CHEMISORPTION OF RADIONUCLIDES ON COMMERCIAL, SYNTHETIC, AND BIOGENIC SORBENTS FOR USE IN-SITU GAMMA SPECTROMETRY

A Thesis

by

MATTHEW TAYLOR ATHON

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Peter H. Santschi
Co-Chair of Committee,	Karl Kaiser
Committee Members,	Patrick Louchouarn
	Glen Fryxell
Head of Department,	Debbie J. Thomas

May 2016

Major Subject: Oceanography

ABSTRACT

Recent nuclear disasters, such as in Fukushima, Japan, have made it evident that there is a need for the capability to efficiently measure radionuclides in-situ in marine and coastal waters. A group at Pacific Northwest National Laboratory (PNNL) is working to develop a novel, in-situ gamma spectrometer that will provide high resolution gamma spectrometry in natural waters after nuclear disasters. This system will utilize high-capacity chemisorbent cartridges that will pre-concentrate radionuclides from water for lower background and more precise gamma measurement using onboard $LaBr_3$ detectors. Although impregnated MnO_2 chemisorbents have been tested for this system previously, there is a demand for improved performance from novel chemisorbents.

In this study, I investigated the particle-water distribution coefficient, K_D, of commercial potassium hexacyanoferrate, Anfezh, and three novel MnO_2 sorbents using small batch experiments and a set a radionuclides (^{7}Be, ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, ^{137}Cs, ^{210}Pb, ^{233}Pa, and ^{234}Th). Results are compared to conventional impregnated MnO_2 to determine if these novel materials display superior sorption of radionuclides from solution. A novel nanostructured MnO_2 sorbent demonstrated K_D performance up to two orders of magnitude greater than traditional impregnated MnO_2. Additionally, biogenic MnO_2 displayed K_D values that were comparable to those of impregnated MnO_2 for most radionuclides and are found naturally at the Savannah River Site. Biogenic MnO_2 are not expected to be used in the in-situ gamma spectrometer, however this is the first study to evaluate their ability to sorb radionuclides. The results of these tests also determined the shelf life of impregnated MnO_2 to be greater than 5 years for most radionuclides tested in synthetic seawater.

I developed a reproducible method for extraction of radiocesium (~80% extraction) from Anfezh after aqueous deployment by mixing Anfezh with NaOH and EDTA inside of a sorbent canister. The results from this work will be applied to future development of PNNL’s gamma spectrometer and marine radiochemical research.

NOMENCLATURE

AFW	Artificial Fresh Water
ASW	Artificial Seawater
GBW	Galveston Bay Water
K_D	Distribution Coefficient
K_{DC}	Distribution Coefficient Including Colloidal Fraction
MnO_2	Manganese Dioxide
PNNL	Pacific Northwest National Laboratory
SAMMS	Self-Assembled Monolayers on Mesoporous Supports

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE Page

LIST OF TABLES

TABLE Page

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

The detection of radionuclides in marine and coastal environments is critical for monitoring water quality, scientific research, and national security issues. Radionuclide contamination at nuclear waste sites and natural waters near historic and recent nuclear contamination incidents are a source of hazardous and highly mobile radioactive species (Johnson et al. 2012). Nuclear disasters, such as the Fukushima Daiichi spill, have released high volatility fission products (e.g. ^{129m}Te, ^{131}I, and ^{137}Cs) into the environment (Kinoshota et al. 2011). Additionally, National nuclear waste sites, such as the Hanford Site in southeastern Washington State, contain billions of gallons of legacy nuclear waste from decades of nuclear processing activities. Large plumes of nuclear waste nuclides (e.g. ^{90}Sr, ^{129}I, ^{137}Cs, and ^{239,240}Pu) that are stored at many of the waste sites are leaking and jeopardizing groundwater used as public drinking water (Xu et al. 2015). In order to better mitigate internal exposure to radionuclides contained in natural waters, efficient radiation monitoring devices need to be developed, optimized, and implemented in marine and coastal environments. It is abundantly clear that the ability to monitor fallout radionuclides in natural waters after spills would help mitigate exposure to emergency responders and inhabitants near the outflow.

Pacific Northwest National Laboratory (PNNL) has spent many years developing a medium-resolution autonomous collection and in-situ detection system that will increase water monitoring capabilities in the event of a nuclear detonation or accidental spill of radionuclides. This novel system will perform pre-concentration for in-situ measurement of γ-emitting radionuclides from natural waters. The in-situ gamma spectrometry capability of the system relies on scintillation detection using a cerium-activated lanthanum bromide ($LaBr_3$:Ce) crystal (Schwantes et al. 2009). A system such as this one has not existed before commercially. Traditional marine gamma spectrometry requires extensive laboratory analysis on pre-concentrated sorbents in order to make reliable radioactivity measurements. Additionally, conventional thallium-activated sodium iodide (NaI:Ti) scintillators produce γ-spectra that can become overwhelmed by natural radionuclides (e.g. ^{40}K and U-Th series) in natural waters (Tsabaris et al. 2008; Wedekind et al. 1999). $LaBr_3$ crystals are more expensive and exhibit unwanted background γ-rays due to the natural inclusion of ^{138}La and ^{227}Ac radionuclides; however, $LaBr_3$:Ce produces a resolution of less than 3 percent at 662 keV compared to approximately 6.5 percent for a comparable sized NaI:Tl scintillator (Milbrath et al. 2006). NaI:Tl scintillators have long been the preferred choice for in-situ gamma ray detection, but the low resolution of NaI:Tl limits its performance in high background γ-ray environments (Zeng et al. 2014).

The in-situ gamma system developed by PNNL will employ onboard high capacity chemisorbent cartridges that will pre-concentrate radionuclides for in-situ measurement and further laboratory analysis (Schwantes et al. 2009). Commercial and synthetic chemisorbents have been tested in the past as a means to extract anthropogenic radionuclides from aqueous environments for use on in-situ gamma systems (Johnson et al. 2011a; Johnson et al. 2011b; Johnson et al. 2012). In particular, manganese dioxide

(MnO_2) chemisorbents are used extensively for extraction and pre-concentration of heavy metals and radionuclides in oceanographic and radiological measurements due to their high sorption capabilities (e.g. Mou et al. 2011; Johnson et al. 2011; Varga, 2007; Baskaran et al. 1992; Mann et al. 1984; Goldberg, 1954). MnO_2 materials display advantageous chemisorption properties via their open crystal structures, high surface area to volume ratio, negatively charged surfaces, and sites of exchangeable cations such as Na^+, K^+, Ca^{2+}, Mn^{2+} (Tebo et al. 2004). In the environment, natural MnO_2 minerals have been known to sorb and sequester dissolved radionuclides and trace metals (e.g. Wang et al. 2012; Adams et al. 2009; Webb et al. 2006; Todd et al., 1988; Bacon et al., 1980; Murray, 1975). Recent developments have allowed researchers to synthesize novel, high surface area MnO_2 sorbents that can potentially improve sorption capabilities of radionuclides from natural waters (Yantasee et al. 2007). Further testing of novel and naturally precipitated MnO_2 will provide an evaluation of sorption performance over traditional chemisorbents used as heavy metal and radionuclide adsorption materials.

In Johnson et al. (2011a, 2011b, 2012), a number of sorbents were tested for their abilities to pre-concentrate target radionuclides using batch and flow aqueous conditions. Sorption performance of impregnated MnO_2, Anfezh, and nanostructured SAMMS sorbents were established by calculating distribution coefficients (K_D) using batch experiments. The average log K_D results produced in those papers ranged from ~1.3 – 5 in artificial sea water for all radionuclides tested, in which MnO_2 was determined to be the best overall traditional sorbent tested. Impregnated MnO_2 sorbents contain variable and inconsistent Mn oxidation states and little MnO_2 content using this recipe (20% by weight), which can limit sorption performance. Additionally, Johnson et al. (2011a, 2011b, 2012) did not provide experimental evidence for shelf life and storage of impregnated MnO_2 or Anfezh that would be stored in sorbent cartridges for immediate use in the event of a nuclear disaster. Novel MnO_2-decorated Self Assembled Monolayers on Mesoporous Supports (SAMMS) and a nanostructured MnO_2 will be tested here as a means to evaluate their sorption performance compared to traditional impregnated MnO_2. Due to the high surface area, unique synthesis (i.e. mesoporous silica and copolymer backbones), and the ability to better control MnO_2 coverage and oxidation state for each sorbent, it is possible for the K_D performance to be improved by orders of magnitude compared to traditional impregnated MnO_2.

This research improves knowledge of the chemisorption of a selection of three synthetic and one biogenically-produced MnO_2. I accomplished this by performing batch experiments using triplicate samples of an impregnated MnO_2 (Varga, 2007), a nanostructured mesoporous MnO_2 (Nayak & Munichandraiah, 2011), a MnO_2-decorated (Mn III, IV) SAMMS high performance nanoporous sorbent (unpublished Glen Fryxell recipe), and a newly discovered, biogenically-produced MnO_2 that is precipitated from a *Chromobacterium* sp. found at the Savannah River Site. I also performed batch experiments using the same batch of impregnated MnO_2 synthesized by Johnson et al. (2011b) in order to determine optimal storage conditions and approximate shelf-life of that particular sorbent in artificial sea water (ASW) and artificial fresh water (AFW). Information about shelf life and storage is necessary for future use of impregnated MnO_2

in cartridges for pre-concentration of radionuclides from marine and coastal waters post-nuclear disaster.

SAMMS MnO_2 sorbents are engineered to provide exceptionally high surface area using nanoporous silica supports (~1000 m^2/g), high density binding sites, and fast sorption kinetics due to their open pore structure. Other SAMMS materials have been shown to be effective heavy-metal sorbents in aqueous conditions (Fryxell et al. 2004; Yantasee et al. 2007; Johnson et al. 2011a,b). This particular recipe of MnO_2 SAMMS has not been investigated for use as a radionuclide adsorbent. The nanostructured MnO_2 that I tested has also not previously been experimented as a radionuclide adsorbent; however, due to its high surface area (~ 200 m^2/g), unique copolymer backbone, and mesoporous structure (pore diameter 8 – 40 nm) I determined that it would be suitable as a radionuclide sorbent.

In addition to MnO_2 sorbents, I investigated the chemisorption capabilities and shelf life of the Russian commercial sorbent, Anfezh. Specifically, I sought to determine how well Anfezh performs as a ^{137}Cs sorbent for use in a deployable, high capacity sorbent cartridge that will be mounted to PNNL's in-situ gamma spectrometer. Anfezh is a potassium ferrohexacyanoferrate compound (attached to a cellulose backbone) that has been designed to selectively extract cesium isotopes from aqueous solutions (Johnson et al., 2011a,b; Remez and Sapozhnikov, 1996). The sorbent cartridge that I tested was developed by PNNL to be reusable for experimentation.

In addition to testing the chemisorption capabilities of Anfezh, I developed a method to chemically destroy the Anfezh contained inside the chemisorbent cartridge and release or desorb the cesium isotopes for further laboratory analysis. Destructive analysis, such as mass spectrometry, could provide isotopic information of the cesium species (e.g. ^{135}Cs/^{137}Cs) that are sorbed onto Anfezh after aqueous deployment. There is an interest by nuclear forensics scientists at PNNL to have the capability to determine stable cesium isotopic signatures in seawater as a means to resolve the origin of nuclear signatures in the event of a nuclear detonation. The methods that I developed to desorb cesium isotopes from Anfezh will be immediately useful for future nuclear forensics studies.

