RADIOACTIVE ELEMENT REMOVAL FROM WATER USING
GRAPHENE OXIDE (GO)

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Radioactive Element Removal From Water Using Graphene Oxide (Go). (May 2014)

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The objective of this research is to test the ability of Graphene Oxide (GO) to attract and hold heavy radionuclides to be mechanically filtered out using an aluminum oxide ceramic filter. The radionuclides of interest are strontium-90, cesium-137 and uranium.

Naturally occurring radioactive materials (NORM) are abundant throughout the earth's crust. Human manipulation of NORM for economic ends, such as mining, ore processing, fossil fuel extraction, and commercial aviation, may lead to what is known as "technologically enhanced naturally occurring radioactive materials" (TENORM). The existence of TENORM results in an increased risk for human exposure to radioactivity. TENORM-producing industries may cause workers to be occupationally exposed to ionizing radiation and may release significant amounts of radioactive material into the environment resulting in the potential for widespread exposure. These industries include mining, phosphate processing, metal ore processing, heavy mineral sand processing, titanium pigment production, fossil fuel extraction and combustion, manufacture of building materials, thorium compounds, aviation, and scrap metal processing[1].

Treatment and decontamination of waste products and contaminated groundwater containing human-made radionuclides, among which the transuranic elements are the most toxic, is an essential task in the clean-up of legacy nuclear sites[2]. The recent accident that included radionuclide release to the environment at the Fukushima Daiichi nuclear power plant in Japan, and the contamination of the water used for cooling its reactor cores, underscores the need for effective treatment methods of radionuclide-contaminated water[3.]

This research hopes to find a less expensive and easier way of cleaning up radioactive accidents and leaks by demonstrating an ability of the GO to effectively and efficiently filter radionuclides from water sources such as rain water runoff or holding tank water.

DEDICATION

To my wife Heather, who has supported my efforts to return to school and finish what I started so many years ago. To my children Payton, Mason and Rebekah, who make me so proud each and every day.

I would not be able to do this without you, nor would I be where I am today.

ACKNOWLEDGEMENTS

NOMENCLATURE

GO   Graphene Oxide

NORM   Naturally Occurring Radioactive Material

TENORM   Technologically Enhanced Naturally Occurring Radioactive Material

^{90}Sr   Strontium-90

^{137}Cs   Cesium-137

TAMU   Texas A&M University

FCML   Fuel Cycle & Materials Lab

PPM   Parts Per Million

TMFD   Tensioned Metastable Fluid Detector

USNRC   United States Nuclear Regulatory Commission

CHAPTER I

INTRODUCTION

Naturally occurring radioactive materials (NORM) are abundant throughout the earth's crust. Human manipulation of NORM for economic ends, such as mining, ore processing, fossil fuel extraction, and commercial aviation, may lead to what is known as "technologically enhanced naturally occurring radioactive materials" (TENORM). The existence of TENORM results in an increased risk for human exposure to radioactivity. TENORM-producing industries may cause workers to be occupationally exposed to ionizing radiation and may release significant amounts of radioactive material into the environment resulting in the potential for widespread exposure. These industries include mining, phosphate processing, metal ore processing, heavy mineral sand processing, titanium pigment production, fossil fuel extraction and combustion, manufacture of building materials, thorium compounds, aviation, and scrap metal processing[1].

Treatment and decontamination of waste products and contaminated groundwater containing human-made radionuclides, among which the transuranic elements are the most toxic, is an essential task in the clean-up of legacy nuclear sites[2]. The recent accident that included radionuclide release to the environment at the Fukushima Daiichi nuclear power plant in Japan, and the contamination of the water used for cooling its reactor cores, underscores the need for effective treatment methods of radionuclide-contaminated water[3.] Such decontamination technologies should be inexpensive, expeditious, effective and environmentally friendly.

An advance in graphite-related materials promises to finally mitigate a long-standing problem for the resource development industries. Graphene oxide (GO), which is non-conductive, hydrophilic and easily suspended in water, is able to clean radionuclide-contaminated liquids by agglomerating contaminants into solids.

