DEGRADATION AND BACTERIAL SURVIVAL ON NUCLEAR-GRADE ION EXCHANGE RESINS AND IMPLICATIONS FOR WASTE MANAGEMENT

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Abstract

Ion-exchange resins are used, among others, for the purification of the moderator of CANDU reactors. The resins are potentially degraded during service due to peroxide and temperature. The resins containing radioactive impurities collected during service are eventually discarded in non-sterile holding tanks or shipping liners, awaiting permanent disposal. In this study, we have investigated the impacts of bacterial survival on resins. We developed protocols to gently degrade resins, simulating damage during service. Resins were then contacted with bacteria. We found that, even though the resins were previously damaged, the impact of bacterial growth on resins (damaged or undamaged) was minimal.

1. Introduction

1.1 Background and statement of the problem

The total energy production from nuclear reactors in Canada was 15.1% in 2004, and in Ontario was 50% [1]. The existing and future reactors will produce benefits such as electricity, but along with positive returns, there will be an increase in the volume of wastes generated. One of the more dominant types of wastes from CANDU-type reactors is ion exchange resins, which contain several radioactive and non-radioactive contaminants, C-14 being dominant and potentially inventory-limiting [2]. Resin performance during reactor operation is important to maintain low ^{14}C emissions [3, 4], and eventually for disposal, since resins will contain most of the ^{14}C inventory [2, 5]. It is also important to examine the resin properties during service and in wastes, as this type of material was not intended for the long-term containment of contaminants.

Carbon-14 is produced primarily by the $^{17}O(n, \alpha)^{14}C$ reaction in the moderator of CANDU-type of reactors [2, 6, 7]. This ^{14}C is readily converted to dissolved CO_2, or bicarbonate ($D^{14}CO_3^-$) to be exact, at the mid-pH (or pD) and oxidizing conditions of the moderator [7]. In turn, the moderator is continuously purified by ion exchange resins, which will pick up the bicarbonate and other impurities by ion exchange. At the end of the service life (up to 2-3 months), the resins are discarded into holding tanks or shipping liners for extended storage. Even if changes in these operations have taken place recently, it was estimated that 6.5 PBq or 29% of the total production of ^{14}C from nuclear reactors sits on resins in Canada alone [5].

Conditions in reactors and the interim storage medium have an impact on the resin properties and integrity, hence the safety of the ^{14}C inventory on resins. For instance, the radiolysis

produces ~2-3 ppm of deuterium peroxide (D_2O_2) in the moderator [4], which can degrade resins, especially in the presence of catalysts such as Fe^{2+} (Fenton reaction; [8]). The potential consequences are a change in capacity (less removal potential), a change in selectivity (displacement of $H^{14}CO_3^-$ by other byproducts) and de-crosslinking, causing fragility and release of resin fragments. In turn, fragments from these stresses could saturate resins prematurely [3]. Conversely, damage by thermal degradation is not likely an issue [9].

1.2 Resin properties and rationale for the study

The spent ion exchange resins are usually placed in holding tanks or storage liners after service, for up to several decades [10]. The resins will be invariably in wet conditions, fully or partially submerged in de-ionized water. These spent resins will contain ions picked up during service (DCO_3^-, NO_3^-, Cl^-, Gd^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Al^{3+} among others [11, 12]), up to potential saturation. If the spent resins were damaged during service, this can result in the release of contaminants. This is very important because the carbonate equilibrium is fragile and it depends upon the pH, competition with resin sites ($\equiv R^{(+)}$), and isotopic exchange with atmospheric CO_2:

$$\equiv R^{(+)}OH^{(-)} + HCO_3^-{}_{(aq)} \leftrightarrows \equiv R^{(+)}HCO_3^{(-)} + OH^-{}_{(aq)} \quad (1)$$

$$HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \leftrightarrows H_2CO_{3(aq)} \quad (2)$$

$$H_2CO_{3(aq)} \leftrightarrows H_2O + CO_{2(gas)} \quad (3)$$

Any change in pH or anion import can affect the carbonate equilibrium and the reactions above. Since it has been postulated [3] that resins may be saturated with other anions, the resin selectivity to bicarbonate may be affected, even if small quantities of competing ions are present in solution. An example of competition is shown here with nitrate (NO_3^-):

$$\equiv R–HCO_3 + NO_3^- \leftrightarrow \equiv R–NO_3 + HCO_3^- \quad (4)$$

Where ≡R is the resin, and the equilibrium constant $K_{HCO_3^-}^{NO_3^-}$ (also the selectivity factor in this case), is given by:

$$K_{HCO_3^-}^{NO_3^-} = \frac{[\equiv R - NO_3^-] \times [HCO_3^-]}{[\equiv R - HCO_3^-] \times [NO_3^-]} \quad (5)$$

The higher the selectivity factor, the higher the affinity for the ion in solution to replace the other ion on the resin. This is important, especially if a resin, pre-loaded with ^{14}C-bicarbonate and potentially damaged in service, is holding a significant contaminant inventory. It just so happens that the resin selectivity for most ions is higher than for bicarbonate [13], hence it is important to determine the limits of this parameter.

