Nanoparticle Injection Technology for Remediating Leaks of CO_2 Storage Formation

Project Number DE-FE0026514

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U.S. Department of Energy

National Energy Technology Laboratory

Mastering the Subsurface Through Technology Innovation, Partnerships and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting

Project Overview: Objectives and Methodology

The overall goal of this project is to develop a new technology that can be used to repair wellbore leakages through the **combination of a nanoparticle injection technique with the simultaneous extraction of harmful ions (e.g. chlorides) out of the leaking area.**

Objective 1: Development of the injection technology for leakage repair.

Electro-migration test unit	Select healing agents	Small-scale wellbore test system	Evaluate effectives with material testing

Objective 2: Development of a new numerical simulation model that can simulate and predict the performance of the new wellbore repair technology.

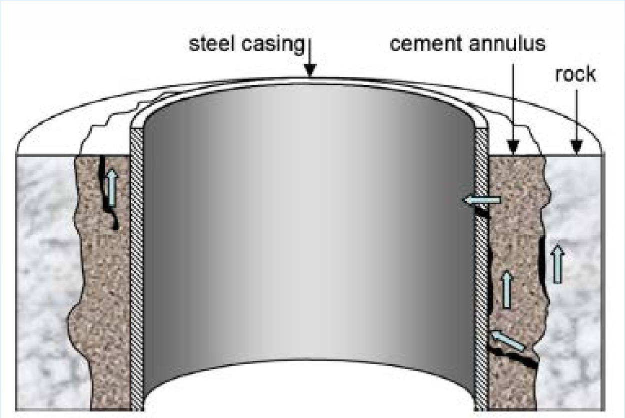
Model particle injection	Model ionic removal

Concept Review

The concept of nanoparticle injection technology is to use an **electrochemical method** to deliver beneficial particles or agents to deteriorating areas. This technology is normally used for underground projects which are difficult to access.

- Ion exchange
- High voltage
- Reverse anode and cathode regions
- Ions diffuse, causing gradient which can drive particles

- Interface between steel casing and cement anulus
- Crack of cement
- Crack of steel casing
- Interface of rock and cement

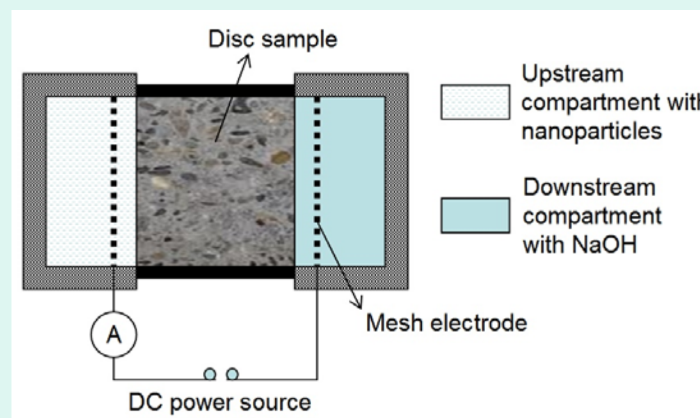


Presentation Outline

Task 2 & 3: Selection of healing agents
Task 5: Evaluate effectiveness
Completed

Task 4: Wellbore test system

Task 6: Numerical modeling

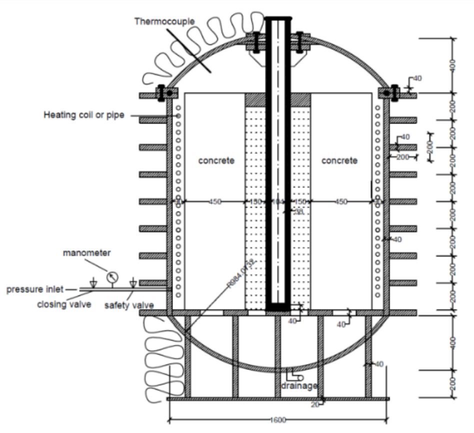


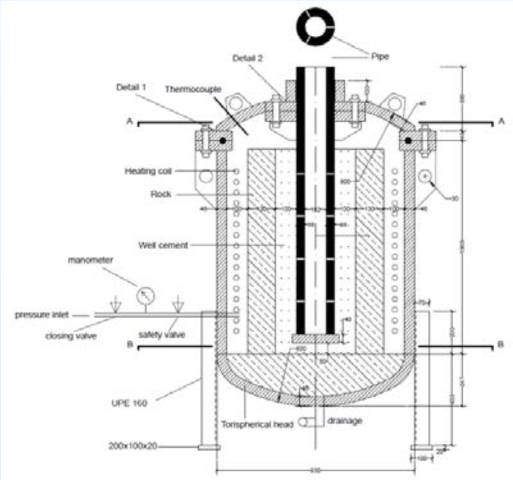
Task 4: Wellbore test system

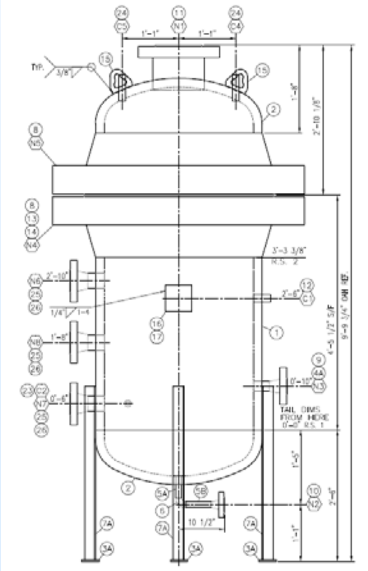
Wellbore Test System

- In the past, the successful story has been presented of nanoparticle injection technology by using desktop unit device under room temperature and atmospheric pressure.
- The objective of building a small-scale prototype wellbore testing system is to simulate the real **environmental condition in the field**, which means capturing downhole conditions such as high temperature and high pressure.

  - 1000 psi internal pressure
  - Heating up to 80°C
  - Standard well pipe
  - 10 feet tall pressure vessel







Evolution of pressure vessel design

Task 4: Wellbore test system

Heating System

Pressure System

Drain System

Sealing System

Task 4: Wellbore test system

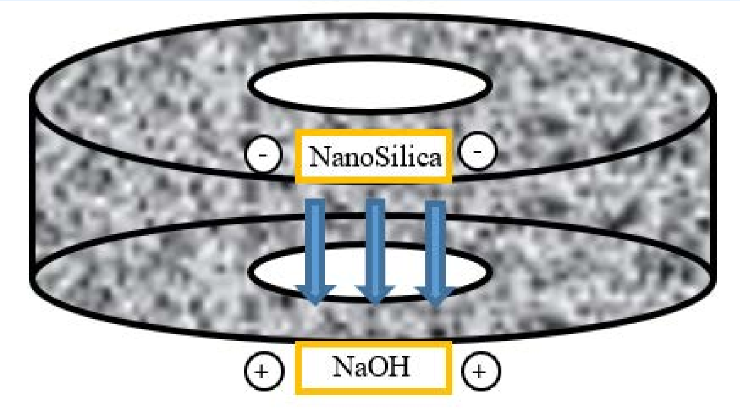
Test Procedure focusing on Environmental Impact on Nanoparticle injection process

