Innovative Treatment of Problematic (Orphan) and Other Organic Wastes: An Excellent Example of International Technology Transfer between the US and the UK - 14119

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ABSTRACT

There are a wide variety of waste streams across the US Dept. of Energy (DOE) complex, many of which have well documented and well proven disposition pathways. There are also a number of waste streams, particularly those containing organics, for which the disposition path is not clear or does not exist at all. For example, waste streams such as dioxins, furans and PCB-laden oils pose a significant issue to the DOE since they cannot be readily treated using existing treatment technologies such as incineration.

The Arvia Organics Destruction Process is based on a patented material, Nyex^{TM} which combines adsorption of organics with electrochemical oxidation to provide an ambient temperature, highly efficient system to convert organic materials to carbon dioxide and water while partitioning radioactive and inorganic constituents into an aqueous stream which can be readily treated by a local effluent treatment plant. The Nyex acts as a catalytic agent and is regenerated during the process which makes the approach both environmentally friendly and cost effective.

The Arvia Organics Destruction Process has been deployed at a Magnox site in the UK to treat radioactively contaminated oils but its efficiency for the treatment of wastes in the DOE complex is unproven.

This paper will give an overview of the Arvia process and describe recent US DOE-funded efforts with a consortium of NuVision Engineering, Arvia Technology and Perma-Fix Environmental Services Inc to demonstrate the Arvia process in the United States. In this project, simulated wastes representing those containing dioxins and furans will be subjected to treatability studies at Arvia's facilities in the UK. Following optimization of the treatment parameters, active wastes from the DOE site at Oak Ridge will be transferred to the Perma-Fix facility in Gainesville, FL for active testing trials.

In addition, the paper will discuss other waste streams which are amenable to treatment using the Arvia process in both the commercial and Government markets including

- the destruction of EHC oil and Fomblin lubricant; organic liquids that are thermally stable
- the destruction of dibutyl glycol in the presence of plutonium contamination
- the destruction of Tellus 46 in the presence of alpha contamination

INTRODUCTION

Operation and decommissioning of nuclear facilities results in the generation of a range of radioactive liquid organic wastes including oils, chelating agents, solvents, corrosion inhibitors and cleaning agents. Many of these wastes are difficult to treat using existing technologies (e.g., incineration) as a result of their radioactive content and/or the presence of certain chemical components that preclude these processes from being successfully or economically applied. New, innovative technologies are required for the treatment of these ‘orphan’ or ‘problematic’ wastes.

Arvia has developed a process of adsorption coupled with electrochemical oxidation that has enabled treatment of this category of organic wastes. This process is based on a novel, highly conducting, adsorbent material called Nyex. Treatment is achieved by dissolving or emulsifying the organic waste in water, adsorption of the organic component onto the adsorbent (Nyex) and the regeneration of the adsorbent for reuse by electrochemically oxidizing the adsorbed organic.

The benefits of oxidation of organics as a destructive technology have long been recognised and a range of techniques have been investigated. These include chemical [1], photocatalytic [2], electrochemical [3], supercritical water [4], biological [5] and plasma. None of these alternative oxidation technologies have yet proven technically or economically viable at scale.

Arvia’s process has been demonstrated both on simulant and on real difficult-to-treat liquid organic wastes. A demonstration plant (Figure 1) has treated 10 L of LLW and ILW oil contaminated with alpha radioactivity at the Magnox Ltd nuclear decommissioning site, at Trawsfynydd, in the UK [6]. This joint Arvia/Magnox project [7] showed that the oil could be successfully destroyed using an average regeneration energy of 42.5 kWh/l.

The potential of the Arvia process to treat problem waste streams in the United States is being investigated by a consortium of NuVision Engineering, Arvia Technology and Perma-Fix Environmental Services Inc. Of specific interest are dioxin, furan and PCB-laden organics which exist on the DOE estate. This paper addresses the work taking place on developing a treatment path for these, and other radioactivity-containing orphan waste streams.

EXPERIMENTAL

Baseline Performance

Arvia’s core technology is able to remove organics from solution and electrochemically oxidise them on the surface of its novel adsorbent/ electrode material, Nyex [8]. Typical operation follows the following treatment steps:

1. *Adsorption* – Achieved by mixing the Nyex and effluent through the injection of fluidizing air at the bottom of the reactor. Vigorous mixing and the non-porous nature of the Nyex results in quick adsorption (typically 15 – 30 minutes).

2. *Sedimentation* – When the fluidising air is switched off the dense Nyex particles settle rapidly under the influence of gravity to form a bed (typically 5 – 10 minutes). This bed is formed within a compartment containing an anode and a micro-porous membrane. The cathode is placed behind the separator with an electrolyte solution present to provide conductivity between the separator and the electrode.

3. *Electrochemical Destruction* **–** A direct electric current is passed through the bed which destroys the organic pollutant through anodic oxidation of the organic matter to water, carbon dioxide and small amounts of hydrogen and carbon monoxide. This serves to regenerate the adsorbent. The regenerated adsorbent is then ready for immediate re-use and the whole cycle is repeated. Regeneration time varies depending on the organic adsorbed per cycle.

When applying Arvia's technology to different waste streams, different system operating philosophies have to be applied to balance different organic interactions within the process namely the readiness with which a specific organic is adsorbed and the energy requirement of completely oxidising the organic on the Nyex surface [9]. Another key interaction defining the operating philosophy is the relative hydrophobicity of the organics to be adsorbed and destroyed.

Hydrophobic molecules are readily adsorbed by Nyex hence the process must be geared towards providing sufficient energy to the system to oxidise the adsorbed organics. Hydrophilic molecules are less readily adsorbed hence the process must be geared towards providing sufficient mass transfer in the system to promote adsorption so that the energy applied is utilised efficiently for organics destruction. The following experiments are built around this premise i.e. the fundamental interaction of Nyex with the organic and that subsequent treatment relies on the electron requirements of the particular organics.

