PROCEEDINGS OF

The 20th International Technical Conference on

COAL UTILIZATION & FUEL SYSTEMS

THE YEAR OF COMPLIANCE

March 20-23, 1995
Sheraton Sand Key
Clearwater, Florida, U.S.A.

Endorsing Organizations

- American Public Power Association
- American Society of Mechanical Engineers
  - *Fuels & Combustion Technologies Division*
- CANMET Natural Resources Canada
- Center for Coal Utilization In Japan
- Edison Electric Institute
- Illinois Department of Natural Resources
  - *Office of Coal Development & Marketing*
- International Energy Agency
  - *Coal Liquid Mixtures Group*
  - *Coal Research*
- National Mining Association
- National Rural Electric Cooperative Association
- Ohio Coal Development Office
- U. S. Department of Energy

MASTER

Presented by
Coal & Slurry Technology Association
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DISCLAIMER

WELCOME

On behalf of the Coal & Slurry Technology Association and the U.S. Department of Energy's Pittsburgh Energy Technology Center, I am pleased to welcome you to the 20th International Technical Conference on Coal Utilization & Fuel Systems.

This is a very special year in the history of our international technical conferences—this is our 20th Anniversary. Clearly, there has been a major evolution in the nature and focus of these conferences. We began in 1976 as a strictly technical conference on slurry transportation. The conference was held in Columbus, Ohio, February 3-4, 1976. Looking at that location and that date, I'd say we've greatly improved the conference just by meeting in Clearwater, Florida. Seriously, though, that first conference had just three sessions. The first was "Slurry System Operating Experience and Performance"; the second was "Slurry System Engineering Design Considerations"; and the third session was "Slurry System Planning". It's reassuring to know that while this conference is quite different in content from that first conference, those are still familiar topics that will be covered this year as well. But beyond those still applicable topics, this conference has evolved, with the assistance of our supportive partners at the Pittsburgh Energy Technology Center, to a conference covering all aspects of innovative coal utilization technologies in the United States and worldwide.

The theme of this year's conference is "1995: The Year of Compliance with the Clean Air Act Amendments". Our first panel, which will discuss this topic, has a number of excellent speakers including James McAvoy, Executive Director of the National Coal Council. Other panels include "Privatization & Deregulation of the Electric Utility Industry Worldwide", and "Coal Fines Utilization: Federal Regulation, Recovery, Utilization and Economic Analysis". Recent studies have shown that by preparing, delivering and burning this clean fuel as CWS, the cost of producing electricity can be lower than the current cost based upon using dry, solid coal. Based upon this consideration, the potential CWS market in the U.S. can be 15 to 20 million tons per year (dry basis).

At this year's conference, we are pleased to have two special reports by two of the Association's most supportive members. The first report, about the proposed 500-mile coal pipeline in China, is titled, "Proposed Shanxi to Shandong Coal Slurry Pipeline". It will be given by our chairman, Hank Brolick, of Williams Technologies Inc. The second special report is titled, "A Review of

Recent Slurry Systems Worldwide", and will be presented by longtime CSTA member Tedd Dowd of Pipeline Systems Incorporated.

We are truly honored to have Girard F. Anderson, President of Tampa Electric Company, to give this year's Keynote Address. Mr. Anderson is a much sought after speaker these days and we feel very fortunate that he agreed to share his thoughts with us today. We hope that by having the conference in Clearwater, basically in Mr. Anderson's backyard, we at least simplified his busy travel schedule.

We are pleased to welcome the Endorsing Organizations who have lent their support to the '95 conference. They are: **American Public Power Association; American Society of Mechanical Engineers -- Fuels & Combustion Technologies Division; CANMET Natural Resources CANADA; Center for Coal Utilization, Japan; Edison Electric Institute; Illinois Department of Natural Resources, Office of Coal Development & Marketing; International Energy Agency -- Coal Liquid Mixtures Group and Coal Research Group; National Mining Association (formerly the National Coal Association); National Rural Electric Cooperative Association; Ohio Coal Development Office; and the U.S. Department of Energy.** We thank all of these groups for associating their good names with our conference.

On a sad note, I would be remiss to not mention that this year's conference is dedicated to the memory of William Peters, Pittsburgh Energy Technology Center; and Todd Johnson, Senior Marketing Specialist, Babcock & Wilcox. As many of you know, both these gentlemen were killed in the crash of USAir Flight 427 outside Pittsburgh on September 8, 1994. While we mourn for all those who lost their lives on that flight, many of whom were colleagues of ours from PETC and from industry, Bill and Todd were longtime participants at our technical conferences and will be especially missed and remembered by all of us.

Each year, we strive to improve the conference and be increasingly responsive to the needs of our attendees. We sincerely hope that our technical conference is beneficial in helping you meet the goals and challenges in the year ahead. If you have any comments or suggestions on how we may better serve you, please do not hesitate to raise those issues with us.

Stuart D. Serkin
Executive Director

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APPENDIX (Papers Received after Pagination)

RESULTS FROM SAMPLING FULL-SCALE COAL COMBUSTION SYSTEMS FOR AIR TOXIC EMISSIONS

James D. Wesnor
ABB Environmental Systems
Birmingham, AL

Presented at:
20th International Technical Conference on Coal Utilization & Fuel Systems
Clearwater, FL
March 20-23, 1995

ABSTRACT

Since passage of the Clean Air Act, ABB has been actively developing a knowledge base on the Title III hazardous air pollutants, more commonly called air toxics. In addition to design experience and database acquired in Europe, ABB has conducted source sampling and analysis at commercial installations for hazardous air pollutants to determine the emission rates and removal performance of various types of equipment. Several different plants hosted these activities, allowing for variation in fuel type and composition, boiler configuration, and air pollution control equipment. This paper discusses the results of these investigations.

FULL-SCALE SAMPLING

In the past year, sampled several full-scale facilities in the United States have been sampled by ABB for hazardous air pollutant emissions. The method employed for these field campaigns were similar to those of the EPRI PISCES and USDOE/USEPA programs. In general, the gas streams only were sampled at these facilities, with sampling occurring at the boiler or combustion furnace outlet, air pollution control system inlet (if different from the boiler outlet), any air pollution control system intermediate points if possible, and the stack. Identical test methods and quality control/quality analysis procedures were followed.

General descriptions of the plants discussed in this paper are as follows:

Coal-A:	A utility boiler burning a midwestern bituminous coal. Pollution control systems include an electrostatic precipitator and limestone wet flue gas desulfurization system. Air pollution control equipment designed to and operating at NSPS standards[1]. Sampling points were the coal feed, boiler outlet/ESP inlet, ESP outlet/FGD inlet, and FGD outlet/Stack.
Coal-B:	A new utility boiler burning a bituminous coal. Pollution control systems include a lime-reagent spray dry absorber and fabric filter. Air pollution control equipment designed to and operating at NSPS standards. Sampling points were the boiler outlet/FGD inlet, FF outlet/Stack.
Coal-C:	A utility-scale boiler burning bituminous coals. Pollution control consisted of low NOx burners (ABB's TFS 2000 firing system) and an upgraded electrostatic precipitator. Criteria pollutant emissions met NSPS standards. Sampling points were the boiler outlet/ESP inlet and ESP outlet/Stack.

Although several other plants have been sampled, the data cannot be presented due to confidentiality arrangements, but trends noticed from the data are similar to those expressed in this paper. In addition, ABB has sampled several MSW-fired facilities. The data from this work has been presented and discussed in previous papers.[2]

An independent, qualified stationary source subcontractor conducted the sampling and analysis. The sampling and analysis were done according to the following methods:

Determination of Gas Velocity	EPA Method 1[3]
Determination of Volumetric Flow Rate	EPA Method 2

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[1] NSPS standards denote New Source Performance Standards, which are SO_2 emissions not to exceed 0.6 lb/mmBtu and particulate emissions not to exceed 0.03 lb/mmBtu.

[2] Wesnor, J.D., **Analytical Results From Sampling Full-Scale Combustion Systems For Air Toxic Emissions**, ICAC Forum 94, Nov. 1994.

[3] EPA test methods may be found in the **Code of Federal Regulations, Title 40, Part 60, Appendix A**, published by the Office of the Federal Register, National Archives and Records Administration.

Determination of Gas Composition	EPA Method 3
Calculation of Gas Moisture Content	EPA Method 4
PM10 Emissions	EPA Method 201A
Specific gaseous hydrocarbon emissions	EPA Method 18
Dioxins/Furans	EPA Method 23
Volatile organic emissions	EPA Method 25A
Volatile metal emissions	U.S. SW846-0030
Semi-volatile metal emissions	U.S. SW846-0010
Metal emissions	EPA Draft Method 29

Method 29 samples were analyzed for the following metals: total chromium, cadmium, arsenic, nickel, manganese, beryllium, copper, zinc, lead, selenium, phosphorous, thallium, silver, antimony, barium, and mercury. Title III currently lists only antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium as hazardous air pollutants.

Results are presented as emission factors, with units of pound of pollutant emitted per trillion (10^{12}) Btu coal fired. Results from the field testing are presented in the following tables. Entries noted with "(max)" indicate that the pollutant was not detected and that calculations use the detection limit value. Removal efficiencies noted "(min)" indicate that the actual removal efficiency exceeds the value given, which is calculated using the detection limit value.

TRACE METAL EMISSIONS

The majority of trace metals, at normal air heater outlet temperatures (330-375°F, 165-190°C), are associated with the particulate fraction and either remain in the flyash particle, condense onto the particle surface or exist as a submicron fume. Notable exceptions to this rule would be mercury, selenium, arsenic, which exist primarily as vapors, and to lesser extents, chromium and lead, of which a significant percentage can exist in the vapor phase. Therefore, the efficiency of the particulate control system will determine the collection efficiency of these "particulate-phase" metals, as shown in Table 1, Table 5, and Table 7.

As evidenced by Coal-A results (Table 1), unless the wet desulfurization system achieves a significant degree of additional particulate removal or the wet desulfurization system inlet particulate loading is uncharacteristically high, additional particulate-phase trace metal control will be variable and negligible.

