

An Evaluation of Electrokinetic Transport of Radioactive Species through Concrete for Application as a Non-Destructive In Situ Remediation Technique – 14102

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ABSTRACT

An experimental evaluation was carried out to assess the efficacy of *in situ* electrokinetic treatments of saturated concrete contaminated with radioactive species. The electromigration of K^+ and Cs^+ was assessed through different thicknesses of concrete using an external electric field. Ionic flux and diffusion coefficients, calculated using a Simplified-Nernst-Planck approach, shows values consistent through the work and with comparable studies. The affects of the redox reaction on the physical surface of the concrete samples was also studied; with results showing that strict pH control of the pore solution is needed to prevent corrosion.

INTRODUCTION

Anthropogenic radioactive material, notably fission products from the nuclear fuel cycle entrained within structural concrete, poses one of the largest nuclear decommissioning challenges. In the UK alone there is an estimated 2,800,000 cubic metres of low-level contaminated structural concrete [1]. In contrast to drier environments, where radioactive contamination is localised at the concrete surfaces, environments such as legacy fuel pond structures present particular challenges, e.g. the First Generation Magnox Storage Ponds (FGSMP) Sellafield, UK. Here, large volumes of highly-mobile aqueous fission products, e.g. ^{137}Cs and ^{90}Sr , infiltrate deep within concrete structures through cracks and fissures, as well as the porous concrete matrix itself [2]. The presence of such cracks and fissures in the concrete structure can lead to the leakage of fuel pond water. The highly-radioactive nature of this pond water means that external remediation work on the cracks to prevent further leakage is difficult as the areas concerned are often too radioactive to approach safely. As such, there is an urgent need to decontaminate the concrete of radioactive material so that work can be carried out to alleviate the future leak damage.

Electrokinetic decontamination and remediation methods utilise one of the fundamental properties of dissolved ionic species, their inherent charge. The application of an external electric field, over a saturated environment, causes charged particles, ions, and solids to move toward the electrode of opposite charge. Electrokinetic transport encompasses several phenomena, with *electroosmosis* and *electromigration* being the most relevant to this work. The former term is used to describe macro-scale flow caused by charge migration along capillary walls, and the latter is the migration dissolved ions. The accelerated ionic transport, due to electromigration and electroosmosis, allows ions to be transported at a far faster rate than through pure diffusion alone. Electrokinetic techniques have found widespread use for *in situ* land remediation and decontamination of chlorides, heavy metals and radioactive ions from saturated soils [3]. However, the use of this technique for the decontamination of concrete of radioactive material is still at the laboratory trial stage [4].

The literature on electrokinetic removal of entrained radioactive contaminants in concrete follows

two main themes; 1) the concrete has been removed from site and requires decontamination prior to final disposal, usually in the form of crushed concrete or rubble [5], 2) the concrete, as part of a larger structure or building, requires decontamination prior to being demolished so as to prevent further dispersal of radioactive material [4]. It is the second of these themes that is of particular interest, as the use of an *in situ* decontamination method for saturated concrete can allow structural remediation work to be carried out on structures such as the FGMSP at Sellafield that cannot easily be demolished. This can prolong the life of an aging structure or building and provide for easier final disposal upon decommissioning.

The utilisation of structural steel rebar as an electrode for *in situ* electrokinetic treatment has been documented previously, namely for the re-alkalisation of concrete and for the decontamination of radioactive species from concrete surfaces [6]. However, the use of rebar as an electrode poses difficulties to the electrokinetic remediation, i.e. the use of complexing and chelating agents, of legacy storage ponds as anodic oxidation can cause the corrosion of the rebar electrode [4] an undesirable outcome for a structural support. As the use of complexing and chelating agents are strictly controlled at nuclear sites the remaining option is to utilise the rebar as a cathode and drive contaminants toward it and back into the ponds.

In this paper we describe a simplified *in situ* experimental simulation of the problem described above, whereby the electromigration is used to transport cations through concretes of varying thickness. To maintain a level of realism the cathode material has been selected as mild steel rebar representing the structural rebar to which contaminants are driven. The preliminary results detailing K^+ and Cs^+ transport rates, breakthrough times, and concrete binding capacity are discussed in addition to an evaluation of the affects of *in situ* electrokinetic on the concrete itself.

