RECOVERY OF ALUMINIUM TRICHLORIDE SOLUTIONS USING MEMBRANES

Novel membrane bioreactor technology

FUTURE PRACTICE: Tomorrow’s technology and techniques for profitable environmental improvement
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FR200
SUMMARY

A new technology, the Extractive Membrane Bioreactor (EMB), can be used to recover aqueous streams containing valuable inorganic salts polluted with low concentrations of organic compounds. The technology, developed by Membrane Extraction Technology Ltd (MET), uses non-porous elastomeric membranes to extract the organic contaminants and micro-organisms to metabolise the contaminants to harmless compounds. The use of non-porous elastomeric membranes allows streams which would preclude direct biological treatment to be cleaned without any pre-treatment (eg dilution or neutralisation). The specific case used in this project involves the recovery of a 30% w/v aluminium trichloride solution polluted with benzene, 1,3-dichlorobenzene or toluene at Elf Atochem UK Ltd, Widnes. This material is generated through Friedel-Crafts reactions used for manufacturing aromatic ketones.

The overall aim of the project was to construct an EMB pilot plant capable of treating 2 - 3 tonnes of solution/day over a six-month period, to generate long-term operating data and provide sufficient material to explore commercial opportunities.

Over a nine-month period, the pilot plant was designed, built, installed and commissioned. This work was carried out in parallel with modifications to Elf Atochem’s production facility to provide the aluminium trichloride solution for the trial. Commissioning was carried out at a flow rate of approximately 3 tonnes/day. The results were very promising, with benzene levels below the measurement limit in the clean solution.

Following the commissioning period, the membrane modules had to be rebuilt with a new membrane material (EPDM) due to corrosion problems. During the project, from May to October 1998, the modules showed no signs of chemical degradation. Typically 98 - 99% of the benzene was removed from the solution, however, by the end of the project, improvements in the technique had resulted in a 99.9% removal with benzene concentrations in the treated solution <1 mg/litre. Elf Atochem has used this material in customer trials to verify the commercial possibility of selling the clean solution to the water treatment industry. The market value is dependent on the solution specification and the end use.

Environmentally, the EMB has proved to be a cleaner technology than the state-of-the-art technologies for treating these wastes (steam stripping and carbon adsorption). The use of micro-organisms to biodegrade the contaminants results in elimination of the toxic contaminants and no generation of secondary toxic waste streams. Economically, the EMB is competitive with carbon adsorption and significantly cheaper than steam stripping in terms of both capital and operating costs.

In conclusion, the EMB has proved to be a reliable and easy-to-use technology for cleaning aluminium trichloride solution contaminated with benzene, toluene and other organic compounds. The pilot plant built for this trial has achieved 99.9% removal of the benzene from the AlCl₃ solution. The EMB is cost-competitive with the current state-of-the-art technologies and also has less environmental impact.
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1 INTRODUCTION

1.1 FRIEDEL-CRAFTS CHEMISTRY AND ALUMINIUM TRICHLORIDE

Friedel-Crafts reactions are used to manufacture many ring-substituted aromatic molecules\(^1\), eg:

- benzophenone and substituted benzophenones (UV curing, sunblocks);
- isobutylacetophenone (intermediate in Ibuprofen synthesis);
- 2’,4’-dichloroacetophenone (agrochemical intermediate).

These reactions proceed via an aluminium trichloride (AlCl\(_3\)) complex, which is subsequently de-complexed in water to yield product and aqueous AlCl\(_3\) solution. For each tonne of product, 2 - 3 tonnes of 30% w/v AlCl\(_3\) solution is obtained. The untreated solution is contaminated with product and solvent and as such is classified as a hazardous waste. Disposal costs are approximately £50/tonne AlCl\(_3\) solution. However, upon removal of the toxic organics, the AlCl\(_3\) solution has value\(^2\) as a flocculant in wastewater treatment.

1.2 EXTRACTIVE MEMBRANE BIOREACTOR (EMB) TECHNOLOGY

Many toxic organic molecules can be readily biodegraded by naturally occurring, specialised micro-organisms under ideal conditions. However, the inorganic content (eg high acidity, alkalinity or salt concentration) of many hazardous waste streams precludes direct biological treatment.

The Extractive Membrane Bioreactor (EMB)\(^3\) technology overcomes this problem, by using membranes to extract the toxic organic molecules from the waste stream into a separate aqueous phase where the toxic organic molecules can be biodegraded under ideal conditions\(^4\).

