DOCUMENTATION FOR REVISED EMISSION FACTORS: SECTION 7.5 - IRON AND STEEL PRODUCTION AND SECTION 7.2 - COKE MANUFACTURING

by

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NOTICE

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ABSTRACT

Under several EPA contracts, JACA Corp. has collected emission test reports for iron and steel operations. Under this EPA work assignment, JACA reviewed in-house test reports and developed emission factors for iron and steel operations for pollutants that are not included in the 1986 update of Section 7.5 (Iron and Steel Production) and Section 7.2 (Coke Manufacturing) of AP-42. Specifically, the following operations were addressed: Sintering-windbox, basic oxygen furnaces, electric arc furnaces, argon oxygen decarburization, steel teeming, coke pushing, coke oven gas desulfurization, and combustion stacks.

The development of the emission factors are discussed in this document. The revised AP-42 sections are contained in appendices.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA -- atomic absorption spectrophotometry
AOD -- argon oxygen decarburization
AP-42 -- EPA publication entitled Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources
BOF -- basic oxygen furnace
COG -- coke oven gas
COS -- carbonyl sulfide
EAF -- electric arc furnace
EFMS -- Emission Factor Methodologies Section
EIB -- Emission Inventory Branch
EPA -- U.S. Environmental Protection Agency
ESP -- electrostatic precipitator
gr/dscf -- grains per dry standard cubic feet
kg/Mg -- kilograms per megagram
lb/ton -- pounds per ton
MEA -- monoethanolamine
MM -- million
NSPS -- New Source Performance Standards
NYDEC -- New York Department of Environmental Conservation
PADER -- Pennsylvania Department of Environmental Resources
PSD -- Prevention of Significant Deterioration
PM -- particulate matter
SIP -- state implementation plan
SPG -- Springer gas
Tons/hr -- tons per hour
μm -- micro meters

SYMBOLS

CS_2 -- carbon disulfide
H_2S -- hydrogen sulfide
NO_x -- nitrogen oxides
Pb -- lead
SO_2 -- sulfur dioxide
SO_3 -- sulfur trioxide

SECTION 1

OVERVIEW

INTRODUCTION

The Emission Factor Methodologies Section (EFMS) of the Emission Inventory Branch (EIB) has responsibility for developing and maintaining the document Compilation of Air Pollutant Emission Factors, AP-42, which is a basic source of emission factors used in preparation of State Implementation Plans (SIPs), economic analyses, review of Prevention of Significant Deterioration (PSD) applications, New Source Review permit applications and other Federal, State and local agency assessments of air pollution sources. Emission factors are one primary tool used to determine source contribution to pollutant levels within a specific geographic area. Therefore, they affect source control and permit decisions as well as SIP emission inventory development covering several source types.

Under several EPA contracts, JACA Corp. has collected emission test reports for iron and steel operations. Under this EPA work assignment, JACA reviewed in-house test reports and developed emission factors for iron and steel operations for pollutants that are not included in the 1986 update of Section 7.5 (Iron and Steel Production) and Section 7.2 (Coke Manufacturing) of AP-42. Specifically, the following operations and pollutants were addressed:

- Sintering-windbox: sulfur dioxide (SO_2) and nitrogen oxides (NO_x)
- Basic oxygen furnace (BOF): SO_2 and NO_x
- Electric arc furnace (EAF): SO_2 and NO_x
- Argon oxygen decarburization (AOD): particulate matter (PM), particle size distribution, and lead (Pb)
- Steel teeming: particle size distribution
- Coke pushing: SO_2
- Coke oven gas (COG) desulfurization: SO_2 and sulfur compounds (hydrogen sulfide, carbonyl sulfide, and carbon disulfide)
- Combustion stack: Pollutants to be specified at a later date.

The development of the emission factors for each operation and pollutant are discussed in the remaining sections of this document. Appendix A contains the revised AP-42 Section 7.5, document. Appendix A contains the revised AP-42 Section 7.5, and Appendix B contains the revised AP-42 Section 7.2. Apendix C contains copies of key pages of the test reports that are discussed in this document.

EMISSION FACTOR RATING SYSTEM

The emission factors are based on data from several sources. A rating system is used to convey the reliability and accuracy of the data from an individual test report as well as the emission factor that is subsequently developed from the test data.(1) The rating system for data from an individual report is as follows:

A - Tests performed by a sound methodology and reported in enough detail for adequate validation. These tests are not necessarily EPA reference method tests, although such reference methods are certainly to be used as a guide.

B - Tests that are performed by a generally sound methodology but lack enough detail for adequate validation.

C - Tests that are based on an untested or new methodology or that lack a significant amount of background data.

D - Tests that are based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The rating system for the emission factor is as follows:

A - Excellent. Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough to minimize variability within the source category population. A source category is generally a single process.

B - Above average. Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. As in the A rating, the source category is specific enough to minimize variability within the source category population.

C - Average. Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A rating, the source category is specific enough to minimize variability within the source category population.

D - Below average. The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are footnoted in the emission factor table.

E - Poor. The emission factor was developed from C- and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always footnoted.

Both of these standard rating systems are used throughout this document.

REFERENCES FOR SECTION 1

1. Air Management Technology Branch, Office of Air Quality Planning and Standards. Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1980, 55 pp.

SECTION 7

COKE PUSHING

SUMMARY

An emission factor for SO_2 is included for coke oven pushing in the revised AP-42 Section 7.2. The following is a summary of the emission factor:

Type of operation	Suggested emission factor rating	Emission factor kg/Mg (lb/ton) coal charged
Coke pushing, uncontrolled (includes non-pushing periods)	D	SO_2:0.043 (0.086)

The SO_2 emission factor is based on a single B-rated test and, therefore, a D emission factor rating is proposed. Table 7-1 provides a summary of the test data.

SULFUR DIOXIDE DATA

The single SO_2 test is summarized in this section.

Test 24: Bethlehem Steel Corp./Burns Harbor, IN[1]

During March 1975, Clayton Environmental conducted testing of coke side emissions on the Battery 1 shed. The testing was conducted under contract to EPA to quantify the nature and extent of emissions. The authors noted that the continuous average estimated shed capture efficiency was 85 percent.

SO_2 emissions were measured using Method 8. The measurements were made on a continuous basis. An emission factor was calculated as follows:

Emission rate = 12.6 lb/hr (average)

Coke production rate = 35 ton/charge (average) wet coal feed

Average number of pushes = 4.9 push/hr (average during sampling period). Assume average number of charges/hr is equal to the average number of pushes/hr.

Capture efficiency of hood = 85 percent or 15 percent escaping capture

Emission factor:

Table 7-1. SUMMARY OF EMISSION FACTOR FOR COKE OVEN PUSHING

Plant/Location	Source description	Pollutant	Test method	No. of test runs	Emission factor[a]	Proposed test rating
Bethlehem Steel Corp./Burns Harbor, IN	Coke pushing, uncontrolled	SO_2	Method 8		0.043 (0.086)	B

[a] Kilograms per megagram (pounds per ton) of dry coal charged.

$$\frac{12.6\ \text{lb}}{\text{hr}} \times \frac{\text{hr}}{4.9\ \text{charges}} \times \frac{\text{charge}}{35\ \text{ton coal}} \times \frac{1}{0.85} =$$

$$0.086\ \text{lb/ton coal}\ (0.043\ \text{kg/Mg coal})$$

A B rating is proposed for the test data. This is a very comprehensive test series, however, all of the supporting data sheets are contained in appendices which are not included with the test report.

REFERENCES FOR SECTION 7

1. Clayton Environmental Consultants, Inc. Source Testing of a Stationary Coke-Side Enclosure, Burns Harbor Plant, Bethlehem Steel Corporation, Chesterton, Indiana (Volume 1 of 12). U.S. Environmental Protection Agency, Washington, D.C., EPA-340/1-76-012, May 1977, 128 pp.

SECTION 8

COKE OVEN GAS DESULFURIZATION

SUMMARY

Emission factors for SO_2 and sulfur compounds (carbon disulfide, hydrogen sulfide, and carbonyl sulfide) have been included in revised AP-42 Section 7.2. The emission factors are summarized below and on Table 8-1:

Type of operation	Suggested emission factor rating	Emission factor kg/1,000 m^3 COG (lb/1,000 ft^3 COG) as SO_2
COG desulfurization incinerator	E	SO_2 0.74 (0.046)
Scrubber (contactor) inlet	E	Sulfur Compounds: 15.8 (0.98)
Scrubber (contactor) outlet	E	Sulfur Compounds: 0.48 (0.030)

The suggested emission factor rating for all source categories is E because the emission factors are based on C-rated test reports. There was a general lack of process data or plant description in the test reports.

Sulfur recovery from coke oven gas (COG), is done by wet oxidation or absorption stripping processes. There are approximately eight major types of commercially available processes.[1] All of the available test reports have poorly documented or non-existent sections on process information or facility descriptions. Because of the variety of commercial processes involved, the number of possible sampling sites, possible configuration differences, and the E emission factor rating, the COG desulfurization emission factors are presented as a footnote on AP-42 Table 7.2-1.

SULFUR DIOXIDE DATA

SO_2 data is available from three facilities. The tests were conducted at incinerator stacks. The test data is summarized in this section.

Test 25: Allied Chemical/Ashland, KY[2]

TABLE 8-1. SUMMARY OF EMISSION FACTORS FOR COKE OVEN GAS DESULFURIZATION

Plant/location	Source description	Pollutant	Test method	No. of test runs	Emission factor[a]	Suggested test rating
Allied Chemical/ Ashland, KY	Tail gas incinerator	SO_2	Method 6	18	0.80 (0.050)	C
Republic Steel/ Cleveland, OH	Incinerator	SO_2	Method 8	14	0.55 (0.034)	C
Shenango Inc./Neville Island, PA	Incinerator	SO_2	Method 6	12	0.88 (0.055)	C
Allied Chemical/ Ashland, KY	Exit of Sulfiban process[b]	Sulfur compounds[c]	GC	18	0.42 (0.026)	C
Republic Steel/ Cleveland, OH	Scrubber (contactor) inlet	Sulfur compounds[c]	GC and wet chemistry	13	12.02 (0.75)	C
	Scrubber (contactor) outlet	Sulfur compounds[c]	GC and wet chemistry	14	0.30 (0.019)	C
Shenango Inc./ Neville Island, PA	Scrubber inlet	Sulfur compounds[c]	GC and wet chemistry	12	19.40 (1.21)	C
	Scrubber outlet	Sulfur compounds[c]	GC and wet chemistry	12	0.71 (0.044)	C

[a] Kilograms per 1,000 cubic meters (pounds per 1,000 cubic feet) of coke oven gas as sulfur dioxide equivalents.
[b] Assume equivalent to scrubber or contactor.
[c] Includes carbon disulfide, carbonyl sulfide, and hydrogen sulfide.

In January 1979, York Research Corp. conducted testing of the Sulfiban process for the Claus plant tail gas incinerator stack. The Sulfiban process consists of scrubbing raw COG and Springer gas (SPG) from the ammonia concentration section with monoethanolamine (MEA) solution. The desulfurized COG is returned to plant's users or sold. Acid gas regenerated from the MEA solution flows to the Claus plant where elemental sulfur is produced. Tail gas from the Claus plant is incinerated.

Eighteen SO_2 samples of the Claus plant incinerator stack were collected using Method 6. The results are reported in pounds of SO_2/million cubic feet of COG (lb SO_2/MM ft^3 COG). The average of the 18 test runs is 49.74 lb SO_2/MM ft^3 COG. Normalizing this to lb/1,000 ft^3 COG yields 0.050 lb SO_2/1,000 ft^3 COG or 0.80 kg SO_2/1,000 m^3 COG.

A C rating is proposed for the tests. This rating was selected for several reasons: 1) the process is not well documented and 2) there were errors in the sample calculations for SO_2.

<u>Test 26: Republic Steel/Cleveland, OH[3]</u>

In 1981, BCM conducted testing on the Sulfiban COG desulfurization system serving No. 1 Coke Plant Batteries 1, 2, 3, and 4. The testing program included sampling at the incinerator stack using EPA Method 8. Fourteen test runs were conducted. Results are reported in hydrogen sulfide (H_2S) gr/100 dscf COG.

The average of the tests is 12.1 H_2S gr/100 dscf COG. To express this as an SO_2 equivalent, complete oxidation of H_2S to SO_2 was assumed. Using this assumption, 1 lb of H_2S is equivalent to 1.88 lb of SO_2. Converting the test results from gr/100 dscf of COG as H_2S to lb/1,000 dscf COG as SO_2:

$$\frac{12.81 \text{ gr as } H_2S}{100 \text{ dscf}} \times \frac{\text{lb}}{7{,}000 \text{ gr}}$$

$$\times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S}$$

$$= 0.034 \text{ lb/1,000 ft}^3 \text{ COG as } SO_2 \text{ (0.55 kg/1,000 m}^3\text{)}$$

The report contains field data sheets, calculations, descriptions of test methods but lacks a description of the process that was tested. An appendix reports that testing shall be conducted under maximum loading conditions, but there is no statement in the report that testing was done under maximum conditions. A C rating is proposed for this test report because of the lack of process information.

Test 27: Shenango Inc./Neville Island, PA[4]

BCM conducted SO_2 tests at the incinerator stack at the desulfurization plant on June 12 and 13, 1980. The purpose of the tests was to determine if the desulfurization unit was meeting the manufacturer's specifications and local air pollution regulations. Twelve SO_2 samples were collected using Method 6.

Results are reported in gr/100 dscf of COG as H_2S. The results were expressed as an SO_2 equivalent using the procedure described under Test 26. The average results are 20.38 gr/100 dscf as H_2S. The emission factor was calculated as follows:

$$\frac{20.38 \text{ gr as } H_2S}{100 \text{ dscf}} \times \frac{\text{lb}}{7{,}000 \text{ gr}} \times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S}$$

$$= 0.055 \text{ lb}/1{,}000 \text{ ft}^3 \text{ COG } (0.88 \text{ kg}/1{,}000 \text{ m}^3) \text{ as } SO_2$$

The test report includes original data sheets and calibration sheets. However, there is no description of the plant or operations. A C rating is proposed.

SULFUR COMPOUNDS DATA

Data is available from three facilities for testing of H_2S, carbonyl sulfide (COS), and carbon disulfide (CS_2) at several points within the COG desulfurization plant. For purposes of consistency, the H_2S, COS, and CS_2 data were expressed as SO_2 equivalents and summed to yield total sulfur compounds as SO_2 equivalents.

