INCINERATION OF POLYCHLORINATED BIPHENYLS

A. F. Pier
Corporate Engineering Division
Monsanto Company
St. Louis, Mo.

Introduction

Polychlorinated biphenyls (PCB's), manufactured by Monsanto Company, have many good qualities. They're versatile, stable, and non-combustible under normal conditions of use.

It wasn't until the late '60's - with the revolution in analytical procedures and improved detection methods - that we found out this wasn't the whole PCB story. Preliminary evidence showed that PCB's were accumulating in the environment and having adverse effects. Further research confirmed that the more highly chlorinated biphenyls are not readily biodegradable and disappear from the environment slowly.

At that time, PCB's were sold primarily as transformer fluids under the trade name Aroclor, Inerteen, and Pyranol, and as heat transfer fluids under the trade name Therminol FR. It became evident to us that we had several things to do:

discontinue any PCB sales where product use involved danger of loss to the environment;

ensure that any PCB's we did sell were for "closed systems" only, where there was no danger of loss to the environment;

develop a method of destroying PCB's after they were used.

Thus, we discontinued all Therminol FR sales. We restricted any PCB sales to "closed systems", such as transformer fluids. And this paper deals with the last program, destroying waste PCB's.

Destroying PCB's

Incineration, of course, was the most obvious method to try. As I said, Aroclors and Therminols do not support combustion under normal conditions of use. But, laboratory tests showed these materials could be burned in a bench-scale refractory-lined

incinerator, if it were preheated to a temperature of 1800° to 2000°F and some auxiliary fuel added.

Development of Incineration Technique

In March, 1970, tests were run on Aroclor 1242 (42% chlorine) and Aroclor 1260 (60% chlorine) in the John Zink Company pilot plant thermal oxidizer at temperatures of 1600, 1800, and 2000°F. Both Aroclors were burned successfully, although the 1260 required auxiliary fuel to maintain a stable flame. Samples of the flue gas were analyzed for PCB's, HCl and chlorine. High levels of destruction of the PCB's were achieved, and the formation of chlorine, which would be more difficult to scrub out of the flue gas than HCl, was low.

In May, 1970, further tests on Aroclor 1260 were run to determine the effects of higher temperatures. The thermal oxidizer was operated at 2000, 2400, and 2800°F and at residence times of 1.2 to 1.9 seconds. As expected, the level of destruction of the Aroclor 1260 was higher than that attained in the March test, and chlorine levels in the flue gas remained low.

Installation of Full-Scale System

Based on the pilot plant results a system to burn 1250 pounds per hour of PCB's was designed and installed at Monsanto's Sauget, Illinois, plant. The full scale system consists of a Thermal oxidizer, a quench pot, a Venturi scrubber to remove particulate, and a packed scrubber to remove HCl. This system is shown in Figure 1. The thermal oxidizer section is designed to operate at a temperature of 2200 to 2800°F and a residence time of 2.5 seconds. Water is used as the quenching and scrubbing liquor. The scrubber system was designed to meet the following requirements on emissions to the atmosphere:

HCl	5 lb/hr. maximum
Cl_2	50 ppm maximum
Particulate	.05 gr/scf maximum

The scrubber system has consistently operated well within these limits.

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The design rate of 1250 pounds per hour has been attained for short periods of time. However, the average operating rate, for reasons noted below, has been about 900 pounds per hour.

Operation of the System

The incinerator system was designed to destroy wastes which contain a high percentage of Aroclors, and which have heats of combustion ranging from9000 BTU per pound for Aroclor 1242 to 6000 BTU per pound for Aroclor 1260. However, much returned waste contains large percentages of hydrocarbon solvents used to flush out heat transfer systems. These solvents have heats of combustion of about 17,000 BTU per pound. Since the incinerator has a constant capacity for heat release, the capacity for solvents on a pound basis is correspondingly reduced.

Early in the operation of the incinerator system, the scrubber liquor and the scrubber off gas were monitored for PCB's to determine the level of destruction. At operating temperatures above 2200^{o}F essentially all of the PCB's are destroyed. Current practice is to operate the oxidizer at 2500^{o}F to provide a wide margin of safety.

Mechanical Problems

A number of mechanical problems were encountered in the startup and operation of the oxidizer-scrubber system, primarily with the refractory lining in the oxidizer and the polyester lining in the scrubber. The refractory originally installed in the burner plenum and the oxidizer chamber was a high chrome basic brick. A basic brick was selected to resist attack by the lime present in some of the waste materials as well as the chlorine and HCl released in the combustion of straight chlorinated hydrocarbons.