This process is made possible by using dense phase membranes (eg silicone rubber), as these membranes prevent ionic species (acids, bases, etc) from permeating through them and affecting the micro-organisms\(^5\). A schematic diagram of the operating principle is shown in Fig 1.

The technology was developed by Membrane Extraction Technology Ltd (MET) and is demonstrated in this project by Elf Atochem UK Ltd, Widnes.

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\(^3\) The EMB technology was invented at and patented by Imperial College, London (PCT/GB92/01719 Treatment of Aqueous Media Containing Organic Material) and is being developed and commercialised by Membrane Extraction Technology Ltd (MET).


Fig 1  Operating principle of Extractive Membrane Bioreactor technology

1.3 AIMS AND OBJECTIVES OF THE ATOMET PROJECT

The overall aim of the ATOMET project was to use the Extractive Membrane Bioreactor (EMB) technology to treat a minimum of 2 - 3 tonnes/day of an aluminium trichloride (AlCl₃) solution made during a Friedel-Crafts acylation reaction at Elf Atochem, Widnes. Once it had been treated, this solution was to be evaluated as a value-added product.

A number of technical and commercial objectives were set to achieve the project aims.

1.3.1 Technical objectives

- Achieve consistent reduction of organic concentrations to acceptable levels for sales.
- Determine the best EMB plant configuration for achieving these removal levels.
- Establish membrane lifetime and durability in the face of acidic aluminium chloride solutions and occasional upset periods in which pure organic phase may contact membranes.
- Demonstrate the robustness of EMB technology in the face of changing organic content in waste.

1.3.2 Commercial objectives

- Establish the suitability of treated AlCl₃ solution as a water treatment chemical.
- Demonstrate the potential of EMB technology for energy and capital plant savings over alternative technologies (steam stripping, carbon adsorption).
- Establish the process economics of EMB technology as a recovery process.
- Gain acceptance of the EMB process as an easy to operate and reliable unit operation.
2 DESCRIPTION OF THE PROJECT

The project was scheduled in five stages, as shown in Table 1. Stages 1, 2 and 3 form Phase I of the project and Stages 4 and 5 form Phase II.

Table 1 Project outline

<table>
<thead>
<tr>
<th>Stage</th>
<th>Tasks</th>
<th>Steps taken</th>
</tr>
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</table>
| 1. Design and hazard analysis | Detailed design of pilot unit and connections to Elf Atochem production plant. Hazard analysis following Elf Atochem’s hazard study procedures. | ■ Establish pilot plant design.  
■ Prepare Process and Instrumentation Diagram (P+ID) for pilot plant.  
■ Review and revise P+ID through MET in-house hazard reviews.  
■ Elf Atochem and MET personnel to carry out hazard study on final design.  
■ Prepare detailed mechanical drawings of pilot plant.  
■ Prepare detailed mechanical drawings of location for pilot plant.  
■ Prepare detailed mechanical drawings of service connections to pilot plant and process connections to Elf Atochem’s production plant. |
| 2. Construction              | Procurement and assembly of pilot plant items. Preparation of service connections, construction of concrete plinths and bunds, and installation of storage tanks and pipework at Widnes. | ■ Get tenders for (a) construction of pilot plant frame and mounting of process equipment, and (b) electrical wiring and control panel.  
■ Procure process plant equipment for assembly.  
■ Assemble pilot plant.  
■ Pipe services (air, steam and water) to pilot plant location.  
■ Install AlCl₃ solution storage tanks and process pipework. |
■ Connect services (air, electricity, steam and water) and process pipework.  
■ Check all sensor and control functions.  
■ Train site operators in system operation.  
■ Ship culture inoculum (micro-organisms) to site.  
■ When culture begins to grow, set pilot plant running with continuous flow of AlCl₃ solution. |
| 4. Operation                 | Operate unit on site and produce saleable AlCl₃ solution.             | ■ Operate pilot plant at 100 litres/hour AlCl₃ solution or more.  
■ Monitor removal efficiency and mass transfer coefficient.  
■ Minimise added nutrient flow.  
■ Continuously maintain culture during trial for rapid inoculation in case of process upset. |
| 5. Evaluation                | Evaluate total treatment costs based on operating data and construction costs. | ■ Use data on membrane lifetime, power consumption and manpower requirements to recalculate EMB costs.  
■ Compare EMB costs with existing data for alternatives (steam stripping, carbon adsorption) generated by Elf Atochem design studies. |
3 PROJECT IMPLEMENTATION

3.1 STAGE 1 - DESIGN AND HAZARD ANALYSIS

Design work on the pilot plant started on commencement of the project (February 1997). The design basis used for the project was:

- 250 litres/hour AlCl₃ solution;
- 50 mg/litre benzene in AlCl₃ solution;
- 99% removal required.