The radionuclides used to test the K_D of these MnO_2 sorbents and Anfezh include: ^{7}Be, ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, ^{137}Cs, ^{210}Pb, ^{233}Pa, and ^{234}Th. Each of these radionuclides is of significance in marine and coastal detection using gamma spectrometry. ^{7}Be ($T_{1/2}$ = 53 days) is produced cosmogenically, exists primarily as Be(II) in the ocean, and has been used widely as a proxy for air-sea interface and upper ocean mixing studies due to its particle reactivity (Yang et al. 2013; Silker et al. 1968). ^{57}Co ($T_{1/2}$ = 271.8 days) typically occurs as Co (II) in natural waters and can be used as an analog for the fission product ^{60}Co (Johnson et al. 2011b). ^{106}Ru ($T_{1/2}$ = 1.017 years) exists as Ru (II & VI) in natural seawater and is a common nuclear fission product. ^{125}Sb ($T_{1/2}$ = 2.758 years) is strongly hydrolyzed in natural seawater, exists predominantly as Sb (III & V), and forms from nuclear fission. ^{133}Ba ($T_{1/2}$ = 10.538 years) is an alkaline Earth element that occurs in natural waters as the free cationic species Ba (II) and can be used as an analogue for Ba isotopes that are nuclear fission products (i.e.^{140}Ba). ^{137}Cs ($T_{1/2}$ = 30.07 years) is an alkali metal element that occurs typically as the free cation Cs

(I) in natural waters, and is a widely studied nuclear fission product (Johnson et al. 2011b). ^{210}Pb ($T_{1/2}$ = 22.3 years) is a particle reactive radionuclide produced by the decay of ^{238}U and is used extensively in oceanography to study particle fluxes (Yang et al. 2013). ^{233}Pa ($T_{1/2}$ = 26.967 days) is a particle reactive element that can be produced as a result of the nuclear fuel cycle (Lung and Gremm 1998). ^{234}Th ($T_{1/2}$ = 24.10 days) is also a particle reactive element that results from the decay of its parent radionuclide, ^{238}U, typically exists as Th (IV) complexes in seawater, and is useful as a tracer in determining particle fluxes in the upper ocean (Santschi et al. 2006). Testing this set of radionuclides will be useful for determining the effectiveness of these synthetic and commercial sorbents for reliable radionuclide pre-concentration after nuclear disasters and for oceanographic research.

CHAPTER II

COMPARISON OF NOVEL AND TRADITIONAL MANGANESE OXIDES FOR CHEMISORPTION OF RADIONUCLIDES

INTRODUCTION

Monitoring radioactive contamination in the event of a nuclear disaster requires rapid and reliable methods of pre-concentration of radionuclides from large volumes of water. After pre-concentration, the radioactivity can be quantified by using in-situ-onboard detectors, such as used in the gamma spectrometer developed by PNNL, or by transferring the sorbent cartridges to a laboratory for traditional high resolution gamma spectrometry. Manganese oxides have been a primary focus for sorption of radionuclides due to their relatively high selectivity towards metals and resistance to radiation damage (Koulouris et al. 2000). In the event of a nuclear disaster, forensic and radiochemical researchers can use in-situ spectrometry and chemisorption to assess the distribution of radionuclides into the surrounding aqueous environment.

A novel in-situ gamma spectrometer is currently being developed by researchers at PNNL. This novel system will employ the use of onboard $LaBr_3$ scintillation detectors and sealed cartridges containing sorbents needed for radionuclide pre-concentration. Previous research has tested the sorption capabilities of many different sorbents that could be employed in the system (Johnson et al. 2011a; Johnson et al. 2011b; Johnson et al. 2012). The use of composite sorbents containing impregnated MnO_2 is expected due to their wide range of selectivity of radionuclides; however, additional testing of novel MnO_2 chemisorbents that could produce higher (>1 order of magnitude) K_D than traditional MnO_2 is necessary.

In this study, I investigated the chemisorption of a selection of MnO_2 sorbents for nine radionuclides in a synthetic sea water. The purpose of these experiments is to evaluate if novel MnO_2 chemisorbents produce higher distribution coefficients (K_D) than traditional impregnated MnO_2 sorbents for radionuclides in aqueous environments. The experiments used here have been modeled after the procedures used in Johnson et al. (2011b). Ultimately, sorbents that display efficient chemisorption and the ability to effectively sequester target radionuclides will be recommended for use in cartridges on PNNL's in-situ gamma spectrometer after nuclear disaster scenarios.

I thus synthesized three novel MnO_2 sorbents using recipes from Glen Fryxell and from the literature including: mesoporous nanostructured MnO_2 (Nayak and Munichandraiah 2011), SAMMS-MnO_2 decorated with Mn^{+3} oxidation states, and SAMMS MnO_2 decorated with Mn^{+4} oxidation states. These sorbents provide advantages over traditional MnO_2 via their high surface area (200 – 1000 m^2g^{-1}), better control of the chemical structure of the MnO_2 (i.e. oxidation states and defect sites), and the unique materials used to assemble the sorbents (i.e. silica gel and Pluronic P123 triblock copolymer). None of these MnO_2 sorbents have been previously tested for their radionuclide chemisorption capabilities. I employed these MnO_2 as triplicates samples in batch experiments to determine their K_D for the following radionuclides: ^{7}Be, ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, ^{137}Cs, ^{210}Pb, ^{233}Pa, and ^{234}Th. The latter 3 radionuclides are used in oceanographic studies for particle cycling. Batch experiments are justified for use of chemisorption determination because they were conducted using identical conditions as in the batch experiments of Johnson et al. (2011b), which they compared to column experiments. This allows one to objectively compare the results of this study to the former one.

In addition to K_D, I determined the shelf life of traditional impregnated MnO_2 by comparing these K_D results using the same batch of impregnated MnO_2 synthesized by Johnson et al. (2011b) to K_D data from their research. The batch of impregnated MnO_2 synthesized by Johnson et al. (2011b), and has been stored in a sealed glass container in the laboratory since 2008. Optimal storage conditions of impregnated MnO_2 were determined in this research by performing batch experiments using fresh MnO_2 stored in dry and deionized water-saturated conditions. Data regarding the optimal storage and shelf life of impregnated MnO_2 is necessary for individuals that plan to store this sorbent in deployable cartridges for long periods (i.e. >5 years) of time.

MATERIALS AND METHODS

A series of batch experiments were performed that are modeled after the methods used by Johnson et al. (2011b). Batch experiments were performed as a means to determine distribution coefficients (K_D) of each radionuclide between artificial seawater (ASW) and MnO_2 chemisorbents. ASW was used for testing the performance of the MnO_2 chemisorbents in an ideal marine environment (salinity = 35‰). The ASW was synthesized using protocols taken from the Marine Biological Laboratory of Woods Hole Oceanographic Institute. Each experimental tube containing ASW was buffered using 50 mM Tris-25 mM HCl to keep the ASW pH at 8.0 ± 0.1. This synthetic seawater does not contain the same concentration of natural colloidal macromolecular impurities that natural waters contain, which can influence sorption of radionuclides to sorbent particles. In K_D experiments for shelf life evaluation of impregnated MnO_2, an artificial fresh water (AFW) was synthesized as well using the same procedures as used in Johnson et al. (2011b). This synthetic water was buffered the same way as ASW in order to keep a pH of 8.0 ± 0.1.

I tested the chemisorption of a selection of 3 synthetic (impregnated MnO_2, nanostructured mesoporous MnO_2, SAMMS MnO_2) and one biogenic MnO_2. The impregnated MnO_2 was synthesized using procedures from Varga (2007), in which MnO_2 is coated on an anion exchange resin (Biorad AG 1-X4 Cl form). The nanostructured mesoporous MnO_2 was synthesized using procedures from Nayak and Munichandraiah (2011). This porous resin is prepared by the reduction of $KMnO_4$ by using the tri-block copolymer P123 (Sigma Aldrich). The copolymer acts as a reducing and structure directing-agent, and allows for the surface area to be controlled (Nayak and Munichandraiah 2011). SAMMS are technologically advanced, high performance sorbents developed by scientists at PNNL. SAMMS can be functionalized to target many different metal sorbates for various applications. MnO_2-SAMMS is synthesized from an unpublished recipe by Glen Fryxell, in which silica gel is used as the support, and the Mn-containing reagents are added at different quantities and heated overnight at 150 °C in a vacuum oven. The different ratios of Mn-containing reagents allow the surface of the SAMMS to become decorated with different oxidation states of Mn (i.e. Mn +3, Mn +4, mixed oxidation). Lastly, biogenically-produced MnO_2 is one that was isolated by members of the Laboratory of Oceanographic and Environmental Research at Texas A&M University at Galveston (unpublished research) from a *Chromobacterium* sp. found at the Savannah River Site in South Carolina. This biogenic MnO_2 is relevant because it has not yet been characterized, nor has it been studied for its role in the fate of radionuclides at Savannah River Site. This selection of MnO_2 sorbents will provide a comparison of traditional and novel chemisorbents that could be used for pre-concentration of radionuclides released to aquatic environments after nuclear disasters.

The set of nine radionuclides were added to batch experiments by standardizing them into two working cocktail solutions of 0.1M HCl. The cocktail solutions were split into one containing ^{7}Be, ^{210}Pb, ^{233}Pa, and ^{234}Th, and another containing ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, and ^{137}Cs. The cocktails were separated into oceanographic radionuclides and nuclear fission product-related radionuclides. Each cocktail was created by adding approximately equal activities of each radionuclide to a Teflon beaker, and then heating the solution to incipient dryness (without boiling) using a heating block. The remaining material was then reconstituted using 150 µL of 0.1M HCl. Standard cocktails were then counted using HPGe gamma spectrometry to quantify the counts per minute (cpm) for each radionuclide that would be added to each batch experiment. The radiotracers were added at concentrations that were identical to those used in Johnson et al. (2011a, 2011b, 2012) for the sake of evaluating sorption differences for shelf life of impregnated MnO_2. It was determined that at these metal concentrations, the solution would not be supersaturated in relation to solid phase formation and each were added less than or equal to most metal's natural concentrations (Johnson et al. 2012).

Batch experiments involving ^{7}Be, ^{210}Pb, ^{233}Pa, and ^{234}Th were separated into particulate, colloidal, and dissolved fractions using 0.45 µm and 3 kDa centrifugal filters (Pall Corporation). The activities of each fraction were used to calculate the K_{DC} for each radionuclide and MnO_2 sorbent. K_{DC} is defined as the distribution coefficient including the colloidal fraction. These radionuclides were separated in this fashion due to their particle-reactive nature as they are considered to be active in the colloidal fraction. ^{233}Pa was added in equilibrium with ^{237}Np, which is known to not sorb to particles, so in-growth of ^{233}Pa in the dissolved phase was accounted for in each K_{DC} calculation.

Batch experiments involving ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, and ^{137}Cs were separated by centrifugation without the use of filters. Johnson et al. (2011b) determined there was greater than 99% sorbent mass recovery using this method, and these radionuclides are not considered active in the colloidal phase. For each of these radionuclides the K_D was calculated rather than $K_{DC.}$

K_{DC} batch experiments involved combining 15 mg of MnO_2 chemisorbent with 14 mL of ASW and 1 mL of 50 mM Tris-25mM HCl buffer inside the membrane of a 0.45 µm centrifuge filter. All radionuclides were combined at similar activities in a cocktail standard of 0.1 M HCl. A 5 µL aliquot of the radionuclide cocktail was added to the sorbent-ASW slurry, and the sample tubes were placed on a shaker table for 100 minutes of equilibration. Previous experiments by Johnson et al (2011b) determined that 100 minutes of mixing allowed for equilibration of all the radionuclides. The tubes were centrifuged at 4000 RPM for 20 minutes to separate the sorbent particles from the water fraction. The retained sorbent particles were collected by rising the filter with Mili-Q water and transferring the suspended sorbent particles to 5 mL counting tubes for gamma spectrometry. The filtrate was then transferred to a 3 kDa centrifuge filter membrane and centrifuged at 4000 RPM for 30 minutes to separate the colloidal and truly dissolved fractions. The retentate was defined as the colloidal fraction of the MnO_2 chemisorbent and was collected for gamma spectrometry by rinsing the filter with 5 mLs of Mili-Q water. The filtrate was then collected for gamma spectrometry and defined as the truly dissolved fraction.

K_D batch experiments involved mixing 50 mg of MnO_2 sorbent with 50 mL of solution (49 mL ASW + 1 mL tris buffer) in a 50 mL centrifuge tube. A 5 µL aliquot of radionuclide cocktail was added to the slurry, and the tubes were then placed on a table shaker for 100 minutes. Experiment tubes were then centrifuged at 4000 RPM and separated into particulate and dissolved fractions by carefully pipetting the solution out of the centrifuge tube. All sorbent particles were then transferred from the centrifuge tube to a 10 mL gamma counting tube using 1.5 mL of deionized water to re-suspend and transfer the particles.

Gamma spectrometry was performed using a Canberra high-purity germanium (HPGe) well detector. The activities of ^{7}Be (477.6 keV), ^{57}Co (122.1 keV), ^{106}Ru (via its daughter ^{106}Rh, 511.8 keV), ^{125}Sb (427.9 keV), ^{133}Ba (356 keV), ^{137}Cs (661.7 keV), ^{210}Pb (46.5 keV), ^{233}Pa (312 keV), ^{234}Th (63.5 keV) were determined. Samples were counted until peak area errors were less than 5% for each radionuclide. The activities in each fraction were used to calculate the K_{DC}, in which the particulate fraction is defined as particulate plus colloidal. The equation used is as follows:

$$K_{DC} = \frac{(Ap+Ac)}{A_d}\frac{V}{m} \ (\frac{L}{kg}) \qquad \text{(II-1)}$$

In the equation above, *Ap* is the total activity in the particulate fraction, *Ac* is the total activity in the colloidal fraction contained on the 3 kDa membrane, *Ad* is the total activity in the truly dissolved fraction, *V* is the volume of the water used in the batch experiment (15 mL), and *m* is the mass of the sorbent (15 mg).

