

# DEVELOPMENT OF AN ELECTROCHEMICAL OXIDATION PROCESS FOR THE TREATMENT OF LANDFILL LEACHATES

K. KAUR BSc., PhD\*, J. CHURCHLEY BSc. MCIWEM\*\*  
and N. KANDHOLA\* BSc., MSc..

## ABSTRACT

Some landfill site operators use wastewater treatment plants for the discharge of complex leachate waste. However, for the water company involved in managing the wastewater plant, leachates can pose a problem to the quality of the effluent, due to the high levels of Chemical Oxygen Demand (COD), ammonia and inorganic metal constituents.

Electrochemical oxidation of landfill leachate has been successfully used by researchers<sup>(1,2,3,4)</sup> with current densities of 5 to 100 mA/cm<sup>2</sup>. A new laboratory system has been developed which utilises a low current density of 2.42 mA/cm<sup>2</sup> and the performance has been evaluated with synthetic and 'real' landfill leachates from 2 wastewater sites.

This system reduces COD of synthetic mixtures by 58%, with complete removal of ammonia. For real leachates, 5 out of 8 samples resulted in ammonia reduction, with 2 samples experiencing approximately 60% COD reduction. Power costs for treatment have been determined and the potential for a full-scale installation considered.

**Key words: Ammonia; COD; electrochemical; landfill leachates; power; oxidation**

\*WatStech Ltd. The Technology Centre, Wolverhampton Science Park,  
Wolverhampton, WV10 9RU, UK.

\*\*Sewer Trent Water Ltd., Technology Development, Avon House, St. Martins Road,  
Finham, Coventry CV3 6PR, UK.

This paper was presented at CIWEM's National Conference 13-15 September 2004, Bretton Hall,  
Wakefield, UK.

## INTRODUCTION

### Summary of landfill leachate legislation and control

There are currently 1,500 landfill sites in England & Wales<sup>(5)</sup> receiving a total of approximately 100 million tonnes of waste per year. These sites can and do produce leachates, it has been estimated up to 276 litres can be produced per tonne of waste landfilled<sup>(6)</sup>. If these leachates are discharged to the water environment they can have major polluting or toxic effects. Therefore, stringent European legislation for the operation, management and control of landfill sites (Landfill

Directive 99/31/EC) has been introduced, this has been implemented in England & Wales through the Landfill Regulations (2002). This legislation includes procedures for water control and discharge of leachate in a controlled manner, with reporting requirements for annual emissions in terms of substances from a 'pollution inventory list'. However, leachate production from a landfill can last for decades, therefore treatment options are being introduced by some landfill operators to minimise the pollution risk and to comply with legislation.

## Description of landfill leachate quality

Landfill leachate is a complex mixture of inorganic and organic compounds. This waste can cause problems to wastewater plant processes, as well as being difficult to treat, due to the high concentration of refractory organic compounds that are not very biodegradable (sometimes termed 'hard COD'). The biodegradability can be measured by Biochemical Oxygen Demand (BOD), generally BOD is a small fraction of the COD in landfill leachates indicating poor biodegradability. The 'young' leachates (also termed acetogenic) have high BOD to COD ratios and therefore are more biodegradable, however old leachates (termed methanogenic) have low BOD to COD ratios. Typically 'old' leachates contain BOD to COD ratios of less than 0.20.

The types of organics present in leachates are variable and dependent on the type of waste present in the landfill. Paxeus<sup>(7)</sup> tested different landfill leachates and found more than 200 individual organic compounds and classes of compounds with concentrations ranging from less than one to several hundred µg/l. In leachates, high molecular weight (HMW) compounds are mainly humic acids and carbohydrates, the low molecular weight (LMW) compounds are mostly carboxylic compounds.

## Electrochemical treatment of leachates

### Effect on organics

Electrochemical treatment of landfill leachates has been found to successfully reduce COD and ammonia at laboratory<sup>(1)</sup> and pilot-scale<sup>(4)</sup>. Chiang *et al.*<sup>(1)</sup> indicated that the removal of COD was 52-58% after 6 hours batch electrochemical oxidation and over 80% for ammonia (NH<sub>4</sub><sup>+</sup>). There are two mechanisms suggested for this process, direct and indirect oxidation. The indirect oxidation is the main reaction pathway for landfill leachate treatment and results in the formation of hypochlorite ions when chloride is also present<sup>(8)</sup>. The direct oxidation of organics by the electrochemical processes can achieve about 40% reduction in COD.

Other effects of the electrochemical process have been noted by Panizza *et al.*<sup>(9)</sup> who found that colour was reduced by 80-94% from a real chemical wastewater. They suggested that this dramatic reduction in colour was due to oxidation of polyaromatic compounds, first to colourless intermediates and then to carbon dioxide. They indicated that when no chloride was present a 40% reduction in COD occurred, but there was no change in colour, with the addition of chloride 100% COD and colour reduction was mediated.