There are realistically three strategies for ensuring that radioactive materials don't cause harm to people or the environment:

1) Separation,

2) Isolation,

3) Transmutation, a nuclear reaction by bombarding the material with neutrons or protons from an accelerator or a reactor to form isotopes with short half-lives.

The last approach, while highly effective, is developmental and prohibitively expensive to consider for anything less radioactive than spent nuclear fuel, so the only realistic options are separation and isolation. The role that GO can play in these options is separation.

The invention of a GO filtration system originated through an international collaboration led by the efforts of James Tour in the Nanomaterial's Research Lab at Rice University in Houston and Stepan Kalmykov in the Environmental Radioactivity Research Lab at Moscow State University. Although it is still in a stage of development, it is being introduced in a variety of systems configurations through the efforts of VSW Water Purity, LLC, in Grapevine, Texas. In this system, GO powder is suspended in water and coagulates when heavy metal ions are introduced to the solution. It is then easily separated by sedimentation or rough mechanical filtering.

The properties of GO suspended in solution make it a promising material in rheology and colloidal chemistry[4,5]. The hydrophilic GO produces stable suspensions when dispersed in liquids and shows excellent adsorption capacities due to its relatively vast and highly accessible surface area, lack of internal surfaces, which usually cause slow cation-sorbent interactions, and its significant negative charge[6,7,8].

Low-valence ions, such as in Ca^{2+} and Fe^{2+}, also adsorb onto GO's surface, but, unlike high-valence ions, they don't disrupt the suspension. Thus for low-valence ions, adsorption is reversible and insignificant. Conveniently, anions such as Cl^- and CO_3^{2-}, being negatively charged, are not attracted to GO. So neither of these species interferes with radionuclide adsorption. This preference to heavy radioactive ion adsorption by GO not only allows for a more effective concentration of radioactive materials into solids, but also allows for their use in non-desalinated water, where many other sorbents fail. Furthermore, GO is combustible as well as biodegradable, which means that NORM and TENORM could be turned into radioactive ash, which results in more compact waste.

NORM and TENORM concentrations are usually very low, a few parts per trillion, but they can still be easily detected and can pose preventable hazards to living things. Ideally, radionuclide cleanup procedures would produce clean water while concentrating radioactive materials into a small, solid, manageable volume.

The goal of this project is to identify specific absorption rates associated with the GO filtration process using varied concentrations of radionuclides, chlorides, carbonates and various other light

and heavy ions. This research could lead to the significant reduction in NORM and TENORM storage capacities as well as cost of storage of radioactive material.

CHAPTER II

METHODS

Sample Preparation

Preparing samples for this experiment requires that certain precautions be taken. First, all samples should be prepared in the fume hood in order to contain any harmful fumes and or radioactive material. Lab coat, goggles and gloves taped to the sleeves of the lab coat are required as well.

In order to prepare a solution of 1 part per million (ppm) of uranium, a sample of uranium oxide (UO2) will be used. Nitric acid (HNO_3) will break down the UO_2 and create a water soluble salt of uranyl nitrate ($UO_2 \cdot (NO_3)_2$). This salt will then be dissolved in deionized water to produce a 1ppm solution of uranium. Once the sample solution has been produced, it should be stored in a glass container with a cap. The cap of the container should be taped to ensure a good seal and to prevent a possible release of radioactive material. The container should also be labeled with its contents, the date of creation and the name of person who created it. This container should then be stored in a radioactive safety locker.

Preparation of a solution containing 0.5 ppm of ^{137}Cs and 0.5 ppm of ^{90}Sr, for a total of 1 ppm concentration of radioactive elements will use a slightly different technique. Strontium nitrate ($Sr \cdot (NO_3)_2$) and cesium nitrate ($Cs \cdot NO_3$) salts will be added directly to deionized water in order to create the solution. Once this has been accomplished, trace amounts of radioactive isotopes Cs^{137} and Sr^{90} will be added to the solution. Once the sample solution has been produced, it should be stored in a glass container with a cap. The cap of the container should be taped to ensure a good

seal and to prevent a possible release of radioactive material. The container should also be labeled with its contents, the date of creation and the name of person who created it. This container should then be stored in a radioactive safety locker.

