

**Destruction of Volatile Organic
Compound (VOC) Emissions by
Photocatalytic Oxidation (PCO): Final
Report (ESHCOO3)**

SEMATECH and the **SEMATECH logo** are registered service marks of SEMATECH, Inc.

Destruction of Volatile Organic Compound (VOC) Emissions by Photocatalytic Oxidation (PCO): Final Report (ESHCOO3)

Technology Transfer # 97013236A-ENG

SEMATECH

February 28, 1997

Abstract: This report summarizes the experimental activities at National Renewable Energy Laboratory (NREL) and at KSE to investigate the use of photocatalytic oxidation (PCO) as a volatile organic compound (VOC) control technology for point-of-use (POU) application in the semiconductor industry. It contains the results of laboratory-scale testing using an NREL-developed photocatalyst as well as experiments using proprietary KSE photocatalysts and presents estimates of the cost of ownership (COO) of PCO for POU applications.

Keywords: Photocatalytic Oxidation, Cost of Ownership, VOC Abatement, Volatile Organic Compounds

Authors: Edward J. Wolfrum, Roberto Rabago, Avtar S. Jassal

Approvals: Avtar S. Jassal, Project Manager
Walter Worth, Program Manager
Scott Elrod, Director
Laurie Modrey, Technical Information Transfer Team Leader

Table of Contents

1	EXECUTIVE SUMMARY	1
2	INTRODUCTION/BACKGROUND.....	1
2.1	Project History	1
2.2	End-of-Pipe versus Point-of-Use VOC Control	2
2.3	The Evolving Design Basis.....	3
3	EXPERIMENTAL	4
3.1	NREL Experiments.....	4
3.2	Small-Scale Reactor Tests	4
3.3	Large-Scale Reactor Tests	6
3.3.1	Spike and Long-Term Tests.....	6
3.4	KSE Experiments.....	10
3.5	Discussion and Comparison of Results	12
4	SIZE AND COST ANALYSIS	13
4.1	PCO Cost Analysis	13
4.2	Comparison with Conventional Treatment Costs.....	13
5	CONCLUSIONS AND RECOMMENDATIONS.....	15
6	REFERENCES.....	15

List of Figures

Figure 1	Photocatalytic Oxidation of a Three-Component Mixture of Methanol, Isopropanol, and Acetone using DeGussa P25 TiO ₂ Photocatalyst.....	2
Figure 2	Schematic Diagram of the Small-Scale Reactor Test Assembly at NREL.....	5
Figure 3	Performance of NREL Photocatalyst in Small-Scale Reactor Assembly	6
Figure 4	Schematic Diagram of the Large-Scale Reactor Test Assembly at NREL.....	7
Figure 5	Parts Cleaning Bench Data as a Function of Total Time on Stream.....	8
Figure 6	Behavior of a PCO System Exposed to Intermittent Spikes of Methanol	9
Figure 7	Long-Term Photocatalyst Activity Test.....	10
Figure 8	Photocatalytic Destruction of Methanol Using KSE Photocatalyst.....	11
Figure 9	Photocatalytic Destruction of Methanol Using KSE Photocatalyst A.....	12

List of Tables

Table 1	Comparative Photocatalyst Performance for Methanol Destruction, KSE Inc.....	11
Table 2	Results of SEMATECH COO Analysis for 1000 CFM, 500 ppmv Methanol POU Treatment System Options.....	14

Nomenclature and Abbreviations

CFM	Cubic Feet per Minute
COO	Cost of Ownership
CRADA	Cooperative Research and Development Agreement
EOP	End of Pipe
FRP	Fiberglass Reinforced Plastic
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
HAP	Hazardous Air Pollutant
LPM	Liters per Minute
NDA	Non-disclosure Agreement
NREL	National Renewable Energy Laboratory
PCO	Photocatalytic Oxidation
POU	Point of Use
TOC	Total Organic Carbon
VOC	Volatile Organic Compound

1 EXECUTIVE SUMMARY

This report summarizes the experimental activities at National Renewable Energy Laboratory (NREL) and at KSE to investigate the use of photocatalytic oxidation (PCO) as a volatile organic compound (VOC) control technology for point-of-use (POU) application in the semiconductor industry. It contains the results of laboratory-scale testing using an NREL-developed photocatalyst as well as experiments using proprietary KSE photocatalysts and presents estimates of the cost of ownership (COO) of PCO for POU applications.

The testing at KSE was performed for two reasons: 1) to collect adequate experimental data to permit KSE to provide a cost estimate of a full-scale treatment system and 2) to investigate the performance of the KSE photocatalytic system.

Based on the experimental results, NREL and KSE, Incorporated independently developed estimates for the capital and operating costs of a 1000 cubic feet per minute (CFM) photocatalytic oxidation system. NREL then used the SEMATECH COO model to determine COO. These results suggest that a 1000 CFM PCO system would have a COO of approximately \$25,000–\$30,000 per 1000 CFM. The SEMATECH estimate for current end-of-pipe (EOP) thermal technologies is approximately \$20,000 per 1000 CFM.

Based on results of the COO model, it appears unlikely that photocatalytic oxidation will cost less on a “per CFM basis” than existing EOP technologies. However, a number of specific cases indicate that POU technologies in general and photocatalytic oxidation in particular may provide a cost-effective alternative to (EOP) technologies. However, the actual costs of these specific cases are not well-captured by the COO model.

It was determined that PCO technology, like other catalytic technologies, is not suited for VOC emissions containing hexamethyldisilazane (HMDS) because of rapid catalyst deactivation, which would lower the overall performance of the POU technology.

2 INTRODUCTION/BACKGROUND

Researchers at the NREL have been working with SEMATECH under a CRADA to investigate the use of PCO as a VOC control technology for POU application in the semiconductor industry.

The goal of the final phase of the NREL/SEMATECH CRADA was to provide SEMATECH with as accurate an estimation as possible of the COO of a PCO system for a POU application. To accomplish this goal, NREL cooperated with KSE, Incorporated, a company currently developing photocatalytic oxidation as an air pollution control technology.

