Arvia Organics Destruction: An Innovative Treatment Approach for Dioxins, Furans and Other Problematic (Orphan) Organic Wastes - 16262

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ABSTRACT

The safe and efficient disposal of radionuclide-contaminated organic wastes is a key component in the lifecycle of a nuclear power plant. Technologies are available for the processing of some of these wastes although there are a number of waste streams for which the disposition path is not clear or does not exist at all. For example, waste streams such as dioxin, furan and PCB-laden oils & aquoues organic matrices pose an issue for the US Dept. of Energy complex. These wastes present a challenge as they cannot be readily treated using existing treatment technologies because of legislative and material constraints such as gaseous phase radioactivity discharge limits, waste elemental content, by-product generation and waste resistance to thermal decomposition.

Alternate methods of organics destruction can circumvent some of these issues by using different mechanisms of organics oxidation. One such innovative method, known as the Arvia organics destruction process, combines adsorption with electrochemical combustion and offers such an alternative. This technology, based on a patented material, Nyex^{TM} that is able to act as both an adsorbent and as an electrode, allows the electrochemical combustion of adsorbed organics to occur on the material's surface. The result is the destruction of organics whilst the bulk of inorganic and radionuclide components remain in the aqueous phase. These components can subsequently be treated using existing waste processing technologies.

This paper outlines recent work conducted on demonstrating the Arvia process against the destruction of dioxin, furan and PCB-laden wastes that demonstrates that the technology successfully removes these target species to below discharge standards in the aqueous phase. Based on these successful trials a test unit has been designed to demonstrate the process on actual radioactive wastes at the DOE Oak Ridge facility. During commissioning at Arvia's facility the unit achieved a destruction rate of over 1.5 ml of 100% organic waste per hour. The unit is currently at a partner laboratory facility based at Oak Ridge National Laboratories and has recently completed a further suite of simulant trials which are reported here.

The above work showcases the development, testing and initial application of an innovative technology, first presented to the industry at the Waste Management 2012, as another option for the treatment of challenging wastes with expensive,

complex or no current disposal routes. Over the years the technology has gone through a number of proving stages culminating in the testing on real orphan wastes based at the Oak Ridge Facility. The Arvia Organics Destruction Cell technology adds to the portfolio of available treatment technologies and will help facilitate the decommissioning and waste disposal responsibilities of the nuclear industry.

1. INTRODUCTION

1.1 Innovative Technology for Problem Liquid Organic Waste Destruction

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. In this particular case the wastes both carry codes that require incineration and preclude incineration as treatment methods hence leaving the wastes with no practicable disposal path. 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 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 and Arvia Technology. Of specific interest are dioxin, furan and PCB-laden organics which exist on the DOE estate. These F027-coded liquid organic wastes do not currently have a disposal pathway as regulations on their F027 content and their radioactive content preclude existing technologies from being used in their disposal. This paper addresses the work taking place on developing a treatment path for these, and other radioactivity-containing orphan waste streams, using the Arvia process.

1.2 Introduction to Arvia's Process

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]. Nyex is an engineered, carbonaceous material proprietary to Arvia. It is a granule and roughly 1 mm in diameter. The system is known as the Organics Destruction Cell (ODC). 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 (Figure 1). This work focuses on the use of a reversing current configuration of the Arvia technology outlined in Figure 1 for the treatment of a fixed inventory of wastes in a batch treatment operation.

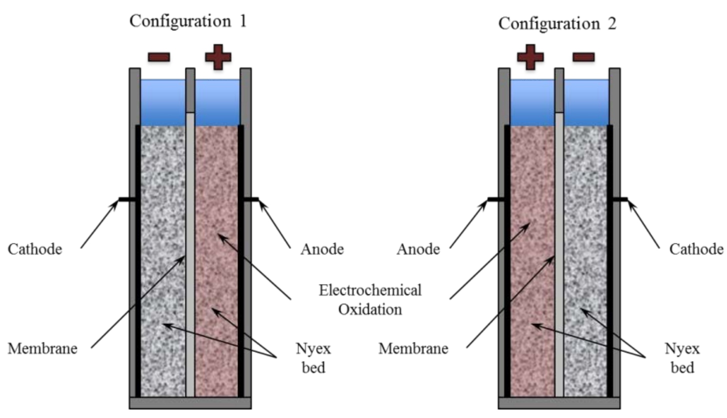


Figure 1: Reverse current version of Arvia's organics destruction cell technology showing the two configurations of operation.