We should also be able to obtain samples of typical rain water run-off and storage water from the Fukishima Daiichi nuclear reactor site in Japan.

System Set-Up

This experiment will use a 1000 mL beaker as a collection basin and a 125 mL Erlenmeyer flask as a sample solution origin and radionuclide infused sludge collector. A variable speed peristaltic pump will be used to move the sample from the origin through the filter and back to the flask in order to prevent contamination. Autoclavable tubing will be used for this process and an aluminum oxide ceramic filter will separate the radioactive sludge from the clean water, which will move through the filter by osmosis and collect in the 1000 mL beaker. The radioactive sludge, which is actually radionuclides attached to the grapheme oxide, will collect in the original flask until no more water can be removed. This entire set-up will be placed inside a large plastic bin which has been fitted with a rubber strip to enhance sealing of the top to the base. This is to prevent any possible release of radioactive material. The tubing will be attached to the filter and fixed using clamps.
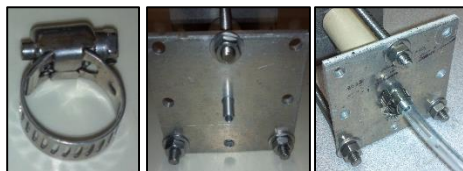

Fig. 1a - Inlet   Fig. 1b - Outlet

Procedure

The first step in the procedure is to take readings of the sample solutions. The uranium samples will be read using a tensioned metastable fluid detector (TMFD). This detector is a new type of detector that was developed by researchers at Purdue University in partnership with Texas A&M University and various national laboratories, and is being tested here at Texas A&M University. This detector can detect alpha emissions in solution. The cesium and strontium samples will be read using a liquid scintillation detector. The water from Fukishima Daiichi nuclear reactor site in Japan will be read using both methods. Once base readings have been performed on the samples, grapheme oxide powder will be added to the samples.

Once the graphene oxide has had a chance to absorb the radionuclides from the solutions, we will begin the filtration process. The tubing from the inlet side of the filter will be inserted into the peristaltic pump and then into the bottom of the 125 mL Erlenmeyer flask containing the solution of radionuclides and graphene oxide. The tubing from the outlet side of the filter will be placed into the flask as well, but at a higher level than the suction side. This will allow for the sample to be self-mixed during the filtration process.
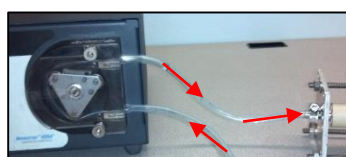
Fig. 2a & 2b   ⟶   Indicates direction of flow

Fig. 3

The filter will be placed over the 1000 mL beaker for the collection of the filtered water. A flow reducer will be placed on the discharge side of the filter which will add a slightly higher pressure to build up inside the filter to facilitate osmosis through the filter. This will allow the fresh water to drain into the beaker while the radioactive sludge continues back to the original flask.
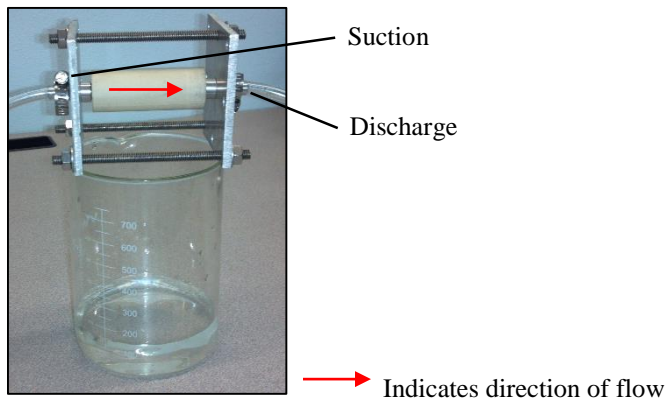

