Nanoparticle Injection Technology for Remediating Leaks of CO2 Storage Formation

Project Number DE-FE0026514

Yunping Xi

University of Colorado at Boulder

Mija Hubler, Thomas Dewers, and Pania Newell

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

August 13-16, 2018

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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.

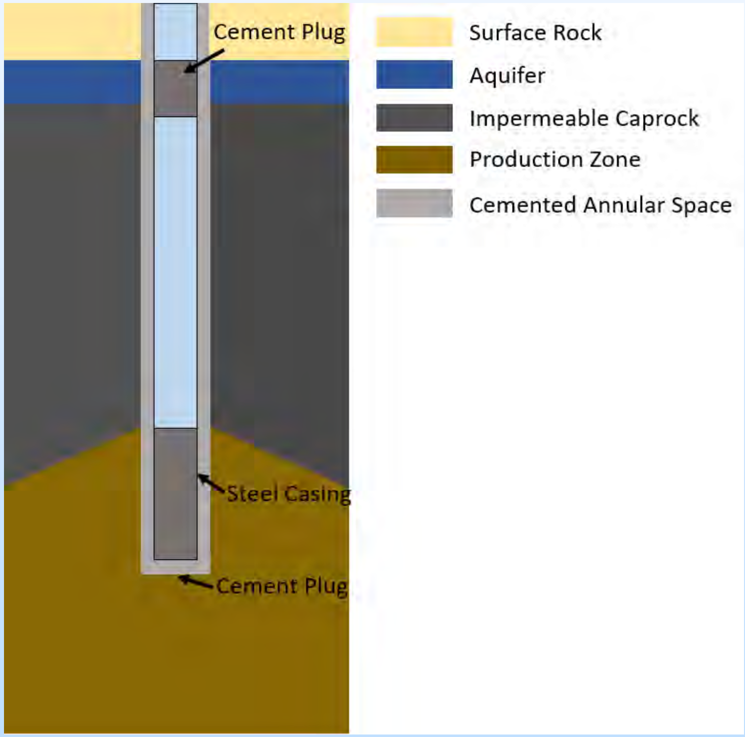
Electro-migration test unit	Select healing agents	Small-scale wellbore test system	Evaluate effectives with material testing

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

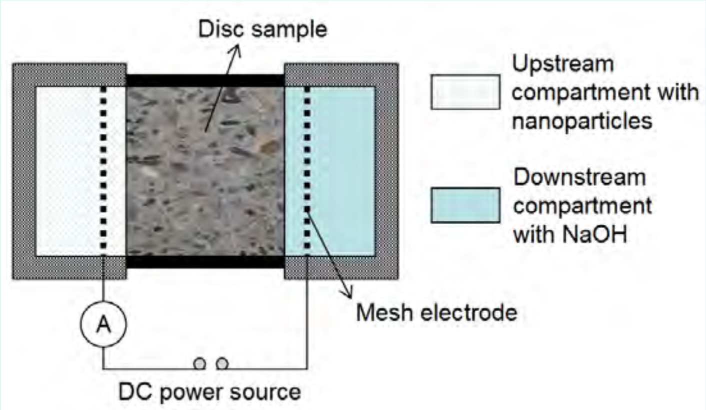
The concept of electrochemical technology is to use ionic exchange to deliver particles or repair agents to deteriorating areas. Usually this methodology will be adopted for the area which is difficult to reach, such as underground CO2 storage formations.



- Ionic exchange
- External current
- Anode and cathode regions
- Reduce corrosion damage

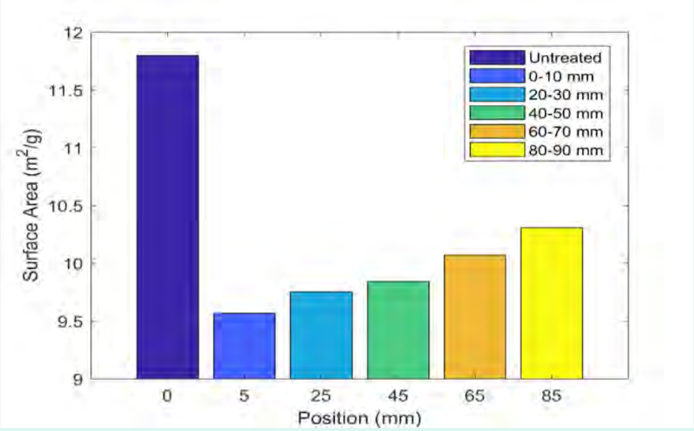
Presentation Outline

Task 2 & 3: Selection of healing agents

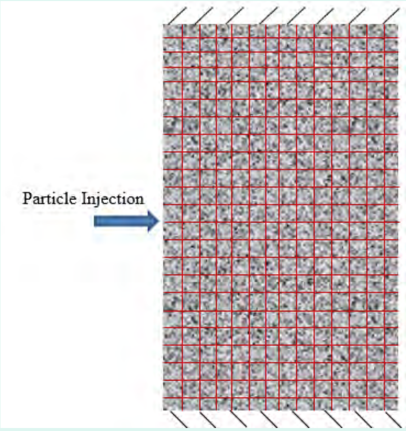


Task 4: Wellbore test system

Task 5: Evaluate effectiveness



Task 6: Numerical modeling



Task 2 & 3: Selection of healing agents

Table 1: Sample notation and producer specifications of nanoparticles used for treatments.

Specimen	Particle	Size	Charge	Content (wt.%)	Surface (m^2/g)	pH	
S1	S	7 nm	⊖	30	320-400	9.7-10.3	7nm nanosilica
S2	S	22 nm	⊖	40	130-155	9-9.5	22nm nanosilica
SF	S	$5-10^{*}\mu m$	⊖	9	$8^{\dagger}$	11.3-11.7	Fumed silica
SA	S/A	24 nm	⊕	30	n/a	4.2	Nanoalumina coated nanosilica
AL	A	50 nm	⊕	20	n/a	4	50nm nanoalumina

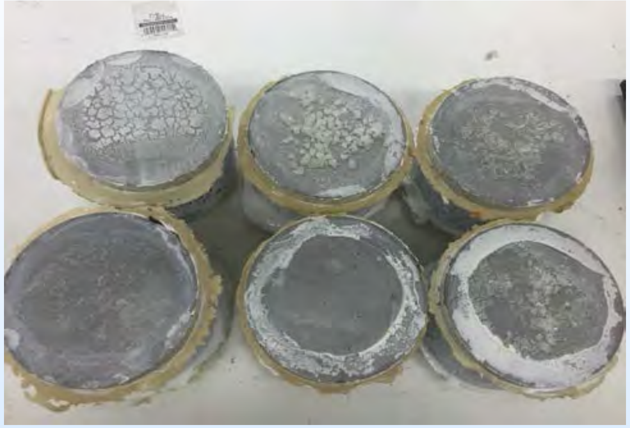
Note: S=SiO_2; A=Al_2O_3; *(80% $1-5\mu m$), † ref. [58]

- Injection into 50 mm thick cylindrical specimens made of class-G oil well cement with 42% porosity.
- During the injection, the electric current was monitored and the total charge passed through the samples was logged.
- Two kinds of samples were tested, non-aged and aged. Aging was performed by a thermal load (90°C for 8 days) which can cause severe cracking in the cement.
- After the test, the formation of particle agglomeration resulted in a reduction of the particle penetration. Chemical surfactants and new nanoparticles have been used.

