Adsorbent Alkali Conditioning for Uranium Adsorption from Seawater:

Adsorbent Performance and Technology Cost Evaluation

Fuel Cycle Research & Development

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SUMMARY

The Fuel Resources program of the Fuel Cycle Research and Development program of the Office of Nuclear Energy (NE) is focused on identifying and implementing actions to assure that nuclear fuel resources are available in the United States. An immense source of uranium is seawater, which contains an estimated amount of 4.5 billion tonnes of dissolved uranium. This unconventional resource can provide a price cap and ensure centuries of uranium supply for future nuclear energy production. NE initiated a multidisciplinary program with participants from national laboratories, universities, and research institutes to enable technical breakthroughs related to uranium recovery from seawater. The goal is to develop advanced adsorbents to reduce the seawater uranium recovery technology cost and uncertainties. Under this program, Oak Ridge National Laboratory (ORNL) has developed a new amidoxime-based adsorbent of high surface area, which tripled the uranium capacity of leading Japanese adsorbents.

Parallel efforts have been focused on the optimization of the physicochemical and operating parameters used during the preparation of the adsorbent for deployment. A set of parameters that need to be optimized are related to the conditioning of the adsorbent with alkali solution, which is necessary prior to adsorbent deployment. Previous work indicated that alkali-conditioning parameters significantly affect the adsorbent performance. Initiated in 2014, this study had as a goal to determine optimal parameters such as base type and concentration, temperature, and duration of conditioning that maximize the uranium adsorption performance of amidoxime functionalized adsorbent, while keeping the cost of uranium production low.

After base-treatment at various conditions, samples of adsorbent developed at ORNL were tested in this study with batch simulated seawater solution of 8-ppm uranium concentration, batch seawater spiked with uranyl nitrate at 75-100 ppb uranium, and continuous-flow natural seawater at the Pacific Northwest National Laboratory (PNNL). Fourier Transform Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Scanning Electron Microscopy (SEM), and elemental analysis were used to characterize the adsorbent at different stages of adsorbent preparation and treatment. The study can be divided into two parts: (A) investigation of optimal parameters for KOH adsorbent conditioning and (B) investigation of other possible agents for alkali conditioning, including cost analysis on the basis of uranium production. In the first part of the study, tests with simulated seawater containing 8 ppm uranium showed that the uranium adsorption capacity increased with an increase in the KOH concentration and conditioning time and temperature at each of the KOH concentrations used. FTIR and solid state NMR studies indicated that KOH conditioning converts the amidoxime functional groups into more hydrophilic carboxylate. The longer the KOH conditioning time, up to three hours, the higher was the loading capacity from the simulated seawater solution which is composed of only uranyl, sodium, chloride, and carbonate ions.

Marine testing with natural seawater, on the other hand, showed that the uranium adsorption capacity of the adsorbent increased with KOH conditioning temperature, and gradually decreased with increasing KOH conditioning time from one hour to three hours at 80 ºC. This behavior is due to the conversion of amidoxime to carboxylate. The carboxylate groups are needed to increase the hydrophilicity of the adsorbent; however, conversion of a significant amount of amidoxime to carboxylate leads to loss in selectivity toward uranyl ions. Thus, there is an optimum KOH conditioning time for each temperature at which an optimum ratio between amidoxime and carboxylate is reached. For the case of base conditioning with 0.44 M KOH at 80 ºC, the optimal conditioning time is 1 hour, with respect to the highest uranium loading capacity from natural seawater.

Uptake of other metal ions such as V, Fe, and Cu follows the same trend as that of uranium. Also, the uptake of Ca, Mg, and Zn ions increased with increasing KOH conditioning time, probably due to

formation of more carboxylates, which leads to conversion of uranium-selective binding sites to less selective sites.

In the second part of the study, inorganic based reagents such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), cesium hydroxide (CsOH), as well as organic based reagents such as ammonium hydroxide (AOH), tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), triethylmethylammonium hydroxide (TEMAOH), tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TBAOH), in addition to KOH, were used for alkaline conditioning. NaOH has emerged as a better reagent for alkaline conditioning of amidoxime-based adsorbent because of higher uranium uptake capacity, higher uranium uptake selectivity over vanadium, and lower cost over the other candidate alkaline reagents.

The findings lead to significant economic impacts, as the use of NaOH conditioning in place of KOH results in a 21-30% decrease in the cost of uranium production.

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ACRONYMS

AOH	Ammonium hydroxide
ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
Bi	Biot number
CMPEI	Carboxymethylated polyethyleneimine
DOG	Degree of grafting
DNA	Deoxyribonucleic acid
FR	Fluidized reactor
HDPE	High density polyethylene
HSAB	Hard / soft acid and base theory
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
JP	Japanese prepared sorbent
NICA	Non-ideal competitive adsorption
ORNL	Oak Ridge National Laboratory
PBR	Packed bed reactor
PNNL	Pacific Northwest National Laboratory
poly(TFE-E)	poly(tetrafluoroethylene-*co*-ethylene)
RIGP	Radiation-induced graft polymerization
RSMAS	Rosenstiel School of Marine & Atmospheric Science of the University of Miami
SP	Suspension polymerization
TGA	Thermogravimetric analysis
TMAOH	Tetramethyl ammonium hydrohide
TEAOH	Tetraethyl ammonium hydroxide
TEMAOH	Triethyl methyl ammonium hydroxide
TPAOH	Tetrapropyl ammonium hydroxide
TBAOH	Tetrabutyl ammonium hydroxide
UM	University of Miami

1. INTRODUCTION

The current mission of the Fuel Resources subprogram of the Fuel Cycle Research and Development program of the DOE Office of Nuclear Energy (NE) is to identify and implement actions to assure that economic nuclear fuel resources remain available in the United States. Seawater contains more than 4 billion tonnes of dissolved uranium at a concentration of 3.3 ppb. Combined with a suitable extraction cost, this unconventional seawater resource can potentially provide a price cap and ensure centuries of uranium supply even with aggressive world-wide growth in nuclear energy applications.

NE-5 initiated a multidisciplinary team from national laboratories, universities, and research institutes in 2011. The team seeks to take advantage of recent developments in (1) high performance computing, (2) advanced characterization instruments, and (3) nanoscience and nanomanufacturing technology to enable technical breakthroughs related to uranium recovery from seawater. The program goal is to develop advanced adsorbent materials to reduce the seawater uranium recovery technology cost and uncertainties. The R&D investment strategy is focused on developing advanced adsorbents that can simultaneously enhance uranium adsorption capacity, selectivity, kinetics, and materials durability. As a result of this investment strategy, Oak Ridge National Laboratory (ORNL) has developed a new amidoxime-based adsorbent of high surface area, which tripled the uranium capacity of leading Japanese adsorbents that were proven in field marine testing. Parallel efforts have been focused on the optimization of the physicochemical and operating parameters used during the preparation of the adsorbent for deployment.

Previous work indicated that alkali-conditioning parameters affect the adsorbent performance. A study was initiated in 2014 with the goal to determine optimal parameters such as base type and concentration, temperature, and duration of conditioning that maximize the uranium adsorption performance of an amidoxime functionalized adsorbent with minimum structural effects. Several alternative base solutions were investigated, and it was determined that NaOH solution is the most cost-effective, performance-enhancing base for adsorbent alkali conditioning. This work has been concluded and the results have been compiled in this milestone report.

2. BACKGROUND INFORMATION

A 2011 study by the Organization for Economic Co-operation and Development estimated that, at the current consumption rate, the global conventional reserves of uranium (7.1 million tonnes) could be depleted in roughly a century. Therefore, it is of significant interest to look for resources of uraniun other than the conventional terrestrial uranium ores. Seawater is a potential source of a vast amount uranium (around 4.5 billion tonnes), albeit at a low concentration of 3.3 ppb[1].

Capturing uranium from seawater is a challenging task that requires consideration of chemical, transport, and process design aspects. The concentration of uranium in seawater is on the order of 1.4×10^{-8} mol L^{-1} (3.3 ppb) and is the anionic triscarbonato-uranate (VI) $(UO_2(CO_3)_3)^{4-}$ species under the prevailing conditions[2]. The major problems pertaining to the development of a suitable uranium recovery system from seawater are due to the low concentration, the stability of triscarbonato uranate (VI), and the large excess of competing ions[2-4].

Poly(acrylamidoxime) (pAO) has been found to be chemically suitable for uranium recovery from seawater during the last few decades. The proposed deployment system uses braided textile adsorbents surface functionalized with an amidoxime ligand; the positively-buoyant adsorbent is moored to the ocean floor to passively collect uranium. In this work, pAO adsorbents have been prepared by electron beam

induced grafting of acrylonitrile (AN) and itaconic acid (ITA) onto a "hollow-gear" shaped poly(-ethylene-) host fiber with subsequent conversion of AN to AO groups by treatment with hydroxylamine.

One of the key factors affecting uranium uptake from seawater in pAO-based adsorbents is alkaline conditioning. It is well documented that alkaline conditioning of pAO adsorbent is necessary before its deployment for uranium extraction[5, 6] to enhance the uranium loading capacity. It is claimed that the enhancement is due to two primary reasons: i) increased hydrophilicity[6-19] and ii) conversion of open-chain amidoxime into cyclic imidedioxime.[17, 20, 21] Although several reports have been published on this topic, no systematic work has been performed so far to investigate the optimum reaction parameters of alkali conditioning for the pAO-based adsorbents. In this report, such parameters as concentration, temperature, and time of the KOH treatment have been studied with the objective to identify the optimum conditioning parameters to maximize uranium uptake capacity from seawater while minimizing structural effects on the adsorbent. In addition, investigation for alternate alkaline reagents, other than KOH, was carried out, and an economic assessment was performed on the basis of altered uranium adsorption from seawater and/or lower chemical cost.

3. Experimental Design

Two types of fiber adsorbents have been selected for evaluation toward optimizing the alkali-conditioning parameters, as discussed below in this report. Multiple chemical and physical characterization techniques have been employed to strengthen the conclusions related to the adsorbent performance for each parameter investigated. Experiments of uranium uptake from seawater have been performed in this study using batch and continuous-flow reactors at ORNL and at marine sites at PNNL (state of Washington) and RSMAS (University of Miami). The conditions and results of tests with seawater are described below.

3.1 Adsorbent Preparation

Polyethylene (PE) based adsorbent fibers were prepared by radiation-induced graft polymerization (RIGP) at the NEO Beam Electron Beam Cross-linking Facility (Middlefield, OH). The co-extruded polylactic acid (PLA) was completely removed by submerging the fibers in excess THF at 65-70 °C overnight before RIGP. The pre-weighed dry fiber samples were placed inside double-layered plastic bags within a plastic glove bag and sealed under nitrogen. The fibers were irradiated in the presence of dry ice using a translation table cycling the fibers for 16 passes under the electron beam to a dose of approximately 200 ± 10 kGy using 4.4-4.8 MeV electrons for approximately 22 minutes. After irradiation, the fibers were immersed in 300-mL pressure bottles containing de-gassed grafting solutions of AN and ITA in DMSO. The pressure bottles were then placed in an oven at 64 °C for 18 hours. After grafting, the fibers were drained from the solution and washed with DMF to remove unreacted monomers and homo polymers, rinsed with methanol, and dried at 50 °C under vacuum. The grafted polyacrylonitrile (pAN) fibers were weighed to calculate the percent degree of grafting (%DOG), determined gravimetrically from pre-irradiation and post-grafting weights of co-polymers onto the trunk polymer (Eq 1):

$$\%DOG = \frac{\left(wt_{AG} - wt_{BG}\right)}{wt_{BG}} x100 \tag{1}$$

where wt_{BG} = dry weight before grafting and wt_{AG} = dry weight after grafting.

The grafted AN groups in pAN fibers samples were converted to pAO groups by treating with 10 wt % hydroxylamine hydrochloride in 50/50 (w/w) water/methanol (previously neutralized with KOH) at 80 °C

for 72 h. The resulting adsorbent was designated as the AF series. The adsorbent samples were then washed under vacuum filtration with deionized water, rinsed with methanol, and allowed to dry at 50 °C under vacuum.

3.2 Alkaline conditioning of amidoximated fibers

The amidoximated fibers were treated with 0.44M alkaline solutions at temperatures of 60 ºC, 70 ºC, or 80 ºC for periods of 1 h, 2 h, or 3 h. The alkaline conditioned samples were immediately filtered and washed with DI water until the pH was neutral, with uranium adsorption studies immediately subsequent.

3.3 Capacity Evaluation

3.3.1 Simulated seawater screening for uranium adsorption determination

Batch experiments with synthetic seawater were conducted at the The University of Tennessee at Knoxville (UTK). The simulated seawater screening solution consisting of 193 ppm sodium bicarbonate, 25,600 ppm sodium chloride, and 8 ppm uranium from uranyl nitrate hexahydrate was prepared in 18.2 $M\Omega$ cm^{-1} water. The pH of the test solution was approximately 8. The concentrations of sodium and bicarbonate were selected to be similar to those of seawater. A sample of the solution was collected prior to adsorbent addition to determine the initial uranium concentration. Each of the alkaline-conditioned adsorbent samples was then equilibrated with 750 mL of simulated seawater solution for 24 hours at room temperature with constant shaking at 400 rpm. After contacting for 24 hours, an aliquot was taken and the initial and final solutions were analyzed using inductively coupled plasma-optical emission spectroscopy (Perkin Elmer Optima 2100DV ICP-OES) at 367 nm. The uranium adsorption capacity is determined from the difference between initial uranium concentration and final uranium concentration, using Eq 2. The ICP-OES was calibrated using 6 standard solutions ranging from 0-10 ppm, which were prepared from 1000 ppm uranium in 5 wt % nitric acid stock solution, and a linear calibration curve was obtained. A blank solution of 2–3 wt % nitric acid was also prepared, and control blanks were monitored between samples to ensure no uranium was carried over into the next analysis. In addition, a solution of 5 ppm yttrium in 2 wt % nitric acid was used as an internal standard, which was prepared from 1000 ppm stock solution (High-Purity Standards, North Charleston, USA).

$$\text{Uranium (U) adsorption capacity} = \left[\frac{Initial\ [U]\left(\frac{mg}{L}\right) - Final\ [U]\left(\frac{mg}{L}\right)}{g\ of\ dry\ adsorbent} \right] \times \text{Soln. vol. (L)} \qquad (2)$$

3.3.2 Uranium adsorption kinetics in batch reactors using seawater

Adsorption experiments were performed using two batches of seawater, each containing different concentrations of uranium. Natural coastal seawater from Charleston, South Carolina, was used after filtration (0.45um), while seawater spiked at ~75 ppb uranium was prepared by simply adding uranyl nitrate hexahydrate to the aforementioned costal seawater. Batch reactor experiments with natural seawater were performed at the Oak Ridge National Laboratory (ORNL). The amounts of natural and spiked costal seawater used for batch adsorption experiments are five gallons and one liter, respectively. Adsorbents (5-10 mg) were freely suspended in seawater after conditioning with 0.44M alkaline solutions at designated temperatures and time-periods. An initial seawater sample of 1 mL was collected prior to addition of adsorbent. The containers were shaken constantly at 100 rpm at room temperature. This shaking frequency was proven sufficient for fluidized fibers to adsorb uranium in the reaction-limited regime, *i.e.* in the presence of bicarbonate ions[6]. 1-mL samples were collected periodically using a volumetric pipette, over a period of 20 days for the spiked seawater and 56 days for natural seawater.