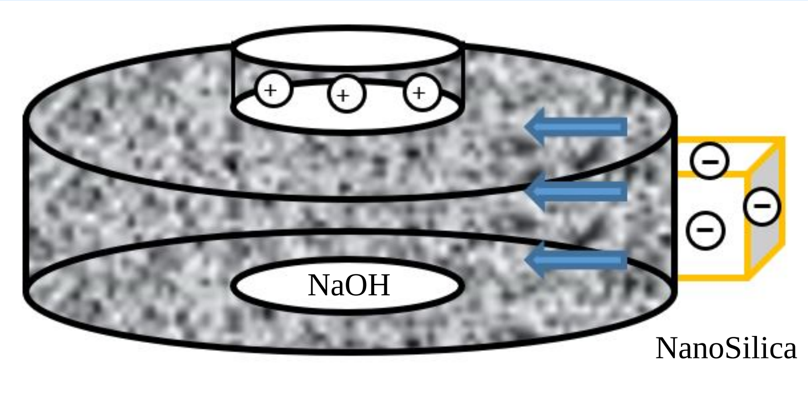
Tests:

- Room Temperature and Atmospheric Pressure
- High Temperature and Atmospheric Pressure
- Room Temperature and High Pressure
- High Temperature and High Pressure (future)

Nanoparticles Used:

- Colloidal Nanosilica (CNS)
- Nanoalumina
- Nanogel





Task 4: Wellbore test system

Materials and Methods

W/C: 0.44

Mixing Procedure:

15sec of 4000 rpm followed by 35sec of 12000 rpm

Demold at 24 hours and submerge for 48 hours

Injection: 60 V and 100 hours

Measure the weight of the samples under oven dry and saturated surface dry conditions

Task 4: Wellbore test system

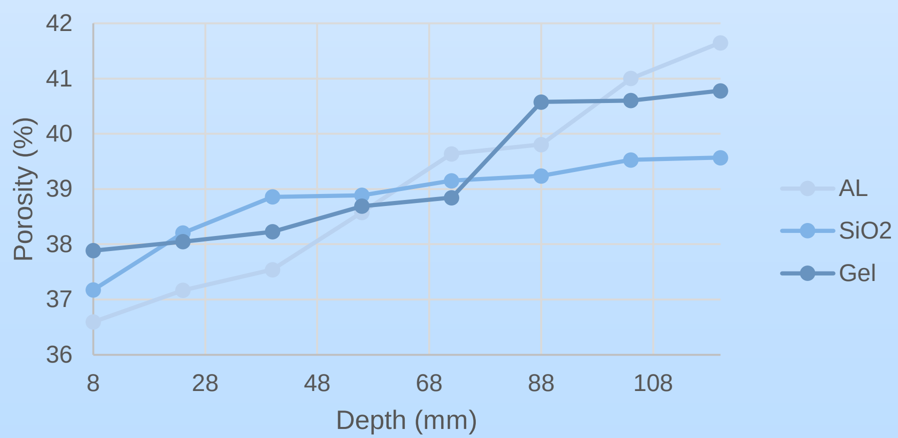
Test Results

- Porosity changes under Room Temperature and Atmospheric Pressure

	Untreated (%)	**2/3 into sheath (%)**	**1/3 into sheath (%)**	**Relative Porosity Change (%)**	**Charge Passed**
Injection I	43.05	41.71	41.12	3.06	2286±377
Injection II	42.73	42.21	41.69	1.81	4541±307

- Porosity changes under High Temperature and Atmospheric Pressure

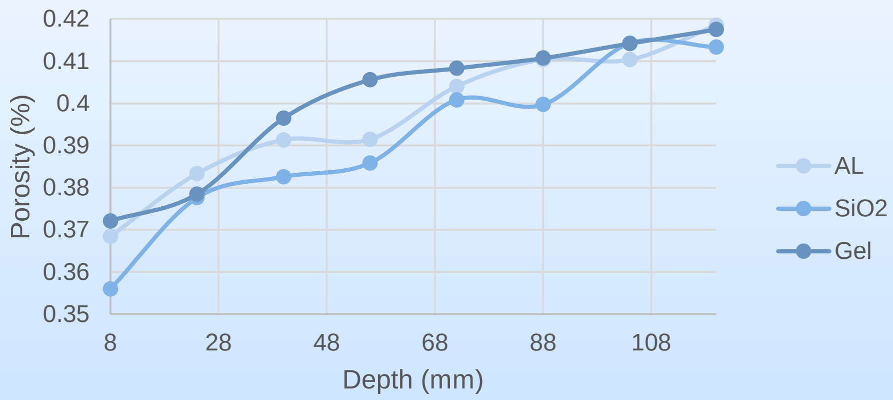
	Porosity (%)	**Relative Porosity Change (%)**	**Charge Passed**
Untreated	41.68	0	0
Nanoalumina	39.00	6.44	575
Nanosilica	38.83	6.85	3048
Nanogel	39.21	5.93	12928



Task 4: Wellbore test system

- Porosity changes under Room Temperature and High Pressure

	Porosity (%)	Relative Porosity Change (%)	Charge Passed
Untreated	41.97	0	0
Nanoalumina	39.72	5.35	733
Nanosilica	39.13	6.78	2414
Nanogel	40.04	4.60	11346



Agglomeration of nanoparticles

Task 4: Wellbore test system

Conclusion

- The heating and pressurizing system is built and tests were conducted by using the pressure vessel.
- From the results collected from the tests, it can be seen that both high temperature and high pressure can accelerate the hydration process. The porosity of the sample is decreased as a result of the accelerated curing.
- The nanosilica shows the best performance for nanoparticle injection, based on the decrease of the porosity. The nanogel provided the lowest porosity change.
- 2 more test will be conducted: the high temperature-pressure coupling test and the large-scale test. The large-scale test will build a full-size underground structure with steel casing and surrounding rock. This test will evaluate the possibility of using nanoparticle injection technology in the field. Results will be included in the final report of this project.

Task 6: Numerical modeling

Injection of Nanoparticles

- A general framework of numerical modeling was be developed to describe the proposed electrochemical injection technology.
- 2D mesh, 1D diffusion + migration.
- Governing Equations:

Nernst-Planck Equation:

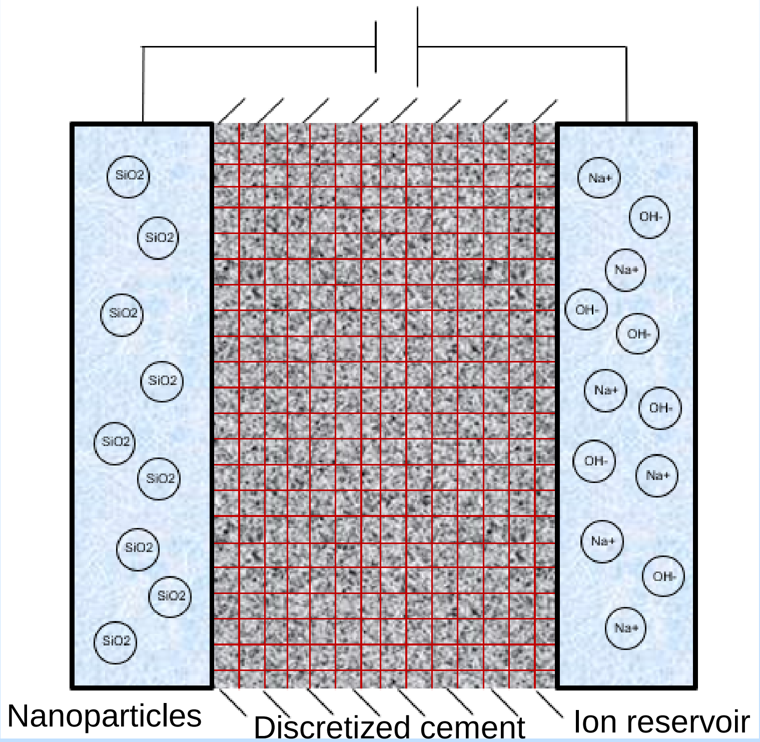
Ion concentration

$$\frac{\partial C_{it}}{\partial t} = \frac{\partial C_{it}}{\partial C_i}\frac{\partial C_i}{\partial t} = \nabla(D_i \nabla C_i + z_i D_i \left(\frac{F}{RT}\nabla\Phi\right) C_i + C_i D_i \nabla(ln\gamma_i))$$

Poisson's Equation:

Electrical potential

$$\tau\nabla^2\Phi = -\frac{F}{\varepsilon_0\varepsilon_r}\sum_{i=1}^{n} C_i z_i$$



- Red circles mark the two variables which need to be solved.