Task 2 & 3: Selection of healing agents

- Chemical Surfactants

  - Methylcellulose ✔
  - Ethanol
  - Propanol
  - Sodium Dodecyl Sulfate ✔
  - Gum Arabic



Surface agglomeration

- New Nano-solutions

From previous researches, new nano-silica solutions seemed to be effective to prevent the agglomeration. That is the SiO_2 in tetraethoxysilane (TEOS). (Li et al., 2016)

Recently, there is a new type of nano-particle that has a potential to be used in oil and gas industry, named nano-gel, which includes polyacrylamide (PAM) nanogel and methylene bisacrylamide as the crosslinker. (Ding et al., 2017)

Task 2 & 3: Selection of healing agents

Non-Aged	Average Porosity (%)	Relative Porosity Change %)	Charge Passed
NanoSiO_2	40.07	4.59	6155
NanoAl_2O_3	41.56	2.42	1384
Meth	39.99	4.8	7990
SS	40.45	3.69	7013
Nanogel	40.83	2.79	7287
TEOS	40.14	4.43	7115

Aged	Average Porosity (%)	Relative Porosity Change %)	Charge Passed
NanoSiO_2	38.80	7.61	12233
NanoAl_2O_3	38.95	7.27	1969
Meth	37.91	9.75	9064
SS	38.38	8.61	11994
Nanogel	38.46	8.42	13768
TEOS	38.84	7.53	18201

Task 2 & 3: Selection of healing agents

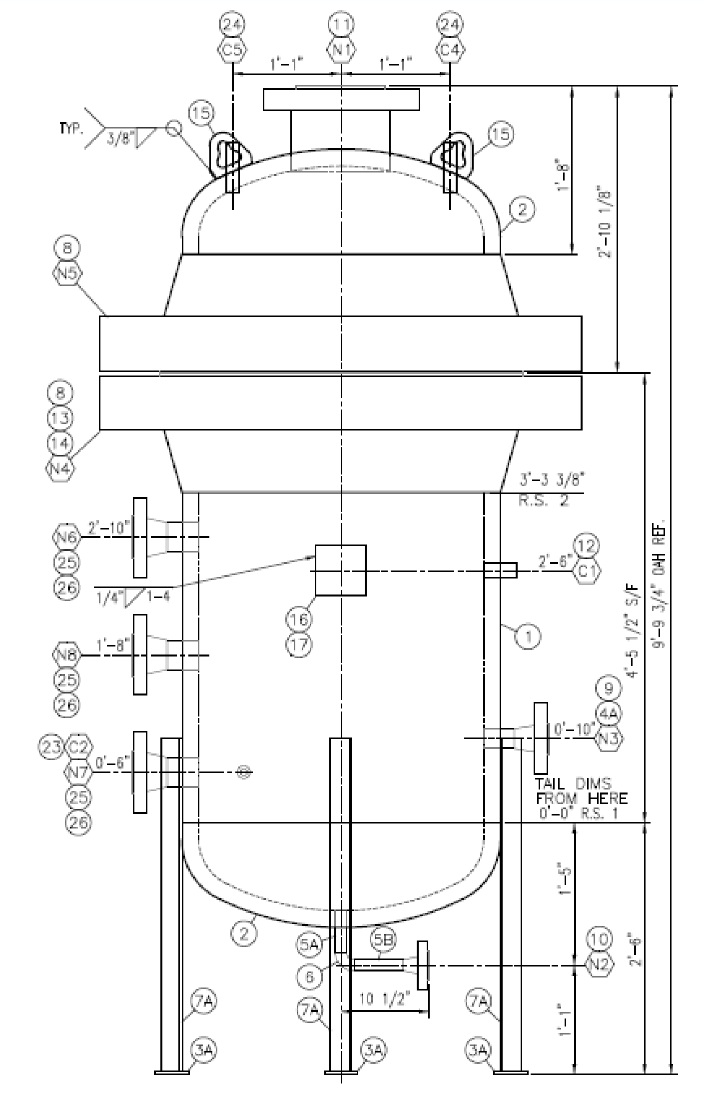
Conclusions

- An effective nanoparticle injection technology was developed. The desktop device was successfully used for injecting the nanoparticles.
- The agglomeration of the nanoparticles is an important issue since it can directly affect the effectiveness of the nanoparticle injection technology.
- Compared with Nanoalumina, Nanosilica is a better injection solution with more reduction of porosity.
- The Nanosilica mixed with Sodium Dodecyl Sulfate and Nanogel showed better performance for aged samples compared with original Nanosilica.
- The Nanosilica mixed with Methylcellulose is the most effective injection solution for intact samples.
- The Nanogel is the most effective injection solution for aged samples

