Nanoparticle Injection Technology for Remediating Leaks of CO₂ Storage Formation
Project Number DE-FE0026514

Collaborators
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Pania Newell and Thomas Dewers, Sandia National Labs
Outline

- Benefit to the program
- Objectives and methodology
- Task and subtask description
- Accomplishments to date
- Synergy opportunities
- Summary
Benefit to the Program

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

• 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.
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 effectiveness 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
Task 2: An electro-migration test unit

The basic idea: Electrochemical repair techniques are used for repairing reinforced concrete structures. Further development of this technology for repairing well cement.

- Ion exchange
- High voltage
- Reverse anode and cathode regions
- Ions diffuse, causing gradient

Electrochemical Chloride Extraction (ECE) technologies were used to remove chloride ions in concrete.
Task 3: Selection of healing agents

- Nano-SiO$_2$ can **improve** cement workability and strength, **increase** resistance to water penetration, and help to control the leaching of calcium.
- Nano-Fe$_2$O$_3$ can **provide** self-sensing capabilities and improve strength.
- Nano-Al$_2$O$_3$ can **increase** the modulus of elasticity.
- Nano-clay can **enhance** mechanical performance, the resistance to chloride penetration, and the self-compacting properties of cement.

Select based on size, charge, and permanence

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Task 4: Small-scale wellbore test system

- **Purpose**
  A small-scale prototype wellbore test system will be developed based on the electro-migration unit system to be developed in Task 2 and Task 3. The prototype system will be used to simulate the real environment in the field.

- **Principal wellbore conditions to be simulated**
  - steel casing
  - cementing
  - rock surroundings
  - brine

- **Approach**
  - Development of a small-scale technology prototype
  - Based on a packer cement squeeze process
  - Development of a counter electrodes system
Task 5: Evaluation of the effectiveness

- **Purpose**
  Characterize and evaluate the effectiveness of the cementitious materials enhanced with nanoparticles.

- **Evaluation Goals**
  - Which combination of materials and processes provide the best healing performance?
  - How are the mechanical and transport properties of the material affected?
  - How effectively are the ions removed during the injection process?

- **Approach**

  Fabricate systematically undamaged and damaged samples
  - Mechanical loading
  - Added porosity
  - High temperature

  - Macroscopic strength, stiffness and transport characterization
  - Microscopic material structure characterization
  - Fracture testing and analysis

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Task 6: Numerical models

- Used to simulate the entire transport process for nanoparticle injection and ionic removal process.
- A multi-physics framework of the model will be established and the coupling effects among the state variables involved in the injection system will be taken into account.
- Used to predict the performance of the new technology for repairing leakage of wellbores.

Sierra Mechanics

Kayenta: quasi-static behavior of porous geomaterials

- Pressure sensitive
- Non-associative plastic behavior
- Non-linear elasticity
- "Cap" yield surface in stress space
- Shear-induced dilatation
Accomplishments to Date
Task 2 - Development of an electro-migration unit system

Sample Preparation according to API Spec. for Class G well cements:
- w/c: 0.44
- size: 100 x 90 mm Cylinder
- curing: 7 days in water

Upstream: Nanoparticles (30 – 40% weight)
Downstream: 0.3 N NaOH (+ polarity)
External Current: 10 V
Running Time: 12 hrs
Temperature: 49 °C
Measuring the Injected Particles

Method 1: Porosity Measuring using ASTM C830

This method can be used to compare the total porosity change of the sample before and after the injection test, which can indirectly prove the particles injection effectiveness.

\[
Porosity = \frac{W_{SSD} - W_{OD}}{\rho_{water}} \cdot v_{sample}
\]

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Measuring the Injected Particles

Method 2: BET Method
The adsorption of gas molecules on the internal material surfaces is used to obtain the pore size distribution and deduce the penetration depth.
Task 2 - Development of an electro-migration unit system

Measuring the Injected Particles

Method 3: Conductivity Test

After the Nano-Particle injection, the voids and pores may be filled by Nano-SiO₂. Air is a better insulator than particles. Thus, the idea is to re-run the RCPT test and check the how much the conductivity changes.