K_D was determined by counting the activity in the particulate and dissolved fractions. The equation used to calculate K_D is as follows:

$$K_D = \frac{A_p}{A_d}\frac{V}{m} \ (\frac{L}{kg}) \qquad \text{(II-2)}$$

In the equation above, A_p is the total activity in the particulate fraction, A_d is the total activity in the truly dissolved fraction, V is the volume of the water used in the batch experiment (50 mL), and m is the mass of the sorbent (50 mg).

The K_{DC} and K_D were determined by normalizing to total sorbent mass used in each batch experiment and to the mass of MnO_2 in each sorbent. MnO_2 content of each sorbent was determined by dissolution of MnO_2 and quantification of Mn using atomic absorption spectrometry (Varian). The rationale for the two ways of calculation is so that the influence of MnO_2 content on radionuclide sorption can also be evaluated. Johnson et al. (2011b) normalized their K_D values only to sorbent mass in their batch experiments.

The shelf life of impregnated MnO_2 was determined by performing batch experiments using the same batch of impregnated MnO_2 synthesized and tested in Johnson et al (2011b). The sorbent was stored in the LOER in an air-tight container at room temperature conditions for six years. I then compared data from these experiments to the data produced by Johnson et al (2011b) by performing t-tests to determine if we observed differences that are statistically different. If there was a significant difference between identical radionuclides and test water, then the shelf life of the sorbent was described as being less than 6 years. Optimal storage condition evaluation was done by storing fresh impregnated MnO_2 in dry and saturated deionized water conditions. K_D batch experiments were performed similarly as described above in ASW and artificial fresh water (AFW). T-tests were performed on the data to determine if there were statistical differences between the K_D of the storage conditions.

RESULTS AND DISCUSSION

A series of batch experiments involving five different MnO_2 sorbents were performed in order to determine if there is an improvement in chemisorption of nine different radionuclides over impregnated MnO_2. The following figures contain the average log K_{DC} and K_D results from these batch experiments. Each data point is presented with error bars that represent the standard deviation of the mean for triplicate samples.

In Figure 1, the average log K_{DC} results of nanostructured, biogenic, and impregnated MnO_2 is presented. The impregnated MnO_2 shown here was freshly synthesized in 2014 using the same recipe as used in Johnson et al. (2011b). Traditional, oceanographic research radionuclides (^{7}Be, ^{210}Pb, ^{233}Pa, and ^{234}Th) were tested to evaluate the capabilities of these sorbents in a marine context. Each of these radionuclides are gamma-emitters and have been used extensively in oceanography tracer studies involving particle export flux from the upper ocean (e.g. Bacon et al. 1996; Feng, Cochran, and Hirschberg 1999;Baskaran and Santschi 2002; Buesseler et al. 2008). K_{DC} values presented here were normalized to the total mass of the sorbent used.

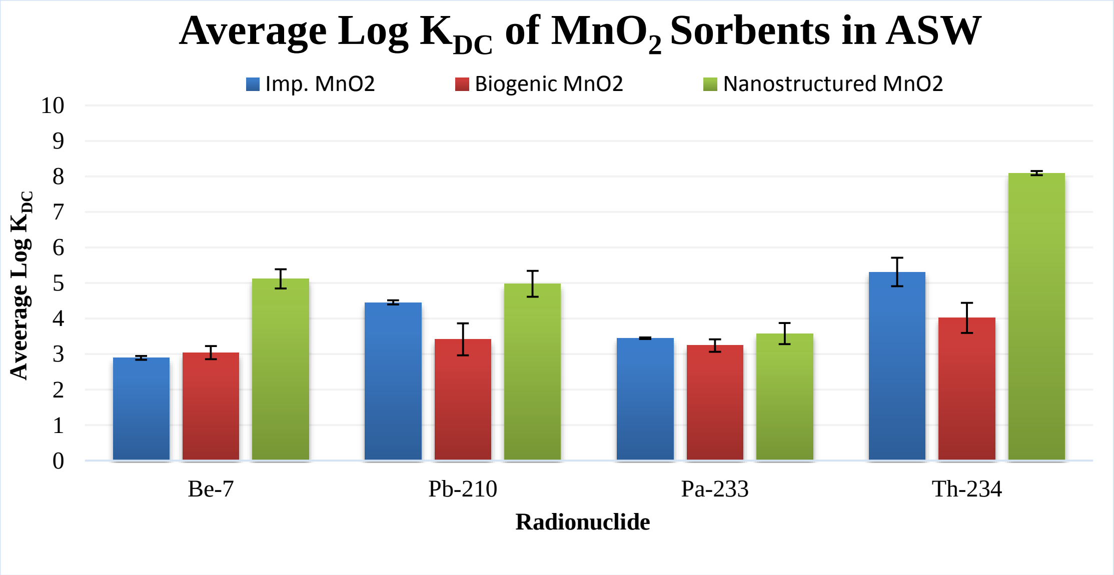

Figure 1: Average Log K_{DC} of Impregnated, Nanostructured, and Biogenic MnO_2 Sorbents in Artificial Seawater (ASW)

MnO_2 produced log K_{DC} values that were comparable to impregnated MnO_2 for ^{7}Be (3.76±0.18 vs 3.59±0.05 log K_{DC}) and ^{233}Pa (3.24±0.18 vs 3.45±0.02 log K_{DC}); however, impregnated MnO_2 produced K_{DC} values that were more than an order of magnitude greater than biogenic MnO_2 for ^{210}Pb (4.46±0.06 vs 3.42±0.45 log K_{DC}) and ^{234}Th (6.03±0.40 vs 4.74±0.42 log K_{DC}). This particular biogenic MnO_2 has not yet been characterized, however it is likely not well constructed for use in cartridges for pre-concentration chemisorption of radionuclides from marine or coastal environments. MnO_2 sorbents employed in pre-concentration cartridges would need to contain consistent MnO_2 coverage, particle size, and purity. Biogenic MnO_2 is likely to be coated by cellular material that could influence sorption capabilities, thus making it an improbable candidate for usage as a sorbent. Nevertheless, this biogenic MnO_2 is precipitated by bacteria found at the Savannah River Site, which is contaminated by anthropogenic radionuclides. The K_{DC} results from this study will be applied to additional experiments in the future to determine how this natural MnO_2 can influence the fate of anthropogenic radionuclides found at the Savannah River Site.

Nanostructured MnO_2 produced K_{DC} values that were numerically greater than impregnated and biogenic MnO_2 for every radionuclide in ASW. Nanostructured MnO_2 produced average K_{DC} values that was up to two orders of magnitude greater than impregnated MnO_2 for ^{7}Be (log K_{DC} 5.69±0.27 vs 3.59±0.05) and ^{234}Th (log K_{DC} 8.09±0.06 vs 6.03±0.40), and log K_{DC} that were 0.5 greater than impregnated MnO_2 for ^{210}Pb (4.98±0.36 vs 4.46±0.06). This nanostructured sorbent has a much greater surface area than impregnated MnO_2 (~250 m^2g^{-1} vs 18 m^2g^{-1}) and is composed of a tri-block copolymer backbone that contains terminal hydroxyl groups where metals could sorb. This mesoporous, nanostructured MnO_2 was designed to perform in electrochemical supercapacitor studies; however, evidence shows that it produces greater K_{DC} values for these radionuclides over those using impregnated MnO_2 under the same conditions.

In Figure 2, the average Log K_{DC} values for the same sorbents and radionuclides as in Figure 1 are presented. The K_{DC} values presented here differ by the K_{DC} calculation, in which the K_{DC} in Figure 2 is normalized to the mass of MnO_2 in each sorbent. The purpose of this data is to evaluate the influence of MnO_2 content (percentage) on the sorption of these particular radionuclides. The MnO_2 content percentage by weight for the sorbents is as follows: impregnated MnO_2 (2.23%), biogenic MnO_2 (26.47%), and nanostructured MnO_2 (12.57%).

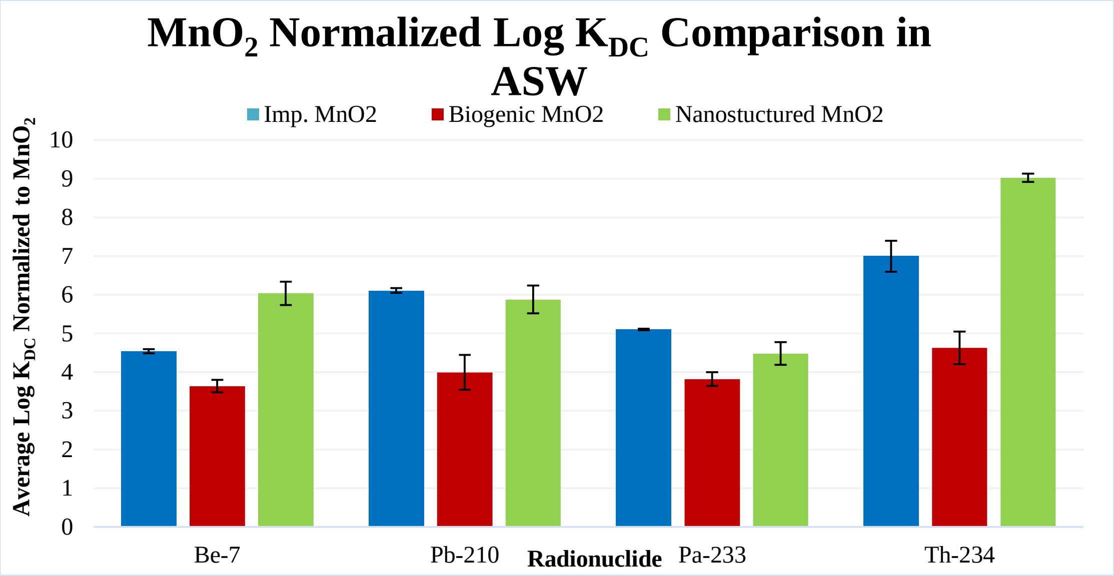

Figure 2: Average log K_{DC} Normalized to MnO_2 Content in Artificial Seawater (ASW)

The log K_{DC} data for the sorbents and radionuclides shown in Figure 2 are greater than the log K_{DC} values from Figure 1. This is expected as the sorption is attributed to the smaller mass of MnO_2 in each sorbent rather than the total mass of sorbent, which is mostly sorption backbone material. Impregnated MnO_2 displayed the greatest improvement to its K_{DC} over the other sorbents and exceeded the results of nanostructured MnO_2 for ^{210}Pb and ^{233}Pa. This is to be expected as its MnO_2 content is much less than the other materials.

Batch experiments using fresh impregnated, biogenic, nanostructured, and SAMMS MnO_2 were conducted in order to evaluate K_D for ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, and ^{137}Cs in ASW. These experiments were modeled after Johnson et al. (2011b), in which centrifugation filters were not used to separate the solution into particulate, colloidal, or dissolved fractions. Figure 3 displays the average log K_D results from the batch experiments. The radionuclides tested in these batches were used to mimic Johnson et al. (2011b). As expected, each sorbent produced minimal log K_D (0.81-1.71 average log K_D) for ^{137}Cs, which is due to its properties as a monovalent alkali metal.