In some cases, gas-side data indicate possible mercury control in electrostatic precipitators. This has been reported in several early studies, with mercury removal as high as 66 %. Although this is more common in older data, the recently released USEPA/USDOE data was consistent with this trend. For cases with significant positive removal efficiencies, closure of the mercury material balance could not be achieved, thus making it doubtful that any significant, reliable control of mercury vapor phase emissions could be achieved by particulate control alone at typical cold-side temperatures (275-350°F). The mercury "removal" reported is more of an indication of the uncontrolled variability of Method 29 sampling than an indication of actual removal.

Primary control of vapor-phase trace metals, primarily mercury, selenium, and arsenic, will occur in the desulfurization system. Vapor-phase metals will be controlled by condensation and subsequent absorption into the wet desulfurization system scrubbing liquor or adsorption onto the captured particulate in a dry desulfurization system. At air heater outlet temperatures, selenium and arsenic are fractionally partitioned between the particulate and vapor phases[4] while mercury exists entirely as a vapor. In most instances, the trace metal concentration of the vapor-phase metals will not be sufficiently high to promote complete condensation onto the particulate surface.

For a wet desulfurization system to effectively capture the vapor-phase metals, the compound must be in a water-soluble form. If the metal compound is partitioned between a water-soluble and water-insoluble form, the wet desulfurization system will provide efficient control (above 90%) of the water-soluble form and little control of the water-insoluble form. This is best demonstrated with mercury removal efficiencies.

Wet desulfurization system mercury emissions are addressed in Table 2. In most cases, mercury removal efficiencies for the particulate control system varied greatly, often swinging to large negative values. Mercury removal efficiencies by wet desulfurization systems vary widely between facilities. Data on partitioning between ionic (dominantly water-soluble $HgCl_2$) and elemental (water-insoluble Hg) forms has not available until recently.[5] Recent data support the above assertion that nearly all of the water-soluble form is removed by the wet desulfurization system while all of the insoluble form passes through the unit and is emitted from the stack. For mercury, once absorbed, the water-soluble ionic form can be reduced to the elemental form by the sulfite ions in the scrubber liquor.[6] Once the solubility limit is reached, the reduced mercury will desorb from the scrubber liquor and be emitted from the stack. In this case, there will be a net increase in elemental mercury flow through the desulfurization system, a phenomenon that has been noted in laboratory and field data.

In most cases, trace elemental addition through the desulfurization reagent will not be significant. Particulate-phase metals will either dissolve in the scrubbing liquor or remain in their solid form, where they will be purged from the system with the desulfurization sludge/product. Vapor-phase metals may enter the flue gas through the reduction/desorption mechanism described above.

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[4] I have labeled them as "vapor-phase" metals because their particulate phase removal efficiencies are usually below 90%, and stand out when compared to the remaining trace metals.

[5] Hg_2Cl_2 is thermodynamically unstable at normal flue gas conditions and will decompose into $HgCl_2$ and Cl_2 gas. HgO and CH_3Hg have not yet been identified in flue gas.

[6] Munthe, J., Z.F. Xiao and O. Lindqvist, **The Aqueous Reductions of Divalent Mercury by Sulfite**, Water, Air, and Soil Pollution, 56, 621-630, 1971. Although this is an old source, the data has recently been confirmed by several other examiners.

In general, outlet emissions of trace metals are lower from dry desulfurization systems than wet systems, due to use of fabric filters. In general, fabric filters achieve better control of micron and sub-micron particulates than electrostatic precipitators, and collect more of the particulate-phase pollutants. The dust cake allows for a higher degree of adsorption of the vapor-phase pollutants. Also, in a dry desulfurization system, the particulate acts as a nucleation seed for the calcium oxide/sulfite; thus, the particle size increases through a spray dryer, reducing the fraction of micron and sub-micron particles. These larger particles are then collected by the fabric filter.

Analysis of test data for dry desulfurization systems (Table 5) has shown collection efficiencies for particulate phase metal compounds in excess of 95 % ,which equals or exceeds the performance of wet desulfurization systems. The effectiveness of dry desulfurization systems in collecting these compounds is attributable to the high collection efficiency of sub-micron particles achievable in fabric filters.

Vapor-phase trace metals (primarily mercury, selenium, and arsenic) are also controlled to higher levels by a dry desulfurization system. The primary control mechanism is the condensation onto flyash particles and subsequent collection by the fabric filter. Field data has shown that dry desulfurization systems achieve higher collection efficiencies of these vapor-phase compounds, due to the lower particulate collection temperature, and to a lesser effect, gas filtration and adsorption by the dust bed.

In a wet desulfurization system, the particulate collection device operates at the air heater outlet temperature. Removing the particulate at this temperature will not allow the degree of condensation and adsorption available at the operating temperatures of a fabric filter following a DFGD system. Also, the precipitator removes the flyash from the gas path, whereas the fabric filter uses the flyash to form a filtration bed. The gas residence time of the flyash in a fabric filter is much greater than that of a precipitator, allowing additional time and contact for adsorption of volatile compounds. When one further considers the additional benefit of unburned carbon as an adsorbent, it is very easy to reconcile the higher collection efficiencies found for fabric filters in the field data.

ORGANIC REMOVAL EFFICIENCIES

Uncontrolled organic pollutant emissions are much lower than trace metal emissions, in most cases by two or three orders of magnitude. Benzene, toluene, phenol and naphthalene are the most prevalent and consistently detected organic compounds in coal-combustion flue gas.

The organic removal efficiencies will be controlled by the same mechanisms as the trace metal pollutants. Particulate-phase organics, usually higher molecular weight hydrocarbons, will condense onto the flyash as the gas temperature is lowered, allowing removal to the extent that particulate material is controlled. Vapor-phase organics will condense onto available particulate surface, either flyash or sulfite/sulfate carryover, and be collected by impaction with the spray droplets or mist eliminator, absorbed into the scrubbing liquor, or emitted from the stack.

Dioxin and furan emissions from a wet desulfurization system are shown in Table 3. The more toxic cogeners were not found in detectable quantities at 10^{-5} lb/TBtu. Schmidt and Brown reported detects at 10^{-7} and 10^{-6} lb/TBtu for 2,3,7,8-TCDD/F[7]. Emission factors for dioxin/furan cogeners are six to eight orders of magnitude below metal emissions. From the data obtained, it would be difficult to state with certainty whether any significant removal was found.

Total hydrocarbon emissions increased across a wet desulfurization system, as shown in Table 4. If the desulfurization system is operating in a closed-loop configuration, any cleaning solvents or lubricating oils washed from the pad into the washwater sumps could find their way into the scrubbing liquor loop. It is common procedure to use reclaim water from the pad wash-down sumps as reagent slurry water or mist eliminator wash water. In these cases, the lube oils and solvents will find their way into the scrubbing liquor where the higher volatility compounds will be stripped from the scrubbing liquor and be emitted from the stack. This trend was noticed in the data from Coal-A sampling, but the hypothesis has not been confirmed.

The organic removal efficiencies for a dry desulfurization system will be controlled by the similar mechanisms as the trace metal pollutants. Higher molecular weight (less volatile) hydrocarbons will be removed to the extent that particulate material is collected by the fabric filter. Vapor-phase organics will condense onto available particulate surface, including unburned carbon, and be collected by the fabric filter. As with the vapor-phase metals, field data for dry desulfurization systems indicate control efficiencies in excess of wet desulfurization systems, primarily due to the use of a fabric filter and avoidance of recycling lubricants into the process water loop.

Several concerns have been raised about the effect of low NOx combustion on organic emissions. Initial hypotheses were that the more extreme firing conditions in the furnace would increase organic emissions at the boiler outlet, a concern rising from the increased non-combusted material in the flyash. From the Coal-C data, ABB found that organic compound emissions were exacerbated by low NOx firing, with the volatile compounds being more affected by the firing system (Table 8). Volatile organic compound (with boiling points lower than 100°C) emissions increased by a factor of 5, while semivolatile organic compound emissions increased by a factor of 2. This data is consistent with that being reported by other investigators.[8]

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[7] Schmidt, C.E., T.D. Brown, **Results from the Department of Energy's Assessment of Air Toxic Emissions from Coal-Fired Power Plants**, International Joint Power Generation Conference, Oct. 1994.

[8] Dismukes, E.B., **Measurement of Chemical Emissions under the Influence of Low NOx Combustion Modifications**, Southern Research Institute, Oct. 1993.

Table 1. Coal-A Metal Emission Factors and APC Removal Efficiencies.

Pollutant	Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency	WFGD Emission Factor, lb/TBtu	WFGD Removal Efficiency
Antimony (Sb)	136 ± 22	15 (max)	89.0 % (min)	16 (max)	No Additional
Arsenic (As)	941 ± 235	23 (max)	97.6 % (min)	25 (max)	No Additional
Barium (Ba)	3467 ± 1020	12 (max)	99.7 % (min)	7 (max)	Not Available
Beryllium (Be)	56 ± 15	1 (max)	98.2 % (min)	1 (max)	No Additional
Cadmium (Cd)	40 ± 3	2.3 ± 0.8	94.2 %	1 (max)	56.5 % (min)
Chromium (Cr)	824 ± 99	795 ± 104	3.5 %	4.3 ± 0.8	99.5 %
Copper (Cu)	576 ± 150	30 ± 8	94.8 %	15 (max)	50.0 % (min)
Lead (Pb)	750 ± 174	26 ± 14	96.5 %	22.5 ± 1.5	13.5 %
Manganese (Mn)	1090 ± 204	76 ± 9	93.0 %	4 (max)	94.8 % (min)
Nickel (Ni)	1369 ± 435	479 ± 344	65.0 %	10 (max)	97.9 % (min)
Phosphorous (P)	4412 ± 2280	65 (max)	98.5 %	76 (max)	No Additional
Selenium (Se)	721 ± 94	642 ± 129	11.0 %	393 ± 94	38.8 %
Silver (Ag)	14 (max)	2 (max)	Not Avail	3 (max)	No Additional
Thallium (Tl)	141 (max)	20 (max)	Not Avail	25 (max)	No Additional
Zinc (Zn)	2009 ± 23	45 ± 7	97.8 %	24 ± 10	46.7 %

Table 2. Coal-A Mercury Emission Factors and APC Removal Efficiencies.

Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency	WFGD Emission Factor, lb/TBtu	WFGD Removal Efficiency
8.2	7.3	10.9 %	1.2	83.1 %
6.4	10.7	-67.6 %	4.0	62.0 %
4.8	6.9	-46.0 %	1.6	77.2 %

Table 3. Coal-A PCDD/PCDF Emission Factors and APC Removal Efficiencies.

PCDD/PCDF Cogener	Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency	WFGD Emission Factor, lb/TBtu	FGD Removal Efficiency	APC Removal Efficiency
2,3,7,8 TCDD	$2.3 * 10^{-6}$ (max)	$9.6 * 10^{-6}$ (max)	Not Avail	$3.2 * 10^{-6}$ (max)	Not Avail	Not Avail
1,2,3,7,8 PeCDD	$1.2 * 10^{-5}$ (max)	$6.7 * 10^{-6}$ (max)	Not Avail	$1.9 * 10^{-6}$ (max)	Not Avail	Not Avail
1,2,3,4,7,8 HxCDD	$1.5 * 10^{-5}$ (max)	$9.4 * 10^{-6}$	Not Avail	$3.3 * 10^{-6}$ (max)	64.4 % (min)	Not Avail
1,2,3,6,7,8 HxCDD	$2.8 * 10^{-5}$	$1.5 * 10^{-5}$	44.0 %	$2.2 * 10^{-6}$ (max)	85.6 % (min)	92.0 % (min)
1,2,3,7,8,9 HxCDD	$3.1 * 10^{-5}$	$2.1 * 10^{-5}$	32.3 %	$2.5 * 10^{-6}$ (max)	88.0 % (min)	91.9 % (min)
1,2,3,4,6,7,8 HpCDD	$1.8 * 10^{-4}$	$1.1 * 10^{-4}$	37.2 %	$8.5 * 10^{-6}$	92.4 %	95.2 %
1,2,3,4,6,7,8,9 OCDD	$2.9 * 10^{-4}$	$2.7 * 10^{-4}$	7.5 %	$2.1 * 10^{-5}$	92.1 %	92.7 %
Total PCDD	$5.6 * 10^{-4}$ (max)	$4.4 * 10^{-4}$ (max)		$4.3 * 10^{-5}$		92.3 %
2,3,7,8 TCDD Eq PCDD	$3.0 * 10^{-4}$ (max)	$2.8 * 10^{-4}$ (max)		$2.6 * 10^{-5}$		91.5 %
2,3,7,8 TCDF	$1.1 * 10^{-5}$	$6.6 * 10^{-6}$ (max)	38.9 % (min)	$7.9 * 10^{-6}$ (max)	Not Avail	27.2 % (min)
1,2,3,7,8 PeCDF	$1.4 * 10^{-5}$ (max)	$7.5 * 10^{-6}$	Not Avail	$1.2 * 10^{-6}$ (max)	84.3 % (min)	Not Avail
2,3,4,7,8 PeCDF	$3.6 * 10^{-5}$ (max)	$1.6 * 10^{-5}$	Not Avail	$1.2 * 10^{-6}$ (max)	92.6 % (min)	Not Avail
1,2,3,4,7,8 HxCDF	$1.4 * 10^{-4}$	$5.7 * 10^{-5}$	59.5 %	$2.0 * 10^{-6}$ (max)	96.5 % (min)	98.6 % (min)
1,2,3,6,7,8 HxCDF	$3.6 * 10^{-5}$ (max)	$1.6 * 10^{-5}$	Not Avail	$1.3 * 10^{-6}$ (max)	92.3 % (min)	Not Avail
2,3,4,6,7,8 HxCDF	$5.0 * 10^{-6}$ (max)	$3.5 * 10^{-6}$	Not Avail	$2.3 * 10^{-6}$ (max)	35.1 % (min)	Not Avail
1,2,3,7,8,9 HxCDF	$7.0 * 10^{-5}$ (max)	$2.6 * 10^{-5}$	Not Avail	$1.6 * 10^{-6}$ (max)	93.7 % (min)	Not Avail
1,2,3,4,6,7,8 HpCDF	$2.2 * 10^{-4}$	$8.1 * 10^{-5}$	62.4 %	$3.6 * 10^{-6}$ (max)	95.5 % (min)	98.3 % (min)
1,2,3,4,7,8,9 HpCDF	$2.3 * 10^{-5}$ (max)	$1.8 * 10^{-5}$	Not Avail	$2.2 * 10^{-6}$ (max)	87.4 % (min)	Not Avail
OCDF	$7.1 * 10^{-5}$	$5.9 * 10^{-5}$	17.3 %	$2.5 * 10^{-6}$ (max)	95.7 % (min)	96.5 % (min)
Total PCDF	$6.2 * 10^{-4}$ (max)	$2.9 * 10^{-4}$ (max)		$2.6 * 10^{-5}$ (max)		
2,3,7,8 TCDD Eq PCDF	$8.9 * 10^{-6}$ (max)	$4.2 * 10^{-6}$ (max)		$1.1 * 10^{-6}$ (max)		
Total PCDD+PCDF	$1.2 * 10^{-3}$ (max)	$7.3 * 10^{-4}$ (max)		$6.9 * 10^{-5}$ (max)		
2,3,7,8 Eq PCDD+PCDF	$3.1 * 10^{-4}$ (max)	$2.9 * 10^{-4}$ (max)		$2.7 * 10^{-5}$ (max)		

Table 4. Coal-A Organic Emission Factors and APC Removal Efficiencies.

Pollutant	Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency	WFGD Emission Factor, lb/TBtu	WFGD Removal Efficiency
Formaldehyde	40.9	3.7	91.0 %	1.6	56.8 %
Total Hydrocarbons	17,500	7800	55.4 %	17,900	-129.5 %

Table 5. Coal-B Metals Emission Factors and APC Removal Efficiencies.

Pollutant	Boiler Emission Factor, lb/TBtu	SDA/FF Emission Factor, lb/TBtu	SDA/FF Removal Efficiency
Antimony (Sb)	33 ± 2	0.37 (max)	98.9 % (min)
Arsenic (As)	118 ± 20	0.37 (max)	99.7 % (min)
Barium (Ba)	192 ±11	0.87 ± 0.26	99.6 %
Beryllium (Be)	69 ± 3	0.16 ± 0.16	99.8 %
Cadmium (Cd)	2.0 ± 0.1	1.24 ± 1.05	36.0 %
Chromium (Cr)	895 ± 67	1.24 ± 0.31	99.9 %
Copper (Cu)	522 ± 30	2.27 ± 0.68	99.6 %
Lead (Pb)	266 ± 22	0.86 ± 0.56	99.7 %
Manganese (Mn)	347 ± 16	1.68 ± 1.14	99.5 %
Mercury (Hg)	10.3 ± 0.3	0.95 (max)	90.8 % (min)
Nickel (Ni)	548 ± 58	2.10 ± 0.65	99.6 %
Phosphorous (P)	6,463 ± 712	7.5 ± 2.5	99.9 %
Selenium (Se)	128 ± 3	0.37 (max)	99.7 % (min)
Silver (Ag)	0.8 ± 0.1	0.19 ± 0.03	74.9 %
Thallium (Tl)	1.4 ± 0.4	0.37 (max)	69.0 % (min)
Zinc (Zn)	642 ± 43	18.6 ± 10.7	97.2 %

Table 6. Coal-B Organic Emission Factors and APC Removal Efficiencies.

Pollutant	Boiler Emission Factor, lb/TBtu	SDA/FF Emission Factor, lb/TBtu	SDA/FF Removal Efficiency
Total Non-CH_4 Hydrocarbons	100 (max)	333 ± 205	Not Calculated

Table 7. Coal-C Metal Emission Factors and ESP Removal Efficiencies.

Pollutant	Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency
Antimony (Sb)	37	ND	Not Avail
Arsenic (As)	60	0.1	99.8 %
Barium (Ba)	2377	2	99.9 %
Beryllium (Be)	61	0.3	99.5 %
Cadmium (Cd)	17	0.7	95.9 %
Chromium (Cr)	903	16.9	98.1 %
Copper (Cu)	1005	3.8	99.6 %
Lead (Pb)	502	6.5	98.7 %
Manganese (Mn)	335	3.1	99.1 %
Mercury (Hg)	2.2	1.2	45.5 %
Nickel (Ni)	803	6.6	99.2 %
Phosphorous (P)	4876	35.5	99.3 %
Selenium (Se)	202	45.5	77.5 %
Silver (Ag)	ND	ND	Not Avail
Thallium (Tl)	1.5	ND	Not Avail
Zinc (Zn)	289	8.3	97.1 %

Table 8. Coal-C Organic Emission Factors and ESP Removal Efficiencies.

Firing Condition and Pollutant	NOx Emissions (ppm @ 3 % O_2)	Boiler Emission Factor, lb/TBtu	ESP Emission Factor, lb/TBtu	ESP Removal Efficiency
Normal, VOC	239	10.1	3.4	66.3 %
Low NOx, VOC	168	47.9	11.2	76.6 %
Normal, SVOC	239	64.5	114.4	-77.4 %
		60.8	113.5	-86.7 %
Low NOx, SVOC	168	80.9	163.4	-102.0 %
		126.2	90.0	28.7 %

TRACE ELEMENT BEHAVIOUR DURING COMBUSTION OF DIFFERENT COALS IN AN EXPERIMENTAL FURNACE

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Abstract

This work has been performed in the frame of an ENEL experimental program (CATOCA project), aimed to investigate the relationship between the coal characteristics and its behaviour during combustion. The experiments have been carried out in a 50 kWt vertical furnace equipped with a pulverized coal burner. The operating conditions of the plant were optimized in order to reach the best practical combustion efficiency and maintained as steady as possible for all the tests. More than sixty elements (major, minor and trace) in the fuels and related particulate matter were analysed by ICP/MS and IC for seven coals of different geographical origin and rank [6]. Fourteen elements (As, Ba, Br, Cd, Cl, Hg, I, Mo, Ni, S, Sb, Se, Sn, Zn), with tendency to transfer into stack gas as vapour phase, were sampled. A dedicated system named TRIS (TRace Inorganic Sampler), mainly consisting of a cooled train of solid adsorbers, was adopted. The analyses were performed by INAA. The concentrations of the elements in the stack gas, both in the particulate matter and in the vapour phase, are reported for all types of coal. The volatilization degree and the distribution between solid and vapour phase for each different coal are also included.