Task 6: Numerical modeling

Model Input parameters

Faraday	Universal gas	Temp	Permittivity vacuum, water at 25C	
$F\ (C/mol)$	$R\ (J/mol/K)$	$T\ (K)$	$\varepsilon_0 (C/V/m)$	ε_r
9.648×10^{-4}	8.314	298	8.854×10^{-12}	78.3

	Si	Na	OH	Cl	K
Charge Number	-4	+1	-1	-1	1
Diffusion Coefficient (cm^2/min)	7.86×10^{-6}	8×10^{-5}	3.16×10^{-4}	1.22×10^{-4}	1.17×10^{-4}
Binding Capacity	0.5	0.5	0.5	0.5	0.5

Boundary Conditions

Field Variables	Silica (g/g)	Sodium(g/g)	Hydroxide (g/g)	Chloride (g/g)	Potassium (g/g)	Electrostatic Potential (V)
Initial Conditions	0	1.13×10^{-4}	1.03×10^{-4}	1.03×10^{-4}	1.03×10^{-4}	0
Boundary Conditions						
x=0	3.96×10^{-5}	Flux	Flux	Flux	Flux	0
x=L	Flux	1.25×10^{-3}	1.15×10^{-3}	Flux	Flux	20

Assumptions made:

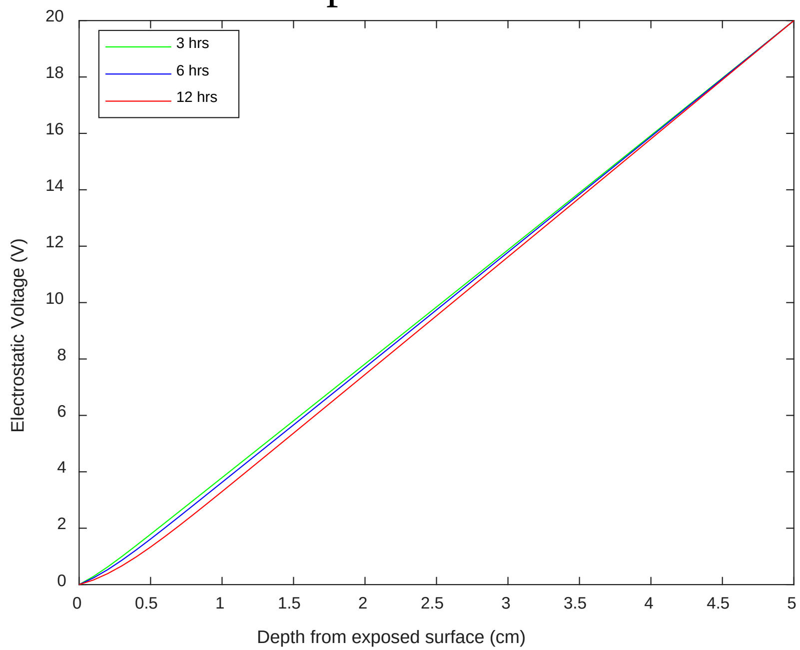
(1) Neglect chemical activities.

(2) Binding Capacity and Diffusion Coefficient are constants.

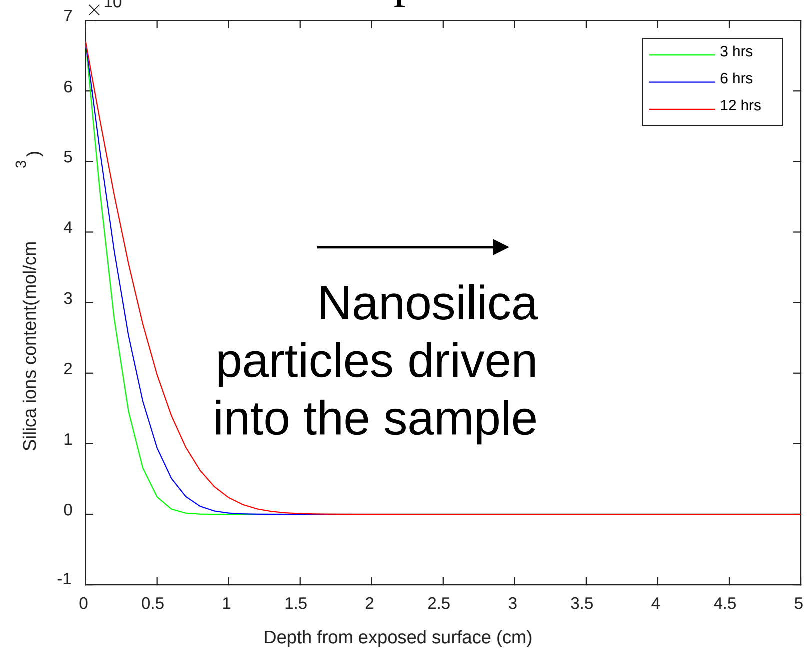
Task 6: Numerical modeling

Results

Voltage calculated at various depths with time



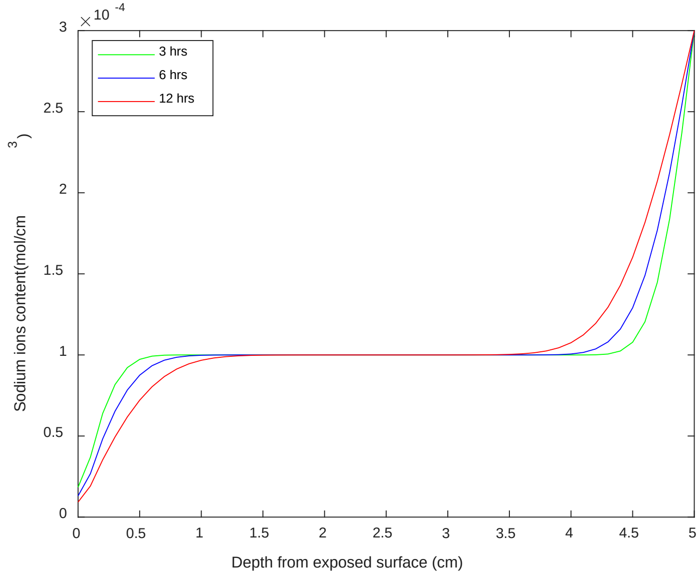
Silica Nanoparticle content at various depths with time