Suction

Discharge
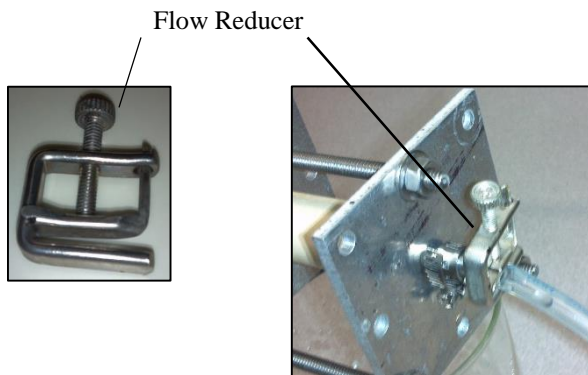
→ Indicates direction of flow

Fig. 4

Flow Reducer

Fig. 5a & 5b

Once the filter is properly hooked up to the pump and the sample solution is in place, the pump can be turned on at a flow rate of ≥ 4.0 on the flow speed controller on the pump.

FLOW SPEED

Fig. 6

Allow the system to run for at least 2-3 minutes to allow the filter to become saturated with water. Then adjust the flow speed controller and the flow reducer to allow for active filtration through the filter without a buildup of pressure or sludge at the discharge due to the flow reducer.
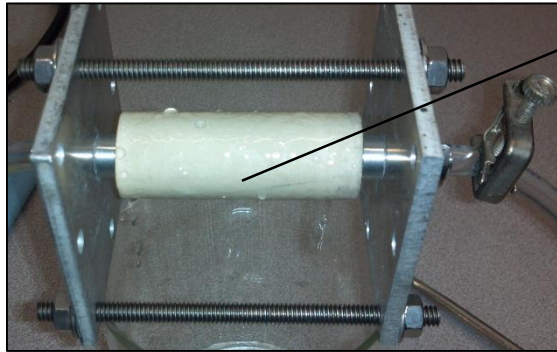
Fig. 7

Once the sample solution has been reduced to the point of no longer being able to be pumped and active filtration has stopped, turn off the pump and remove the filter from the system. The filter will contain radioactive material at this point and should be treated as such. Place the filter into a bag labeled as radioactive and label the time and date. The filtered water should be placed into a clean and verified non-radioactive container to be measured independently of the rest of the sample. The filter and the radioactive sludge will also be measured.

The goal of this experiment is to successfully remove all of the radioactive elements from the water, leaving the water as inert and harmless as possible. To ensure viability and reliability, this experiment will be tested on deionized water as well as slightly chlorinated water.

CHAPTER III

DISCUSSION

Graphene Oxide (GO) has been shown to be an effective agent in the removal of the naturally occurring, non-radioactive elements Strontium and Cesium from water[4,5] this work has been done by Tour et al. at Rice University. The design and purpose of this research has been to test the ability of GO in the removal of the radioactive isotopes Sr^{90} and Cs^{137}, and Uranium from water. Unfortunately, the arrival of GO to our facility here in the Fuel Cycle and Materials Lab at Texas A&M University from Rice University has been delayed, so no evolutions of the experiment have yet taken place. The reason behind this delay has in part been due to some new motivations that have been developing over the past few months. The reason behind this redirection of focus is that there is a need for an additional process in the treatment of Fracking water. This additional process concerns the removal of Naturally Occurring Radioactive Material (NORM) from Fracking water before the water can be returned to the ground and it is believed that the GO filtration process can accomplish this safely and quickly. Researching the effective removal of radioactive elements from water using GO is still an ongoing research project, however, recent attention to the removal of Uranium and other trans-Uranic elements from water has begun to take more precedence over the removal of Cs^{137} and Sr^{90} per the initial and ongoing motivation, which is the clean-up of the nuclear reactor accident at Fukushima Daiichi Nuclear Power Plant in Japan and other legacy nuclear sites. What follows will be a discussion of what has been accomplished regarding this project, where this research is heading in the near future and the implications of successful experiments of this research.