Arvia Demonstration Cells and Pilot Plant

Arvia has two configurations of its technology: a catholyte system which is based around traditional electrochemical cell technology and a reverse current system in which the polarity of the cell is switched intermittently and the two sides of the electrochemical cell play the role of both the anode and the cathode. The plants used in the data shown in this paper are as follows:

Arvia ODC1B20 Small Scale Reverse Current Configuration Cell

The ODC1B20 cell has an electrode area of 400 cm^2 and holds 1 kg of Nyex. It operates the reverse current version of the Arvia process in which the Nyex adsorbent behaves as an adsorbent, an electrode material in the anode and as a solid electrolyte in the cathode. A schematic of this cell is shown in Figure 1.

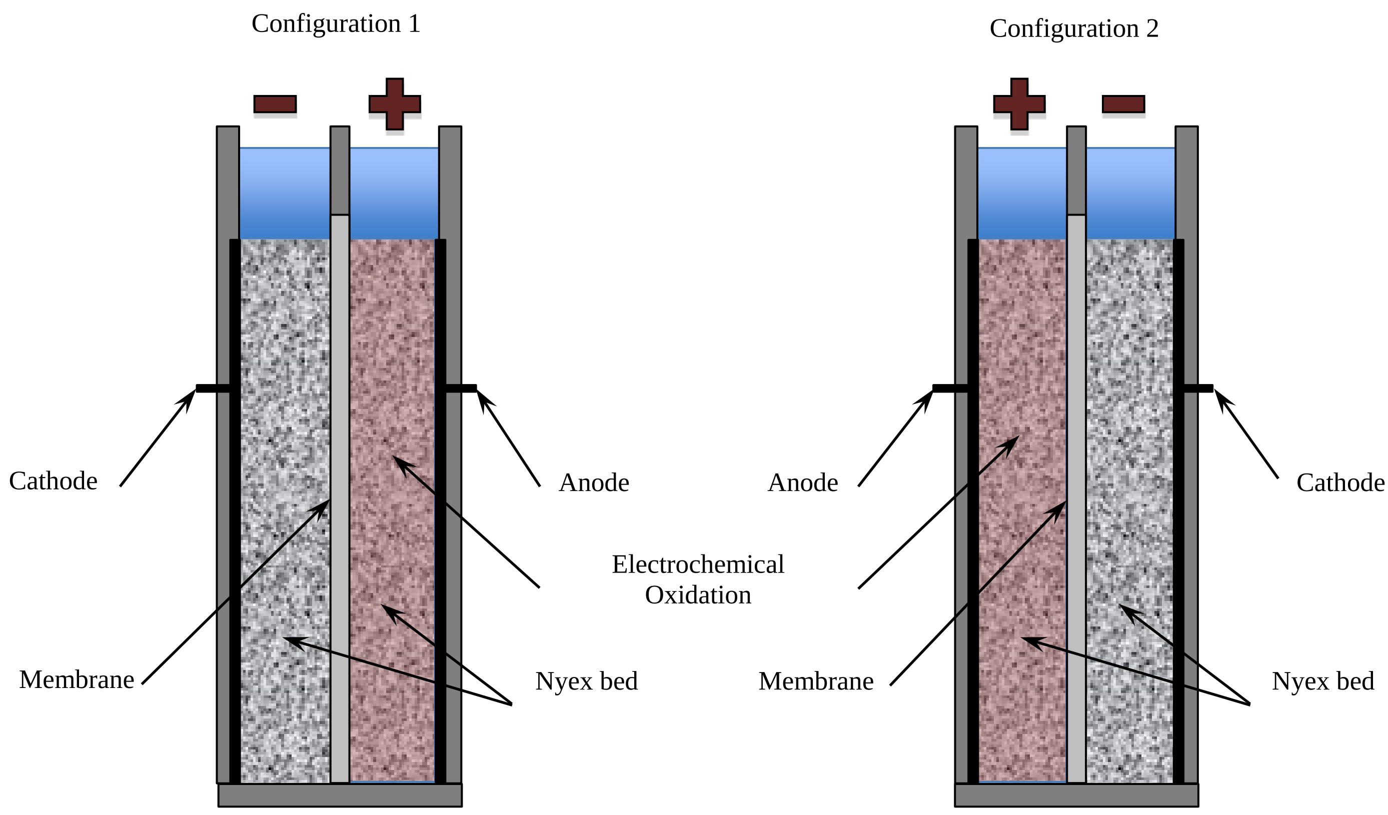

Figure 1: Reverse current version of Arvia's organics destruction cell technology showing the two configurations of operation.

Arvia MORC Small Scale Catholyte Configuration Cell

This unit has an electrode area of 50 cm^2 and holds 100g Nyex. It operates the catholyte system version of the Arvia process in which the Nyex adsorbent behaves both as an adsorbent and as an electrode material in the anode. A schematic of this cell is shown in Figure 2.

Arvia 10 Cell Pilot Plant Demonstration Scale Catholyte Configuration Cell.

This unit has 10 cells each of 23,424 cm^2 electrode area each and holds a total of 35 kg of Nyex. It operates the catholyte system version of the Arvia process in which the Nyex adsorbent behaves both as an adsorbent and as an electrode material in the anode. Its basic design is the same as shown in Figure 2 except at a larger scale with 10 cells in series.

