Nanoparticle Injection Technology for Remediating Leaks of CO_2 Storage Formation

Project Number DE-FE0026514

Collaborators

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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.

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.

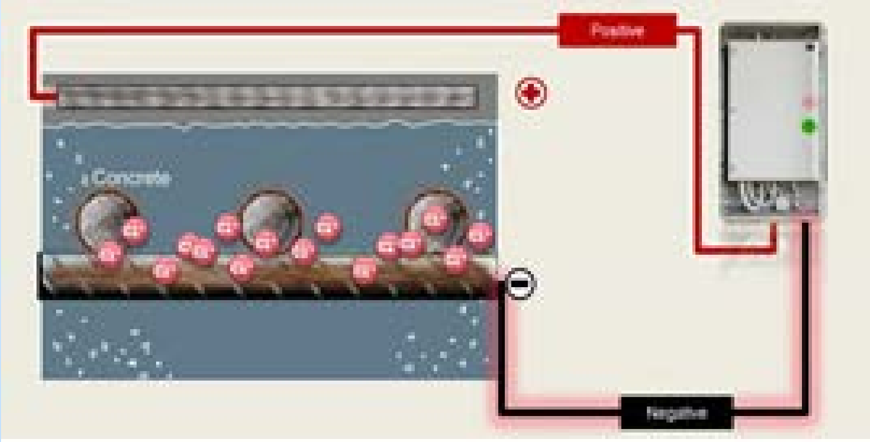
Model particle injection	Model ionic removal

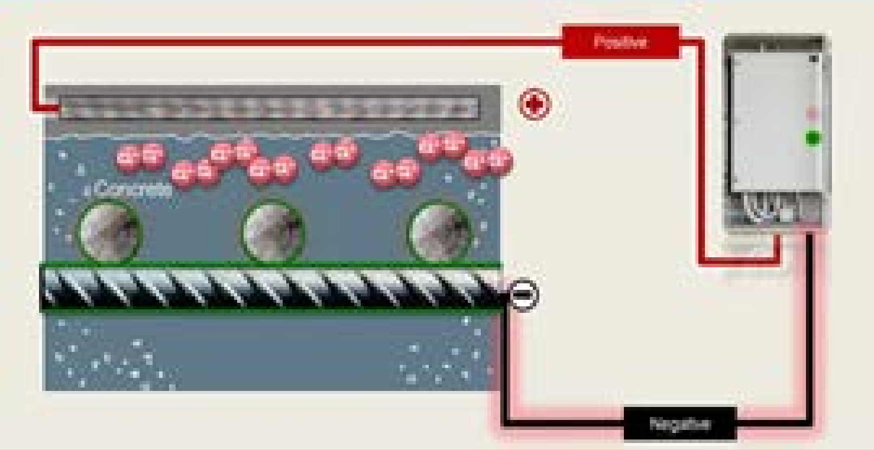
Task 2: An electro-migration test unit

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

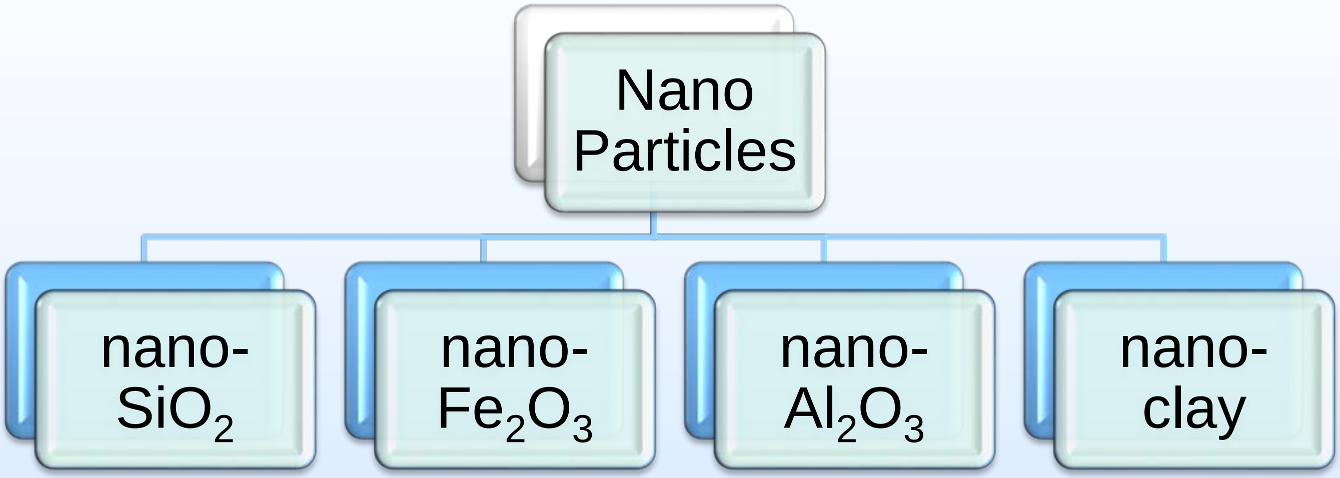
- Ion exchange
- High voltage
- Reverse anode and cathode regions
- Ions diffuse, causing gradient

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_2O_3 can **provide** self-sensing capabilities and improve strength.
- Nano-Al_2O_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