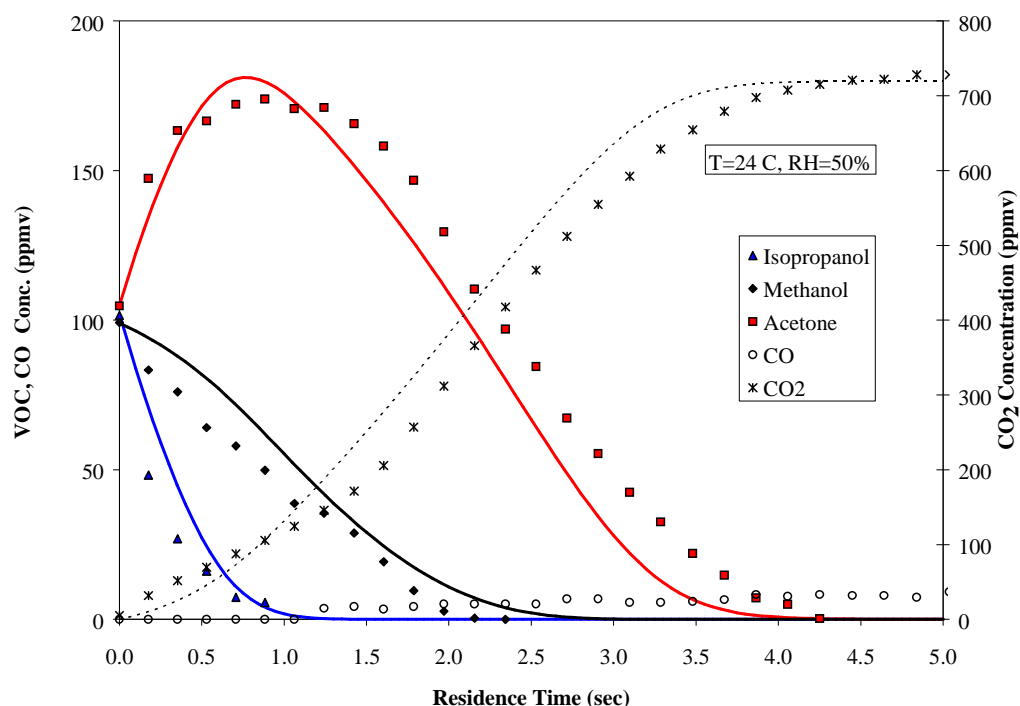
2.1 Project History

SEMATECH and NREL initiated a CRADA in 1994 to determine whether PCO could be used as a POU control abatement technology for VOCs.

The approach that NREL has taken in this project has been to conduct a series of laboratory experiments to accurately measure the reaction kinetics of a number of organic compounds likely to be present in POU applications. Conceptual designs of large-scale systems were developed based on these laboratory measurements to establish estimates for capital and operating costs. These estimates were then inserted into a SEMATECH model to calculate COO.

Earlier work on this project [1, 2, 3] demonstrated that PCO could completely destroy some commonly used VOCs such as acetone, isopropanol, and methanol, but could not effectively destroy HMDS due to rapid catalyst deactivation. Figure 1 shows a representative data set. The reactor modeling results demonstrate that the performance of a multicomponent stream can be predicted based upon the kinetic behavior of individual components.

The key variable in the cost of any catalytic system is the activity of the catalyst. A significant portion of the activity in this CRADA has been in the area of photocatalyst development. As a result, NREL has developed a number of advanced photocatalysts with catalytic activities that have substantially decreased the cost of PCO technology for air treatment. For example, the catalyst used in Figure 1 resulted in the production of carbon monoxide. Later work using platinum-doped TiO_2 not only destroyed VOCs more quickly, but also left CO (<0.5 ppmv) undetectable for all VOCs tested under all reaction conditions.



Note: Reactor model (lines) showed excellent agreement with experimental data

Figure 1 Photocatalytic Oxidation of a Three-Component Mixture of Methanol, Isopropanol, and Acetone using DeGussa P25 TiO_2 Photocatalyst

2.2 End-of-Pipe versus Point-of-Use VOC Control

There has been much discussion regarding the applicability of POU versus EOP VOC control in the semiconductor industry. To date, the industry has yet to adopt a method for comparing EOP and POU techniques that is generally acceptable to all its members. One method, SEMATECH's COO model, presents the total cost of a VOC control technology in terms of "cost per thousand CFM."

NREL believes that it is inappropriate to compare POU and EOP technologies on a per thousand CFM basis simply because of their different scales. Given the economies of scale inherent in larger-scale chemical processes, it is unlikely that any VOC control device treating 1000 CFM could be competitive on a per thousand CFM basis with a 50,000 CFM system employing the same technology. For any air pollution control technology, smaller systems are more expensive in terms of cost per thousand CFM than larger systems [4, 5].

However, under certain plant-specific conditions, a POU technology could be the most cost-effective solution. For example, each of the following four scenarios represent likely cost-effective POU applications:

1. An incremental capacity expansion is planned for a facility, and the existing EOP system is already operating at its design limit.
2. A particular stream contains a contaminant that is difficult to treat with the existing EOP system. Additional control for that specific contaminant is required.
3. A new stream-producing device cannot be easily connected to the existing EOP system because of location or because critical operations would have to be shut down to connect the new device.
4. Plant operating philosophy views each stream-producing operation as a self-contained, standalone process.

The first three scenarios involve modifications to an existing plant. The costs of these modifications are not easily accommodated by the current COO model, which estimates installation costs as a multiplier to the equipment capital cost. For example, with scenario 3, it is difficult to imagine how the installation costs could be accurately captured by the existing COO model.

Scenario 4 is attractive if a particular VOC control device malfunctions. Because the VOC control is attached directly to the discrete stream-producing process, only that process would be rendered inoperable during the time required to bring the VOC control device back on line. Again, the COO model does not readily reflect the operational and cost advantages of such an approach.

It is largely beyond the scope of this CRADA, and beyond the expertise of the NREL researchers involved in this project, to determine the relative merits of POU and EOP treatment technologies. However, an evaluation based solely on the cost per 1000 CFM treated does not adequately assess the relative merits and drawbacks of either approach.

2.3 The Evolving Design Basis

The early laboratory work on this project involved a three-component, equimolar mixture (isopropanol, acetone, methanol) with a total concentration of approximately 400 ppmv. This early work clearly demonstrated that acetone was the mixture's rate-limiting compound, and thus subsequent work used acetone as the model compound. Acetone recently has been excluded from the definitions of VOCs by the Environmental Protection Agency on the basis that it has negligible photochemical activity [6], making its control less critical to SEMATECH.