Test 28: Allied Chemical/Ashland, KY[2]

Tests for H_2S, COS, and CS_2 were conducted during Test 25 at the point where the desulfurized COG line exits the Sulfiban process. The tests were conducted using gas chromatography with flame photometric detection. The method described in the report appears to be similar to EPA Method 15. The results are reported in pounds of equivalent SO_2 per million cubic feet of COG produced for H_2S, COS, and CS_2. The SO_2 equivalent results were summed for each of the 18 test runs. The average total sulfur compounds (H_2S, COS, and CS_2) expressed as an SO_2 equivalent is 25.96 lb/MM ft^3 COG. To express the results in the units selected for the emission factor, the results were divided by 1,000. Therefore, the total sulfur emission factor is 0.026 lb/1,000 ft^3 COG (0.42 kg/1,000 m^3 COG) as SO_2 equivalent.

There is a wide range in the results for the tests - 7.76 to 133.43 lb/MM ft^3 COG as SO_2 (total sulfur compounds) - with no explanation provided by the authors. The largest range is among the H_2S results which range from 0.04 to 118.9 lb/MM ft^3 as SO_2.

A C rating is proposed for the test data because the report lacks a description of the process and because there is no explanation regarding the wide range of results.

Test 29: Republic Steel/Cleveland, OH[3]

The Test 26 sampling program also included testing for H_2S, COS and CS_2 at the scrubber (contractor) inlet and outlet. Fourteen tests were conducted at the outlet site and 13 at the inlet site.

H_2S was sampled using a modified version of Method 11. The method was modified to accommodate the higher concentrations of H_2S that are present in COG. COS and CS_2 were sampled using an absorbing alcoholic potassium hyroxide solution.

Test results are reported in H_2S gr/100 dscf of COG. The average for the contactor inlet and outlet are 280 and 7.2 H_2S gr/100 dscf of COG, respectively. Converting to SO_2 equivalents and emission factor units:

Contactor inlet -

$$\frac{280 \text{ gr as } H_2S}{100 \text{ dscf}} \times \frac{\text{lb}}{7{,}000 \text{ gr}} \times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S \text{ equivalent}}$$

$$= 0.75 \text{ lb}/1{,}000 \text{ ft}^3 \text{ COG } (12.02 \text{ kg}/1{,}000 \text{ m}^3) \text{ as } SO_2$$

Contactor outlet -

$$\frac{7.2 \text{ gr as } H_2S}{100 \text{ dscf COG}} \times \frac{\text{lb}}{7{,}000 \text{ gr}} \times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S \text{ equivalent}}$$

$$= 0.019 \text{ lb}/1{,}000 \text{ ft}^3 \text{ COG } (0.30 \text{ kg}/1{,}000 \text{ m}^3) \text{ as } SO_2$$

A C rating is proposed for the data because of the lack of process description in the test report and because a standard method (Method 15) was not used for the COS and CS_2 tests.

Test 30: Shenango, Inc./Neville Island, PA[4]

Test 27 also included testing for COS, CS_2, and H_2S at the scrubber inlet and outlet. A total of 12 samples were taken at each location. A modified version of Method 11 was used to accomodate the higher concentrations of H_2S that are found in COG. COS and CS_2 were sampled using absorption in alcoholic potassium hydroxide.

Results are reported in gr/100 dscf as H_2S for H_2S and organic sulfur (COS and CS_2). The H_2S and organic sulfur results expressed as H_2S equivalents were summed. The average total sulfur inlet and outlet values are 451.94 and 16.36 gr/100 dscf as H_2S. Converting to emission factors:

Inlet -

$$\frac{451.94 \text{ gr as } H_2S}{100 \text{ dscf COG}} \times \frac{\text{lb}}{7{,}000 \text{ gr}} \times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S \text{ equivalent}}$$

$= 1.21 \text{ lb}/1{,}000 \text{ ft}^3$ COG ($19.40 \text{ kg}/1{,}000 \text{ m}^3$) as SO_2 equivalent

Outlet -

$$\frac{16.36 \text{ gr as } H_2S}{100 \text{ dscf COG}} \times \frac{\text{lb}}{7{,}000 \text{ gr}} \times \frac{10}{10} \times \frac{1.88 \text{ lb } SO_2 \text{ equivalent}}{1 \text{ lb } H_2S \text{ equivalent}}$$

$= 0.044 \text{ lb}/1{,}000 \text{ ft}^3$ COG ($0.71 \text{ kg}/1{,}000 \text{ m}^3$) as SO_2 equivalent

A C rating is proposed for the test data because of the lack of process description in the test report and because a standard method (Method 15) was not used for determining CS_2 and COS emissions.

REFERENCES FOR SECTION 8

1. United States Steel. The Making, Shaping and Treating of Steel, 10th Edition. Association of Iron and Steel Engineers, Pittsburgh, PA, 1985, 1,572 pp.

2. York Research Corporation. Test Report for Allied Chemical Corporation, Semet-Solvay Division, Ashland, Kentucky 41101 on the Sulfiban Process. York Research Corporation, Stamford, CT, YRC No. 1-9868-02, March 1979.

3. Beer, R.G. Evaluation of the Desulfurization Facility at the Cleveland Plant of Republic Steel Corporation, Cleveland, Ohio. BCM Project No. 00-4178-13, Betz, Converse, Murdoch, Inc., Pittsburgh, PA, September 1981.

4. Turina, P. Compliance and Guarantee Evaluation of the Desulfurization Facility, Neville Island Plant, Shenango Incorporated, Pittsburgh, Pennsylvania. BCM Project No. 00-4810-03, Betz, Converse, Murdoch, Inc., July 1980.

Appendix B

Revised AP-42 Section 7.2: Coke Manufacturing

7.2 COKE MANUFACTURING

7.2.1 Process Description

Metallurgical coke is manufactured by destructive distillation of coal in a byproduct coke oven battery. The distillation, termed "coking", is accomplished in a series of ovens in the absence of oxygen. Volatile compounds are driven from the coal, collected from each oven, and processed in an adjacent plant for recovery of combustible gases and other coal byproducts. Virtually all metallurgical coke is produced by this process, termed the "byproduct" method. Metallurgical coke is used in blast furnaces for production of iron.

Coke is produced in narrow, slot type ovens constructed of silica brick. A coke oven battery may have a series of 10 to 100 individual ovens, with a heating flue between each oven pair. Ovens are charged with pulverized coal, through ports in the oven top, by a larry car traveling on tracks along the top of each battery. After charging, the ports are sealed, and the coking process begins. Combustion of gases in burners in the flues between the ovens provides heat for the process. Coke oven gas from the byproduct recovery plant is the common fuel for underfiring the ovens at most plants, but blast furnace gas and, infrequently, natural gas may also be used.

After a coking time typically between 12 and 20 hours, almost all volatile matter is driven from the coal mass, and the coke is formed. Maximum temperature at the center of the coke mass is usually 1100 to 1150°C (2000 to 2100°F).

After coking, machinery located on tracks on each side of the battery removes the vertical door on each end of an oven, and a long ram pushes the coke from the oven into a rail quench car, whence it goes to a quench tower, where several thousand gallons of water are sprayed onto the coke mass to cool it. The car then discharges the coke onto a wharf along the battery for further cooling and drainage of water. From here, coke is screened and sent to the blast furnace or to storage in outdoor piles.

After the coke is pushed from an oven, the doors are cleaned and repositioned, and the oven is then ready to receive another charge of coal. Figure 7.2-1 is a diagram of a typical byproduct coke process.

During the coking cycle, volatile matter driven from the coal mass is collected by offtakes located at one or both ends of the oven. A common collector main transports the gases from each oven to the byproduct recovery plant. Here, coke oven gas is separated, cleaned and returned to heat the ovens. Only 40 percent of recovered coke oven gas is required for underfiring, and the remainder is used throughout the steel plant. Other coal

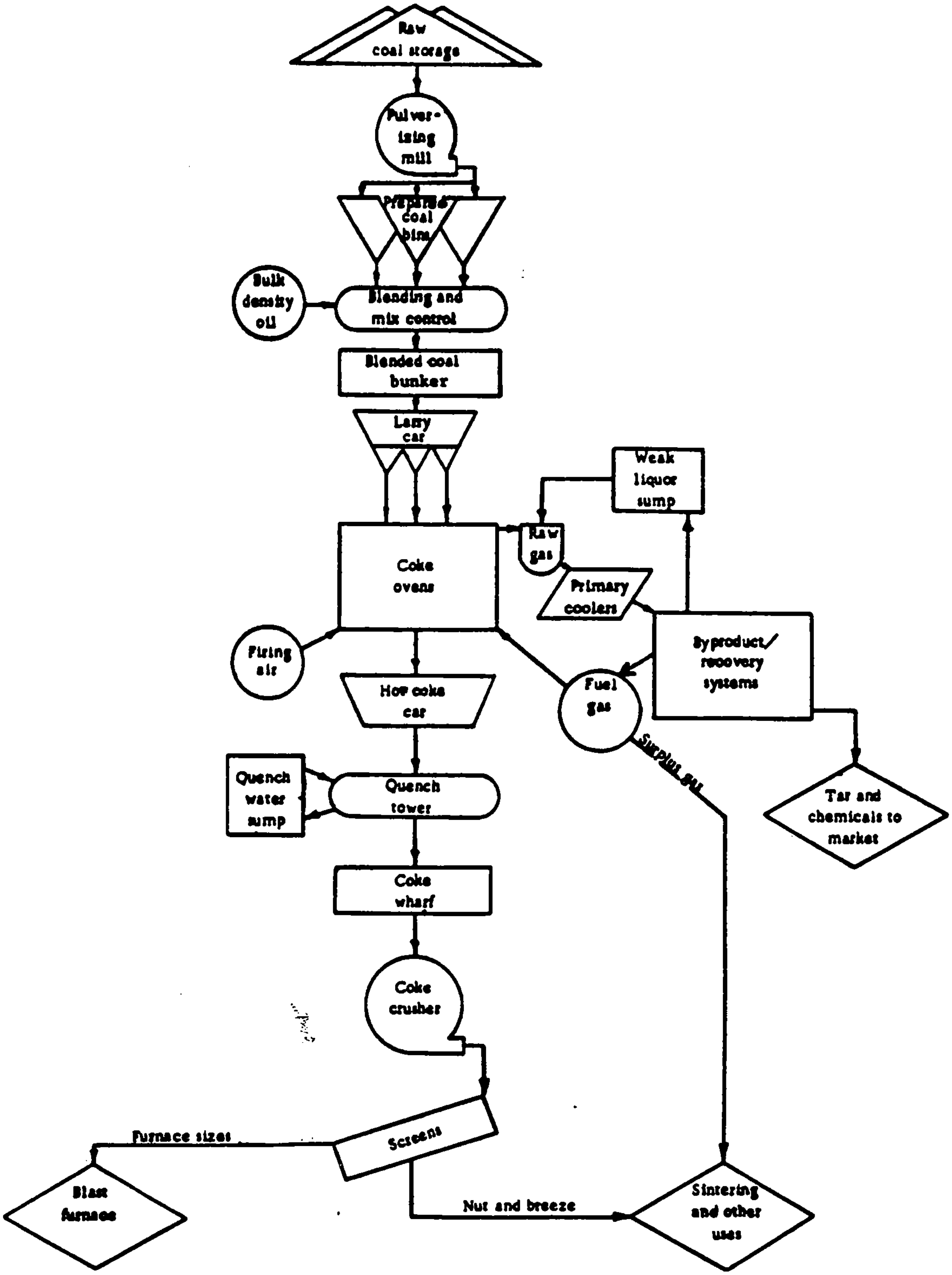


Figure 7.2-1. The major steps in the carbonization of coal with the byproduct process.

byproducts also are recovered in the byproduct plant for reuse, sale or disposal.

7.2.2 Emissions and Controls

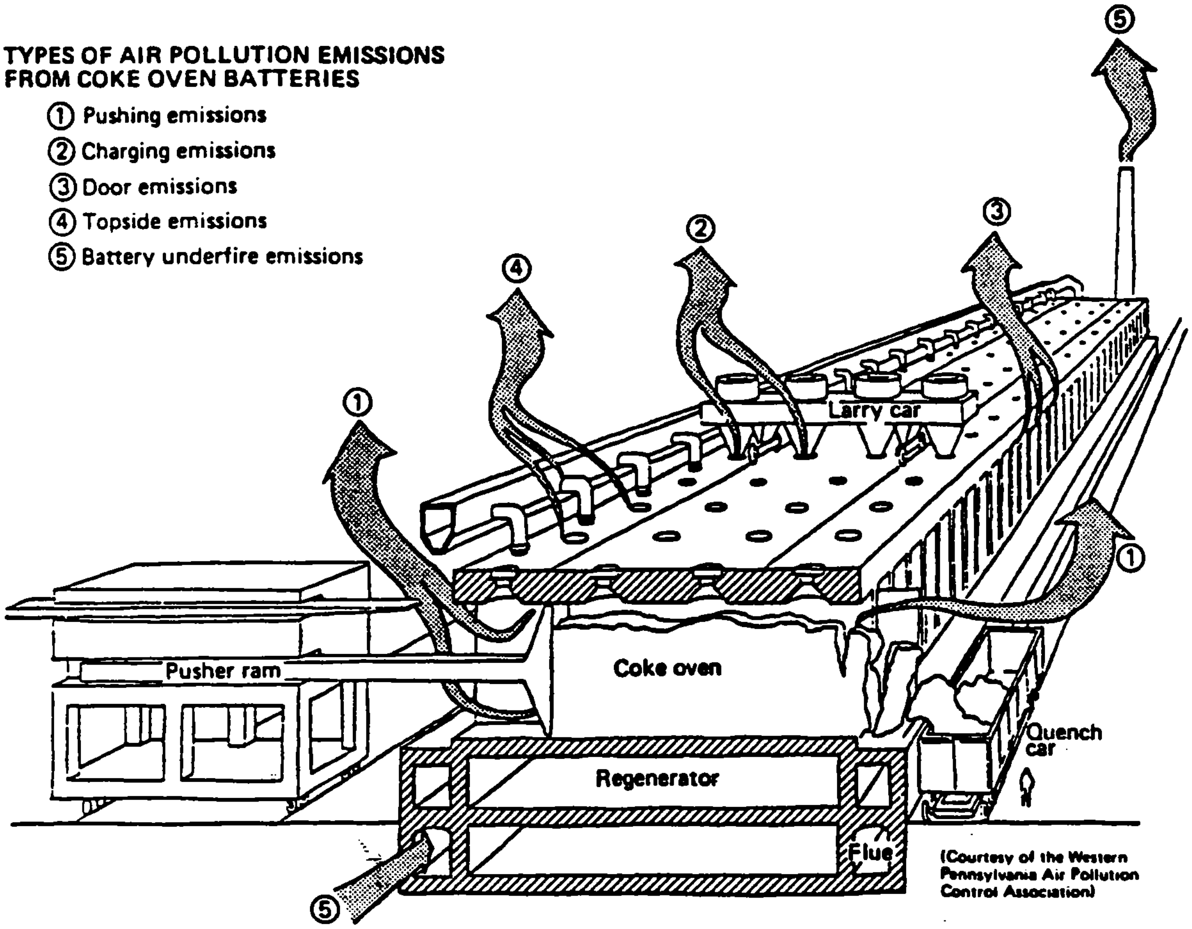
Particulate, volatile organic compounds, carbon monoxide and other emissions originate from several byproduct coking operations: (1) coal preparation, (2) coal preheating (if used), (3) charging coal into ovens incandescent with heat, (4) oven leakage during the coking period, (5) pushing the coke out of the ovens, (6) quenching the hot coke and (7) underfire combustion stacks. Gaseous emissions collected from the ovens during the coking process in the byproduct plant are subjected to various operations for separating ammonia, coke oven gas, tar, phenol, light oil (benzene, toluene, xylene) and pyridine. These unit operations are potential sources of volatile organic compound emissions.

