

# Ionizing-Radiation Induced Synthesis of a Novel Alumina-acrylic Nanogels for Immobilizing Chloride Ion Transport in Concrete

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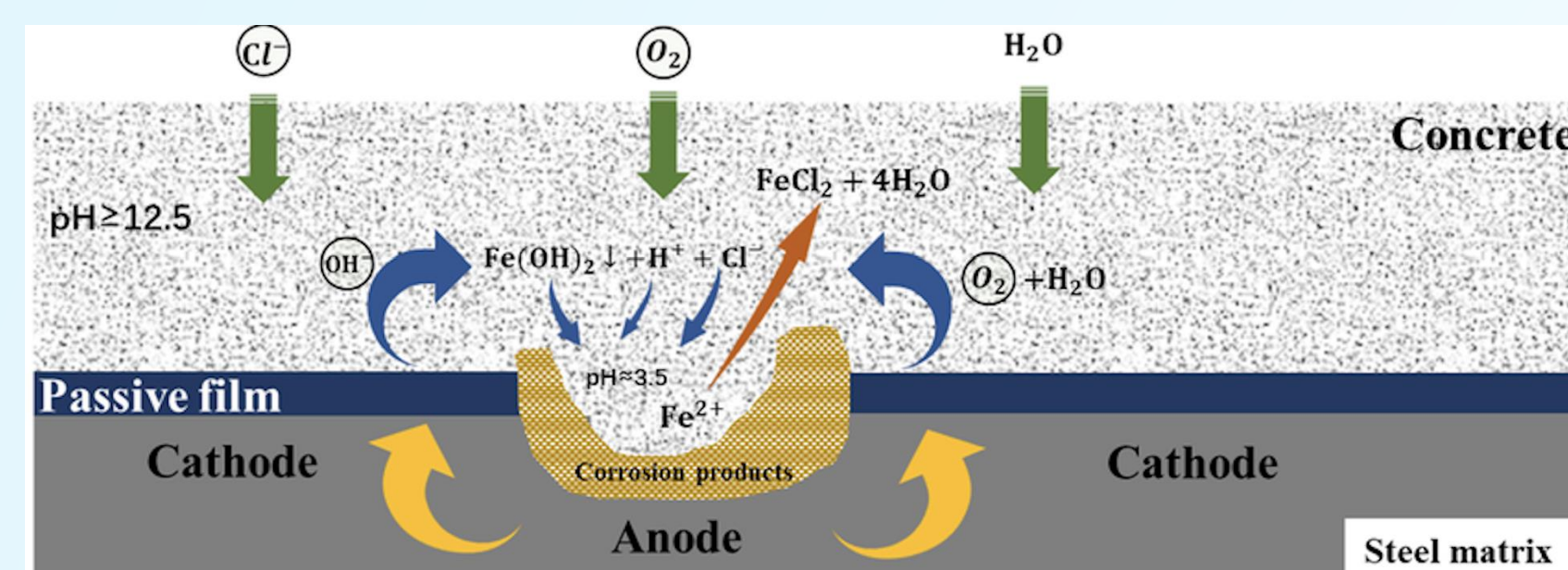
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## Introduction

