Stack Emissions and Ash Characterization Data from a State of the Art Municipal Waste Resource Recovery Facility

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INTRODUCTION

Montgomery County, Maryland, is located outside of Washington, D.C. In 1987, the County implemented an Integrated Solid Waste Management Program which provided for a Waste-to-Energy municipal solid waste Resource Recovery Facility (RRF) as the County's central disposal facility for municipal waste. On February 12, 1993, the Maryland Department of Environment (MDE) issued a Permit to Construct (PTC) the RRF. Construction of the facility started in March 1993 and was completed in May, 1995. The RRF, which is constructed adjacent to a coal-fired power plant near Dickerson Maryland, consists of three units. Each unit is designed to combust 600 tons of refuse per day and generate approximately 20 megawatts (MW) of electricity.

Northeast Maryland Waste Disposal Authority (NEA) is the legal owner of the facility. Ogden Martin Systems of New Jersey (Ogden) is the full service vendor, who designed, constructed and operates the facility.

Waste is transported to the RRF by rail from the County's Waste transfer station located in Rockville, approximately 20 miles away. The County's residential, commercial and office waste as well as yard waste and recyclables are brought to the Transfer Station daily by trucks. The trucks are checked by County staff for potential hazardous substances. If any hazardous materials are found, the waste is not accepted by the County. The accepted waste is unloaded into the pit at the Transfer Station. The waste in the pit is again inspected for any hazardous substances. If any household hazardous substances are found, they are sent to the County's Household Hazardous Waste Collection Center. The recyclables are sent to the County's Material Recycling Facility (MRF) located adjacent to the Transfer Station. Non-processibles are sent to the Oaks landfill by truck. The non-recyclable and burnable waste is loaded in to specially designed balers that compact the waste in to 30-ton 37-foot logs. These logs are slid into 40-foot long intermodal containers. The containers are sealed with internal air bladders to prevent leakage, and loaded on to specially designed trailers and transported to the railyard approximately 500 feet from the Transfer Station. Although the RRF is designed to burn 1800 tons of waste per day, only 1200 tons of waste currently arrives at the Transfer station. Each rail carriage holds two 30-ton containers. Therefore, twenty carriages are needed to transport the 1200 tons of waste per day from the Transfer Station to the RRF.

When the loaded rail units arrive at the rail yard adjacent to the RRF every morning, the containers are lifted by an overhead MiJack crane and lowered on to specially designed trucks with tipping chases. The trucks take the containers to the RRF tipping floor. The waste is dumped into the 205-foot long, 65-foot wide and 30-foot deep pit by inclining the containers at a 70-degree angle.

After combustion of the waste, the residue is again loaded into the intermodal containers and taken

to the rail yard for transporting back to the County's Transfer Station. The ash-containers are then trucked approximately 10 miles to a landfill for disposal in a monofill.

Only two of the three units of the RRF are generally operating on any given day to combust the approximately 1200 tons of waste currently being shipped to the RRF.

The facility consists of three water wall boiler units, each unit combusting approximately 600 tons of waste per day (TPD) and generating approximately 20 megawatts (MW) of electricity. The facility is equipped with the state of the art Air Pollution Control (APC) System that consists of a reverse air fabric filter baghouse, spray dryer and activated carbon injection system for the control of organics, trace metals, acid gases, and mercury. A selective non-catalytic reactive system (SNCR) is installed for the control of nitrogen oxides (NOx). In addition, direct lime injection system in to the boiler further controls the acid gases, and addition of dolomitic lime to the ash minimizes leaching of metals from the ash when it is deposited in a landfill. Atmospheric discharge is through a 275-foot tri-flue stack (Figure 1). Technical information pertaining to the facility is presented in Tables 1, 2 and 3.

A Service Agreement signed by NEA and Ogden requires Ogden to conduct several engineering and environmental compliance tests to demonstrate that the facility can operate within the prescribed conditions in the Service Agreement before the facility can be accepted by the County and the Authority. The emission guarantees in the Service Agreement are based on stack test results from the vendor's best performing facilities. On May 5, 1995, the Maryland Department of Environment (MDE) issued a temporary Permit to Operate that required the vendor to conduct compliance tests within 180 days of start-up to demonstrate that the facility can operate in compliance with the permits issued by the Agency.

The facility commenced temporary operations on May 9, 1995. Compliance tests were conducted from July 24, 1995 to August 4, 1995. These tests included stack emissions and ash characterization programs. The facility passed all compliance tests that were required by NEA's Service Agreement and MDE's temporary operation permit. On November 8, 1995, the RRF received an Air Permit to Operate and a Waste Disposal Permit from MDE. The Air Permit to Operate is valid until October 31, 2000, and the Waste Disposal Permit is valid until February 9 1998.

MDE's Air Permit to Operate requires that stack emission tests for certain pollutants be conducted quarterly for each combustion train for the first year of operation after initial compliance testing, and annually thereafter. The pollutants to be tested are: particulates, nitrogen oxides, sulfur dioxide, carbon monoxide, hydrogen chloride, sulfuric acid mist, non-methane hydrocarbons, fluorides, mercury, cadmium, beryllium, lead and total dioxins and furans. For certain other pollutants, stack emissions testing are conducted on one combustion train rotated quarterly for the first three years of operation. These pollutants are: chlorophenols, polychlorinated biphenyls, chlorobenzenes,

ammonia, total chromium, chromium $_{\rm VI}$, copper, zinc, antimony, arsenic, barium, cobalt and selenium. MDE's Waste Disposal Permit required ash characterization prior to the startup of commercial operations of the facility. However, the County required quarterly ash testing during the first year of operation.

As required by MDE's air permit, compliance tests were conducted in August 1995 and quarterly tests during the first year of operation in December 1995, February 1996, May 1996 and August 1996. During the second year of operation, quarterly stack testing for one combustion train (Unit 2) was conducted in November 1996.

SAMPLING AND ANALYTICAL METHODS

Stack Air Emissions

As required by MDE's Air Permit to Operate, emissions tests were conducted for each unit in accordance with the protocol approved by MDE. The test methods are listed in Table 4.

Combustion Residue Characterization.

