A. Project Title and Date:

Catalytic Treatment of Hydrogen Peroxide in IBM Semiconductor Wastewater
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B. Primary Sponsor:

International Business Machines (IBM) Corporation Microelectronics Division

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The International Business Machines (IBM) East Fishkill semiconductor manufacturing site has modified its wastewater treatment scheme to replace its chemically intense hydrogen peroxide treatment system with one that uses a small amount of a renewable and biodegradable enzyme to catalyze the natural decomposition of hydrogen peroxide into water and oxygen. The catalytic reduction of hydrogen peroxide process has been continuously online since the beginning of 2010 and is currently patent-pending.

This application is not eligible for either the small business or academic award but applies to Focus Area 2: Industry Sponsor for the Use of Greener Reaction Conditions.

All research, bench, and pilot scale investigation was completed at the IBM 300mm semiconductor wafer facility in Hopewell Junction, NY. The full-scale treatment system was constructed there and started up at the end of 2009.

Abstract

In 2003, IBM East Fishkill (EFK) began an initiative with the New York State Department of Environmental Conservation to significantly reduce total dissolved solids (TDS) in the site's final effluent discharge to a small receiving stream. Over the next six years, IBM EFK investigated alternative technologies to remove sources of TDS from our manufacturing wastewaters and wastewater treatment processes, including the treatment of hydrogen peroxide. The largest quantity of hydrogen peroxide in site wastewater is present in the ammonia/hydrogen peroxide wastewater from semiconductor manufacturing. The former and existing wastewater treatment scheme includes the hydrogen peroxide removal process followed by an ammonia separation step, in which the wastewater is distilled for ammonium hydroxide removal. Through the end of 2009, the peroxide removal process was the industry standard: sodium bisulfite reduction, followed by sodium hydroxide neutralization. Both of these chemicals contributed high levels of TDS to our wastewaters and final effluent discharge, and were becoming increasingly expensive.

In early 2009, a catalytic enzyme process was qualified to replace the existing sodium bisulfite process to remove peroxide from the ammonia wastewater. This process uses a small quantity of enzyme to catalyze the decomposition of peroxide waste into water and oxygen, without contributing TDS to the site final effluent discharge and at a fraction of the cost. The process design incorporated existing building equipment as much as possible, and was flawlessly integrated into the existing treatment system. Design and construction of the full-scale peroxide treatment system was started and completed in 2009, with startup continuing through March 2010. This new treatment process eliminates use of 38% sodium bisulfite (510,000 gallons/year) and the subsequent 50% sodium hydroxide (135,000 gallons/year) for acid neutralization, and reduced chemical costs by $675,000 / year. The catalytic reduction of hydrogen peroxide process has been continuously online since the beginning of 2010 and is currently patent-pending.

Additional Project Details

Hydrogen peroxide is conventionally treated in wastewater by neutralizing it with a reducing agent. Until 2009, IBM East Fishkill used sodium bisulfite ($NaHSO_3$) to reduce hydrogen peroxide into water, producing sodium, Na^+, and sulfate, SO_4^{2-}, ions.

$$NaHSO_3 + H_2O_2 \rightarrow Na^+ + H^+ + SO_4^{2-} + H_2O \quad (1)$$

The resulting acidity created by this reaction had to be further neutralized with sodium hydroxide (NaOH).

$$H^+ + NaOH \rightarrow Na^+ + H_2O \quad (2)$$

The consequences of this treatment included high concentrations of both sodium and sulfate salts in the wastewater, the byproducts of the reactions to remove hydrogen peroxide. Alone, these benign salts pass through wastewater treatment systems into the receiving water body with no consequence, except as contributors to the final effluent's total dissolved solids (TDS) concentrations. However, a noted increase in reproductive toxicity at IBM's final effluent led to the correlation that higher levels of TDS can impact the relative health of the associated receiving water fauna, especially the vulnerable water flea.