Polcaro *et al.*<sup>(10)</sup> reported that electrochemical degradation of 2-chlorophenol was more efficient when chloride of approximately, 1000 mg/l was added. The

mechanism was summarised as oxidation of chlorophenol to quinonic compounds, followed by ring-opening to form aliphatic acids (predominantly oxalic acids) and finally mineralisation to carbon dioxide.

### Treatment of ammonia (ammonium NH<sub>4</sub><sup>+</sup>)

Direct electrochemical oxidation of ammonia is a slow process, however in the presence of chloride (hence chlorine) the removal of ammonia is significant. The chlorine produced from chloride can react indirectly with ammonia and organics containing an amino group to form chloramines. The mechanism for removal of ammonia is similar to the 'breakpoint reactions' of ammonia with chlorine/hypochlorite to form chloramines, the final product is the formation of nitrogen gas.

Chiang *et al.*<sup>(1, 2)</sup> reported that ammonia of 2600 mg/l was completely removed from landfill leachate using 7500 mg/l chloride, this is an approximately, 1:3 ratio for ammonia to chloride. They suggested that there is simultaneous removal of COD and ammonia in leachates. However, the ammonia reaction with chlorine/hypochlorite is the dominant process.

## Electrochemical treatment system design

### Current density and power used

Laboratory electrochemical units used by other researchers have applied 5 to 100 mA/cm<sup>2</sup> current densities<sup>(1, 3, 4, 10)</sup>. At these current densities it was suggested by some researchers that current efficiency is independent of current density and the amount of COD removed was only dependent on the charge supplied per unit volume<sup>(3)</sup>.

The power consumed is a key factor for assessing the economics for electrochemical treatment of landfill leachates. Chiang *et al.*<sup>(1)</sup> used current densities of 6 to 25 mA/cm<sup>2</sup> and they calculated that 144 kWh/m<sup>3</sup> is required to achieve a final effluent target of 500 mg/l COD and 0 mg/l ammonia, however this increases to 216 kWh/m<sup>3</sup> if the COD target is 200 mg/l. They indicated that by using a higher current intensity the power required was 103 kWh/m<sup>3</sup> and this was recommended to save time and space for the treatment process.

### Type of electrodes

The types of electrodes used in electrochemical processes are variable and typical types are titanium anodes coated with oxides of tin or lead, with a stainless steel cathode<sup>(1, 3, 10)</sup>. Other combinations of titanium-coated anodes are ruthenium/tin/lead dioxides or oxides<sup>(9)</sup> and ruthenium oxide only. Panizza *et al.*<sup>(9)</sup> also tested other non-coated electrodes such as titanium with platinum and carbon, alongside traditional coated electrodes. They found that titanium/platinum electrodes offered better performance than the others tested.

## Development of a new electrochemical system

The system used in this project was typical of systems available, but operated at lower current densities. This low current density system has been evaluated for the reduction in COD and ammonia using synthetic leachates to assess the reaction mechanisms. The performance of the system was also assessed for the treatment of a number of real leachates from wastewater treatment sites operated by Severn Trent Water Ltd.

## METHODS & MATERIALS

### Design of the laboratory electrochemical system

A laboratory electrochemical system has been specifically built for this project by Advanced Oxidation Ltd. (Wrexham, UK) and incorporates a number of key features, such as a mesh design electrode structure, anodes coated with ruthenium and iridium dioxide and a patented power supply system. Details of the electrodes are shown in Table 1.

Table 1. Details of electrodes used for the electrochemical system

Parameter	Description
Total number of electrodes (all titanium)	13
Number of cathodes	7
Number of anodes (coated with ruthenium/iridium dioxide)	6
Dimensions of electrodes	20.9 cm x 12.5 cm x 4.0 cm
Thickness of electrodes	0.1 cm
Gap between electrodes	0.2 cm
Total surface area of all electrodes	6679.4 cm <sup>2</sup>
Active surface area (60%)	4127.6 cm <sup>2</sup>
Current density range for active surface	1.21 to 2.42 mA/cm <sup>2</sup>

The electrode pack was housed within a glass vessel of 3 litres capacity for batch treatment and the solution was recirculated at 1 l/min. volumetric flow rate to maintain mixing. Photographs of the electrochemical system are shown in Figure 1 (a & b). Voltage was controlled to achieve set current densities and recorded to determine power usage.

