

# DIOXIN REDUCTION TECHNOLOGY

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The papers in this session are primarily concerned with reducing the dioxin load from a process on the environment by using techniques that prevent dioxins from ever forming in the process involved or those that use various techniques within the process to destroy dioxins formed during the process. Among the technologies reported those concerned with incineration are the most prominent but there are two papers (PIRARD and ANDERSON) that are concerned with dioxins generated by steel making sinter plants. There are also about 10 papers being presented in a posture session on this subject. All but a few are concerned with using various techniques to reduce dioxins generated during incineration in municipal incinerators using techniques of filtration and catalytic or heat destruction of PCDD/F and other chlorinated compounds.

MOGAMI describes a catalytic filter system that combines the well know bag filters with a catalytic felt substrate to reduce dioxin emissions in both batch and continuous municipal incinerators in Japan. His data from actual tests on two different plants show that this system can reduce PCDD/F emissions well below the 0.1ng TEQ/Nm<sup>3</sup> regulation value. This result was achieved during steady state as well as in the usually high emission phases of start up and shut down. A special PTFE membrane filter captures sub-micron particulates and protects the catalytic felt from contamination/poisoning. No data is given on the life and maintenance history of the system.

TAKEYA discusses the design of a retrofitted large MSW in the Tokyo area that employs natural gas reburning to reduce dioxin emissions by creating a high temperature reburning zone with better mixing in the combustion chamber. The system re-circulates 3-15% of the total exhaust gas to insure mixing of the natural gas during combustion. Systematic investigations since 1998 on this system used in this incinerator show that under optimized conditions the dioxins can be reduced down to the regulations of 0.1ng I-TEQ/Nm<sup>3</sup> for new incinerators.

FUJIOSHI takes another approach to reducing generation of dioxins during incineration by attacking and immobilizing the precursors of dioxins early in the incineration process so they are not available for absorption and formation of dioxins on the catalytic fly ash. An inhibitor composed of powdered active alkaline compounds is introduced just prior to the electrostatic precipitator. This technique reduces dioxins not only in the flue gas but in the fly ash as well. Using only 300mg/Nm<sup>3</sup> of inhibitor the dioxins in the outlet gas of the ESP was decreased by 79 % to 0.04ng-TEQ/Nm<sup>3</sup> and the concentration in the fly ash was decreased by 90% to 0.06ng-TEQ/g. The fly ash result is important since the fly ash contains over 90% of the total dioxin emissions. This seems to be a very simple and effective method to reduce total dioxin emissions.

PIRARD has applied the inhibition methods that reduce the catalytic activity of fly ash

developed for MSW to a Belgium sintering plant. Her studies of the dioxin reduction effect of functionalized amines were done both in the laboratory and in plant tests. The laboratory tests using TEA and MEA measured the effect of temperature, amount of inhibitor in the range of 0.5-2.0 wt. percent and contact time on reduction of dioxins formed on the fly ash. Results indicated that global inhibition yields of up to 90 % were obtained. Inhibition tests done in parallel in a sinter plant gave results in good agreement with those in the laboratory. In the plant tests it was noted that sufficient time after injection was required to saturate all the process sites where fly ash was deposited. Considering the large gas volume flows from such industrial processes, it is important to use such methods to reduce dioxin pollution from them. (See ANDERSON)

BASSETTI has tested a pilot catalytic reactor for the combined removal of dioxins and Nox placed after the fabric filtration unit in the Bolzano, Italy MSW plant. Since the unit operates at the same temperature as the exit gas of the filter (~210C) the complexities and expense of preheating the exit gas is avoided. Effective operation at this temperature is made possible by a new type of monolithic base low temperature catalyst. Analytical results were obtained not only for the PCCD/F, PHA AND PCB compounds in the laboratory but for the inorganic micro pollutants by continuous monitoring with an FTIR analyzer. In the test of 1000 hrs duration the feasibility of achieving a 90% reduction of dioxins and 70%+ for Nox simultaneously was shown. Life of the catalyst bed and its performance were quite adequate for industrial applications.

INOUE reports the results of a very thorough study of catalytic decomposition of dioxins by manganese oxide-TiO<sub>2</sub> based catalysts, both in the pellet and honeycomb form. As a first step ortho-dichlorobenzene was used as a model compound to survey performance of the catalysts. Catalysts chosen from this step were then tested for their dioxin decomposition activities using three 2,3,7,8 substituted dioxin congeners. In a final step dioxin removal activities of the catalysts were determined in the exhaust stream of a fluidized bed incinerator equipped with a bag filter. In applying the honeycomb Fe/MnOx catalyst to the flue gas of a municipal incinerator dioxin decomposition activity of 92% was obtained, which is ~10% higher than that found for the conventional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst.

MA investigated the operation of a large MSW in Taiwan for a 2-month period to determine how well the unit conformed to controlled criteria and government enforced regulations. The air pollution control devices consist of lime plus activated charcoal injection into a semi-dry scrubber and a bag house filter. Detailed analyses of the waste composition revealed that its variations had no effect on dioxin emission behavior. Three sampling periods were made of the slag, fly ash and stack gases during the 2 month period with analytical results showing dioxin removal efficiency between 97% to 99%, giving values that are well within the permitted levels. This study is important to gain public acceptance of MSW because Taiwan, like Japan, lacks landfill sites and must use incineration for its waste.

ANDERSON discusses the source of dioxin emissions from integrated iron and steel making sinter plants in the UK. Earlier study has shown that emissions from the main waste gas stacks of the five UK sinter plants were in the range of 0.28 to 4.4 ng-I-TEQ/Nm<sup>3</sup> with an overall mean of 1.21 ng I-TEQ/Nm<sup>3</sup> for 94 measurements. This is close to the achievable release limits. These studies are

to investigate means to further reduce dioxin emissions and is concerned with the dioxin formation mechanism in these processes. The sinter process is an agglomeration process in which iron ore fines, fluxes, fuel in the form of coke and recycle material from other processes are fused together to form a clinker-like material. The waste gases from this process are passed through windlegs (ducts) and on to an ESP where fly ash is precipitated. Just as in MSW incinerators this dust in the ducts and ESP is the major source of dioxins. It was noted that dioxin emissions were greater when waste gas temperature in the windlegs from the sinter bed to the ESP was near 250C. Because the temperature of the ESP was 160C and the windlegs range was 60 to 220C, both below the optimum range of 250 to 450C for catalytic activity of the fly ash, it was postulated that dioxins were formed within the sinter bed, ahead of the flame front and condensed later on the ESP dust. This concept is puzzling because it does not take into account the fact that a very catalytically active fly ash can generate considerable dioxins at temperatures between 200 and 250C. Urea addition in these tests in small amounts (50 kg/hour) to the raw sinter mix gave a 50% reduction of PCDD/F emissions, confirming earlier work, but higher amounts (100-150kg/hr) provided at best an 80% total suppression. (See PIRARD)