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case study bulletin

CL:AIRE case study bulletins provide a source of information on the characterisation and remediation of specific sites in the UK. This bulletin provides a review of the 11 year operation of the SEREBAR groundwater treatment system which was described in CL:AIRE publication TDP17.

SEREBAR – A Review of 11 Years of Operation

1. INTRODUCTION

The SEquential REactive BARrier (SEREBAR) Groundwater Treatment system is a Permeable Reactive Barrier (PRB), which was constructed on a former gasworks site in 2003. It was one of the first biologically based PRB systems installed in the UK and was primarily a research project which was to be operated at a commercial scale. The project was funded through the BBSRC DTI LINK Bioremediation programme with support from Secondsite Property (now National Grid Property) and Parsons Brinckerhoff (now WSP). SEREBAR has been in operation since 2004 and this bulletin provides a review of the systems' performance over the period 2004 to 2015.

The SEREBAR project forms one of the longest running research projects of its kind in the world and one of the few which have provided active contamination management on a commercial scale. The research was undertaken by a multidisciplinary team from Queen's University Belfast, NERC Centre for Ecology & Hydrology, Oxford and University of Surrey, led by the principal investigator Prof. Robert Kalin (now at the University of Strathclyde). The academic partners undertook the original laboratory investigation, modelling and design of the SEREBAR system prior to installation of the system by Keller Ground Engineering with their subconsultant RD Geotech. The background to the project is documented in detail in TDP17 (CL:AIRE, 2008) and some of the early performance data was published in a paper in Environmental Science and Technology (Gibert *et al.*, 2007).

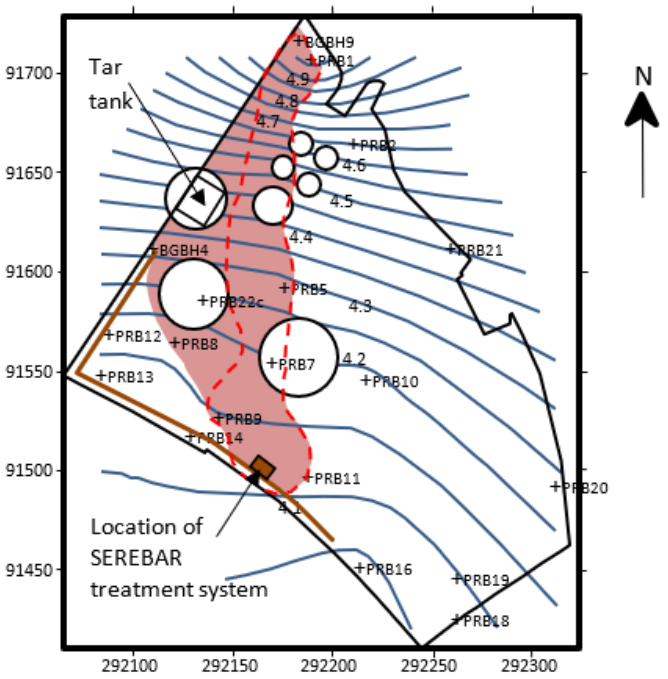

Figure 1: Plan of. the site, showing the groundwater gradient (blue), the location of the slurry wall and treatment system (brown), historic below ground tanks (black), extent of the current contaminant plume (pink) and approximate area of shallow alluvial valley (red dashed line).

2. SITE DESCRIPTION

The site was part of a gasworks, which was originally constructed in 1836 as a small gasworks which operated low temperature directly fired horizontal retorts. The gasworks expanded in 1849 towards the adjacent canal to the north. Following local nuisance complaints in 1877, the city authorised an engineer to inspect the gasworks. He condemned them as unworkable, due to the lack of any logic in the way they had been developed. In 1878, work began on rebuilding and expanding the gasworks to an increased capacity of 2 million ft3 per day. In 1912, the works were remodelled, introducing the use of continuous vertical retorts. There were a further 4 additions of continuous vertical retorts in the period up to 1930. The site also operated a Carburetted Water Gas (CWG) plant, an oil gas plant and had its own chemical works, including a tar distillery. In 1942, the site was hit by two 500 kilogram bombs, which destroyed a large tank and the ammonia plant. The works were again rebuilt in 1952, to make it one of the major gas production facilities in the region. The gasworks ceased gas production in 1971.