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Task 3: Selection of healing agents

Select Healing Agents

- Selection based on the penetration depth into the region to be repaired and enhancement of the properties of repaired materials.
- The healing agents will comprise of particles + cement slurry
- Pre-requisition: Negative surface charge
- Potentials: Aluminum Oxide, Silica Dioxide, Fumed Silica, Nano Clay, Calcium Carbonate

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</table>
Task 3: Selection of healing agents

Particle Size Effect

![Graph showing the relationship between SiO2 size (nm) and avg. porosity change (%). The x-axis represents avg. porosity change (%) ranging from 0 to 500, and the y-axis represents SiO2 size (nm) ranging from 0 to 14. The graph shows a linear trend with points at 0.83, 1.81, and 12.70.]
Task 3: Selection of healing agents

Generation of Distressed Well Cement

1. Cast using the API method and Class G cement in a high speed well cement mixer.

2. The samples are demolded after 2 days and cured for 7 days in water.

3. A preload at 70% of the strength of the sample in a 2min load exposure to engage the material and simulate a start of service condition.

4. Samples are aged at a consistent high temperature for 1, 3, or 7 days at 170°C to represent the ageing processes observed in concrete in an accelerated manner.

5. At the end of the ageing period the samples are again loaded to 70% of the strength of the sample to open the any cracks or defects.
Task 4: Small-scale wellbore test system

(A) Installation of one electrode rod through one of the squeeze points. The other electrode could be the steel casing, or a rod through another squeeze point.

(B) A packer cement squeeze process inside steel casing (Dusseault et al. 2014).

(C) Small-scale wellbore test system
Task 4: Small-scale wellbore test system
Task 5: Evaluation of the effectiveness

Fracture mechanics equation for cracking potential (toughness):

\[
J = \frac{(1-v_m^2)}{2E_m}\left[ \frac{v_m}{(1-v_m^2)} \frac{1}{(1-v_m^2)} \text{tr}(\sigma \cdot \sigma) - \frac{\nu_m}{(1-v_m^2)} \left( \text{tr}(\sigma)^2 \right) \right] + \frac{1}{1-p} \left( \frac{1}{2E_m} \{4\text{tr}(\sigma \cdot \sigma) \cdot (\text{tr}(\sigma)^2) \} + 2\pi \text{A} \cdot \text{Crack density, } \alpha \right) + \frac{1}{2E_m} \left( \text{A} \cdot \pi ab \left[4\text{tr}(\sigma \cdot \sigma) \cdot (\text{tr}(\sigma)^2) \right] \right)
\]
Task 5: Evaluation of the effectiveness

Fracture testing and analysis:

“Short rod testing is perhaps the most unequivocal and scale-independent method for testing cylindrical samples in Mode I”

Features:
- Slotted cylinders
- Chevron connection
- In-Situ pressure vessel
- Hydraulic actuator
- Sustains a chloride environment

Sensenny and Pfeifle, 1984
Ouchtlerlony, 1989, 1990

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Task 5: Evaluation of the effectiveness

H = hydrostatic, UCS = unconfined compression test, T = triaxial
Test 3T was performed at constant confining pressure of 17.3 MPa
Test 4T was performed at constant confining pressure of 34.5 MPa
Task 5: Evaluation of the effectiveness

- The unload-reload loops are used to track evolution of elastic moduli during plastic yielding (elastic-plastic coupling).
- Estimates of failure surface (dashed line) and initial yield (solid) surface from the 4 tests.
Task 6: Numerical models

Kayenta material model for damage characterization

- Kayenta continuous yield surface
  - (a) 3D view: Principal stress space with the high pressure “cap”
  - (b) Side view: Using cylindrical coordinate system
  - (c) The Octahedral view: Looking down at the hydro stat (Brannon et al., 2009)
Task 6: Numerical models