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**

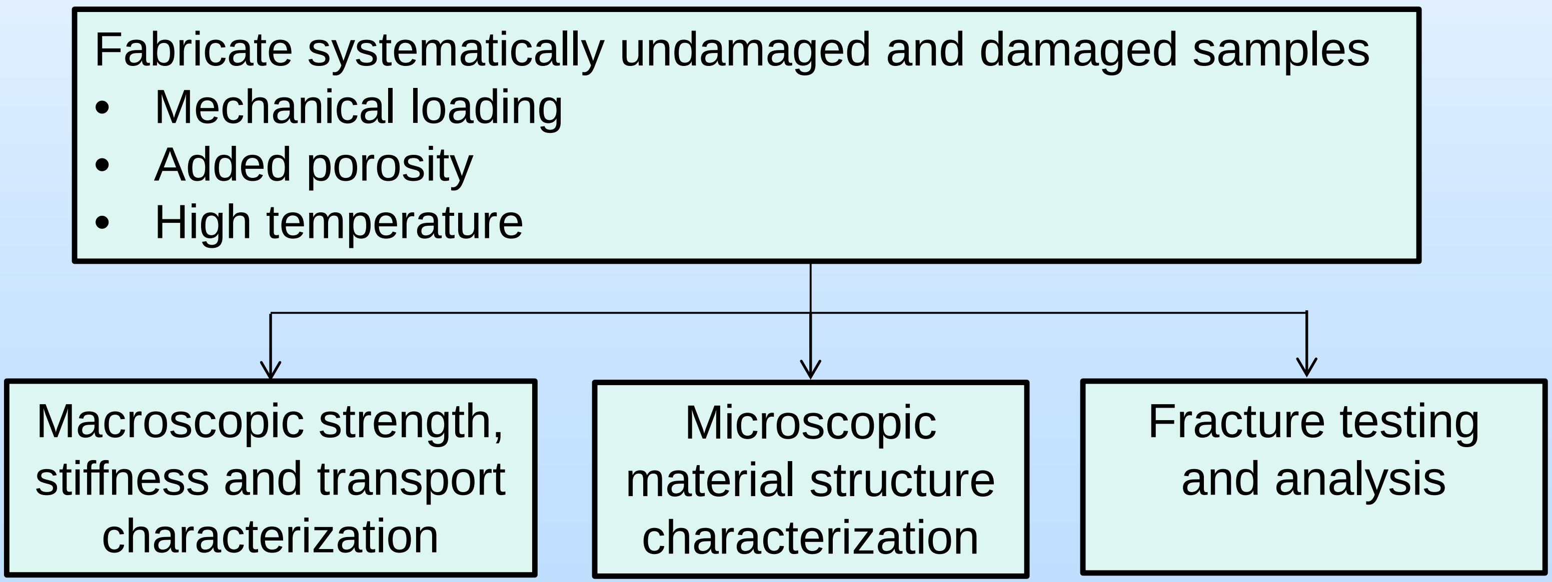
  - Development of a small-scale technology prototype
  - Based on a packer cement squeeze process
  - Development of a counter electrodes system

Task 5: Evaluation of the effectiveness

- **Purpose**

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

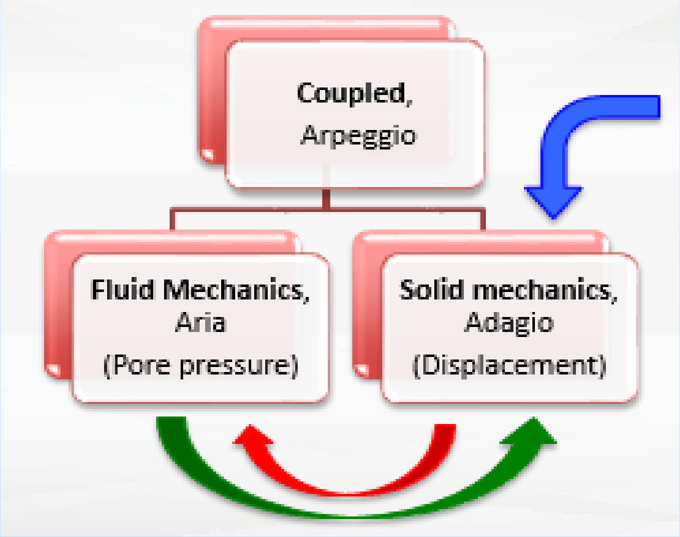
- **Evaluation Goals**
  - Which combination of materials and processes provide the best healing performance?
  - How are the mechanical and transport properties of the material affected?
  - How effectively are the ions removed during the injection process?
- **Approach**



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



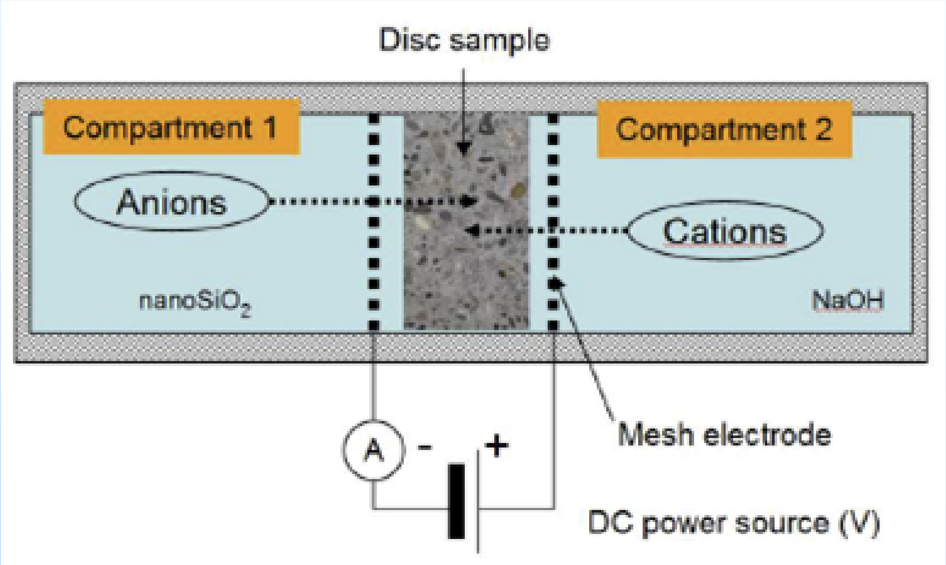
Kayenta: quasi-static behavior of porous geomaterials

- 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: Nanopaticles (30 – 40% weight)
Downstream: 0.3 N NaOH (+ polarity)
External Current: 10 V
Running Time: 12 hrs
Temperature: 49 °C

Task 2 - Development of an electro-migration unit system

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.