MATERIALS & METHODS

Concrete and Experimental Rig

The concrete samples were mixed with a ratio of 3:2:1 (coarse aggregate, siliceous sand, Ordinary Portland Cement), in accordance with the European Standard EN196-1. Concrete samples were taken from the central section of a 150mm long concrete cylinder 110mm in diameter that was sliced into 20, 35, and 65 mm sections. The transport experiments were carried out in an analytical phantom, described by Parker *et al* (2013) [7]. The sections were fitted tightly inside the analytical phantom of the same internal diameter to ensure a leak proof assembly. The total sample surface area exposed to ionic transport in each electrode compartment was 95cm^2 . Figure 1 shows a photograph of the experimental setup.



Figure 1. The analytical phantom, housing the concrete sample between the anode compartment, left, and the cathode compartment, right.

Electric Field and Electrodes

A potential of 60 V was applied across the electrokinetic cell for each concrete sample (EL302T, Thurlby Thandar Instruments, UK). Based on studies conducted by ...a current limit of 70 mA was set so that the effects of a temperature increase (confirmed by temperature measurements, not shown) on the pore solution were mitigated, and electroosmotic flow was minimised. The change in electrical current in the system was monitored throughout the experiment.

Compartment Solutions

For the experiments the 1 litre cathode compartment were filled with 0.03g ml⁻¹ potassium chloride (KCl) solutions and the same volume anode compartments filled with doubly de-ionised water (DDW). To compensate for the generation of acidic and alkaline fronts in the cell, which in the case of an acidic front can substantially corrode the concrete surfaces, 0.01g m⁻¹ of sodium hydroxide (NaOH) was added to each electrode compartment to maintain pH values above 12.

Experimental Monitoring

The electrolyte solutions in each compartment were monitored over the course of the experiments for ⁴⁰K content using a bespoke thallium-doped sodium iodide well counter. We previously developed the first method of using ⁴⁰K as a safe, radioactive surrogate of ¹³⁷Cs for use in radiometric monitoring so as to replicate analytical techniques that would be used in the field [8]. 40ml aliquot solution were taken from each compartment every 24 hours and counted for 2 hours. The 40 ml sample solutions were also subject to pH (pH 510 Meter, Eutech Instruments) conductivity and Total Dissolved Solids (TDS) measurements (Jenway 4200 Conductivity Meter) to validate the radiometric potassium content, and to analyse the evolution of pH conditions. Following analysis the 40 ml samples were replaced into their respective electrolyte compartments. Using the relationship shown in Figure 2 it is possible to calculate the total

potassium concentration in a 40 ml aliquot.

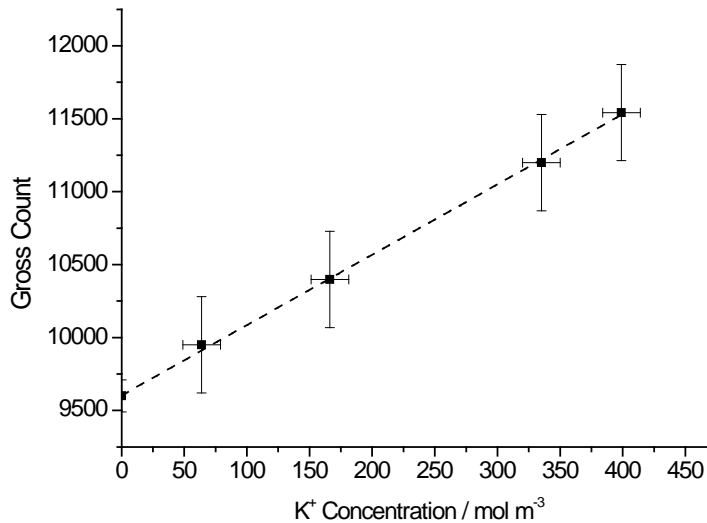


Figure 2. The relationship between the gross count and potassium concentration of a 40ml KCl sample , where $y = mx+c$, $m = 4.74 \pm 0.1$, $c = 9629 \pm 28.2$.