Detection

94.6% of the time, Cs^{137} decays by emitting β's at 512 keV and reduces to $Ba^{137(m)}$ which emits a γ at 662 keV to stabilize at Ba^{137}. We use a High Purity Germanium (HPGe) Detector to characterize the γ emission spectrum which peaks at 662 keV. Sr^{90} decays to Y^{90} by emitting β's at 546 keV. Y^{90} then decays to Zr^{90} by emitting β's at 2280 keV. We can use a liquid scintillation detector to characterize these β-emissions as well as the β-emissions from Cs^{137} by observing the energy peaks. Uranium decays primarily by a series of α-emissions and β-emissions. Because the decay of the daughter products of uranium have very short half-lives compared to uranium, it is difficult to determine the governing decay scheme from the α-emissions, but because α's don't travel in water very well, detection of uranium in water is very difficult. However, we have an experimental detector called the Tensioned Metastable Fluid Detector (TMFD) that can detect α's in solution. By using the TMFD, it can be determined if uranium or other α-emitting trans-uranic elements are present in solution and if so, approximately how much based on the activity of the sample.

Expected Activity of Samples

A solution containing natural strontium and cesium spiked with the radioactive isotopes Sr^{90} and Cs^{137} was created. The isotopes were obtained from storage following experimentation performed by Braden Goddard for his Master's thesis on "Development of a Real-Time Detection Strategy for Material Accountancy and Process Monitoring during Nuclear Fuel Reprocessing Using the UREX+3a Method" submitted in December 2009. These samples contained the following quantities:

Cs, Sr : FPEX Prod 1:

Sr^{90} – 8.66E-09 grams

Cs^{137} – 2.02E-08 grams

Then by using the equation $\lambda = \frac{\ln 2}{t_{1/2}}$ to obtain the radioactive decay time constants (λ) for each

isotope, it was determined that the following quantities of each isotope was remaining:

Sr^{90} ($t_{1/2}$ = 28.79 yr, λ = 0.024076 yr^{-1})   –   7.41E-09 grams

Cs^{137} ($t_{1/2}$ = 30.17 yr, λ = 0.022975 yr^{-1})   –   1.79E-08 grams

This information paired with the specific activity (SA) of each isotope obtained from the United

States Nuclear Regulatory Commission (U.S.NRC), expected count rates were calculated for the

sample to determine the expected level of activity in the sample solution[9].

SA of Sr^{90} = 8.70E+01 $^{Ci}/_g$ → Activity of Sr^{90} = 5.73E+04 counts per second

SA of Cs^{137} = 1.41E+02 $^{Ci}/_g$ → Activity of Cs^{137} = 3.84E+04 counts per second

➔   Total activity expected from sample = 9.57E+04 counts per second

A solution containing uranium was created by treating depleted reactor fuel (UO$_2$) with Nitric

Acid (HNO$_3$) to create uranyl nitrate (UO$_2$·(NO$_3$)$_2$) which is a water soluble salt. This salt was

then dissolved in water to create the solution.

The amount of UO$_2$·(NO$_3$)$_2$ required to create a 100mL sample solution was determined by using

the following equations:

$$wt\% = \frac{wt_{element}}{wt_{sample}}$$

1ppm = 0.998859 $^{mg}/_L$

U	1(238.0300 $^g/_{mol}$)	= 238.0300 $^g/_{mol}$
O	8(15.9994 $^g/_{mol}$)	= 127.9952 $^g/_{mol}$
N	2(14.0070 $^g/_{mol}$)	= 28.0140 $^g/_{mol}$
Total wt		= 394.0392 $^g/_{mol}$

%U in $UO_2 \cdot (NO_3)_2$ = 0.604076955 = 60.41%

➔ 0.165353 mg $UO_2 \cdot (NO_3)_2$ is required to make a 1ppm solution of uranium

This information paired with the specific activity (SA) of uranium obtained from the United States Nuclear Regulatory Commission (U.S.NRC), the expected count rate was calculated for the sample to determine the expected level of activity in the sample solution[9].

