Preliminary Development in the Synthesis of Alumina-acrylic Polymer Nanoparticles for Immobilizing Chloride Ion Transport in Concrete

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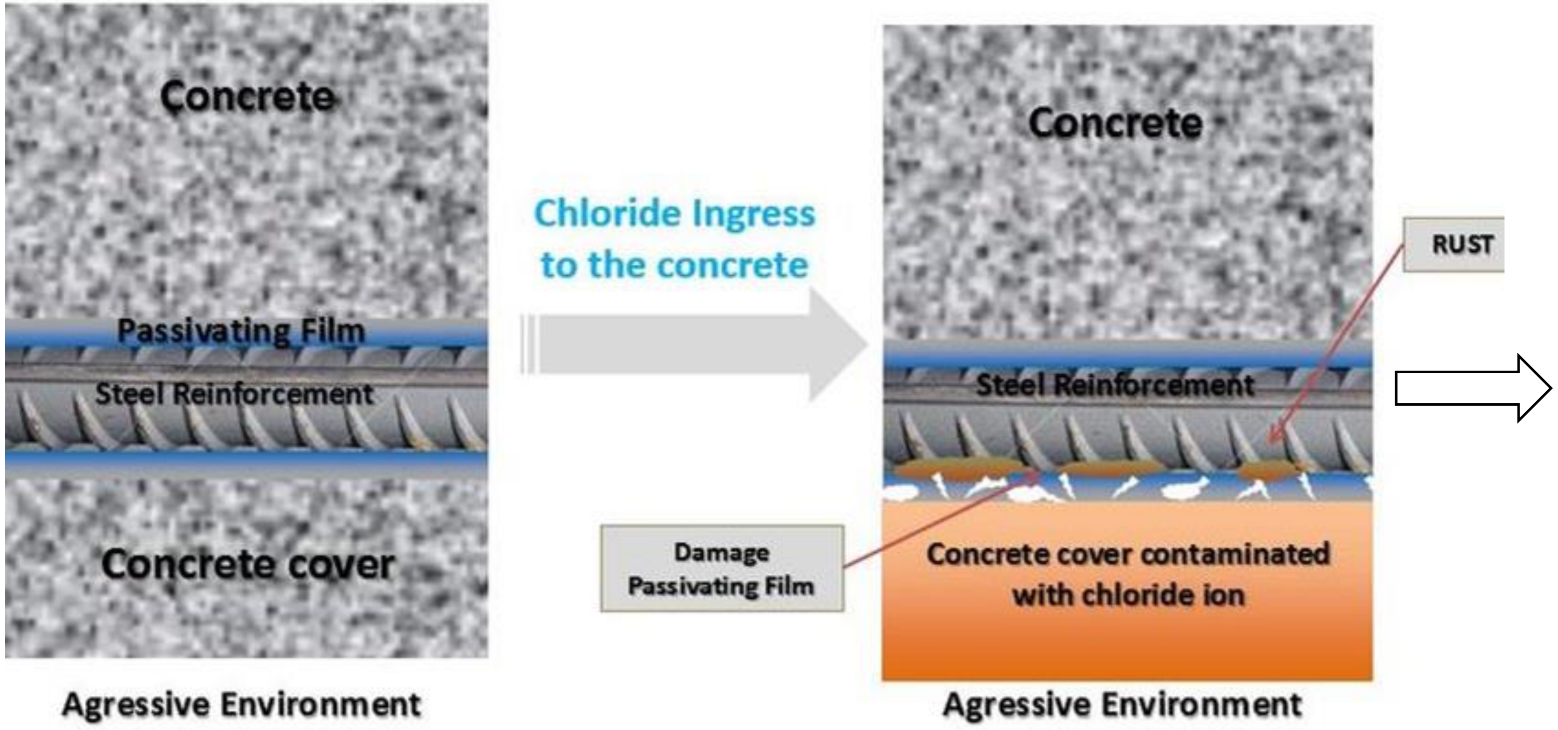
Presentation Outline

- Chloride induced corrosion of imbedded steel reinforcement in concrete structures
- Radiolytic synthesis of metal encapsulated nanogels
  - Indirect encapsulation
  - Direct encapsulation
- Experimental Set-up
- Preliminary Results
  - Nanogel characterizations
  - Performance in pore water solutions

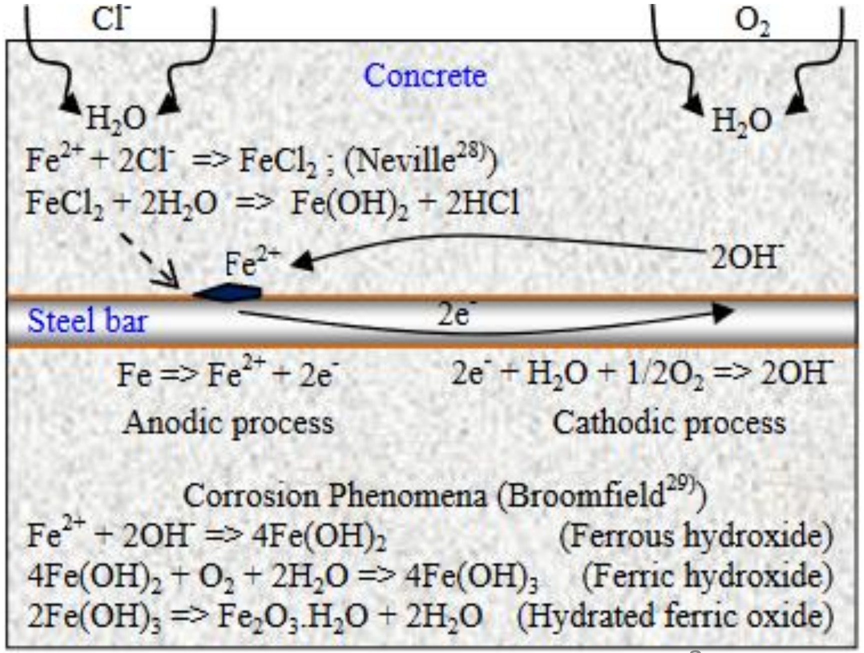
Chloride induced corrosion of rebar

- Primary way through which infrastructure loses integrity.
  - High repair costs or in extreme situations can lead to structural collapse

- **Free chloride ions** penetrate the oxide film that exists around the steel rebar
- When steel corrodes, the rust has a higher volume putting internal stresses on the surrounding concrete which results in crack formations



Sutrisno, Wahyuniarsih et.al (2017) Jurnal Teknologi. 79. 10.11113/jt.v79.5370.