Previous studies have used destructive testing to monitor isotope transport through concrete. This involves the collecting of mortar depth profile samples for subsequent acid digestion and *ex situ* analysis, using Atomic Absorption Spectroscopy (AAS) [9]. However, the benefit of using a detectable, but non-hazardous, potassium source is that the assessment of the extent of ⁴⁰K radioactivity, and therefore total potassium concentration, throughout the concrete sample can be achieved accurately and non-destructively. Before, during, and after the experimental regime on a 35 mm sample, the concrete was removed from the analytical phantom and placed in the detection setup. The slice was measured twice for two hours, first with the side in contact with the anodic solution closest to the detector and secondly with the side in contact with the catholyte. This non-destructive method gives an overview of the level of uniformity in radioactivity, and therefore K⁺ contamination, without altering the concrete structure. Any discrepancy between the anode side count and cathode side count would highlight a lack of uniformity, as the concrete slice attenuates the 1461 keV γ rays [10].

RESULTS AND DICUSSION

Figure 3 shows the change in cathodic gross count for three different thicknesses (20, 35 and 65 mm respectively) of concrete sample over the course of 500 hours application of the 60 V external electric field.

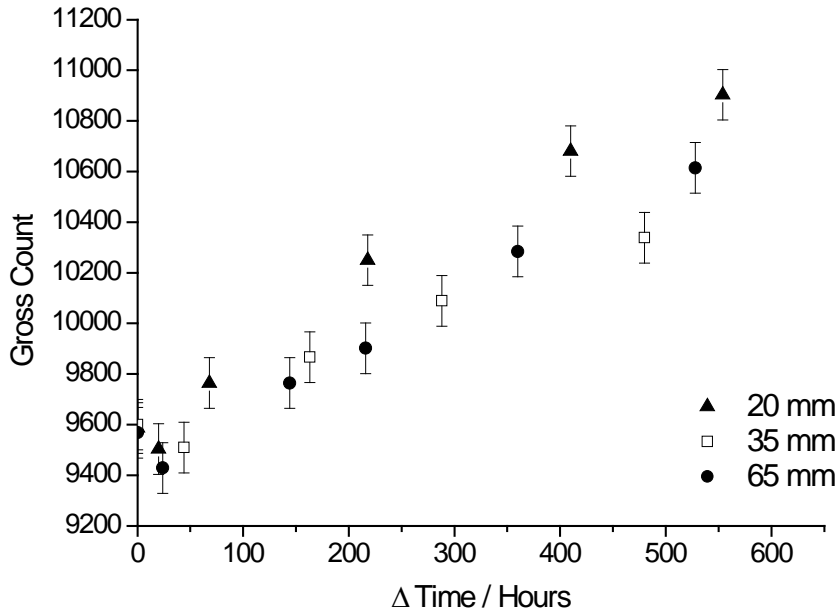


Figure 3. Change in gross count from 40 ml aliquots taken periodically from the catholyte solution for three concrete thicknesses.

It can be seen from Figure 3 that the rate of change in K^+ in the catholyte is consistent across the three samples used. Using the relationship between gross count and K^+ concentration, shown in Figure 2, it is possible to calculate the change in catholyte concentration. Figure 4 shows the linear regressions of the concentration change for the three concrete samples.

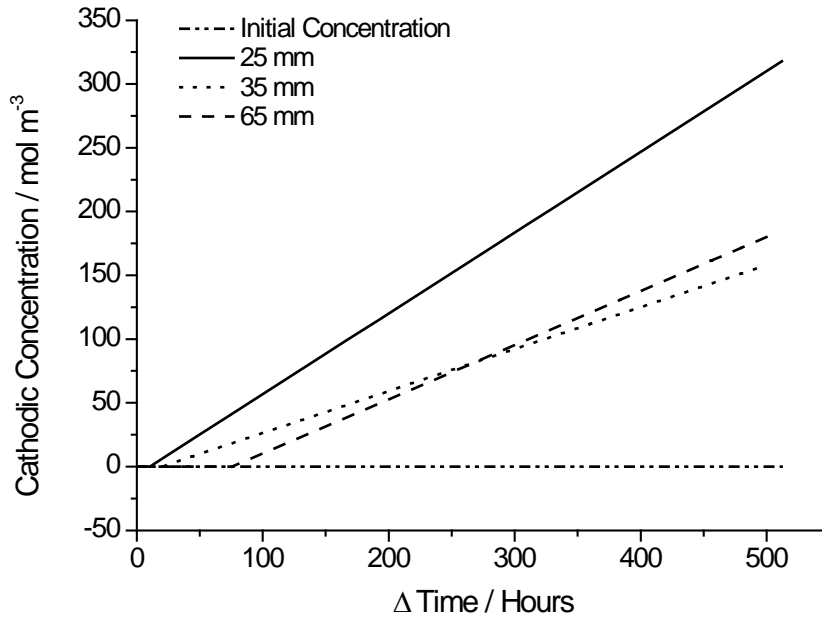


Figure 4. Linear regression analysis, and ionic breakthrough plot, of the concentration change for the three samples.