The treatment system designs used for the cost analysis presented in this report were based on a 1000 CFM stream containing 500 ppmv methanol. (Methanol is defined by the EPA as a

Hazardous Air Pollutant [HAP]). This design basis could correspond to any of the four scenarios presented above.

Methanol was used as a model compound for the laboratory work because it is easily destroyed in thermal treatment systems often used as EOP technologies. However, methanol removal efficiency by granular activated carbon (GAC) or zeolite absorption is relatively low (~50%), so it may cause problems for otherwise efficient EOP systems employing these technologies.

3 EXPERIMENTAL

The experimental work was performed at two locations. NREL researchers tested a 10 CFM reactor assembly and a 5 LPM reactor assembly, both using an NREL-developed photocatalyst at their laboratories; KSE, Inc. researchers tested a proprietary 5 LPM photocatalytic reactor assembly at their laboratories.

NREL initiated a pilot-testing program with KSE to provide SEMATECH with supplier data. KSE, Inc. is currently building a number of large-scale (100–1000 CFM) PCO reactor systems for VOC control; they have had several successful large-scale demonstrations treating such compounds as hexane [6] and pentane [7]. KSE performed a number of experiments at their expense and have given NREL pilot test data that summarize the results of their experiments as well as estimates of the capital and operating costs of a full-scale PCO reactor system.

An analysis of the testing at KSE was performed by an independent consultant (formerly of NREL), who monitored the testing to ensure good laboratory practices were followed and who reviewed a portion of the KSE data.

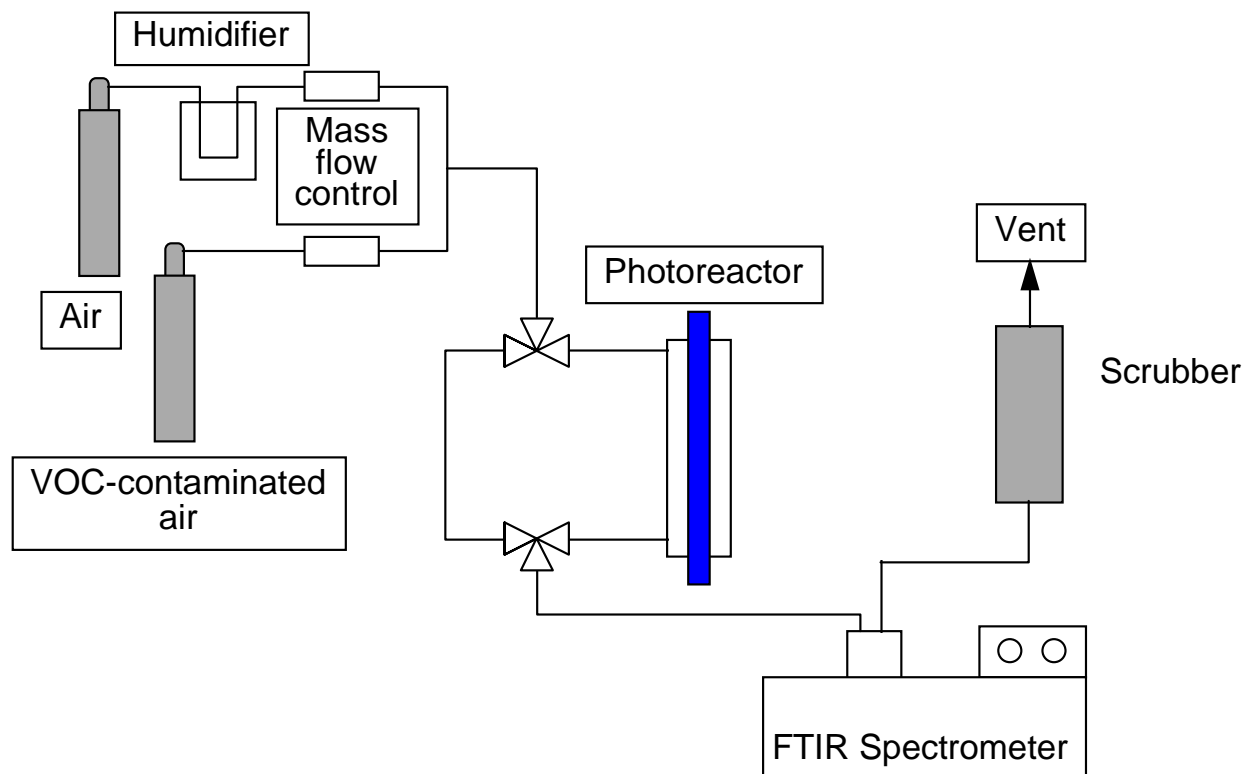
3.1 NREL Experiments

The experimental work at NREL used two reactor assemblies. The small-scale reactor assembly provided data to compare the performance of the NREL and KSE catalyst systems. The large-scale tests addressed issues raised in earlier work, including catalyst lifetime, and allowed in-depth analysis of the “spiking” phenomenon, where very high concentration (>1000 ppmv) spikes of pollutant intermittently enter the photocatalytic reactor system.

3.2 Small-Scale Reactor Tests

A schematic diagram of the small-scale reactor assembly is shown in Figure 2. It is the same assembly used for the majority of the previous work done on this project. A Fourier transform infrared (FTIR) spectrometer (Nicolet IMPACT 400D) was used to measure the VOC concentration in either the inlet or outlet air stream, although not in both simultaneously. The FTIR could also detect and quantify reaction intermediates and products.

