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

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**Purpose:**

Chloride-induced corrosion poses a significant threat to the structural integrity of concrete. This type of corrosion occurs when chloride ions penetrate the concrete and reach the steel reinforcements, which can happen in marine environments or due to de-icing salts. It is a leading cause of concrete failure and reduces the service life of steel-reinforced concrete. One way to prevent this type of corrosion is to limit the diffusion of chloride ions from reaching the steel reinforcements. One effective method to achieve this is by increasing the chloride binding capacity of the concrete. By doing so, the corrosion rate of rebar can be significantly reduced. The primary focus of this work is to use ionizing radiation to synthesize novel alumina-encapsulated nanogels, which will be optimized by varying radiation conditions to enhance the binding of free chloride ions.

**Methods:**

This work utilizes high-speed electrons generated by an 11 MeV linear electron accelerator (see Figure 1) located at the Medical-Industrial Radiation Facility (MIRF) in the National Institute of Standards and Technology (NIST). The accelerator operates on a pulsed beam with a pulse width of approximately six microseconds and a repetition rate of 120 pulses per second. The calibration of the electron beam is done using radiochromic film dosimetry, as shown in Figure 1c. The calibration vials are equipped with films, both in the front and at the back. These films react to ionizing radiation by triggering the dye within them, resulting in a color change. The energy absorbed by the films is then measured using a Thermo Scientific GENESYS 20 Visible Spectrophotometer. Three factors that affect dosimetry are sample geometry, type of sample, and the overall setup configuration.

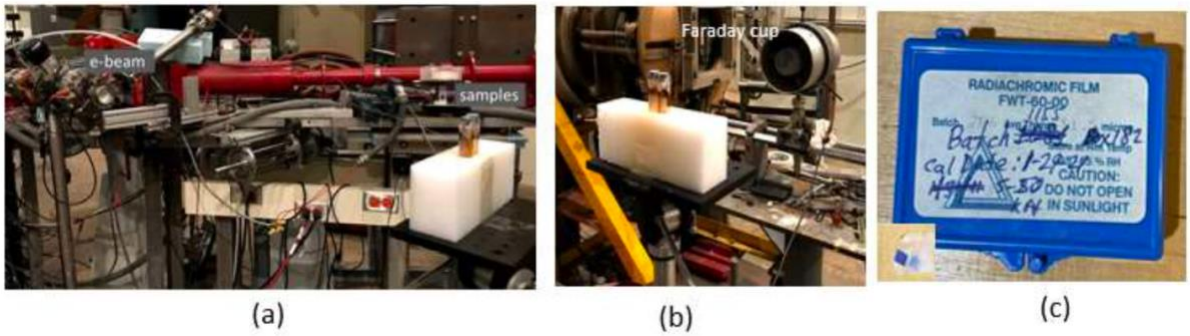


*Figure 1. (a) Electron beam set up at MIRF (b) Faraday cup measures the current and is used to determine the dose administered to the samples (c) Radiochromatic films used to calibrate the instrument*

The samples are made up of diluted aqueous solutions of polymers. It is important to note that the radiation does not have a direct interaction with the polymer. Rather, the polymer reacts with the short-lived reactive species that are produced during water radiolysis.

The amount of energy that is deposited in water depends on the type of ionizing radiation used. When low-LET radiation, such as electron accelerator radiation, is used, energy is deposited in distinct and spaced-out regions, which are called “spurs,” “blobs,” and short-tracks (see Figure 2). The energy

deposition in water is not uniform. Once the short-lived reactive species are produced from the splitting of water, they quickly diffuse throughout the solution and react with different solutes, such as polymers.