### Sample analysis

The system was allowed to reach steady state prior to the start of the experiments and a typical batch experiment was for 6 hours duration. Samples were taken from within the vessel at specific time intervals during treatment and analysed immediately using standard analytical techniques<sup>(1)</sup>. Some of the colorimetric methods were supplied as HACH™ tests kits (Camlab, Cambridge, UK) and completed using the HACH™ DR2010 Spectrophotometer. When samples were outside the range of the methods used, dilution with distilled water was included as part of the analysis and chlorine residual was neutralised with sodium thiosulphate. Some analysis of Semi-Volatile Organic Carbons (SVOCs) using standard Gas



a) Front view of the system



b) Inside view of system (with electrode pack & vessel)

Figure 1. Photographs of the electrochemical system

Chromatography Mass Spectrometry (GCMS) analysis was completed at Severn Trent Laboratories Ltd. (Coventry, UK).

### Synthetic and real landfill leachate composition

A synthetic mixture was developed that was based on Kamenev et al.<sup>(2)</sup> and contains a range of compounds, in particular chloride concentration of 1000 mg/l, ammonia (NH<sub>4</sub><sup>+</sup>) of 250 mg/l and COD of 1000 mg/l. The typical composition of the synthetic mix is shown in Table 2. The organic and inorganic compounds were supplied by Acros (Fisher Scientific, Loughborough, UK) or Scientific & Chemical (Bilston, UK) as analytical grade.

The humic acid used was initially purchased from Acros, but this was later changed to Sigma Aldrich (Sigma Aldrich, Dorset, UK) and contained 92.5% organics with 7.5% inorganics. The theoretical COD (ThCOD) was used to assist with determining the amount of organics used in the mixture. Some of the inorganic element concentrations varied due to changes in the type of compounds used in the mixture e.g.

Table 2. Composition of typical synthetic leachate

Organics	Formula	Conc. as mg/l	Inorganic elements	Formula	Conc. as mg/l
Phenol	C <sub>6</sub> H <sub>5</sub> OH	105.05	Sodium	Na	504.9 to 554.7
2 chlorophenol	C <sub>6</sub> H <sub>4</sub> ClO	25	Magnesium	Mg	60.7
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	25	Calcium	Ca	178.8 to 90.4
Acetic acid	CH <sub>3</sub> COOH	37.5	Potassium	K	100
Propionic acid	C <sub>2</sub> H <sub>5</sub> COOH	26.3	Iron	Fe	30
Humic acid	/	270	Sulphate	SO <sub>4</sub>	718.7 to 955.2
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	277.77	Chloride	Cl	1081.9 to 955.9
<b>Total ThCOD</b>		<b>1078.8</b>	Phosphate	PO <sub>4</sub>	243
			Ammonium	NH <sub>4</sub>	250
			Carbonate	CO <sub>3</sub>	208.2
			Hydroxide	OH	29.7

Table 3. Quality of the synthetic leachate measured using standard techniques

Analytical parameter	Units	Range of results
Alkalinity	mg/l as CaCO <sub>3</sub>	230
Conductivity	µS/cm	5000 to 6012
Colour	°Hazen	2400 to 2667
TOC (total organic carbon)	mg C/ l	330 to 291
COD	mg/l	952 to 983
BOD	mg/l	400 to 421.3
BOD/COD	Ratio	0.42 to 0.43
UV absorbance (1/10 <sup>th</sup> dilution )	At 254nm (1cm pathlength)	0.710 to 0.953
Iron residual	mg Fe/l	21.3
Chloride	mg Cl/l	1075 to 1330
Oxidation Reduction Potential (ORP)	MV	+211.7 to +262.3
Ammonia	mg NH <sub>3</sub> /l	232 to 240
Total Nitrogen	mg N/l	240

Table 4. Quality of real landfill leachate samples from sites A & B

Analytical parameter	Site A – sample no.					Site B – sample no.		
	1	2	3	4	5	1	2	3
pH	7.67	8.13	8.04	7.64	7.42	7.46	7.95	7.59
Conductivity	1611	4460	1250	1290	1570	2610	4210	2520
Colour (°Hazen)	1180	560	890	740	1050	560	1770	1150
TOC mgC/l	208	/	269	118	156	104	118	113
COD mg/l	1540	451	1406	1297	1486	1557	1580	2670
BOD mg/l	311	96.5	407	240.6	358.5	135.8	331.4	265
BOD/COD ratio	0.20	0.21	0.29	0.19	0.24	0.09	0.21	0.10
UV abs. (1/10 <sup>th</sup> 254nm)	1.432	0.422	0.913	0.840	1.257	0.405	0.825	0.407
Iron mgFe/l	/	2.76	8.41	5.0	7.47	11.50	7.44	/
Chloride mg/l	3563	/	2118	2473	3229	5935	6876	5211
ORP mV	+152	+163	+131	+116	-115	+169	-463	+277
Ammonia mg/l	/	219	875	/	1095	525	/	/
Total nitrogen mg/l	/	160	/	/	1150	650	1050	400

magnesium chloride changed to magnesium sulphate. The quality of the synthetic leachate produced was determined using the standard analytical techniques and the data is shown in Table 3.

