Decontamination of Organic Wastes Containing Radionuclides – 15122

Thomas J. Unsworth*, Nigel W. Brown**, Simon M. Pimblott*
*University of Manchester, Dalton Cumbrian Facility, Westlakes Science and Technology Park, Moor Row, Cumbria, CA24 3HA, United Kingdom,
thomas.unsworth@postgrad.manchester.ac.uk
**Arvia Technology Ltd, Daresbury Innovation Centre, Daresbury, WA4 4PS, United Kingdom

ABSTRACT

The Arvia Process is being adapted for use in the nuclear industry for the decontamination of oils containing radionuclides. This waste treatment process uses adsorption followed by electrochemical oxidation as an alternative technique to conventional incineration. A study has been carried out on components of the Arvia Process with the aim of understanding the changes in chemistry due to ionizing radiation. Samples of adsorbent in water have been exposed to gamma-rays from a Co-60 irradiator at absorbed doses of 3, 19, and 304 kGy. Preliminary results show that the concentration of inorganic ions and carbon in the water increased as a function of dose. This increase suggests that degradation of the adsorbent may take place at high doses. Further characterization of the microstructure and adsorption studies post-irradiation are planned.

INTRODUCTION

Radioactive organic liquids (ROLs) present a unique set of challenges to the decommissioning and waste treatment industries. Hydraulic oils, lubricants, scintillation liquids, and organic solvents become contaminated by radionuclides during their use in nuclear operations. Conventional treatment by means of incineration can be unsuitable or unable to comply with limits set by environmental bodies [1, 2].

Arvia Technology Ltd was formed in 2007 and operates in the field of research and development of water purification technology. The earliest publications by researchers working with Arvia Technology established a water treatment process of adsorption followed by electrochemical oxidation, now known as the Arvia Process [3, 4]. The process used a proprietary carbon based adsorbent material with the trade name Nyex 100.

Since 2004, the process has undergone significant research and development. Improvements have included batch and continuous process designs, optimum current and regeneration cycles and adsorbent material properties. A variety of contaminants have been treated. In 2011, a pilot scale organic waste treatment rig was successfully demonstrated [5]. It destroyed 10 litres of radioactive oils on the Magnox Trawsfynydd site. The technology now requires more research into the behaviour of radioactive oils and the effects of ionizing radiation on the Arvia Process.

Irradiation by gamma-rays was chosen as the topic for a radiological study. The treatment of emulsified contaminated oils involves exposure of components of the Arvia Process to ionizing radiation including gamma-rays. The products formed from water radiolysis (e_{aq}^-, $H^\cdot$, $^\cdot OH$, H_2,

H_2O_2, and H_3O^+) could enhance the degradation process in addition to direct damage by irradiation [6]. Organic liquids produce an even wider variety of products when irradiated. In addition, there has been little research into the effects of gamma-ray irradiation on adsorbent effectiveness. For ion exchange resins, which are commonly used in the nuclear industry, researchers have found reductions in adsorption capacity due to exposure to ionizing radiation [7, 8] and the release of gases and other degradation products [9, 10]. These studies use different materials but the experimental techniques will be utilized in this study.

Ionizing radiation can interact with graphite causing structural defects. This phenomenon has been widely studied due to the use of graphite as a moderator in nuclear reactors [11]. Recent studies have investigated the effects of gamma-ray irradiation on graphite [12], graphene [13] and multi-walled carbon nanotubes [14]. The use of X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy have produced a variety of results.

This research will attempt to study the effects of ionizing radiation on a carbon based adsorbent material in water while also examining the changes in functionality of adsorbents used in the Arvia Process.

EXPERIMENTAL METHODS

Adsorbent Preparation

Nyex 1000 is the adsorbent grade used in the majority of recent studies by researchers working with Arvia Technology [15–17]. This material was supplied as flakes with no internal surface area. The material is non-porous and as a result has a much lower surface area than traditional carbonaceous adsorbents like activated carbon. A newer grade of adsorbent, Nyex 2105, and an intermediate grade, Nyex 2104 have also been supplied for this study. The morphology of Nyex 1000 and Nyex 2105 can be compared in Fig. 1. Nyex 2105 is more grain like and less sticky than Nyex 1000.

Fig. 1: Photograph of Nyex 1000 (left) and Nyex 2105 (right)

The adsorbent manufacturing process for Nyex adsorbents leaves impurities on the surface of the material, which leach over time when the material is immersed in water. The first treatment step involves washing the adsorbent to remove excess ionic compounds and other contaminants. This step also separates the majority of the fine flakes.

20 g of Nyex adsorbent was weighed and placed into a sintered glass disc funnel filter (porosity 4). The funnel was placed on a Büchner flask attached to a water tap. 100 ml of deionized water was added to the Nyex adsorbent and the mixture was stirred vigorously to release any fines. The supernatant was removed and collected for analysis and the remaining water was sucked through the funnel. This procedure represents one wash cycle.