1.3 The presence of bacteria in nuclear wastes

Bacteria can survive in most wet environments as long as nutritional and energy requirements are met [14]. Bacteria have been found in biofilms of nutrient-depleted environments such as in nuclear fuel pools [15], and in ultrapure water systems [16]. Conditions in spent resin holding tanks or liners are expected to be similar, e.g., wet (fully or partially submerged in water), scarce in nutrients, of moderate temperature and radiation, and non-sterile. It is thus possible, or highly likely, to find bacteria with spent resins. Nutritional requirements may be met if the resin backbone can be used as a carbon source, and if other ions, picked up during service and concentrated on resins, are available as potential nutrients.

Bacterial growth on resin wastes is an additional factor which must be understood and incorporated into a complete assessment of the stability of radiocontaminants on waste resins. Unknown effects of bacteria include the excretion of by-products, which could displace ions previously exchanged on the resins, and formation of biofilms which can provide a micro-environment for life and that may affect ion exchange. We need to have a closer look at the integrity and the chemical properties of resins, and the effects of bacteria on these wastes to determine if contaminants, such as C-14, can remain immobile.

1.4 Objectives

The main objective of this work is to determine if a bacterium, *Ralstonia pickettii*, isolated in de-ionized systems, is capable of growing on damaged anion exchange resins. We had to develop a new protocol to gently damage resins, similarly but beyond expected service conditions. We have also customized and developed protocols to measure resin damage: ion exchange capacity (total and strong-based), moisture content, selectivity, and Total Organic Carbon (TOC) release. This work is breaking new grounds to assess the consequences of resin damage for the safety of ^{14}C on resins in wastes, and in addition, this has a potential benefit for reactor service.

2. Methods

2.1 Resin degradation set-up

The resin degradation set-up (Figure 1; see [8, 9]) was modified for small volumes of resin (<15 mL). An alternate batch set-up was also used, for larger volume of resins (~1 L; figure not shown). The intent was to gently degrade resins, slightly beyond expected service conditions. It is known that resin degradation is affected by heat [9], peroxide [3, 8] and catalysts [8], so the conditions to expose resins were set according to these factors:

$$\begin{matrix}\text{Resin damage} \\ \text{[TOC release]}\end{matrix} \propto \text{Resin quantity} \times \begin{bmatrix}\text{peroxide} \\ \text{concentration}\end{bmatrix} \times \begin{bmatrix}\text{catalyst} \\ \text{concentration}\end{bmatrix} \quad (5)$$

The catalyst and peroxide concentration and temperature were held constant, hence the main variable was the time. The exposure time to peroxide was normalized in units of ppm-hour. The ion exchange resins used were NRW-37 LC from Purolite (Batch # 385/02/3). The resins were received as a mixed bed of nuclear grade A-400 and C-100, in OH^- and H^+ form,

respectively. Resin handling, capacity, cleaning and conditioning were modified ASTM methods [17]. Further details on this set-up and for the resin degradation protocols are reported separately [18].