Introduction

During combustion processes, inorganic matter undergo several transformations: entering into the combustion chamber, coal particles receive, due to irradiation, an amount of heat that they swell up and shatter. Pyrolysis products burn, while the environment on particle surfaces becomes reducing. Due to the above conditions, breaking of bonds between elements and organic network take place, and some elements pass directly into gas phase. The elements in the vapour phase can have either the same oxidation number or change to a reduced state.

When the organic material has almost completely burnt, the environment on particle surfaces become oxidizing; in such a way many elements turn into their oxides.

Leaving the zone at high temperature, some elements at vapour state condense on particle surfaces. The above phenomena can take place both before and after the filtering systems. Some species, which have a low boiling temperature, can also remain in the vapour phase at stack (Hg, etc.).

The vaporization phenomena depend on both the temperature reached by the coal particle, and the volatility of the compound.

The temperature may vary considerably from particle to particle, explaining the heterogeneous characteristics of the aerosol produced by coal combustion.

The volatility of the compound can partially explain the heterogeneous distribution of elements in the vapour phase, but some elements having a high volatility can be blocked in the partially melted fly ashes because of diffusion difficulties.

Experimental tests aiming to the study of elements' distribution in the micronic particulate matter have been carried out [1-2]. They show good results and repeatibility for what concerns group composition. On the contrary, in sub-micronic field, the distributions are unpredictable [3-4], both between elements and among several authors. This is mainly due to plant conditions variability and to the sampling system used.

The purposes of the present work are:

- the evaluation of the distribution between solid and gaseous phase for some elements whose emission are ruled by Italian law;
- a tentative classification of elements in the vapour phase following their behaviour during combustion of different coals
- the verification of the applicability of a special sampling system (dedicated to heavy metal sampling in gas phase) to the sampling of gaseous halogens and Sulphur.

Some previous works regarded a mass balance for these elements, and some unbalances have been attributed to an emission in gaseous phase.

In this experimentation, a special sampling system for the gaseous phase, equipped with solid adsorbers, has been used.

The difficulties found in the elements extraction from the adsorbers drove the choice of the analytical methods on INAA (Instrumental Neutron Activation Analysis), directly applied on solid adsorbers.

Experimental

Plant facilities

This work has been carried out in the frame of an ENEL experimental program aimed to study the relationship between the characteristic of coals and their behaviour during combustion. The tests have been carried out on a 50 kWth vertical furnace equipped with a pulverized coal burner. The operating conditions of the plant have been optimized in order to get the best combustion efficiency and maintained as steady as possible for the whole campaign.

Seven bituminous coals, with different characteristics and geographical origin have been tested. Every coal has been milled to obtain a particle size distribution similar to the one normally used in power plants (80% < 200 mesh).

The test facility mainly consists of an adiabatic combustion chamber (0.033 m^3 volume), followed by a water cooled section (0.098 m^3) and a stack pipe. The burner (based on a IFRF design) was equipped with a turbulence generator allowing a variable swirl number. In fig. 1 a draft of the test facility is represented.

The furnace performance has been controlled and optimized by mean of a data acquisition system, which allows a continuous monitoring of both plant parameters and the concentrations of gaseous combustion products.

Each coal has been burnt during one or more tests and flue gas samples for each test have been taken in the stack pipe.

The following scheme summarizes the experimental plan:

Num. of Tests	Coal
4	Poland
3	Mapco USA
3	McCall USA
2	South Africa
2	Sulcis Italy
1	Venezuela
1	Colombia

The characteristics of the fuels are summarized in Tab. 1, while the operating conditions of the plant are reported in the References [5]

Sampling system

The TRIS (TRace Inorganic Sampler) that has been used for the tests is represented in fig. 2.

The gas is sampled using an heated probe, in order to avoid condensations inside the probe itself. The heated section contains also a ceramic filter, for the separation of particulate matter.

After filtration, the gaseous sample is cooled down to 5 °C in a glass impinger, in order to separate water. Then the sample is passed through several trap of activated carbon, where the elements are captured.

After the system there are a membrane pump and a gas meter.

For each test, the following samples have been obtained:

- particulate matter on a glass fiber filter;
- condensed water
- activated carbon traps.

Analytical procedures

The particulate matter has been solubilized by mean of acid mixtures (HNO_3, HF), using autoclaves and microwave chambers. The solutions obtained by this process and the condensed water have been analysed by a Mass Spectrometer coupled with an ICP, and the halogens have been characterized by Ion Chromatography.

The elements trapped in the activated carbon have been analysed by mean of Instrumental Neutron Activation Analysis.

The solid adsorbers have been irradiated and analysed at the Nuclear Facility of the University of Pavia, Italy.

Results and discussion

The distribution of elements emission has been reported in the Tables 2a-2b. The results are expressed in µg/Nm3, normalized for a 6 % Oxygen concentration in flue gases. For each coal three columns are reported:

- the first is the concentrations of elements in the vapour phase (adsorbers + condensed water);
- the second one is the concentrations on the particulate matter;
- the third one is percentage of distribution of elements in the gas phase respect to the sum particulate + gas.

The concentrations have been expressed as averaged results of several tests, as reported in section 3.1.

Taking into account that plant conditions were subjected to variations, due to both the coal feeding system and the temperature controls of the furnace, the reproducibility of the tests was acceptable.

The analysis of the particulate matter by ICP-MS, allowed the characterization of 70 elements (major, minor and traces) [6]. Cl, S, Br and I have not been measured on the solid phase, because of the small amount of sample available. Moreover, for these elements, the results of the analyses of the gas phase are low and extremely variable, confirming that the sampling method used is not suitable for halogens. Standard methods (alkaline solutions) are recommended for the sampling of halogens and Sulphur in the gas phase.

The INAA technique, applied on the active carbon gas adsorbers, allowed the analysis of 22 elements only, with the exclusion of some important elements such as Pb, Be, F. This limit is due to the INAA technique itself. Moreover, another interesting element, Cu, has not been considered because it is present as a strong impurity (together with Na, Al, Ca) in the activated carbon. [7]

A common behaviour observed is the very high percentage (> 60 %) of Mercury present in the gas phase for all the coal tested. The Sulcis coal (Italy) has the lowest degree of Hg volatilization; this is due to the high mineral matter content of this typical Italian brown coal. It is also evident that for this coal, almost all the elements show a lower degree of volatilization.

Another elements which shows a similar behaviour to Hg (% in gas phase > 50) is Cadmium. This element often follows a VCM (Volatilization-Condensation Mechanism) and shows the highest concentration in the finest fly ash, where it can be both inside the vitreous matrix of the particle and, in oxide form, on particle surfaces. As a matter of fact, a previous study carried out on a coal-fired power plant [8] gave the following results expressed as enrichment factors:

Bottom Ash	0.01
Hopper Ash	0.20
Particulate at Stack	2.19

In the tests carried out on the experimental furnace, the high level of Cd in the gas phase is probably due to both the different thermal profile of the furnace itself and the higher temperature of flue gas at sampling point (about 180 °C).

A further elaboration of the element concentrations in the gas phase, made a classification following the scheme suggested by Klein [9] and Coles [10] in their "chemical studies of stack fly ash". These subdivisions come from previous geological studies made by Goldschmit, and consist of a grouping of elements following their natural occurrences: silicates associations, Sulphur association, native Fe occurrence and natural gases.

Group	Behaviour
silicates association	poor volatility
Sulphur association	high volatility
Fe native affinity	intermediate behaviour
natural gas	very high volatility

Coles took into account the scheme above and, on the basis of experimental tests on coal fired plants, grouped the elements found in the fly ash in four behaviour classes.

First group is constituted by elements whose concentrations are constant in the different kind of solid emissions (bottom ash, fly ash and particulate matter); they don't undergo vaporization phenomena.

The second group' s elements show an enrichment in the particulate matter respect to bottom ash. This behaviour is due to a volatilization-condensation mechanism.

Third group shows an intermediate behaviour.

Fourth group is constituted by elements with high volatility. They pass through the stack mainly in vapour phase.

Tab. 3 shows the concentrations of the elements (expressed as µg/Nm3, normalized for the initial concentration of the element itself in the fuel) in the gas phase measured in our tests, following the Coles classification.

Rb, Cs and Mn belong to the first Coles group. They have a good correlation, as shown in Fig. 3.

Rb and Cs are isomorphic in sulphate compounds, while Mn is present mainly as oxide, carbonate and silicate. This difference is shown by the distributions in tabs. 2a-2b.

Second group' s elements are mainly present in coal as sulphides. Cadmium shows the highest degree of volatilization, followed by Tin and Selenium (fig. 4). The first two elements could also belong to the fourth group. This is probably due to the high temperature of the sampling point. Tin behaviour may also depend on the mineral form in which it is present in the fuel.

Data in tab. 3 and in fig. 5 show the low volatilization degrees of elements belonging to group three. During combustion, these elements are mainly changed into low-volatile oxides.

The fourth group contains Hg, S and Halogens. Only Hg (fig. 6) has been correctly sampled and measured, due to the reasons above. The degree of volatilization measured confirms the Hg tendency to be present as vapour at the temperature of the sampling point.

Conclusions

The tests have been carried out on an experimental facility. Some combustion parameters distinctive of this plant, such as:

- the residence time and temperature profiles of the furnace;
- the environment around the particles, which has a major influence on the vaporization and aerosol formation

can be different from power plant ones.