From this brief description, it is apparent that the gasworks had been subject to numerous rebuilds and as the gas making technology evolved, so did the by-products formed. More detail on the operation of former gasworks is provided in Thomas (2014). At the start of the project in 2004, two gasholders were still in operation, these have since been decommissioned and removed, along with many of the buildings. At the current time (2017) there is still an operational gas distribution plant present at the site.

The site is generally flat with a gradual slope towards the site boundary in the southern and south-eastern corner, where the land was substantially raised historically and supported by retaining walls. The outline of the site, showing key features is represented in Figure 1.

Site Geology

The site ground conditions were investigated intensively between 2000 and 2003 with several phases of investigation and groundwater monitoring reported in detail in TDP17 (CL:AIRE, 2008). In brief, the following typical ground conditions were found at the site: Made ground (thickness of 0.9 m to 3.4 m) comprised a variety of different soil types, ranging from sandy silts to gravels, with fragments of anthropogenic material such as brick and clinker in most the exploratory holes. Natural ground comprised of inter-bedded alluvial clay, silt or sand (2.5 m to 4.6 m thick) which grade laterally into river alluvial gravels (maximum thickness of 3.0 m).

Beneath the Gravels is a bedrock of Permian breccia-conglomerates, sandstones, with subordinate mudstones, the top of which is weathered.

The site geology is shown pictorially in Figure 2. A shallow alluvial valley (Figure 1) was detected during the investigation within which pockets of tar had been identified.

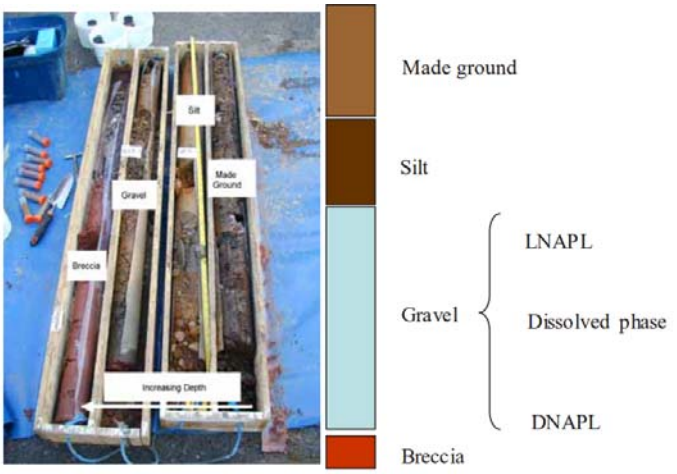

Figure 2. Stratigraphic sequence from the SEREBAR site.

Hydrogeology

The low hydraulic conductivity of the weathered breccia limits the vertical movement of the groundwater. The overlying alluvial sediments can be regarded as a single unconfined layer. Groundwater was encountered in the gravels across the site at a depth of between about 4 and 5 m below ground level (bgl). Monitoring prior to the installation of the SEREBAR system indicated that the groundwater flowed in a southerly direction in the alluvium as shown in Figure 1, under a hydraulic gradient of approximately 0.022. To the north of the site are a canal and marina complex, beyond which is a river. The marina had been suspected to recharge the groundwater at the site. Groundwater monitoring at the site had demonstrated that elevated concentrations of both polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethyl benzene and xylenes (BTEX) compounds were present, which had previously been shown to be risk drivers at the site.

3. REMEDIATION OPTIONS

It was decided that, given the shallow groundwater underlain by highly impermeable breccia and active plant restricting access, a risk management option was best suited to the site. The relatively new concept (at the time) in Britain of a biologically-based PRB, was identified as the most suitable option, even though such an application was novel. This followed a year after the Environment Agency had published their PRB guidance and who were active partners in the research project (Environment Agency, 2002).

The PRB concept encompasses a barrier installed below ground to capture and treat contaminated groundwater. The barrier may be permeable and comprise reactive media to treat contamination directly, or alternatively it can comprise an impermeable 'wall' that directs the contaminant plume to a permeable treatment zone or system. More detailed descriptions of PRBs can be found in CL:AIRE Treatability Bulletin TrB2 (CL:AIRE, 2011).

4. ORIGINAL DESIGN

SEREBAR was designed to remove a range of potential groundwater contaminants associated with gasworks. These included PAHs and BTEX. It comprised two impermeable bentonite slurry barrier walls extending 175m along the south western site boundary and 70m along the north western site boundary. The barrier walls act to deflect groundwater into the treatment zone of the SEREBAR system, comprising an oil-water separator (to remove non-aqueous phase liquid (NAPL)) and six steel chambers containing media that facilitate sequential treatment stages (Figure 3).