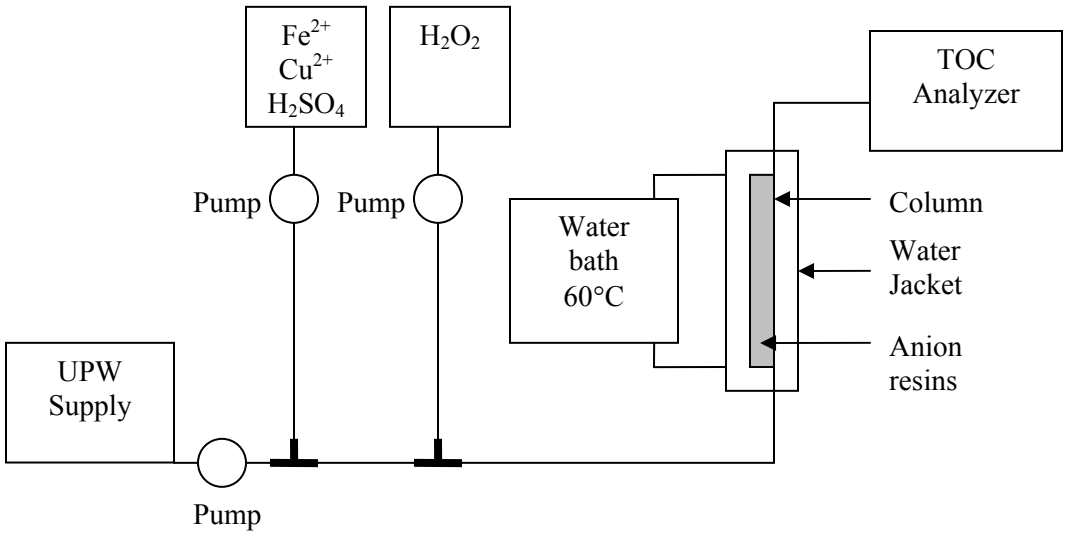

Figure 1: modified column (on-line) system used to damage anion exchange resins.

2.2 Indicators of Resin Damage

The indicators of resin damage were the TOC release, the change in moisture content, the capacity (total and strong), and the selectivity. Our approach was to set the basic properties of resins, as-received and damaged by peroxide, and compare the incremental damage of the resins (damaged and undamaged) when they are exposed to bacteria.

The TOC released from damaged resins was measured using a Sievers TOC analyzer model 800. The TOC was measured using the analyzer's on-line mode directly on the column set-up (Figure 1). The detection limit is 0.05 ppb TOC ± 3%. The units of resin damage were normalized to *quantity of TOC × (mL of resin bed × time)*$^{-1}$.

The moisture content, a measure of resin de-polymerization, was a modified ASTM method [17, 18], on approximately 5 ml of anion exchange resins. The precision among replicates was ±0.5 to 1.9%, and changes in moisture content of 5% or more were significant. The capacity was also a modified ASTM method [17, 18], on 5 mL of resin. Both capacity measurements (total and strong base capacity) were reproducible within 2% among replicates.

For the selectivity, approximately 5 mL of anion exchange resins were pre-saturated with HCO_3^-. A nitrate ion spike, corresponding to 20% of the total resin capacity, was added to the solution. Both ions (NO_3^- and HCO_3^-) were analysed in the supernatant water by ion chromatography. The procedure was repeated until the NO_3^- spike reached 100% of the calculated resin capacity. The amount of nitrate adsorbed on the resin was plotted against the mole fraction of NO_3^- loaded on the resin exchange sites, for 5 data points per determination; this gave the selectivity factor.

2.3 Bacteria

A local ultra-pure water Milli-Q system was sampled at Laurentian University. The most abundant colony was identified as *Ralstonia pickettii* with 99.9% assurance (GAP EnviroMicrobial Services, London, ON). The growth of pure *R. pickettii* cultures was done in oligotrophic medium containing 300 mg/L of glucose [16]. Replicates with other carbon sources were done with 100, 10, 1 and 0 mg/L glucose. Additional growth curves were performed with dead *R. pickettii* cells as a carbon source, representing a value of 10 and 1 mg/L carbon [19].

The growth curves of bacteria with resins were done with cleaned up broth to have only the bacteria and resins as sources of Carbon. The anion exchange resins were pre-converted to the Cl^- form, so that the Cl^- ion found in solution would indicate resin degradation by the bacterium or displacement by metabolites. These resin-bacteria containers were kept in this condition for 6 months. Sampling for the Cl^- content was measured initially, after 2 and 6 months.

Cell counts of *R. pickettii* were performed by serial dilutions and streak plating technique, on Mueller-Hinton agar plates, cultivated at 25 °C. The statistical analysis was the ANOVA single factor at the 95% confidence level, using the Microsoft Excel spreadsheet.

3. Results

3.1 TOC release rates for the degradation experiments

The TOC values for resins degrading in the column (on-line) mode were normalized and plotted against time (Figure 2). The maximum normalized TOC release rates for the 6 trials are given in Table 1. For the batch set up, the normalized TOC release rate was determined at the end of the degradation (interim release rates are not available because of the set-up). A system blank, done with clean resins without peroxide and catalyst, is also shown for comparison.