Songkram Piyamahant et al (2013) Journal of JSCE, Vol. 1, 162-180

Immobilization of chloride

1. **Physical adsorption** by calcium-silicate-hydrate gel
2. Reduce permeability through **pore-ceiling**
3. **Chemical binding** to form precipitates known as Friedel or Kuzel Salts

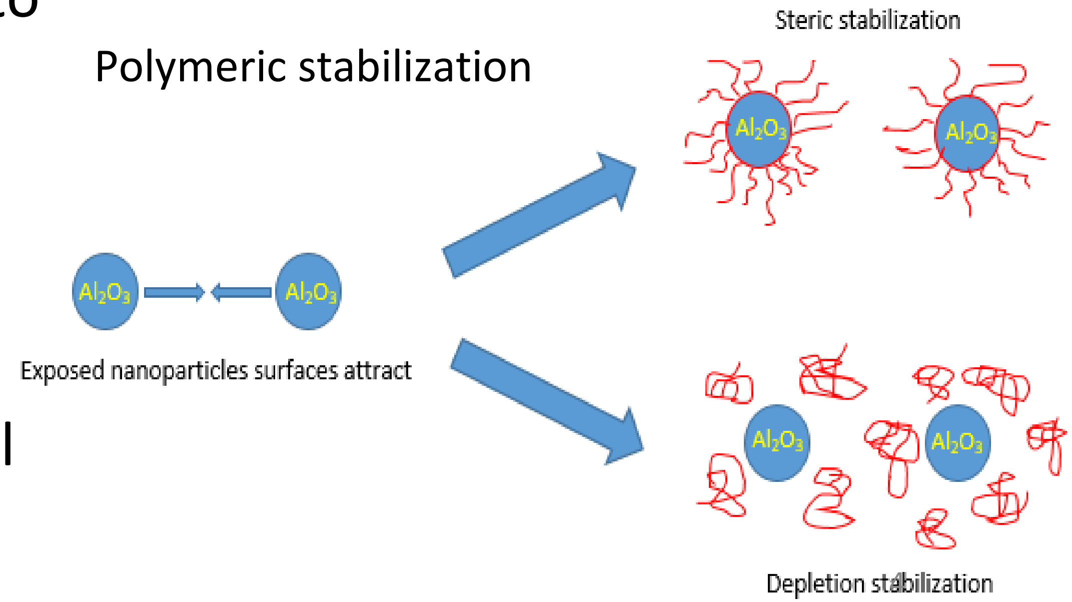
https://www.tuf-bar.com/chloride-induced-steel-corrosion-and-solutions/

Addition of **nano-aluminum oxide (aka nano-alumina)** has shown to increase the bound chloride content up to 37%.

Nano-alumina also has a pore refining effect as nanoparticles are finer than cement powder

<ins>**Challenge :**</ins> Nanoparticle agglomeration makes optimal dosages hard to determine.

Polymeric stabilization



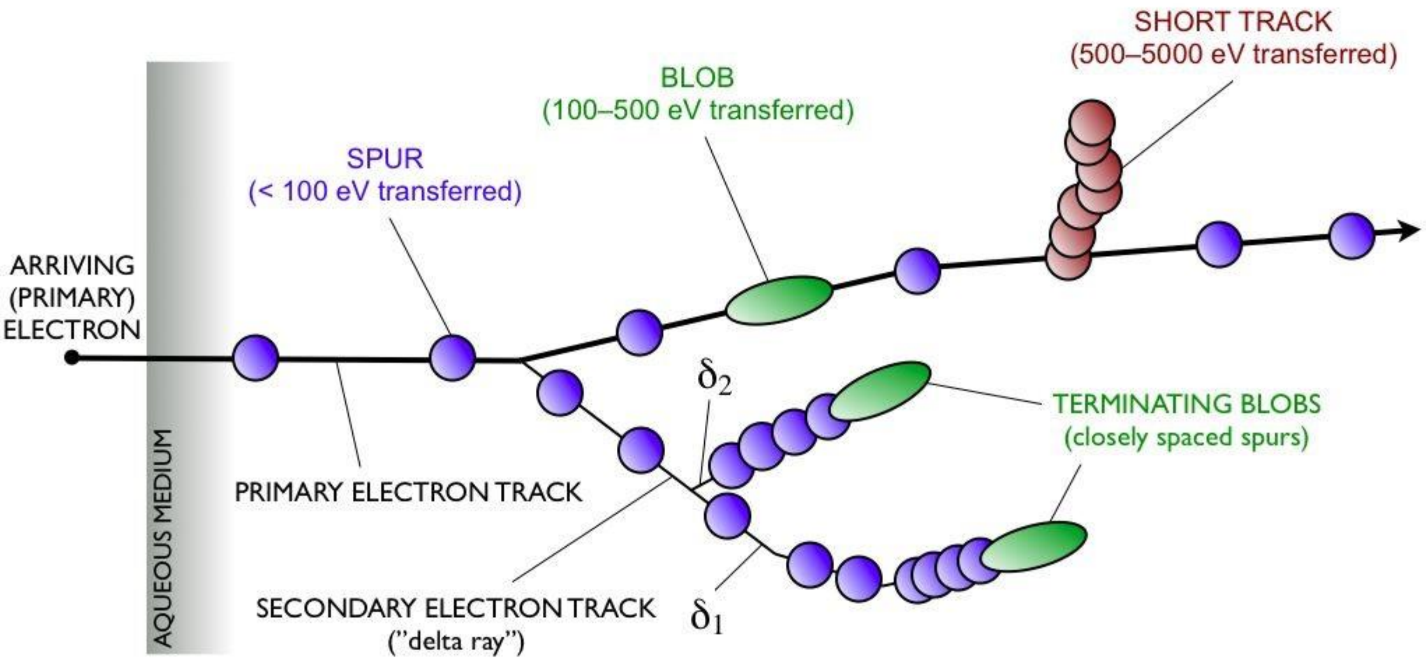
Research Goals

1. Synthesize polymeric nanogels that contain aluminum oxide nanoparticles using e-beam radiation.
   - Direct vs Indirect
   - Fine tune the size, morphology of the gels changing parameters such as dose, dose rate, temperature, starting concentrations, etc.
   - **Allow chloride ions to selectively permeate structure while improving dispersion of aluminum oxide.**

2. Test how the alumina nanogels compare to bare alumina nanoparticles at scavenging chloride ions in simulated pore water solutions.

