Florida Department of Environmental Regulation

Twin Towers Office Bldg. ● 2600 Blair Stone Road ● Tallahassee, Florida 32399-2400

Bob Martinez, Governor
Dale Twachtmann, Secretary
John Shearer, Assistant Secretary

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION
NOTICE OF PERMIT AMENDMENT

Mr. Randy Thompson
Environmental Department
Florida Crushed Stone Company
Post Office Box 490300
Leesburg, Florida 34749-0300

June 13, 1990

Enclosed is an amendment for construction permits Nos. AC 27-118674 and PSD-FL-091 for Florida Crushed Stone Company to conduct performance tests on the cement kiln while burning tire derived fuel with coal at the existing facility located approximately 3.5 miles NW of Brooksville, Hernando County, Florida. This amendment is issued pursuant to Section 403, Florida Statutes.

Any party to this amendment has the right to seek judicial review of the amendment pursuant to Section 120.68, Florida Statutes, by the filing of a Notice of Appeal pursuant to Rule 9.110, Florida Rules of Appellate Procedure, with the Clerk of the Department in the Office of General Counsel, 2600 Blair Stone Road, Tallahassee, Florida 32399-2400; and by filing a copy of the Notice of Appeal accompanied by the applicable filing fees with the appropriate District Court of Appeal. The Notice of Appeal must be filed within 30 days from the date this amendment is filed with the Clerk of the Department.

Executed in Tallahassee, Florida.

STATE OF FLORIDA DEPARTMENT
OF ENVIRONMENTAL REGULATION

C. H. Fancy, P.E.
Chief
Bureau of Air Regulation

Copy furnished to:

B. Thomas, SW District
J. Koogler, P.E., K&A
C. Shaver, NPS
J. Harper, EPA

CERTIFICATE OF SERVICE

The undersigned duly designated deputy clerk hereby certifies that this NOTICE OF PERMIT AMENDMENT and all copies were mailed before the close of buisness on 6-13-90.

FILING AND ACKNOWLEDGEMENT FILED, on this date, pursuant to §120.52(9), Florida Statutes, with the designated Department Clerk, receipt of which is hereby acknowledged.

	6-13-90
Clerk	Date

Final Determination

The construction permit amendment request has been reviewed by the Department. Public Notice of the Department's Intent to Issue was published in The Tampa Tribune on May 4, 1990. The letter amendment and attachments were available for public inspection at the DER's Southwest District and Bureau of Air Regulation (Bureau) offices.

A comment was received on the proposed action from Mr. Bruce Mitchell, with the Bureau, in an Interoffice Memorandum. The comment identified mercury as a pollutant of concern in Florida and the need to conduct tests for it. Therefore, the following will be added to No. 4 of the letter amendment:

Pollutant/Pollutant Category	Test Method
• Mercury	EPA Method 101 or 101A

Attachment to be incorporated:

12. Interoffice Memorandum from Mr. Bruce Mitchell dated May 17, 1990.

The Bureau will incorporate the change into the appropriate area of the letter amendment, as reflected in the final determination. It is recommended that the letter amendment be issued as drafted, with the above revision and attachment incorporated. This letter amendment shall be attached to construction permits Nos. AC 27-118674 and PSD-FL-091, and shall become a part of the permits.

THE TAMPA TRIBUNE

Published Daily

Tampa, Hillsborough County, Florida

RECEIVED

MAY

DER - BAQM

State of Florida
County of Hillsborough }

Before the undersigned authority personally appeared James L. Gonnering, who on oath says that he is Assistant Comptroller of The Tampa Tribune, a daily newspaper published at Tampa in Hillsborough County, Florida; that the attached copy of advertisement being a LEGAL NOTICE

in the matter of ISSUE A PERMIT AMENDMENT

was published in said newspaper in the issues of May 4, 1990

Affiant further says that the said The Tampa Tribune is a newspaper published at Tampa, in said Hillsborough County, Florida, and that the said newspaper has heretofore been continuously published in said Hillsborough County, Florida, each day and has been entered as second class mail matter at the post office in Tampa, in said Hillsborough County, Florida, for a period of one year next preceding the first publication of the attached copy of advertisement, and affiant further says that he has neither paid nor promised any person, firm, or corporation any discount, rebate, commission or refund for the purpose of securing this advertisement for publication in the said newspaper.

Sworn to and subscribed before me, this 10 *day*

of May *, A.D. 19*90

Debra Lynne Bouchard

(Seal)

Notary Public, State of Florida
My Commission Expires Jan. 6, 1993
Bonded Thru Troy Fain - Insurance Inc.

The Department of Environmental Regulation hereby gives notice of its intent to issue a permit amendment to FCSC (Florida Crushed Stone Company), Environmental Department, P.O. Box 490300, Leesburg, Florida 34749-0300, to conduct a performance test on the cement kiln while burning tire derived fuel (TDF) with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this amendment is to allow FCSC to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal. The proposed project will occur at the applicant's existing facility located approximately 3.5 miles NW of Brooksville, Hernando County, Florida. The Department is issuing this intent to issue for the reasons stated in the proposed letter amendment to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

A person whose substantial interests are affected by the Department's proposed permitting decision may petition for an administrative proceeding (hearing) in accordance with Section 120.57, Florida Statutes. The petition must contain the information set forth below and must be filed (received) in the Office of General Counsel of the Department at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400, within fourteen (14) days of publication of this notice. Petitioner shall mail a copy of the petition to the applicant at the address indicated above at the time of filing. Failure to file a petition within this time period shall constitute a waiver of any right such person may have to request an administrative determination (hearing) under Section 120.57, Florida Statutes.

The Petition shall contain the following information:

(a) The name, address, and telephone number of each petitioner, the applicant's name and address, the Department Permit File Number and the county in which the project is proposed;

(b) A statement of how and when each petitioner received notice of the Department's action or proposed action;

(c) A statement of how each petitioner's substantial interests are affected by the Department's action or proposed action;

(d) A statement of the material facts disputed by Petitioner, if any;

(e) A statement of facts which petitioner contends warrant reversal or modification of the Department's action or proposed action;

(f) A statement of which rules or statutes petitioner contends require reversal or modification of the Department's action or proposed action; and

(g) A statement of the relief sought by petitioner, stating precisely the action petitioner wants the Department to take with respect to the Department's action or proposed action.

If a petition is filed, the administrative hearing process is designed to formulate agency action. Accordingly, the Department's final action may be different from the position taken by it in this Notice. Persons whose substantial interests will be affected by any decision of the Department with regard to the application have the right to petition to become a party to the proceeding. The petition must conform to the requirements specified above and be filed (received) within 14 days of publication of this notice in the Office of General Counsel at the above address of the Department. Failure to petition within the allowed time frame constitutes a waiver of any right such person has to request a hearing under Section 120.57, F.S., and to participate as a party to this proceeding. Any subsequent intervention will only be at the approval of the presiding officer upon motion filed pursuant to Rule 28-5.207, F.A.C.

The application is available for public inspection during business hours, 8:00 a.m. to 5:00 p.m., Monday through Friday, except legal holidays, at:

Department of Environmental Regulation
Bureau of Air Regulation
2600 Blair Stone Road
Tallahassee, Florida
32399-2400

Department of Environmental Regulation
Southwest District Office
4520 Oak Fair Boulevard
Tampa, Florida 33610-7347

Any person may send written comments on the proposed action to Mr. C. H. Fancy at the Department's Tallahassee address. All comments mailed within 14 days of the publication of this notice will be considered in the Department's final determination.

2642 5/4/90

ATTACHMENT 12

For Routing To Other Than The Addressee

To: ______________________ Location: ______________
To: ______________________ Location: ______________
To: ______________________ Location: ______________
From: ____________________ Date: __________________

State of Florida
DEPARTMENT OF ENVIRONMENTAL REGULATION

Interoffice Memorandum

TO: Florida Crushed Stone File: AC 27-118674
FROM: Bruce Mitchell
DATE: May 17, 1990
SUBJ: Comments - Public Notice

Due to the concerns about mercury in Florida, I recommend that FCS perform emissions tests for this highly toxic pollutant, both prior to burning TDF and during the TDF trial burn.

BM/plm

Florida Department of Environmental Regulation

Twin Towers Office Bldg. ● 2600 Blair Stone Road ● Tallahassee, Florida 32399-2400

Bob Martinez, Governor Dale Twachtmann, Secretary John Shearer, Assistant Secretary

June 6, 1990

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

Mr. Randy Thompson
Environmental Department
Florida Crushed Stone Company
Post Office Box 490300
Leesburg, Florida 34749-0300

Dear Mr. Thompson:

Re: Amendment to Construction Permit No. AC 27-118674 and PSD Permit No. PSD-FL-091 to Conduct Performance Test(s) on the Cement Kiln While Burning Tire Derived Fuel (TDF) with Coal.

The Department has reviewed the request that you provided on March 14, 1990. We have also considered the Department's legal authority to allow you to conduct the requested performance test(s). Paragraph 403.061(15), Florida Statutes (F.S.) authorizes the Department to consult with any person proposing to construct, install, or otherwise acquire a pollution control device or system concerning the efficacy of such device or system, or the pollution problem which may be related to the source, device, or system. Paragraph 403.061(16), F.S., authorizes the Department to encourage voluntary cooperation by persons in order to achieve the purposes of the state environmental control act. Paragraph 403.061(18), F.S., authorizes the Department to encourage and conduct studies, investigations, and research relating to the causes and control of pollution. Florida Administrative Code (F.A.C.) Rule 17-2.250(5) authorizes the Department to consider variations in industrial equipment and make allowances for excess emissions that provide practical regulatory controls consistent with the public interest.

In accordance with the provisions of Paragraphs 403.061(15), (16) and (18), F.S., and F.A.C. Rule 17-2.250(5), you are hereby authorized to performance test the cement kiln while burning TDF with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this activity is to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF with coal under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal.

The performance test(s) shall be subject to the following conditions:

1. The permittee shall notify, in writing, the Department's Southwest District and Bureau of Air Regulation (BAR) offices at least 15 days prior to commencement of the performance test(s). A written report shall be submitted to these offices within 45 days upon completion of the last test run.

2. Prior to or after conducting tests on TDF and coal (Post-tests), performance tests (Pre-tests) shall be conducted while firing 100% coal for all of the identified pollutants and pollutant categories in order to establish background levels, unless performance tests have already been conducted and the results can be provided to the Department. These tests, "Pre-tests" (i.e., coal only), shall be compared to the post-tests (TDF and coal) to determine if:

   a) PSD review is required, which includes a construction permit application package and appropriate processing fee; or,

   b) the current construction and PSD permits can be amended to allow the use of TDF with coal.

3. All post-test results shall be compared to "actual emissions" for PSD review purposes (see Region IV, U.S. EPA's letter dated April 4, 1990).

4. The contents of Dr. John B. Koogler's letter received March 14, 1990, are adopted by reference, with exceptions to part A, of which the following pollutants/pollutant categories will also be tested for:

Pollutant/Pollutant Category	Test Method
o Metals (continued)	
Barium	EPA Method 5
Copper	
Nickel	
Iron	
Vanadium	
o PCDDs and PCDFs	EPA Method 23
o PAHs (polynuclear aromatic hydrocarbons)	Modified Method 5
o Benzene	EPA Method 18
o Mercury	EPA Method 101 or 101A

5. An ultimate analysis of the particulate filter(s) shall be required. Also, an ultimate analysis of a representative sample(s) from the baghouse hopper shall be required.

6. This authorized performance test(s) shall not result in the release of objectionable odors pursuant to F.A.C. Rule 17-2.620(2).

7. Performance testing shall immediately cease upon the occurrence of a valid environmental complaint by a citizen or other party, or a nuisance or danger to public health or welfare. Performance testing shall not resume until appropriate measures to correct the problem have been implemented.

8. The performance test(s) shall be conducted under the direct supervision and responsible charge of a professional engineer registered in Florida.

9. This Department action is just to authorize the performance tests on the cement kiln while firing coal and TDF only. The firing of TDF after the last performance test run is completed will be deemed a violation of the current permits, AC 27-118674 and PSD-FL-091.

10. Complete documentation of any TDF usage in the cement kiln shall be required (i.e., start-up and testing).

11. The Department shall be notified in writing on the date of the last test run completion.

12. From the initial date of using TDF, which shall be documented in writing to the Department, the permittee shall be limited to 45 days to stabilize the cement kiln and to submit notification of performance testing. If additional time is needed, the permittee shall provide the Department with documentation of the progress accomplished to date and shall identify what is left to be done in order to achieve stabilization of the cement kiln for performance testing purposes.

13. Attachments (see Attachment Section) are incorported.

The Department has relied on the information referenced in the attachments and conversations with representatives of the FCSC, U.S. EPA-Region IV, and Department of Interior's National Park Service in authorizing this permit letter amendment to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

A copy of this letter and its attachments shall be attached to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

Sincerely,

Dale Twachtmann
Secretary

DT/plm

Attachments

c: B. Thomas, SW Dist.
J. Koogler, P.E., K&A
C. Shaver, NPS-Air
J. Harper, EPA

Attachment Section

1. Final Emissions Test Report of April, 1988, for the Modesto Energy Company's Waste Tire to Energy Facility, Westley, California, received January 18, 1989. Confidential;
2. Federal Register, Volume 52, No. 167, issued August 28, 1987; pages 32597-32600; "Assessment of Zinc and Zinc Oxide as Potentially Toxic Air Pollutants;"
3. "Engineering Study on Burning a Mixture of Coal and Rubber Tire Chips at the United Power Association Elk River Power Station;" Milos Tomaides and Alan Trowbridge; MPCA Reg. #06054;
4. "Measurement of Polynuclear Aromatic Hydrocarbons and Metals from Burning Tire Chips for Supplementary Fuel," by John Drabek and Jay Willenberg, both with the State of Washington Department of Ecology, presented to the 1987 TAPPI Env. Conf., April 26-29, 1987, in Portland, Oregon;
5. "Rubber Tires, A Hazardous Fuel?," by William deBoisblane with the Bay Area AQD, dated March 6, 1985;
6. "Conversion of Scrap Tires to Energy and Its Environmental Issues," by Mark W. Hope with Waste Recovery, Inc., presented to APCA Int. Speciality Conf., October 9-12, 1988;
7. Federal Register, Volume 54, No. 243, issued December 20, 1989; pages 52190-52201; "Standards of Performance for New Stationary Sources; 40 CFR 60, Appendix A - Addition of Methods for Measurement of PCDDs and PCDFs, and Hydrogen Chloride Emissions from Stationary Sources;
8. Dr. John B. Koogler's letter received January 25, 1990;
9. Dr. John B. Koogler's letter received February 6, 1990;
10. Dr. John B. Koogler's letter received March 14, 1990; and,
11. Ms. Jewell A. Harper's letter dated April 4, 1990, and received April 9, 1990.
12. Interoffice Memorandum from Mr. Bruce Mitchell dated May 17, 1990.

Florida Department of Environmental Regulation

Twin Towers Office Bldg. • 2600 Blair Stone Road • Tallahassee, Florida 32399-2400

Bob Martinez, Governor   Dale Twachtmann, Secretary   John Shearer, Assistant Secretary

April 30, 1990

CERTIFIED MAIL-RETURN RECEIPT REQUESTED

Mr. Randy Thompson
Environmental Department
Florida Crushed Stone Company
Post Office Box 490300
Leesburg, Florida 34749-0300

Dear Mr. Thompson:

Attached is one copy of the proposed letter amendment to air construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091 for Florida Crushed Stone Company (FCSC) to performance test the cement kiln while burning tire derived fuel (TDF) with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this letter amendment is to allow FCSC to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF with coal under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal.

Please submit any written comments you wish to have considered concerning the Department's proposed action to me.

Sincerely,

C. H. Fancy, P.E.
Chief
Bureau of Air Regulation

CHF/BM/plm

Attachments

c: B. Thomas, SW Dist.
J. Koogler, P.E., K&A
C. Shaver, NPS-Air
B. Beals, EPA

BEFORE THE STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION

In the Matter of
Application for Amendment by:

FCSC
P. O. Box 490300
Leesburg, Florida 34749-0300

DER File No. AC 27-118674
PSD-FL-091

INTENT TO ISSUE

The Department of Environmental Regulation hereby gives notice of its intent to issue an amendment (copy attached) for the proposed project as detailed in the application for an amendment specified above. The Department is issuing this Intent to Issue for the reasons stated in the attached letter amendment.

The applicant, FCSC (Florida Crushed Stone Company), requested on March 14, 1990, to the Department of Environmental Regulation for authorization to performance test the cement kiln while burning tire derived fuel (TDF) with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this amendment is to allow FCSC to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal. The proposed project will occur at the applicant's existing facility located approximately 3.5 miles NW of Brooksville, Hernando County, Florida.

The Department has permitting jurisdiction under Chapter 403, Florida Statutes, and Florida Administrative Code Chapters 17-2 and 17-4. The project is not exempt from permitting procedures. The Department has determined that an amendment is required for the proposed work.

Pursuant to Section 403.815, F.S. and DER Rule 17-103.150, F.A.C., you (the applicant) are required to publish at your own expense the enclosed Notice of Intent to Issue. The notice shall be published one time only within 30 days, in the legal ad section of a newspaper of general circulation in the area affected. For the purpose of this rule, "publication in a newspaper of general circulation in the area affected" means publication in a newspaper meeting the requirements of Sections 50.011 and 50.031, F.S., in the county where the activity is to take place. The applicant shall provide proof of publication to the Department, at the address specified within seven days of publication. Failure to publish the notice and provide proof of publication within the allotted time may result in the denial of the amendment.

The Department will issue the amendment with the attached conditions unless a petition for an administrative proceeding (hearing) is filed pursuant to the provisions of Section 120.57, F.S.

A person whose substantial interests are affected by the Department's proposed permitting decision may petition for an administrative proceeding (hearing) in accordance with Section 120.57, Florida Statutes. The petition must contain the information set forth below and must be filed (received) in the Office of General Counsel of the Department at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400. Petitions filed by the permit amendment applicant and the parties listed below must be filed within 14 days of receipt of this intent. Petitions filed by other persons must be filed within 14 days of publication of the public notice or within 14 days of receipt of this intent, whichever first occurs. Petitioner shall mail a copy of the petition to the applicant at the address indicated above at the time of filing. Failure to file a petition within this time period shall constitute a waiver of any right such person may have to request an administrative determination (hearing) under Section 120.57, Florida Statutes.

The Petition shall contain the following information;

(a) The name, address, and telephone number of each petitioner, the applicant's name and address, the Department Permit File Number and the county in which the project is proposed;

(b) A statement of how and when each petitioner received notice of the Department's action or proposed action;

(c) A statement of how each petitioner's substantial interests are affected by the Department's action or proposed action;

(d) A statement of the material facts disputed by Petitioner, if any;

(e) A statement of facts which petitioner contends warrant reversal or modification of the Department's action or proposed action;

(f) A statement of which rules or statutes petitioner contends require reversal or modification of the Department's action or proposed action; and

(g) A statement of the relief sought by petitioner, stating precisely the action petitioner wants the Department to take with respect to the Department's action or proposed action.

If a petition is filed, the administrative hearing process is designed to formulate agency action. Accordingly, the Department's final action may be different from the position taken by it in this notice. Persons whose substantial interests will be affected by any decision of the Department with regard to the application(s) have the right to petition to become a party to the proceeding. The petition must conform to the requirements specified above and be filed (received) within 14 days of publication of this notice in the Office in General Counsel at the above address of the Department. Failure to petition within the allowed time frame constitutes a waiver of any right such person has to request a hearing under Section 120.57, F.S., and to participate as a party to this proceeding. Any subsequent intervention will only be at the approval of the presiding officer upon motion filed pursuant to Rule 28-5.207, F.A.C.

Executed in Tallahassee, Florida.

STATE OF FLORIDA DEPARTMENT
OF ENVIRONMENTAL REGULATION

C. H. Fancy, P.E.
Chief
Bureau of Air Regulation

Copies furnished to:

B. Thomas, SW Dist.
J. Koogler, P.E., K&A
C. Shaver, NPS-Air
B. Beals, EPA

CERTIFICATE OF SERVICE

The undersigned duly designated deputy clerk hereby certifies that this NOTICE OF INTENT TO ISSUE and all copies were mailed before the close of business on 4-30-90.

FILING AND ACKNOWLEDGEMENT
FILED, on this date, pursuant to §120.52(9), Florida Statutes, with the designated Department Clerk, receipt of which is hereby acknowledged.

Kim Tober 4-30-90
Clerk Date

State of Florida
Department of Environmental Regulation
Notice of Intent to Issue

The Department of Environmental Regulation hereby gives notice of its intent to issue a permit amendment to FCSC (Florida Crushed Stone Company), Environmental Department, P. O. Box 490300, Leesburg, Florida 34749-0300, to conduct a performance test on the cement kiln while burning tire derived fuel (TDF) with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this amendment is to allow FCSC to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal. The proposed project will occur at the applicant's existing facility located approximately 3.5 miles NW of Brooksville, Hernando County, Florida. The Department is issuing this Intent to Issue for the reasons stated in the proposed letter amendment to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

A person whose substantial interests are affected by the Department's proposed permitting decision may petition for an administrative proceeding (hearing) in accordance with Section 120.57, Florida Statutes. The petition must contain the information set forth below and must be filed (received) in the Office of General Counsel of the Department at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400, within fourteen (14) days of publication of this notice. Petitioner shall mail a copy of the petition to the applicant at the address indicated above at the time of filing. Failure to file a petition within this time period shall constitute a waiver of any right such person may have to request an administrative determination (hearing) under Section 120.57, Florida Statutes.

The Petition shall contain the following information:

(a) The name, address, and telephone number of each petitioner, the applicant's name and address, the Department Permit File Number and the county in which the project is proposed;
(b) A statement of how and when each petitioner received notice of the Department's action or proposed action;
(c) A statement of how each petitioner's substantial interests are affected by the Department's action or proposed action;
(d) A statement of the material facts disputed by Petitioner, if any;
(e) A statement of facts which petitioner contends warrant reversal or modification of the Department's action or proposed action;
(f) A statement of which rules or statutes petitioner contends require reversal or modification of the Department's action or proposed action; and

(g) A statement of the relief sought by petitioner, stating precisely the action petitioner wants the Department to take with respect to the Department's action or proposed action.

If a petition is filed, the administrative hearing process is designed to formulate agency action. Accordingly, the Department's final action may be different from the position taken by it in this Notice. Persons whose substantial interests will be affected by any decision of the Department with regard to the application have the right to petition to become a party to the proceeding. The petition must conform to the requirements specified above and be filed (received) within 14 days of publication of this notice in the Office of General Counsel at the above address of the Department. Failure to petition within the allowed time frame constitutes a waiver of any right such person has to request a hearing under Section 120.57, F.S., and to participate as a party to this proceeding. Any subsequent intervention will only be at the approval of the presiding officer upon motion filed pursuant to Rule 28-5.207, F.A.C.

The application is available for public inspection during business hours, 8:00 a.m. to 5:00 p.m., Monday through Friday, except legal holidays, at:

Department of Environmental Regulation
Bureau of Air Regulation
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Department of Environmental Regulation
Southwest District Office
4520 Oak Fair Boulevard
Tampa, Florida 33610-7347

Any person may send written comments on the proposed action to Mr. C. H. Fancy at the Department's Tallahassee address. All comments mailed within 14 days of the publication of this notice will be considered in the Department's final determination.

Florida Department of Environmental Regulation
Twin Towers Office Bldg. • 2600 Blair Stone Road • Tallahassee, Florida 32399-2400
Bob Martinez, Governor · Dale Twachtmann, Secretary · John Shearer, Assistant Secretary

April 30, 1990

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

Mr. Randy Thompson
Environmental Department
Florida Crushed Stone Company
Post Office Box 490300
Leesburg, Florida 34749-0300

Dear Mr. Thompson:

Re: Amendment to Construction Permit No. AC 27-118674 and PSD Permit No. PSD-FL-091 to Conduct Performance Test(s) on the Cement Kiln While Burning Tire Derived Fuel (TDF) with Coal.

The Department has reviewed the request that you provided on March 14, 1990. We have also considered the Department's legal authority to allow you to conduct the requested performance test(s). Paragraph 403.061(15), Florida Statutes (F.S.) authorizes the Department to consult with any person proposing to construct, install, or otherwise acquire a pollution control device or system concerning the efficacy of such device or system, or the pollution problem which may be related to the source, device, or system. Paragraph 403.061(16), F.S., authorizes the Department to encourage voluntary cooperation by persons in order to achieve the purposes of the state environmental control act. Paragraph 403.061(18), F.S., authorizes the Department to encourage and conduct studies, investigations, and research relating to the causes and control of pollution. Florida Administrative Code (F.A.C.) Rule 17-2.250(5) authorizes the Department to consider variations in industrial equipment and make allowances for excess emissions that provide practical regulatory controls consistent with the public interest.

In accordance with the provisions of Paragraphs 403.061(15), (16) and (18), F.S., and F.A.C. Rule 17-2.250(5), you are hereby authorized to performance test the cement kiln while burning TDF with coal at 15% of the total (100%) Btu heat input (i.e., TDF @ 15% and coal @ 85%). The purpose of this activity is to obtain the data necessary to determine whether the cement kiln is capable of accommodating TDF with coal under the cement kiln's present physical configuration and what regulations the cement kiln will be subject to if it is to be permitted to burn TDF with coal.

The performance test(s) shall be subject to the following conditions:

1. The permittee shall notify, in writing, the Department's Southwest District and Bureau of Air Regulation (BAR) offices 15 days prior to commencement of the performance test(s). A written report shall be submitted to these offices within 45 days upon completion of the last test run.

2. Prior to or after conducting tests on TDF and coal (Post-tests), performance tests (Pre-tests) shall be conducted while firing 100% coal for all of the identified pollutants and pollutant categories in order to establish background levels, unless performance tests have already been conducted and the results can be provided to the Department. These tests, "Pre-tests" (i.e., coal only), shall be compared to the post-tests (TDF and coal) to determine if:

   a) PSD review is required, which includes a construction permit application package and appropriate processing fee; or,

   b) the current construction and PSD permits can be amended to allow the use of TDF with coal.

3. All post-test results shall be compared to "actual emissions" for PSD review purposes (see Region IV, U.S. EPA's letter dated April 4, 1990).

