

## Uranium adsorption behaviour of amidoximated fibers under coastal ocean conditions

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### ABSTRACT

Uranium is a naturally occurring trace element in seawater. Research has been on-going to develop selective adsorbents to bind uranium in seawater to harvest this element from the ocean as a sustainable source for nuclear power generation. This study tested amidoxime-based polymer A18, currently one of the most promising adsorbents, in a variety of coastal ocean conditions. Also tested was the extraction of uranium from fibers with 3M  $\text{KHCO}_3$  and their subsequent adsorption capacity upon reuse. Overall, fibers were negatively affected by biofouling, where adsorption was reduced by up to 70% for fouled fibers; higher than laboratory predictions. Increasing temperature correlates positively with uranium adsorption as long as biofouling is not beyond 115% weight increase. Fiber reuse did not prove effective as it was found that total harvested uranium was analogous for single-use 56-day deployment fibers and for those used multiple times over 84 days, with  $\text{KHCO}_3$  extraction between uses. Reuse of the fibers is therefore not recommended and revised extraction methods are needed for reuse to become cost-effective.

### 1. Introduction

The ocean constitutes an unconventional reserve of naturally-occurring uranium that could be harvested for future energy needs. With growing markets for low-carbon electricity generation, and increasing energy demands worldwide, demand for nuclear energy is projected to increase in the foreseeable future (OECD, 2018). Much of this capacity is expected to increase in east Asia, whereas a decline in capacity is continuing in North America as older reactors close and are not replaced. Uranium for reactors is currently supplied through terrestrial mining, presently occurring in 19 countries worldwide, as well as from secondary sources such as reprocessed fuel or re-enrichment of depleted tailings. In 2016 only Canada and South Africa were able to domestically supply enough uranium for their reactors (OECD, 2018). The oceans, containing dissolved uranium at 3.3 ppb on average (Ku et al., 1977), have the potential to be a reserve for countries without terrestrial resources, allowing for a secure and reliable source.

Research has been on-going since the 1950s to develop selective adsorbents that would bind dissolved uranium and allow for its extraction on an economically favourable scale. These studies are examined at length by Abney et al. (2017). Laboratory and field tests have included a variety of adsorbent materials starting with inorganic

materials, followed by organo-functionalized polymers and, beginning in 1979, amidoxime-functionalized polymer adsorbents (Egawa and Harada, 1979). At present, 40 years later, amidoxime-based polymers are still being optimized but have been identified as having the highest adsorption capacity in laboratory settings (Abney et al., 2017; Dungan et al., 2017) and have been successfully tested at larger scale in Japan (Parker et al., 2018). While initial amidoximated materials had poor mechanical strength, the introduction of radiation-induced graft polymerization (RIGP), to enable a trunk material to be functionalized with polyacrylonitrile, then converted to polyamidoxime, allowed for ocean deployments (Tamada, 2010; Seko et al., 2004a). Marine tests were conducted in Japan starting in 1999 using amidoxime-functionalized polyethylene fabric sheets. Overall they were able to collect approx. 1 kg of uranium oxide (“yellowcake”) using 350 kg of fabric exposed for a total of 240 days with elution of U every 20–90 days (Seko et al., 2003). Further development led to kelp-like fiber structures with adsorption rates as high as 1.5 g-U/kg-ads (Seko et al., 2004b). Additional field studies of various grafted material have been conducted in India (Prasad et al., 2009), Korea (Jang et al., 2000), China (Chen et al., 2017), and the United States (Gill et al., 2016). In 2011 the U.S. Department of Energy launched a campaign to optimize extractive fiber technologies and conduct laboratory and field studies that led to this

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research.

Specifically, this study used adsorbent containing acrylonitrile as well as a vinylphosphonic acid, prepared by radiation induced graft polymerization onto a high surface area polyethylene trunk (Das et al., 2016). These polymers have been found to adsorb uranium up to 3.52 g-U/kg-ads (grams uranium per kilogram adsorbent) after 24 h exposure to synthetic seawater spiked with 8 ppm uranyl in a laboratory setting, and at 3.35 g-U/kg-ads using natural seawater filtered to 0.45  $\mu\text{m}$  and normalized to salinity of 35 practical salinity units (psu) (Das et al., 2016). Uranium is considered conservative in seawater due to the linear relationship between uranium concentration relative to salinity (Owens et al., 2011; Not et al., 2012). All data presented have been normalized to a mean oceanic salinity of 35 psu for comparative purposes between experiments and results from other studies.

The production of fibers and ocean deployment costs for uranium adsorbing fibers are currently a hindrance to large-scale production. Terrestrially-mined uranium oxide ( $\text{U}_3\text{O}_8$ ) in 2016 averaged between USD 77/kgU and USD 120/kgU (OECD, 2018), the lowest since 2005. In order to achieve this price point, given the large capital cost of manufacturing fibers, they would need to be reused numerous times to be economically viable (Dungan et al., 2017; Byers and Schneider, 2016; Byers et al., 2018). This requires efficient collection and stripping of uranium from the fibers without damaging them. While laboratory and filtered water tests have shown great leaps in adsorbent capacity in recent years (Abney et al., 2017), as well their ability to be reused in a laboratory setting (Kuo et al., 2017), these fibers have not been tested in the open coastal ocean environments in which they would need to be deployed for commercial use. This study provides results of seawater trials and examines the reuse of fibers deployed in the coastal Atlantic Ocean at the Woods Hole Oceanographic Institution (WHOI) in Massachusetts, USA.

## 2. Methods

### 2.1. Experimental design

Over the course of two years, uranium adsorbing fibers were deployed three times at a dock at WHOI, twice in an indoor flume receiving filtered ambient seawater at WHOI and once off a dock at the Massachusetts Maritime Academy (MMA) in Bourne, Massachusetts, USA (Table 1). The first experiment (Exp 1) from May to July 2015 was a simultaneous dock-flume experiment at WHOI to examine the effects of filtered versus unfiltered seawater on the adsorption of uranium. A second dock only experiment (Exp. 2) at WHOI from September to November 2015 examined different enclosure types, and biofouling effects on the uptake of uranium at 5 and 12 m. From July to September 2016 an additional filtered water flume experiment (Exp. 3) was conducted with higher water flow (4.6 cm/s vs. 2.0 cm/s). A WHOI dock experiment (Exp. 4) from August to November 2016 examined the reuse of fibers following the extraction of uranium. Finally fibers were also

deployed (Exp. 5) at the MMA from October to December 2016. The MMA fibers were then compared with those deployed at WHOI.