The wet cake was allowed to equilibrate in a beaker for two days releasing evaporated water which condensed on the glass of the beaker. Nyex adsorbent is known to interact poorly with water after being dried in a vacuum oven. For this reason, it is beneficial to allow the cake to remain slightly wet. A small quantity (5 g) of the washed adsorbent cake was placed into a vacuum oven for 24 hours at -1000 mbar and 40 °C. Following heating, the sample was re-weighed and the reduction in mass enabled calculation of adsorbent content and water content for the adsorbent cake.

Adsorbent Characterization

Brunauer Emmett Teller (BET) surface area and porosity measurements were carried out using a Micromeritics Tristar II 3020 analyzer using full adsorption desorption isotherms of nitrogen gas. Raman spectroscopy measurements were carried out using a Bruker RamanScope III using a 532 nm laser. The Raman peaks were integrated using the peak analysis tools in OriginPro software. Prior to analysis, samples were dried in a vacuum oven at 40 °C and -1000 mbar. At least three measurements were taken using BET analysis and at least five measurements were taken using Raman spectroscopy analysis for accuracy.

Sample Irradiation

The Co-60 irradiator used for this project was supplied by Foss Therapy Inc (see Fig. 2). The irradiator was loaded with 535.4 TBq of Co-60 on the 24th of February 2012. Samples placed in the sample chamber are subjected to gamma-rays at dose rates dependent on their distance from the source in accordance with the R^2 law.

Fig. 2: Co-60 irradiator

To determine the radiation dose to an irradiated sample, ferrous sulphate (Fricke) dosimetry was selected as the most appropriate dosimetry method for this study. The dosimeter was created by adding $FeSO_4$ to an aerated acid matrix of H_2SO_4 and water. When Fe^{2+} is irradiated, it is oxidized to Fe^{3+} with the chemical yield $G(Fe^{3+})$ of 15.5. This oxidation also happens in natural light, so solutions are kept covered in aluminium foil. The absorbed dose D can be found by using Eq. 1 [18].

$$D = 9.65 \times 10^6 \left[\frac{OD_i - OD_n}{\Delta\varepsilon \rho l G(Fe^{3+})} \right] \quad \text{(Eq. 1)}$$

Analysis by ultraviolet-visible spectroscopy (UV-Vis) at 304 nm yields the values OD_i and OD_n, which are the optical densities of the irradiated and non irradiated dosimeter respectively. l is the optical path length used in UV-Vis (1 cm), ρ is the density of the system (1.024 $g.cm^{-3}$) and $\Delta\varepsilon$ is the difference in molar extinction coefficient of Fe^{2+} and Fe^{3+} (2174 $dm^3.mol^{-1}.cm^{-1}$).

Fricke dosimetry was carried out using 10 ml of Fricke solution in four 20 ml radiolysis vials in a sample rack approximately 2 cm from the Co-60 source. It was determined that an average dose rate of 322 $Gy.min^{-1}$ was effectively applied to samples in all four positions. The nature of radioactive decay means that the activity of the Co-60 source will decrease over time. The activity of a source C_t at time t can be found using the expression given in Eq. 2, where C_0 is the initial source activity and the decay constant λ is equal to 0.693 divided by the half-life of the source [19]. The half-life of Co-60 is 5.27 years.

$$\frac{C_t}{C_0} = e^{-\lambda t} \quad \text{(Eq. 2)}$$

Irradiated water and Nyex adsorbent mixtures were analyzed for ion and carbon content. Anions and cations were detected by ion chromatography (IC) using a Thermo Scientific Dionex ICS2100 and ICS1600 respectively. Organic and inorganic carbon in solution was detected by total organic carbon (TOC) analysis using an Analytik Jena Multi N/C 2100S.

RESULTS AND DISCUSSION

Adsorbent Characterization

Table I shows the results of BET analysis of Nyex 1000 and Nyex 2105 using samples of mass 0.5 g. The measured surface area of Nyex 1000 was found to be nearly three times higher than that of Nyex 2105, possibly due to a greater number of fines and lower material density. The measured pore volumes are very low and so cannot be considered accurate, but this result gives a strong indication that Nyex has no internal surface area. BET surface area analysis will be repeated on irradiated samples in the future.