Typical operation for a batch system includes the following concurrent treatment processes:

1. *Adsorption* – Achieved by mixing the Nyex and effluent through the injection of effluent into the reactor through a Nyex bed. The effluent can be fed from the top or bottom of the bed depending on system requirements. Effective mass transfer and the non-porous nature of the Nyex results in quick adsorption from the effluent.

2. *Electrochemical Destruction* **–** A direct electric current is passed through the bed while the effluent is passing through the reactor. This current 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, now free to remove further organic from the system.

These processes are shown in the diagram in Figure 2 which is the basic model for the different configurations of cells demonstrated in this work. In this case a bottom feed configuration was used as opposed to the top feed shown in the figure.

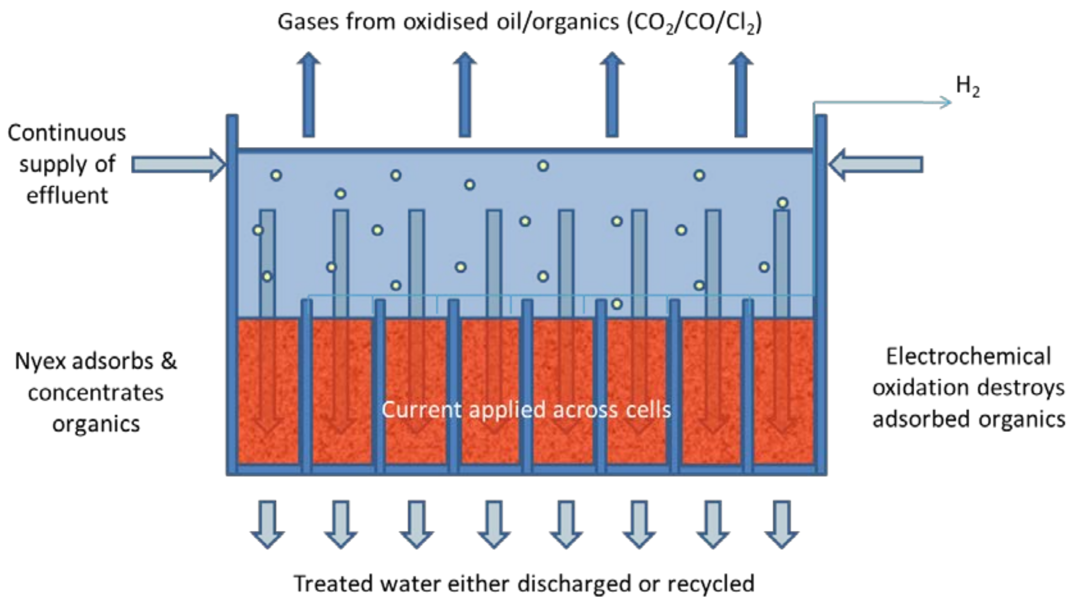


Figure 2: Arvia technology's continuous treatment process shown here in top-feed configuration. Effluent can also be injected from the base of the cell.

When applying Arvia's technology to a waste inventory, different system design and operation parameters have to be taken into consideration. The readiness with which a specific organic is adsorbed affects the energy requirement of completely oxidising the organic on the Nyex surface [9]. This has an impact on the rate of organics destruction per treatment cell and the overall energy cost of treatment per unit organic. This variation in performance has led to Arvia using a feasibility study followed by a pilot plant approach when considering new applications.

To determine the size of a plant appropriate for a specific treatment application the rate at which organics are destroyed needs to be balanced by the number of cells required to deliver this destruction. A larger plant has implications both in terms of capital cost and secondary waste production from the process. The balance between these two parameters – in other terms, the balance between rate of treatment and volume reduction achieved – drive differences in plant sizes given waste characteristics and end user requirements.

2. EXPERIMENTAL

To determine technology efficacy for the treatment of dioxin, furan and polychlorinated biphenyl (PCB) laden wastes a number of experiments have been conducted and reported in earlier publications [10]. Here the studies conducted at the partner facility at Oak Ridge are reported.

Two chemical classes were selected for testing: pentachlorophenol (PCP) and a blend of polychlorinated biphenyls (PCBs; Aroclor 1016 and Aroclor 1260 – both standard PCB compositions). PCP is a stable F027 labelled compound that can form dioxin/furan species as it oxidises; the PCBs are also stable polychlorinated compounds and can form dioxins/furans during oxidation. Successful oxidation of these species is a reliable indicator that the system would be able to destroy dioxin/furan species present. Further, oxidation of these species with minimal generation of dioxin/furan species as reaction intermediates would be a positive indicator for process efficacy for F027 labelled waste treatment.