$$Porosity = \frac{\frac{w_{SSD} - w_{OD}}{\rho_{water}}}{v_{sample}}$$

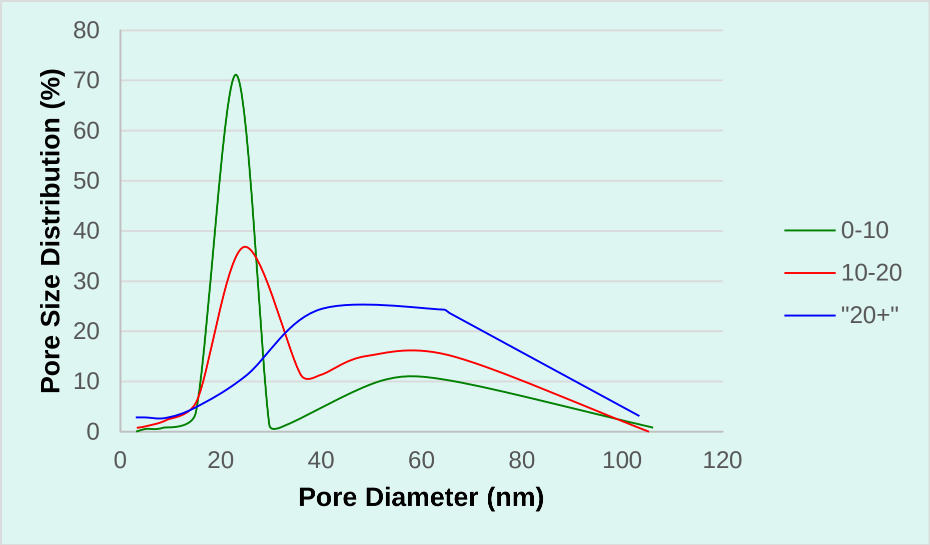
7 nm			
Untreated	V cm^3	Porosity	Avg.
	716.67	0.2010	0.2077
	706.38	0.2143	
Treated	V cm^3	Porosity	Avg.
	708.59	0.1961	0.1993
	713.89	0.2025	
22 nm			
Untreated	V cm^3	Porosity	Avg.
	701.23	0.2188	0.2081
	720.69	0.1974	
Treated	V cm^3	Porosity	Avg.
	711.37	0.2053	0.1900
	719.40	0.1746	
5000 nm			
Untreated	V cm^3	Porosity	Avg.
	713.79	0.3449	0.3529
	710.65	0.3608	
Treated	V cm^3	Porosity	Avg.
	711.37	0.2032	0.2258
	716.78	0.2484	

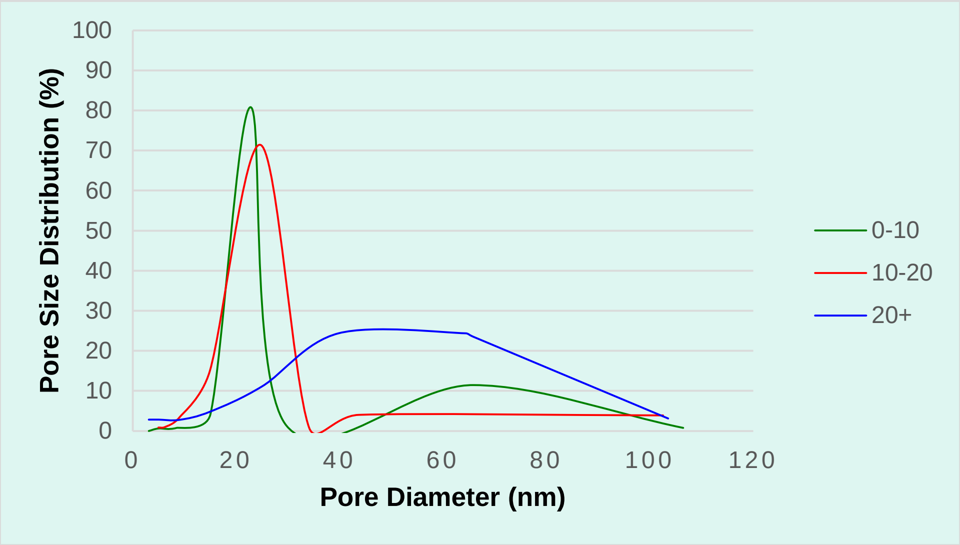
Task 2 - Development of an electro-migration unit system

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.





12 hr test

24 hr test

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-SiO_2. 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.

	Treated	**Original**
Charge Passed (Coulomb)	15733	14721

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

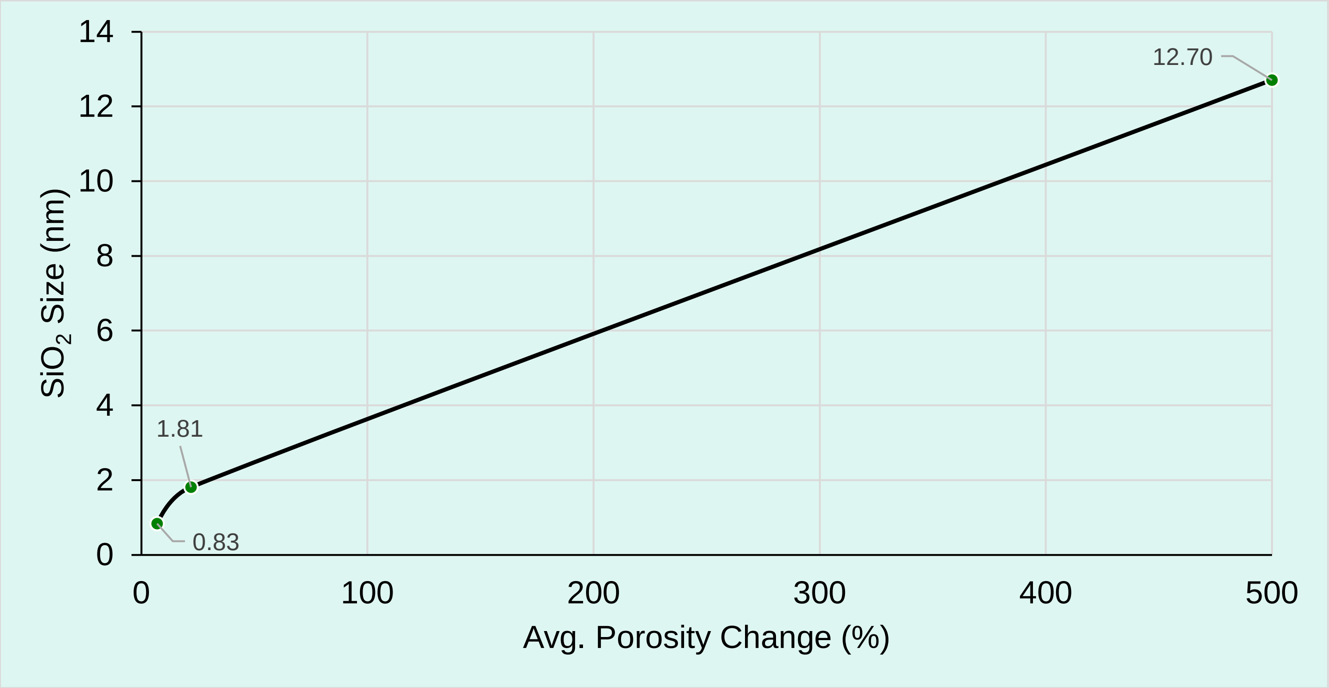
- Pre-requisition: Negative surface charge

- Potentials: Aluminum Oxide, Silica Dioxide, Fumed Silica, Nano Clay, Calcium Carbonate

Al_2O_3			
Untreated	V cm^3	Porosity	Avg.
	715.34	0.2713	0.2594
	713.79	0.2475	
Treated	V cm^3	Porosity	Avg.
	716.67	0.2474	0.2514
	722.75	0.2553	

Task 3: Selection of healing agents

Particle Size Effect



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.