There are common trends in the replicate degradation patterns, but there were also some divergences. All of them had a fairly uniform TOC release rate for the first ~60 hours. The degradation rate increased markedly for runs #1, 2 and 4 between ~60-90 h of exposure, whereas the increase was gradual for runs #3, 5 and 6. The reasons of the divergences were not investigated in detail; we used resins from the same batch, the pump set-up, the flow rate and the chemicals were the same between replicates. We also know from experience that the column set-up yields reproducible results [9]. Despite the variations, the TOC release rates were well above the system blank, without catalysts and peroxide (Table 1). In comparison, the instant release rate from the batch set-up gave a similar TOC value.

3.2 Bulk indicators of resin damage

The other bulk indicators of resin damage, i.e., the moisture content, the capacity (total and strong), and the selectivity factor are summarized in Table 2 for the resins degraded using the on-line mode. Most of these indicators showed significant changes. The moisture content

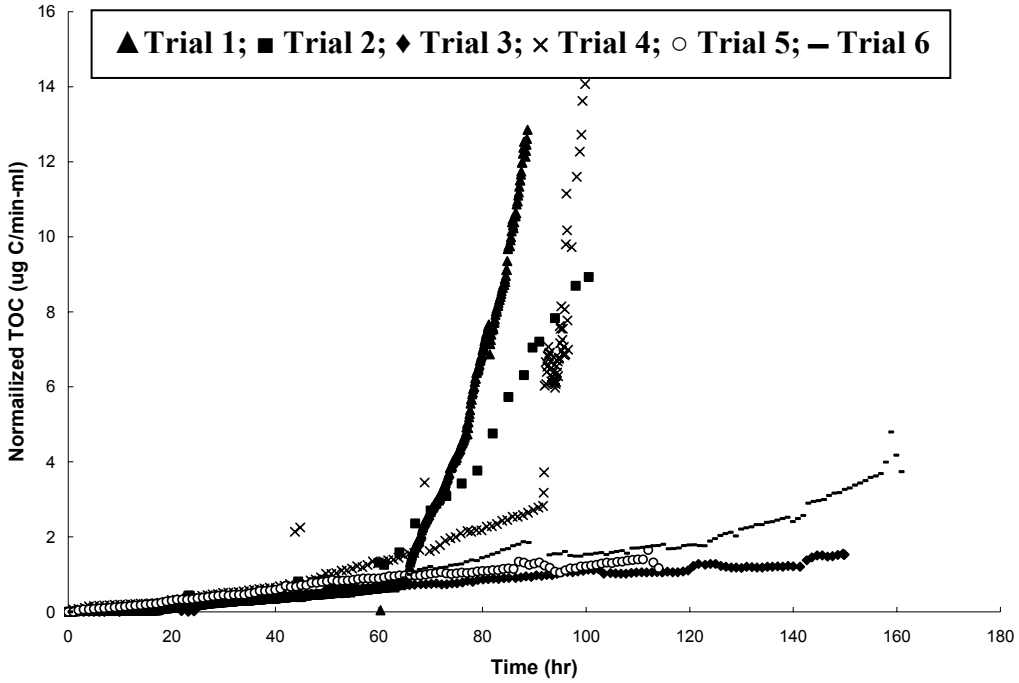

Figure 2: Variations of the normalized Carbon release rate, in μg C (min × mL resin)$^{-1}$, with time (hr) for anion exchange resins damaged in a column set-up.

Table 1: Maximum normalized TOC release rates for anion exchange resins damaged under both column and batch set-ups.

Run No	TOC release rate[a] μg C (min × mL resin)$^{-1}$	Run No	TOC release rate[a] μg C (min × mL resin)$^{-1}$
1 – column mode	13	4 – column mode	14
2 – column mode	9.0	5 – column mode	1.3
3 – column mode	1.5	6 – column mode	4.0
Batch mode	4.3	System blank (clean resin)	0.0037

[a]Calculation: = [TOC] × (Flow rate through resin bed) / Volume of resin; [9].

increased, indicating some resin depolymerization; the capacity (total and strong-base) both decreased, indicating that exposure to peroxide and catalysts affected the ion exchange sites; the

selectivity factor decreased appreciably, without being necessarily statistically significant. The interpretation of this change is under investigation [18].