Inductively coupled plasma mass spectroscopy (ICP-MS, Thermo Scientific X-Series II) was used for quantitative analysis. Sample aspiration was performed at 100 μL/min with a Teflon SP nebulizer coupled to an Elemental Scientific Inc. PC[3] and Fast combination spray chamber. Matrix effects were corrected by adding internal standards containing Bi, In, Sc, Tb, Y (High Purity Standards ICP-MS-IS-2, Perkin-Elmer, consisting of 100 ppb Bi, In, Sc, Tb, Y in 2% nitric acid) offline before sample introduction. The average of six replicate measurements per sample was used to quantify uranium-238 against a 6-point calibration curve. Prior to sample analysis, semi-quantitative full-mass-range survey scans were collected. Control blanks were measured between samples. Standards NASS-5 (seawater) and CASS-6 (seawater), supplied by the National Research Council of Canada, were used for seawater quality-control experiments. High-purity nitric acid (2%, Optima, Fisher Scientific) was used as the sample diluent and carrier phase.

3.3.3 Flow-through column tests with natural seawater

Investigations were performed at PNNL-MSL over 56 days using natural seawater flowing through columns (Figure 1). Adsorbent performance was assessed and characterized in terms of adsorbent capacity and kinetics by varying alkaline conditioning parameters, such as temperature and time. The quality of seawater was quantitatively monitored for pH, temperature, salinity, and trace-metal concentrations over the experimental period. The average uranium concentration observed in this study was slightly lower than the normal uranium concentration of 3.3 ppb [for a salinity of 35 practical salinity units (psu)] in seawater. Marine testing was performed using filtered (0.45 μm) seawater at a temperature of 20 ± 2 °C and at a flow rate of 250 mL/min, using an active pumping system (Figure 1). Glass wool and glass beads were used as packing materials for the columns.
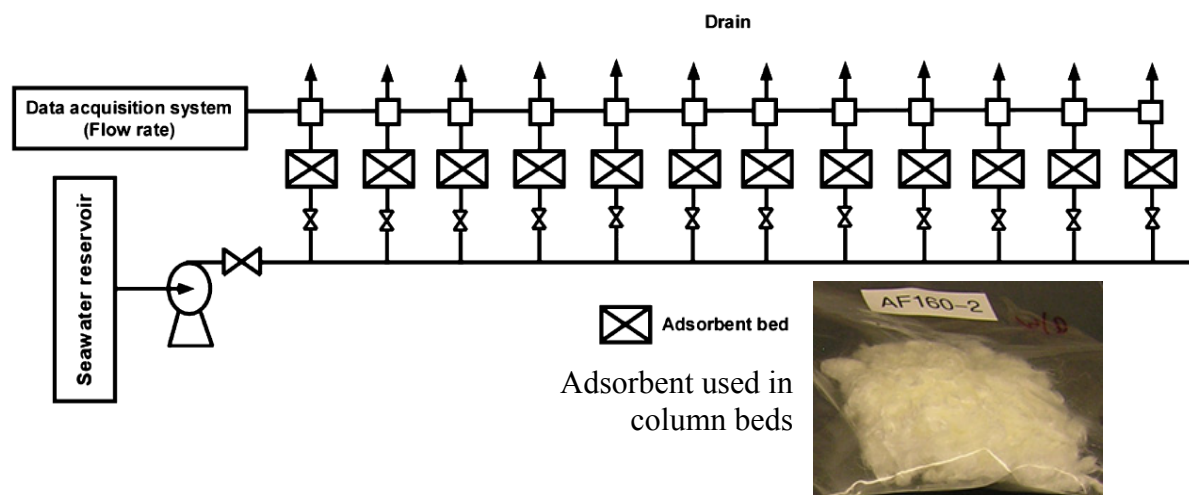
Figure 1. Schematic diagram of flow-through experiments using a parallel configuration at PNNL-MSL.

Approximately 50 mg of adsorbent samples were treated with 0.44 M of respective alkaline solution at various temperatures, e.g., 60, 70, and 80 °C for different time periods, e.g., 1, 2, and 3 hours prior to packing into columns 1-inch in diameter and 6-inches in length, fabricated from all-plastic components, mostly polyvinylchloride and polypropylene. Glass wool and 5-mm glass beads were used to ensure adsorbent fibers remained fixed in place inside the column. Seawater pumped from Sequim Bay, WA, was filtered through 0.45-μm polypropylene cartridges before entering the columns for the continuous-flow adsorption experiments. The temperature of the incoming seawater was maintained at 20±1 °C using an all-titanium immersion heater. A temperature logger equipped with a flexible hermetically sealed RTD sensor probe (OMEGA Engineering, Stamford, CT, USA) and an in-line turbine-style flow sensor (Model

DFS-2W, Digiflow Systems) were used to monitor the temperature and flow rate, respectively, with a 10-minute interval between measurements. The salinity and pH of the seawater were monitored daily using a hand-held salinometer (Model 30, YSI) and pH meter (Orion 3 STAR, Thermo). The adsorbents were removed from the columns after a certain period of exposure and desalted by thoroughly rinsing with DI water, followed by drying in a heating block. The dried and weighted adsorbents were digested with a 50% aqua regia solution at 85 °C for 3 hours. Samples were further diluted with DI water to be in the desired concentration range for analysis. The concentrations of uranium and metals were analyzed using a Perkin-Elmer Optima 4300DV ICP-OES, with quantification based on standard calibration curves.

4. Results and Discussion

4.1 Investigation for optimum alkaline conditioning parameters using potassium hydroxide

A high-surface-area polyethylene-fiber adsorbent (AF160-2) developed at the Oak Ridge National Laboratory (ORNL) by radiation-induced graft polymerization of acrylonitrile and itaconic acid was used for optimization of the conditioning parameters. The grafted nitriles were converted to amidoxime groups by treating with hydroxylamine. The amidoximated adsorbents were then conditioned with potassium hydroxide (KOH) by varying different reaction parameters such as KOH concentration (0.2, 0.44, and 0.6 M), duration (1, 2, and 3 h), and temperature (60, 70, and 80 ºC). Elemental analysis was performed at different steps of the preparation processes. Adsorbent screening was then performed with simulated seawater solutions containing sodium chloride and sodium bicarbonate, at concentrations found in seawater, and uranyl nitrate at a uranium concentration of ~ 7-8 ppm and pH 8. The uranium adsorption capacity in simulated seawater screening solution gradually increased with conditioning time and temperature, for all KOH concentrations. It was also observed that the adsorption capacity increased with an increase in concentration of KOH for all the conditioning times and temperatures.

Adsorption kinetics testing was performed with spiked seawater in batch reactors and natural seawater using flow-through experiments to determine uranium adsorption capacity with varying KOH conditioning time and temperature. Based on uranium loading capacity values of several AF160-2 samples, it was observed that changing KOH conditioning time from 3 to 1 h at 60, 70, and 80 ºC resulted in increase of the uranium loading capacity in seawater, which did not follow the trend found in laboratory screening with stimulated solutions. Longer KOH conditioning times lead to significantly higher uptake of divalent metal ions, such as calcium and magnesium, which is a result of amidoxime conversion into less selective carboxylate. FTIR and solid state NMR characterization studies were performed to monitor functional group transition during KOH conditioning. Morphology comparisons of adsorbent samples treated at different conditioning parameters have been performed using scanning electron microscopy (SEM) images.

4.1.1 Elemental analysis

The degree of adsorbent grafting was determined to be ~300%. The weight gain after amidoximation with 10 wt % hydroxylamine at 80 ºC for 72 h was ~30%. Results from elemental analysis are shown in Table 1. The nitrogen and oxygen percentage in the electron beam grafted material confirms that AN and ITA are grafted onto PE at an 85:15 weight ratio. The percent weight increase of nitrogen and oxygen in the amidoximated AF160-2 indicates significant conversion of acrylonitrile into amidoxime. The difference in the total percentage of elements confirms deprotonation of the amidoxime functional groups on conditioning with KOH. It can also be postulated that loss of nitrogen with gain of oxygen following conditioning with 0.44 M KOH indicates degradation or conversion to another functional group.

Table 1. Results of C, H, N, O elemental analysis

Sample ID	Elements (wt %)				
	C	H	N	O	Total
PE hollow fiber	84.88	15.77	< 0.5	< 0.5	~100
Grafted AF160-2	67.08	8.16	18.54	6.12	~100
Amidoximated AF160-2	48.95	8.13	20.15	22.53	~100
AF160-2 – 0.44 M KOH @80C for 3 h	45.43 (48.33)	7.6 (8.08)	16.88 (17.95)	24.27 (25.82)	~94* (100)**

*The rest (6%) is potassium.
**The values in parentheses were calculated on the basis of 100%.

