An Evaluation of Levels of Chlorinated Aromatic Compounds in ECO LOGIC Process Stack Outputs

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Abstract

Testing was performed on the ECO LOGIC Process to verify regulatory compliance during the commercial-scale treatment of transformer oil. The oil contained high levels of PCBs (approximately 50%), chlorobenzenes (approximately 30%), and PCDDs and PCDFs (0.17 to 0.40 ppm). Levels of PCBs, PCDDs and PCDFs in stack outputs were calculated to be approximately 10,000 times lower than Ontario Ministry of Environment and Energy (MOEE) criteria at the nearest receptor (point of impingement). Levels of dioxin TEQs were approximately 25 times lower than the risk-based Acceptable Source Impact Level for the State of Washington. Levels of dioxin TEQs in stack gas were similar to levels recorded during the combustion of household heating fuel, and lower than other recorded sources including waste incineration, wood burning, and oil and gas furnaces.

Introduction

In April and May, 1996, ECO LOGIC conducted commercial-scale performance testing of the ECO LOGIC Process at a site in Ontario. During this testing, high-strength polychlorinated biphenyl (PCB) oil containing significant levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as contaminants, was processed. Analysis of system outputs showed that at least 99.99999 percent of the PCBs had been destroyed, and that 99.999 to 99.9999 percent of the PCDDs and PCDFs had been destroyed. Levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents (dioxin TEQs) in the stack gas were approximately 15 picograms per cubic metre of air.

This paper presents a brief discussion of the ECO LOGIC Process and the testing program, and evaluates stack output, receptor, and ambient air levels of dioxin TEQs during oil processing.

Description of the ECO LOGIC Process

The ECO LOGIC Process involves the gas-phase reduction of organic compounds in the presence of hydrogen at temperatures of 850°C or higher. Chlorinated hydrocarbons such as PCBs and PCDD/Fs are chemically reduced to methane and hydrogen chloride (HCl), while non-chlorinated organic contaminants, such as PAHs, are reduced substantially to methane and minor amounts of other light hydrocarbons. The HCl produced can be recovered as acid or neutralized in a caustic scrubber downstream of the process reactor.

The gas-phase chemical reduction takes place in a reactor. The gas generated from this reduction is then passed through a series of scrubbers to remove particulate, hydrogen chloride, carbon monoxide and trace hydrocarbons. The resulting clean gas, called product gas, is comprised primarily of methane and hydrogen. This gas is reused in the system as a fuel or sweep gas, or catalytically reformed to recover hydrogen. Excess product gas is combusted in a burner train. Regulatory testing is performed on the stack gas resulting from the burning of the product gas in the presence of combustion air drawn in from the site ambient air. It should be noted that the internal reuse of the product gas does not constitute an additional treatment component. The product gas is recycled within the system purely as a means of output disposition and in order to recover the energy which has been produced. It was clearly proven in the ECO LOGIC's 1992 USEPA SITE Demonstration that:

> *"Although the result was not listed as a primary or secondary objective for the demonstration, destruction and removal efficiencies (DREs) for PCBs in the scrubbed reformed gas were essentially equal to the DREs achieved at the boiler stack. This shows that combustion of the reformed gas in the boiler is not required to complete PCB destruction."* (1)

Analytical Results

Table 1 provides a characterization of the input oil that was processed during the performance tests. Table 2 provides a summary of dioxin TEQs for the performance test samples in the input oil, combustion air, product gas and stack gas. As can be seen by the blank levels on this table, there appears to have been considerable interference during sampling and analytical activities.

The input oil contained approximately 50 percent PCBs and from 25 to 35 percent chlorobenzenes. All PCDF congeners were detected at very high levels (up to 2,200,000 pg/g), whereas all PCDD congeners except OCDD were below detection limits ranging from approximately 400 to 1000 pg/g.

Product gas created from the reduction of PCBs, PCDDs and PCDFs in the reactor contained detectable levels of PCDDs and PCDFs. However, blank levels were the same or higher than recorded levels, indicating that the levels are artifactual, and a result of sampling or analytical interference. Data has not been blank-subtracted, and therefore represents "worst-case" levels.