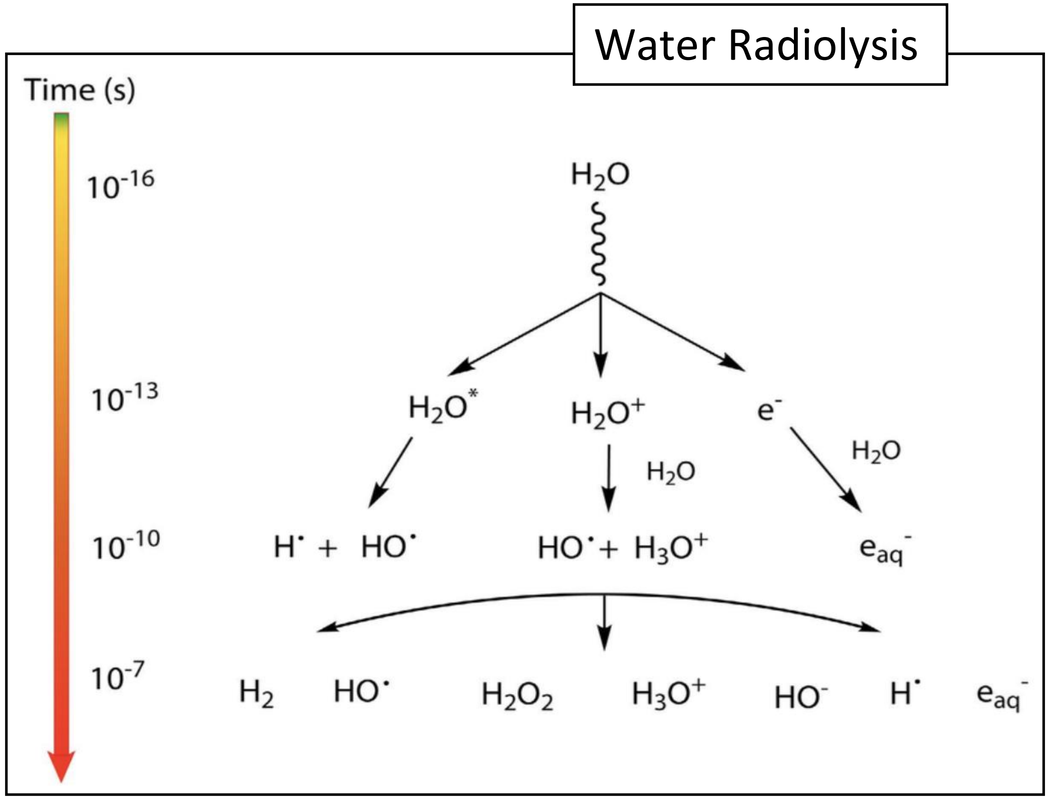
Energy Deposition by Low Linear Energy Transfer (LET) particles

A cluster of reactive ionized species is referred to as a "spur."



nonhomogeneous

Energy deposition by fast electrons occurs in discrete and spaced-out events called spurs, blobs and short tracks. These clusters are where the radiolysis products are concentrated.

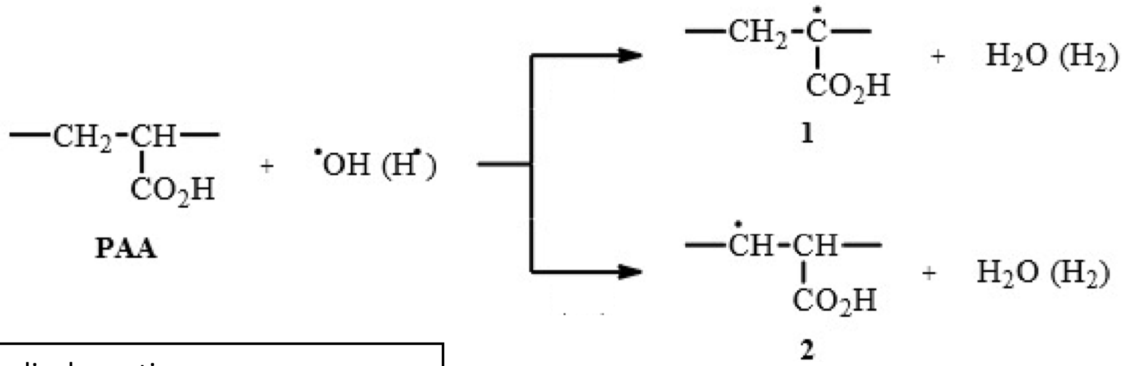


Most of the energy is adsorbed by water. Any effect on the polymer/metal is through **secondary interactions** between the reactive species generated through water radiolysis