Among the results for the resins damaged in the batch mode, only the TOC release rate showed a consistent and significant change (Table 1). The other bulk indicators showed changes but these were not consistent or statistically significant among aliquots (results not shown). This was likely due in part to the lower amount of control on the reagent levels, although the peroxide level was measured and adjusted on a daily basis. In addition, mixing was minimal to avoid physical damage to resins, hence, contact between the reagents and the resins may not have been intimate. Nevertheless, we judged that the resins were sufficiently damaged to warrant their exposure to bacteria.

Table 2: Summary of changes in resin properties from the on-line degradation set-up.

Damage indicator	----- Initial -----		----- Final -----		Relative change*
	Avg	Range	Avg	Range	
Moisture content average (% mass)	54.1	49.2-61.5	60.8	56.3-68.4	4 to 17%**
Total capacity (mEq/mL resin)	1.06	0.99-1.14	0.85	0.69-1.01	-5 to -40%**
Strong base capacity (" ")	0.91	0.84-0.93	0.67	0.57-0.73	-18 to -38%**
Selectivity factor (unitless)	4.28	-	2.49	1.58-3.27	-24 to -63%***

*Average of 6 trials, n = 3 per trial; **significant; ***two of samples out of 6 showed a significant difference.

3.3 Bacteria growth

3.3.1 Cultures not contacted with resins

The growth curves for *R. pickettii* in the standard and oligotrophic broths gave the viable cell counts and generation times shown in Table 3. Each determination was done in triplicate. For comparison, the growth curve data for the dead cell-based broths are also shown. We have observed a general trend: the higher the glucose content as a carbon source, the shorter the generation time. The generation times at 0 mg/L of glucose were difficult to measure because serial dilutions always included other sources of organic C from cell debris; the other replicates using cell debris had generation times close to those without glucose addition.

Table 3: Viable cell count at stationary phase and generation times for *R. pickettii* grown in oligotrophic broth with various glucose and carbon sources (room temperature).

Conditions	Viable cell count CFU/mL	Generation time, min	Conditions	Viable cell count CFU/mL	Generation time, min
---------- Source of C: glucose ----------			---------- Source of C: dead cells ----------		
300 mg/L	9.4×10^{12}	23.7			
100 mg/L	2.07×10^{10}	39.3			
10 mg/L	3.20×10^{10}	26.8			
1 mg/L	3.47×10^{9}	40.3			
0 mg/L #1	1.17×10^{10}	54.5	10 mg C/L	1.90×10^{6}	219
0 mg/L #2	7.70×10^{5}	245	1 mg C/L	1.37×10^{6}	231

3.3.2 Cultures of bacteria contacted with resins

All the bacteria were able to grow both in the presence of damaged and undamaged ion exchange resins. There were no statistical differences in moisture content, ion exchange capacity (total and and strong base capacity), for *R. pickettii* growth in contact with resins (damaged or undamaged; results not shown). The comparison was made before and after inoculation (6 months incubation time). There was a measured change in selectivity values, however these were not statistically significant at the 95% confidence level (Table 4).

Table 4: Summary of resin selectivities (damaged and undamaged) before and after exposure to bacteria for 6 months.

	Selectivity before	Selectivity after	Change
Undamaged	4.28 ± 0.86*	2.97 ± 0.29**	-30.6% ± 6.7%**
Damaged	3.72 ±1.22*	2.55 ± 0.42**	-31.5% ± 11.3%**

*Standard deviation on one determination (5 data points)
**Standard deviation on the average of 6 determinations (5 data points per determination).

3.3.3 Changes in chloride content in cultures contacted with resins

The difference in chloride content $[Cl^-]$ in the solution contacting the resin was an indicator of competition which released this anion from the resins. This was given by:

$$[Cl^-]_{released} = [Cl^-]_{final} - [Cl^-]_{initital} \quad (6)$$

A negative value indicates an uptake, whereas a positive value indicates a release. The data in Figure 3 shows that the Cl^- ion was picked up and not released for the resins contacted with bacteria (all were negative values), whereas the control did not show definite trend after 6 months.