The dioxin and furan content was tested in both the aqueous and on the solid Nyex phase. The goal of this assessment was to demonstrate that both the treated water and the used Nyex could be disposed of within regulatory (RCRA) limits.

The work was broken into 3 separate experiments; these experiments together with their objectives are described below. The notation ‘2’ represents that these experiments were run as part of Phase 2 of the project. Removal of the target species from the aqueous phase was measured on a per experiment basis; the system’s ability to deliver removal was calculated by mass balance over the total system. In all cases approximately 20 L of solution was treated over 72 hour runs.

Experiment 2.A – Treatment of PCBs in Water

The successful treatment of PCBs would be a reliable indicator of the efficacy of the Organics Destruction Cell (ODC) technology for the treatment of dioxin and furan contaminated wastes. Here PCBs were dosed in water to simulate an aqueous waste containing dioxin/furan species. Dosing was conducted at the 30 ug/l level of two PCB blends - Aroclor 1016 and Aroclor 1260 and repeated 3 times over a 72 hr period. The aqueous phase was analysed after each dose.

Experiment 2.B – Treatment of PCP in Water

The above was repeated with PCP dosed at the 10 mg/l level. Again the aqueous phase was analysed after each dose. Here the higher levels of PCP were representative of F027 species such as chlorophenols which can occur at these levels in problematic waste streams. The PCP was supplied at a 97.99% and was expected to contain dioxin and furan species so these were also tested for to allow for a dioxin-furan mass balance to be conducted to demonstrate the destruction of these challenging components.

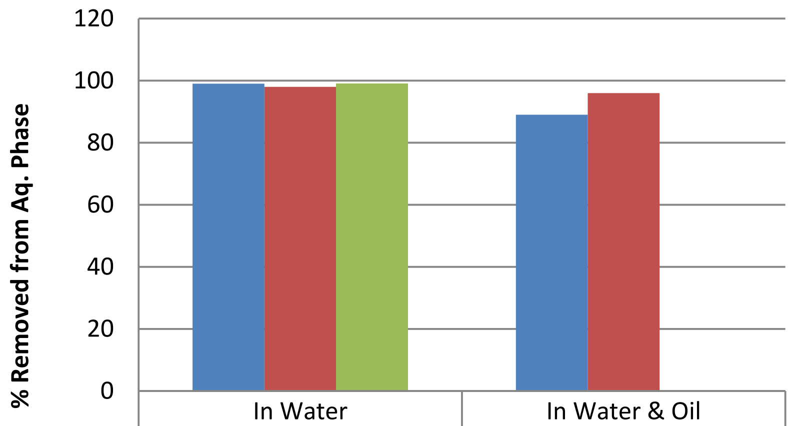
Experiment 2.C – Treatment of PCB's in Water and Oil

Experiment 2.A was repeated with the addition of nonanol (used as an oil surrogate as a result of its properties) at approximately 300 mg/l. This simulated wastes in which the dioxin and furan species would be at concentrations at orders of magnitude below other organics that would be competing for treatment. Again the aqueous phase was tested for the target components.

After the experiments were completed the Nyex was sampled and a composite of the liquids from the different experiments was taken in order to determine the dioxin/furan content of the Nyex and liquid in the ODC. The results are presented by category not by experiment.

3. RESULTS AND DISCUSSION

Removal of PCP and PCBs from the Aqueous Phase



	In Water	In Water & Oil
Aroclor 1016	99	89
Aroclor 1260	98	96
PCP	99	N.A.

Figure 3: Removal of PCP and PCB's from Water and from Water with Oil

Figure 1 shows the removal of the PCB's and PCP from the water matrix. In both cases effective removal was seen at over 98%. The PCBs were also tested in a water and oil matrix. In this case removal was poorer at above 89% however this was expected as the oil would compete with the Nyex for the sorption of the PCBs from solution. PCP was not tested in an oil – water matrix.

Removal of PCP and PCBs from the System

The removal of these species was determined by completing a mass balance over the system taking into account species found on the Nyex, in the aqueous phase and the amount of species transferred into the treatment tank. It must be noted that the amount of component lost by adsorption in the holding tank was insignificant with the exception of PCP in which approximately 1.5% was found on the walls of the holding tank.