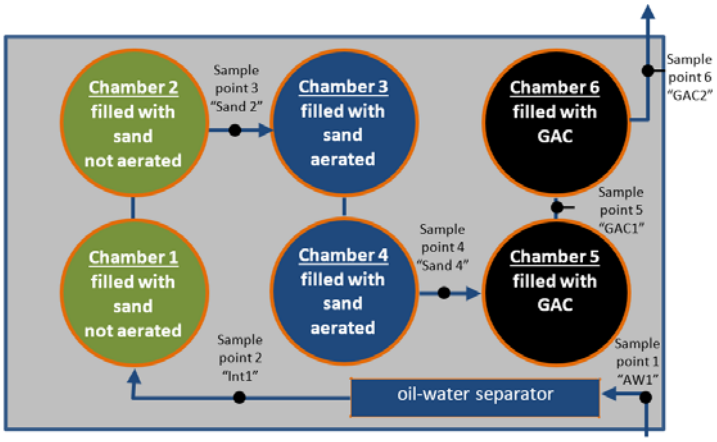

Figure 3. Schematic of the SEREBAR system, showing the contents of each chamber and the sampling locations.

The first and second chambers contain sand and were designed to biodegrade more complex organic compounds (4-6 ring PAH such as benzo[g,h,i]perylene) under anaerobic conditions. The third and fourth chambers also contain sand, but were aerated creating conditions for the biodegradation of simpler organic compounds such as benzene and naphthalene. The fifth and sixth chambers (GAC1 and GAC2) contain granular activated carbon (GAC) and were designed to adsorb any recalcitrant organic compounds and to provide a backup should the biodegradation capacity of the system be insufficient. The sample points were located prior to entry into the system (AW1), after the interceptor (INT1), after chamber 2 (Sand 2), after chamber 4 (Sand 4) and after both chambers filled with GAC (GAC1 and GAC2).

The data from each sample point show the relative performance of that part of the system, with INT1 showing the performance of the interceptor, Sand 2 showing the performance of the anaerobic biodegradation, Sand 4 showing the performance of the aerobic biodegradation and GAC 2 showing the performance of the two GAC chambers. AW1 and GAC1 were the compliance points for water entering and leaving the treatment system. GAC1 was located prior to the final chamber, chamber 6 which was provided as an additional fail safe and polishing step, should the systems treatment capacity fail prior to this.

5. MODIFICATIONS TO THE DESIGN

Interceptor

The original oil-water separator was fabricated from rendered blockwork. It proved unreliable and was replaced with a prefabricated steel unit. In 2008 it was decided to utilise the potential for aerobic biodegradation offered by the oil-water separator by installing an air sparge system. This changed the treatment sequence within the SEREBAR system from Anaerobic →

Aerobic → GAC to Aerobic → Anaerobic → Aerobic → GAC. Whereas the four sand-filled chambers provided a habitat for sessile (attached) bacteria, the aerated oil-water separator provided a new habitat for planktonic (free floating) bacteria, allowing these types of bacteria to colonise the interceptor. Air was only sparged in the first two baffles of the interceptor, to ensure that the aeration would not be carried over into the two anaerobic canisters (SAND 1 & SAND 2).

Pump

Pump reliability has been problematic, due to the low pumping rate of between 500 and 1700L/d required. Such borehole pumps were not available at the time of construction. A Grundfos SQ 1-35 borehole pump was installed which was designed for use at a much higher discharge, so it had been modified with a control system that allowed it to pump at a sub-optimal rate. This increased wear, making the pump cut out occasionally, due to overheating or the deposition of ferric iron precipitates from the oxidation of the iron-rich groundwater. The deposition of iron within the wider system has been problematic, especially on the few steel pipes and valves, where it has had to be removed. The re-infiltration well has also had to be redeveloped three times to remove iron precipitate which had been blocking the well screen. In 2012, the original Grundfos borehole pump was replaced with a Williamson Cased 400 series peristaltic pump calibrated to operate at 1000 litres per day. This increased the reliability of the pump dramatically, although it limited the ability to change the discharge rate.