The mixture was adjusted to pH 7 using potassium dihydrogen phosphate (1M) and sodium hydroxide (1M), 3 litres was prepared for each experiment. Some of the quality data such as for COD and ammonia was converted to normalised values (i.e. value after treatment ÷ initial value before treatment) to allow for comparison of performance when initial values were different.

The 'real' landfill leachates were composed of variable COD (range 451 to 2670 mg/l), ammonia (range 219 to 1095 mg/l) and chloride (range 2118 to 6876 mg/l) concentrations. These real leachates were collected from two wastewater sites (Site A in the West Midlands and Site B in the East Midlands) both sites are operated by Severn Trent Water Ltd. and receive leachates from landfill sites for treatment. The samples were all collected during November 2002 to January 2003.

A total of 5 samples were collected from Site A, samples 2 and 3 from Site A were as mixed leachates from the main reception tank and have been subject to some preliminary treatment by settlement. The other samples from Site A were taken directly from the delivery tanker and have had no pretreatment. A total of 3 samples were taken from Site B and these have had no pretreatment. The quality of the real leachates taken from Sites A and B was determined using the standard analytical techniques and the data is shown in Table 4.

## RESULTS & DISCUSSION

### Treatment of synthetic leachates

#### Oxidation of organics

The changes in organics during electrochemical treatment of the synthetic leachates were monitored using COD, colour, UV absorbance at 254nm, BOD/COD ratio (Figure 2 a, b, c & d) and TOC. The COD reduction was approximately, 58% when chloride was included in the mixture, without chloride this was only 27%. Changes in colour were significant and approximately, 95% reduction was achieved with chloride, but only 51% without chloride (Figure 3 a & b). For UV absorbance at 254nm, with chloride after 6 hours of treatment the UV is reduced by 58% from the initial value. These changes in UV absorbance are not observed when no chloride is present and only 8% reduction in UV is measured after treatment. Also, the synthetic leachate BOD/COD ratio is approximately, 0.40, after 6 hours of treatment with chloride this increases by 37%, without chloride the increase is only 4%. Data not shown indicated that TOC decreased by 30% from the initial value after 6 hours of treatment with chloride, without chloride the reduction was 20%.

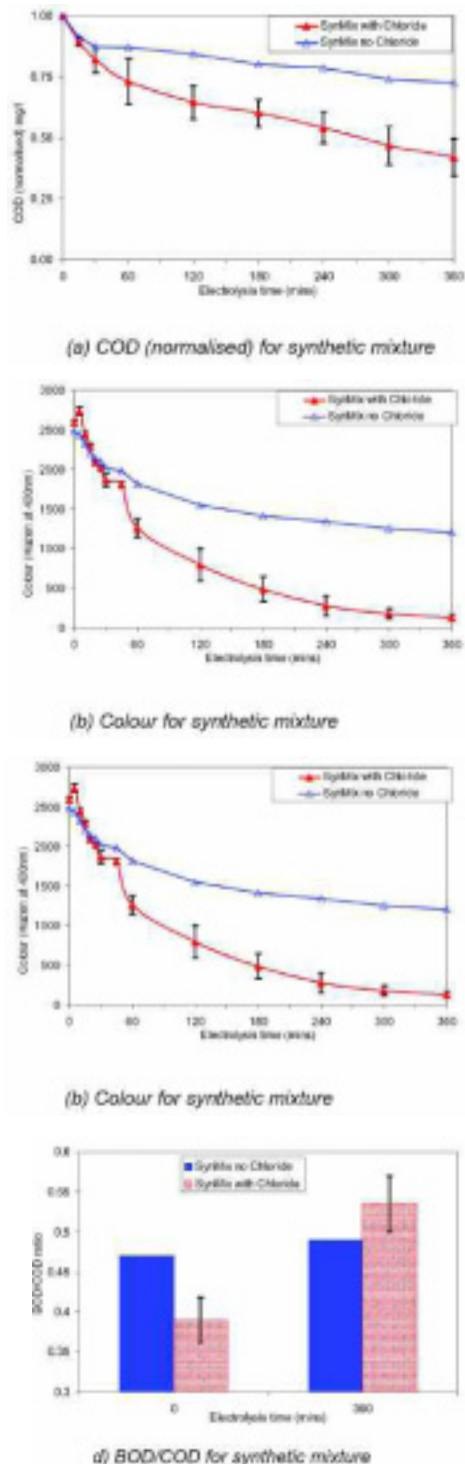


Figure 2. (a-d) Changes in organics for synthetic leachates (with & without chloride) during electrochemical treatment (error bars relate to n = no. of experiments = 2 or 4)