Coal preparation consists of pulverizing, screening, blending of several coal types, and adding oil or water for bulk density control. Particulate emissions are sometimes controlled by evacuated or unevacuated enclosures. A few domestic plants heat coal to about 260°C (500°F) before charging, using a flash drying column heated by combustion of coke oven or natural gas. The air stream that conveys the coal through the drying column usually is passed through conventional wet scrubbers for particulate removal before discharge to the atmosphere.

Oven charging can produce emissions of particulate matter and volatile organic compounds from coal decomposition. The stage, or sequential, charging techniques used on virtually all batteries draw most charging emissions into the battery collector main and on to the byproduct plant. During the coking cycle, volatile organic emissions from the thermal distillation process occasionally leak to the atmosphere through poorly sealed doors, charge lids and offtake caps, and through cracks which may develop in oven brickwork, the offtakes and collector mains. Door leaks are controlled by diligent door cleaning and maintenance, rebuilding of doors, and in some plants, by manual application of lute (seal) material. Charge lid and offtake leaks are controlled by an effective patching and luting program.

Pushing coke into the quench car is another major source of particulate emissions, and if the coke mass is not fully coked, also of volatile organic compounds and combustion products. Most batteries use pushing emission controls such as hooded, mobile scrubber cars; shed enclosures evacuated to a gas cleaning device; or traveling hoods with a fixed duct leading to a stationary gas cleaner. The quench tower activity emits particulate from the coke mass, and dissolved solids from the quench water may become entrained in the steam plume rising from the tower. Trace organic compounds also may be present.

The gas combustion in the battery flues produces emissions through the underfire or combustion stack. If coke oven gas is not desulfurized, sulfur oxide emissions accompany the particulate and combustion emissions. If oven wall brickwork is damaged, coal fines and coking decomposition products from a recently charged oven may leak into the waste combustion gases. Figure 7.2-2 portrays major air pollution sources from a typical coke oven battery.



(Courtesy of the Western Pennsylvania Air Pollution Control Association)

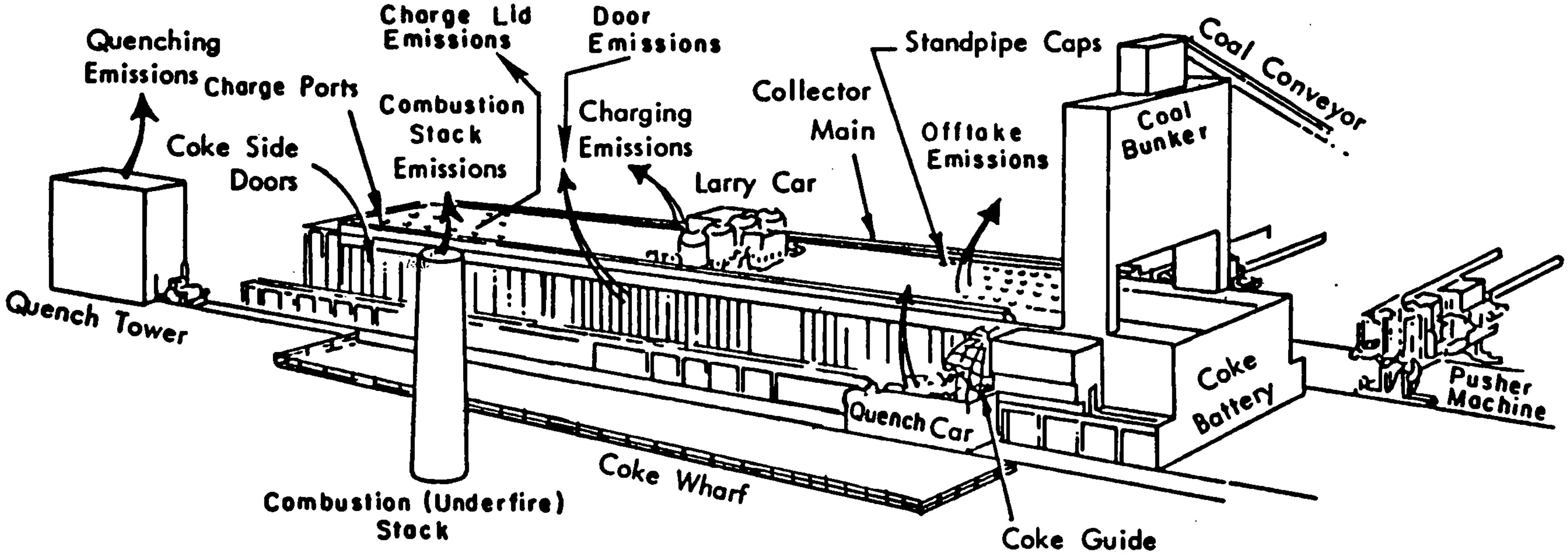


Figure 7.2-2. Byproduct coke oven battery, with major emission points shown.

Associated with the byproduct coke production are open source fugitive dust operations from material handling. These operations consist of unloading, storing, grinding and sizing of coal; and screening, crushing, storing and loading of coke. Fugitive emissions may also result from vehicles traveling on paved and unpaved surfaces. The emission factors available for coking operations for total particulate, sulfur dioxide, carbon monoxide, volatile organic compounds, nitrogen oxides and ammonia are given in Table 7.2-1. Table 7.2-2 gives available size-specific emission factors. Figures 7.2-3 through 7.2-13 present emission factor data by particle size. Extensive information on the data used to develop the particulate emission factors can be found in References 1 and 21.

TABLE 7.2-2. SIZE SPECIFIC EMISSION FACTORS FOR COKE MANUFACTURING

Process	Particulate emission factor rating	Particle size (μm)	Cumulative mass % ≤ stated size	Cumulative mass emission factors		Reference source number
				kg/Mg	lb/ton	
Coal preheating Uncontrolled	D	0.5	44	0.8	1.5	6
		1.0	48.5	0.8	1.7	
		2.0	55	1.0	1.9	
		2.5	59.5	1.0	2.1	
		5.0	79.5	1.4	2.8	
		10.0	97.5	1.7	3.4	
		15.0	99.9	1.7	3.5	
			100	1.7	3.5	
Controlled with venturi scrubber	D	0.5	78	0.10	0.20	6
		1.0	80	0.10	0.20	
		2.0	83	0.10	0.21	
		2.5	84	0.11	0.21	
		5.0	88	0.11	0.22	
		10.0	94	0.12	0.24	
		15.0	96.5	0.12	0.24	
			100	0.12	0.25	
Coal charging Sequential or stage	E	0.5	13.5	0.001	0.002	7
		1.0	25.2	0.002	0.004	
		2.0	33.6	0.003	0.005	
		2.5	39.1	0.003	0.006	
		5.0	45.8	0.004	0.007	
		10.0	48.9	0.004	0.008	
		15.0	49.0	0.004	0.008	
			100	0.008	0.016	
Coke pushing Uncontrolled	D	0.5	3.1	0.02	0.04	8-13
		1.0	7.7	0.04	0.09	
		2.0	14.8	0.09	0.17	
		2.5	16.7	0.10	0.19	
		5.0	26.6	0.15	0.30	
		10.0	43.3	0.25	0.50	
		15.0	50.0	0.29	0.58	
			100	0.58	1.15	
Controlled with Venturi scrubber	D	0.5	24	0.02	0.04	8,10
		1.0	47	0.04	0.08	
		2.0	66.5	0.06	0.12	
		2.5	73.5	0.07	0.13	
		5.0	75	0.07	0.13	
		10.0	87	0.08	0.16	
		15.0	92	0.08	0.17	
			100	0.09	0.18	
Mobile scrubber car	D	1.0	28.0	0.010	0.020	14
		2.0	29.5	0.011	0.021	
		2.5	30.0	0.011	0.022	
		5.0	30.0	0.011	0.022	
		10.0	32.0	0.012	0.024	
		15.0	35.0	0.013	0.023	
			100	0.036	0.072	

(Continued)

TABLE 7.2-2. (CONTINUED)

Process	Particulate emission factor rating	Particle size (µm)	Cumulative mass % ≤ stated size	Cumulative mass emission factors		Reference source number
				kg/Mg	lb/ton	
Quenching Uncontrolled (dirty water)	D	1.0	13.8	0.36	0.72	15
		2.5	19.3	0.51	1.01	
		5.0	21.4	0.56	1.12	
		10.0	22.8	0.60	1.19	
		15.0	26.4	0.69	1.38	
			100	2.62	5.24	
Uncontrolled (clean water)	B	1.0	4.0	0.02	0.05	15
		2.5	11.1	0.06	0.13	
		5.0	19.1	0.11	0.22	
		10.0	30.1	0.17	0.34	
		15.0	37.4	0.21	0.42	
			100	0.57	1.13	
With baffles (dirty water)	D	1.0	8.5	0.06	0.11	15
		2.5	20.4	0.13	0.27	
		5.0	24.8	0.16	0.32	
		10.0	32.3	0.21	0.42	
		15.0	49.8	0.32	0.65	
			100	0.65	1.30	
With baffles (clean water)	D	1.0	1.2	0.003	0.006	15
		2.5	6.0	0.02	0.03	
		5.0	7.0	0.02	0.04	
		10.0	9.8	0.03	0.05	
		15.0	15.1	0.04	0.08	
			100	0.27	0.54	
Combustion stack Uncontrolled	D	1.0	77.4	0.18	0.36	16-18
		2.0	85.7	0.20	0.40	
		2.5	93.5	0.22	0.44	
		5.0	95.8	0.22	0.45	
		10.0	95.9	0.22	0.45	
		15.0	96	0.22	0.45	
			100	0.23	0.47	

TABLE 7.2-1. EMISSION FACTORS FOR COKE MANUFACTURING[a]
EMISSION FACTOR RATING: D (except Particulate)

Type of operation	Particulate emission factor rating[b]	Particulate[b]		Sulfur dioxide[c]		Carbon monoxide[c]		Volatile organics[c,d]		Nitrogen oxides[c]		Ammonia[c]	
		kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Coal crushing													
with cyclone	D	0.055	0.11	-	-	-	-	-	-	-	-	-	-
Coal preheating													
Uncontrolled[e]	C	1.75	3.50	-	-	-	-	-	-	-	-	-	-
With scrubber	C	0.125	0.25	-	-	-	-	-	-	-	-	-	-
With wet ESP	C	0.006	0.012	-	-	-	-	-	-	-	-	-	-
Wet coal charging[f]													
Larry car													
Uncontrolled	E	0.24	0.48	0.01	0.02	0.3	0.6	1.25	2.5	0.015	0.03	0.01	0.02
With sequential charging	E	0.008	0.016	-	-	-	-	-	-	-	-	-	-
With scrubber	E	0.007	0.014	-	-	-	-	-	-	-	-	-	-
Door leak													
Uncontrolled	D	0.027	0.54	-	-	0.3	0.6	0.75	1.5	0.005	0.01	0.03	0.06
Coke pushing													
Uncontrolled	B	0.58	1.15	0.043	0.086	0.035	0.07	0.1	0.2	-	-	0.05	0.1
With ESP[g]	C	0.225	0.45	-	-	-	-	-	-	-	-	-	-
With venturi scrubber[h]	D	0.09	0.18	-	-	-	-	-	-	-	-	-	-
With baghouse[h]	D	0.045	0.09	-	-	-	-	-	-	-	-	-	-
With mobile scrubber car[j]	C	0.036	0.072	-	-	-	-	-	-	-	-	-	-
Quenching													
Uncontrolled													
Dirty water[k]	D	2.62	5.24	-	-	-	-	-	-	-	-	-	-
Clean water[m]	D	0.57	1.13	-	-	-	-	-	-	-	-	-	-
With baffles													
Dirty water[k]	B	0.65	1.30	-	-	-	-	-	-	-	-	-	-
Clean water[m]	B	0.27	0.54	-	-	-	-	-	-	-	-	-	-

(Continued)

TABLE 7.2-1. (CONTINUED)

Type of operation	Particulate emission factor rating[b]	Particulate[b]		Sulfur dioxide[c]		Carbon monoxide[c]		Volatile organics[c,d]		Nitrogen oxides[c]		Ammonia[c]	
		kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Combustion stack													
Uncontrolled (COG)	A	0.234	0.47	2.0[n]	4.0[n]	-	-	-	-	-	-	-	-
Uncontrolled (BFG)	A	0.085	0.17	-	-	-	-	-	-	-	-	-	-
With ESP (COG)	D	0.046	0.091	-	-	-	-	-	-	-	-	-	-
With baghouse (COG)	D	0.055	0.11	-	-	-	-	-	-	-	-	-	-
Coke handling													
With cyclone[p]	D	0.003	0.006	-	-	-	-	-	-	-	-	-	-
Combined operations[q]	D	-	-	-	-	-	-	-	-	-	-	-	-
Coke oven gas desulfurization[r]	-	-	-	-[r]	-[r]	-	-	-	-	-	-	-	-

[a] Expressed as units/unit of coal charged. Dash = no data. ESP = electrostatic precipitator. COG = coke oven gas. BFG = blast furnace gas.

[b] Reference 1.