TABLE I: BET surface area and porosity results for Nyex 1000 and Nyex 2105

	Nyex 1000	Nyex 2105
Surface area ($m^2 \cdot g^{-1}$)	2.01 ± 0.08	0.66 ± 0.04
Pore volume ($cm^3 \cdot g^{-1}$)	0.00181 ± 0.00002	0.00074 ± 0.00012

Table II shows the results of Raman spectroscopy analysis. The peak locations are a close fit to the literature data for graphite, which give 1350 cm^{-1} for the D peak and 1580 - 1600 cm^{-1} for the G peak, although the standard deviation is quite large. The ratios of I_D/I_G were calculated as 0.4 for Nyex 1000 and 0.34 for Nyex 2105. Literature values vary from 0.29 for unirradiated graphite and 0.86 for multi-walled carbon nanotubes. The standard deviation is quite large, but consistent with the values reported in the literature. Raman spectroscopy will be repeated on irradiated samples in the future.

TABLE II: Raman spectroscopy results for Nyex 1000 and Nyex 2105

	Nyex 1000	Nyex 2105
D peak location (cm^{-1})	1346.67 ± 2.89	1350 ± 0.35
G peak location (cm^{-1})	1575.08 ± 3.83	1580.75 ± 1.52
I_D/I_G ratio	0.40 ± 0.07	0.34 ± 0.06

Irradiation Experiments

An intermediate grade of material, Nyex 2104 was used for these experiments. 0.5 g of washed Nyex 2104 was irradiated in 10 ml deionized water. Samples were irradiated at dose rates of 322 $Gy.min^{-1}$. Four samples were irradiated for each value of absorbed dose. Values of absorbed dose were varied based on the length of time samples spent in the Co-60 irradiator. Control

samples which were not being irradiated were kept in a water bath at 40 °C, which is the temperature measured inside the irradiator.

Fig. 3 shows the results from IC analysis and TOC analysis of water after irradiation. IC detected a wide range of anions and cations, only sulphate and sodium ions are represented here. The concentration of sulphate and sodium ions increased with increasing gamma-ray doses. This increase is possibly due to damage to the material structure causing the release of intercalated species. Both inorganic carbon and total carbon content increase with increasing gamma-ray doses, which could represent the radiolytic degradation of the material. These preliminary results show that the adsorbent material in water is affected by gamma-ray irradiation. Further investigation into the changes in microstructure of the material, available surface area, and adsorption capacity are needed to draw reliable conclusions.

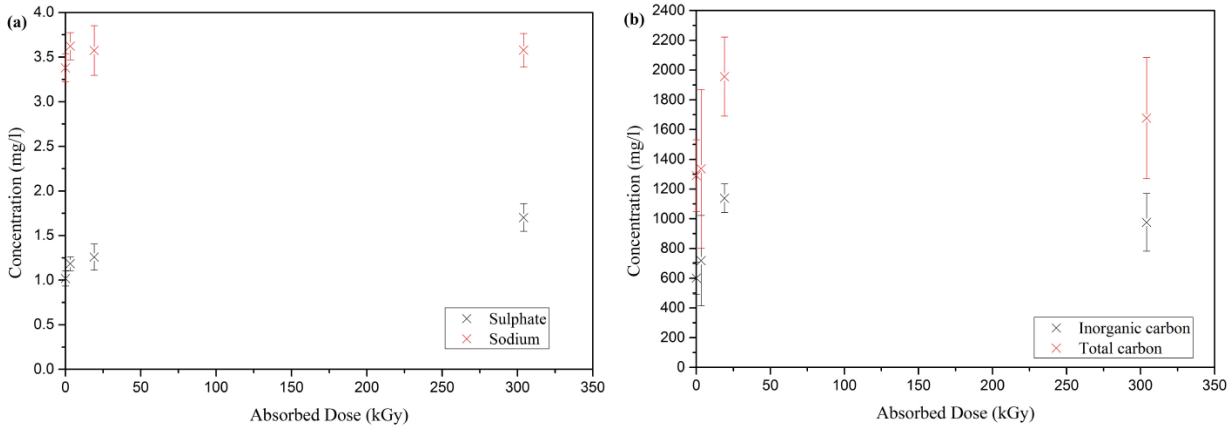

Fig. 3: (a) IC measurements of sulphate and sodium ion concentration and (b) TOC measurements of carbon concentration in water containing Nyex 2104 subject to gamma-ray irradiation

CONCLUSIONS

The early stages of this investigation suggest that irradiation of Nyex adsorbent in water with gamma-rays causes small but measurable changes to the material. Increased concentrations of ions in solution suggest damage to the structure of the adsorbent material and increased concentrations of carbon suggest that radiolytic degradation takes place. These claims could be supported further with analysis of microstructure changes in the material such as XRD and Raman spectroscopy, and techniques such as XPS could give a more detailed and accurate picture of the surface chemistry.

Further research is required to more fully understand the effects of ionizing radiation on the functionality of the adsorbent and the efficiency of the Arvia Process in a radioactive environment. Experiments using emulsified oil spiked with small quantities of ions to simulate the interaction of organics with ions are planned. These future studies will be comparative between the older grade of Nyex 1000 and newer grade Nyex 2105.

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