Used widely in semiconductor manufacturing, hydrogen peroxide is a large component of several wastewater streams at the IBM EFK site. The subsequent treatment of the peroxide waste generated a large portion of the TDS in the combined effluent. By targeting the highest contributor of TDS in this process, IBM could reduce the component of TDS added as treatment chemicals.

The most elementary hydrogen peroxide reaction is its decomposition. It is thermodynamically favorable for hydrogen peroxide to decompose into water and oxygen, although the rate at which this happens is dependant on many factors, including concentration, temperature, pH, etc. Many substances, like metals, or enzymes, can catalyze its decomposition, releasing oxygen and generating only water as an aqueous byproduct.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (3)$$

The chosen replacement technology for the existing bisulfite treatment method needed to meet stringent requirements and be compatible with subsequent wastewater treatment processes. Not only did it need to be effective for the specific ammonia/hydrogen peroxide wastewater that is generated by semiconductor manufacturing, but it needed to provide a significant net reduction of TDS (which eliminated all conventional treatment options) without addition of other undesirable ions. There were several other constraints because the subsequent ammonia wastewater distillation process step, which generates an ammonium hydroxide product for commercial sale, was critical to the overall operation of the site wastewater treatment systems and waste minimization activities. The new process needed to operate at a low pH to prevent loss of ammonia gas, and could not introduce chemicals or change wastewater characteristics that would foul the ammonia distillation column or contaminate the ammonium hydroxide product.

Following several years of investation and laboratory testing, a commercial, aqueous fungal enzyme was chosen as the most favorable solution. The enzyme, an *Aspergillus niger* catalase dervied from microbial fermentation, catalyzes the decomposition of hydrogen peroxide through a covalently bound heme group, Fe(III), which acts an oxygen acceptor and donor to catalyze the reaction.

$$H_2O_2 + Fe(III) \rightarrow H_2O + Fe(IV)O^+ \quad (4)$$

$$Fe(IV)O^+ + H_2O_2 \rightarrow H_2O + O_2 + Fe(III) \quad (5)$$

The selected technology was subjected to a long evaluation process by IBM EFK before full-scale implementation. Rigorous peroxide removal optimization, pH, biodegradation, offgasing, and fouling tests were conducted before the new treatment scheme was established.

This replacement treatment technology challenged all major disadvantages of the previous method. By eliminating chemicals and reducing the chemical volumes, the project reduced potential hazards to employees, tanker offloading labor, and greenhouse gases associated with truck emissions. The catalytic peroxide removal process does not produce a wastewater discharge concern at the expense of other media. The only byproducts are water and oxygen. The process does not cause any increase in sludge generation, there are no additional air emissions, and the enzyme is biodegradable once exhausted.

The new process was incorporated seamlessly into existing buildings and systems. Two unused tanks in the path of the wastewater transfer pipeline were repurposed as catalytic reaction tanks, with minimal piping, instrumentation, or other mechanical upgrades necessary, reducing the amount of new construction required. Existing variable frequency drives were employed for energy savings, and exhaust systems were installed to address operational and safety concerns associated with deentrainment and accumulation of oxygen within the treatment system. The previous treatment scheme was left untouched as an active backup system.