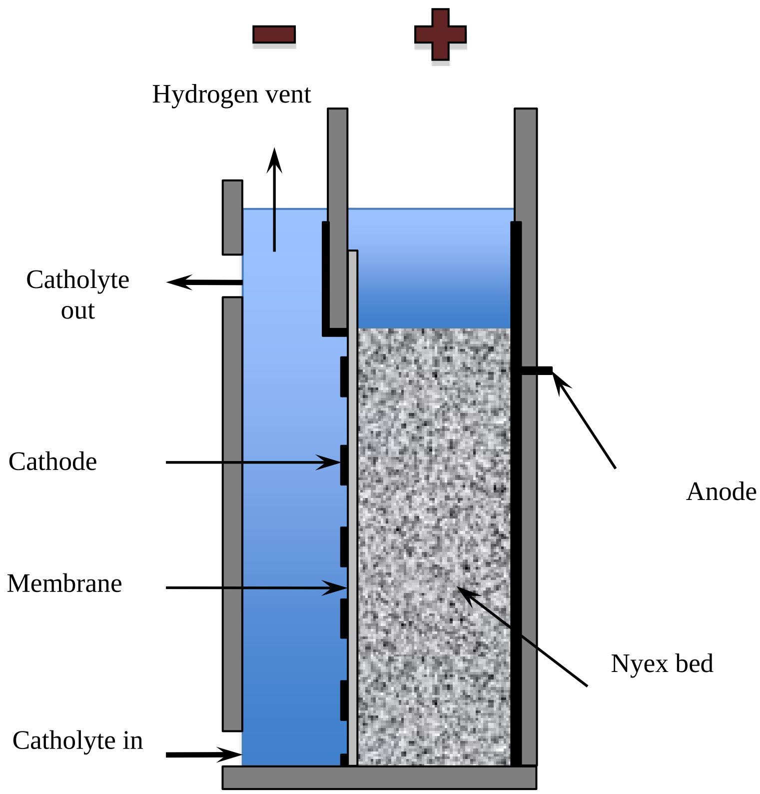

Figure 2: Catholyte version of Arvia's organics destruction cell technology

Waste Streams of Interest

Dioxin, Furan and PCB-Containing Organics

Dioxin, Furan and PCB species can, as a generalization, be considered as hydrophobic compounds. They have a $LogK_{ow}$ coefficient of order 6, which is comparable to that of oils. This suggests that they will be adsorbed well by the Nyex adsorbent and be readily treated by the Arvia process. Considering treatment of dioxin, furan and PCB bearing wastes the characteristics of the supporting organic matrix will influence the rate at which the dioxins, furans and PCBs are adsorbed from solution and subsequently treated.

Two model compounds, 1,3 – butanediol ($LogK_{ow}$ -0.29) and 1- nonanol ($LogK_{ow}$ 3.77) were used to model both a hydrophilic and hydrophobic supporting organic matrix so that the Arvia process’ performance against the two extremes of operation could be demonstrated. The destruction of 2g of supporting organic waste containing µg amounts of Dioxin, Furan and PCBs in 2 L of solution will be demonstrated in Arvia's ODC 1B20 demonstration cell. The cell will be operated at a current density of 10 mA/ cm^2 and the operating philosophy is varied to reflect the interaction between the waste and the adsorbent.

EHC Oil and Fomblin Oil

EHC and Fomblin oils are thermally stable oils that are used in a number of nuclear applications including vacuum and hydraulic pumps. EHC oil can be treated using Arvia's standard methodology and results from Arvia's ODC 1B20 unit are presented in this paper. The Fomblin had to be loaded on to dry Nyex at significantly higher concentrations than usual and then loaded into an Arvia MORC organics destruction cell for treatment.

Dibutyl Glycol

Dibutyl glycol is a solvent that is used in the cleaning of chemical analysis equipment. It forms a component of some of the inventory of 'wastes without current disposal routes' on the Sellafield site. Arvia treated dibutyl glycol in its ODC 1B20 cell to demonstrate the technology's efficacy for the treatment of solvents used in the nuclear industry.

Tellus 46 Hydraulic Oil

Radioactivity contaminated mineral based oil can originate from industrial hydraulic systems and power transmission systems on nuclear sites. Arvia is currently working with Magnox Ltd on the development of a solution to treat 2 m^3 of contaminated oil on the Magnox Trawsfynydd site. As part of this process Arvia conducted a pilot unit trial on the Magnox site using its Titan demonstration unit on active waste. This was able to destroy 10 L of waste and the results were presented in a technical report [7]. This work has been supplemented with a long term study conducted at Arvia's facilities running an Arvia catholyte 10 cell unit over 1000 hours. This data is presented in this paper.

Analysis

Analysis can broken out into two major analysis types: analysis of aqueous phase organic content and analysis of the organic on the adsorbed phase. Aqueous phase analysis was carried out by chemical oxygen demand (COD) testing and total organics carbon (TOC) testing [10,11]. Both techniques give an indication of the total organic content of the aqueous phase but cannot give any indication as to the nature of the different organic species present. When specific organic type analysis was required, gas chromatography with flame ionization detection (GC-FID) and mass spectrometry (GC-MS) was used.

Analysis of the solid phase requires an extraction step followed by an analysis step. Extraction was carried out using hexane. Analysis techniques varied from the use of fluorescence testing, to total petroleum hydrocarbon analysis (TPH). Another method used was analysis by supercritical CO_2 extraction [12]. It was possible to extract the organic from the Nyex using supercritical CO_2 and measure the mass change of the Nyex hence demonstrating how much of the previously adsorbed oil had been destroyed.

RESULTS AND DISCUSSION

Baseline Performance

Two example compounds representing extremes in the range of hydrophobicities, 1,3 - butanediol and 1 – nonanol, were selected to demonstrate the effect of this parameter on the operating philosophy of the Arvia 1B20 unit. Isotherms were produced in the aqueous concentration range of 0-1000 ppm and are shown in Figure 3. It is clear from this data that the more hydrophobic 1-nonanol is much more readily adsorbed by Nyex than the 1,3-butanediol. This effect is significant and is a difference of over 2 orders of magnitude in adsorption, on a per Nyex mass basis, above aqueous phase concentrations of 100 ppm. This difference has implications on the operating philosophy of the Arvia process, which relies on adsorption followed by separation and subsequent electrochemical oxidation of the adsorbed organics, as the orders of magnitude difference in amount adsorbed results in orders of magnitude different amounts of current required per adsorption/separation/regeneration cycle. Further, to achieve treatment to a particular discharge consent, the number of adsorption/separation/regeneration cycles is also vastly different as the amount of organic removed each time depends on the relative adsorptive capacity of the Nyex for the different materials.

