 potential leakage. Metal crosslinking agents such as Cr^{3+}, Zr^{+} are commonly used for CO_2 leakage control.

A. Syed (2014) used HPAM as base polymer, and applied Chromium (III) acetate as crosslinker to test the CO_2 permeability reduction ability of HPAM based polymer. In his research, when used sandstone cores saturated with 3% saline brine, the permeability reduction to CO_2 could reach more than 99%. In higher salinity conditions (12 to 25%), the permeability reduction to CO_2 could still reach nearly 90%. Durucan et al. (2016) used PAM crosslinked with Zn^{2+} to seal the sandstone cores. The results indicated that the permeability reduction to gas reached 99% percent.

3.4.3. CO_2 Triggered Polymer. Gelation time control is a big challenge for gel treatment. To solve this problem, Li et al (2015) have proposed a new type of material based on the CO_2 sensitive gel system, which is a modified polyacrylamide-methenamine-resorcinol gel system. CO_2 dissolved into formation water will reduce the pH to 3-4, and provide an acid environment. Methenamine can release methanal (formaldehyde) in an acidic and a high-temperature environment. The released methanol can react with polyacrylamide (PAM) and resorcinol to generate phenolic resin via a polycondensation process. The phenolic resin can react further with PAM to produce linear polymers to block formation channels (Noller 1965; Xing et al. 2005).

The results of Li et al. (2015) have shown that at 70 °C and 20,000 ppm formation water salinity environments, the CO_2-sensitive gel could reduce 97% - 99% of the water permeability in a low permeability core (59.6 to 120.2 md). However, when the temperature (90□), water salinity (200,000ppm), and core permeability (1698.5md) were increased, the reduction to permeability decreased to 90% - 93%.

The advantage of this gel system is that it can be stable in an acid environment. The limitation is that the permeability reduction effectiveness is not well enough, and need further test to realize the permeability reduction efficiency to gas.

3.4.4. Silicate Gel. According to Lakatoset et al. (1999), silicate gels could control unwanted fluid flow because they have (a) low initial viscosities so that they can penetrate deep formation (b) enough high-environmental conditions (temperature, acid) resistance, (c) cost-effective, (d) environmentally friendly, and (e) easy to remove if an unexpected accident happens.

Burns et al. (2008) mentioned a new type of silica gel which was named as Silica Polymer Initiator (SPI) gel. This gel system contains sodium silicate, an organic initiator such as a polyacrylamide derivative. The SPI gel has a gelation time ranges from hours to several days. The SPI gel system has different properties and can be used in different ways by adjusting sodium to silicate ratio, which are shown in Table 3.14. The SPI gel is four to ten times stronger than cross-linked polyacrylamide (PAM) systems (Burns et al. 2008).

Table 3.14. Properties and application methods of SPI gels
(Data source: Burns et al., 2008)

Gel type	Sodium silicate to initiator ratio	Gel time at 40°C	pH range	Application method
Weak SPI gel	0.5 – 1.1	30 – 65 hours	7 – 8	Conformance control
Firm SPI gel	1.1 – 2.0	4 – 29 hours	8 – 10	Casing repair

Compared with traditional silicate gels, the SPI gel demonstrates a new type of silicate gel which is more elasticity and possessing delayed gelation control. However, calcium concentrations and formation water salinities have shown considerable influences on SPI gel, so it may not be used in a saline aquifer. Oglesby et al. (2016) have proved that the SPI gel was effectiveness in CO_2 flooding.

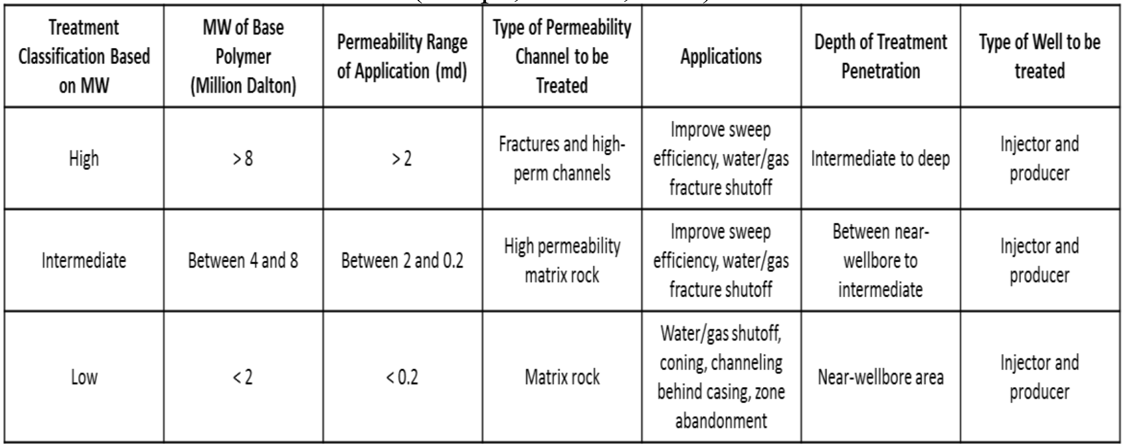
3.4.5. Factors Impacting Gel Performance. Many factors influence gel system performance. The first one is gel type. The components of gel system could be adjusted to fit for different environments. For example, as Table 3.13 shows, OCP systems with various of base materials, crosslinkers, and additives, can work at variable temperature ranges.

The molecular weight (MW) of base polymer affects gels application methods. Crespo et al. (2014) mentioned that when the base polymer MW is small, higher polymer concentration is required to form gel with reasonable gelation time, and viscosity buildup attributed to crosslinking is very sharp, approaching a right-angle set. However, when the MW of base polymer is high, lower concentration polymer is used, and the gel strength build up is gradual and can take several minutes to hours to reach full strength, which is beneficial at when large fluid volumes are used to reach deep into the formations. Table 3.15 shows the connections between polymer MW and polymer application area.

Base polymer and crosslinker concentration will affect gel performance. The increase of crosslinker concentration causes the reduction of gelation time. The increase of polymer and crosslinker concentration can improve gel viscosity and gel strength. According to the research of Hadi Mosleh (2016), HPAM/PAM based polymer gel which has lower polymer to crosslinker ratio results in higher gel strength.

Formation conditions such as temperature, pH, and salinity also affect gel performance. The increase of temperature and pH will reduce gel gelation time. Based on the introduction in Section 3.4.2, although HPAM/PAM crosslinked with metal agents have high permeability reduction to CO_2, however, these gel systems are still easy to be affected by environmental conditions. For example, with the increase in temperature and salinity, gels plugging performance decrease (Gu et al., 2015). The increasing of pH will reduce gel crosslinking, and result in lower viscosity and gel strength. Based on Gu et al. (2015), considering both strength and stability, the best range of pH value is 7~8.

Table 3.15. Conformance gels applications based on MW of base polymer (Crespo, F. et al., 2014)



Treatment Classification Based on MW	MW of Base Polymer (Million Dalton)	Permeability Range of Application (md)	Type of Permeability Channel to be Treated	Applications	Depth of Treatment Penetration	Type of Well to be treated
High	> 8	> 2	Fractures and high-perm channels	Improve sweep efficiency, water/gas fracture shutoff	Intermediate to deep	Injector and producer
Intermediate	Between 4 and 8	Between 2 and 0.2	High permeability matrix rock	Improve sweep efficiency, water/gas fracture shutoff	Between near-wellbore to intermediate	Injector and producer
Low	< 2	< 0.2	Matrix rock	Water/gas shutoff, coning, channeling behind casing, zone abandonment	Near-wellbore area	Injector and producer

3.4.6. Advantages and Limitations. The advantages of gel systems including wide applicability, high-temperature stability, CO_2 resistance, and relatively low viscosity before gelation (high injectability). Furthermore, according to Aird (2014), gel systems have high permeability reduction ability (for example the OCP systems could reduce 100% water permeability, or 83% CO_2 permeability).

The limitation is also significant; it is that the gel systems do not have enough plugging time. In the previous operations, gel systems were used as conformance control agents and did not need to stay in formation for a very long time. However, long enough remaining time (decades) in formation is required for a leakage control sealant. The high-temperature and high-pressure conditions in formation can reduce the gel system stable time, and leads to the decomposition of gel system. Besides, according to the research of Paul et al. (2013), polymer gel is only effective in sealing fractures with widths less than 1/4 mm. Future studies should focus on improving the working time of gel systems under formation conditions.

3.5. RESIN SYSTEMS

Resin systems are strong materials for use in blocking and plugging unwanted fluid flow in the wellbore and the very near-wellbore region in the oilfield.

3.5.1. Common Used Resin Systems. Resins exhibit the same flow-flowing property as cement, and can they be irreversibly set to hard, rigid, and solid (Morris et al., 2012). Based on the chemistry compositions, oilfield commonly used base resins include epoxy resins, phenolic resins, and furan resins. Among these materials, epoxy resins are the fittest for CO_2 leakage control and the most widely used resin types (Petrowiki).

All these resin systems have high-temperature stability, and wide compressive strength ranges. Basic information of the three commonly used resins in oilfield are shown in Table 3.16. The resin systems are not sensitive to acid, salinity, and pH. Therefore, compared with traditional Portland cement, resin systems are more stable under acid downhole environment. For these reasons, resin systems are suitable for CO_2 storage and leakage control.

Table 3.16. Basic information of base resins (Data from Petrowiki)

Resin Type	Application Temperature, ℃		Compressive Strength, MPa
	Normal	Max	
Epoxies Resin	21-55	205	6.895 – 137.9
Phenolic Resin	32-77	232	
Furans Resin	15-177	371	

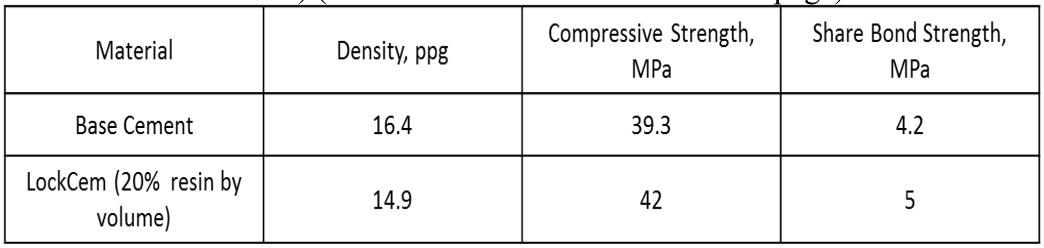
A resin system usually contains base resin and hardener. The hardener is used to react with resin and form cross-linking structure to improve resin strength. Amine-based hardener is one of the most commonly used hardener types.