4. The contents of Dr. John B. Koogler's letter received March 14, 1990, are adopted by reference, with exceptions to part A, of which the following pollutants/pollutant categories will also be tested for:

<u>Pollutant/Pollutant Category</u>	<u>Test Method</u>
o Metals (continued)	
Barium	EPA Method 5
Copper	
Nickel	
Iron	
Vanadium	
o PCDDs and PCDFs	EPA Method 23
o PAHs (polynuclear aromatic hydrocarbons)	Modified Method 5
o Benzene	EPA Method 18

5. An ultimate analysis of the particulate filter(s) shall be required. Also, an ultimate analysis of a representative sample(s) from the baghouse hopper shall be required.

6. This authorized performance test(s) shall not result in the release of objectionable odors pursuant to F.A.C. Rule 17-2.620(2).

7. Performance testing shall immediately cease upon the occurrence of a valid environmental complaint by a citizen or other party, or a nuisance or danger to public health or welfare. Performance testing shall not resume until appropriate measures to correct the problem have been implemented.

8. The performance test(s) shall be conducted under the direct supervision and responsible charge of a professional engineer registered in Florida.

9. This Department action is just to authorize the performance tests on the cement kiln while firing coal and TDF only. The firing of TDF after the last performance test run is completed will be deemed a violation of the current permits, AC 27-118674 and PSD-FL-091, and shall be dealt with as such.

10. Complete documentation of any TDF usage in the cement kiln shall be required (i.e., start-up and testing).

11. The Department shall be notified in writing of the time and date of the last test run completion.

12. From the initial date of using TDF, which shall be documented in writing to the Department, the permittee shall be limited to 45 days to stabilize the cement kiln and to submit notification of performance testing. If additional time is needed, the permittee shall provide the Department with documentation of the progress accomplished to date and shall identify what is left to be done in order to achieve stabilization of the cement kiln for performance testing purposes.

13. Attachments (see Attachment Section) are incorporated.

The Department has relied on the information referenced in the attachments and conversations with representatives of the FCSC, U.S. EPA-Region IV, and Department of Interior's National Park Service in authorizing this permit letter amendment to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

A copy of this letter and its attachments shall be attached to the construction permit No. AC 27-118674 and PSD permit No. PSD-FL-091.

Sincerely,

Dale Twachtmann
Secretary

DT/plm

Attachments

c: S. Smallwood, DARM
C. Fancy, BAR
B. Thomas, SW Dist.
J. Koogler, P.E., K&A
C. Shaver, NPS-Air
B. Beals, EPA

Attachment Section

1. Final Emissions Test Report of April, 1988, for the Modesto Energy Company's Waste Tire to Energy Facility, Westley, California, received January 18, 1989. Confidential;

2. Federal Register, Volume 52, No. 167, issued August 28, 1987; pages 32597-32600; "Assessment of Zinc and Zinc Oxide as Potentially Toxic Air Pollutants;"

3. "Engineering Study on Burning a Mixture of Coal and Rubber Tire Chips at the United Power Association Elk River Power Station;" Milos Tomaides and Alan Trowbridge; MPCA Reg. #06054;

4. "Measurement of Polynuclear Aromatic Hydrocarbons and Metals from Burning Tire Chips for Supplementary Fuel," by John Drabek and Jay Willenberg, both with the State of Washington Department of Ecology, presented to the 1987 TAPPI Env. Conf., April 26-29, 1987, in Portland, Oregon;

5. "Rubber Tires, A Hazardous Fuel?," by William deBoisblane with the Bay Area AQD, dated March 6, 1985;

6. "Conversion of Scrap Tires to Energy and Its Environmental Issues," by Mark W. Hope with Waste Recovery, Inc., presented to APCA Int. Speciality Conf., October 9-12, 1988;

7. Federal Register, Volume 54, No. 243, issued December 20, 1989; pages 52190-52201; "Standards of Performance for New Stationary Sources; 40 CFR 60, Appendix A - Addition of Methods for Measurement of PCDDs and PCDFs, and Hydrogen Chloride Emissions from Stationary Sources;

8. Dr. John B. Koogler's letter received January 25, 1990;

9. Dr. John B. Koogler's letter received February 6, 1990;

10. Dr. John B. Koogler's letter received March 14, 1990; and,

11. Ms. Jewell A. Harper's letter dated April 4, 1990, and received April 9, 1990.

ATTACHMENT 1

Confidential

ATTACHMENT 2

Use/Production. (S) Abrasion resistance enhancing for thermoplastic resins. Prod. range: Confidential.

Dated: August 17, 1987.

Denise Devoe,

Acting Director, Information Management Division, Office of Toxic Substances.

[FR Doc. 87-19657 Filed 8-27-87; 8:45 am]

BILLING CODE 6560-50-M

Assessment of Zinc and Zinc Oxide as Potentially Toxic Air Pollutants

[AD-FRL-3253-6]

AGENCY: Environmental Protection Agency (EPA).

ACTION: Notice of zinc and zinc oxide assessment (Zn/ZnO) results and solicitation of information.

SUMMARY: This notice announces the results of EPA's assessment of Zn/ZnO as candidates for regulation under the Clean Air Act (CAA). The Agency has concluded that the health date for Zn/ZnO is insufficient to determine their carcinogenic, mutagenic, or teratogenic potential following inhalation exposures. Adverse respiratory effects have been associated with inhalation exposure to Zn/ZnO fumes and dusts. Similarly, exposure to total particulate matter, which may contain Zn/ZnO, has been associated with adverse respiratory effects. Primary national ambient air quality standards (NAAQS) for particles having diameters of less than or equal to 10 microns (PM_{10}) have been established to protect the general public from such adverse respiratory effects. Therefore, no regulation under the CAA directed specifically at controlling emissions of Zn/ZnO is appropriate at this time.

Given the limited opportunity for prior public review of the health and exposure information incorporated in this notice, the Agency is soliciting comment and information pertinent to the determination made today. A further notice will be published only if public comments or additional information suggest a need to revise EPA's conclusion. This finding has no effect on the regulation of Zn/ZnO as particulate matter to attain the NAAQS for particulate matter. In addition, this notice does not preclude any State or local air pollution control agency from specifically regulating emission sources of Zn/ZnO.

DATES: Written comments pertaining to this notice must be received on or before November 27, 1987.

ADDRESSES: Submit comments (duplicate copies are preferred) to: Central Docket Section (A-130), Environmental Protection Agency, Attn: Docket No. A-87-09, 401 M Street SW., Washington, DC 20460.

Availability of related information: Information on the availability of the documents "Summary Review of the Health Effects Associated with Zinc and Zinc Oxide: Health Issue Assessment," EPA 600/8-87/021F, and "Zinc/Zinc Oxide Preliminary Source Assessment," EPA 450/3-87-008, can be obtained from ORD Publications, CERI-FR, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, OH 45268 (Telephone: 513-569-7562). The above document and other information on the sources, emissions, and environmental fate of Zn/ZnO are summarized in several reports which are found in Docket No. A-87-09, located in the Central Docket Section of the U.S. Environmental Protection Agency, South Conference Center, Room 4, 401 M Street SW., Washington, DC 20460. The docket may be inspected between 8:00 a.m. and 4:00 p.m. on weekdays, and a reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Robert M. Schell, Pollutant Assessment Branch (MD-12), Strategies and Air Standards Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 (Telephone: 919-541-5519 commercial; 629-5519 FTS).

SUPPLEMENTARY INFORMATION: The EPA initiated an assessment of Zn/ZnO based on the large production volume and the potential for adverse health effects associated with exposure to Zn/ZnO in ambient air. In the course of this assessment, the Agency collected relevant information currently available and today's notice provides a summary of this information on the following topics: production and uses, sources and emissions, health effects, monitored ambient air concentrations, exposure and risk estimates and existing regulations.

Production and Uses

Zinc is used extensively to galvanize iron and steel. The element also readily combines with other metals, imparting the characteristics of workability at low temperatures; corrosion resistance; and finishes for use in die-casting alloys, brass, and other common alloys. Zinc displays a vigorous reducing power, liberating hydrogen from sulfuric and hydrochloric acid. This property is the basis for the use of zinc dust or mossy zinc in many commercial organic chemical processes (EPA, 1987a).

Zinc oxide is principally used to activate the vulcanization of rubber. It also helps protect rubber by its opaqueness to ultraviolet light and its high thermal conductivity. A newer use of zinc oxide utilizes its photoconductive and electrostatic properties in office photocopying applications. One of the oldest uses of zinc oxide is in the treatment of burns, infections, and skin diseases. It is also used to give white paints good concealing power, in the manufacture of opaque and certain types of transparent glass, and in the manufacture of porcelain enamels for sheet iron and vitreous enamels for cast iron (EPA, 1987a).

Sources and Emissions

Zinc is the 24th most abundant element and represents about 0.02% of the earth's crust. Zinc blende or sphalerite (ZnS) is the most important ore, yielding about 90% of the metallic zinc produced (Merck, 1976). Natural sources of zinc (e.g., windblown soil, volcanic emissions) have been estimated to constitute about 13% of the total emissions to the atmosphere (Nriagu, 1979).

Anthropogenic Zn/ZnO are emitted to the ambient air from a variety of sources. Table 1 presents a summary of general source categories which emit Zn/ZnO and their estimated emissions (EPA, 1987b; Vandenberg, 1987). Table 1 also lists the number of facilities and maximum annual facility emissions estimates for each source category, where available. Based on the available information, primary zinc and zinc oxide smelters appear to be the largest individual sources of anthropogenic air emissions of Zn/ZnO.

TABLE 1.—SOURCES AND EMISSIONS OF ATMOSPHERIC ZINC AND ZINC OXIDE [a]

Source category	Number of facilities	Estimated emissions to the atmosphere (Mg/yr)		Highest Annual Emissions per Facility (Mg/yr)	
		Zn	Zn0	Zn	Zn0
Primary Zn/Zn0 Production	5	49.9	198	25.2	139
Iron and Steel Production	319	600	2400	15.8	36.7
Metallurgy [b]	NA [c]	NA	NA	16.2	NA
Miscellaneous [d]	NA	NA	NA	0.1	0.3

[a] EPA, 1987b, Vandenberg, 1987.

[b] Includes secondary zinc/zinc oxide industry, brass and bronze production, plating, etc.

[c] Not available.

[d] Includes pigments/paints, semiconductors, business machines, glass/ceramics, detergents, etc.

Health Effects

The available health effects information summarized in the document "Summary Review of the Health Effects Associated with Zinc and Zinc Oxide: Health Issue Assessment" (EPA, 1987a), are reviewed in this section. General statements made in this notice regarding zinc usually pertain to inorganic zinc compounds. Reference is made to specific zinc compounds when only compound-specific information is available.

Zinc is an essential element necessary for the growth and development of all animals, including humans. The essential nature of zinc is based on its role as an integral part of some metalloenzymes, a cofactor in regulating the activity of zinc dependent enzymes, and as a structural and functional component of biomembranes. In addition, zinc plays an important role in the metabolism of proteins and nucleic acids, is essential for the synthesis of deoxyribonucleic acid and ribonucleic acid, and it may control metabolic processes through the formation and/or regulation of the activity of zinc-dependent enzymes. Recommended dietary allowances have been established, with a greater concern generally associated with zinc deficiencies, rather than with less often seen toxic effects associated with excessive zinc intake.

Inhaled zinc can be absorbed across the alveolocapillary membrane, depending on the particle size, solubility, and functional state of the lungs. Similarly, orally administered zinc can be absorbed across the gut mucosa. Zinc may also be absorbed across the skin.

Numerous studies indicate that the body attempts to control the zinc balance homeostatically according to need by regulating the extent of absorption of dietary zinc and the rate of fecal excretion of stable zinc. Absorbed zinc is distributed to muscle, bone, liver, kidney, hair and some endocrine glands. In humans the highest concentrations of zinc are found in the male reproductive system. Zinc is mainly excreted by the gastrointestinal tract.

Zinc oxide has been shown to cause chromosomal damage in the form of an increased frequency of hyperdiploid cells in the bone marrow of noninbred white rats at concentrations of 0.1 and 0.5 mg/m³. An increase in the frequency of structural aberrations of the chromosomes and hyperdiploid cells was seen when human lymphocytes were exposed *in vitro* to zinc acetate at concentrations of 7.0 to 20.0 μg/ml. An interpretation of this report is difficult because the category of aberrations referred to as hyperdiploid cells is not one generally used by cytogeneticists in discussing this type of study. Additionally, the frequency of structural aberrations at 20 μg/ml was slightly less than the frequency at 7 μg/ml. Zinc oxide was not mutagenic at levels of 100 to 5000 μg/plate in the *Salmonella* reversion assay.

There are no data which suggest that a zinc level over that required for normal growth and development is teratogenic. A greater risk of malformations is expected in regard to zinc deficiency. Zinc also appears to offer a degree of protection against the teratogenic effect of cadmium. There are several animal studies and one human study which suggest that the ingestion of high levels of zinc may have an adverse impact on reproduction. Three premature births and one stillbirth occurred in a small group of women ingesting 40.5 mg zinc/day during the third trimester of pregnancy. However, because of the small sample size and lack of a control group, the results from this study are difficult to interpret. No adverse effects on the outcome of pregnancies were observed in a group of seven women supplemented with 81 mg zinc/day during the third trimester of pregnancy. Also, adverse effects on the outcome of pregnancies were not reported in a group of women supplemented with 8.1 mg zinc/day in addition to dietary zinc intakes of from 9.3 to 11.3 mg/day.

A positive carcinogenic response resulting from zinc administration has been only observed following injection of zinc salts into the testes of fowl and rats. Tumors always developed near the site of injection, with some authors doubting the usefulness of the technique employed if only injection site tumors developed. The injection route of exposure is unlikely to be encountered by man, thus one could conclude that testicular tumors in fowl and rats resulting from the injection of zinc salts into the testes are of limited predictive value.

There is no evidence that the inhalation, ingestion or parenteral administration of zinc induces the formation of tumors. There is, however, a considerable amount of information which indicates that the administration of zinc is indirectly involved in tumor formation as a growth promoter or inhibitor. In some animal studies, zinc deficient diets have been found to promote the development of chemically-induced cancers, whereas zinc-adequate and zinc-supplemented diets provided a protective barier against tumor formation. In other animal studies, zinc-adequate or zinc-supplemented diets facilitated the development of chemically-induced cancers. Also, examinations of cancerous tissues in humans have shown that the zinc level deviates from that found in noncancerous tissue. The EPA's Carcinogen Assessment Group (CAG) has concluded that the overall weight-of-evidence for zinc and its inorganic salts suggests that data are not sufficient to determine its carcinogenic potential for humans. Therefore, based on EPA's Guidelines for Carcinogen Risk Assessment (EPA, 1986a), CAG has classified zinc in Group D (not classifiable as to human carcinogenicity) (EPA, 1987a).

Adverse health effects associated with occupational exposures to airborne zinc oxide fumes and/or dust are primarily manifested by respiratory symptoms. Zinc oxide fumes, as well as fumes of many other heavy metals, have been shown to cause an acute illness called metal fume fever in workers exposed to high concentrations in confined occupational settings. This condition is typically characterized by influenza-like symptoms (e.g., headache, fever, nausea, sensations of chills or warmth, and general aches and pains) that occur within a few hours after exposure and may persist for one to two days.

While data are limited, it has been estimated that metal fume fever generally does not occur at zinc oxide levels below 15 mg/m^3. Some eastern European literature report the occurrence of metal fume fever in workers repeatedly exposed to zinc oxide levels averaging as low as 5 mg/m^3.

The Occupational Safety and Health Administration (OSHA) adopted an 8-hour time weighted average permissible exposure limit of 5 mg zinc oxide/m^3, and the American Conference of Governmental Industrial Hygienists (ACGIH) has established an 8-hour time weighted average threshold limit value (TWA–TLV) of 5 mg/m^3 for zinc oxide fumes and a TWA–TLV of 10 mg/m^3 for zinc and zinc oxide dusts to protect against nuisance effects at high dust concentrations in the work environment (ACGIH, 986).

Monitored Ambient Concentrations

Data contained in the EPA's National Aerometric Data Bank indicate the highest monitored annual average ambient concentraiton of zinc is approximately 2.65 $\mu g/m^3$ (Hunt et al., 19[illegible]). Additional information in the literature show annual atmospheric zinc concentrations range from 0.03–27 ng/m^3 in remote locations and from 0.1 to 1.7 $\mu g/m^3$ in urban areas (EPA, 1987a). The highest available ambient air concentration of zinc measured for a 24-hour period was approximately 115 $\mu g/m^3$ located near a point source (Faoro, 1986). Ambient monitoring data specifically for zinc oxide was unavailable.

Exposure Estimates

Estimates of long-term (annual average) human exposure to atmospheric Zn/ZnO emitted from specific or representative facilities for each source category identified in EPA's source assessment for Zn/ZnO (EPA, 1987b) were calculated using the Human Exposure Model (HEM). The HEM estimated concentrations to which populations living within 50 kilometers of specific sources may be exposed. For sources in the primary Zn/ZnO production source category and for several production facilities in the iron and steel source category, site-specific modeling was conducted. Model sources representative of the other facilities within the iron and steel, matallurgy and miscellaneous source categories were used, with maximum reported emission estimates used in the modeling exercise. The results of these modeling analyses indicated a maximum annual zinc concentration of 10.7 $\mu g/m^3$ and a maximum annual zinc oxide concentration of 3.0 $\mu g/m^3$ (Vandenberg, 1987).

In order to assess the potential for adverse noncancer health effects from short-term exposure to Zn/ZnO, a conservative screening modeling analysis was performed using time-adjusted annual emission rates for facilities likely to have emissions resulting in the highest short-term exposures. These facilities included primary Zn/ZnO smelters, a steel producer, two model iron and steel manufacturing furnaces and a facility from the miscellaneous source category (Doll, 1987a, 1987b). Worst case assumptions for source configuration, location, meteorological conditions and terrain effects were applied.

The highest predicted concentrations exceed the 24-hour primary PM_{10} NAAQS for particulate matter by an order of magnitude. While available monitoring data for particulate matter indicate that there are exceedances of this standard in the vicinity of some primary Zn/ZnO smelters, actual total particulate matter measured (containing zinc as well as other particulates) do not confirm ambient concentrations as high as those predicted by the screening technique (Vandenberg, 1987). In addition, fractionation of particulate matter from monitoring sites in close proximity to a source having high predicted concentrations of zinc demonstrate zinc concentrations as high as approximately 10 $\mu g/m^3$, a concentration that is lower than the 24-hour PM_{10} NAAQS for a particulate matter (Pezze and Albert, 1987).

Existing Regulations

Particulate matter, which may or may not contain Zn/ZnO, has been associated with an increased incidence of adverse respiratory effects in both occupationally-exposed people and in the general public. An analysis of the health effects associated with exposure to particulate matter and the concentrations required to elicit these effects is contained in the EPA staff paper (EPA, 1986b) and the criteria document on particulate matter (EPA, 1986c). Primary NAAQS have been established under section 109 of the CAA to protect the general public from adverse respiratory effects for both short-term (24-hours) and long-term (annual) exposure periods. These levels are 150 $\mu g/m^3$ and 50 $\mu g/m^3$, respectively, measured as PM_{10} (i.e., particles having diameters of less than or equal to 10 microns)(EPA, 1987c).

The National Institute for Occupational Safety and Health, OSHA and ACGIH have adopted regulations or have made recommendations for an occupational 8-hour time weighted average level of 5 mg/m^3 for zinc oxide fumes and 10 mg/m^3 for dusts. These levels are designed to protect the average healthy worker that may be repeatedly exposed to zinc or zinc oxide fumes or dusts, day after day, from adverse health effects (ACGIH, 1986).

The Office of Drinking Water has adopted a secondary drinking water standard of 5 mg/liter for organoleptic reasons (EPA, 1985). Zinc and some zinc compounds are currently listed as hazardous substances under section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Further, under section 101(14) of CERCLA, Reportable Quatities (RQs) are established for substances specified in the CERCLA, as well as substances listed or designated under certain sections of the Clean Water Act, CAA (section 112), the Resource Conservation and Recovery Act and the Toxics Substances Control Act (EPA, 1986d). Section 103(a) of the CERCLA requires that any release to the environment (including the air) in any 24-hour period that is equal to or greater than 1000 pounds of zinc must be reported to the National Response Center (telephone 800–242–8802 or 202–426–2675 for the Washington, DC metropolitan area). The 24-hour period refers to the period within which a reportable quantity of a hazardous substance is released in order for the release to be considered reportable; it does not refer to the time available for a person to report a release. Such reporting must occur immediately.

Conclusions

The Agency concludes that the data available at this time are insufficient to indicate health concerns that require further regulation of Zn/ZnO emissions under the CAA. The target levels identified for protection against adverse respiratory effects associated with exposure to Zn/ZnO were the primary PM$_{10}$ NAAQS for particulate matter. These levels were selected on the basis that the respiratory effects elicited by particulate matter containing or not containing Zn/ZnO are equivalent. Available data on the ambient particle size distribution of zinc indicate that the mass median diameter is 1.13 µm (Milford and Davidson, 1985). Therefore, the PM$_{10}$ levels identified to protect public health are appropriate for protecting against adverse effects associated with exposure to Zn/ZnO.

Protective levels were not identified for metal fume fever. Available information indicates that metal fume fever is an acute occupational hazard confined to the immediate work place. It is associated with exposure to fumes or fine dusts of many heavy metals (e.g., zinc, copper, manganese) which are generated during certain work practices (e.g., welding or cutting metals, galvanizing iron). Metal fume fever is a transitory acute effect and appears to be more a function of the physical form(s) of a metal rather than a specific metal. As noted above, the most appropriate benchmark for this decision on Zn/ZnO was judged to be the PM$_{10}$ NAAQS for particulate matter.

Given the findings presented here, the long-term (annual) Zn/ZnO concentrations measured or estimated to be present in the ambient air are below the health effects levels associated with exposure to Zn/ZnO. In contrast, the concentrations predicted from the short-term modeling exercise indicate a potential cause for concern, since these concentrations exceed the 24-hour primary PM$_{10}$ NAAQS for particulate matter. Criteria air pollution control programs have been established, or will be revised if needed, to control particulate matter emissions in order to attain the NAAQS for particulate matter in all areas. Zinc and zinc oxide, as particulate matter, are controlled under these efforts. Therefore, Federal regulatory activity specifically directed at regulating Zn/ZnO under the CAA is not warranted at this time. The EPA's decision not to separately regulate Zn/ZnO under the CAA has no effect on the regulation of particulate matter, which may include Zn/ZnO.

The EPA invites comments and submission of information pertinent to the determination made today. A further notice will be published if public comments or other additional information suggest a need to reevaluate today's findings and revise EPA's present conclusions.

Date: July 31, 1987.

Don R. Clay,

Acting Assistant Administrator for Air and Radiation.

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[FR Doc. 87-19773 Filed 8-27-87; 8:45 am]

BILLING CODE 6560-50-M

[OPTS-59246A FRL# 3254-1]

Certain Chemicals; Approval of a Test Marketing Exemption

AGENCY: Environmental Protection Agency (EPA).

ACTION: Notice.

SUMMARY: This notice announces EPA's approval of an application for test marketing exemption (TME) under section 5(h)(6) of the Toxic Substances Control Act (TSCA), TME-87-20. The test marketing conditions are described below.

FOR FURTHER INFORMATION CONTACT: Robert Wright, Premanufacture Notice Management Branch, Chemical Control Division (TS-794), Office of Toxic Substances, Environmental Protection Agency, Rm. E-611, 401 M Street SW., Washington, DC 20460, (202-382-7800).

SUPPLEMENTARY INFORMATION: Section 5(h)(1) of TSCA authorizes EPA to exempt persons from premanufacture notification (PMN) requirements and permit them to manufacture or import new chemical substances for test marketing purposes if the Agency finds that the manufacture, processing, distribution in commerce, use and disposal of the substances for test marketing purposes will not present any unreasonable risk of injury to health or the environment. EPA may impose restrictions on test marketing activities and may modify or revoke a test

ATTACHMENT 3

ENGINEERING STUDY ON BURNING
A MIXTURE OF COAL AND RUBBER
TIRE CHIPS AT THE UNITED POWER ASSOCIATION
ELK RIVER POWER STATION

RECEIVED
JAN 24 1989
DER-BAQM

By

Milos Tomaides
and
Alan Trowbridge

MPCA Requisition Number 06054

Prepared For

United Power Association
Elk River, MN [illegible]

and

Minnesota Pollution Control Agency
Division of Solid Waste
1935 West County Road B2
Roseville, MN [illegible]

- SCHRIPTEK/ Tim Brady

DISCLAIMER

This report has been reviewed by the Minnesota Pollution Control Agency and United Power Association and has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Minnesota Pollution Control Agency and United Power Association, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

ENGINEERING STUDY ON BURNING
A MIXTURE OF COAL AND RUBBER
TIRE CHIPS AT THE UPA
ELK RIVER POWER STATION

MPCA Requisition Number 06054

1 INTRODUCTION

MMT Environmental, Inc. (MMT) was authorized by United Power Association to perform a study on the burning of a mixture of sub-bituminous coal and shredded automobile tires. The tests were performed at the Elk River Power Station. The purpose of the study was to collect sufficient amounts of information and test data to allow the following assessments:

(a) Technical feasibility of such a fuel combination with respect to reliable operation of the fuel handling equipment, boiler, and fly ash control equipment.

(b) Economic feasibility of such a fuel combination.

(c) Compliance of the process with existing air quality regulations.

Three (3) complete tests were performed, each of one-day duration. On May 30, 1979, a 100 percent coal test was performed. A 95 percent coal - 5 percent tires test and a 90 percent coal - 10 percent tires test were performed on June 4 and June 7, 1979, respectively. The test results and related conclusions are presented in this report.

2 SUMMARY OF TEST RESULTS

The short-term tests on burning a mixture of coal and rubber tire chips have proven the feasibility of such an approach for the United Power Association, Elk River plant operating conditions. The test results and observations of the plant equipment operation are summarized as follows:

2.1 Fuel Handling

(a) Open-belt type conveyors which were used to convey and mix the coal and rubber worked quite reliably.

(b) The dump type feed-scale worked on the mixture of rubber chips and coal without difficulties.

(c) The mechanical stoker spreader handles the coal/rubber chip mixture adequately.