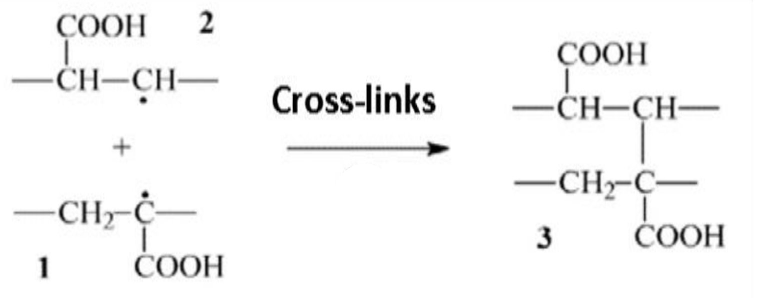
Indirect Irradiation Approach

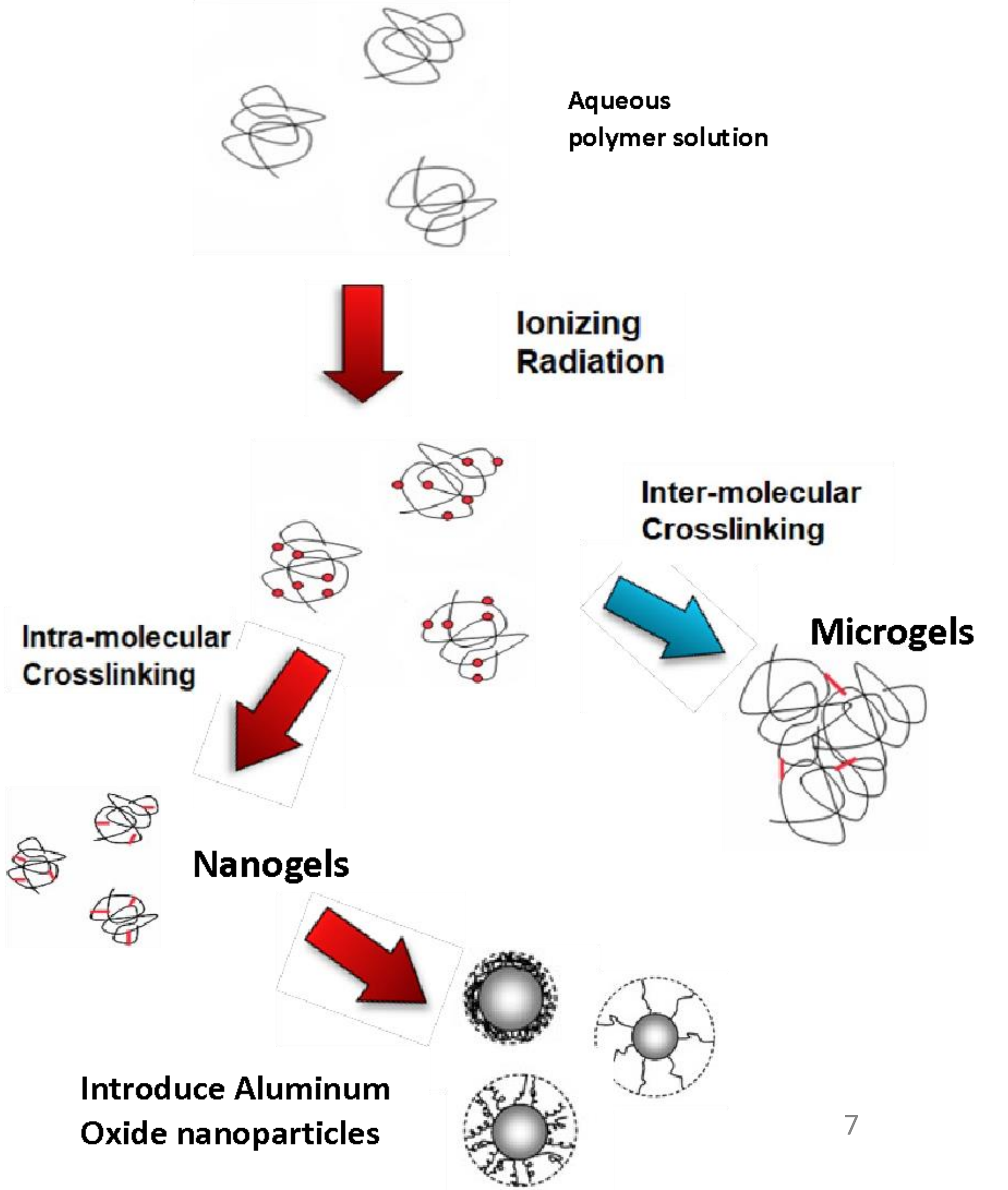
1. Radical crosslinking to synthesize poly(acrylic acid) nanogels
2. Incorporation of nano aluminum oxide into the gels after the irradiation

Hydrogen abstraction on PAA backbone



Radical reactions





Direct Irradiation Approach

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- The irradiated solutions are **simultaneously** subjected to induce **intra-molecular crosslinking of PAA polymers** and **the reduction of Al^{3+}** from precursor metal salts (i.e. $AlCl_3*6H_2O$).
- Ionizing radiation can induce the reduction of metals in aqueous solutions through the production of **solvated electrons** (strong reducing species). **Equation (1)**
- Certain alcohols (i.e. 2-propanol and isopropanol) are added as •OH and •H radical scavengers to help promote reduction of metal ions in aqueous solutions. **Equations (2)-(4)**

$$Al^{3+} + 3e^{-}_{aq} \rightarrow Al^{0} \quad (1)$$

$$OH\bullet + CH_3CH(OH)CH_3 \rightarrow H_2O + H_3CC\bullet(OH)CH_3 \quad (2)$$

$$H\bullet + CH_3CH(OH)CH_3 \rightarrow H_2 + H_3CC\bullet(OH)CH_3 \quad (3)$$

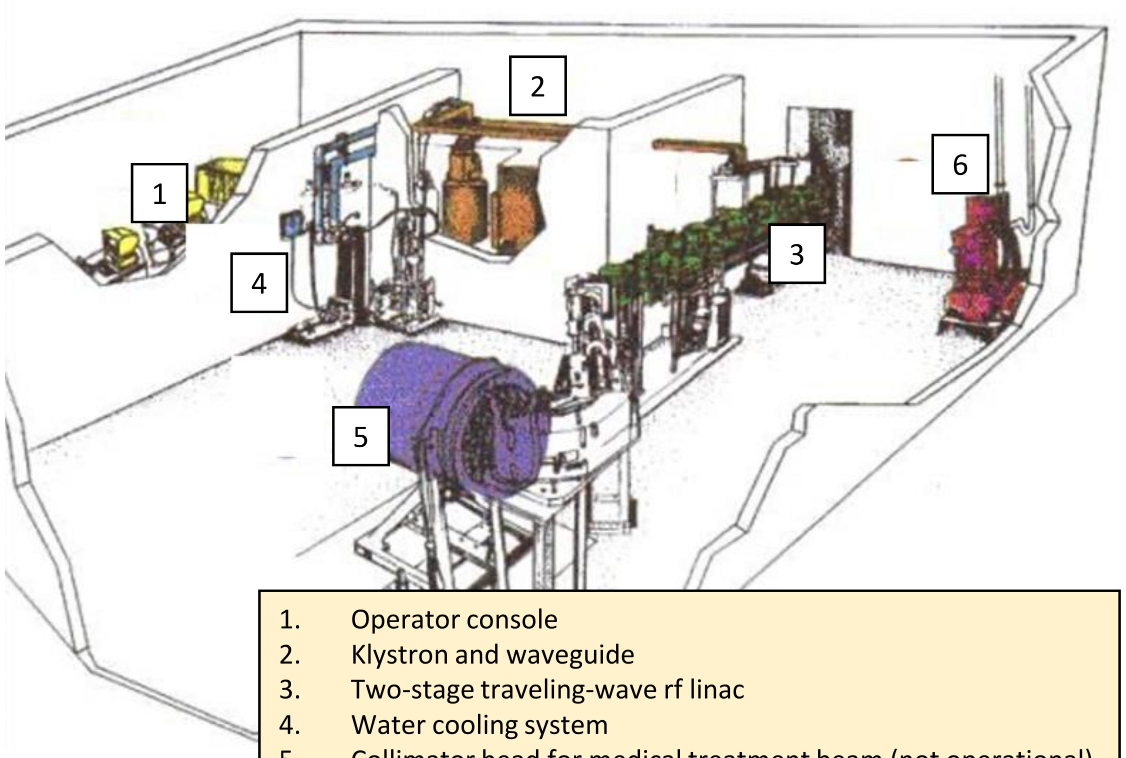
$$Al^{3+} + 3(H_3-CC\bullet(OH)CH_3) \rightarrow 3(CH_3-CO-CH_3) + Al^{0} + 3H^{+} \quad (4)$$

$$PAA + Al^{0} + O_2 \rightarrow PAA\text{-}Al_2O_3 \quad (5)$$

Experimental

Irradiations were performed at the Medical Industrial Radiation Facility (MIRF) at the National Institute of Science and Technology (NIST)

dose rate $\propto 1/r^2$



1. Operator console
2. Klystron and waveguide
3. Two-stage traveling-wave rf linac
4. Water cooling system
5. Collimator head for medical treatment beam (not operational)
6. Motor generator

