



## American Coke and Coal Chemicals Institute

1255 Twenty-Third Street, NW • Washington, DC 20037-1174 • (202) 452-1140 • Fax: (202) 833-3636

March 22, 1999

Mr. Frank Anscombe  
U.S. Environmental Protection Agency  
Region 5 (G-17J)  
77 West Jackson Boulevard  
Chicago, IL 60604

Mr. Darryl Hogg  
Canada Ontario Agreement Coordination  
Ministry of Environment  
40 St. Clair Avenue West, 12th Floor  
Toronto, Ontario M4V 1M2

Re: BMI's December 12, 1998, Draft Report Implicating Coke  
Production as a Possible "Suspect Source" of OCS Emissions

Gentlemen:

I am writing on behalf of the AISI/ACCCI Coke Oven Environmental Task Force (COETF), concerning a 12 December 1998 draft report entitled "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources". The draft report was prepared by Batelle Memorial Institute (BMI) for the EPA.

- 1 The COETF (see Enclosure 1) was formed in 1996 by the American Iron and Steel Institute (AISI) and the American Coke and Coal Chemicals Institute (ACCCI) to address environmental issues of concern to the industry. The COETF represents all 20 U.S. companies that produce metallurgical coke, including nine integrated steel companies operating 14 coke plants (40 batteries) and 11 independently owned/operated "merchant" companies operating 11 coke plants (28 batteries). The COETF also represents two Canadian companies that produce coke.

The COETF is vitally interested in the draft report because it implicates coke production as a possible "suspect source" of OCS emissions. Upon first learning of the draft report via its involvement in the Council of Great Lakes Industries (CGLI), the COETF provided CGLI with the results of effluent testing at Stelco Inc.'s Lake Erie Steel Company. These results, which showed no detectable OCS in coke plant effluent (see Enclosure 2), were provided to CGLI for submittal to Great Lakes Binational Toxics Strategy (BNTS) OCS Workgroup. CGLI submitted this information to the Workgroup on March 1 (see Enclosure 3).

Messers. Anscombe and Hogg  
BMI's December 12, 1998, Draft Report Implicating Coke Production as a  
Possible "Suspect Source" of OCS Emissions  
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- 2 Subsequently, the COETF retained Dr. Laura L. Kinner (Emission Monitoring Inc.), to evaluate the potential for OCS formation in coke ovens. Dr. Kinner, an expert in coal chemistry, has concluded that " ... the formation of OCS during coal coking operations is not implicated by the reaction mechanisms, nor do laboratory studies or actual emissions data support it" (see Enclosure 3). A copy of Dr. Kinner's resume is enclosed for your information (see Enclosure 4)

In consideration of the above, we believe the evidence is compelling that coke plants are not a source of OCS and hereby request that coke production be removed as a suspected source of OCS emissions. Please call me if you have any questions.

Sincerely,



David C. Ailor, P.E.  
Director of Regulatory Affairs

Four Enclosures

cc (w/o Attachment to Enclosure 3):

COETF (see Enclosure 1)  
Jeff Wentz (Acme Steel Company)  
Bob Ajax (Ajax & Associates)  
Marty Dusel (Citizens Gas & Coke Utility)  
George Kuper (CGLI)  
Ian Shaw (Dofasco, Inc.)  
Gary Quantock (DTE Energy Services)  
Laura Kinner (Emission Monitoring Inc.)  
Steve Sands (Geneva Steel)  
Gerald Kendrick (Jewell Coal & Coke)  
Traci Self (Koppers Industries, Inc.)  
Mary Lou Harmon (LTV Steel Company)  
David Menotti (Shaw, Pittman, Potts & Trowbridge)  
Bob Bloom (Tonawanda Coke Corporation)  
Nancy Hirko (USS)

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AISI/ACCCI Coke Oven Environmental Task Force

Bill West, Co Chairman	LTV Steel Company
Ron McCollum, Co Chairman	USS Clairton
Mark Poling	ABC Coke
Jack Garzella	Acme Steel Company
Steve Felton	AK Steel Corporation
George Ossman	Bethlehem Steel Corporation
Wade Kohlmann	Citizens Gas & Coke Utility
Danny Lewis	Empire Coke Company
Russ Christensen	Geneva Steel
Buster Stewart	Gulf States Steel, Inc.
George Bradley	Indiana Harbor Coke Company
Greg Shamitko	Koppers Industries, Inc.
Jack Heintz	National Steel Corporation
Mike Mehalovich	New Boston Coke Corporation
Nick Buchko	Shenango Inc.
Bobby Fisher	Sloss Industries Corporation
Tim Huxley	Stelco Inc.
Mark Kamholz	Tonawanda Coke Corporation
Bill Samples	Wheeling-Pittsburgh Steel Corporation

ENCLOSURE 2

**Stelco Inc.**  
General Office  
Stelco Tower  
Hamilton, Ontario  
L8N 3T1  
(905) 528-2511 ext 4201  
fax (905) 577-4441  
e-mail environ2@stelco.ca

1999-02-10

Mr. David C. Ailor, PE  
Director of Regulatory Affairs  
American Coke and Coal Chemicals Institute  
1255 Twenty-Third Street, NW  
Washington, DC 20037

  
~~Dear Mr. Ailor:~~

**Subject: OCS in Effluent - Test Results from Stelco**

The Ontario government tested integrated steel plant effluents in 1989 and 1990 for various pollutants including OCS, as part of its Municipal/Industrial Strategy for Abatement (MISA).