Fly ash from the baghouse is carried via ash conveyors and is combined with residue from the scrubber and bottom ash from the boiler ash dischargers. Dolomitic lime is added to the ash between the scrubber and the baghouse to stabilize the ash to bind the metals. Combined ash samples are collected at a location after the ferrous material has been removed so that the sample represents the ash as it leaves the site. In accordance with the requirements of MDE's Waste Disposal Permit, an ash residue characterization program was conducted within 90 days of startup of the RRF. The program was designed in accordance with USEPA's draft guideline document entitled "Sampling and Analysis of Municipal Refuse Incinerator Ash", "Guidance for Sampling and Analysis of Municipal Waste Combustion Ash for the Toxicity Characteristics", and other supporting documents. The ash sampling methods are listed in Table 9. The ash testing program was repeated quarterly after the initial compliance test. A total of six quarterly tests have been conducted over the last eighteen months.

DISCUSSION OF RESULTS

Stack Emissions

A total of five stack tests were conducted on units 1 and 3, and six tests on unit 2. Of the six tests, five were conducted by Clean Air Engineeribg and one test was conducted by Entropy. The County screened these consultants for their compliance record. The results are reported by Ogden in Environmental Test Reports^{1,2,3,4,5,6}. MDE's permit limits for organics and acid gases are standardized

to 7% O₂ and for particulates and metals to 12% CO₂. EPA's requirements for organics as well as metals are standardized to 7% O₂. Therefore two sets of stack emission test results were reported, one standardized to 7% O₂ and the other to 12% CO₂. However, the difference between the two sets of results is generally less than five percent. These results are summarized in Tables 5 to 8. The emission limits required by MDE's Permits, the NEA's Service Agreement and the USEPA are also listed in these Tables. The results for selected compounds are discussed below.

Organics.

A total of 16 samples of dioxins and furans were collected between August 1995 and November 1996. The overall maximum and minimum concentrations of total dioxins in the flue gas are 7.06 and 0.26 ng/dscm @ 7% O₂ respectively. MDE's Permit limit is 30 ng/dscm @ 7% O₂. The overall maximum and minimum dioxin concentrations expressed as 2-3-7-8TCDD (EPA 89 TEF or ITEF) are 0.004 ng/dscm @ 7% O₂ and 0.0142 ng/dscm @ 7% O₂, compared to the NEA's Service Agreement requirement of 1 ng/dscm @ 7% O₂. The results of total dioxins obtained in the quarterly tests from each of the three units are shown in Figure 2. The results indicate that no specific data point is consistently highest or any test series consistently the highest. This means that the variations from test to test or unit to unit may be nothing more than random noise. Flue gas concentrations of PCBs, PAHs, Chlorophenols and Chlorobenzenes were below laboratory detection limits. These detection limits are shown in Table 4.

Particulates and Trace Metals.

From the data obtained in the six stack tests conducted so far, the range of particulate concentrations in the flue gas is from 0.00016 to 0.0018 gr/dscf @ 12% CO2 compared to MDE's permit limit of 0.01 gr/dscf @ 12% CO2. In all six stack tests, mercury was found above detection limits. The overall maximum and minimum concentrations of mercury in the flue gas are 76.9 and 1.8 microg/dscm @ 7% O2 respectively compared to EPA's requirement of 80 microg/dscm @ 7% O2. The results of mercury flue gas concentrations in the quarterly tests from each of the three units are shown in Figure 3. In three stack tests, cadmium was below laboratory detection limits of 0.06 microg/dscm @ 7% O2. The range of detected concentrations of cadmium in the flue gas is 0.2 to 0.63 microg/dscm @ 7% O2 compared to EPA's requirement of 40 microg/dscm @ 7% O2. In three stack tests, lead was below laboratory detection limits of 0.1 microg/dscm @ 7% O2 compared to EPA's requirement of 490 microg/dscm @ 7% O2 compared to EPA's requirement of 490 microg/dscm @ 7% O2 compared to EPA's requirement of 490 microg/dscm @ 7% O2. The results indicate that there is no seasonal trend in the metals.

Acid Gases and Nitrogen Oxides.

The range of detected 3-hour average concentrations of sulfur dioxide (SO₂) in the flue gas is 0.1 to

15.2 ppmv @ 7% O₂ compared to MDE's permit limit of 30 ppmv @ 7% O₂. The removal efficiencies ranged from a maximum of 99.9% to a minimum of 92.4% compared to MDE's permit requirement of 85% removal efficiency. The range of 1-hour average concentrations of hydrogen chloride (HCl) in the flue gas is 8.0 to 21.8 ppmv @ 7% O₂ compared to MDE's permit limit of 25 ppmv @ 7% O₂. The removal efficiencies ranged from a maximum of 98.1% to a minimum of 95.9% compared to MDE's permit requirement of 95% removal efficiency. The range of 24-hour average concentrations of nitrogen oxides (NO_x) in the flue gas is 151 to 177 ppmv @ 7% O₂ compared to MDE's permit limit of 180 ppmv @ 7% O₂.

Combustion Residue Characterization

A total of six quarterly ash characterizations have been done over the last eighteen months. The results are reported by Ogden in Environmental Test Reports^{7,8,9,10,11,12}. In all six quarterly ash characterization programs conducted so far, volatile/semivolatile organics, herbicides and pesticides were below detection limits. Therefore, only trace metal results are presented in Table 10, and are discussed below.

Trace Metals.

In all six quarterly ash characterization programs, arsenic, selenium and silver were below laboratory detection limits. These detection limits are shown in Table 10. Cadmium was found in all six tests but lead was only detected in three of the six tests while mercury was detected in four of the six tests. Barium and chromium were detected in only one test. The sampling results and regulatory thresholds are presented in Table 8. The range of 90% upper confidence interval concentration of cadmium in the ash was 0.019 to 0.434 mg/liter compared to the regulatory threshold value of 1.0 mg/liter. The range of detected 90% upper confidence interval concentration of lead in the ash was 0.051 to 0.44 mg/liter compared to the regulatory threshold value of 5.0 mg/liter. The range of detected 90% upper confidence interval concentration of mercury in the ash was 0.0006 to 0.0038 mg/liter compared to the regulatory threshold value of 0.2 mg/liter.

SUMMARY AND CONCLUSIONS

This paper summarizes stack emissions and ash characterization data obtained in six quarterly tests conducted over an eighteen month period for the Montgomery County Waste-to-Energy Resource Recovery facility (RRF) located near Dickerson, Maryland. The facility started testing and temporary operations in May 1995. The first stack test was a compliance test conducted in August 1995 to demonstrate to the County, NEA and the Maryland State that the facility can comply with all applicable permit conditions prior to the issuance of an operation permit by the Maryland Department of Environment (MDE). In November 1995, MDE issued the operation permit. Subsequent to this date, five quarterly tests have been conducted. The last quarterly test reported in

this paper was conducted in November 1996. Of all the stack emissions, dioxin and mercury levels in the flue gas are of focal interest both from a regulatory compliance perspective and public perception.