3.5.2. Review of Some Resin System. This section will introduce some resin systems include Halliburton WellLock® resin, thermal activated resin, CO_2-triggered resin, and double network water-absorbent resin (DNWR).

3.5.2.1. Halliburton WellLock® resin. Epoxy resin crosslinked with polymer is the most widely used type of resin systems. Halliburton invented a temperature active polymer resin system which is the WellLock® resin system. This system applies a cross-linking reaction between an amine hardener and epoxides, resulting in a cured three-dimensional infinite polymer network. The target temperature of the system is between15.56 and 93.3°C, and the compressive strength is from 34.47 to103.4 MPa (5 to 15 Kpsi), and the tensile strength ranges from several hundred psi to larger than two thousand psi. The density and viscosity of the WellLock® resin can be adjusted by field conditions (Based on the introductory page of Halliburton).

Resin system can be used as cement additive to help improve cement properties. Halliburton invented the LockCem™ cement, which uses Portland cement mixes with the WellLock® resin system. As Table 3.17 shows, the LockCem™ cement has lower density and higher strength than Portland cement. The advantages of LockCem™ cement help it work better in well operations. The field application methods of WellLock® resin and LockCem™ cement are shown in Figure 3.22.

Table 3.17. LockCem™ Cement: WellLock resin & Portland Cement (20% resin by volume) (Based on Halliburton LockCem™ page)



Material	Density, ppg	Compressive Strength, MPa	Share Bond Strength, MPa
Base Cement	16.4	39.3	4.2
LockCem (20% resin by volume)	14.9	42	5

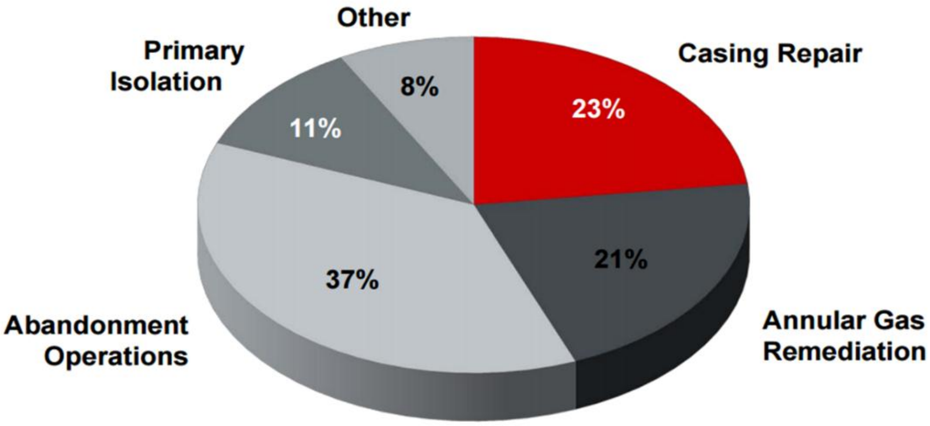


Figure 3.22. WellLock® Resin and LockCem™ application methods based on 400^+ case histories (Paul Jones, Halliburton, 2016)

3.5.2.2. Thermal activated resin. The thermal activated resin is a particle free, multi-component polymer resin based plugging material, with a curing process activated by temperature. By adjusting the initiation of curing process and curing time, thermal activated resin can suit determined temperature of formation. The most common thermal activated resins include, polyester, epoxy, phenolic, vinyl ester, polyurethane, silicone, and polyamide-imide resin (Corrosionpedia, 2017).

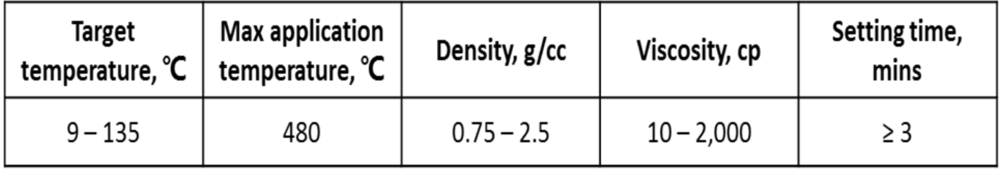
Some properties of thermal activated resin are shown in Table 3.18. The thermal activated resin is a low viscosity resin system that can deeply penetrate formations and seal small channels. Some additives which are needed during the thermal activated resin making process are listed below (Knudsen et al., 2014):

- Curing Initiator (liquid): Adjust curing time (Catalyst react with polymer resin)
- Accelerators (liquid): Speed the curing process
- Inhibitors (liquid): Slow curing process time
- Viscosifier: Increase the resin viscosity
- Weight Fillers (solid): Control system weight/density to a specific number
- TAR Cleaner: Remove residual thermal activated resin from equipment
- TAR Solvent: Dissolve and remove undesirable thermal activated resin plug after its hardened

Thermal activated resin is a CO_2-resistance material. The performance of thermal activated resin exposure to CO_2 is shown in Table 3.19. From this table, we can find that after 12 months, the permeability of resin sample did not increase much, and the compressive strength was almost same with the initial conditions, or even bigger.

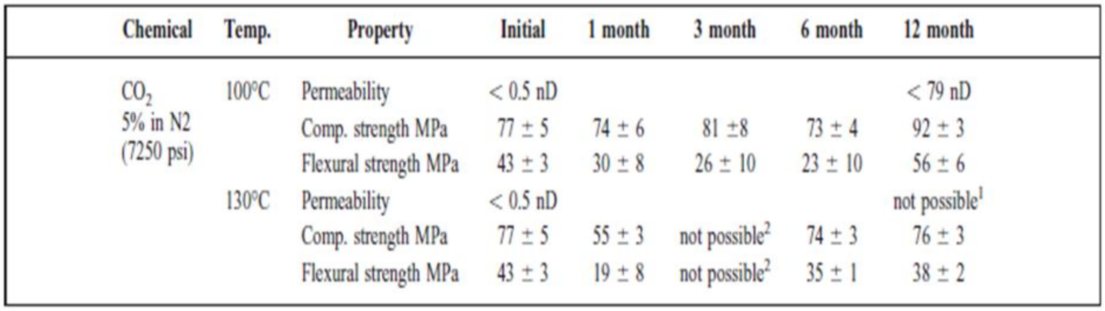
The thermal activated resin can also be cement additive because it has better properties when comparing with cement. Table 3.20 shows the comparison between thermal activated resin and cement.

Table 3.18. Properties of thermal activated resin (Knudsen et al., 2014)



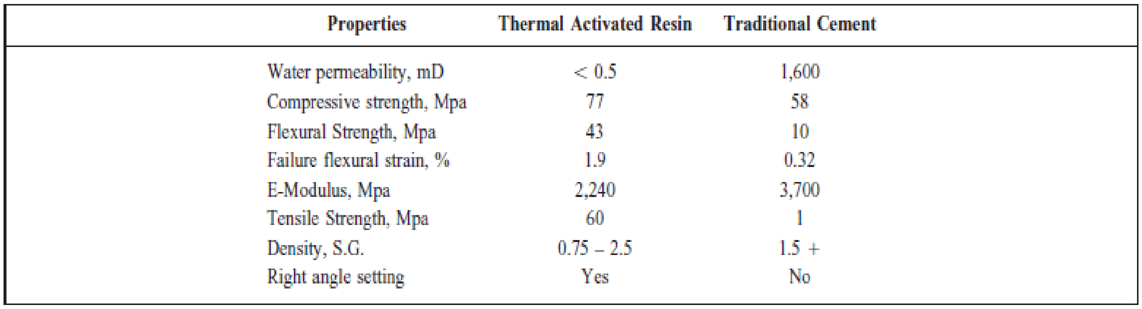
Target temperature, ℃	Max application temperature, ℃	Density, g/cc	Viscosity, cp	Setting time, mins
9 – 135	480	0.75 – 2.5	10 – 2,000	≥ 3

Table 3.19. Thermally activated resin exposure to CO_2 (Beharie et al., 2015)



Chemical	Temp.	Property	Initial	1 month	3 month	6 month	12 month
CO_2 5% in N2 (7250 psi)	100°C	Permeability	< 0.5 nD				< 79 nD
		Comp. strength MPa	77 ± 5	74 ± 6	81 ±8	73 ± 4	92 ± 3
		Flexural strength MPa	43 ± 3	30 ± 8	26 ± 10	23 ± 10	56 ± 6
	130°C	Permeability	< 0.5 nD				not possible[1]
		Comp. strength MPa	77 ± 5	55 ± 3	not possible[2]	74 ± 3	76 ± 3
		Flexural strength MPa	43 ± 3	19 ± 8	not possible[2]	35 ± 1	38 ± 2

Table 3.20. Comparison between thermal activated resin and Portland cement (Knudsen, K. et al., 2014)



Properties	Thermal Activated Resin	Traditional Cement
Water permeability, mD	< 0.5	1,600
Compressive strength, Mpa	77	58
Flexural Strength, Mpa	43	10
Failure flexural strain, %	1.9	0.32
E-Modulus, Mpa	2,240	3,700
Tensile Strength, Mpa	60	1
Density, S.G.	0.75 – 2.5	1.5 +
Right angle setting	Yes	No

3.5.2.3. CO_2-triggered resol phenol-formaldehyde resin system. This resin system contains alkaline catalysts. Hence, the CO_2-triggered resin system can react with CO_2. Through this way, the resin system can be solidified. However, from Li et al (2016)'s experiments, the CO_2 plugging performance of this resin is not well enough, only 30.5%. The compressive strength of this resin is lower than the epoxy resin system. Temperature, salinity, pH, and additives have shown influences on the resol phenol-formaldehyde resin system. Based on these limitations, the resol phenol-formaldehyde resin is not suitable to treat CO_2 leakage problems. However, future study can pay attention to using additives to improve resol phenol-formaldehyde resin properties.

