Celgene Corporation has developed a reactor based biological treatment system for the degradation of methylene chloride. The process utilizes a naturally occurring microorganism to completely mineralize methylene chloride to water, carbon dioxide and chloride salts. A pilot plant case history for a GE Plastics production facility in Mt. Vernon, IN is given. This technology is effective for the treatment of either aqueous or vapor streams.

Methylene chloride (dichloromethane, DCM), a suspect carcinogen on the EPA Priority Pollutant list, is an industrial solvent commonly used in aerosols, degreasing operations, paint stripping and as a solvent in the plastics, photographic film, and pharmaceutical industries. U.S. Industry reported that 130 million pounds of DCM were released into the environment in 1989 (Figure 1).

Recently enacted regulations such as the Clean Air Act and the Pollution Prevention Bill have placed increased pressure on DCM users to find an adequate means of reducing the emissions of this hazardous compound. In current practice, methylene chloride in aqueous streams is adsorbed onto granular activated carbon (GAC) and then incinerated. For air emissions, methylene chloride is controlled by carbon adsorption, condensation or thermal oxidation. For selected contaminated groundwater, vacuum extraction followed by incineration of the vapor has also been practiced. While GAC adsorption treatment is widely accepted for many hydrocarbons, it is not particularly efficient at treating DCM contamination in aqueous systems. At DCM concentrations of 500-5000 ppm, loadings on F-300 GAC (Calgon) are on the order of 20-75 mg DCM/gm GAC. With the establishment of lower discharge limits into water, it is not clear if GAC treatment can, in practical terms, meet the new, more stringent treatment guidelines.

SOLUTION: CELGENE'S BIOTREATMENT SYSTEM

One of the advantages of using Celgene’s biologically based system for the treatment of process wastes which contain DCM is the complete destruction of the toxic compound. Researchers at Celgene have successfully isolated naturally occurring microorganisms capable of using methylene chloride as the sole source of carbon and energy. One such organism, designated CEL5002, is capable of completely degrading DCM. The biochemistry of DCM metabolism in this organism has been completely described and is understood. Initial studies clearly documented that CEL5002 degrades DCM with the stoichiometric release of 2 moles of chloride per mole of DCM consumed according to the following equation:

\[ \text{DCM Dehalogenase Reaction} \]
\[ \text{CH}_2\text{Cl}_2 + \text{Enzyme-GSH} \rightarrow \text{E-GS-CH}_2\text{Cl} + \text{HCl} \rightarrow \text{E-GS-CH}_2\text{OH} + \text{HCl} \rightarrow \text{E-GSH} + [\text{CH}_2\text{O}] \rightarrow \text{biomass} + \text{CO}_2 + \text{H}_2\text{O} \]

The rate limiting factor in this process is the dechlorination step. The assimilation of formaldehyde into the biomass is very rapid with no evidence of trace levels of formaldehyde in the external medium.
Protocols for the growth and immobilization of CEL5002 at the pilot and plant scales have been demonstrated.

The bacteria have been immobilized onto a variety of supports allowing degradation to be performed and optimized for many different reactor configurations. To maximize biodegradation and minimize the potential for air stripping, lab scale trickle bed columns have been operated in a down-flow mode with co-current air flow. Aqueous waste containing DCM was fed into the column at rates achieving an empty bed contact time of 30 minutes. Under these conditions, input concentrations of 400 ppm of DCM are reduced to less than 5 ppb in the effluent. Since the degradation of DCM results in the liberation of 2 equivalents of HCl, pH control is a necessary and important feature in the operation of this system. Excess biomass can be easily removed by backflushing the reactor. Lab scale trickle bed systems have been in continuous operation for over 12 months. Rates of DCM degradation of 1 gm-DCM/L-hour column volume are commonly observed for the trickle bed reactors. The down-flow trickle bed reactor concept also has been used to treat vapor streams containing DCM. Treatability of DCM in vapor streams is similar to that seen with aqueous streams.

The DCM degradation process also has been conducted in fluidized bed reactors (FBR). Celgene engineers have modified a FBR system to meet the special requirements of the DCM degradation process. These modifications include pH control and enhanced oxygen delivery systems.

**CASE HISTORY**

Celgene has successfully demonstrated degradation of a methylene chloride process stream for General Electric Plastics at their facility in Mt. Vernon, Indiana. The treated stream was a steam stripper bottom solution which contained DCM and other trace organics. GE effluent requirement was less than 5 ppm (non-detection limit). This level was maintained despite influent DCM fluctuations from 500-4000 ppm. Additional results from the study are shown in Figure 2.

In conclusion, Celgene has developed a biological process for the efficient and economic treatment of a major hazardous pollutant. Some of the benefits of Celgene's biotreatment system are listed in Figure 3.