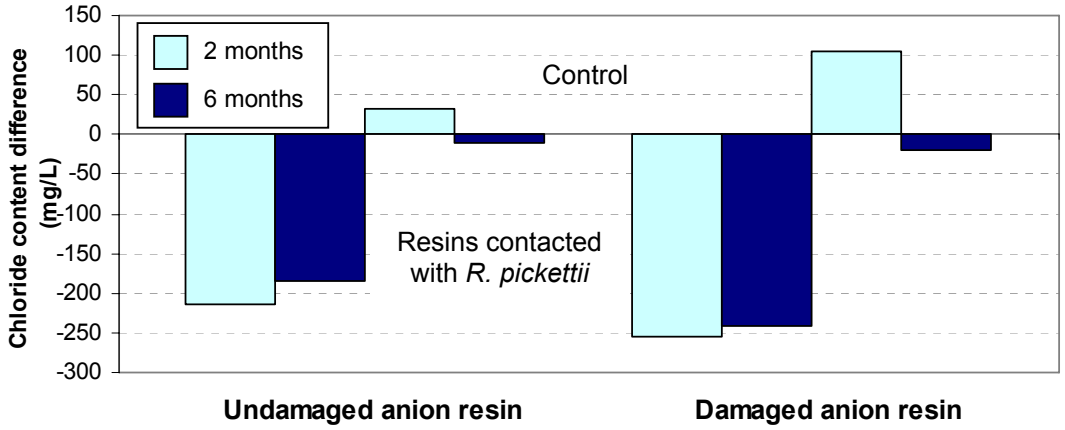

Figure 3: difference in chloride content for resins contacted and not contacted with *R. pickettii*.

4. Discussion and conclusion

The resin degradation protocol was developed to have a limited amount of damage to the resin. The peroxide contact time ranged from ~4400 to 8000 ppm-hour, which brackets the range expected in the moderator (up to ~6000 ppm-hour). The conditions in our set-up were harsher than in reactors because the presence of the main catalyst (e.g., Fe^{2+}) was held constant throughout the exposure, and the temperature (60 °C) was at the upper end of expected service conditions. Although the temperature and the peroxide concentration were higher than expected in a CANDU-type HWR moderator, this does not affect the initiation of the reaction [9]. Damage to resins occurred for the on-line (column) set-up, but the damage was less obvious for the batch set-up. The TOC release rate was the most discriminant indicator of damage. The selectivity factor, which is a new potentially important parameter, showed some promise, although some work is needed to decrease the standard error.

The growth of *R. pickettii* followed typical patterns, e.g., lag phase, exponential phase, stationary phase. After 100 hours, the plate count started to become erratic, in part because the bacterium is naturally slow-growing. Growth was also slow in carbon-deprived medium, and to meet minimal nutritional needs, the bacteria likely went under cryptic growth. This phenomenon has been observed elsewhere under similar conditions [16], when the nutritional requirements of bacteria are met from the cellular debris of dead cells.

Ralstonia pickettii was able to grow on undamaged and damaged resins. The bulk damage indicators showed an increase in resin capacity (strong and total), and decreases in moisture content in some aliquots, but by in large, the trends were inconclusive. Some of these changes were consistent with the formation of a biofilm, which can block resin pores by the addition of extracellular polymeric substances (EPS; [20]). EPS have a complex structure, and can trap dead and viable cells, they can act as a sticky substance and traps nutrients traveling in the surrounding environment [20]. This could explain the change in selectivity factor for resins, before and after contact with bacteria. It has been noted that the selectivity factor changed by the same amount (Table 4), whether the resins were degraded or not.

The changes in chloride ion in solution originated from the anion resin (the resin was pre-saturated with Cl^- prior to incubation). Since the decreases of the chloride ion in solution were substantial, compared to the control, a likely explanation is a pick-up by the bacteria or trapping in a biofilm. It is known that biofilms can act as ion concentrators [20, 21]. Although we did not sample for biofilms, these could form in nutrient-poor pools containing resins.

In summary, we found that resin properties (damaged or undamaged) did not conclusively change upon exposing resins to bacteria, there was no significant change in moisture content (indicative of resin back-bone attack), Cl^- ions (surrogate for functional group attack) were not released from their pre-exchanged sites on resins, rather, there was a pick-up of the Cl^- anion from solution. The selectivity of nitrate over bicarbonate was slightly lower upon contact with bacteria, suggesting that bicarbonate was held more strongly and it was more impervious to competition. It is likely that biofilms formed, and biofilms usually provide a buffer against changes that could affect exchange with resins.

If these conditions were extended to existing resin wastes containing C-14, we could not find a negative impact of bacteria on resin properties: resin integrity and contaminant retention. This would imply that there would be no adverse effects for waste management, on the short term at least. If biofilms form on resins, this may prove to be beneficial in isolating contaminants, as opposed to being detrimental.

More work is needed to investigate the leaching or exchange rates from resins on longer-term experiments. In addition, this work was dealing exclusively with anion exchange resins (damaged and undamaged), experiments should be done to determine the impact of damaged cation resins, for a whole-system assessment.

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