3.5.2.4. Double network water-absorbent resin (DNWR). The DNWR is a polymer crosslinked resin system which contains two independently crosslinked networks (Yang-Ho N. et al., 2004). The first network is a rigid polyelectrolyte and the second one is a flexible neutral polymer (Lai et al., 2010). The first network can tolerance high tensile stress while it is brittle by itself. Hence that, the second network is designed for relaxing stress. This structure can provide high strength and prevent crack development. As Figure 3.23 shows, when the compressive pressure from the formation (black arrows in Figure 3.23) acting on the DNWR, the second network can absorb and disperse the pressure to the first network (white arrows in Figure 3.23) so that the influence of pressure is reduced.

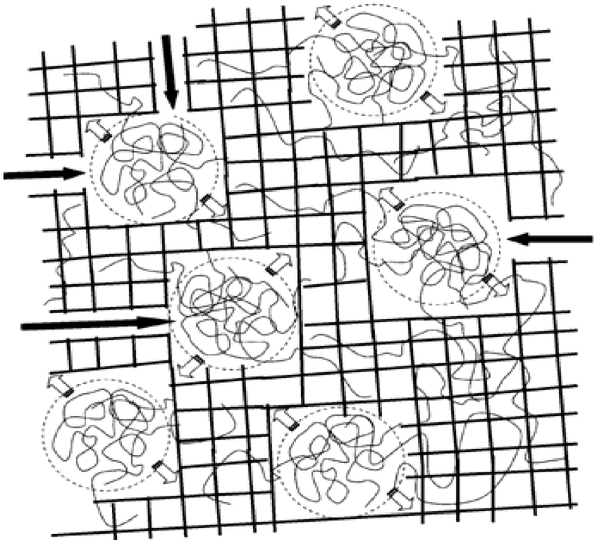


Figure 3.23. Structural model of DNWR (Lai et al., 2010)

Because of the structure advantage, the compressive strength of DNWR could reach 17.2 MPa, which is 20 times larger than single network gels (Lai et al., 2010). DNWR also has great thermal stability, and it can work at formation with the temperature of 150°C for more than 30 days. DNWR is not sensitive to pH and salinity, so it has good chemical stability. The DNWR can be employed as deep formation fluid migration control agent as it has resistance to high-pressure and high-temperature.

The plugging mechanisms of DNWR including deformability, absorbability, and swelling property. DNWR has good deformability, so the formation pressure difference can help squeeze DNWR into formation fracture and fill the loss formation automatically. As Figure 3.24 shows, after being squeezed into fractures, hydration happens to the hydrophilic groups on polymer chains because the existence of the high-temperature and water in the formation, so the polymer chains can spread and gather to plug the fractures. The polymer chains can also adsorb on the surface of rock to improve the sealing performance. As Figure 3.25 shows, when DNWR particles are inside the fractures, they can enlarge their volume by absorbing formation water. Through this way, DNWR particles can fill and compact the formation fractures. According to Lai et al (2010) the DNWR swelling ratio is five to ten times of original weight.

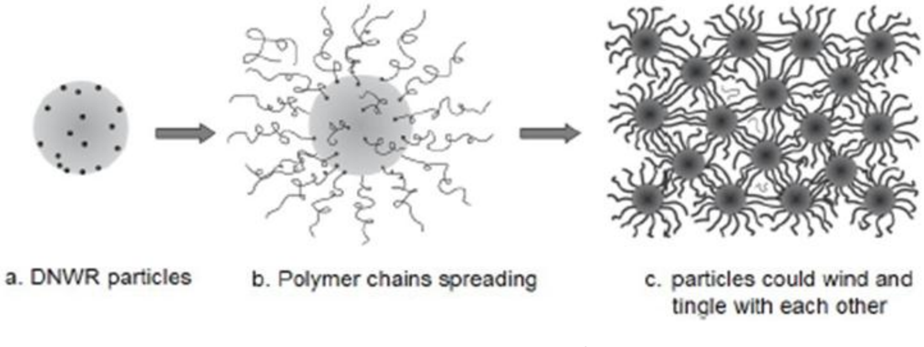


Figure 3.24. DNWR plugging mechanism in the fracture (Lai, X. L. et al, 2010)

3.5.3. Advantages and Limitations. The advantages of resin systems include high bonding strength, good thermal stability, changeable viscosity and setting time, long life, and favorable chemical inertness (acid-resistance).

However, there are still limitations for resin systems such as expensive, relatively complex preparation, low injectability. Overall, the resin systems are materials which have huge potential but have not been widely used.

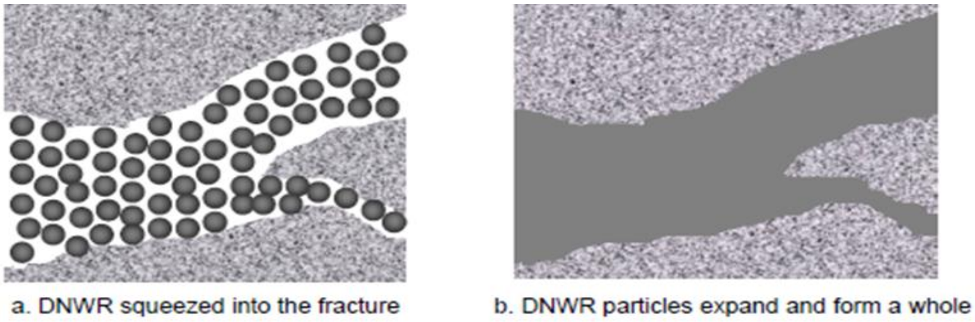

a. DNWR squeezed into the fracture
b. DNWR particles expand and form a whole

Figure 3.25. DNWR swelling and plugging process (Lai, X. L. et al, 2010)

3.6. BIOFILM BARRIERS AND BIOMINERALIZATION

This section will focus on biofilm barriers and biomineralization. Figure 3.26 describes the application areas of these two materials.

3.6.1. Biofilm Barriers and Biomineralization/MICP Introduction. Biofilm are microorganism assemblages firmly attached to a surface, which form and are encased within self-produced extracellular polymeric substances (EPS), a hydrated matrix of mostly polysaccharides and proteins (Costerton and Stewart, 2001; Lewandowski and Beyenal, 2007). Biofilms can reduce subsurface formation porosity and permeability, and then reduce upward CO_2 leakage.

Microbial (or biofilm) induced carbonate precipitation (MICP) which is also called biomineralization, uses mineral trapping and solubility trapping mechanisms to improve CO_2 storage. The equations in Figure 3.27 demonstrate the biomineralization process. The mechanism is using biofilm to produce and induce urea hydrolysis, then reacting with Ca^{2+} ions in formation water to form the $CaCO_3$ precipitate. In this process, HCO_3^- is used to provide CO_3^{2-} for forming carbon precipitate, this reaction can increase the solubility of CO_2, and reduce the CO_2 volume in the subsurface. Solubility trapping indicates CO_2 dissolves in the brine and forms H_2CO_3. The formed $CaCO_3$ precipitate could be the mineral trapping materials to reduce the porosity and permeability of the underground formation. MICP can also be applied to cement repairing and cement properties improving. For example, bacteria S. pasteurii plays an important role in increasing the compressive strength of fly ash concrete by up to 22% at the age of 28 days (Navneet et al., 2011)

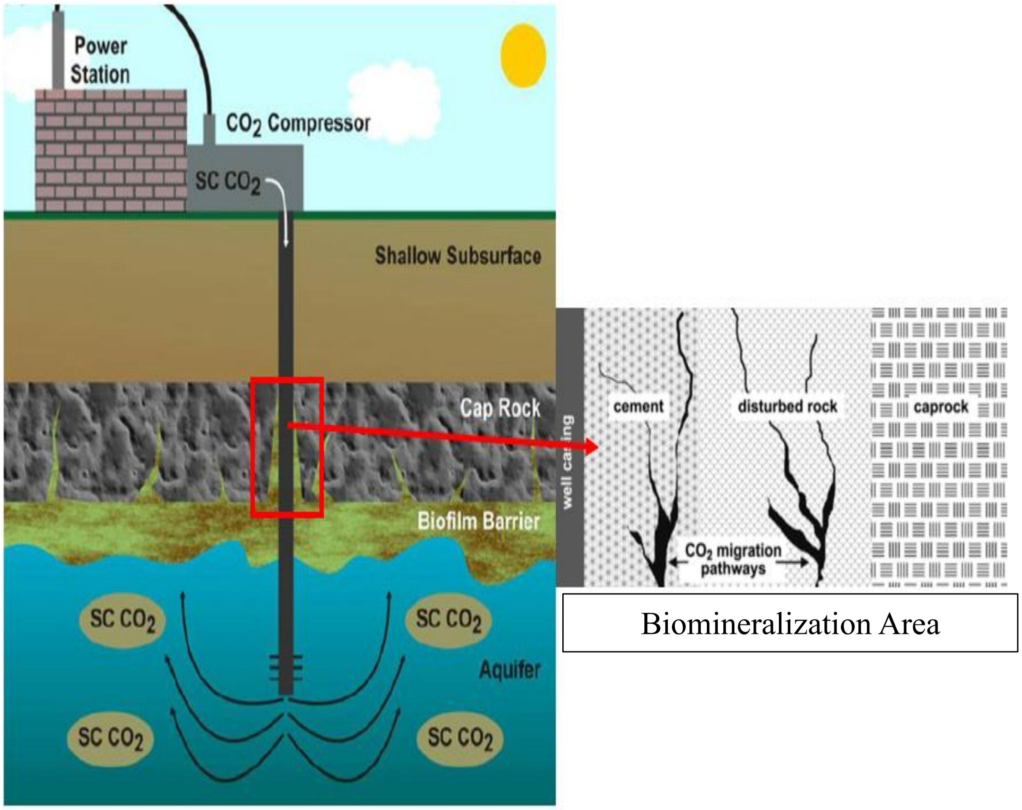


Figure 3.26. Biofilm barriers and MICP reduce the upward CO_2 leakage through formation fracture and near wellbore area pathways (Based on Andrew C. Mitchell et al., 2008 and A. B. Cunningham et al., 2011)

Biofilm plugging (biofilm barrier and MICP) materials include microorganisms, Ca^{2+} ions, urea, and nutrient feed. The microorganisms are used for forming biofilm barrier and induce calcium precipitation. The Ca^{2+} ions providing the precipitation materials, and the urea can also help adjust the pH to a weak alkaline environment is good for the growth of most types of bacteria. The nutrient feed is the supply for the growth of biofilm.