### 2.2. Fiber preparation

All experiments used the A18 adsorbent braid prepared by Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee, USA. The fibers are high-surface-area polyethylene fibers prepared by irradiation followed by immersion in an acrylonitrile and vinylphosphonic acid (VPA) grafting solution. Following a wash with N,N-dimethylformamide the nitriles are converted to amidoxime groups. Particulars regarding adsorbent type and preparation of the fibers can be found in Das et al. (2016) where adsorbent A111 is identical to A18 used in this study. The fibers function as uranyl ( $\text{UO}_2^{2+}$ ) binds to active open-chain or cyclic amidoxime group (Ladshaw et al., 2017a). Fibers have been found to perform better in the presence of the VPA however reasons for this are unclear and under further investigation (Das et al., 2016).

The prepared fibers were dried at 50 °C to achieve a stable weight. For experiments quantifying biofouling (Exp. 2, 4, 5) fibers were weighed into 100 mg bundles (Fig. 1A) that were tied together using nylon thread and labelled. All fibers were then conditioned at 80 °C for 1 h in a 2.5 wt% KOH solution at a rate of 1 ml KOH per 1 mg of adsorbent. This deprotonates the carboxylic acids and swells the fibers for contact with seawater. The fibers were then rinsed until they reached a neutral pH and stored in deionized water until use. Pre-weighing the fibers dry for experiments 2, 4 and 5 enabled us to quantify biological growth on the fibers during deployment by comparing the pre- and post-deployment weights.

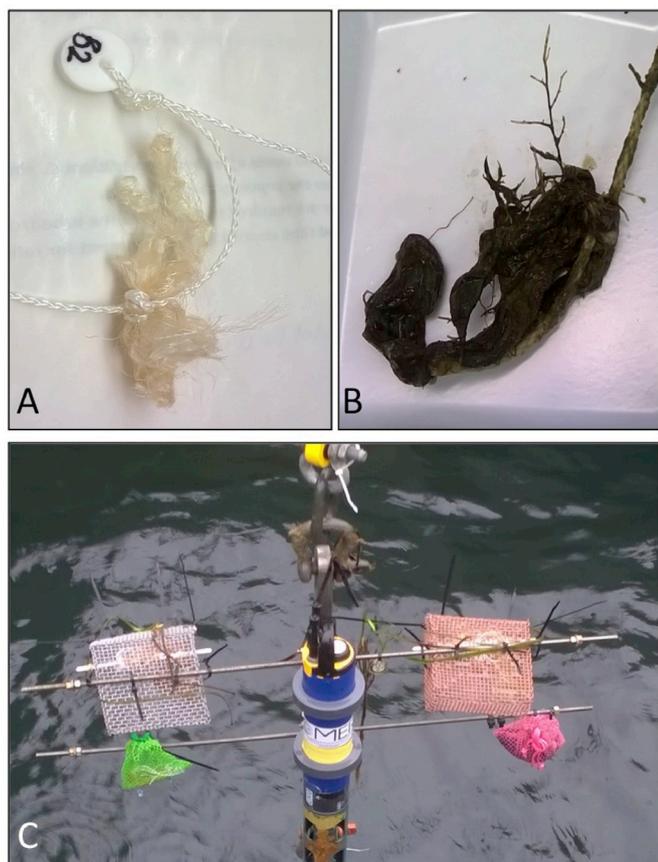
### 2.3. Ocean dock experiment locations and procedures

WHOI is located on the Atlantic coast in southwestern Massachusetts, USA. Ocean experiments were conducted on the WHOI dock exposed to unfiltered Atlantic seawater. An aluminium bar was suspended at 5 m (Exp. 1, 2, 4) and 12 m (Exp. 2, 4) depths. Two horizontal bars extending from an aluminium truss contained salinity and temperature sensors as well as fibers contained in nylon mesh bags (5 mm openings). For Experiment 2 fibers were also deployed in type 430 Stainless Steel or copper woven wire cloth, both with 5.16 mm openings and 1.19 mm diameter wire, resulting in an open area similar to that of the nylon mesh bags (Fig. 1C). Fibers were sampled weekly from the various enclosures. Currents were measured using either an acoustic Doppler (Exp. 1, 2) or an Aquadopp Profiler (Nortek) (Exp 4). Temperature, salinity and pH were measured continuously at 15 min intervals using a YSI EXO multiparameter Sonde (Exp. 1, 2, 4).

The fibers were also deployed in nylon mesh bags at the Massachusetts Maritime Academy (MMA) in Bourne on Buzzards Bay, Massachusetts, USA (Exp. 5). The bags were attached to an aluminium rod at 6 m depth off of a floating dock. These were sampled weekly in conjunction with samples from a moving system testing enclosure types

**Table 1**  
Environmental conditions during deployment of amidoxime-based fibers for uranium adsorption.

#	Experiment	Location	Depth	Average water flow	Max. temperature (°C)	Min. temperature (°C)	Average temperature (°C)	Average salinity (psu)	Average pH
1	Flume-Dock Parallel 2015	WHOI Flume	flume	2.0 cm/s	23.1	16.5	18.4 ± 1.4	32.1 ± 0.2	7.82 ± 0.10
		WHOI Dock	5 m	7.2 cm/s	22.9	14.3	18.6 ± 1.8	32.1 ± 0.3	7.55 ± 0.28
2	Biofouling mitigation 2015	WHOI	5 m	9.2 cm/s	20.7	11.8	15.3 ± 2.0	32.1 ± 0.4	8.21 ± 0.10
		Dock	12 m	9.2 cm/s	20.5	11.8	15.3 ± 2.0	31.9 ± 0.4	8.21 ± 0.13
3	Flume increased velocity 2016	WHOI Flume	flume	4.6 cm/s	23.9	19.8	22.5 ± 2.1	32.5 ± 0.3	8.00 ± 0.37
4	Fiber reuse 2016	WHOI	5 m	9.8 cm/s	25.6	9.2	18.4 ± 4.4	32.4 ± 0.2	8.01 ± 0.12
		Dock	12 m	9.8 cm/s	24.8	7.7	18.3 ± 4.4	32.4 ± 0.2	8.04 ± 0.11
5	Mass Maritime Academy 2016	MMA	6 m	8.4 cm/s	17.8	5.3	11.1 ± 3.0	31.7 ± 0.8	8.18 ± 0.10



**Fig. 1.** (a) AI8 adsorbent weighed and tied into a mini-braid. (b) A mini-braid post deployment after 49 days at 5 m depth in a steel cage (fall 2015). (c) Deployment of YSI and fibers inside steel (upper left), copper (upper right) and nylon bags at the WHOI dock (Exp. 2).

described further in [Haji et al. \(2019\)](#). Currents were measured using a tilt current-meter by Lowell Instruments and salinity and temperature were measured using a HOBO Salt Water Conductivity/Salinity Data Logger (Onset).