Figure 4 & Figure 5 demonstrate the effect of hydrophobicity from the process perspective. Figure 4 shows the predicted treatment profile of 1,3-butanediol with time and the effect of the hydrophobicity limitation – that the amount removed (and destroyed) per cycle was very limited as a result of Nyex's limited adsorptive affinity for the hydrophilic compound, and that this requires a significant number of adsorption-regeneration cycles to achieve treatment. It is of note that the treatment time calculated is a function of the amount of time required to pass sufficient charge through the system to destroy the adsorbed organics, and the mixing time (15 minutes) required per cycle.

Figure 5 depicting the treatment of 1-nonanol is in complete contrast to Figure 4. Here, the interaction between the organic and Nyex is no longer the limiting factor; the limiting factor is the charge passed through the system. This results in relatively few adsorption-regeneration cycles required for treatment, but each cycle is much longer as the amount of organic to be destroyed is much larger than in the case of 1,3-butanediol.

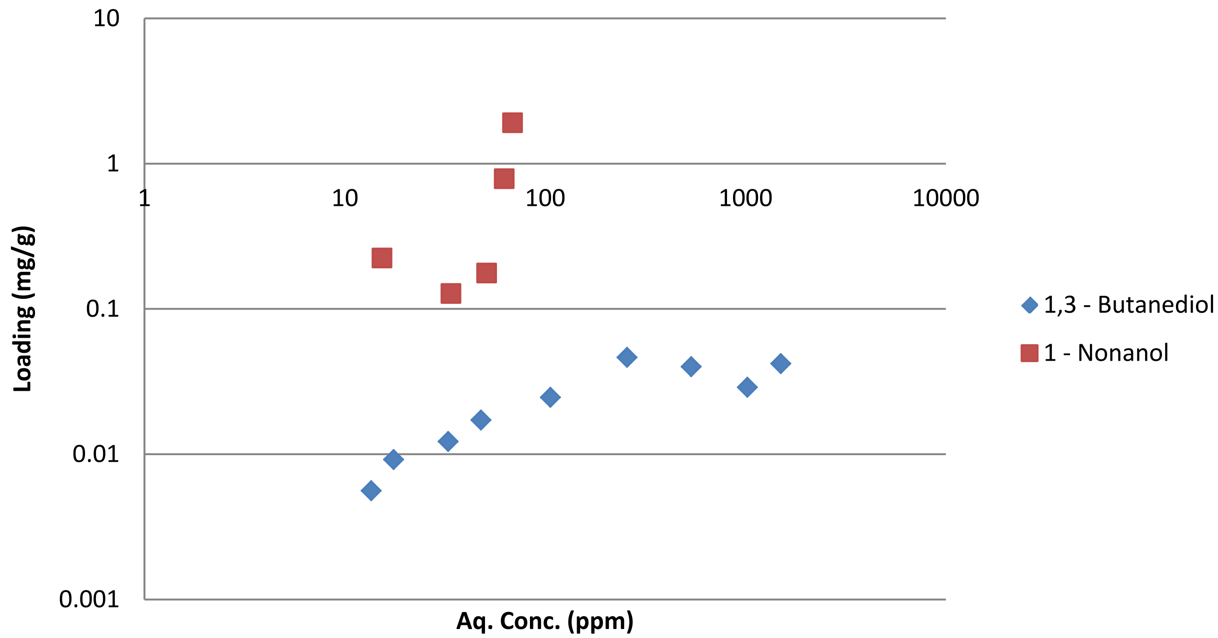

Figure 3: Isotherms for 1,3-butanediol and 1-nonanol

The net effect of this range in interaction types based on organic hydrophobicity results in different treatment rates and efficiencies. The treatment of equivalent concentrations (by mass) of 1-nonanol and 1,3-butanediol against time is shown in Figure 6. This comparison demonstrates that the treatment of hydrophilic organics takes significantly longer than that of hydrophobic organics as a result of the much greater number of cycles required and the mixing associated with each cycle, despite lower regeneration times required per cycle. Figure 6 demonstrates the operating range of Arvia's 1B20 demonstration unit and actual unit performance is expected to fall between the two extremes of treatment for most organics processed of comparable carbon chain length.

