CL:AIRE Technology Demonstration Project (TDP) Bulletins provide a summary of CL:AIRE approved Technology Demonstration Projects. TDPs have passed through the CL:AIRE application and review process, and represent demonstration for the specific conditions in which they are applied. This bulletin describes two field applications of the Arvia™ process for removing organic contaminants from groundwater.

Demonstration of the Arvia™ process of adsorption coupled with electrochemical regeneration for the on-site, *ex situ*, decomposition of organic contaminants in groundwater

1. INTRODUCTION

Groundwater treatment to remove organic pollutants is often achieved using Granular Activated Carbon (GAC) or other treatment processes followed by GAC. GAC is usually considered the best practical option, however it is purely a concentration process as the pollutant is only transferred from one phase to another. The loaded GAC must then be disposed of (via landfill or incineration) or regenerated. Regeneration is often regarded as the most environmentally friendly and commercially viable option (San Miguel *et al*., 2001), but this will only occur if the volumes involved are sufficient. Hence there is potential for environmental impact through incineration, disposal to landfill or regeneration.

The Arvia™ process introduces a fundamentally new approach to adsorption technology, using a non-porous, highly-conducting, carbon adsorbent. It is based on research undertaken in the School of Chemical Engineering and Analytical Sciences at the University of Manchester, with commercialisation being undertaken by the spin out company, Arvia Technology Ltd. An independent technical review of the technology by Hyder Consulting Ltd as part of the initial funding round concluded that the innovation had the potential to be disruptive in the market place, as well as being described as "*refreshingly straightforward*". They calculated "*the operational costs of Nyex and GAC are impressive; with Arvia figures approximately half that of GAC*".

Two applications of the process are reported, treatment of a complex range of organics at an agro-chemical research centre by Vertase F.L.I. Ltd and the removal of diesel, petrol and associated decomposition products from a petrol station remediation by Geo² Ltd.

In the Arvia™ process the pollutants are removed by a proprietary adsorbent, Nyex™, which is then regenerated electrochemically, rendering the organic pollutants into harmless gases and water. As well as achieving effective treatment, the technology offers significant cost benefits compared to competing technologies for a wide range of applications along with low environmental impact since the energy use is low and little or no chemicals are required.

The Arvia™ technology is based on two key elements:

Figure 1: The Arvia™ continuous treatment unit – the Arvia™ Gemini.

- A novel, non-porous, highly conducting carbon-based adsorbent material (Nyex™) for the adsorption of organic contaminants that is capable of rapid electrochemical regeneration.
- A treatment process capable of adsorption and electrochemical regeneration within a single unit, using either batch or continuous operation.

The unit design is elegant and robust with no internal moving parts as hydrodynamic control is achieved through fluid injection. It has a number of major advantages over existing processes, from both technological and sustainability perspectives:

- On-site treatment and destruction
- Reduced transportation
- Lower material requirements
    - -No waste sludge or secondary effluent is produced
    - -Addition of chemicals is minimised or avoided

- -Fast adsorption & regeneration results in low adsorbent requirements
  - -No loss of adsorbent or capacity on regeneration
- Low energy requirement
  - -On-site regeneration is achieved at room temperature and pressure
  - -High conductivity adsorbent gives a low cell voltage
- Re-use of treated water possible as nothing is added to the water
- Preferential removal of potentially toxic, aromatic and chlorinated compounds
  - -Pre-treatment to remove these compounds allows biological treatment (often a cheaper option)
- Simple operation and scale up
  - -No internal moving parts
  - -Unit is skid mounted for easy installation
  - -Easy scale up as electrochemical cells can be added in series or parallel
  - -Can be operated in batch or continuous modes

These benefits result in a lower cost treatment process with significantly less environmental impacts.

The Arvia^{TM} process relies on adsorption to achieve the same result as activated carbon, but the Nyex^{TM} adsorbent can then be electrochemically regenerated on site within the same process unit to achieve complete destruction of the organic pollutants. This adsorbent can then be reused, reducing the amount of adsorbent required on site. The Arvia^{TM} process comprises three stages:

- ***Adsorption*** - Adsorption is achieved by mixing the Nyex^{TM} and effluent through fluidising the adsorbent particles, where vigorous mixing and the non-porous nature of the Nyex^{TM} results in quick adsorption.
- ***Sedimentation*** - Sedimentation is achieved when the fluidising air is switched off and the dense Nyex^{TM} particles settle rapidly under the influence of gravity to form a bed.
- ***Electrochemical Destruction*** - Two electrodes are placed either side of the bed of particles and a direct electric current is passed through the bed which destroys the pollutant through direct and indirect oxidation of the organic matter to water, carbon dioxide and a small amount of hydrogen. This serves to regenerate the adsorbent. The regenerated adsorbent is then ready for immediate reuse and the whole cycle is repeated.

This process can operate in both batch and continuous modes.

2. AIMS AND OBJECTIVES

The aim of this project was to demonstrate that the Arvia^{TM} process could treat groundwater, specifically looking at a relatively "simple" petrol station ground remediation project and a "complex" agro-chemical research centre groundwater. The specific objectives were:

- To compare field results with laboratory trials.
- To compare batch and continuous operation.
- To report on the comparable performance of GAC and Nyex^{TM}.
- To calculate the carbon footprint of GAC and Nyex^{TM} in a real application.

This involved the pilot scale demonstration of the novel technology, treating pumped groundwater from two contaminated sites.

3. PROJECT DESCRIPTIONS

This section describes the two projects that were undertaken as part of the technology demonstration project.

3.1 Site 1 – Agro-chemical Research Site

3.1.1 Site Description

The site is a former agro-chemical facility being remediated by Vertase F.L.I.. The ground and groundwater were heavily contaminated and the site contained a number of boreholes from where effluent was pumped to a storage tank. From here the effluent was passed to the effluent treatment works before discharge to a local stream. Treatment involved air-stripping, biological oxidation in filter beds and GAC adsorption. The Arvia^{TM} process was used to polish the biologically treated effluent and all effluent from the Arvia^{TM} process was returned to the existing on-site treatment process to ensure compliance with the existing discharge consents. A list of the contaminants in the biologically treated effluent is given in section 4.1.