The unit was started up on waste PCB's containing no lime. After one month of operation, the brick lining showed general deterioration, sanding, and loss of strength, with spalling in localized areas. Analysis of the brick (Fig. 2) showed severe losses of MgO and S_2O_2. It was concluded that the brick was

being attacked by chlorine or phosphorous in the oxidizer atmosphere. Phosphorous is not a normal component of Aroclors, but is believed to have been in some of the waste received.

Since the predicted life of the original refractory was low, a search was started for a brick that would give better service. Samples of alumina brick containing from 70 to 90% Al_2O_3 were tested in the furnace. The samples were exposed to chlorine and HCl gases released from the PCB's during the test period, but were not exposed to any lime. Under these conditions, the alumina brick was much more resistant to attack than the basic brick. The resistance increased at higher alumina levels. When the present brick lining reaches the end of its effective life, it will be replaced with 90% alumina brick.

The packed scrubber column is constructed of polyester lined steel. After a month and a half of operation, there were a number of failures in the polyester lining. Inspection disclosed that there was no chemical attack on the liner, but that large areas had disbonded from the steel shell. Visual and microscopic examination of the shell revealed that the surface had not been properly sandblasted prior to application of the lining. The original lining was removed, the interior surface were sandblasted, and a new polyester lining applied. The new lining has maintained its bond to the shell, and only minor repairs have been required.

The original lining was also eroded at the flue gas inlet nozzle. It was concluded that the erosion was caused by small particles spalled from the brick in the oxidizer and trapped in the water in the quench pot. In the original installation, water from the quench pot was used as make-up for the Venturi scrubber as shown in Figure 3. Water containing the brick dust was accelerated to a high velocity in the Venturi scrubber and impinged on the wall of the packed scrubber column. The problem was solved quite simply by using water only from the bottom of the scrubber column to supply the Venturi.

Operating Permit Requirements

The incinerator system is operated under a permit from the Illinois Environmental Protection Agency, which places limits on emissions of PCB's, HCl, chlorine, and particulate.

Under the terms of the permit, continuous monitoring of HCl and chlorine emitted from the scrubber stack is required. Statistical studies of the data obtained show that the unit is operating well within the permit levels of five pounds per hour HCl and 50 ppm chlorine. For example, an analysis of 64 readings of chlorine levels gave the following results:

Average, $\bar{x}$ = .7158 ppm
Standard Deviation, $\bar{\sigma}$ = .2072
$3\bar{\sigma}$ = .6216
99% Confidence interval, 1.3374 ppm

The 99% confidence level states that there is a 99% probability that the emission of chlorine will be less than 1.3374 ppm, well below the 50 ppm specified in the permit.

In addition, under the terms of the permit, pilot plant tests are required on the incineration of any new waste materials before they can be fed to the plant incinerator. Tests on several additional wastes have been carried out in the John Zink Company pilot unit. The cost of a pilot plant test ranges from $3000 to $5000 depending on the amount of sampling and analytical work required.

Conclusions

In conclusion, we were successful in developing a method of destroying PCB's. The thermal oxidizer scrubber has performed well in achieving high levels of destruction and in controlling losses of particulate, chlorine, and HCl to the atmosphere.

We have made a great deal of progress in solving our mechanical, refractory, and corrosion problems. But our challenges remain in the areas of high maintenance costs and low on-stream time. The current charge to our customers for incinerating PCB's of 3¢ per pound is close to the actual operating cost.

In essence, then, we're getting the job done very effectively. But, as with many environmental-control problems, we found once again that solutions are expensive, time-consuming, and based primarily on a strong technical effort.