OCS was below detection at all facilities including Stelco Inc.'s Lake Eric Steel Company, which produces over 600,000 tons of coke annually, but due to an unfortunate error made in recording the data the government earmarked Lake Erie Steel Company as an OCS emitter.

Lake Erie Steel Company effluent measured less than 0.0026 ug/l OCS i.e., below detection limit, for all samples taken between November 1989 and June 1990, the government test period. The RMDL was 0.010 ug/l.

Enclosed are copies of correspondence between Stelco and Mr. Daryl Hogg, a consultant working for the Ontario Ministry of Environment and Environment Canada on Great Lakes issues including the Binational Agreement.

The result of that dialogue was the conclusion by government that the Iron and Steel Sector is not a source of OCS, and they now reflect this in their OCS survey.

Best regards,



F.R. Kent  
Environmental Program Specialist

cc T.F. Huxley

# Canada Ontario

June 11, 1998

FRK 06/15  
c.c. G. Saldanha  
T. Hurley

orig to  
file with  
"COA"

Mr. Ross Kent  
Environmental Program Specialist  
Stelco Inc.  
General Office  
100 King St. West  
Hamilton, Ontario  
L8N 3F1

12 Floor  
40 St. Clair Avenue West  
Toronto, Ontario  
M4V 1M2  
Tel. (416) 314-3931

Dear Mr. Kent:

Thank you for your letter of May 26, 1998, concerning the Octachlorostyrene release number for the Lake Erie Steel Company Ltd. (LESC).

Your letter and the MISA records from LESC indicating that OCS levels were below detection limits over the MISA sampling period in question are presently under review. Once I have received concurrence on your findings, I will inform you. In the interim period, the OCS number attributed to the iron & steel sector in the COA inventory of tier I/II substances has been removed, and replaced with a notation that the release number is under review.

If you have any questions on the above matter please contact me.

Yours truly,



Darryl Hogg  
COA Stream 2 Coordination

cc. Ian Smith  
Tom Tseng

NOTE TO FILE 02/10/99

D. Hogg confirms that Iron and Steel sector is NOT a suspect for OCS.

He concurs that an error was made in MOE 1990 REPORT.

He is involved in BINAROUND Agreement on GL talks.

per Telecon D. Hogg / FRK. FRK.



## **Potential of Octachlorostyrene Formation from Coke Ovens**

Laura L. Kinner Ph.D.<sup>1</sup>  
Emission Monitoring Incorporated  
8901 Glenwood Ave.  
Raleigh, NC

### **Introduction**

A draft report entitled "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources" was prepared by Battelle Memorial Institute (12/22/98) for the U.S. EPA. The Battelle Report discusses the toxicity and environmental persistent nature of OCS, and presents a detailed list of sources known and suspected to emit OCS. All of the "documented sources" of OCS emissions identified in Table 2 of the report have chlorine as a reactant or by-product of the process. All of the "highly probably" sources of OCS emissions are identified as incinerative in nature and/or have chlorine as a reactant or by-product of the process. Coke production is identified as a possible "suspect source" of OCS emissions.

This paper addresses the potential of OCS formation from coke ovens.

### **Coke Formation by Coal Pyrolysis**

Coke formation is not like the other processes identified in the Battelle Report as emitting OCS. The coking process is not incinerative and does not involve the addition of chlorine. Coke is formed by thermally treating coal in the absence of excess oxygen (pyrolysis).

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<sup>1</sup> Dr. Kinner received her Ph.D. from the University of Missouri in 1992. Her dissertation research focussed on gasification of hazardous wastes using coal chars. This work entailed detailed studies of various coals and the reaction mechanisms of pyrolysis, gasification and combustion relative to the destruction highly chlorinated hazardous and radioactive mixed wastes.

Coal is highly amorphous and varies significantly by geographical location and age. Coal can be represented as aromatic and hydroaromatic sub-units with functional groups at their periphery forming a cross-linked structure. The functional groups are mainly hydrocarbon (methylenic or ethylenic) in nature, but can also be composed of sulfur, nitrogen, metals and halogen atoms. Elements such as chlorine generally comprise less than 0.5% of the coal structure. X-ray analysis of coals shows that the cyclic sub-units arrange themselves in polymeric layers becoming more ordered (graphitic) depending on coal rank.<sup>2</sup> In general coal is ranked by hardness; anthracite > bituminous > sub-bituminous > lignite.