Table 1 CHARACTERISTICS OF INPUT OIL

Compound		*Test 1*	*Test 2*	*Test 3*
Total Chlorobenzenes	(ppm)	293010	332580	256470
	(%)	29.3	33.3	25.6
Total PCBs	(ppm)	480000	540000	510000
	(%)	48	54	51
Dioxin TEQs	(ppt)	167930	201719	397506
	(ppm)	0.17	0.20	0.40
Total CBs, PCBs and TEQs	(%)	77.5	87.5	77.0

Table 2 DIOXIN TEQS IN PERFORMANCE TEST SAMPLES

Location	*Method Blank*	*Field/Filter Blank*	*Test 1*	*Test 2*	*Test 3*
Input Oil (pg/g)	-	-	113030	145919	298506
Product Gas (pg/m³)	35	68	38	32	25
Combustion Air (pg/m³)	0.21	0.38	0.48	0.62	0.48
Stack Gas (pg/m³)	5.8	7.9	21	19	16

Stack Output Characteristics

Stack gas is produced from the burning of product gas and combustion air. As indicated on Table 2, dioxin TEQ test data was in the same order of magnitude as the blank data.

Referring to Table 3, levels of tetra-substituted PCDDs are similar to those found in the field blank. With the exception of Test 1, penta- and hexa-substituted PCDDs are also present at similar levels to those found in the field blank. The level of penta-substituted PCDD in Test 1 is higher than in the field blank, but in the same order of magnitude. Levels of hepta- and octa-substituted congeners show typically higher levels, as is common in combustion samples. Levels of all PCDD congeners are in the same order of magnitude as the field blank. Levels of PCDF congeners are generally higher than the blank data. In some cases (particularly Test 3), levels are more than an order of magnitude higher.

In general, the stack gas contained primarily PCDFs; PCDD blank levels indicated sampling and analytical interference had occurred. As discussed in a companion paper (2), the PCDFs were likely a result of the presence of PCBs in air drawn into the burner train of the stack, while it was firing PCB-free product gas generated from the reduction of PCBs in the Process.

Table 3 PCDDS AND PCDFS IN STACK GAS (pg/m³)

PCDD/PCDF Congener	*Method Blank*	*Field Blank*	*Test 1*	*Test 2*	*Test 3*
2,3,7,8-TCDD	< 1.2	3.8	2.7	5.3	3.9
1,2,3,7,8-PeCDD	1.8	2.8	13	3.7	2.0
1,2,3,4,7,8-HxCDD	< 2.1	5.5	4.7	7.5	6.4
1,2,3,6,7,8-HxCDD	< 1.3	< 1.2	< 1.2	3.3	1.9
1,2,3,7,8,9-HxCDD	< 1.7	2.8	5.2	5.7	3.0
1,2,3,4,6,7,8-HpCDD	5.1	11	27	29	27
OCDD	35	60	87	77	150
2,3,7,8-TCDF	1.4	2.3	6.9	16	27
1,2,3,7,8-PeCDF	< 0.76	0.92	7.9	8.6	5.2
2,3,4,7,8-PeCDF	< 0.76	< 0.81	6.7	6.8	8.6
1,2,3,4,7,8-HxCDF	< 1.2	< 1.9	8.2	13	10
1,2,3,6,7,8-HxCDF	< 0.81	< 1.3	5.2	6.8	5.4
2,3,4,6,7,8-HxCDF	< 1.2	< 2.0	< 1.2	6.4	12
1,2,3,7,8,9-HxCDF	2.8	< 2.1	2.7	3.3	3.4
1,2,3,4,6,7,8-HpCDF	1.5	3.5	17	26	75
1,2,3,4,7,8,9-HpCDF	< 1.2	< 1.0	2.7	4.0	12
OCDF	5.5	3.9	10	13	250

Discussion

Comparison of Stack Outputs to Criteria

Concentrations of stack gas compounds were subjected to dispersion modelling to determine the concentrations at the point where the plume from the stack has maximum impact on receptors at ground level (the "Point of Impingement", or POI). The POI criteria regulated by the Ontario Ministry of Environment and Energy (MOEE) for total PCBs and dioxin TEQs are 0.45 $\mu g/m^3$ and 15 pg/m^3, respectively. Modelled results for PCBs and PCDDs/PCDFs at a typical site are provided in Table 14. The highest levels found in the stack for the three tests were chosen for this table, to show the maximum impact from waste processing. While there was obvious interference on PCDD levels from sampling and analytical procedures, data was not blank-corrected, and therefore results and interpretation are "worse-case".

Included in Table 14 is the risk-based Acceptable Source Impact Level (ASIL) for dioxin TEQs for the State of Washington. The ASIL is the concentration of a compound in the outdoor atmosphere in any area which does not have restricted or controlled public access, that is used to evaluate the air quality impacts of a single source. The risk-based ASIL is the annual average concentration, in $\mu g/m^3$, that may cause an increased cancer risk of one in one million.