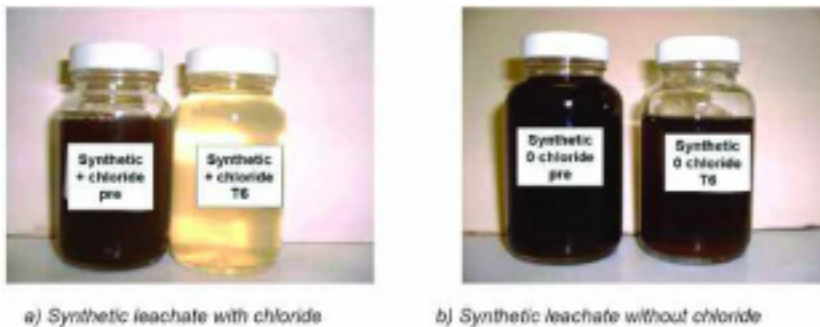


Figure 3. Photographs of synthetic leachates prior to (pre) and after electrochemical treatment for 6 hours (T6) with & without chloride

The oxidation of organics using the electrochemical process has been well documented by other researchers and from this project the data verifies the previous findings, indicating that in the presence of chloride effective treatment can be achieved. Chiang *et al.*<sup>(9)</sup> found that the pollutant removal efficiency depends strongly on the electrolyte present in the wastewater, by increasing the concentration of chloride to 5000 mg/l in a real landfill leachate the removal efficiencies could be increased by approximately 40% for COD.

From the changes observed in UV and BOD/COD ratio it is proposed that structural modifications occur resulting in the possible conversion of 'hard' COD to biodegradable components. Chiang *et al.*<sup>(13)</sup> indicated that during electrochemical treatment the humic acid organic characteristics were affected, within the first hour a change in the UV scan indicated that derivatives were being formed and as the electrochemical process proceeded these derivatives were destroyed. They indicated that the high molecular weight (HMW) compounds are converted to low molecular weight (LMW) compounds.

A reduction in TOC following electrochemical treatment was a general phenomenon and this could be a result of some mineralisation of organics to CO<sub>2</sub> and water with possibly volatilisation. However, iron residual was monitored and decreased by 67 to 100% after electrolysis of the synthetic leachate and with significant changes in colour observed this may have been via a process of electroflocculation/coagulation of organics or colour forming compounds.

The optimum chloride concentration was not determined from these experiments and further work would be required to elucidate the minimum chloride concentration required to mediate effective electrochemical treatment. Some workers<sup>(9)</sup> have used chloride concentrations ranging from 1000 to 10,000 mg/l. This was to achieve reduction in COD by 50% with 1000 mg/l chloride to 97% COD reduction with 10,000 mg/l chloride.

**Indirect oxidation and changes in chlorid**

For synthetic leachates, the initial chloride concentrations were an average of 1190 mg/l. The reduction in chloride during electrochemical treatment was approximately 86% (Figure 4) and formation of chlorine was in excess of 200 mg/l.

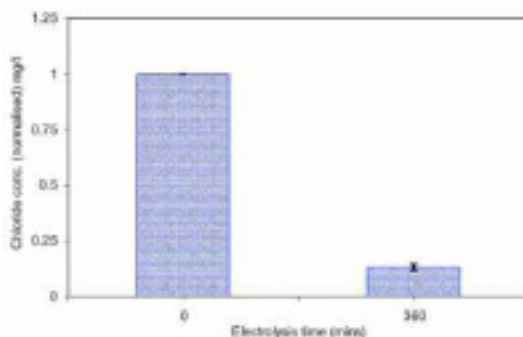


Figure 4. Chloride concentration (normalised) before and after electrochemical treatment of synthetic leachates (n = no. of experiments = 2)

Electrolysis of chloride solutions leads to the formation of 'active chlorine' (chlorine, hypochlorous acid and hypochlorite ion), in the pH ranges 6-9 hypochlorous acid and hypochlorite ion dominate. Chiang *et al.*<sup>(2)</sup> indicates that anodic oxidation of chloride to 'active chlorine' is a two electron transfer reaction. The following Equations (1-3) outline the changes in the formation of 'active chlorine' from electrolysis of chloride<sup>(9)</sup>.

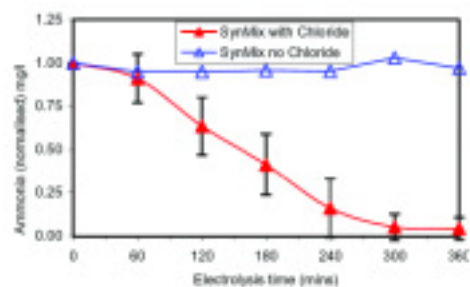


Chiang *et al.*<sup>(14)</sup> tested the influence of different anions (sulphate, nitrate and chloride) on the treatment of landfill leachates and found that chloride was the most effective because it can promote the indirect oxidation effect by formation of chlorine/hypochlorite.