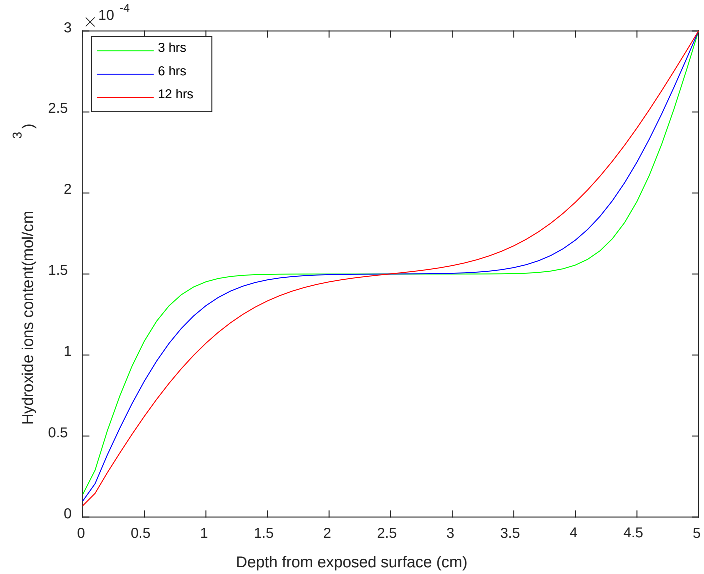


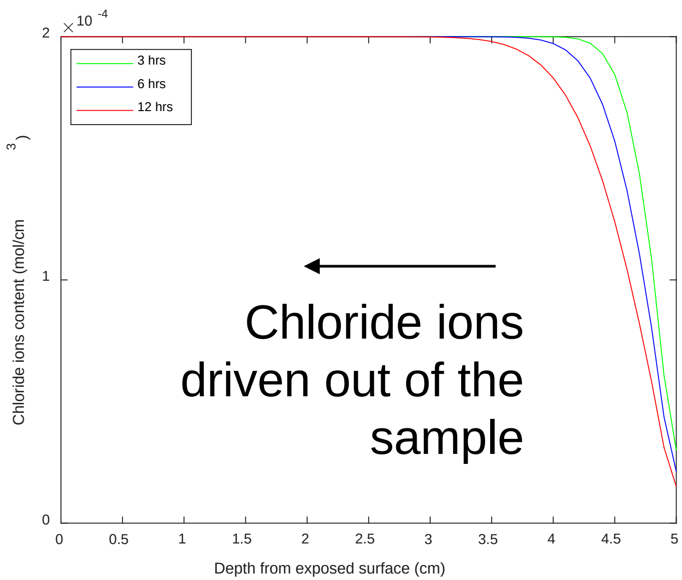
Calculated using silica ion charge and molar mass of nanoparticle

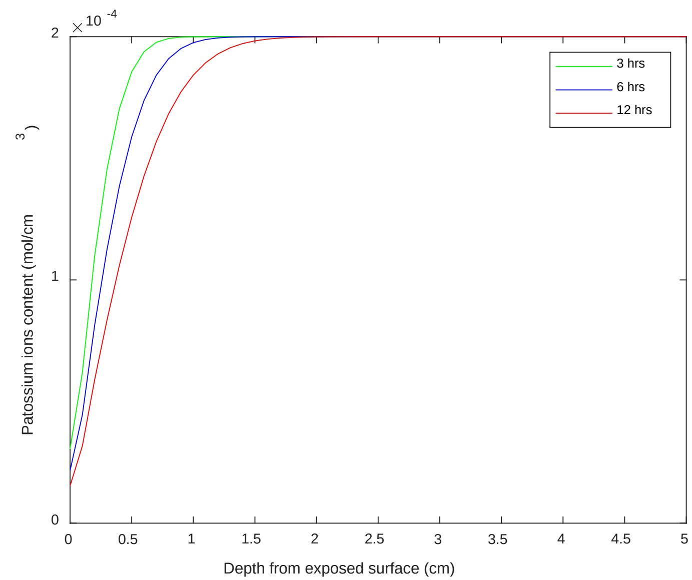
Task 6: Numerical modeling

Concentration of other ions







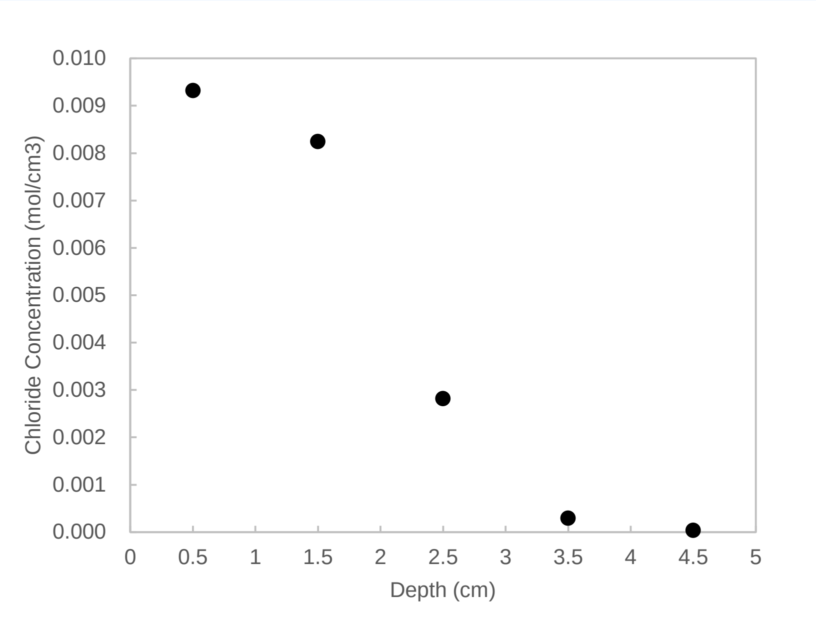


Task 6: Numerical modeling

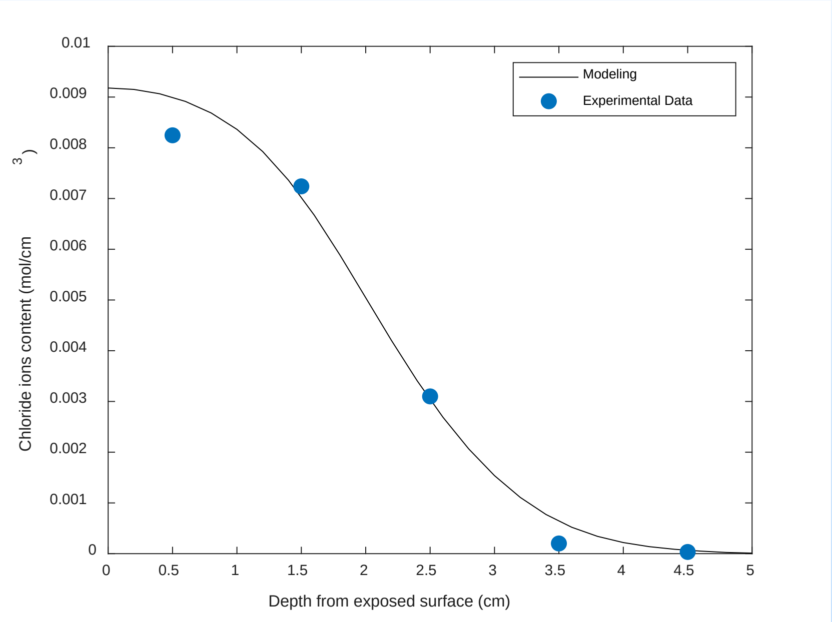
Model Validation

(1) ASTM C1202 (ASTM C1202) rapid chloride permeability test can be conducted. The result is used as the initial condition in the model.

(2) Run nanoparticle injection model, collect the chloride profile again and compare with the model prediction.



Initial Condition from Experiment



Final Condition after Injection

Task 6: Numerical modeling

Conclusion

- The coupled numerical model have been built and solved considering both concentration of ions and electrical potential.
- A multi-ions diffusion model has been successfully applied. Clear trends of the movement of different ions have been obtained.
- In validation work, the chloride profile obtained from the experimental study has be introduced as the input parameters. Later, the simulated result has compared with the result obtained from nanoparticles injection test. The simulated result is close to the result from experimental study.
- The material model has not been considered, which means the diffusion coefficient should not be a constant during the injection process simulated in the model.

