A COMMERCIAL APPLICATION OF
VIROFLOW™ TECHNOLOGY

CASE STUDY: TREATMENT OF HEAVY METALS AND ACIDITY AT H.J. ENTHOVEN AND SONS, SOUTH DARLEY, UNITED KINGDOM

"Results of this project have clearly shown that the application of ViroFlow™ Technology and the use of ElectroBind™ reagent to treat Enthoven's wastewater stream was extremely effective in reducing metal contaminants and acidity to below emissions targets."

*Dosing tanks for ElectroBind™ (left)
Close up of ElectroBind™ and mixer
prior to dosing (above)*

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BACKGROUND

H.J. Enthoven and Sons is the largest producer of recycled lead in Europe, and part of the world's largest lead group, Quexco Inc, with lead operations in seven countries. Enthoven produces annually around 75,000 tonnes of lead products, and has expanded its interests into battery strip production and recycling of the polypropylene components from scrap batteries.

The Enthoven site at South Darley, in the Darley Dales, on the edge of the Peak District National Park occupies about 10.5 acres in the centre of a 250-acre estate. Part of the site has been recognised by the Nature Conservancy Council and English Nature as a "Site of Special Scientific Interest". The estate has been naturally forested for centuries and is home to a large variety of wildlife. In 1984, the wooded area was extended by planting poplars and other English hardwoods selected by ornithologists, and since then many copses have been planted, providing improved woodland walks for locals and visitors.

Lead has been mined on the Enthoven site since Roman times. The current site was originally called the Mill Close Mine, one of the most valuable lead mines in Great Britain. The smelter itself was established by Mill Close Mines in 1934 and was bought in 1941 by H.J. Enthoven and Sons, a London-based lead producer. From 1970 to 1994 the company was owned by the Royal Dutch Shell Group, during which the operations were substantially replaced and upgraded. Since 1994 the company has been owned by Quexco, Inc., a privately held U.S. company based in Dallas, Texas.

Previous laboratory and on-site trials by Virotec Europe demonstrated the ability of its ViroFlow™ Technology, incorporating the application of ElectroBind™ reagent, to treat soluble metals in Enthoven's wastewater effluent effectively. In particular, concentrations of cadmium (Cd), lead (Pb) and zinc (Zn) could be reduced to below current consent levels by direct addition of ElectroBind™ with a reaction period of 30-45 minutes.

APPLICATION METHOD

Full-scale treatment of Enthoven's effluent by direct addition of the ElectroBind™ reagent was assessed at the site. The objectives of the on-site project were to:

1. Assess the efficiency of treating Enthoven's wastewater treatment plant influent by direct addition of the ElectroBind™ reagent;
2. Investigate and determine the optimum ElectroBind™ dose rate;
3. Assess the specific ElectroBind™ reagent blend type that was most effective in removing heavy metals; and;
4. Assess the impact of reducing or omitting the addition of other chemical additives on treatment efficiencies.

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ElectroBind™ was prepared as a 20% (w/v) slurry in an IBC ($1m^3$), stirred with an overhead mixer, and fed to the influent stream using a calibrated peristaltic pump. Addition of ElectroBind™ was restricted to the normal working hours of the wastewater treatment plant but settled sludge was continuously recycled.

Figure 1: Raw inlet channel running diagonally from top left to centre of photo; ferric chloride is typically dosed in the circular drum, centre, to aid the settling of solids prior to treatment.

Figure 2: Overhead view of the pre-conditioning tank where raw inlet influent is mixed thoroughly prior to chemical dosing.

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Figure 3: Overhead view of the IBC containing ElectroBind™ and mixer, centre left, and raw inlet work running diagonally from lower left to upper right.

Figure 4: ElectroBind™ being dosed into Tank 1.

Figure 5: Close up of ElectroBind™ and mixer prior to dosing.

Figure 6: ElectroBind™ was dosed into Tank 1, the first tank at the bottom of this photo; TMT and Amerfloc would be routinely dosed in the next two tanks (seen under plant operators).

