

## THE PREVENTION OF DIOXIN FORMATION IN WASTE INCINERATION

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### Introduction

Waste incineration is one of the major contributors to atmospheric dioxin/furan (PCDD/F) levels. Paradoxically, incineration is the most widely used method of destroying dioxins. Nevertheless, dioxins do form in incinerator flue gas by way of a regeneration process. As the combustion gases cool below 300-400°C, trace dioxin precursor compounds are concentrated by adsorption on fly ash. The adsorbed compounds are then converted to dioxins by reaction with metal chlorides in the ash<sup>(1,2,3)</sup>. A fraction of the dioxins that form on the ash vaporize to the stack gas; the rest remain in the ash.

Powdered activated carbon (PAC) is widely used to adsorb dioxins from the waste combustion gases. In industrial practice, both powdered lime (for acid gas neutralization) and PAC are injected into the flue gas. These are removed, along with the fly ash, by either a fabric filter or an electrostatic precipitator. Conventional PAC is a catalyst that promotes the formation of dioxin, and the total amount of dioxin generated (gas + ash) is greatly increased by PAC<sup>(4)</sup>. The USEPA field test data cited<sup>(4)</sup>, show that activated carbon generates five times as much dioxin in the ash as would be present without it. This is not surprising, given the fact that PAC is normally made from coal, and can contain as much as 20% ash along with reactive and catalytic transition metals. The object of this study was to develop a transition metal-free PAC that would resolve the problem of contaminated ash and also prevent the formation of dioxins in waste incineration flue gas.

### Experimental Method and Materials

From a study of the role of PAC, it was concluded that a more appropriate sorbent than PAC would be one that was transition metal-free, so that dioxin formation from the adsorbed organics would be prevented. An activated carbon was therefore prepared by treating PAC to remove halogen acid-reactive metals to obtain a modified PAC, called "Diox-Blok". In March 2001, a series of stack tests were made at the K municipal waste (MSW) incinerator in Korea, comparing the effect of the injection of PAC with "Diox-Blok" on PCDD/F formation. Tests were made injecting "Diox-Blok" at two dosage rates, 0.5 kg/ton of waste burned (1.75 kg/hr) and 1.0 kg/ton waste (3.3 kg/hr). Analyses were made for (PCDD/F) and also the dioxin precursor compounds, chlorobenzenes and chlorophenols.

The K MSW flue gas system comprised a waste heat boiler, followed by a baghouse fabric filter. Flue gas treatment consisted of lime injection for acid gas neutralization and PAC injection. In flue gas treatment systems, a PCDD/PCDF congener shift usually occurs, resulting in an increase in toxic equivalents (ITEQ)<sup>(5)</sup>. Accordingly, base-line tests were made using lime injection alone, without PAC or "Diox-Blok" addition, to establish reference emission levels..

## Results and Discussion

The results of the stack test analyses for PCDD/F and the dioxin precursor compounds are presented in Table I:

**Table I**

Results of K Incinerator Stack Tests  
Dioxin and Dioxin Precursor Emissions

Test	Dosage Kg/ton	PCDD/F ng/Nm <sup>3</sup>	ITEQ ng/Nm <sup>3</sup>	% ITEQ Removal	Precursors* ng/Nm <sup>3</sup>
Lime only		3.42	0.134	97.5	947.33
Diox-Blok	0.5	1.38	0.025	99.2	610.24
Diox-Blok	1.0	0.44	0.012	99.8	354.79
PAC	1.0		0.060		

\*Analyzed Precursors: Chlorbenzenes and Chlorophenols

The base-line stack emission value for lime injection-only was 3.4 ng/Nm<sup>3</sup>, equivalent to an ITEQ removal efficiency of 97.5%. This dioxin control efficiency is notably higher than has been previously been reported for lime-injection-only baghouses operating on municipal or medical waste incinerators. A review revealed that the K baghouse operates at temperature of 130°C, which is a much lower temperature than the 200°C used in conventional baghouse design. The effect of the lower temperature on dioxin removal is equivalent to a "rapid quench" for the flue gas, a known method for lowering dioxin formation.

The "Diox-Blok" was very effective in reducing the already low dioxin emissions. At a dosage rate of 1.0 kg/ton waste burned, "Diox-Blok" gave a 91% reduction in the initially low 0.134 ng/Nm<sup>3</sup> of the base lime-only run

Also of note is the fact that, at a dosage rate of 0.5 kg/ton waste, "Diox-Blok" gave an ITEQ of 0.025 ng/Nm<sup>3</sup>, as compared to an ITEQ of 0.06 ng/Nm<sup>3</sup> for PAC at 1.0 kg/ton waste. In other words, at half the dosage rate of PAC, "Diox-Blok" gave a 40% lower ITEQ emission than PAC.

The primary function of "Diox-Blok" is not to adsorb dioxins after they have been formed, but to prevent their formation. This is accomplished by preferential dioxin precursor adsorption. "Diox-Blok" is injected into the gas at a point where adsorption by fly ash would normally begin. Because the "Diox-Blok" has a far greater adsorption area and capacity for precursor compounds such as the chlorophenols and chlorobenzenes than does the fly ash, it minimizes or blocks adsorption by the fly ash. Because the halogen-acid reactive metals have been removed from the

“Diox-Blok”, dioxin formation from the adsorbed precursors does not occur. It therefore follows that the use of “Diox-Blok” should show enhanced dioxin precursor removal from the flue gas, and also reduced baghouse discharge ash content.

As per Table I, analyses of the likely dioxin precursor compounds, chlorophenols and chlorobenzenes, present in the gas, showed reductions of 1/3 and 2/3, at the two respective “Diox-Blok” dosage rates, compared to the lime-only reference run. These data may be taken as partial verification of the theoretical basis for the use of the fly ash competitive adsorption approach. However, of more importance is the reduction of dioxin levels in the baghouse discharge ash. Disposal of this contaminated material is a problem.

Baghouse ash is a fine, easily-dispersed low-density powder. Consequently, unless the solids are treated and consolidated before being sent to a landfill, any dust can become a readily-inhalable, dioxin-loaded, PM<sub>10</sub> constituent. While gaseous toxics in stack emissions are diluted and dissipated, contaminated dust can vector dioxin concentrates directly to human lungs. Thus, the effect of “Diox-Blok” on the dioxin content of the ash was of direct interest. The results of the ash analyses for the Table I test data are given in Table II.

**Table II**  
K Incinerator Stack Tests  
Dioxin Content of Baghouse Ashes

Test	Dosage Kg/ton	PCDD/F Ng/g	ITEQ ng/g
Lime only		309.70	12.085
Diox-Blok	1.0	95.13	5.02

With a dosage rate of 1.0 kg/ton of waste burned, “Diox-Blok” reduced the PCDD/F ash content by 69% and the ITEQ content by 58.5%. In view of the fact that conventional PAC acts to multiply the ash dioxin content by factors of up to 5, the significant decrease in ash dioxins obtained with “Diox-Blok” clearly differentiates it from PAC. “Diox-Blok” is now in commercial use in incinerator emission control systems in the U.S., New Zealand and the U.K..

**References:**

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