CO_2(g) Dissolution and Disassociation.

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O(l) \leftrightarrow H_2CO_3 \qquad (2)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (3)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (4)$$

Ureolysis.

$$CO(NH_2)_2 + H_2O \rightarrow NH_2COOH + NH_3 \qquad (5)$$

$$NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3 \qquad (6)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (7)$$

$$2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^- \qquad (8)$$

$$HCO_3^- + H^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2H_2O \qquad (9)$$

Overall Ureolysis and $CaCO_3$ Precipitation.

$$NH_2CONH_2 + 2H_2O \leftrightarrow 2NH_4^+ + CO_3^{2-} \qquad (10)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s) \qquad (11)$$

Figure 3.27. Equations of microbial (or biofilm) induced carbonate precipitation (Andrew C. Mitchell et al., 2010)

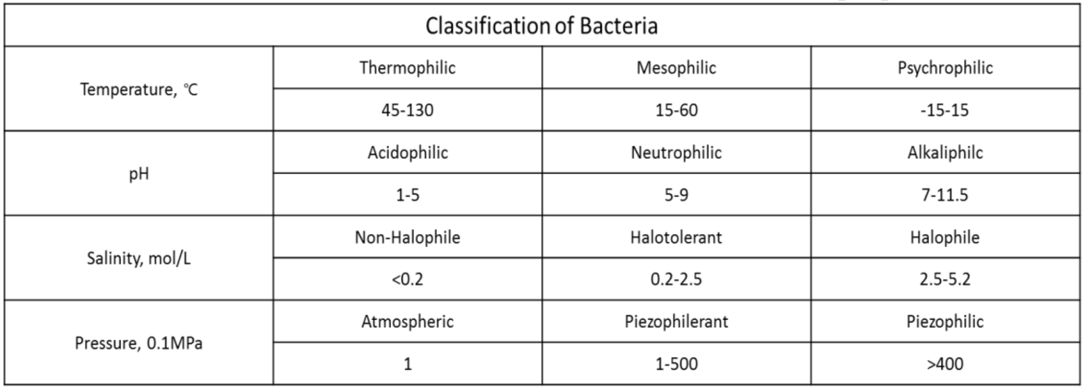
Several challenges are existing when considering the use of this technology in relevant subsurface CO_2 storage site conditions including elevated temperatures, pressures, and the presence of supercritical CO_2 (Phillips et al., 2012).

As the subsurface CO_2 is usually in supercritical phase, so the biofilm barrier should grow under an environment which has pressure larger than 7.4MPa, temperature larger than 32°C, and weak-acid condition. However, urea hydrolysis needs an appropriate environment, so that, the optimum conditions for MICP need a temperature between 20 to 37°C, and weak-alkaline environment (Mitchell, 2008). Hence that, the compositions of initial materials should be adjusted to provide favorable conditions for biomineralization.

3.6.2. Factors Impacting Biofilm Barriers and Biomineralization. Factors include bacteria type, temperature, pH, urea and calcium ions concentrations can affect biofilm barrier growth and biomineralization. These factors show impacts on MICP because they can affect urease activity and calcium precipitation.

3.6.2.1. Bacteria types. Based on the hereditary characters and physical properties, the bacterias used for CO_2 sequestration containing thermophilic bacteria, mesophilic bacteria, psychrophilic bacteria, acidophilic bacteria, alkaliphiles bacteria, halophilic bacteria, and piezophilic bacteria. Table 3.21 introduces some properties of these types of bacteria. In the field application, different types of bacterias can be mixed to improve the biofilm properties.

Table 3.21. Classification of bacteria based on different properties



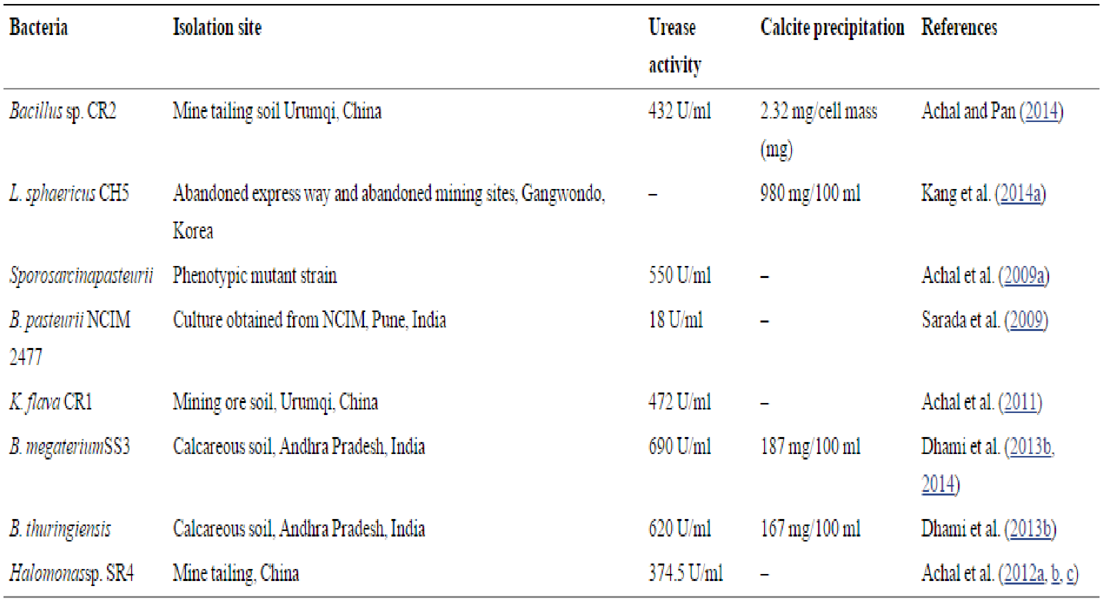
Classification of Bacteria			
Temperature, ℃	Thermophilic	Mesophilic	Psychrophilic
	45-130	15-60	-15-15
pH	Acidophilic	Neutrophilic	Alkaliphilc
	1-5	5-9	7-11.5
Salinity, mol/L	Non-Halophile	Halotolerant	Halophile
	<0.2	0.2-2.5	2.5-5.2
Pressure, 0.1MPa	Atmospheric	Piezophilerant	Piezophilic
	1	1-500	>400

The urease is one of the most important parts in biomineralization, each kind of bacteria produces different amount of urease. The researchers have investigated many types of bacteria which could produce urease, and are shown in Table 3.22 (Periasamy Anbu et al., 2016).

3.6.2.2. Temperature, pH, and salinity. Temperature can decide the catalysis between urease and urea as same as other enzymatic reactions. For most ureases, the optimum reaction temperature ranges from 20 to 37 °C (Mitchell 2008).

PH value influences calcite precipitation because urea hydrolysis only happens at specific pH ranges where the urease can be active. Previous studies (Gorospe et al. 2013; Stocks-Fischer et al. 1999) reported pH at 8.0 is the most suitable for keeping urease activity. Urease activity decrease with the rise of pH. Weak alkaline conditions were found to favor the formation of CO_3^{2-} from HCO_3^- that leads to calcification of the bicarbonate generated (Knoll, A. H., 2003)

Table 3.22. Information of different types of urease-producing bacteria (Periasamy Anbu et al., 2016)



Bacteria	Isolation site	Urease activity	Calcite precipitation	References
Bacillus sp. CR2	Mine tailing soil Urumqi, China	432 U/ml	2.32 mg/cell mass (mg)	Achal and Pan (2014)
L. sphaericus CH5	Abandoned express way and abandoned mining sites, Gangwondo, Korea	–	980 mg/100 ml	Kang et al. (2014a)
Sporosarcinapasteurii	Phenotypic mutant strain	550 U/ml	–	Achal et al. (2009a)
B. pasteurii NCIM 2477	Culture obtained from NCIM, Pune, India	18 U/ml	–	Sarada et al. (2009)
K. flava CR1	Mining ore soil, Urumqi, China	472 U/ml	–	Achal et al. (2011)
*B. megaterium*SS3	Calcareous soil, Andhra Pradesh, India	690 U/ml	187 mg/100 ml	Dhami et al. (2013b, 2014)
B. thuringiensis	Calcareous soil, Andhra Pradesh, India	620 U/ml	167 mg/100 ml	Dhami et al. (2013b)
*Halomonas*sp. SR4	Mine tailing, China	374.5 U/ml	–	Achal et al. (2012a, b, c)

Dupraz (2009) used B. pasteurii ATCC11859 strain and brine from Dogger aquifer (Paris Basin, France) to study the influence of salinity on biomineralization. Dupraz adjusted the brine salinity ranged from 5,800 ppm to 35,000 ppm. The results have proved that salinity increase in a suitable range could help increase pH, provide appropriate conditions for calcium precipitating, and shorten the precipitate beginning time. The mechanism by which salinities positively affect ureolysis rates is likely related to the effect of sodium ions on exchanges of urea and calcium between cells and medium (Dupraz et al., 2009).