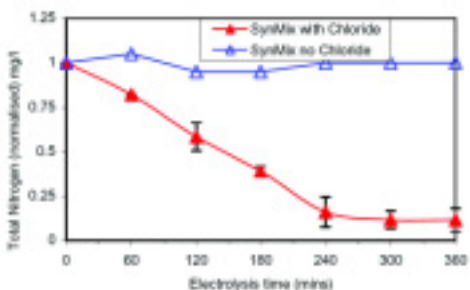
### Electrochemical ammonia reduction

In the experiments using the synthetic leachates, it was found that direct oxidation of ammonia did not occur, however in the presence of chloride (hence chlorine) the removal of ammonia was significant (as shown in Figure 5 a & b). The 'active chlorine' produced from chloride can react indirectly with ammonia and organics containing an amino group to form chloramines.

In the presence of compounds that exert a chlorine demand (e.g. ammonia or organics) the 'active chlorine' concentration will be reduced. The mechanism for removal of ammonia is similar to the 'breakpoint reactions'<sup>(2)</sup> with the formation of chloramines and finally nitrogen gas. This reaction is dominant, but a simultaneous reduction in COD can also occur.



a) Ammonia (normalised concentration)



b) Total nitrogen (normalised)

Figure 5. Changes in ammonia and total nitrogen in synthetic leachates during electrolysis (n = no. of experiments = 2 to 4)

The reaction of ammonia with chlorine/hypochlorite results in approximately 90% removal within 4 hours, without the

addition of chloride 0% change was observed. Other researchers<sup>(1, 2, 4)</sup> have also found similar effective removal of ammonia from leachates. The final product is nitrogen gas and the removal of nitrogen from the system was confirmed by the measurement of total nitrogen (N) content of the solution initially and after 6 hours of treatment (Figure 5), in the majority of cases this resulted in 88.5% reduction in total N content. This is an important environmental aspect of the electrochemical process with no requirement for a separate disposal route for the by-products, since the ammonia pollutant is converted into a non-toxic gaseous form

### Formation of chlorinated organics - Semi-volatile Organic Carbons (SVOCs)

Since indirect oxidation of organics by the chlorine/hypochlorite reaction is the main reaction pathway for landfill leachate electrochemical treatment, the formation of chlorinated organics can pose more concerns in terms of toxicity of the final effluent. Samples from synthetic leachates with and without chloride addition prior to and after 6 hrs of treatment were analysed for SVOCs. Recovery of the organics is only approximately 12% for phenol and 49% for 2-chlorophenol, however the results can provide an indication of performance (Table 5). It can be seen that the predominant SVOCs present in the synthetic leachate prior to treatment, are phenol and 2-chlorophenol. After treatment these SVOCs are reduced by 99.9% after 6hrs of electrochemical treatment with the addition of chloride. In the absence of chloride, the reduction of these two components after treatment is 78%. In addition, the formation of other organic compounds after treatment is 3 times greater in concentration in the absence of chloride as compared to when chloride is present.

Polcaro *et al.*<sup>(10)</sup> suggested that organo-chlorinated compounds can be formed, but their concentration was low. Chiang *et al.*<sup>(1)</sup> also indicated that total organic halogens (TOX) were approximately 13 mgCl/l before electrochemical treatment and after this was reduced to 2 mgCl/l. They also indicated that the BOD/COD ratio was increased from 0.06 to between 0.36 and 0.76, indicated that biodegradability of the organics was increased.

### Treatment of real leachates

The quality analysis of the real leachates before treatment has been summarised in Table 4 and after treatment for 6 hours the quality data has been converted to % change in Table 6 (displayed as a positive or negative change as compared to the before treatment analysis).

The COD reduction is in the region of 14-21% for samples Site A 1, 3, 4 & 5, however for sample 2 approximately 62% reduction in COD was observed. The COD is also reduced by

**Table 5.** SVOC analysis for synthetic leachate before and after 6hrs electrochemical treatment, with and without chloride addition

SVOC analysis	Before with chloride µg/l	After 6hrs with chloride µg/l	Before no chloride µg/l	After 6hrs no chloride µg/l
Phenol	12700	1.4	12600	2750
2-chlorophenol	12300	10.9	11200	2480
2-methylphenol	6.3	0	18.9	3.4
4-methylphenol	3.3	0	0	43.8
2,4-dichlorophenol	0	26.8	0	46.6
2,4,6-trichlorophenol	0	26.1	0	58.4
Napthalene	0	3.3	0	31.2
Diethylphthalate	0	1.9	0	3.9
Bis(2 ethylhexyl)phthalate	0	0	136	0

**Table 6.** Change in quality of real landfill leachate samples from sites A & B after 6hrs electrochemical treatment, as % increase (+) or % decrease (?) from initial value