[c] References 2-3.

[d] Expressed as methane.

[e] Exhaust gas discharged from series of primary and secondary cyclones used to separate flash dried coal from hot gas.

[f] Charged coal has not been dried.

[g] Emissions captured by coke side shed.

[h] Emissions captured by traveling hood.

[j] Emissions captured by quench car enclosure.

[k] Dirty water ≥5000 mg/l total dissolved solids.

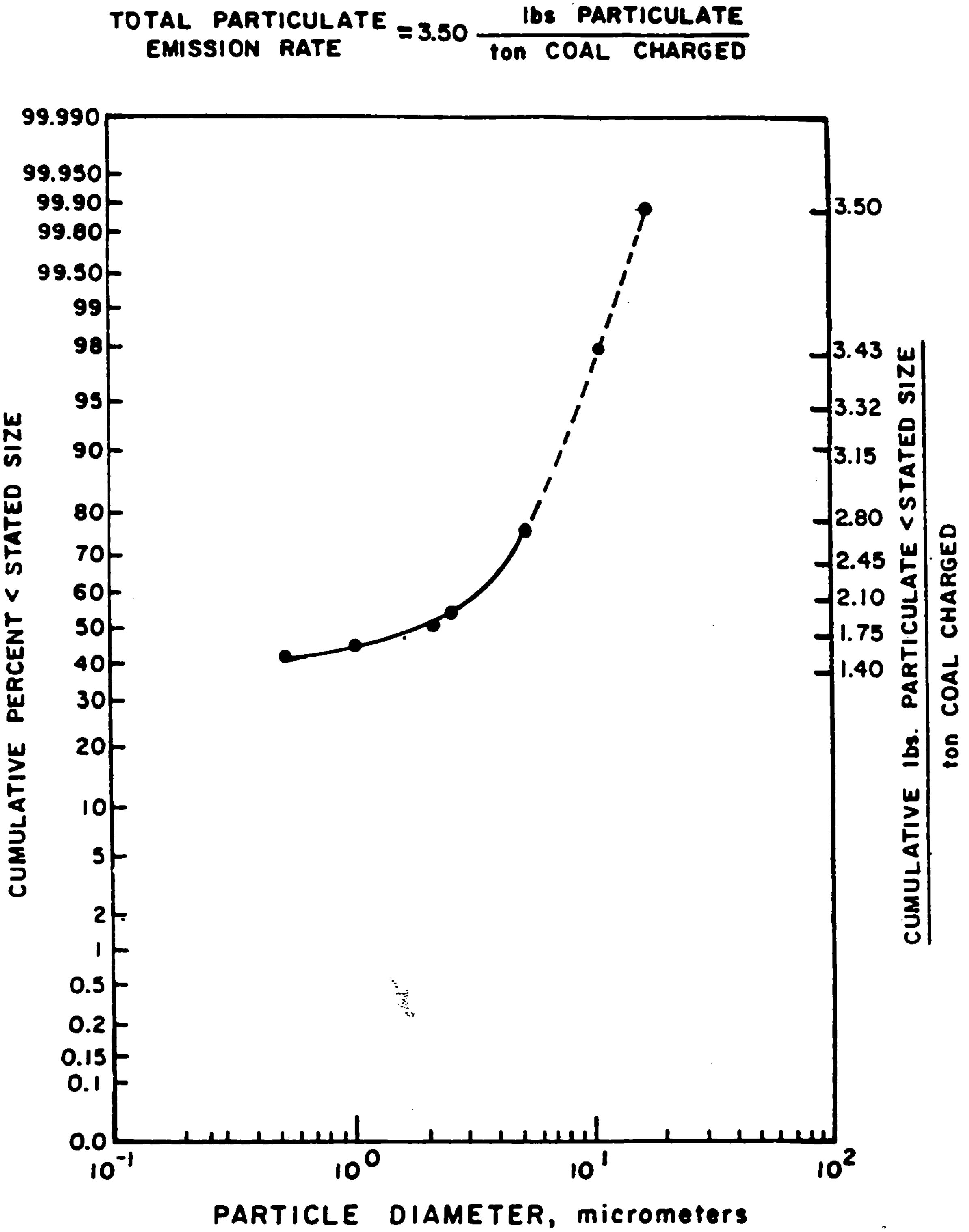
[m] Clean water ≤1500 mg/l total dissolved solids.

[n] Reference 4. Factor for SO_2 is based on these representative conditions: (1) sulfur content of coal charged to oven is 0.8 weight %; (2) about 33 weight % of total sulfur in coal charged to oven is transferred to coke oven gas; (3) about 40% of coke oven gas is burned during underfiring operation, and about 60% is used in other operations where the rest of the SO_2 [3 kg/Mg (6 lb/ton) of coal charged] is discharged; (4) gas used in underfiring has not been desulfurized.

[p] Defined as crushing and screening.

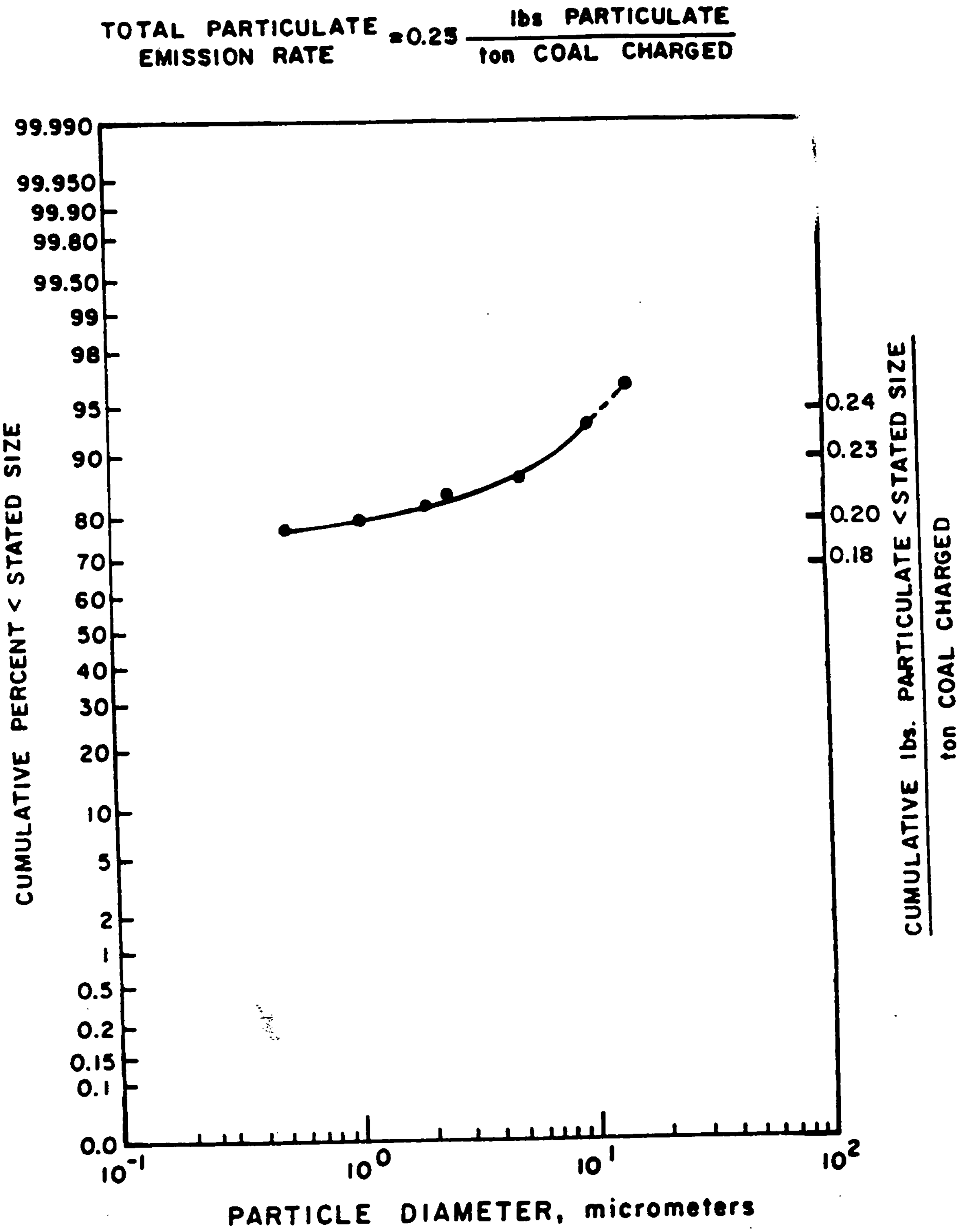
[q] References 19-20. Uncontrolled lead emissions are 0.00018 kg/Mg (0.00035 lb/ton).

[r] Emission factor rating E for SO_2 and sulfur compound data. SO_2 emission factor for incinerator is 0.74 kg/1,000 m^3 (0.046 lb/1,000 ft^3) of coke oven gas (COG). The emission factor for sulfur compounds (carbonyl sulfide, carbon disulfide and hydrogen sulfide) from the contactor (or scrubber) is 15.8 kg/1,000 m^3 (0.98 lb/1,000 ft^3) of COG as SO_2. The emission factor for sulfur compounds from the contactor (or scrubber) outlet is 0.48 kg/1,000 m^3 (0.030 lb/1,000 ft^3) of COG as SO_2.



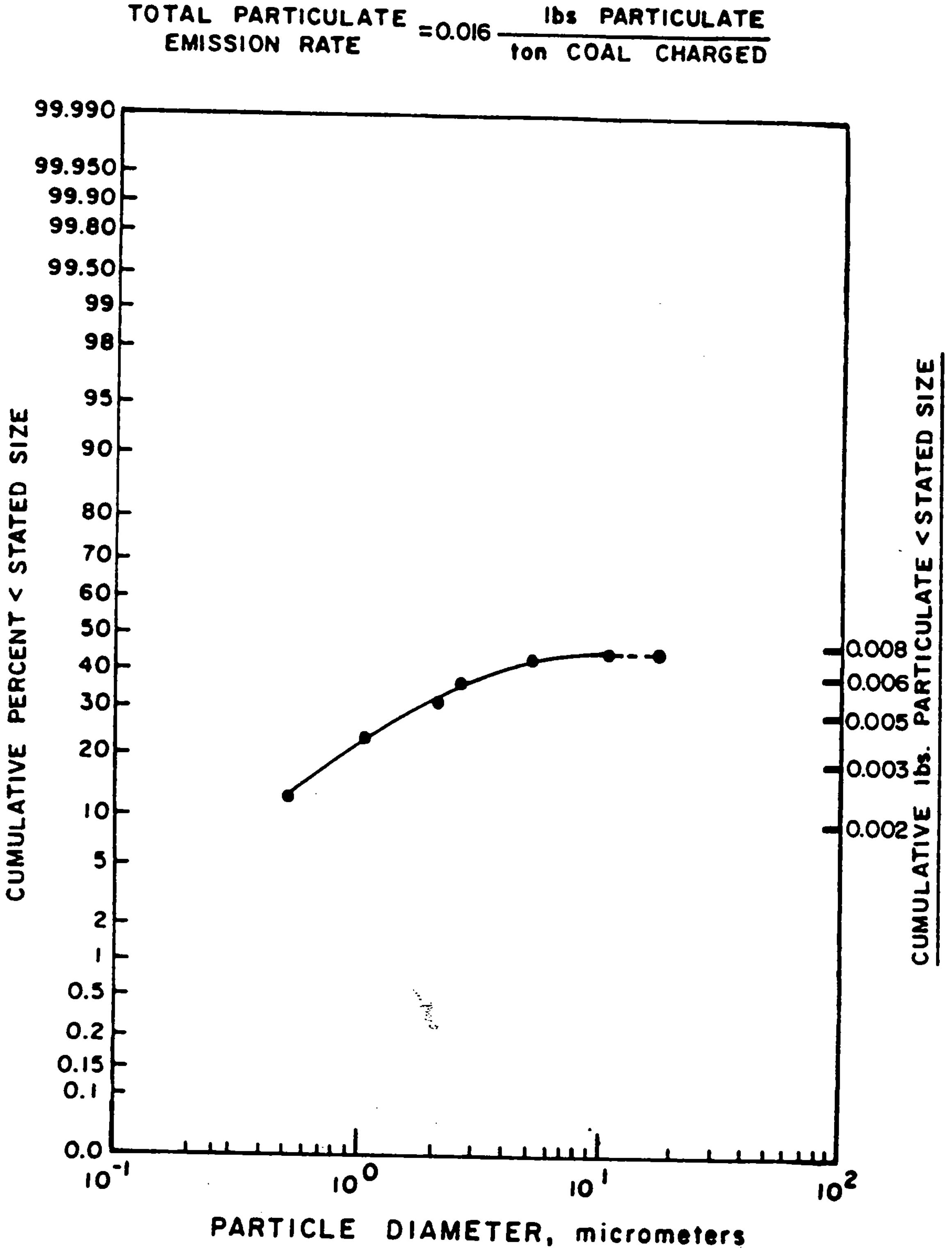
Note: Extrapolated to the 15 μm size, using engineering estimates.

Figure 7.2-3. Coal preheating (uncontrolled).