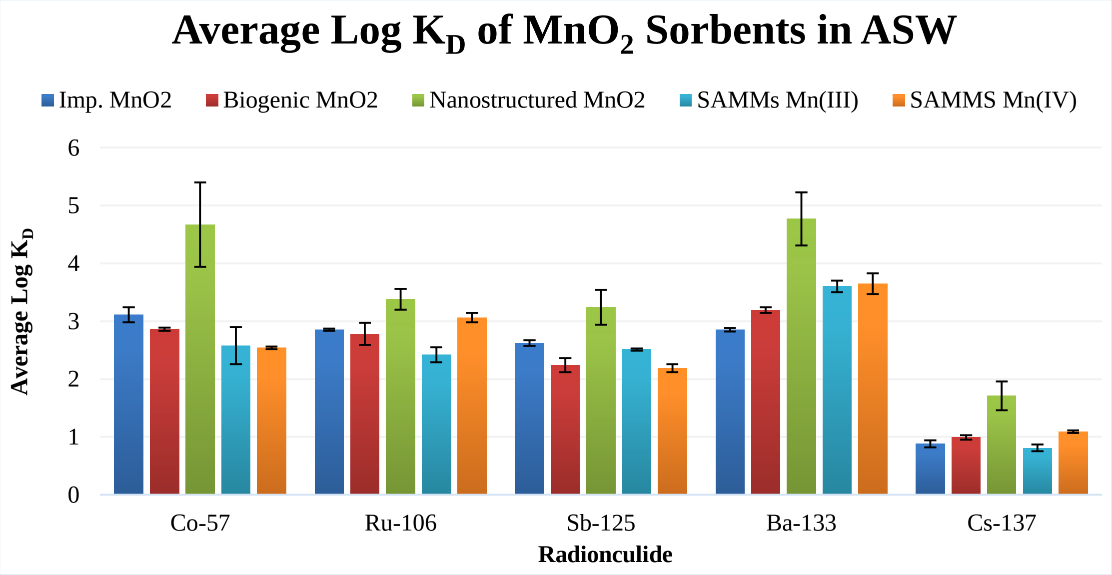

Figure 3: Average Log K_D of Impregnated, Biogenic, Nanostructured, and SAMMS MnO_2 Sorbents in Artificial Seawater (ASW)

The nanostructured MnO_2 sorbent performed similarly as it did in previous K_{DC} experiments. The average log K_D was numerically greater than other MnO_2 for each radionuclide. In comparison to fresh impregnated MnO_2, the nanostructured produced average log K_D values that were more than an order of magnitude greater for some radionuclides (^{57}Co- 4.7±0.7 vs 3.1±0.1 and ^{133}Ba- 4.8±0.5 vs 2.9±0.03). It produced greater log K_D values for ^{106}Ru (3.4±0.2 vs 2.9±0.02), ^{125}Sb (3.2±0.3 vs 2.6±0.1), and ^{137}Cs (1.7±0.3 vs 0.9±0.1). These results prove that the nanostructured MnO_2 is an effective sorbent for many different radionuclides in ASW. Nanostructured MnO_2 was previously used exclusively in supercapacitor studies; however, it is my recommendation that nanostructured MnO_2 be considered for pre-concentration of radionuclides for in-situ gamma spectrometry due to its superior log K_D to impregnated MnO_2 in ASW.

SAMMS-MnO_2 resins were synthesized with different amounts of Mn(III,IV) in the Mn(IV) structure in an attempt to improve its chemisorption capabilities for these radionuclides. All recipes for SAMMS resins were suggested by Glen Fryxell of Battelle, who is the designer of these materials. There were improvements to the K_D of impregnated MnO_2 using SAMMS MnO_2 resins for specific isotopes. Mn +3-SAMMS showed improvement in log K_D over impregnated MnO_2 for ^{133}Ba (3.6±0.1 vs 2.9±0.03), however it produced lower values for the rest of the radionuclides. Mn +4-SAMMS displayed improved log K_D results over impregnated MnO_2 for ^{106}Ru (3.1±0.1 vs 2.9±0.02), ^{133}Ba (3.7±0.2 vs 2.9±0.03), and ^{137}Cs (1.1±0.02 vs 0.9±0.06). Neither of these sorbents improved the log K_D performance by orders of magnitude like originally hypothesized. Although these SAMMS materials are advanced in their design, they will likely need to be chemically altered for use as a substitute of impregnated MnO_2 in chemisorbent cartridges. Future improvement to SAMMS-MnO_2 could involve the addition of Fe to the structure of the MnO_2 to create more reactive binding sites, or the recipes for SAMMS synthesis could include different combinations of Mn-containing reagents to improve Mn coverage of the silica backbone.

Novel biogenically-produced MnO_2 was included in these batch experiments in order to determine its chemisorption capabilities for ^{57}Co, ^{106}Ru, ^{125}Sb, ^{133}Ba, and ^{137}Cs compared to impregnated MnO_2. Biogenic MnO_2 yielded numerically greater average log K_D values than impregnated MnO_2 for ^{133}Ba (3.2±0.1 vs 2.9±0.03) and ^{137}Cs (1.0±0.04 vs 0.9±0.1), however it produced log K_D values that were less than impregnated MnO_2 for each of the remaining radionuclides. This biogenic MnO_2 has proven to sorb all of the radionuclides in batch experiments by an average log K_D range of ~1 - 4.75. As before, this particular biogenic MnO_2 does not outperform synthetic MnO_2 sorbents. This biogenic MnO_2 needs to be further characterized to determine its morphology and chemical structure (i.e. oxidation states). All K_D results using biogenic MnO_2 will be incorporated in future characterization studies to help determine how this MnO_2 influences the fate of anthropogenic radionuclides at the Savannah River Site.

In Figure 4, the log K_{DC} values using the same sorbents and radionuclides as Figure 3 is presented as K_{DC} data normalized to MnO_2 content. As before, the purpose of this data is to evaluate the influence of MnO_2 content on the sorption of these radionuclides to the tested MnO_2 sorbents. The MnO_2 content as percentage by weight is as follows: impregnated MnO_2 (2.23%), biogenic MnO_2 (26.47%), nanostructured MnO_2 (12.57%), SAMMS Mn(III) (9.98%), and SAMMS Mn(IV) (11.25%).

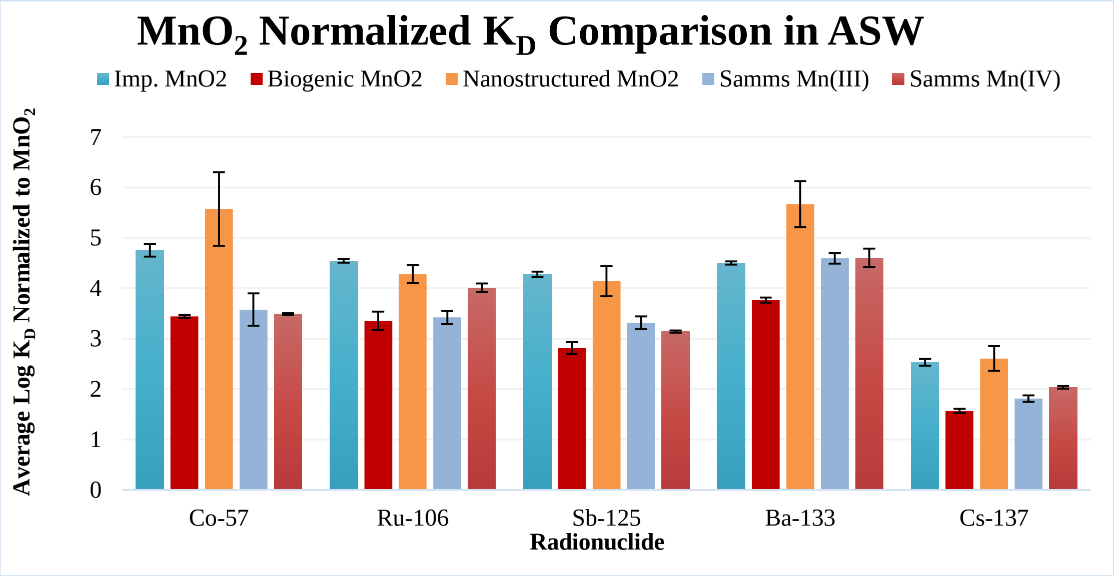

Figure 4: Average Log K_D Normalized to MnO_2 Content in Artificial Seawater (ASW)

In Figure 4 the results are similar to those in Figure 2. For each sorbent, the log K_D is calculated to be greater than K_D normalized to total mass of sorbent. The relatively small mass of MnO_2 in impregnated MnO_2 results in a log K_D that is greater than for each of the other sorbents, with the exception of nanostructured MnO_2, using the same radionuclides. Nanostructured MnO_2 produces the greatest K_D values for ^{57}Co, ^{133}Ba, and ^{137}Cs. These results help convey that the relative amount of MnO_2 can influence the sorption of these radionuclides from aqueous solution.

Table 1: Average Log K_D Results of All Radionuclides Using MnO_2 Sorbents in Artificial Seawater (ASW)

Radionuclide	Fresh Impregnated MnO_2	Nanostructured MnO_2	SAMMs Mn (III)	SAMMS Mn (IV)	Biogenic MnO_2	Johnson MnO2 (2011b)	Wet MnO_2	Old MnO_2
^{7}Be	3.59±0.05	5.69±0.27	N/A	N/A	3.76±0.18	N/A	N/A	N/A
^{57}Co	3.11±0.13	4.67±0.73	2.58±0.32	2.54±0.02	2.86±0.03	3.16±0.37	2.52±0.04	3.09±0.04
^{106}Ru	2.85±0.02	3.38±0.18	2.42±0.13	3.06±0.08	2.78±0.19	3.04±0.21	2.93±0.06	2.86±0.01
^{125}Sb	2.62±0.05	3.24±0.30	2.51±0.02	2.19±0.07	2.24±0.12	2.75±0.15	2.52±0.04	2.83±0.07
^{133}Ba	2.85±0.03	4.77±0.46	3.60±0.10	3.65±0.18	3.19±0.05	3.57±0.3	2.75±0.02	2.83±0.02
^{137}Cs	0.88±0.06	1.71±0.25	0.81±0.06	1.09±0.02	0.99±0.04	1.01±0.03	2.53±0.01	N/A
^{210}Pb	4.46±0.06	4.98±0.36	N/A	N/A	3.42±0.45	N/A	N/A	N/A
^{233}Pa	3.45±0.02	3.58±0.30	N/A	N/A	3.24±0.18	N/A	N/A	N/A
^{234}Th	6.03±0.40	8.09±0.06	N/A	N/A	4.74±0.42	N/A	N/A	N/A

MnO_2 impregnated anion exchange resins that were used in Johnson et al. (2011b) were retested for ^{57}Co, ^{125}Sb, ^{133}Ba, and ^{106}Ru adsorption. Figure 3 and Figure 4 display the impregnated MnO_2 K_D results of the comparison between Johnson et al. (2011b) and these 2014 experiments using ASW and AFW. The purpose of these results is to evaluate if there are statistical differences between K_D values using the same batch of impregnated MnO_2 after six years of storage. Additionally, the results of the wet storage K_D is presented as Wet MnO_2. Old MnO_2 represents the retest of the same batch of MnO_2 synthesized and tested by Johnson et al. (2011b), while Fresh MnO_2 is a 2014 batch of impregnated MnO_2 using the same Varga (2007) procedures.

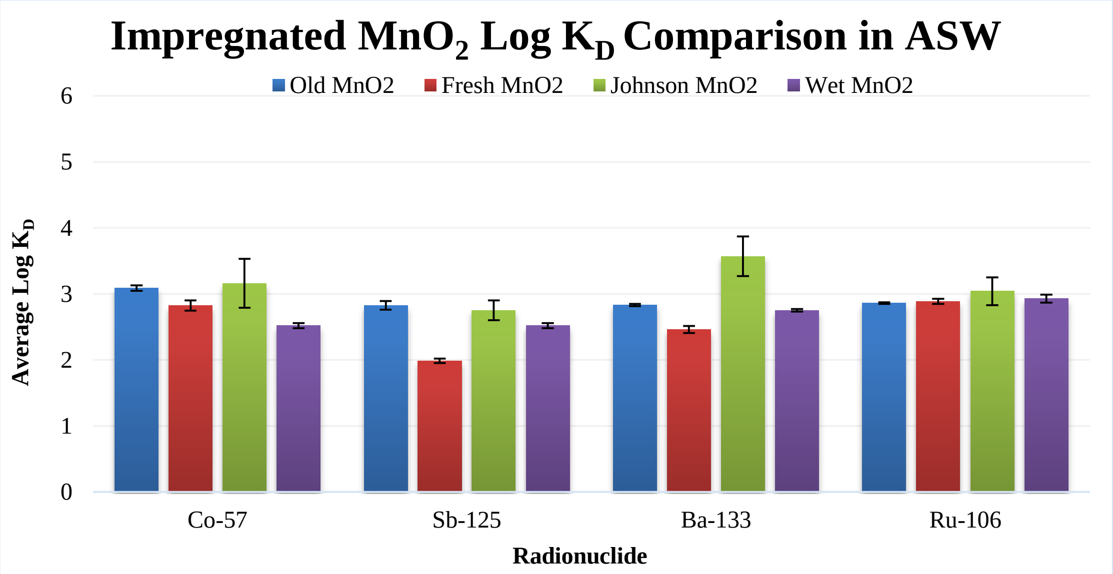

Figure 5: Average Log K_D Comparison of Impregnated MnO_2 Sorbents in Artificial Seawater (ASW)

In Figure 5, the comparison of Old MnO_2 and Johnson MnO_2 is established to evaluate the shelf life of impregnated MnO_2 in ASW. Generally, the Old MnO_2 impregnated anion exchange resins performed either the same in artificial seawater, or slightly less efficient for some radionuclides (e.g. ^{57}Co, ^{106}Ru, ^{133}Ba). However, results were similar when compared to newly synthesized MnO_2 impregnated anion resins, suggesting that there might have been slight differences in experimental execution rather than degradation of the sorbent over 5-6 years. T-test analysis ($p<0.01$) reveals that there is no statistical difference between the same MnO_2 resin tested by Johnson et al., (2011b), and its retest in 2014 for ^{57}Co ($P = 0.76$), ^{106}Ru ($P = 0.47$), and ^{125}Sb ($P = 0.22$) in ASW. Using this information, the shelf life for impregnated MnO_2 is determined to be greater than five years for these radionuclides in ASW.