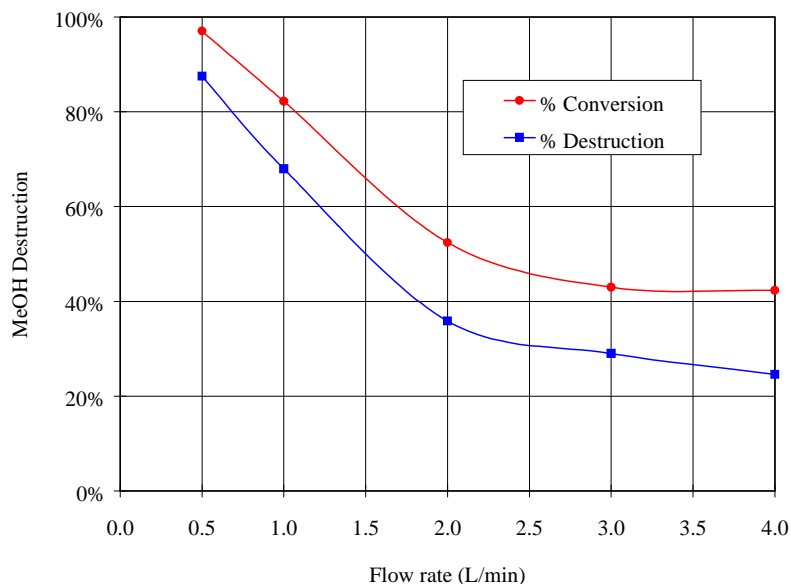
The photocatalytic reactor was of annular reactor geometry, with inner and outer Pyrex walls of 35 mm and 54 mm outside diameter (OD), respectively. The bed depth was 4 cm, giving an empty bed volume of 50 cm³. The reactor contained 50 grams of 3 mm soda lime glass beads coated with 0.5 wt% platinum-impregnated TiO₂ photocatalyst developed at NREL. The reactor was illuminated by an 8 W black light lamp (NEC, F8T5BLB). The flowrate through this reactor assembly was varied between 0.5 and 5 LPM, and the initial inlet methanol concentration was varied between 100 and 500 ppmv.



Note: This assembly is identical to those used by NREL in previous work on this CRADA.

Figure 2 Schematic Diagram of the Small-Scale Reactor Test Assembly at NREL

The results of these tests are shown in Figure 3, which compares methanol destruction to flowrate. The data in Figure 3 demonstrate that methanol photocatalytic oxidation produces a byproduct, methyl formate. No carbon monoxide or formaldehyde was identified, although the FTIR can identify these at sub-ppmv levels and quantify concentrations above 1 ppmv. When the photocatalytic reactor assembly is operated under conditions that give complete methanol conversion, no intermediates are seen. However, such data are not useful for kinetic analysis.



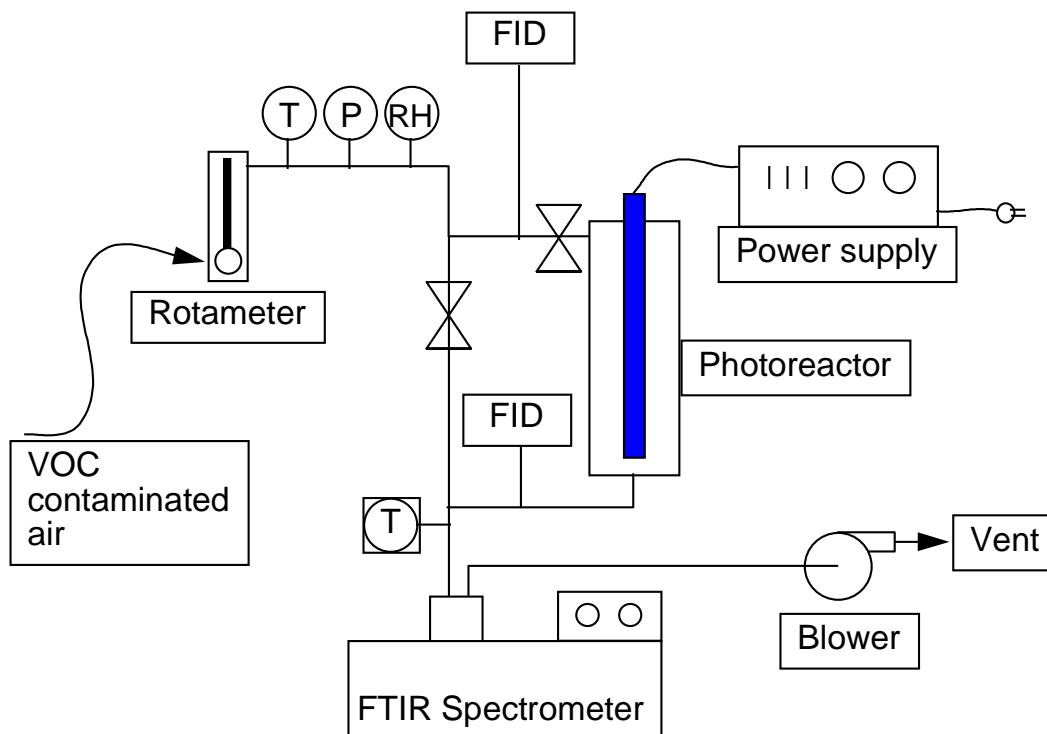
Note: Inlet methanol concentration 500 ppmv, reactor temperature 41°C.

Figure 3 Performance of NREL Photocatalyst in Small-Scale Reactor Assembly

3.3 Large-Scale Reactor Tests

The large-scale reactor tests used dual flame ionization detectors (FIDs) (California Analytical Instruments Model 300-FID) running simultaneously on the inlet and outlet. The data were continuously collected using National Instruments' Virtual Benchlogger software. An FTIR spectrometer (Nicolet IMPACT 400D) was used to measure either the reactor inlet or outlet. This configuration continuously monitored the total organic carbon (TOC) in the system and periodically identified all compounds in the inlet and outlet stream.

The large-scale reactor was of annular geometry, with a 1.5" OD 40 W nUV lamp (Sylvania F40T12BLB) surrounded by a 3" inner diameter (ID) sleeve. The NREL photocatalyst (0.5 wt% Pt-TiO₂) was coated on a proprietary aluminum support, which provided good light distribution in the photoreactor without excessive pressure drop. The reactor length was 44", giving an illuminated reactor volume of approximately 3 liters. A schematic of the large-scale reactor assembly is shown in Figure 4.



Note: Dual FID detectors were used for continuous emission monitoring. FTIR was used to identify and quantify reaction intermediates and products.