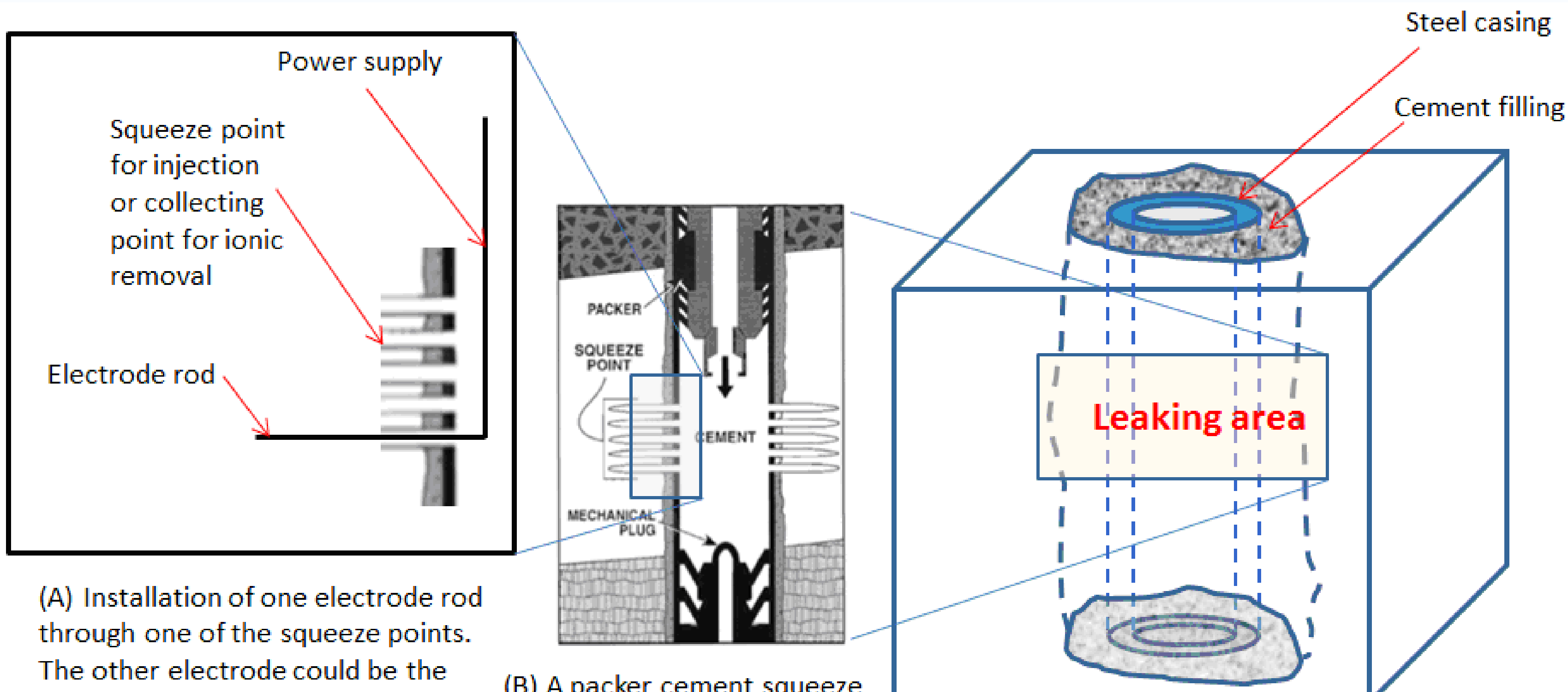
2. The samples are demolded after 2 days and cured for 7 days in water.