In field applications, selecting bacteria that use for forming biofilm barrier should base on the required conditions. Table 3.23 has listed some bacterias' growing conditions.

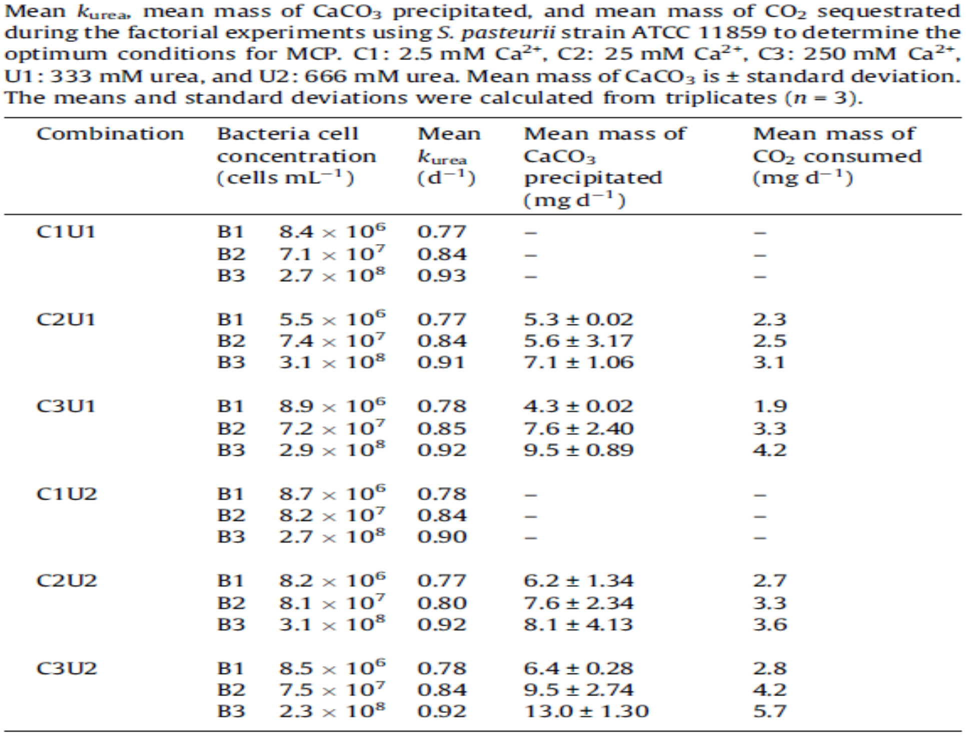
3.6.2.3. $ScCO_2$ challenge. Peet et al. (2015) did experiments and proved that $ScCO_2$ could reduce spores' viability, so supercritical CO_2 has an adverse effect on biofilm barriers growth. Mitchell (2008) used $ScCO_2$ to challenge cores which were plugged by biofilm materials (Shewanella, Frigidimarina) and found that the permeabilities of the cores were increased a little, which means $ScCO_2$ do has influence on biofilm growth.

Table 3.23. Growth conditions of types of bacteria which can be used for CO_2 sequestration (Eugenio-Felipe U. Santillan,2015; Peet, K. C. et al., 2015; Achal, V. et al., 2009; Avinash. D. Patil, Nandkishor. Patil., 2013; Ono and Cuello, 2004)

Types	Example Isolation Site	Growth Temperature,°C	Growth Pressure, MPa	Growth pH	Growth Salinity
Lactobacillus	Crystal Geyser, Utah, U.S.A	25-45	CO_2: 0.1-1.0	4-8	NaCl 11,700-17,550 ppm
Bacillus sp. strain	Formation Water, 1,528–1,534 m, 55 °C; Frio-2, Texas	23-55	Formation Pressure: 15	4-10	0-60,000 ppm
Micro Algae	Marine and Fresh Water	15-26	-	Neutral pH	-

3.6.2.4. Bacterial cell, urea, and Ca^{2+} concentrations. Based on Table 3.24, the increase of bacterial cell concentration has shown a positive effect on the calcium precipitation, and the positive effect also happened when the urea concentration was increased (Okwadha et al., 2010).

Table 3.24. Calcium and urea concentrations effect on urea hydrolysis and calcium precipitation (Okwadha et al., 2010)



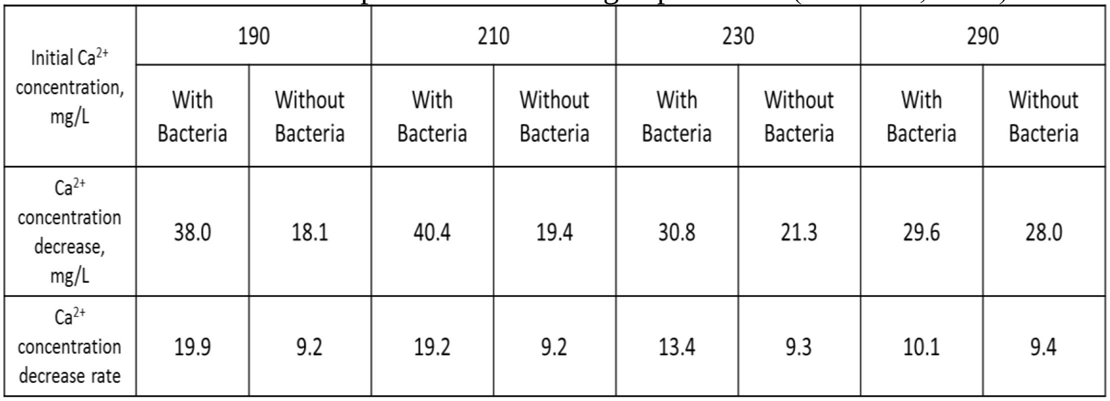
Mean k_{urea}, mean mass of $CaCO_3$ precipitated, and mean mass of CO_2 sequestrated during the factorial experiments using *S. pasteurii* strain ATCC 11859 to determine the optimum conditions for MCP. C1: 2.5 mM Ca^{2+}, C2: 25 mM Ca^{2+}, C3: 250 mM Ca^{2+}, U1: 333 mM urea, and U2: 666 mM urea. Mean mass of $CaCO_3$ is ± standard deviation. The means and standard deviations were calculated from triplicates ($n = 3$).

Combination	Bacteria cell concentration (cells mL^{-1})		Mean k_{urea} (d^{-1})	Mean mass of $CaCO_3$ precipitated (mg d^{-1})	Mean mass of CO_2 consumed (mg d^{-1})
C1U1	B1	8.4×10^6	0.77	–	–
	B2	7.1×10^7	0.84	–	–
	B3	2.7×10^8	0.93	–	–
C2U1	B1	5.5×10^6	0.77	5.3 ± 0.02	2.3
	B2	7.4×10^7	0.84	5.6 ± 3.17	2.5
	B3	3.1×10^8	0.91	7.1 ± 1.06	3.1
C3U1	B1	8.9×10^6	0.78	4.3 ± 0.02	1.9
	B2	7.2×10^7	0.85	7.6 ± 2.40	3.3
	B3	2.9×10^8	0.92	9.5 ± 0.89	4.2
C1U2	B1	8.7×10^6	0.78	–	–
	B2	8.2×10^7	0.84	–	–
	B3	2.7×10^8	0.90	–	–
C2U2	B1	8.2×10^6	0.77	6.2 ± 1.34	2.7
	B2	8.1×10^7	0.80	7.6 ± 2.34	3.3
	B3	3.1×10^8	0.92	8.1 ± 4.13	3.6
C3U2	B1	8.5×10^6	0.78	6.4 ± 0.28	2.8
	B2	7.5×10^7	0.84	9.5 ± 2.74	4.2
	B3	2.3×10^8	0.92	13.0 ± 1.30	5.7

However, when comes to the calcium ions concentration, the results become more complex than that of bacteria cell and urea concentrations. According to the previous reports (Okwadha et al., 2010 and Liu et al., 2013), we can realize that bacteria can help facilitate calcium precipitate, while the increase in calcium concentration may not improve the forming of the precipitate.

The optimum range of Ca^{2+} concentration for MICP is from 25mg/L to 250mg/L, and if the concentration of calcium ions is higher than 500mg/L, the efficiency of calcite precipitation will decrease because too much Ca^{2+} shows a negative effect on bacterial metabolism (Okwadha et al., 2010). For example, Table 3.25 illustrates 190mg/L is the best for Synechococcus induced calcite precipitation. The optimum numbers of the bacterial cell, urea, and Ca^{2+} concentrations are various, and these numbers have connection with reactions environments and bacterial types.

Table 3.25. Consumption of Ca^{2+} during experiments (Li & Fan, 2013)



Initial Ca^{2+} concentration, mg/L	190		210		230		290	
	With Bacteria	Without Bacteria	With Bacteria	Without Bacteria	With Bacteria	Without Bacteria	With Bacteria	Without Bacteria
Ca^{2+} concentration decrease, mg/L	38.0	18.1	40.4	19.4	30.8	21.3	29.6	28.0
Ca^{2+} concentration decrease rate	19.9	9.2	19.2	9.2	13.4	9.3	10.1	9.4

3.6.3. Advantages and Limitations. The advantages of using biofilm or biomineralization to plug CO_2 include 1) biofilm has low viscosity, so it can be used in near wellbore area; 2) bacteria materials are environmental friendly; 3) biomineralization process can be controlled by varying the concentration of Ca^{2+} and the nutrient feed.

The main potential limitation of microbial enhanced CCS is the ability of microorganisms to withstand high pressure and SC-CO_2 (Mitchell. et al., 2010). Some other limitations include 1) the distribution of $CaCO_3$ is not homogeneous, most deposits are formed at the inlet part; 2) the bacteria and nutrition feed are expensive; 3) Some types of bacteria are not good for human health. Future researchers could pay more attention to promoting biofilms' environmental adaptive capacity and improving the distribution of carbonate calcium precipitation.