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Based on previous laboratory trials, the optimum ElectroBind™ dose rate was adjusted according to the flow rate of influent coming into the wastewater treatment plant.

Two different types of ElectroBind™ were applied in the project. ElectroBind™ reagent "Blend A" was added to Tank 1 immediately after the pre-conditioning tank, where influent pH was about 2.3 (Samples 1-20). ElectroBind™ reagent "Blend B" was added to Tank 2, where influent pH was about 8.7 (Samples 21-26).

Enthoven routinely added: a) ferric chloride at the end of the inlet works to flocculate and settle solids; b) TMT (a 15% aqueous solution of organo-sulphide trimercapto-s-triazine, tri-sodium salt) in Tank 2; and c) Amerfloc coagulant to Tank 3 to process the wastewater more effectively. During this project to evaluate the effectiveness of ViroFlow™ Technology, the addition of TMT and Amerfloc coagulant was stopped just prior to Sample 5 until end of the project; ferric chloride addition was stopped just prior to Sample 13 until end of the project.

Inlet and treated samples were filtered, using 0.2 µm Microsart syringe filters, and analysed for pH and soluble metals. An in-line voltammetry system was used for metals analysis during the project, with results confirmed by ICP at a later date. The pH readings were taken with a Schott bench meter. Inlet Samples 1-12 were taken from Tank 1, prior to the ElectroBind™ addition point. Inlet Samples 13-26 were taken from the raw inlet channel just prior to ferric addition. A comparison of samples taken from Tank 1 and the raw inlet channel is summarised in Table 1. Treated samples were taken from the weir of the final clarifier after Tank 3.

RESULTS

Table 1 records the quality of the raw inlet influent with respect to pH, lead, zinc and copper. Inlet pH remained fairly constant throughout the sampling period, with Tank 1 pH ranging from 2.28-2.45 (average 2.37) and raw inlet values ranging from pH 1.28-1.49 (average 1.36). Concentrations of soluble lead ranged from 2.8-7.1 mg/L, with an average of 4.0 mg/L. Soluble zinc concentrations ranged from 6.7-115.8 mg/L, with an average of 45.5mg/L. Soluble cadmium concentrations in Samples 1 to 4, which ranged from 14.2-42.7 mg/L (average 27.8 mg/L), were significantly higher than those in Samples 5 to 26, 0.53-7.1 mg/L (average 3.5 mg/L).

Table 2 summarises the reagent application conditions for the project. Ferric chloride, TMT and Amerfloc coagulant were dosed into the influent waste stream in the usual manner at the beginning of the trial, in combination with ElectroBind™ Blend A. From Sample 5 onwards, the dosing of TMT and Amerfloc were omitted from the process. The addition of ferric chloride was omitted from the process from Sample 12 onwards.

Table 3 shows the analytical data for the treated samples. Metal removal efficiencies have been calculated using values for the previous inlet assays; e.g. calculation of metal removal efficiencies for Sample 4 was done using inlet Sample 3 results. Note: Sample 1 was taken 45 minutes after initial dosing of ElectroBind™.

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TABLE 1: QUALITY OF INFLUENT PRIOR TO TANK 1 (SAMPLES 1-20) AND TANK 2 (SAMPLES 21-26)