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

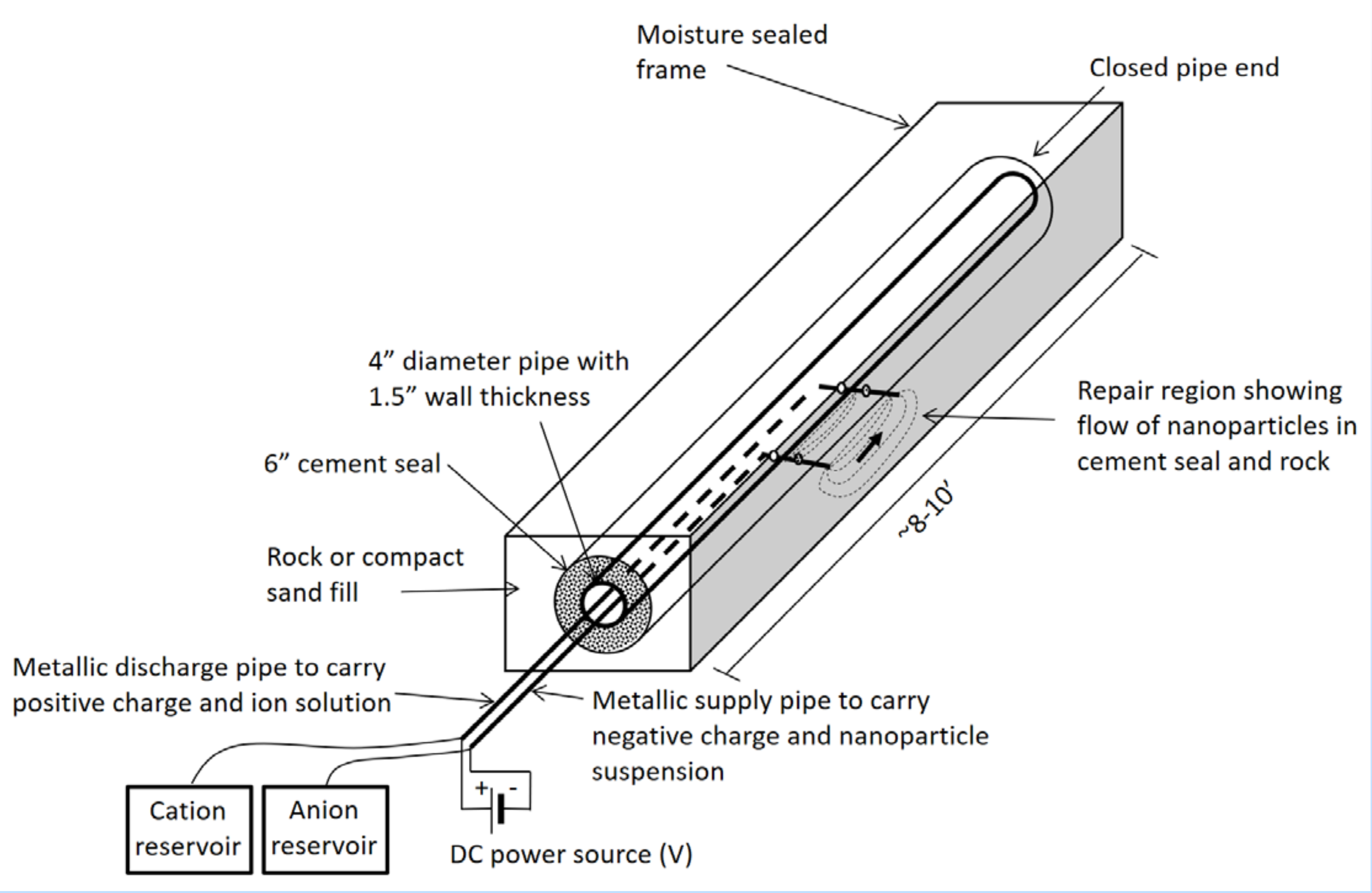


(A) Installation of one electrode rod through one of the squeeze points. The other electrode could be the steel casing, or a rod through another squeeze point.

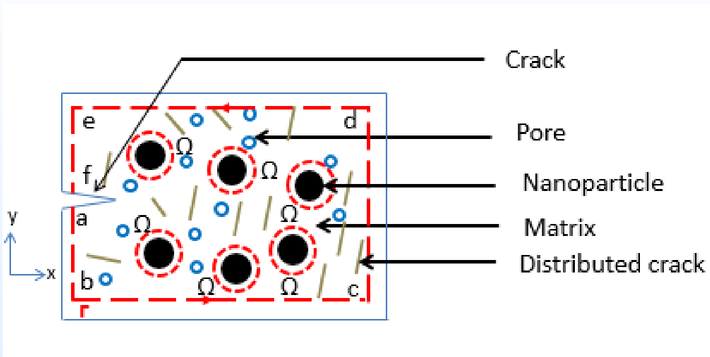
(B) A packer cement squeeze process inside steel casing (Dusseault et al. 2014).

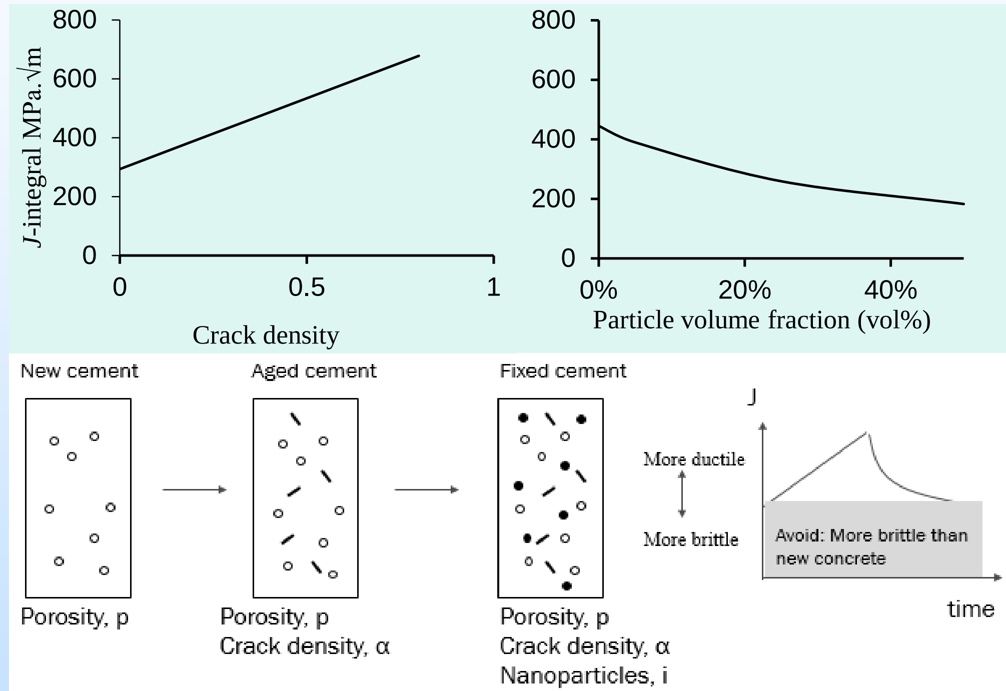
(C) Small-scale wellbore test system

Task 4: Small-scale wellbore test system



Task 5: Evaluation of the effectiveness





Fracture mechanics equation for cracking potential (toughness):

$$J = \frac{(1-\nu_m^2)}{2\,E_m}\left[\left(1+\frac{\nu_m}{(1-\nu_m^2)}\right)\mathrm{tr}(\sigma.\sigma)-\frac{\nu_m}{(1-\nu_m^2)}(\mathrm{tr}\sigma)^2\right]+\left[\frac{1}{1-p}\,\frac{1}{2E_m}\{p[4tr\,\sigma.\sigma-(tr\,\sigma)^2]+2\pi\,\sigma.\sigma:\alpha\}\right]+\left[\frac{1}{2E_m}\,\frac{1}{A}\,[\pi ab[4tr\,\sigma.\sigma-(tr\,\sigma)^2]]\right]$$