2.2 Boiler

(a) The short-term tests did not result in any malfunction of boilers because of adding rubber chips to the coal.

(b) A coal/rubber chip mixture of about 5 percent rubber chip content appears to burn at higher temperatures compared to 100 percent coal or 10 percent rubber chips. This most probably results in a higher thermal efficiency of the boiler when about a 5 percent rubber chip/coal mixture is burned.

(c) Soot blowing and pulling of bottom ashes from the boiler were normal during all rubber chip burning tests.

(d) The tests show no increased danger of boiler corrosion for up to 10 percent rubber tire chips coal mixture

(e) The amounts of gaseous and particulate pollutants generated by the boiler did not increase with an increasing rubber chip content up to 10.4 percent.

(f) The amount of fine carbon black aerosol generated by burning rubber tire chips increased with the increasing rubber chip content in the fuel.

(g) It is recommended that a 6 percent rubber chip content in the coal not be exceeded for continuous burning of the coal/rubber tire chip mixture for the boilers tested. The limit must be tested for other boilers on an individual basis.

2.3 Fly Ash Control System

(a) The baghouse operated properly and maintained a very high collection efficiency throughout the tests.

(b) Particulate emissions were well in compliance with existing mass emission and visible emission regulations for all test runs.

(c) The presence of carbon black particles from burning rubber chips increased the rate of baghouse pressure drop rise. As a result, the baghouse may require more frequent cleaning for continuous burning of rubber chips.

(d) When cyclone fly ash collectors are used to control the boiler air emissions, the maximum allowable content of rubber chips will be limited by the 20 percent opacity regulation on visible stack emissions.

3 DESCRIPTION OF TESTED FACILITIES

The combustion tests were performed at the Elk River Power Station of United Power Association. Under evaluation was the performance and reliability of three (3) main groups of technological equipment, namely: the fuel handling system, boilers, and fly ash control system. These systems are described in this section.

3.1 Fuel Handling

The layout of the fuel supply conveyors is shown in Figure 1. The coal is normally transported from either open pile storage on the east side of the plant property or coal car dump bins located in the coal unloading building. The coal is transported by open-type rubber belt conveyors.

For the rubber chip burning test, the rubber chips were transported from the open storage and continuously dropped from the rubber chip conveyor onto the fuel mixture conveyor. The coal was brought to the fuel mixture conveyor from the coal car dump bins by a perpendicularly located conveyor. The mixture of fuels was transported into the steam plant building and continuously fed into coal bins located above each of the four (4) fuel feed-scales.

Each of the two (2) stoker boilers tested has two feed scales. Boiler #I is served by feed-scales #F11 and #F12. Boiler #II is served by feed-scales #F21 and #F22.

The fuel from the feed-scale hopper continues to flow into Model 24 Super Spred mechanical spreaders. There are four (4) spreaders per boiler.

3.2 Boilers

The boilers tested were Units #1 and #2 stoker fired Springfield boilers designed to burn coal, No. 2 fuel oil, No. 6 fuel oil, or natural gas. The primary fuel for these boilers is raw, unwashed coal delivered [illegible] from the mine. Each boiler is rated at [illegible] pounds per hour

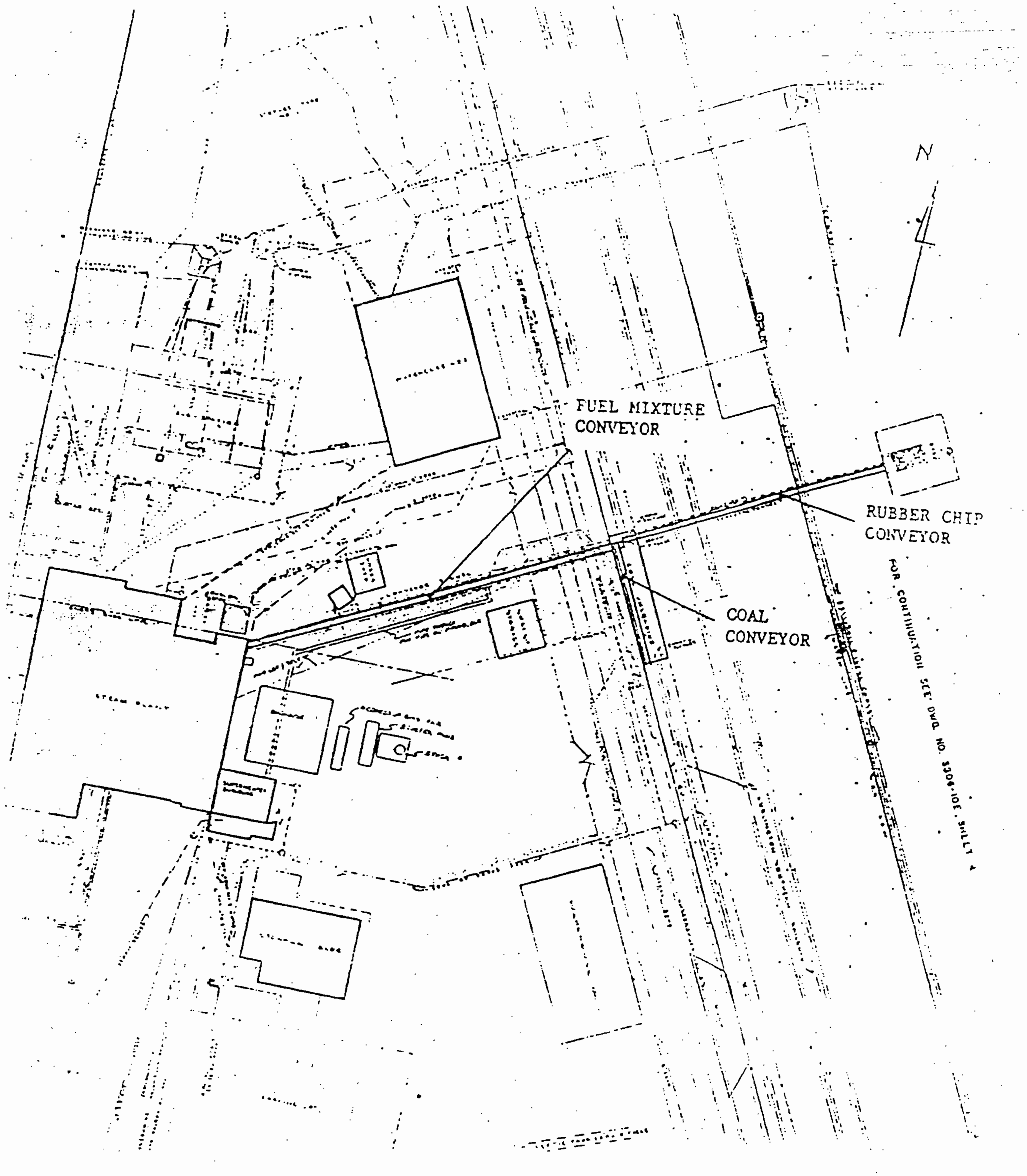

Figure 1. Layout of United Power Association, Elk River, MN Power Plant Facilities

of steam with a gross heat input of 170 x 10^6 Btu per hour. Details on the boiler design are summarized in Table 1.

3.3 Fly Ash Control System

The fly ash is collected from the flue gas in a Research-Cottrell Model #324-12, 264, Series 8 baghouse. The baghouse consists of eight (8) separate modules installed downstream of the boiler as shown in Figure 2.

The flue gas from the individual boilers flows through a duct (Stack #1, Stack #2, Stack #3). Each duct serves one of the three boilers. Boiler #3, which is a pulverized coal unit, was not in operation during the rubber burning tests.

The baghouse is designed for the following parameters:

Maximum throughput, ACFM	280,000
Maximum temperature, °F	360
Bags, glass fiber treated	
Bag diameter, in.	8
Bag length, ft.	22
Maximum baghouse pressure drop, in. w.g.	6
Air to cloth ratio	2.3:1
Maximum inlet dust load, gr/acf	3

Baghouse operation is fully automated. Reverse cleaning of the bags is initiated either automatically at a preselected maximum baghouse pressure drop or manually. The individual baghouse compartments are cleaned in sequence starting with #1 through #8. The total baghouse cleaning cycle is approximately 20 minutes. When all three boilers are running, the cleaning is initiated approximately every 3 hours

Table 1. Boiler Design Parameters

BOILER, Manufacturer	SPRINGFIELD BOILER Co.
Type	2 DRUM - BENT TUBE
Diameter of Drums	60" ID & 42" ID
Length of Drums	17'-6"
Sq. Ft. Surface	11000
Size and Spacing of Tubes	3¼" OD ON 6¾" 2½" OD ON 5¼"
Kind of Tubes	SEAMLESS
SUPERHEATER, Manufacturer	SPRINGFIELD BOILER Co.
Type	2 STAGE - INTERBANK
Sq. Ft. Surface	4040 SQ.FT.
Size of Tubes	1¾" O.D.
No. and Size of Headers	3-12¾" O.D.
SUPERHEAT CONTROL, Type	SWARTWOUT SPRAY TYPE
ECONOMIZER, Manufacturer	SPRINGFIELD BOILER Co.
Type	CONTINUOUS LOOP
Sq. Ft. of Surface	4440
Size of Tubes	2" O.D.
No. and Size of Headers	2-10¾" O.D
WATER WALLS, Manufacturer	SPRINGFIELD BOILER Co.
Type	BARE TUBE
Sq. Ft. Surface, Side Walls	[illegible] SQ FT
Rear Wall	680 SQ FT
Roof and Front Wall	1090 SQ FT.
[illegible]	
Tube Spacing	SIDES 6 - REAR FRONT & ROOF 6¾
No. and Size of Headers	6-10¾" O.D.

Table 1. Continued

AIRHEATER, Manufacturer SPRINGFIELD BOILER Co.

Type TUBULAR

Sq. Ft. of Surface 3300

Size and Length of Tubes 2½" OD - 22'-0"

Thickness of Tube Sheets 3/4"

SETTING, Manufacturer SPRINGFIELD BOILER Co

Type STUDDED TILE

Thickness of Refractory: Furnace 3½ Boiler 3

Kind of Refractory: Furnace SP TILE Boiler SL4S TILE

Thickness of Insulation: Furnace 5 Boiler 5

Kind of Insulation: Furnace SELECTED Boiler SELECTED

SPREADER STOKER AND TRAVELING GRATE

Manufacturer Wm. BROS BOILER & MFG. Co.

Type MODEL 24 SUPER SPRED

Number of Feeders 4.

Effective Grate Area 240 SQ. FT.

Type Grate Drive HYDRAULIC

H.P. Feeder Drive Motor (4) ½ H.P. EACH

H.P. Grate Drive Motor (2) 1 H.P EACH

OVER-FIRE AIR BLOWERS, Manufacturer NORTH AMERICAN

Type and Size SERIES 300 TURBO BLOWER

Capacity, Cfm 1700

Pressure, ins. water 17.35

H.P. Driving Motor 7½ H.P 3500 RPM

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Table 1. Continued

CINDER RETURN BLOWER, Manufacturer	SAME AS
Type and Size	OVERFIRE AIR
Capacity, cfm	FAN
Pressure, ins. water	
HP Driving Motor	
FLY ASH COLLECTOR, Manufacturer	BUBAR
Number of Units	AS REQUIRED
Type	LOW DRAFT LOSS
FORCED DRAFT FAN, Manufacturer	AMERICAN BLOWER CORP.
Type and Size	TYPE HS #400 DIDW.
HP Motor	100
Magnetic Drive, Mfgr.	—
Hydraulic Drive, Mfgr.	A.B.CORP TYPE SC #21
INDUCED DRAFT FAN, Manufacturer	AMERICAN BLOWER CORP.
Type and Size	SIROCCO #7 DI 2/3 DW
HP Motor	200
Magnetic Drive, Manufacturer	—
Hydraulic Drive, Manufacturer	A.B.CORP. TYPE SC #27
SOOT BLOWERS, Manufacturer	VULCAN
Material for Heads	CAST IRON
No. High Temp. Elements	FOUR
Material for Elements	[illegible]
No. Medium Temp. Elements	TWO
Material for Elements	VULCROM
[illegible]	[illegible]
Material for Elements	PLAIN STEEL

Table 1. Continued

AIRHEATER, Manufacturer SPRINGFIELD BOILER Co

Type TUBULAR

Sq. Ft. of Surface 13300

Size and Length of Tubes 2½ OD - 22'-0"

Thickness of Tube Sheets 3/4"

SETTING, Manufacturer SPRINGFIELD BOILER Co

Type STUDDED TILE

Thickness of Refractory: Furnace 3½ Boiler 3

Kind of Refractory: Furnace SP TILE Boiler SL4S TILE

Thickness of Insulation: Furnace 5 Boiler 5

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Effective Grate Area 240 SQ. FT.

Type Grate Drive HYDRAULIC

H.P. Feeder Drive Motor (4) ½ H.P. EACH

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OVER-FIRE AIR BLOWERS, Manufacturer NORTH AMERICAN

Type and Size SERIES 300 TURBO BLOWER

Capacity, Cfm 1700

Pressure, ins. water 17.35

H.P. Driving Motor 7½ H.P 3500 RPM.

Table 1. Continued

SAFETY VALVES, Manufacturer FOSTER

Type and Size TYPE 38 SV - 1-1½", 2", 2½"

WATER COLUMNS AND GAUGE GLASSES

Manufacturer JERGUSON

Type HIGH-LOW ALARM

BLOWOFF VALVES, Manufacturer HANCOCK

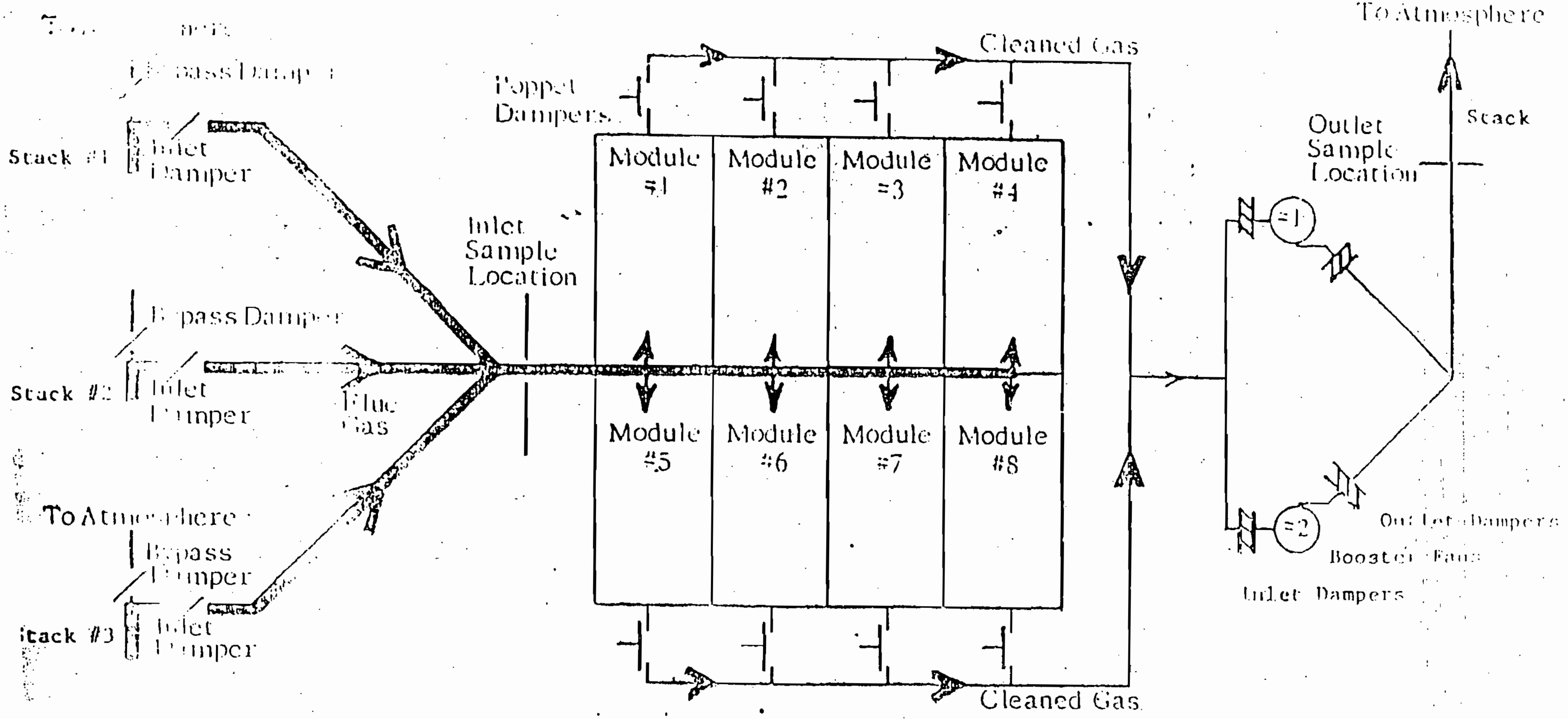
Type and Size 8137 WB - 8137 WB - 1½"

Nozzle Sizes 1½"

No. & Size Feed Water Connections 2-3"

Size Saturated Steam Connection 1½"

Size Superheated Steam Connection 56-1¾"



W. R. Smit
July, 1978

Figure 2. Elk River Baghouse
Flue Gas Schematic Diagram

TEST RESULTS

The results of the combustion test have been divided into information regarding: fuels, boiler, boiler effluent, and fly ash control system, as summarized in this section.

4.1 Fuels

The parameters related to fuels determined during the individual test days were: the coal and rubber mixing ratio, fuel feed rates, and fuel properties.

4.1.1 Mixing Ratio

As shown in Appendix A9, the actual content of rubber chips mixed with coal was:

0 percent by weight for Test #I (5/30/79)
6.3 percent by weight for Test #II (6/4/79)
10.4 percent by weight for Test #III (6/7/79)

4.1.2 Fuel Feed Rates

The fuel feed rates are shown on the field test forms in Appendix B11. The results are summarized in Table 2.

4.1.3 Fuel Properties

The results of the analyses of coal samples are presented in Appendix C7. The results of rubber tire chip analyses are presented in Appendix C8. The identification of coal and rubber samples that were analyzed is presented in Appendix C6. The coal burned was Montana Coalstrip 1 1/4 x 0 inches. The rubber was premium non-steel belted tire chips sized up to 2 inches maximum. No tire side walls were included in the chips. The tires used to prepare chips were only polyester type.

No significant deviations among individual samples of coal and rubber ships were detected. Therefore, the average results of the fuel analyses have been calculated and are summarized in Table 3 for coal samples and Table 4 for rubber samples. From these tables, the as-received heating values of the 6.3 percent/93.7 percent coal/rubber chip mixture were 9105 Btu/lb and 9400 Btu/hr, respectively.

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Table 2. Fuel Burning Rate (LB/HR) For 0%, 6.3% and 10.4% Tire Burning Tests

Time	Test I (0%)				Test II (6.3%)				Test III (10.4%)			
	Boiler I		Boiler II		Boiler I		Boiler II		Boiler I		Boiler II	
	F11	F12	F21	F22	F11	F12	F21	F22	F11	F12	F21	F22
0900	----	----	----	----	2600	2800	2000	3800	7600	8800	7200	12600
1000	5800	7800	5600	5200	6800	6200	6200	9400	6400	8200	7800	8400
1100	7200	8800	6400	10200	5400	5400	5400	8000	8400	9800	7800	8800
1200	7400	8400	6400	8600	6800	5400	6400	10000	6000	7000	6600	7000
1300	7800	8200	6000	8200	6400	5600	6200	8800	7000	9000	8000	9000
1400	10000	10200	8000	10000	5400	5800	6800	7400	6200	7800	6000	6200
1500	6800	6600	5200	7400	6000	5800	7400	7800	5200	8400	5400	9600
1600	8200	8800	6000	9800	7600	5600	8200	9000	6200	9200	5600	10200
1700	7400	7800	5600	8600	5600	4400	5800	6800	5400	9000	5400	9400
1800	8000	9200	6200	9600	6600	4800	6400	7200	----	----	----	----
1900	7200	8600	5400	8600	----	----	----	----	----	----	----	----
Total, LB	75800	84400	60800	86200	59200	51800	60800	78200	58400	77200	59800	81200
Total Per Boiler, LB	160200		147000		111000		139000		135600		141000	
Total Per Test, LB	307200				250000				276600			
Rate Per Boiler, LB/HR	16020		14700		11684		14632		15066		15666	
Rate Per Plant, LB/HR	30720				26316				30733			

Table I. Summary of Coal Analyses

Parameter	Average Values For Each Test Day Test #I	Test #II	Test #III
Moisture, %	22.47	22.14	22.78
Ash, %	10.26	9.60	8.83
Volatile Combustible Matter, %	27.50	27.80	28.20
Fixed Carbon, %	39.78	40.47	40.20
Sulfur, %	0.70	0.71	0.44
B.T.U. wet per pound	8650	8810	8780
B.T.U. dry per pound	11154	11314	11429
Total Carbon, %	50.80	51.80	50.75
Hydrogen, %	3.70	3.85	3.70
Oxygen, %	11.10	10.90	11.75

All % contents are by weight.

Average higher heating value of the coal used was 11299 Btu/lb.

Average lower (as-received) heating value was 8747 Btu/lb.

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Table [illegible]. Summary of Tire Chip Analyses

Parameter	Average Values For Each Test Day Test #II	 Test #III
Moisture, %	0.71	1.14
Ash, %	3.00	3.68
Volatile Combustible Matter, %	65.49	63.71
Fixed Carbon, %	30.81	31.48
Sulfur, %	1.26	1.46
B.T.U. wet per pound	15880	15880
B.T.U. dry per pound	15988	16062
Total Carbon, %	85.10	85.05
Hydrogen, %	6.75	6.30
Oxygen, %	2.75	2.00

All % contents are by weight.

Average higher heating value was 16025 Btu/lb.

Average lower (as-received) heating value was 15880 Btu/lb.

4.2 Boiler

Information and test results related to the boiler operation are presented in the following paragraphs. They are listed separately to cover: fuel feeding, combustion, bottom ash, and boiler output.

4.2.1 Fuel Feeding

No specific problems were experienced with the fuel feeding and spreading onto the grate. No change in the operation of the feeders was noticed while burning up to 10.3 percent of rubber chips. The only noticeable change was that during the 6.3 percent rubber chip test, the fuel feeders had to be throttled to feed less fuel compared to the first day and third day tests.

The fuel feed rates are summarized in Table 2 separately for each boiler and each feeding scale.

4.2.2 Combustion

As inspected visually, the flames above the grate were longer and hotter during the 6.3 percent rubber test compared to the 100 percent coal test, primarily in Boiler #1. Also, the 6.3 percent rubber test resulted in generation of more black smoke at the end of the flames. The 10.4 percent rubber test resulted in a shorter flame, but large quantities of smoke were generated from the flames filling up the boiler combustion chamber.

Otherwise, the boiler operation was regular without any malfunctions on any of the test days. The soot blow was normal and was performed about once every eight (8) hours on the average.

4.2.3 Bottom Ash

Bottom ashes were pulled approximately every five (5) hours. No significant differences were found among the individual test days. The bottom ash appeared much hotter and with more clinkers on the 10.4 percent rubber test day.

Identification of bottom ash samples which were analyzed is described in Appendix C6. The results of the bottom ash analyses are presented in Appendix C9 and Table 5.

Table 5. Summary of Bottom Ash and Fly Ash Analyses for Combustible Matter, Sulfur Trioxide, and Zinc

	Average Content Per Test Day, % weight		
Sample Identification	Combustible Matter	Sulfur Trioxide	Zinc
Test #I			
Bottom Ash	3.77	0.82	0.0009
Fly Ash	26.22	0.38	0.022
Test #II			
Bottom Ash	1.89	1.11	0.0040
Fly Ash	24.32	0.58	0.532
Test #III			
Bottom Ash	2.65	0.91	0.0065
Fly Ash	30.70	0.42	0.784

4.2.4 Boiler Output

The boiler output was very steady on all test days. Each boiler generated about 10 megawatts continuously. The boiler output parameters are presented in Appendix B11.

4.3 Boiler Effluent

The stack test results are presented separately for boiler gaseous effluent and fly ash effluent. The field test data is presented in Appendixes A1 through A8, B1 through B9, and C1 through C5.

4.3.1 Gaseous Effluent

(a) Flow Rate. Test results are summarized in Table 6 for the baghouse inlet and outlet.

(b) Temperature. Dry bulb temperatures are presented in Table 6 for the baghouse inlet and outlet. Also presented are dew-point temperatures as measured at the baghouse inlet only.

(c) Gas Composition and Gas Emission Rates. The results of ORSAT analyses are summarized in Table 6. The emission rates of the main gaseous pollutants are presented in Table 7.

4.3.2 Fly Ash Effluent

(a) Emission Rates. Particulate emission rates are presented in Table 7 for the baghouse inlet and outlet.

(b) Size Distribution. Fly ash samples as identified in Appendix C6 were sieve analyzed for particle size distribution. The results are presented in Appendix C9. The average size distributions of fly ash for individual test days are summarized in Table [illegible].