During this initial period of the project, the design evolved through a process of information gathering, design and hazard review. One of the key pieces of information that came to light was the viscosity of the AlCl₃ solution. Information provided by Elf Atochem showed that viscosities up to 20 cP could be expected (depending on concentration and temperature of the AlCl₃ solution).

The primary concern with such a viscous fluid is the pressure drop in the membrane modules; the higher the viscosity, the higher the pressure drop. The elastomeric membrane tubes used in the EMB technology have a maximum operating pressure which gives an upper limit to the flow rate. As the mass transfer coefficient is a function of the flow rate (Reynolds number), lower flow rates reduce the rate of mass transfer attainable in the system.

In parallel with this project, MET was developing process-scale shell and tube membrane modules (denoted MET 200 series) as part of a DTI-sponsored SPUR through SMART award. The design of these modules allows either the wastewater or biological medium to flow through the tubes, with the other phase flowing through the shell.

The data obtained for these modules in trials on a caustic waste were convincing and performance calculations based on published theory/correlations were verified at process-scale⁶. On the basis of these measurements, it became clear that for a given wastewater flow rate, higher mass transfer coefficients and lower pressure drops could be obtained by flowing the wastewater in the shell-side of the modules (see Table 2).

<table>
<thead>
<tr>
<th>Module</th>
<th>Mass transfer coefficient (10⁻⁶ m/s)</th>
<th>Pressure drop/module (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MET 200 (flow in tube)</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>MET 200 (flow in shell)</td>
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Design calculations showed that for a flow of 100 litres/hour of AlCl₃ solution, a membrane area of ~120 m² is required to provide 99.9% removal (~50 mg/litre reduced to <0.05 mg/litre) of the organic solvents. This corresponds to 12 MET 200 modules. The pressure drop in the shell-side of the modules is high enough that the pressure must be ‘boosted’ every so often by intermediate pumps to prevent excessive shell-side pressures collapsing the membrane tubes. Flow sheet and general layout diagrams of the design are shown in Figs 2 and 3. Following completion of the process and instrumentation diagram, a hazard review was carried out by MET which was subsequently approved by Elf Atochem.

To provide a feed of AlCl₃ solution for the project and a storage tank for processed material, Elf Atochem designed a system that connects the pilot plant to the production plant and solution storage tank. The feed system was designed to minimise the probability of large volumes of organic solvent phase from entering the pilot plant. The system is shown in Fig 4.

The process plant installed by Elf Atochem separates carried-over organic phase so that it can be recovered. To promote phase separation, the AlCl₃ solution (ex quench vessel) is passed through a heat exchanger. This reduces the solution temperature from ~80°C as it leaves the production plant to ~40°C in the phase separation tank.

The phase separation tank design allows the AlCl₃ solution to underflow into the AlCl₃ feed tank (minimising disturbance of the organic layer) and recovery of the organic layer is possible through overflow or drain arrangements in the tank. The AlCl₃ solution is then pumped from the feed tank through the membranes in the pilot plant, and the treated (pollutant-free) AlCl₃ solution is collected in the storage tank.
Fig 2 Flow sheet of ATOMET pilot plant
Fig 3  General layout of ATOMET pilot plant
Fig 4  Connections from existing production facility to ATOMET pilot plant
3.2 STAGE 2 - CONSTRUCTION

Before ordering equipment to be used in the pilot plant, engineering standards were agreed with Elf Atochem. The location of the plant is in a Zone 1 hazardous area and consequently only flameproof electrical equipment and intrinsically safe instrumentation were used. Industrial good practice was adhered to where no formal standards were available.

The size of the pilot plant made it difficult to assemble in MET’s facilities, so it was assembled in situ at Widnes; the largest individual item was the steel frame for the membrane modules and process plant. This was fabricated as a single piece, of overall dimensions 7 m (l) by 2 m (w) by 2 m (h).

Contracting out the assembly work was considered. However, this was beyond the project budget, hence the pilot plant was assembled by MET engineers. The MET 200 series membrane modules are a proprietary technology and were manufactured by MET for the project. MET 200 SR (silicone rubber) membrane modules were used, as a laboratory feasibility study and material compatibility tests had shown silicone rubber to be an appropriate membrane material. A total of 14 modules were manufactured; 12 modules for installation in the pilot plant plus two spares. Membrane module manufacture took place during August and September 1997 and assembly of the pilot plant was carried out between mid-September and mid-November 1997.