Task 5: Evaluation of the effectiveness

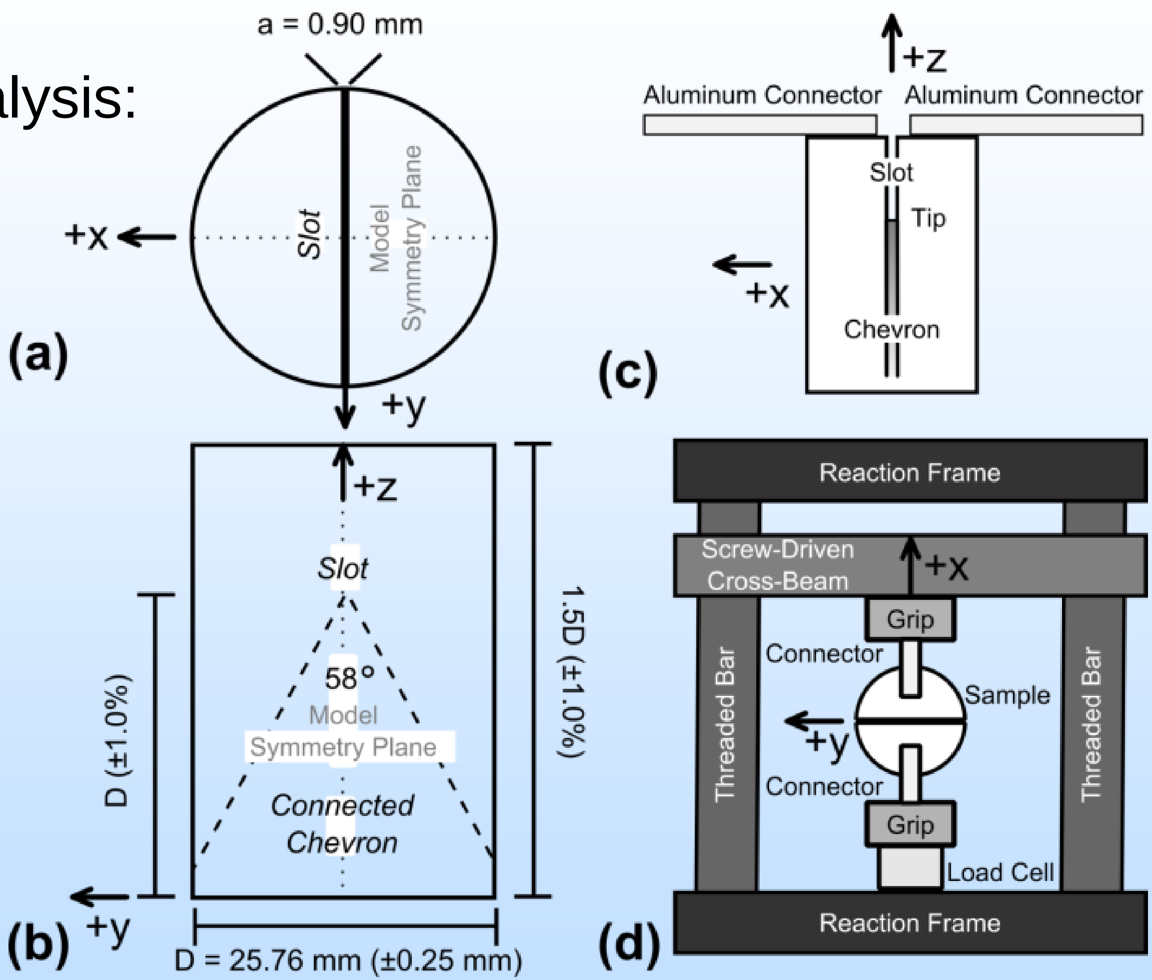
Fracture testing and analysis:

> *"**Short rod testing** is perhaps the most unequivocal and scale-independent method for testing cylindrical samples in Mode I"*

Sensenny and Pfeifle, 1984
Ouchtlerlony, 1989, 1990

Features:

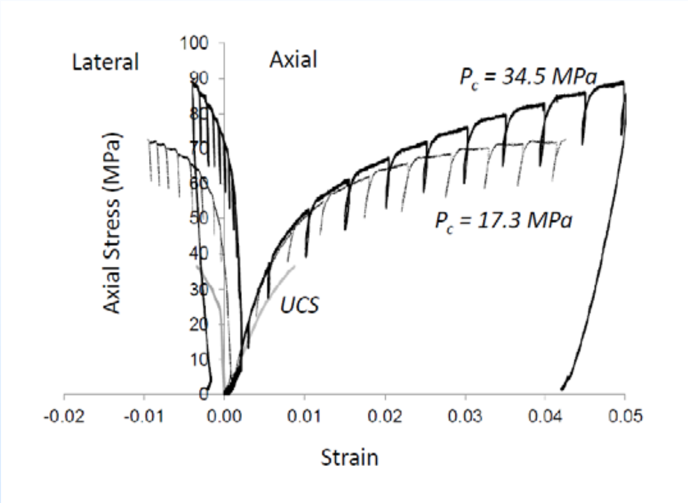
- Slotted cylinders
- Chevron connection
- In-Situ pressure vessel
- Hydraulic actuator
- Sustains a chloride environment