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Table 6. Summary of Main Parameters of Boiler Gaseous Effluent

Test Description			Parameter				
			Gas Temperature, °F	ORSAT Analysis, $CO_2/O_2/CO$	Flow Rate, ACFM	Flow Rate, DSCFM	Dew Point °F
Test #I (0% Rubber)	In	1-1	302	6.9/12.8/0.1	182450	114220	70
		1-2	313	7.4/12.6/0.0	197320	121710	72
		1-3	318	7.4/12.6/0.0	182170	112120	73
		Ave.	311	7.2/12.7/0.0	187310	116020	72
	Out	1-1	297		178890	112450	--
		1-2	308	7.2/12.8/0.0	185980	116680	--
		1-3	313	7.4/12.6/0.0	180600	112030	--
		Ave.	306	7.3/12.7/0.0	181820	113720	--
Test #II (5% Rubber)	In	2-1	296	7.9/12.1/0.0	160260	102820	74
		2-2	301	8.1/11.7/0.1	173590	109640	75
		2-3	302	7.7/12.5/0.1	175190	109520	75
		Ave.	300	7.9/12.1/0.1	169680	107330	75
	Out	2-1	291		176810	111560	--
		2-2	296	8.0/12.0/0.1	175530	110600	--
		2-3	297	7.8/12.4/0.1	170150	106050	--
		Ave.	295	7.9/12.2/0.1	174160	109400	--
Test #III (10% Rubber)	In	3-1	298	5.4/15.2/0.2	173600	109640	75
		3-2	301	6.4/13.8/0.0	167580	106210	76
		3-3	299	7.6/12.6/0.0	160900	100240	75
		Ave.	299	6.5/13.9/0.1	167360	105360	75
	Out	3-1	293	7.3/12.7/0.0	172110	107890	--
		3-2	296	5.7/14.4/0.0	170250	106370	--
		3-3	294		168810	105790	--
		Ave.	294	6.5/13.6/0.0	170390	106680	--

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Table 7. Summary of Emission Rates of Various Pollutants

Test Description			Heat Input	Parameter									
				Particulate Emission Rate		Sulfur Dioxide Emission Rate		Sulfuric Acid(1) Emission Rate		Nitrogen Dioxide Emission Rate		Chloride (as Cl^-) Emission Rate	
			MBTU/HR	LB/HR	LB/MBTU	LB/HR	LB/MBTU	LB/HR	LB/MBTU	LB/HR	LB/MBTU	LB/HR	LB/MBTU
Test #I	In	1-1	292.54	931	3.18	474	1.62	0	0	105*	0.37*	10.5	0.036
(0% Rubber)		1-2	269.01	735	2.73	445	1.65	0	0	213	0.83	13.9	0.050
		1-3	257.77	440	1.71	434	1.68	0	0	202	0.78	0.0	0.000
		Ave.	273.11	702	2.54	451	1.65	0	0	208	0.81	8.1	0.029
	Out	1-1	292.54	2.81	0.010								
		1-2	269.01	4.54	0.017	380	1.41	4.0	0.015	202	0.78		
		1-3	257.77	9.11	0.035								
		Ave.	273.11	5.49	0.021								
Test #II	In	2-1	241.38	799	3.31	87*	0.36*	---	-----	181	0.75	5.4	0.022
(5% Rubber)		2-2	252.67	1137	4.50	451	1.78	1.6	0.006	174	0.72	8.9	0.035
		2-3	226.94	602	2.65	449	1.98	24.9	0.110	204	0.85	23.1*	0.102*
		Ave.	240.33	846	3.49	450	1.88	13.3	0.058	186	0.77	7.2	0.029
	Out	2-1	241.38	4.84	0.020								
		2-2	252.67	3.94	0.016	454	1.80	3.6	0.014	144	0.58		
		2-3	226.94	1.88	0.008								
		Ave.	240.33	3.55	0.015								
Test #III	In	3-1	312.20	666	2.13	454	1.45	24.7	0.079	155	0.55	5.1	0.016
(10% Rubber)		3-2	281.75	389	1.38	229*	0.81*	22.6	0.080	156	0.55	17.5	0.062
		3-3	286.12	635	2.22	434	1.52	----	-----	---	----	0.6	0.002
		Ave.	293.36	563	1.91	444	1.49	23.7	0.080	156	0.55	7.7	0.027
	Out	3-1	312.20	2.14	0.007								
		3-2	281.75	2.40	0.009	430	1.53	3.3	0.012	90	0.30		
		3-3	286.12	3.28	0.011								
		Ave.	293.36	2.61	0.009								

*Starred values not used in calculations of average.

(1) Expressed as sulfuric acid--actually combination of SO_3 and H_2SO_4

Table 8. Average Fly Ash Size Distribution For the Three Test Days

Test	Tire Content By Mass, %	Mass of Particles Larger Than Size Shown, % 2000 μm	425 μm	150 μm	75 μm	0 μm
#I	0	0.2	2.6	44.8	84.9	100
#II	6.3	0.0	1.2	18.0	50.4	100
#III	10.4	0.0	3.4	31.3	64.1	100

Also analyzed, under an optical microscope, were samples of the catch from the stack sampling train. The mass median diameter of fly ash particles collected on the backup filter was about 5 μm for Test Day #I, about 10 μm for Test Day #II, and 17 μm for Test Day #III. Samples from Test Day #II and Test Day #III contained much more carbon black chain aggregates compared to Test Day #I samples. Also, samples from Test Day #I were dark gray compared to samples from Test Day #II and Test Day #III which were black.

(c) Composition. Results of chemical analyses of fly ash samples are presented in Appendix C9. As seen from these results, the only variation was detected on sulfur trioxide and zinc. The average values for individual test days are summarized in Table 5.

(d) Visible Emissions. No visible emissions were observed on the stack during the entire test. The only visible emissions appeared for several seconds during the beginning of the baghouse cleaning cycle. This event is recorded on a chart of the transmissometer readout as shown in Appendix B13.

4.4 Fly Ash Control System

The operating parameters of the fly ash control system for the individual test days are presented in Appendixes B10 and B12. Other pertinent information is described in the following paragraphs.

4.4.1 Mode of Operation

The baghouse was operating throughout the tests with all eight compartments active. The cleaning of the bags was initiated manually when [illegible] pressure drop [illegible] This is normal operating conditions when the baghouse serves three boilers including the pulverized coal boiler, the cleaning cycle is initiated automatically at about 7.5 in. w.g. baghouse pressure drop. Duration of complete cleaning cycle of the baghouse was approximately 20 minutes.

4.4.2 Gas Flow Rates and Temperatures

Gas flow rates and temperatures at the baghouse inlet were measured using baghouse panel gauges. The results are presented in Appendix B10. More accurate are the flow rates and temperatures actually measured with stack sampling equipment as summarized in Table 6.

4.4.3 Dust Loads

Dust loads at the baghouse inlet and outlet are shown in Table 7.

4.4.4 Pressure Drops

Pressure drops of the baghouse and the individual compartments are presented in Appendix B10.

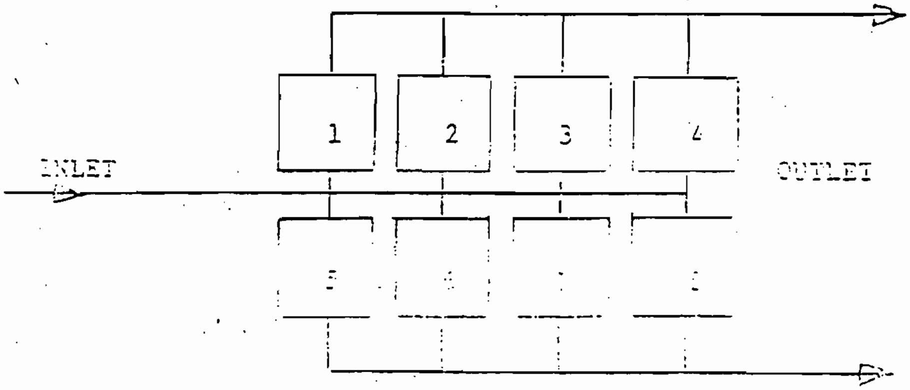
(a) Rate of Increase. To demonstrate the influence of varying quality of the fly ash depending upon the type of fuel burnt, a rate of increase in the baghouse pressure drop and the pressure drop of the individual compartments was calculated. The results are summarized for each test day in Table 9.

(b) Bag Cleaning Effectiveness. The bag cleaning effectiveness was determined from the reduction of the baghouse pressure drop before and after the cleaning cycle expressed in percent of the pressure drop before the baghouse cleaning. This reduction was 29 percent, 18 percent, and 15 percent for [illegible] percent sulfur, [illegible] percent sulfur, and [illegible] percent sulfur, respectively.

Table 9. Rate of Increase of Baghouse Pressure Drop on Individual Test Days

Baghouse Module #	Rate of Increase, in. per hour Test #I	Test #II	Test #III
1	0.07	0.15	0.20
2	0.05	0.23	0.27
3	0.08	0.33	0.33
4	0.07	0.30	0.30
5	0.07	0.37	0.20
6	0.08	0.23	0.27
7	0.07	0.30	0.33
8	0.08	0.30	0.33
Total Baghouse	0.07	0.30	0.30

Location of Modules



5 DISCUSSION OF TEST RESULTS

The tests offer the following observations and conclusions:

5.1 Fuel Handling

The rubber chips did not create any significant problems during their handling and transport. The transportation of rubber chips and coal on two separate belt conveyors and their mutual mixing on a third conveyor was quite successful. The mixing ratio was simply controlled by changing the amount of one of the two materials being transported to the mixing conveyor. The same can be accomplished by changing the speed of the conveyors.

The mixture of up to 10.4 percent rubber chips and coal did not result in any difficulties in the operation of the dump type feed-scale. The mixture was also easily handled by ordinary mechanical fuel spreaders and allowed for a normal, evenly spread layer of fuel on the grate.

5.2 Boiler Performance

Both boilers operated normally throughout the tests. Fuel spreading, quality of flames, size of burning region, and bottom ash properties were comparable for all test runs.

The only detectable differences in the boiler performance when comparing the test results of the individual test days were as follows:

(a) Reduced fuel feed rate on the 6.3 percent rubber chip test day

(b) Obviously higher temperature of the burning fuel on the 6.3 percent rubber chip test day

(c) Noticeably more [illegible] in the boiler on the 10.4 percent rubber chip test day

(d) Content of combustible matter in the fly ash and bottom ash was lowest for the 6.3 percent rubber chip test, indicating better combustion during that test (ϵ). Increasing content of zinc in the fly ash with increasing content of rubber chips.

The above observations suggested that the burning conditions were favorable on the 6.3 percent rubber test day. To assess the possible influence of burning rubber chips on that day, the overall boiler heat utilization factor was calculated for each boiler and each test day. The results are summarized in Table 10.

From this table, the heat utilization factor of the boilers when operating on 100 percent coal is between 0.87 and 0.89 percent. Considering the type of boilers, this factor is much higher than would be anticipated. This means that either the steam flow meters were measuring a higher flow rate than actual or the feed-scale was feeding more than 200 pounds of fuel per dump. The accuracy of the scale is suspect in this case.

Increase of the heat utilization factor in Boiler #I on the second test day should be noted. The heat utilization factor calculated for that test was in excess of 1.0, which is normally not possible. Because of the suspect accuracy of the feed-scale, only a relative difference between heat utilization factors measured on various days should be considered.

The heat utilization factor of Boiler #II was significantly lower on the second test day. This difference may indicate that the feed-scale of Boiler #I was dumping much more than 200 pounds of fuel on that day. This is possible, but notes from the boiler operation show that the fuel spreader had to be throttled on Boiler #I that day to maintain a constant 10 megawatts boiler output. The analyses of other boiler operating parameters do not offer any clues to this apparent discrepancy in the boiler #I heat utilization factor.

By combining the observation of the quality of fuel combustion in Boiler #I on the second test day with the results of fly ash analysis for combustible matter and the heat utilization factor calculations, it is believed that the combustion efficiency on the second test day in Boiler #I was more favorable than on the other test days. One possible explanation is that by better balancing of the amount of top and bottom

Table 10. Heat Utilization Factor for 0%, 6.3%, and 10.4% Tire Burning Test[x1]

Parameter	Test I (0%) BI	Test I (0%) BII	Test I (0%) SUM	Test II (6.3%) BI	Test II (6.3%) BII	Test II (6.3%) SUM	Test III (10.4%) BI	Test III (10.4%) BII	Test III (10.4%) SUM
Fuel Burning[x2] Rate, LB/HR	16020	14700	30720	11684	14632	26316	15066	15665	30731
Combined Lower Heating Value, BTU/LB		8747			9105			9400	
Heat Input, MBTU/HR	140	129	269	106	134	240	142	147	289
Steam Gener. Rate, 1000 LB/HR	105	100	205	105	98	203	102	98	200
Content, BTU/LB	1164	1153	1158	1158	1153	1155	1158	1158	1158
Heat Output, MBTU/HR	122	115	237	122	112	234	118	114	232
Boiler Heat Utilization Factor[x3]	0.87	0.89	0.88	1.15	0.84	0.98	0.83	0.78	0.80

[x1] Calculated for fuel heating values on as-received basis (lower heating value) comparing heat input in fuels with heat output in steam.

[x2] Assumed coal scale capacity of 200 lb per each dump. Calculated as a ratio of "Heat Output" and "Heat Input".

[x3] Steam heat content less heat in the boiler make-up water (approx. 860 psig and 340° F).

combustion air in Boiler #1, the higher heating value of rubber chips resulted in a higher combustion temperature and, consequently, more efficient use of combustibles in the fuels. Although an objective explanation would require more testing, the test results suggest that the combustion of rubber chips may, up to a certain content, improve the thermal boiler efficiency.

No differences were observed in the effectiveness of the soot blowing nor was any need for more frequent soot blowing experienced during the tests. However, it must be emphasized that burning tests of longer than one day's duration would be required to be able to generalize this observation.

5.3 Boiler Effluent

The total flow rate of the flue gas remained constant for all test days as seen in Table 6. Also, the effluent temperatures, both wet bulb and dew point, did not change appreciably. A relatively constant dew point temperature indicates that the sulfur oxide emissions, primarily sulfur trioxide, were independent of the amount of rubber chips burned within the range tested. This observation is also supported by the results of sulfur dioxide and sulfuric acid (combined sulfuric acid and sulfur trioxide) emission tests as presented in Table 7. The emissions of nitrogen oxide and chloride were also constant for all practical purposes.

As seen in Table 7, it can be concluded that the quality of gaseous effluent from the boiler does not depend appreciably upon the amount of rubber chips burned within the range tested.

The amount of particulate emissions varied for individual test days. When this variation was compared with the variation for separate test runs for each day, it was found to be about the same. It can be concluded that the mass of particulate emissions did not change appreciably.

On the other hand, the size distribution of the particulate [illegible] and the quality [illegible] depend [illegible] upon the amount of rubber chips burned. The test results indicate that the particulate emissions consisted of fly ash generated by coal burning and carbon black aerosol generated by burning the rubber chips. This observation is supported by the changing color of fly ash samples from gray for 100 percent coal to black for 10.4 percent tire chips. It is further supported by an optical analysis of the fly ash samples from the baghouse and stack sampling train. The optical analysis showed a large quantity of carbon black chain aggregates attached to other fly ash particles whenever rubber was burned. The chains, consisting of about 0.5 μm primary particles, were longer and bigger for 10.4 percent rubber test runs than for 6.3 percent rubber test runs. Finally, the observation is supported by a chemical analysis of the fly ash (shown in Table 5) in which the amount of combustible matter increased with an increasing rubber content. The portion of the fly ash which was generated by coal burning maintained a relatively constant size distribution. This conclusion is supported by the size analysis of fly ash presented in Table 6.

The only other change in chemical composition of the fly ash was the increased content of zinc with the increasing content of rubber chips, as shown in Table 5. The fly ash samples appear to be alkaline, as presented in Appendix C9-3. This does not mean that the carbon black agglomerates are not slightly acidic.

The presence of carbon black particles must be changing the adhesive properties of the fly ash, making the fly ash more difficult to remove from the surface of the heat exchanger and the surface of the filter fabric.

The quality and chemical composition of the bottom ash was constant and independent of the content of rubber chips within the limits tested.

The changed quality of the gaseous and particulate effluent from the boiler was not significant enough to complicate the performance of the boiler except that the soot blowing may possibly have to be performed more often. The corrosion potential of the effluent did not change enough to result in operational [illegible]

Total sampling time per test run: 60 minutes

Port Identification: Ports were labeled A to F with Port A
being on the west end.

Point Identification: Points within each port were labeled
from 1 to 5 with 1 being farthest from the port.

<u>Baghouse Outlet (Stack)</u>

Stack inside diameter: 96 inches

Distance to flow disturbance
Number of duct diameters before port: 5.8
Number of duct diameters after port: 6 (estimate)

Required number of sampling points: 28

Actual number of sampling points used: 32

Number of ports: 4

Points per port: 8

Sampling time per point: 2 minutes

Total sampling time per test run: 64 minutes

Port Identification: Ports were labeled A to D in a clockwise
direction with port A facing the north.

Point Identification: Points within each port were labeled
from 1 to 8 with point 1 being farthest from the port.

6.2 Testing Equipment

The boiler and baghouse operation was monitored with standard plant equipment and instruments. The following standard instruments were used to collect all pertinent operational parameters:

Temperatures - thermocouple

Steam pressure - pressure gauge (Bourdon tube)

Best Available Copy

Pressure drop in baghouse - Magnehelic gauges

Opacity - EPA approved transmissometer

To measure the amount of fuel (coal or coal/rubber chip mixture), two feed scales per boiler were used. The scales are a product of the Beaumont Birch Company, Philadelphia, Pennsylvania. The scales are set to feed **approximately 200 pounds of coal per balance dump. The counter which counts the number of scale dumps was used to monitor the fuel input.**

Particulate testing in the boiler before the baghouse and in the stack was performed using two standard EPA type sampling trains.

Manufacturer: Research Appliance Company

Model: RAC Stacksamplr

Probes: Inlet test - 10 foot with stainless steel lines
Outlet test - 5 foot with pyrex lines

Nozzles: Stainless steel

Filter media: Type A/E glass fiber
100mm effective filtration diameter

6.3 Testing and Analytical Procedures

Testing and analytical procedures employed in this study were as follows:

6.3.1 Boiler Operation

The boiler operation parameters were determined and recorded every hour. The following parameters were measured:

Coal consumption

Tire chip consumption

Flue gas temperature

O_2 flue gas content

[illegible]

Steam temperature and pressure

Two (2) coal samples per day

Two (2) tire rubber samples per day

Four (4) bottom ash samples per day

The only procedure which requires special description is how the fuel and bottom ash samples were obtained. The fuel to be analyzed was collected by randomly removing approximately a one-pound sample from each of the four feeding scales. A total of about twenty pounds was removed, put on one pile, mixed, and the pile reduced to about a four-pound sample by the standard quartering technique. This sample was manually screened to separate all rubber. The resulting coal and rubber samples were separately weighed and stored for analysis. By comparing the weights of the rubber and coal samples, the actual rubber content in the fuel was determined.

The bottom ash sample was obtained by removing about fifty pounds of bottom ash while pulling the ashes. This amount was shoveled out of the bottom ash chute to cover the whole width of the boiler. A final sample was obtained by mixing and quartering the original fifty-pound sample down to about five pounds.

A special test was performed on the boiler to observe the quality of the flame in the boiler and also to determine the quality of bottom ash. Both parameters were determined visually.

6.3.2 Baghouse Operation

The boiler operation parameters were determined and recorded every hour. The following parameters were measured:

Particle concentration before and after the baghouse

Particle size from the baghouse hopper

Particle size from the sampling train

[illegible]

Temperature before and after the baghouse

Moisture content before and after the baghouse

Gas composition before and after the baghouse

Plume opacity

Total baghouse pressure drop

Individual compartment pressure drop

Frequency and sequence of baghouse cleaning

On ash sampling test procedures, caution must be exercised in interpreting results from the fly ash sampling tests. United Power Association (UPA) is concerned that a number of the initial fly ash samples were not as representative as they could have been. As the test procedure progressed, somewhat better techniques were developed; however, the fly ash sample still does not provide an accurate representation of the ash collected by the baghouse.

The problem is that fly ash drops out in various portions of the flue gas duct as it leaves the boiler. The first place that the fly ash drops out is in the air preheater section. In this area fairly heavy particles begin to fall out. A portion of these particles are reinjected into the boiler. Previous tests have indicated there can be 50 percent carbon in the air preheater area. As the flue gas enters the bottom of each baghouse module, the heavier particles tend to drop into the bottom of the ash hopper and the relatively fine particles are carried by the flue gas and collect on the filter bags.

The initial samples of fly ash were collected from 9-inch poke holes in the bottom of the fly ash hoppers. Since these poke holes fill up with the heavier particles, the samples were not representative of all the particulate collected in the baghouse.

A more representative fly ash sample was obtained by changing the collection procedure. Initially, the ash collection system cleaned the ash [illegible] through a cleaning cycle and, subsequent to that, a sample of ash was pulled off the bottom of the fly ash hopper. In order to reduce the influence of stratification on the sample of fly ash, the ash removal system was allowed to pull the ash from the hopper for 20 seconds and then the sample was removed from the hopper. This provided a representative sample of the ash as it came out of the ash hoppers.

One problem experienced in this particular sampling procedure was that the upstream hoppers, #1 and #5, tend to have very light loads of fly ash. Therefore, it was very easy not to have a sufficient amount of material for an accurate sample after some ash had been pulled out during the ash removal process. On hoppers #1 and #5, a sample was collected prior to the start of the ash cleaning process and another after the ash cleaning process had been in operation for one cycle.

With respect to the fly ash sampling during the tire test burn, the first sample taken during the 100 percent coal burning operation was not representative because the sample consisted of ash that was in the bottom of the fly ash hopper. The second sample obtained during the 100 percent coal burning operation was taken after cleaning of the baghouse and was somewhat more representative. The samples taken during the 5 percent and 10 percent tire chip test burn were as representative of the fly ash as possible. There is still concern that these do not necessarily reflect the exact proportions of heavy ash which collects in the bottom of the ash hoppers or fine ash which collects on the bags.

6.3.3 Analysis of Ash and Fuel Samples

Three samples of fly ash were analyzed from each test day for: manganese, zinc, boron, potassium, and sodium. The analytical technique used was atomic absorption.

Four samples of bottom ash were analyzed from each test day for the same elements as fly ash.

A duplicate analysis of fly ash and bottom ash leachate was performed on the 10 percent rubber chip test samples. The leachate was analyzed for: arsenic, boron, cadmium, iron, lead, manganese, nickel, and zinc using the atomic absorption technique. Standard EPA techniques for wastewater were used to analyze the leachate for: chlorides, phosphorus, and phenol.

All fly ash and bottom ash samples were also analyzed for acidity. In this test, distilled water was shaken with each sample in a 2:1 ratio and the resulting pH values were measured and recorded.

A standard sieving technique was used to analyze the size of fly ash samples.

6.3.4 Stack Sampling and Analytical Procedures

General

In order to determine the pollutant emission rate from stationary sources, the EPA (Environmental Protection Agency) has established a series of reference methods which specify the manner in which tests must be performed. These reference methods are found in the Code of Federal Regulations under Title 40 - Protection of Environment; Chapter 1 - Environmental Protection Agency; Subchapter C - Air Programs; Part 60 - Standards of Performance for New Stationary Sources; Appendix A - Reference Methods.

Unless otherwise noted, the tests presented in this report were performed according to the EPA Reference Methods. A brief description of the test procedures used follows

Preliminary Determinations

The number of sampling points and their locations within the duct was determined according to EPA Method 1. The number of points required is based on the distance (duct diameter) of undisturbed flow both up and downstream of the sampling location.

Preliminary measurements to determine the stack pressure, temperature, and range of velocity heads were made by traversing the duct with a pitot tube and thermocouple as per EPA Method 2.

Determination of Particulate, Sulfur Dioxide, and Sulfuric Acid Emissions

The particulate, sulfur dioxide (SO_2), and sulfuric acid (H_2SO_4) emissions were determined per EPA Methods 5 and 8. In the combined procedure, the effluent is isokinetically withdrawn from the source. Particulate matter in the effluent is collected on a glass fiber filter which is maintained at a temperature of 248 ± 25 degrees Fahrenheit. The particulate mass, which includes any material which condenses at the filtration temperature, is determined gravimetrically after removal of uncombined water. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated and collected by bubbling the filtered effluent through a series of absorbing solutions. Both sulfur dioxide fractions are then measured by the barium-thorin titration method.

The sampling train (see Figure 3) consists of a heated glass-lined sampling probe with attached thermocouple and S-type pitot tube. The probe attaches to the front sample case which houses an all glass in-line filter holder in a temperature controlled environment. The back sample case houses several moisture condensing impingers and a desiccant column. The first impinger contains an 80 percent isopropanol solution for the collection of sulfuric acid and sulfur trioxide. The second and third impingers each contain a 3 percent hydrogen peroxide solution for the collection of sulfur dioxide. The sample case is connected via an umbilical cord to the control unit which contains the vacuum pump, dry-test meter, calibrated orifice, orifice pressure indicator, velocity pressure indicator, [illegible] parative controls. The [illegible] is [illegible] heated [illegible] separately [illegible] temperature readout.

A representative particulate sample was acquired by sampling for equal periods of time at the center of a number of equal area regions [illegible]

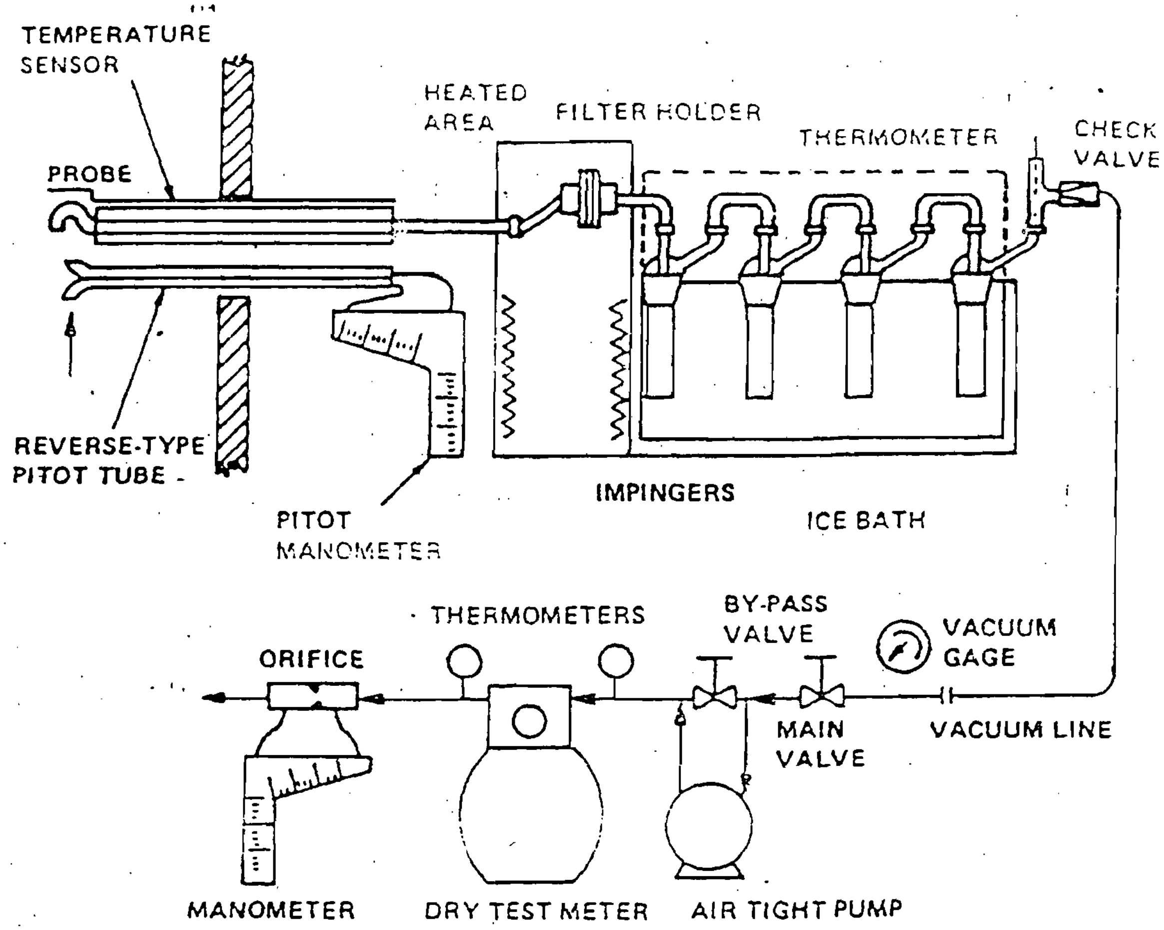


Figure 3. The EPA Method 5 particulate sampling train.

were measured and the sampling rate rapidly adjusted to isokinetic conditions with the aid of a nomograph. Sample gas drawn into the nozzle (size determined by preliminary measurements) flowed through the probe to the glass fiber filter where the particulates were collected. The gases then passed through an ice-cooled condenser and desiccant column which quantitatively sorbed all moisture from the gas stream. The gas then passed through the vacuum pump, the dry-test meter, and the calibrated orifice.