The feed tank system was designed by Elf Atochem engineers and construction was contracted out. The construction was carried out in five stages. Stage one was the preparation of the plant area which involved creating a bunded area and concrete plinths for the tanks, heat exchanger and pilot plant. The second stage involved erecting steelwork for mounting the AlCl₃ solution phase separation/feed tank system. Installation of the tanks and heat exchanger constituted stage three. Piping the new tanks and pilot plant into the existing process plant pipework was stage four. The final stage was to provide service utilities to the pilot plant (low pressure steam, electricity, air and water). This work was carried out from September to December 1997.

3.3 STAGE 3 - INSTALLATION AND COMMISSIONING

Following construction, commissioning of the AlCl₃ solution feed system and pressure testing of the process pipework was completed in mid-December 1997.

3.3.1 Hydraulic commissioning

Connection of the utilities and electricity to the pilot plant was completed during mid-late November 1997. This was followed by a period of hydraulic (water) commissioning during late November/early December 1997. The aim of this was to ensure that all parts of the pilot plant operated satisfactorily and were correctly calibrated prior to commissioning the plant with AlCl₃ solution and micro-organisms. No major problems were encountered and it was completed by the second week of December.

3.3.2 AlCl₃ commissioning

The bioreactor was inoculated with benzene/toluene-degrading micro-organisms from existing EMB pilot plants three weeks before commissioning started with the AlCl₃ solution. During this period the bacteria were acclimatised to the operating conditions of the bioreactor (30°C, pH 7) and were maintained on benzene/toluene. Rapid bacterial growth was noted within two days of inoculation.
Treatment of the AlCl$_3$ solution started on 16 December, and the plant was run for over 130 hours to provide commissioning data. During this period, the plant treated over 20 tonnes of AlCl$_3$ solution (approximately 3 tonnes/day). Samples of the AlCl$_3$ solution entering and leaving the pilot plant were taken daily and analysed for the presence of benzene and benzophenone (reactant/solvent and product of the acylation reaction), and samples of the biomedium were taken for chemical oxygen demand (COD) analysis. These results are shown in Figs 5, 6 and 7.

**Fig 5** Benzene concentrations in the AlCl$_3$ solution entering and leaving the ATOMET pilot plant during the commissioning period

**Fig 6** Benzophenone concentrations in the AlCl$_3$ solution entering and leaving the ATOMET pilot plant during the commissioning period
Throughout the commissioning period the benzene concentration in the AlCl₃ solution leaving the pilot plant was below the detection limit of the analysis (Fig 5), which suggests that removal efficiencies in excess of 99.9% (with respect to benzene) were achieved. Also, the variation in the inlet concentration of benzene did not appear to have any effect on the removal efficiency. Significant amounts of benzophenone were also removed from the AlCl₃ solution (Fig 6); below 10 mg/litre benzophenone at the inlet, the outlet concentration was below the detection limit, and when the inlet concentration peaked at 36 mg/litre a removal efficiency of 90% was still achieved.

The relatively low COD concentration in the biomedium of approximately 200 mg/litre (Fig 7) suggests that the biomass yield (per kg benzene) is low and that conversion of benzene to carbon dioxide is high. This means that the biomedium overflow does not constitute a significant secondary waste stream.

Overall, the results obtained during the commissioning period were promising. They showed that by using the EMB system it is possible to reduce the concentration of dissolved toxic organics in the AlCl₃ solution to less than 1 mg/litre. This allows the solution to be recovered without generating any secondary pollution. The pilot plant operated successfully during commissioning without any major problems occurring.

### 3.4 STAGE 4 - OPERATION

After the commissioning period (Phase I), the pilot plant was mothballed for a month while the operational results were reviewed with the Environmental Technology Best Practice Programme. When Phase II began, one month later, the pilot plant was re-tested and it was found that several of the membrane modules had developed leaks. By ‘sacrificing’ two modules it was found that the membrane tubes had been severely corroded.
Laboratory trials prior to the ATOMET project had not revealed any such problems, yet the chemical attack on the silicone rubber membrane material was severe and of a type not previously seen by MET. The attack by the AlCl₃ solution resulted in the presence of discrete blisters on the membrane surface, which weakened the membrane (as measured by the tube’s burst pressure) and small pinhole leaks were seen.

In an attempt to replicate this damage in the laboratory, a number of trials were carried out. It was subsequently found that the chemical attack was promoted by compounds containing carbon-oxygen double bonds (particularly benzoyl chloride, one of the reactants), and this was also reproduced in experiments carried out in Elf Atochem’s development laboratory. It is hypothesised that an AlCl₃-benzophenone complex, formed as part of the reaction, remains stable during quenching and is present in the solution to be treated.