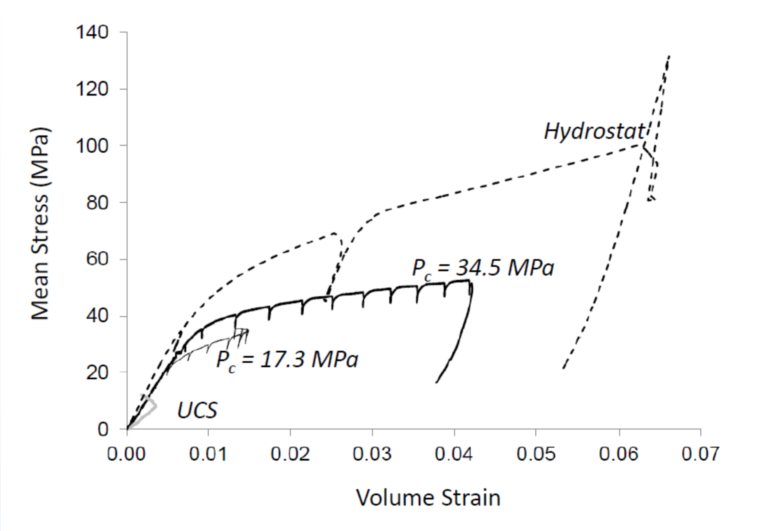


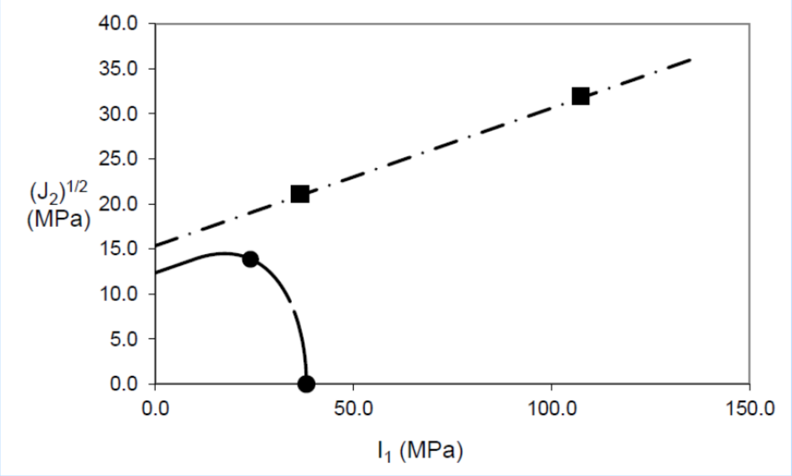
Task 5: Evaluation of the effectiveness

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



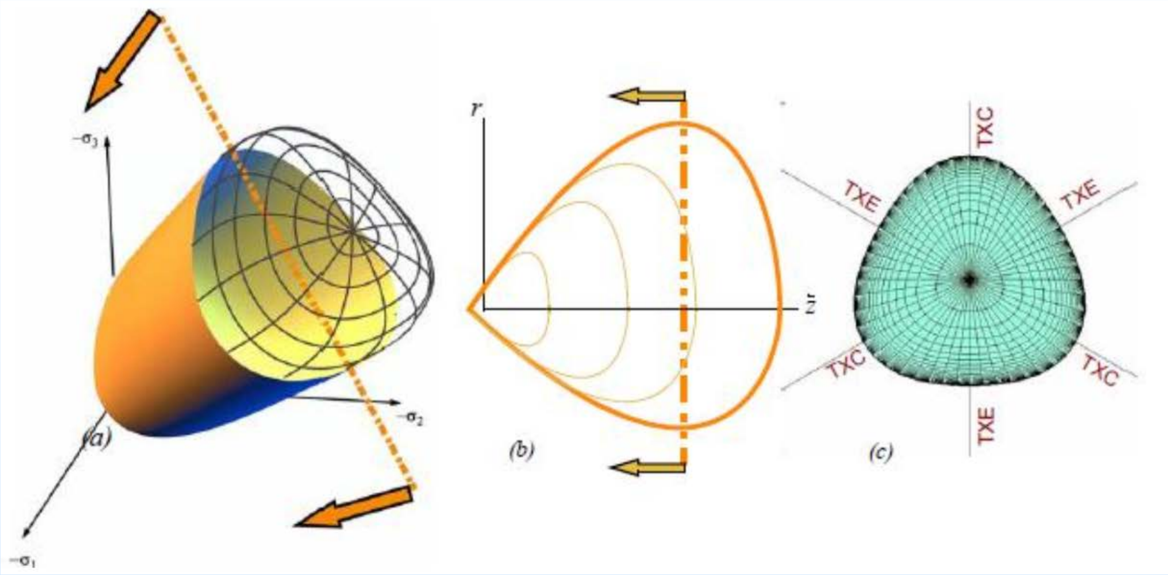




- The unload-reload loops are used to track evolution of elastic moduli during plastic yielding (elastic-plastic coupling).
- Estimates of failure surface (dashed line) and initial yield (solid) surface from the 4 tests.

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:

$$\frac{\partial C_i}{\partial t} = \nabla\left(\underbrace{D_i \nabla C_i}_{\text{diffusion}} + \underbrace{z_i D_i \left(\frac{F}{RT} \nabla \Phi \right) C_i}_{\text{electrical migration}} + \underbrace{D_i C_i \nabla(\ln \gamma_i)}_{\text{chemical activity}} + \underbrace{C_i V_x}_{\text{advection}} + \underbrace{D_{i-H} \nabla H}_{\text{moisture effect}} + \underbrace{D_{i-T} \nabla T}_{\text{temp. effect}} \right)$$

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

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

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

$$\frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial T}\frac{\partial T}{\partial t} = \nabla\left(D_{T-i}\nabla C_i + D_T \nabla T + D_{T-H}\nabla H\right)$$

Task 6: Numerical models

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

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

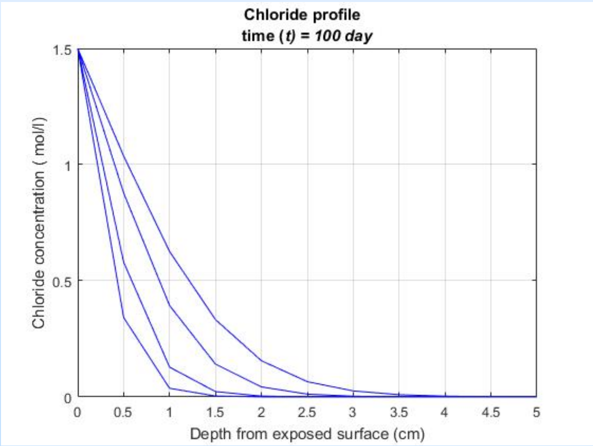
Will be used to determine the electrostatic potential ϕ with an externally applied current

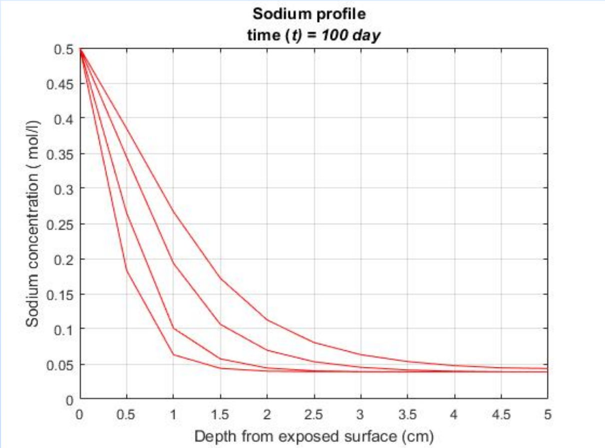
The porosity and tortuosity(τ) of well cement depend on the extent and type of the injected healing agent(s), therefore the transport parameters in the model depend on the nano- and microstructures of the well cement, which will be updated in the simulation process.