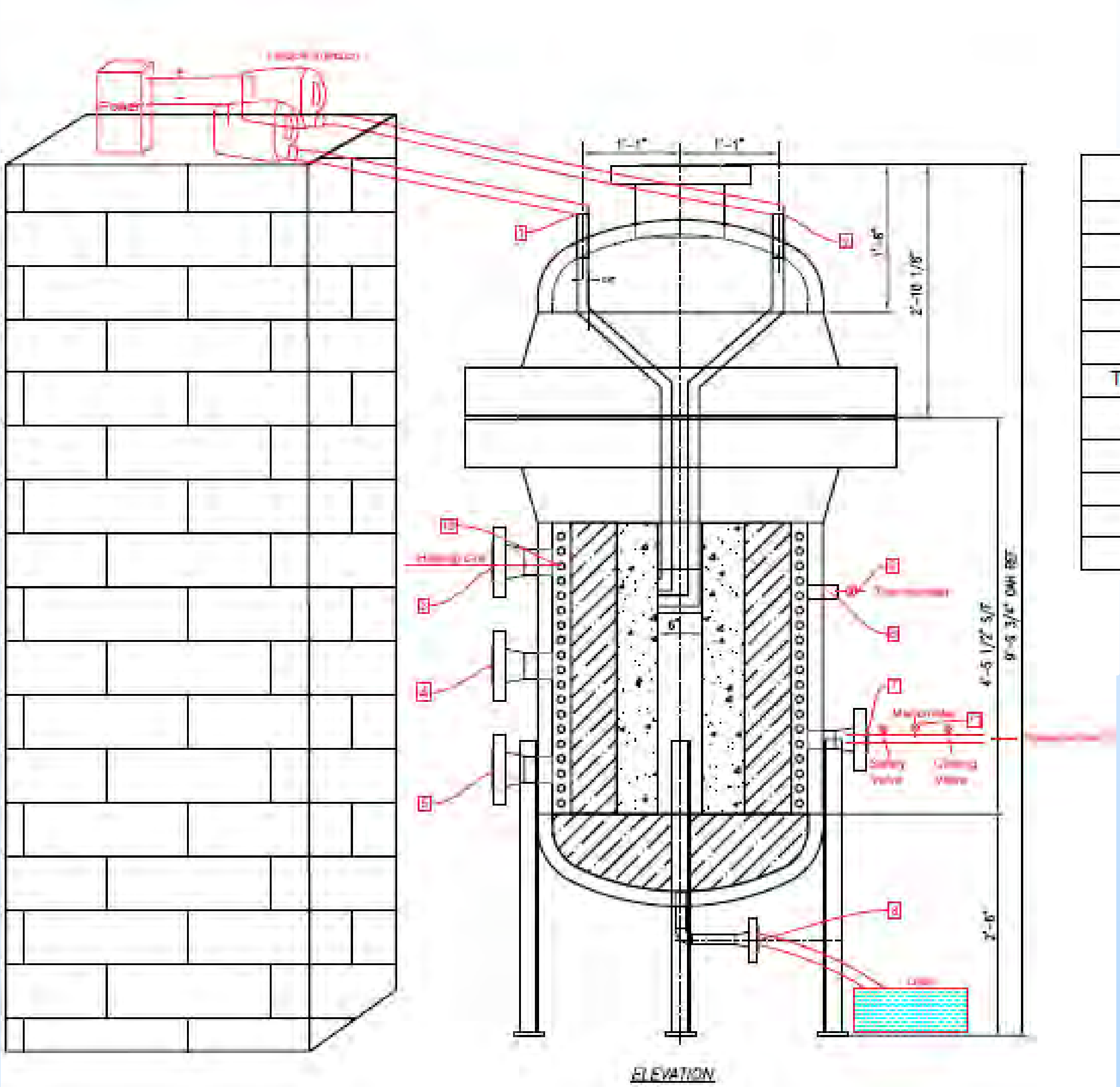
Task 4: Wellbore test system

Goal: develop a small-scale prototype wellbore testing system; and use it to simulate the real environment in the field.

- 12 MPa internal pressure
- Heating up to 80°C
- Full sized well pipe can be used
- 10 feet tall pressure vessel



Task 4: Wellbore test system



NAME	DIAMETER (in)	Thread Pitch (in)
Top Fill Hole 1	0.64	NO
Top Fill Hole 2	0.64	NO
Heating Hole 3	2.30	NO
Heating Hole 4	2.30	NO
Heating Hole 5	2.30	NO
Thermocouple Hole 6	0.88	0.08
Pressure Inlet Hole 7	1.50	NO
Drain Hole 8	0.60	NO
Thermometer 9	0.83	0.07
Heating Coil 10	0.74	0.06
Menometer 11	0.83	0.07

Task 4: Wellbore test system

Task 4: Wellbore test system

Rock Surrounding

Cement Pump

Heating Coil

The Gage that Transfer Air Pressure to Fluid Pressure

Task 4: Wellbore test system

- Setup Procedure

  1. Place a concrete block inside the vessel using a crane
  2. Install wall and bottom (plastic) separator.
  3. Insert steel casing and lid assembly
  4. Stress bolts
  5. Connect the cement pump and fill annulus with cement through the tube
  6. Fill with brine and pressurize
  7. Conduct particle injection test

- Experimental Plan for the next step of project

  Totally six testing variables need to be considered:

  1. Temperature
  2. Pressure
  3. Nanoparticles
  4. Injection duration
  5. Voltage of the external power
  6. Distance between injection tubes

Task 4: Wellbore test system

Step 1: Standard test: The same parameters as desktop test will be used

Step 2: Temperature effect: Increase the temperature to 40°C and 80°C

Step 3: Pressure effect: Increase the pressure to 4 MPa, 8 MPa, and 12 Mpa.

Step 4: Combined temperature and pressure effect:
Setup the temperature to 80°C and pressure to 12 Mpa.

Step 5: Nanoparticles from Tasks 2 and 3: Nanosilica with 7 nm diameter, Nanogel, and Nanosilica treated by Methylcellulose.

Step 6: External voltage: 20 V and 40 V.

Step 7: Injection duration: 12 hours and 24 hours.

Step 8: Injection distance: 6 7/8” and 13 3/4”.

Totally 24-30 tests are planned based on the combinations of testing variables

Task 4: Wellbore test system

Summary

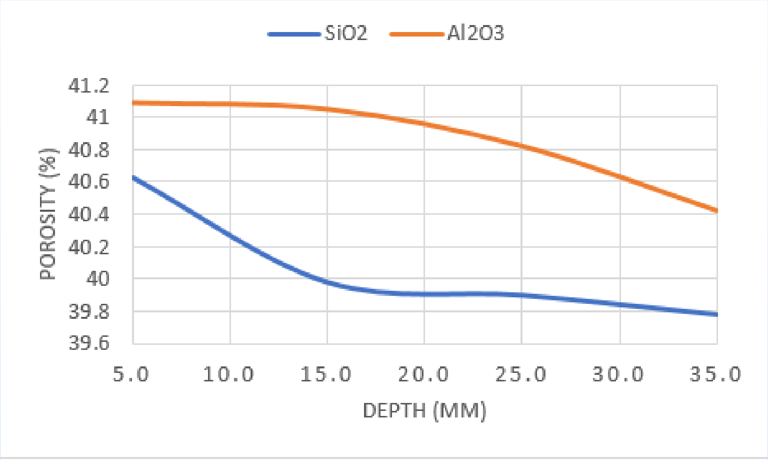
- The small-scale wellbore system has been successfully built which can generate similar environment as underground wellbore environment with high temperature, high moisture, and high pressure.
- All necessary parts of the pressure vessel have been ordered: heating coil, cement pump, hydraulic pump, etc.
- Various testing variables have been identified, and an experimental plan was designed, and systematic tests will be conducted in the future.
- In order to open the lid, a hydraulic wrench with high torque has to be purchased.