The temperature of the sampling point is higher than the temperature of the stack in a standard power plant.

For these reasons, the behaviour of elements as Sn and Cd should be investigated on a standard power unit. A mass balance should be made, in order to understand the efficiencies of sampling and analysis.

The TRIS sampling system seems to be suitable for heavy metals. The elements are quantitatively captured by solid adsorbers.

The TRIS doesn't appear to be good for halogens sampling.

Another problem of this sampling system is connected to the INAA analytical methods: some elements cannot be detected (Pb, F, Be).

The degree of volatilization of several heavy metals has been obtained, and a classification in groups has been made, and compared with some literature fly ash classification. Some similarities have been observed and discussed.

As expected, in this classification, some little discrepancies have also been found. They can be explained assuming different models of formation between particulate matter and gas. In previous works on sub-micronic particles, difficulties in classification of elements have already been found.

The coals which show higher degrees of volatilization for almost the elements analyzed are Venezuela and Poland.

The coal which shows the lowest degrees of volatilization for all the elements is Sulcis. This result has been confirmed by laboratory volatilization tests [8].

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TABLE I

Characteristics of the coals.

Coal type	NCV [a] kJ kg-1	GCV [a] kJ kg-1	C/H [b]	LTA [b] %	FC/VM
Italian Sulcis	20130	21231	12.5	24.2	0.97
Columbian	28897	30082	14.5	7.8	1.58
Venezulane	27604	28876	14.0	4.4	1.66
U.S.A. Mapco	29278	30400	15.4	8.3	1.75
Polish	31929	33005	15.9	12.8	1.96
U.S.A. Mc Call	31640	32695	17.1	6.6	2.39
South-African	26670	27620	17.7	16.5	2.40

NCV, GCV	Net, Gross Calorific value	LTA	Low Temperature Ash
C/H	Carbon to Hydrogen ratio from ultimate analysis	FC	Fixed Carbon from proximate analysis
		VM	Volatile Matter from proximate analysis
[a]	as received	[b]	dry basis

Tab. 2a - Elemental distribution in particulate matter and gas

Coal	Colombia			Venezuela			SulcisII Italy			South Africa		
µg/Nm3												
Element	Gas	Part. Matter	% Gas	Gas	Part. Matter	% Gas	Gas	Part. Matter	% Gas	Gas	Part. Matter	% Gas
S	6285	0	N.D.	4526	0	N.D.	31771	0	N.D.	7901	0	N.D.
Cl	24674	0	N.D.	25702	0	N.D.	6971	0	N.D.	6745	0	N.D.
Ti	93	24343	0.38	20	8979	0.22	94	82158	0.11	237	96377	0.24
V	3	1235	0.22	5	365	1.28	1	12009	0.01	10	1576	0.66
Cr	1	1232	0.10	1	453	0.21	12	3992	0.29	15	1592	0.91
Mn	50	2031	2.41	81	1295	5.86	4	3414	0.13	74	3419	2.12
Fe	4500	98110	4.39	74	38115	0.19	578	205052	0.28	2616	76232	3.32
Co	0	200	0.01	0	47	0.07	2	500	0.32	3	695	0.40
Ni	6	1116	0.53	10	340	2.83	6	3328	0.19	14	1331	1.01
Zn	49	1175	4.01	7	333	2.09	18	6047	0.30	40	1822	2.15
As	10	172	5.73	10	69	12.97	1	4419	0.02	8	278	2.80
Se	5	53	9.07	5	75	5.88	13	108	10.38	4	8	34.79
Br	197	0	N.D.	136	0	N.D.	59	0	N.D.	66	0	N.D.
Rb	29	15	66.21	7	10	40.87	1	682	0.09	27	2	92.49
Mo	0	217	0.01	0	83	0.23	1	3273	0.03	1	202	0.39
Cd	32	14	69.34	33	3	91.62	19	67	21.87	32	17	65.33
Sn	39	32	55.39	238	124	65.72	12	148	7.49	47	248	16.01
Sb	1	62	1.92	1	19	7.27	1	227	0.49	1	62	2.12
I	61	0	N.D.	59	0	N.D.	11	0	N.D.	135	0	N.D.
Cs	6	10	35.55	1	5	13.31	0	168	0.00	246	7	97.35
Ba	111	5194	2.10	44	2264	1.92	86	30083	0.28	102	14884	0.68
Hg	3	1	83.10	5	0	93.97	3	2	63.21	10	1	89.50

Tab. 2b - Elemental distribution in particulate matter and gas									
Coal	Mapco USA			McCall USA			Poland		
µg/Nm3									
Element	Gas	Part. Matter	% Gas	Gas	Part. Matter	% Gas	Gas	Part. Matter	% Gas
S	6374	0	N.D.	21356	0	N.D.	8185	0	N.D.
Cl	66425	0	N.D.	60945	0	N.D.	49854	0	N.D.
Ti	89	54012	0.16	73	44068	0.17	312	47166	0.66
V	9	1202	0.71	4	1841	0.19	11	2329	0.46
Cr	2	1228	0.17	1	1420	0.08	8	1409	0.53
Mn	38	1017	3.59	24	1211	1.95	55	5466	1.00
Fe	429	50935	0.84	27	65303	0.04	512	109268	0.47
Co	3	425	0.79	9	325	2.58	2	637	0.27
Ni	8	891	0.94	7	1087	0.61	4	1779	0.25
Zn	58	621	8.54	28	418	6.26	35	1517	2.23
As	2	236	0.96	2	239	0.97	2	269	0.73
Se	9	104	7.59	6	37	14.72	6	21	21.21
Br	618	0	N.D.	265	0	N.D.	260	0	N.D.
Rb	15	140	9.67	11	40	21.40	9	56	13.34
Mo	1	89	0.88	1	143	0.53	0	203	0.04
Cd	20	16	55.49	10	4	73.84	204	18	91.68
Sn	123	54	69.58	1	18	6.67	43	95	31.27
Sb	1	37	2.74	1	52	1.83	1	160	0.33
I	124	0	N.D.	41	0	N.D.	240	0	N.D.
Cs	0	20	1.42	0	12	1.62	0	35	0.81
Ba	191	7010	2.66	118	6228	1.87	104	14581	0.71
Hg	3	0	88.85	2	1	75.65	2	1	65.44

Tab. 3

Tab. 3 - Relative volatilization degrees								
ug/Nm3/ppm in coal								
Group 1	Coal	Colombia	Mapco	McCall	Poland	SouthAfrica	SulcisII	Venezuela
	Cs	10.1	0.6	0.3	0.2	210.8	0.0	3.8
	Rb	6.0	5.9	2.6	1.4	14.6	0.1	6.0
	Mn	1.4	2.0	1.3	0.6	1.4	0.1	3.1
Group 2	Coal	Colombia	Mapco	McCall	Poland	SouthAfrica	SulcisII	Venezuela
	As	5.7	1.3	0.5	1.0	6.4	0.1	9.3
	Cd	1185.8	691.7	540.3	1850.7	728.5	40.6	1861.4
	Sn	99.2	257.3	2.9	41.5	33.0	19.4	406.6
	Sb	1.7	2.1	0.7	0.4	3.7	1.2	4.9
	Se	6.7	21.5	4.4	10.8	8.5	2.8	1.4
	Zn	2.9	7.9	4.0	1.7	3.1	0.5	1.3
Group 3	Coal	Colombia	Mapco	McCall	Poland	SouthAfrica	SulcisII	Venezuela
	V	0.1	0.7	0.1	0.4	0.6	0.0	0.5
	Cr	0.1	0.2	0.1	0.4	0.7	0.3	0.2
	Ni	0.7	1.0	0.6	0.2	1.1	0.2	2.6
	Co	0.0	0.7	1.6	0.2	0.4	0.2	0.0
	Ba	0.6	2.0	0.8	0.4	0.3	0.4	0.6
Group 4	Coal	Colombia	Mapco	McCall	Poland	SouthAfrica	SulcisII	Venezuela
	Hg	28.0	68.4	60.7	33.8	64.7	20.2	175.6

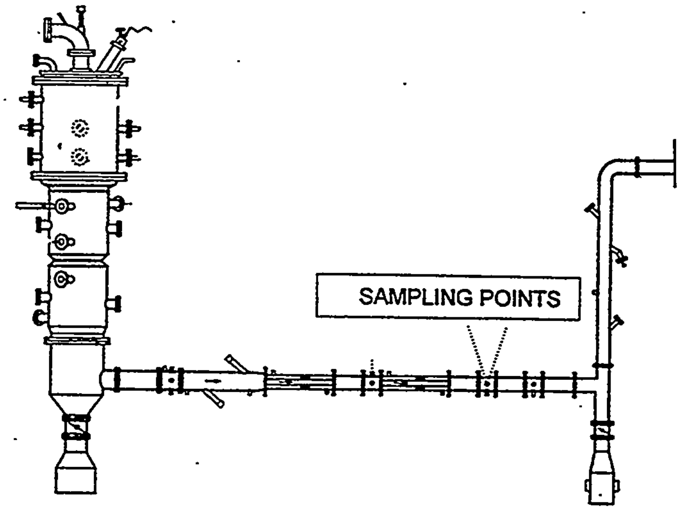
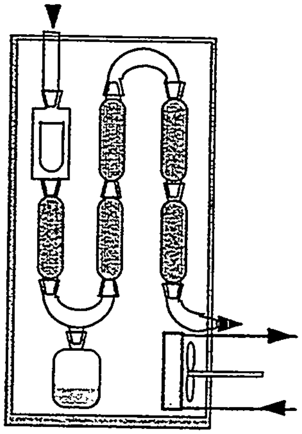