Task 6: Numerical modeling

Chemical Composition and Mechanical Properties of Well Cement under Carbonation Reactions

Initial mineral composition of well cement

Mineral Composition	C_3S	C_2S	C_3A	C_4AF
% by mass	56	25.7	2	16.3

Hydration reaction

$$C_3S + 5.3H \rightarrow 0.5C_{3.4}S_2H_8 + 1.3CH$$

$$C_2S + 4.3H \rightarrow 0.5C_{3.4}S_2H_8 + 0.3CH$$

$$C_4AF + 2CH + 10H \rightarrow 2C_3(A,F)H_6$$

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$

$$C_3A + 0.5C_6AS_3H_{32} + 2H \rightarrow 1.5C_4ASH_{12}$$

$$C_3A + CH + 12H \rightarrow C_4AH_{13}$$

After the hydration process

Volume Fraction	%
V_{CH}	18.16
V_{CSH}	57.99
V_{W}	0.54
V_{cp}	9.24
V_{AL}	14.08

Task 6: Numerical modeling

Volume fractions change due to the **carbonation reactions**

$$\left\{\begin{array}{c}
CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \\
Ca(OH)_2 + 2H^+ + CO_3^{2-} \rightarrow CaCO_3 + 2H_2O \\
Ca(OH)_2 + H^+ + HCO_3^- \rightarrow CaCO_3 + 2H_2O \\
C - S - H + 2H^+ + CO_3^{2-} \rightarrow CaCO_3 + SiO_xOH_x \\
C - S - H + H^+ + HCO_3^- \rightarrow CaCO_3 + SiO_xOH_x \\
CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \\
2H^+ + CaCO_3 \leftrightarrow CO_2 + Ca^{2+} + H_2O
\end{array}\right.$$

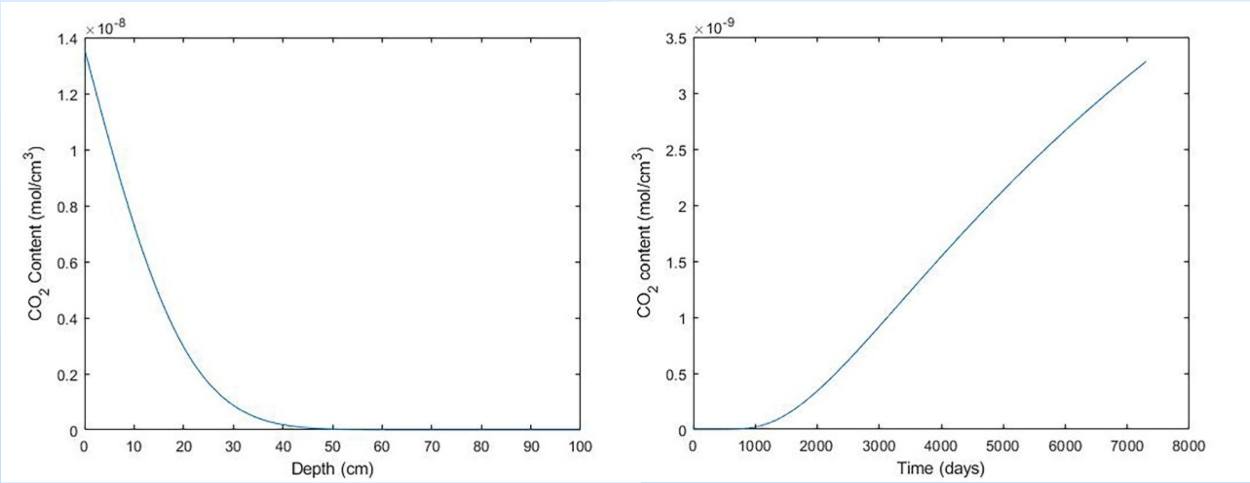
Carbonation reaction rate:

$$R_i = K_i \times [i] \times [CO_2]$$

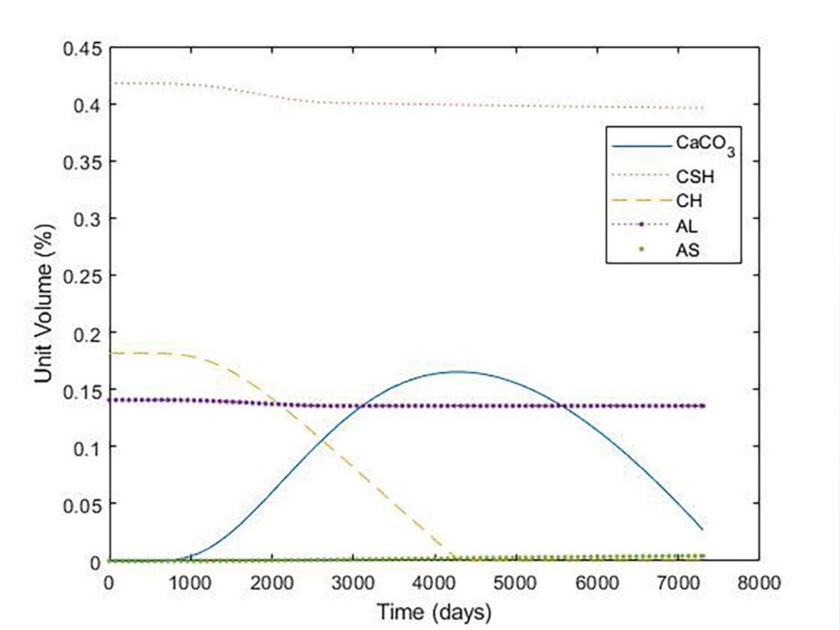
CO_2 profile:

$$C(x,t) = C_s \times \left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

predicted by the error function solution of 1D CO_2 diffusion equation

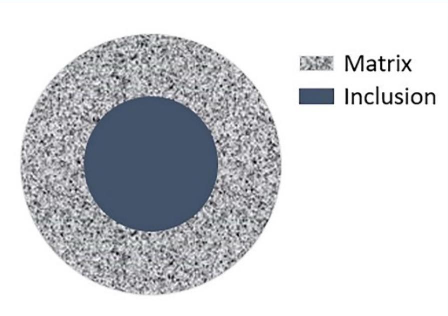


Task 6: Numerical modeling



- Modulus of elasticity change due to carbonation reaction

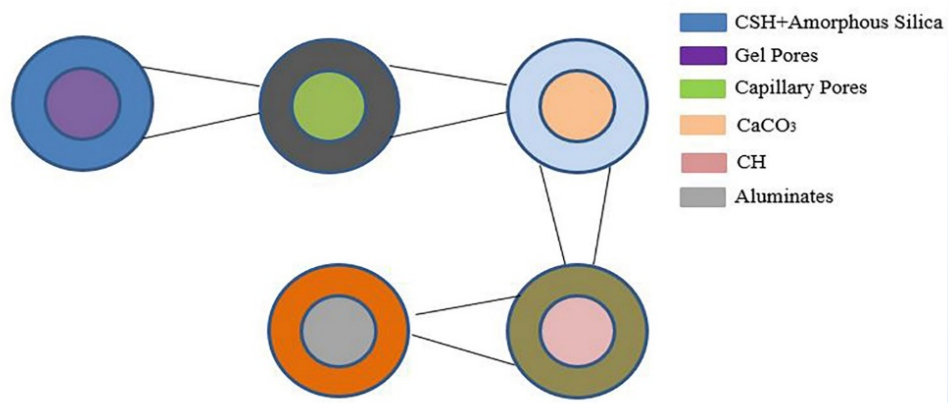
$$E_{eff} = E_{matrix}\left(1 + \frac{f_{inclusion}}{\left(\frac{1-f_{inclusion}}{3}\right) + \left(\frac{1}{\frac{E_{inclusion}}{E_{matrix}} - 1}\right)}\right)$$