The site was not being used and the only activity on the site was the operation of the effluent treatment plant. This plant was operating at up to 40 m^3/hr to prevent the migration of contaminated groundwater from the site. The Arvia^{TM} unit treated a portion of the effluent after biological treatment. Space was not an issue and the Arvia^{TM} pilot plant was delivered in a standard 10 foot (3.05 m x 2.44 m x 2.59 m) iso-container.

Although the site is disused, the water treatment plant remained operational to treat the contaminated groundwater. Operation of this plant fell under the existing site health and safety regulations. This included access to site, evacuation and fire fighting. A site water treatment operator remained on-site to ensure the correct operation of the works. The site was manned on a 24 hour basis.

3.1.2 Technology Demonstration Support Issues

The site is one which has caused significant local interest and there was concern that no additional publicity should be generated which could cause local issues. To prevent this, a detailed risk assessment was undertaken prior to delivering the container to reduced any possible impacts on the local environment.

3.1.3 Technology Demonstration Set Up

This project involved a priority site containing a mix of organic contaminants. The Arvia^{TM} pilot unit treated this groundwater using both batch (the Arvia^{TM} Sequential Batch Reactor (SBR)) and continuous (the Arvia^{TM} Gemini unit) processes. The approach taken was to operate each unit under a range of different processing parameters to optimise performance.

Figures 1 and 2 show the Gemini and Figure 3 shows the SBR. Both were housed within a single 10 foot container.

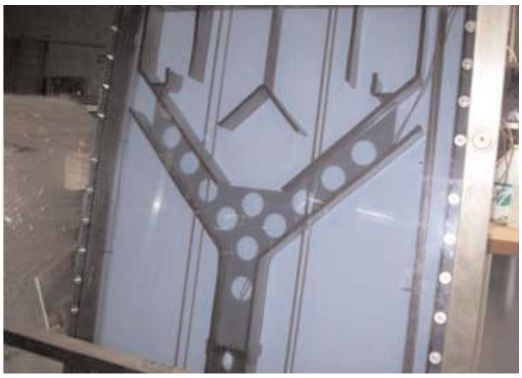

Figure 2: Internal configuration of the Gemini unit.

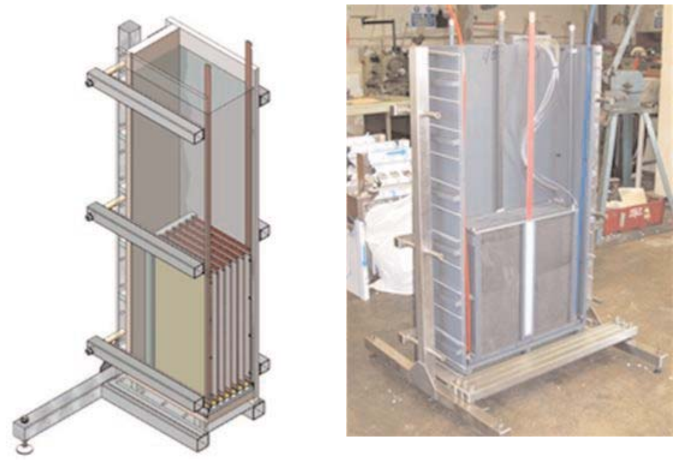

Figure 3: (Left) Image through multi-cell Sequential Batch Reactor (SBR) showing cell arrangement. (Right) Photograph of multi-cell SBR under construction.

3.1.4 Technology Demonstration Operation

During the trials the data/analysis in Table 1 was recorded.

3.1.5 Technology Demonstration Close Out

No waste was generated on site for disposal.

3.2 Site 2 – Petrol Station Site

3.2.1 Site Description

The site was a petrol station in Lancashire that was being remediated prior to redevelopment. The soil and groundwater were contaminated with petrol and diesel hydrocarbons along with their degradation products. Part of the treatment process entailed pumping groundwater to a surface treatment plant comprising oil-water separation, air stripping and GAC adsorption.

Geo^2 Remediation Limited partnered with Arvia Technology Limited to undertake field trials of the new Arvia^{TM} process to remove petrol/diesel contaminants from groundwater with a view to implementing future full scale treatment. The field trial utilised the Arvia^{TM} 6 cell pilot scale sequential batch reactor (Figures 1, 2 & 4) from December 2009 to February 2010 as part of a Dual Phase Vacuum Extraction system removing LNAPL from a petroleum site.

3.2.2 Technology Demonstration Support Issues

A site trial was arranged at an active remediation site with the clients' permission to assess the practicalities of a full scale plant. A risk assessment and method statements were prepared to consider any potential risks. The effluent after treatment was returned to the existing plant up stream of the GAC column so that no untreated effluent would be discharged. Effluent discharge was under the site's existing discharge consents.

3.2.3 Technology Demonstration Set Up

The pilot unit was supplied to site as a pre-commissioned containerised unit. Power was supplied by a connection to the electrical supply on the existing treatment unit. Effluent was taken up stream of the GAC adsorption columns and was stored in a 500 litre container prior to use.

3.2.4 Technology Demonstration Operation

Initial assessment to prove the treatability of the effluent was undertaken at the laboratory scale using the Arvia^{TM} mini-sequential batch reactor (mini-SBR) (Figure 4). The on-site work was carried out using the Arvia^{TM} 6 cell pilot scale sequential batch reactor (SBR) (Figure 5) situated in a container.

Table 1: Data recorded or samples for analysis during the optimisation stage.

Parameter/ Determinand	SBR	Gemini
Current	Each cycle	Yes
Cell voltage	Every 5-15 minutes during regeneration cycle	Every 60 minutes
Air flow rates	Each cycle	Yes
Mixing time	Each cycle	N/A
Settlement time	Each cycle	N/A
Regeneration time	Each cycle	N/A
Temperature	At start and finish of each cycle	Every 2 hours during first 6 hours – influent and effluent. Final reading taken after 24 hours operation
pH	At start and finish of each cycle – measured on site	Every 2 hours during first 6 hours – influent and effluent. Final reading taken after 24 hours operation
Chemical Oxyen Demand (COD)	At start and finish of each cycle – measured on site	Every hour during first 6 hours – influent and effluent. Final reading taken after 24 hours operation
Catholyte pH	At start and finish of each cycle – measured on site	N/A – controlled by pH controller. Volume of acid dosed recorded daily
Suspended solids	At start and finish of each cycle – measured at the Arvia^{TM} Labs	Daily sample – measured at the Arvia^{TM} Labs
Total Organic Carbon (TOC)	At start and finish of each cycle – measured at the Arvia^{TM} Labs	Every hour during first 6 hours – influent and effluent. Final reading taken after 24 hours operation
Conductivity	At start and finish of each cycle – measured on site	Every 2 hours during first 6 hours – influent and effluent. Final reading taken after 24 hours operation
Effluent flow rate/Batch volume	At start of each cycle	Every 2 hours
Organic contaminants	Once per set of operating parameters	Once per set of operating parameters

Figure 4: The Arvia™ mini-sequential batch reactor.