Table 14 COMPARISON OF PCB AND PCDD/PCDF LEVELS TO CRITERIA

Compound	*POI Criteria regulated by the MOEE*	*10^{-6} Risk ASIL Annual Average*[1]	*Highest Modelled Level at Receptor/POI*
PCBs	0.45 $\mu g/m^3$	--	0.000037 $\mu g/m^3$
Dioxin TEQs	15 pg/m^3	0.03 pg/m^3	0.0012 pg/m^3

[1] *State of Washington*

The results from Table 14 show that the levels of PCBs and PCDDs/PCDFs at POI are 10,000 times lower than the MOEE POI criteria, and levels of PCDDs/PCDFs at POI are approximately 25 times lower than the 10^{-6} risk-based ASIL.

Comparison of Stack Outputs and Recorded Ambient Air Levels to Other Sources

Table 15 presents a summary of dioxin TEQs from various sources. Table 16 presents a summary of the ambient air data collected during performance testing, as well as the corresponding stack output dioxin TEQ level. The stack output dioxin TEQs are lower than most documented levels for other sources, such as waste incinerators, wood burning and oil and gas furnaces. Levels are similar in magnitude to the dioxin TEQs generated when burning "normal" charcoal briquettes for domestic heating (approximately 10 to 20 pg/m^3).

The values detected in the ambient air during testing are all within the same order of magnitude, with the exception of Test 2, and all are in the very low 0.1 to 0.01 pg/m^3 range. At these extremely low levels it is unlikely that there is any significant difference in the levels found in the samples. The levels detected in ambient air during oil processing are in fact from 35 to 135 times lower than the MOEE ambient air quality criteria for dioxin TEQs of 5 pg/m^3. The ambient levels of dioxin TEQs during the testing are also very similar to the typical ambient levels in North America and Europe (approximately 0.1 pg/m^3). These factors indicate that the dioxin TEQs in the stack output had no

effect on the ambient levels, because of the extremely low dioxin TEQ levels resulting from dispersion.

Table 15 DIOXIN TEQS FROM VARIOUS AIR SOURCES

Air Source		*TEQ (pg/m³)*	*Reference*
ECO LOGIC Performance Test*		20 17 18	--
HWI Flue Gas		200 300	3
Combustion of "Salt" Briquettes**		87 134 106 109	4
Combustion of "Normal" Briquettes**		13 21 10 15	4
MSW Incinerator		200 - 63000	5
Hazardous Waste Incinerator		100 - 500	5
Wood Combustion	Natural Waste Wood	20 - 1800 2700 - 14000	5
Oil Furnace		30 - 300	5
Gas Combustion		70 - 100000	5
Ambient Air	North America Europe	0.0949 ± 0.24 (n=84) 0.108 (n=454)	6

* Field Blank = 7.9 pg/m³

**"normal" briquettes: chlorine content of 300 ppm; "salt" briquettes: chlorine content of 2000 ppm

Table 16 WORST-CASE DIOXIN TEQ LEVELS IN AMBIENT AIR AND STACK GAS DURING PERFORMANCE TESTING

Test	*Ambient Air Dioxin TEQ Level Relative to Site (pg/m³)*				*TEQ Level in Stack (pg/m³)*	*TEQ Level at POI (pg/m³)*
	North	*East*	*South*	*West*		
Field Blank	--	--	--	--	7.9	--
Test 1	0.073	0.073	0.079	0.083	20	0.0012
Test 2	0.123	0.112 0.103	0.144	0.128	17	0.00093
Test 3	0.068	0.057	0.072	0.072	18	0.0011

Conclusions

- the test matrix contained high levels of PCBs (approximately 50%), chlorobenzenes (approximately 30%), and PCDDs and PCDFs (0.17 to 0.40 ppm)
- levels of PCBs, PCDDs and PCDFs were approximately 10,000 times lower than MOEE criteria for Point Of Impingement
- stack gas contained primarily PCDFs (PCDDs were generally non-detect or a result of sampling or analytical interference)
- levels of dioxin TEQs were approximately 25 times lower than the risk-based Acceptable Source Impact Level for the State of Washington
- levels of dioxin TEQs in the ambient air around the demonstration site were not affected during oil processing; ambient levels around the site are similar to ambient levels for North America and Europe
- levels of dioxin TEQs in stack gas were similar to levels recorded during the combustion of household heating fuel, and lower than other recorded sources including waste incineration, wood burning, and oil and gas furnaces

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