The regression analysis of the cathodic concentration change, Figure 4, allows for the calculation of the rate of steady state ionic flux, J ($\text{mol m}^{-2}\text{s}^{-1}$), of potassium migrating through the phantom. The value for J can be determined at steady-state conditions using the following equation [11]:

$$J = \frac{\Delta c V}{S \Delta t} \quad \text{Eq. 1}$$

where Δc is the change in cathodic concentration over the time interval Δt (s), V is the cathodic volume (m^3) and S is the surface area of the concrete sample (m^2). Using the calculated steady state ionic flux value it is possible to solve the Simplified-Nernst-Plank equation, obtaining diffusion coefficient, D_{SNP} ($\text{m}^2 \text{s}^{-1}$) for the cationic migration:

$$D_{SNP} = \frac{J R T l}{z F c E} \quad \text{Eq. 2}$$

where z is the valence of ionic species, c is the anodic concentration, F the Faraday constant ($96484.6 \text{ C mol}^{-1}$), R the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$), E the electric potential (V), and l the thickness of the concrete sample (m). The use of the Simplified-Nernst-Plank equation is appropriate in this instance as the phantom evaluation experiments satisfy the assumptions detailed by Andrade (1993) necessary for the derivation of Equation 2. These assumptions are that convection and diffusion are both negligible compared to the migration; that the slowest process is the only one considered relevant i.e. processes through the concrete sample; the concrete sample is thin enough for steady-state conditions to be reached within hours; and that the ionic concentration in one chamber of the cell is far greater than the other.

Table 1 shows the calculated ionic flux and diffusion coefficient values for the three concrete samples, as well as the derived time of ionic breakthrough.

TABLE I. Calculated values for the time of ionic breakthrough, flux, and Simplified-Nernst-Planck diffusion coefficients for the three thicknesses of concrete

Concrete Thickness (mm)	Breakthrough Time (Hours)	J (mol m ² s ⁻¹)	D_{SNP} (m ² s ⁻¹)
20	10.5	1.85 ×10 ⁻³	3.81 ×10 ⁻¹¹
35	20.2	9.62 ×10 ⁻⁴	3.46 ×10 ⁻¹¹
65	75.7	1.24 ×10 ⁻³	8.29 ×10 ⁻¹¹

The values in Table 1 show that rates of ionic flux, and therefore the diffusion coefficients, are consistent across the three samples. This is to be expected, given the same initial starting conditions. Despite similar ionic flux values, the significant difference between the experiments is the time taken to achieve ionic breakthrough, i.e the time for the K⁺ ions to traverse through the sample and into the cathode compartment. The time taken to achieve breakthrough is inherently linked to the thickness of the sample, and also to the applied external potential. Figure 5 shows the relationship between the time taken to achieve K⁺ breakthrough and the electric potential over the sample.

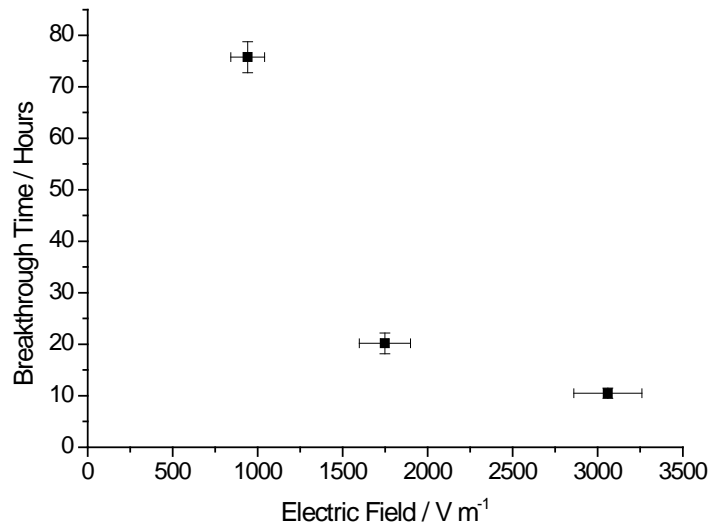


Figure 5. Relationship between the electric potential over the concrete and the sample thickness.