4.1.2 Scanning Electron Microscopy (SEM)

SEM images were collected using a JOEL, JSM-6060 SEM at 4 kV. The cross sectional pictures of the grafted, amidoximated, and dried AF160-2 fibers (Figure 2) clearly demonstrate the hollow gear definition with good gear lengths and an increase in fiber diameter after amidoximation. SEM images of KOH-conditioned AF160-2 fibers are shown in Figure 3. From these images, it can be concluded that: i) the amidoximated fibers swell further on KOH conditioning, ii) the fibers retain their hollow gear definition even after 3 hours of KOH conditioning, and iii) the fibers are substantially deformed after 24 hours of KOH conditioning. It should be emphasized here that SEM imaging was performed under vacuum, which also affects the state of the adsorbent fibers.
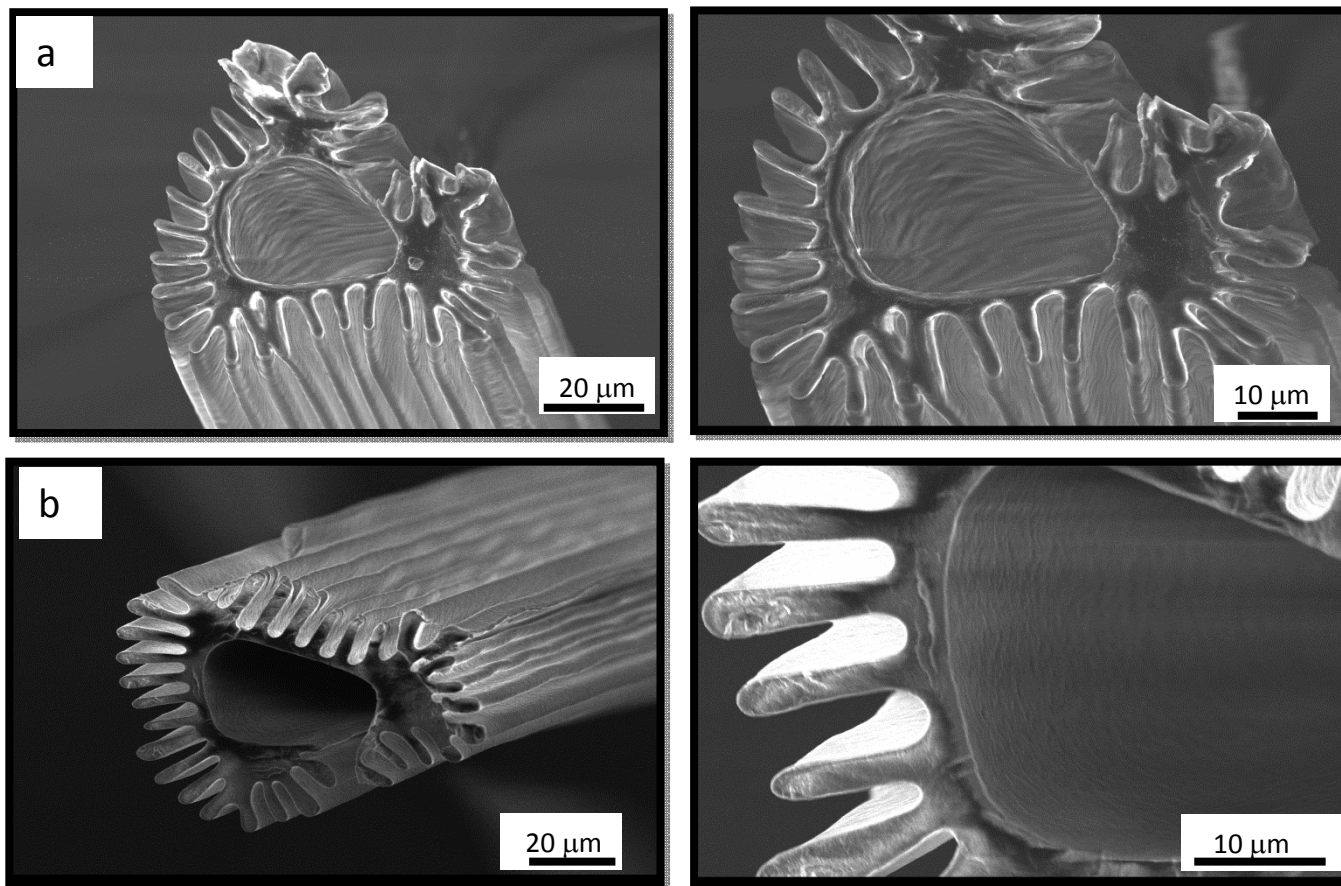
Figure 2. SEM images of grafted AF160-2 fiber (a) and amidoximated AF160-2 fiber (b).
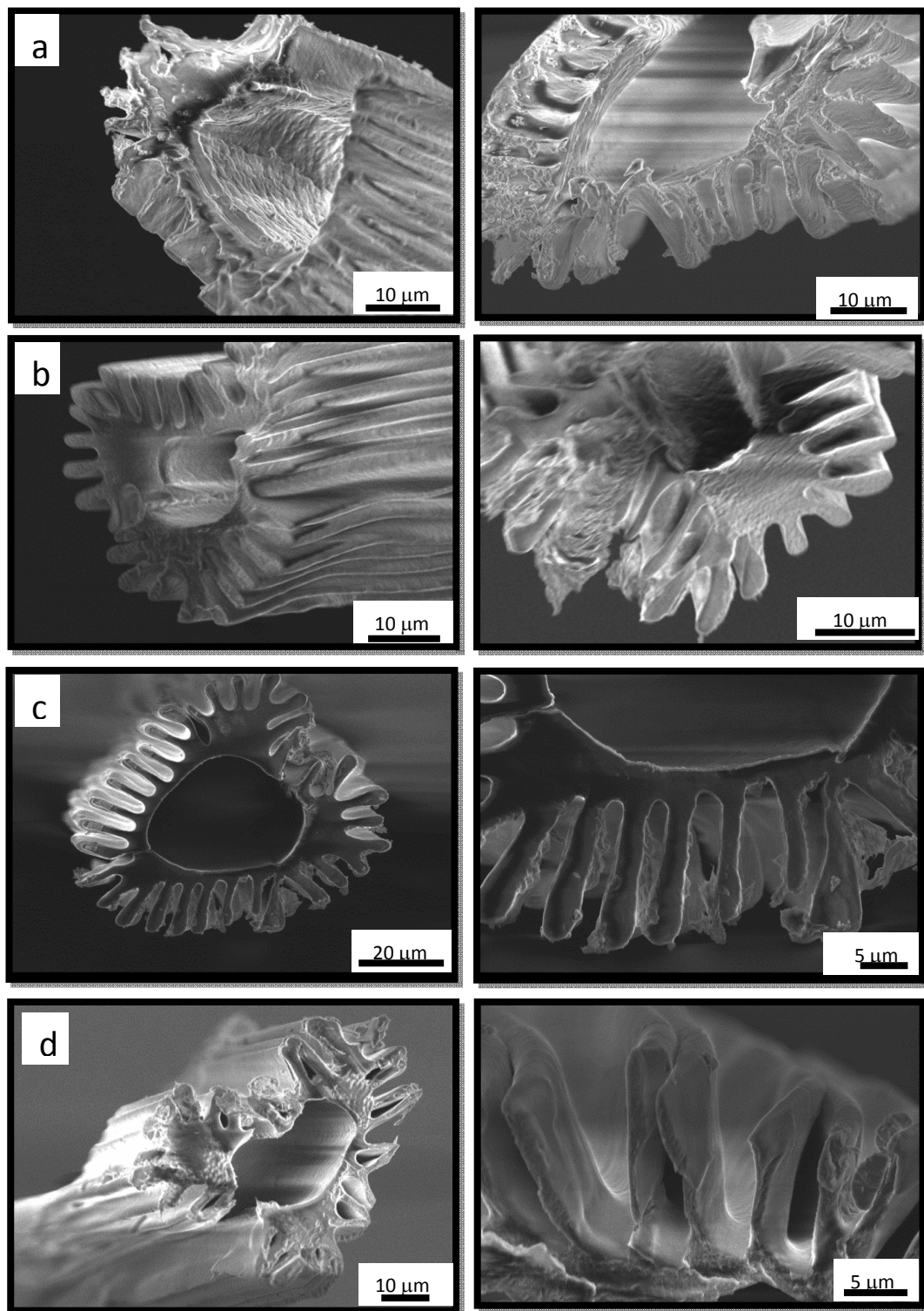
Figure 3. SEM pictures of dried AF160-2 fiber after conditioning with 0.44M KOH at 80 °C for different time-periods: (a) one hour, (b) two hours, (c) three hours and (d) 24 hours.

4.1.3 Fourier Transform Infrared (FTIR) spectrometry

FTIR spectra of the AF160-2 fiber samples were collected on a Perkin Elmer Frontier FTIR with a single-bounce diamond attenuated total reflectance (ATR) accessory at 4 cm^{-1} resolution and averaged over 16 scans. FTIR spectra at various steps of the adsorbent preparation are shown in Figures 4 and 5. The major peaks in Figure 4 are given in Table 2. The appearance of a stretch at 2247 cm^{-1} (Figure 4b), representing the C≡N stretch, suggests grafting of acrylonitrile onto the polyethylene. The split features at 1723cm^{-1} and 1670 cm^{-1} represent the two carbonyl stretches of itaconic acid. The disappearance of the nitrile stretch (2247 cm^{-1}) and appearance of N-H (3391, 3267 cm^{-1}), C=N (1644 cm^{-1}), C-N (1277 cm^{-1}), and N-O (935 cm^{-1}) (Figure 4c) can occur after conversion of the nitrile group to amidoxime (AO).
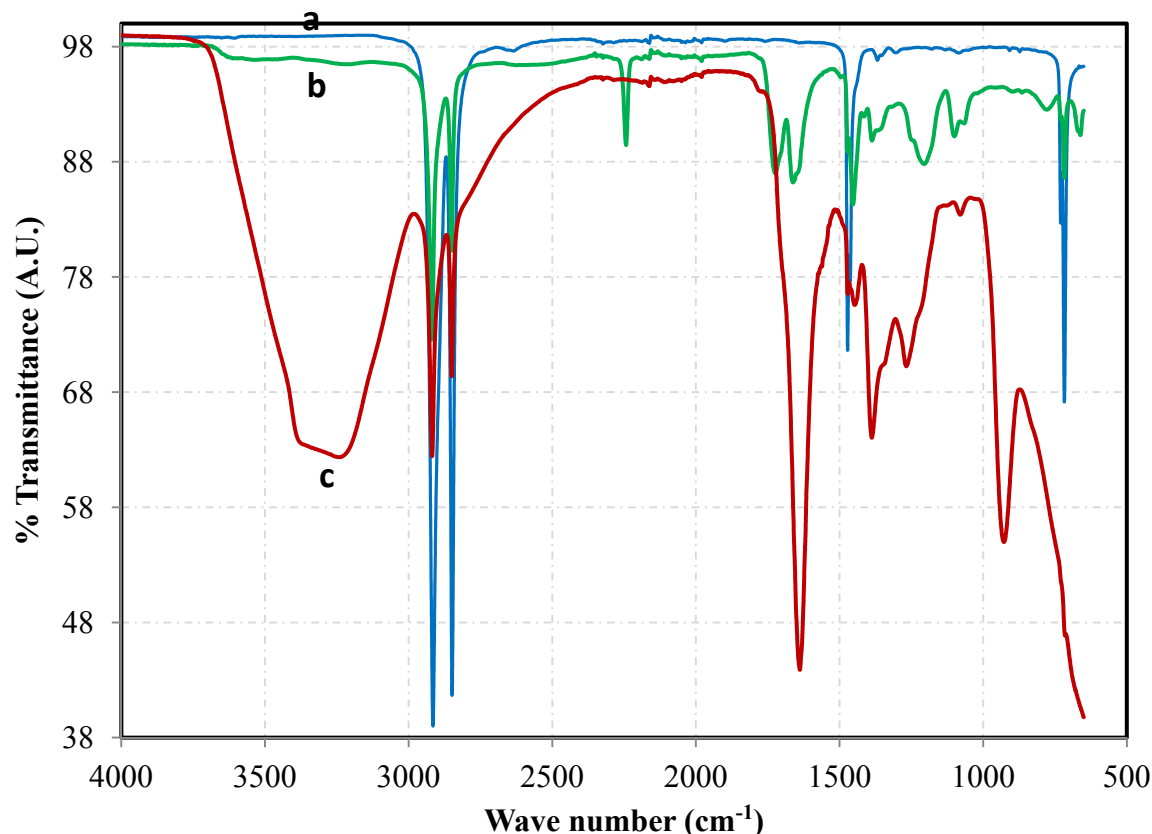
Figure 4. FTIR spectroscopy of (a) PE hollow fiber, (b) AN grafted PE (AF160-2) fiber, and (c) amidoximated AF160-2 fiber.

The effect of KOH conditioning on the FTIR-ATR of the grafted polymers is shown in Figure 5. The gradual decrease in intensity or disappearance of N-O stretch at 935 cm^{-1} and the C-N stretch at 1277 cm^{-1} and appearance of the new band at 1565 cm^{-1}, ascribed to carbonyl stretch from carboxylate, with increasing KOH conditioning time-period, can be described with the help of percent transmittance ratios shown on Table 3. The N-O vs C=N and C-N vs C=N ratios do not change significantly up to 3 hours KOH conditioning, but the complete disappearance of N-O after 24 hour indicates destruction of the AO functional group.

Appearance of the new band at 1560 cm^{-1} (i.e., C=O stretch) is a result of formation of carboxylate due to hydrolysis of the amidoxime (AO) upon KOH conditioning (see reaction scheme in Figure 6). The gradual increase in 1560 cm^{-1} vs 1640 cm^{-1} transmittance ratio also supports the fact that formation of

carboxylate increases with KOH conditioning time. Significant gradual loss in % transmittance of the N-O stretches at 935 cm^{-1} with increasing KOH conditioning time suggests gradual degradation of active AO binding sites and thus may completely disappear after 24 hours.

Table 2. Assessment of functional groups in the AF160-2 adsorbent from characteristic absorption bands in the FTIR spectra shown in Figure 4

Plot	Characteristic absorption (cm^{-1}) bands	Functional group (origin)	Type of vibration
a	2915, 2850	C-H (PE)	Stretching
	1470	C-H (PE)	Bending
	720	CH$_2$ (PE)	Rocking
b	2660-2370	O-H (ITA)	Stretching
	1721, 1668	C=O (ITA)	Stretching
	1390, 1450	C-O-H (ITA)	Bending
	1100,1215	O-C (ITA)	Stretching
	2247	C≡N (AN)	Stretching
c	3200-3400	N-H (AO)	Stretching
	1644	C=N (AO)	Stretching
	1277	C-N (AO)	Stretching
	935	N-O (AO)	Stretching
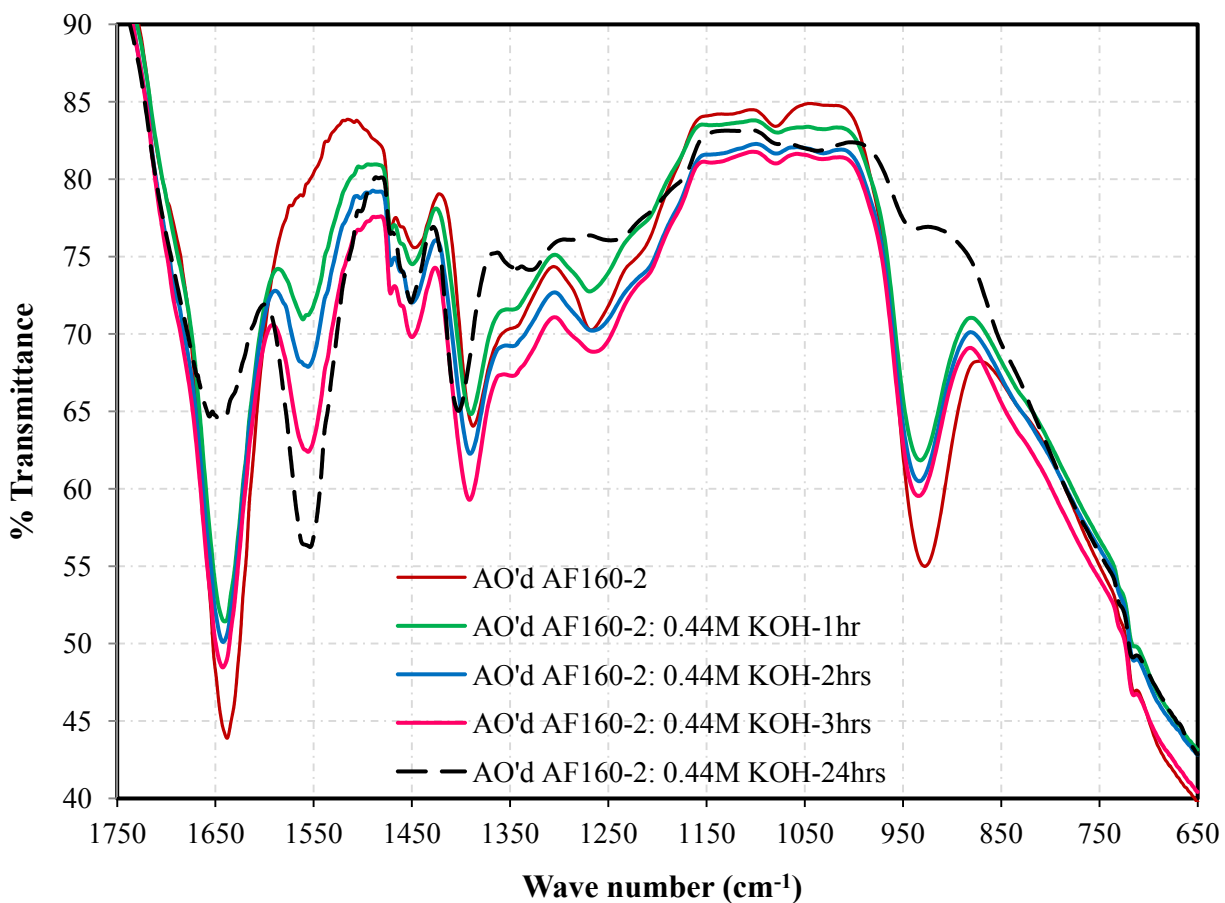
Figure 5. IR spectra of amidoximated AFI60-2 fibers after alkali conditioning with 0.44 M KOH for different time periods.