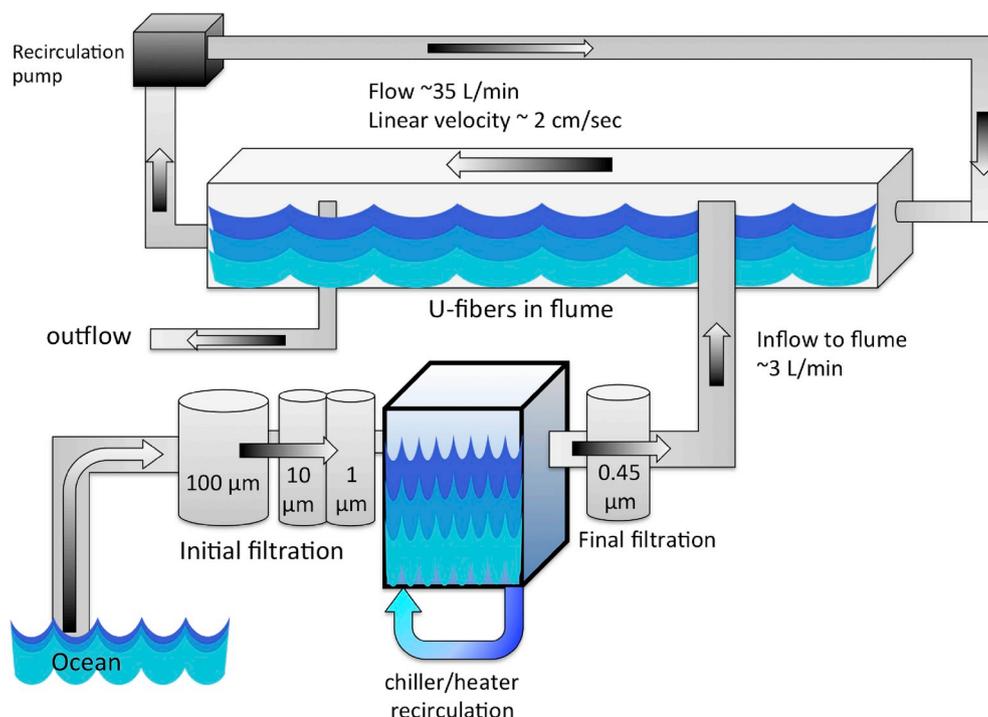
#### 2.4. Flume experiment procedures

The flume experiments were performed at WHOI Shore Lab where a seawater delivery system provides ambient seawater to a shore-based laboratory. The flume was designed by [Gill et al. \(2016\)](#) at the Pacific Northwest National Laboratory (PNNL) in Sequim, Washington, USA and follows the method described in [Gill et al. \(2016\)](#). In brief, seawater is actively pumped to the lab and filtered to  $0.45\ \mu\text{m}$  to remove most biological organisms. Water is then fed at three locations into a 185 cm long by 15 cm wide and 22 cm deep flume at a rate of approximately 3 l/min. A recirculating centrifugal water pump was used to recirculate water within the flume ([Fig. 2](#)). The linear velocity of the current in the flume could be adjusted from 2 cm/s to 5 cm/s. The flume was made of opaque plexiglass to prevent light from entering during the experiment in order to reduce biological growth. Temperature controls after the initial filtration were available to warm or cool the water depending on need. For Experiment 1, the dock parallel study, water temperatures were matched to the concurrent dock temperatures. For the second flume experiment, water was set to  $20\ ^\circ\text{C}$  but averaged  $22.5\ ^\circ\text{C}$  due to ambient room temperature and malfunction of the water chiller.

In the flume, braided adsorbent was secured to polyethylene tubing adhered to the base of the flume. Salinity, pH and temperature were measured on weekdays, as was the water for trace metals. Probes were calibrated as required. Snippets ( $\sim 100\ \text{mg}$ ) of fiber were removed weekly and analysed for uranium and other metals.

#### 2.5. Fiber sampling

Fibers were sampled in both the flume and dock either by cutting small pieces (approx. 100 mg) from a single large braid using titanium coated stainless steel scissors or removing one to three of the pre-weighed bundles at each time point. The remaining fibers were kept



**Fig. 2.** Shore Laboratory flume set up at WHOI.

wet during all sampling and the apparatus was immediately redeployed. Once sampled, fibers were stored in clean 15 ml vials.

## 2.6. Uranium extraction from fibers for reuse

Fiber bundles for uranium extraction and reuse (Exp. 4) were removed from the ocean and placed in 10 ml of Milli-Q clean water in individual 15 ml test tubes. They were brought back to the lab where they were shaken and rinsed two more times with 10 ml of DI water to remove sediments and any loose biological material. In new centrifuge tubes the fibers were centrifuged and remaining liquid was poured off. The fibers were submerged in 10 ml of 3M  $\text{KHCO}_3$  at 40 °C for 24 h to strip the uranium per previously established protocols (Pan et al., 2017).  $\text{KHCO}_3$  was used in place of less costly  $\text{NaCO}_3\text{-H}_2\text{O}_2$  because it was found to be more efficient with less fiber damage in a laboratory setting. As well the desorption of U was greater with  $\text{KHCO}_3$  versus the  $\text{NaCO}_3\text{-H}_2\text{O}_2$  treatment. The supernatant was poured into trace-metal clean vials for analysis. The fibers were then soaked in 0.5M NaOH at 20 °C for 3 h then rinsed and stored in 10 ml DI water until they were redeployed in the ocean. Some fibers were not deployed but instead digested in acid, as described in the following section, to analyse trace metals that were not removed during the extraction process.