Of the sixteen samples obtained in the six stack tests conducted for the three units, nine samples of total dioxins in the flue gas were less than 1 ng/dscm @ 7% O₂. Four samples were between 1 and 2 ng/dscm @ 7% O₂ and two samples were between 3 and 4 ng/dscm @ 7% O₂. The remaining sample, the maximum reported in this paper is 7.06 ng/dscm @ 7% O₂. A comparison of these values with the data obtained from other facilities that have similar air pollution control equipment, indicate that the dioxin levels recorded in the stack tests of Montgomery County Facility are the lowest values recorded by any other currently operating modern facility in the United States. Activated carbon injection system proved to be effective not only for mercury control, but also for dioxin and trace metal control.

Of the sixteen mercury samples obtained in the six stack tests conducted for the three units, fifteen samples were less than 51 microg/dscm @ 7% O₂. Only one sample (76.9 microg/dscm @ 7% O₂), the maximum reported in this paper came close to the EPA's requirement of 80 microg/dscm @ 7% O₂. Of the fifteen samples which were below 51 microg/dscm @ 7% O₂, eight samples were less than 20 microg/dscm @ 7% O₂ and the remaining seven samples were between 20 and 51 microg/dscm @ 7% O₂. Mercury removal efficiencies exceeded 93% compared to EPA's requirement of 80% removal efficiency.

The results of ash characterization programs indicate that all organics are below detection limits. Of the trace metals, cadmium, lead and mercury are present in detectable quantities. However, the maximum lead concentrations were less than 10% of the regulatory threshold and the maximum mercury concentrations were less than 2% of the regulatory threshold. The maximum concentrations of cadmium were less than 50% of the regulatory threshold. Most recent tests indicated that cadmium is the only metal that is present in detectable quantities.

References:

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TABLE 1. Technical Information for the Montgomery County Waste-to-Energy Resource Recovery Facility

Waste-to-Energy System	Three 600 tons-per-day (TPD) mass-burning waterwall furnaces with Martin reverse-reciprocating grates and ash handling system
Waste Type	Municipal residential, commercial and office waste
Guaranteed Throughput	558,450 tons per year (1530 TPD)
Boiler Design	865 psig/830 deg F superheater outlet conditions
Air Pollution Control Equipment	Dry flue gas scrubbers, direct lime injection system into boilers, reverse air fabric filter baghouses, nitrogen oxide control with Selective Non Catalytic Reactive (SNCR) system and mercury control with activated carbon injection system. Scrubber Inlet Temp: 440 deg F Scrubber Outlet Temp:295 deg F
Gross Energy Generation at Rated Capacity	54 MW
Net Energy Generation at Rated Capacity	48 MW
Customer	Potomac Electric Power Company (PEPCO)
Special Features	Waste is transported by rail in closed containers. Combustion residue, after ferrous materials recovery is also transported by rail in closed containers

Table 2. Reagents used in the Air Pollution Control and Ash Leaching in 1996

	(Average Amount	s in Pounds per Ton of	Refuse Burned)	
Pebble Lime	Hydrated Lime	Dolomitic Lime	Ammonia	Carbon
15.0	3.1	12.8	1.8	1.7

Table 3. Combustion Residue and Ferrous Materials generated in 1996

Percent by ofRefuse I	
Combustion Residue	Ferrous
26.1	3.0

TABLE 4. Stack Emissions Test Methods

Parameter	Test Method	Location
Particulate Matter (PM)	EPA Method 5	Stack
Particulate Matter <10 micr. (PM10)	EPA Method 201A	Stack
Sulfur Dioxide (SO2)	EPA Method 6C	Inlet/Stack
Hydrogen Chloride (HCl)	EPA Method 26	Inlet/Stack
Total Fluorides (HF)	EPA Method 13B	Stack
Carbon Monoxide (CO)	EPA Method 10	Inlet
Sulfuric Acid Mist	EPA Method 8	Stack
Nitrogen Oxides (NOx)	EPA Method 7E	Stack
Mercury (Hg)	EPA Method 101A	Inlet/Stack
Dioxins/Furans (PCDD/PCDF)	EPA Method 23	Stack
Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Chlorophenols, Chlorobenzenes	SW846 - 0010	Stack
Ammonia (NH3)	EPA Method 26	Stack
Carbon Dioxide (CO2)	EPA Method 3A	Inlet/Stack
Oxygen (O2)	EPA Method 3A	Inlet/Stack
Multi Metals: Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Total Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Nickel (Ni), Selenium (Se), Zinc (Zn)	EPA Method 29	Stack
Non-Methane Hydrocarbons (NMHC)	EPA Method 25A	Stack
Hexavalent Chromium (Cr6)	BIF Cr ₆	Stack
Opacity	EPA Method 9	Stack

TABLE 5. Stack Emissions Test Results - Organics

Flue Gas Concentration in nanograms per dry standard cubic meter (ng/dscm @ 7% O ₂)	Unit 1	Unit 2	Unit 3	MDE Operating Permit Standards	EPA's Standards promulgated on 10/31/95	NEA Service Agreement Requirements
Dioxins (Total)	0.29 - 1.41	0.294 - 7.06	0.26 - 3.51	30 (4-hr)	30	None
EPA 89 TEF	0.004	0.012	0.014	None	None	1.0° 0.9°
PCBs	<2661	<4454	<2300			
Total PAHs	<3959	<4575	<6445			13,400
Chlorophenols	<3673	<15,431	<18,069			
Chlorobenzenes	<3670	<6976	<8148			

TABLE 6. Stack Emissions Test Results - Trace Metals

Flue Gas Concentration, microg/dscm @ 12% CO ₂ or 7% O ₂	Unit 1	Unit 2	Unit 3	MDE's Operation Permit Standards @ 12% CO ₂	EPA's Standards promulgated on 10/31/95 @ 7% O ₂	NEA Service Agreement Requirements @ 12% CO ₂
Arsenic (As)	<0.21 - 0.23	0.15 - <0.2	<0.19 - 0.37	None	None	26 ^b
Beryilium (Be)	<0.05 - <0.06	<0.04 - <0.06	<0.04 - <0.06	0.36	None	0.88* 0.82 ^b
Cadmium (Cd)	0.06 - 0.63	0.06 - 0.25	0.04 - 0.12	None	40	64.4 ^b
Chromium (Cr)	<0.16 - 0.83	<0.17 - <0.5	<0.2 - 6.0	None	None	465 ^b
Cr _{VI}	0.11 - <0.32	0.13 - <0.46	0.15 - <0.40	None	None	None
Nickel (Ni)	<0.16	<0.15	0.26			444 ^b
Lead (Pb)	<0.1 - <1.07	<0.2 - <3.3	<0.4 - 13.8		490	2702° 537 _b
Mercury (Hg)	5.0 - 77.0	12.4 - 47.0	1.8 - 51.0		80 85% removal	130 80% Remov ^{ab}

