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Prevention of Dioxin Formation in Medical Waste Incineration

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Introduction

The original Beco incineration emission control technology was developed in 1985 for a toxic metal fluoride/chloride fume incinerator at a large glass company in Tennessee. The process consisted of a "dry/wet" scrubbing sequence in which the incinerator off-gas was cooled, contacted with an alkaline powder, baghouse-filtered, and then wet-scrubbed for final removal of traces of acid gases. The process, with several improvements, was next applied to a medical waste incinerator (MWI) at Hamot Medical Center at Erie, Pennsylvania, in 1989.

Annual Hamot Medical stack testing was required by the Pennsylvania State DER, and this gave a continuing data base on dioxin and mercury emissions. These data, as well as extensive EPA field test data on MWI emission control (1) systems allowed analysis of the effect of various air pollution control system parameters on these emissions. The results of this Beco effort were reported in several AWMA and seminar papers covering a four-year period (2-4). The investigation of the chemical behavior of dioxin formation has led to the development and patenting of a method for preventing the formation of dioxins and furans in cooling of waste incineration combustion gases, a method and sorbent now called "Diox-Blok". This paper will review the development and application of the "Diox-Blok" method for prevention of dioxin formation. For the purposes of this paper, the polychlorinated dibenzo dioxins, comprising the tetra- through the octa-chlorinated homologs, and the polychlorinated dibenzofuran analogs, will be generically referred to simply as "dioxins".

The "Diox-Blok" method of preventing dioxin formation was necessarily based on data on the reaction chemistry and a postulated mechanism of formation. Chemically, dioxins are formed from aromatic precursor compounds such as chlorobenzenes, chlorophenols, polychlorinated diphenyl ethers, polychlorinated biphenyls, benzo-furans, and benzo-dioxins, all of which may be referred to as "pre-dioxins".

In order to distinguish among the published formation mechanisms for the polychlorinated dioxins and furans, and claims for their removal, it is helpful to know the physical state of the dioxins and their chemical precursors in incinerator flue gases. Figure 1 shows the vapor pressure curve for 2,3,7,8-tetrachlorodioxin (TCDD), the most toxic of the dioxin compounds,

plotted from the data of Rordoff (5). To condense TCDD, the partial pressure would have to be greater than that shown by the curve. However, the range of TCDD concentration associated with the burning of medical and municipal wastes (6,7) is also shown. It is obvious that the concentration of TCDD in combustion gases is many orders of magnitude less than the vapor pressure curve. Therefore, the TCDD in combustion gases can exist only as a gas or an adsorbed phase, i.e., "vapor or particulate form".

If the dioxins themselves exist only in gaseous form, even at low temperatures, then the lower molecular weight pre-dioxin compounds must also be gases. The concentration of both the pre-dioxins and dioxins in the cooled combustion gases is in the microgram or nanogram per cubic meter range. At these dilute chemical concentrations, it is virtually impossible for the chemical formation of dioxins to occur in the gas phase. The law of mass action indicates that chemical reactions involving these trace gas quantities would be so kinetically slow that they could not take place to any extent in the very short time the gas remains in the combustion exhaust train.

Concentration of Pre-Dioxins

For dioxin-generating reactions to occur, a means must exist for gathering and concentrating the pre-dioxins into sufficient concentrations for these compounds to react. It is fairly well-established that fly ash serves the necessary adsorption-concentrator function for dioxin generation (7, 8). As the gas cools to a favorable adsorption temperature, generally below 300°C, precursor compounds are adsorbed and concentrated by the fly ash. It has also been shown by Altwicker (8) that the carbon fraction in the fly ash can itself be a source of the pre-dioxin organic compounds, particularly at higher post-combustion temperatures. Thus, the fly ash can serve as both a generator of organic compounds and a concentrator for these compounds.