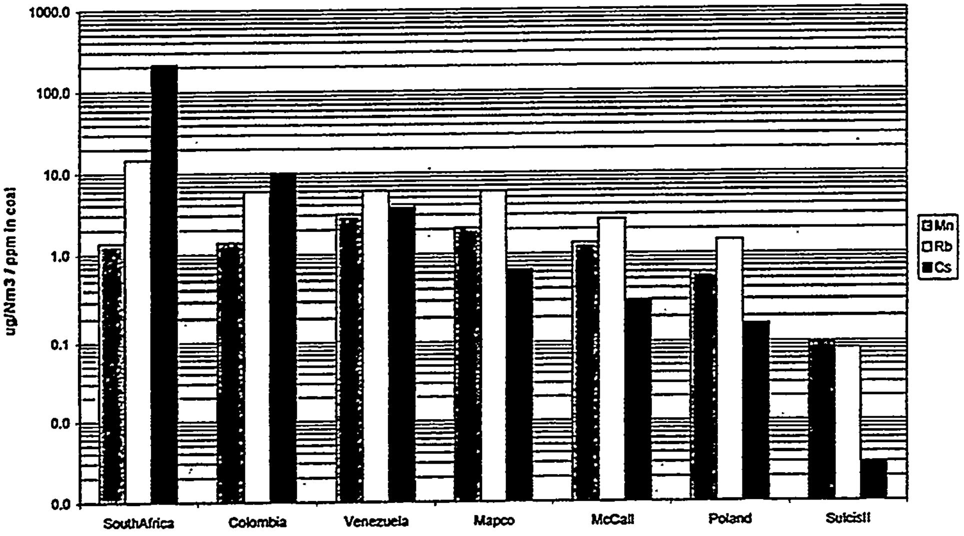
FIGURE 1

Fig.2 TRIS Sampling System



DISTR.XLS

Fig. 3 - Group 1



DISTR.XLS

Fig. 4 - Group 2

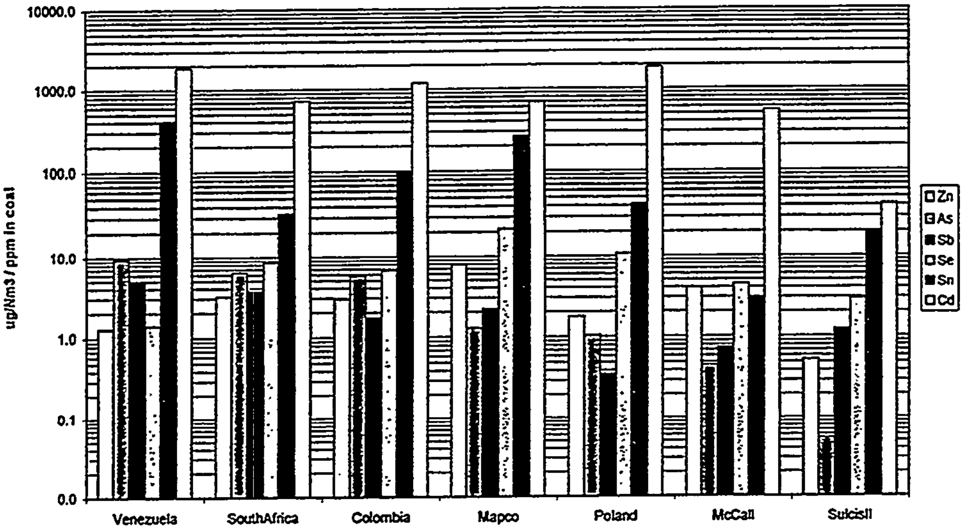


Fig. 5 - Group 3

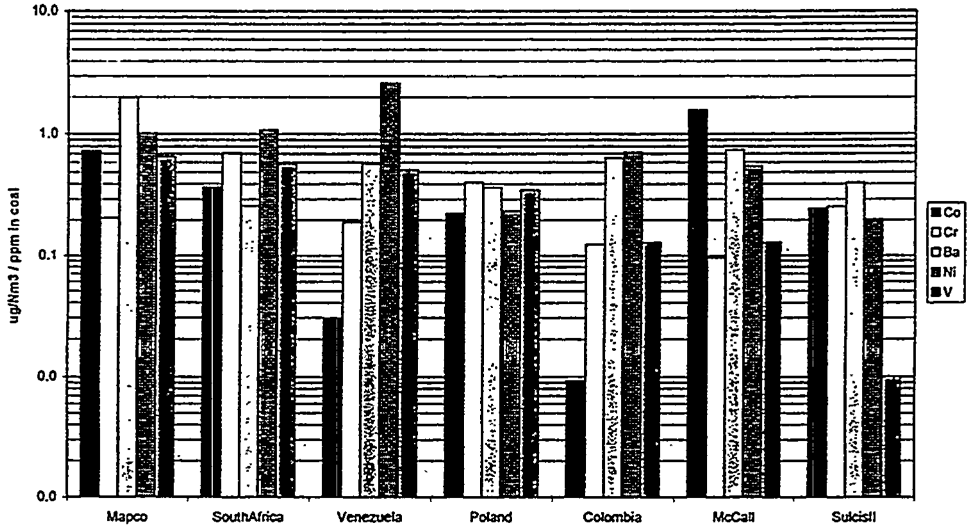
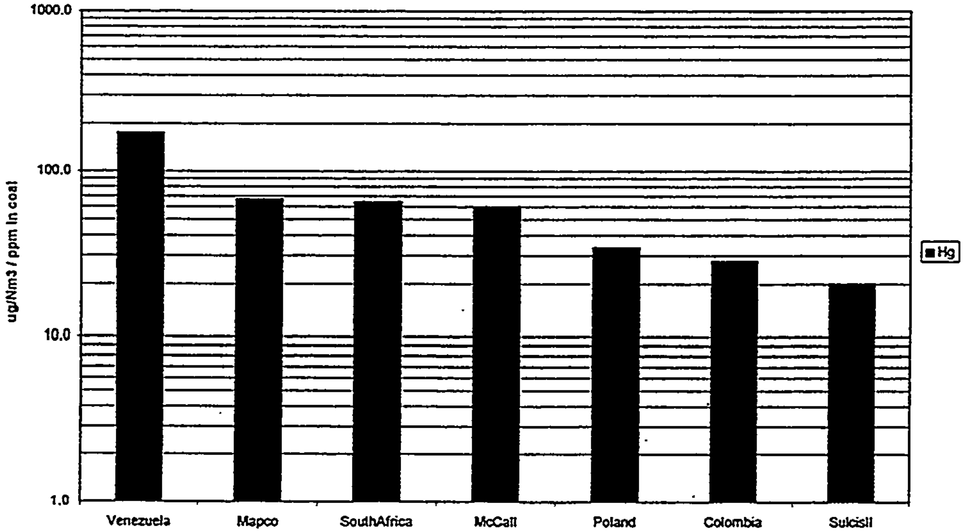


Fig. 6 - Group 4



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A Systems Approach to Risk Assessment: Application to Methylmercury from Coal Combustion

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INTRODUCTION

Two special studies of mercury (Hg) in the environment are being prepared for Congress in response to the Clean Air Act Amendments of 1990. The National Institute of Environmental Health Sciences has prepared a draft report on the maximum acceptable average daily human intake levels for mercury,[1] and the U.S. Environmental Protection Agency has prepared a draft study of mercury emissions from major anthropogenic sources and their environmental effects.[2] These studies are to be used in an analysis of the need to regulate mercury emissions from utilities, which are currently exempted from the hazardous air pollution regulations in the Amendments. In support of this forthcoming regulatory analysis, The Department of Energy (DOE) asked Brookhaven National Laboratory (BNL) to perform a probabilistic assessment of the health risks associated with Hg from coal-fired power plants.[3-5] The objective of the assessment is to estimate the incremental health risks that might ensue from a typical coal-fired power plant, together with their uncertainties, taking into account existing background levels and the actual adverse health effects that have previously been associated with exposure to various Hg species.

Mercury has a long history of association with adverse neurological effects at high exposure levels. The most important current exposure pathway has been found to be ingestion of fish containing methylmercury (MeHg), which is the end product of bioconcentration moving up the aquatic food chain. Mercury can enter natural waters from either industrial discharges or from atmospheric deposition of various inorganic Hg compounds. Because of the worldwide background and the existence of local emissions sources, Hg deposition must be considered on local, regional and global scales. The regulatory technical challenge presented by methylmercury is to protect public health without foreclosing an appreciable a portion of the food supply or impacting on the lifestyles of North American native populations.

This paper presents an abbreviated account of the DOE/BNL risk assessment, as viewed from a systems perspective. We review the structure of the model, the sources of data used, the assumptions that were made, and the interpretation of the findings. Since publication of the first risk assessment report[3], we have refined our estimates of local atmospheric dispersion and deposition and "calibrated" the pharmacokinetic portion of the model against observations.

THE BNL RISK ASSESSMENT MODEL

The probabilistic risk assessment model combines probability distributions for a number of input parameters that define exposure to a toxic agent, and then compares the resulting distribution of exposures to the levels at which adverse health effects have been observed. The resulting risk is thus defined as the product of the probability of exposure at some level times the probability of experiencing an adverse effect at that exposure level. This assessment comprises an assembly of 3 modular "subsystems":

1. the global Hg background, which defines the Hg intake and status of persons not exposed to current anthropogenic emissions,
2. the impacts of current anthropogenic emissions over and above that background,
3. the information necessary to describe human health effects that might be expected at various exposure levels.

Because of the recycling and persistence of mercury in the environment, some portion of today's background may have originated as anthropogenic emissions in previous years. We describe the elements of the model in terms of the sequence of calculations from emission source to receptor, with accumulation in freshwater fish as an important intermediate point in the chain.

Emissions and Control Processes

The model powerplant is assumed to be located near a lake in the upper Midwest and to have a capacity factor of 75%. In order to allow for a range of generation capacities and coal Hg contents, we assumed the product of nameplate rating and Hg concentration to be 250 ppm-MW, which corresponds to annual Hg emissions of about 560 kg. This allows for, say, a 1000 MW plant burning coal with 0.25 ppm Hg or a 2500 MW plant burning coal at 0.1 ppm Hg or combinations of values in-between. We note that this assumed emission rate corresponds to the upper end of the range of Hg emissions from U.S. power plants.[2] We assume that the plant is equipped with state-of-the art electrostatic precipitators that remove 10% of the Hg, but we do not consider the environmental effects of Hg in the solid waste stream in this assessment.