Task 5: Evaluate effectiveness

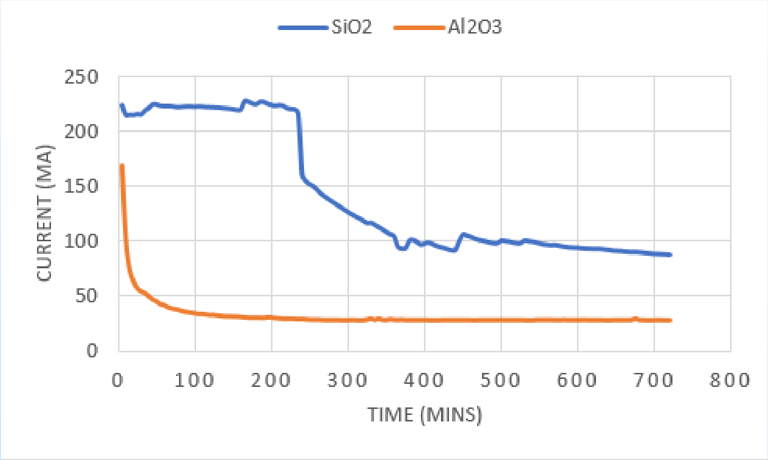
How to prove the injection technology?

1. Porosity should be reduced because the nanoparticles can fill pores and cracks
2. Conductivity should be reduced because the conductivity of nanoparticles is low

Method 1: Porosity test



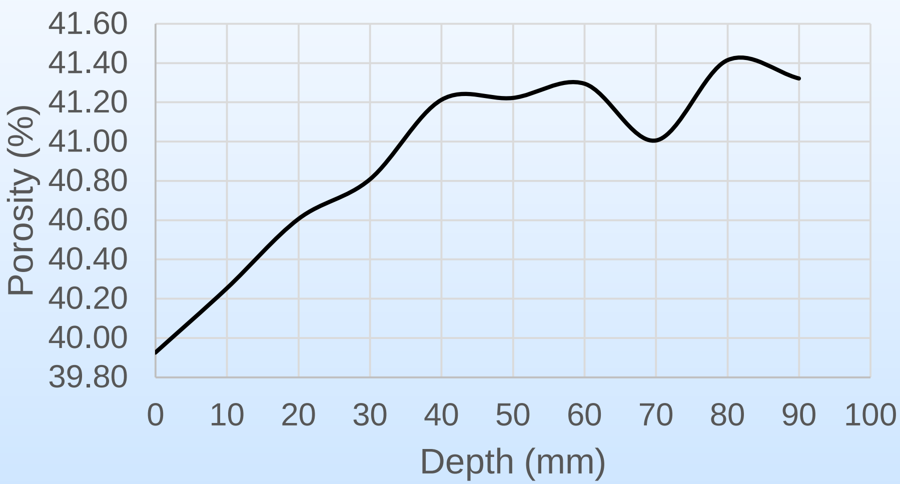
Method 2: Conductivity Test

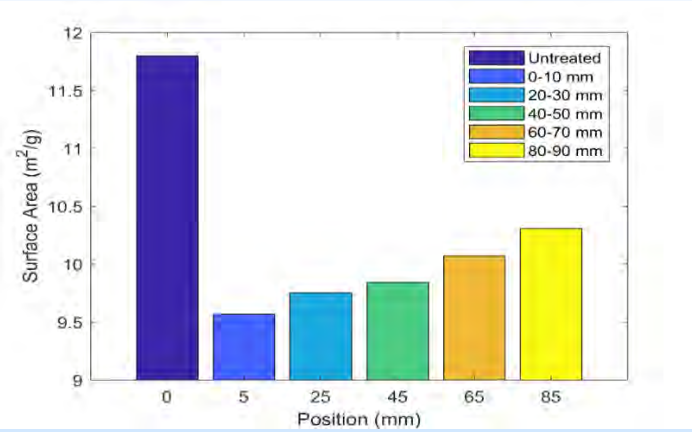


Initial test of Method 1 showed that the porosity of repaired samples decreased from the side close to nanoparticles to the far side, this is because the testing samples are not long enough, more particles have already been injected into deep part of the sample.

Task 5: Evaluate effectiveness

Method 3: BET Test
- Long Sample Considered: 200 mm length

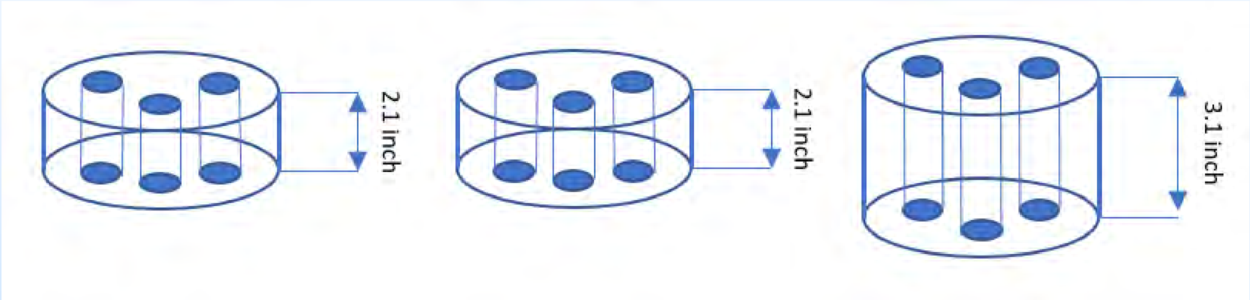




- The result from Method 3 proved the assumption made in Method 1.
- The profile of surface area also showed that the internal surface areas closer to the injection side are lower because the nanoparticles filled some of pores and cracks.