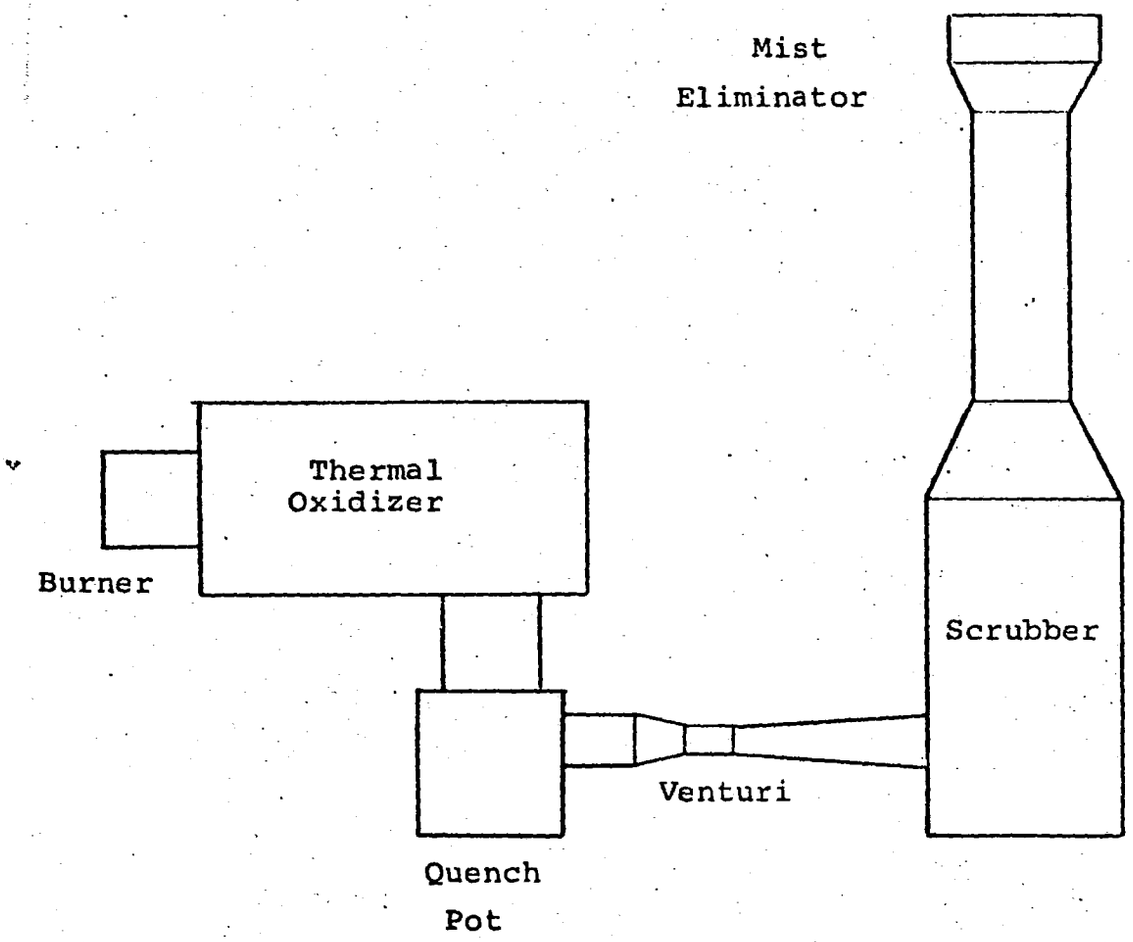

Fig. 1 - Oxidizer - Scrubber System

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Component	Original Analysis wt. %	Hot Face Analysis wt.%
MgO	39-42	20.5
Fe_2O_3	9.5-11	7.6
Cr_2O_3	21-23	27.4
CaO	0.5-1	.12
SiO_2	4.5-5.5	.20
Al_2O_3	20-22	40.6
P_2O_5	0	3.5

Fig. 2 - Analysis of Initial Brick Lining

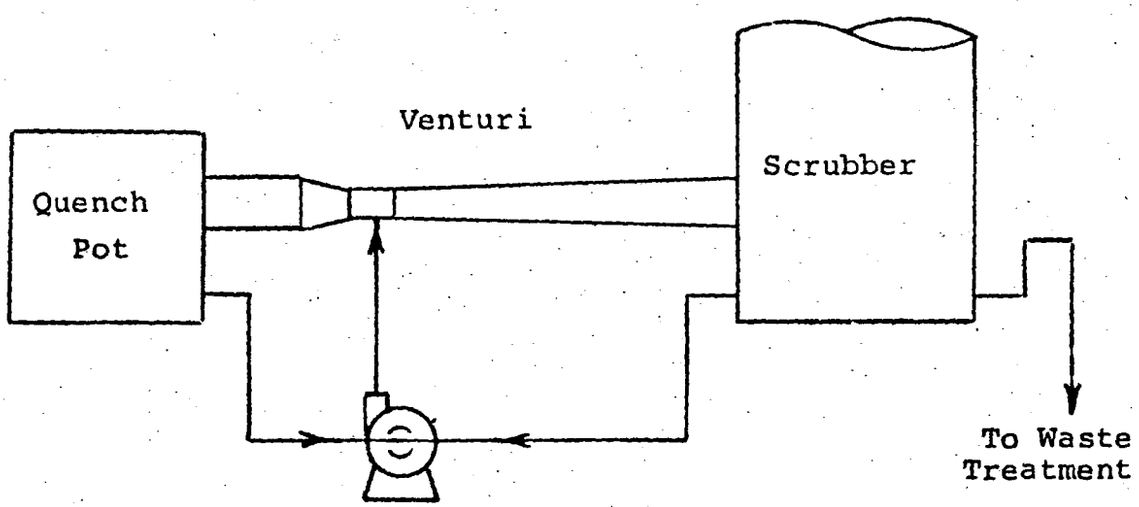

Fig. 3 - Scrubber Water System

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