Impregnated MnO_2 sorbents were stored in wet and dry conditions to compare K_D performance. Batch experiments using each storage condition revealed that storage of impregnated MnO_2 in deionized water for 5 months yielded numerically higher K_D values in artificial seawater for the following radionuclides: ^{125}Sb (2.5 ± 0.04 vs 2.0 ± 0.03), ^{133}Ba (2.8 ± 0.02 vs 2.5 ± 0.01), and ^{106}Ru (2.9 ± 0.1 vs 2.9 ± 0.04). The results for ^{57}Co were numerically less for wet storage than dry storage of impregnated MnO_2. T-test analysis ($p<0.01$) confirmed that each wet storage K_D was significantly different from dry storage. For future use of impregnated MnO_2 inside of cartridges on an in-situ gamma spectrometer, I recommend that the sorbent be stored in sealed, deionized water-saturated containers for optimal K_D performance in seawater for radioisotopes of Sb, Ru, Ba, and Ru.

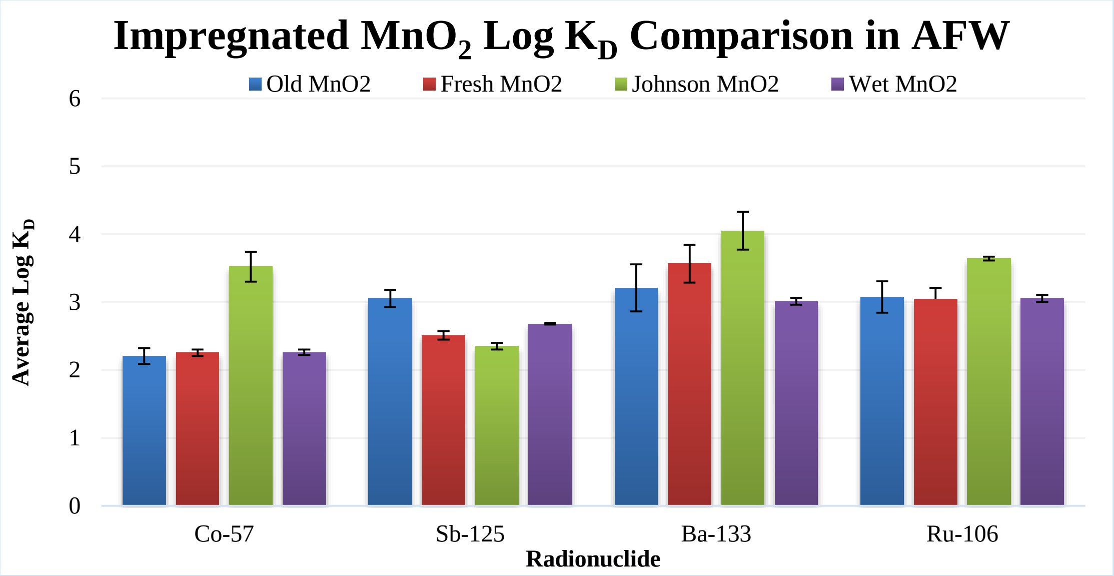

Figure 6: Average Log K_D Comparison of Impregnated MnO_2 Sorbents in Artificial Fresh Water (AFW)

In Figure 6, the results of batch experiments in AFW are presented to evaluate the shelf life of impregnated MnO_2 for this set of radionuclides. Old MnO_2 produced average log K_D that was numerically less than Johnson MnO_2 for every radionuclide except ^{125}Sb (3.1±0.1 vs 2.4±0.1). Fresh MnO_2 produced average log K_D values that were approximately the same as Old MnO_2 for ^{57}Co (2.3±0.1 vs 2.2±0.1) and ^{106}Ru (3.1±0.2 vs 3.1±0.2), and it exceeded the average log K_D for ^{133}Ba (3.6±0.3 vs 3.2±0.4). T-test analysis ($p<0.01$) reveals that AFW batch experiments yielded wet storage K_D values that were not significantly different than dry MnO_2 storage. Based on these results, impregnated MnO_2 sorbents used in synthetic fresh water analyses are unaffected by saturated storage conditions and can be stored either wet or dry for optimal K_D performance.

CONCLUSIONS

The K_D performance of a selection of novel MnO_2 sorbents using nine radionuclides was performed in ASW in order to compare to traditional impregnated MnO_2. In all cases, nanostructured MnO_2 was found to outperform impregnated MnO_2 K_D by 1-2 orders of magnitude for all radionuclides of interest. SAMMS-MnO_2 showed higher affinity towards ^{133}Ba than impregnated MnO_2, however it yielded lower K_D for all other radionuclides. SAMMS-MnO_2 did not perform as expected in this research, and it is my recommendation that its structure needs to be improved chemically in order to be substituted for impregnated MnO_2 as a radionuclide adsorbent. Biogenically-produced MnO_2 produced log K_D that was slightly higher than impregnated MnO_2 for ^{7}Be, ^{133}Ba and ^{137}Cs; however, this biogenic MnO_2 needs to have its morphology and chemical composition characterized in order to better understand its sorption mechanisms.

MnO_2 content of each sorbent was measured in order to evaluate its effect on the sorption of radionuclides from solution. Although nanostructured MnO_2 still displayed the greatest K_D and K_{DC} value for most radionuclides, Impregnated MnO_2 contained relatively the least MnO_2 content in its structure and thus showed orders of magnitude improvement over its K_D and K_{DC} value when normalized to total sorbent mass.

The shelf life and optimal storage condition of impregnated MnO_2 was evaluated by performing K_D batch experiments in ASW and AFW. It has was determined that the shelf life of impregnated MnO_2 is greater than five years for ^{57}Co, ^{125}Sb, and ^{106}Ru in

ASW. In AFW, the shelf life is determined to be less than five years for each radionuclide at the significant level of $p<0.01$.

CHAPTER III

ANFEZH CHEMISORPTION AND DESORPTION OF RADIOCESIUM

INTRODUCTION

Radiocesium isotopes (i.e. ^{134,137}Cs) are well-studied contaminants of nuclear spills and legacy waste sites. In March 2011, the Fukushima Dai-Ichi nuclear power plant was critically damaged by an earthquake and subsequent tsunami that resulted in the accidental release of an estimated 12 to 41 PBq of ^{137}Cs. This event represents the largest release of radionuclides to the ocean in human history (Pike et al. 2013). Events such as these are relevant due to the significant health concerns associated with radioactive isotopes of Cs. In particular, ^{137}Cs carries considerable health risks due to its emission of gamma energy, relatively long half-life ($T_{1/2}$ = 30.17 y), and its high chemical solubility in natural waters. Cs metal behaves similarly to potassium and can be readily absorbed into the soft tissues of the body, which can cause thyroid cancer, asthma, heart problems, reproductive damage, and mutagenic disorders (Olatunji et al. 2015). Due to their prevalence after nuclear disasters and inherent dangers, radioisotopes of Cs are among the most critical risks for humans in the event of a nuclear catastrophe.

The assessment of radionuclide contamination after a nuclear disaster can be done by means of in-situ spectrometry and pre-concentration chemisorption. In-situ chemisorption of radionuclides from natural waters allows for analytes to be concentrated into compact cartridges that can be easily transported for further analysis.

These methods allow researchers to strip trace metals and radionuclides from large volumes (greater than 200 liters) of water, thus improving the sensitivities of their measurements (Mann and Casso 1984). In addition to cesium measurement in natural waters, the treatment of low, medium, and high-level contaminated nuclear wastes is gaining national attention. Commercial cesium-specific chemisorbents have been tested for pre-concentration of radiocesium from marine waters in other studies (e.g. Johnson et al. 2011a; Johnson et al. 2011b; Johnson et al. 2012). A sophisticated and efficient in-situ spectrometry and pre-concentration response to a nuclear disaster involving a release of radionuclides to marine environments is needed to evaluate potential health risks to first-responders.

In the event of a spill of radioactive waste to the marine environment, pre-concentration will be performed using various chemisorbents that are efficient at sorbing target radionuclide species. The composite sorbent used here, Anfezh, is regularly used for the rapid determination of radioactive cesium species in natural waters, milk, and other aqueous media (Remez and Sapozhnikov 1996). Anfezh is a patented, cesium-specific chemisorbent that was formulated by the Russian-Canadian company Compomet-Cantec in Ekaterinburg, Russia. Anfezh is characterized as a potassium hexacyanoferrate, or Prussian blue, compound supported by a cellulose backbone. Over the course of its use, Anfezh has proven to be effective for pre-concentration of radiocesium from deep and surface waters. Anfezh has a certified efficiency for radiocesium of 98 ± 1% (Remez and Sapozhnikov 1996). Anfezh is available directly from its current parent company, Eksorb, for the use of radionuclide pre-concentration.

Commercial chemisorbents, such as Anfezh, would be a first-choice for use in cartridges contained on an in-situ, first-response device in the event of a nuclear spill.

There is a demand from the Measurement and Signatures Intelligence (MASINT) initiative of the U.S. Defense Intelligence Agency for the testing of the chemisorption and desorption of radionuclides, storage, and shelf-life determination of the commercial sorbent, Anfezh. I performed each of the listed experiments requested by MASINT. The results of these experiments will be employed for the future use of Anfezh as a radionuclide chemisorbent on the novel, in-situ gamma spectrometer that has been developed by PNNL. I tested the chemisorption of Anfezh using five different radionuclides and three test waters, determined a novel method for the desorption of ^{137}Cs from Anfezh needed for mass spectrometry analysis, briefly determined if there are detrimental effects to Anfezh from wet versus dry storage conditions, and I determined the shelf life of Anfezh stored at room temperature conditions by performing K_D batch experiments using 6-year-old Anfezh.

MATERIALS AND METHODS

Batch experiments were performed as a means to determine the K_D between Anfezh and five different radionuclides using two synthetic waters, artificial seawater ASW) and artificial fresh water (AFW), and one natural 0.45 µm filtered Galveston Bay Water. These batch experiment methods were replicated from Johnson et al. (2011b) in order to perform a t-test comparison of Anfezh K_D for shelf life determination. In previous experiments by Johnson et al (2011b), centrifugation of the sorbent separation of particulate and dissolved fractions was shown to reliably recover greater than 99% of the original sorbent mass, so I did not use centrifugal filters in these experiments.

K_D batch experiments were performed by combining 50 mg of Anfezh and 50 mL test water (49 mL of water + 1 mL of 50 mM Tris/25 mM HCl buffer) in a 50 mL centrifuge tube. A 5 µL aliquot of working radionuclide cocktail (standardized in 0.1M HCl) was added to each sample, and then placed onto a shaker for 100 minutes equilibration. After shaking, the samples were centrifuged at 4000 RPM for 15 minutes to separate the particulate and dissolved fractions. The dissolved fraction was then separated from each tube by pipetting it into another centrifuge tube. Then 1.5 mL of deionized water was used to transfer all of the Anfezh particles into a gamma counting tube. A 2 mL aliquot of the dissolved fraction was then placed into a gamma counting tube. Each fraction was then counted using gamma spectrometry. As before, metal radiotracer concentrations were added less than or near environmental concentrations.

Gamma spectrometry was performed using a Canberra high-purity germanium (HPGe) well detector. The activities of ^{57}Co (122.1 keV), ^{106}Ru (via its daughter ^{106}Rh, 511.8 keV), ^{125}Sb (427.9 keV), ^{133}Ba (356 keV), and ^{137}Cs (661.7 keV) were determined. Samples were counted until peak area errors were less than 5% for each radionuclide. All radionuclides were applied using a working-standard cocktail of 0.1 M HCl. The cocktail was developed by applying all radionuclides at similar activities, heating to incipient dryness, and finally standardizing the solution using 0.1M HCl. The K_D was calculated by counting each fraction using gamma spectrometry, in which each sorbent or water fractions were counted until the counting error was less than 5%. The formula used to determine K_D is as follows:

$$K_D = \frac{Ap}{A_d}\frac{V}{m}\ \left(\frac{L}{kg}\right) \qquad \text{(III-2)}$$

In Equation 2, *Ap* is the total activity in the particulate fraction, *Ad* is the total activity in the truly dissolved fraction, *V* is the volume of the water used in the batch experiment (50 mL), and *m* is the mass of the sorbent (50 mg). I determined the K_D values of all five radionuclides to assess their affinity for Anfezh particles in the three different aqueous conditions (i.e. different salinity and pH).