Combining the flux equations with the mass conservation equations:

\[ \frac{\partial C_i}{\partial t} = \nabla \left( D_i \nabla C_i + z_i D_i \left( \frac{F}{RT} \nabla \Phi \right) C_i + D_i C_i \nabla \left( \ln \gamma_i \right) + C_i V_x + D_{i-H} \nabla H + D_{i-T} \nabla T \right) \]

- diffusion
- electrical migration
- chemical activity
- advection
- moisture effect
- temp. effect

For ionic removal, the chemical activity and advection could be ignored.

The governing equations for the moisture and heat transport in cement are:

\[ \frac{\partial w}{\partial t} + \frac{\partial w}{\partial H} \frac{\partial H}{\partial t} = \nabla \left( D_{H-i} \nabla C_i + D_H \nabla H + D_{H-T} \nabla T \right) \]

\[ \frac{\partial Q}{\partial t} + \frac{\partial Q}{\partial T} \frac{\partial T}{\partial t} = \nabla \left( D_{T-i} \nabla C_i + D_T \nabla T + D_{T-H} \nabla H \right) \]
Additional equations are needed to account for the electrostatic potential

(i) Electroneutrality

\[ \sum_{i=1}^{n} z_i c_i = 0 \]

Will be used to determine initial conditions of ion concentration

(ii) Poisson’s equation

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

Will be used to determine the electrostatic potential \( \phi \) with an externally applied current

The porosity and tortuosity(\( \tau \)) of well cement depend on the extent and type of the injected healing agent(s), therefore the transport parameters in the model depend on the nano- and microstructures of the well cement, which will be updated in the simulation process.
Numerical simulations are performed on a rectangular concrete sample 3 cm by 5 cm. The sample is exposed to 0.5 mol/L NaCl and 0.5 mol/L CaCl$_2$ solutions on the top surface, and the other boundaries are assumed to be insulated.

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<th>species</th>
<th>K</th>
<th>Na</th>
<th>Cl</th>
<th>OH</th>
<th>Ca</th>
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<td>-1</td>
<td>+2</td>
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<td>D$_{Cl}$</td>
<td>3.9x10^{-11}</td>
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Synergy Opportunities

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

**In the current session**
- P2 – Using mineral precipitation method.
- P3 – Using microbially-induced calcite precipitation.
- P7 – Using nanocomposite materials for wellbore seal repair

**Other sessions**
- Applications of nanoparticles for *hydraulic fracturing*

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

- The nanoparticle injection technology is effective in the small scale.
- The size of nanoparticle is important for the effectiveness of the repair method.
- Several methods are being developed to generate distressed well cement and exam the repaired well cement.
- Numerical models are being developed to simulate the ionic transport process in porous well cement.

Future Work

- More nano- and micro-particles will be tested.
- Lab-scale testing system will be developed.
- Mechanical properties of repaired well cement will be examined.
- Numerical models will be developed to simulate the repairing process.
Appendix
Organization Chart

Lead Institution: University of Colorado at Boulder
PI: Yunping Xi

University of Colorado at Boulder
PI: Yunping Xi
Tasks 1, 2, 4, 5, 6
Co-PI: Mija Hubler
Tasks 2, 3, 4 and 5
Key personnel: Jiri Nemecek
2, 3, and 4

Sandia National Laboratory
Co-PI: Pania Newell
Tasks 1, 6
Co-PI: Tom Dewers
Task 5

University of Colorado at Boulder
Graduate Student 1
Tasks 2, 3, 4, 5
Graduate Student 2
Tasks 2, 3, 4, 6

Summer program at Sandia National Lab
Graduate Student 1
Participate Task 5, working with Dr. Dewers
Graduate Student 2
Participate Tasks 6, working with Dr. Newell

Biweekly phone conferences will be held to discuss project progress and plans, and resolve any issues

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