Figure 4 Schematic Diagram of the Large-Scale Reactor Test Assembly at NREL

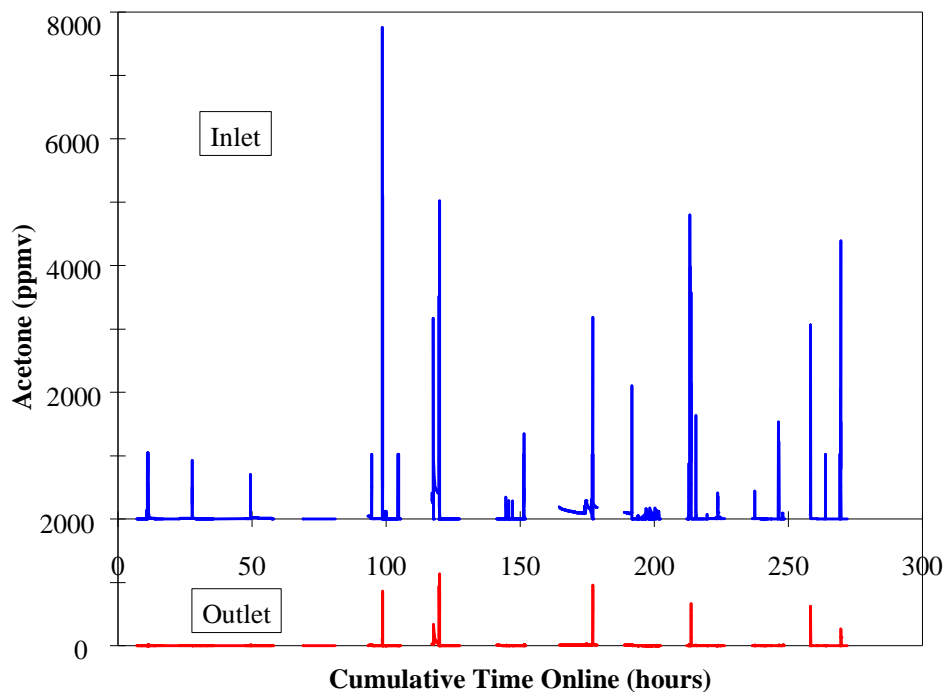
3.3.1 Spike and Long-Term Tests

The field experiments performed at Hewlett-Packard earlier in this project [3] demonstrated that PCO could destroy intermittent spikes of acetone that were present at significantly higher concentrations than what the unit was originally designed. This field data are presented in Figure 5. Similar results were also obtained for an ethyl lactate emission stream from a planar coating track.

Figure 6 presents laboratory data to demonstrate this spiking phenomenon using methanol. The reaction conditions were set to provide approximately 65% conversion of the methanol (100 ppmv methanol, 3 scfm flowrate). This conversion was selected to easily monitor deviations from the steady-state conversion value. The inlet methanol concentration was rapidly increased and then quickly returned to the nominal value. This process was repeated several times; each time the reactor destroyed the vast majority of the methanol spike. However, as shown in Figure 6, for several minutes immediately after the fourth spike (~20 min), the outlet methanol concentration was higher than the inlet concentration.

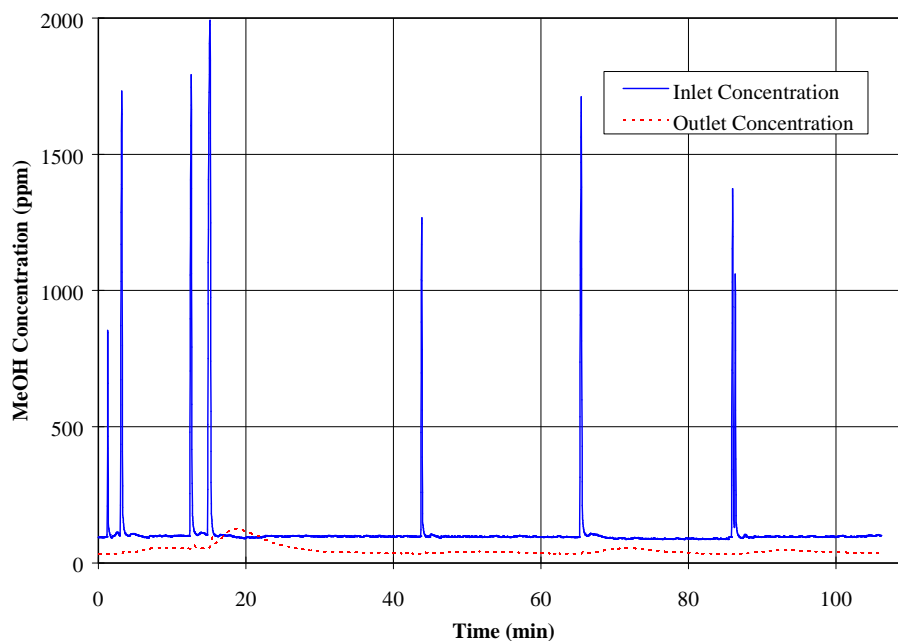
Although not obvious because of the time scale in Figure 6, this spike lasted significantly longer than the previous and subsequent ones, so the reactor saw a much larger “plug” of methanol entering the reactor. The methanol breakthrough is due to methanol desorbing from the photocatalyst surface; it is not an artifact of the analytical equipment. However, the reactor achieved a time-averaged value of 60% conversion even when including the breakthrough phenomenon. That is, the NREL photoreactor, when operated under conditions designed to provide 65% destruction of a continuous 100 ppm stream, destroyed 60% of the methanol present

in a stream where the inlet concentration was rapidly varying up to 20 times the steady-state value.



Note: Top curve is inlet VOC concentration; bottom curve is outlet VOC concentration. VOC emissions from this source were almost entirely acetone, based on FTIR analysis. Time-averaged conversion was 96%. No reaction intermediates were seen. Data from a SEMATECH member company [3].

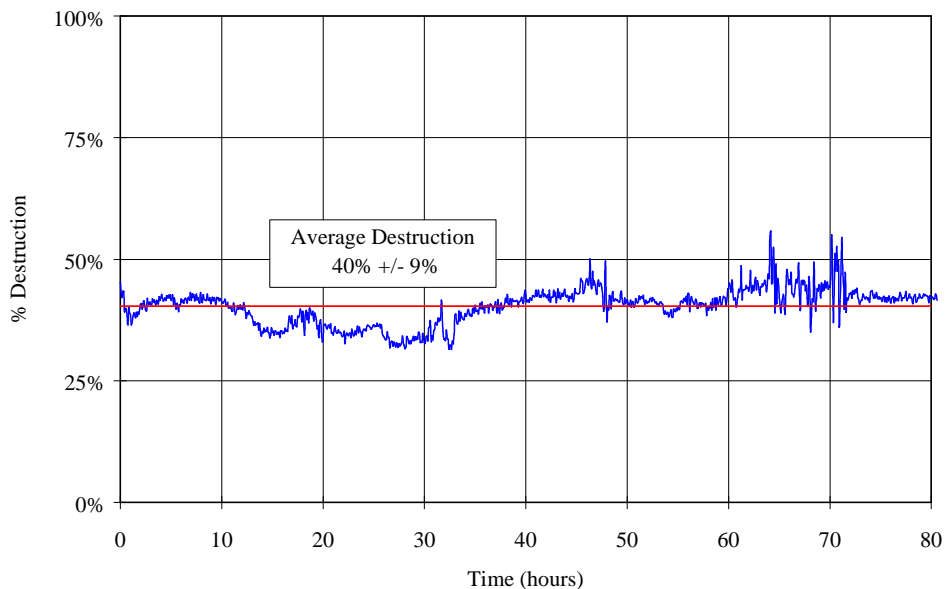
Figure 5 Parts Cleaning Bench Data as a Function of Total Time on Stream



Note: Inlet methanol concentration 100 ppmv, flowrate 3 CFM, reactor temperature 41°C. The time-averaged treatment efficiency remained within 5% of original design efficiency.