I determined the shelf-life of Anfezh stored in room temperature conditions by performing batch experiments using the same batch of Anfezh used by Johnson et al. (2011b) that has been stored in sealed glass container located in the Laboratory for Oceanographic and Environmental Research at Texas A&M University at Galveston since 2008, and freshly manufactured Anfezh that was purchased in 2014. I performed triplicate batch experiments in the same fashion as listed before. The data from these experiments was used to compare to the data produced by Johnson et al. (2011b). I performed t-test analyses of the data to determine if these experiments using the same batch of Anfezh used in 2008 is significantly different after 6 years of storage. Data that is significantly similar or different will help me determine the shelf life of Anfezh for particular radionuclides.

Experiments to chemically destroy Anfezh’s structure and desorb ^{137}Cs were performed by testing small-scale (50 mg) quantities of Anfezh and reagents (1-5 mLs) in 10 mL counting tubes (e.g., using various acids, bases, or reductants). Tubes were capped and placed onto a shaker to ensure adequate mixing of Anfezh and desorption reagent. Equilibration times varied from short scale (100 minutes) to longer scale (48 hours). Information from Eksorb, the manufacturer of Anfezh, mentioned that under alkaline conditions (pH 11-12) the Anfezh would desorb cesium. Due to the lack of literature on the effect of strongly alkaline conditions on cesium sorbed to Anfezh, experiments begun by testing bases (i.e. NaOH and NH_4OH) and some acids for comparison (i.e. HNO_3 and oxalic acid) at different molar concentrations (i.e. 0.01 M, 0.1 M). I quantified desorption of ^{137}Cs by counting pre and post mixing using gamma spectrometry. Small scale experiments proceeded until greater than 50% desorption of cesium was reproduced three times. I performed identical experiments using larger quantities of sorbent (~20 g) and reagent (~500 mL) in 1 L Teflon beakers.

After performing large and small batch desorption experiments, I filled the sorbent cartridge from PNNL to full capacity with Anfezh (~10 g). I then circulated water containing a spike of ^{137}Cs through the cartridge continuously using a peristaltic pump. After that, I circulated 0.1 M NaOH for a minimum of 12 hours. The activity of the desorbed ^{137}Cs was determined by taking an aliquot of the NaOH solution and counting it using an HPGe gamma spectrometer (Canberra). I repeated this procedure three times to determine reproducibility for a sorbent cartridge that has been deployed in an aqueous environment.

RESULTS AND DISCUSSION

A series of batch experiments were conducted to evaluate the effectiveness of Anfezh as a sorbent for use in a cartridge on an in-situ gamma spectrometer, and to determine the shelf life of Anfezh stored in room temperature conditions. The K_D results for Anfezh, chosen radionuclides, and test waters is described below. In each figure below: Old Anfezh corresponds to Anfezh that was purchased and tested by Johnson et al. (2011b) and has been stored in the laboratory since 2008, Johnson Anfezh corresponds to the data taken from Johnson et al (2011b), and Fresh Anfezh represents a new Anfezh purchased in 2014.

In Figure 7, the average log K_D of Anfezh in ASW is presented. Average log K_D values ranged from values of ~1 – 4 for this selection of radionuclides. The K_D produced by the Fresh Anfezh was greater than any other variant of Anfezh displayed here. As expected, the numerically highest log K_D values were produced using ^{137}Cs in which the values ranged from 3.2-3.9. The Old Anfezh produced higher log K_D values than Johnson et al. (2011b) for all radionuclides. It is difficult to explain the improvement over Johnson Anfezh using the Old Anfezh. Each batch experiment I performed was done using the same materials and methods as Johnson et al. (2011b). A possible explanation is that there were slight systematic differences in the execution of the same procedure. Additionally, it is unclear whether Johnson's results were reported using triplicate samples of each sorbent. The compounding effects of procedural differences and lack of replicates could explain the difference of up to an order of magnitude of K_D for some radionuclides using the same batch of Anfezh.

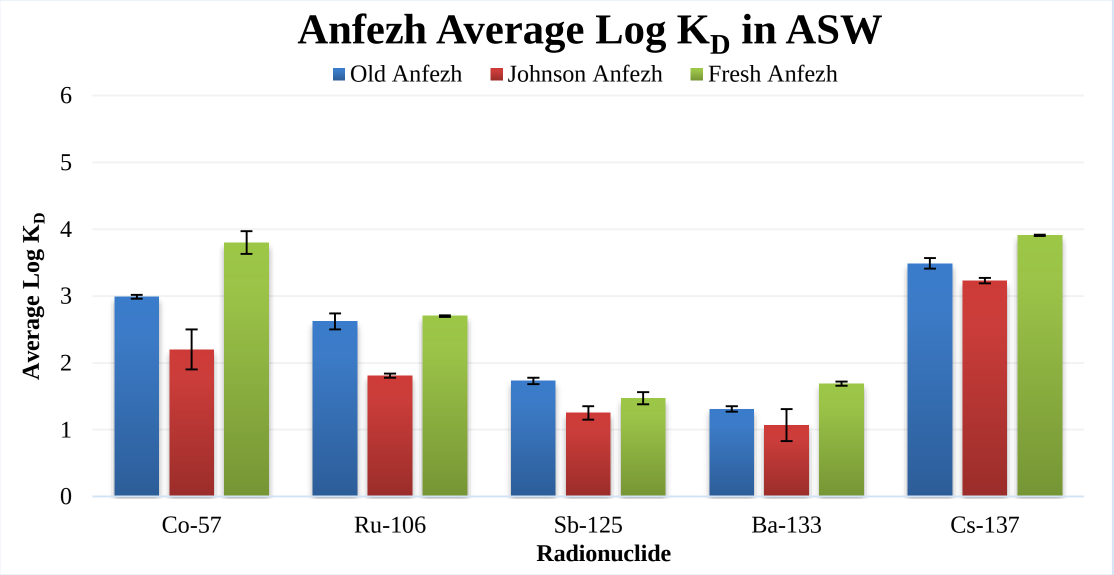

Figure 7: Average Log K_D of Anfezh in Artificial Seawater (ASW)

In Figure 8, the average log K_D of Anfezh in AFW is presented. Similar to ASW, the Fresh Anfezh produced higher K_D values for all radionuclides; however, the K_D value for ^{125}Sb was lower than the Johnson Anfezh and Old Anfezh. The numerically highest average log K_D values were produced by ^{137}Cs using each sorbent. Johnson Anfezh produced higher log K_D than the Old Anfezh for ^{57}Co, ^{106}Ru, ^{125}Sb, and ^{137}Cs. Old Anfezh produced higher log K_D values than Johnson et al (2011b) for ^{133}Ba.

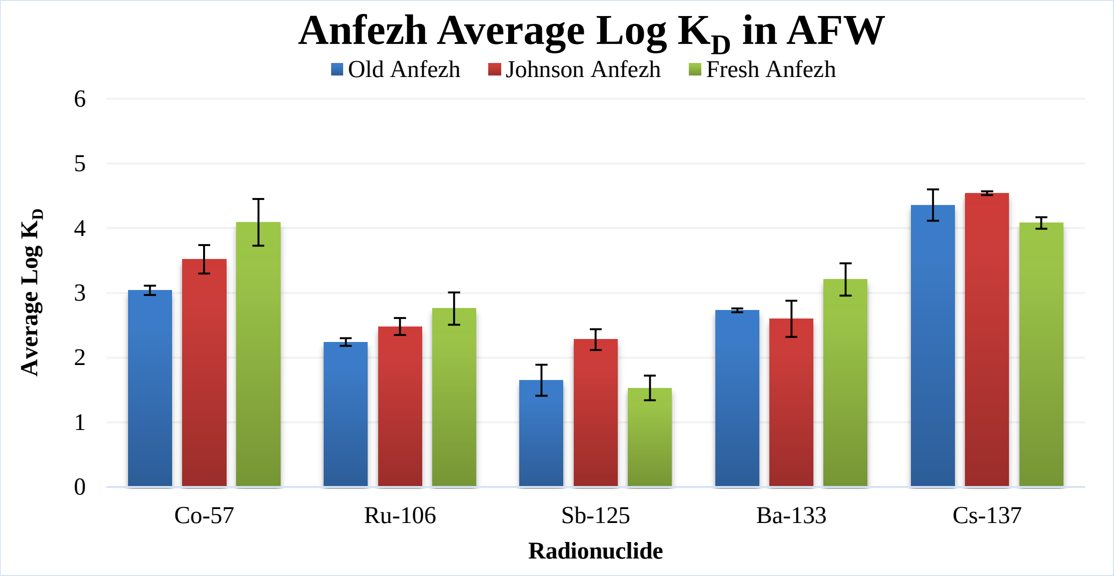

Figure 8: Average Log K_D of Anfezh in Artificial Fresh Water (AFW)

In Figure 9, the data produced by batch experiments using Old Anfezh and filtered GBW is presented. Johnson et al. (2011b) did not perform batch experiments using this particular water and sorbent. The highest average log K_D values were produced by ^{137}Cs, followed by ^{57}Co and ^{106}Ru. The average log K_D of ^{137}Cs was lower in GBW than in ASW or AFW. This water was filtered using 0.45µm glass fiber filters to remove any sediment particles, however organic matter and colloidal particles are likely present in solution. The presence of natural macromolecular and micro-particles in the GBW will likely complex the radionuclides in batch solution, which would reduce the sorption of ^{137}Cs to Anfezh.

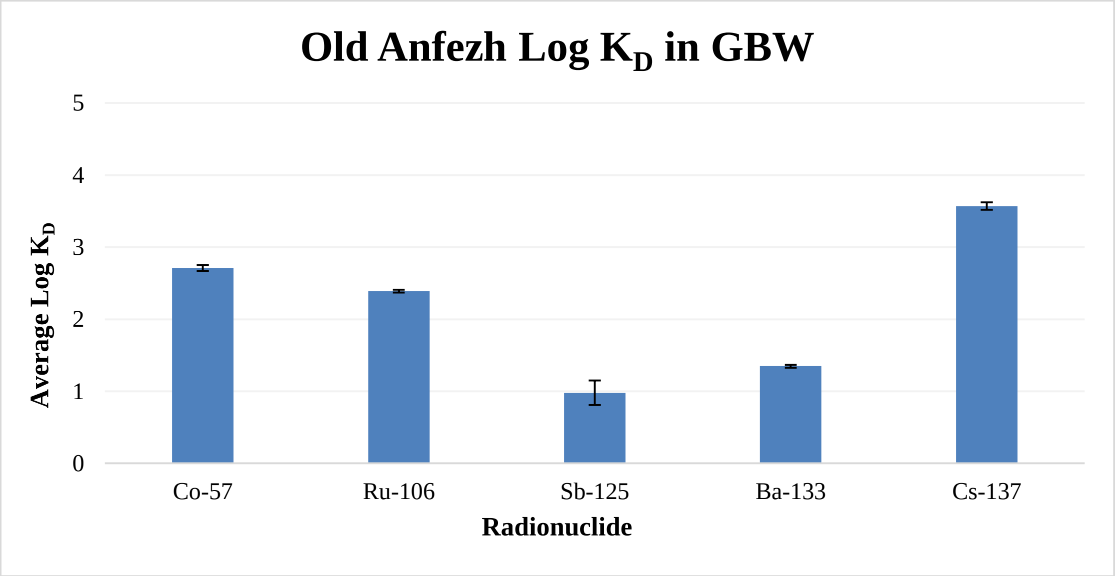

Figure 9: Average Log K_D of Old Anfezh in Galveston Bay Water (GBW)

In Table 2, the average log K_D data from each of the previous graphs is presented. The deviation given is the standard deviation of the mean using triplicate samples.