This complex is sufficiently hydrophobic that it can permeate into the membrane and hydrolyse within the membrane itself. This liberates hydrochloric acid, which breaks down the silicone rubber. Such a complex would have a finite half-life (possibly a few hours or less), which may explain why the chemical attack was not observed in the original laboratory trials. Thus, a replacement membrane material had to be located.

A review of the literature provided a list of elastomers that are resistant to AlCl₃ solutions (eg Viton, EPDM (ethylene-propylene-diene monomer), nitrile rubber). Any of these materials may make suitable membranes, however testing was carried out on EPDM as it is readily available commercially in tubular form and it is known in the literature to be selective for aromatic hydrocarbons.

Material compatibility tests on EPDM were carried out in parallel with determining the cause of the silicone rubber corrosion. These tests showed that there was no change in burst pressure of EPDM tubing under conditions which corroded the silicone rubber tubing (it could not be burst at >6 bar - the maximum pressure of the compressed air system). These tests suggested that EPDM is significantly more chemically resistant than silicone rubber and should stand up to the operating conditions of the pilot plant. Measurement of mass transfer through the EPDM tubing in a measurement cell showed good correlation with theoretical predictions with values up to $4.5 \times 10^{-6}$ m/s obtained for benzene at Reynolds numbers comparable with pilot plant operation. This is greater than the mass transfer coefficient used as a basis for pilot plant design. Prior to installing EPDM membrane modules in the pilot plant, tests with both benzene-containing and toluene-containing AlCl₃ solutions were carried out using a laboratory-scale shell and tube membrane module (nominal 1 inch, as opposed to 2 inches at pilot plant scale). An average mass transfer coefficient (based on inlet and outlet concentrations from the module at a specific point in time) of $2.5 \times 10^{-6}$ m/s was obtained, see Fig 8.

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On the basis of these results in the laboratory, four of the pilot plant membrane modules were rebuilt with EPDM tubing. Using EPDM membranes required a change in the module manufacturing process which reduced the available membrane area by 25%. These modules were operated on the pilot plant for six weeks with both benzene-containing and toluene-containing AlCl₃ solutions provided from 800-litre intermediate bulk containers. There was no sign of membrane degradation. Fig 9 shows the results obtained over this period expressed as mass transfer coefficients. As can be seen, the results are consistent with those obtained in the laboratory (Fig 8).

**Fig 8** Mass transfer data from laboratory-scale EPDM membrane module

**Fig 9** Mass transfer data from pilot-scale EPDM membrane module
It was observed with these EPDM modules that the pressure drop/module on the pilot plant was low, <0.1 bar/module, compared to 0.6 bar/module in the laboratory. The original silicone rubber modules averaged a 1 bar/module pressure drop. The difference in pressure drop suggested that the AlCl₃ flow in the pilot plant modules was channelling and by-passing the membrane surface. So, to achieve the design mass transfer coefficient ($3 \times 10^{-6}$ m/s), the flow through the membrane shell was modified by inserting inert packing inside the module shell. This reduces the flow area, so increasing the fluid velocity over the membrane tubes, which increases the mass transfer coefficient but also increases the module pressure drop. In early May 1998, six improved EPDM modules were installed in series with the original silicone rubber membrane modules and performance was compared.

Installation of the improved design modules allowed organic-free AlCl₃ solution to be generated from benzophenone- and $p$-chlorobenzophenone-derived AlCl₃ solutions by a single pass through the membranes. During May, material was processed and stored for use in customer trials. The process was operated at 30 litres/hour for 10 days (~245 hours), at 80 litres/hour for 5.5 days (~130 hours) and at ~200 litres/hour for 2 days (~50 hours) until production of the AlCl₃ solution stopped. The data obtained during this period is summarised in Figs 10 and 11 for benzene and benzophenone respectively. During this period $p$-chlorobenzophenone was also produced, which did not affect the bacteria as no accumulation in the biomedium was observed.

![Fig 10 Data for benzene removal during May 1998](image-url)
During June 1998 there was no production of AlCl₃ solution and the pilot plant and membrane modules were modified in preparation for restarting the AlCl₃ solution treatment. The plant was started up on 10 July (t=0 hours). Due to the nature of the production process, variations in solution strength, density, viscosity, organic contaminant concentrations and solids content have occurred, and brief production shutdowns occurred in mid-July and mid-August. Graphs summarising the data gathered during July and August 1998 are shown in Figs 12, 13, 14 and 15.