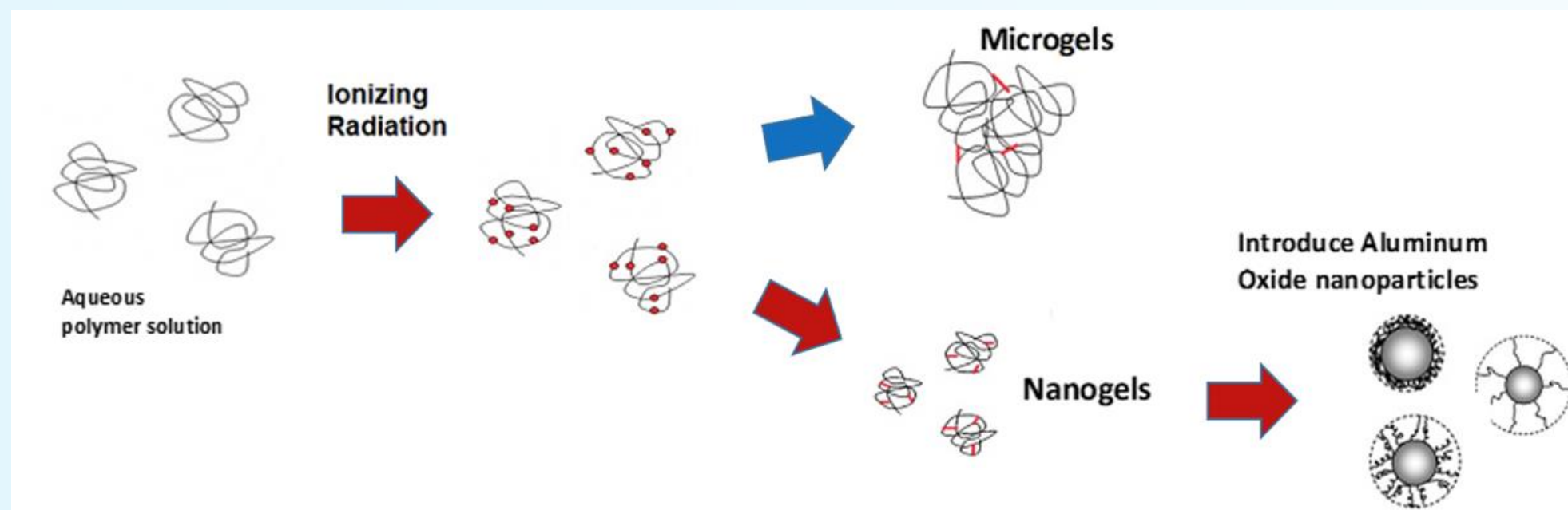
Chloride-induced corrosion is a common cause of structural damage to concrete reinforced with steel. This occurs when chloride ions penetrate the surface, leading to rust formation around the rebar, which in turn causes cracks due to internal stresses caused by volume expansion.



Wang, et al. (2023) Research Progress of Macrocell Corrosion of Steel Rebar in Concrete. Coatings. 13. 853. 10.3390/coatings13050853.

Cement production accounts for approximately 8% of global CO<sub>2</sub> emissions, one of the largest any single industry contributes. While practical alternatives to cement are being researched, it's essential to adopt sustainable cement practices to minimize harm in the meantime.

The chemical binding of chloride ions through the addition of alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles can decelerate the corrosion process by decreasing the diffusion of chloride ions. However, determining the optimal dosage for the addition of alumina nanoparticles to increase cement binding capacity is challenging owing to their tendency to agglomerate. Encapsulating nanoparticles into polymeric nanogels can enhance their stability and dispersion, thus presenting a viable solution to this challenge.