3.7. NANOPARTICLES

Nanoparticles are very useful in carbon sequestration. Nanoparticles could be used as additives to improve the performance of foams, silica gel, and cement. Nanoparticles solution could also help enhance CO_2 storage by controlling CO_2 fluid mobility, decreasing CO_2 fingering, and finally reduce CO_2 leakage risks in deep saline aquifers.

3.7.1. Nanoparticles Classifications. Nanoparticles are particles between 1 and 100 nanometers in size. Based on particle size and component, the classifications of nanoparticles have been shown in Table 3.26 and 3.27 (Words in red mean commonly used nanoparticles).

Table 3.26. Classification of nanoparticles based on particle size (Based on the United States Environmental Protection Agency)

EPA Description	Particle Diameter, µm
Super Coarse	$d_{pa} > 10$
Coarse	$2.5 < d_{pa} \leq 10$
Fine	$0.1 < d_{pa} \leq 2.5$
Ultra Fine	$d_{pa} \leq 0.1$

Table 3.27. Classification of nanoparticles based on particle compositions

Type	Examples
Metallic Nanoparticles	Au, Ag, Ni, Co, Pt, Fe
Carbide Nanoparticles	SiC
Metallic Oxide Nanoparticles	SiO_2, ZnO, Fe_2O_3, Al_2O_3, TiO_2, $BaTiO_3$
Inorganic Salt Nanoparticles	CdS, CdSe, $CaCO_3$, AgCl
Organic Nanoparticles	Polymeric Nanoparticles

3.7.2. Nanoparticles as Foams Stabilizers. Nanoparticles can promote the foam stability by adsorbing on the interface of gas and liquid to improve the interface's mechanical strength. Nano-silica is the most commonly used foam additive, sometimes fly ash nanoparticle has also been used. Based on previous research (Singh et al., 2015), the fly ash nanoparticle contains 63.35% SiO_2, 20.7% Al_2O_3, 5.52% Fe_2O_3, 4.17% CaO, and some other oxides.

Many parameters can affect nanoparticle foams stability, such as particle size, particle concentration, salinity, temperature, and pressure. Horozov (2008) indicated that nanoparticles which can be used for forming foam should have the particle size between several nanometers and several micrometers. Hariz (2012) demonstrated 5nm particles could form more stabilized and smaller foam than particle which has a 20nm particle size in the same experimental conditions. This happened because with the same concentration, smaller particles have larger quantity, larger surface area, and distribute more homogeneous than larger size particles. However, Arezoo et al. (2017) mentioned that relatively larger particle size is good for foam stability based on the contact angle theory.

According to the research of Yu et al (2012), under 25°C, 1500psi condition, more foam was formed when the concentration of particle increased from 4000 ppm to 6000 ppm. The reason is higher particle concentration can improve the stabilization of foam. However, when the particle concentration growing to a certain degree, the particles may gather together and lead to larger particle size, and large particle size is harm for foam generation.

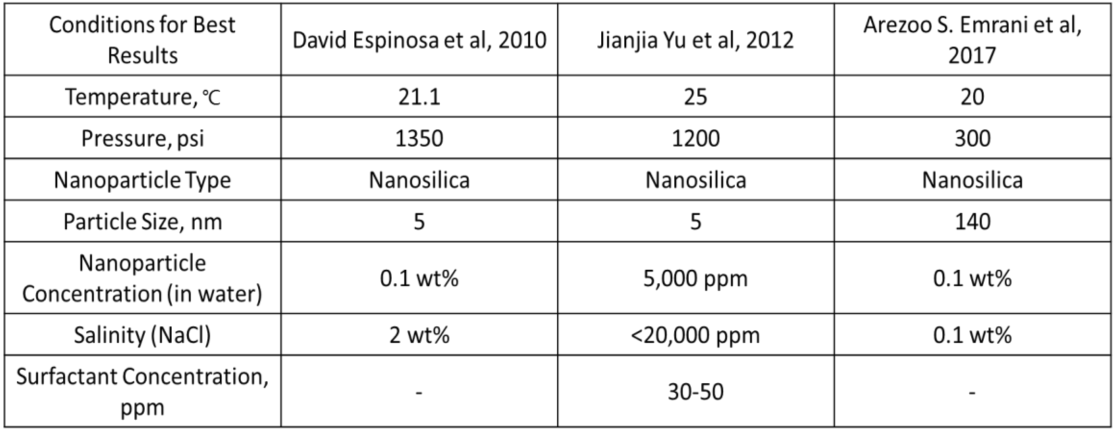
Salinity affects nanoparticle CO_2 foam by two ways. On one side, the increase of salinity could increase the hydrophobicity of nanoparticle, and this is conducive to nanoparticle adsorption on the gas-liquid interface. On the other hand, the increase of salinity leads to aggregation of the nanoparticles and reduces foam generation. Yu et al (2012) demonstrated that under 5000 ppm concentration of nano-silica condition, as the concentration of NaCl increased from 0 ppm to 50,000 ppm, the generation of CO_2 foam was inhibited.

Yu et al (2012) indicated when the pressure was between 1200 psi to 2000 psi, the height of CO_2 foam was increasing with the growing pressure, while the foam stabilization was decreasing. A higher temperature could accelerate the thermal motion of nanoparticles and against nanoparticles absorption. When the test temperature was increased from 25°C to 60°C, the foam stabilization reduced, and there was no foam generated when the temperature was above 60°C.

Adding a small amount of surfactant is useful for nano-silica CO_2 foam generation. Yu et al (2012) have shown that more foam was generated under room condition with 5000 ppm nano-silica, and surfactant concentration was between 30 ppm and 50 ppm.

Overall, the favorable conditions for nano-silica lab experiments are listed in Table 3.28 below. With different additives and experimental environments, the favorable conditions can be various. In the field applications, nanoparticles should be set based on field conditions.

Table 3.28. Favorable conditions for nano-silica as foam additive
(Based on Jianjia Yu et al., 2012; David Espinosa et al., 2010; Arezoo.S.E et al., 2017)



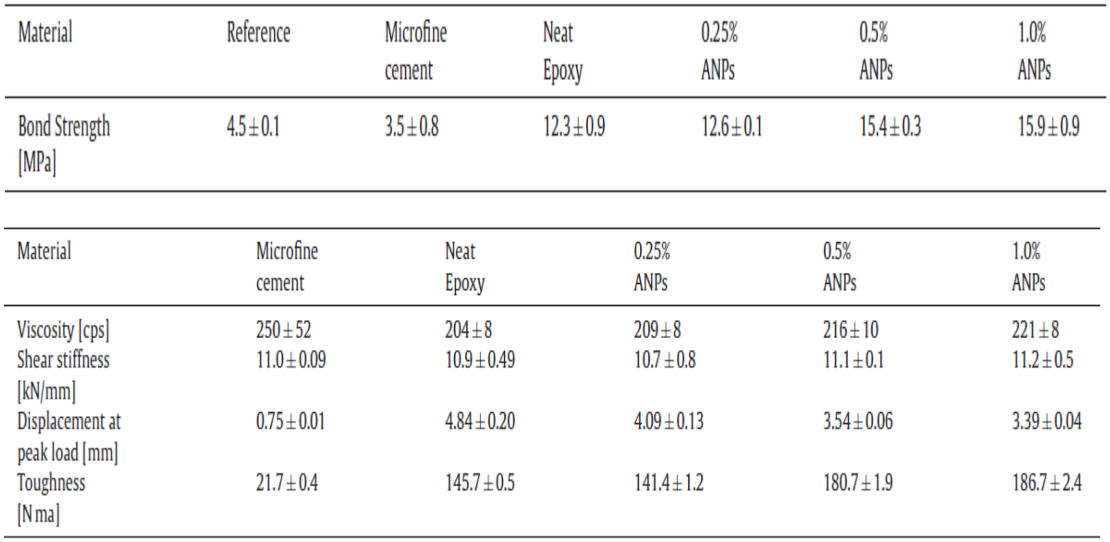
Conditions for Best Results	David Espinosa et al, 2010	Jianjia Yu et al, 2012	Arezoo S. Emrani et al, 2017
Temperature, ℃	21.1	25	20
Pressure, psi	1350	1200	300
Nanoparticle Type	Nanosilica	Nanosilica	Nanosilica
Particle Size, nm	5	5	140
Nanoparticle Concentration (in water)	0.1 wt%	5,000 ppm	0.1 wt%
Salinity (NaCl)	2 wt%	<20,000 ppm	0.1 wt%
Surfactant Concentration, ppm	-	30-50	-

B. Aminzadeh et al. (2013) mentioned that pre-positioning a dispersion of nanoparticles (for example nano-silica) above or within potential leakage pathways such as fractures, faults, and abandoned wells could help form CO_2/brine foam when CO_2 transmits through the paths. This method could help slow or even prevent CO_2 leakage.

3.7.3. Nanoparticles as Cement Additives. Cement repair materials should be flexible, have relatively low shrinkage, and low viscosity. Moneeb Genedy et al (2016) suggested that polymer based materials are optimal repair materials to achieve those requirements. Furthermore, polymer combined with metallic materials has very high bond strength. Some other materials such as nano-barite and nano-silica can also help improve cement properties.

Moneeb Genedy et al (2016). presented a type of polymer nanocomposite called Aluminum Nanoparticles (ANP)-epoxy nanoparticles for restoring well seal integrity. According to his research, the ANP was added into the epoxy resin and mixed at 110℃ for 2 hours. This process was used to reduce the resin viscosity and improve ANP dispersion. The hardener was also added into the mixture, the ratio of hardener to the resin by mass was 1:2.2. The viscosities of different materials were measured under room temperature. Table 3.29 shows the properties of ANP added cement compared with cement without ANP, and proves that ANP-epoxy nanoparticles could improve the cement properties, for example, the increase of bond strength and the reduction of viscosity, then make it more appropriate for well cement seal integrity.