**Fig 11 Data for benzophenone removal during May 1998**

During June 1998 there was no production of AlCl₃ solution and the pilot plant and membrane modules were modified in preparation for restarting the AlCl₃ solution treatment. The plant was started up on 10 July (t=0 hours). Due to the nature of the production process, variations in solution strength, density, viscosity, organic contaminant concentrations and solids content have occurred, and brief production shutdowns occurred in mid-July and mid-August. Graphs summarising the data gathered during July and August 1998 are shown in Figs 12, 13, 14 and 15.

**Fig 12 Benzene concentrations during July/August 1998**
Fig 13  Removal efficiency for benzene during July/August 1998

Fig 14  Benzophenone concentrations during July/August 1998
The benzene inlet concentration was variable, with concentration peaks in excess of 250 mg/litre and an average inlet of concentration of ~180 mg/litre. Despite this, the outlet concentration averaged 2 - 3 mg/litre (high of 5.6 and low of <0.1 mg/litre). The exceptions to this occurred during start-up, when the biomass in the system was building up and minor changes to the operation of the plant were being made, and when solids (crystalline aluminium chloride, benzoic acid (reaction side-product) and/or benzophenone) were present in the solution flowing through the system. It is hypothesised that the solids ‘trap’ benzene such that it cannot readily dissolve in the AlCl₃ solution and hence is not extracted through the membrane. Apart from these periods, the percentage of benzene removed has been consistently high - in the range 97 - 99.5%, averaging 98+%. By the end of the project, further modifications to the pilot plant allowed 99.9% removal of benzene to be achieved consistently.

The inlet concentration of benzophenone is also variable; inlet concentrations between 2 - 120 mg/litre were measured. However, the concentration is typically 20 - 30 mg/litre. During this period an average benzophenone removal of 70 - 80% was recorded, and typical outlet concentrations of 5 - 10 mg/litre were measured (high of 130 mg/litre and low of 0.5 mg/litre). The large variation in concentrations is reflected in the percentage removal, which shows significant scatter around a mean of ~75% removal.

Benzophenone is difficult to treat consistently, as it appears that small variations in the production process allow varying amounts of both dissolved and solid benzophenone to enter the pilot plant. Dissolved benzophenone is readily extracted, however, due to the nature of benzophenone (it crystallises at 50°C and is highly hydrophobic) it dissolves extremely slowly from its solid form and can pass through the system before it is extracted.
Throughout the period May to October 1998, the ATOMET pilot plant generated clean AlCl₃ solution. The benzene concentration in this material was reduced by over 98%, and removals of 99.9% were achieved consistently by the end of the project.

Since the problems with the silicone rubber membrane have been overcome, no problems have been observed with the EPDM membranes despite the corrosive nature of the AlCl₃ solution and the presence of the organic compounds. Since the EPDM membranes were installed in May 1998, test samples of the membrane tubes have been periodically removed and tested. After six months there is no loss of strength of the material (as measured by burst pressure).

During the project, products based on the solvents benzene and toluene and the acid halides benzoyl chloride and 4-chlorobenzoyl chloride have been made. The switch from one product to another has not affected the EMB system. Observations of the removal of benzene/toluene and the biological performance suggest that the micro-organisms coped with these changes. In the laboratory, micro-organisms have been enriched to biodegrade 1,3-dichlorobenzene, the one solvent not used during the project.
5 ENVIRONMENTAL AND ECONOMIC BENEFITS OF THE PROJECT

The number of direct alternatives to EMB technology for recovering AlCl₃ solutions is limited. For example, the relatively low level of organic contaminants and high inorganic content makes it uneconomic to incinerate the material. The state-of-the-art treatment technologies for cleaning this type of material are steam stripping and carbon adsorption. Also, carbon adsorption is a well-established technology for polishing gas or liquid streams. It is either installed as a regenerative system or used as ‘disposable’ containers.

5.1 ENVIRONMENTAL BENEFITS

A major advantage of the EMB technology over the alternatives is that it eliminates the organic compounds at source rather than concentrating them. The use of micro-organisms to biodegrade the contaminants means that harmless materials such as carbon dioxide, water, chloride ion and more bacteria are generated from the toxic contaminants.

Both steam stripping and carbon adsorption work on the principle of concentrating the pollutant to provide smaller volumes of material for disposal. In both cases, residues are generated that require additional treatment or disposal: condensate contaminated with organics is generated through steam stripping, and carbon adsorption generates saturated carbon which has to be disposed of or cleaned (which in turn generates more waste). The amount of toxic wastes generated by each of these technologies, as well as waste generated by disposal, is summarised in Table 3.