Atmospheric Processes

The model tracks the fates of 3 Hg species through the atmosphere: elemental Hg (Hg^0), reactive Hg (Hg^{++}), and particulate Hg (Hg_p). Hg^{++} is the most important species for local impacts, since its high solubility leads to rapid washout and deposition in the near field downwind of the plant (ca. 50 km). Based on early experimental results,[6] we assumed that 75% of the emitted Hg is in the form of Hg^{++}. Results computed by the U.S. Environmental Protection Agency (EPA) for several coal-fired power plants in the range 900-1100 MW were used to estimate the near-field atmospheric dispersion ratios (Figure 1). The peak cumulative average concentrations and thus deposition occur about 2-10 km from the plant. By the time the emissions travel 50 km from the stack, local concentrations are reduced by an order of magnitude or more, such that their impact on the existing background becomes negligible. Approximately 5-8% of the stack Hg emissions are deposited (wet + dry) within a 50 km radius from the stack. We assume that the remainder of the emitted Hg becomes part of the global background.

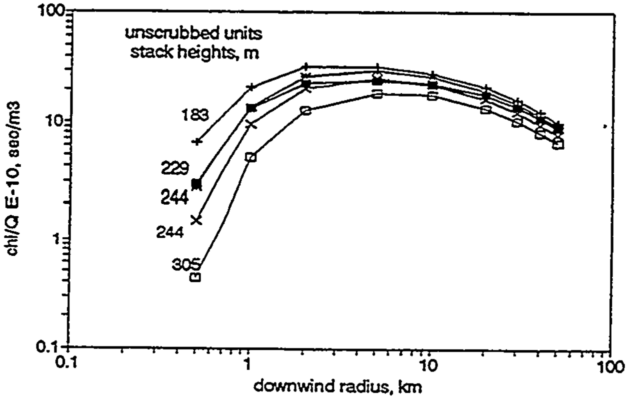

Figure 1. Dispersion factors for annual average concentrations from coal-fired power plants in the Eastern U.S., 900-1100 MW. Values are cumulative average concentrations (g/m^3) out to the specified radius, averaged around the compass, divided by annual emissions (g/s).

Although we found little reliable data on the parameters controlling mercury deposition from power plant plumes, our model compares well with measurements of wet deposition of Hg downwind of a municipal waste incinerator.[7] There is more information on the relevant atmospheric processes for background Hg, but these data may not apply to the near field (i.e., footprint) of a plume.

Probabilistic consideration of all of the vagaries of powerplant design, location, Hg emissions, transport, deposition, and bioaccumulation would entail cumulative uncertainties of several orders of magnitude. To preclude these uncertainties from dominating the risk assessment, we constrained the variability in the net effect of anthropogenic deposition above background through use of an "impact factor", representing the percentage increase in local deposition averaged over a nearby waterbody, with respect to the deposition expected from background Hg sources alone. Based on our dispersion analysis and measured background data, the impact factor was assigned a uniform probability distribution from 1.5 to 3.0 (50% to 200% increase over background). This factor includes the effects of Hg deposited on land in the watershed and subsequently transported into the lake. All other factors remaining equal, the impact factor would be proportionately lower for lower rates of Hg emissions or for a smaller fraction of Hg^{++} in the stack plume.

Baseline Mercury Levels in Seafood

We found substantial variations in the fish mercury concentrations reported in the literature for a given species. Some of this variation may be due to differences in laboratory techniques over time and the reporting of total Hg vs. MeHg, but the main sources of variability within a given species appear to be fish size and age. In addition, for freshwater species, the levels of dissolved organic carbon (DOC) and pH of the water body from which the fish were taken can affect Hg levels. We were not able to identify an effect of watershed/lake surface area ratio on Hg content from the available data, which raises questions as to the mobility of Hg deposited in a watershed. There is some recent evidence that the presence of wetlands along the lake shore may be an important factor with respect to the role of DOC.[8] The variations among the average levels of Hg between different fish species were of about the same order as those within a given species, and were probably related to the trophic level of the fish. MeHg from tuna is the largest source of dietary Hg for most Americans; average Hg concentrations are around 0.2 ppm. For other kinds of seafood, there was no difference between average mercury levels in shellfish and finfish; both were about 0.1 ug/g. Mercury levels for freshwater game fish such as pike, walleye or bass averaged about 0.3 ug/g and were more variable. There was the suggestion of a downward trend in fish Hg concentrations over time, especially for canned tuna, but this could not be confirmed statistically. Better data on fish mercury levels are needed.

Effects of Local Hg Deposition on Fish Hg Content

The above considerations apply to the baseline fish mercury concentrations, including the distributed regional effects of existing coal combustion. To estimate the incremental local effects of a hypothetical powerplant, we assume proportionality between local mercury deposition from the atmosphere and the mercury content of local (freshwater) fish. Thus, an impact factor of 1.5 corresponds to a 50% increase in the Hg content of the freshwater fish consumed, with respect to the baseline case.

Fish Consumption Rates

In order to derive fish consumption statistics appropriate for this assessment, we found it necessary to combine data from various sources. For example, much of the detailed data on distributions of seafood consumption date from 1973-74, but overall per capita consumption has increased substantially since then. We used the trend data from national overall production statistics to adjust the older distributional statistics upward to more nearly reflect current consumption levels, but this procedure may entail errors if public preferences for certain species have changed over the years. We find good support from both surveys and production statistics for an overall average per capita fish consumption rate of about 25 g/d, with a 95th percentile level of about 80 g/d. These consumption figures correspond to about 43 and 87 fish meals per year, respectively; the maximum number of fish meals in the simulation was about one per day. Surveys indicate that about 95% of the U.S. population consumes at least some fish over the course of a year.

Meals of tuna fish are assumed to have vary from 26-130 g each; all other fish portions are assumed to be vary between 100-300 g each. However, we also assume a (positive) relationship between body mass and the size of the fish meals consumed, which resulted in a mean intake parameter for the baseline case of 0.032 ug/kg/day and 0.055 ug/kg/day for the impact case. The average correlation between the number of fish meals and body mass in this simulation was 0.66, which is higher than was reported from a survey in Canada.[9] That survey only looked at total food consumption for all ages and found a linear correlation of about 0.33 with body mass. The lower correlation could have resulted in part from the nonlinearity introduced by including teenagers in the sample.

The Pharmacokinetics of Ingested MeHg

In contrast to both carcinogenic and irritant air pollutants, the dose* metric of practical concern for MeHg is neither the maximum rate of acute intake or the total accumulated intake, but the equilibrium body burden that is attained as a balance between quasi-steady rates of intake and excretion. The concept of the "reference dose" (the amount that may be consumed over a lifetime without adverse consequences[2]) would thus appear to be inappropriate here. The overall body burden of MeHg controls health responses and is directly related to measurable levels of MeHg in blood and hair, which serve as biomarkers. Because, as a practical matter, a high body burden of MeHg can only be obtained by eating fish more often (with a normal diet), the averaging process that takes place over time with respect to individual dose increments obtained from eating disparate meals is an important feature of the pharmacokinetics. Monte Carlo simulations were used to develop an empirical model of this process, which is given by

$$\log(GSD) = -1.211 + 1.766\log(GSD_0) + 0.5\log(f^*k) \qquad [1]$$

where GSD and GSD_0 are the geometric standard deviations of the original and modified fish Hg distributions, f is the frequency of consumption, and k is the elimination constant (k=ln[2]/half-life). The GSDs were reduced by about 40% at the mean according to this relationship, thus narrowing the distribution of body burdens with respect to the distribution of intake rates. Figure 2 shows how the (geometric) standard deviation of body burden decreases as the frequency of consumption increases; eating fish more often increases the mean body burden but reduces its variability. One measure of the suitability of this model may be made by comparing the variability of the simulation results with the variability of observations of blood and hair Hg. The observed data from various sources have GSDs ranging from 1.4 to 2.8; the equivalent values for body burden from our simulations were 1.74 and 2.05, depending on assumptions. If metabolic averaging is not considered, typical MeHg intake GSD values obtained by combining the distributions of Hg concentration and fish consumption can exceed 3.0[10]. Important parameters in this model that are required to predict the equilibrium body burden of MeHg include body mass and the half-life of MeHg in the body. Conversion from body burden to blood and hair concentrations requires other parameters: the fraction of Hg in blood, the volume of blood, and the hair-blood ratio. The nominal blood-body burden ratio was 0.7 with a GSD of 2.0. The distribution of hair/blood ratios was selected to match the 12 studies listed by the U.S. Environmental Protection Agency,[2] which had a weighted mean ratio of 276.

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*Although it is common in the risk assessment literature to refer to the amount ingested as the "dose," strictly speaking, the term should be reserved to indicate the amount received by the for target organ, in this case, the brain.

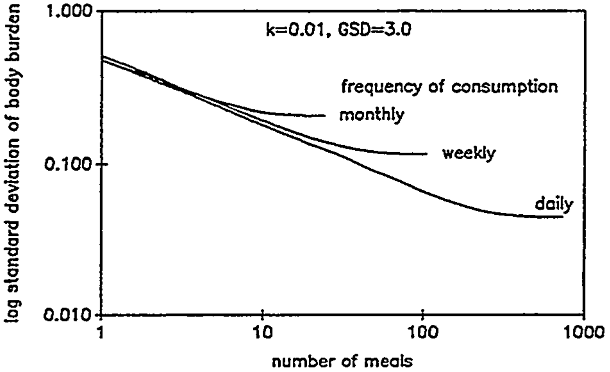

Figure 2. Simulated reduction in the standard deviation of body burden as a function of number of fish meals consumed in the time to reach equilibrium, with an underlying GSD of 3.0. (k = elimination constant)

Results of the Simulations. In order to confirm the suitability of the assumptions made in the model, comparisons were made with a set of hair MeHg concentration data first reported by Smith *et al.*[11] These data were obtained from a "demographically balanced" national sample of women of childbearing age in all 50 states. Hair samples were obtained from 1437 women and were analyzed for MeHg by gas chromatography. Food intake diaries were also completed and the average MeHg intake for the 1009 individuals reporting seafood consumption was about 1 ug/day. The highest recorded MeHg intake was 14.3 ug/d. In order to match this rate of MeHg intake for model "calibration" purposes, we deleted the freshwater fish portion of our dietary intake distribution; this yielded very good correspondence. The relevant statistics of this simulation are compared to the sample data in Table I and the hair Hg frequency distributions are compared in Figure 3. The agreement is seen to be excellent, which validates the model parameter values selected to represent MeHg intake (except for freshwater fish) and the pharmacokinetics. It is also interesting that the observed distributions of MeHg in hair are similar for those who reported eating fish and those who did not. Possible explanations include inaccurate diaries, other sources of MeHg, or confusion between Hg and MeHg peaks in the gas chromatography. Smith (personal communication, December 1994) reported a (log-log) correlation between hair Hg and dietary intake of about 0.59; we obtained a value of 0.53 from the simulation. We thus concluded that the baseline parameters selected for these simulations and their frequency distributions were consistent with observations. Simulations were then performed for the cases of interest, with freshwater fish included in the dietary intake as described above. The statistics derived from these simulations are given in Table II.