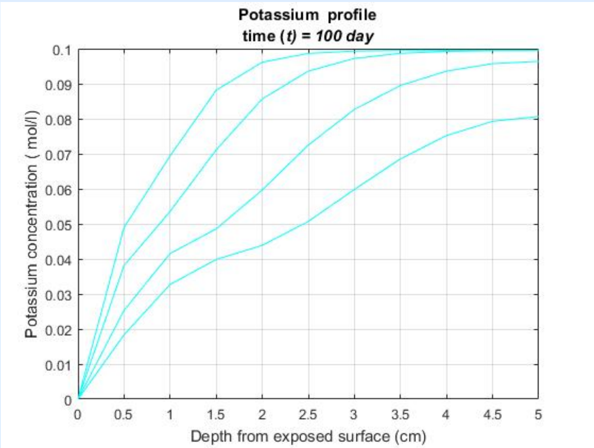
Task 6: Numerical models

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.

species	K	Na	Cl	OH	Ca
charge number	+1	+1	-1	-1	+2
diffusion coefficient, D_{Ci} /($m^2.s^{-1}$)	$3.9x10^{-11}$	$3.9x10^{-11}$	Dcl	$3.9x10^{-11}$	$3.9x10^{-11}$
boundary condition at top surface of concrete sample/($mol.L^{-1}$)	0	0.5	1.5	0	0.5
initial condition in pore solution/($mol.L^{-1}$)	0.0995	0.0389	0	1.384	0
water-cement ratio, w/c			0.55		
volume fraction of aggregate, g_i			0.65		







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.

Summary

Conclusions

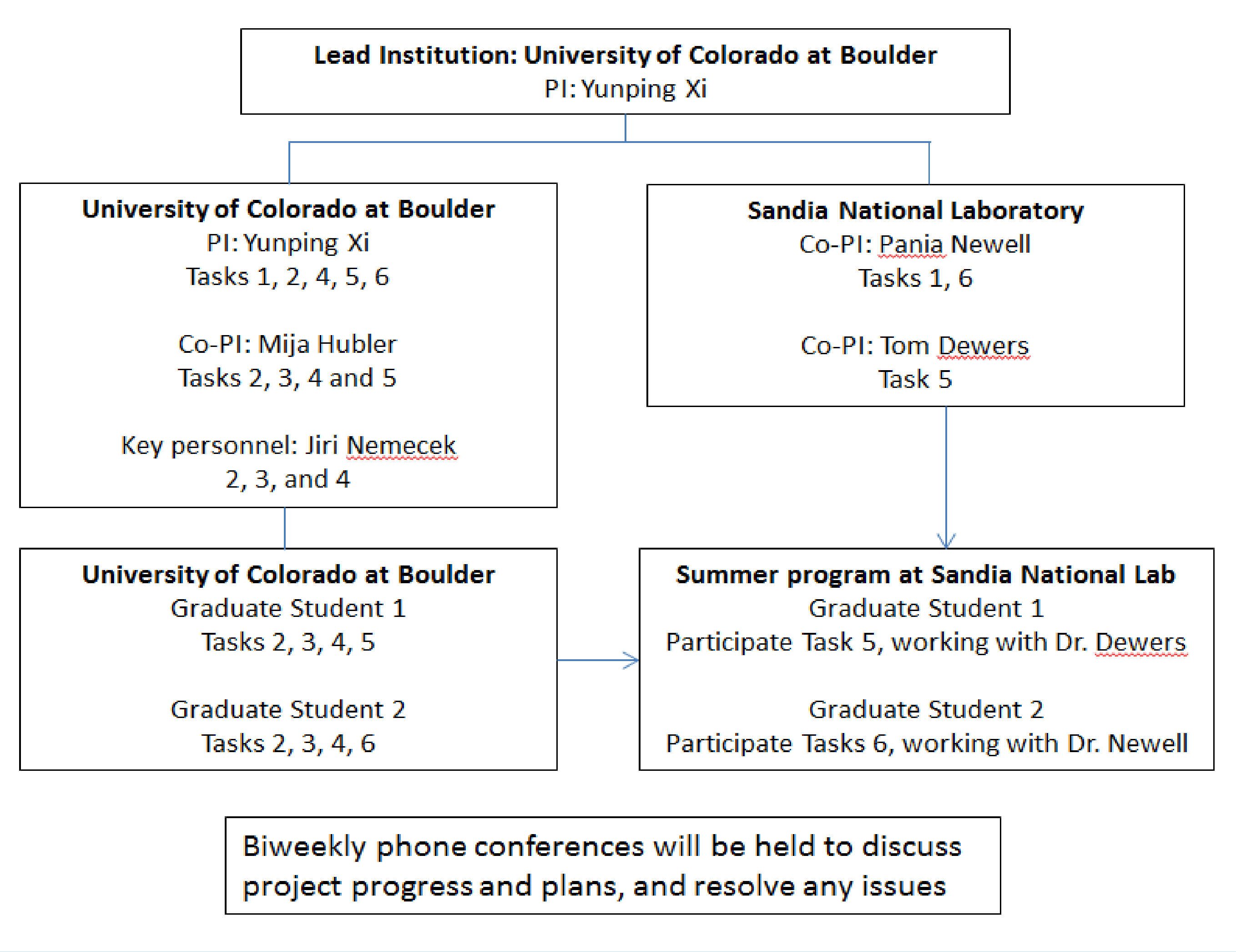
- The nanoparticle injection technology is effective in the small scale.
- The size of nanoparticle is important for the effectiveness of the repair method.
- Several methods are being developed to generate distressed well cement and exam the repaired well cement.
- Numerical models are being developed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



Proposed Schedule

		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 by Kayenta and Sierra Mechanics												**Model**

Bibliography

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- Hubler, M.H., Xi, Y., Newell, P., and Dewers, T., "Electrochemical Nanoparticle Injection Technology for Remediating Leaks." American Geological Society, Dec. 2016.