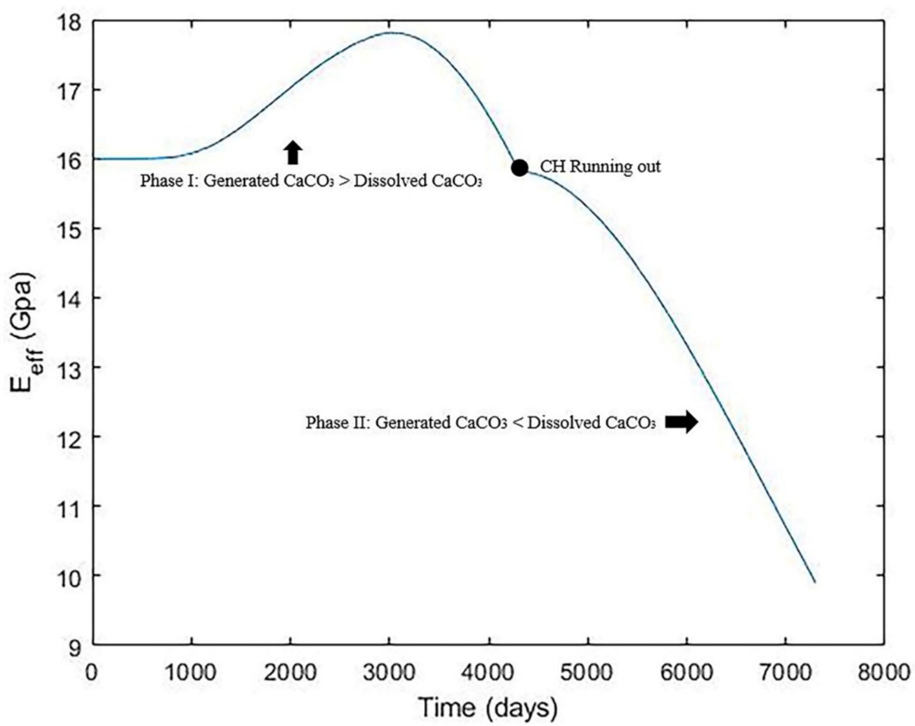
Task 6: Numerical modeling

Generalized self-consistent (GSC) model

Multiscale structure of cement



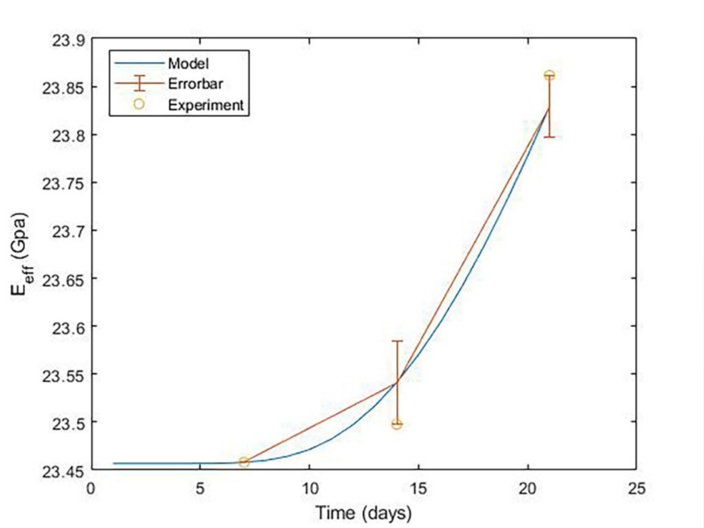
Changes of mechanical properties during the carbonation reactions

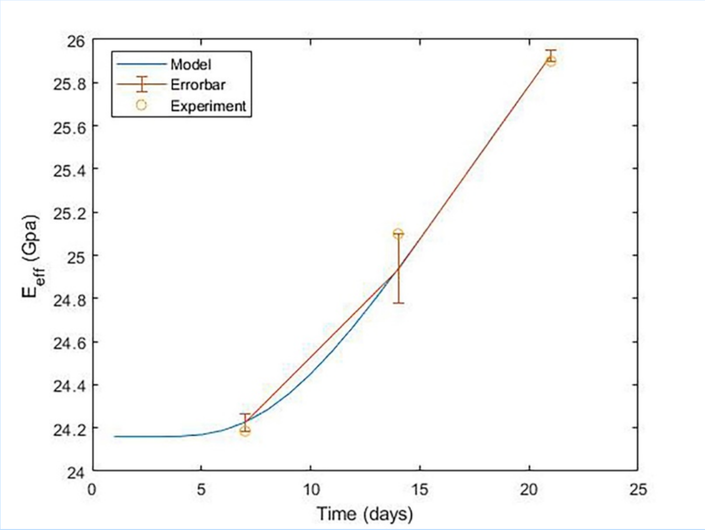


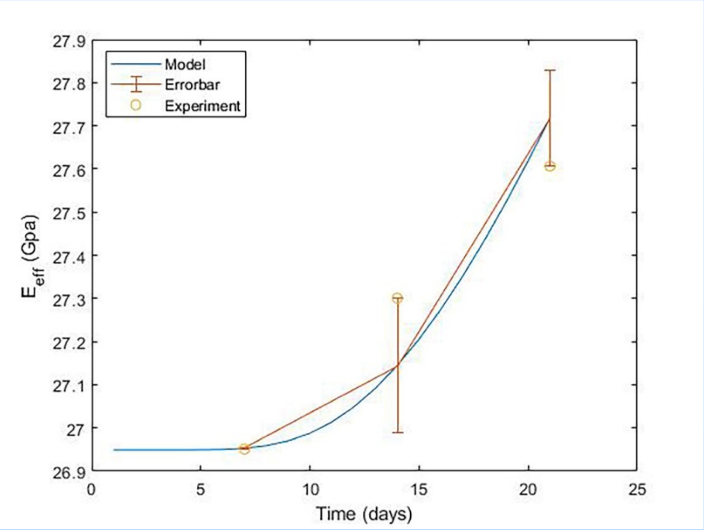
Task 6: Numerical modeling

Model Validation – published results

w/c ratio	Water (kg/m³)	Cement (kg/m³)	Sand (kg/m³)	Gravel (kg/m³)
0.4	219	548	611	950
0.5	217	434	727	950
0.6	190	317	875	950







Task 6: Numerical modeling

Conclusion

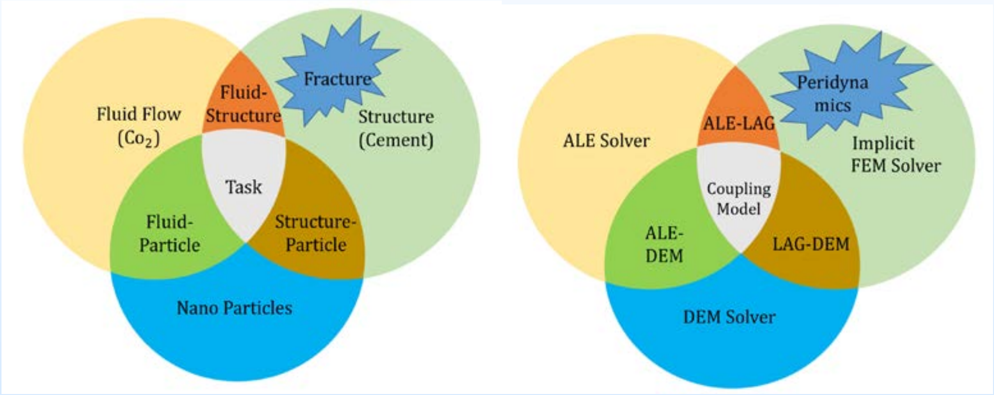
- The phase transformations of Class G cement during the carbonation process were predicted by the use of stoichiometric models.
- The generalized self-consistent (GSC) model was used to characterize the changes of mechanical properties during the carbonation reactions.
- The model was validated through the comparison with published experimental results of elastic modulus of carbonated concrete.