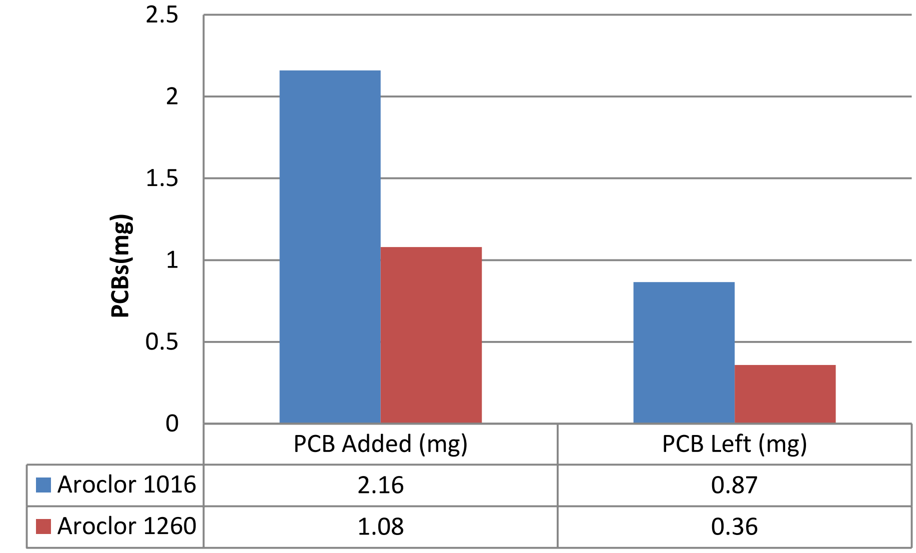


Figure 4: PCB System Balance

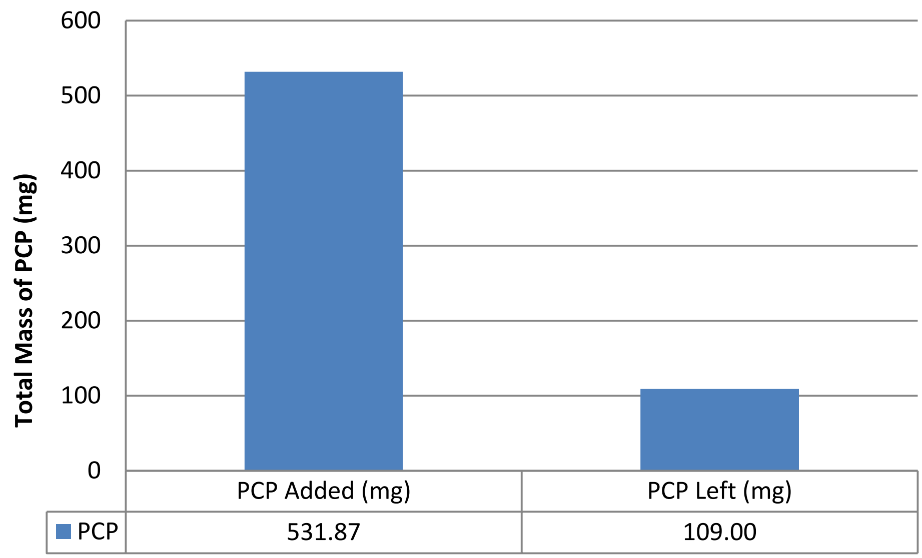


Figure 5: PCP System Balance

Figure 2 and 3 show the system balances for PCBs and PCP respectively. It is clear that in both cases there is significant removal of the species implying that the species underwent oxidation during treatment in the ODC. This conjecture could be confirmed with further experimentation. The PCP, dosed at a higher concentration into the system, is removed more effectively than the PCBs. This is a result of the concentration of the species that affects rate of oxidation. In previous work conducted by Arvia it is shown that components at the mg level are removed more quickly than at the ug level.