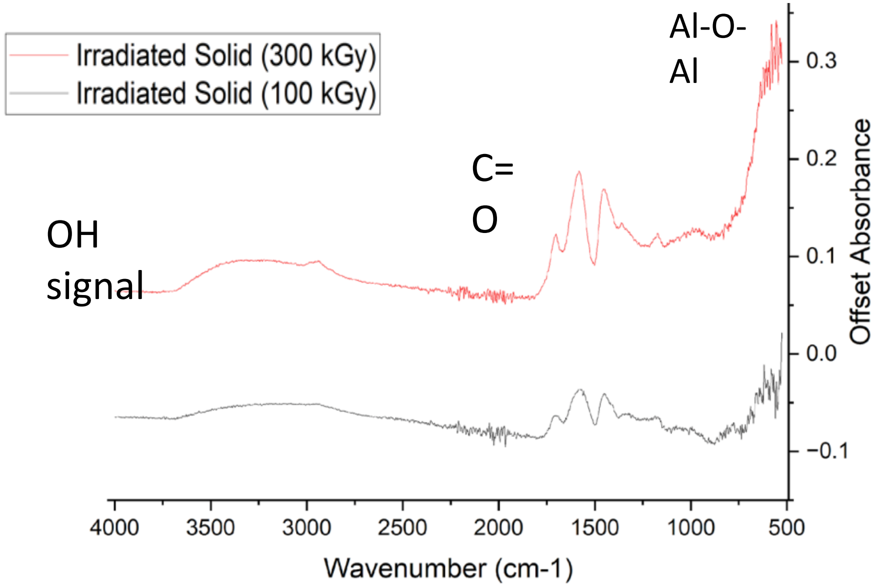
<u>Irradiation Conditions</u>

Electron energy: 11 MeV
Pulsed Beam
Pulse width: ~ 6 µs
Repetition rate: 120 pulses per second
Dose Rate : 350 kGy/hr
Ambient temperatures

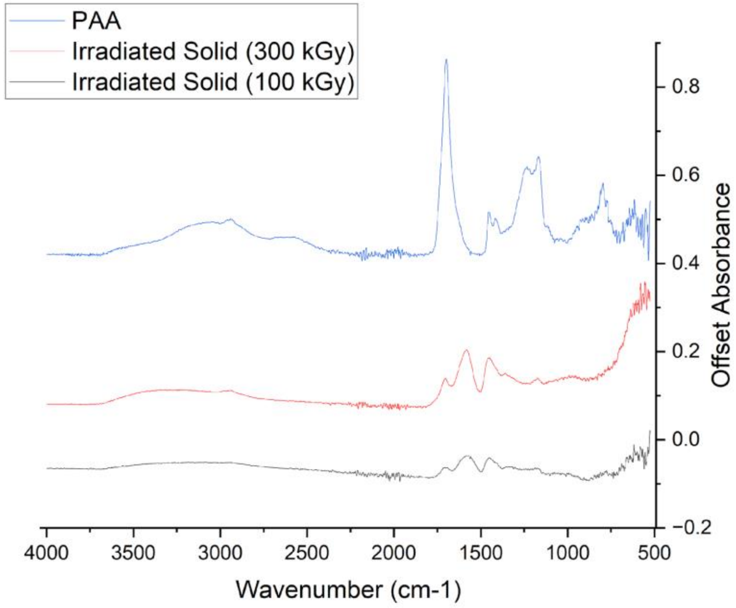
Preliminary Results

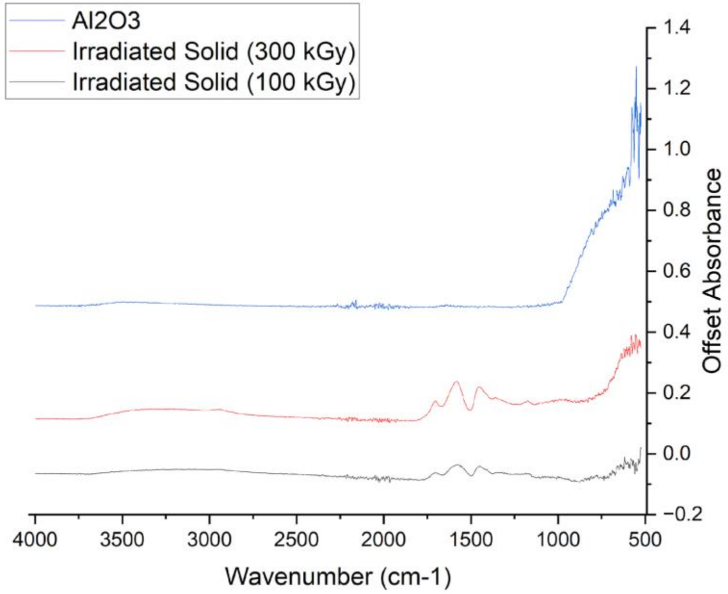
1. Characterization of nanogels synthesized using the direct methodology
    1. FTIR
    2. UV-Vis Spectroscopy
    3. Dynamic Light Scattering
    4. Zeta Potential
2. Chloride scavenging experiments
    1. Nanogel vs bare alumina performance in pore water solutions
    2. Characterization of precipitate