Vandalism

SEREBAR was originally installed on a secure active depot. Over the past twelve years, the site has become vacant and the buildings largely demolished, leaving an exposed and less secure site. As a result, the SEREBAR system has suffered vandalism.

Most of SEREBAR is installed below ground and is therefore relatively robust against vandalism. The control systems, however, were installed in an above ground cabinet. After an act of vandalism in 2012, fences, buildings, equipment and cabling were damaged and had to be replaced. In order to minimise the risk of electrocution from a repeat offence, the cables were buried below ground.

6. COMPARATIVE PERFORMANCE OVER 11 YEARS OF OPERATION

The SEREBAR system has been operational since 2004 at flow rates ranging from 320 L/d to 4000 L/d, with corresponding hydraulic residence times in each of the six chambers of 19 days and 1.5 days, respectively. SEREBAR was tested at a range of flow rates as part of the initial research as described in TDP17. At low flow rates (320-520 L/d) the majority of contaminant removal (>93%) occurred biologically within the oil-water separator and the aerated chambers. At high flow rates (1000-4000 L/d) and following the installation of a new oil-water separator (prior to its aeration), most contaminant removal (>80%) again occurred biologically within the aerated chambers. Since 2006 SEREBAR has operated at a flow rate of 1000L/day giving a residence time of 6 days in each chamber.

Average annualised concentrations for three of the contaminants of concern, benzene, naphthalene and phenanthrene are presented in Figures 4, 5 and 6. AW1 is the monitoring point immediately before entering SEREBAR, GAC1 is the compliance point after the first canister of GAC and PRB16 is the sentinel well which monitors for migration around the southern end of the PRB.

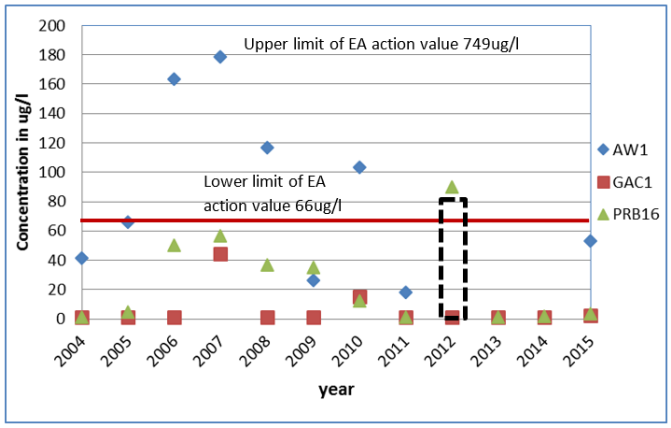

Figure 4. Annual performance of benzene remediation by the SEREBAR System, black hashed area = period when hydraulic control lost due to vandalism.

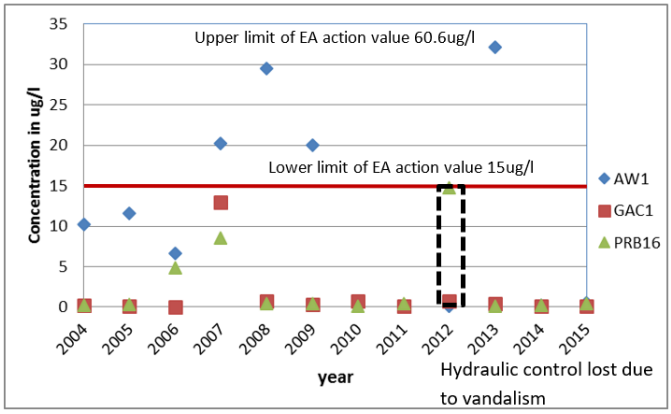

Figure 5. Annual performance of naphthalene remediation by the SEREBAR System, black hashed area = hydraulic control lost due to vandalism.

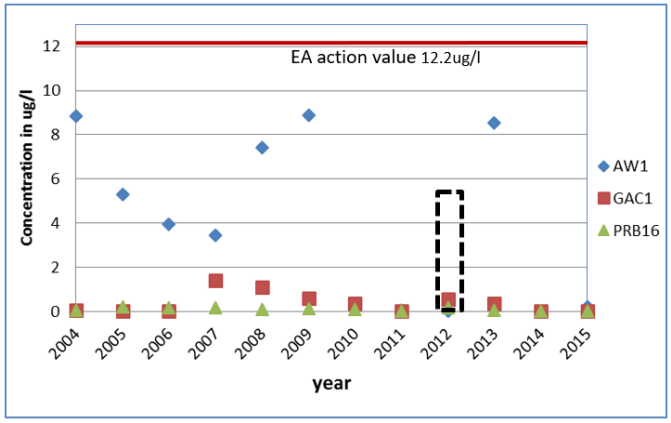

Figure 6. Annual performance of phenanthrene remediation by the SEREBAR System, black hashed area = period when hydraulic control lost due to vandalism.