Dioxins & Furans Treatment by the ODC

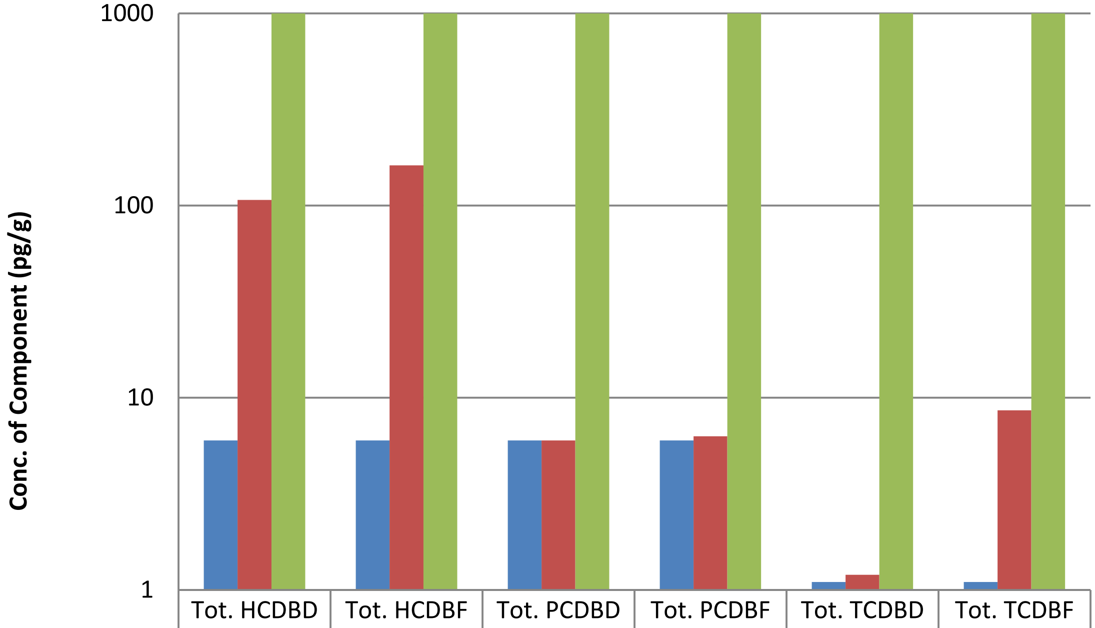
The dioxin and furan content was measured both on the Nyex and in the aqueous phase at the end of the experiments. The data is presented in Figure 4 and Figure 5 with Table 1 outlining the abbreviations used.

Table 1: Dioxin and furan Congeners with Abbreviations

Congeners	Abbreviation
Total Hexachlorodibenzo-p-dioxins	Tot. HCDBD
Total Hexachlorodibenzofurans	Tot. HCDBF
Total Pentachlorodibenzo-p-dioxins	Tot. PCDBD
Total Pentachlorodibenzofurans	Tot. PCDBF
Total Tetrachlorodibenzo-p-dioxins	Tot. TCDBD
Total Tetrachlorodibenzofurans	Tot. TCDBF

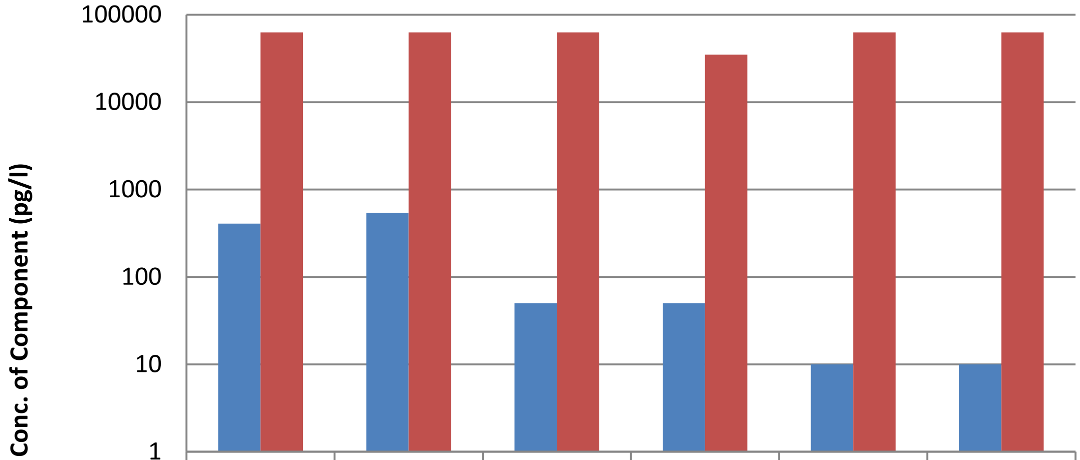
The work conducted by Arvia in Phase 1 demonstrated that Nyex, as a material containing carbon, had some naturally occurring dioxin and furan species on its surface. As a result a ‘zero’ and an after treatment measurement were required. These two measurements together with the RCRA discharge standard are shown in Figure 4. It is clear from the figure that there was an increase in dioxin and furan content measured before and after the treatment of the PCBs and PCP; specifically HCDBD and HCDBF are seen. This echoes the data generated during Phase 1 during the treatment of TCP which showed an increase in Tetrachlorodibenzofuran (TCDBF). At this stage it was not clear whether this increase was a result of the partial oxidation of the different species resulting in the increase of different reaction intermediates or whether they originate from contaminants in the chemical used to spike the species in (Technical grade PCP can contain up to 0.1% dioxin and furan). Importantly the limited amount of dioxin and furan found did not lead to the Nyex becoming out of specification with regards to RCRA disposal limits. This finding was repeated in the aqueous phase shown in Figure 5.