Dioxin Formation Mechanisms

While the fly ash provides the organic reactants and conditions necessary for dioxin formation, both the formation of the pre-dioxins and their conversion to dioxins requires a chlorination reagent. This reagent is hydrochloric acid; in the absence of hydrochloric acid gas in the combustion gases, dioxins are not formed. However, the evidence indicates that HCl is not the direct chlorinating reagent. With chemical quantities near the limits of measurement, it has been difficult to determine the precise chlorination chemistry. In consequence, there have been an abundance of theories, most of which involve "catalytic" mechanisms. The evidence supporting catalytic formation is indirect, and none of the catalytic theories has led to any practical means for controlling dioxin formation.

Fundamental studies by Hoffman, Eiceman and co-workers (10) have shown that post-combustion dioxin formation on fly ash proceeds by direct chemical reaction. The final dioxin reaction involves chlorination of adsorbed aromatic pre-dioxins, through an intermediate inorganic compound. Hoffman and Eiceman showed that the active chlorinating agent was ferric chloride, FeCl_3 , formed by reaction of HCl with the surface atoms of iron contained in the fly ash structure. Experiments showed that the amount of aromatic chlorination was exactly equal to the

amount of the reduction of FeCl_3 to unreactive Fe^{+2} . Thus, the reaction appears to be stoichiometric, not catalytic. The relationship between fly ash iron content and dioxin formation was confirmed by Glasser, et al.. (11). These investigators measured the emissions for many hospital incinerators in California, and found that the higher the iron content of the fly ash, the higher the dioxin content of the flue gas.

If dioxins are manufactured in the fly ash "factory", their transfer to the gas phase would appear to be the result of a desorption or "distillation" process. As the rate of dioxin generation increases with decreasing temperature, the fly ash adsorption capacity goes to saturation. The dioxin congeners distill over in the order of their fugacities, so that the lower molecular weight dioxin congeners would preferentially transfer to the gas phase. Assuming transfer to be an equilibrium process, this fractionation process would tend to enrich the gas phase in the lower molecular weight, more toxic, dioxins, but also leave significant residual dioxin content in the fly ash.

Control Methods

There are two general approaches to dioxin control: (a) preventing the gaseous emissions of dioxins to the stack, and (b) prevention of dioxin formation. The most widely used current method of control of gaseous dioxin emissions from waste combustion processes is carbon adsorption. This has taken various forms, including fixed and moving carbon beds, but the most conventional method is injection of fine powdered activated carbon, either dry, or with a lime slurry in spray-drying neutralization of HCl.

Activated Carbon

Activated carbon is now in fairly widespread use as an adsorbent of dioxins from flue gas, post-formation. Figure 2 is a plot of EPA field test data for a 700 lb/hr MWI incinerator, equipped with a dry lime injection/fabric filter APC system. As can be seen, activated carbon is a fairly effective sorbent for removing dioxins from the gas. However, Figure 2 is an incomplete and misleading description of the total system; it portrays only the transfer of gas-phase dioxins to solid-phase adsorbed dioxins.

Although Figure 2 shows activated carbon to provide excellent dioxin adsorption capability, the carbon also has a very unfortunate multiplying effect on the total amount of dioxin in the system (gas + baghouse discharge + ash). Activated carbon results not only in a dioxin-contaminated baghouse discharge and total ash, but also in a highly increased dioxin "make" for the total system. USEPA field test data (Figure 3) show that, while it may remove dioxins from the gas, activated carbon generates five times as much dioxin in the ash as does zero carbon usage. This is not surprising, given the fact that activated carbon is normally made from coal, and can contain as much as 20-25% ash. The coal ash provides all the reactive transition metal oxides necessary for indirect chlorination via HCl.

As Figure 3 shows, the total dioxin content of the system increases with increasing carbon usage. Obviously, if the dioxins are not reporting to the gas, the excess dioxins made by activated carbon are retained by the carbon. As anyone knows who has handled powdered activated carbon, the material is a very fine, easily-dispersed low-density powder. Consequently, unless the ash is treated and consolidated before being sent to a landfill, the highly-fugitive carbon dust can become a readily-inhalable, dioxin-loaded, PM₁₀ constituent. Gaseous toxics in stack emissions may be diluted and dissipated, while contaminated dust can vector dioxin concentrates to human lungs.