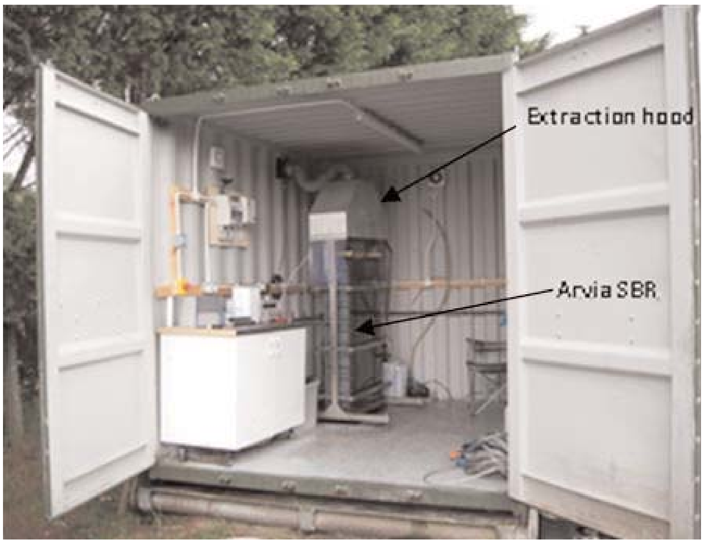

Figure 5: The Arvia™ batch treatment unit (the SBR) – inside the container.

3.2.5 Technology Demonstration Close Out

No waste was generated on site for disposal.

4. RESULTS AND DISCUSSION

In this section the results of the on-site trials are reported, first for the agro-chemical research site and then for the petrol station.

4.1 Site 1 – Agro-chemical Research Site

A sample of effluent from the biological filter outlet was taken for analysis to determine the quality of feed to the Arvia™ process. Since the only priority pollutants at levels above the limit of detection were found in the OP/ON (ON is Organonitrogen Pesticides and OP is Organophosphorus Pesticides) and Phenoxy Acid Herbicide analytical suites, analysis of the trial samples was only undertaken using these specific suites (Table 2).

4.1.1 Laboratory scale treatment using mini-SBR

Initial treatment was undertaken on the laboratory scale and this showed that the organic pollutants in the groundwater, as measured by chemical oxygen demand (COD), could be removed to below the detection limit (4 mg/l) using the Arvia™ process (Figure 6). This work was intended to prove that the groundwater could be treated and no attempt was made to optimise the process at this stage.

Laboratory treatment involved treating 2 litres of the site groundwater (after air stripping and biological treatment) in the mini-SBR (Figure 4) over a number of cycles with the same batch of adsorbate. Treatment conditions are given in Table 3.

From this data it was possible to calculate the operating performance of the system. The major use of energy within the Arvia™ process is typically the energy for electrochemical regeneration. The laboratory cell used in this work was operating at a power of 2.1 Watts, giving an energy requirement for

Table 2: Typical influent concentration

Determinand	Influent (mg/l)	Method	LOD (μg/l)	Analytical Suite
Dimefox	0.2	GC-MS	0.1	OP/ON
Ethofumesate	0.3	GC-MS	0.1	OP/ON
Hempa	6.5	GC-MS	0.1	OP/ON
Schradan	4.6	GC-MS	0.1	OP/ON
Simazine	0.34	GC-MS	0.01	OP/ON
Dicamba	1.6	GC-MS	0.1	Phenoxy acid
Dichloroprop	0.1	GC-MS	0.1	Phenoxy acid
Mecoprop	0.2	GC-MS	0.1	Phenoxy acid
PAAH	<0.1	GC-MS	0.1	Phenoxy acid
1,2-dichlorobenzene	<1	GC-MS headspace	1	VOC
1,2-dichloroethane	<1	GC-MS headspace	1	VOC
Cis-1,2-dichloroethylene	<1	GC-MS headspace	1	VOC
Cyclohexane	<10	GC-MS headspace	10	VOC
Tetrachloroethylene	<1	GC-MS headspace	1	VOC
Toluene	<1	GC-MS headspace	1	VOC
Trichloroethylene	<1	GC-MS headspace	1	VOC
Vinyl chloride	<1	GC-MS headspace	1	VOC
Xylene	<1	GC-MS headspace	1	VOC
2,4,6-trichlorophenol	<10	GC-MS	10	SVOC
2-methyl-4,6-dinitrophenol	<10	GC-MS	10	SVOC
4-chloro-2-methyl phenol	<10	GC-MS	10	SVOC
Bis (2-chloroethyl) ether	<10	GC-MS	10	SVOC
Phenol	<50	GC-MS	10	SVOC

Notes

PAAH - Phenoxy acetic acid herbicide: MCPA (4-chloro-2-methylphenoxyacetic acid)
GC-MS - Gas Chromatography-Mass Spectrometry
OP/ON - Organophosphorus pesticides/Organonitrogen pesticides
VOC/SVOC - Volatile Organic Compounds/Semi-volatile Organic Compound

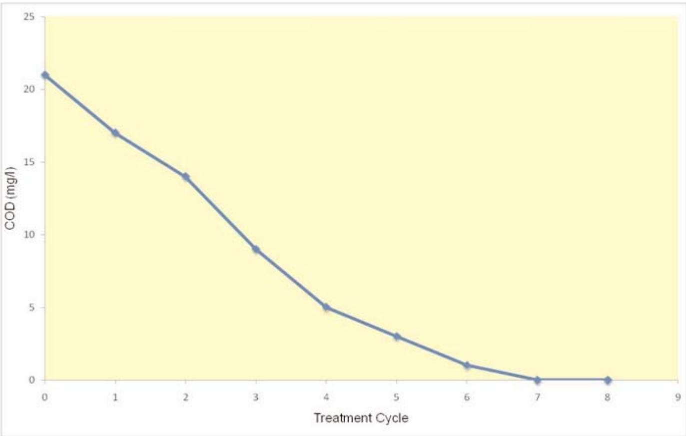

Figure 6: Removal of organic contaminants on the laboratory scale using initial batch of adsorbate.