The extracted solute (~10 ml) was filtered through a 0.45  $\mu\text{m}$  25 mm nylon filter with polypropylene housing using a syringe and sent to PNNL for analysis. There, a 1 ml aliquot was taken and slowly neutralized with 0.25 ml of  $\text{HNO}_3$  before diluting with 5% $\text{HCl}$ :2% $\text{HNO}_3$ . Samples were analysed on a PerkinElmer 4300 inductively coupled plasma optical emission spectrometer (ICP-OES). Quantification was based on a standard calibration curve covering the sample concentration range. Standard reference material showed between 95% and 99% recovery throughout the run. Replicate samples showed relative percent differences of 1%–2%. Tests by the laboratory found that Mg and Zn showed approximately 10% wall-binding in the tubes due to the basic nature of the material.

## 2.7. Uranium and trace metal analysis on fibers

The adsorbent fibers were rinsed three times with 10 ml of DI water to remove loosely-held sediment, salts and biological growth. Rinsing was not necessary for fibers that had been through the elution process and not re-deployed. Fiber bundles were untied if necessary and the fibers were then dried at 50 °C for 48 h to achieve a steady weight. They were then weighed to compare initial and final weights. Fibers were then sent to PNNL where they were digested in 10 ml of high-purity (Optima, Fisher Scientific) 50% aqua regia acid mixture (3:1; hydrochloric: nitric acids) for 3 h on a heating block at 85 °C. Trace metal analysis was conducted on a Thermo Scientific ICapQ inductively coupled mass-spectrometer (ICP-MS) and based on a standard calibration curve which covered the sample concentration range.

## 2.8. Seawater sampling and analysis

Seawater samples were taken at the dock using a peristaltic pump with tubing going to either 5 m or 12 m depths. These were filtered in-line with a SingleUse® 0.45  $\mu\text{m}$  hydrophilic PES disposable groundwater filter into HDPE acid cleaned bottles. Samples were acidified with nitric acid (Ultrex II J.T. Baker Ultrapure) to 0.2% and sent to PNNL for analysis. At PNNL samples were diluted 20 fold with high-purity deionized water and analysed using a Thermo ICapQ ICP-MS as described in Gill et al. (2016). Analysis of U and other trace-elements in seawater is non-trivial due to the matrix effects of Na (Wood et al., 2016). For this reason a standard addition calibration method was used whereby instrument calibration curves were prepared using seawater 20-times diluted with deionized water and then spiked at 0.1, 0.2, 0.3 and 0.4  $\mu\text{g/L}$  U, as well as a 2% nitric acid blank in dilute seawater, for a five point calibration. Standard reference material (CASS-5, nearshore

seawater reference material for trace metal from the National Research Council Canada) was analysed every 10 samples and showed recovery of 96% and higher during analysis. Replicate samples showed relative percent differences between 1% and 2%.

## 3. Results & discussion

### 3.1. Effects of biofouling

Uranium adsorbing amidoxime-based fibers have mostly been tested in a laboratory setting devoid of living organisms. In the ocean however biological organisms, dissolved particulate and organic matter may compete for nucleation sites on the fibers or coat fibers, reducing their ability to adsorb uranium. Biofouling contributors could include microorganisms, algae, or animals, all of which were observed on the fibers during all ocean deployments. Larger “loose” organisms such as mussels, shrimp, algae, tunicates and crabs were also all observed on fibers when they were removed from the ocean, however their abundance was not measured. It was beyond the scope of this project to identify organisms found on the fibers. While enclosing fibers with small pore size mesh could prevent some fouling, the less than 100  $\mu\text{m}$  pore size required would also severely impede water flow, necessary for greater U adsorption.

Experiment 1 (2015) compared fibers exposed to filtered seawater in a flume to those exposed to natural coastal ocean waters. While the braids in the flume had higher uranium uptake overall, it was not until after the 42nd day that this became more significant (Fig. 3). After the 49-day experiment the flume fibers had adsorbed 3.4 g-U/kg-ads whereas the dock fibers had adsorbed only 2.3 g-U/kg-ads. Flume results are comparable to Kuo et al. (2018) who found flume fibers at 20 °C adsorbed 3.6  $\pm$  0.1 g-U/kg-ads after 56 days. The dock fibers did not gain, and may have even lost, U after 35 days. This may have coincided with increased biological activity as waters warmed. Increased water temperatures have been found in other flume and modelling studies to have a positive correlation with uranium adsorption (Kuo et al., 2018; Ladshaw et al., 2017a), reflected here as the flume fibers were able to continue adsorption unimpeded by biofouling. As fibers for Experiment 1 were cut off one larger braid and not pre-weighed, measurements of fouling or loss of material were not possible.

In Experiment 2, 4 and 5 in autumn 2015 & 2016 biofouling was quantified by weighing the fibers dry prior to the experiment and weighing them again, dry, following exposure in the ocean. While no way was devised to account for lost material during the experiment it was found that an average of 5% weight was lost during the KOH conditioning. It is possible more material was lost during deployment as grazing marine organisms were observed on the fibers and so biofouling determined by weight in this study may be an underestimate to a small degree.

Following ocean exposure, greater amounts of fouling resulted in lower adsorption of uranium (Fig. 4). Copper is a known toxin to many marine organisms and so Experiment 2 explored using copper, steel and nylon enclosures at 5 and 12 m. A large (5 mm) mesh size was used to allow water flow but prevent larger organisms (fish) from entering the enclosures as they were observed nibbling the algae-covered fibers late in Experiment 1. The use of copper cages did reduce biofouling in 5 m samples with 81%  $\pm$  5% wt. increase versus 254%  $\pm$  11% in the nylon and 321%  $\pm$  10% in the steel. Despite the lesser biofouling, the uranium uptake of fibers by day 49 in the copper enclosure was only 1.7 g-U/kg-ads and they were saturated with copper. The nylon and steel enclosures adsorbed 0.60 and 0.54 g-U/kg-ads respectively, a clear indication of the negative effects of biofouling on uranium uptake.

In the deeper samples, at 12 m depths, biofouling was reduced due to reduced sunlight penetration and the effect of copper was negligible. Sample weights increased by 71%  $\pm$  7% in copper cages, 58%  $\pm$  9% in nylon and 55%  $\pm$  10% in steel. Uranium uptake was within error for all three 12 m enclosures at 1.5  $\pm$  0.1 g-U/kg-ads.