<table>
<thead>
<tr>
<th>Option</th>
<th>Toxic waste generated (kg/m³ AlCl₃ solution)</th>
<th>Energy consumed (MJ/m³ AlCl₃ solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-site disposal</td>
<td>1 300</td>
<td>-</td>
</tr>
<tr>
<td>EMB</td>
<td>0</td>
<td>40¹</td>
</tr>
<tr>
<td>Steam stripping</td>
<td>0 - 10²</td>
<td>756³</td>
</tr>
<tr>
<td>Carbon adsorption (regenerative)</td>
<td>0.5⁴.5</td>
<td>96³</td>
</tr>
<tr>
<td>Carbon adsorption (container)⁶</td>
<td>5⁴</td>
<td>50⁷</td>
</tr>
</tbody>
</table>

¹ Data calculated from pilot plant operation.
² Depends on volume of condensate generated and how this is treated.
³ Based on steam consumption.
⁴ Assumes at saturation 100 g of benzene adsorbs on 1 kg of carbon.
⁵ Assumes carbon can be regenerated 10 times before it must be disposed of.
⁶ Includes energy consumption and secondary waste generation associated with off-site disposal/regeneration of carbon.
⁷ Assumes fluid pumped through bed with 2 kW pump.
Another major contributor to the environmental burden of the technologies is the amount of energy consumed by the treatment process. In the case of the EMB, the energy consumed is in the form of electricity for pumps and steam to heat the bioreactor. The majority of the energy consumed by regenerative carbon adsorption is in the form of steam to recover the used carbon. Steam stripping requires large quantities of steam to heat the AlCl₃ solution to drive off the volatile organics. The energy required for carbon containers includes the energy to manufacture and dispose of the carbon as well as the energy to pump the solution through them. These values are summarised in Table 3.

A more precise picture of the environmental burden would be provided by performing a Life-Cycle Analysis on each technology, which is beyond the scope of this project. Nevertheless, the values outlined in Table 3 provide a crude analysis of the environmental burden. As can be seen in the Table, the energy requirement of the EMB system is low, comparable with activated carbon adsorption and much less than steam stripping. In addition, because the toxic contaminants are biodegraded in the EMB there are no secondary toxic wastes generated. All the other treatment technologies and off-site disposal generate significant secondary wastes. Thus, on the basis of this analysis the EMB offers significant environmental benefits over the state-of-the-art technologies.

5.2 ECONOMIC ANALYSIS OF THE PROJECT

The pre-project base case was disposal of 3 000 tonnes/year of contaminated AlCl₃ solution via a licensed waste disposal outlet at a cost of £50/tonne.

Table 4 summarises the cost comparison between EMB and alternative treatments for recovery or disposal of AlCl₃ solution. In Table 4 the disposal costs have been calculated for 3 500 tonnes/year (compared with the 3 000 tonnes/year of the pre-project base case) to reflect the subsequent developments.

Table 4 assumes 30% AlCl₃ solution containing 180 g/m³ benzene and 20 g/m³ other organics and assumes that the basic infrastructure in terms of pipework, storage tanks, etc for all the technologies is the same. All the assumptions made in Table 3 remain the same.

Steam stripping is a well-established technology which works well for volatile solvents. However, the elevated temperatures and highly corrosive nature of the AlCl₃ solution mean that lined or exotic materials such as hastelloy and titanium alloys have to be used for construction. This requires a large premium in capital investment (see Table 4).

Carbon adsorption can be implemented either in the form of a regenerative system, or as ‘disposable’ containers. The regenerative system requires installation of fixed adsorption beds where the carbon is used and once saturated is recovered in situ. The container system requires minimal plant items to be installed, as the containers are replaced as a whole once they are used up. The regenerative system has a much lower usage of carbon, as it is re-used many times before being replaced. Thus, the capital cost of a container system is minimal compared with a regenerative system (it requires some civil work but no major plant items). The operating cost of a regenerative system may be much higher as it requires high pressure steam (see Table 4).
Table 4  Summary of cost comparison for disposal options

<table>
<thead>
<tr>
<th>Option</th>
<th>Capital cost (£000)</th>
<th>Operating cost (£000/year)</th>
<th>Annualised cost£ (£000/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-site disposal¹</td>
<td>-</td>
<td>193¹</td>
<td>193</td>
</tr>
<tr>
<td>EMB</td>
<td>60</td>
<td>10³</td>
<td>22</td>
</tr>
<tr>
<td>Steam stripping</td>
<td>400²</td>
<td>13²</td>
<td>93</td>
</tr>
<tr>
<td>Carbon adsorption (regenerative)</td>
<td>600²</td>
<td>100²,4</td>
<td>220</td>
</tr>
<tr>
<td>Carbon adsorption (container)</td>
<td>15⁵</td>
<td>27⁶,7</td>
<td>30</td>
</tr>
</tbody>
</table>