Table 3. % Transmittance (%T) ratios among the different functional groups in AF160-2 adsorbent before and after 0.44 M KOH conditioning at 80 °C for different time periods shown in Figure 5

Conditioning time of amidoximated AF-160-2	% T Ratio		
	C=O (1565cm^{-1}) /C=N(1644 cm^{-1})	N-O (935 cm^{-1}) /C=N (1644 cm^{-1})	C-N (1277 cm^{-1}) /C=N (1644 cm^{-1})
Without KOH	-	1.253	1.601
0.44M KOH - 1 hour	0.725	1.202	1.414
0.44M KOH - 2 hours	0.738	1.207	1.401
0.44M KOH - 3 hours	0.777	1.228	1.420
0.44M KOH - 24 hours	1.146	N-O stretch shifted to 950 cm^{-1}	C-N stretch shifted to 1341 cm^{-1}
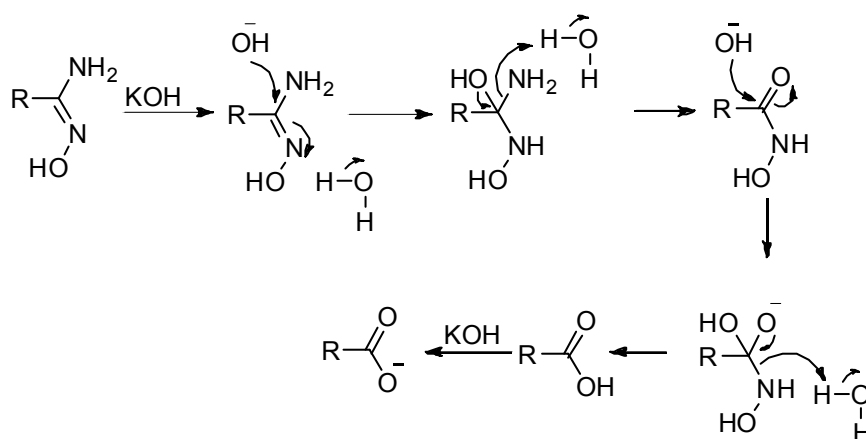
Figure 6. Proposed mechanism of formation of carboxylate from amidoxime on reaction with 0.44M KOH at 80 °C.

The reported pk$_a$ of the amidoxime group is 10.7-10.8, for succinediamidoxime[22]. Therefore, the amidoxime groups present in the AF160-2 adsorbent are prone to be deprotonated in a strong base like 0.44M KOH (the calculated pH is 13.6). Bromberg et al. illustrated that heating the amidoxime in the presence of water could convert it to hydroxamic acid, which further hydrolyses into acrylic acid[22]. The degradation of amidoxime to carboxylate occurs during the KOH treatment (Figure 6). Carboxylate formation can be supported by the increase of the oxygen content of the fibers (Table 1), as well as the peak intensity increase at 1565 cm^{-1} vibrational stretching (Figure 5). The formation of carboxylate from amidoxime during KOH conditioning was previously demonstrated on small-molecule model compounds[23]. Similar conversion can also be observed using solid-state NMR after treatment of the AF160-2 fiber with KOH at 80 ºC for three hours (Figure 7). The signals at 149 ppm and a shoulder centered at 157 ppm (Figure 7a) are ascribed to cyclic imidedioxime and open-chain amidoxime, respectively. The increase in the peak at 180 ppm is ascribed to the increased content of carboxylate, as shown in Figure 6. The following reaction (eq. 3) may occur during base conditioning for long periods of time:

(3)
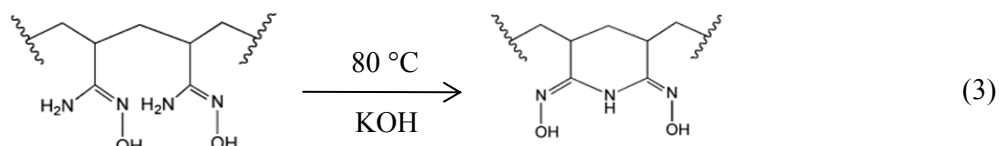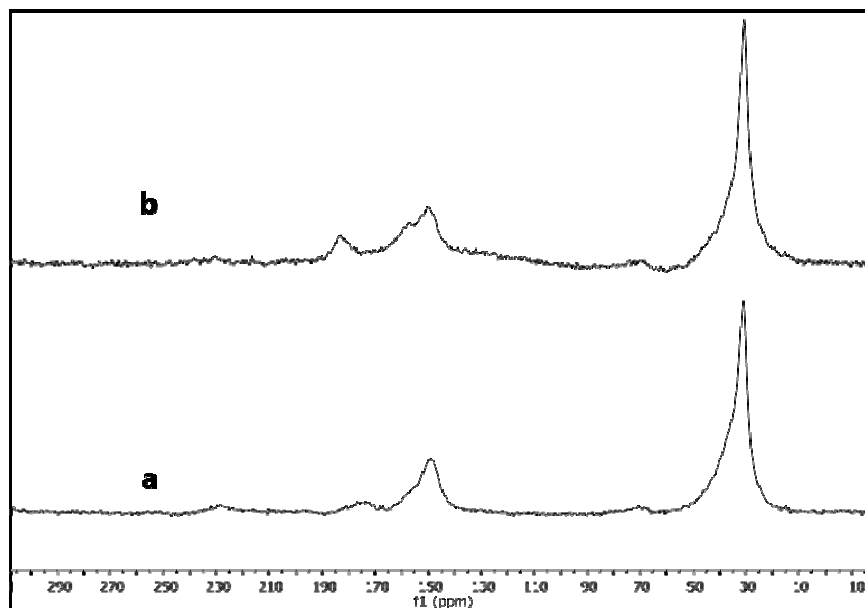
Figure 7. The solid state NMR of amidoximated fiber (a) and the fiber
after KOH treatment for three hours at 80 ºC (b).

4.1.4 Simulated seawater screening

The uranium loading capacities of AF160-2 without KOH conditioning was found to be zero after 24 hours of contact with the 8-ppm U simulated seawater screening solution. The uranium loading capacities of AF160-2 after conditioning with 0.2 M, 0.44 M, and 0.6 M KOH (using 1 mg adsorbent per mL base solution) at 60 ºC, 70 ºC, and 80 ºC for 1 hour, 2 hours, and 3 hours are shown in Figure 8. The adsorption capacity was higher with higher KOH concentration for any conditioning time period and temperature. Results shown in Figure 8, demonstrate a trend for the adsorbent performance in terms of uranium adsorption capacity with KOH concentration: 0.6 M > 0.44 M > 0.2 M. Uranium adsorption gradually increases with conditioning time (i.e., 1 h through 3 h) using 0.2 M and 0.44 M KOH. It is also notable that there is no significant effect of conditioning time on uranium adsorption capacity for 0.6 M KOH conditioning at 80 ºC.
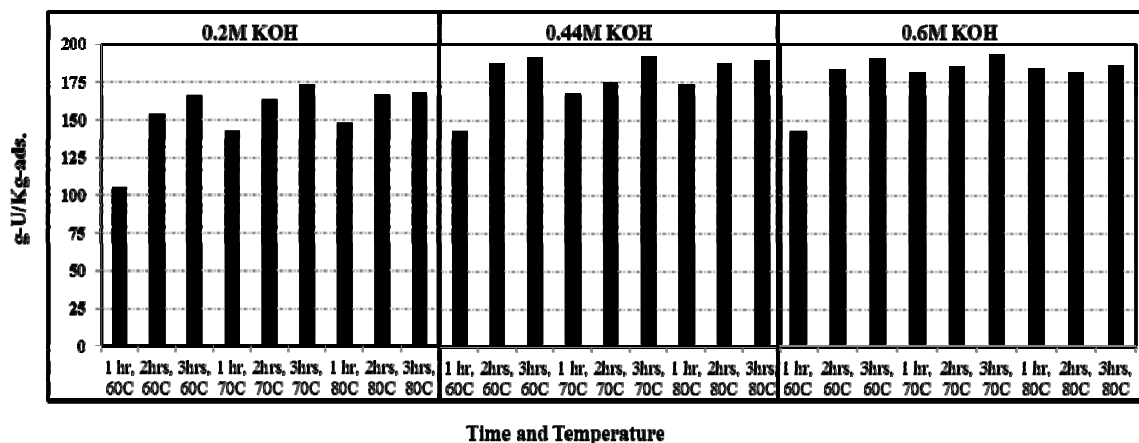
Figure 8. Uranium loading capacities of AF160-2 after 24 h in screening solution, spiked with uranyl ions at 8 ppm, after conditioning with 15 mL of 0.2 M, 0.44 M, and 0.6 M KOH at 60 ºC, 70 ºC, and 80 ºC for 1h, 2 h, and 3h duration at each KOH concentration.

4.1.5 Uranium uptake kinetics in batch reactors

The results of uranium uptake kinetics in 1-L seawater spiked with 75-ppb uranyl nitrate are shown in Figure 9. The rate of uranium uptake increases as the KOH conditioning time increases from 45 minutes up to 120 minutes. However, the uranium uptake rate slows down after 180 minutes KOH conditioning of the adsorbent. It is also notable that the total uranium uptake capacities after KOH conditioning for 75, 120, and 180 minutes are comparable despite the fact that the rate of uptake decreases for 180 min (3 h) KOH conditioning. These results indicate that KOH conditioning for a longer time-period may not be helpful for higher uranium uptake capacity from natural seawater.
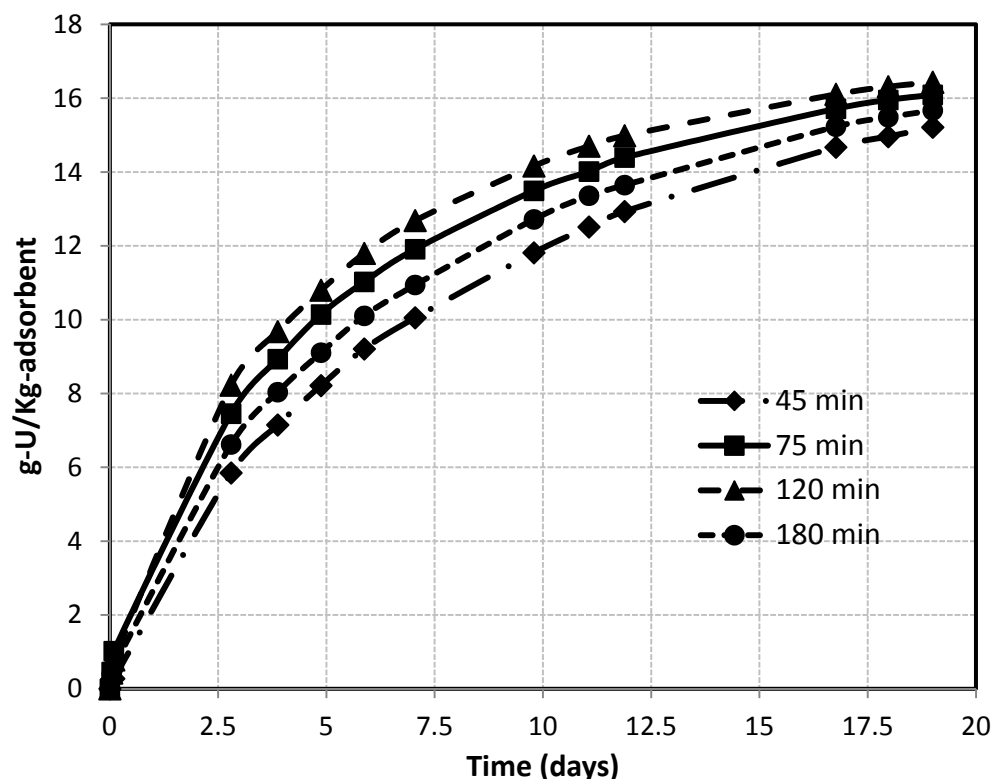
Figure 9. Uranium uptake histories by AF160-2 adsorbent from 1-L seawater spiked with 75-ppb uranyl nitrate. The adsorbent fibers were conditioned with 0.44 M KOH for 45, 75, 120, and 180 min at 80 ℃ prior to addition in seawater.

4.1.6 Field seawater testing

The AF160-2 adsorbent performance with natural seawater, carried out at PNNL-MSL with filtered water from Sequim bay for 56 days in flow-through columns, is shown in Figure 10. The amidoximated AF160-2 adsorbent samples were treated with 0.44 M KOH at three different temperatures, i.e., 60 ℃, 70 ℃, and 80 ℃ for three different time periods, i.e., 1 h, 2 h, and 3 h at each temperature. As can be seen in Figure 10, the uranium adsorption capacity after KOH conditioning at 70 ℃ is higher than that after KOH conditioning at 60 ℃. It is also notable that the uranium adsorption does not vary significantly with KOH conditioning time at 70 ℃. More interestingly, although AF160-2 has the highest uranium adsorption (~4 g-U/Kg-ads.) after KOH conditioning at 80 ℃ for one hour, the capacity gradually decreases with increasing conditioning time from one hour to three hours. These results suggest that: 1) base-

conditioning of the adsorbent is necessary in enhancing the uranium adsorption capacity and 2) longer alkaline contact at 80 ℃ reduces the uranium adsorption capacity. Thus, conditioning of the AF160-2 adsorbent with 0.44 M KOH at 80 ℃ for one hour can be considered optimal for highest uranium uptake capacity.