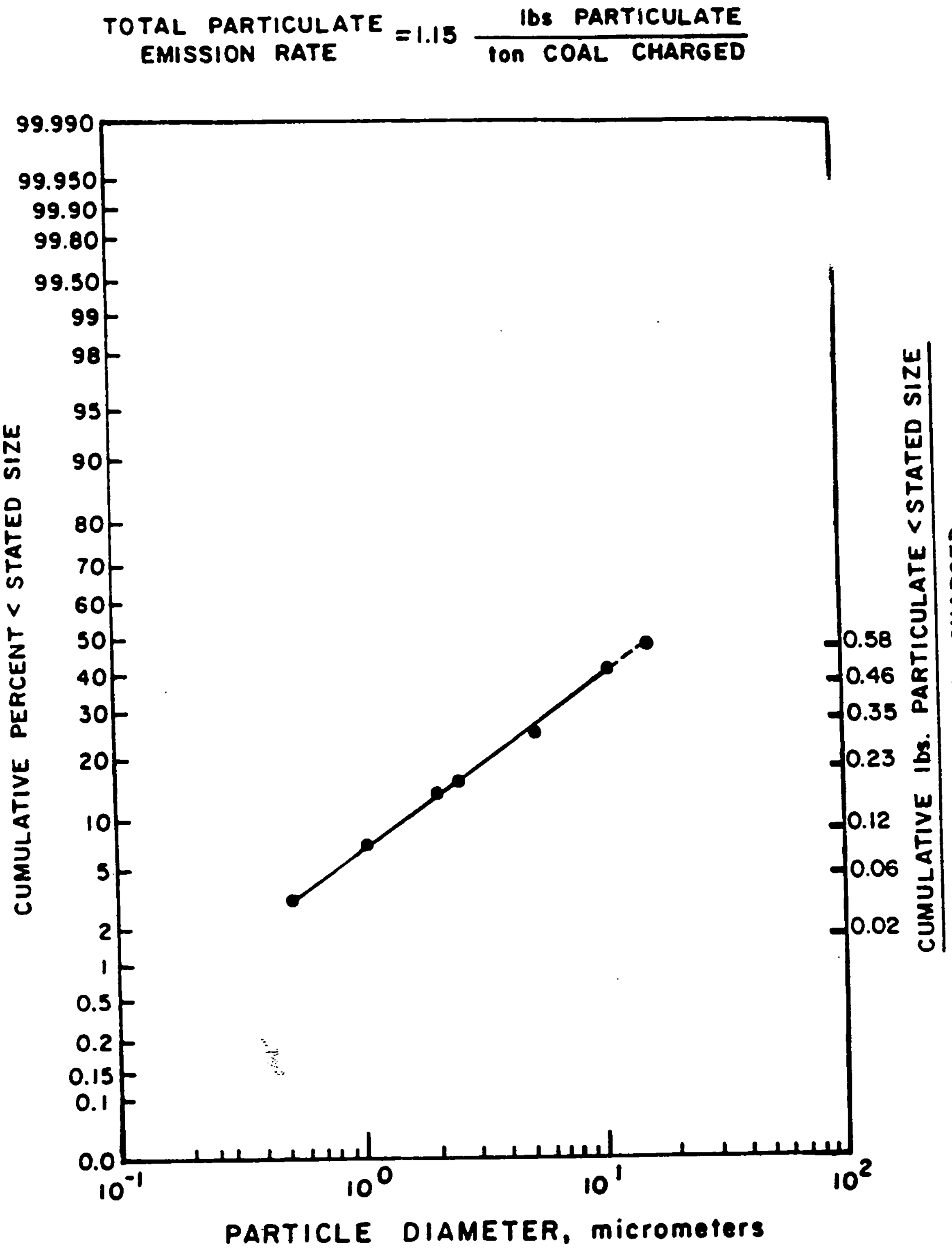
Note: **Extrapolated to the 15 μm size, using engineering estimates.**

Figure 7.2-4. Coal preheating (controlled with scrubber).



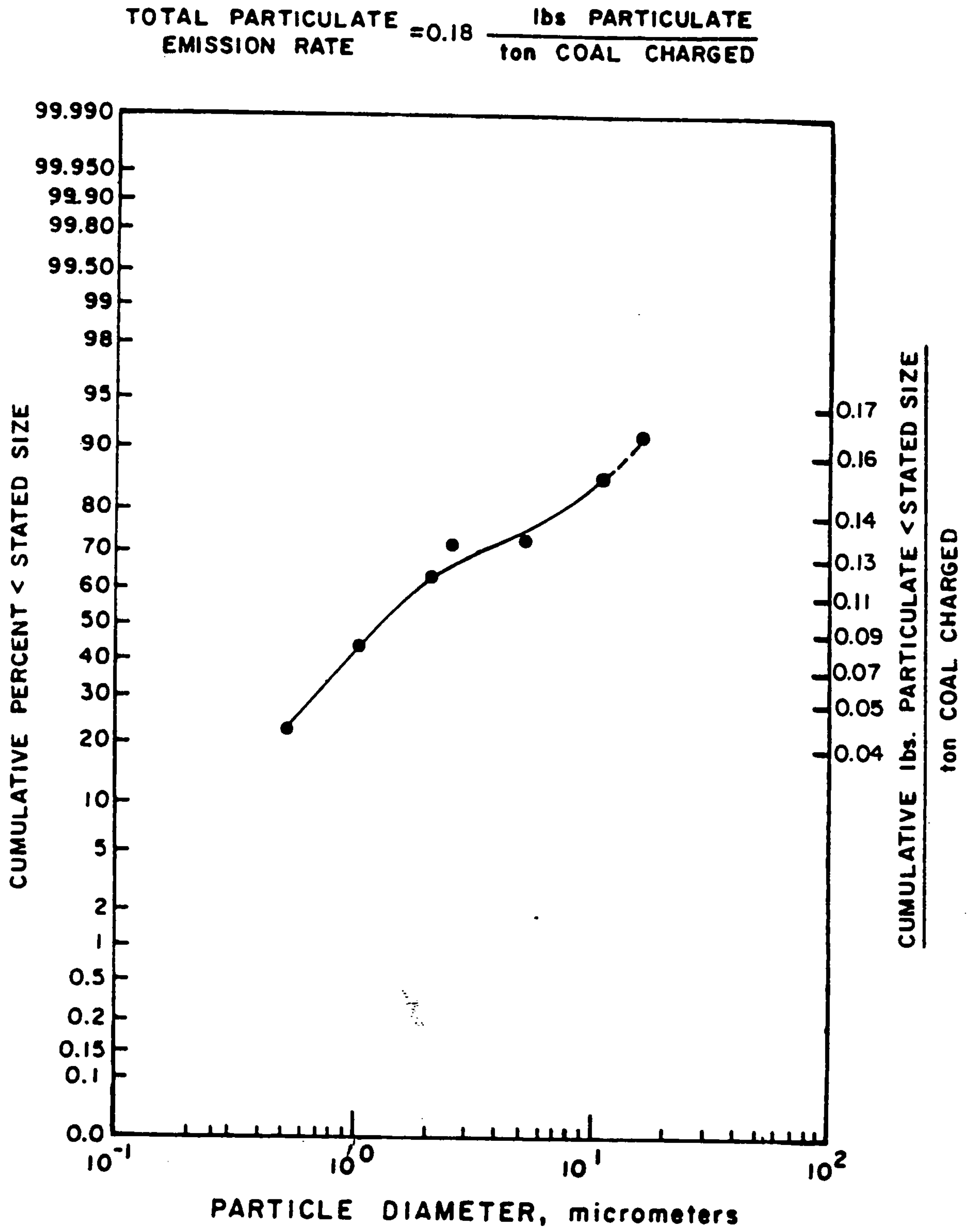
Note: Extrapolated to the 15 μm size, using engineering estimates.

Figure 7.2-5. Coal charging (sequential) average of 2 tests.



Note: Extrapolated to the 15 μm size, using engineering estimates.

Figure 7.2-6. Pushing (uncontrolled) average of 6 sites.



Note: Extrapolated to the 15 μm size, using engineering estimates.

Figure 7.2-7. Pushing (controlled with scrubber) average of 2 sites.

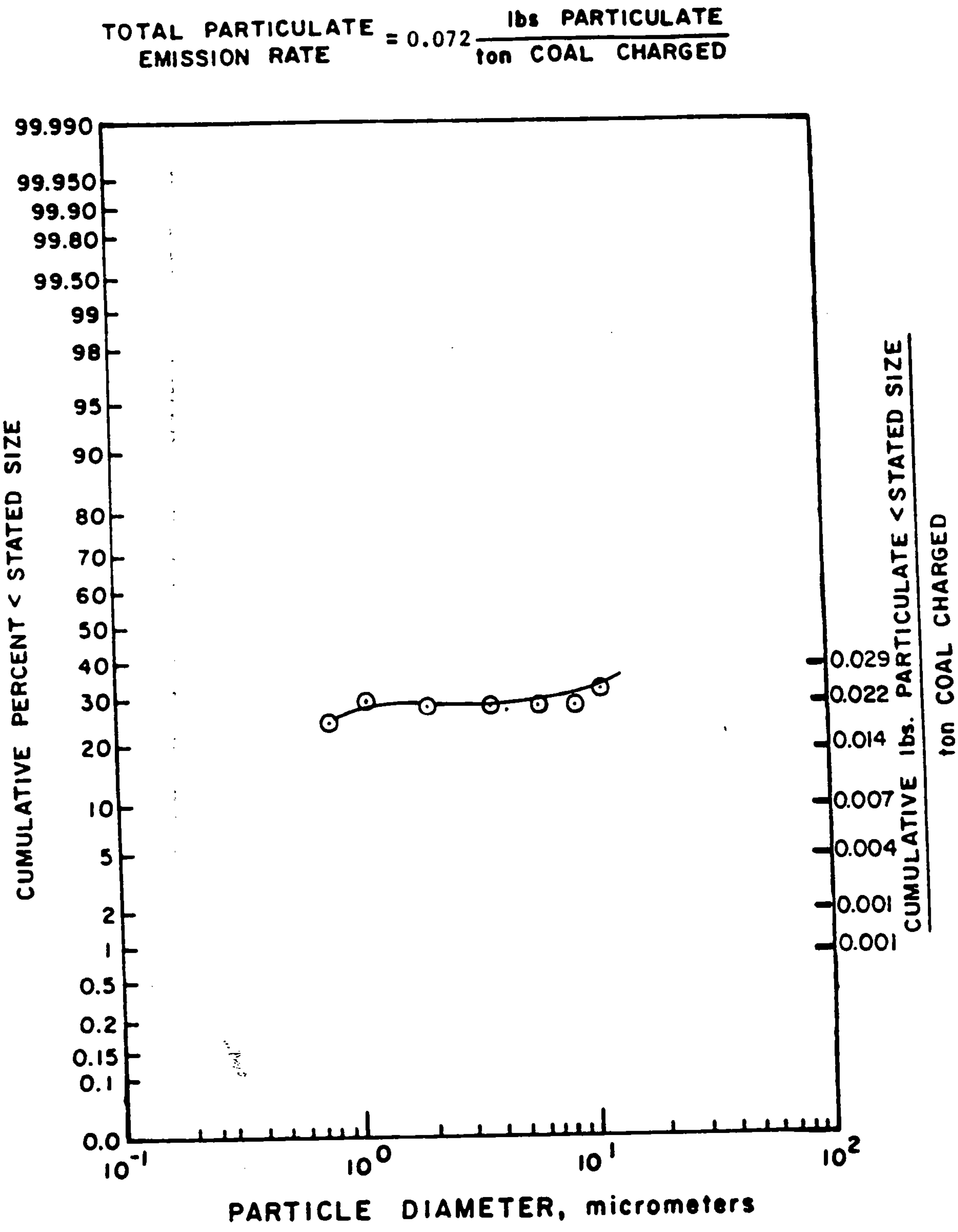


Figure 7.2-8. Mobile scrubber cars.

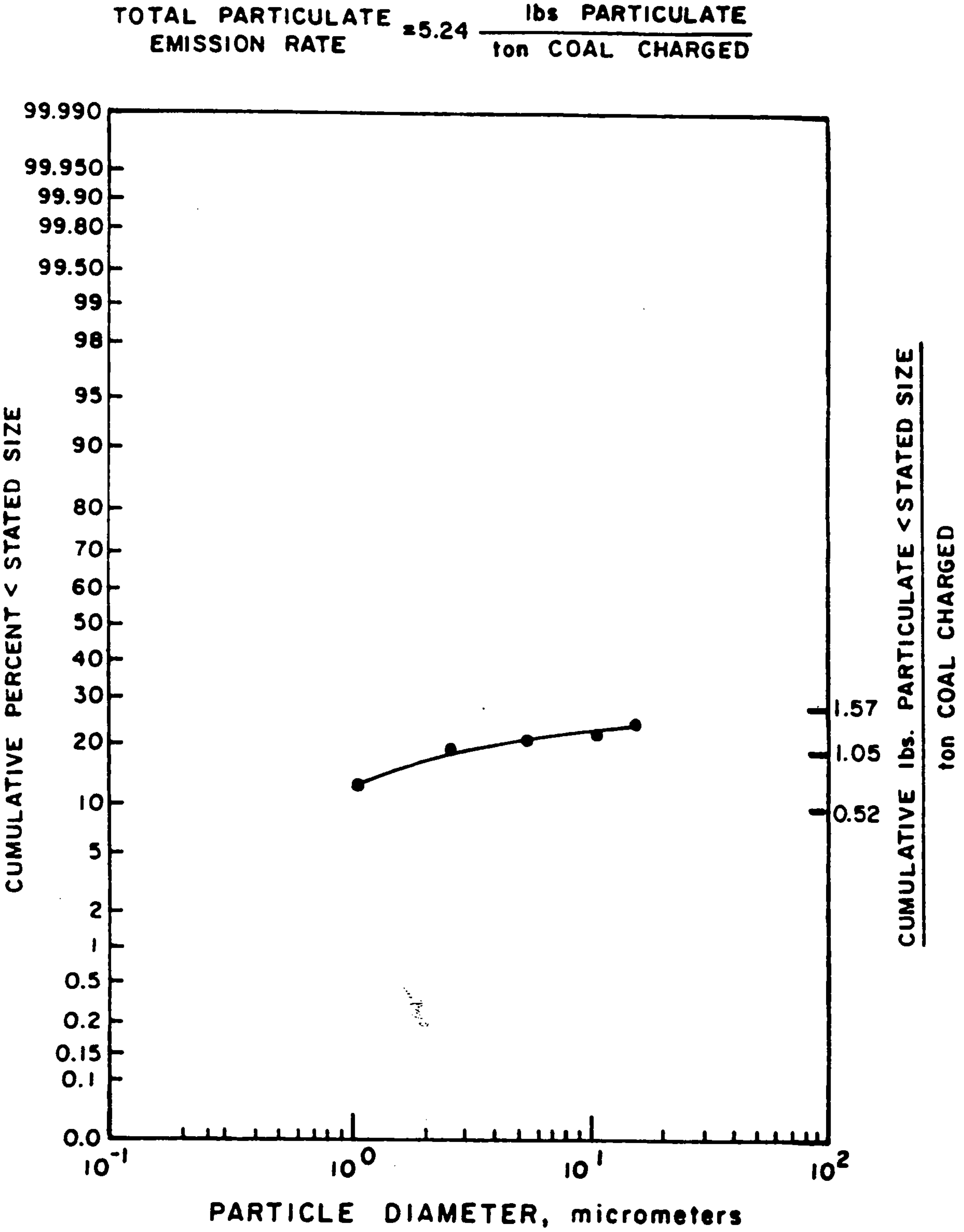


Figure 7.2-9. Quenching (uncontrolled) dirty water >5,000 mg/L TDS.