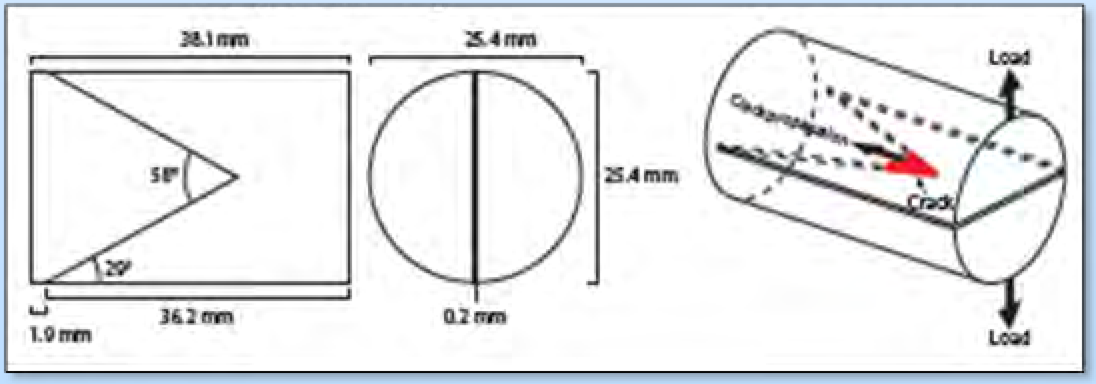
Task 5: Evaluate effectiveness

- Small cylinders collected from large cylinders by using Water Jet Cutting.
- Cylinders came from different types of samples: intact samples, aged samples, and repaired samples.
- Small cylinders will be used to determine mechanical properties of the samples. Compression tests, tension tests, and fracture tests will be conducted.



Sample Geometry

Schematic of Test



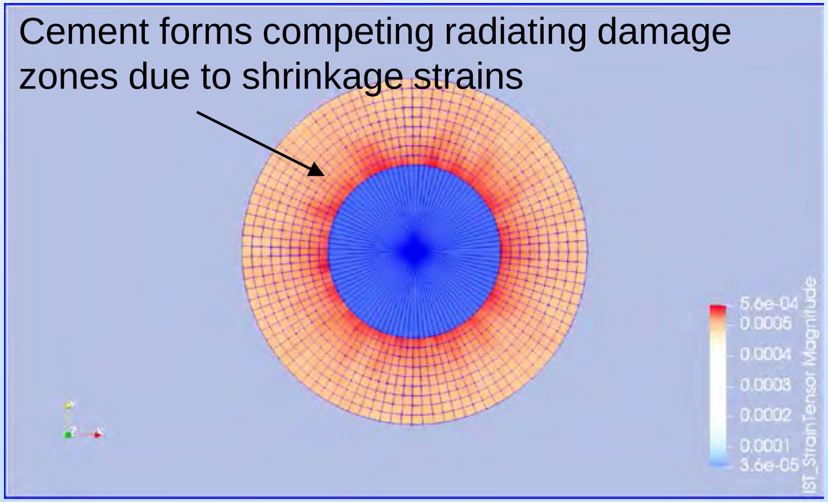
Task 5: Evaluate effectiveness

Objective: Study crack development and structure to understand how particles will enter the leakage network.

Method: Digital image correlation study of well cement ring test.

Previously showed **crack initiation** is sensitive to steel sheath modulus

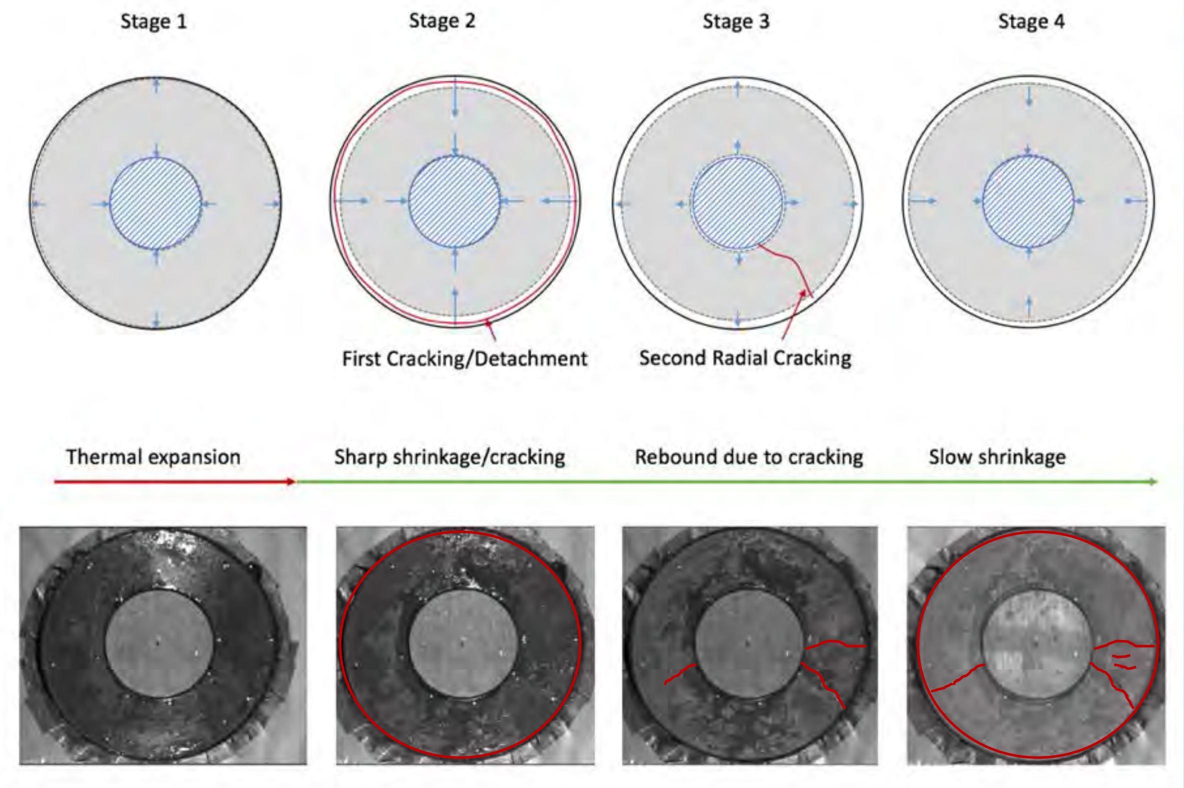
Recently studied **cracking stages** experimentally and compared with numerical models:



Model statistically distributed properties in the cement elements and isotropic damage model for interface elements.

Task 5: Evaluate effectiveness

Strain behavior of the entire section showed four characteristic stages.



<u>Insights:</u>

- Initially a large number of particles will fill the damaged area around the sheath.
- Particles may travel down a radial crack and enter space caused by sheath detachment.
- Once the dominant radial crack is filled, particles will primarily move through convection into the cement matrix.

Task 6: Numerical modeling

Injection of Nanoparticles

- A general framework of numerical modeling is under development to characterize the electrochemical injection technology.