By analyzing the dioxin and furan content of the PCP a system balance could be conducted for the dioxin and furan contents observed to give an indication if the observed dioxins and furans were predominantly a result of oxidation byproducts or an artefact of the removal of dioxin and furan species added into the system with the PCP dose. The results are shown in Table 2.



	Tot. HCDBD	Tot. HCDBF	Tot. PCDBD	Tot. PCDBF	Tot. TCDBD	Tot. TCDBF
New Nyex	<6	<6	<6	<6	< 1.1	< 1.1
Used Nyex	107	162	6	6.3	1.2	8.6
Treatment Standard	1000	1000	1000	1000	1000	1000

Figure 6: Dioxin and Furan content of Nyex Before and After Matrix Treatment



	Tot. HCDBD	Tot. HCDBF	Tot. PCDBD	Tot. PCDBF	Tot. TCDBD	Tot. TCDBF
Liquid After Treatment	407	540	<50	<50	<10	<10
Treatment Standard	63000	63000	63000	35000	63000	63000

Figure 7: Dioxin and Furan content of the Aqueous Phase

Table 2: Dioxin and furan content of PCP added and system dioxin and furan balance. Note negligible dioxin/furan found in aq. phase.

	PCP Dioxin/Furan Content Results (pg/g)	Dioxin/Furan added to system with PCP (pg)	Mass of Dioxin/Furan measured in System (pg)	Dioxin/Furan Added/Removed from System	
Tot. HCDBD	12200000	6478200	8062160	24%	More
Tot. HCDBF	20800000	11044800	10834560	2%	Less
Tot. PCDBD	18800	9982.8	41280	314%	More
Tot. PCDBF	46600	24744.6	43344	75%	More
Tot. TCDBD	1430	759.33	8256	987%	More
Tot. TCDBF	4810	2554.11	59168	2217%	More

From Table 2 it is understood that the dioxin and furan species measured would have resulted from a combination of the generation of oxidation by-products of the

PCP and addition as a result of the purity of PCP added (97%) as the amount added to the system is below that measured at the end. This is in keeping with earlier works that observed the production of furan species during the oxidation of TCP. Further work is ongoing to understand the relative contributions of these species.

4. CONCLUSIONS AND RECOMMENDATIONS

Based on the data generated during the Phase 2 trials the following can be concluded:

1. F027 and F027-like components can be removed from the aqueous phase, even at low levels, and can still be removed in the presence of oils at proportionately higher concentrations that would compete with the target organic species for uptake onto Nyex.

2. A system mass balance demonstrated the removal of PCP and PCBs from the system with proportionately more PCP removed than PCB. This is thought to be as a result of the relative concentrations in the systems of the two species.

3. The treatment of the dioxin/furan precursors used (PCP and PCB) did not result in a significant generation of dioxin and furan species. The levels observed were measured at below RCRA levels on both the Nyex and the aqueous phase meaning that they could be candidates for disposal within regulatory limits.

4. A system dioxin and furan balance suggested that the dioxin and furan species measured could not be simply explained by the amounts added in the PCP dose hence some formation (see point 3) of these species had occurred most likely as a result of incomplete PCP oxidation byproducts.

From the above it can be concluded that the technology has the potential to play a role in the treatment of hard to treat F027 wastes on the DOE estate as it can treat F027 species (PCP, PCBs) and generates limited amounts of dioxin/furan species as oxidation breakdown products. Further work is planned to test the system against real F027 contaminated wastes to generate operational data as a pilot for determining appropriate system scale up parameters and operational performance.

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