Leak checks to detect any dilution air being pulled into the sampling line were performed at the beginning and end of each test run and also when and if any sample line connections (except probe) were broken.

Gas composition was determined per EPA Method 3. Grab samples were collected and analyzed for carbon dioxide, oxygen, and carbon monoxide using a standard ORSAT analyzer.

After completion of each test run, the sampling train was removed to the clean-up area for sample recovery. The filter was removed from the filter holder and placed in Container #1. The probe and all connecting glassware (except cyclone) in front of the filter were rinsed with 80 percent isopropanol and the rinsings were placed in Container #2. The particulate matter collected in the cyclone was transferred to Container #3. The remaining particulate matter in the nozzle, probe, cyclone, and all connecting glassware in front of the filter was quantitatively transferred to Container #4 by means of a distilled water wash followed by an acetone wash. A stiff brush was used in the probe cleaning step to help dislodge deposits. The volume of liquid in the first impinger was measured and transferred to Container #5. This impinger was then rinsed with 80 percent isopropanol and the rinsings added to Container #5. The volume of liquid in each of the remaining impingers (desiccant column excluded) was measured and quantitatively transferred to Container #6. These impingers and their connecting glassware were then rinsed with distilled water and the [illegible] liquid and [illegible] contents transferred to [illegible] waste solvent container.

Sample analysis was performed at MMT's laboratory. The filter was desiccated to constant weight (Weight A, see Note below). The contents of Container #3 were transferred to a tared beaker and desiccated to constant weight (Weight C). The contents of Container #4 were transferred to a tared beaker, evaporated without heat to near dryness, and desiccated to constant weight (Weight B). The contents of Container #2 were filtered through a tared filter. The filter was dried at 100° C and then desiccated to constant weight (Weight D). The filtered liquid was added to Container #5. The total mass of particulate matter collected during each test run is the summation of Weights A, B, C, and D.

The filter and the material collected in the cyclone were added to Container #5. The sulfur dioxide (Container #6) and the sulfuric acid (Container #5) samples were then each made up to volume and an aliquote titrated using the barium-thorin method.

NOTE: All items were desiccated at 68 ± 10° F for a period of at least 24 hours and then weighed to the nearest 0.1 mg in a balance room where the relative humidity was less than 50 percent. The desiccation/weighing procedure was repeated at intervals of at least six (6) hours until a constant weight (± 0.5 mg) was obtained.

Determination of Nitrogen Oxide Emissions

The concentration of nitrogen oxides (except nitrous oxide) in the effluent stream was determined per EPA Method 7. In this procedure, a grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

Determination of Chloride Emissions

The concentration of chloride compounds in the effluent stream was determined by drawing a known volume of gas through a midget impinger containing acetate buffer. [illegible] by titration.

Determination of Particle Size Distribution

Particle size distribution of the dust samples collected in the sampling train was determined by optical microscopy.

ATTACHMENT 4

MEASUREMENT OF POLYNUCLEAR AROMATIC HYDROCARBONS AND METALS FROM BURNING TIRE CHIPS FOR SUPPLEMENTARY FUEL

John Drabek
Air Quality Engineer
State of Washington
Department of Ecology
4350 150th Ave. N.E.
Redmond, WA 98052

Jay Willenberg
Air Quality Engineer
State of Washington
Department of Ecology
4350 150th Ave. N.E.
Redmond, WA 98052

ABSTRACT

Air emissions of polynuclear aromatic hydrocarbons (PNAs) and heavy metals air emissions from two wood fired power boilers and a lime kiln were measured. The samples were taken when the sources were burning their normal fuel and when the fuel was supplemented with tire chips. The results indicate increased particulate emissions, primarily due to increased zinc, when tires are burned and little or no change in PNA emissions. Results compare well with air emission measurements from other tire burning sources and wood burning sources. The suitability of the Modified Method 5 PNA technique is also discussed.

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INTRODUCTION

Scrap tires that are not recycled constitute a serious solid waste problem, but also offer energy conservation opportunities through their use as solid fuel. If burned alone tires or tire chips would require specially designed incinerators. However, under some conditions they can be burned as a co-fuel at existing facilities with little modification (1). In Washington at least three pulp mills have burned tire chips as co-fuel.

Complaints from residents in the vicinity of one of these pulp mills generated interest in the Washington Department of Ecology to determine what emissions may be coming from the burning of tires as an auxiliary fuel in a wood fired boiler at the mill. Ecology is also interested in identifying emissions of toxic air contaminants and determining their significance.

A literature search revealed that polynuclear aromatic hydrocarbons (PNAs) and some heavy metals, such as zinc, arsenic and chromium, are potential air emissions from burning of tires. This paper reports results of measurements to determine if burning tire chips as a co-fuel generates significantly more emissions of toxic air contaminant than if tire chips were not burned. The paper also discusses the sampling methodology and problems encountered with sampling particulate and volatile toxic air contaminants.

SAMPLING OBJECTIVES

In sampling for toxic pollutants it must be recognized sensitive methods do not exist for many substances. Also, to sample for too broad a range of compounds would be extremely costly and complex. In most cases, careful selection of a specific set of target pollutants is adequate to determine if significant quantities of most compounds are emitted.

In the case of burning tires a literature search indicated that target pollutants should be polynuclear aromatic hydrocarbons and heavy metals. PNAs have received much attention in studies of air pollution because some of these compounds are highly carcinogenic (2). They are a class of compounds consisting of various arrangements and substitutions of multiple benzene rings and are known to be produced by the incomplete combustion of fossil fuels, wood and other organic materials. Therefore, PNAs are likely to be produced by incomplete combustion of tires.

To look for all of the PNA class of compounds quantitatively would be prohibitive from an analytical and cost standpoint. The more exotic compounds could not be accurately quantified because standards for these substances could not be obtained. Some of these standards, if available cost approximately $3,000/gram.

The sixteen PNAs listed in EPA Method 610, see Table 1, were judged to be the most technically feasible and environmentally significant compounds. It was felt that these compounds would be most environmentally significant. In addition our laboratory has had considerable experience with the analytical procedures.

Another good choice for target compounds are heavy metals. Heavy metals are associated with cancers of the lungs and kidneys, fetus malformation, insomnia, stupor, coma, joint muscle pain, nausea and vomiting. Previous work also indicated they might be present in air emissions from tire burning sources. The particular heavy metals that we decided to analyze for are listed in Table 1.

Table 1 Target Pollutants

Polynuclear Aromatic Hydrocarbons
Listed in EPA Method 610

- Naphthalene
- Acenaphthylene
- Acenaphthene
- Fluorene
- Phenanthrene
- Anthracene
- Fluoranthene
- Pyrene
- Benzo(a)Anthracene
- Chrysene
- Benzo(b)Fluoranthene
- Benzo(k)Fluoranthene
- Benzo(a)Pyrene
- Dibenzo(a,h)Anthracene
- Benzo(ghi)Perylene
- Indeno(1,2,3-cd)Pyrene

Heavy Metals

- Arsenic
- Barium
- Cadmium
- Chromium
- Copper
- Iron
- Lead
- Nickel
- Vanadium
- Zinc

Selecting a sampling procedure is difficult because PNAs can exist as particulate or gases and change phases with different sampling conditions. Traditionally, investigations of airborne PNAs have been confined to particles collected on glass fiber filters (3). For relatively nonvolatile PNAs, such as benzo(a)pyrene, filter collection might be acceptable. However, recent studies have shown that the 3 to 4 ring PNAs are largely in vapor form in ambient air because of their volatility and are therefore not retained by filters (4). Additionally, organic compounds can be present in the gas phase or adsorbed onto particles (e.g. dust, fly ash, water droplets etc.). The fraction retained by filters decreases with increasing temperature and increases with decreasing molecular weight (5). In choosing a sampling procedure it is therefore important to select a method that would collect both gases and solid PNAs.

There are other reasons to analyze for both phases. Certain components may be slowly driven from the captured particles during sampling; whereas, certain gas phase components may adsorb to filter media, hence appearing in the particle sample. In general, compounds less volatile than anthracene will be retained on the filter at around 420 degrees K. There were at least six target PNAs less volatile than anthracene and several more volatile (6).

MODIFIED METHOD 5

The Modified Method 5 was selected to determine the emission rates of:

1. Total particulate
2. PNAs
3. Heavy metals.

This method is a modification of the standard EPA Method 5, see Fig.1. The train was modified by adding a cooler-condenser and an adsorbent cartridge between the filter and the first impinger. Normal Method 5 sampling procedures were followed. Particulate PNAs and metals are extracted from the filter with more volatile PNAs collected on the solid adsorbent.

The solid adsorbent chosen was XAD-2, which is a synthetic adsorbent structurally comprised of a styrene-divinylbenzene copolymer, an organic synthetic plastic. An advantage of the organic polymeric adsorbents is the absence of "active sites", which can lead to irreversible adsorption of certain polar compounds.

Each of the processes tested were controlled by a wet scrubber producing stack gases with 10-30 percent water vapor. In order to sample large volumes of air with a small amount of adsorbent, it is necessary for the adsorbent not to collect the water. Organic polymeric adsorbents such as XAD-2 have this feature. Inorganic adsorbents like silica gel, alumna, Florisil, and molecular sieves are considerably more polar than the organic polymeric adsorbents, leading to the efficient collection of polar materials, such as water.

An inverse relationship exists between the adsorbent temperature and the retention volume. Therefore, large volumes of stack gas may be sampled, using a reasonable quantity of adsorbent, if the trap is cooled to prevent appreciable losses of the most easily eluted components. To accomplish this a water cooled-condenser is necessary downstream of the heated filter and upstream of the XAD-2 trap.

ANALYTICAL PROCEDURE

PNAs were extracted from the filter and XAD-2 using methylene chloride. These extracts were concentrated and analyzed using high performance liquid chromatography (HPLC) with ultraviolet and fluorescent detectors. Selected XAD-2 samples were spot checked using gas chromatography with mass spectrometer (GC/MS) according to EPA Method 625.

Metals were extracted from the filters with nitric acid and hydrogen peroxide and analyzed using atomic absorption. Probe rinses were mixed with nitric acid and hydrogen peroxide and similarly analyzed. Blank values were subtracted from the sample values in calculating emission rates.

QUALITY ASSURANCE

A major deleterious property associated with the use of polymeric sorbents as collection media is the contamination of the product as received from the manufacturer. Users of XAD-2, as received from the manufacturer have experienced resin contamination, qualitatively consistent from lot to lot. The PNA naphthalene has been found in quantities of 470 ug per gram of XAD-2 suggesting that the extractable contaminants are either residuals from the resin manufacturing process (e.g. starting materials or secondary by-products) or artifacts from the degradation of the polymer itself during storage and handling, subsequent to the manufacturing process (7).

A rigorous cleanup prior to use in sampling is required. The most widely accepted clean up procedure was used by the Ecology Environmental Laboratory. The XAD-2 resin, although originally cleaned by Supelco to EPA specifications was cleaned again by soxhleting for eight hours each with chromatography grade methanol, hexane, methylene chloride and diethylether. The resin was then air dried and about 19 grams placed in each resin cartridge and held in place with solvent extracted glass wool. As further quality control a blank XAD-2 cartridge and filter were carried to the sample site. These were analyzed to assess contaminants of the collection media both in the field and in the laboratory. The blank analysis attests to the elimination of media contamination. All PNAs blank values were below the detectable limit. For naphthalene this is equivalent to a contaminant concentration of less than 0.07 ug per gram of XAD-2.

Other problems with solid adsorbents are artifact formation or chemical transformation of some adsorbed materials through the interaction with stack gases like NO_x and SO_x. Nitro PNA derivatives can be formed from reaction of nitric acid, NO_2, and N_2O_5 on sorbed material. Also, sunlight can influence the integrity of sorbed material. This phenomena has been shown to promote insitu degradation of photochemically active species such as PNAs. Precautions must be taken to shield sample filters from sun or room light. To shield the XAD-2 from light the cartridges were wrapped in aluminum foil.

There is some evidence to suggest the structure of XAD-2 will break down into organic components at elevated temperatures. The condenser prevents this by reducing sample gas temperature. In additio the temperature of the resin was monitored during sampling.

FACILITIES SAMPLED

The MM5 sampling procedure was used to measure emissions where tire chips were burned as a co-fuel in two hog fuel boilers and a lime kiln. Tires were used as an alternate fuel replacing all or part of the oil in the hog fuel boilers. The lime kiln was fired with tire chips as a co-fuel with natural gas. The fraction of heat input received from the tire chips ranged from two to fifteen percent. In each case the sources were asked to operate the facilities normally when tires were burned and as they would if tires were not available. All three sources were located in Washington state at different locations and under different management.

Source A

Source A is a hog fuel boiler built in 1977 that was designed to produce about 90,000 kg/hr (200,000 lb/hr) of steam. The particulate control equipment for this source consisted of a 600 tube multiclone operated with 90 to 100 mm water pressure drop and a venturi scrubber operating with a pressure drop between 300 and 400 mm water.

While waste wood is the primary fuel the boiler is normally operated with between three and eight percent of the heat input coming from auxiliary fuel; oil or tire chips. During the testing about 500 kg/hr of tires were burned representing about seven percent of the heat input. When oil was used as auxiliary fuel about 400 kg/hr were burned representing about five percent of the heat input.

Source B

Source B is a hog fuel boiler that was originally built as an oil boiler in 1952 and later converted to burn hog fuel by Combustion Engineering. Oil or tire chips are still used as auxiliary fuel to increase combustion efficiency. The particulate control equipment consisted of a multiclone followed by a variable throat venturi scrubber with about 300 mm of water pressure drop.

When tire chips were burned they contributed about two percent of the heat input and oil contributed about eleven percent with hog fuel contributing the remaining. When tire chips were burned oil contributed about twelve percent of the heat input.

Source C

Source C is a lime kiln built in about 1980 and equipped with an Air-Pol variable throat venturi scrubber which is normally operated at 700 to 750 mm of water pressure drop.

The kiln normally burns natural gas and recently has been supplementing the gas with tire chips on an experimental basis. During the test about 15 percent of the heat input came from tire chips.

RESULTS

Emissions of PNA and metals were measured while the sources were both burning tire chips as a co-fuel and when the processes were fired without tires chips. Most of the operating parameters were held constant with the exception of the change in the fuel. In each case an increase in particulate emissions was noted as shown in Table 2. Much of the increase in particulate emissions from the hog fuel boilers can be attributed to increased emissions of zinc, as shown in Table 3. Other heavy metals emissions that increased when tires were burned are arsenic which increased from 0.2 gm/hr to 0.5 gm/hr at Source B and an increase of chromium from 3 gm/hr to 13 gm/hr at Source C.

Table 2 Effects of Auxiliary Fuel on Particulate Emissions

	Particulate Emissions Rate	
Source	Not burning tires, gm/hr	Burning tires, gm/hr
A	21,000	29,000
B	5,000	7,000
C	4,000	7,000

Table 3 Effects of Auxiliary Fuel on Zinc Emissions

Source	Zinc Emissions Rate Not burning tires, gm/hr	Burning tires, gm/hr
A	1,400	22,200
B	210	1,400
C	1	20

The hog fuel boiler at Mill A experienced increases in emissions of anthracene and phenanthrene with the use of tires. On the other hand the emissions of several heavy metals increased with the burning of oil as a supplemtary fuel, as shown in Table 4.

Table 4 Effects of Auxiliary Fuel on Emissions of PNAs and Metals From a Hog Fuel Boiler at Mill A

Pollutant	Emissions Rate, gm/hr Burning oil	Burning tires
Zinc	1440	22,200
Vanadium	90	0.6
Nickel	66	5.4
Lead	58	12
Phenanthrene (PNA)	41	72
Chromium	5.4	3.0
Cadmium	4.2	3
Anthracene (PNA)	1.2	2.4

The higher emissions rates of lead, nickel, vanadium and chromium may come from metals in the oil. As shown in Table 5 these metals are typically in fuel oil ash (8).

Table 5 Typical Oil Ash Analysis

Constituent	Weight %
Iron	23.0
Vanadium	19.6
Nickel	11.9
Chromium	1.4
Lead	0.2
Copper	0.1

The increased emissions of zinc measured from each mill during the burning of tires is supported by literature sources. For bench tests of a tire incinerator for Modesto Energy Company, CA (9), emissions of zinc oxide comprised fifty one percent of particulate emissions. W. L. Cox (10) reports one to two percent zinc oxide present in tires which burns to ash. Zinc was found in water run off from the Everett, Washington tire fire (11). Zinc was also found in the smoke plume from the Rhinehart tire fire in Winchester, Virginia, at a concentration of 122 ug/m^3, an order of magnitude times higher than lead, at 11 ug/m^3, or iron, at 14 ug/m^3 (12).

The total of the PNA emissions measured from the burning of wood and auxiliary fuel at Sources A and B are compared in Table 6 with emission estimates derived from emission factors reported in a 1985 inventory of toxic emissions in the State of Washington (13). Considering the uncertainty of applying universal emission factors to a specific source, these emission rates are reasonably close. The PNA emissions are also in the same ranges as reported by the National Council of the Paper Industry for Air and Stream Improvement (14) and the EPA as shown in Table 7.

Table 6 Comparison of Emission Rates for Total PNA

	PNA Emissions	
	Measured gm/hr	Estimate gm/hr
Source A	120	27
Source B	7.2	18

Table 7 Comparison of PNA Emission Factors

Pollutant	Mill A ug/kg	Mill B ug/kg	NCASI ug/kg	EPA ug/kg
Anthracene	72	10	64	---
Phenanthrene	3060	450	108	5043
Fluoranthene	3354	371	7	884
Benzo(a)Anthracene	1820	474	25	642
Chrysene	18	14	8	216
Benzo(a)Pyrene	nd	8	7	323
Benzo(ghi)Perylene	nd	48	6	---
Benzo(b)Fluoranthene & Benzo(k)Fluoranthene	18	29	10	413

COMMENTS

The increase in emissions of zinc that was expected from the literature review was verified. Zinc is probably emitted in the form of a very fine particulate that may be generated as zinc in tire chips, is evaporated in the combustion chamber and condensed in the form of zinc oxide as the combustion gases cool. Such a mechanism would result in most of the zinc leaving the boiler in the form of fly ash or fine particulate. This fine particulate can only be collected by high efficiency air pollution control equipment. Hence, it would be reasonable to require a review of the efficiency of air pollution control equipment prior to using tire chips as an auxiliary fuel.

The evidence suggests that all three sources tested are capable of burning tire chips as auxiliary fuel without significantly increasing the emission of polynuclear aromatic hydrocarbons. It is also likely that such emissions would not increase as long as the combustion conditions are properly maintained.

Using the emission factors developed here it is estimated that the emissions from all commercial and industrial wood fired boilers in Washington is about 6.6 tons per year. Emissions from residential wood combustion are estimated to be about one hundred times as much at 690 tons per year.

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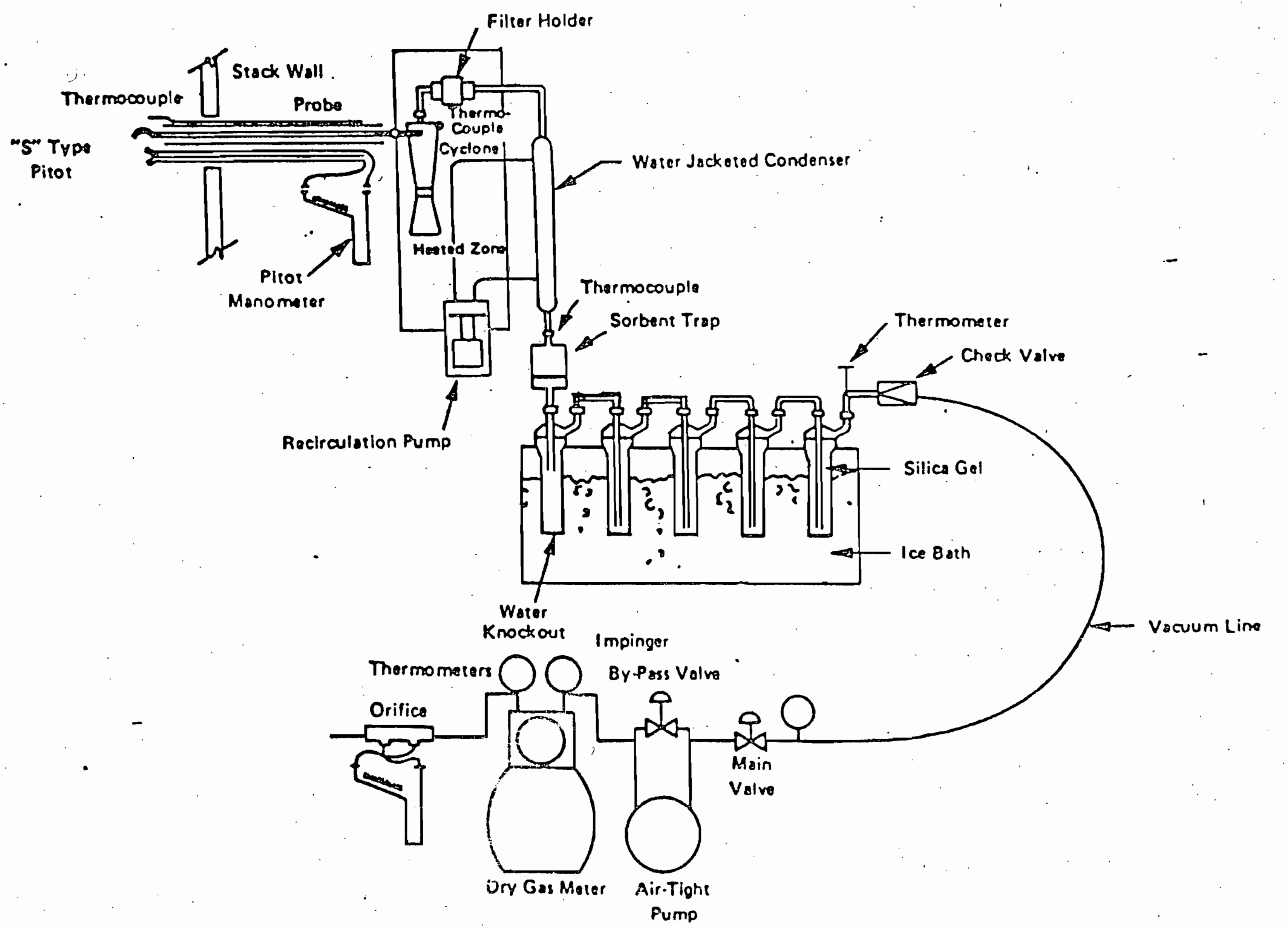


Figure 1: MM5 Train schematic diagram

ATTACHMENT 5

RUBBER TIRES, A HAZARDOUS FUEL?

Over the last few years I have had numerous discussions with eager individuals interested in burning rubber tires as a fuel. I have heard of valleys filled to the brim with rubber tires just waiting to be burned. I personally have contributed my share of Big O's to this ever growing heap over the years. I must admit, that I had preconceived visions of billowing black smoke rising unrelentlessly to the sky. From strictly a heating value viewpoint, rubber tires are an excellent fuel, having a heating value twice that of wood and about 75% of fuel oil, but is it hazardous to burn them?

Just recently the Bay Area AQMD granted Louisiana-Pacific (L-P) a permit which will allow them to burn up to 42 tons/day of rubber tire fuel in their waste wood boiler. Although this may seem like a large quantity, it represent no more than ten percent of the total heat input to this large 550 million Btu/hr boiler and a small fraction of the available supply of tires. Before a permit was issued to L-P they were required to conduct two test burn programs under the supervision of our District and the California Air resources Board. This boiler is controlled by a electrostatic precipitator followed by a wet scrubber for SO2. Both of these devices are considered Best Available Control Technology (BACT) by our District.

The purpose of these test burns was two fold. Firstly, it was L-P's burden to demonstrate that hogged rubber tire fuel could be burned in this unit without significantly increasing already permitted emissions of the so called criteria pollutants. The District was particularly concerned that emissions of NOx not be increased since

L-P was already operating under a variance for exceeding their permitted level. The effect on emissions of SO2 and particulate matter (PM) was also of concern, considering the sulfur content of rubber tires(~1 to 2 %S) and the dense particulate formation associated with the open burning of rubber tires. Secondly, and perhaps more importantly, there was concern that hazardous air emissions might result. It is well known that rubber tires contain many trace metals including; lead, mercury, nickel, cadmium, zinc and others.