Table 3: Treatment conditions for laboratory scale treatment of an agro-chemical groundwater.

Parameter	Value
Adsorption time	15 minutes
Settlement time	5 minutes
Regeneration time	15 minutes
Regeneration current	0.5 A
Typical cell voltage	4.2 V

regeneration of 1.8 kWh/m^3. This is based on a charge passed of 75 C/mg COD. The theoretical charge for electrochemical regeneration is of the order of 12 C/mg COD and typically Arvia would expect a charge passed to be around 20 C/mg COD. Hence it is expected that optimisation work would reduce the energy required, although this was not investigated at laboratory scale.

4.1.2 Continuous Treatment - Gemini Trial

The Gemini unit was used to treat groundwater over a period of time using a combination of different flow rates (5 – 30 l/hr) and currents (1 – 5 A). From this data the electrical energy (per m^3) used for regeneration could be calculated and was compared with the COD removal rates (Figure 7). Whilst Figure 7 demonstrates that increasing the energy results in greater COD removal, it is shown more clearly in Figure 8, where the average COD removal for a range of energy inputs is shown. For this groundwater the energy to reduce the COD to below the limit of detection would be 1.6 kWh/m^3.

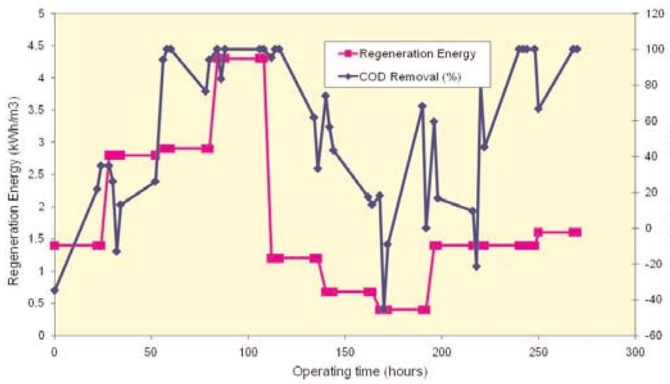

Figure 7: Performance of the Gemini unit over time. Data points are shown for the plant operating at different flow rates and currents.

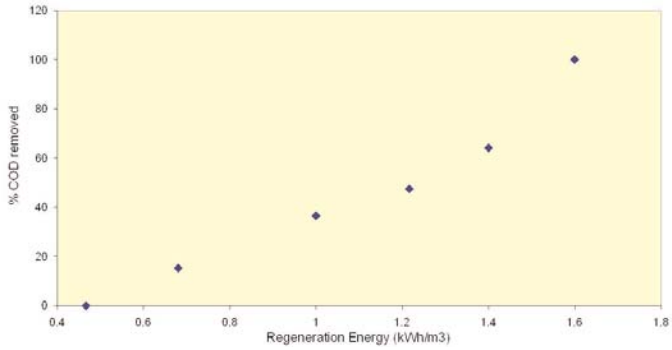

Figure 8: Summary of the data averaged from Figure 7 showing the effect of increasing regeneration energy on COD removal (using data from trials with flow rates up to 15 l/hr).

This does not give a full picture as it became apparent during the trial period that when operating the system at the higher flow rates, the limiting factor was the adsorptive capacity of the Nyex™, rather than the energy being applied during regeneration. At flow rates of 30 l/hr the COD removal rate was very limited whatever the regeneration current applied, demonstrating that it was the adsorption phase that was the limiting factor (probably due to the limited time for adsorption). At 5 and 15 l/hr, COD removal to below the level of detection could be achieved by passing the correct current through the cell.

The charge passed through the system at 1.6 kWh/m^3 was around 66 C/mg COD, very similar to the results obtained from the laboratory scale.

Subsequent trials have shown that scale up of the Gemini unit to a multi-cell system is problematic due to the hydrodynamics within the adsorption zone. A revised multi-cell design has now been developed and tested.

4.1.3 Batch Treatment - SBR Trial

The SBR was operated by filling the treatment unit with 60 litres of groundwater, agitating for 30 minutes, settling for 10 minutes and then regenerating for 15-30 minutes under different conditions. Figure 9 shows the effect of operation of the unit over a range of conditions.

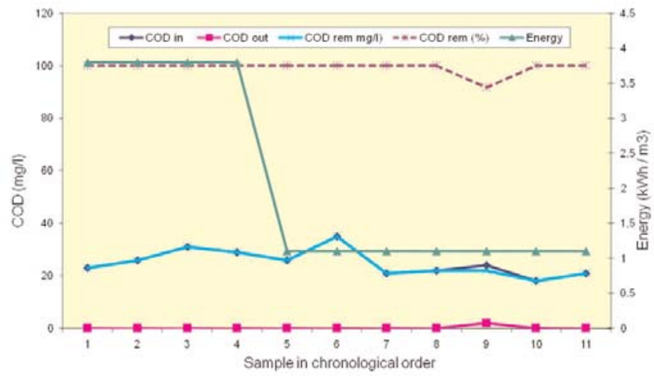

Figure 9: COD and regeneration requirements over a range of operating conditions.

From this data it can be seen that full removal of the incoming COD was achieved. After this period there was a drop in performance of the system. This was found to be due to oxidation of the stainless steel fittings introducing air into the sparging system at the bottom of the unit due to the strong oxidising conditions generated during regeneration. This was proven by taking samples from the top of the unit during agitation when it was found that the adsorbent loading within the tank was too low. Hence the system was again being limited by adsorption rather than by regeneration. Replacement of the stainless steel components with plastic eliminated the problem.