"Diox-Blok" Sorbent

The basic difficulties with activated carbon are: (a) it operates too late in the process, removing dioxins only after they have been formed by the fly ash, and (b) it contains reactive metal oxides and itself becomes a dioxin generator. From a study of the field data, it was concluded that a more appropriate sorbent would (a) remove the pre-dioxins, and (b) not contain chlorinatable metal oxides.

Because fly ash is the chemical "factory" where dioxins are made, preventing the dioxin precursor compounds from adsorbing on the fly ash would abort the dioxin formation process. A simple method of accomplishing this is to deliberately add a sorbent material having higher area and more active sorption capabilities than fly ash to the gas at temperatures above the precursor adsorption temperature "window". Most importantly, such sorbents would be relatively free from the transition metals that are capable of forming reducible chlorides. This defines the necessary properties of a "Diox-Blok" sorbent.

"Diox-Blok" is a modified sorbent specifically formulated to adsorb dioxin pre-dioxins. The action of "Diox-Blok" to prevent dioxin formation by adsorption of precursors is predicated on fly ash as the PCDD/F factory. By using a sorbent with more active area than the fly ash for competitive adsorption of the precursors as the gas cools down through the adsorption temperature "window", the precursors are kept off the fly ash. "Diox-Blok" accomplishes two things: (a) the fly ash is "starved" of organic reactants, and (b) the chemically inert "Diox-Blok" prevents conversion of its adsorbed organic compounds to dioxins. Unlike activated carbon, "Diox-Blok" does not cause dioxin-contaminated ash problems. Because the concentration of dioxin precursors in flue gas is extremely low, only nominal injection rates of "Diox-Blok" are required, of the order of 0.5-1 lb/ton of waste burned.

Field Results

Beginning in 1993, "Diox-Blok" technology was incorporated in Beco "Alka/Sorb" dry/wet emission control trains built for three regional 20 tonne/day biomedical waste incineration units in the United Kingdom. Over the last four years, the effective suppression by "Diox-Blok" of

dioxin formation has been repeatedly verified in all of these units. Table I lists the stack test data for one of these installations, King' s College Hospital, London. The results shown for the dioxins (PCDD/PCDF) are for two successive years, 1994 and 1995.

Stack tests at all three regional medical waste incineration plants, including King' s College, have shown the dioxin level to be consistently at 0.006 ng/DSCM, NATO TEQ, 11% O₂. This is just twice the minimum detection level of 0.003 ng/DSCM. These results were obtained at a "Diox-Blok" sorbent feed rate of only 1 lb/ton of waste burned. Tests with varying sorbent feed rates established that reduction of "Diox-Blok" to 0.5 lb/ton increased dioxin/furan stack emissions to only 0.02 ng/DSCM, still well below the EU mandated level of 0.1 ng/DSCM NATO TEQ. This value compares with an activated carbon feed rate of 3 lbs/ton (1) for equivalent dioxin stack emissions.

Effects Of System Design On Dioxin Formation

The excellent field results of the use of "Diox-Blok" were obtained in an air pollution control system, the "Alka/Sorb" Process, specifically designed to avoid secondary dioxin generation. This process is shown schematically in Figure 4. Design attention was given to material selection to avoid corrosion in the low temperature regions of the gas treatment train. In corroded systems, iron oxide surfaces can supplement and substitute for fly ash as a dioxin generator. Iron oxide provides both a dioxin precursor adsorption medium together with a reactant, Fe₂O₃, for low-temperature reaction with HCl. Some of the system design aspects that have to be implemented to minimize secondary dioxin formation and to optimize the use of "Diox-Blok" include:

1. Minimization of metallic iron and iron compounds in the waste burned.
2. Rapid quench of the hot gas, for example, in a waste heat boiler or spray drier.
3. Corrosion-resistant boiler tubes.
4. Corrosion-resistant materials for equipment at temperatures below 300oC.