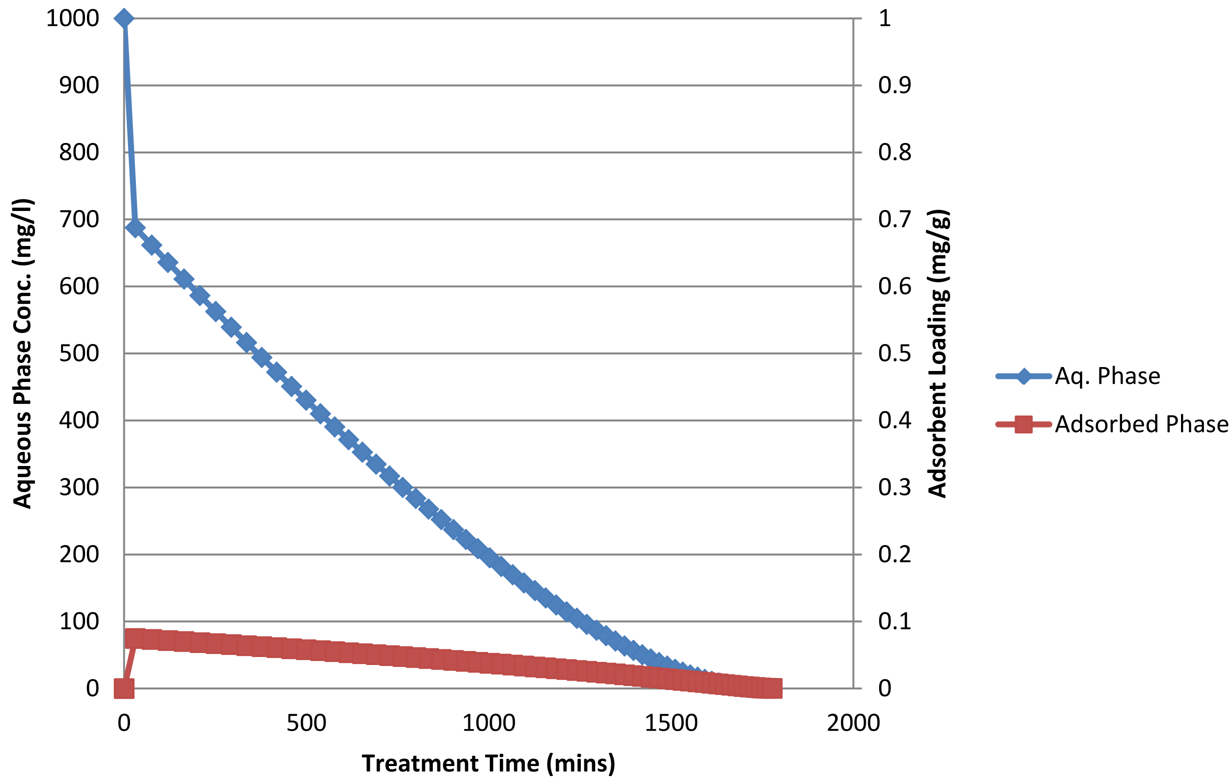

Figure 4: 1,3-butanediol expected treatment profile. The large drop in aqueous phase concentration in the first cycle is a result of dilution as the prepared organic matrix is added to a wetted Nyex bed

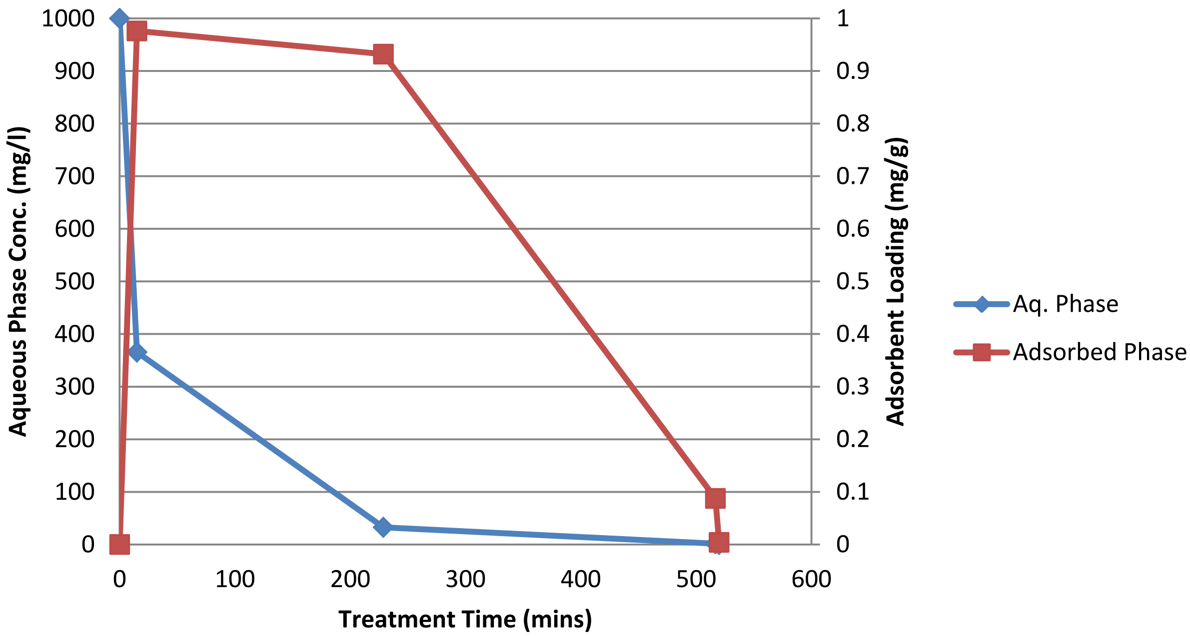

Figure 5: 1-nonanol expected treatment profile. The effect of dilution in this case is obfuscated by the large uptake of 1-nonanol by the Nyex