EPA 89 TEF: EPA's 1989 Toxicity Equivalent Factors for dioxins/furans

a: NEA Service Agreement Compliance Test Requirement

b: NEA Service Agreement Annual Average Requirement

^{7%} O2: adjusted to 7% oxygen in dry gas at standard conditions

TABLE 7. Stack Emissions Test Results - Acid Gases, NOx, CO & NH3

Flue Gas Concentration ppmv @ 7% O ₂	Unit 1	Unit 2	Unit 3	MDE's Operation Permit Standards	EPA's Standards promulgated on 10/31/95	NEA Service Agreement Requirements
Sulfur Dioxide (SO ₂)	1.4 - 15.2	0.14 - 7.03	2.1 - 10.2	30	31	30
Removal Efficiency %	95.5 - 98.8	92.4 - 99.9	93.8 - 97.5	85	75	85
Hydrogen Chloride (HCl)	8.0 - 16.7	9.9 - 21.8	8.2 - 19.1	25	31	30 ^a 25 ^b
Removal Efficiency %	97.1 - 98.1	96.1 - 97.5	95.9 - 97.9	95	95	90 ^{ab}
Nitrogen Oxides (NOx)	151 - 168	154 - 168	153 - 177	180 (24h)	200	180 ^{sb}
Carbon Monoxide (CO)	16.8 - 31.2	11.4 - 25.6	18.0 - 31.8	200 (1h) 50 (24h)	100 (4h)	50°
Ammonia (NH ₃)	1.4 - 8.7	<0.11 - 4.7	2.2 - 4.7	None	None	None

TABLE 8. Stack Emissions Test Results - Fluorides, NMHC, H2SO4 Mist, Particulates and PM10

Flue Gas Concentration in grains per dry standard cubic foot (gr/dscf @ 12% CO2)	Unit 1	Unit 2	Unit 3	MDE's Operation Permit Standards	EPA's Standards promulgated on 10/31/95	NEA's Service Agreement
Fluorides	<0.02 - <0.283	<0.02 - <0.207	<0.02 - <0.220	3.1	None	None
Nonmethane Hydrocarbons (NMHC)	0.1 - <1.2	0.1 - <1.2	0.2 - <1.2	4.4 (3h)	None	None
Sulfuric Acid Mist	0.0184 - 2.51	0.0507 - 2.85	0.0484 - 2.75	20 (3h)	None	None
Particulates	0.00016 - 0.0018	0.00024 - 0.0012	0.00024 - 0.00074	0.01	None	0.01
PM10	<0.0007	<0.0007	<0.0007	0.01 (3h)	0.012	0.01 ^{ab}

a: Service Agreement Compliance Test Requirement,

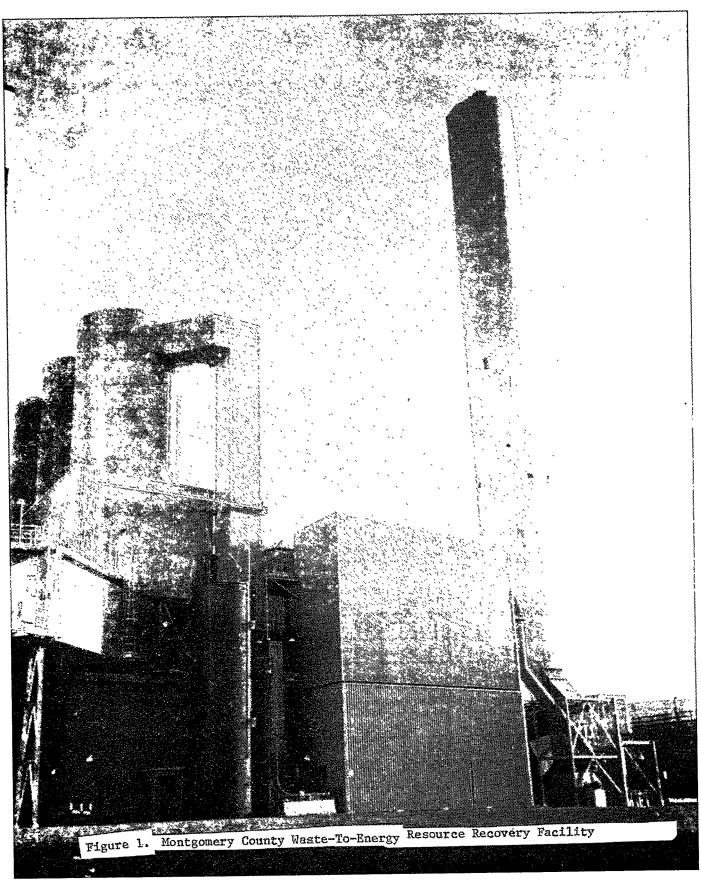
b: Service Agreement Annual Average Requirement