The clear trend from Figure 5 is that increasing the electric potential-per-metre significantly increases the rate of ionic breakthrough. However, the extent of this connection is dependent on the particular characteristics of the concrete and cement used. Further experimental work, including, a greater number of concrete samples and comparisons with related transport models, is needed to fully explore this relationship.

Caesium Transport

Whilst potassium, in the form of KCl, provides a valid surrogate in which to study electrokinetic transport of Group I elements through concrete, there remain subtle differences between it and the particular isotope of interest in this study, namely caesium. Using a method developed by Parker *et al* (2013) we have begun to radiometrically study the electromigration of Cs^+ through concrete [12]. Placing a K^+ loaded ion exchange (IX, Lewatit Monoplus 108 KR) resin barrier on the cathode side of the concrete we have monitored the displacement of K^+ ions caused by Cs^+ traversing through a 20 mm concrete sample and into the resin matrix. For these experiments the anolyte had a Cs^+ concentration of 60 mol m^{-3} , with 30 g of IX as the barrier. The total exchange capacity (TEC) of the resin allows for all of the available Cs^+ to be exchanged onto the resin. Figure 6 shows the change in K^+ concentration in the catholyte resulting from the Cs^+ migrating through the concrete and into the resin, the same 61 V electric potential was applied as in the previous experiments.

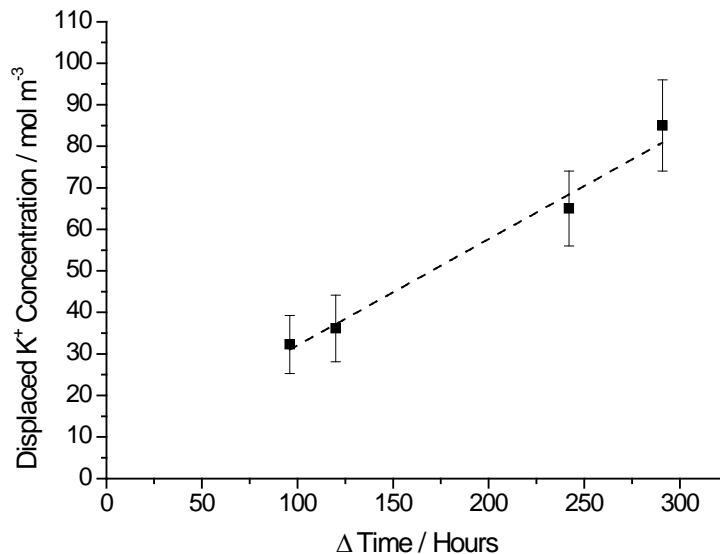


Figure 6. Change in gross count of catholyte solution as a result of Cs^+ displacing K^+ from an ion exchange material after migrating through a 20mm concrete sample.

From Figure 6 it can be seen that after 300 hours a K^+ concentration of $\sim 85 \text{ mol m}^{-3}$ is reached. Given that the initial Cs^+ anolyte concentration was 60 mol m^{-3} , it is clear that additional potassium has migrated from the concrete sample itself, as potassium is a partial constituent of concrete.

Analysis of the data of Figure 6 using Eq.1 & 2 results in ionic flux and diffusion coefficient values of $J = 6.7 \times 10^{-4}$ and $D_{SNP} = 9.25 \times 10^{-11}$, for the transferred Cs^+ . The values seen for the Cs^+ transport are consistent with those seen for K^+ in this work and similar to those observed by Frizon *et al* (2005), for Cs^+ through 18 mm thick concrete [9].

Despite similarities between studies, caution must be taken in drawing definite conclusions

between studies. The method of detecting Cs^+ transport through displaced potassium is still in its infancy and more work is need to validate it, especially given the high levels of initial ^{40}K , and therefore overall potassium, in the concrete samples, see Figure 7. Furthermore, the difference in concretes provides the biggest variation between experiments of this type, both in composition, curing times etc. Slight variations in these factors could cause significant differences in porosity, turtuosity, and binding capacity rendering comparisons between different works redundant.