Adsorption of other metal ions such as V, Fe, Cu, and Zn from seawater is shown in Figure 11. It is notable that adsorption of vanadium was significantly higher, as compared to that of uranium. The iron uptake was comparable to uranium uptake. It is also interesting to see that uptake of vanadium and iron gradually decreases with increasing KOH conditioning time from one hour through three hours at 80 ℃, while uptake of zinc slightly increases. It could, therefore, be briefed that the uptake of V, Fe, and Cu follows the same trend as that of uranium in both of the above conditioning parameters, while the uptake of Zn does not. It was also observed that adsorption of Ca^{2+} and Mg^{2+} increases, as the KOH conditioning period increases, which is similar to the behavior of Zn^{2+}. This phenomenon is probably due to the formation of more carboxylates with increasing KOH conditioning time, leading to more degradation of selective binding AO sites. This trend was not obvious in laboratory experiments because the screening solution did not comprise Ca, Mg, V and other competing ions.
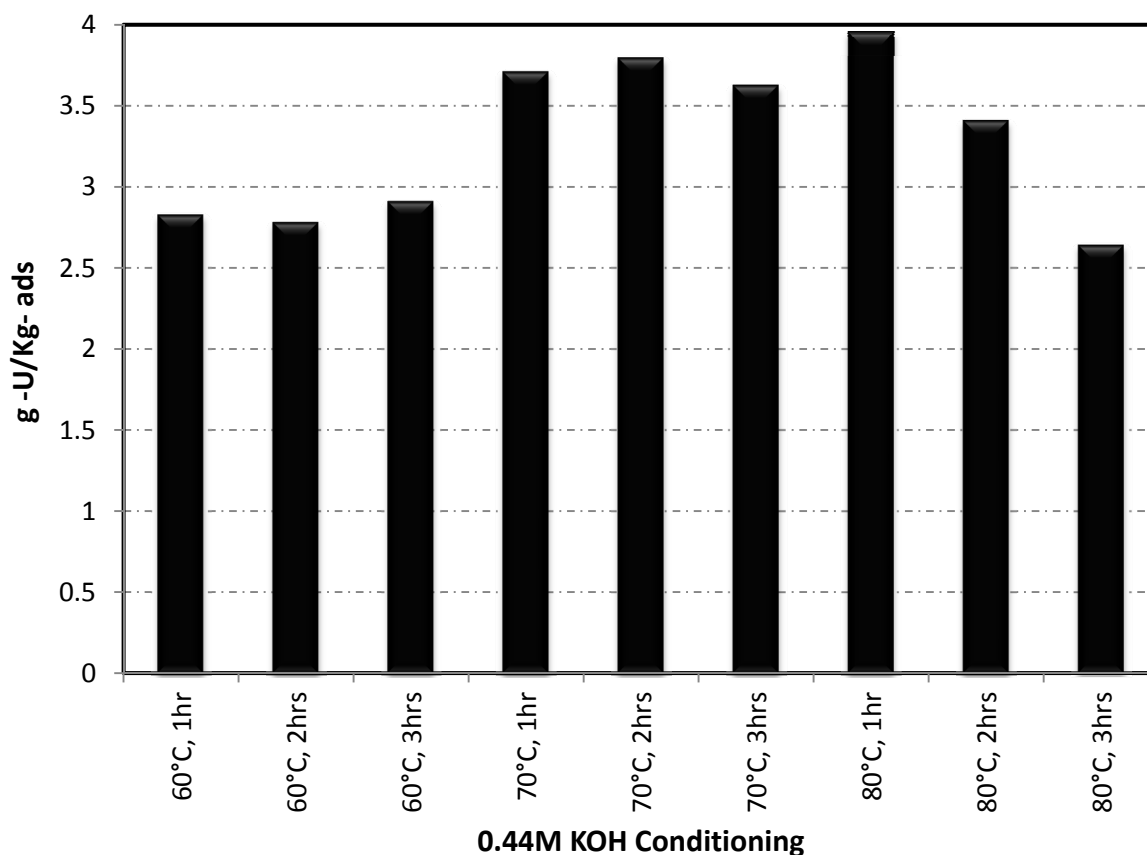
Figure 10. Uranium adsorption capacities of AF160-2 after 56 days contact with Sequim bay seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 60 ℃, 70 ℃, and 80 ℃ for three time periods, i.e., 1 h, 2 h, and 3 h at each temperature.
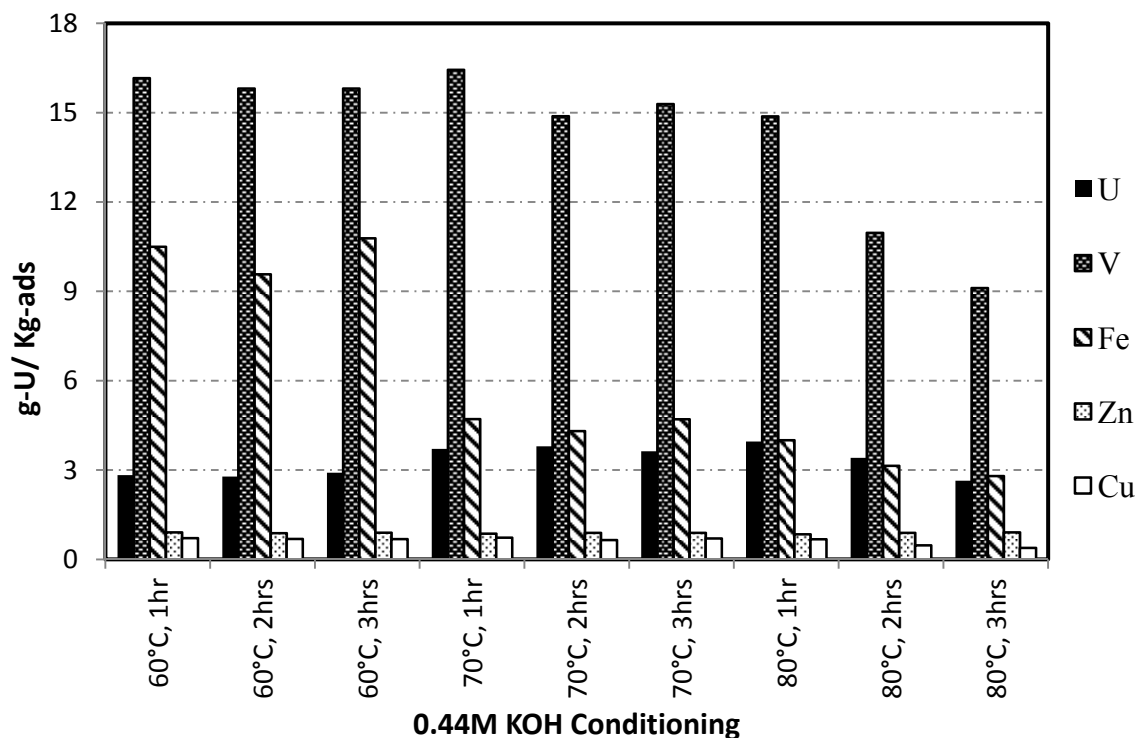
Figure 11. Loading of U, V, Fe, Zn, Cu, Ca and Mg by AF160-2 after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M KOH at 60 ºC, 70 ºC, and 80 ºC for three time periods, i.e., 1 h, 2 h, and 3h at each temperature.

4.1.7 Conclusions on KOH conditioning parameters

Simulated seawater screening tests with high uranyl concentration showed that the uranium adsorption capacity increased with an increase in the KOH concentration and conditioning time and temperature at each of the KOH concentrations. FTIR and solid state NMR studies indicated that KOH conditioning converts the amidoxime functional groups into more hydrophilic carboxylate and probably cyclic imidedioxime. The longer the KOH conditioning time, up to three hours, the higher is the loading capacity from the simulated seawater screening solution, which is composed of only uranyl, sodium, chloride, and carbonate ions.

Field testing with natural seawater, on the other hand, showed that the uranium adsorption capacity of AF160-2 increased with KOH (0.44M) conditioning temperature, and gradually decreased with increasing KOH conditioning time from one hour to three hours at 80 ºC. This behavior is due to the conversion of amidoxime to carboxylate. The carboxylate groups are needed to increase the hydrophilicity of the adsorbent; however, conversion of a significant amount of amidoxime to carboxylate leads to loss in selectivity toward uranyl ions. Thus, considering single use of the adsorbent, there is an optimum KOH conditioning time for each base-conditioning temperature at which an optimum ratio between amidoxime and carboxylate is reached. For the case of base conditioning with 0.44 M KOH at 80 ºC, the optimal conditioning time is approximately 1 hour, with respect to the highest uranium loading capacity from real seawater. It should be noted, however, that for multiple uses of the adsorbent involving several adsorption/elution cycles, if base-conditioning has to be performed before each adsorption cycle, a less than the optimum time period should be used each time. This is because of the fact that the conversion of

amidoxime to carboxylate is irreversible, which means that the density of carboxylate groups will keep increasing as the number of adsorption/elution cycles increases. Thus, in a real adsorbent deployment scenario, if base-conditioning has to be performed before adsorption, its duration should be determined based on the expected number of cycles. For example, if six is the most economical number of cycles, using amidoxime-based adsorbents, base conditioning before each adsorption step with 0.44 M KOH at 80 ºC should last for 15-20 min. It should also be noted that the optimal conditioning parameters may be different for adsorbents containing different monomers or acids. Thus, a base-conditioning study is recommended for each type of adsorbent to fine tune the base-conditioning parameters.

Uptake of other metal ions such as V, Fe, and Cu follows the same trend as that of uranium. Also, the uptake of Ca, Mg, and Zn ions increased with increasing KOH conditioning time, probably due to formation of more carboxylates, which leads to conversion of uranium-selective binding sites to less selective sites.

The results of this study are useful in the selection of optimal values of the parameters involved in preparing amidoxime-based adsorbent for uranium uptake from seawater.

4.2 Alternative Alkaline Conditioning and Economic Evaluation

The AF1 adsorbent prepared at the Oak Ridge National Laboratory by radiation-induced graft polymerization (RIGP) with acrylonitrile and itaconic acid onto high-surface-area polyethylene fibers was selected for alternative alkaline conditioning studies. Besides chemical structure examination by FTIR spectroscopy, the effects of various alkaline conditioning parameters such as the type of alkaline reagent, reaction temperature, and reaction time were also investigated with respect to uranium adsorption capacity from simulated seawater and natural seawater. Specifically, comparisons between sodium hydroxide and potassium hydroxide as conditioning agents have been performed with respect to both performance and cost.

4.2.1 Fourier Transform Infrared (FTIR) spectrometry

FTIR spectra of the AF1 fiber samples were collected on a Perkin Elmer Frontier FTIR with a single-bounce diamond attenuated total reflectance (ATR) accessory at 4 cm^{-1} resolution and averaged over 16 scans. The stretching frequencies at 2244 cm^{-1} and 1720 cm^{-1} represent the C$\equiv$N and carbonyl groups, respectively, and thus can be used to determine the grafting of acrylonitrile and itaconic acid onto the polyethylene. The disappearance of nitrile stretch and appearance of N-H (3390, 3265 cm^{-1}), C=N (1640 cm^{-1}) and N-O (930 cm^{-1}) can also verify conversion of the nitrile to amidoxime (AO). Figure 12 describes the effect of conditioning with 0.44M NaOH at 70 ºC for different time-periods. The gradual decrease in intensity, or disappearance of N-O stretch at 930 cm^{-1}, and appearance of the new band at 1560 cm^{-1} are due to conversion of amidoxime into carboxylate with increasing NaOH conditioning time-period.
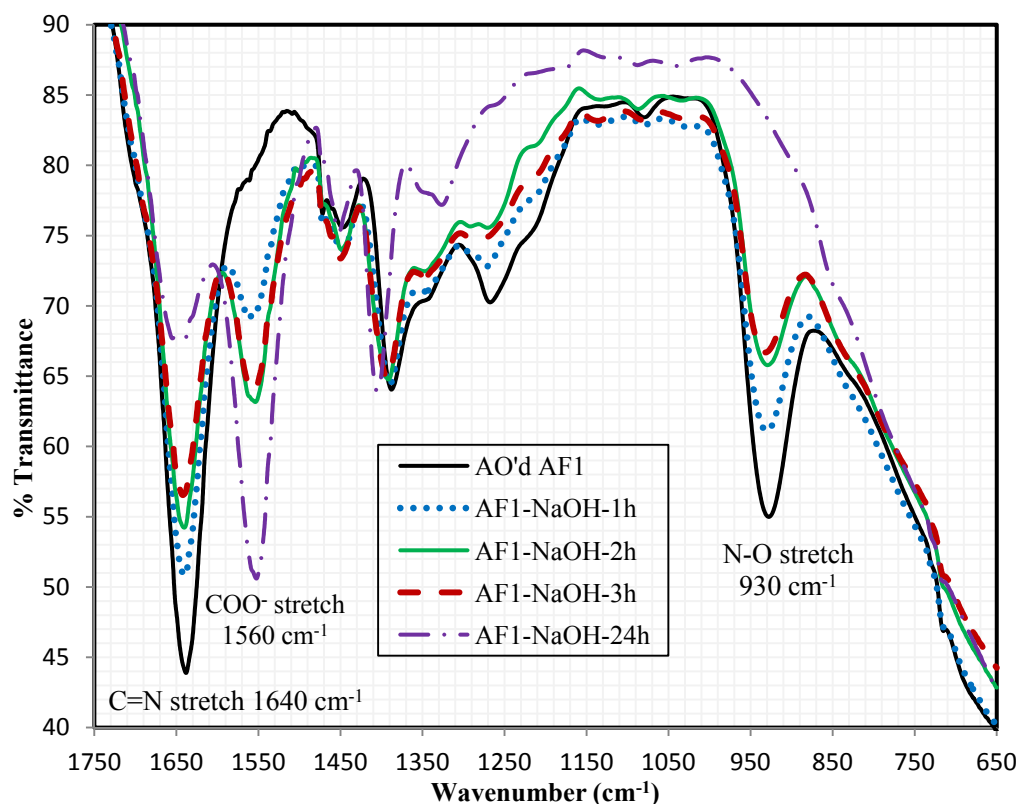
Figure 12. FTIR spectra of amidoximated AF1 fibers after conditioning with 0.44 M
NaOH at 70 ºC for different time periods.