The concentrations of the Contaminants of Concern (CoC) have fluctuated considerably over the past 11 years. Typically concentrations of organic compounds entering the system have generally decreased since 2011, but in all cases they were treated effectively by the SEREBAR system.

As a result of the vandalism at the end of 2011, a loss of control over the hydraulic regime occurred. This resulted in an increase in the concentration of both benzene and naphthalene observed at the sentinel well (PRB16) located at the southern end of the slurry wall

(PRB13). Following repairs mid-2012, hydraulic control was re-established and concentrations at PRB16 subsequently declined.

A review of all the data collated to date is presented in Table 1, which shows average concentrations at monitoring point AW1, GAC1 and PRB16. Typically, biodegradation efficiencies of the selected CoC by SEREBAR have been between 80 and 90%, although lower treatment efficiencies were observed for toluene and xylenes. With most of the degradation occurring in the oil-water separator and the anaerobic sand filled canisters.

Table 1: Average percentage decrease in contaminants of concern during 11 years of operation.

	Conc. (µg/l) entering SEREBAR AW1	Conc. (µg/l) at compliance point GAC1	Conc. (µg/l) at PRB16 sentinel well	% decrease
Naphthalene	11.38	1.93	2.62	83.07
Phenanthrene	4.23	0.41	0.13	90.26
Pyrene	1.45	0.17	0.43	88.42
Benzene	91.72	8.34	27.58	90.91
Toluene	4.14	1.86	1.62	62.30
Ethylbenzene	19.94	3.86	5.92	80.63
Xylene	16.15	5.75	2.70	67.00
Cyanide	558.65	271.34	146.82	51.43

One notable change in the SEREBAR system has been the gradual increase in the concentration of total cyanide entering the system (Table 2). The cyanide was approximately 95% complexed from with generally less than 5% of the free form. Given the iron rich groundwater the predominant form of the complexed cyanide would be hexacyanoferrate. The site investigations undertaken prior to the installation of the SEREBAR system identified no major source of cyanide contamination within the site. The purifiers, typically the process which generated cyanide rich wastes, had been located beyond the site boundary and not up-gradient of SEREBAR. For this reason no specific cyanide treatment was incorporated in the system. Microscale Zero Valent Iron (ZVI), a highly reactive form of iron, whose particle size is a few micrometres, had been considered as a treatment option at the research stage.

Cyanide concentrations have continually increased year on year, which in turn has led to concern over whether this would harm the systems performance and whether it would breach the agreed remedial target for total cyanide of 1.44 mg/l (1440 µg/l). Average total cyanide concentration in the infiltration well (AW1), the monitoring point within the SEREBAR system (GAC1) and at the sentinel well (PRB16) are presented in Table 2.

SEREBAR has periodically (2004-2006, 2008 & 2012-2015) demonstrated some capacity to treat both free and complex cyanide.

Table 2. Annual average concentrations of total cyanide entering (AW1) SEREBAR, at the compliance point (GAC1), and at the sentinel well (PRB16).

	Total cyanide concentration in µg/l					
Year	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
AW1	171.0	188.6	202.2	215.0	345.2	221.4
GAC1	14.0	50.5	27.7	241.9	236.0	334.3
PRB16	119.6	133.6	210.5	117.4	60.3	97.0
Year	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**
AW1	263.8	215.0	387.0	2545.0	250.0	3342
GAC1	421.3	465.5	27.5	307.5	215.0	1092
PRB16	124.7	96.5	62.1	103.0	136.0	373

The mechanism is unclear as to whether it is absorbing to iron that has precipitated within the system, or whether the cyanide is being biodegraded. The increased concentrations observed at the compliance point over AW1 in 2007 and between 2009 and 2011, suggests that the cyanide may also desorb from the system.