Fourier-transform infrared spectroscopy

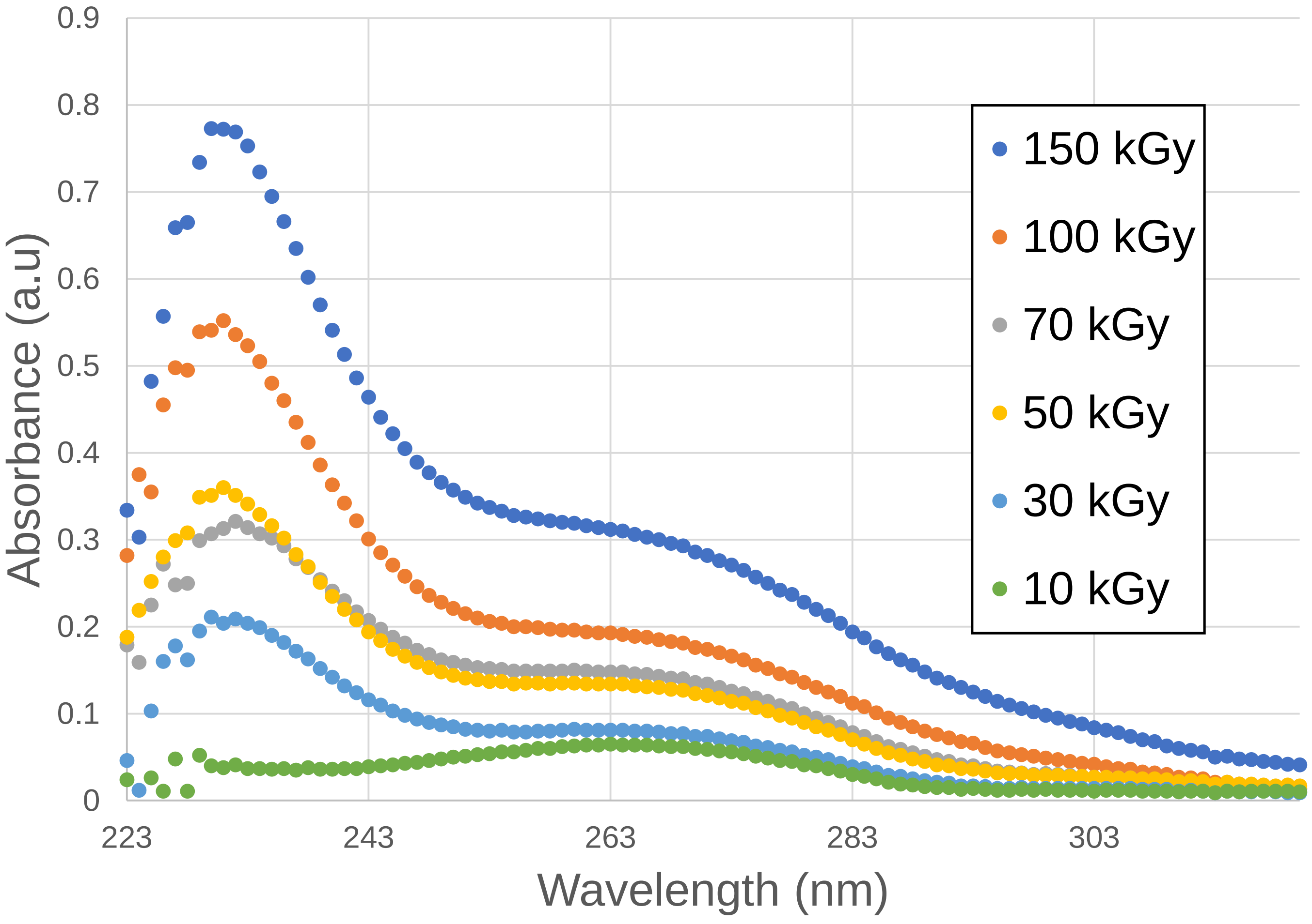


FTIR is a technique used to obtain an infrared spectrum of absorption or emission of solids, liquids, or gases. Molecules vibrate, stretch and bend in characteristic ways when they absorb infrared radiation.

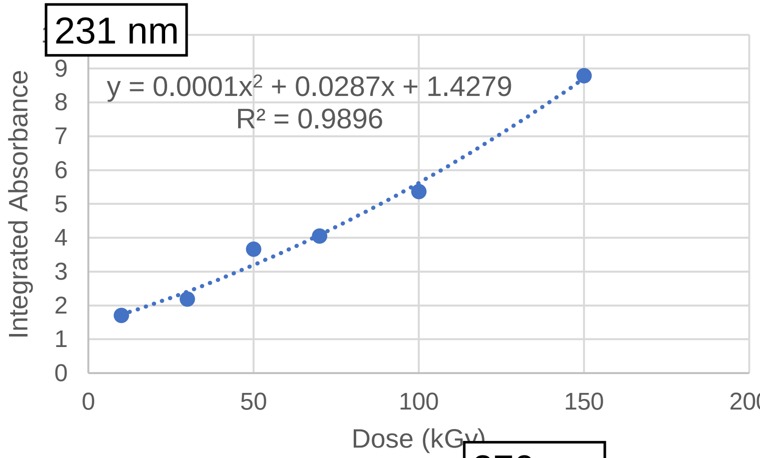


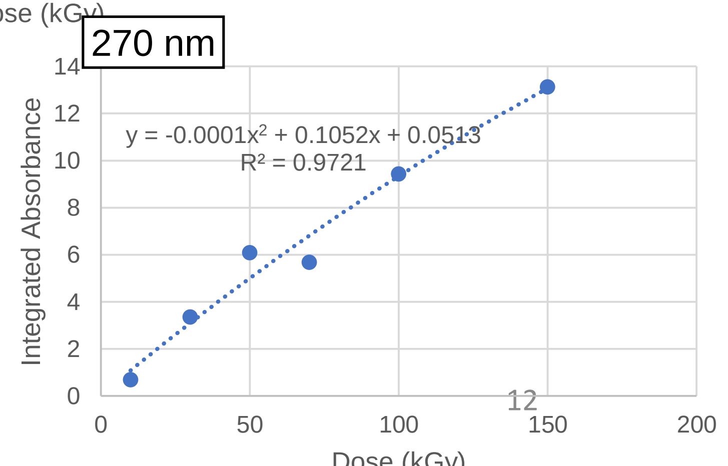


UV-VIS



UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.





The increase in intensity of the absorption band with increasing radiation dose, indicates a higher alumina yield.