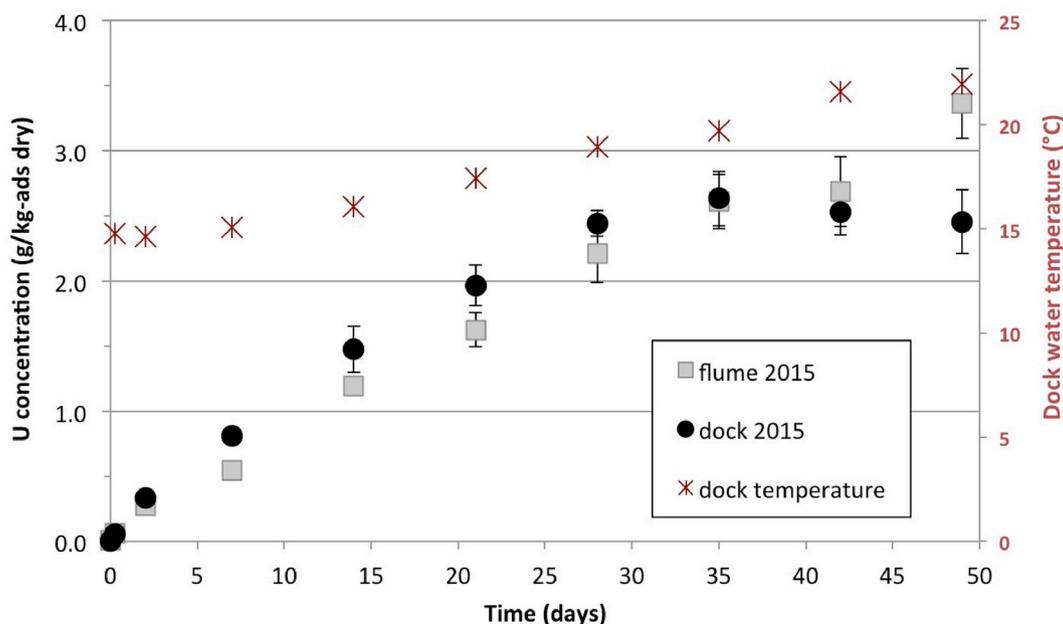


Fig. 3. Concentration of uranium adsorbed to fibers over a 49-day experiment in nylon bags at the WHOI dock (black circle) and the flume (squares). Flume temperature measurements mimicked the dock temperature, shown on the secondary Y-axis. Error bars indicate the relative percent difference between duplicate samples, for samples without duplicate analyses the average percent difference (8%) is used.

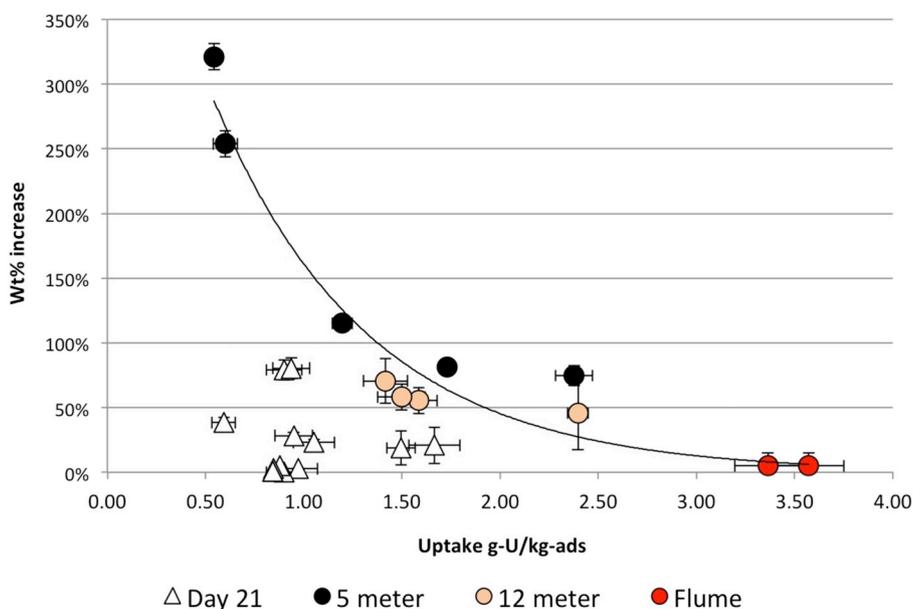


Fig. 4. Weight percent increase versus uranium uptake. Uranium adsorbed (g-U/kg-ads) by day 49 (circles) and day 21 (triangles) versus percent weight increase of fibers over that time at 5 m (black), 12 m (gray) and in the flume (striped). The trendline is for day-49 results only and the goodness of the fit ( $r^2$ ) of this exponential relationship is 0.89.

A flume test at PNNL found a 30% decrease in U adsorption when comparing a flume with sunlight (and therefore biofouling) to one without sunlight (and limited biofouling) after 42 days of exposure to natural seawater filtered to 150  $\mu\text{m}$  (Park et al., 2016). This study found that fouling reduced adsorption by as much as 70% when comparing the steel or nylon to copper enclosed fibers at 5 m during the same time period. Fibers from the darkened flume filtered to 0.45  $\mu\text{m}$  were found to have no biofouling observable by eye and weight measurements showed  $\pm 5\%$  change. The effects of biofouling on uranium uptake were not observed by day 21 when measuring trends across all experiments. By day 49, a clear inverse relationship between biofouling and uranium adsorption was observed.