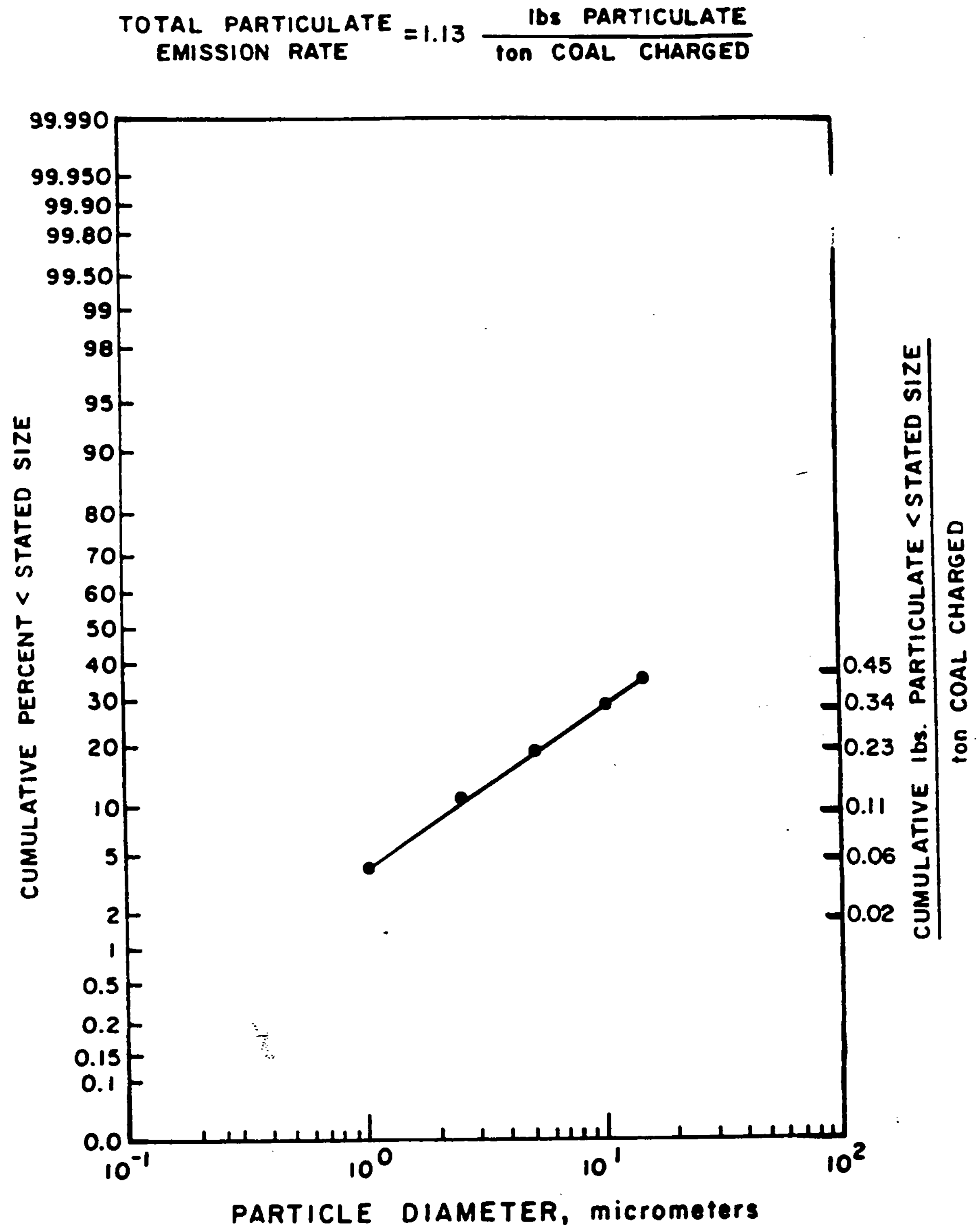


Figure 7.2-10. Quenching (uncontrolled) clean water <1,500 mg/L TDS.

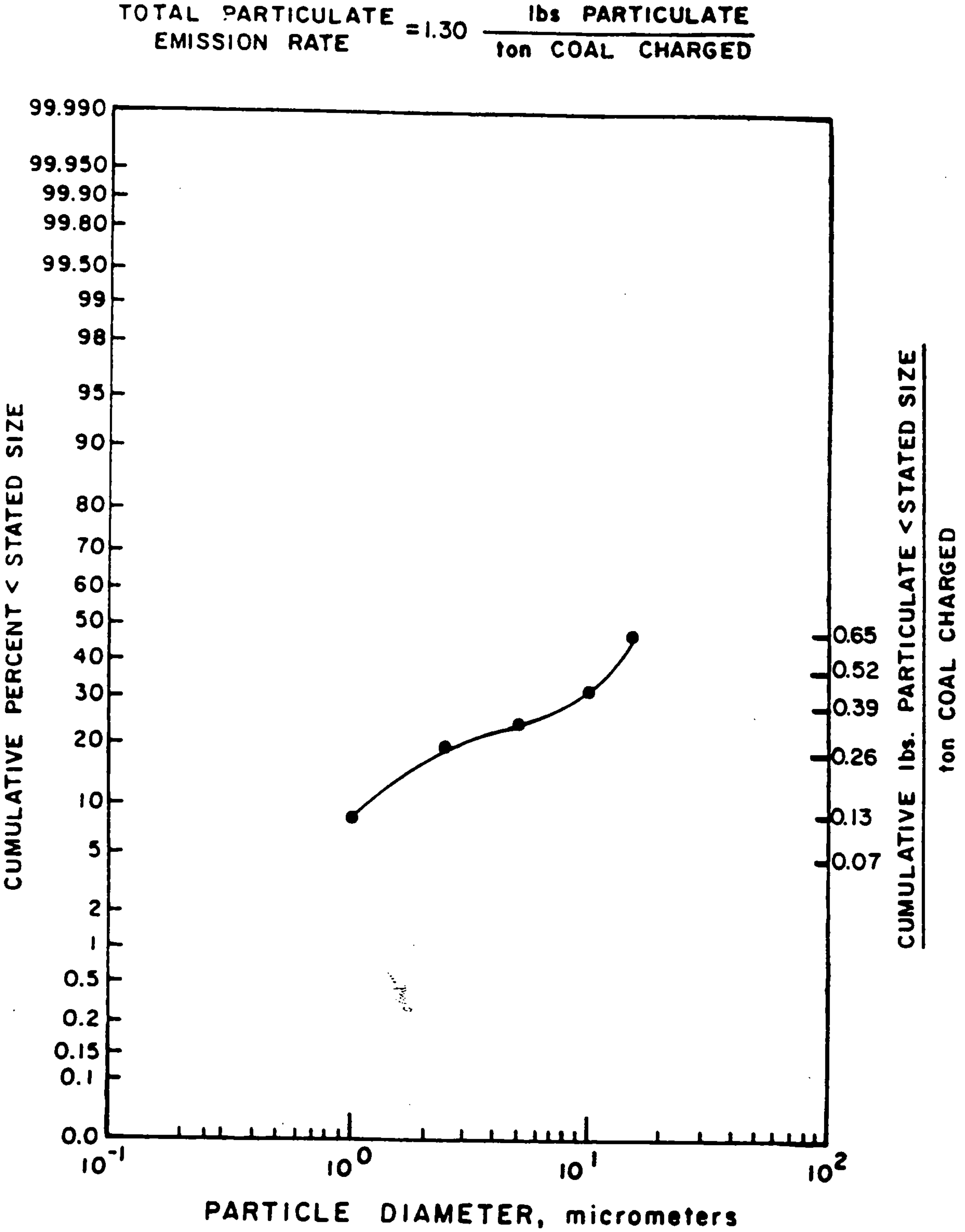


Figure 7.2-11. Quenching (controlled with baffles) dirty water >5,000 mg/L TDS.

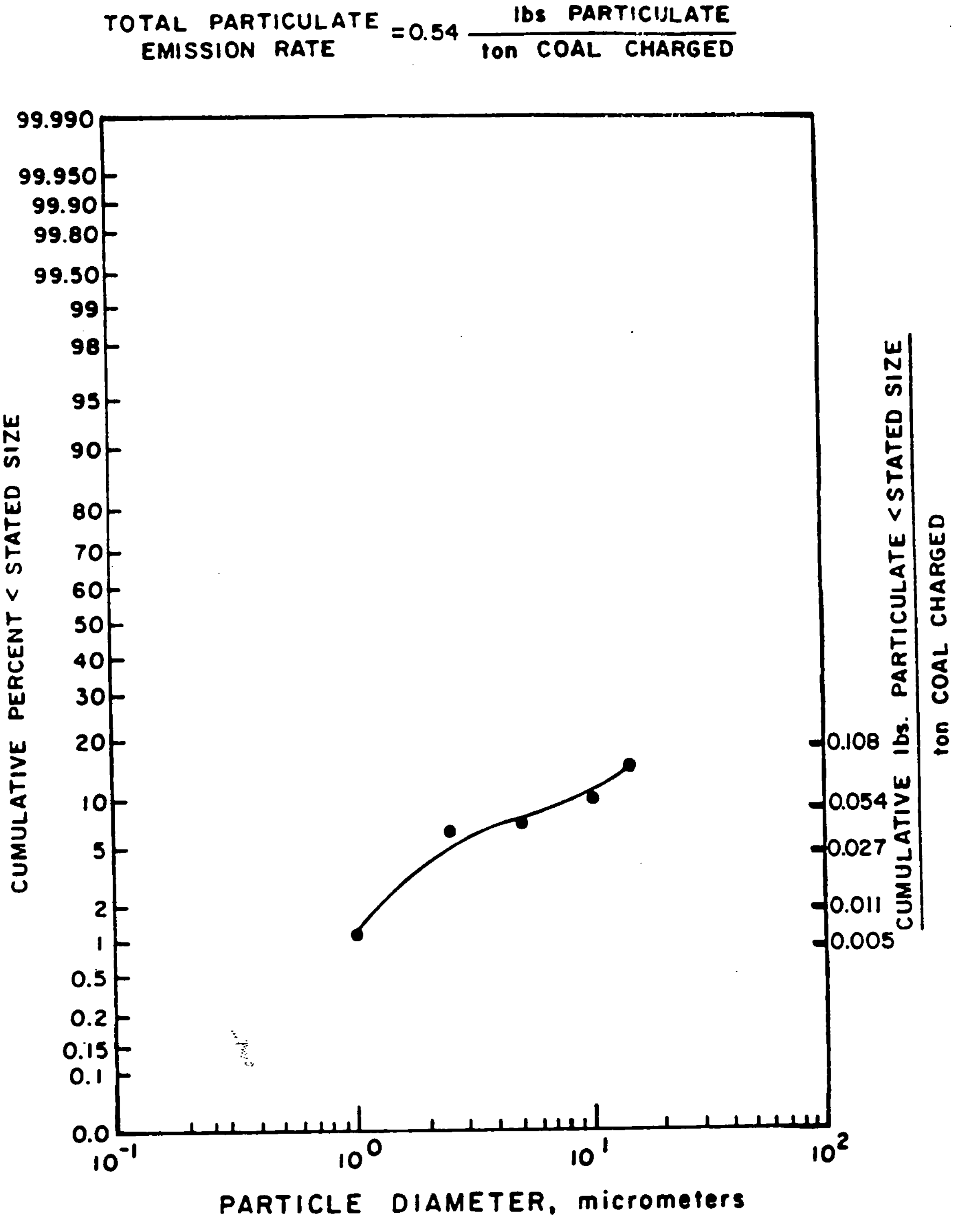
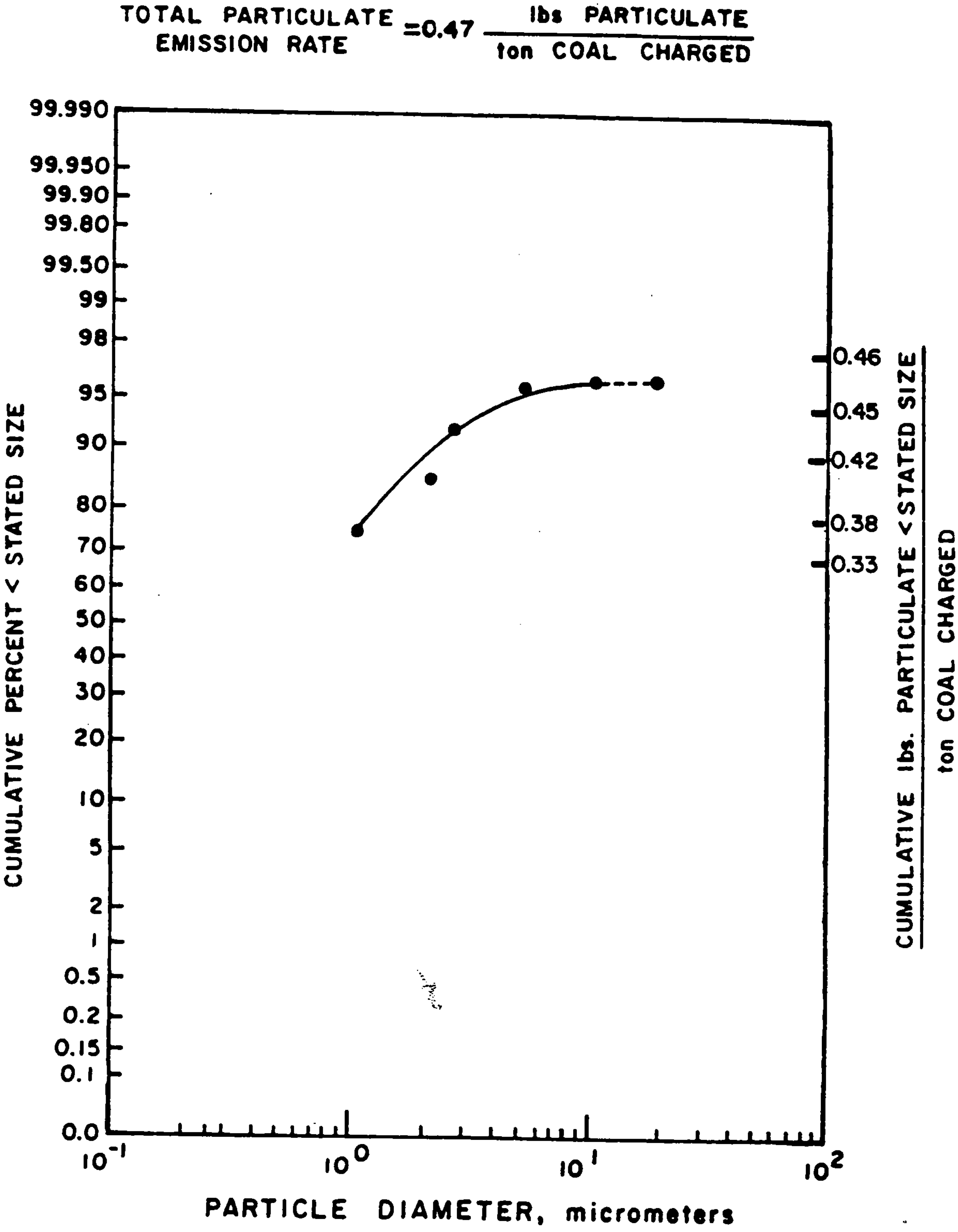


Figure 7.2-12. Quenching (controlled with baffles) clean water <1,500 mg/L TI



Note: Extrapolated to the 15 μm size, using engineering estimates.