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FIGURE 1
VAPOR PRESSURE OF 2,3,7,8-TCDD

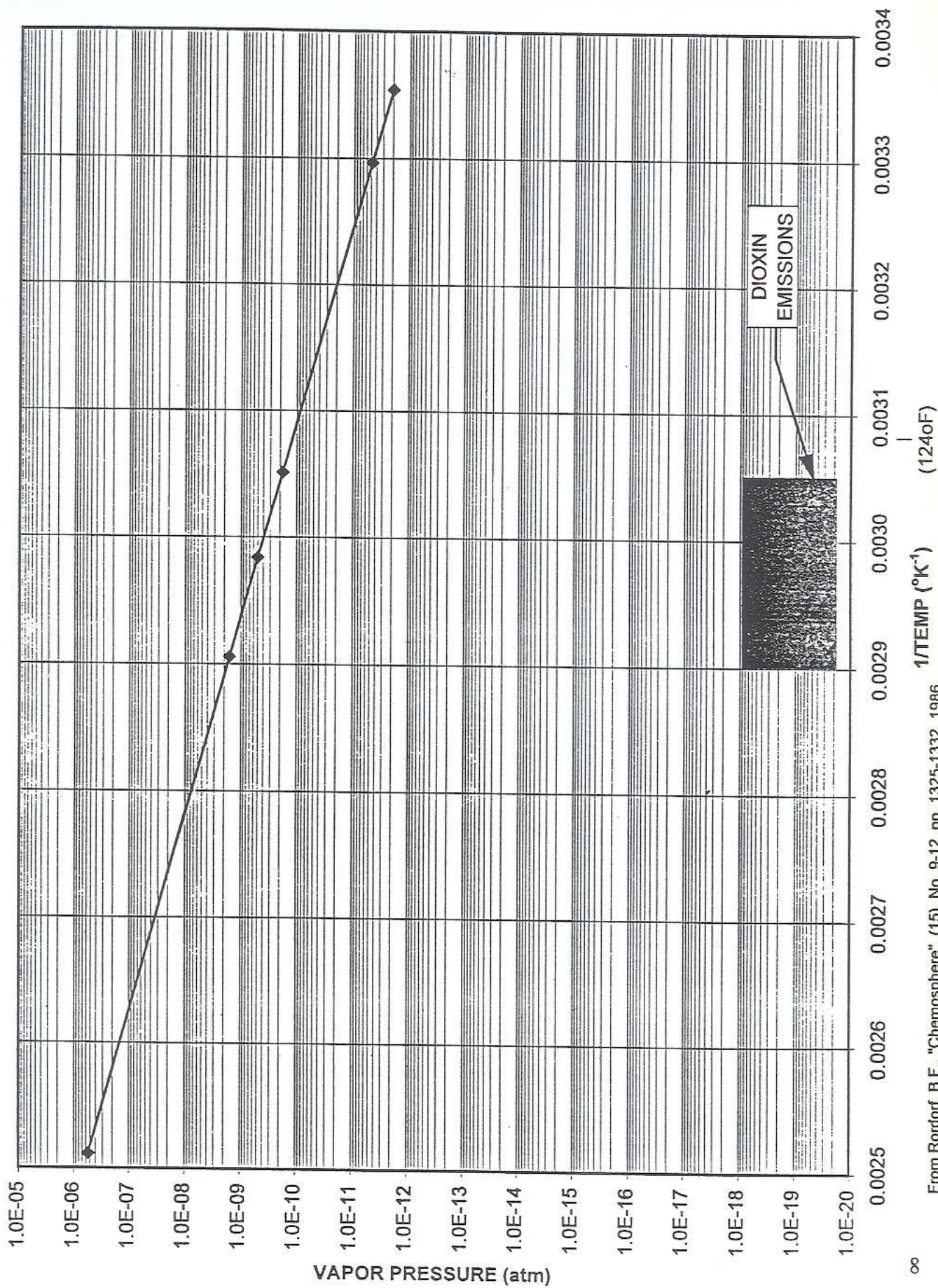