Dynamic Light Scattering

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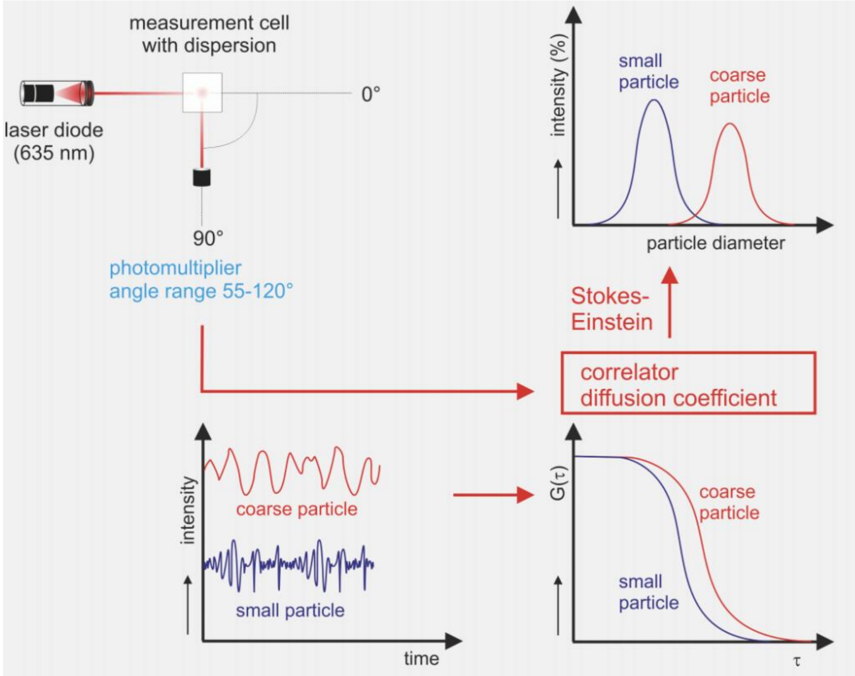
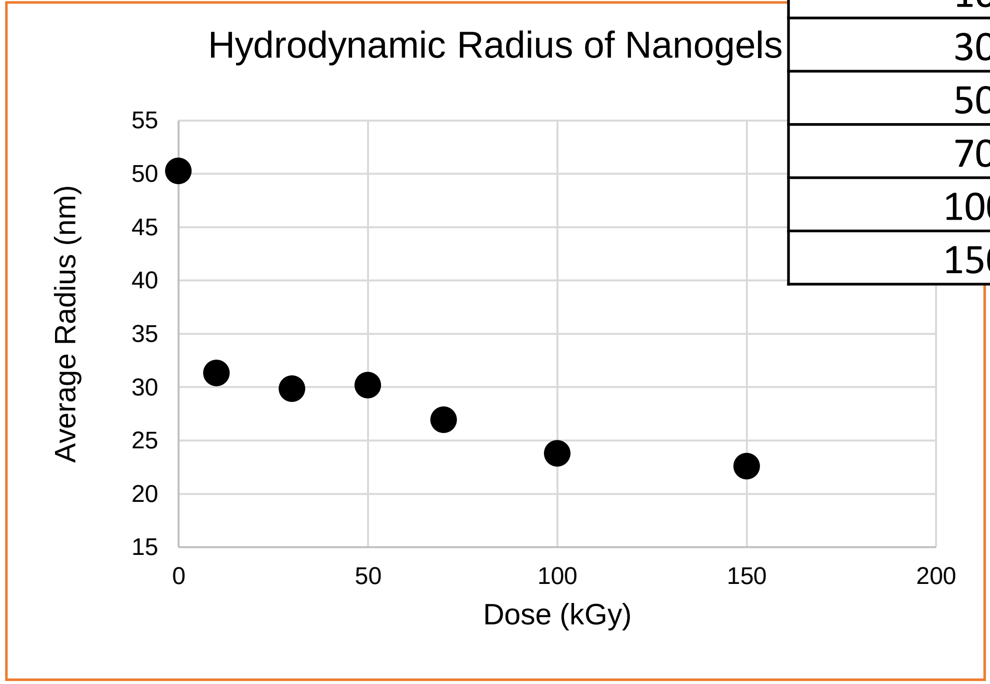
DLS is a technique for measuring the size and size distribution of molecules





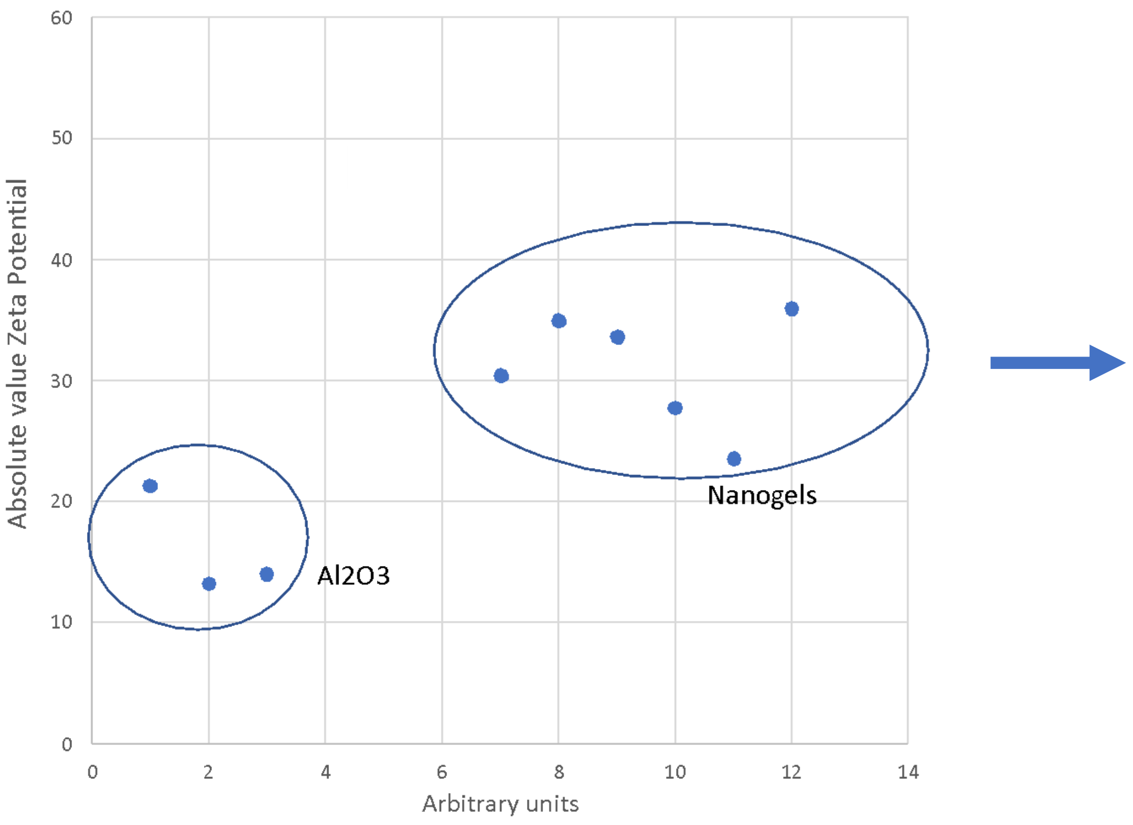
Dose (kGy)	Avg size (nm)
0	50.27
10	31.33
30	29.85
50	30.20
70	26.95
100	23.79
150	22.59