Figure 6 Behavior of a PCO System Exposed to Intermittent Spikes of Methanol

The large reactor was also used to perform multiple experiments to determine the amount of deactivation the photocatalyst undergoes. These data, shown in Figure 7, indicate that the NREL photocatalyst retained its activity throughout the experiment. The modest fluctuation in conversion is due to fluctuations in the inlet concentration, flowrate, and temperature over the course of the experiment. These results agree with much longer lifetime studies performed at the earlier field test [3].



Note: Inlet methanol concentration 100 ppmv, flowrate 3 CFM, reactor temperature 41°C. The slight variation in treatment efficiency over the course of the experiment is due to reactor inlet concentration and temperature fluctuations. Reactor maintained its original efficiency over the course of the experiments.

Figure 7 Long-Term Photocatalyst Activity Test

3.4 KSE Experiments

The experimental work performed at KSE, Inc. had two purposes: 1) it investigated the performance of the KSE photocatalytic system, and 2) it provided enough information for KSE to design and cost a full-size system. The test assembly was conceptually identical to the one used for the small-scale reactor tests performed at NREL, except that in addition to the analytical equipment used by KSE, NREL also provided analytical equipment for some of these tests. This equipment consisted of a portable gas chromatograph (MTI P200 GC) equipped with dual thermal conductivity detectors. The portable GC identified and quantified the reactants, intermediates, and products of the oxidation reaction, with a sensitivity of approximately 1 ppmv. Two photocatalysts, identified only as A and B, were tested by KSE. The catalyst formulations, as well as their preparation methods and their methods of deployment, are proprietary to KSE. The results of these tests are shown in Figure 8, Figure 9, and Table 1.

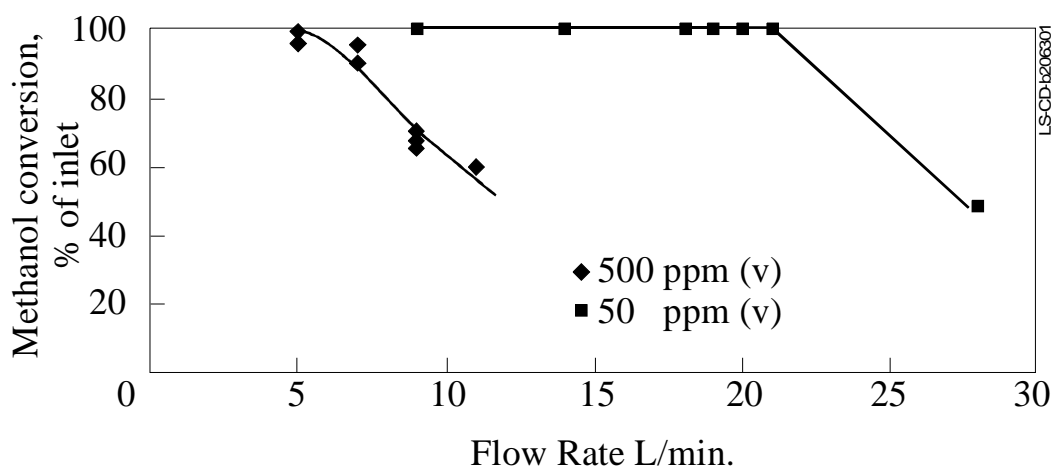
Figure 8 shows the effect of flowrate on methanol destruction using KSE catalyst A. Decreased flowrates result in increased residence times and therefore in increased methanol conversions. For conversions less than 100%, methyl formate and one other unidentified intermediate were seen. KSE used the data in Figure 8, along with the NREL data in Figure 3 to perform a qualitative comparison of the NREL and KSE catalysts. This comparison is discussed in detail below.

The results of long-term catalyst stability tests on KSE catalyst A are shown in Figure 9. Over a period of almost 1000 hours, the KSE data for catalyst A showed no measurable loss in activity.

Table 1 Comparative Photocatalyst Performance for Methanol Destruction, KSE Inc.

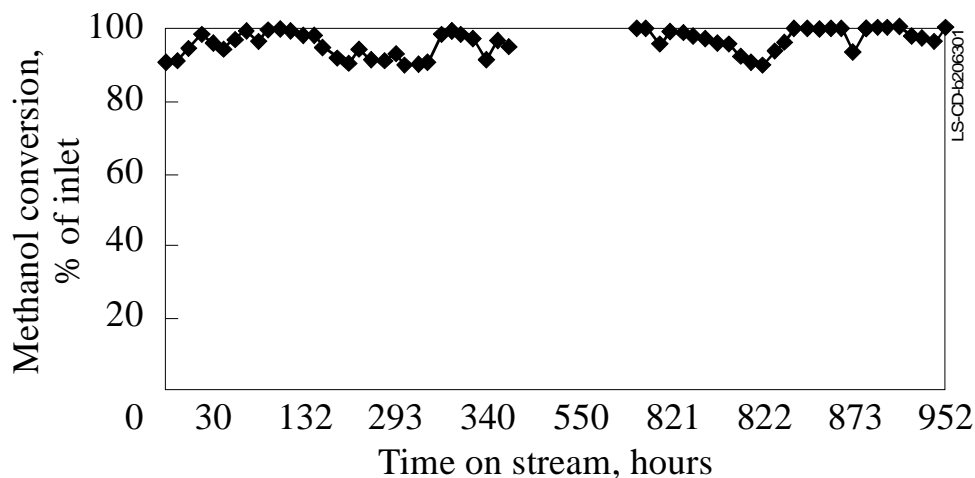
Catalyst Identification, Methanol Concentration	Relative First Order Rate Constant ¹	% of Total Products Converted to CO ₂
NREL Catalyst, 500 ppmv	1.0	87 ²
KSE Catalyst A, 500 ppmv	5	100 ³
KSE Catalyst A, 50 ppmv	19	100 ³
KSE Catalyst B, 50 ppmv	17	100 ⁴

Table Notes: 1) Comparisons of rate constants between laboratories requires comparable ultraviolet (UV) sources and utilization, which has not been confirmed in this work. 2) Methyl formate was the only intermediate seen with the NREL catalyst. 3) At less than 100% destruction of methanol, low concentrations of methyl formate were observed in the reaction products. 4. At all conversions of methanol, from 30% to 100% destruction, no byproducts were observed in the reactor effluent.