Table 2: Average Log K_D of Anfezh in Artificial Seawater, Artificial Fresh Water, and Galveston Bay Water

ASW	**Sorbent**	^{57}**Co**	^{106}**Ru**	^{125}**Sb**	^{133}**Ba**	^{137}**Cs**
	Old Anfezh	2.99 ± 0.03	2.62 ± 0.12	1.73 ± 0.05	1.31 ± 0.04	3.49 ± 0.08
	Johnson Anfezh	2.20 ± 0.30	1.81 ± 0.03	1.25 ± 0.10	1.07 ± 0.24	3.23 ± 0.04
	Fresh Anfezh	3.80 ± 0.17	2.70 ± 0.01	1.47 ± 0.09	1.69 ± 0.03	3.91 ± 0.01
AFW	Old Anfezh	3.04 ± 0.07	2.24 ± 0.06	1.65 ± 0.24	2.73 ± 0.03	4.36 ± 0.24
	Johnson Anfezh	3.52 ± 0.22	2.48 ± 0.13	2.28 ± 0.16	2.60 ± 0.28	4.54 ± 0.03
	Fresh Anfezh	4.09 ± 0.36	2.76 ± 0.25	1.53 ± 0.19	3.21 ± 0.25	4.08 ± 0.09
GBW	Old Anfezh	2.71 ± 0.04	2.39 ± 0.02	0.98 ± 0.17	1.35 ± 0.02	3.57 ± 0.05

Anfezh has again proven to be an effective sorbent for Cs in different test waters. The results from these experiments have shown that in synthetic fresh water, synthetic sea water, and Galveston Bay Water, Cs binds to Anfezh at 1-3 orders of magnitude greater than Co, Sb, Ru, and Ba. In every condition tested, Co produces an average K_D that is about one order of magnitude lower than Cs. Anfezh has a certified efficiency of 98 ± 1% for Cs and an efficiency of 40 ± 5% for Co, so it is expected that the average K_D is inherently lower (Remez and Sapozhnikov 1996).

The shelf life of Anfezh was determined using t-test analysis of the results of these batch experiments using Old Anfezh and the results from Johnson et al. (2011b). If a statistical significant difference was observed at $p<0.01$, then the shelf life of Anfezh for particular radionuclides was considered to be less than 6 years. It is assumed that although this study contains a low number of samples due to the constraints of time, materials, etc., the experimental conditions were duplicated using triplicate batches thus making this t-test appropriate for testing statistical differences between the data. Anfezh sorbents produced results that were statistically indistinguishable to those determined by Johnson et al. (2011b) for ^{137}Cs (its target radioisotope), indicating that the dry-storage shelf life is at least 5 years. At a confidence level of 99%, there was no significant difference between Anfezh average log K_D in Johnson's data and the retest using the same Anfezh sorbent for artificial sea water ($P=0.04$) or artificial fresh water ($P=0.24$). Dry weight normalized log K_D for Cs^{137} in artificial seawater was determined as 3.49 ± 0.08, while Johnson et al. (2011b) determined 3.2 ± 0.04 for identical conditions in 2008/2009. Log K_D for artificial freshwater was determined as 4.4 ± 0.2, while Johnson et al. (2011b) obtained 4.5 ± 0.03. The similar performance suggests that Anfezh resins have a shelf life of at least 5-6 years for use in ASW and AFW. The batch of Anfezh used in these tests was stored in a sealed glass container under ambient laboratory conditions (~18°C) for six years. Results from these tests indicate that Anfezh can be stored in a sealed sorbent cartridge at ambient laboratory conditions for up to six years and be used reliably for Cs adsorption in synthetic fresh or marine waters.

Leaching experiments were performed in order develop verified methods of extraction of Cs^{137} sorbed to the commercial chemisorbent, Anfezh. Initially, small-scale trials were conducted using hot (~60°C) and room temperature (~18°C) oxalic acid, nitric acid, hydroxylamine, ammonium hydroxide, and 30% hydrogen peroxide for mixing times of 100 minutes to 48 hours; however, each of those reagents failed to desorb greater than 40% of the ^{137}Cs sorbed to Anfezh. Soon after those tests, I experimented using 0.01M and 0.1M sodium hydroxide (NaOH), in which each reagent immediately (< 30 minutes mixing) started to visibly alter the color of Anfezh from blue to gray and the solution turned orange. This color change is likely due to the rapid oxidation of Fe(II) to Fe(III) in the structure. After 24 hours of mixing, the NaOH turned from orange to green. The result of this color change is possibly due to the hydrolysis of the cyanide bonds found in the Anfezh's ferrocyanide structure. After 100 minutes mixing time, the addition of 0.1M NaOH extracted 71% of the ^{137}Cs sorbed to Anfezh. The same reaction vessel was allowed to mix for 24 hours, in which the total percentage of ^{137}Cs desorbed from Anfezh was increased to 73.7%. The addition of 0.01M NaOH was not as effective, however, and extracted 1.9% of the sorbed ^{137}Cs from Anfezh after 100 minutes mixing. One might infer that there was not an adequate concentration of hydroxide present to oxidize the ferrocyanide when the concentration of NaOH is 0.01M rather than 0.1M, although O_2 is the oxidant.

It was believed that some of the ~30% remaining Cs sorbed to the Anfezh must be held by incomplete oxidation of the ferrocyanide framework by O_2 in NaOH and that the digested iron in the mixture could flocculate and inhibit Cs from entering the solution. To attempt to further improve desorption of Cs from Anfezh, 1M ethylenediaminetetraacetic acid (EDTA) was added to the NaOH solution and was allowed to mix with the Anfezh for 100 minutes. This reaction increased desorption of Cs from Anfezh to 79.98%. EDTA is a hexadentate ligand that can chelate the digested iron that was possibly inhibiting Cs from releasing into solution. An increase of ~9% of Cs extracted from Anfezh is progress towards the goal of producing a method that extracts the highest percentage of Cs from Anfezh that has been deployed in natural environments. In Figure 10, the results of the small-scale leaching experiments is presented. Each value is based on single trials using the stated reagents. NaOH leaching was reproduced in later single batch trials.

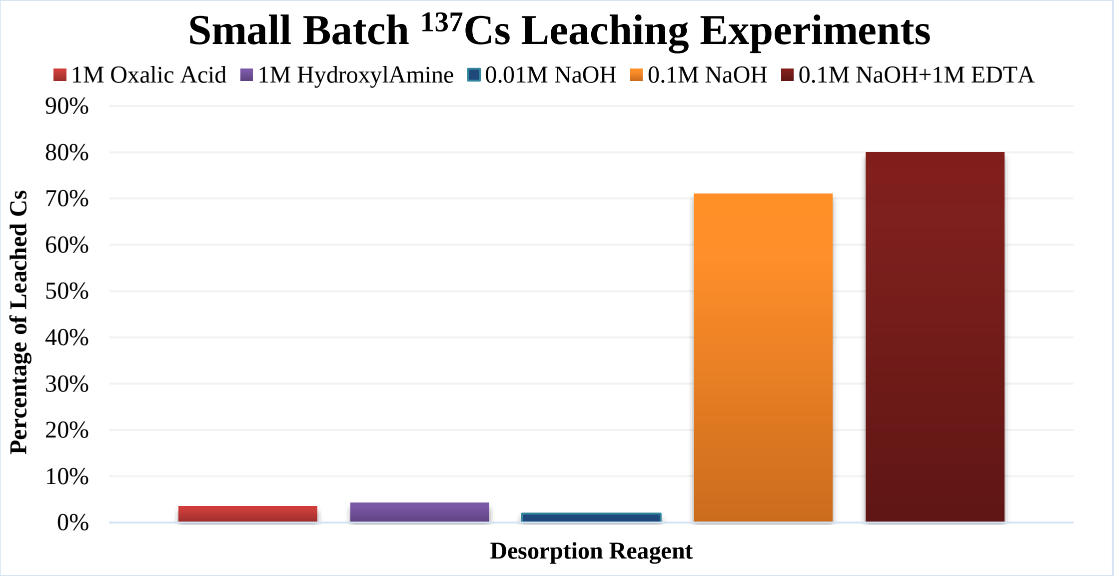

Figure 10: Percentage Desorption of ^{137}Cs from Anfezh Using Leaching Reagents

After NaOH plus EDTA was determined to be the most effective reagents for desorption of Cs from Anfezh, large-scale desorption experiments were tested using the same ratio of 2 mLs NaOH for every 50 mg of Anfezh. The experiment was performed in a Teflon beaker. The result of the large-scale (~20g of Anfezh) leaching experiment was that the total percentage of added ^{137}Cs leached from Anfezh was 50.51%. This experiment was completed using properly-scaled amounts of Anfezh, NaOH, and EDTA. The percentage of leached Cs is ~30% less than the small-scale experiments due to inadequate homogenization of the reaction contents. During each small-scale experiment the reaction tubes were rapidly and evenly mixed using a vortex tube shaker for maximum homogenization. The large-scale experiment, however, was too large to reliably and safely mix thoroughly without a loss of solution. Nevertheless, 50%

extraction of added Cs from Anfezh using real-world quantities of sorbent and reagents is more representative of the capabilities of this method of batch extraction.

Following the large-scale leaching experiment, the method of NaOH and EDTA ^{137}Cs extraction was implemented three times using the sorbent cartridge developed by PNNL. The extraction of ^{137}Cs in these trials was an average of 83.15 ± 6.21% after 48 hours of total cycling of NaOH and EDTA. The higher percentage of Cs desorption using the cartridge versus the batch conditions is expected due to the complete coverage and homogenization of the solution inherent with pumping the solution continuously through the Anfezh using a peristaltic pump. A method of Cs extraction from Anfezh does not currently exist in the published literature. Due to the reproducibility of this method, it has potential for use in laboratories that have deployed a sorbent cartridge containing Anfezh and would like to perform further destructive analysis of the adsorbed analytes. This method could specifically benefit nuclear forensic scientists who want to establish stable Cs isotopic signatures in marine or coastal environments.

CONCLUSIONS

A series of batch experiments using Anfezh and three test waters (ASW, AFW, and GBW) were conducted in order to determine the K_D and effectiveness of Anfezh as a radionuclide pre-concentration chemisobent. In all conditions, Anfezh produced log K_D values that were the highest using ^{137}Cs, its target radionuclide. The second highest K_D for Anfezh in all conditions was ^{57}Co. Each of these results are expected because Anfezh has a certified efficiency of 98 ± 1% for Cs and an efficiency of 40 ± 5% for Co (Remez and Sapozhnikov 1996). The shelf life of Anfezh was determined to be greater than six years for ^{137}Cs ($P = 0.27$) in AFW after t-test analysis of K_D from Johnson et al. (2011b) and the 2014 retest of K_D using the same batch of Anfezh purchased in 2008. The K_D t-test comparison of ^{137}Cs in ASW was statistically significant ($P = 0.01$), so the shelf life is said to be less than 6 years for Anfezh in ASW. Based on these results, Anfezh is an excellent choice for a commercial sorbent that can adsorb radiocesium and cobalt species that have been released after a nuclear disaster. Anfezh would likely be used in close association with a MnO2 sorbent that can better sequester particle reactive radionuclides (i.e. Th, Be, and Po).

Leaching experiments were performed to develop a method to chemically desorb Cs that has sorbed to Anfezh after aqueous deployment. It was determined that the combination of 0.1M NaOH and 1M EDTA produced the highest percentage of Cs extracted from Anfezh at ~80%. This method was performed on Anfezh contained in a sorbent cartridge developed by PNNL, in which it produced a final percentage of Cs extraction of 83.15 ± 6.21% after three trials. This method will be immediately useful for researchers looking to quantify the isotopic information of Cs that has adsorbed to Anfezh from natural seawater.

CHAPTER IV

OVERVIEW CONCLUSION

PNNL has spent several years developing a novel in-situ gamma spectrometer that will be used to determine radionuclide contamination post nuclear disaster. The system will rely on pre-concentration of radionuclides to help eliminate the natural background of gamma emitting radionuclides (e.g. ^{40}K) in seawater, and will produce an estimated one to three orders of magnitude lower limit of detection over gamma measurement alone (Schwantes et al. 2009). The system is not yet in production, so optimization of the sorbents that will be used for radionuclide pre-concentration is imperative. The results of these experiments demonstrate that the K_D values of a selection of radionuclides and chemisorbents will be useful for applications in cartridges on the gamma system; they are discussed below.

Batch experiments were conducted to determine the K_D for nine radionuclides, six sorbents, and three test waters in support of the in-situ gamma system developed by PNNL. Three novel MnO_2 sorbents were tested to evaluate if they produce K_D values that are superior to the currently preferred MnO_2 radionuclide sorbent, impregnated MnO_2 (Varga, 2007). Of those novel MnO_2 sorbents only one of them, nanostructured MnO_2 (Nayak and Munichandraiah 2011), produced K_D values that were one to two orders of magnitude greater than impregnated MnO_2 in ASW. This sorbent was previously used exclusively in superconductor studies, so this is the first study to test for its ability to sequester various radionuclides from aqueous solution. Its ability to sorb greater amounts of the radionuclides tested likely results from its higher surface area, its complex copolymer backbone that acts as a directing agent during synthesis, and its mesoporous structure.