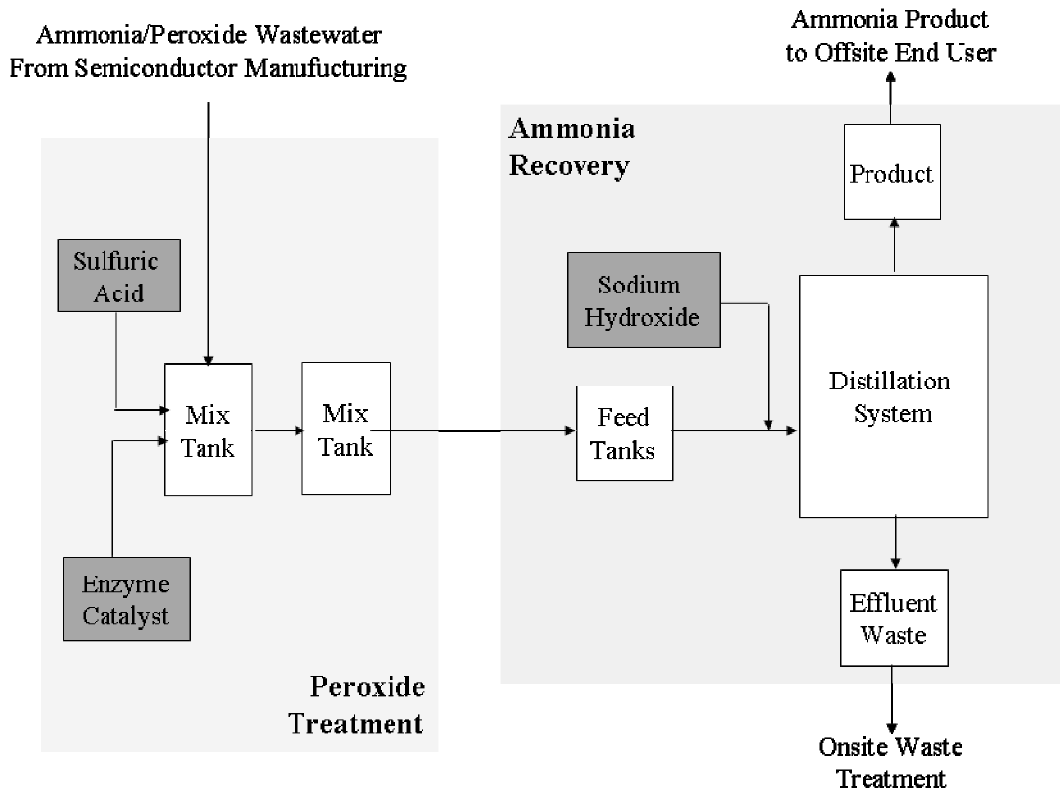

Figure 1: Revised Ammonia-Peroxide Wastewater Treatment Scheme

By converting IBM EFK's treatment system to the catalytic technology, this installation was first of a kind in the semiconductor industry. Although the particular catalase has been used for peroxide waste neutralization in other industries, those applications had much lower peroxide concentrations, and different waste characteristics. The enzyme was chosen from extensive research and testing on alternative processes and catalysts to match the site wastewater characteristics and requirements. The process is currently patent-pending.

Because of the highly complex requirements for integration into the existing waste treatment processes, all bench and pilot testing was completed on site by IBM EFK personnel. This included construction and operation for four weeks of a scaled-down ammonia distillation column to assess the potential for column fouling before moving forward with full-scale construction.

The former process used over 645,000 gallons/year in inorganic and hazardous treatment chemicals. Instead, this project substituted only 200 gallons/year of a biodegradable and renewable enzyme, thus eliminating hundreds of thousands of gallons/year in treatment chemicals. The significant reduction in TDS in IBM EFK's wastestream will benefit aquatic biota through improved receiving water quality. Additionally, by replacing sodium bisulfite and the resulting caustic with the enzyme catalyst (200 gallons/year), IBM has avoided 162 chemical tanker shipments from Buffalo, NY to Hopewell Junction, NY, a 400 mile route from our supplier to our manufacturing facility. Over 129,000 truck miles have been avoided, resulting in the avoidance of 270 tons of greenhouse gas emissions, to the beneift of local traffic and air quality. The reduction of 3-4 tanker deliveries per week also reduced potential hazards to employees and tanker offloading labor.

In addition, wastewater treatment spending has decreased by over $675,000 per year. The project lowered capital costs by avoiding purchase of new building materials and reusing existing building space and equipment.

The catalytic reduction of hydrogen peroxide process is currently patent-pending. In 2011, the project won two awards: The Excellence in Environmental Engineering Grand Prize for Small Projects from the American Academy of Environmental Engineers in January 2011, and the National Polution Prevention Roundtable MVP2 Award in September 2011.