SA of U   = 3.60E-07 $^{Ci}/_g$ ➔ Activity of U   = 1.33 counts per second

How Graphene Oxide Works

The amphiphilic GO produces stable suspensions when dispersed in liquids[6] and shows excellent sorption capacities. Previously it was shown that GO enables effective removal of Cu,[10] Co and Cd,[11] Eu,[12] arsenate[13] and organic solvents.[14] The surface of GO is functionalized with epoxy, hydroxyl and carboxyl moieties; the formation and composition of GO has been extensively studied.[7,8] The surface moieties are well-suited for interaction with cations and anions.

a) Updated chemical structure
proposed by Gao and colleagues
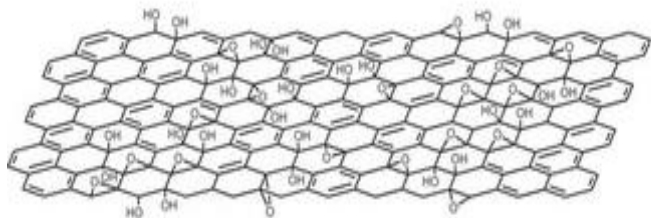
a) The chemical structure of a single sheet of Graphene Oxide according to the Lerf–Klinowski model[15, 16].
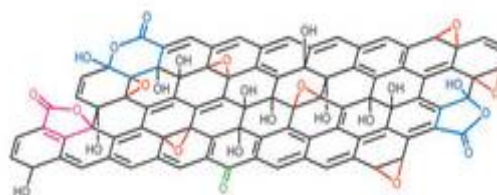
b) An updated chemical structure proposed by Gao and colleagues[17].

The fast sorption kinetics are likely due to GO's highly accessible surface area[7, 8] and its lack of internal surfaces that usually contribute to the slow kinetics of diffusion in cation–sorbent interaction. The fast kinetics are important for practical applications of GO for removal of cationic impurities. GO has a high sorption capacity towards U, Sr, Am and Eu cations as determined from the sorption isotherms. Even at a GO concentration as low as 0.038 $^g/_L$, the saturation limit is not reached.

Low-valence ions such as in calcium and iron also adsorb onto GO's surface, but, unlike high-valence ions, they don't destabilize the suspension. That itself leads to the formation of stable complexes, completely immobilizing the cations. Thus for low-valence ions, adsorption is reversible and insignificant. Conveniently, anions such as chloride and carbonate, being negatively charged, are not attracted by GO, so neither of these species interferes with radionuclide adsorption[2].

The selectivity of heavy radioactive ion absorption by GO against lighter ions, the ones that yield water salinity, not only allows more effective concentration of radioactive materials into solids,

the volume of which is the only price-determining factor in the radionuclide recycling process, but also allows their use in non-desalinated water, where many other sorbents fail[2, 3].

Implications

GO is also combustible as well as biodegradable. This means that NORM and TENORM material could be turned into radioactive ash, the smallest practically achievable volume and mass.
There is currently no large-scale production of GO, mainly because no application to date has demanded large quantities of the environmentally friendly material. A chemical company, AZ Electronic Materials, is in the development phase of scaling-up Rice University's GO synthesis method. This new application will encourage the bulk manufacture of GO at prices significantly below that of the most common sorbents, ion exchange resins and clays.

The application of GO is not limited to production water filtration. Biodegradable, permeable reactive barriers could be constructed around NORM and TENORM-affected facilities as additional environmental protection[6]. Together with GO's outstanding ability to clog porous media, including clays and porous rock formations, these barriers could minimize leakage of radioactive materials into the environment[11,12].

GO demonstrated high sorption affinity towards the most toxic radionuclides from various solutions and is found to be much more effective when compared to bentonite clays or activated carbon in actinide removal from liquid nuclear wastes. The GO-containing radionuclide could be easily coagulated and precipitated. The simplicity of industrial scale-up of GO, its high sorption capacity and its ability to coagulate with cations makes it a promising new material for responsible

radionuclide containment and removal. And if GO's radionuclide absorption can be reversed, it would allow for more sophisticated recycling procedures and perhaps even making it possible to mine radioactive materials from wastewater. For now, this Nano-technological breakthrough of capturing radioactive materials on GO, burning the GO and disposing of the compacted radioactive waste could invigorate the mining business while offering attractive options for the oil/gas and nuclear power industries.

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