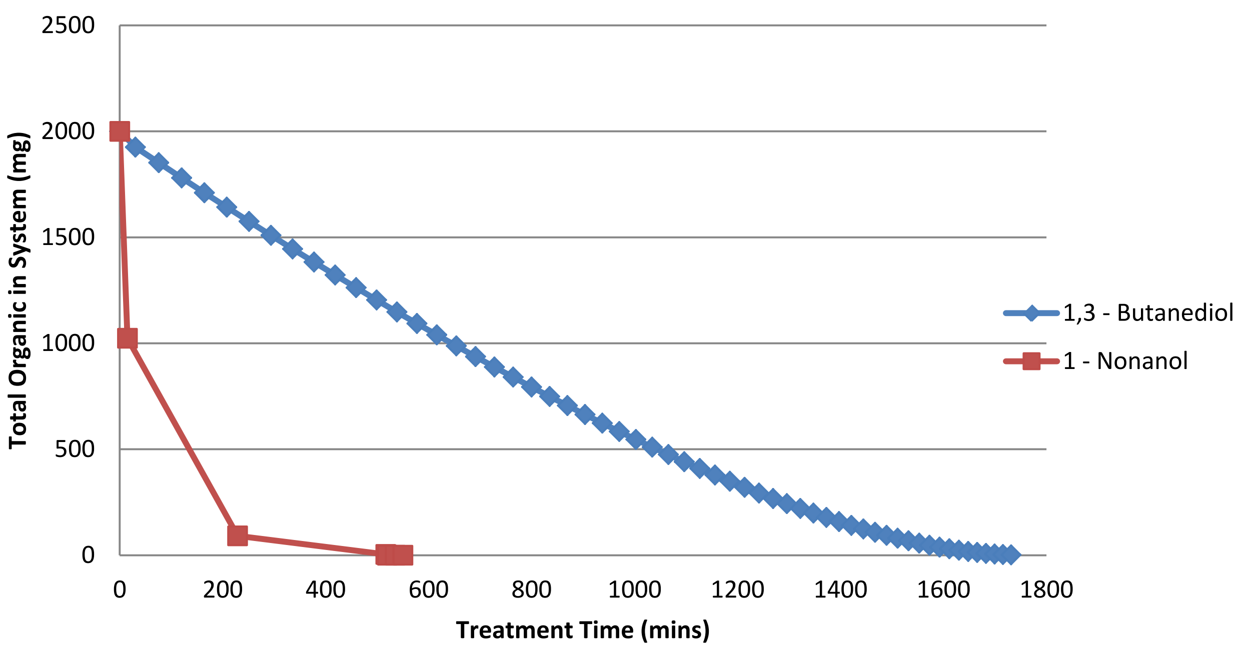

Figure 6: Comparison of the treatment of 1-nonanol and 1,3-butanediol against time

Dioxin, Furan and PCB Laden Organics

The above example compounds, 1,3-butanediol and 1-nonanol, were used as the supporting organic matrix for a dioxin, furan and PCB containing simulant waste. Treatment parameters based on the above work were used and the dioxin, furan and PCB concentration was followed with treatment time. At this time this work is ongoing. Results will be presented at the conference.

EHC Oil and Fomblin Oil

Work conducted demonstrated that the process was able to adsorb and destroy EHC and Fomblin high thermal stability oils. Figure 7 demonstrates the oxidation of Fomblin on Nyex. As a result of its properties large quantities of the Fomblin oil had to be added to a dry bed of Nyex. Despite being a departure from Arvia's typical adsorption-regeneration process in terms of both oil adsorption mechanism and quantity of oil adsorbed, Figure 7 demonstrates that oil destruction was achieved.

EHC oil was also tested. This oil could be treated using Arvia's standard treatment methodology. Both the aqueous phase and solid phase concentration were followed and are shown in Figure 8. The results demonstrate that the EHC could be both adsorbed, in keeping with its hydrophobic character, and oxidized after being adsorbed. A comparison of the energy requirement for the oxidation of the different oil types studied is shown in Table 1.