Removal of the organics to below the COD limit of detection was achieved by a regeneration energy input of 1.1 kWh/m^3. This is equivalent to a charge passed of 54 C/mg COD. Again this is line with the results from both laboratory batch treatments and from the continuous Gemini trial.

For both continuous and batch treatment, the charge passed is still higher than expected. There are two possible reasons for the higher than expected charges required.

1. Complex organics require a higher charge to achieve oxidation than simpler molecules.
2. System was adsorption limited so that some of the electrical charge passed through the Nyex™ was not used for organics destruction as the organic loading was lower than expected.

The second reason is believed to be most likely as decreasing the flow rate for the Gemini system from 15 to 5 l/hr, but keeping the regeneration energy at 1.4 kWh/m^3, increased the COD removal rate from 28% to 100%. In addition when there was failure of the air sparging system in the SBR, there was reduced removal of organics, from the 100% in the trials described above, down to 65%. Hence the adsorptive loading of the Nyex™ must be considered in the design of the treatment unit.

Comparing the results obtained for the small scale batch reactor and the larger scale multi-cell pilot reactor showed comparable results, indicating that scale up is not an issue. This has been fully supported by a subsequent larger scale batch plant in the nuclear industry (Brown *et al.*, 2013). However follow-up trials on a larger continuous process have highlighted that the existing design of single cell system cannot be easily scaled up to multi-cell systems, due to hydrodynamic problems. This has led to a revised continuous process design that has significant advantages over the Gemini unit (Brown and Roberts, 2011).

4.1.4 Priority Pollutants

As well as assessing the removal of organics as measured by COD, Arvia also looked to follow the removal of specific priority pollutants as discussed above and comparing whether these compounds would be preferentially removed during treatment.

Figure 10 shows the rates of removal of COD from the Gemini trials at various regeneration currents whilst using a flow rate 5 l/hr. These trials demonstrate that at a fixed flow rate, it is the regeneration current that controls the degree of treatment required. This means that the degree of treatment that the groundwater receives can be controlled.

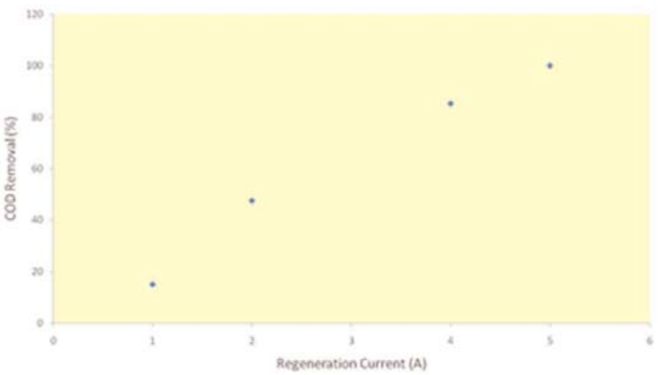

Figure 10: Comparison of the removal of COD at various regeneration currents at a continuous flow rate of 5 l/hr.

Table 4 below shows that, with the exception of Dicamba, all the priority pollutants identified are being removed to below the detection, even when the removal of COD is still very low. This suggests that the process is preferentially removing these specific compounds. However it also highlights that limited removal of Dicamba is occurring. It is believed that this is due to its high solubility which means that it preferentially remains in the aqueous phase rather than adsorbing onto the Nyex™ particles. Activated carbon is likely to find this specific compound difficult to remove as well due to its high solubility.

Table 4: Level of priority pollutants in influent (Infl.) and effluent (Effl.) at different regeneration currents at a flow rate of 5 l/hr. All units in µg/l.

Determinand	Current 1A		Current 2A		Current 4A		Current 5A	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
Dimefox	0.1	<0.1	0.1	<0.1	0.2	<0.1	<0.1	<0.1
Ethofumesate	0.3	<0.1	0.4	<0.1	0.4	<0.1	0.3	<0.1
Hempa	9.2	<0.1	8.4	<0.1	11	<0.1	7.8	<0.1
Schradan	5.1	<0.1	4.3	<0.1	3.7	<0.1	3.5	<0.1
Simazine	0.26	1.1[a]	0.3	<0.1	0.33	<0.1	0.31	<0.1
Dicamba	0.4	0.4	0.2	0.2	0.3	0.2	0.3	0.3
Dichloroprop	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mecoprop	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PAAH*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[a] this result is being treated as erroneous as it is higher than the influent levels in all samples analysed.

The performance of the SBR in the removal of priority pollutants was also investigated. Figure 11 shows that increasing the regeneration time (and hence the regeneration energy), gives improved performance of the system in terms of COD removal.

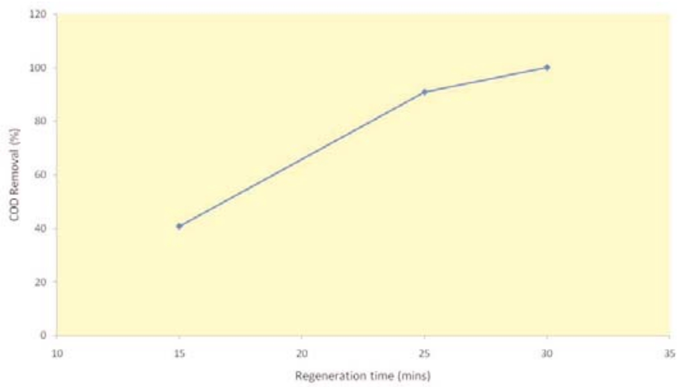

Figure 11: Comparison of the removal of COD with the regeneration time with an applied current of 10A.

As before the samples were analysed for a number of priority pollutants (Table 5).

Table 5: Level of priority pollutants in influent and effluent at different regeneration times at a current of 10 A. All units in µg/l. Note that there are differences in the limit of detection due to different quantities of sample available for testing.

Determinand	Regen Time 15 mins		Regen Time 25 mins		Regen Time 30 mins	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
Dimefox	0.2	<0.3	0.2	<0.1	0.1	<0.2
Ethofumesate	<0.2	<0.3	0.3	<0.1	0.9	<0.2
Hempa	16	<0.3	9.9	<0.1	10	<0.2
Schradan	10	<0.3	5.2	<0.1	7.3	<0.2
Simazine	1.1	<0.02	0.66	0.07	1.1	<0.02

As with the Gemini trials, removal of the priority pollutants is preferentially achieved with the concentration of effluents below the limits of detection with all regeneration times (with the exception of Simazine being detected in the regenerated for 25 minutes sample).