- Governing partial differential equations:

Nernst-Planck Equation:

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

Poisson's Equation:

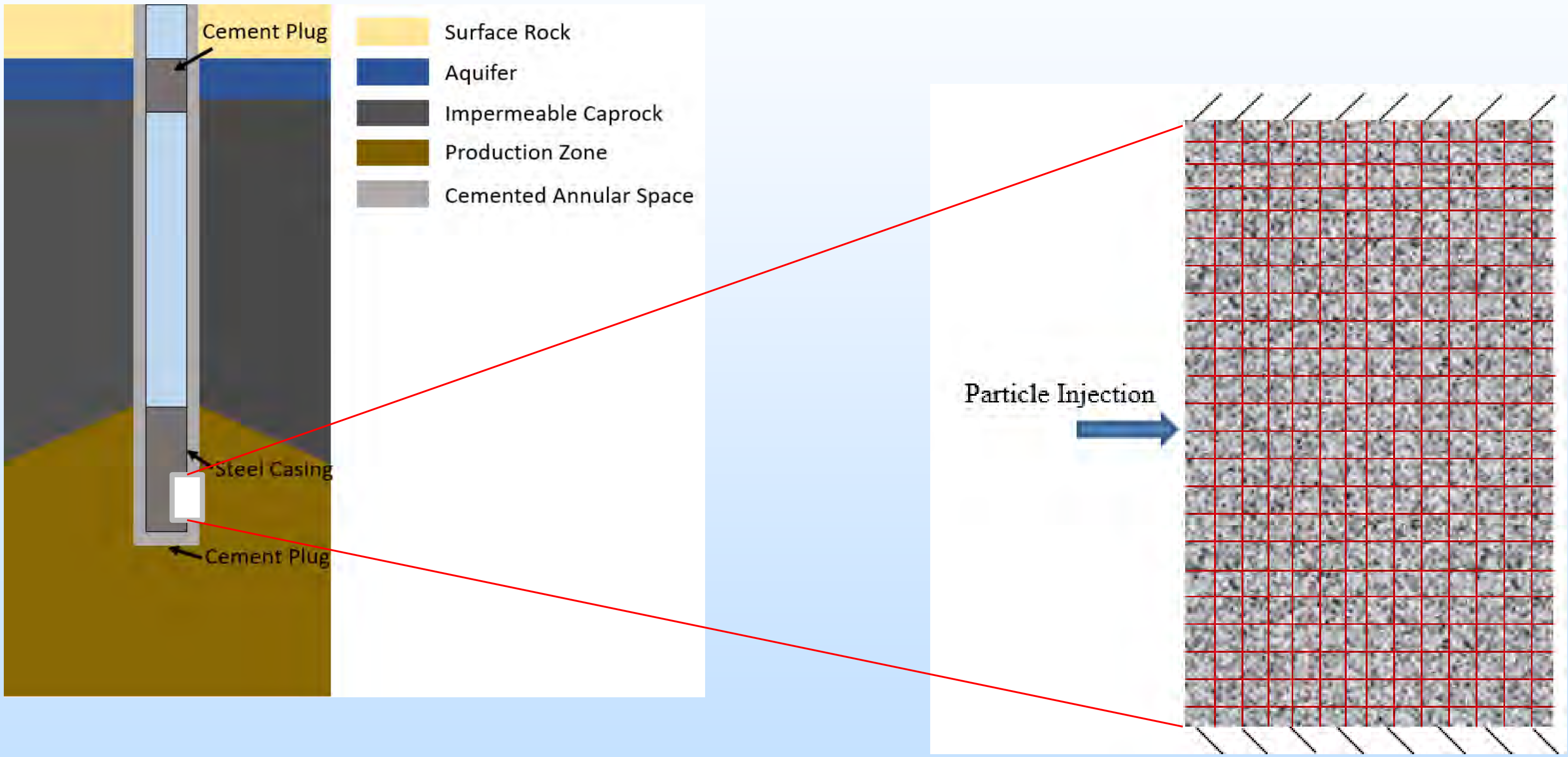
$$\tau\nabla^2\Phi = -\frac{F}{\varepsilon_0 \varepsilon_r}\sum_{i=1}^{n} C_i z_i$$

Red circles are for the two types of variables need to be solved:

- Ci is the concentration of diffusing species including the nanoparticles. Multi-species transport can be handled, such as chloride and nanoparticles
- Φ is the electric potential in the system

Task 6: Numerical modeling

Simulation of the nanoparticle injection process



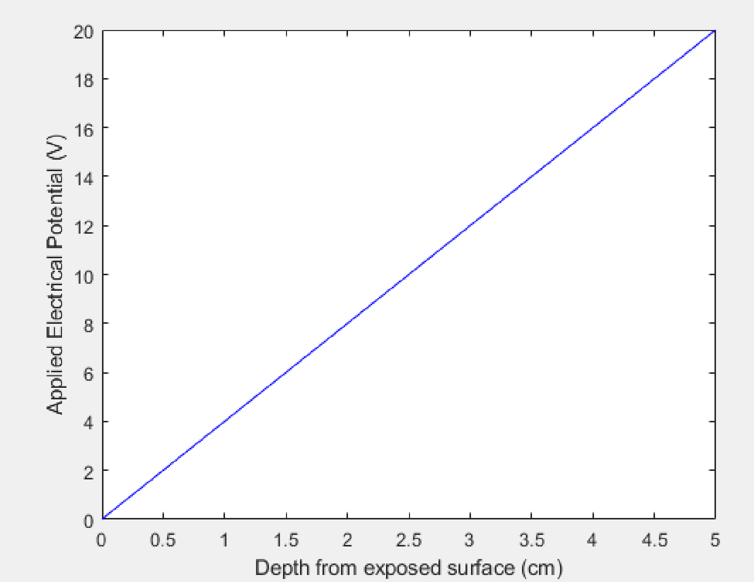
Simulation of the nanoparticle injection process by a 2D finite element mesh (could be horizontal or vertical injection depending on the characteristics of the leaking site)

Task 6: Numerical modeling

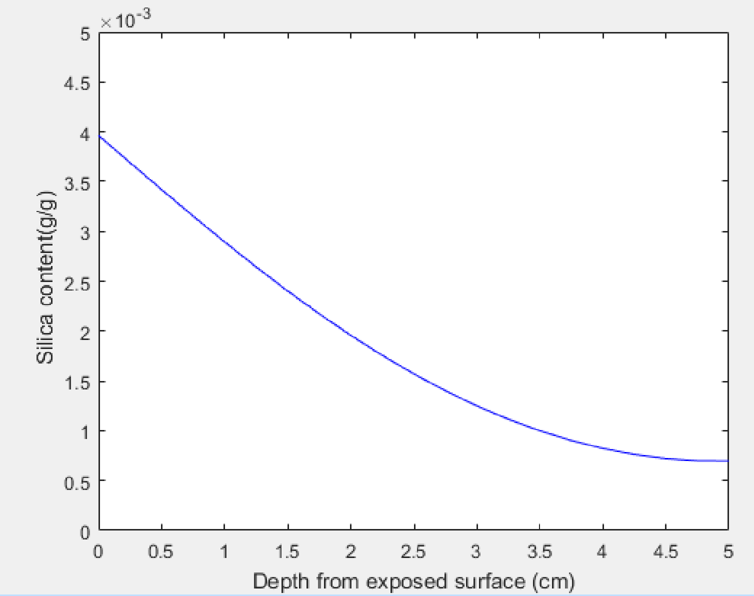
- Preliminary results

(1) Consider one type of diffusing species (nanosilica particles with negative surface charges) and an assumed linear distribution of electrical potential (20 V to 0 V).
(2) Neglect chemical activities (the last term on the right hand side of Nernst-Planck Equation).
(3) Assume binding capacity and diffusion coefficient are constants.