Table 3.29. Properties of different repair materials (Moneeb Genedy et al., 2016)



Material	Reference	Microfine cement	Neat Epoxy	0.25% ANPs	0.5% ANPs	1.0% ANPs
Bond Strength [MPa]	4.5±0.1	3.5±0.8	12.3±0.9	12.6±0.1	15.4±0.3	15.9±0.9

Material	Microfine cement	Neat Epoxy	0.25% ANPs	0.5% ANPs	1.0% ANPs
Viscosity [cps]	250±52	204±8	209±8	216±10	221±8
Shear stiffness [kN/mm]	11.0±0.09	10.9±0.49	10.7±0.8	11.1±0.1	11.2±0.5
Displacement at peak load [mm]	0.75±0.01	4.84±0.20	4.09±0.13	3.54±0.06	3.39±0.04
Toughness [N ma]	21.7±0.4	145.7±0.5	141.4±1.2	180.7±1.9	186.7±2.4

Amin. A. et al (2017) mentioned use barite nanoparticles to reduce the cement fluid loss. Cement fluid loss is one important reason which causes the decrease of cement physical properties because of the loss of fluid increases cement density and leads to a higher differential pressure. These changes of properties increase the possibility of cement fracture and loss. So, controlling the cement fluid loss is an important way to keep cement seal integrity, and reduce CO_2 leakage.

Different mass of barite nanoparticles was added to Portland cement. The cement slurry compositions are shown in Table 3.30. The barite nanoparticle size in this research ranged from 19 nm to 49 nm. Researchers tested two samples with different Nano-barite and hydroxyethyl cellulose (HEC) under 71°C, 2000 psi condition, and found that barite nanoparticles do not have a direct effect on cement thickening time.

Table 3.30. Compositions of cement slurry
(Amin. A et al., 2017)

	Base Case	**1% NP**	**2% NP**	**3% NP**
Portland Cement (gr)	432.5	432.5	432.5	432.5
Water	432.5	432.5	432.5	432.5
HEC (gr)	3	3	3	3
Barite (gr)	161.5	150.5	129	109.5
Barite NPs (gr)	0	11	32.5	52

Some other materials can also help promote cement properties and reduce CO_2 leakage. Nazari and Riahi (2010) studied titanium oxide nanoparticles could help improve cement compressive strength and reduce water permeability. Bahadori and Hosseini (2012) had demonstrated that nano-silica could fill the cement microstructure better and improve the cement physical properties. Shiyi Zhang et al. (2014) showed that nano-kaolinite can help enhance cement concrete acid-resistance. After 60 days exposure, the surface erosion of the modified cement with 1% nano-kaolinite clay weakens and compared with the ordinary Portland cement, the strength degradation ratio decreases by 27.23%. Lu et al. (2015) illustrated that nano-clay, nano-silica, and nano-titanium could improve cement bonding strength.

The relationships between different cement slurries average fluid loss and barite nanoparticles concentration are shown in Figure 3.28 below. Barite nanoparticles has an advantage compares to other nanoparticles, which is relatively low cost of material.

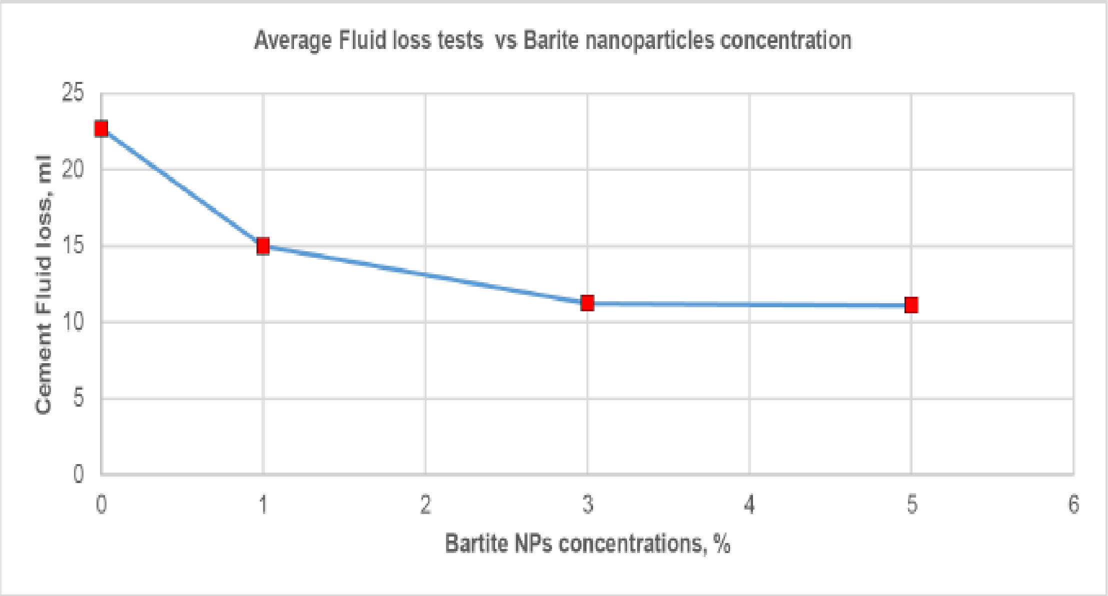


Figure 3.28. The relationship average fluid loss of cement with different barite nanoparticles concentrations (Amin. A et al., 2017)

3.7.4. Nanoparticles Reduce CO_2 Leakage in Deep Saline Aquifers. Before CO_2 brine on the top layer mixed with underlying brine in the saline aquifer, there will be a period called instability onset time. During this period, CO_2 could easily come up and may lead to the leak of CO_2. Farzam Javadpour and Jean-Philippe Nicot (2010) mentioned that inject CO_2 with nanoparticles (10nm) could enhance the density contrast between CO_2-rich brine and the resident brine. Therefore, the addition of nanoparticle helps improve the convective mixing and to decrease the instability onset time.

Based on their numerical results, we can find out that the injected nanoparticles-CO_2 flow penetrates deeper and has less overriding or finger than the CO_2 plume without nanoparticles (Figure 3.29 and Figure 3.30). Hence that, more convective mixing of nanoparticles-CO_2 will improve CO_2 downward movement, reduce CO2 overriding and fingering, then reduce the unstable onset time, and finally decrease CO_2 leaks through the caprock.

Sui & Li (2016) compared the CO_2 flooding performance between a brine saturated core and a nanoparticle solution saturated core. They found out that CO_2 mobility in the nanoparticle solution saturated core was less than in the brine saturated core. They also known that the nanoparticle solution could dissolve more CO_2 than the brine at the same conditions. These results illustrated that the nanoparticle solution can help reduce CO_2 fingering, control CO_2 mobility, and improve CO_2 storage.

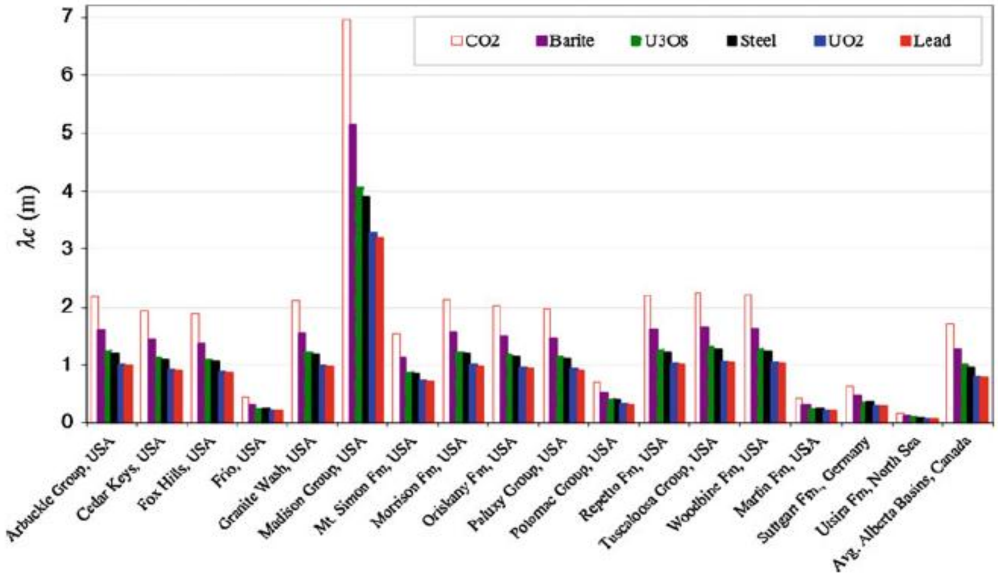


Figure 3.29. Effect of different NP materials on the wavelength of fingers (λc) on 18 different deep saline aquifers worldwide
(Farzam Javadpour and Jean-Philippe Nicot, 2010)

3.7.5. Nanoparticles Fillers Improving Silicate/Polymer Gel Properties.

Lakatoe. L et al. (2012) indicated that introducting SiO_2 nanoparticles to the silicate/polymer gels could help enhance some properties so that the gel would be more suitable for blocking channels.