When coal is subjected to the pyrolytic conditions encountered during the coking process, the weakest bonds in the cross-linking structure rupture. This thermal decomposition, or cracking, causes two free radicals to be formed for every bond broken. Coal pyrolysis end products are: coke (devolatilized coal) and gaseous mixtures of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> (methane), water and lighter hydrocarbons. These products differ greatly from those of combustion: noncombustible residue (ash), CO<sub>2</sub> and H<sub>2</sub>O.<sup>3</sup>

An important reactive intermediate of coal pyrolysis is atomic hydrogen [H•], sometimes referred to as nascent hydrogen. The amount of available nascent hydrogen formed during combustion is negligible compared to that formed during pyrolysis.

### **Potential of Octachlorostyrene Production during Coal Coking**

The atomic hydrogen produced during coal pyrolysis reacts with other hydrogen atoms to produce H<sub>2</sub>, and participates in reactions with other gaseous free radicals and the hot coal surface. Formation of octachlorostyrene in coal pyrolysis systems is not favored because: 1) chlorine free radicals cleaved from the coal surface during thermal cracking will combine with the nascent hydrogen to form hydrochloric acid (HCl), 2) nascent hydrogen abstracts chlorine from the hot coal surface (dehydrochlorination) forming HCl, and 3) alkylchloride free radicals (RCl•) cleaved from the coal surface during thermal cracking will combine with nascent hydrogen or other alkyl free radicals to produce low molecular weight organochloride compounds such as chloromethane, chloroethane, etc.

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2. Cartz, L. and Hirsch, P.B., "A Contribution to the Structure of Coals from X-Ray Diffraction Studies," Proceedings from the Royal Society of London, 1960, A252, 557-602.

3. Campbell, J.H., "Kinetics Studies of Gas Evolution During Pyrolysis of Subbituminous Coal," American Chemical Society, Division of Fuel Chemistry, 1991, 21, 7, 94.

The immediate consumption of chlorine and alkyl chloride free radicals by nascent hydrogen eliminates a multi-step chlorination reaction involving styrene to produce the fully chlorinated compound OCS.

### **Supporting Data**

Pyrolysis and gasification studies were conducted using coal char as a substrate for hexachlorobenzene (HCB) to determine the potential of coal char pyrolysis to dehydrochlorinate hazardous wastes.<sup>4</sup> In these studies, mass balances achieved for chlorine determined that HCB sorbed onto coal char was effectively dechlorinated to HCl and chlorides as determined by analysis of effluent gas and the pyrolyzed chars. No highly chlorinated organic compounds were detected in these studies.

The fact that OCS formation during coking operations is not probable is further supported by information contained in the Battelle Report (cited above) and from data gathered by Bethlehem Steel Corporation (see Attachment). The Battelle report states that:

*"In general, it appears that whenever hexachlorobenzene (HCB) and chlorinated dibenzodioxins (CDDs) are formed, there is potential that OCS is formed"*

Therefore, the absence of HCB and CDDs would indicate that formation of OCS is not favored.

In the Bethlehem study, untreated effluent samples collected from a coke oven battery using XAD resin were analyzed for semi-volatile compounds by SW846-8270. The results from these analyses indicate no emissions of HCB, or any other chlorinated organic compound from the testing conducted at Bethlehem at stack concentrations of approximately 7.5 parts per trillion (using the level of detection reported by Great Lakes Analytical). Method 18 samples were analyzed for volatile compounds using SW846-8240 analysis procedures during this same testing program. Results from these analyses indicated that one run had methylene chloride contamination as indicated by the field blank. No other organochlorine compounds were detected in any sample at stack concentrations approximating 0.1 parts per billion (using the level of detection reported by Air Toxics LTD). Given these data, it seems highly improbable that OCS is emitted from coal coking operations.

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<sup>4</sup> Kinner, L.L., Manahan, S.E., "Mechanistic Study of the ChemChar Process Using Hexachlorobenzene as a Surrogate for Monitoring reaction Products," *Chemosphere*, 24 (12) 1867-1884. (1992).

Table 4. of the Battelle Report also contains a list of source categories and their potential to emit OCS. In this Table, carbon reactivation furnaces are listed as having negligible dioxin emissions and negligible potential to emit OCS. It is unlikely that coke production would have a greater potential of OCS emissions relative to carbon reactivation furnaces.

### **Conclusions**

The formation of octachlorostyrene during coal coking operations is not implicated by the reaction mechanisms, nor do laboratory studies or actual emissions data support it. Therefore, coke production should be removed as a suspected source of OCS emissions from Table 2 of the Battelle Report.

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