It should be noted that the presence of Natural Organic Matter (NOM) within the groundwater is likely to effect the regeneration energy required as this organic will also be oxidised. In the site trials no attempt has been made to identify the energy required to destroy the NOM compared with the priority pollutants. However it is anticipated that the majority of the energy used is for NOM removal as this is present in mg/l quantities compared with the priority pollutants at the µg/l level. These trials show that treatability studies for each case are likely to be required and that a surrogate may not adequately reflect the performance of the system.

4.2 Site 2 – Petrol/Diesel Contamination

4.2.1 Laboratory Scale Treatment using Mini-SBR

Laboratory scale treatment showed that the organic pollutants (as measured by COD) in the groundwater could be removed to below the limit of detection (LOD - 4 mg/l) using the Arvia^{TM} process (Figure 12). This involved treating 500 ml of the site effluent after aeration and oil/water separation in the mini-SBR over a number of cycles with the same batch of adsorbate. Treatment conditions are given in Table 6.

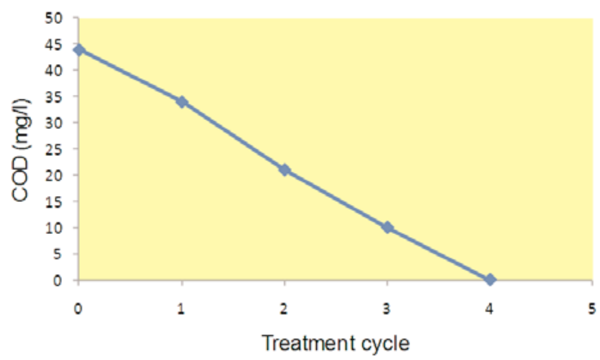

Figure 12: Removal of organic contaminants on the laboratory scale using initial batch of adsorbate

Table 6: Treatment conditions for laboratory scale treatment of petrol station groundwater.

Parameter	Value
Adsorption time	15 minutes
Settlement time	5 minutes
Regeneration time	10 minutes
Regeneration current	0.5 A
Typical cell voltage	4.2 V

From this data it was possible to calculate the operating performance of the system. The laboratory cell used in this work was operating at a power of 2.1 Watts, giving an energy requirement for regeneration of 2.8 kWh/m^3. This is based on a charge passed of 54.5 C/mg COD.

4.2.2 Batch Treatment – SBR Trials

From this data the initial trial conditions on the 6-cell pilot SBR were established. On-site treatment using the pilot scale replicated the removal of the organics over a number of cycles using fresh effluent for each cycle (Figure 13). Whilst the process has been shown to work more efficiently at warm temperatures, the field trial has shown high efficacy at the low environmental temperatures occurring over the winter of 2009/2010. This field trial is based on achieving organics removal (as measured by COD) to below the limit of detection, in one treatment cycle.

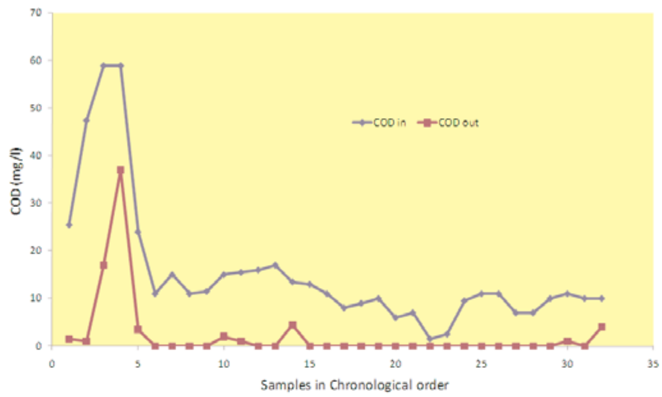

Figure 13: Incoming and treated COD concentrations

The initial results were taken during commissioning when the incoming COD was varying and the process parameters were being established. The regeneration energy required to achieve treatment over this period is given in Figure 14.

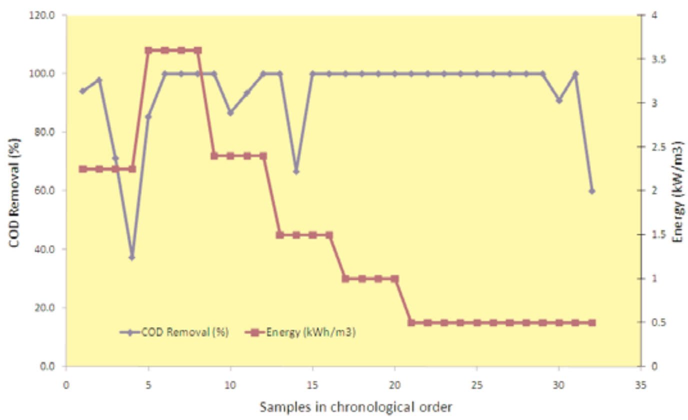

Figure 14: Energy required for treatment

As seen in Figure 14, removal of the organics to below the COD limit of detection could be achieved whilst running at lower energy levels than identified on the laboratory scale. This was because of the lower organic loading and less over treatment. The charge passed when treating at 0.5 kWh/m^3 was calculated at around 10 C/mg COD, in line with the theoretical value.

4.2.3 Proposed Full Scale Design

In order to provide an insight into the scale of plant required for this application, an outline design is proposed below. The design parameters that have been used to scale up the treatment plant are given in Table 7.

Table 7: Design parameters.