Note: Effect of flowrate on conversion. Diamonds: 500 ppmv inlet methanol concentration; Squares: 50 ppmv inlet methanol concentration

Figure 8 Photocatalytic Destruction of Methanol Using KSE Photocatalyst A



Note: Long-term photocatalyst stability test. Inlet methanol concentration approximately 500 ppmv; flowrate 5 lpm.

Figure 9 Photocatalytic Destruction of Methanol Using KSE Photocatalyst A

3.5 Discussion and Comparison of Results

There is excellent agreement between the small-scale and large-scale NREL tests. Although the reactors differed in flowrate, power, and volume by an order of magnitude, after accounting for these differences, the efficiencies of the two reactors differed by less than 5%.

The NREL photocatalyst showed significant thermal activity as well. For methanol, an order of magnitude increase in rate is seen when the reaction temperature is increased from approximately 40°C to approximately 70°C. This in turn leads to a significantly smaller reactor size for a given conversion. The steady-state reactor temperature for photocatalytic reactors (due to heat emitted by the fluorescent lamps) is approximately 40°C. Methanol has a very modest reaction exotherm, approximately 2°C per 100 ppmv methanol in the feed stream for complete destruction. However, the supplementary heat necessary to afford a 30°C increase in reactor temperature is significantly smaller than that needed to raise the temperature of the reactor to 350°C, the operating temperature of thermal catalytic systems. The requirement for this modest heating is due to the NREL catalyst's dual photocatalytic/thermal catalytic activity.

A qualitative comparison of the KSE, Inc. and NREL catalysts is seen in Table 1. The relative first order rate constants were determined by assuming first order kinetics. With this assumption, the rate constant is calculated as $\ln[C_{in}/C_{out}]/t_{res}$. A direct comparison between the two photocatalytic systems is very difficult, because the two systems used different light sources and very different catalyst formulations. Such a comparison is of limited utility without specific information regarding the reactor geometry, particularly the relative light intensities in different reactors. However, since all KSE experiments were performed using the same reactor geometry, comparisons among the KSE results are valid.

The relative performance of the KSE photocatalyst for treatment of a 500 ppmv and a 50 ppmv stream, as shown in Figure 8, is significant. The same photocatalyst shows significantly higher activity for the 50 ppmv stream than for the 500 ppmv stream. The KSE photocatalyst performs about 4X better on the 50 ppmv stream than on the 500 ppmv stream. Since these measures are taken from the same reactor system, their relative magnitudes are significant. The cause of the

higher activity at lower inlet methanol concentrations is probably due to methanol saturating the catalyst surface, which leads to a reaction rate largely independent of concentration. If the absolute reactivity (amount of pollutant destroyed per time) at the lower concentration run is the same as at the higher run, the activity of the lower concentration run is considered higher. This behavior, which has been seen in many photocatalytic studies, is indicative of complex reaction kinetics. Note also that the KSE photocatalyst shows no thermal activity; without illumination, no reactant destruction occurs.

4 SIZE AND COST ANALYSIS

SEMATECH's COO model was used to develop cost estimates for photocatalytic oxidation as a VOC control technology. The critical inputs to the COO model are the capital cost of the PCO reactor and the utility costs. The COO model assumes a number of standard multipliers to calculate the final ownership costs. The design basis used for the cost analysis was a 1000 scfm stream containing 500 ppmv methanol. The rationale for choosing this design basis was presented earlier.

4.1 PCO Cost Analysis

The kinetic data presented in the previous section were used to determine the size of a full-scale unit. NREL developed the capital and operating costs for the NREL photocatalyst system. In this report, as in previous work, NREL has used a literature correlation [8] between system power and total system cost. This correlation has been regarded as accurate by one of NREL's industrial partners. KSE, Inc. provided capital cost information for KSE's proprietary catalyst system.

The conceptual design of the NREL reactor is a 75 lamp system (each lamp 48" long, drawing 62 W), operating at 70°C. Such a reactor would have dimensions of approximately 4' x 4' x 4'. Very modest supplemental heating is necessary to achieve this operating temperature, as discussed previously. The reactor could be manufactured from fiberglass-reinforced plastic (FRP), with significant cost savings over a similar reactor made from stainless-steel. The cost of such a system would be approximately \$60,000. This is in agreement with both the literature correlation NREL has used in the past and an approximate calculation based on materials of construction and required construction labor hours.

KSE supplied a cost estimate for a 50 ppmv inlet methanol, 1000 CFM treatment system. The KSE cost estimate (like the two thermal catalytic oxidation quotes discussed below) does not include an amortized catalyst replacement charge. This charge, plus an annual charge for lamp replacement, would likely add 10–20% to the COO of the KSE system.

4.2 Comparison with Conventional Treatment Costs

NREL contacted suppliers to determine the relative costs of conventional VOC control technologies. They were given the design basis presented above and asked for quotes for capital costs and estimates of operating/maintenance costs. Table 2 lists the inputs to and the results from the SEMATECH COO analysis for the four treatment systems considered.

Table 2 Results of SEMATECH COO Analysis for 1000 CFM, 500 ppmv Methanol POU Treatment System Options

Quote Source		Capital Cost (\$K)	Electric Load (kW)	Fuel Load (MMBTU/hr)	COO (\$/scfm)
KSE, Incorporated	PCO	46	6.9	0	\$23
NREL	PCO	60	5.0	0.1	\$28
Wolverine (MA) Corporation	Thermal Catalytic	127	9.4	1.0	\$58
Alzeta Corporation	Thermal Catalytic	80	1.2	0.22	\$34

Note: Data from NREL and KSE are for PCO systems. Data from Wolverine and Alzeta are for thermal catalytic oxidation systems. KSE quotation data are for a 50 ppmv methanol treatment system.