Task 6: Numerical modeling

Multi-Physics modeling of feasibility of nanoparticle injection

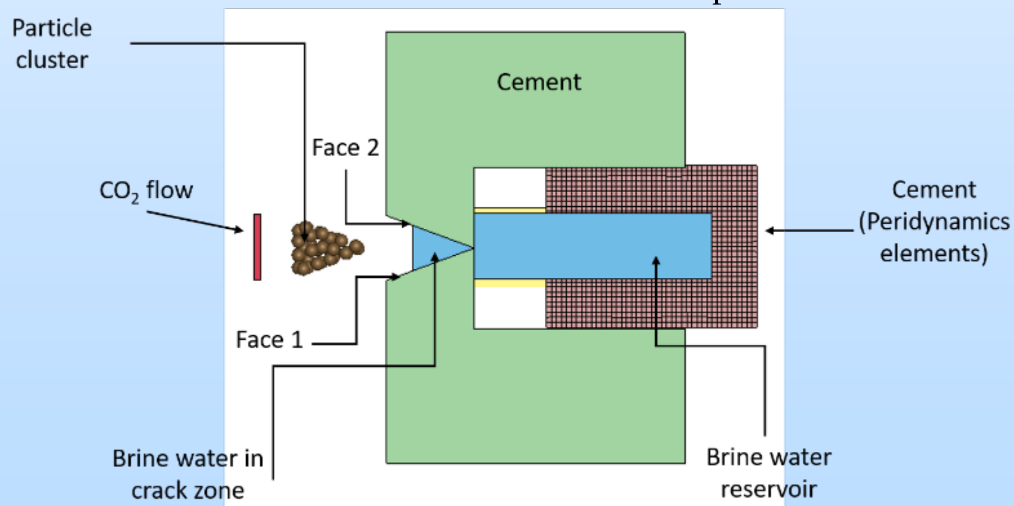
Work conducted at UoU

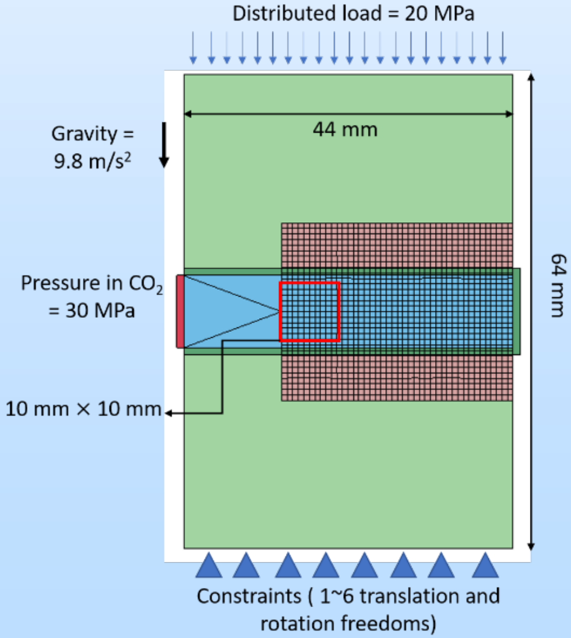
A multi-phase numerical modeling strategy was set-up using LS-Dyna.



Coupled-ALE (Arbitrary-Lagrangian-Eulerian)-DEM (Discrete Element Method)-peridynamics model

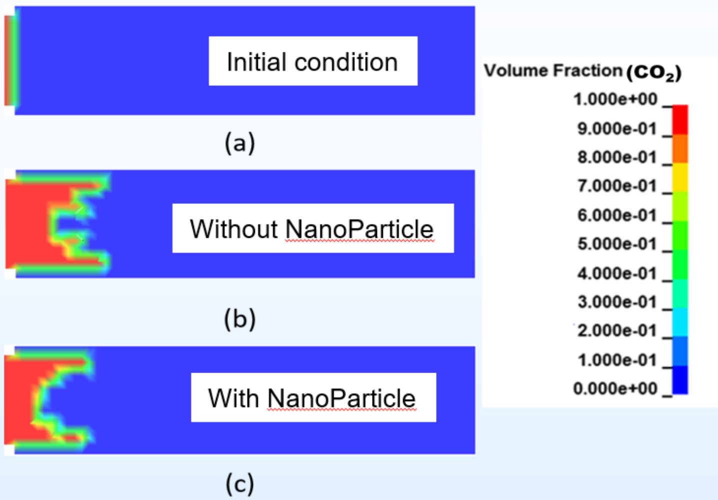
Pressures measured on Faces 1 and 2 for various particles.



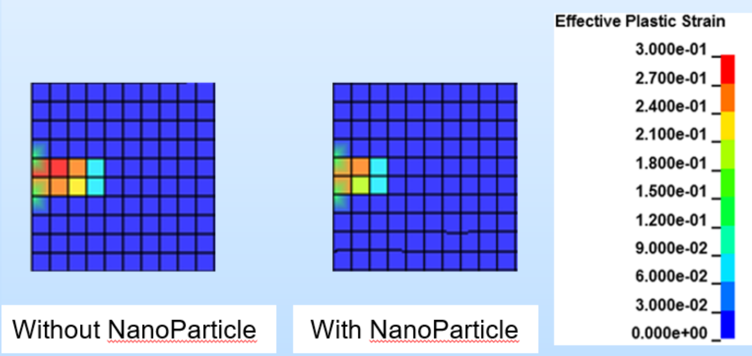


Task 6: Numerical modeling

CO_2 movement in the crack zone

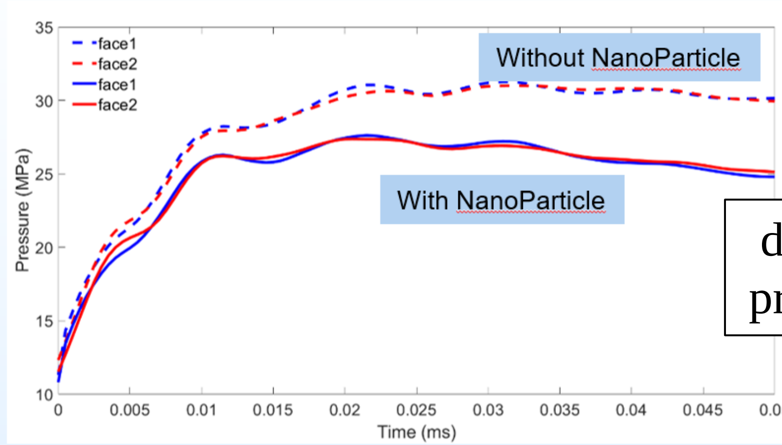


Fracture propagation at crack tip



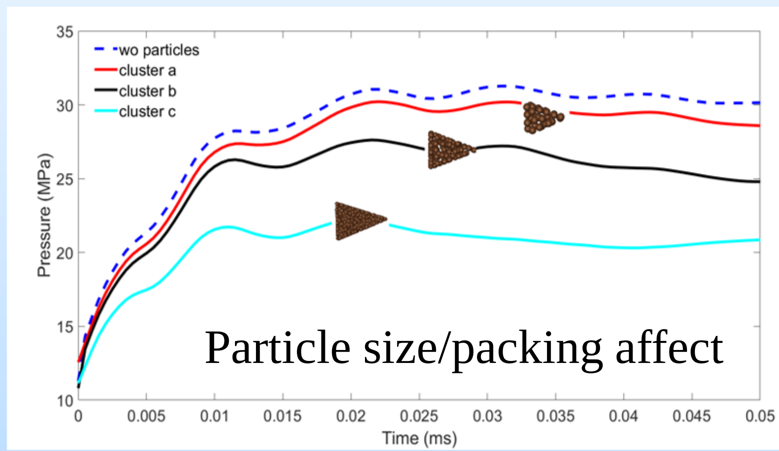
Reduction of plastic strain

Imposed pressure on crack surface



drop in pressure

Different particle clustering



Task 6: Numerical modeling

Conclusion

- A numerical modeling strategy coupling ALE compressible fluid solver, DEM solver, and Peridynamic solver has been built to model the fracture mitigation effect of nanoparticle injection technology within the LS-Dyna framework.
- The numerical model shows that the nanoparticle can effectively reduce the imposed pressure on crack surfaces, and consequently, the fracture propagation at crack tips can be remediated.