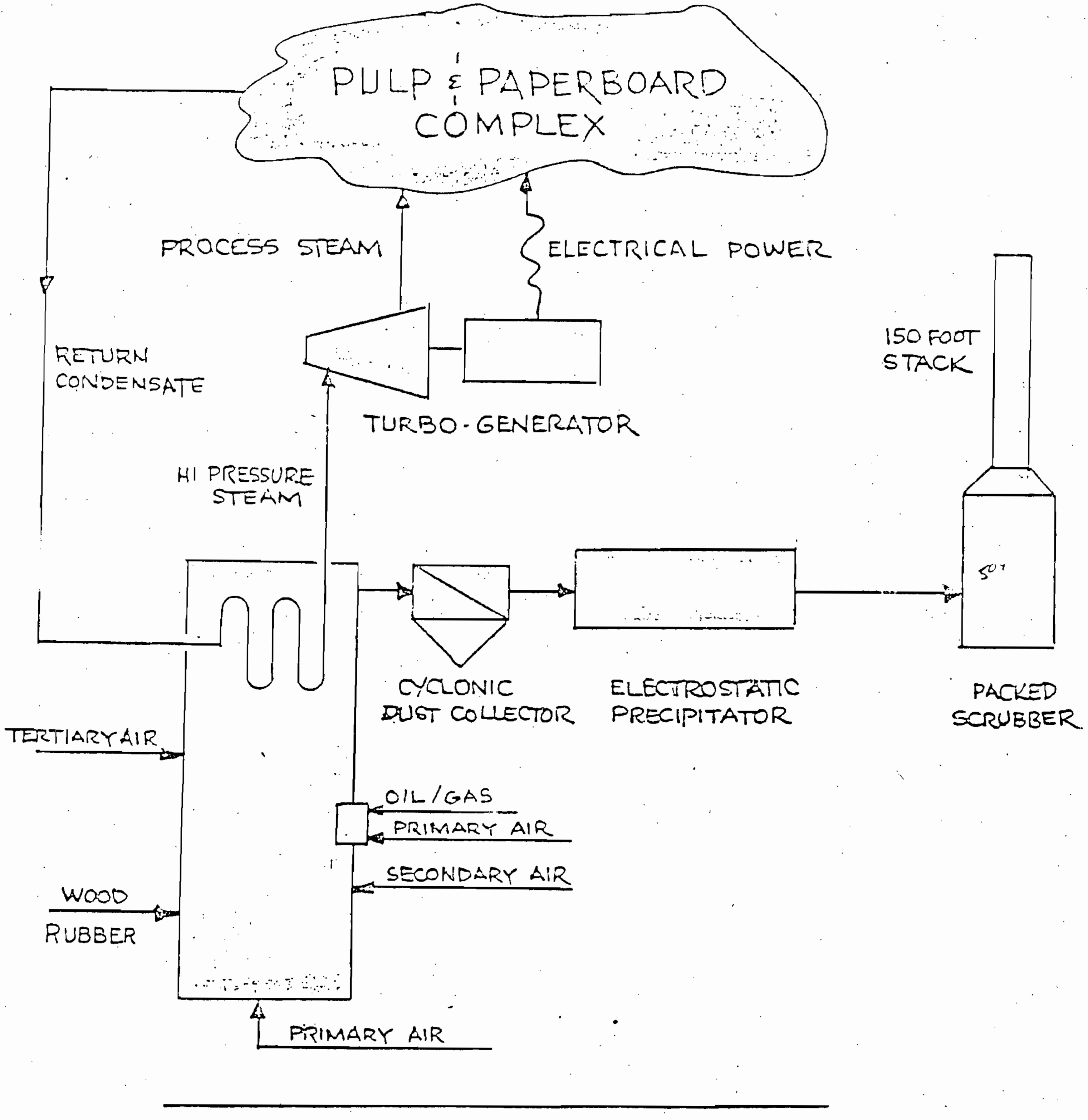
This boiler is equipped with continuous emission monitors for both NOx and SO2 so it was relatively easy to determine what the total emissions of these contaminants were during the test burn periods. However, the waste wood boiler is not base loaded and must handle the large swings in the steam demand of the paper mill resulting in considerable variations in combustion parameters and resulting emission. Therefore, it was difficult to determine conclusively, a significant correlation between percent rubber tires burned and emissions, particularly those of NOx. In spite of this difficulty, it was concluded from the test results, that NOx emissions were probably not increased, while both SO2 and PM showed slight increases. It should be noted that considering both the normal accuracy of the monitors and source test methods used, all changes in emissions noted were in the probable noise level of the data itself.

Composite particulate samples were collected by L-P during stack testing and analyzed for the metals listed above.? Based on the analyses of these samples, the daily emissions of these metals were estimated to be; 8.6 lb of zinc, 0.12 lb of cadmium, 0.05 lb of nickel, 0.006 lb of lead and 0.007 lb of mercury. The zinc emission represents approximately six percent of the total particulate matter emitted and corresponds to a stack concentration of less than one ppm as ZnO. Considering the significant dispersion of these emission which would result before they reach ground level, they would not be expected to constitute a health hazard.

In addition L-P is required by the Regional Water Quality Control Board to conduct periodic tests for toxic compounds in the ash collected from the boiler grate, the sand seperator and electrostatic precipitator in order to determine if the ash can be placed in a landfill. To date, no restrictions have been placed on the land disposal of this ash based on these tests.

In conclusion, I must say that the jury is still out as to whether or not rubber tires can be burned in all combustion devices without creating a hazardous air emission or a hazardous solid waste ash. The L-P boiler is well equipped with air pollution controls for particulate matter, SO2, and HCl. The boiler's solid fuels are supplemented at all times with gas or oil to assure temperatures are maintained high enough to guarantee complete combustion. Although rubber tires are not classified as a hazardous waste under RCRA and their controlled combustion not prohibited under any known regulations, we should proceed with caution in permitting their use as a fuel. Additional testing for metals and other contaminants which may be present in the stack emissions or the ash should be performed on a periodic basis until this question is fully resolved.

By
William deBoisblanc
Manager, New Source Review
Bay Area AQMD
March 6, 1985



WASTE WOOD POWER BOILER

EXHIBIT I

EXHIBIT III ASH ANALYSIS WITH 10% RUBBER FUEL

Louisiana Pacific Corporation
test date: March 6, 1984
by Curtis & Tompkins, Ltd.

Results: E P Toxicity, all metals reported as mg/liter in the final extract

Parameter	sample 1	sample 2	sample 3	Allowable
Arsenic	<0.2	<0.2	<0.2	5.0 ✓
Barium	<5	<5	<5	100 ✓
Beryllium	<0.5	<0.5	<0.5	0.75
Cadmium	<0.1	<0.1	0.34	1.0 ✓
Chromium,+6	<0.5	<0.5	<0.5	5. ✓
Lead	0.3	trace<0.1	trace<0.1	5.0 ✓
Mercury	<0.1	<0.1	<0.1	0.2 ✓
Nickel	<0.1	<0.1	<0.1	20
Selenium	<0.1	<0.1	<0.1	1.0 ✓
Silver	<0.1	<0.1	<0.1	5.0 ✓
Zinc	9.1	26.1	189	250

Sample 1 - boiler grate ash
Sample 2 - sand seperator ash
Sample 3 - precipitator ash

Composite Ash - WFB   Analysis by ULTRACHEM

Results: E P Toxicity, all metals reported as mg/L in the final extract.

Parameter	Sample	Allowable Limit
Arsenic	0.018	5.0
Barium	<2	100
Cadmium	<0.2	1.0
Chromium, Hexavalent	<0.5	5.0
Lead	<0.5	5.0
Mercury	<0.02	0.2
Selenium	<0.2	1.0
Silver	<0.2	5.0

Nutrient Levels

Parameter	as Received	Dry Basis	
Moisture, loss at 105°C, % w/w	39.1	-	
Potassium, K, % w/w	1.17	1.92	2.3
Nitrogen, N, % w/w	<0.04	<0.07	
Phosphorous, P, % w/w	0.013	0.021	0.05

Submitted by,

Michael Lynch

Michael Lynch
Manager, Technical Services

ML/dfh

Best Available Copy

LABORATORY CERTIFICATE

- Doug Robbi[illegible]
CONTACT PERSON
w/ LAB

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Laboratory No.	84h112	*Reported*	8/15/84
Preliminary No.	8314	*Sampled*	-------
		Received	7/25/84

For LOUISIANA PACIFIC CORPORATION

Report on 7 samples of Rubber Chips

Mark Shipping Order No. 9-56-688
Sample Nos. as below

	Mark	Nitrogen(N),%	Sulfur(S),%
1)	13th Comp	0.19	1.49
2)	20th Comp	0.18	1.36
3)	9th July	0.20	1.52
4)	July 10th	0.19	1.38
5)	July 11th	0.18	1.40
6)	July 12th	0.54	1.49
7)	July 13th	0.19	1.50

Curtis & Tompkins Ltd.

SAMPLES DISCARDED 30 DAYS AFTER RECEIPT UNLESS OTHERWISE REQUESTED

CAPCOA TECHNICAL SEMINAR

[illegible]
At 15th & P St. Conference Room
Sacramento, California

Incineration of Hazardous Materials

10:00 am	Introduction	- Jan Bush
10:05 am	Incineration of Misc. Haz. Wastes	- Don Ames, ARB
11:00 am	Burning of Reclaimed or Used Oil	- Bob Barham, ARB
11:30 am	Burning tires	- Bill DeBoisblanc, BAAQMD
12:00 pm	Lunch	
1:00 pm	Infectious Waste Incineration	- Bill Dennison, SCAQMD
1:45 pm	Waste Gas Incineration	- Ken Kitchingman, EPA
2:15 pm	Residential Wood Burning	- Earl Withycombe, MCAB

After each presentation there will be time for questions and discussion of the material presented. The format is intentionally informal and designed to maximize exchange of information and views. An abstract from each presentor is desireable for reference by those unable to attend the Seminar. It will be included in a CAPCOA Newsletter.

ATTACHMENT 6

SUMMARY OF WEST COAST EXPERIENCE WITH EMISSION FROM WOOD-RESIDUE FIRED BOILERS WHILE BURNING TIRE DERIVED FUEL (TDF) AS A SUPPLEMENTAL FUEL

WASTE TIRE UTILIZATION IN SOLID FUEL BOILERS AN ALTERNATIVE FUEL AND IT'S EMISSIONS

Mark W. Hope, Waste Recovery, Inc.

I GENERAL OVERVIEW

Tire derived fuel (TDF) is an alternative fuel that has received acceptance and creditability with the pulp and paper industry over the last 5 years. The most rapidly growing commercial use for scrap tires in the world today is incineration for heat recovery. With a high latent heat content of 15,000 Btu/lb, the burning of tire chips has been found to be profitable in a number of power generation facilities.

A general review of TDF is included here to cover appropriate application, material characteristics, economics and environmental concerns. Costs associated with various fuels in the Pacific Northwest are summarized in Table 1. Specifics with regards to these issues are drawn from a number of companies who have experience with TDF and for more detailed information you are encouraged to contact them directly. It is extremely important to note that emission rates, contaminant routes, handling characteristics and economic return may differ due to the difference among the many combustion and control systems, even if they appear similar.

TABLE 1 WESTERN OREGON FUEL COSTS - 1984

		Gross $/MMBtu	Net Fuel Cost/1000# Steam
*Sawmill Hog Fuel	8.50/ton	0.94	1.45
*TDF - Chopped Tires	50.00/ton	1.67	2.23
Coal - 11,000 Btu/lb	40.00/ton	1.81	2.41
Straw - 12 Mo. Supply	37.50/ton	2.50	3.33
RDF	31.00/ton	2.80	4.00
Logging Residue Chips	24-36.00/grn ton	2.67-4.00	4.11-6.15
Natural Gas Incentive	.42/therm	4.20	5.07
Wood Pellets	68.00/ton	4.00	5.13
No. 6 Heavy Oil	26.00/bbl	4.20	5.25
Natural Gas Industrial	.49/therm	4.90	5.90
Natural Gas Residential	.64/therm	6.40	7.71
Fuel Oil Residential	1.03/gal	7.30	9.12
Dry Cord Wood Residential	80.00/cord	6.00	12.00
Electricity Residential	.42/Kwh	12.30	13.67

*Limited supply
One therm = 100,000 Btu

A. TDF Analysis and Handling Characteristics

TDF is a refined scrap tire. More specifically, it is a scrap tire which has been shredded and processed to a fairly clean rubber chip roughly 1 inch to 2 inches in size. Waste Recovery's TDF is free of bead wire, has 70 percent or more of the belt wire removed and has a conservative Btu value of 15,500/lb.

Wire removal is important to eliminate ash and material conveying problems. TDF with the inherent wire will increase grate cleaning time, ash clinker and create problems with conveying systems due to its tendency to hang up and conflict with magnetic check systems. A quality TDF can be blended and fed into boilers via existing solid fuel systems without modification. To date facilities using TDF are stoker fired and traveling, pinhole or fixed grate boilers. Some caution must be used when replacing coal in a coal only boiler due to grate ash insulation considerations. Rubber has less ash and burns at a higher temperature than coal. To date trials to replace coal have established a 50-50 mix as a good mix in one particular boiler trial. This boiler used a baghouse as primary emission control.

Specially designed material handling and metering systems are imperative to provide a constant, consistent and precise blend rate with the normal solid fuel. An alternative to a metered mix is mixing TDF directly in the pile of solid fuel. Problems with mixing the pile are:

(1) Slugging of the system with TDF which if a large enough concentration reaches the boiler, it can momentarily throw the stack out of compliance and unnecessarily increase steam which wastes fuel.

(2) No guarantee of the mixture rate, percentage of rubber to solid fuel. By mixing rubber directly in the pile one cannot realize a continuous even feed. Thus one may experience a loss of economic benefit due to the lack of a continuous synergistic effect of burning TDF with other fuels.

(3) Environmental constraints limit the quantity of TDF that is ultimately used. Uneven feed rates place further limits on TDF usage due to surging which may create upset conditions.

(4) Cost of handling TDF is actually higher since time must be spent attempting to evenly mix it in the solid fuel pile rather than charging a metering hopper once per shift or less.

The benefits and economic return on a metering unit are as follows:

(1) Even Mixing With Solid Fuel - This is perhaps the most important aspect since the even blending of TDF with other solid fuels increases the efficiency of the boiler. When other solid

fuels have a high moisture content the combustion efficiency and energy recovery drops drastically. If moisture content is high enough one might even create an energy sink. However, it has been proven that by using an even mixture of TDF (15,500 Btu/lb) with hog fuel that has 53 percent or more moisture (8,000 Btu/dry lb) to bring the heat value down onto the grate that TDF not only maintains the combustion of poor quality hog fuel but also contributes significantly to the steam demand without having to rely on oil or natural gas. The metering unit distributes TDF with the main solid fuel such that its heat value is not so isolated to certain feed surges or areas on the grate. If the fuel moisture is not an issue one still realizes an overall efficiency increase due to the competitive cost of a higher Btu value TDF, higher burning temperatures, low moisture and low ash.

(2) Less Employee Time in Handling TDF - A metering unit can be designed to store a shift quantity of TDF. Better yet, it can be fully automated to allow for truck dumping into the unit.

(3) A metering unit allows the boiler operator immediate control of the TDF feed rate as with the other solid fuel system. Such control would allow for more cost effective use of TDF. Specifically, if the fuel system shuts down then TDF can be shut down, and if poor quality fuel creates poor boiler performance than a variable speed control to the TDF metering unit would allow the operator to compensate by increasing the TDF feed rate.

In summary, a TDF metering unit allows better control of fuel feed, reduces employee handling time, saves energy dollars and ensures environmental compliance. One should calculate yearly energy savings based on average boiler efficiency increase (probably somewhere around 3 to 6 percent) when blending TDF with other solid fuels. Be sure to factor in an average moisture value since TDF's best operational benefits are with wet fuels. Based on similar experience elsewhere, the ROI on a TDF metering unit would be 1 year or less.

II TDF ANALYSIS AND ENVIRONMENTAL CONCERNS

An analysis of TDF is presented in Table 2. Specific TDF concerns are the fixed carbon 27.96 percent volatile matter 66.64 percent and ash 4.78 percent. Elements of concern are the sulfur 1.23 percent and zinc 1.52 percent. All other elements are of insignificant quantities when the burning of TDF is a smaller percentage of the solid fuel demand. If burning TDF as a primary fuel then trace elements (less than 0.5 percent) such as chromium, cadmium and lead should be evaluated as a component of the ash. Uses to date verify that these elements would be found in a compounded form and normally pass EP toxicity tests.

Carbon and volatile matter are evaluated for fuel characteristics and would verify TDF as a quality fuel for boilers. TDF is being blended with both coal and wood waste around the

United States. Beneficial advantages have been demonstrated in both applications. No obnoxious odors have been observed during its use in low or high concentrations.

An ash content of 4.78 percent is average as compared to wood species (1.8 percent) and much less than most coal which has an average ash content of 12 percent. Thus one can expect to see very little change, if any, in ash quantities from a wood fired boiler and less ash from coal fired boilers. With a quality TDF, i.e. no wire, ash handling time would remain the same.

TABLE 2 PROXIMATE AND ULTIMATE ANALYSIS AND METAL ANALYSIS OF TIRE-DERIVED FUEL (TDF)*

Proximate Analysis	Percent by Weight As Peceived	Percent by Weight Dry Basis
Moisture	0.62	-
Ash	4.78	4.81
Volatile Matter	66.64	67.06
Fixed Carbon	27.96	28.13
	100.00	100.00
Ultimate Analysis		
Moisture	0.62	-
Ash	4.78	4.81
Carbon	83.87	84.19
Hydrogen	7.09	7.13
Nitrogen	0.24	0.24
Sulfur	1.23	1.24
Oxygen (by difference)	2.17	2.39
	100.00	100.00
Elemental Analysis		
Zinc	1.52	1.53
Iron	2.52	2.54
Calcium	0.378	0.379
Chlorine	0.149	0.150
Chromium	0.0097	0.0087
Fluoride	0.0010	0.0010
Cadmium	0.0006	0.0006
Lead	0.0065	0.0065
Heat Value	Btu/lb	kJ/kg
HHV	16,250	37,798
HV_{ave}	15,500	36,053
TDF Combustion	°F	°C
Tires Ignite	550 - 650	288 - 343
Carbon Begins to Burn	842	450
Carbon Completely Burnt	1202	650

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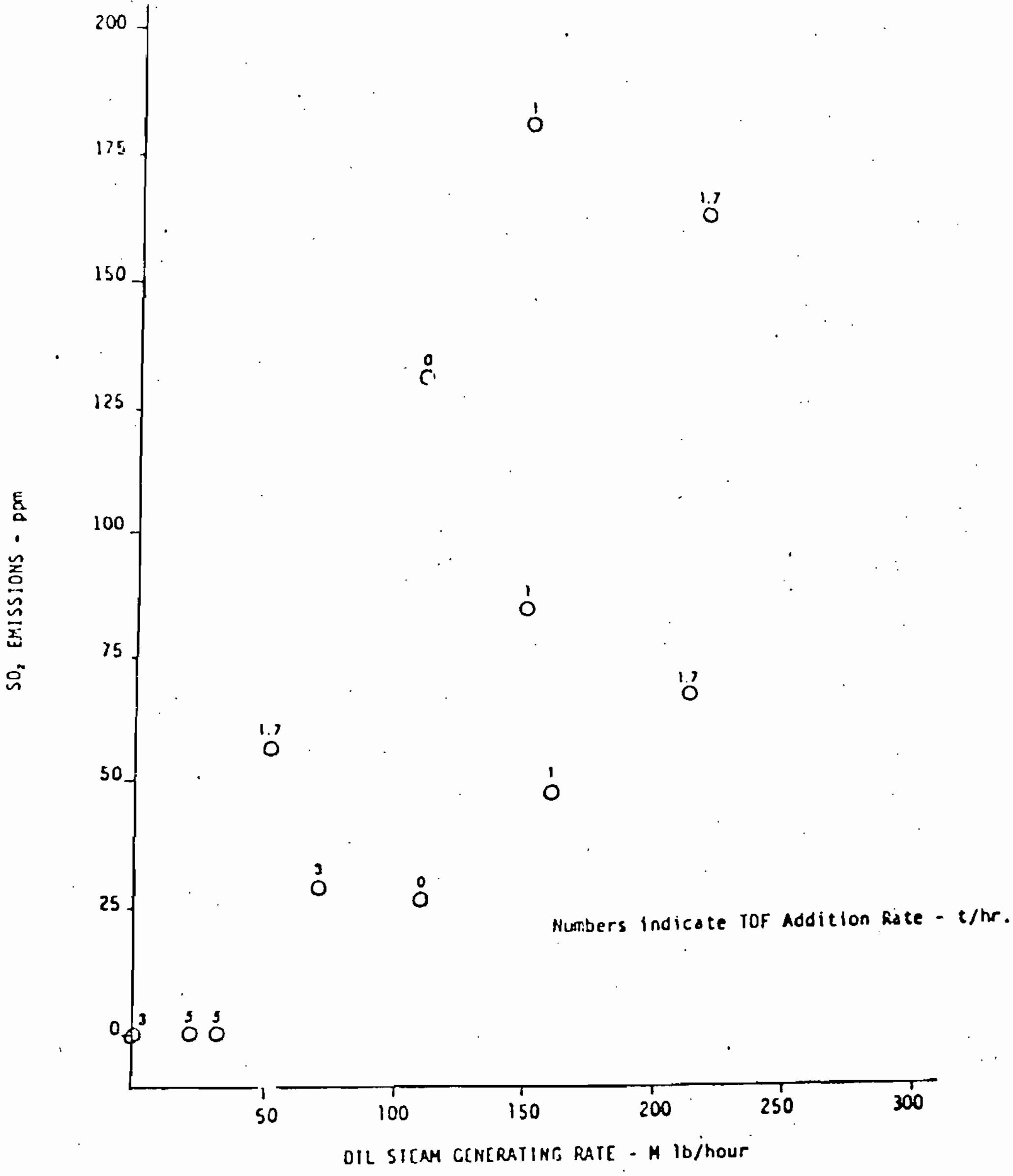
*Sources: TDF produced from scrap passenger and commercial tires, free of bead wire.

Sulfur content of TDF is within the legal limits of most state's limit for heavy residual fuel oil (1.5 percent). Previous trials and current uses have demonstrated TDF's ability to bring the heat value to the boiler's grate when burning wet hog fuel thus reducing oil demand to sustain steam loading. In this case the actual SOx emissions will actually be reduced as demonstrated in Figure 1. If a boiler uses only wood and/or low sulfur coal, then a slight SOx increase would be observed when burning TDF. Each boiler with its fuel mix must be evaluated to determine any SOx changes as this is a function of its fuel mix, both historic and proposed.



Numbers indicate TDF Addition Rate - t/hr.

FIGURE 1

SO_2 EMISSIONS DURING TDF ADDITION AS A FUNCTION OF OIL STEAM GENERATING RATE

Zinc is usually the most significant element of concern due to its concentration. Furthermore, zinc is an element that normally is not found in boiler emission and effluent systems. Industry's use of TDF for the past several years have offered operating experience to define the extent of zinc pollution and that it can be dealt with. Whether zinc is an issue to be dealt with is specific to the quantity of TDF used and type of emission control system. Results from the analysis of three ash samples for zinc are presented in Table 3.

TABLE 3 SUMMARY OF BOTTOM ASH AND FLY ASH ANALYSES FOR COMBUSTIBLE MATTER, SULFUR, AND ZINC

	Average Content Per Test Day, Percent Weight		
Sample Indentification	Combustible Matter	Sulfur	Zinc
Test #1			
Bottom Ash	3.77	0.82	0.0009
Fly Ash	26.22	0.38	0.022
Test #2			
Bottom Ash	1.89	1.11	0.0040
Fly Ash	24.32	0.58	0.532
Test #3			
Bottom Ash	2.65	0.91	0.0065
Fly Ash	30.70	0.42	0.784

Test #1 - 0% Rubber
Test #2 - 6.3% Rubber
Test #3 - 10.4% Rubber
Primary Fuel - Coal

When TDF is burned, zinc becomes entrained in the air flow. Particle size distribution of uncontrolled particulate matter emitted from a boiler while firing TDF at rates of 0, 6.3, and 10.4 percent by mass are presented in Table 4. Due to its fine particle size and high carbon content it is more difficult for wet scrubbers than electrostatic or bag houses to control particulate emissions. Some particulate will exit the stack, however, an electrostatic and bag house will allow one to burn TDF in much higher concentrations because they are much more efficient in dealing with TDF particulate. This has been demonstrated by both the power utilities and pulp and paper industry.

TABLE 4 AVERAGE FLY ASH SIZE DISTRIBUTION FOR THE THREE TEST DAYS

		Mass of Particles Larger Than Size Shown, Percent				
Test	Tire Content by Mass Percent	2000 um	425 um	150 um	75 um	0 um
# 1	0	0.2	2.6	44.8	84.9	100
# 2	6.3	0.0	1.2	18.0	50.4	100
# 3	10.4	0.0	3.4	31.3	64.1	100

Test # 1 - 0% Rubber
Test # 2 - 6.3% Rubber
Test # 3 - 10% Rubber
Primary Fuel - Coal

TDF particulate exiting the stack could affect opacity and grain loading. There is no zinc limit as an air pollutant other than that as a particulate. Since the zinc particulate is small, any great concentration will dramatically affect opacity since the particles will condense with the moisture in the air fairly rapidly causing a blue haze. However, when burning TDF in concentration appropriate with the emission system, this should not be a problem.

Washington State classifies most waste using a fish bioassay LC_{50} and derived toxicity response in addition to the standard RCRA listing criteria. Zinc concentrations in the ash may complicate the aquatic toxicity test since certain forms of aquatic life are sensitive to zinc. Because of the high pH of a dry ash, the zinc would be compounded, insoluable and non-toxic. Landfill testing of dry ash containing 35 percent zinc has shown no significant quantities of zinc leaching to either the groundwater or receiving streams. (Whiteson Landfill, McMinneville, Oregon 1974 to 1979).

Wet fly ash can become a part of the effluent which normally is treated through a wastewater treatment system. Zinc may become an issue here due to aquatic life's sensitivity to it. Two areas of immmediate concern would be the microbial action in the biological treatment system and in the receiving stream. Since solubility of zinc is a function of pH, actual experience has shown the zinc to percipitate and become part of the sludge in a treatment system. Significant quantities of zinc have not been detected in biological treatment system effluent and none has been detected at a discharge point to receiving streams where primary and secondary treatment occurs. Wet ash analysis has been conducted where the fly ash from a multi-clone and blow down from a wet scrubber has entered the wastewater treatment system as a matter of practice. (Western Kraft, Albany, Oregon).