For the design basis used, catalytic oxidation appears to be better than conventional technology for POU. Alzeta Corporation also manufactures adsorption systems using hydrophobic zeolites that could treat the 1000 scfm stream. However, company representatives recommended their catalytic oxidization systems because the relatively high methanol inlet concentration (500 ppmv) in the stream to be treated would result in a concentrated methanol stream from the zeolite regeneration step that was very close to the upper limit permitted for most industrial facilities (25% of the lower explosion limit [LEL]).

The catalytic oxidation units quoted by Wolverine Corporation (MA) and Alzeta Corporation have significantly different capital costs. The Wolverine unit is designed for installation in a more rugged environment than the Alzeta unit. Alzeta has a number of catalytic oxidation units installed in semiconductor manufacturing plants throughout the U.S. and is familiar with the semiconductor business. The differences in the capital cost quotes from Alzeta and Wolverine are due in part to slightly different assumptions on suppliers' parts. Both were asked to quote a system without a separate air handling system, but Wolverine included a 10 hp blower to move the air. The electricity used to run the blower accounts for most of the 9.2 kW needed for this system. The differences in fuel load are due to the differences in heat recovery efficiency. Both units exchange heat between the inlet and outlet streams, but the Alzeta unit is somewhat more efficient. Both of these quotes are to be considered preliminary. Both firms offered to provide a more detailed quotes, including explicit charges for catalyst replacement, based on an actual stream to be treated.

NREL had previously estimated the COO for photocatalytic oxidation based on its current photocatalyst to be approximately \$35,000 per thousand CFM treated. [9] The slightly smaller value in this report results from the change in the design basis from acetone to methanol; methanol is easier to photocatalytically treat, so the resulting treatment system is less expensive to purchase and to operate.

The conclusions regarding the relative costs of photocatalytic and thermal catalytic oxidation treatment systems should be viewed with caution. The thermal catalytic oxidation cost estimates are actual system quotes for readily available, existing systems. Thermal catalytic oxidation is a well-understood, widely used, robust technology that has been successfully used in many applications [10]. Photocatalysis is a new technology currently under development, so very long-term reliability and operating data are not yet available.

A direct comparison between thermal catalytic and photocatalytic oxidation technologies is very difficult. It is not NREL's intention to promote photocatalysis at the expense of thermal catalysis. However, the comparison above shows that photocatalytic oxidation may be a cost-competitive technology. These results are consistent with previous NREL studies [5].

5 CONCLUSIONS AND RECOMMENDATIONS

Both PCO and conventional technologies such as thermal catalytic oxidizers could be used in POU applications in the semiconductor manufacturing industry for emissions that do not contain HMDS. It is unlikely that the COO of such systems would be less expensive—on a per CFM basis—than conventional EOP treatment systems. Niche applications exist where a POU system is the most cost-effective solution when other factors, particularly installation costs, not currently well-captured by the SEMATECH COO model are included.

The detailed design and construction of PCO reactor assemblies for VOC destruction depends on detailed knowledge of the stream to be treated. Very specific information about the identity and concentration of the various pollutants, the flowrate of the stream, and the intermittence of the flow are critical to the design of the system.

These conclusions about the relative costs of photocatalytic and thermal catalytic oxidation treatment systems should be viewed with caution. The thermal catalytic oxidation cost estimates are actual system quotes for readily available, existing systems. The cost estimates for the photocatalytic oxidation systems are based on experimental data and costing methodologies developed by NREL and KSE for this report.

6 REFERENCES

- [1] C.S. Turchi, R. Rabago, *Benchscale Testing of Photocatalytic Oxidation (PCO) to Destroy Volatile Organic Compound (VOC) Emissions*, SEMATECH Technology Transfer Report #95042791A-ENG, April 28, 1995.
- [2] C.S. Turchi, R. Rabago, A. Jassal, *Destruction of Volatile Organic Compound (VOC) Emissions by Photocatalytic Oxidation (PCO): Benchscale Test Results and Cost Analysis*, SEMATECH Technology Transfer Report #95082935A-ENG, August 31, 1995.
- [3] C.S. Turchi, R. Rabago, A. Jassal, *Destruction of Volatile Organic Compound (VOC) Emissions by Photocatalytic Oxidation (PCO): Field Test Results*, SEMATECH Technology Transfer Report #96083084A-ENG, February 29, 1996.
- [4] AIChE Center for Waste Reduction Technologies, *Current and Potential Future Industrial Practices for Reducing and Controlling Volatile Organic Compounds*, American Institute of Chemical Engineers, New York, September 1992.
- [5] Turchi, C.S., E.J. Wolfrum and R.A. Miller, *Gas-Phase Photocatalytic Oxidation: Cost Comparison with Other Air Pollution Control Technologies*, "NREL/TP-471-7014, Presented at Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, Canada, June 25-30, 1994

- [6] *Federal Register*, 40 CFR Part 51, pp. 31633-31637.
- [7] J.R. Kittrell, C.W. Quinlan, J.W. Shepanyk, "Photocatalytic Destruction of Hexane Eliminates Emissions in Contact Lens Manufacture," Paper # ES96-51, AWMA Emerging Solutions to VOC & Air Toxics Control, Clearwater Beach, FL February 28-March 1, 1996.
- [8] J.R. Kittrell, C.W. Quinlan, E.K. Zimmerman, "Pentane Emissions Control by Photocatalytic Technology in the Expandable Polystyrene Industry," Paper # 95-FA146.04, Air & Waste Management Association (AWMA) 89th Annual Meeting and Exhibition, Nashville, TN, June 23-28, 1996.
- [9] R. Notarfonzo, W. McPhee, "How to Evaluate a UV/Oxidation System," *Pollution Engineering*, October 1994 pp. 74-76.
- [10] E.J. Wolfrum, SEMATECH ES&H PTAB Meeting, Austin, TX, May 1996.
- [11] R.M. Heck, R.J. Farrauto, *Catalytic Air Pollution Control: Commercial Technology*, New York: Nostrand Reinhold (1995).

**SEMATECH Technology Transfer
2706 Montopolis Drive
Austin, TX 78741**

<http://www.sematech.org>