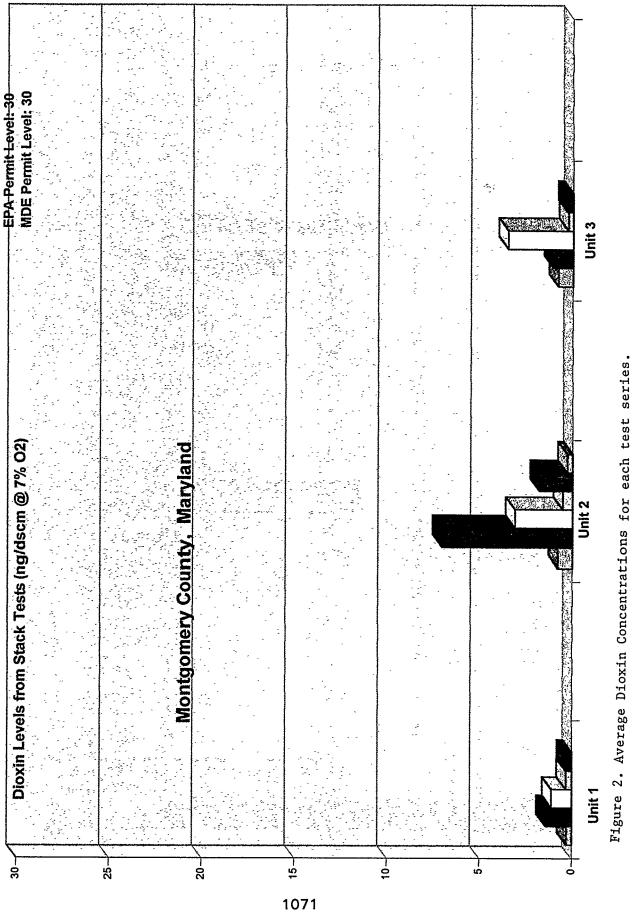
TABLE 9. Ash Testing Methods

Parameter	Analytical Method ^b
TCLP Metals ^a	
Arsenic	3010 and 6010A (ICP)
Barium	3010 and 6010A (ICP)
Cadmium	3010 and 6010A (ICP)
Chromium	3010 and 6010A (ICP)
Lead	3010 and 6010A (ICP)
Mercury	7471 (CVAA)
Selenium	3010 and 6010A (ICP)
Silver	3010 and 6010A (ICP)
Other TCLP Constituents	
Volatiles	8260 (GC/MS)
Semi volatiles	8270 (GC/MS)
Pesticides & Herbicides	8080 and 8150 (GC)
2.0 Moisture	160.3
(a) EPA Method 1311, Toxic Ch (b) ICP: Inductively Coupled Pla GC: Gas Chromatograph	aracterization Leaching Procedure sma Spectroscopy CVAA : Cold Vapor Atomic Absorption GC/MS: Gas Chromatograph and Mass Spectroscopy

Table 10. Ash Characterization Results from Six Quarterly Tests - Metals

Metals	Lowest Detection Limit	90% Upper Conf. Interval* (milligrams per liter)	Regulatory Threshold** (Milligrams per Liter)
Arsenic	0.028	ND	5.0
Barium	0.26	0.47 (1)	100
Cadmium	0.001	0.019 - 0.434 (6)	1.0
Chromium	0.001	0.018 (1)	5.0
Mercury	0.0003	0.0006 - 0.0038 (4)	0.2
Lead	0.003	0.051 - 0.44 (3)	5.0
Selenium	0.03	ND	1.0
Silver	0.019	ND	5.0
*: SW-846 (b)	**: 40 CFR Part 261 ND	: Not Detected (): Number of Test	ts in which the metal is detected





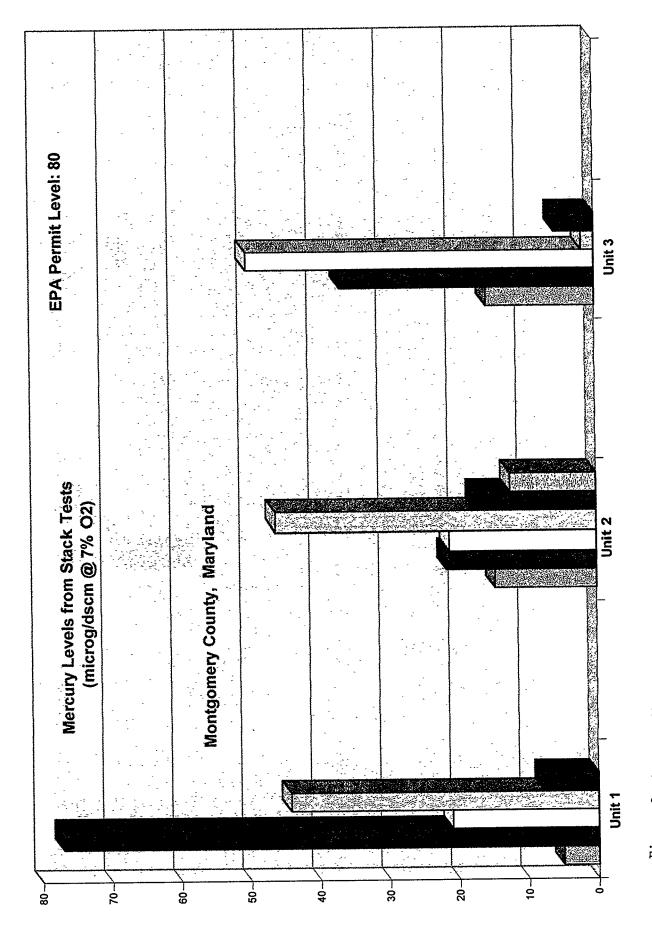


Figure 3. Average Mercury Concentrations for each test series.

Developing Laboratory Test Facilities to Evaluate Carbon Based Materials to Control Mercury Emissions

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ABSTRACT

Changes in carbon technology and new applications for the technology have led to the development of a research and testing facility which can be used to evaluate new carbons and formulations quickly, and at a relatively low cost. Märker Umwelttechnik GmbH has developed a testing facility that simulates the thin layer of adsorbent on a fabric filter through which a simulated flue gas can be passed. A novel development in this flue gas simulation system is the use of mercuric chloride (HgCl₂) instead of elemental mercury (Hg°). Most research into mercury adsorption has been conducted using elemental mercury while in most municipal waste combustors (MWCs), HgCl₂ makes up about 85% of the total mercury emissions.

This paper discusses the development of the test facility and describes how it is used to develop new adsorption products. A comparison of laboratory test results to actual field testing will be presented to illustrate the value of this system.

INTRODUCTION

Regulatory requirements for the control of mercury emissions are becoming ever more stringent and their implementation more speedy. In light of this fact and in response to its need to provide both timely and cost effective service its clients needs, Märker Umwelttechnik GmbH (Märker) set out to develop a testing facility to simulate the thin layer of carbon or Sorbalit® on a fabric filter. This test facility has enhanced Märker's ability to promptly and economically evaluate product formulations by replicating the actual operating conditions in the field. Typical conditions simulated include flue gas concentrations of moisture and HCl, gas temperature and fabric filter materials and layer thickness.