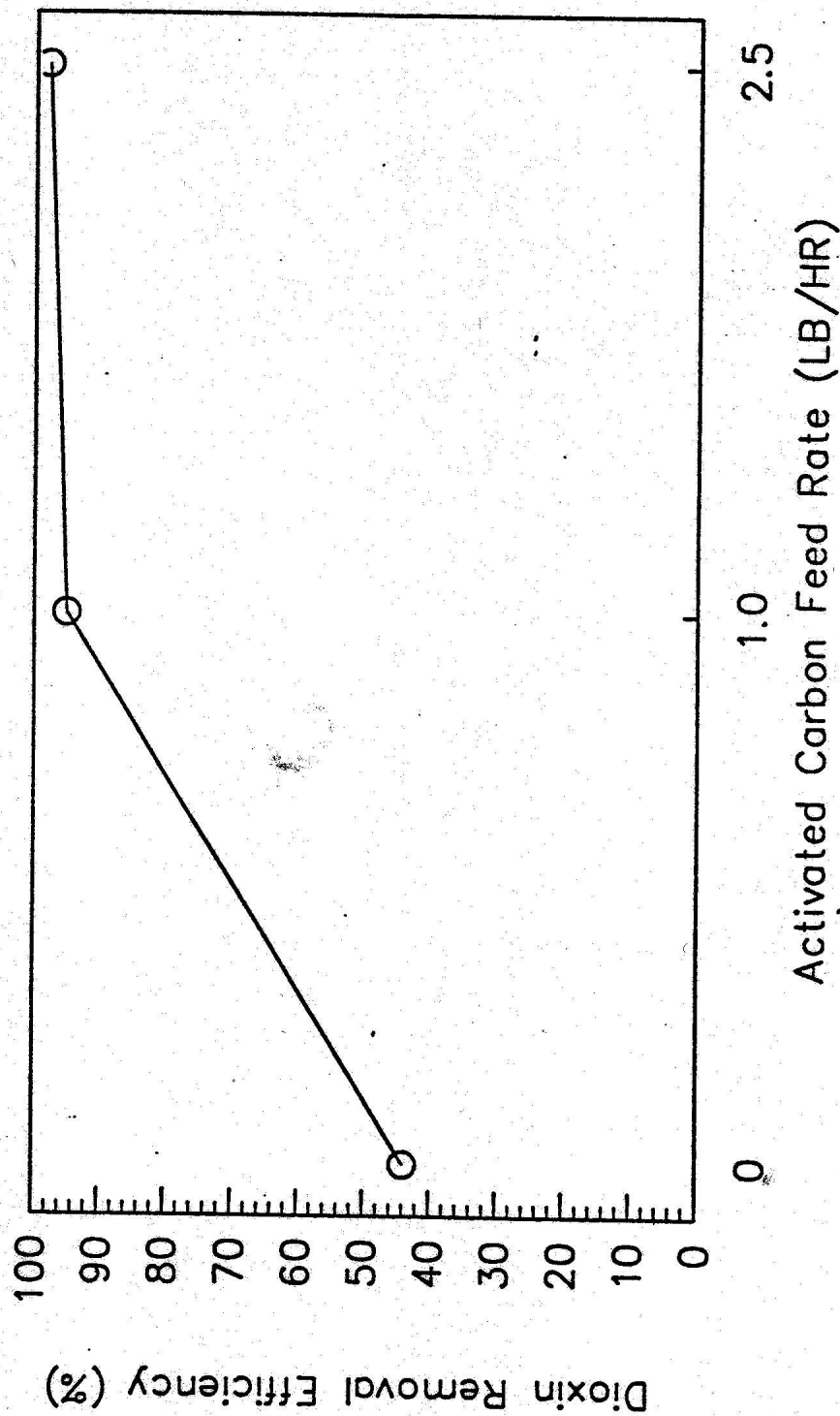
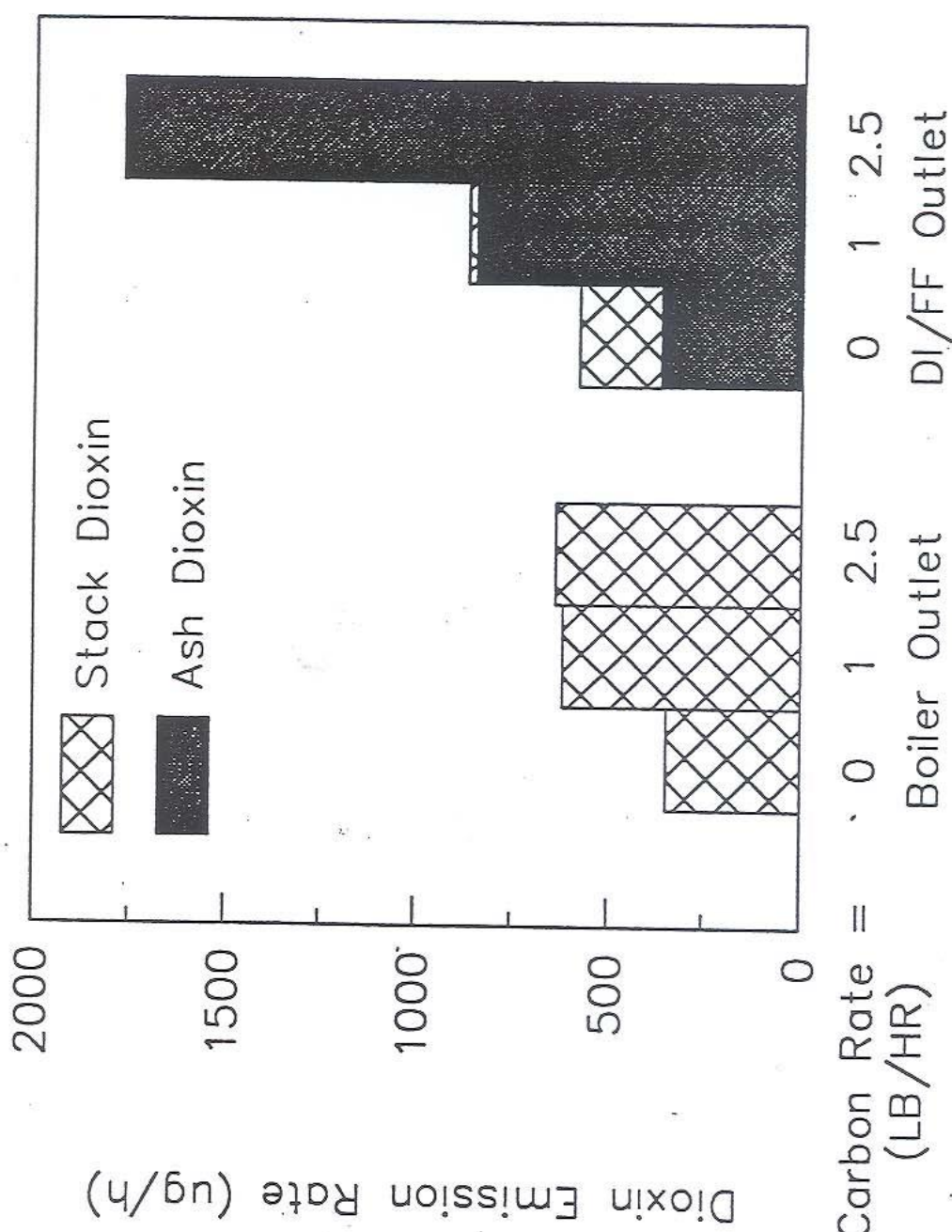