## Methodology

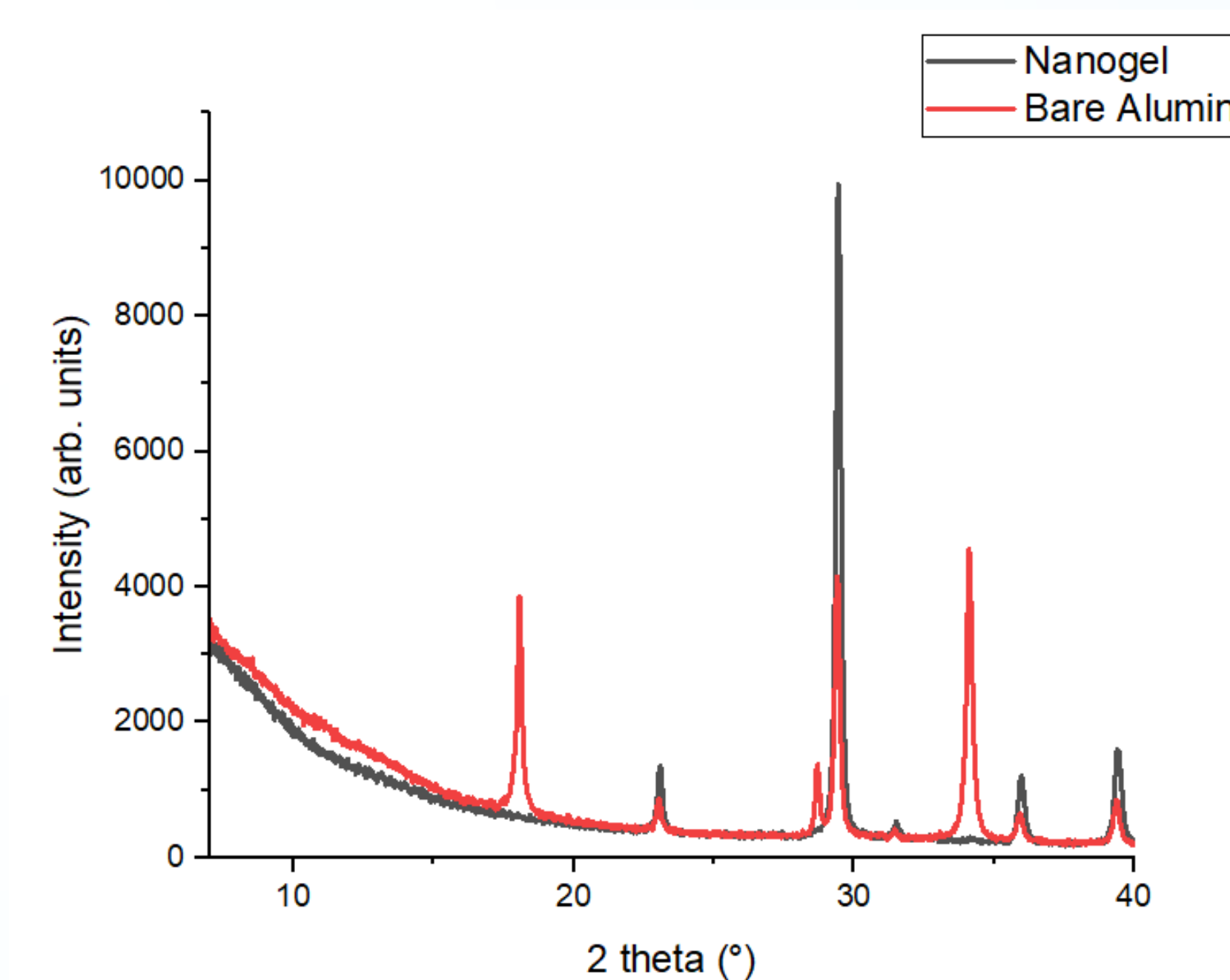
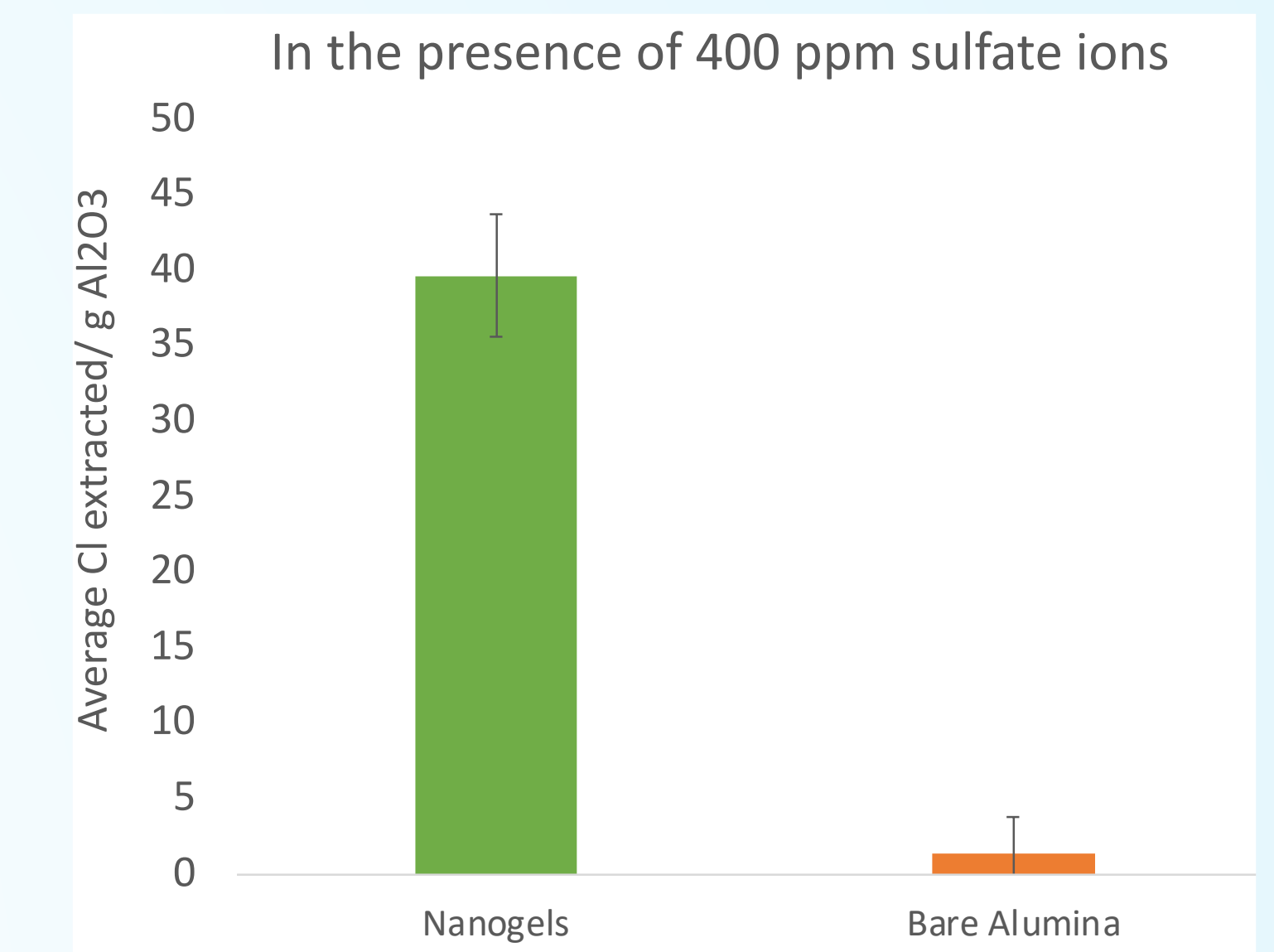
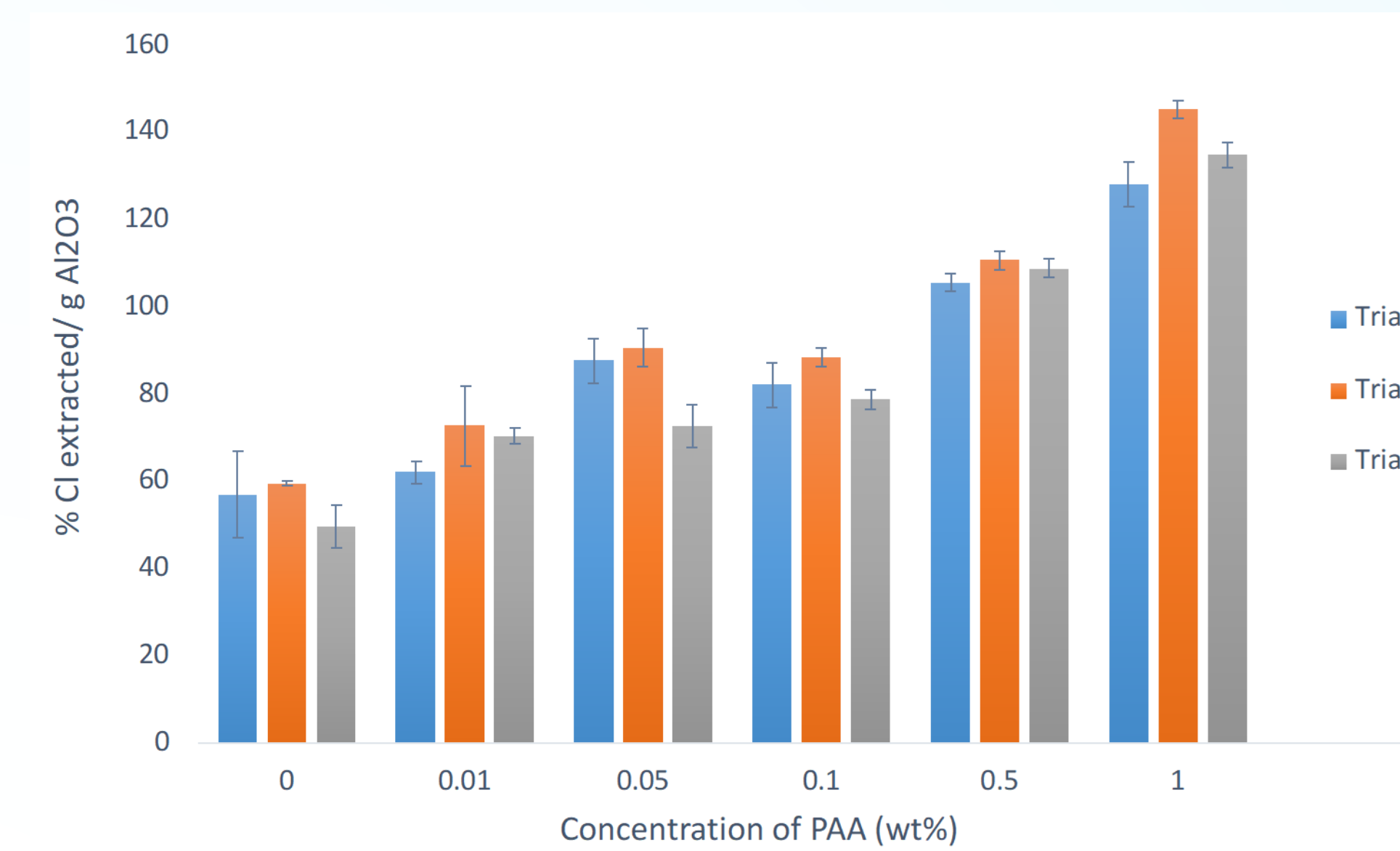
This study uses low-LET ionizing radiation to synthesize nanogels that can encapsulate alumina nanoparticles. The performance of these nanogels is studied in simulated pore water solutions to test their effectiveness in binding free chloride ions. The precipitate formed after contact with the nanogels is also analyzed to better understand the nature of the chloride binding.