Concrete Binding

Figure 7 shows the γ -ray count detected from the concrete sample before electrokinetic treatment, after 400 hours of treatment and when electric current dropped to 0 A. Potassium is a naturally occurring radioactive material (NORM) and a constituent of the concrete sample. This is evident in the initial count data recorded prior to the contamination phase with a net count of ~8200 equating to a potassium content of 11.5g/kg within the concrete sample. The application of the electric field during the first 400 hours uniformly contaminates the concrete sample with potassium, increasing the potassium content of the concrete to 17.1g/kg of concrete. The further application of the electrokinetic regime phase reduces the radioactivity level in the concrete by 70% to 12g/kg until electric current drops to 0 A. Given the initial catholyte concentration of 400 mol m^{-3} , the decontamination efficiency is in agreement with computational studies and experimental studies of a comparable design [9, 13].

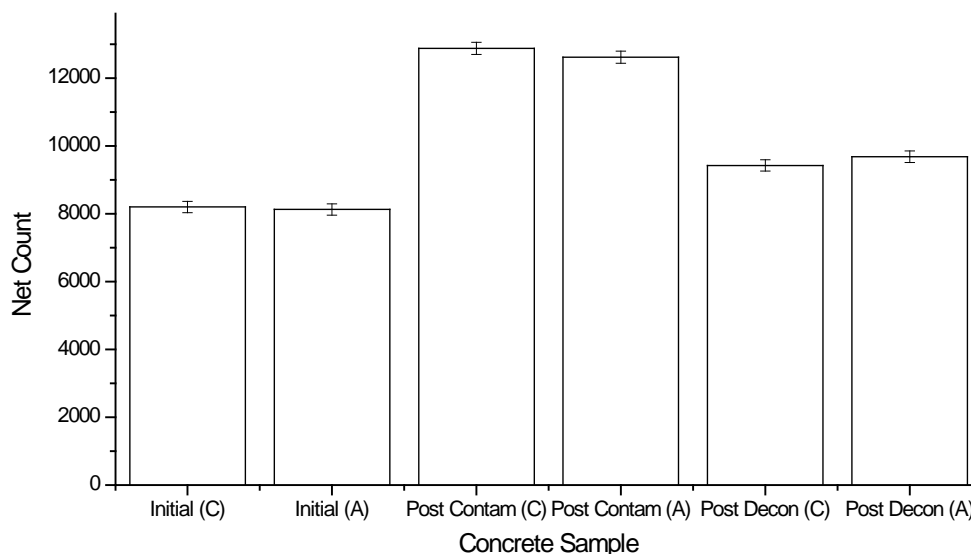


Figure 7. Radiometric count from potassium contamination at 0, 400, end of the experimental regime, C is cathode side, A is the anode side of the concrete sample.

As the current dropped to 0 A, and therefore no further electromigration of ions took place, in Figure 7, the fact that there is still a level of K^+ suggests that there is a mass of potassium irreversibly bound within the concrete matrix. Taking into account the initial bound concentration

of potassium and the proportion of irreversibly adsorbed K^+ , the application of an electrokinetic regime produces a decontamination factor between 3.45-5.77, where the decontamination factor is defined as the ratio between degree of highest contamination and the level at the end of the experiment. Despite being lower than the decontamination factors reported in related works, these preliminary studies still represents, a more efficient means of non-destructively decontaminating concrete than a range of chemical methods [14].

Affects on Concrete

A fundamental objective of the use of *in situ* electrokinetic remediation is that it is non-destructive. Thus, any affects that the electrochemical reactions have on the concrete need to be monitored and analysed. Of the chemical processes occurring during the application of the electrokinetic technique that of greatest concern is the generation of an acidic front at the anode which can be the primary cause of concrete corrosion. Figure 8 shows the change in pH at the anode and cathode in two experimental runs on a 35mm concrete sample where the pH was uncontrolled in one, Figure 8 A, and a second where it was kept at a level found in FGMSW waters (~pH 12), Figure 8 B [2].