### 3.2. Effects of temperature

Previous studies using synthetic sterile laboratory seawater, filtered seawater (Kim et al., 2014; Kuo et al., 2018) and with models (Ladshaw et al., 2017b) have shown that increased temperature results in higher uranium adsorption. Overall the reactions between the main species of uranium in seawater, uranyl ( $\text{UO}_2(\text{CO}_3)_3^{4-}$ ) and amidoxime ligands are endothermic and thus capacity increases with increasing temperature (Leggett et al., 2016). Due to the multi-variable nature of the coastal ocean environment, many factors affect adsorption; however the numerous experiments performed at WHOI at different times of year in the same marine environment allowed for an examination of the effects

of temperature. A trend of increasing adsorption with increasing temperature was observed (Fig. 5). The dock fibers with less than 115% weight increases due to biofouling followed this trend. Results from the two samples with the greatest fouling (nylon mesh with 254% wt. increase and steel cages with 321% wt. increase in Experiment 2) were not included with these results due to the overwhelming effect of fouling. Biofouling also positively correlates with temperature increases. Given the reduced amount of biofouling on the 12 m samples, submerging samples to decrease light penetration appears to be an effective way of reducing biofouling, as temperature differences were negligible ( $\pm 0.1$  °C) between the two depths. Water velocity has been shown to have an influence on the adsorption of U to the fibers (Ladshaw et al., 2017b) but these results are not obvious in our sampling due to the more influential effects of temperature and biofouling. Of the two data points representing flume samples in Fig. 5, the one with higher adsorption (3.6 g-U/kg-ads) showed both higher average temperature ( $22.5 \pm 2.1$  °C) and higher flow rates (4.6 cm/s) compared with the fiber that adsorbed 3.4 g-U/kg-ads at a flow rate of 2.0 cm/s and temperature of  $18.4 \pm 1.4$  °C.

### 3.3. Fiber reuse

The capital cost of fiber production is calculated to be the largest economic factor associated with using uranium adsorbing fibers (Kim et al., 2014; Byers and Schneider, 2016). Therefore the ability to effectively strip uranium from the fibers without damaging them, allowing them to be reused, is an important concern. Previously, acid-based leaches have been used for this task but were found to damage the fibers beyond use (Pan et al., 2017; Kuo et al., 2018). Pan et al. (2017) tested a 3M  $\text{KHCO}_3$  solution and found near total extraction of uranium and no loss of capacity after six 42-day cycles using simulated seawater. Upon exposure to  $\text{KHCO}_3$ , uranyl ions, bound to amidoxime ligands, are converted to uranyl tris-carbonato complexes and dissolve in the solution. Kuo et al. (2017), using the same 3M  $\text{KHCO}_3$  extraction with natural filtered seawater, report an extraction proportion of 85% of adsorbed uranium. This experiment found an average extraction of 54% for fibers following their first use exposed to natural unfiltered coastal seawater (Table 2). Higher extractable uranium was observed during the earlier, warmer experiments, and where higher overall uranium

adsorption was also observed. The decrease per use in the ability to extract U is an important consideration if the goal is to reuse the same fibers multiple times (Byers and Schneider, 2016; Byers et al., 2018).

Because reuse experiments at WHOI were performed over a fall season with decreasing water temperatures, new unused fibers were deployed as controls with the reused fibers. With the initial (single) use at 5 m  $59\% \pm 4\%$  of uranium was extracted after 28 days and  $54\% \pm 6\%$  after 42 days. On second deployment at 5 m, after 28 days the reused fibers showed 50% extractable U whereas the control fibers had 62%. For the third use the controls showed 53% extractable U while the reused fibers showed 38% at 5 m. At 12 m results were effectively the same (within error) for the first use (Table 2). The second use showed 55% extractable U for the control but only 38% for the reused fiber, and the third use showed 38% for the control and 36% for the reused fiber. It is unclear why the control fiber elution proportion declined but this may have been due to the overall reduction in adsorbed uranium of both the reused and control fibers, due to the decreased water temperature by time of the third use in the autumn. The 42-day experiment showed little difference between the control and reused fibers where 49% and 46% of the uranium was extracted from the controls at 5 and 12 m (respectively) and 46% and 43% was extracted from the reused fiber at 5 and 12 m on the second use. We have no explanation why the extraction efficiency is more consistent with the controls after 42-day exposures versus 28 days but overall lower adsorption over this colder time-period may be a factor. Examination of the amidoxime ligand through Fourier transform infrared spectroscopy (FTIR) by Kuo et al. (2017) following fiber reuse, indicated increasing degradation with increased usage perhaps explaining some of the reduced adsorption capacity.

Other elements were less effectively removed from fibers using  $\text{KHCO}_3$  (Fig. 6) with magnesium averaging 37%, zinc 22%, calcium 4% and copper, iron and vanadium all less than 1%. These percentages were consistent with subsequent fiber reuse and showed no significant trend toward increased or decreased extracted concentration. These findings are in contrast to those of Pan et al. (2017) who, using filtered natural seawater, found elution proportions of 95% for Mg, 35% for Zn, 25% for Cu, 47% for Fe and 33% for V. This variation in extractability may have been due to the use of filtered seawater by Pan et al. (2017). As well, in this study fibers were extracted and the  $\text{KHCO}_3$  solute was measured for trace elements. The fiber was then acid digested to analyse for un-eluted

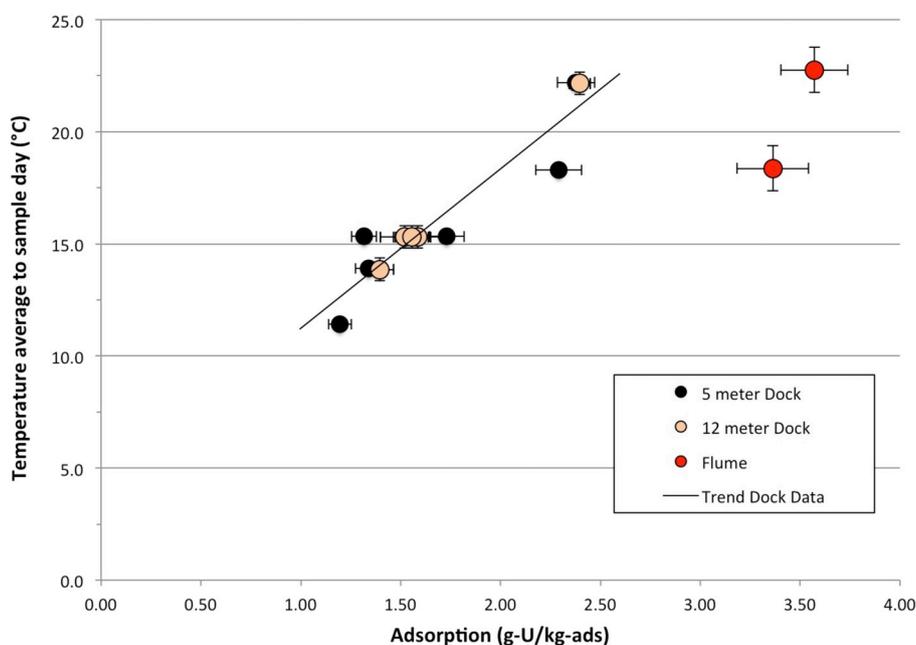
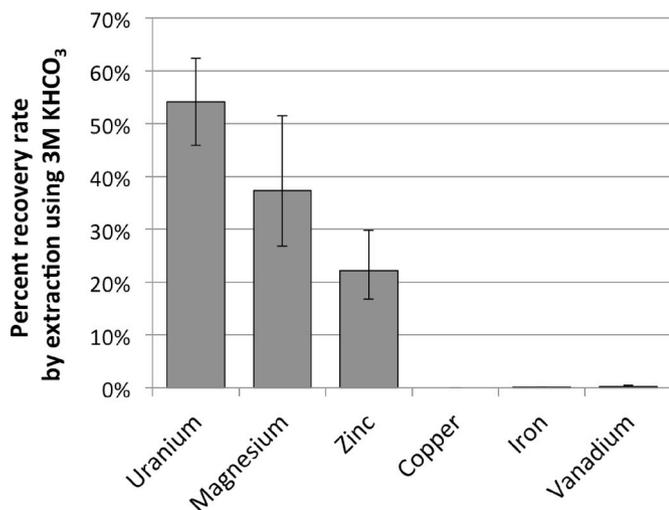