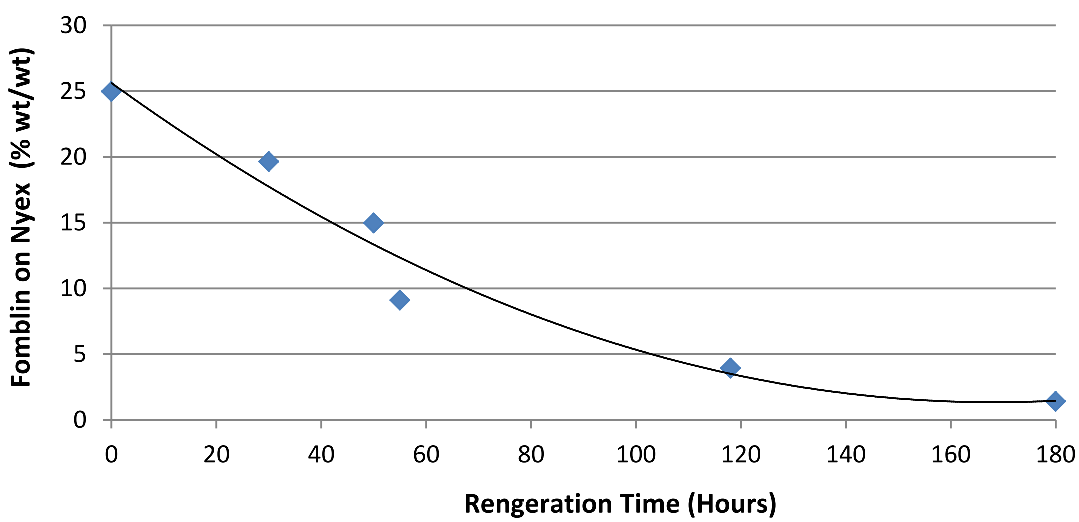

Figure 7: The destruction of Fomblin oil by the Arvia process

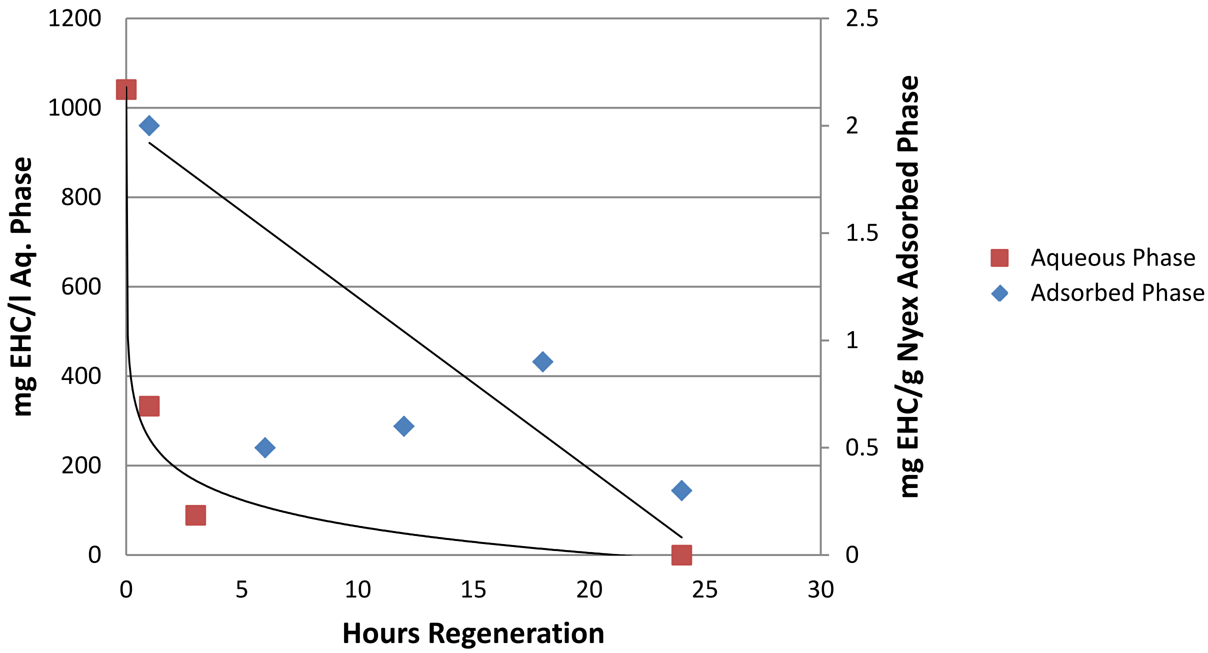

Figure 8: Treatment of EHC oil using the Arvia ODC1B20

Table 1: Organic destruction rate comparison (by mass) of different oils

Oil	**Organics Destruction Rate/m^2 Electrode at 10 mA/cm^2 (g/hr)**
Tellus 46	0.26
Fomblin	0.22
EHC	0.23

Dibutyl Glycol

Dibutyl glycol was treated in Arvia's ODC 1B20 in preparation for trials to be undertaken at the National Nuclear Laboratories (NNL's) Central Laboratory against the Sellafield site on lab waste comprising dibutyl glycol contaminated with plutonium. Preparatory work demonstrated that the isotherm obtained (Figure 9) combined with the model predicting performance based on the isotherm and expected current efficiency was able to accurately predict the performance of the cell for butyl diglycol adsorption and destruction. This comparison is shown in Figure 10. It is of note that the large initial drop in system aqueous phase for the first adsorption cycle is a result of dilution by the water pre-adsorbed on the Nyex. This result gave confidence in Arvia's ability to devise an appropriate unit operating philosophy for the operation of the unit on site at NNL.