Sample	Influent Analysis			
	pH	Metals (mg/L)		
		Lead	Zinc	Cadmium
1	2.3	4.0	58.7	14.2
2	2.3	4.6	105.9	27.9
3	NT	3.9	55.6	42.7
4	NT	7.3	79.1	26.3
5	2.4	3.3	26.1	3.8
6	2.3	7.1	82.3	4.1
7	2.3	3.8	42.6	5.6
8	2.4	3.1	46.4	3.0
9	2.4	3.1	36.0	7.1
10	2.4	3.9	37.9	5.3
11	2.3	3.4	73.8	5.9
12	2.2	3.4	32.6	4.2
13	1.4	5.1	39.0	4.2
14	1.3	5.0	115.8	5.0
15	1.2	2.8	11.1	1.4
16	1.3	3.8	34.7	2.3
17	NT	2.9	63.7	2.3
18	NT	4.5	8.6	0.58
19	NT	4.7	21.0	1.4
20	1.2	3.8	21.1	1.6
21	1.3	3.0	53.1	5.8
22	1.4	3.2	71.9	5.6
23	NT	4.0	25.4	2.7
24	1.3	3.2	17.3	2.9
25	1.3	3.1	15.4	2.4
26	1.3	3.1	6.7	0.53

Note: 1) NT = Not Taken, 2) the plant was taken off-line between samples 17 and 18 due to screen maintenance.

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TABLE 2: PROJECT APPLICATION PARAMETERS

Sample	ElectroBind™ Type (A/B)	ElectroBind™ Dose Point	Influent pH at Dose Point	Ferric Chloride Addition (on/off)	TMT Addition (on/off)	Amerfloc Coagulant Addition (on/off)
1	A	Tank 1	2.3	on	on	on
2	A	Tank 1	2.3	on	on	on
3	A	Tank 1	2.3	on	on	on
4	A	Tank 1	2.3	on	on	on
5	A	Tank 1	2.3	on	off	off
6	A	Tank 1	2.3	on	off	off
7	A	Tank 1	2.3	on	off	off
8	A	Tank 1	2.3	on	off	off
9	A	Tank 1	2.3	on	off	off
10	A	Tank 1	2.3	on	off	off
11	A	Tank 1	2.3	on	off	off
12	A	Tank 1	2.3	on	off	off
13	A	Tank 1	2.3	off	off	off
14	A	Tank 1	2.3	off	off	off
15	A	Tank 1	2.3	off	off	off
16	A	Tank 1	2.3	off	off	off
17	A	Tank 1	2.3	off	off	off
18	A	Tank 1	2.3	off	off	off
19	A	Tank 1	2.3	off	off	off
20	A	Tank 1	2.3	off	off	off
21	B	Tank 2	8.7	off	off	off
22	B	Tank 2	8.7	off	off	off
23	B	Tank 2	8.7	off	off	off
24	B	Tank 2	8.7	off	off	off
25	B	Tank 2	8.7	off	off	off
26	B	Tank 2	8.7	off	off	off

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TABLE 3: TREATED WASTEWATER ANALYSIS AND METAL REMOVAL EFFICIENCIES

Sample	pH	Metals (mg/L)			Removal Efficiences (%)		
		Lead	Zinc	Cadmium	Lead	Zinc	Cadmium
1	9.3	0.04	0.07	0.21	99.0	99.8	98.5
2	9.3	0.15	0.11	0.33	96.3	99.8	97.6
3	NT	0.11	0.16	0.38	97.6	99.8	98.6
4	NT	0.11	0.17	0.47	97.1	99.6	98.9
5	9.4	0.16	0.09	0.17	97.8	99.8	99.3
6	9.4	0.23	0.06	0.07	93.1	99.7	98.1
7	9.3	0.02	0.04	0.01	99.7	99.9	99.7
8	9.5	3.70	0.07	0.03	3.15	99.8	99.4
9	9.3	0.35	0.31	0.11	88.8	99.3	96.3
10	9.3	0.27	0.17	0.15	91.3	99.5	97.8
11	9.4	0.60	0.15	0.02	84.8	99.6	99.6
12	9.3	0.33	0.16	0.02	90.3	99.7	99.6
13	9.3	0.03	0.08	0.06	99.1	99.7	98.5
14	9.4	<0.01	0.05	0.02	>99.8	99.8	99.5
15	9.3	0.10	0.07	0.04	98.0	99.9	99.2
16	9.2	0.05	0.11	0.07	98.2	99.0	95.1
17	NT	0.16	0.09	0.02	95.8	99.7	99.0
18	NT	<0.01	0.07	0.02	>99.6	99.8	99.1
19	NT	<0.01	0.08	0.03	>99.7	99.0	94.8
20	9.3	<0.01	0.09	0.02	>99.7	99.5	98.6
21	9.4	0.12	0.06	0.16	96.9	99.7	90.1
22	9.6	0.23	0.06	0.08	92.3	99.8	98.6
23	9.6	0.04	0.04	0.01	98.7	99.9	99.8
24	9.5	0.13	0.04	0.03	96.7	99.8	98.9
25	9.5	0.11	0.04	0.02	96.6	99.7	99.3
26	9.5	0.08	0.07	0.03	97.4	99.5	98.7