Fig. 5. Temperature average versus uranium adsorption (g-U/kg-adsorbent) after 49 days at 5 and 12 m in the coastal ocean, and in the WHOI flume. The trend line is indicated for the dock water samples only with an  $r^2$  fit of 0.88. Data from 5 m Exp. 2 were not included due to the extreme biofouling effects.

**Table 2**

Percent uranium extractable by  $\text{KHCO}_3$  elution relative to total uranium by acid digestion on fibers following 28-day and 42 day exposures. Uncertainties indicate one standard deviation of triplicate samples; \* indicates average uncertainty used.

	First Use	Second Use		Third Use	
	% U Extracted	% U Extracted control	% U Extracted Reuse	% U Extracted control	% U Extracted Reuse
28 day 5 m	59% $\pm$ 7%	62% $\pm$ 11%*	50% $\pm$ 11%*	53% $\pm$ 11%*	38% $\pm$ 11%*
28 day 12 m	61% $\pm$ 15%	55% $\pm$ 11%*	38% $\pm$ 11%*	38% $\pm$ 11%*	36% $\pm$ 11%*
42 day 5 m	54% $\pm$ 6%	49% $\pm$ 8%	46% $\pm$ 10%	–	–
42 day 12 m	62% $\pm$ 16%	46% $\pm$ 10%	43% $\pm$ 15%	–	–



**Fig. 6.** Recovery of elements by extraction using 3M  $\text{KHCO}_3$  relative to full acid digestion of fibers. Averaged from 5 to 12 m control (single use) fibers in the 28-day reuse experiments. Error bars indicate one standard deviation.

elements. Pan et al. (2017), in contrast, used acid to digest fibers, then used a second sample for the extraction procedure. The extracted fiber was then acid digested and total extracted U in this case was the difference between the two digested samples rather than direct measurement of the  $\text{KHCO}_3$  solution. In summary,  $\text{KHCO}_3$  is not an effective way to desorb U from fibers exposed to seawater as there would be a considerable decrease in the efficiency of the fibers.

Because of the incomplete U extraction by  $\text{KHCO}_3$ , we find that when fibers are acid digested the total adsorption of uranium onto reused fibers is comparable to the control fibers (Fig. 7). However taking into account that the reused fibers start with considerable U at time zero, the overall addition of U during the repeated use is less than half that of the control fibers in all cases.

Given the decreasing uranium adsorption with reuse, as well as the less extractable uranium on the fibers, it is not clear from this study that reusing fibers is more effective than a single, longer deployment followed by acid digestion for total U extraction (Table 3). For example using the same fiber three times for 28 days with  $\text{KHCO}_3$  extraction results in  $2.8 \pm 0.3$  g-U/kg-ads versus  $2.7 \pm 0.4$  g-U/kg-ads with a single, 56-day use (Table 3), which are not significantly different from each other.

### 3.4. Other considerations: salinity, pH, flow rate

A challenge of multiple experiments in a coastal ocean environment over several seasons is controlling for the various factors that may affect adsorption over time. In addition to temperature and biological growth, salinity, pH and flow rates are factors that affect the fibers (Endrizzi et al., 2016; Zhang et al., 2005; Ladshaw et al., 2017b). Salinity in the area is relatively constant ranging from 31.7 to 32.6 psu during these experiments, constraining the average uranium concentrations to

between 2.7  $\mu\text{g/L}$  and 3.0  $\mu\text{g/L}$ . The presence of salts and bicarbonate has been found to retard uranium adsorption (Ladshaw et al., 2016) however the variation of salinity across the experiments is minimal and would have limited effect on uranium adsorption when comparing experiments. pH of the solution can affect both the speciation of U(VI) as well as the surface charge of the fiber materials. pH in these experiments varied by approximately 1 pH unit with the WHOI dock experiment in fall 2015 having the highest pH at  $8.2 \pm 0.3$  and the WHOI dock in spring 2015 having the lowest pH at  $7.3 \pm 0.3$ . This variation in pH is small and changes in adsorbed uranium speciation were beyond the scope of this study. Other studies have found that sorption rates are highest to amidoxime functional groups at pH 7.0 and higher (Zhang et al., 2005) and that there is little change in aqueous species distribution between pH 6 and 8, where  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  complexes with  $\text{UO}_2^{2+}$ - $\text{CO}_3^{2-}$  represent over 90% of species (Endrizzi et al., 2016). While flow rate has been shown to have a significant effect on uranium adsorption (Ladshaw et al., 2017b), the effects of biofouling and temperature are greater and mask that of flow in these studies. The two flume experiments with flows of 2.0 cm/s and 4.6 cm/s had the highest uranium adsorption rates ( $3.4 \pm 0.2$  g-U/kg-ads and  $3.6 \pm 0.2$  g-U/kg-ads respectively). In contrast, all dock experiments with flows between 8.2 cm/s and 9.8 cm/s showed at most  $2.8 \pm 0.4$  g-U/kg-ads in what was the warmest overall experiment in fall 2016.