Some dry fly ash is currently being used as a soil amendment to adjust soil pH. If zinc is a component of that ash, then maximum cumulative loading requirements are placed on its application the same as with a municipal sewage sludge. Because the zinc is compounded and fairly insoluable, it would have a low availability to plants. Specifically, zinc will usually remain insoluable as $Zn(OH)2$ and plant uptake will be restricted. Limits in concentration of specific elements in sewage sludge for soil application, concentrations measured in ash from boilers burning TDF as a portion of their fuel and cumulative loading rates when applied on land are presented in Table 5.

The average background levels of zinc in surface water is 10 ug/L. Recommended standard after a mixing zone is 47 ug/L for freshwater, for a 24 hr period; and 58 ug/L for saltwater, for a 24 hr period.

TABLE 5 METAL CONTENTS OF SLUDGES APPROPRIATE FOR AGRICULTURAL LAND APPLICATIONS, CONCENTRATION IN ASH FROM BOILER FIRING TDF AS A FUEL SUPPLEMENT AND MAXIMUM LOADING FOR A SOIL WITH A CATION EXCHANGE CAPACITY OF 5 TO 15 (mg/100g)

Element	Sewage Sludge Conc. (mg/kg)[1]	Flyash Conc.	Maximum Loading (kg/ha)[1]
Zn	2000 ppm	5000 ppm (10#/ton)	1000
Pb	1000	110 (0.2 #/ton)	500
Cu	800	240 (0.5 #/ton)	250
Ni	100	52 (0.1 #/ton)	100
Cd	25	2	10

[1] Guidelines for land applications of wastewater and sludges, Oregon Department of Environmental Quality (May 18, 1981).

Methods for assessment of the impact of the discharge of zinc included:

(1) Evaluate whether or not zinc escapes existing environmental control systems.

(2) Burn TDF in low proportions relative to the primary solid fuel.

(3) Maintain a neutral or higher pH in the scrubber discharge and document the contribution of zinc.

(4) Prepare a zinc balance of the system.

III SUMMARY

Generally most states have been very receptive to industry's interest to test and use TDF. Tires have been a historic disposal problem and alternative beneficial uses are encouraged. It is important that industry work closely with environmental control agencies to test and demonstrate its use within environmental limits. Relative to other industrial process and environmental testing, trials to demonstrate an ongoing ability to use TDF in an industrial boiler as supplemental fuel are fairly simple.

A recommended approach to procede with a TDF trial for its approval as an alternative/supplemental fuel would be:

(1) Contact the state pollution control agency to inform them of your interest to examine TDF as an alternative fuel. Express your interest to conduct a preliminary trial.

ATTACHMENT 7

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 60

Standards of Performance for New Stationary Sources; Appendix A—Addition of Methods for Measurement of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Hydrogen Chloride Emissions From Stationary Sources

[AD-FRL-3694-2]

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule and notice of public hearing.

SUMMARY: The purpose of this proposed rule is to add Method 23, "Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources," and Method 26, "Determination of Hydrogen Chloride Emissions from Stationary Sources" to Appendix A of CFR part 60. These methods are being proposed to determine compliance with subparts Ca and Ea of part 60.

A public hearing will be held, if requested, to provide interested persons an opportunity for oral presentation of data, views, or arguments concerning the proposed rule.

DATES: *Comments.* Comments must be received on or before March 5, 1990.

Public Hearing. If anyone contacts EPA requesting to speak at a public hearing by January 10, 1990, a public hearing will be held February 7, 1990, beginning at 10 a.m. Persons interested in attending the hearing should call the contact mentioned under **ADDRESSES** to verify that a hearing will be held.

Request to Speak at Hearing. Persons wishing to present oral testimony must contact EPA by January 10, 1990.

ADDRESSES: *Comments.* Comments should be submitted (in duplicate if possible) to: Air Docket (LE-131), Attention: Docket Number A-89-11, U.S. Environmental Protection Agency, room M-1500, 1st Floor, Waterside Mall, 401 M Street SW., Washington, DC 20460.

Public Hearing. If anyone contacts EPA requesting a public hearing, it will be held at EPA's Emission Measurement Laboratory Building, Research Triangle Park, North Carolina. Persons interested in attending the hearing or wishing to present oral testimony should notify Gary McAlister, Emission Measurement Branch (MD-19), Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-1062.

Docket. Docket No. A-89-11, containing materials relevant to this rulemaking, is available for public inspection and copying between 8 a.m. and 3:30 p.m., Monday through Friday, at EPA's Air Docket, room M-1500, 1st Floor, Waterside Mall, 401 M Street SW., Washington, DC. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Gary McAlister or Roger Shigehara, Emission Measurement Branch (MD-19), Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-1062.

SUPPLEMENTARY INFORMATION:

I. The Rulemaking

Under subparts Ca and Ea, the EPA is proposing to regulate emissions from municipal waste combustors (MWCs) which will include setting emission limits for polychlorinated dibenzo-p-dioxins (PCDDs, CDDs, or dioxins), polychlorinated dibenzo furans (PCDFs, CDFs, or furans), and hydrochloric acid (HCl). There are presently no methods published in 40 CFR part 60, appendix A, to measure any of these pollutants. This action would propose one method to measure the PCDDs and PCDFs and another method to measure the HCl.

Summary of Reference Methods

Method 23 is used to measure the emission of PCDDs and PCDFs from MWCs. A sample is withdrawn isokinetically from the stack through a probe, a filter, and a trap packed with a solid adsorbent. The PCDDs and PCDFs are collected in the probe, on the filter, and on the solid adsorbent. The PCDDs and PCDFs are extracted from the particulate matter and the adsorbent with a hot organic solvent. The extracted PCDDs and PCDFs are separated by capillary gas chromatography and then each isomer is identified and measured with mass spectrometry (GC/MS). The total PCDDs and PCDFs are the sum of the individual isomers. Toxicity factors are not used in the calculation.

Method 26 is used to measure the emission of HCl from MWCs. A sample is withdrawn at a constant rate from the stack through a probe and impingers filled with a dilute acid. The HCl is collected in the impinger solution. The chloride ion is separated by ion chromatography and measured by a conductivity detector.

Background

In 1983, the American Society of Mechanical Engineers (ASME) recognized that the testing for PCDDs and PCDFs needed to be standardized. In February of 1984, the ASME convened a committee of government representatives, testing consultants, equipment manufacturers, and incinerator operators to write a standard procedure for PCDDs and PCDFs. This eventually distributed as a draft ASME protocol in December of 1984. The procedure that we are proposing was derived from this draft ASME protocol. We are proposing significant changes in the quality assurance requirements and the solvents used to recover the sample. Because more labeled compounds are available, the proposed method will require additional labeled internal standards and surrogate compounds which will provide better representation of the entire range of PCDDs and PCDFs. Under the proposal the filter and solid adsorbent would be extracted in the laboratory with toluene to assure a high PCDD and PCDF recovery efficiency. Additionally the proposed sample recovery solvents used for rinsing the sample train glassware in the field would be acetone followed by methylene chloride with a final quality assurance rinse using toluene. EPA will continue to review the toluene field rinse quality assurance results and continue to evaluate the desirability of replacing methylene chloride with toluene for field rinsing sample glassware.

II. Administrative Requirements

A. Public Hearing

A public hearing will be held, if requested, to discuss the proposed test methods in accordance with section 307(d)(5) of the Clean Air Act. Persons wishing to make oral presentations should contact EPA at the address given in the **ADDRESSES** section of this preamble. Oral presentations will be limited to 15 minutes each. Any member of the public may file a written statement with EPA before, during, or within 30 days after the hearing. Written statements should be addressed to the Air Docket address given in the **ADDRESSES** section of this preamble.

A verbatim transcript of the hearing and written statements will be available for public inspection and copying during normal working hours at EPA's Air Docket in Washington, DC (see **ADDRESSES** section of this preamble).

B. Docket

The docket is an organized and complete file of all the information submitted to or otherwise considered by EPA in the development of this proposed rulemaking. The principal purposes of the docket are: (1) To allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process and (2) to serve as the record in case of judicial review (except for interagency review materials) [section 307(d)(7)(A)].

C. Office of Management and Budget Review

Executive Order 12291 Review. Under Executive Order 12291, EPA must judge whether a regulation is "major" and, therefore, subject to the requirement of a regulatory impact analysis. The proposal of these test methods is not major because it will not have an annual effect on the economy of $100 million or more; it will not result in a major increase in costs or prices; and there will be no significant adverse effects on competition, employment, investment, productivity, innovation, or on the ability of U.S.-based enterprises to compete with foreign-based enterprises in domestic or export markets. Any burden resulting from the use of these methods is considered in the burden estimate for the regulation requiring the use of these methods.

D. Regulatory Flexibility Act Compliance

Pursuant to the provisions of 5 U.S.C. 605(b), I hereby certify that this attached rule, if promulgated, will not have an economic impact on small entities because no additional costs will be incurred from this action.

This proposal does not contain any information collection requirements subject to OMB review under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*

List of Subjects in 40 CFR Part 60

Air pollution control, Municipal waste combustors, MWCs, Polychlorinated dibenzo-p-dioxins, Polychlorinated dibenzofurans, Hydrogen chloride.

Dated: November 30, 1989.

William K. Reilly,

Administrator.

The EPA proposes to amend title 40, part 60 of the Code of Federal Regulations as follows:

1. The authority citation for part 60 continues to read as follows:

Authority: 42 U.S.C. 7401, 7411, 7414, 7416, 7601.

2. Appendix A is amended by addin Methods [illegible] and 26 to read as follows.

Appendix A—Reference Methods

* * * * *

Method 23—Determination of Polychlorina Dibenzo-p-Dioxin Polychlorinated Dibenzofurans From Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources.

1.2 Principle. A sample is withdrawn fr the gas stream isokinetically and collected the sample probe, on a glass fiber filter, an on a packed column of adsorbent materia The PCDDs and PCDFs are extracted from the sample, separated by high resolution g chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampl train used in this method is shown in Figure 23-1. The train is identical to that describe in Section 2.1 of Method 5 of this appendix with the following additions:

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel plated stainless steel, quartz boroslicate glass.

BILLING CODE 6560-50-M

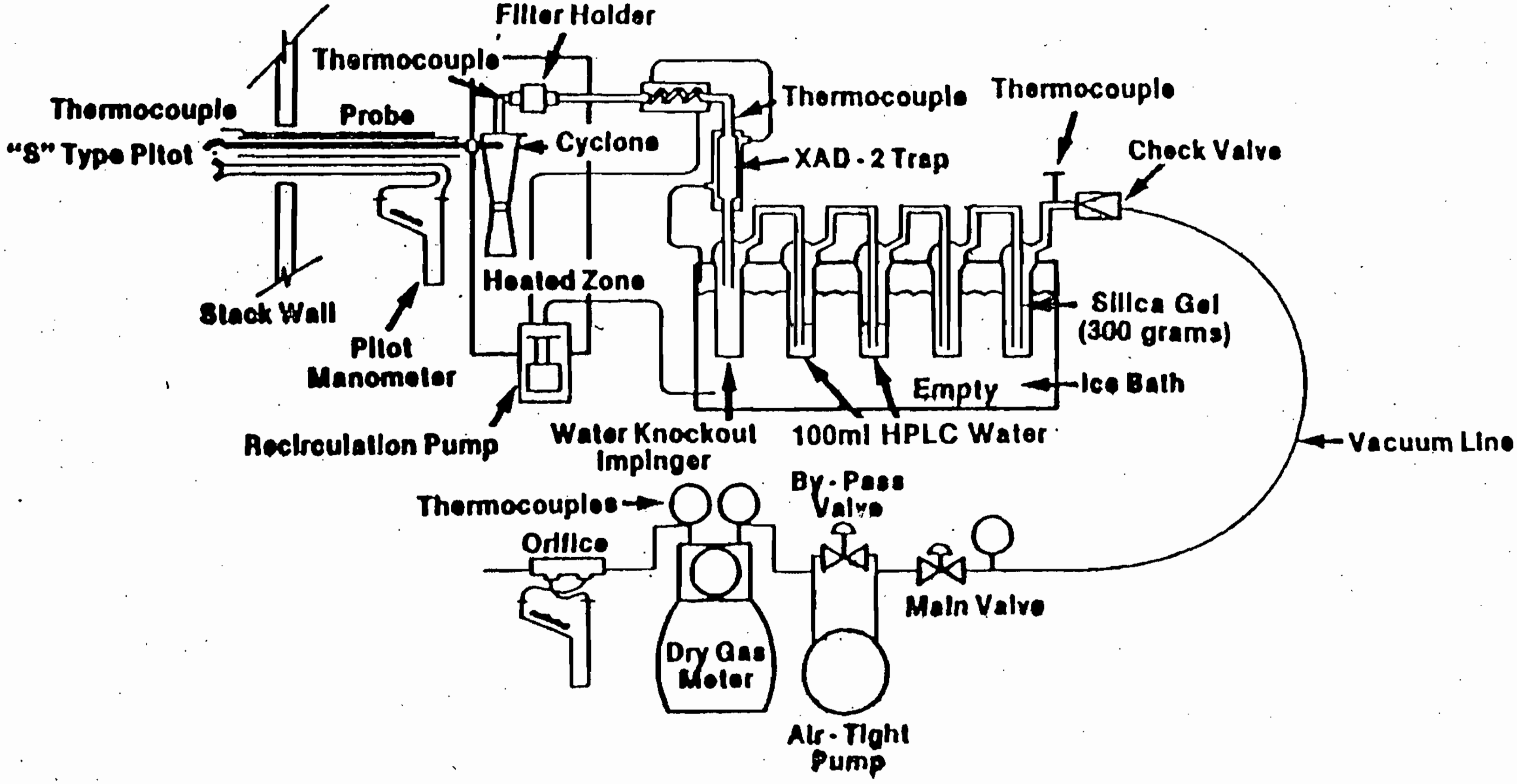


Figure 1. CDD/CDF Sampling Train Configuration

BILLING CODE 6560-50-C

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon coated wire.

2.1.2 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.1.3 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.4 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon or aluminum foil to cap-off the sample exposed sections of the train.

2.2.2 Wash Bottle. Teflon, 500-ml.

2.2.3 Probe Liner and Probe-Nozzle Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or aluminum foil.

BILLING CODE 6560-50-M

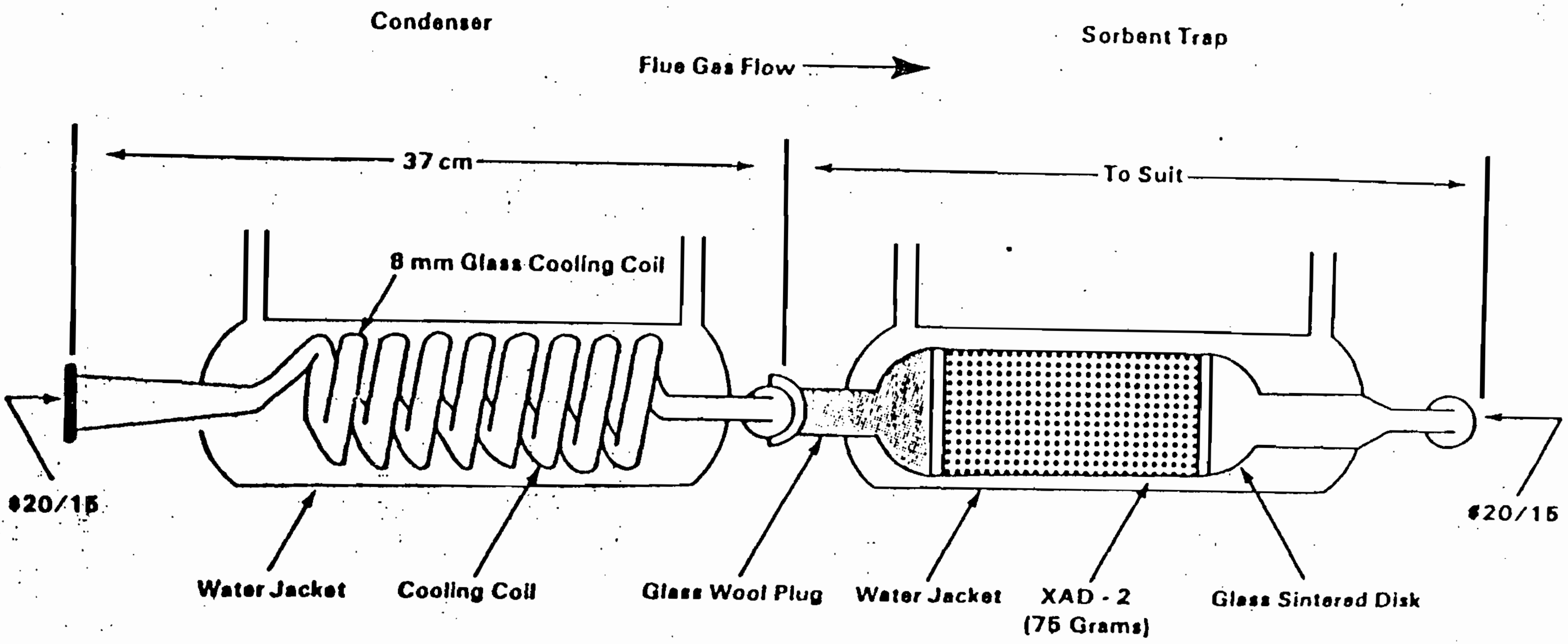


FIGURE 2. CONDENSER AND SORBENT TRAP FOR COLLECTION OF GASEOUS PCDDs AND PCDFs

BILLING CODE 6560-50-C

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Metal Storage Container. Air tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.5 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.6 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

2.3.7 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.8 Separatory Funnels. Glass, 2-liter.

2.3.9 Gas Chromatograph. Consisting of the following components:

2.3.9.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C and performing programmed increases in temperature at rates of at least 3 °C/min.

2.3.9.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.9.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.9.4 Capillary Columns. A fused silica column, 60 m × 25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m × 25 mm ID coated with SP-2331.

2.3.10 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.11 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.12 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (Reapproved 1978) (incorporated by reference—see § 60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of three hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the bed of silica gel and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and retain it for analysis. Remove the filters and dry them under a clean N_2 stream. Store the filters tightly wrapped in cleaned aluminum foil.

3.1.1.2 Quality Control Check. Analyze the toluene extract from Section 3.1.1.1 as described in Sections 5.2 and 5.3. If any TCDD or TCDF is present at a concentration above the minimum detectable level, repeat the cleaning procedure and reanalyze the extract until no TCDD or TCDF is detectable.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10–15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene chloride	Extract for 22 hours.
Methylene chloride (fresh).	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers as shown in Figure 23-3.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The rate of flow should be high enough to gently agitate the particles but not high enough to cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual methylene chloride as well as TCDDs and TCDFs.

3.1.2.3.1 Methylene Chloride Residue.

3.1.2.3.1.1 Extraction. Weigh a 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.1.2 Analysis. Inject a 5 μl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10% OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C until it reaches 250 °C; return to 30 °C after 1000 seconds.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 2.5 μl of methylene chloride into 100 ml of toluene. This corresponds to 100 μg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.3.2 TCDDs and TCDFs. Extract the sample as described in Section 5.1.1. Analyze the extract as described in §§ 5.2 and 5.3. If any of the TCDDs or TCDFs are present at concentrations above the MDL, the adsorbent must be recleaned by repeating the last step of the cleaning procedure. The MDL can be calculated as ½ of the theoretical minimum quantifiable level (TMQL). The TMQL is calculated in § 9.8.

3.1.2.4 Storage. The adsorbent must be used within four weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with Teflon film and elastic bands.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of hexane, dried in a 110 °C oven, and stored in a hexane-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a hexane-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide quality.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. Reagent grade.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide Grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Isooctane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 ml of isooctane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of isooctane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of isooctane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module shall be cleaned as described in section 3A of the Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples. Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They should not be loaded in the field. Fill a trap with 20 to 30 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container or wrapped in aluminum foil.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter sealed until just prior to assembly or until sampling is about to begin.

Note: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger.

4.1.3.3 Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50.C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the TCDDs and TCDFs.

4.1.4 Leak-Check Procedure. Same as Method 5, § 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, § 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking which could contaminate the sample shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

4.2.2 Absorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Cyclone Catch. If the optional cyclone is used, quantitatively recover the particulate into a glass container and cap.

4.2.4 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first by brushing while rinsing three times each with acetone and then by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder, the connecting line between the filter and the condenser, and the condenser, if using a separate condenser and absorbent trap, sequentially, three times each, with acetone and methylene chloride. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.5 Container No. 3. Repeat the rinsing described in section 4.2.4 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.6 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight. 4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger.

5. Analysis

5.1 Sample Extraction.

5.1.1 Container No. 1. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Suspend the adsorbent module directly over the extraction thimble described in section 5.1.1. The glass frit of the module should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module with toluene into the beaker containing the thimble. Add the XAD–2 glass wool plug to the thimble, add the contents of container No. 1, and add the concentrate from Section 5.1.2. For low level samples, add 20 ul of the internal standard solution (section 3.3.20), for high level samples, add 100 ul of the solution. Low level samples are those samples that contain less than 200 pg of any TCDD of TCDF. Cover the XAD–2 in the thimble with the cleaned glass wool plug to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. The thimble is placed in the extractor, and the toluene contained in the beaker is added to the solvent reservoir. Additional toluene is added to make the reservoir approximately two—thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5–6 times per hour. Extract the resin for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 5 ml. Use nitrogen evaporation to further reduce the sample to about 1 ml. Split the sample in half. Store one half and analyze the other according to the procedures in sections 5.2 and 5.3.

5.1.2 Container No. 1. Transfer the contents directly to the glass thimble of the extractor and extract them simultaneously with the XAD–2 resin.

5.1.3 Container No. 2. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus as described in section 5.1.1.

5.1.4 Container No. 3. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract according to the procedures in sections 5.2 and 5.3.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the bottom 0.5 inch from the tip of a 9-ml disposable Pasteur pipette. Insert a filter paper disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane and 2 ml of hexane. Discard these eluates. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 4 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts in a freezer, shielded from light, prior to analysis.

5.3 Analysis. Analyze the sample using a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. A 1 to 5 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the SP 2331 column to measure the 2,3,7,8 tetra-chlorodibenzofuran isomer.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise ballistically to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 8000–10000 m/e.

5.3.2.2 Ionization Mode. Electron impact, 70 eV.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 4.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M+/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 5.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions shown in Table 4 for a given analyte shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRTs found in the continuing calibration.

5. The signal to noise for all monitored ions must be greater than 2.5.

6. The confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDFs, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDDs or PCDFs in its homologous series. For example the $^{13}C_{12}$-1,2,3,4-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$-1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$-1,2,3,[illegible] 6,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2 for low level samples or Table 3 for high-level samples. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 6. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 5.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject one µl of solution number 4 from Table 2 or solution number 3 from Table 3. Calculate the relative response factors (RRF's) for each compound and compare each of them to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 6. In addition the ion-abundance ratios shall be within the allowable control limits shown in Table K.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDDs and PCDFs that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25% of the lower of the two peaks.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the adsorbent cartridge of each train before each test.

7.2 Internal Standard Percent Recoveries. Recoveries of the internal standards must be between 40 to 130% for the tetrathrough hexachlorinated compounds while the range is 25 to 130% for the higher hepta- and octachlorinated homologues. If the internal standards do not meet the recovery requirements, the data will still be acceptable provided that the signal is equal to or greater than ten times the noise level.

7.3 Surrogate Recoveries. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. All recoveries shall be between 70 and 130%. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70%, the sampling runs must be repeated. As an alternative the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

7.4 Toluene Quality Assurance Rinse. Report the results of the toluene quality assurance rinse separately from the total sample catch. Do not add it to the total sample.

8. Quality Assurance

8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed.

8.2 Audit Procedure. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for any enforcement agency within seven days is not required.

8.3 Audit Sample Availability. The audit sample may be obtained by writing:

Source Test Audit Coordinator (MD-77B),
Quality Assurance Division, Atmospheric
Research and Exposure Assessment
Laboratory, U.S. Environmental Protection
Agency, Research Triangle Park, NC 27711

or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA regional office or the appropriate enforcement agency. The STAC will return the EPA response to the laboratory being audited. Include this EPA response with the results of the compliance samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent analyses for any enforcement agency during the seven-day period.

8. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ci} = Integrated ion current of the two ions characteristic of compound i in the calibration standard.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A^*_{cs} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

Ai = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_s = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_s = Concentration of the compound of interest in the most dilute calibration solution, pg/µl.

m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.

m^*_{ci} = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.

m^*_i = Mass of internal standard i added to the sample, pg.

m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.

m_s = Mass of surrogate compound i in the calibration standard.

RRF_i = Relative response factor.

RRF_{rs} = Recovery standard response factor.

V = Final extract volume, µl.