Because of mercury's great volatility and the variety of its binding forms, the process of controlling mercury and its compounds is a difficult one. Due to their high vapor pressures even at low temperatures, mercury and its compounds are present in the flue gas mainly as gas phase materials. Also, depending upon the quantity of chloride in the stack gas, the flue gas components, the combustion process and the operating conditions of the plant, mercury may be present in a variety of forms in the flue gas. In passage through the gas path of a plant, conversion reactions between individual species can and do take place. In addition to its elementary form, mercury is emitted mostly as $HgCl_2$ and other mercury compounds such as mercury sulfide or mercury oxide may also be present albeit to a much smaller degree. Further, mercury bound as $HgCl_2$ predominates in the flue gas of most waste combustion processes such as MWCs, MWIs and HWIs where the $HgCl_2$ component of the mercury emissions can be as much as 85% to 95% of the total. Typically for fossil fuel fired boilers, mercury bound as $HgCl_2$ is 50% or less in the flue gas.

Historically, most researchers have evaluated carbon adsorption on the basis of elemental mercury removal which Märker scientists did not believe would provide representative results of actual field conditions. Since elemental mercury by virtue of its smaller molecular size (~3.6Å) is not as easily adsorbed as HgCl₂ (~5.4Å) or HgSO₄ (~5.3Å), projections of mercury removal requirements for waste incineration processes based on the assumption that elemental mercury needed to be removed would overestimate the carbon requirement. Since open hearth coke (HOK) which is a residual coke material with a reduced surface area than activated carbon costs about DM 590/tonne (\$360/ton) and activated carbon depending on activation

method and impregnation method, costs from DM 1700 - DM 14,000 /tonne (\$1,000 - \$8,500/ton) such an assumption was both expensive and wasteful.

Therefore, Märker concluded that to determine representative total mercury emissions and removal efficiencies both in the field and in the laboratory, it is generally both sufficient and representative to detect only the HgCl₂ component. Further, the increase in regulatory activity with regard to acid gases and heavy metals in general and to mercury emissions specifically, increased client urgency for Märker to develop product formulations which were both effective in controlling emissions and yet economically attractive. In response to this urgent client need for optimized product formulations, and in light of the high costs and time frames associated with field testing, Märker designed a test facility specifically geared to generating mercury laden test gases and simulating field conditions so that various product formulations could be easily, effectively, and inexpensively evaluated.

TEST FACILITY DESCRIPTION

Reference test gases are essential for determining the adsorbtivity of a product formulation. The mercury test gases now available in pressure cylinders are characterized by good stability, but in some cases the indicated concentrations differ considerably from actual values. To ensure high test gas quality, a test gas generator system has been developed for accurately generating mercury in the form of HgCl₂. The principle of gas diffusion, in which a carrier gas (N₂ & O₂ mixture) controlled by a mass-flow regulator is conducted through a temperature-controlled gas cell, is used for this purpose. A test gas with a reference mercury content can be generated in the Märker laboratory test facility at constant conditions (temperature, volumetric flow).

The laboratory test setup allows a known quantity of mercury, as $HgCl_2$ to be passed through the substance to be tested (typically activated carbon or Sorbalit®) within a given time and the residual content of mercury exiting the test material can then analytically determined. This procedure allows conclusions concerning the adsorbtivity of individual substances to be drawn.

The laboratory test setup is designed with the following components:

- ♦ Test Gas Station: This consists of a 40 liter test gas cylinder filled with a mixture of nitrogen and 10% oxygen.
- Gas metering: The metering is performed using a Tylan instrument which operates on the basis of the thermal conductivity of gases.
- ♦ Hg metering: The metering is performed by using a hose pump to aspirate a solution of HgCl₂ from a glass container into a U-tube evaporator thru a Teflon tube immersed in the solution. The glass container is set onto a laboratory scale. The hose pump is set at about 0.2 g/min. The quantity of HgCl₂ is determined with precision by means of the difference in the laboratory scale readings at the beginning and end of a test.

- ♦ U-Tube Evaporator: This serves to evaporate the HgCl₂ solution, mix it with the test gas, and introduce the gas mixture into the reactor. The evaporator consists of a glass U-tube in an electrically heated oven which operates at a temperature of 640°C. Test gas from the test gas station is heated in the first part of the U-tube and mixed with the HgCl₂ solution in the second part using glass wool or glass beads to facilitate evaporation of the HgCl₂ solution and mixing of the gases. All connections are made with standard laboratory connections.
- Adaptor: This is a glass tube wrapped in heating tape and connects the evaporator outlet to the inlet of the reaction tube via ground glass tapered joints.
- Reactor: It consists of heated enclosure which contains a reaction tube containing the substance being tested (e.g. activated carbon or Sorbalit®). The reactor chamber is heated and maintained at the desired temperature. The test substance is contained within the reactor tube as a one (1) cm thick layer imbedded between layers of densely packed quartz wool. Figure 1 is a sketch of the reactor tube which illustrates the main components. Figure 2 is a photo of the reactor tube set into the heated enclosure.
- ♦ End piece: It is attached to the reactor via a ground glass tapered joint and provides an interconnection to the adsorption bottle and is equipped with a thermovell for the insertion of a thermocouple positioned as closely as possible to the test substance layer.
- Adsorption bottle: This contains 40 ml of 10% HNO₃. The gases from the reactor are passed through the HNO₃ solution to precipitate Hg from the test gas stream.
- Gas meter: The precise test gas volume through the system is determined using a calibrated gas meter. Test gas flow is readily determined using a stop watch in conjunction with the meter readings.

Figure 3 is a photo of the test system. The HgCl₂ solution is aspirated by means of a gas pump and fed into the evaporator through a Teflon nozzle and mixed in a layer of glass wool or glass beads. In the evaporator, the HgCl₂ solution is evaporated, introduced and thoroughly mixed into the hot test gas upstream of the reactor. In the reactor, the mercury-laden test gas flows through the layer of the substance by which the mercury is adsorbed. The test gas stream containing the unadsorbed mercury is then directed into the HNO₃ solution in the adsorption bottle to precipitate mercury from the gas stream. The mercury content of this solution is determined and compared with the initial value. The degree of mercury removal by the test substance can then be calculated.

TEST PROCEDURE

Prior to testing, the reaction tube is loaded with a densely packed layer of quartz wool about three (3) cm long. Then 250 mg of the test substance together with two (2) grams of quartz sand are weighed into the reaction tube and are mixed and compressed into a dense structure using quartz wool in the tube.