## 4. Conclusions

This study, conducted under varying coastal ocean conditions, tested amidoxime-based polymer adsorbent A18 to understand the effects of temperature, biofouling and reuse on the adsorption of uranium. While teasing apart the specific mechanisms for each variable was not possible due to the complex matrix of seawater and changing ocean conditions, results show a clear trend of increased adsorption with increased temperature, and decreased adsorption with increased biofouling. It should be noted that biofouling will differ with local conditions, and it is lessened in lower temperatures, as well as with less light, suggesting that cooler, deeper water, with less light penetration, may be an improvement to this issue. The use of copper was shown to be an ineffective solution to biofouling at 5 m due to the adsorption of copper to the fibers. The release of Cu may have been catalysed by light as this effect was not observed for samples at 12 m depth. It was outside the scope of this research to quantify the surface coverage or identify organisms on the fibers but this is an important avenue for future studies.

The effects of reusing fibers after both 28-day and 42-day deployments appear to indicate that a single, long deployment of 56 days followed by acid digestion of samples results in a similar yield of uranium compared to multiple exposures followed by the less efficient extraction method developed to reuse these fibers. Considering the likely increased cost associated with recovery, elution and re-deployment, further study is needed to improve this extraction method if fibers are to be reused in ocean environments.

Finally, other effects not considered in these experiments that warrant further investigation include the loss of material in the ocean, either by physical abrasion or by animals that were observed eating fibers or associated biological material on fibers. On a large scale deployment, these losses would decrease U recovery and could become a significant

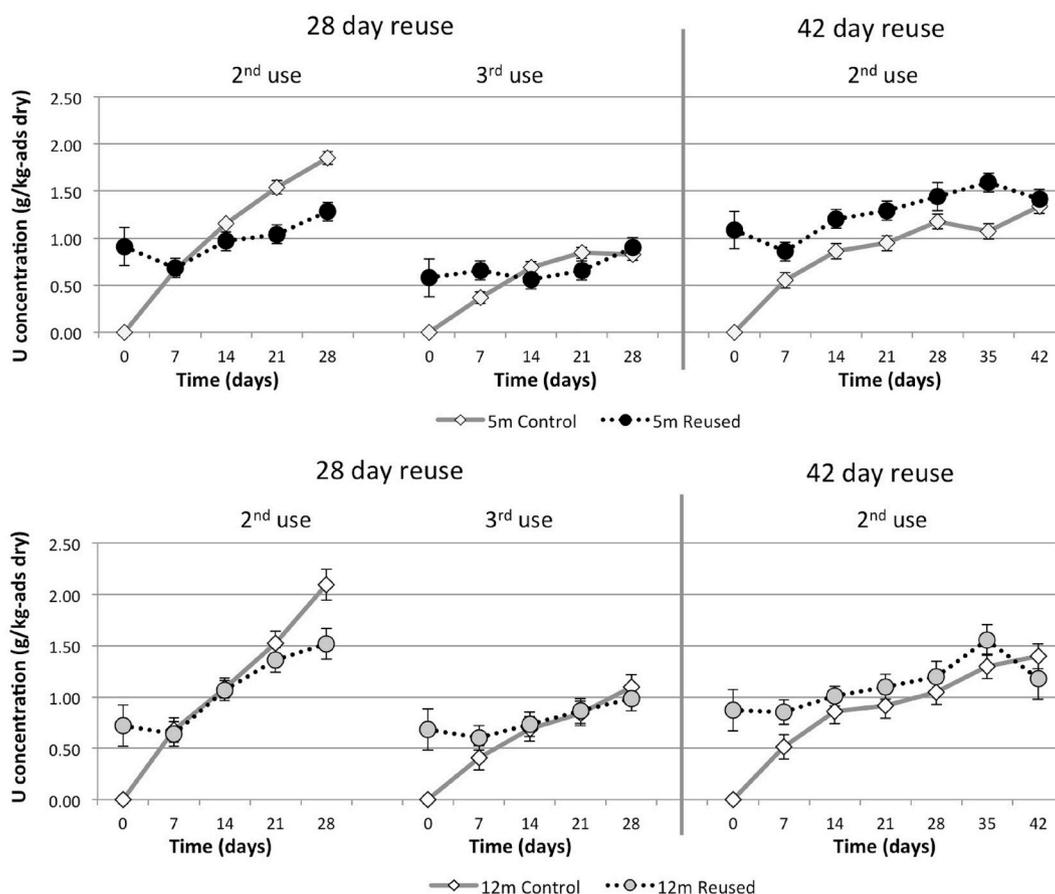


Fig. 7. Uranium adsorption on fibers with U sorption determined by acid digestion. Comparing control (1st use fibers) and reused fibers deployed simultaneously for either 28 (left) or 42 (right) days and at 5 m depth (top) or 12 m depth (bottom). Error bars indicate one standard deviation of triplicate samples.

Table 3

Total harvestable uranium calculated from the sum of extractable uranium by KHCO<sub>3</sub> between uses and with acid digestion of the fibers following their terminal use. Uranium from the 56-day experiment was harvested by acid digestion only. All data in g-U/kg-ads.

	28 day deployments		42 day deployments		56 day deployment	
	5 m	12 m	5 m	12 m	5 m	12 m
1st use extraction	1.31 ± 0.08	1.14 ± 0.10	1.27 ± 0.06	1.42 ± 0.12	–	–
2nd use extraction	0.64 ± 0.13	0.56 ± 0.02	0.65 ± 0.07	0.51 ± 0.08	–	–
3rd use extraction	0.34 ± 0.08	0.36 ± 0.03	–	–	–	–
Final fiber acid digestion	0.56 ± 0.09	0.62 ± 0.06	0.49 ± 0.05	0.67 ± 0.07	2.78 ± 0.42	2.65 ± 0.31
SUM	2.86 ± 0.38	2.69 ± 0.21	2.41 ± 0.18	2.60 ± 0.27	2.78 ± 0.42	2.65 ± 0.31

source of plastic in the ocean. This research contributes to the growing body of ocean-deployment studies that will enable us to determine suitable placement for fibers, both geographically and in the water column. While harvesting uranium from the ocean using amidoxime-based fibers has the potential to be an alternate source to traditional terrestrial uranium mining, before we can accurately determine the economics of large scale U extraction (such as Flicker Byers et al., 2018), further study is warranted under varying ocean conditions.

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**Appendix A. Supplementary data**

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.pnucene.2019.103170>.

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