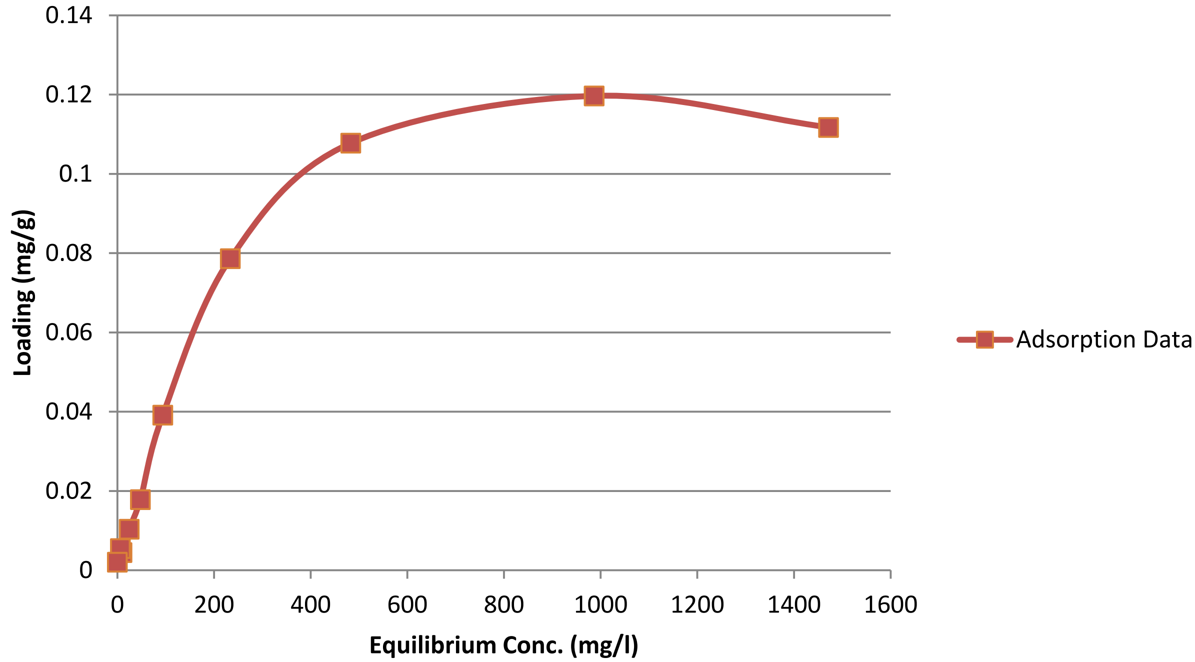

Figure 9: Adsorption isotherm for butyl diglycol

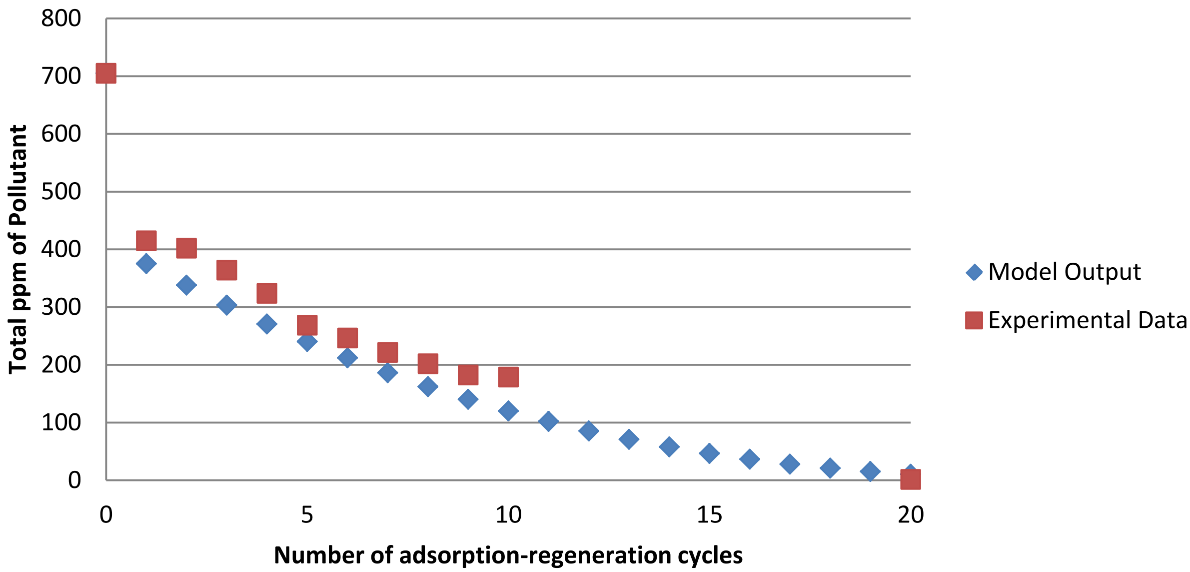

Figure 10: Predicted ODC1B20 performance for butyl diglycol destruction compared to measured performance

Tellus 46 Hydraulic Oil

At WM13 Arvia presented results from its Titan demonstration plant at Magnox. As further supporting work in the demonstration of the technology for the Magnox site Arvia is running a 1000 hour oil destruction trial using Tellus 46 as the example oil. Figure 11 compares the amount of oil added to the system on a per Nyex mass basis with the measured amount of oil during the trial. From Figure 11 the rate of oil destruction is shown to be approximately 15.4 ml of oil per hour by both the fluorescence method and the TPH method used in the analysis.

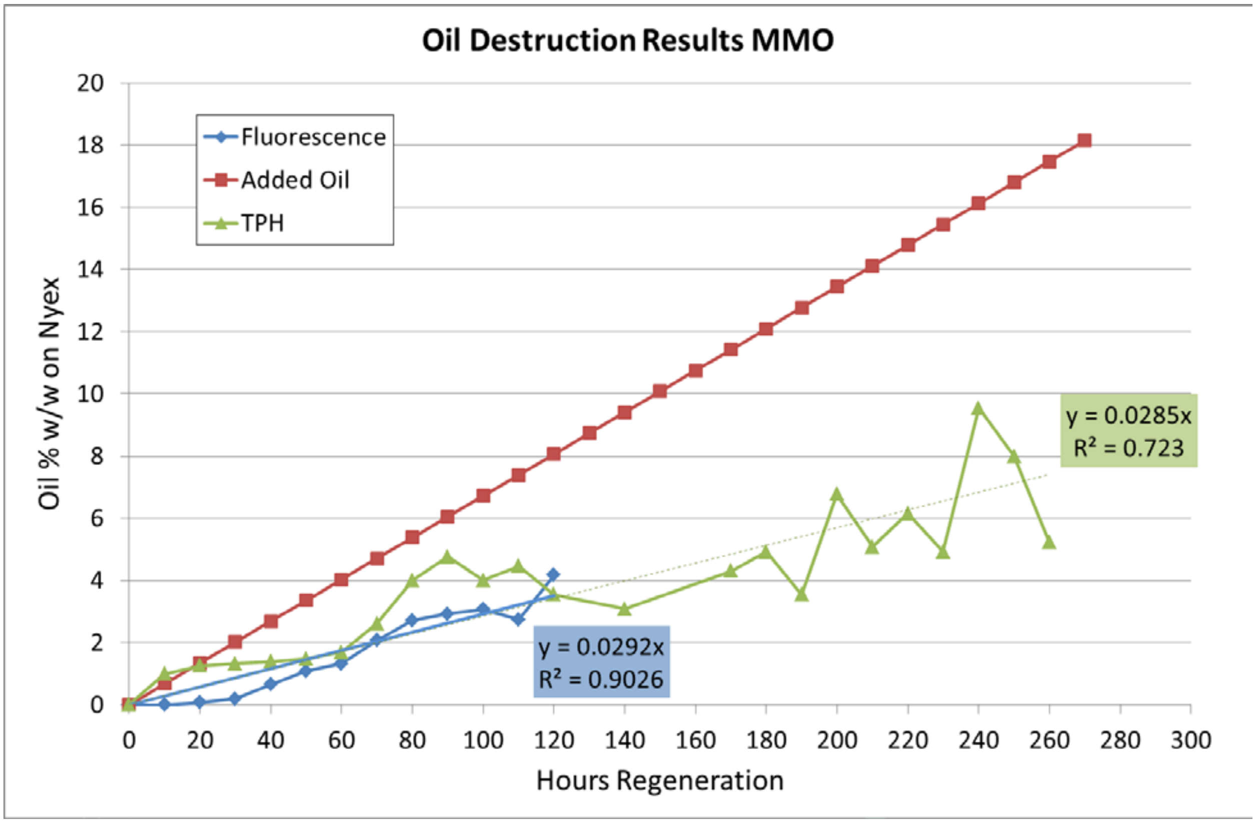

Figure 11: Oil destruction on Arvia's 10 cell demonstration unit

CONCLUSIONS

The presented data demonstrates how Arvia's organics destruction technology has begun to be successfully applied to different organic waste stream types. There is a difference in technology performance between different organics of different chemical and physical properties and these differences have to be managed by different operating philosophies. The development of an operating philosophy able to manage both hydrophobic and hydrophilic organics is currently ongoing as an internal research project.

Results from the treatability trials as part of the collaboration of between Arvia, NuVision and PermaFix with the DOE are not yet available but will be presented at the conference and included in an updated version of the paper.

ACKNOWLEDGEMENTS

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