Accomplishments to Date

– Selected best healing agents.
– Completed desk top electro-migration testing.
– Completed the design and development of a lab scale wellbore testing system (the pressure vessel) for full size testing of a wellbore system.
– Conducted the studies using the pressure vessel.
– Completed different testing methods to measure porosity distribution in well cement.
– Completed the numerical modeling of nanoparticle injection technology and carbonation effect onto well cement.

Lessons Learned

– **Unanticipated research difficulties.** The pressure vessel is more difficult to handle than anticipated due to the large cap.

Synergy Opportunities

The injection method may be used for sealing (healing) agents other than nano- and micro-particles.

In the other ongoing projects

Using mineral precipitation method.

Using microbially-induced calcite precipitation.

Using nanocomposite materials for wellbore seal repair

Other projects

Applications of nanoparticles for *hydraulic fracturing*

The evaluation methods and the simulation models may also be used for other technology.

Project Summary

- All stages of numerical and bench-scale technology assessment are complete.
- Next steps:
  - large scale lab test
  - X-ray imaging of fluid flow around cement sample with nanoparticles

Appendix

These slides will not be discussed during the presentation, but are mandatory.

Benefit to the Program

The overall goal of the project is to develop a new technology that can repair cement casing leakage of the wellbore and reduce the risk of steel corrosion. The leakage problem will be solved by injecting nanoparticles electrochemically so the cement materials will be densified, and the corrosion risk will be reduced by removing some of the harmful ions in the system.

Program goals addressed:

- Develop and validate technologies to ensure 99 percent storage permanence;
- Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.

Benefit to the Program

Project benefits:

- Development of advanced materials and methods that have the ability to prevent or remediate detected leaks in complicated environments under a variety of pressure, temperature, and chemical conditions to ensure CO_2 permanence within the storage formation;
- Theoretical and numerical models to demonstrate potential long-term (i.e., at least 50 years) feasibility and effectiveness of the new technology.

Project Overview
Goals and Objectives

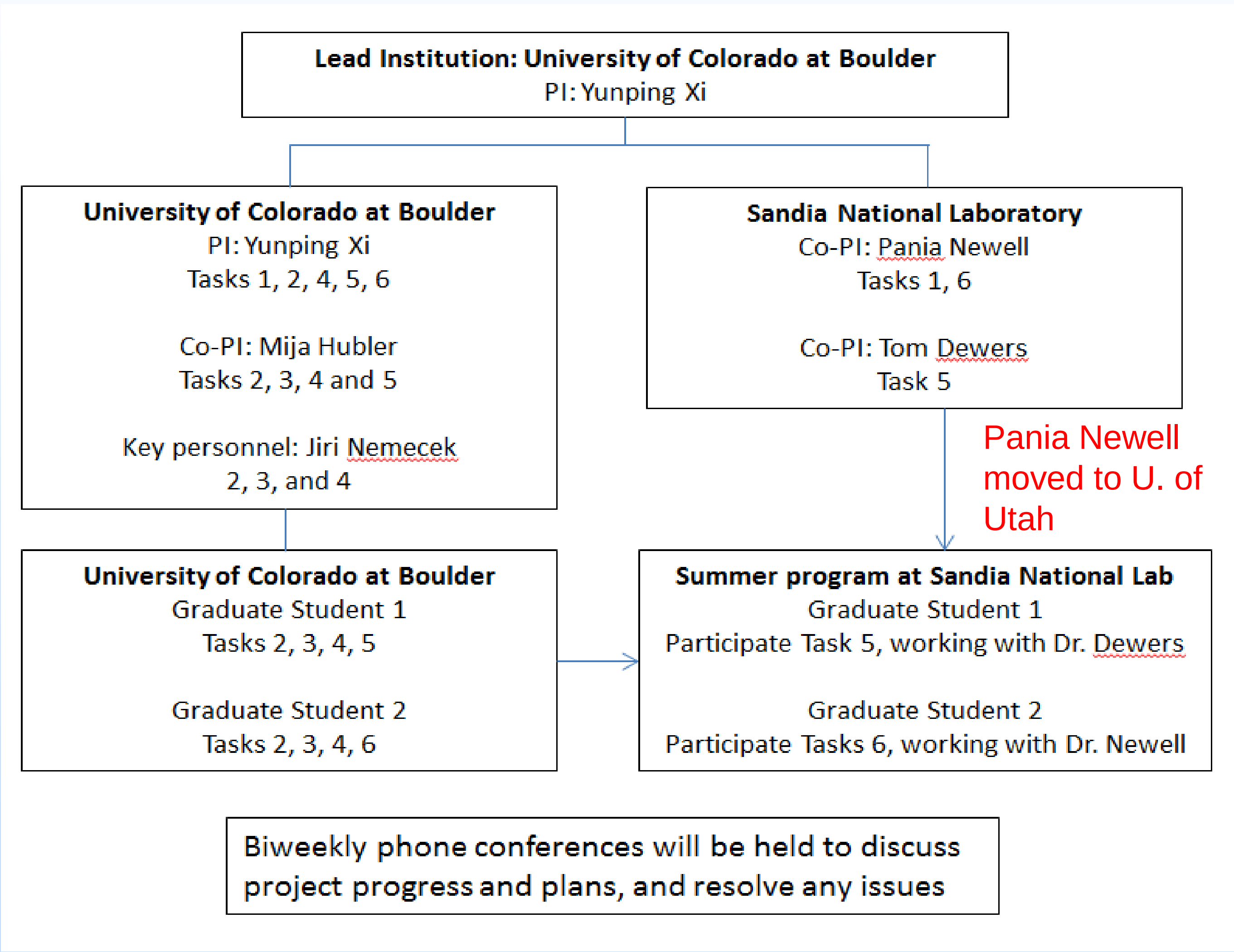
Objective 1: Development of the injection technology for leakage repair

Success criteria: we will seal artificially damaged samples and evaluate their mechanical properties and ultrasonic properties to reveal improvement.

Objective 2: Development of a new numerical simulation model that can simulate and predict the performance of the new wellbore repair technology

Success criteria: we will compare numerical results with experiments for validation.

Organization Chart



Gantt Chart

		Year 1: Budget Period 1				Year 2: Budget Period 2				Year 3: Budget Period 3			
Task #	Task	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr
1	Project Management, Planning and Reporting												
1.1	Project Management Plan	PMP											
1.2	Project Planning and Reporting			Presentation	Report				Report				**Final Report**
2	Development of an electro-migration unit system and testing							Presentation					
2.1	Development of an electro-migration unit system												
2.2	Testing with the electro-migration unit system												
3	Selection of Healing agents									**Report**			
3.1	Nanoparticle testing												
3.2	Nanoparticle based slurry testing												
3.3	Selection of healing agents												
4	Small-scale wellbore test system												**Presentation**
	Design and construction of test system												
5	Evaluation of the effectiveness of the technology												**Report**
5.1	Strength, stiffness, and transport properties												
5.2	Microscopic study												
5.3	Fracture testing and analysis												
6	Numerical modeling and verification												
6.1	Numerical modeling for ionic removal												
6.2	Numerical modeling for injection of healing agents												
6.3	Numerical modeling of fracture using Kayenta and Sierra Mechanics												**Model**

Bibliography

Journal articles:

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