Novel SAMMS-MnO_2 sorbents were tested as well, yet they failed to produce higher K_D values than for impregnated MnO_2 for all but three radionuclides (i.e. ^{106}Ru, ^{133}Ba, and ^{137}Cs). SAMMS sorbents are advanced in their design, yet this kind of MnO_2 lacks the ability to outperform impregnated MnO_2 overall. This is likely due to a synthesis issue, such as incomplete MnO_2 coverage of the mesoporous silica that forms the backbone of SAMMS. SAMMS rely on molecular self-assembly using a mesoporous silica backbone to support the functional group interface that binds radionuclides in solution, thus an incomplete layer of MnO_2 would leave bare silica which would inhibit the overall sorption capabilities (Fryxell et al. 2007). MnO_2 coverage of silica could be improved by applying longer (>12 hours) mixing upon the initial addition of the Mn-containing reagents.

Novel biogenic MnO_2 produced by a *Chromobacterium* sp. treated with Mn was also tested for its ability to sequester radionuclides from solution for the first time during this study. While it failed to produce K_D that was greater than impregnated MnO_2 for all radionuclides, it displayed that it has the capability to sorb radionuclides from solution. This biogenic MnO_2 is produced by bacteria found at the Savannah River Site and could potentially influence the fate of anthropogenic radionuclides that have contaminated the environment. This sorbent will not likely be useful for pre-concentration of radionuclides for gamma spectrometry, however it is necessary to examine its role in radionuclide mobility in the environment. Future studies will need to characterize this biogenic MnO_2 using mass spectrometry and x-ray diffraction due to its unknown morphology and chemical characteristics.

In addition to MnO_2, a commercial potassium hexacyanoferrate sorbent, Anfezh, was tested for its K_D using five radionuclides, and a novel method of desorption of radiocesium from Anfezh was developed. As expected, Anfezh produced K_D values that were orders of magnitude greater for ^{137}Cs (its target radionuclide) than for ^{57}Co, ^{106}Ru, ^{125}Sb, and ^{133}Ba. Anfezh relies on cation exchange of the potassium in its structure, so monovalent alkali metals will sorb most effectively (Johnson et al. 2011b). Radiocesium is a high-risk fission product of nuclear processing activities due to its relatively long half-life ($T_{1/2} = 30.07$ years) and radiotoxicity. For these reasons, Anfezh's reliable and efficient extraction (98 ±1%) of Cs from solution make it a prime candidate for use in sorbent cartridges on PNNL's gamma spectrometer. It will likely be used in sequence of a MnO_2-containing sorbent for a wider range of radionuclide pre-concentration capability.

A novel method of desorption of Cs from Anfezh contained in a sorbent cartridge was developed in this study that reliably extracts ~80% of sorbed Cs. A method such as this does not currently exist in the published literature. Researchers that want to determine stable Cs isotopic ratios for forensic or oceanographic research will be able to employ this method prior to chemical preparation for mass spectrometry.

The results of this study are beneficial towards the full-scale operation of the in-situ gamma spectrometer developed by PNNL. MnO_2 sorbents are among the most versatile materials for sequestering a wide variety of fission and activation products that are released after nuclear disasters. The combination of impregnated and nanostructured MnO_2 and Anfezh will be most effective for pre-concentration of radionuclides for direct in-situ gamma measurement.

Future studies will need to address radionuclide-loading capacity and the volume of water used for optimal adsorption when using these sorbents in disaster scenarios. PNNL's gamma spectrometer will utilize radionuclide sorbents inside of a sorbent cartridge, so realistic sorption parameters need to be explored. Practical sorption capabilities of these sorbents using natural sea water and river water pumped-through the cartridge will be useful for final production of the in-situ gamma spectrometer.

REFERENCES

Adams, James P, Robert Kirst, Lance E Kearns, and Mark PS Krekeler. 2009. "Mn-oxides and sequestration of heavy metals in a suburban catchment basin of the Chesapeake Bay watershed." *Environmental Geology* 58 (6):1269-1280.

Bacon, Michael P, Peter G Brewer, Derek W Spencer, James W Murray, and John Goddard. 1980. "Lead-210, polonium-210, manganese and iron in the Cariaco Trench." *Deep Sea Research Part A. Oceanographic Research Papers* 27 (2):119-135.

Baskaran, M, David J Murphy, Peter H Santschi, James C Orr, and David R Schink. 1993. "A method for rapid in situ extraction and laboratory determination of Th, Pb, and Ra isotopes from large volumes of seawater." *Deep Sea Research Part I: Oceanographic Research Papers* 40 (4):849-865.

Fryxell, Glen E, Shas V Mattigod, Yuehe Lin, Hong Wu, Sandy Fiskum, Kent Parker, Feng Zheng, Wassana Yantasee, Tom S Zemanian, and R Shane Addleman. 2007. "Design and synthesis of self-assembled monolayers on mesoporous supports (SAMMS): The importance of ligand posture in functional nanomaterials." *Journal of Materials Chemistry* 17 (28):2863-2874.

Goldberg, Edward D. 1954. "Marine geochemistry 1. Chemical scavengers of the sea." *The Journal of Geology*:249-265.

Johnson, B. E., P. H. Santschi, R. S. Addleman, M. Douglas, J. D. Davidson, G. E. Fryxell, and J. M. Schwantes. 2011a. "Collection of fission and activation product elements from fresh and ocean waters A comparison of traditional and novel sorbents." *Applied Radiation and Isotopes* 69 (1):205-216. doi: 10.1016/j.apradiso.2010.07.025.

Johnson, B. E., P. H. Santschi, R. S. Addleman, M. Douglas, J. Davidson, G. E. Fryxell, and J. M. Schwantes. 2011b. "Optimization and evaluation of mixed-bed chemisorbents for extracting fission and activation products from marine and fresh waters." *Analytica Chimica Acta* 708 (1-2):52-60. doi: 10.1016/j.aca.2011.08.017.

Johnson, B. E., P. H. Santschi, C. Y. Chuang, S. Otosaka, R. S. Addleman, M. Douglas, R. D. Rutledge, W. Chouyyok, J. D. Davidson, G. E. Fryxell, and J. M. Schwantes. 2012. "Collection of Lanthanides and Actinides from Natural Waters with Conventional and Nanoporous Sorbents." *Environmental Science & Technology* 46 (20):11251-11258. doi: 10.1021/es204192r.

Kinoshita, Norikazu, Keisuke Sueki, Kimikazu Sasa, Jun-ichi Kitagawa, Satoshi Ikarashi, Tomohiro Nishimura, Ying-Shee Wong, Yukihiko Satou, Koji Handa, and Tsutomu Takahashi. 2011. "Assessment of individual radionuclide distributions from the Fukushima nuclear accident covering central-east Japan." *Proceedings of the National Academy of Sciences* 108 (49):19526-19529.

Koulouris, G, B Slowikowski, R Pilviö, T Bostrom, and M Bickel. 2000. "Pre-concentration of actinoids from waters: a comparison of various sorbents." *Applied Radiation and Isotopes* 53 (1):279-287.

Lung, Michel, and Otto Gremm. 1998. "Perspectives of the thorium fuel cycle." *Nuclear Engineering and Design* 180 (2):133-146.

Mann, D. R., L. D. Surprenant, and S. A. Casso. 1984. "Insitu Chemisorption of Transuranics from Seawater." *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment* 223 (2-3):235-238. doi: Doi 10.1016/0167-5087(84)90653-7.

Mann, Don R, and Susan A Casso. 1984. "In situ chemisorption of radiocesium from seawater." *Marine Chemistry* 14 (4):307-318.

Milbrath, Brian D, Bethany J Choate, Jim E Fast, Walter K Hensley, Richard T Kouzes, and John E Schweppe. 2007. "Comparison of LaBr 3: Ce and NaI (Tl) scintillators for radio-isotope identification devices." *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 572 (2):774-784.

Mou, Juan, Guoju Wang, Wenxian Shi, and Shouwei Zhang. 2011. "Sorption of radiocobalt on a novel γ-MnO2 hollow structure: effects of pH, ionic strength, humic substances and temperature." *Journal of Radioanalytical and Nuclear Chemistry* 292 (1):293-303.

Murray, James W. 1975. "The interaction of metal ions at the manganese dioxide-solution interface." *Geochimica et Cosmochimica Acta* 39 (4):505-519.

Nayak, Prasant Kumar, and N Munichandraiah. 2011. "Mesoporous MnO 2 synthesized by using a tri-block copolymer for electrochemical supercapacitor studies." *Microporous and Mesoporous Materials* 143 (1):206-214.

Olatunji, Michael Adekunle, Mayeen Uddin Khandaker, HNM Ekramul Mahmud, and Yusoff Mohd Amin. 2015. "Influence of adsorption parameters on cesium uptake from aqueous solutions-a brief review." *RSC Advances* 5 (88):71658-71683.

Pike, SM, KO Buesseler, CF Breier, H Dulaiova, K Stastna, and F Sebesta. 2013. "Extraction of cesium in seawater off Japan using AMP-PAN resin and quantification via gamma spectroscopy and inductively coupled mass spectrometry." *Journal of Radioanalytical and Nuclear Chemistry* 296 (1):369-374.

Remez, VP, and Yu A Sapozhnikov. 1996. "The rapid determination of caesium radionuclides in water systems using composite sorbents." *Applied Radiation and Isotopes* 47 (9):885-886.

Schwantes, Jon M, Raymond S Addleman, Joseph D Davidson, Matthew Douglas, D Meier, O Dennis Mullen, M Myjak, Mark E Jones, Mitchell L Woodring, and Bryce Johnson. 2009. "Medium-resolution autonomous in situ gamma detection system for marine and coastal waters." *Journal of Radioanalytical and Nuclear Chemistry* 282 (3):889-895.

Tebo, Bradley M, John R Bargar, Brian G Clement, Gregory J Dick, Karen J Murray, Dorothy Parker, Rebecca Verity, and Samuel M Webb. 2004. "Biogenic manganese oxides: properties and mechanisms of formation." *Annu. Rev. Earth Planet. Sci.* 32:287-328.

Todd, James F, Robert J Elsinger, and Willard S Moore. 1988. "The distributions of uranium, radium and thorium isotopes in two anoxic fjords: Framvaren Fjord (Norway) and Saanich Inlet (British Columbia)." *Marine Chemistry* 23 (3):393-415.

Tsabaris, C, C Bagatelas, Th Dakladas, CT Papadopoulos, R Vlastou, and GT Chronis. 2008. "An autonomous in situ detection system for radioactivity measurements in the marine environment." *Applied Radiation and Isotopes* 66 (10):1419-1426.

Varga, Zsolt. 2007. "Preparation and characterization of manganese dioxide impregnated resin for radionuclide pre-concentration." *Applied Radiation and Isotopes* 65 (10):1095-1100.

Webb, SM, CC Fuller, BM Tebo, and JR Bargar. 2006. "Determination of uranyl incorporation into biogenic manganese oxides using X-ray absorption spectroscopy and scattering." *Environmental Science & Technology* 40 (3):771-777.

Wedekind, Ch, G Schilling, M Grüttmüller, and K Becker. 1999. "Gamma-radiation monitoring network at sea." *Applied Radiation and Isotopes* 50 (4):733-741.

Xu, Chen, Daniel I Kaplan, Saijin Zhang, Matthew Athon, Yi-Fang Ho, Hsiu-Ping Li, Chris M Yeager, Kathleen A Schwehr, Russell Grandbois, and Dawn Wellman.

2015. "Radioiodine sorption/desorption and speciation transformation by subsurface sediments from the Hanford Site." *Journal of Environmental Radioactivity* 139:43-55.

Yantasee, Wassana, Cynthia L Warner, Thanapon Sangvanich, R Shane Addleman, Timothy G Carter, Robert J Wiacek, Glen E Fryxell, Charles Timchalk, and Marvin G Warner. 2007. "Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles." *Environmental Science & Technology* 41 (14):5114-5119.

Zeng, Ming, Zhi Zeng, Jirong Cang, Xingyu Pan, Tao Xue, Hao Ma, Hongchang Yi, and Jianping Cheng. 2015. "A Prototype of LaBr3: Ce in situ Gamma-Ray Spectrometer for Marine Environmental Monitoring." *arXiv preprint arXiv:1504.04466*.