Parameter % change (+ is increase or - is decrease)	Site A – sample no.					Site B – sample no.		
	1	2	3	4	5	1	2	3
Colour	-55	-88	-75	-77	-61	-80	-73	-78
TOC	/	/	-12	0	-3	-5	-4	-4
COD	-14	-62	-21	-16	-15	-64	-33	-28
BOD/COD ratio	-5	+124	+28	+74	0	+14	+29	-80
UV abs. (1/10 <sup>th</sup> 254nm)	-37	-51	-39	-36	-42	-7	-43	-14
Iron	/	-100	-100	-71	-80	-61	-56	/
Chloride	-17	/	-19	-19	-20	-62	-37	-70
Ammonia	/	-100	-15	/	-12	-70	/	/
Total nitrogen	/	-75	/	/	0	-69	-76	-100

28- 33% for samples 2 & 3 taken from Site B, however for sample 1 the COD was reduced by 64%. The chloride concentrations for these sites were variable and may have been a contributing factor. The chloride concentration in real leachates is greater than 1000 mg/l, with values up to 7000 mg/l being measured in some instances. The reduction in chloride 12 concentration varies between 17 to 70%. The chlorine produced in these real leachates after 6hrs of treatment is also in excess of that noted for synthetic leachates. All samples show a reduction in UV absorbance after treatment, with Site A sample 2 exhibiting a decrease of greater than 50%. For some samples TOC is reduced but the changes are not significant in comparison to synthetic leachates.

The changes in colour during electrochemical treatment for all the real leachates are significant with final colour values reduced by 55-88%, especially for Site A sample 2 and Site B sample 1 which also experience the highest decrease in COD. For Site B sample 2 the initial colour was exceptionally high (almost black) and this was effectively reduced (Figure 6). The real leachate samples have low initial BOD/COD ratios, in general less than 0.30, in some instances these are lower than 0.10 (Site B sample 1). Overall, after 6hrs of treatment the BOD/COD ratios are increased for Site A samples 2, 3, & 4 and

Site B samples 1 and 2. This increase in biodegradability is most significant for Site A sample 2, which also experiences a corresponding COD and colour reduction.



a) Site A sample 2



b) Site B sample 2

**Figure 6.** Photographs of real leachates prior to (pre) and after electrochemical treatment for 6hours (T6) for Sites A and B



The changes in ammonia were monitored for some of the samples and Site A sample 2 electrochemical treatment resulted in 100% removal of ammonia, with a 70% decrease for Site B sample 1. Some data is not available due to problems with analytical equipment. However, total nitrogen results indicate that the same pattern is observed as for changes in ammonia concentration. The total nitrogen content of the solution is reduced significantly for Site A sample 2 and Site B samples 1, 2 and 3 all resulting in nitrogen changes greater than 69%.

### Power usage and full-scale operational considerations

Power usage is dependent on the current density of the electrodes in this system (Advanced Oxidation Ltd.), which is approximately, 2.42 mA/cm<sup>2</sup> and is typically 40 times lower than for similar systems used by other researchers<sup>(15)</sup>. For the synthetic and real leachates used in this project the power usage recorded is in the region of 85 to 96 kWh/m<sup>3</sup>. This is lower than the power required for real leachates reported by other researchers<sup>(1, 15)</sup> who recorded values of 103 to 216 kWh/m<sup>3</sup>. These researchers also suggested that the power usage could be reduced by 38% using pre-treatment of leachates, such as coagulation with ferric chloride or adsorption onto granular activated carbon (GAC)<sup>(1, 15)</sup>. The electrochemical system used in this project could be an economical process as the costs for 6 hours of treatment are less than £5/m<sup>3</sup>, based on the power usage alone (assuming £0.05 kWh). The process would require minimal ancillary chemicals or additional power. In this respect, the process is economically favourable in comparison to other powerful oxidation processes. Schumann et al.<sup>(16)</sup> compared ozone and electrochemical processes for oxidation of non-ionic surfactants. They indicated that ozone is more efficient in terms of its selectivity for degradation of aromatic rings, but the electrochemical system is a more cost-efficient process for the generation of oxidising agents. However, as indicated and observed from the treatment of real leachates, that pre-treatment would be beneficial to optimise the operating costs for this process. In addition, the production of excess chlorine that is not consumed by the reactions within the electrochemical system may influence post-treatment options. In general, it is considered that the process could assist with improvements in water quality and reduction of the pollution risk from landfill leachates. Sustainability of this process was not assessed in this project, but if it is compared to other advanced oxidation processes it can be considered as a viable alternative.

## CONCLUSIONS

1. The electrochemical system developed in this project was successfully applied for the treatment of synthetic and real landfill leachates.
2. Typically approximately, 60% reduction of COD for the synthetic leachates and for some real leachates was mediated via indirect oxidation mechanism with the formation of chlorine from chloride
3. Some samples exhibited increases in BOD/COD ratios, indicating increase in biodegradability and reductions in UV absorbance at 254nm suggest that changes to organic structure occur.
4. Changes in colour were significant and resulted in colourless solutions for some samples, even when minimal change in COD was observed.
5. Reduction in ammonia was up to 100% for some samples and occurs via indirect reaction with chlorine/hypochlorite and concentration of chloride was key to the performance of the system.
6. This system utilises lower current densities than those typically used by other researchers and overall power usage for this system is between 85 to 96 kWh/m<sup>3</sup>
7. This unit did achieve similar results as for high current density systems indicating that this has the potential for application to full-scale plants. However, optimisation of the process is required to reduce operating costs and this may require consideration of pre and post treatment options.