Assumed Linear Electrical Potential

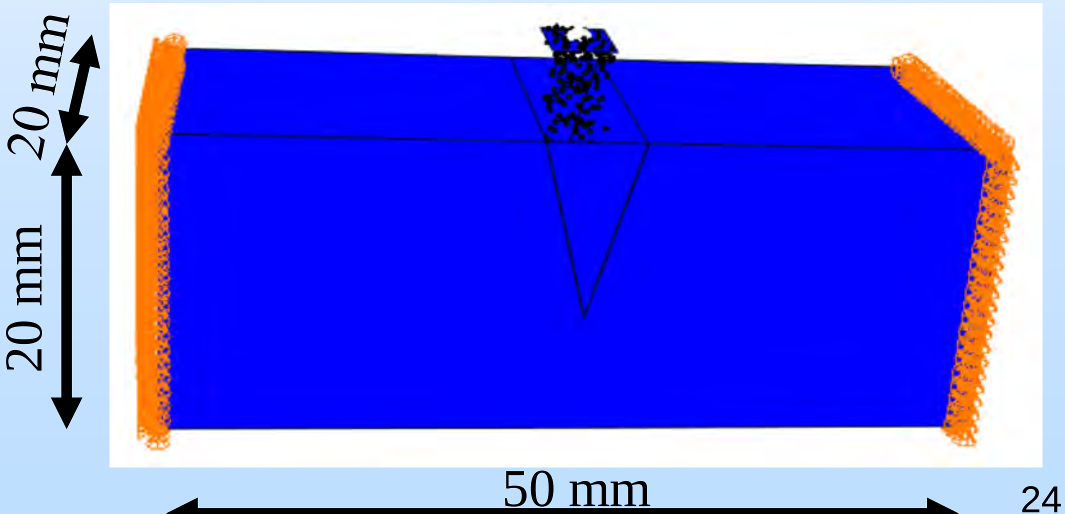


Concentration of Silica Ions after 12 hrs

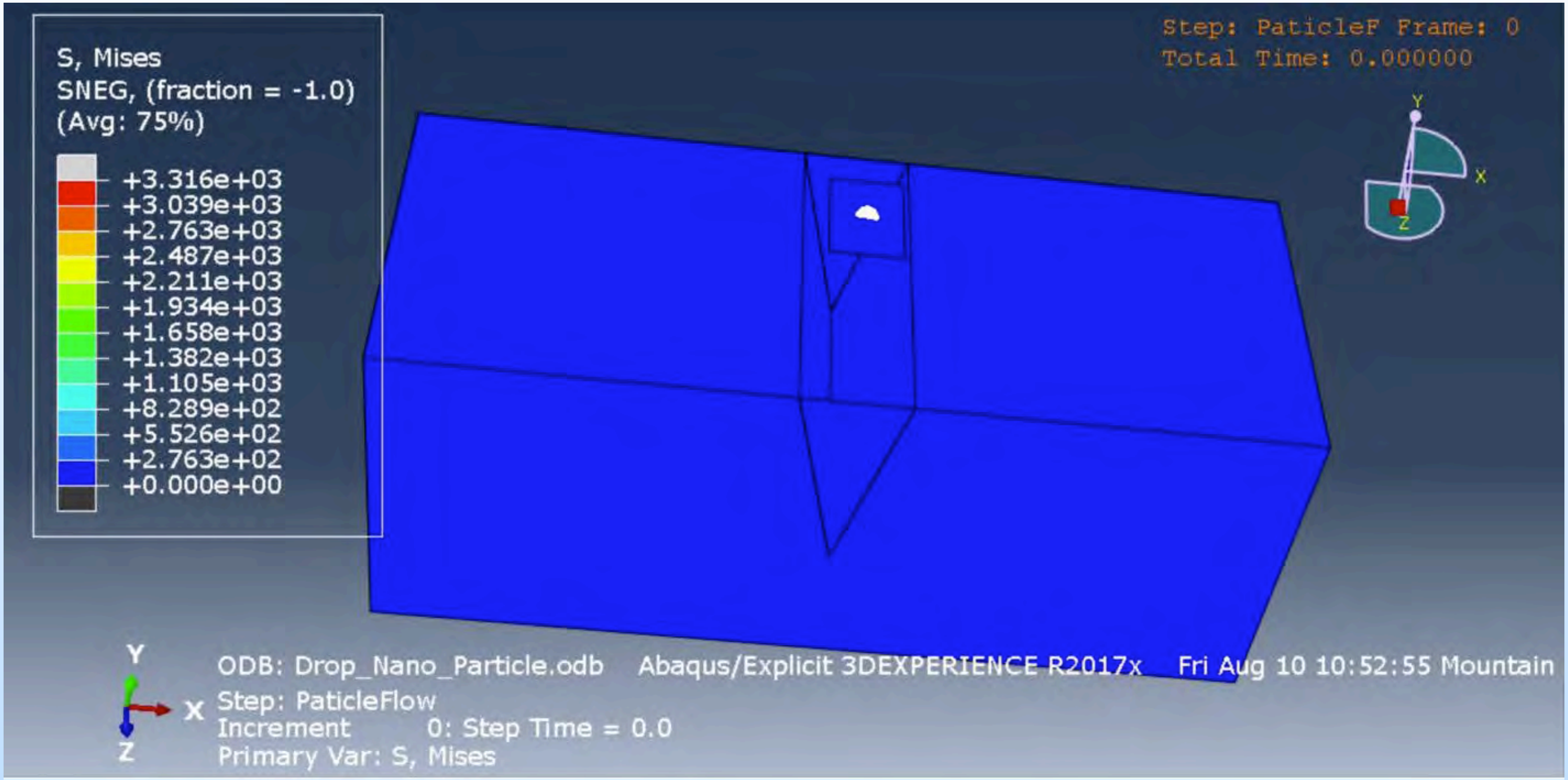


Task 6: Particle-crack interaction

- Simulation was completed using DEM modeling method in Abaqus.
- Particle property:
  - Amount: 1000 particles
  - Stiffness: 100 GPa
- Concrete property
  - Stiffness: 168 GPa
  - Contact stiffness: 300 GPa