The concentrations entering SEREBAR were significantly below the remedial target of 1440µg/l until 2013, when two exceedances were recorded in the infiltration well (AW1). This situation occurred again in 2015 and has continued into 2016. Since 2012 SEREBAR has proved capable of treating cyanide, decreasing the concentration entering the system considerably. The degradation is occurring in the aerated oil-water separator (50% decrease observed) and the first two anaerobic sand filled chambers (a further 40% decrease) (Gibert *et al.*, 2007). The biodegradation of iron-cyanide complexes from gasworks has been proven previously to degrade to nitrate and carbon dioxide. There has been uncertainty over whether this has been mediated by photolysis of the iron cyanide complex (Hommelgaard *et al.*, 1998). In the case of SEREBAR photolysis can be ruled out, but the biodegradation of cyanide has not been proven, although Pseudomonads have been detected in the system (Ferguson *et al.*, 2007). Pseudomonads have previously been reported to biodegrade metal-cyanide complexes in the cyanide rich water from gold mining leach operations (Mudder and Whitlock, 1984). Within the SEREBAR groundwater, cyanide is in competition against ammonium and nitrate to provide a nitrogen source for those organisms degrading the organic compounds under aerobic and anaerobic conditions (Robinson *et al.*, 2006). SEREBAR evidently has the capacity to treat high levels of cyanide, but the mechanism is unstable and would benefit from further investigation.

7. IMPROVED UNDERSTANDING OF THE SITE

The cause of the increasing cyanide concentration in the groundwater is unclear and has led to further investigations at the site to better understand the contaminant sources migrating into SEREBAR. Various decommissioning and redevelopment works have taken place on the wider footprint of the former gasworks, most

notably in the area of the former purifiers, the part of a gasworks typically associated with cyanide contamination. A geochemical investigation of the site groundwater also showed that cyanide-rich groundwater with its own distinct major ion chemistry and isotopic signature was migrating from off-site across the boundary (See BGBH4 Figure 1) of the northern end of the wall into the flow path upstream of SEREBAR.

Studies undertaken on DNAPL samples obtained from a former tar tank (rectangular feature on Figure 1) and boreholes between this and SEREBAR, identified the tar as originating from the vertical retort plant. Although some characteristics of Carburettor Water Gas tar were observed, in some of the samples, both processes operated up stream of the SEREBAR system (McGregor *et al.*, 2012). This has provided some certainty over the point at which these tars originated on site.

8. CHANGES IN THE GROUNDWATER REGIME SINCE INSTALLATION

A comparison of the site wide groundwater data, pre-installation of the SEREBAR system (2000-2003) and after ten years of operation in 2014, has shown the groundwater conditions to have remained very similar across this period. Whilst groundwater flow in 2013 was influenced by the slurry wall, the general flow remains to the south. Groundwater concentrations of the CoC have not shown any considerable change between data sets, with the exception of cyanide as described. The contaminant plume has remained as depicted in red in Figure 1. However, DNAPL and LNAPL detections are less frequent and less extensive in the results obtained in 2013.

9. ECONOMIC CONSIDERATIONS

The economics of the SEREBAR system were first considered in TDP17, which estimated construction and 10 year operation costs to be £1.58m. These predicted costs have been very accurate, with the actual cost close to £1.54m, mainly due to not having to replace the GAC media and slightly lower monitoring costs.

10. CONCLUSIONS

The SEREBAR system has proved to be an effective contaminant source management system, preventing migration of the contaminant plume beyond the PRB over the past 11 years. Except for situations where the system was vandalised, the SEREBAR system has performed very effectively, maintaining hydraulic control over the contaminant plume, treating the target compounds and some compounds, such as cyanide, that it was never designed to treat.

The main reliability issue was the pump, however, by switching to a peristaltic pump, this has made the system more reliable. The GAC canisters have generally provided an effective polishing step, removing remaining contaminants to acceptable concentrations before discharge down-gradient of SEREBAR (overall CoC mass removal >95%). The SEREBAR system was probably over engineered for the expected CoCs. This has, however, provided the flexibility to counter localised changes in groundwater contamination and the increasing cyanide concentration in particular. Aerating the oil-water separator has proved useful in increasing the biodegradation capacity of the system and is now helping to effectively treat a bulk of the CoC and cyanide. Any future design could be modified to benefit from these observations.

This project has shown how an industrial collaborative research project can deliver a commercial scale system in a short timescale (3 years), which has now been operating since 2004.

ACKNOWLEDGEMENTS

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