The system is then prepared for the test as follows:

- The evaporator is turned on and temperature set and maintained at 640°C.
- The end piece is attached to the reaction tube which contains the previously charged test substance and a thermocouple is inserted via a thermowell fitted into the end piece.
- ► The adsorption bottle containing 40 ml of 10% HNO₃ is attached to the end piece.
- Prior to starting up the reactor, the cooling water supply to the reactor infrared oven must be turned on.
- The reactor infrared oven is turned on and the reactor is heated to the desired temperature (typically, 180 300°C). In addition for heating, the test gas feed to the gas cylinder at the main valve must be opened and set to a pressure of 1 bar.
- ► The test gas flow is set at 1.8 l/m using the Tylan instrument.
- When the reactor has reached the desired temperature, the test gas flow is turned off again
- The fixed setting for the HgCl₂ solution is about 0.2 g/m. The actual quantity pumped is precisely determined by scale reading which is set to "zero", the HgCl₂ solution container is set up on the scale, and the Teflon tube is connected to the hose pump.
- At the end of these preparations, the gas meter and the scale readings are noted and the values recorded.
- The Teflon nozzle is then introduced into the evaporator and the test is begun. To start a test, the test gas feed must be opened and the pump turned on.
- ► The duration of a test is ten (10) minutes.
- During the test, the temperature of the adaptor must be kept at 100°C and the reaction temperature constant.
- ► Values are logged every two (2) minutes.
- If condensation appears in the evaporator or in the adaptor, it should be removed with a hot air blower.

When the test is over;

- The pump and test gas are turned off and the Teflon nozzle is removed from the evaporator.
- The scale and the gas meter readings are noted and recorded in the test log.

- The adsorption bottle with the hose is pulled off and the frit and the hose are rinsed. The rinsing are transferred to a 100-ml measuring cylinder and the quantities noted and recorded. The rinsing are then places in a 250-ml sample bottle and labeled.
- Lastly, the reaction tube is removed from the reactor and cleaned.

As stated previously, the amount of HgCl₂ into the reactor is determined by weight difference of the HgCl₂ solution container. However, this value is confirmed for all tests by running a blank sample (i.e. with an empty reactor tube) and measuring the HgCl₂ concentration as though the reactor tube had been charged with reagent.

NEW PRODUCT DEVELOPMENT

The Märker test facility has greatly improved the evaluation and development process for new Sorbalit[®] /Sorbalime[™] products by reducing both testing time and cost factors while markedly improving the reliability of the test results. Previous to Märker's development of the test facility, the most reliable source of data was gathered from the full-scale testing of a new application. Typically (and obviously), the full-scale testing method was not only very expensive by any economic measure in terms of labor and time but in that the information gathered could not be considered either typical or reproducible. The result was that the final product material was ultimately developed by the "fine tuning" of intermediate product formulations.

The development of product formulations involves variations in product carbon content, sulfur content, and product type as well as the use of a whole range of carbon sources (e.g. coconut shell, wood, coal etc.) and suppliers (e.g. Calgon and Norit). In addition, new applications requiring mercury removal continually surface which require an expeditious response by Märker from both marketing and regulatory reasons.

As a result of these pressing needs, the Märker analytical department set out to define and refine a laboratory scale analytical methodology in the new product developmental cycle rather than being required to continually "fine tune" each new product formulation on a full scale until it was optimized.

COMPARISON OF LABORATORY AND FIELD TESTING RESULTS

Table 1 is illustrative of the test results gathered using the test facility. As shown in the table, an initial test is run using a blank tube (containing no substance) to confirm that the system has been properly set up and that the reference values are as indicated.

Test 1 was performed on a test substance consisting of a 250 gram sample of Sorbalit® containing 5% openhearth carbon. An average (over three test runs) of 6.8 micrograms (μ g) of mercury (as HgCl₂) were passed through the test substance using the 90% nitrogen/10% oxygen carrier test gas. The average mercury (as

 $HgCl_2$) exiting the test substance over the three test runs was 0.27 micrograms (μg) yielding a collection efficiency of 96.0% for the test.

Test 2 was performed on a test substance consisting of a 250 gram sample of ground up pellets of hydrated lime mixed with 5% activated carbon, 0.5% sulfur and 5% Bentonite. An average (over three test runs) of 6.8 micrograms (μ g) of mercury (as HgCl₂) were passed through the test substance using the 90% nitrogen / 10% oxygen carrier test gas. The average mercury (as HgCl₂) exiting the test substance over the three test runs was 0.20 micrograms (μ g) yielding an apparent collection efficiency of 97.1% for the test.

Test 3 was performed on a test substance consisting of a 125 gram sample of Sorbalit® containing 7.5% open-hearth carbon and 10% Portland cement. An average (over four test runs) of 4.02 micrograms (μ g) of mercury (as $HgCl_2$) were passed through the test substance using the 90% nitrogen / 10% oxygen carrier test gas. The average mercury (as $HgCl_2$) exiting the test substance over the four test runs was 1.48 micrograms (μ g) yielding an apparent collection efficiency of 63.3% for the test.

The table illustrates the variations in the test substance type and quantity as well as the mercury quantity and concentration which can be inexpensively, expeditiously simulated, and reproduced in the test facility thus enhancing Märker's ability to economically and reliably optimize its products to its clients' needs.

Since the test facility is a recent addition to Märker's technical services department, laboratory testing comparisons to field tests are limited. However, Märker has performed both laboratory and field tests for a MWC in WI Geiselbullach. The results are as follows:

Location	Operating Temperature, °C	Hg Total Quantity In μg/m³	Hg Total Quantity Out μg/m³	% Hg Removal
Test Facility	180	300	45	85.0%
WI Geiselbullach	200	260	13	95.0%

CONCLUSIONS

In response to regulatory requirements for the control of mercury emissions which created urgency on the part of Märker's client industries, Märker designed a testing facility to simulate the thin layer of sorbent on a fabric filter has enhanced its ability to promptly and economically evaluate product formulations in response to both its internal needs and to clients demands. Testing to date using this facility confirms that mercury laden test gases can be synthesized to simulate almost any client application. As a result, we can now quickly and economically evaluate various product formulations geared to the simultaneous control of mercury and other pollutant emissions such as HCl.

Major savings in terms of both cost and time, together with test results which are more reliable and representative are the hallmark for the use of the Märker test facility. The typical cost for performing a test

in the Märker test facility is in the range of \$600 - \$1,000 per sample while the cost of performing mercury tests in the field is in excess of \$10,000.

Test results of various formulations have provided valuable information concerning the effectiveness of using open-hearth carbon, activated carbon, Portland cement, Bentonite and various sulfur compounds. The test facility's ability to test these product formulations and vary the amounts as well as the types of additives has enhanced client confidence in Märker's products to provide them with effective emissions control coupled with quantifiable cost savings.