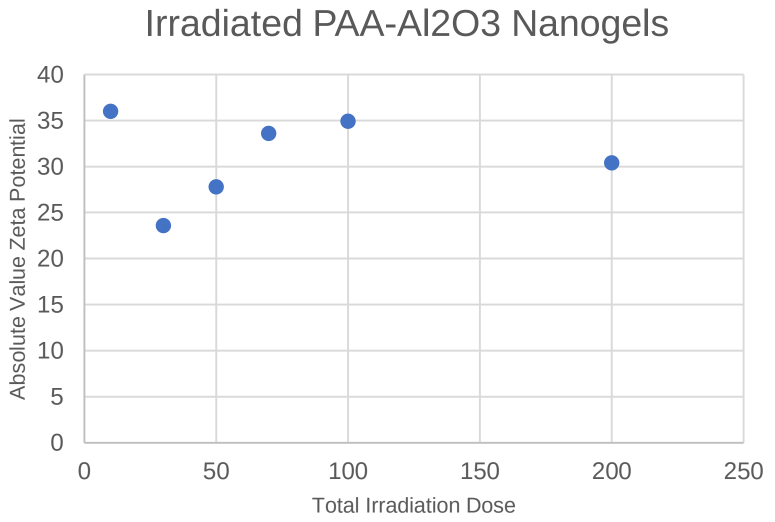
Bare alumina nanoparticle clusters (~200 nm)

Higher doses lead to formation of nanogels with smaller hydrodynamic radii on average.

Zeta Potential

Zeta potential is the net surface charge of a particle suspended in solution. The tendency of particles to agglomerate can be analyzed by magnitude of the zeta potential.





Pore water analysis

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- Saturated $Ca(OH)_2$ (and KOH) aqueous solution is spiked with a fixed amount of chloride ions ($CaCl_2$ or NaCl).
  - *The mixture is kept under in a nitrogen glove box to prevent Ca from precipitating into $CaCO_3$ and causing a pH drop.*
- Al_2O_3 nanoparticles or nanogels are introduced and allowed to stir for 1 hr.
- The precipitate is isolated and analyzed.
- **Mohr's method** is used on the filtrate to determine final chloride concentration.

Preliminary Results

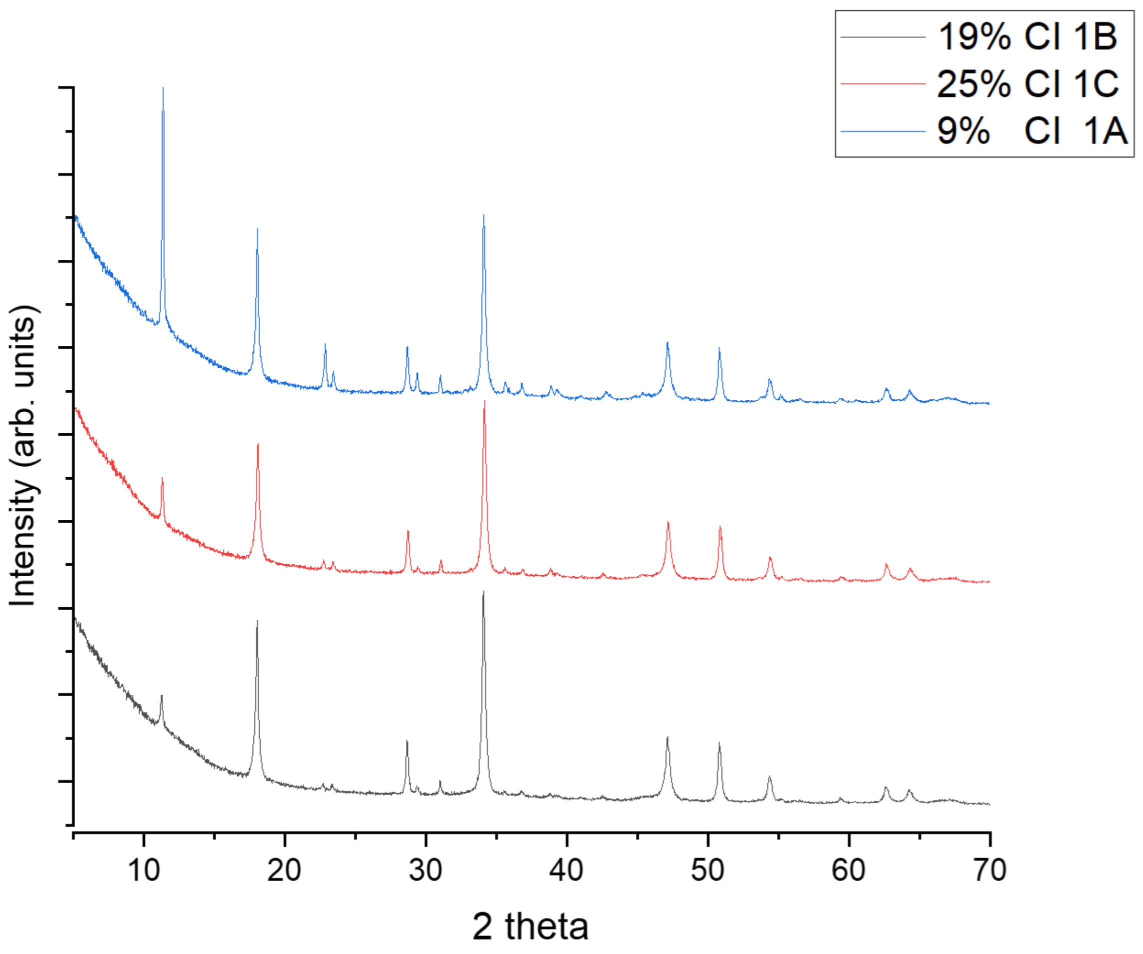
Pore water simulation were used to test the efficiency of the gels to chemically bind chloride ions.

The nanogels performed much better than the bare alumina nanoparticles!

Pore water System : 10g Ca(OH)2 + 2g CaCl2		
Nanogel: Indirect 50 kGy PAA-Al2O3		
Experiment	PAA-Al2O3 NGs (g)	Cl extracted
A	**0.2**	**24%**
B	0.5	34%
C	1	30%
	Bare alumina	
D	**0.2**	**8%**

Friedel Salt Characterization

$Ca_2Al(OH)_6(Cl, OH) \cdot 2\ H_2O$ Friedel Salt



X-ray Diffraction a technique employed to determine the crystal structure of a material

Characteristic peaks for Friedel Salt formation observed verifying the binding of free chloride ions.

Focus of Future Experiments

- Synthesize nanogels that will optimize chloride extraction from pore water simulation experiments

- Cast nanogels into mortar bars for measurement of Cl diffusion coefficient

Thank you for your attention!

Questions?