## ACKNOWLEDGEMENTS

This project was sponsored by Severn Trent Water Ltd. The authors wish to thank Severn Trent Water Ltd. and the University of Wolverhampton for permission to publish this paper. The opinions expressed are those of the authors and do not necessarily reflect the views of Severn Trent Water Ltd. The authors would like to thank the contributions made to this project by Dr. Sandy Alexander and Mr. David Bray from Advanced Oxidation Ltd. The authors also thank the current and previous WatStech Group members who have provided technical advice and access to facilities for this project.

## REFERENCES

1. CHIANG, L.C., CHANG, L.E. AND WEN, T.C. Electrochemical Treatability of Refractory Pollutants in Landfill Leachate. *Hazardous Waste & Hazardous Materials*, 1995a, **12**, (1), 71.
2. CHIANG, L.C., CHANG J.E. AND WEN, T.C. Indirect Oxidation Effect in Electrochemical Oxidation Treatment of Landfill Leachate. *Water Research*, 1995b, **29**, (2), 671.

3. COSSU, R., POLCARO, A.M., LAVAGNOLO, M.C., MASCIA, M., PALMAS, S. AND RENOLDI, F. Electrochemical Treatment of Landfill Leachate: Oxidation at Ti/PbO<sub>2</sub> and Ti/SnO<sub>2</sub> Anodes. *Environmental Science & Technology*, 1998, 32, (22), 3570.
4. ROWLEY, A. and STRATTON-CAMPBELL, D. *In The Electrochemical Treatment of Landfill Leachate: Final Report*, (report no. CT1048), C-Tech Innovation Ltd. 2002.
5. ENVIRONMENT AGENCY. Landfill, website <http://www.environmentagency.gov.uk/subjects/waste>, 2004.
6. NORTHAMPTON UNIVERSITY. Landfill Leachate, Phytoremediation at UCN. website <http://oldweb.northampton.ac.uk/aps/env/landfillleachate/leachate.htm>
7. PAXEUS, N. Organic Compounds in Municipal Landfill Leachates. *Water Science & Technology*, 2000, 42, (7-8), 323.
8. RAJESHWAR, K. AND IBANEZ, J. *Environmental Electrochemistry, Fundamentals and Applications in Pollution Abatement*. Academic Press Inc. 1997.
9. PANIZZA, M., BOCCA, C. AND CERISOLA, G. Electrochemical Treatment of Wastewater containing Polyaromatic Organic Pollutants. *Water Research*, 2000, 34, (9), 2601.
10. POLCARO, A.M., PALMAS, S., RENOLDI, F. AND MASCIA, M. On the Performance of Ti/SnO<sub>2</sub> and Ti/PbO<sub>2</sub> Anodes in Electrochemical Degradation of 2-chlorophenol for Wastewater Treatment. *Journal of Applied Electrochemistry*, 1999, **29**, 147.
11. GREENBERG, A.E., TRUSSELL, R.R. AND CLESCERI, L.S. *Standard Methods for the Examination of Water and Wastewater*, (16th Ed.), American Public Health Association, 1985.
12. KAMENEV, I., PIKKOV, L., KAMENEV, S. AND KALLAS, J. Landfill Leachate Under Combined Oxidation Treatment. In *Proceedings of the 15th World Ozone Congress*, International Ozone Association, London, Sept. 2001.
13. CHIANG, L.C., CHANG J.E. AND WEN T.C. Destruction of Refractory Humic Acid by Electromechanical Oxidation Process. *Water Science and Technology*, 2000, **42**, (3-4), 225.
14. CHIANG, L.C., CHANG J.E. AND TSENG S.C. Electrochemical Oxidation Pretreatment of Refractory Organic Pollutants. *Water Science and Technology*, 1997, 36, (2-3), 123.
15. CHIANG, L.C., CHANG, J.E. AND CHUNG, C.T. Electrochemical Oxidation Combined with Physical-Chemical Pretreatment Processes for the Treatment of Refractory Landfill Leachate. *Environmental Engineering Science*, 2001, **18**, (6), 369.
16. SCHUMANN, U., GLUSCHKE, M., GRUNDLER, P. AND MIKOLAJCZYK, L. Reaction Pathways in Electrochemical Oxidation of Non-Ionic Surfactants. *Tenside Surfactants Detergents*, 1998, **35**, (5), 379.