This research employs high-speed electrons that are generated by an 11 MeV linear electron accelerator, located at the Medical-Industrial Radiation Facility (MIRF), at the National Institute of Standards and Technology (NIST). The accelerator operates on a pulsed beam with a pulse width of roughly six microseconds and a repetition rate of 120 pulses per second. Radiochromic film dosimetry is used to calibrate the electron beam. Calibration vials, equipped with films, are placed both in the front and back, responding to ionizing radiation by activating the dye within them, leading to a noticeable color change. The energy absorbed by the films is then measured using the ThermoScientific GENESYS 20 Visible Spectrophotometer. It is vital to consider sample geometry, sample type, and overall setup configuration, affecting dosimetry.

There are multiple variables that need to be considered while optimizing the alumina-nanogel material. These include dose, dose rate, solution concentration, temperature, etc. Testing the effectiveness of all the different nanogels in cementitious materials is impractical, as it will be a costly, time-consuming and a challenging task. Therefore, we will first test the nanogel materials' effectiveness in binding chloride ions in simulated pore water solutions. Chloride ions are carried through concrete pores by water that is mostly saturated with Ca(OH)<sub>2</sub> and KOH (known as 'pore water solutions'). We can simulate a high pH pore water system in the lab and compare how the nanogels perform compared to bare alumina nanoparticles. These pore water experiments must be conducted in an inert environment in a glove box to avoid the formation of CaCO<sub>3</sub>, which lowers the pH of the solution. Mohr's method is used to determine bound chloride content.

## Results

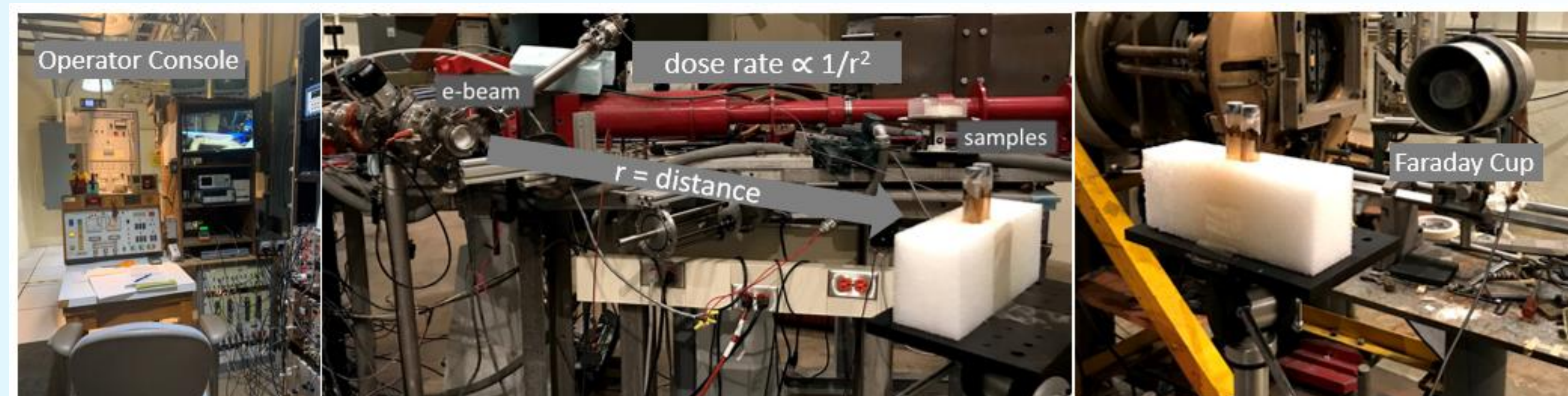
Nanogels are more effective at binding free chloride ions than bare alumina in simulated pore water systems. Thus far, it has been established that the optimal polyacrylic acid (PAA) for binding chloride ions in solution has a molar mass of 450,000 kDa and is irradiated at 70 kGy. Higher concentrations of PAA bind more chloride ions. Concrete structures are also susceptible to sulfate attacks that can reduce the bound chloride content and accelerate corrosion. However, these nanogels have emerged as a potential solution to mitigate the effects of sulfate attacks. Since sulfate ions are larger than chloride ions, they cannot easily penetrate the nanogel structure and disturb the bound chloride concentrations.



