CATALYTIC OXIDATION OF TRICHLOROETHYLENE AND PERCHLOROETHYLENE MIXTURES

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ABSTRACT

Catalytic oxidation is one of the demonstrated treatment alternatives currently available for treatment of air born contaminants. Halogenated hydrocarbons, however, have been difficult to treat by catalytic oxidation due to the poisoning effects of halogens on conventional catalysts. Improvements in catalyst technology using precious metal hybrid formulations have increased the capability to treat halogens. The recalcitrant nature of PCE has remained a challenge for catalytic treatment, until recently.

Allied Signal has recently developed a new formulation to address the challenge of oxidizing PCE. In January 1993 this new catalyst was installed and tested in an oxidizer at the Savannah River Site in South Carolina. The catalytic oxidizer was connected to a vapor extraction system treating a mixture of trichloroethylene (TCE) at a concentration of approximately 80 ppm and PCE at approximately 150 ppm.

Results of this operation verify the effectiveness of the new catalytic material in treating halogenated compounds in general, and PCE in particular.

CATALYTIC OXIDATION OVERVIEW

Catalytic Oxidation is a technology that has been used since the early 1970's for the control of volatile organic compounds (VOCs) emanating from a wide range of industrial applications. This technique involves heating the contaminated air to temperatures ranging from 500 to 900°F. The exact temperature depends on the contaminant to be removed. The heated air is passed over a catalytic material which causes the contaminants to oxidize them completely, at temperatures lower than would be possible with thermal oxidation.

Typically the catalyst materials come from the noble metals group. Platinum has been commonly used either by itself or in combination with other noble metals. Palladium has also been used.
Title III of the 1990 Clean Air Act identifies 189 hazardous compounds as Air Toxics and requires implementation of control technologies to reduce their emissions. Of the 189 hazardous compounds, 154 can be oxidized catalytically. These compounds can be organized into four main categories:

- **Hydrocarbons**
  - example: benzene
- **Halocarbons**
  - example: trichloroethylene
- **Nitrogen Compounds**
  - example: hydrogen cyanide
- **Oxygen Compounds**
  - example: formaldehyde

Catalytic oxidation converts these compounds to safer end products (carbon dioxide, water vapor, nitrogen, oxygen, and hydrogen chloride).

Traditionally, catalysts have been vulnerable to deactivation from several groups of poisons. One of these groups, the halogen elements, is referred to as suppressants, and can interfere with the kinetics of the catalytic reaction and deactivate it. This has made TCE and PCE difficult compounds to treat with a catalytic oxidizer unit.

Halogenated compounds have affected the long term durability of the catalyst materials, and inhibited short term performance. Recent innovations in the development and design of catalysts include formulations that are resistant to deactivation.

The recalcitrant nature of PCE has made it one of the most difficult materials to oxidize. Allied Signal has conducted extensive research in this area and has developed a new formulation of catalyst which, according to Allied Signal, oxidizes PCE in an efficient and cost effective manner.

**TEST PROCEDURES**

At the Savannah River Site (SRS) in South Carolina, the Westinghouse Savannah River Company (WSRC) is field-testing many technologies for use in remediating soil, groundwater and air contaminated with TCE and PCE. This testing is being done under the Integrated Demonstration Project. The best technologies will be used in future full-scale remediation systems at SRS.

One of the field tests was for Methanotrophic Bioremediation of TCE. This complex project tests a variety of new technologies, including horizontal wells, air sparging, vapor-phase injection of nutrients, and cometabolic bioremediation. Also tested was a catalytic oxidation treatment method for TCE and PCE-contaminated vapors produced from the vapor extraction system which were part of the methanotrophic
bioremediation project.

The on site equipment consists of an air/methane injection system and a vapor extraction system. The vapor extraction system consists of a vacuum blower and an off-gas treatment system. The vacuum blower pulls 240 SCFM of air at -10 Inches Hg, from a horizontal well. This airstream contains PCE (approximately 150 ppm) and TCE (approximately 80 ppm). The vapor enters an oxidizer where it passes over the catalytic material. There is a Kilowatt Hour Meter dedicated to this oxidizer which monitors electrical use, and there is no primary heat recovery unit. This system is illustrated in Figure 1.

Gas samples were taken daily before the blower and at the exhaust stack. These samples were analyzed on site by a field laboratory. The equipment used for the analytical work consisted of a Hewlett-Packard Gas Chromatograph model 5890. The system has a packed column connected to a thermal conductivity meter for analysis of methane and CO₂, and a capillary column connected to a flame ionization detector for analysis of volatile organic compounds (TCE, PCE, vinyl chloride, dichloromethane, and dichloroethylene). All of the process equipment and the on site laboratory was designed, installed, and operated during the term of the project by ECOVA Corporation, an environmental services company located in Redmond, Washington.

To test the catalytic oxidation of TCE and PCE a new formulation of Allied Signal’s HDC catalytic material was installed in the oxidizer on January 21, 1993. ECOVA operated the oxidizer with the new catalytic material from January 21 to April 30, 1993. The material consisted of four beds of catalyst, each one identical to the drawing in Figure 2.

RESULTS

Oxidation Efficiency

After installation, considerable attention was given to optimizing operating conditions. This primarily meant determining the minimum oxidizer temperature at which effluent concentrations of chlorinated hydrocarbons would meet discharge requirements.

Table 1 shows the results obtained during the three months of testing. Initially, poor reduction efficiency was obtained for PCE because temperatures were low. Over a period of several days the oxidizer temperature was incrementally raised and samples taken to analyze
conversion efficiency. This resulted in reduction efficiency for PCE of 95% or better for the duration of the test period. TCE was oxidized below detectable limits (5 ppm) at a temperature of 750°F. Table 2 shows the same data as Table 1, only sorted by catalyst temperature.

PCE required temperatures of 825°F, before effluent concentrations were below detectable limits. All daughter products of incomplete combustion were below detectable levels.

**Energy Efficiency**

Table 3 shows the electrical power usage per day for the oxidizer. Prior to January 21, 1993, the system was operated in a thermal mode. After the new catalytic material was installed, the oxidizer temperature was lowered from 1500°F to approximately 825°F.

Electrical consumption per day during the thermal mode was approximately 2000 KWHR. While operating in the catalytic mode, electrical consumption per day was approximately 1000 KWHR.

**Life Time Expectancy**

The duration of this test was just slightly over three months. This is insufficient time to establish expected useful lifetimes.

Currently, Allied Signal is conducting laboratory tests on this material to confirm useful life. The warranted temperature of this material is 900°F, and long term tests are being performed that monitor destruction efficiency at approximately 1000°F.

**CONCLUSIONS**

This particular catalyst successfully achieved efficient oxidation of PCE. Because destruction of PCE has been difficult in the past, determining this ability was of primary importance.

Halogen suppression was not a problem. Suppression occurs when the halogens interfere with the kinetics of the catalytic oxidation reaction. If this were to occur, the suppression would be evident immediately. Since reduction efficiency was in excess of 95%, this past problem with catalysts does not appear to be a factor.

The catalyst has not been in use long enough to establish, with confidence,
an expected useful life. Because other similar catalytic materials for treating TCE have demonstrated economically efficient life expectancies, determining this aspect of the new catalysts performance abilities was of less importance than reduction efficiency.

At $0.03/KWHR, (the cost of electricity at SRS) use of this oxidizer cost approximately $30.00 per day.

This catalytic material appears to have useful applications in the remediation of sites contaminated with PCE. It achieves good reduction efficiency and does not seem to suffer from halogen suppression. Currently, it is being considered for use at SRS for full scale treatment systems.