A summary of the FTIR spectra of the AF1 samples after conditioning with 0.44M of different alkaline solutions at 70 ºC for 1h is shown in Figure 13. The stretching frequency at 1560 cm^{-1} appears as a result of formation of carboxylate due to hydrolysis of the AO upon alkaline conditioning with 0.44 M of potassium hydroxide (KOH), sodium hydroxide (NaOH), tetramethylammonium hydroxide (TMAOH) [tetraethylammonium hydroxide (TEAOH), triethylmethylammonium hydroxide (TEMAOH), tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TBAOH) were also used, but are not included in the figure], except for Na$_2$CO$_3$ and AOH. It is believed that formation of carboxylate is very important for the adsorbent ability to adsorb uranium. AF1 adsorbent, therefore, was not expected to adsorb uranium after alkaline conditioning with Na$_2$CO$_3$ and AOH.
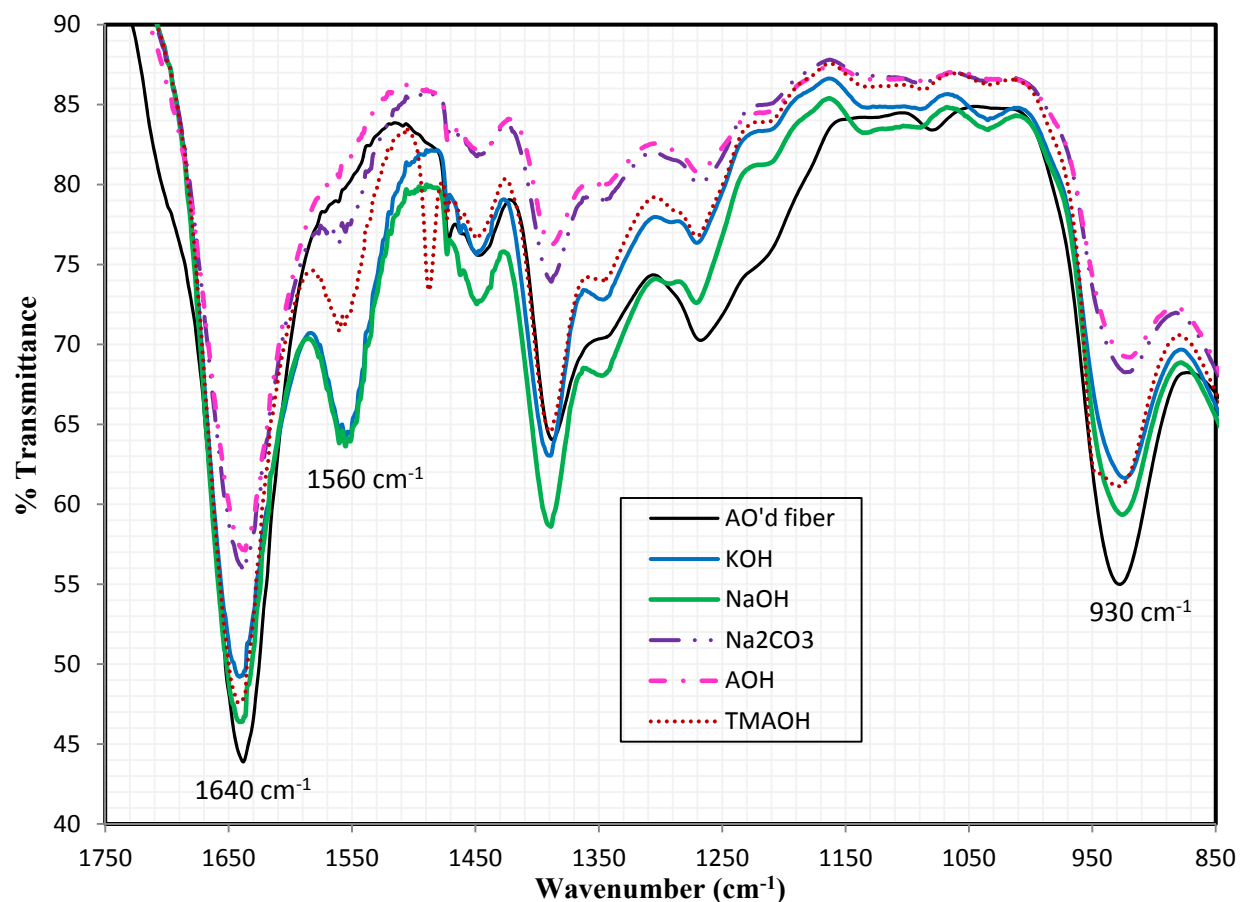
Figure 13. FTIR spectra of amidoximated AFI fiber after conditioning with 0.44 M of different alkaline solution at 70 ºC for 1h.

4.2.2 Simulated seawater screening test

The uranium adsorption efficiency of AF1 adsorbent was tested with simulated screening solution spiked with 8 ppm uranium after conditioning with 0.44 M of different alkaline solutions at 70 ºC for 1h. The uranium adsorption capacities of the AF1 samples after contact with the screening solution for 24 hours are shown in Figure 14. The adsorption capacity for uranium was almost zero without any alkaline conditioning. The uranium adsorption capacity was found to be comparable upon conditioning with KOH and NaOH. As discussed in the previous section, conditioning with Na$_2$CO$_3$ and AOH indeed resulted into practically zero uranium adsorption capacity, probably due to the fact that deprotonation is important for the preparation of the adsorbent and conversion of a portion of the amidoxime group into carboxylate

is also necessary to increase the hydrophilicity of the adsorbent. However, other ammonium hydroxide solutions (i.e., TMAOH, TEMAOH, TEAOH, TPAOH and TBAOH) were also proven to be potential effective reagents for alkaline conditioning towards higher uranium adsorption capacity.
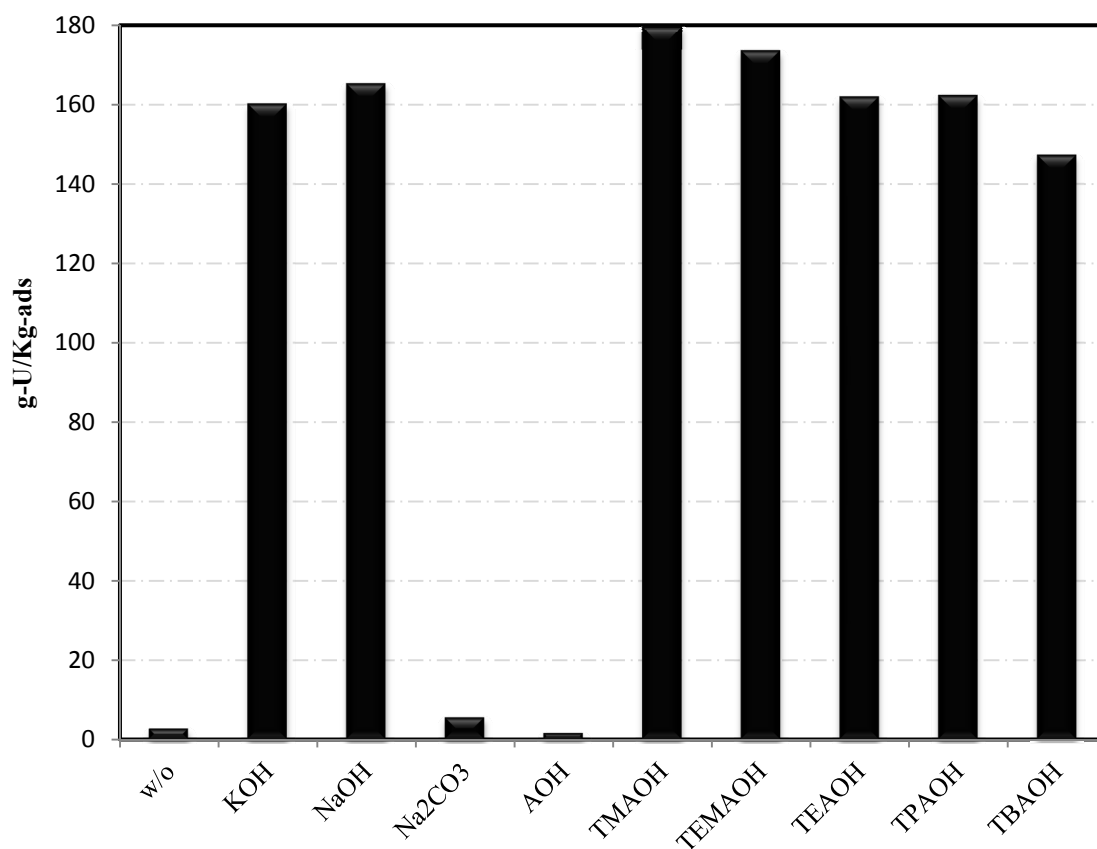
Figure 14. Uranium adsorption capacities of AF1 adsorbent fibers, conditioned with 15 mL of 0.44 M of different alkaline solutions at 70 ºC for 1h, after 24 h in screening solution spiked with 8 ppm uranyl ions.

4.2.3 Uranium adsorption kinetics in batch reactors

Two AF1 adsorbent samples of approximately 8 mg each were treated with 0.44 M KOH and NaOH, at 70 ºC for 1 h. The samples were then placed in 5-gallon seawater containers, shaken at 100 rpm, to study the kinetics of uranium uptake from coastal seawater obtained from Charleston, SC. One-mL solution samples were drawn periodically for ICP-MS analysis of uranium. From the solution uranium concentrations, the amount of uranium adsorbed was estimated through a mass balance. Results of uranium adsorption versus time are presented in Figure 15, where it is shown that the uranium uptake kinetics is faster for the KOH-conditioned sample than for the NaOH-conditioned sample. This result probably explains the reason behind selection of KOH over NaOH for alkaline conditioning by the Japanese scientists, even though it is more expensive than NaOH.
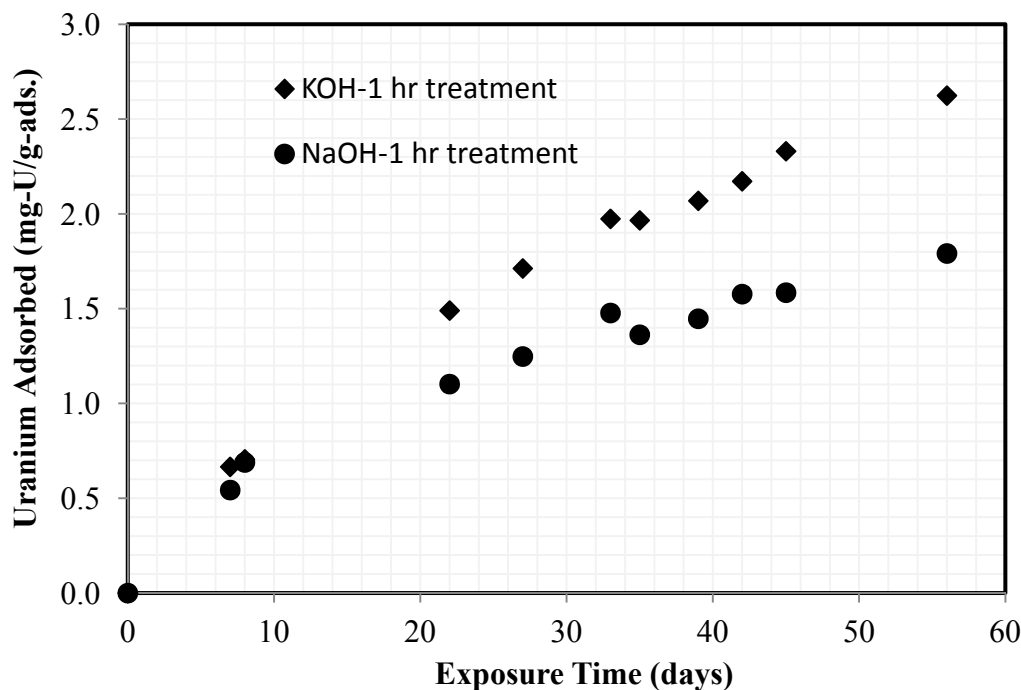
Figure 15. Adsorption kinetics of uranium by same-batch AF1 adsorbent samples after 56 days contact with coastal seawater in 5-gallon batch reactors. The adsorbent samples were treated with 0.44 M of KOH and NaOH at 70 ºC for 1 h.

4.2.4 Field seawater flow through column testing

The performance of the AF1 adsorbent for uranium adsorption from natural seawater was tested at PNNL-MSL with filtered seawater from Sequim Bay, for 56 days in flow-through columns. The amidoximated AF1 adsorbent samples were treated with 0.44 M KOH or NaOH at three different temperatures, i.e., 60 ºC, 70 ºC, and 80 ºC for three different time periods, i.e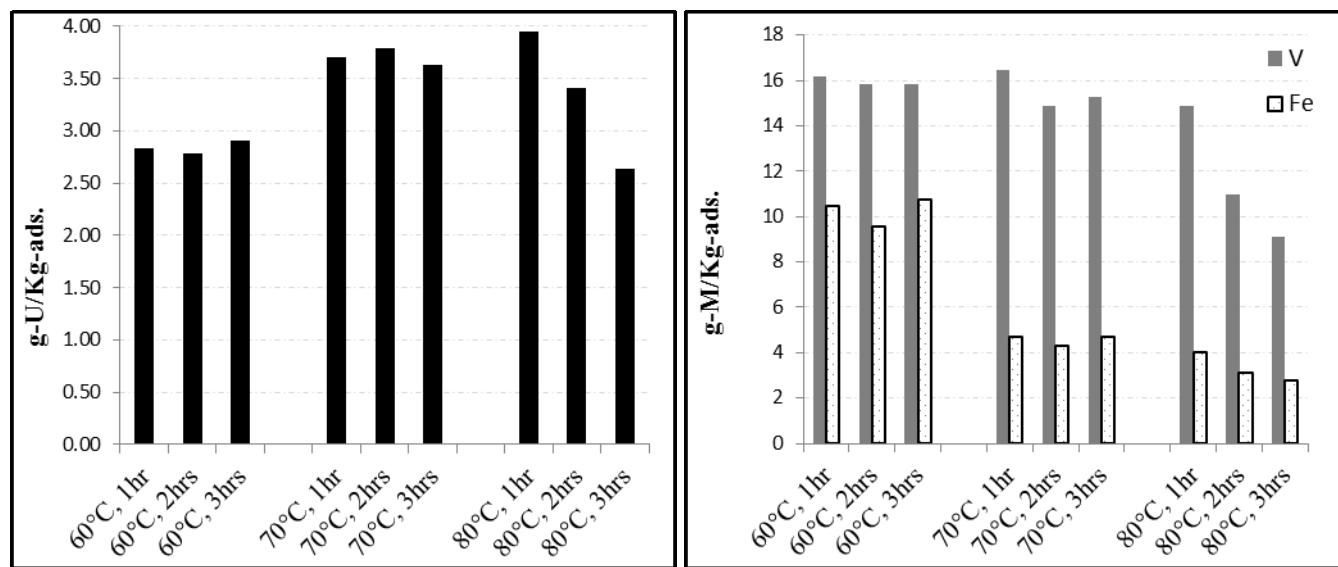., 1 h, 2 h, and 3 h at each temperature. The adsorption capacity of uranium along with vanadium and iron by AF1 after conditioning with 0.44 M of NaOH and KOH is shown in Figure 16. The uptake of other metal ions from seawater was lower. The uranium uptake seems to be optimum after alkaline conditioning at 80 ºC for 1h and 70 ºC for 1 h with KOH and NaOH, respectively.