NT = Not Taken

CONCLUSION

For this purposes of this discussion, we assume that the lead result at Sample 8 is an anomaly (either analytical error or highly elevated lead concentrations in the influent) because there are no related trends or similar results. It is noted that because ElectroBind™ dosing rates were continuously adjusted as a function of influent flow rates and not as a function of contaminant input loads (i.e. a combination of flow rates and contaminant concentrations), any large periodic increases in contaminant concentrations in the influent could result in short term decreases in treatment efficiencies. It may be possible to eliminate such short-term decreases in treatment efficiencies by adding a modest excess of the treatment reagents to provide a safety margin to allow for periodic spikes in contaminant concentrations in the influent fluids. Alternatively, a ballast tank could be used to provide more averaging of influent compositions.

> *Zinc*

Zinc removal was excellent throughout sampling period with a removal rate of 99%-99.9%. All zinc concentrations in treated effluent were well below the treatment target of 0.3 mg/L.

> *Lead*

When dosing either ElectroBind™ reagent Blend A or Blend B, lead removal efficiencies ranged between 92% and 99.8%. Some of this variation can be explained by the variation in the input lead concentrations, but there is also an indication that most effective lead removal occurred between samples 13 and 20, where ElectroBind™ reagent A was dosed without the addition of ferric chloride, TMT or Amerfloc. It should also be noted that during this sampling period (i.e., between samples 13 and 20) wastewater treatment plant operation was stopped briefly for screen maintenance, which could have affected results. Interestingly, lead removal efficiencies at Samples 5 to 12, when ElectroBind™ dose rate was increased, were not as high as at lower dose rates, with removal efficiencies of 84%-99.7%. With the exception of Samples 8 and 11, all lead concentrations in the treated effluent were below Enthoven's consent targets of 0.5 mg/L.

> *Cadmium*

The cadmium result at Sample 21 was calculated using the results of the previous day's inlet sample and was the first sample taken that day. It may therefore not be a true reflection of treatment efficiency. If this result is omitted, cadmium removal efficiencies were 94%-99.8% throughout the project. With the exception of samples corresponding to abnormally high cadmium concentrations in the influent during the period of Samples 2-4, all cadmium concentrations in treated effluent were below Enthoven's consent targets of 0.5 mg/L.

Comparison of the use of ElectroBind™ reagents Blend A and Blend B showed no differences with respect to zinc and cadmium removal efficiencies. However, there is some evidence to suggest that ElectroBind™ reagent Blend A removed lead more effectively than ElectroBind™ reagent Blend B.

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Results of this project have clearly shown that the application of ViroFlow™ Technology and the use of ElectroBind™ reagent to treat Enthoven's wastewater stream was extremely effective in reducing metal contaminants and acidity to below emissions targets.

Moreover, the effectiveness of the treatment was even more pronounced after Sample 13 when all other chemical additives—ferric chloride, TMT and Amerfloc—were no longer added to the wastewater stream. The results of this project show that Enthoven can scale back or even completely eliminate the addition of ferric chloride, TMT and Amerfloc, thereby reducing expenditure on these reagents, simplifying plant operations, reducing the use of hazardous chemicals on site, and more consistently meeting effluent discharge standards.

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