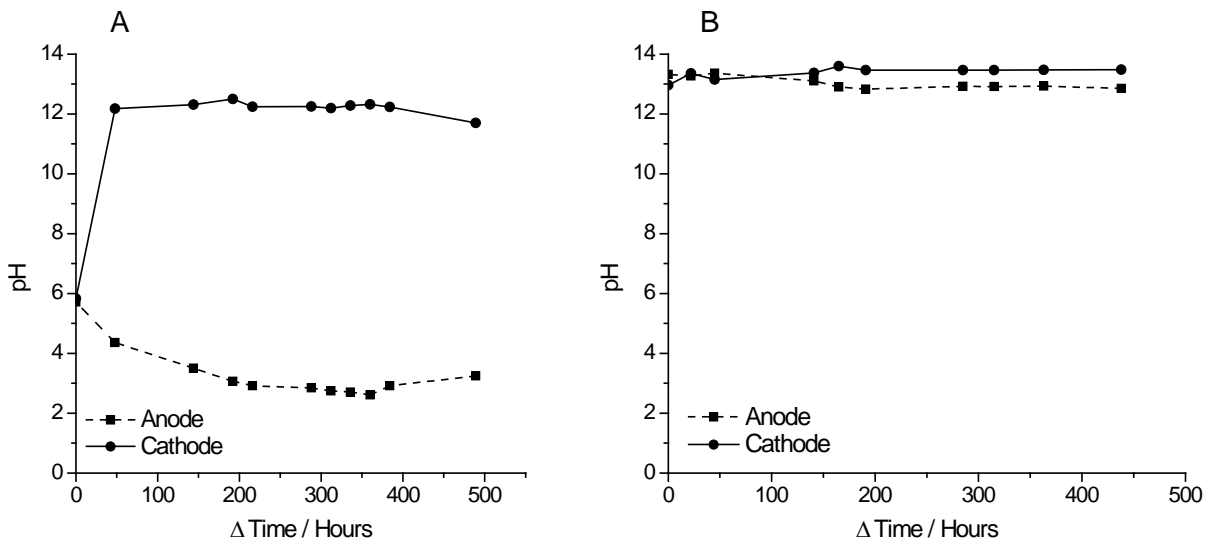


Figure 8. Comparison of pH changes in an uncontrolled (A) and a controlled experiment (B)

The effect of the pH difference on the concrete after 500 hours is pronounced. Figure 9 shows the anodic faces of the two concrete samples from Figure 8 A & B, after washing with DDW. Whilst the concrete in the pH controlled environment showed no visual corrosion, the concrete sample without pH control suffered from significant cementitious erosion. The extent of the erosion was homogenous over the exposed cement face with approximately 2 mm of face corroded, no significant erosion was observed on the coarse aggregate binder.



Figure 9. Photographs showing the physical affects that pH control has on the concrete surface, left pH controlled, right uncontrolled.

Any *in situ* application of the technique would therefore require constant monitoring and control of the electrolyte which, given the particular problems at FGMSP sites, is not straightforward as the electrolyte is the pond water saturates the concrete. It would be highly undesirable for any corrosion to occur on the exposed surfaces of FGMSP walls as this could lead to an increase in the rate leaching of pond waters to the point where the flow rate of radioactive solutions caused by head pressure surpasses the ionic flux rate back toward the pond from electromigration.

The work detailed above provides for a simplified experimental description of conditions faced in real-world decommissioning scenarios. FGSMP contain over 50 years of radioactive waste, in various stages in their decay chains and oxidation state. An electrokinetic decommissioning method designed to drive positive ions back into a fuel pond, e.g. $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^+$, will cause negatively charged ions, $^{131}\text{I}^-$ to migrate out of the concrete to the external surfaces, potentially exacerbating the situation. As such further work is required to study more complex, multi-species examples.

CONCLUSIONS

Given that *in situ* electrokinetic techniques have not yet found widespread used in the remediation of concrete, the significant conclusions from this work which demonstrate the potential of the method are:

- That consistent rates of ionic flux have been observed through increasing thicknesses of concrete, for both K^+ and Cs^+ .
- That the results also show a level of similarity with comparable literature studies using more conventional electrode configurations and computational model.
- That we have demonstrated the need to maintain strict pH control of the pore/electrode solutions to prevent concrete erosion.

- Shown the feasibility of using structural reinforcement bar as a cathode for the electrokinetic decontamination of the surrounding concrete.
- Preliminary analysis suggests *in situ* decontamination factor between 3.45-5.77, higher than some chemical methods.

Based on the preliminary results, further work will focus on the accurate analysis of Cs⁺ transport through concrete, the application on real-world contaminated concrete and utilisation of structural rebar embedded within concrete.

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