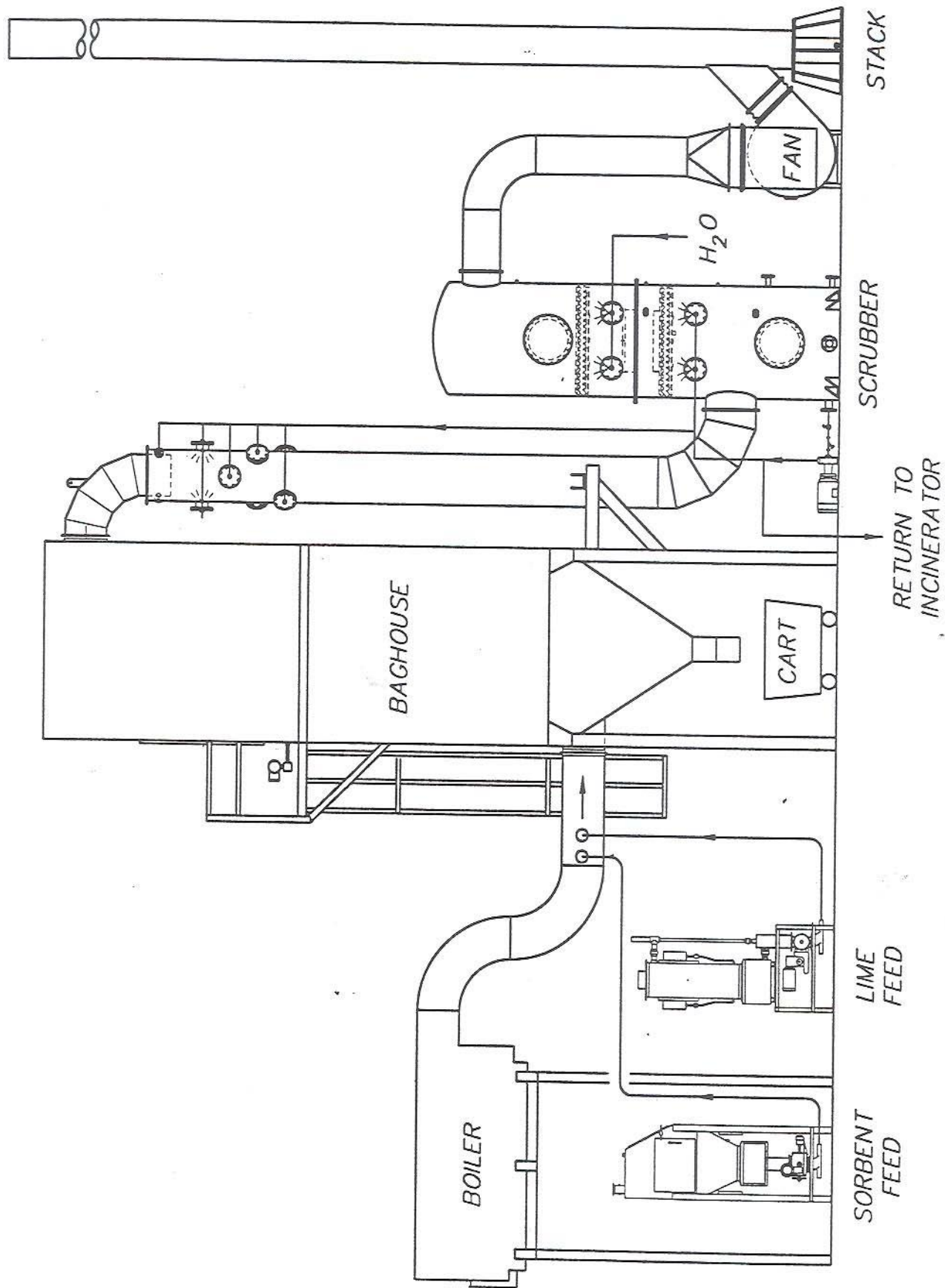
Figure 2.
Effect of Carbon Injection Rate on Dioxin Emissions.



EPA Field Test Data: Reference (1)

Figure 3.
Dioxin Distribution: Medical Waste Incinerator





BECO ALKA/SORB ZERO LIQUID DISCHARGE
FIGURE 4