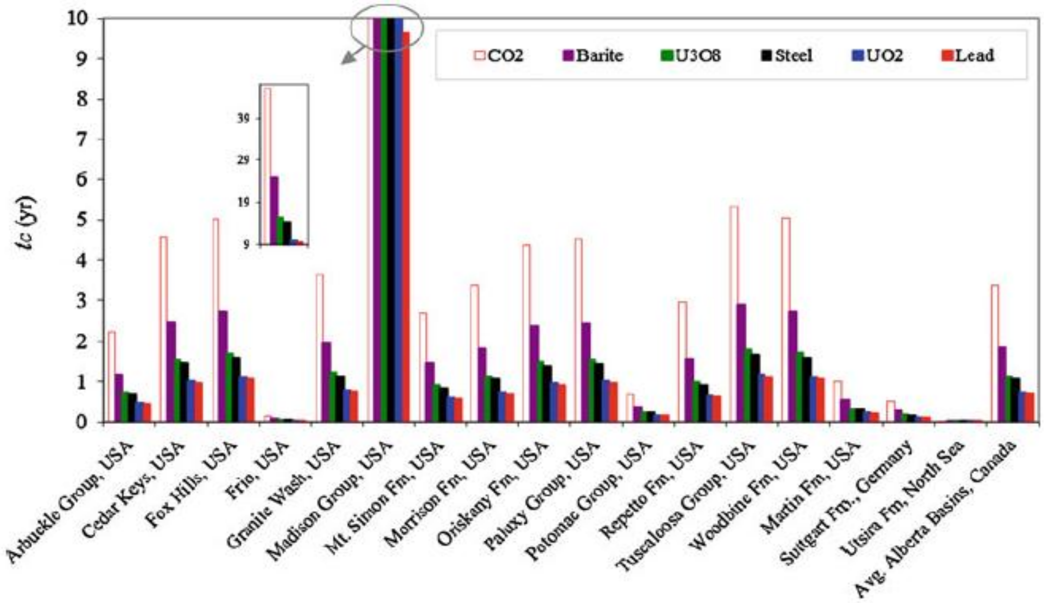


Figure 3.30. Effect of different NP materials on onset time of convective mixing (tc) on 18 different deep saline aquifers worldwide
(Farzam Javadpour and Jean-Philippe Nicot, 2010)

The research of Lakatoe shows that, firstly, the stability of silicate/polymer gel system can be affected by nanoparticle size and concentration. Smaller particle size could improve gel stability, and the optimum nano-silica size in the experiments is between 12 and 15 nm. However, relatively higher nanoparticle concentration (above 5-7 g/L) may reduce the gel stability. Secondly, nano-silica can increase the gel viscosity, besides, accelerating gel gelation and setting processes (Table 3.31), thus makes the gel more appropriate as a blocking agent. With a higher concentration of nanoparticles, the effect of high temperature on silicate/polymer gel setting time is much less than at lower nanoparticles. Thus, the gel systems thermal stability is increased.

3.7.6. Advantages and Limitations. The advantages of using nanoparticles to reduce CO_2 leakage include 1) nanoparticles can change different properties of leakage control materials; 2) nanoparticles have good physical and chemical stability; 3) nanoparticles are environmentally friendly. The limitation is that some types of nanoparticles are relatively expensive and need complex producing process, for example polymeric nanoparticles.

Table 3.31. Temperature effect on silicate/polymer gels setting times
(Based on Lakatos. L et al., 2012)

Temperature	Setting time at 30 °C, min	Setting time at 50 °C, min	Setting time difference, min
Nano-silica 0 g/l	150	50	100
Nano-silica 15g/l	25	10	15

3.8. SUMMARY OF SEALANTS

After introducing various types of sealants, application methods, properties, advantages, limitations, and some other information are summarizing as follows:

1) CO_2 sealants have various functions and could be used to solve different leakage problems. The detailed information is shown in Table 3.32.

2) Sealants have their properties and suitable application conditions. Table 3.33 demonstrates the properties of some sealants. In the field applications, sealants should be chosen based on the practical conditions. Applying additives like nanoparticles could help adjust sealants properties.

3) In the CO_2 storage and leakage remediation processes, many factors affect the performance of sealants such as temperature, pressure, pH, salinity, curing time, and the components ratio of sealants. So far, the high-temperature, high-pressure, and acid environment conditions of the CO_2 storage formations are still the challenge for CO_2 sealants.

4) Each type of sealant has its advantages and limitations, and are shown in Table 3.34. In the field applications, to adjust the operations， the advantages and limitations are all needed to be considered.

5) Future development of sealants should focus on the comprehensive application of different types of sealants and sealant properties improvement. Comprehensive application of sealants means using multiple sealing materials in stages to help enhance sealing performance. It is suggested that the following two aspects should be taken to help improve sealant properties. The first one is adjusting sealants components proportions to fit the environmental conditions, and the second one is using additives to promote sealants stability.

Table 3.32. Sealant types and application methods

Sealants Type	**Applicative Area**	**Principle of Plugging/Remediation**
Cements	Wellbore and near wellbore leakage	Simply plugging
Geopolymer Cements	Wellbore and near wellbore leakage	Simply plugging
Foams	Leakage through; Porous media	Surfactant solution reacting with CO_2 and forming foams to reduce CO_2 mobility
Gel Systems	Leakage through small fractures; Porous media; Casing repair	Selective plugging and reducing CO_2 leakage
Resins	Wellbore and near wellbore leakage	Simply plugging
Biofilm Barriers	CO_2 storage sites (Saline aquifers & Depleted oil/gas reservoirs)	Microorganism growth and plugging the top of CO_2 storage sites
Bio-mineralization (MICP)	Wellbore leakage; Small fractures in formation	Bacteria inducing urea hydrolysis, then reacting with Ca^{2+} ions in formation water to form $CaCO_3$ precipitate
Nanoparticles	Wellbore, reservoirs, and saline aquifers	As cements, foams, gels additives to improve plugging performance; Injected with brine as hydraulic barrier

Table 3.33. Properties of sealants which have been mentioned

Properties/ Sealants	**Properties Ranges of Sealants**			
	Portland Cement	**Aluminate-Calcium Cement**	**Geopolymer Cement**	**CO_2 Foam (CD 1045TM)**
Target Temperature (℃)	38-80	< 110	40-100	< 50
Compressive Strength/Pressure Tolerance (MPa)	42.5-72.5	50-85	55-90	< 10
pH	> 7	> 7	NS	> 5
Salinity Tolerance (ppm)	NG	NG	NG	> 20,000
Viscosity (cp)	NG	NG	NG	200
Setting/Gelation Time (mins)	45-390	30-360	40-120	NG
Properties/ Sealants	**Organic Crosslinked Polymer Gel**	**HPAM/PAM Based Gel**	**Silicate Gel**	**WellLock® Resin**
Target Temperature (℃)	4-204	37-114	< 200	15.56-93.3
Compressive Strength/Pressure Tolerance (MPa)	< 17.93	NG	< 17.5	34.74-103.4
pH	Neutral or Weak Alkaline	5.5-9	0-4/7-10	NS

Table 3.33. Properties of sealants which have been mentioned (cont.)

Salinity Tolerance (ppm)	NG	1,300-185,000	< 120,000	NS
Viscosity (cp)	30-30,000	< 15,000	2-10,000	Varied
Setting/Gelation Time (mins)	240-360	60-12,000	4-65	Varied
Properties/ Sealants	**Thermal Activated Resin**	**Double Network Water-Absorbent Resin**	**Biofilm Barriers (Bacillus sp. strain)**	**Biomineralization (MICP)**
Target Temperature (℃）	9-150	150	23-55	32-37
Compressive Strength/Pressure Tolerance (MPa)	75-77	< 17.2	< 30	9-10
pH	NS	NS	4-10	7-9.5
Salinity Tolerance (ppm)	NS	NS	< 60,000	NG
Viscosity (cp)	10-2,000	NG	NG	NG
Setting/Gelation Time (mins)	≥ 3	NG	NG	NG
NG - Not Given, NS - Not Sensitive				

Table 3.34. Advantages and limitations of different sealants

Sealants Type	**Advantages**	**Limitations**
Cements	High mechanical strength; High permeability reduce ability; Cost-effective	Some types of cement have limited acid resistance and high temperature stability
Geopolymer Cements	High mechanical strength; High permeability reduce ability; High temperature and acid resistance; Low CO_2 emission during the producing process	Complex making process; Could harmful to human health; Geopolymerization process is sensitive, easy to be effected by temperature
Foams	Low price; Salinity tolerance; High injective ability	Short working time; Low mechanical strength; Not enough high temperature stability
Gel Systems	High injective ability; High permeability reduce ability; High temperature stability; CO_2 resistance	Not enough working time; Selectivity permeability reducing and fracture sealing; Low mechanical strength
Resins	High bonding strength; Good thermal stability; Changeable viscosity and setting time; Long working time; Acid resistance	Expensive; Relatively complex preparation; Usually been limited to shallow reservoir applications
Biofilm Barriers	High injective ability; Environmental friendly	Some types of bacteria are not good for human health; Not cost-effective (nutrition feed for bacteria are expensive); Low stability under high pressure condition
Biomineralization (MICP)	Biomineralization process could be controlled by varying the concentration of Ca^{2+} and the nutrient feed	The distribution of $CaCO_3$ is not homogeneous;
Nanoparticles	Widely used; Good physical and chemical stability; Environmental friendly	Some types of nanoparticle are expensive

4. CONCLUDING REMARKS

This research provided a comprehensive review of CO_2 leakage problems, remediation methods, and sealants for CO_2 storage or leakage. Based on review, the following conclusions can be drawn:

1 Depleted oil and gas reservoirs and deep formation saline aquifers provide great potential as CO_2 storage sites.

2 CO_2 leakage pathways can be divided into geological leakage pathways and engineering leakage pathways.

3 Seven types of CO_2 leakage sealants were classified and reviewed in this thesis including: cement, geopolymer, foam, gel, resin, biofilm barrier, biomineralization, and nanoparticles. Among all these materials, cements are the most widely used sealants.

4 Thermal-stability is a great challenge for most materials and should be evaluated under supercritical CO_2 condition.

5 An ideal sealant for CO_2 sequestration needs to be high-temperature, high-pressure and acid tolerant. It should be environmental friendly and cost effective.

6 It is quite challenging to deliver plugging materials into the in-depth of a reservoir where leakage occurs.

7 Future development of CO_2 leakage control sealants should focus on the synergy effect of different types of sealants for combined application and the improvement of sealants properties.

8 Future researchers could focus on optimizing sealants components ratio and using additives to improve sealants properties.

9 Nanoparticles are strongly recommended to be additives for sealant properties improvement.

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VITA

Shudai Peng was born on 07/02/1993. He received his Bachelor of Engineering degree in Geological Engineering from China University of Petroleum (Beijing) in July 2015. In December 2017, he earned his Master of Science degree in Petroleum Engineering from Missouri University of Science and Technology, Rolla, Missouri.