The uranium adsorption, in general, decreases gradually with increasing conditioning time at 70 ºC and 80 ºC. It is also interesting to note that uranium adsorption is higher for conditioning at 60 ºC with 0.44 M NaOH as compared to that with 0.44 M KOH. This particular observation may be significant in efforts to decrease the cost of uranium extraction from seawater. Vanadium is being considered as the main competitive ion for uranium extraction from seawater[24]. The overall vanadium uptake by AF1 is slightly less for adsorbent conditioned with NaOH as compared to the capacity of adsorbent conditioned with KOH. These flow-through-column studies were carried out using two different AF1 samples prepared at different batches, and the difference observed is within the range of variability observed from different batches.

Using AF1 adsorbent samples from the same batch, flow-through-column studies were conducted to determine the effects of conditioning with 0.44 M of KOH, NaOH, CsOH, TEMAOH and TMAOH at 70 ºC for 1 h. CsOH was used mainly for comparison with NaOH and KOH, specifically, with respect to the

(a) 0.44M KOH

(b) 0.44M NaOH
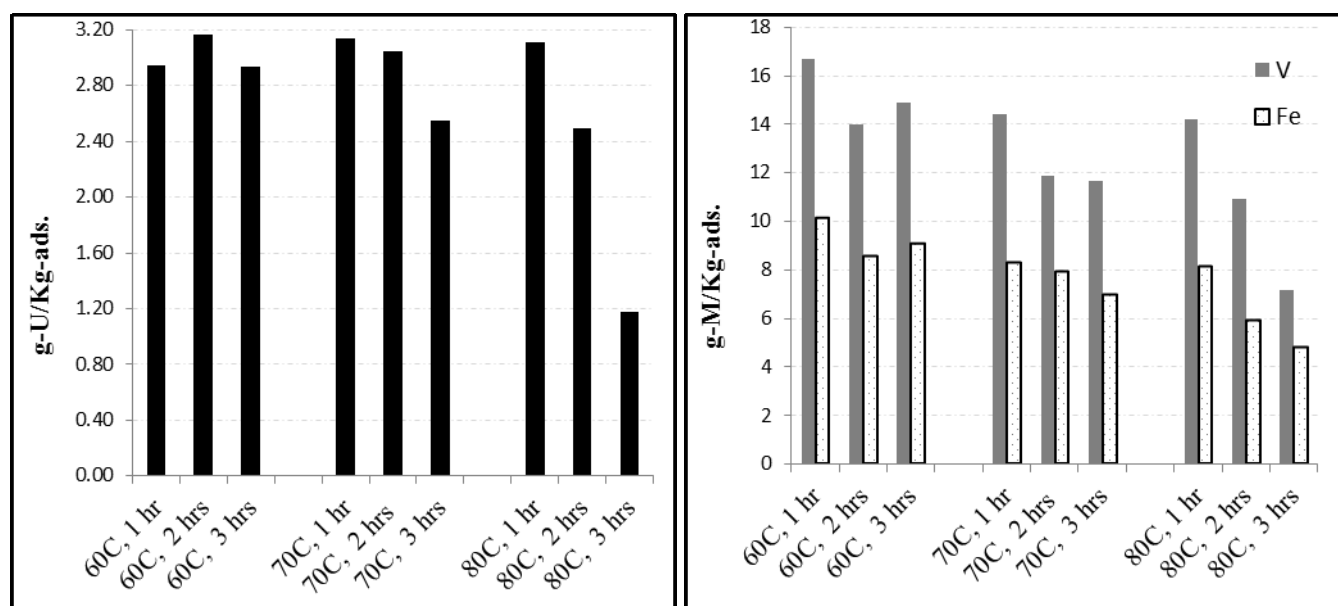
Figure 16. Adsorption of U, V, and Fe by AF1 after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M of KOH and NaOH at 60 ºC, 70 ºC, and 80 ºC for three time periods, i.e., 1 h, 2 h, and 3h at each temperature. Reported adsorption capacities were normalized to 35 psu seawater.

diffusion of Na^+, K^+, and Cs^+ ions through the adsorbent polymer. A summary of uranium uptake after an exposure time of 56 days with seawater in flow-through columns is shown in Figure 17. It can be seen that the AF1 adsorbent has the highest uranium adsorption capacity (3.89 g-U/Kg-ads) after conditioning with 0.44 M of NaOH at 70 ºC for 1 h as compared to the other alkaline reagents. Thus, the same-batch AF1 adsorbent resulted in a 3.2% enhancement of uranium uptake for conditioning with NaOH over KOH. However, previous column experiments from PNNL-MSL, for a different batch of AF1 samples conditioned for 1 and 3 h at 70 ºC, showed a decrease in uptake for fibers conditioned with NaOH as compared to KOH, as seen in Figure 18.
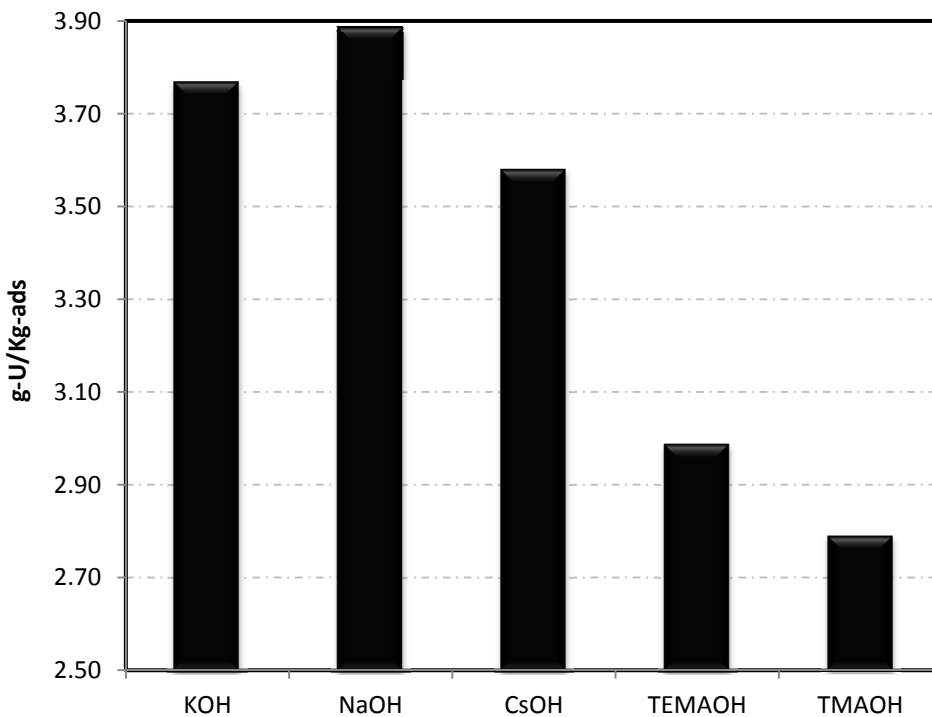
Figure 17. Adsorption of uranium by same-batch AF1 samples after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M of KOH, NaOH, TMAOH, and TEMAOH at 70 ºC for 1 h.
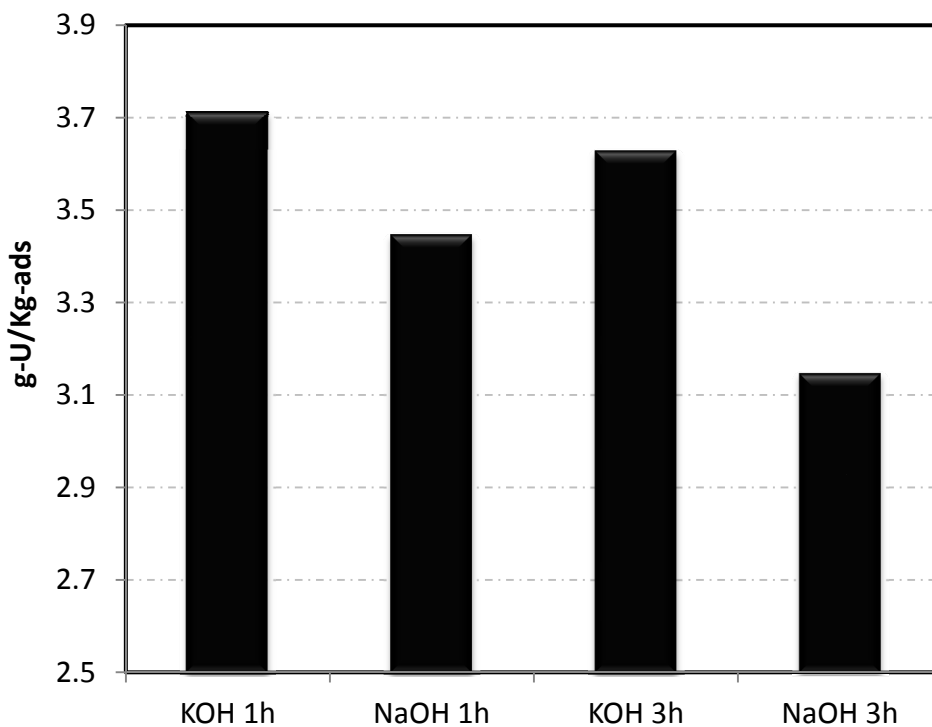
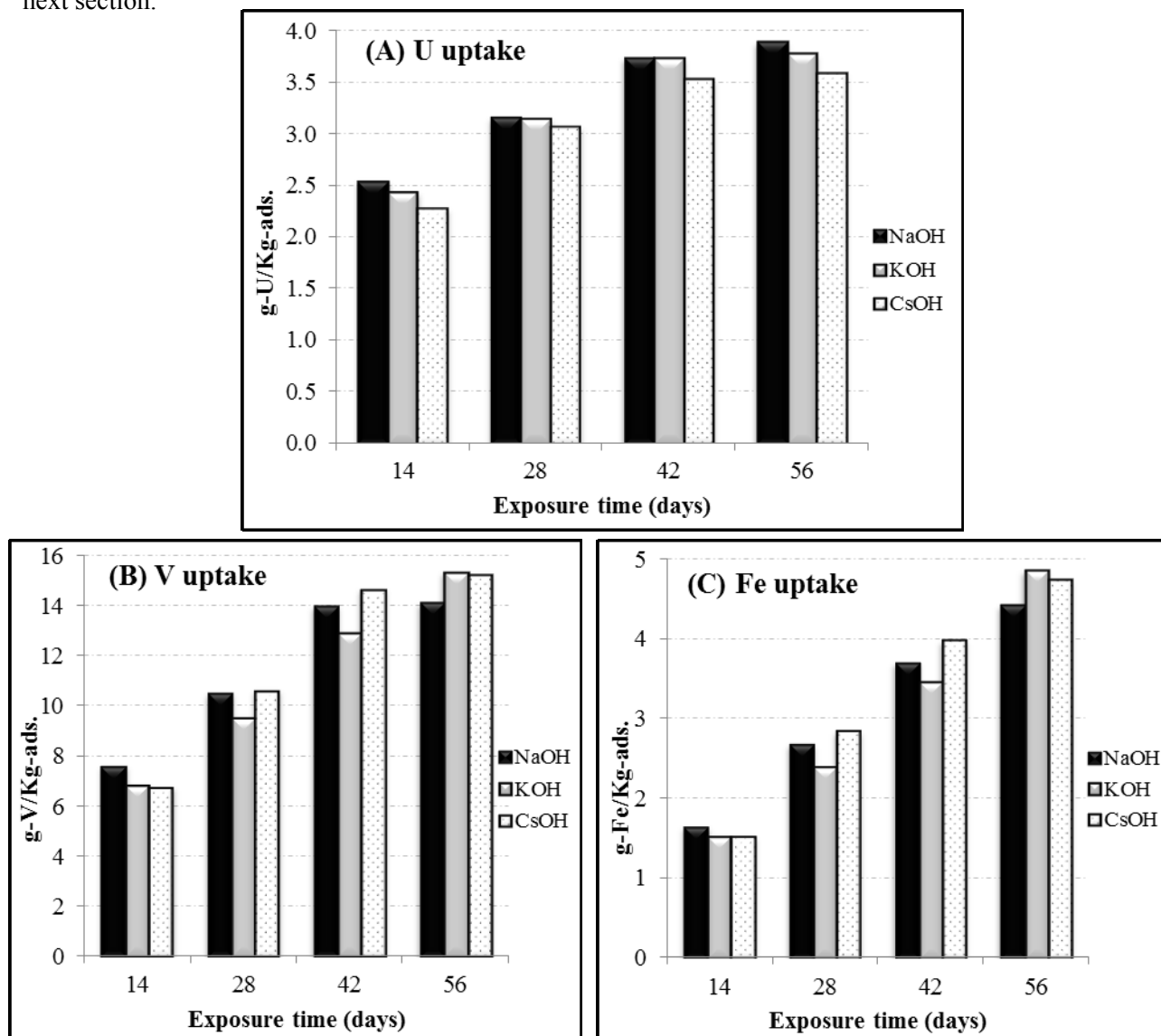**Figure 18.** Adsorption of uranium by a different batch of AF1 samples after 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M of KOH and NaOH at 70 ºC for 1 h and 3 h.