9.2 Relative Response Factor.

$RRF = 1/n \sum^{n} A_{ci}\, m^*_{ci} / (A^*_{ci}\, m_{ci})$ Eq. 23-1

9.3 Concentration of the PCDDs and PCDFs.

$C_i = m^*_i A_i / (A^*_i RRF_i V_{extract})$ Eq. 23-2

9.4 Recovery Standard Response Factor.

$RRF_{rs} = A^*_{ci}\, m_{rs} / (A_{rs}\, m^*_{ci})$ Eq. 23-3

9.5 Recovery of Internal Standards (R^*).

$R^* = (A^*_i\, m_{rs} / A_{rs}\, RF_{rs}\, m^*_i) \times 100\%$ Eq. 23-4

9.6 Surrogate Compound Response Factor.

$RRFs = A^*_{ci}\, m_s / (A_{cs}\, m^*_{ci})$ Eq. 23-5

9.7 Recovery of Surrogate Compounds (R_s).

$R_s = (A_s\, m^*_i / A^*_i\, RRF_s\, m_s) \times 100\%$ Eq. 23-6

9.8 Theoretical Minimum Quantifiable Level (TMQL).

$TMQL = C_s V / R^*$ Eq. 23-7

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TABLE 1.—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-2,3,1,6,7,8 HpCDF	100
Surrogate Standards:	
$^{37}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,1,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS (LOW)

Compound	Concentrations (pg/μL)—Solution No.—				
	1	2	3	4	5
Unlabeled analytes:					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5	10	50	500	1000
OCDF	5	10	50	500	1000
Internal standards:					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate standards:					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	5	50	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Alternate standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery standards:					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS (HIGH)

Compound	Concentrations (pg/μL)—Solution No.—				
	1	2	3	4	5
Unlabeled analytes:					
2,3,7,8-TCDD	5	50	100	500	1000
2,3,7,8-TCDF	5	50	100	500	1000
1,2,3,7,8-PeCDD	25	250	500	2500	5000
1,2,3,7,8-PeCDF	25	250	500	2500	5000
2,3,4,7,8-PeCDF	25	250	500	2500	5000
1,2,3,4,7,8-HxCDD	25	250	500	2500	5000
1,2,3,6,7,8-HxCDD	25	250	500	2500	5000
1,2,3,7,8,9-HxCDD	25	250	500	2500	5000
1,2,3,4,7,8-HxCDF	25	250	500	2500	5000
1,2,3,6,7,8-HxCDF	25	250	500	2500	5000
1,2,3,7,8,9-HxCDF	25	250	500	2500	5000
2,3,4,6,7,8-HxCDD	25	250	500	2500	5000
1,2,3,4,6,7,8-HpCDD	25	250	500	2500	5000
1,2,3,4,6,7,8-HpCDF	25	250	500	2500	5000
1,2,3,4,7,8,9-HpCDF	25	250	500	2500	5000
OCDD	50	500	1000	5000	10000

TABLE 3.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS (HIGH)—Continued

Compound	Concentrations (pg/μL)—Solution No.—				
	1	2	3	4	5
OCDF	50	500	1000	5000	10000
Internal standards:					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate standards:					
$^{37}Cl_4$-2,3,7,8-TCDD	5	50	100	500	1000
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	250	500	2500	5000
Alternate standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	5	50	100	500	1000
Recovery standards:					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 4.—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDDS AND PCDFS

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	354.9792	LOCK	C_9F_{13}	PFK
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
	354.9792	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)

TABLE 4.—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDDS AND PCDFS—Continued

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
	513.8775 442.9728	M+4 LOCK	$C_{12}{}^{35}Cl_6{}^{37}Cl_4O$ $C_{10}F_{17}$	DCDPE PFK

(a) The following nuclidic masses were used: H = 1.007825 C = 12.000000 ^{13}C = 13.003355 F = 18.9984 O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903 S = Labeled Standard

TABLE 5.—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDDS AND PCDFS

Number of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[1]	M/M+2	0.51	0.43	0.59
7[2]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[1] Used only for ^{13}C-HxCDF.
[2] Used only for ^{13}C-HpCDF.

TABLE 6.—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative Response Factors	
	Initial calibration RSD	Daily calibration percentage difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,-PeCDD	25	25
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

* * * * *

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. This method is applicable for determining hydrogen chloride (HCl) emissions from stationary sources.

1.2 Principle. An integrated sample is extracted from the stack and passed through dilute sulfuric acid. In the dilute acid, the HCl gas is dissolved and forms chloride (Cl^-) ions. The Cl^- is analyzed by ion chromatography (IC).

1.3 Interferences. Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences. Another likely interferent is diatomic chlorine (Cl_2) gas which reacts to form HCl and hypochlorous acid (HOCl) upon dissolving in water. However, Cl_2 gas exhibits a low solubility in water and the use of acidic, rather than neutral or basic collection solutions, greatly reduces the chance of dissolving any chlorine present. This method does not experience a significant bias when sampling a 4[illegible] ppm HCl gas stream containing 50 ppm Cl_2. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

1.4 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

1.5 Stability. The collected samples can be stored for up to 4 weeks before analysis.

1.6 Detection Limit. The analytical detection limit of the method is 0.1 $\mu g/ml$.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 26–1, and component parts are discussed below.

2.1.1 Probe. Borosilicate glass, approximately ⅜-in. (9-mm) I.D. with a heating system to prevent moisture condensation. A ⅜-in. I.D. Teflon elbow should be attached to the inlet of the probe and a 1-in. (25-mm) length of ⅜-in. I.D. Teflon tubing should be attached to the open end of the elbow to permit the opening of the probe to be turned away from the gas stream. This reduces the amount of particulate entering the train. This probe configuration should be used when the concentration of particulate matter in the emissions is high. When high concentrations are not present, the Teflon elbow is not necessary, and the probe inlet may be perpendicular to the gas stream. A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result. Instead, a Teflon filter (see § 2.1.5) should be installed at the inlet (for

ATTACHMENT 8

KOOGLER & ASSOCIATES
ENVIRONMENTAL SERVICES
4014 NW THIRTEENTH STREET
GAINESVILLE, FLORIDA 32609
904/377-5822 ▪ FAX 377-7158

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KA 307-90-01

January 24, 1990

Mr. C. H. Fancy
Bureau Chief
Division of Air Resources Management
Florida Department of
  Environmental Regulation
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Subject: Florida Crushed Stone Company
CPL Cement Plant
Brooksville, Florida
Permit AC27-118674
Request for Trial Burn to Test
  Tire-Derived Fuel in the Cement Kiln

Dear Mr. Fancy:

At the request of the Florida Crushed Stone Company and in accordance with conversations that I have had with Mr. Bill Thomas and Mr. Bruce Mitchell of your staff, I would like to request that Permit AC27-118674, issued to the Florida Crushed Stone Company for the construction and initial operation of a dry process Portland cement kiln, be amended to allow a one-time test for burning tire-derived fuel along with coal in the cement kiln. The cement kiln is designed and operated at a feed rate of approximately 123 tons per hour. Heat is provided to the kiln, under conditions of the subject permit, by coal fired at a rate of 10 tons per hour. The resulting heat input to the kiln is 240 million BTU per hour. During the requested one-time test, Florida Crushed Stone will use tire-derived fuel to provide up to 10 percent of the heat input to the kiln, or approximately 24 million BTU per hour.

The cement plant operated by Florida Crushed Stone is a modern, dry process Portland cement plant. The hot gases discharged from the cement kiln pass through a pre-heater where heat is recovered and transferred to the kiln feed. The kiln gases then pass through a baghouse before being discharged to the atmosphere. The baghouse also controls particulate matter emissions from the power/lime plant and a limestone dryer. The stack through which the kiln gases are discharged is equipped with continuous emission monitors for opacity, nitrogen oxides and sulfur dioxide. These monitors can be used to provide a continuous record of stack gas opacity and sulfur dioxide and nitrogen oxides concentrations during the trial period. The dust collected in the baghouse will be disposed of by incorporating it into the kiln feed as is the current practice. As a result, the baghouse dust ends up in the clinker and eventually in the finished product.

A 30-day trial period is requested. During this time, Florida Crushed Stone will evaluate methods of feeding the tire-derived fuel to the cement kiln and will experiment with the quantities of tire-derived fuel that can be used. It is anticipated that the maximum amount of heat that can be provided by tire-derived fuel will be in the range of 24 million BTU per hour; or 10 percent of the heat input to the kiln. During the test period, Florida Crushed Stone will also evaluate the effect of tire-derived fuel on the quality of clinker produced in the cement plant.

During the trial period, Florida Crushed Stone will maintain records of the time periods when tire-derived fuel is fired to the cement kiln. Records will also be maintained documenting the amount of tire-derived fuel fed to the kiln, the procedures for firing the tire-derived fuel, clinker production rates and total heat input to the kiln. Continuous monitoring records from the in-stack opacity, sulfur dioxide and nitrogen oxide monitors will also be available for all periods of time during the test to document the effect of tire-derived fuel on stack emissions.

Consistent with your requirements for other tire-derived fuel tests, Florida Crushed Stone is also proposing emission measurement tests for several criteria and non-criteria pollutants during the trial. As tire-derived fuel will be used to provide only a small fraction (10 percent) of the total heat input to the cement kiln, it is proposed that the emission measurements be conducted on a one-time basis at or near this maximum tire-derived fuel heat input rate.

The emission measurements proposed for the trial burn (at a 10 percent tire-derived fuel heat input rate) will include the following:

Test	Test Method
Particulate Matter	EPA Method 5
Metals Aluminum Arsenic Cadmium Chromium (Total) Lead Zinc	EPA Method 5 filter and probe rinse
Nitrogen Oxides	EPA Method 7

Sulfur Dioxide	EPA Method 6 (in back-half of Method 5 train)
Carbon Monoxide	EPA Method (10)
Volatile Organic Compounds	VOST
Semi-Volatile Organic Compounds	Modified Method 5
Furans and Dioxins	Modified Method 5
CO_2/O_2	EPA Method 3
Stack Gas Flow/Moisture/Temp.	EPA Methods 2 and 4 in conjunction with EPA Method 5

Three replicate test runs will be conducted for each of the measurements listed above. The measurements that are proposed are consistent with those suggested by Mr. Thomas and Mr. Mitchell of you staff. The metals which we propose to test for are metals of potential environmental concern that were measured in significant quantity during a test performed by the Radian Corporation (April 1988) at a waste tire to energy facility in California.

I appreciate your consideration of this request and will provide any additional information that you may require to complete your evaluation of this matter.

Very truly yours,

KOOGLER & ASSOCIATES

John B. Koogler, Ph.D., P.E.

JBK:wa

cc: Mr. Randy Thompson, FCS, Leesburg
Mr. Bill Thomas, FDER-Tallahassee
✓ Mr. Bruce Mitchell, FDER-Tallahassee

ATTACHMENT 9

KOOGLER & ASSOCIATES
ENVIRONMENTAL SERVICES
4014 NW THIRTEENTH STREET
GAINESVILLE, FLORIDA 32609
904/377-5822 ▪ FAX 377-7158

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KA 307-90-01

February 2, 1990

Mr. C. H. Fancy
Bureau Chief
Florida Department of
  Environmental Regulation
Northwest District
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Subject: Florida Crushed Stone Company
CPL Plant
Brooksville, Florida
Permit AC27-118674
Amendment to Permit AC27-118674 to Allow
  the Use of Tire-Derived Fuel in the
  Cement Kiln

Dear Mr. Fancy:

The purpose of this letter is to modify the request made in my letter to you dated January 24, 1990. In that letter, I requested that the subject permit be amended to allow a one-time test to investigate the feasibility of burning tire-derived fuel as a supplemental fuel in the dry process Portland cement kiln operated by the Florida Crushed Company near Brooksville in Hernando County, Florida. After further investigation into the use of tire-derived fuel, Florida Crushed Stone feels that the project is feasible and would like to pursue a permanent amendment to the subject permit to allow the use of this fuel as a supplement to coal, which is normally fired to the kiln. I discussed this matter with Mr. Bruce Mitchell of you staff and it was suggested that an amendment to the subject permit would be possible if the new permit conditions were framed in such a way that the Department would have the necessary assurances that the cement kiln will continue to operate in compliance with all existing permit conditions and that the emission rate of any trace organic or inorganic compounds currently unregulated by DER and/or federal regulations will not result in an unacceptable environmental risk. Based on my conversation with Mr. Mitchell, I understand that a bleach plant, presumably associated with a paper mill, recently received an air construction permit that was contingent upon the results of emission measurements and a risk assessment; both of which would be performed after the facility was constructed and in operation.

Based upon my conversation with Mr. Mitchell, I would like to request that the subject permit be amended to allow the use tire-derived fuel in conjunction with coal to provide the necessary heat for the Florida Crushed Stone cement kiln. The tire-derived fuel will be used to provide up to 15 percent of the total heat input to the cement kiln or up to 36 million BTU per hour. The suggested permit conditions related to this amendment include:

A. Within three months following completion of construction, start-up and the achievement of normal and reliable operations, emission measurements shall be conducted on the cement kiln while fired with tire-derived fuel at a firing rate within 10 percent of the maximum permitted rate of 36 million BTU per hour and while the cement kiln is operating, within 10 percent of the permitted kiln feed rate and total heat input rate. The emission measurements will include:

Test	Test Method
Particulate Matter	EPA Method 5
Visible Emissions	EPA Method 9
Metals Aluminum Arsenic Cadmium Chromium (Total) Lead Zinc	EPA Method 5 filter and probe rinse
Nitrogen Oxides	EPA Method 7
Sulfur Dioxide	EPA Method 6 (in back-half of Method 5 train)
Carbon Monoxide	EPA Method (10)
Volatile Organic Compounds	VOST
Semi-Volatile Organic Compounds	Modified Method 5

Furans and Dioxins	Modified Method 5
CO_2/O_2	EPA Method 3
Stack Gas Flow/Moisture/Temp.	EPA Methods 2 and 4 in conjunction with EPA Method 5

Three replicate test runs will be conducted for each of the measurements listed above. As stated in my letter of January 24, 1990 to you, the measurements proposed herein are consistent with those suggested by Mr. Bill Thomas and Mr. Bruce Mitchell of your staff. The metals proposed in the emission measurements program are those of potential environmental concern that were measured in significant quantity during a test performed by the Radian Corporation in April 1988 at a tire-to-energy facility in California.

B. Within one month following receipt of the results of the emission measurements described in Paragraph A, an air toxics screening test shall be conducted using criteria agreed to by the Department and the permittee. In general, the screening test will include the use of an air quality model (the ISC-ST or equivalent), representative of meteorological data and the emission rates of the various unregulated substances measured during the emission test described in paragraph A. The ground-level concentrations of the various substances will be calculated for receptors at the Florida Crushed Stone property line and these concentrations will be compared with ambient guideline concentrations agreed to by the Department and the permittee.

C. The results of the screening tests will be used to determine whether:

1. The measured emission levels are acceptable, or
2. Additional control measures are required to achieve the screening test criteria, or
3. A detailed risk assessment is necessary to ensure that the achievable emissions are acceptable.

D. For any compound or substance addressed in this permit that fails to meet the criteria established in Paragraph B, the permittee shall submit within six months following receipt of the screening test a plan and schedule which addresses the factors identified in Paragraph C. The plan may include recommendations to install control measurements and/or process modifications if needed and available and practical, or may include recommendations to develop a risk assessment to demonstrate that the practically achievable emissions are acceptable.

E. Upon receipt of the results of the emission measurements described in Paragraph A, a determination shall be made regarding the compliance of the cement plant with established permit limits for particulate matter, nitrogen oxides, sulfur dioxide, and opacity. If compliance cannot be demonstrated, the permittee shall not use tire-derived fuel except for test purposes until the plant has been modified to assure compliance with all existing permit conditions.

An air operating permit will not be issued for the cement plant until a satisfactory screening test as described in Paragraph B is submitted to the Department and compliance with existing permit conditions and emission limits as described in Paragraph E is demonstrated or until the plan described in Paragraph D is approved by the Department and implemented by the permittee.

The proposed use of tire-derived fuel as a replacement for up to 15 percent (based on heating value) of the coal fired to the cement kiln is not expected to increase particulate matter, sulfur dioxide, nitrogen oxides emissions, or on the opacity of emissions. These pollutants are those addressed by emission limiting standards in the current permit for the cement plant. The baghouse that controls emissions from the plant will effectively control particulate matter emissions to the levels currently being achieved. The sulfur content of the tires is lower than the sulfur content of the coal currently being fired to the kiln; hence, there should be a reduction in sulfur dioxide emissions. It is anticipated that the tire-derived fuel may also reduce nitrogen oxides.. Nitrogen oxides are primarily a result of the fixation of atmospheric nitrogen and the use of tire-derived fuel will probably result in a more even distribution of the heat release and hence, a reduction in NOx emissions. The baghouse associated with the cement plant is also expected to adequately control the emissions of metals and the semi-volatile organic compounds (by adsorption or condensation).

Based upon the expected operation of the cement plant while firing tire-derived fuel as a supplement to coal; taking into consideration the characteristics of the tire-derived fuel, the amount of tire-derived fuel that will be used, and the normal operating characteristics of the plant; and considering the effectiveness of the air pollution control system associated with the cement plant, it is our opinion that there will be no perceptible differences in emissions from the plant or in operations of the plant. As pointed out to you in my letter of January 24, 1990, the cement plant is equipped with continuous emission monitors for opacity, sulfur dioxide and nitrogen oxides that can be used to monitor the overall performance of the plant and to provide a continuous record of plant emissions while tire-derived fuel is used as a supplemental heat source. Additionally, the test program described herein will define emission rates of trace organic and inorganic compounds and the screening test that is proposed will assess the risk associated with these emissions. All of these factors, coupled with the assurances guaranteed by the proposed permit conditions should allow the Department to grant the requested amendments to the subject permit.

Again, I appreciate you consideration of this request and will provide any additional information that you may require to complete your evaluation of this matter.

Very truly yours,

KOOGLER & ASSOCIATES

John B. Koogler, Ph.D., P.E.

JBK:wa

cc: Mr. Bill Thomas, FDER-Tallahassee
Mr. Bruce Mitchell, FDER-Tallahassee
Mr. Randy Thompson, FCS, Leesburg
Mr. Charles Bush, FCS, Leesburg

ATTACHMENT 10

KOOGLER & ASSOCIATES
ENVIRONMENTAL SERVICES
4014 NW THIRTEENTH STREET
GAINESVILLE, FLORIDA 32609
904/377-5822 ▪ FAX 377-7158

KA 307-90-01

March 13, 1990

Mr. C. H. Fancy
Bureau Chief
Florida Department of
Environmental Regulation
2600 Blair Stone Road
Tallahassee, FL 32399-2400

RECEIVED
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DER - BAQM

Subject: Florida Crushed Stone Company
CPL Plant
Brooksville, Florida
Permit AC27-118674
Request to Burn Tire-Derived Fuel
in the Cement Kiln

Dear Mr. Fancy:

As a follow-up to previous correspondence to your office, to a meeting with Mr. Bill Thomas and Mr. Bruce Mitchell of your staff and to several recent telephone conversations that I have had with Mr. Mitchell, I would like to request, on behalf of the Florida Crushed Stone Company, a modification or amendment that will allow the use of tire-derived fuel as a supplement to coal in the cement kiln permitted by Permit AC27-118674. The tire-derived fuel will be used to provide up to 15 percent of the total heat input to the cement kiln, or up to 36 million BTU per hour.

The cement plant operated by the Florida Crushed Stone Company is a modern dry-process Portland cement plant. The plant is designed for a kiln feed rate of approximately 123 tons per hour and for a clinker production rate of 75 tons per hour. Under conditions of the present permit, heat is provided to the kiln by coal, fired at the rate of 10 tons per hour; resulting in a heat input to the kiln of approximately 240 million BTU per hour. The tire-derived fuel will replace up to 15 percent of this total heat input.

The hot gases exhausted from the cement kiln passed through a pre-heater where heat is recovered and transferred to the kiln feed material. The kiln gases then pass through a baghouse before being discharged to the atmosphere. The baghouse also controls particulate matter emissions from the power/lime plant and from a limestone dryer. The dust collected in the baghouse will be disposed of by incorporating it in with the kiln feed, as is the current practice. As a result, the baghouse dust ends up in the clinker and eventually, in the finished product.

The requested change should not be considered a modification, as modification is defined in Rule 17-2.100(118) as:

> Any physical change in, change in the method of operation of, or addition to a stationary source or facility which increases the actual emissions of any air pollutant, regulated under this Chapter, including any not previously emitted, from any source or facility...

The Florida Crushed Stone Company has committed that there will be no increase in the emission rate of any air pollutant as a result of using tire-derived fuel as a supplement to the coal. The requested change will require an amendment to the existing permit however, as tire-derived fuel is not included as an allowable fuel in the subject permit.

To demonstrate that there will be no increase in the emission rate of any permitted air pollutant or any air pollutant not previously emitted from the cement kiln, the Florida Crushed Stone Company will conduct one set of emission measurements with the cement plant operating under presently permitted conditions to establish a baseline. A second set of emission measurements will then be conducted with tire-derived fuel being used at the maximum anticipated firing rate to demonstrate that there is no increase in air pollutant emission rates above the baseline.

Suggested permit conditions related to this requested amendment include:

A. The permittee shall conduct emission measurements on the cement kiln while fired with coal and operating under presently permitted operating conditions to establish a baseline emission rate for all regulated and unregulated air pollutants. Within three months following the achievement of normal and reliable operations while firing tire-derived fuel, emission measurements shall be conducted on the cement kiln while fired with tire-derived fuel at a rate within 10 percent of the maximum permitted rate of 36 million BTU per hour, and while the cement kiln is operating within 10 percent of the permitted kiln feed rate and total heat input rate. The emission measurements will include:

Test	Test Method
Particulate Matter	EPA Method 5
Visible Emissions	EPA Method 9
Metals Aluminum Arsenic Cadmium Chromium (Total) Lead Zinc	EPA Method 5 filter and probe rinse
Nitrogen Oxides	EPA Method 7
Sulfur Dioxide	EPA Method 6 (in back-half of Method 5 train)
Carbon Monoxide	EPA Method (10)
Volatile Organic Compounds	VOST
Semi-Volatile Organic Compounds	Modified Method 5
Furans and Dioxins	Modified Method 5
CO_2/O_2	EPA Method 3
Stack Gas Flow/Moisture/Temp.	EPA Methods 2 and 4 in conjunction with EPA Method 5

Three replicate test runs will be conducted for each of the measurements listed above. (Note: The metals proposed in the emission measurements program are those of potential environmental concern that were measured in significant quantity during a test performed by the Radian Corporation in April 1988 at a tire-to-energy facility in California.)

B. Upon receipt of the results of the emission measurements described in Paragraph A, a determination shall be made regarding the compliance of the cement plant with established permit limits for particulate matter, nitrogen oxides, sulfur dioxide, and opacity and significant unregulated air pollutants. If compliance cannot be demonstrated, the permittee shall not use tire-derived fuel except for approved test purposes until the plant has been modified to assure compliance with all existing permit conditions.

C. If there should be an increase in the emission rate of one or more substances, the permittee shall submit within six months following receipt of the emission tests a plan and schedule to install control measurements and/or process modifications if needed and available and practical to reduce the emission rate increases to zero. Or, the plan may suggest an alternative permitting strategy.

An air operating permit will not be issued for the cement plant until compliance with existing permit conditions and emission limits as described in Paragraph B is demonstrated or until the plan described in Paragraph C is approved by the Department and implemented by the permittee.

The proposed use of tire-derived fuel as a replacement for up to 15 percent (based on heating value) of the coal fired to the cement kiln will not increase particulate matter, sulfur dioxide, nitrogen oxides emissions, or the opacity of emissions. These pollutants are those addressed by emission limiting standards in the current permit for the cement plant. The baghouse that controls emissions from the plant will effectively control particulate matter emissions to the levels currently being achieved. The sulfur content of the tires is lower than the sulfur content of the coal currently being fired to the kiln; hence, there should be a reduction in sulfur dioxide emissions. It is anticipated that the tire-derived fuel may also reduce nitrogen oxides. Nitrogen oxides are primarily a result of the fixation of atmospheric nitrogen and the use of tire-derived fuel will probably result in a more even distribution of the heat release and hence, a reduction in NOx emissions. The baghouse associated with the cement plant is also expected to adequately control the emissions of metals and the semi-volatile organic compounds (by adsorption or condensation).

Based upon the expected operation of the cement plant while firing tire-derived fuel as a supplement to coal; taking into consideration the characteristics of the tire-derived fuel, the amount of tire-derived fuel that will be used, and the normal operating characteristics of the plant; and considering the effectiveness of the air pollution control system associated with the cement plant, Florida Crushed Stone will commit that there will be no increase in emissions from the plant or changes in the operations of the plant.

As pointed out to you in my previous correspondence, the cement plant is equipped with continuous emission monitors for opacity, sulfur dioxide and nitrogen oxides that can be used to monitor the overall performance of the plant and to provide a continuous record of plant emissions while tire-derived fuel is used as a supplemental heat source. Additionally, the test program described herein will define emission rates of trace organic and inorganic compounds, both under present and proposed operating conditions. All of these factors, coupled with the assurances guaranteed by the proposed permit conditions should allow the Department to grant the requested amendments to the subject permit.

Again, I appreciate your consideration of this request and will provide any additional information that you may require to complete your evaluation of this matter.

Very truly yours,

KOOGLER & ASSOCIATES

John B. Koogler, Ph.D., P.E.

JBK:wa

cc: Mr. Bill Thomas, FDER-Tallahassee
Mr. Bruce Mitchell, FDER-Tallahassee
Mr. Randy Thompson, FCS, Leesburg
Mr. Charles Bush, FCS, Leesburg
Mr. Thomas Mountain, FCS, Brooksville

ATTACHMENT 11

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IV
345 COURTLAND STREET, N.E.
ATLANTA, GEORGIA 30365

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Mr. C. H. Fancy, P.E., Chief
Bureau of Air Regulation
Florida Department of Environmental
  Regulation
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

RE: Florida Crushed Stone (PSD-FL-091)

Dear Mr. Fancy:

This is to acknowledge receipt of your letter dated March 15, 1990, transmitting a request by Florida Crushed Stone to amend their prevention of significant deterioration (PSD) permit to allow the burning of tire derived fuel (TDF) in their cement kiln. The current permit for the source limits the fuel of the kiln to coal only. As discussed between Mr. Bruce Mitchell of your staff and Mr. Gregg Worley of my staff on March 30, 1990, we have the following comments.

Under the scenario presented by the source, the switch to the use of TDF in the kiln would not constitute a major modification for the purposes of PSD provided that the increase in pollutants due to the fuel switch did not exceed significant emissions increase levels. It is important to note that the change in emissions must be evaluated from "old actual" to "new allowable" emissions. The old actual emissions must be based on the previous two years of operating data unless some other period is deemed to be more representative of normal operating conditions. The new allowable emissions will be those emissions which are reflected in the amended permit. Also, it was noted that the list of pollutants to be tested did not include benzene. Since benzene is a pollutant regulated under the Clean Air Act for which a significant emissions rate has not been established, any increase of emissions of benzene would subject the source to PSD.

Thank you for the opportunity to review and comment on this package. If you have any further questions or comments, please do not hesitate to contact Mr. Gregg Worley of my staff at 404/347-2864.

Sincerely yours,

Jewell A. Harper, Chief
Air Enforcement Branch
Air, Pesticides and Toxics
  Management Division