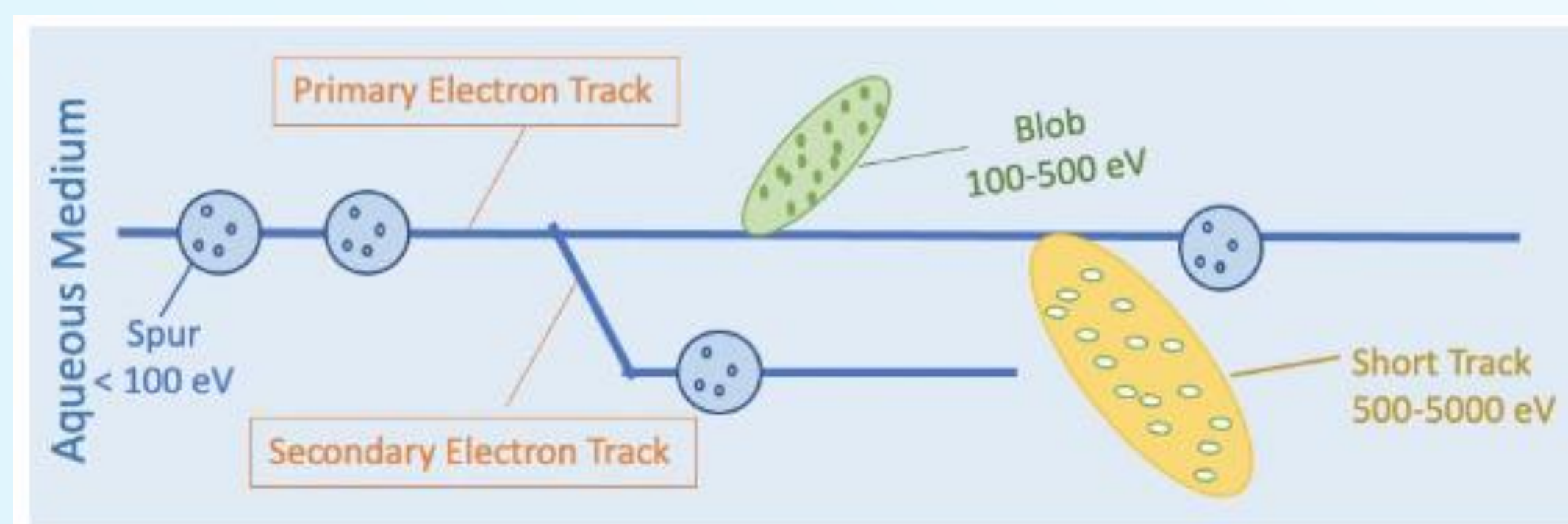
X-ray crystallography (XRD) analysis is a nondestructive technique that can provide the crystallographic structure of solids. Chloride ions chemically bind to cement hydration products to form Friedel salts (FS), complex compounds consisting of a layered double hydroxide with a general formula of Ca<sub>2</sub>Al(OH)<sub>6</sub>(Cl, OH)·2H<sub>2</sub>O. Our pore water experiments confirm the formation of Friedel salts when bare alumina is used. The characteristic XRD peak for FS (2θ = 13.2°) is present in all bare alumina samples. The precipitate formed when nanogels bind chloride ions from the solution is not an FS. This was established with an XRD diffractogram, where the characteristic FS peak is missing for the nanogel precipitates.

The remaining signals on the XRD diffractogram indicate the existence of Ca(OH)<sub>2</sub>. The variation in the strength of the peaks could be due to various reasons such as instrument configurations, sample preparation, larger crystal size, or a greater number of atoms in the crystal.