The uptake of uranium and other metals by AF1 adsorbent was monitored as a function of exposure time. The adsorption history of uranium, vanadium, and iron by the AF1 adsorbent conditioned with 0.44 M of KOH, NaOH, and CsOH, respectively, over a total period of 56 days is shown in Figure 19. Uranium adsorption gradually increased over 56 days by adsorbent conditioned with NaOH, whereas it reached a plateau after 42 days for adsorbent conditioned with KOH or CsOH. This is probably due to the kinetic effect observed in batch experiments. It is also interesting to note that the vanadium was continuously adsorbed over 56 days by adsorbent conditioned with KOH or CsOH, but adsorption was completed after 42 days for adsorbent conditioned with NaOH. The uptake of iron was gradually increased over the period of 56 days and was higher for adsorbent conditioned with KOH or CsOH as compared to iron uptake by adsorbent conditioned with NaOH. Thus, NaOH emerged as a better reagent for alkaline conditioning of the AF1 adsorbent because of higher uranium uptake capacity; higher uranium uptake selectivity over vanadium; and lower cost over the other candidate alkaline reagents. The cost saving per unit mass of uranium produced by using NaOH versus KOH as the alkaline reagent is discussed in the next section.


Figure 19. Adsorption of uranium (A), vanadium (B), and iron (C) by AF1 adsorbent samples as a function of exposure time over 56 days contact with seawater in flow-through columns. The adsorbent samples were treated with 0.44 M of KOH, NaOH, and CsOH at 70 ºC for 1 h.

4.2.5 Economic benefits of NaOH versus KOH alkaline conditioning

A cost analysis of the textile adsorbent technology for recovery of uranium from seawater uses discounted cash flow techniques to follow the life cycle of a unit mass of adsorbent through fabrication, deployment and elution cycles, and disposal[25]. While the cost analysis evolves in tandem with the technology, the majority of the methodology and data sets for the existing analysis mirror those set forth in reference 25 with more recent updates reflected in subsequent analyses[5, 26].

The cost of uranium recovery from seawater is predominantly driven by chemical and raw material expenses. The breakdown shown in Figure 20 is dominated by the production cost of the adsorbent, which includes substrate fabrication and radiation-induced graft polymerization, as well as the elution and regeneration cost. The regeneration cost is in turn dominated by the alkaline solution, which in the previous reference case was KOH. The highlighted regions illustrate the contribution of KOH to the total system cost. The rest of this section will demonstrate the economic benefits of replacing KOH with NaOH in these parts of the procedure.
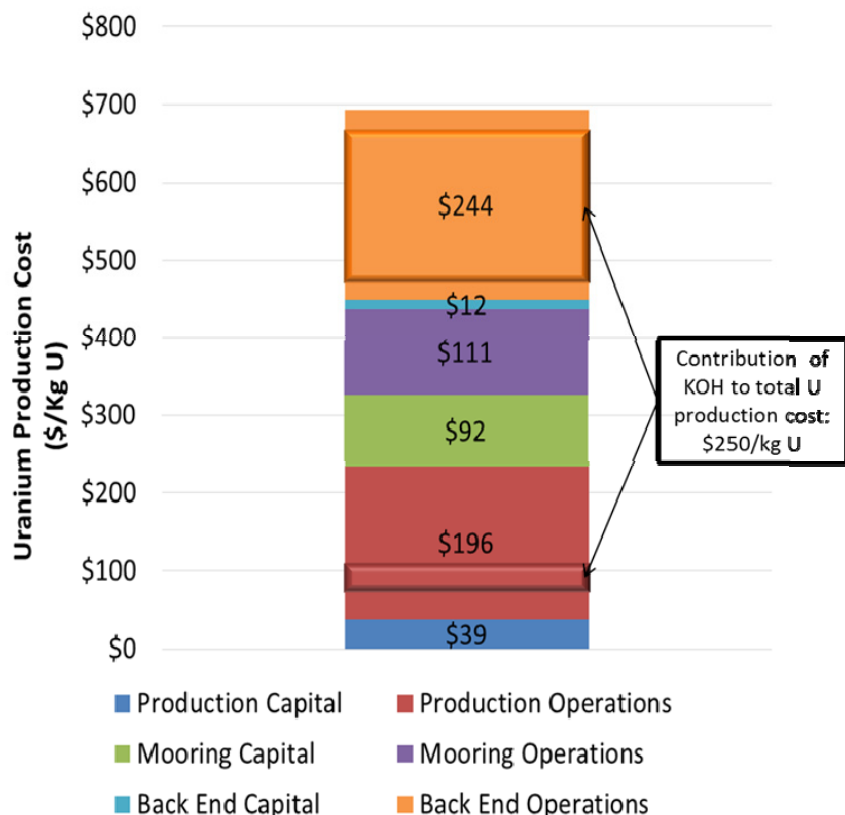
Figure 20. Cost breakdown of uranium production.

The production cost displayed in Figure 20 results from the base case system parameters shown in Table 4. These parameters and the associated system cost do not necessarily reflect the best available technology, which remains under active development.

Table 4. Base case parameters for uranium production system

Degradation Rate (% loss in uptake per re-use)	5
Ocean Temperature ($^{\circ}$C)	20
Alkaline Solution	KOH
Number of Uses of adsorbent prior to disposal	10
Length of Campaign (days)	81

The degradation rate has significant impact on the final cost of recovery. Although re-using the adsorbent circumvents the costly production step, the decreased mass of uranium recovered with each additional use will eventually become low enough to cease outweighing the cost of another deployment. The degradation rate used in this analysis comes from experiments conducted in Japan[27] on a similarly structured adsorbent. The ocean temperature is known to affect uranium uptake, and cost benefits could follow from deployment in warmer waters[28]. The remaining two properties, length of campaign and number of adsorbent uses, are optimized to result in the lowest possible uranium production cost for the given scenario.

A comparison of the two alkaline solutions under consideration can be found in Table 5. The unit costs of NaOH and KOH are obtained from historical data sets[43] as well as vendor quotes, specifically for bulk purchases on the order of tens of metric tons, obtained using Alibaba, a Chinese e-commerce company. Bulk purchases were considered for both commodities to ensure similar economics of scale. Sodium hydroxide is available at roughly half the cost of potassium hydroxide.

Since alkaline consumption is calculated on a stoichiometric basis, the lower molar mass of NaOH results in reduced consumption rates on a unit mass of salt per unit mass adsorbent basis. Given the purpose of deprotonation, 2 moles of potassium or sodium hydroxide are consumed per mole of itaconic acid and 1 mole of base per mole of acrylonitrile present on the adsorbent. Like all other chemicals in the economic analysis, the alkaline solutions are assumed to be used with negligible losses.

Table 5. Comparison of commercially available salts

	Sodium Hydroxide	Potassium Hydroxide
Cost ($/tonne)	$480	$1,050
Molar Mass (g/mol)	40	56

Since the use of sodium hydroxide has been shown to result in a range of effects, ranging from a modest decrease to a small enhancement in capacity, two scenarios are considered. One case considers the adsorbent performance seen in Figure 17, which incorporates a 3% increase in capacity to the cost model. The second case averages the effects on adsorbent uptake seen in Figure 18 to result in a 10% decrease in capacity. The changes in adsorbent performance and the production cost benefits of using NaOH combine to decrease the cost of producing uranium as seen in Table 6.

Table 6. Cost impacts of using sodium vs potassium hydroxide

	Potassium Hydroxide	Sodium Hydroxide Reduced Uptake	Sodium Hydroxide Increased Uptake
Saturation Capacity of fresh Adsorbent (g U/kg ads)	5.42	4.88	5.59
Cost of Uranium ($/kg)	$694	$545	$486
Number of Uses	10	13	15
Soaking Time (days)	81	61	65
Uptake of Fresh Adsorbent (g U/kg ads)	4.24	3.56	4.15

Even if a 10% loss in uptake is suffered by the adsorbent, the use of NaOH is economically advantageous. The economics offered by the lower cost and molar mass of NaOH lead to benefits sufficient enough to outweigh the small decrease in uptake. This chemical replacement leads to a savings of approximately 21-30%, depending on the effect on uptake.

Since the back end cost associated with regenerating adsorbent using NaOH is much lower than that of KOH, the optimal number of adsorbent re-uses increases. The high regeneration cost resulting from KOH use limits the number of economically viable deployment and regeneration cycles, and thus encourages longer optimized soaking times in order to recover more uranium per immersion. In the case of NaOH, a greater number of re-uses is favorable. Subsequently, the production cost does not benefit from these prolonged soaking times, which are associated with decreased rates of uranium uptake and a lowered uranium value due to time value of money effects upon the revenue stream. Note that the uptake of the adsorbent is a function of the saturation capacity and soaking time, so the NaOH-treated adsorbent, which has a shorter optimal soaking time, can exhibit lower uptake than the KOH-treated adsorbent even when it has higher capacity. Figure 21 contrasts the cost breakdown for these two scenarios.
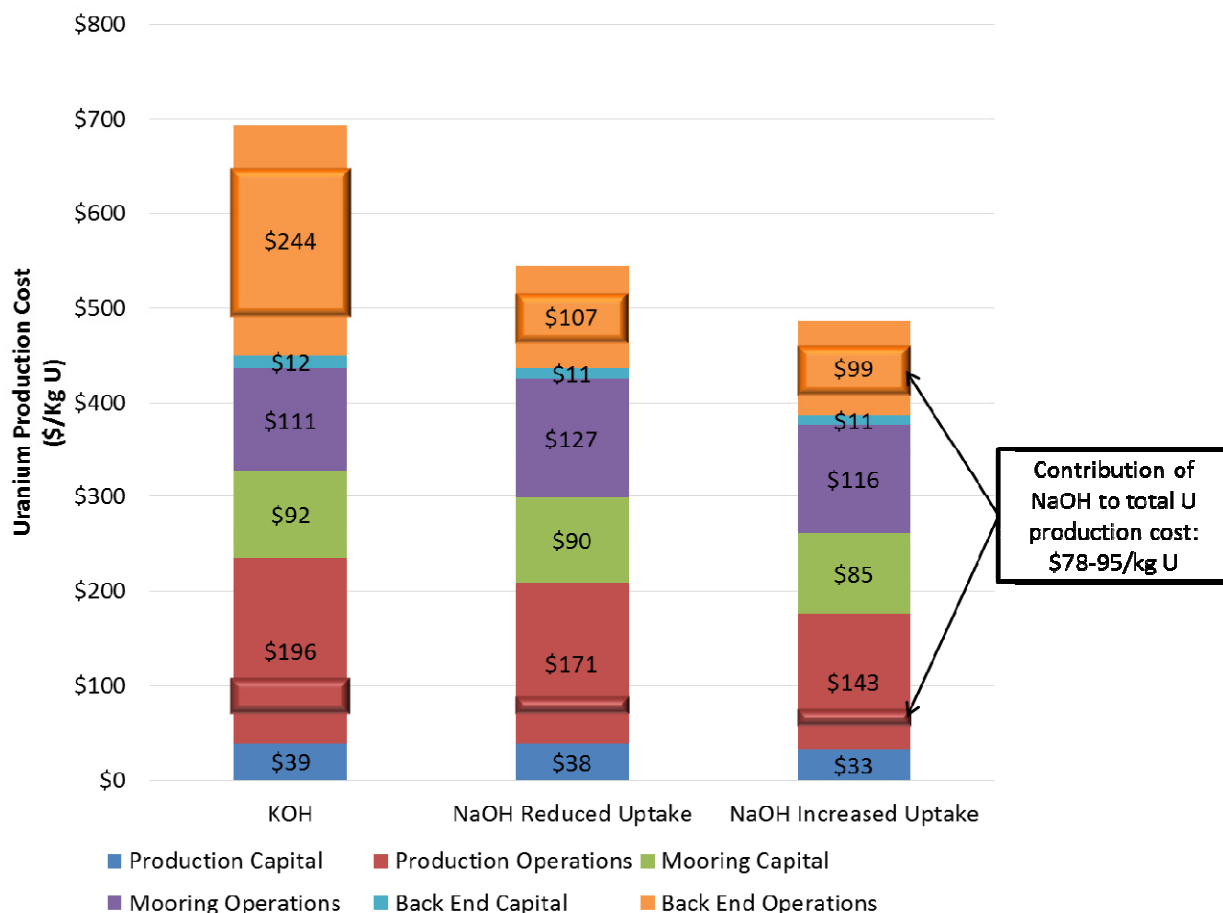
Figure 21. Comparison of uranium production costs.

Since the conditioning process itself is quite similar regardless of which alkaline solution is used, this change is simple to implement and requires no system or design overhauls. Therefore, NaOH is strictly superior to KOH from a cost benefit standpoint, even if it does result in slightly reduced uranium uptake.

4.2.6 Conclusions on alternative alkaline conditioning and economic evaluation

AF1 adsorbent containing acrylonitrile and itaconic acid was successfully prepared by radiation-induced graft polymerization onto high-surface-area polyethylene fiber. Alkaline treatment of the amidoximated adsorbent is important because of formation of carboxylates from part of amidoxime. Investigation on the conditioning parameters such as chemical nature of alkaline, temperature, and time has been successfully demonstrated in this work on the basis of high uranium uptake capacity, selectivity from seawater and its cost effectiveness on the overall process. Inorganic based reagents such as KOH, NaOH, Na_2CO_3, CsOH; as well as organic based reagents such as AOH, TMAOH, TEAOH, TEMAOH, TPAOH and TBAOH were used for alkaline conditioning. NaOH is the best candidate for alkaline treatment among all reagents mentioned above. Conditioning of AF1 adsorbent with 0.44M NaOH at 70 ºC for one hour over conditioning with 0.44M KOH at 80 ºC for 1-3 hours (which has been the usual practice) has been proven to be better for higher uranium uptake capacity as well as uptake selectivity from seawater in 56 days exposure in the flow-through-column study. NaOH, thus emerged as a better reagent for alkaline conditioning of the AF1 adsorbent because of higher uranium uptake capacity; higher uranium uptake selectivity over vanadium; and lower cost over the other candidate alkaline reagents. These findings lead

to significant economic impacts as the use of NaOH conditioning in place of KOH results in a 21-30% decrease in the cost of uranium production.

Acknowledgment

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