¹ Imminent European legislation will limit or remove the landfill option.
² Data provided by equipment vendors or service suppliers.
³ Operating costs are £1 500 for nutrients, £4 000 for membranes and £4 500 for utilities.
⁴ In Elf Atochem’s case the costs of using a carbon adsorption (regenerative) system would be high because of the need for high pressure steam, which is not generated as a by-product at the site.
⁵ Estimated as cost of concrete plinth, bund wall, pipework and pump.
⁶ Includes carbon canisters at £3 000/tonne (data provided by carbon suppliers), estimated rental fee and cranage and transportation of saturated beds.
⁷ The operating cost of the carbon adsorption (container) system for Elf Atochem is particularly low because of the type of contaminants and their concentration. In other situations costs could easily rise to £250 000/year.
⁸ Assumes capital cost charged out over five years.

In addition, there are considerable technical unknowns with activated carbon which make economic analysis difficult. For this comparison, a saturation adsorption of 100 g organic compounds per kg carbon has been assumed (this is consistent with data obtained in MET’s laboratory). However, it is known that competitive adsorption of organic matter and pore blockage can occur in practice, which reduces adsorption efficiency⁹,¹⁰ and increases the frequency with which beds must be changed. Another factor which is difficult to predict, therefore, is the pressure drop through the carbon beds and the likelihood of the beds becoming blocked. Many hazardous wastes contain fine solids (organic or inorganic) which can lodge in the carbon beds increasing the pressure drop and ultimately blocking them. To counteract this, filtration equipment can be installed (though this is expensive for removing fine solids), or a higher than predicted turnover of beds can be accepted. Such costs are not included in Table 4.

Given the cost of disposing of the material to landfill, considerable cost savings can be made by treating the solution, even allowing for the capital cost of each technology (see annualised cost column in Table 4). From Table 4 it is clear that the most cost-effective solution is the EMB. Carbon containers are the next most cost-effective. The cost of activated carbon is also much more sensitive to process variations than the EMB, eg if a process upset occurs and solid material enters the EMB it passes through the system without causing any major damage, however, the same material may block a carbon bed making it unusable and hence needing replacement.

During the course of this project, Elf Atochem has confirmed that there is indeed a market for recovered AlCl₃ solutions. The market value is dependent on the solution specification and on the end use. Therefore, the economic benefit is £50/tonne (avoided disposal costs) plus the margin from the sale of the purified solution (after costs of treatment).

6 CONCLUSIONS

The key conclusions of the ATOMET project are that:

- the EMB has proved to be a reliable, easy-to-use, low maintenance technology;
- EPDM membranes are compatible with the AlCl₃ solution and show no signs of chemical attack after more than six months’ service;
- the EMB can cope with large changes in inlet conditions (ie organic and inorganic content, flow rate and solids) which do not significantly affect the process performance;
- benzene removal efficiencies of 99% can be readily obtained with 25% less membrane area than originally designed;
- the use of micro-organisms to biodegrade the contaminants results in negligible discharges of organic pollutants;
- by the end of the project, 99.9% benzene removal was achieved consistently;
- the EMB has a lower overall environmental burden than its rival technologies;
- the EMB is more cost-effective than alternative technologies.

Further help and advice is available from the Environment and Energy Helpline (0800 585794) which can:

- Send you copies of relevant Environmental Technology Best Practice Programme publications.
- Tell you about environmental and other regulations that could affect your operations.
- Provide free advice and up-to-date information on environmental and energy issues, equipment suppliers and technologies.
- Arrange for a specialist to contact your company if you employ fewer than 250 people, at the discretion of the Helpline Manager.
The Environmental Technology Best Practice Programme is a joint Department of Trade and Industry and Department of the Environment, Transport and the Regions programme. It is managed by AEA Technology plc through ETSU and the National Environmental Technology Centre.

The Programme offers free advice and information for UK businesses and promotes environmental practices that:

- increase profits for UK industry and commerce;
- reduce waste and pollution at source.

To find out more about the Programme please call the Environment and Energy Helpline on freephone 0800 585794. As well as giving information about the Programme, the Helpline has access to a wide range of environmental information. It offers free advice to UK businesses on technical matters, environmental legislation, conferences and promotional seminars. For smaller companies, a free counselling service may be offered at the discretion of the Helpline Manager.