Parameter	Value
Flow rate	40 m^3/d
Influent COD	10 mg/l
COD removal	10 mg/l

The use of these design parameters would result in a treatment plant with the following outline design:
Number of electrodes = 16
Number of stacks = 2
Size of electrodes = 0.25 m * 0.9 m
Size of adsorption/regeneration tank = 1 m by 0.85 m by 2.5 m tall
Estimated regeneration conditions per cell are 23 A @ 4.4 V
Regeneration operating energy requirements estimated at 0.4 – 0.6 kWh/m^3
Regeneration cost would be 2.4 - 3.6 p/m^3 (using energy at 6 p/kWh)

Geo^2 has made the following conclusions based on the results of the trial:

"The use of the Arvia treatment process using carbon-based adsorbent Nyex^{TM} represents a huge leap forward in treatment of aqueous organics in a sustainable manner. Complete destruction of dissolved contaminants is achievable with minimum energy input and no ongoing waste disposal costs (spent activated carbon). There is currently no other treatment technology which can reliably destroy contaminants with such energy efficiency. The method can replace air stripping and carbon adsorption together to reduce overall power requirement of remediation systems. All other aqueous organic effluent treatment technologies require secondary treatment by carbon adsorption as they cannot guarantee total destruction of contaminant".

5. CARBON FOOTPRINT & LIFE CYCLE ANALYSIS

Geo^2 required a reduction in the use of energy and a lower carbon footprint at remediation sites, so methods to remove the use of activated carbon and to reduce the energy requirement were being investigated. Geo^2 used the carbon calculator on www.carbonfootprint.com to assess the carbon footprint of both using GAC and an up-scaled Arvia plant (Section 5.1). In addition Arvia has been working with the Department of Chemical Engineering and Analytical Sciences to undertake a Life Cycle Analysis (LCA) to compare the two processes using their CCalc programme (Section 5.2).

5.1 Carbon Footprint

Adsorption does not result in the destruction of the organic pollutants, purely their transfer from the liquid phase onto the solid adsorbent (usually GAC). After a period of time the GAC becomes fully loaded and must be replaced. The loaded GAC is often disposed of by landfilling (or by incineration with ash to landfill) or it can be regenerated. Industrially thermal methods are the most widely used regeneration method, but these are energy intensive and the GAC requires transportation to specialist off-site regenerators. Regeneration of spent carbon has transport requirements and an approximate energy requirement of 800 kw/h per tonne to regenerate.

In addition the majority of GAC is manufactured from fossil fuels and has a Carbon footprint of approximately 6 tonnes per tonne of GAC produced.

The Arvia^{TM} process had the potential to meet the criteria set out by Geo^2:

- Total removal of GAC
- Reduction in power requirement
- Longevity and reliability
- Sustainability

Geo^2 evaluated the energy consumption of the remediation systems used on site 2 to give a like for like idea of carbon reduction. Geo^2 only included the energy requirement into the comparison for twelve months operation of a system. A comparison for site 1 has not been done as there were no data available on the performance of the GAC.

By using an up-scaled Arvia^{TM} process a saving of 14,162 kw/h per year can be made which equates to approximately 8 tonnes of CO_2. This saving can be made through the removal of transfer pumps and air stripping units which are replaced by the Arvia^{TM} process.

Further to this, each time GAC is regenerated (picked as the most sustainable route for disposal) 800 kw/h per tonne are required. For a system using 2 tonnes GAC which is replaced / regenerated in month six and month twelve of operation, approximately 2 tonnes of CO_2 are added to the equation.

The total carbon saving during a twelve month operation using a full scale Arvia^{TM} plant when compared to GAC (excluding transport) would be approximately 10 tonnes of CO_2. Note the carbon footprint for the manufacture of Nyex^{TM} has not yet been established, but as it is not a high temperature process, it is believed that it is unlikely to be higher than that of GAC.

5.2 Life Cycle Analysis

The University of Manchester undertook a comparative Life Cycle Analysis of the two processes using their CCalc programme. This is an award winning programme that is becoming the standard programme used to assess the full impact of a process over its whole life-time. Their comparison was based on treating 1,000 m^3 of raw water to remove Natural Organic Matter (NOM). A reduction in the carbon footprint of the Arvia^{TM} process compared with GAC of between 23% and 89% was achieved. The difference depends on whether the GAC is regenerated or disposed of to landfill. In addition their analysis showed a significant reduction in other environmental parameters (Table 8). Although their data is still provisional, there is a strong indication that the environmental impact of the Arvia^{TM} process is significantly less than that of GAC adsorption (Jeswani *et al.*, 2012).

6. GASEOUS EMISSIONS

Environmental impacts from the Arvia^{TM} process are low as the system does not produce any secondary waste streams other than waste gases. These gases comprise low quantities of carbon dioxide, hydrogen, carbon monoxide and chlorine. The generated hydrogen is discharged to atmosphere along with the air being used to fluidise the adsorbent in the adsorption zone. This provides immediate dilution of the hydrogen so its concentration is well below the Lower

Table 8: Reduction in a range of environmental parameters using the Arvia^{TM} process compared with GAC (provisional data).

Parameter	Average reduction (%)
Carbon Footprint	67
Acidification Potential	49
Eutrophication Potential	54
Human Toxicity Potential	87
Freshwater Aquatic Ecotoxicity Potential	73
Marine Aquatic Ecotoxicity Potential	84
Terrestric Ecotoxicity Potential	11
Ozone Layer Depletion Potential	74
Photochemical Ozone Creation Potential	30
Abiotic Depletion Potential	72

Explosive Limit (LEL) (Table 9). In addition, the containerised unit has an extractor fan fitted which is interlocked with the power supply to the container. Before power can be obtained at any of the electric points in the container, the fan must be operational and on fan failure, the container is isolated. No off-gas treatment is required.

Table 9: Summary of Key Results (Highest values reported)

Determinand	6-cell SBR	Single cell Gemini
CO_2	0.1%	0.1%
CO	2.2 mg/Nm^3	41.9 mg/Nm^3
Organo-chloro compounds	<4 mg/Nm^3	<3.2 mg/Nm^3
Hydrogen	<0.2%	<0.2%
Chlorine	0.9 mg/Nm^3	1.6 mg/Nm^3

As part of the project on Site 1, analysis of the off-gases was undertaken by Envirocare Ltd (a consultancy specialising in gas monitoring) to prove that there were no health, safety or environmental impacts. Site 1 was chosen as there was a wide range of pollutants in the effluent and site treatment involved both continuous and batch treatment.

As can be seen from the photo, Figure 5, the 6-cell pilot batch cell has a hood over the top to ensure that the hydrogen and waste gases generated are extracted from the container. The Gemini unit has no direct extraction (not required as the system is much smaller, producing only 4% of the hydrogen produced by the 6-cell unit). For the reported values in the Envirocare report (summarised in Table 9), there is significantly less dilution of the gases produced in the case of the Gemini than for the SBR. The installation of a hood would ensure that the exhaust values of this unit would also be very low.