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Table 1. Sorbalit® Research Test Data

	:			H	HgCl ₂ Solution	ц			
Test No.	Reaction Conditions (Adsorbent Weight, mg)	Adsorbent	Reactor Temp °C	$_{\mu g/g}^{Hg}$	HCl Content mg/g	Solution Metered g	Hg Total Quantity In μ g	Hg Total Quantity Out μ g	% Hg Remova
BI	Empty Tube	None	180	1.7	125	4	8.9	6.7	
B2	Empty Tube	None	180	1.7	125	4	8.9	8.9	
¥	250		180	1.7	125	4	8.9	0.49	92.8%
118	250	Sorbalit® with	180	1.7	125	4	8.9	0.19	97.2%
10	250	5% HOK 95% Ca(OH),	180	1.7	125	4	8.9	0.13	98.1%
Av	Average Test 1		180	1.7	125	4	8.9	0.27	%0.96
2A	250	Dravo nellate:	180	1.7	125	4	8.9	0.32	95.3%
2B	250	5% Carbon	180	1.7	125	4	8.9	0.14	%6'.26
2C	250	0.5% Sulfur 5% Bentonite	180	1.7	125	4	8.9	0.13	98.1%
Av	Average Test 2	89.5% Ca(OH) ₂	180	1.7	125	4	6.8	0.20	97.1%
3A	125		180	2.1	125	2.002	4.20	1.70	29.6%
3B	128	Sorbalit® nellets:	180	2.1	125	1.656	3.48	1.30	62.6%
3C	124	7.5% HOK	180	2.1	125	2.001	4.20	1.50	64.3%
3D	125	10% Fortland 82.5% Ca(OH) ₂	180	2.1	125	2.001	4.20	1.40	%2.99
Av	Average Test 3		180	2.1	125	1.915	4.02	1.48	63.3%

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Table 1. Sorbalit® Research Test Data

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		Reaction			Ħ	HgCl ₂ Solution	Œ.			
•	Test No.	Conditions (Adsorbent Weight, mg)	Adsorbent	Reactor Temp °C	Hg Content $\mu g/g$	HCl Content mg/g	Solution Metered g	Hg Total Quantity In μ g	Hg Total Quantity Out μ g	% Hg Removal
	B1	Empty Tube	None	180	1.7	125	4	6.8	6.7	
•	B2	Empty Tube	None	180	1.7	125	4	8.9	8.9	
	14	250		180	1.7	125	4	6.8	0.49	92.8%
	118	250	Sorbalit® with 5% HOK	180	1.7	125	4	8.9	0.19	97.2%
	1C	250	95% Ca(OH) ₂	180	1.7	125	4	8.9	0.13	98.1%
•	Ave	Average Test 1		180	1.7	125	4	8.9	0.27	%0.96
1083	2 A	250	Dravo pellets:	180	1.7	125	4	6.8	0.32	95.3%
3	2B	250	5% Carbon 0.5% Sulfur	180	1.7	125	4	8.9	0.14	94.9%
	3C	250	5% Bentonite	180	1.7	125	4	8.9	0.13	98.1%
,	Ave	Average Test 2	89.5% Ca(OH) ₂	180	1.7	125	4	8.9	0.20	97.1%
	3A	125		180	2.1	125	2.002	4.20	1.70	29.6%
	3B	128	Sorbalit [®] pellets:	180	2.1	125	1.656	3.48	1.30	62.6%
	3C	124	7.5% HOK 10% Portland	180	2.1	125	2.001	4.20	1.50	64.3%
	3D	125	82.5% Ca(OH) ₂	180	2.1	125	2.001	4.20	1.40	%1.99
II	Ave	Average Test 3		180	2.1	125	1.915	4.02	1.48	63.3%

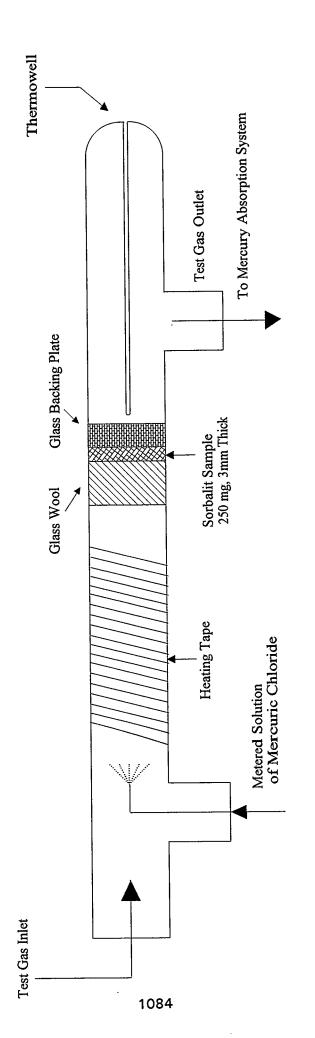


Figure 1. Sketch of Märker's reaction tube assembly.

Figure 2. Reactor tube and oven

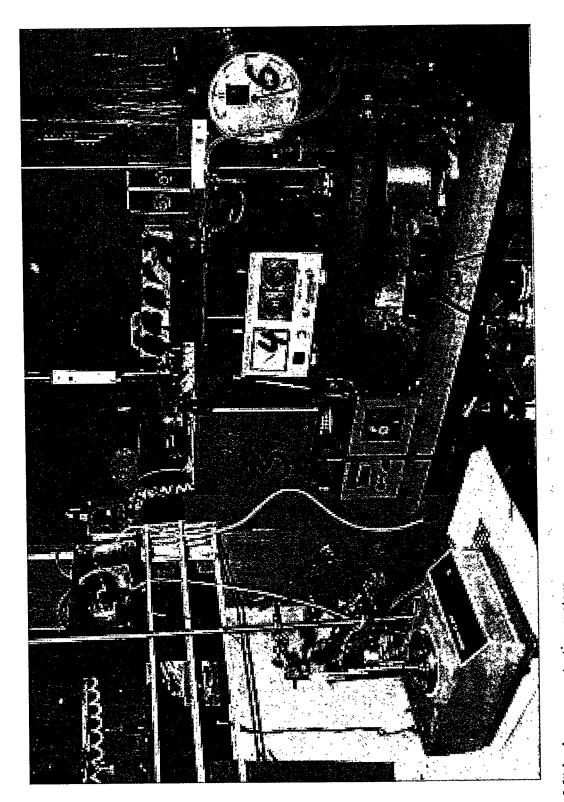


Figure 3. Märker's mercury testing system

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