**Figure 2:** Bioreactor Operating Parameters For Pilot Study At GE, Mt. Vernon, IN

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>DCM influent concentration (ppm)</td>
<td>1270</td>
</tr>
<tr>
<td>DCM effluent concentration (ppm)*</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Average Material Balance (%)</td>
<td>92</td>
</tr>
<tr>
<td>Duration of run (months/days)</td>
<td>&gt; 60 D</td>
</tr>
<tr>
<td>Productivity (g/L-h)</td>
<td>1.4</td>
</tr>
<tr>
<td>Biomass (mg cells/gm GAC wet)</td>
<td>12</td>
</tr>
</tbody>
</table>

*Periodical analysis of grab samples using purge & trap indicated 20-50 ppb DCM.

**Figure 3:** Benefits of Celgene's DCM Biotreatment System

1. Complete mineralization of DCM resulting in innocuous products.
2. Operates at ambient conditions.
3. Tolerant of wide shifts in pH.
4. Stable, reliable, long term operation.
5. Operates efficiently over a wide range of DCM concentrations.
6. Capable of producing high quality effluent (< 5 ppb DCM).
7. The technology has been demonstrated on pilot scale systems.

Celgene, a biotechnology company focusing on the development of biological systems for the treatment of hazardous wastes, was founded in 1986 as a spinoff of the Celanese Corporation Biotechnology unit. For more information about biotreatment systems, contact:

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When and how will the industrialized world clean up the hazardous wastes that continue to pollute air, water and land on our shrinking planet? Across the US, Europe and the Far East, government regulations and public opinion increasingly demand an answer to that multi-billion dollar question.

Although most public attention has focused on existing waste sites resulting from industry's past sins; an enlightened public, along with industrial and regulatory leaders have placed increased emphasis on the longer range solution to the problem of pollution --- stop it at the source. Pollution prevention and waste minimization are fast becoming top priorities for all industrial companies worldwide, and regulatory agencies are beginning to put legislation in place to accelerate this trend.

Conventional physical, chemical and thermal treatment technologies all will play a role in addressing the pollution problem, but each has limitations due to high cost, partial effectiveness, or inappropriate applicability. Celgene has been focused on another solution to the problem --- biological treatment of hazardous waste. Using biotechnology to solve environmental problems "could be --- it should be --- an environmental breakthrough of staggering positive dimensions," says William K. Reilly, Administrator of the U.S. Environmental Protection Agency.

It is well known that naturally occurring microorganisms can degrade many of the pollutants considered toxic. Unfortunately, under the less than ideal conditions found in nature, the natural process is slow and cannot keep up with the large amounts of process waste generated each day. Celgene's in-depth understanding of soil microorganisms allows them to develop biological processes that overcome the limitations found in nature and take advantage of the capabilities of these "biocatalysts" to break down toxic compounds rapidly and effectively.

Celgene’s approach is to carefully select organisms with appropriate enzymes to degrade specific compounds and define the conditions that accelerate the degradation process. Using these organisms or their enzymes as "biocatalysts", Celgene then defines the reactor configuration and overall process system required to apply these biocatalysts to treat a specific waste stream. The result is a practical, cost-effective system that meets the treatment and operational requirements of an industrial plant.

Celgene has focused their initial development efforts on biological treatment of halogenated solvents --- some of the more persistent toxic pollutants found in the environment. As part of this effort, Celgene has developed a novel system for treatment of methylene chloride (DCM). Of the nearly 500 million pounds of this suspect carcinogen produced in the US annually, most of it finds its way into the environment. About one-third of this total is discharged from large industrial facilities where in-process treatment of the waste streams can effectively
address these emissions. Celgene's biotreatment process can reduce the amount of DCM from the parts per thousand levels typically found in aqueous waste streams to parts per billion, turning the toxic compound into carbon dioxide, water and salts.

The biotreatment system has been successfully scaled up for General Electric, Mt. Vernon, Indiana. The unit ran over a 60 day period and averaged 99.92% removal of DCM. The inlet DCM concentration averaged 1270 ppm with effluent concentration below detectable levels. Vent gas measurements indicated less than 0.04% of influent DCM being stripped to the air.

Says Tom Lewis, Vice President and General Manager of Biotreatment, "We are harnessing and accelerating the processes nature has provided. The microbes we employ are naturally occurring, and our technology, therefore, will not face the regulatory obstacles and delays associated with utilization of genetically engineered organisms. This approach allows us to move our technology to the marketplace rapidly, and we can help attack a serious global problem with effective and economical solutions biotreatment provides."

Celgene's technology is based on their deep understanding of the capabilities and limitations of soil microorganisms, and the ability of Celgene scientists to select and manipulate these organisms to develop practical, efficient biocatalysts. By applying these biocatalysts to treatment of waste streams through practical, engineered systems, Celgene scientists and engineers will continue to develop innovative ways to provide solutions to industrial pollution problems.

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