Task 6: Numerical results



Task 6: Numerical modeling

Conclusions and Future Work

- The coupled governing equations for the ionic transport system were developed considering both concentration of ions and the electrical potential.
- A single variable diffusion model was successfully applied to the nanoparticle injection system with an assumption of linear electrical potential.
- The nonlinear electrical potential will be solved together with multispecies transport in the future.
- Chemical activities among different ions will be considered.
- The effect of other variables will be examined such as temperature and pressure, etc.
- The effect of damage level in well cement on the transport process of multispecies will be studied.
- A particle transport model will be developed at University of Utah.

Accomplishments to Date

- Completed the selection of the best healing agents.
- Completed bench-scale electro-migration testing.
- Completed the selection of testing methods to measure the effectiveness of the repair technology.
- A small scale wellbore test system was designed and built.
- An experimental plan was developed for the utilization of the small scale wellbore test system.
- Analytical and numerical models are under development for the nanoparticle injection technology.

Lessons Learned

- Research gaps/challenges

  The development of the pressure vessel is the challenge.
- Unanticipated research difficulties

  The tools for operation of the pressure vessel.
- Technical disappointments
- Changes that should be made next time

  More fund should be allocated in the budget for lab testing.

Synergy Opportunities

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

– Using mineral precipitation method.
– Using microbially-induced calcite precipitation.
– Using nanocomposite materials for wellbore seal repair
- Applications of nanoparticles for hydraulic fracturing

Project Summary

- Key Findings
  - The technology performs as expected on the bench scale platform.
  - Nanosilica mixed with the selected additives and the nano-gel are the most effective ones for the repair technology.
  - A pressure vessel was designed and built that can test a section of full-scale steel casing with well cement under controlled environments.
  - Analytical models were developed for rust penetration, carbonation, stiffness development of the cement, and fracture initiation due to fluid pressure.
- Next Steps
  - Construct and test technology in the large scale lab chamber.
  - Correlate repair technology control parameters to different types of leakage networks.
  - Develop numerical models for the simulation of the particle transport and the repair process.

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

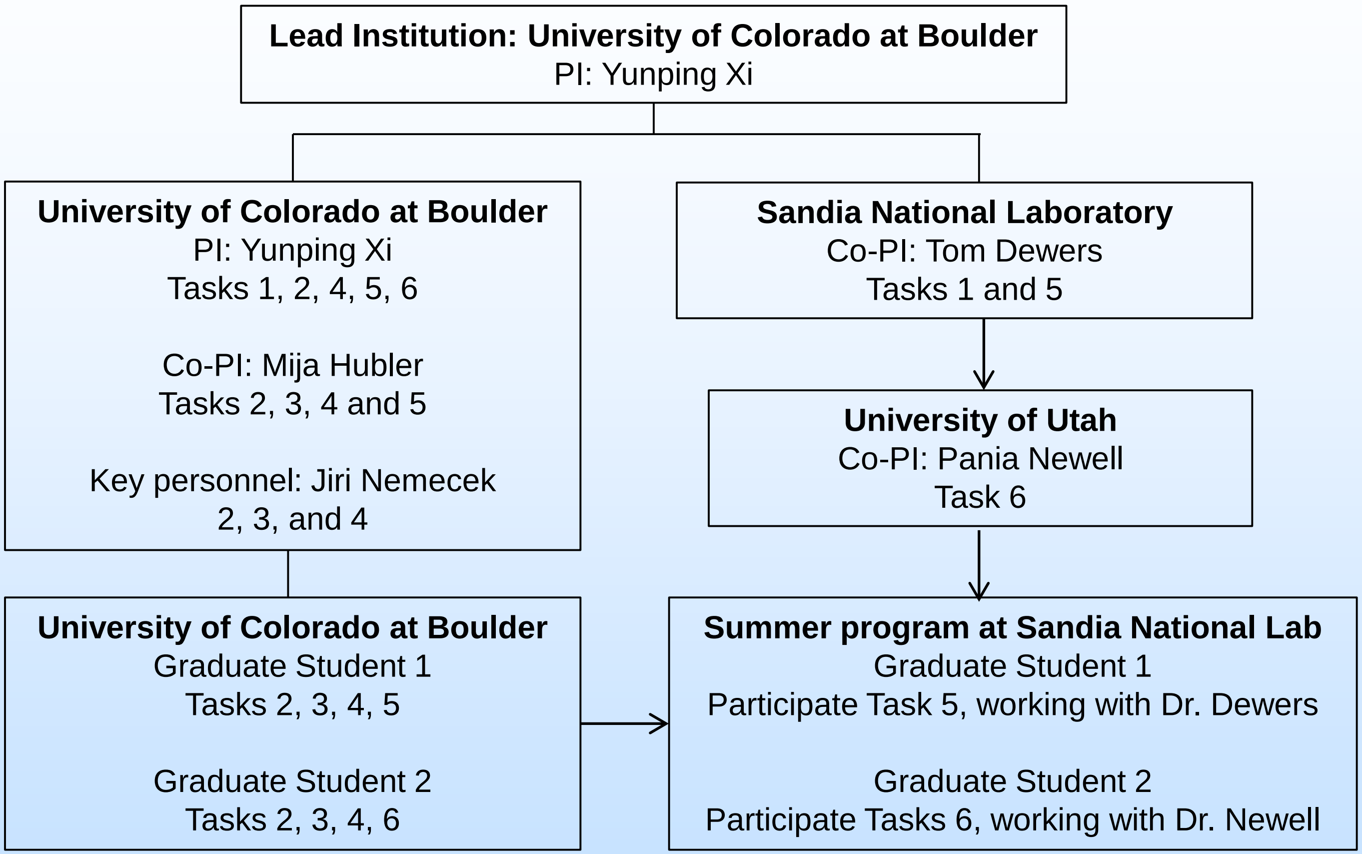
Objective 1: Development of the injection technology for leakage repair

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



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

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

Nemecek, J., Li, L., and Xi, Y. (2017) “Electrokinetic Nanoparticle Injection for Remediating Leaks in Oil Well Cement”, *Construction and Building Materials*, 156, 63-72.