Figure 7.2-13. Combustion stacks (uncontrolled) average of 3 sites.

References for Section 7.2

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16. Stack Test Report for Shenango Steel, Inc., Neville Island, PA, Betz Environmental Engineers, Plymouth Meeting, PA, July 1976.

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Supporting Documents for Section 7:

Coke Pushing

scc# 30300303

EPA-340/1-76-012b
May, 1977

Stationary Source
Enforcement Series

Section 7
Reference 1

SOURCE TESTING OF A STATIONARY COKE-SIDE ENCLOSURE

BURNS HARBOR PLANT
BETHLEHEM STEEL CORPORATION
CHESTERTON, INDIANA

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT
OFFICE OF GENERAL ENFORCEMENT
WASHINGTON, D.C. 20460

1.0 INTRODUCTION

The U.S. Environmental Protection Agency commissioned Clayton Environmental Consultants, Inc. (Task 10, Contract No. 68-02-1408) to quantify the nature and extent of particulate and gaseous emissions typically emanating from the coke side of Coke Battery No. 1 at the Burns Harbor plant of Bethlehem Steel Corporation in Chesterton, Indiana. This information was obtained to help provide a basis for:

1. Development of EPA policy on coke-side coke battery emissions and their control;
2. Assessment of the adequacy of State Implementation Plans to achieve Primary Air Quality Standards in areas contiguous to coke plants; and
3. Assessment of the adequacy of control devices being proposed for abatement of such emissions.

Measurement of the normally fugitive coke-side emissions was facilitated at Burns Harbor by the existence of a permanent, 400-foot long, canopy-type hood, commonly termed "coke-side shed," that semi-enclosed the coke side of Battery No. 1.

The following two major components comprised the coke-side emissions released into the shed:

1. Coke-pushing operation emissions resulting from:
   a. Coke pushing — an intermittent source emission lasting about 15 to 45 seconds and occurring on an irregular basis with an average interval between pushes of 13 minutes;
   b. Quench car movement — an intermittent source emission emanating from the coke in the quench car and lasting

about 15 to 45 seconds, from the end of a coke-oven push until the quench car exits from the shed; and

2. Leaking coke-side doors emissions; in the aggregate, the 82 coke-side doors of Battery No. 1 released emissions at a fairly constant rate.

These two emission components — especially the pushing operation — caused the emissions conveyed through the shed exhaust duct to vary widely with respect to particulate concentration, opacity, chemical composition, temperature, and particle size as a function of time.

Since the shed was installed to capture and transport all of the coke-side emissions to a retrofitted control device (not installed at the time of this study), the original testing protocol specified emission tests only in the (induced draft) duct that exhausted the shed. During the tests, however, visibly-significant quantities of particulate emissions were observed leaking from the shed, indicating that the shed's capture and transport efficiency was less than 100 percent. Therefore, the scope of the project was expanded to provide an estimate of the magnitude of these leaks.

Finally, to be fully responsive to the needs and objectives of this test program, a large number of additional, expected(1,2) air contaminants were measured during this study as shown in Table 1.0-1. The rationale and purposes for sampling each of these materials are given in Table 1.0-2.

The field sampling portion of the study was performed on March 3-7, 1975, after some initial range-finding determinations were made on February 24, 1975. The range-finding determinations included exhaust gas flowrate, moisture content, gas composition

Using these data, pushing operations were found, on an average basis, to account for 76 percent of the overall coke-side particulate emissions, while 24 percent were attributable to non-pushing operations.

2.2 Shed Particulate Capture Efficiency

Because significant visible fugitive emissions were observed escaping from the shed during the study, and in order for EPA to evaluate the cost-effectiveness of the shed concept, it was necessary to evaluate the particulate capture efficiency of the shed.

2.2.1 Evaluation of Shed Capture Efficiency

The efficiency of the shed in capturing and exhausting coke-side emissions from pushing (based upon particulate emission measurements) was found to be approximately 85 percent. Thus, on a "continuous" basis, an average of 15 percent of the particulate emissions escaped from the shed.

2.2.2 Possible Causes of Leakage

Several potential causes for the existence of fugitive particulate emissions have been suggested. These include the following:

1. The overall magnitude of the shed's holding volume appeared to be too small relative to the magnitude of the emissions, and the effective exhaust rate of the shed may have been too low;
2. It is possible that "short circuiting" of the outside air to the exhaust duct occurred; and
3. The shape, size, and location of the holding

TABLE 3.2.2-1

COMPARISON OF KEY PROCESS PARAMETERS (BATTERY NO. 1)

Burns Harbor Plant
Bethlehem Steel Corporation
Chesterton, Indiana
March 3-7, 1975

Parameter	Time Period				
	Before Sampling		During Continuous Particulate Sampling	After Sampling	
	All Data	All Typical* Data		All Data	All Typical* Data
Average Net Coking Time (minutes)	1096	1076	1071	1073	1071
Range of Time Between Pushes (minutes)	3-105	3-99	7-39	5-53	5-53
Average Time Between Pushes (minutes)	13	13	12	13	13
Average Wet Coal Feed Rate (tons/charge)	**	**	35.0	34.8	34.8
Average Coke Production Rate (tons/push)	**	**	25.6	25.4	25.4
Average Number of Pushes/hour	4.4	4.5	4.9	4.5	4.5
Average Coal Moisture Content (percent)	6.7	6.6	6.9	7.3	7.3
Average BTU/lb Coal	1162	1160	1160	1166	1166
Average Shed Evacuation Rate (DSCFM)	295,000 (BSC Data)		268,000	—	

* Typical data is all data other than that for which five (4.5 ± 10%) or more consecutive net coking times were outside of the range of 17-1/4 to 18-1/2 hours, i.e., 1035 to 1110 minutes.

** Information requested but not received.

TABLE 5.5

SUMMARY OF AVERAGE EMISSION RATES OF "OTHER" EMISSIONS

Burns Harbor Plant
Bethlehem Steel Corporation
Chesterton, Indiana
March 3-7, 1975

	Average Emission Rate	
	lbs/hr	kgs/hr
Acetylene	0.4-0.5*	0.2*
Ammonia	0.34-0.44	0.16-0.20
Benzene	4.1	1.9
Benzene Homologues (as C_6H_6)	<1.7	<0.77
Benzo(a+e)Pyrene	0.9-1.2	0.4-0.5
Beta-Naphthylamine	<0.35	<0.16
Carbon Monoxide	6.9*	3.2*
Soluble Chloride	4.6	2.1
Chrysene + Triphenylene + 1,2-Benzanthracene (as Chrysene)	0.8-1.3	0.4-0.6
Complex Soluble Cyanide	0.03	0.01
Insoluble Cyanide	0.01	0.004-0.005
Simple Soluble Cyanide	0.03	0.01
Cyclohexane Insolubles	203	92
Cyclohexane Solubles	291	132
Ethylene & Homologues (as C_2H_4)	147*	67*
Fluoranthene	0.7-1.2	0.3-0.6
Total Light Hydrocarbons (as CH_4)	131*	60*
Hydrogen Sulfide	0.93	0.42
Methane & Homologues (as CH_4)	5.8*	2.7*
Nitrate + Nitrite (as NO_3^-)	0.33-0.40	0.15-0.18
Total Insoluble Phenolics (as C_6H_5OH)	<0.06	<0.03
Total Soluble Phenolics (as C_6H_5OH)	0.89	0.40
Pyrene	<0.86	<0.39
Pyridine	<0.15	<0.07
Insoluble Sulfate	<0.13	<0.05
Total Sulfate	15.7	7.2
Total Sulfite	6.2	2.8
Sulfur Dioxide	12.6	5.7
Sulfuric Acid Mist (as SO_3)	2.2	1.0

* Emissions measured during peak periods. These data have been converted to typical operations; i.e., 4.5 pushes/hour. All other samples were taken on a continuous basis.

Supporting Documents for Section 8:
Coke Oven Gas Desulfurization

Environmental Consultants

Section 8
Reference 2

TEST REPORT
FOR
ALLIED CHEMICAL CORPORATION
SEMET-SOLVAY DIVISION
ASHLAND, KENTUCKY 41101
ON THE
SULFIBAN PROCESS

By

YORK RESEARCH CORPORATION
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STAMFORD, CONNECTICUT 06906

YRC No. 1-9868-02

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1.0 INTRODUCTION

1.1 Test Purpose

The purpose of the test program was to determine regulatory compliance of sulfur emissions from the Sulfiban Process. The equivalent sulfur dioxide emission rates are defined as pounds of sulfur dioxide emitted per million cubic feet of coke oven gas (COG) produced to correspond to the units used by the regulatory agencies.

1.2 Test Location, Type of Process

The Sulfiban Process is located at Allied Chemical Corporation's, Semet Solvay Division, Ashland Coke Plant, Ashland, Kentucky. The two test locations were the desulfurized coke oven gas (sweet coke oven gas - SCOG) line exit the Sulfiban Process and the Claus Plant tail gas incinerator stack.

The basic process consists of scrubbing Raw Coke Oven Gas and Springer Gas (SPG) from the Ammonia concentration section with a monoethanolamine (MEA) solution. The desulfurized (or sweet COG) gas is then returned to plant users or sold. Acid gas regenerated from the MEA solution flows to the Claus Plant where elemental sulfur is produced. Tail gas from the Claus Sulfur plant is then incinerated.

1.3 Test Dates

The comprehensive test effort was conducted from January 10, 1979 through January 13, 1979.

1.4 Pollutants Tested

Over the seventy-two hour test period (continuous) York Research Corporation (YRC) obtained eighteen (18) samples from the SCOG location for analysis of H_2S, COS, CS_2 and SO_2. Simultaneously eighteen (18) samples of the tail gas incinerator stack from the Claus plant were analyzed for SO_2 using EPA Method 6.

1.5 Observers

Officials from the Commonwealth of Kentucky, Department for Natural Resources and Environmental Protection, Division of Air Pollution (KDAPC) were on-site to witness the test program. Messrs. John Jayne, Dan Gray, and Gerald H. Slucher, Environmental Specialist, witnessed the sampling and analytical procedures employed by YRC during the January 10, 1979 through January 13, 1979 test period.

4.3.2 Sulfur Dioxide (SO_2)

After sampling and purging according to EPA Method 6, the impingers (excluding the bubbler) and collecting tubes were rinsed with deionized distilled water and transferred to a labeled polyethylene bottle. The contents were transferred to a volumetric flask and diluted to volume with distilled, deionized water. A suitable aliquot was transferred to an erlenmeyer flask containing isopropanol and thorin indicator. The solution was titrated with standardized 0.0100 N barium chloride to a pink endpoint. The analyses were performed in triplicate each time. The total milligrams of SO_2 was then calculated and utilized to determine the concentration of SO_2 on a dry basis corrected to standard conditions.

4.3.3 Molecular Weight of Desulfurized COG

According to EPA Method 3, a gas sample representative over each test was extracted from the source. analysis (by Orsat) of the gas according to EPA Method 3 applies mainly to fossil fuel combustion process, therefore a gas chromatographic profile was performed each testing day. Briefly, a 0.1 cc sample was injected by means of a heated gas sampling valve/loop system into gas chromatographs employing thermal conductivity and flame ionization detectors. Thermal conductivity detection was used to determine percent levels of H_2, O_2, N_2, CO, CH_4 and CO_2 by comparison to known certified gaseous standards. Flame ionization detection was utilized to determine parts per million (ppm) levels of Benzene, Toluene and Xylene isomers. From these analyses, and the moisture determined by EPA Method 4, the SCOG molecular weight was determined.

4.3.4 Sulfur Gas Analysis of Desulfurized Coke Oven Gas (SCOG)

After sampling, the heated grab samples were analyzed for hydrogen sulfide (H_2S), carbonyl sulfide (COS), sulfur dioxide (SO_2) and carbon disulfide (CS_2) using gas chromatography flame photometric detection. The grab sample was pressurized with mercury and injected via a 1.0 cc heated sample loop/gas sampling valve system into the analytical column and detector for separation and quantification. Known standards of H_2S, COS, SO_2 and CS_2 were used for comparative purposes and the concentrations (ppm) were calculated.

TABLE NO. I-5
SULFUR DIOXIDE EMISSION SUMMARY
SCOG AND TAIL GAS INCINERATOR STACK

Note: All units are in pounds of equivalent SO_2 per million cubic feet of coke oven gas produced.

Test No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Location	-	-	-	-	-	-	-	-	SCOG	-	-	-	-	-	-	-	-	-
	(By Gas Chromatography Analysis)																	
H_2S	39.77	7.78	118.90	0.04	0.04	0.04	37.58	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
COS	4.19	5.50	5.59	6.00	6.59	6.66	4.34	5.45	5.22	4.98	7.41	3.77	5.44	4.70	5.41	5.06	5.29	4.84
CS_2	0.83	9.29	8.94	13.60	9.47	5.16	4.56	6.55	11.50	11.68	17.02	3.95	8.58	5.80	11.18	9.79	11.39	8.94
SO_2	1.32	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	ND	ND	ND	ND
Location	TAIL GAS INCINERATOR STACK (By EPA Method 6)																	
lbs/SO_2/MM/COG	30.82	47.89	26.49	35.44	58.83	30.23	46.97	205.9	56.01	49.44	17.90	42.23	12.94	33.13	49.18	24.19	73.41	54.35
Total Sulfur Compounds	86.93	70.55	160.01	55.17	75.02	42.18	56.00	255.57	72.86	66.23	42.46	50.00	27.09	43.76	65.81	39.08	90.13	68.17

Section 8
Reference 3

EVALUATION
OF THE DESULFURIZATION FACILITY
AT THE
CLEVELAND PLANT
OF
REPUBLIC STEEL CORPORATION
CLEVELAND OHIO

BCM PROJECT NO. 00-4178-13
SEPTEMBER, 1981

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1.0 EXECUTIVE SUMMARY

Republic Steel Corporation retained Betz•Converse•Murdoch•Inc. (BCM) to conduct an evaluation of its Cleveland works Sulfabin desulfurization facility. The Sulfabin system was installed by Black, Sivalls & Bryson, Incorporated (BS & B) of Houston, Texas. The evaluation consisted of 14 test runs. The result of these tests, which are summarized in Table 1, indicate thet the highest emission rate was 34 grains H_2S/100 dscf COG.