From the Envirocare report the following conclusions can be drawn:

1. Hydrogen concentration remains well below the lower explosive limit of 4%
2. Volatile organo-chloro compounds are below the levels of detection
3. An extraction hood over the Gemini would eliminate any problems with carbon monoxide and chlorine concentration
4. The high chlorine concentration reported from the 6-cell SBR occurs at the start of the adsorption phase (when air is blown in for fluidisation releasing any chlorine trapped within the bed). It is significantly lower during the rest of the cycle.

Envirocare concluded that:

"In summary, although there is a certain degree of detection of the pollutants in question, their levels are generally extremely low"

7. LESSONS LEARNED

The cold weather on site 2 experienced during the end of 2009 and the beginning of 2010 resulted in the freezing of the pipes external to the containerised unit whilst the unit was non-operational over the Christmas period. This delayed the start of operations whilst the system thawed out. Designing the unit to allow the drainage of pipes whilst the unit is shut down would prevent this issue. Operation of the unit where climatic conditions are likely to be severe will require an assessment of lagging and trace heating.

A failure of the SBR unit at site 1 occurred due to the corrosion of the stainless steel air inlet fittings due to the strong oxidising conditions occurring during regeneration. These were replaced with plastic fittings to prevent a re-occurrence.

High levels of fast settling suspended solids in the groundwater could result in the presence within the bed of non-conducting material that could cause a reduction in the bed conductivity.

8. ECONOMIC CONSIDERATIONS

This estimate is based on comparing the costs of treatment at Site 2, replacing the GAC column with an Arvia^{TM} unit. It is assumed that all the other operating costs remain the same. Geo^2 were using columns containing 2 tonnes of GAC, which they estimate would be replaced after 6 months operation. Landfill, disposal and replacement of the GAC (ignoring the transportation charge) would be £3,000 per tonne. This would give a GAC replacement cost of £12,000 per annum. In addition there would be the on-site attendance required to supervise the emptying and re-filling of the adsorbers, plus the shut down and re-starting of the plant whilst the GAC was being replaced.

The regeneration cost of operating the Arvia^{TM} unit was calculated to cost 2.4-3.6 p/m^3 (based on 6p/kWh). Assuming that the treatment plant operates for 365 days per year, treating 40 m^3/day, this gives an operating cost of between £350 and £525 per annum.

The capital cost of the Arvia^{TM} system is believed to be higher than the cost of a GAC treatment system as the regeneration equipment is required onsite (although this will be off-set by a smaller inventory of adsorbent and smaller footprint). At this stage it is difficult for an accurate price of a unit to be assessed as each system is currently a one off and there are no benefits from multiple unit manufacture or experienced gained in manufacture. However once a standard design is adopted it is believed that the capital cost will be around one and a half to twice the cost of a comparable GAC system.

9. CONCLUSIONS

The Arvia^{TM} process of adsorption and electrochemical regeneration has demonstrated that it is effective in the removal of aqueous hydrocarbons. Organic contaminants are effectively oxidised rather than the pollutant burden being transferred from one state to another. The Arvia^{TM} process breaks down hydrocarbons to water, carbon dioxide and carbon monoxide, with small quantities of hydrogen produced at the cathode. Low quantities of chlorine can also be produced through the oxidation of chloride ions in the groundwater. This project has demonstrated the process is effective in the treatment of groundwater from different sources using a simple containerised treatment system. The benefits of on-site treatment were highlighted with no need to transport waste materials off site. The treated effluent reached a standard where it could be disposed of via the site's existing discharge consents.

This project has shown that both "simple" and "complex" organics removal can be achieved. The regeneration energy used for treatment in these studies was found to be 1.1 kWh/m^3 and 0.5 kWh/m^3 for the agro-chemical research centre and petrol station groundwater respectively. However the charge passed to achieve these regenerations was greater than anticipated and suggested that there is significant room for further energy reductions. This work suggests that the adsorptive capacity of the Nyex^{TM} must be considered as the limiting factor when treating the low concentrations of organic that can often occur in groundwater situations.

A scale up factor of 300 was used in this project to prove that the process would operate at larger scale. Scale up demonstrated reduced energy requirements (1.1 kWh/m^3) compared with the laboratory scale (1.8 kWh/m^3). In addition a comparison of the continuous and batch process gave similar results with regeneration energy requirements of 1.6 and 1.1 kWh/m^3 respectively.

Removal of a range of identified priority pollutants to below the level of detection (<0.2 µg/l) was achieved treating the agro-chemical research centre groundwater, with the exception of Dicamba which was recorded in the treated effluent at levels up to 0.4 µg/l. This is believed to be due to the high solubility of Dicamba and optimisation work will be required to remove this species to below detectable limits. However, generic organics removal was achieved with treated effluent having CODs below the limit of detection (4 mg/l).

Whilst the work generally showed the preferential removal of pesticides, the minimal removal of Dicamba shows that specific testing will be required to ensure that all required pollutants are removed to the required level. The presence of NOM will mean that regeneration energies are likely to be higher than that required for the identified pollutants.

No process problems were observed when the system was operated in cold conditions where the effluent temperature was less than 5°C. However it highlighted the need for trace heating or lagging when the unit is to be operated in extreme conditions. In addition the strongly oxidising conditions which result during electrochemical regeneration required the replacement of stainless steel fittings with plastic. It should also be noted that the groundwater to be treated should contain relatively small quantities of settleable solids as otherwise they could be trapped within the system, reducing the cell conductivity.

A comparison of the on-site environmental performance of the system with GAC by Geo^2 suggests that there is a significant carbon reduction using the Arvia^{TM} process. A more detailed comparative study by the University of Manchester for a range of environmental effects for the treatment of raw water as opposed to groundwater suggests that the Arvia^{TM} process has much lower environmental impact.

The gaseous emissions were investigated and the independent consultants report concluded that "*although there is a certain degree of detection of the pollutants in question, their levels are generally extremely low*". Off gas removal via local exhaust ventilation without any further treatment should be possible.

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