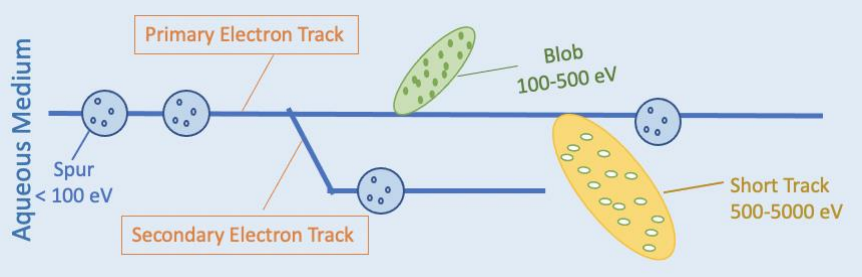


*Figure 2. Energy Deposition of fast electrons in an aqueous medium*

There are three stages in water radiolysis: the *physical stage* (time ranging from initiation to $10^{-15}$ s), the *physio-chemical stage* ($10^{-15}$ to $10^{-12}$ s), and the *chemical stage* ($10^{-12}$ to $10^{-9}$ s).

The reactive species formed during water radiolysis include $e_{aq}^-$, $^{\bullet}OH$, $H^{\bullet}$, $H_2O_2$, $H_2$, $H_3O^+$, $OH^-$. The •OH and H• radicals can abstract hydrogens from the polymer backbone, making them particularly important. It is possible to increase the yield of $^{\bullet}OH$ by bubbling nitrous oxide gas ($N_2O$) throughout the solution, which converts the $e_{aq}^-$ into $^{\bullet}OH$. The general equations for water radiolysis are as follows:

$$H_2O \rightarrow e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H_2O_2, H_2, H_3O^+, OH^- \quad (1)$$

$$N_2O + e_{aq}^- + H_2O \rightarrow {}^{\bullet}OH + OH^- + N_2 \quad (2)$$

$$H_3O^+ + e_{aq}^- \rightarrow H^{\bullet} + H_2O \quad (3)$$

Polymer radicals undergo reactions as they decay. The primary reaction is radical recombination, which creates new C-C bonds (see Figure 3). To form a nanogel, intra-molecular recombination should be more dominant than inter-molecular recombination, which creates a larger macroscopic gel. Modifying parameters like initial polymer concentration, dose rate, and temperature can control which reaction dominates.

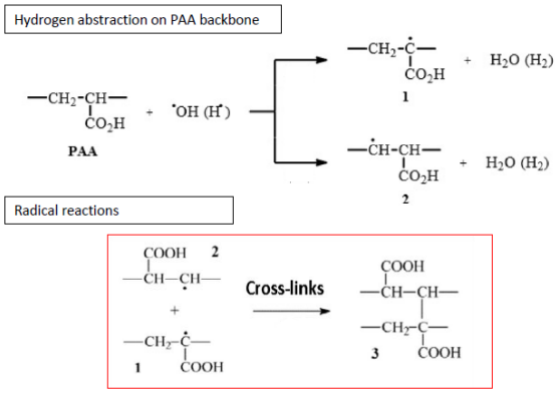


*Figure 3. Polymeric reaction of polyacrylic acid to form chemical crosslinks*

**Results:**

Our research has shown that alumina nanogels have better performance than bare alumina nanoparticles in simulated pore water solutions. Typically, bare alumina can only bind 8-12% of chloride ions, while these alumina nanogels can effectively bind more than 30-40% of chloride ions! X-ray Diffraction results indicate that the chloride-bound precipitate formed with the nanogels is distinct from the one formed with bare alumina. These nanogels show promise in effectively binding chlorine ions in solution, even in the presence of interfering sulfate ions.

**Conclusions:**

Chloride-induced corrosion poses a significant challenge to infrastructure because the cost of repairing damaged rebar is often higher than the initial building costs. Repair expenses alone can account for 3.5-4.5% of a country's national GDP annually. These radiation-induced nanogels show great promise in mitigating this problem. The next phase of this work involves casting the nanogels into cement mortar and studying the chloride diffusion using Rapid Chloride Permeability Testing. Prompt Gamma Neutron Activation Analysis will also be used to build a chloride diffusion profile in mortar samples.

**Relevance to CIRMS:**

This work is part of the first author's dissertation research and is a collaborative effort between NIST and UMD College Park. The study focuses on the impact of ionizing radiation on commercially viable materials that may be used to tackle a major infrastructure challenge of our time. This collaboration is aligned with CIRMS' mission to bring together stakeholders from academia, government, and industry to enhance societal benefits. Additionally, this research seeks to contribute to the scientific understanding of the effects of ionizing radiation on polymeric materials. This knowledge will be beneficial for a variety of fields.