2.0 SCOPE AND OBJECTIVES

The scope of the project was outlined in BCM Proposal No. 18-8249-06 which is contained in Appendix A. The objective of the program was to sample four locations simultaneously every four hours for a 48-hour sampling period in order to determine emissions as H_2S in grains/100 dscf of coke oven gas (COG). The four locations and their respective sample parameters were:

- Contactor Inlet (sour gas) - H_2S, COS + CS_2
- Contactor Outlet (sweet gas) - H_2S, COS + CS_2
- Tail Gas Stream - H_2S, SO_2
- Incinerator Stack - SO_2

3.0 PROCEDURES

The field sampling program and wet chemistry on-site analyses were performed for a 56-hour sampling period for a total of fourteen (14) complete tests. The testing program began at 0100 hours on September 22, 1981 and was ended at 0500 hours on September 24, 1981.

All stack samples were taken at the lower test location but, due to low flows at this location, flow data was taken at the top platform for better accuracy. Flows at the top platform were taken once a day with pilot traverse checks run at the lower location after each test to insure that stack flows had not changed substantially. Stack flows from the upper test location were used in all calculations.

3.1 Field Work

All test and analytical procedures and field data sheets are contained in Appendix B.

3.2 Calculations

Example calculations and field calculations are contained in Appendix C. Republic Steel and BS & B provided flow calculations for the contactor and tail gas locations.

3.3 Calibration

Field equipment calibrations are contained in Appendix D.

4.0 SUMMARY OF RESULTS

Gaseous concentrations at each sampling location were first analyzed directly as either H_2S, SO_2, or $COS-CS_2$, and then converted to concentrations as H_2S because the regulations are based on grains of H_2S/100 dscf COG. Therefore, the flow differential between each location and the sour gas or COG flow had to be accounted for in the calculations. Table 1 summarizes flows and grain loadings for each sample location.

Fourteen (14) test runs were made between 0100 hours on September 22 and 0500 hours on September 24, 1981. As Table 1 indicates, all test runs achieved a total grain loading in the stack and contactor outlet of less than 35 grains H_2S/100 dscf COG. The contactor outlet emissions ranged from 2 to 20 grains H_2S/100 dscf COG. The total grain loading of stack and contactor outlet ranged from 7 to 34 grains H_2S/100 dscf COG.

TABLE 1
DESULFURIZATION DATA SUMMARY

		CONTACTOR INLET		CONTACTOR OUTLET		TAIL GAS		STACK		OUTLET & STACK
Date	Time	Flow dscfh	H_2S gr./ 100 dscf COG	Flow dscfh	H_2S gr./ 100 dscf COG	Flow dscfh	H_2S gr./ 100 dscf COG	Flow dscfh	H_2S gr./ 100 dscf COG	H_2S gr./ 100 dscf COG
9/22	0100	1700808	142	1700888	6	69621	3	139101	4	10
9/22	0600	1751805	244	1751805	16	69620	4	139101	16	32
9/22	0920	1624198	293	1824198	4	68350	5	139101	2	6
9/22	1305	1755578	---	1755578	3	69646	7	139101	4	7
9/22	1705	1742295	303	1742295	6	72401	7	144054	28	34
9/22	2100	1704232	250	1704232	7	*67012	1	144054	8	15
9/23	0040	1769346	252	1769346	20	*74286	1	144054	9	29
9/23	0500	1806827	275	1806827	6	*74776	1	144054	6	12
9/23	0900	1764760	475	1764760	3	76109	9	144054	15	18
9/23	1330	1584273	382	1584273	5	69274	27	144054	15	20
9/23	1700	1841910	254	1841910	7	77192	11	144054	22	29
9/23	2100	1097944	268	1897944	7	77268	8	144054	17	24
9/24	0100	1803033	267	1803033	2	76969	13	144054	17	19
9/24	0500	1803033	235	1803033	9	75239	9	144054	6	15

* H_2S titrations for tail gas no good

REPUBLIC STEEL - DESULFURIZTION TEST PROCEDURES

1.0 EXECUTIVE SUMMARY

Republic Steel Corporation retained Betz•Converse•Murdoch•Inc. (BCM) to conduct an evaluation of its Sulfabin desulfurization facility at its Cleveland Works. Four locations will be sampled simultaneously every four (4) hours for a forty-eight (48) hour sampling period in order to determine emissions as H_2S in grains/100 dscf and removal efficiencies, where applicable. The four locations and their respective sampling parameters are:

- Contactor Inlet (sour gas) - H_2S, COS + CS_2.
- Contactor Outlet (sweet gas) - H_2S, COS + CS_2.
- Tail Gas Stream - H_2S, SO_2.
- Incinerator Stack - SO_2.

The sampling and analytical methods to be used at each location are as follows:

Contactor Inlet (sour gas) - H_2S, COS and CS_2 Sampling

Sampling Method

A Sampling train with five (5) impingers is used (Figure 1):

First impinger contains 100 milliliters (ml) of 0.1 N, H_2SO_4 and a few drops of methyl orange indicator to collect ammonia present in the gas stream. The first impinger removes ammonia which interferes with the H_2S analysis results.

Second and third impingers contain 150 milliliters (ml) each of $Cd(OH)_2$ for H_2S collection. It should be noted that the $Cd(OH)_2$ used here is approximately eight times as concentrated as recommemded in EPA Method Eleven (11) to accommodate the higher concentrations of H_2S present in the coke oven gas (COG). By increasing the concentration, a larger sample volume can be collected and the sampling period can be extended.

Fourth impinger contains 100 milliliters (ml) of alcoholic potassium hydroxide solution for COS and CS_2 collection, according to the following equations:

$$COS + KOE_t \text{ ---- } KS - CO - OE_t$$
$$CS_2 + KOE_t \text{ ---- } KS - CS - OE_t$$

Fifth impinger contains approximately 200 grams of Silica gel for capturing the moisture.

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Laboratory Analysis

H_2S:

The contents of impingers two and three are transferred to a one (1) liter volumetric flask that is then brought to volume with distilled water. A 50 milliliters (ml) aliquot is placed in a stoppered flask containing an excess of acidified iodine solution (0.1 N iodine and 10% hydrochloric acid). The sample is allowed to sit for thirty (30) minutes until the reaction is completed. Four (4) milliliters (ml) of stabilized starch solution is added and the sample is titrated with 0.1 N sodium thiosulfate to the endpoint, the disappearance of any blue color.

COS and CS_2:

The content of fourth impinger is transferred into a 500 milliliter (ml) Erlenmeyer flask, using 80 milliliters (ml) of distilled water to wash out the absorber. The solution is cooled to less than 5°C. Two to three drops of phenolphthalein are added and the solution is slowly neutralized with glacial acetic acid, using three drops in excess after the disappearance of the red color of the indicator. The xanthates are thus converted to reactive xanthic acids which are readily oxidized by iodine.

The acidic solution is nitrated in the flask with 0.1 N iodine solution, keeping the temperature below 5°C. Three to five milliliters (ml) of soluble starch solution are employed as an indicator and the endpoint is taken upon the first appearance of the blue color.

Equations for Calculations

H_2S:

1. $V_{m_{std}} = (528)\ (V_m)\ (P_{bar})\ /\ (29.92)\ (T_m)$

2. $$C_{H_2S} = \frac{\left[(V_I)\ (N_I) - (V_R)\ (N_R)\right] S - \left[(V_I)\ (N_I) - (V_R)\ (N_R)\right] B\ (26.3)\ (V_S)}{(V_A)\ (V_{m_{std}})}$$

Section 8
Reference 4

COMPLIANCE AND GUARANTEE EVALUATION OF THE DESULFURIZATION FACILITY NEVILLE ISLAND PLANT

SHENANGO INCORPORATED
PITTSBURGH, PENNSYLVANIA

BCM PROJECT NUMBER 00-4810-03

JULY 1980

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BERNARD M. CALLI
REGIONAL MANAGER

1.0 INTRODUCTION

In order to reduce the coke plant sulfur emissions, Shenango Incorporated has installed a desulfurization process.

BCM was retained to determine if the desulfurization unit was meeting manufacture specifications and Allegheny County emission limits.

2.0 SCOPE AND OBJECTIVES

The scope of the project was originally defined in BCM proposal number 18-8206-06, a copy of which appears in Appendix A of this report. In summary, sampling and analysis were performed to determine the following parameters.

a. Hydrogen Sulfide (H_2S) - gr/100 DSCF

b. Sulfur Dioxide (SO_2) - gr/100 DSCF

c. Carbon Disulfide (CS_2) - gr/100 DSCF

d. Carbonyl Sulfide (COS) - gr/100 DSCF

3.0 PROCEDURES

A description of the various procedures utilized during the project is outlined below.

3.1 Field Sampling

Field sampling and wet chemistry analysis was accomplished during June 12 and 13, 1980. BCM personnel involved in the project were:

Paul Turina - Scientist

Douglas Seely - Scientist

Kevin Hylton - Scientist

Daniel Petrovay - Technician

Plant coordination between Shenango and BCM was provided by:

J. R. Zwikl - Director of Environmental Control

The following methods were employed during the sampling program:

a. Gaseous hydrogen sulfide was collected as per Method Eleven of the Federal Register, Volume 36, Number 247, December 23, 1971, appropriately amended.

b. Gaseous sulfur dioxide samples were collected as per Method Six of the Federal Register, Volume 36, Number 247, December 23, 1971, appropriately amended.

c. Gaseous carbonyl sulfide and carbon disulfide were sampled via absorption in alcoholic potassium hydroxide.

All sampling methodologies are fully described in Appendix B, pages B-1 through B-2.

3.2 Equipment Calibration

In accordance with accepted procedures published by the U.S. Environmental Protection Agency, gas chromatograph, volume metering equipment, and temperature measuring equipment supplied by BCM had been calibrated before use in the project. Calibration data are listed in Appendix F, pages F-1 through F-4.

3.3 Analytical Procedures

All samples generated during the sampling program were immediately analyzed in the Shenango Laboratory at Neville Island by BCM personnel. The following is a brief outline of the procedures. Complete methodologies are listed in Appendix C of this report, pages C-1 through C-4.

1. Gaseous hydrogen sulfide was determined by absorption in acidified iodine and back-titrated with sodium thiosulfate.
2. Gaseous sulfur dioxide samples were analyzed by titration with barium chloride.
3. Gaseous carbonyl sulfide and carbon disulfide were analyzed by titration with iodine.

3.4 Calculations

Wet chemistry calculations were performed in the field to provide Shenango with immediate preliminary data. The calculations were checked afterwards to assure accuracy.

Raw data generated from the sampling program was combined with the laboratory results and developed through the equations for each methodology. These equations are listed in Appendix C, pages C-3 through C-4.

4.0 RESULTS

4.1 Wet Chemistry Results

The following Tables I, II, III and IV summarize the wet chemistry results. Results are expressed in terms of Coke Oven Gas.

TABLE I

Hydrogen Sulfide (H_2S)
(gr/100 DSCF)

Date	Run No.	Time	Scrubber Inlet	Scrubber Outlet	Tail Gas
6-12-80	1	0700	431.68	10.44	1.63
	2	0900	456.60	7.08	5.31
	3	1100	427.80	7.37	3.60
	4	1300	445.32	12.92	10.16
	5	1500	434.92	10.54	5.53
	6	1700	455.87	6.52	3.11
6-13-80	7	0700	440.84	8.77	7.42
	8	0900	478.54	19.46	2.38
	9	1100	424.36	12.24	1.43
	10	1300	424.75	13.02	1.94
	11	1500	425.99	7.93	No Sample
	12	1700	438.33	11.03	2.09

TABLE II

Organic Sulfur (COS + CS_2)
(gr/100 DSCF as H_2S)

Date	Run No.	Time	Scrubber Inlet	Scrubber Outlet
6-12-80	1	0700	13.61	6.00
	2	0900	14.23	4.84
	3	1100	14.63	5.27
	4	1300	9.61	6.32
	5	1500	20.93	7.44
	6	1700	15.50	5.15
6-13-80	7	0700	8.01	6.12
	8	0900	9.03	4.57
	9	1100	8.87	5.37
	10	1300	7.67	6.28
	11	1500	7.71	5.10
	12	1700	8.49	6.09

TABLE III

Sulfur Dioxide (SO_2)
(gr/100 DSCF as H_2S)

Date	Run No.	Time	Tail Gas	Stack
6-12-80	1	0700	1.52	21.47
	2	0900	0.07	15.38
	3	1100	0.06	18.34
	4	1300	1.12	18.55
	5	1500	0.41	10.66
	6	1700	0.29	9.86
6-13-80	7	0700	0.31	4.77
	8	0900	3.92	24.90
	9	1100	15.53	35.83
	10	1300	0.51	38.75
	11	1500	No Sample	18.87
	12	1700	0.95	27.19

TABLE IV

Total Emission Concentration
(gr/100 DSCF as H_sS)

Date	Run No.	Time	Scrubber Outlet H_2S	Scrubber Outlet Organic Sulfur	Stack SO_2	Total
6-12-80	1	0700	10.44	6.00	21.47	37.91
	2	0900	7.08	4.84	15.38	27.30
	3	1100	7.37	5.72	18.34	31.43
	4	1300	12.92	6.32	18.55	37.79
	5	1500	10.54	7.44	10.66	28.64
	6	1700	6.52	5.15	9.86	21.53
6-13-80	7	0700	8.77	6.12	4.77	19.66
	8	0900	19.46	4.57	24.90	48.93
	9	1100	12.24	5.37	35.83	53.44
	10	1300	13.02	6.28	38.75	58.05
	11	1500	7.93	5.10	18.87	31.90
	12	1700	11.03	6.09	27.19	44.31

Average Emissions Day 1 (6-12-80)	30.77 gr/100 DSCF
Average Emissions Day 2 (6-13-80)	42.72 gr/100 DSCF