## Irradiation Set-Up

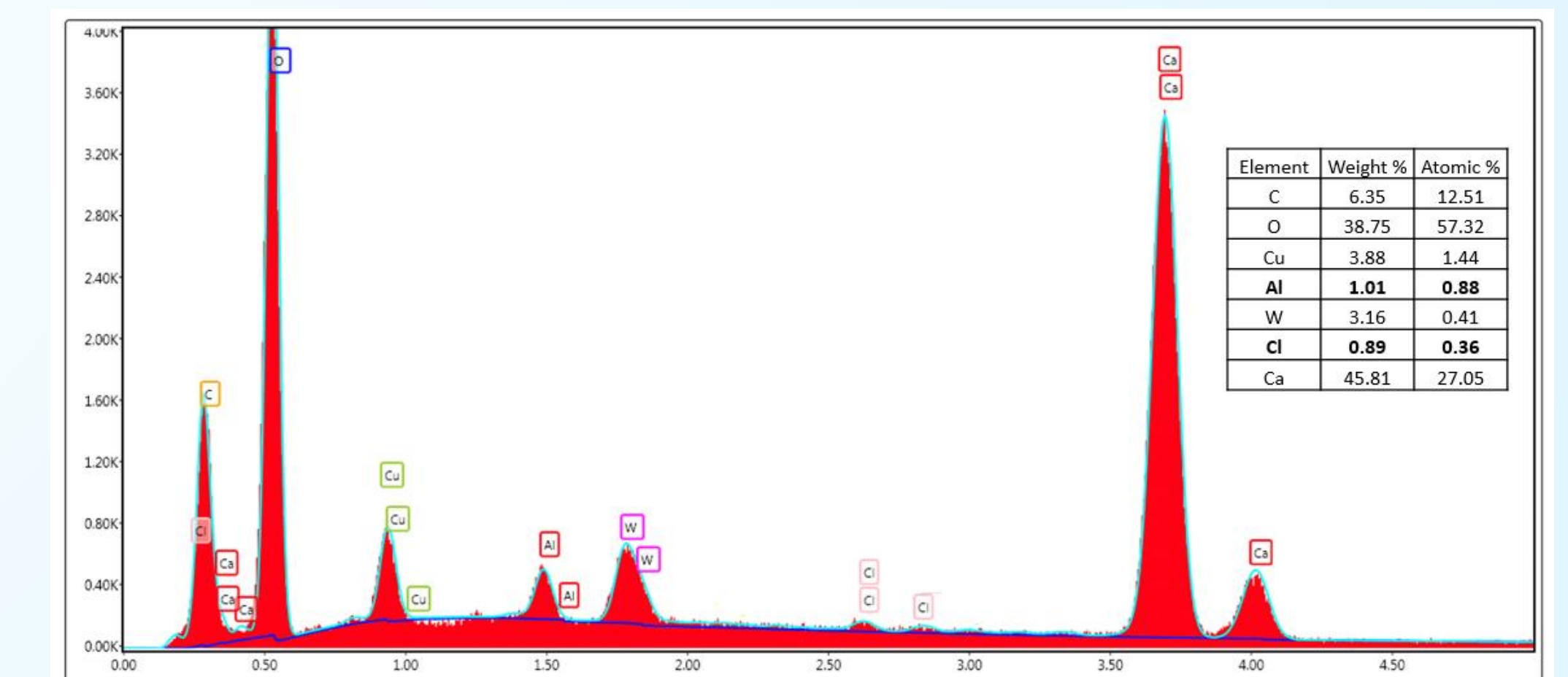


The Medical Industrial Radiation Facility (MIRF) at the National Institute of Standards and Technology



Energy deposition of fast electrons in an aqueous medium.

Energy dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is a technique for analyzing the elements present in a sample and estimating their relative abundance. Chlorine has an absorption peak at approximately 2.6 keV. The EDS analysis confirmed the presence of chloride ions in the precipitate formed with the nanogels.



## Conclusion

The findings of this research indicate that radiation-induced nanogels are more effective than bare alumina nanoparticles in capturing free chloride ions from a simulated concrete pore water solution. The results reveal that the use of bare alumina as a scavenger leads to the formation of chloride ions bound in Friedel Salt complexes, while the use of nanogels prevents the formation of these complexes. Further research is currently being conducted to investigate how chloride ions are bound to the nanogels. This will provide a better understanding of the process and could potentially lead to further improvements in the efficiency of the nanogels. Furthermore, the nanogels have the added advantage of being resistant to sulfate ion attacks, which is not the case with bare alumina nanoparticles. This makes the use of nanogels more reliable for capturing chloride ions in concrete, as it reduces the risk of sulfate ion attacks that can damage the material.