Whereas the distribution of body-burden Hg levels comprises a reasonably tight band, plots show that the scatter is greatly increased for hair Hg, varying by 2 orders of magnitude at a given intake level. This variability has important ramifications with regard to the prediction of risk estimates and the ability to develop accurate exposure-response data from observations. These results showed that the highest hair levels should not be expected to coincide with the highest body burdens or consumption rates, and thus are unlikely to relate to the presence of neurological effects on a 1:1 basis. As a further check on the interrelationships in the model,

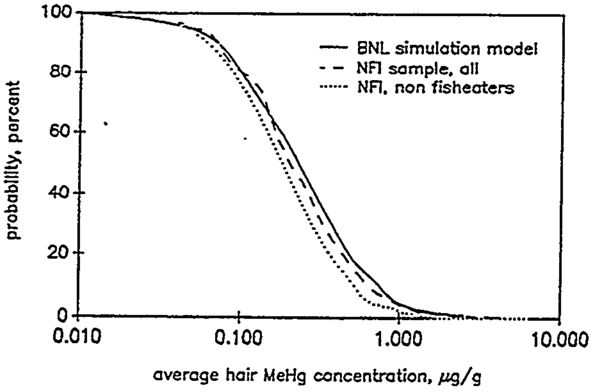

Figure 3. Comparison of simulated and measured^{11} distributions of MeHg in hair.

Table I Comparison of Observed and Predicted MeHg Statistics (n=1000)

parameter	Observed^{10}	Predicted
mean MeHg intake, ug/d	1.0	1.07
median hair concentrations*		
all subjects	0.26 (2.6)#	0.235 (2.56)
fisheaters	0.27 (2.4)	
non fisheaters	0.25 (2.5)	

* measured as MeHg but reported as Hg (ug/g)
\# ( ) = geometric standard deviation

Table II Distribution Statistics Derived from Simulations (n=5000)

	baseline			impact		
parameter	mean	median	95%	mean	median	95%
body mass, kg	73	71	104			
half life, days	72	68	118			
# meals in 5 half-lives	43	36	87			
intake, ug/d	2.5	2.0	5.7	4.3	3.5	10.6
intake parameter, ug/kg/d	0.032	0.029	0.061	0.055	0.047	1.22
body burden, mg/kg	0.0033	0.0027	0.0072	0.0057	0.0046	0.0135
blood concentration, ug/L	0.0029	0.0020	0.0086	0.0050	0.0032	0.015
hair concentration, ug/g	0.82	0.54	2.42	1.40	0.86	4.64

we compared correlations of the log of hair concentration with the MeHg intake per unit of body mass. The simulation produced a correlation coefficient of 0.41, which compares with a correlation of 0.32 between log(hair Hg) and the estimated frequency of fish consumption in a New Zealand sample.[12] These comparisons suggest that, even though hair Hg may be a reliable marker for individual MeHg exposure, the relationships between hair Hg and other measures of MeHg tend to be quite variable across a population. Note also that the inability to reliably measure low Hg concentrations (below the detection limit) will inevitably adversely affect comparisons with predictions that are made on a logarithmic scale.

HEALTH EFFECTS OF MeHg

The central nervous system is the principal target for MeHg, with the potential for effects on sensory, visual, and auditory functions. In adults, low doses may create non-specific symptoms such as paresthesia (tingling of the extremities), malaise, or blurred vision. Higher doses may bring deafness, loss of coordination when walking, and speech disorders, and, in extreme cases, coma and death.[13] Effects on fetal development may represent the most critical class of neurological effects, since the brain is thought to be most sensitive during development. Individuals may vary greatly in their responses to mercury exposure.

Adult Health Effects. Transient paresthesia is perhaps the mildest symptom of adult MeHg poisoning and was selected as the endpoint for this portion of the risk assessment. Data were available on 122 Iraqi adults and older children who consumed Hg-contaminated bread in 1971-1972.[14] Fifty-nine cases of paresthesia were observed, among other more severe neurological symptoms. It should be noted that paresthesia is not uncommon even in unexposed populations; thus some residual or background prevalence rate should be expected, perhaps of the order of a few percent.

Two indices of MeHg exposure were available for this cohort, blood concentrations and estimated consumption of bread. Blood Hg levels were determined an average of 65 days (about 1-1.5 half-lives) after the incident and have been used as an index of MeHg exposure in most previous analyses.[13] This suggests that the relevant (peak) blood concentrations may be about a factor of 2 higher than the measurements reported. Further evidence for this hypothesis is derived from exposure-response data based on the numbers of bread loaves consumed. The exposure-response function is plotted in Figure 4, based on the modified body burdens. A continuous fit to these data based on the logit function is also shown and seems to fit the observations moderately well.

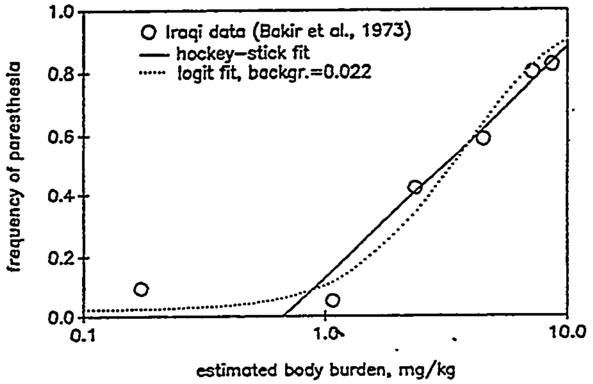

Figure 4. Exposure-response (paresthesia) data from the Iraqi grain poisoning incident. Body burden values have been adjusted to account for the delay in determining peak blood Hg concentrations.

However, Clarkson[15] represented the Iraqi data with threshold or "hockey-stick" models. The top group of data points define a nearly linear relationship quite well, as shown in Figure 4, such that the body-burden threshold depends mainly on the intersection of this diagonal line with the selected background prevalence rate of paresthesia. This methodology leads to an estimated body-burden threshold of onset of adult paresthesia of about 0.75 mg/kg, based on an average body mass of 50 kg for the affected Iraqis.

Congenital Health Effects. Three studies were found in the literature that provided quantitative data suitable for this portion of the assessment. A number of infants were exposed *in utero* during the Iraqi poisoned grain incident of 1971-2. Marsh *et al.*[16] examined 29 Iraqi children, age 4 1/2 to 5, and found that the mothers of the normal children had peak maternal hair Hg levels of 25 ug/g or less (corresponding roughly to average body burdens of 0.14 mg/kg or less). According to the authors, no specific threshold of effects could be identified because of the small sample; the threshold could have been as high as 85 ug/g. Cox *et al.*[17] reported on a much more elaborate analysis of 83 infant-mother pairs from this incident. The mean age of the children was 30 months at the initial interview. They considered frequencies of delayed walking, delayed talking, and of various neurological (CNS) signs. "Increased limb tone and deep tendon reflexes" were the most frequent CNS signs; these symptoms were also noted by Mckeown-Eyssen *et al.*[18] in Cree Indian children at lower maternal hair levels. Note that the definitions of "delayed" walking or talking were somewhat arbitrary and that exact birthdates were sometimes difficult to determine in this population. For this reason, we used the CNS symptom data in our assessment. Cox *et al.* fit logistic and hockey-stick models to these data and developed a data smoothing technique that provided functions of arbitrary shape (Figure 5). The delayed walking and talking exposure-response functions showed a suggestive increase in response around 10 ug/g, with a more definitive rise at around 100 ug/g. The latter point corresponds roughly to the body-burden threshold noted previously for adults. However, the CNS function was more nearly continuous, with the initial rise in response at around 15 ug/g peak maternal hair concentration. The curve-fits to these data suggested risks of CNS signs of 1-2% at peak maternal hair levels of 5 ug/g, for example.[17]

McKeown-Eyssen *et al.*[18] studied a group of Cree Indians in Northern Quebec in 1978. A total of 247 children, ages 12 to 30 months, were identified in four communities known to have experienced high levels of MeHg exposure. The source was fish contaminated by industrial Hg discharges. Hair samples were obtained from the mothers and a medical team examined each child for physical and neurological characteristics. The medical team was blinded to the exposure data. Confounding variables considered included amount of time spent "in the bush," maternal alcohol, tobacco, and caffeine consumption, mother's age, lactation, complications of pregnancy and numbers of previous pregnancies. The most frequent neurological finding was "abnormality of tendon reflex;" 13 boys and 14 girls. When combined with 2 cases of increased muscle tone, 15 "cases" were thus identified among the boys and a statistically significant (p=0.05) relationship was seen with prenatal Hg exposure, in the range from about 2-15 ug/g peak maternal hair concentration. There were no differences in the confounding variables between these 15 and the remaining 82 "controls." No other relationships were seen with Hg in boys, and these conditions were not associated with Hg exposure in girls. However, incoordination was negatively associated (p=0.07) with Hg exposure in girls. We find that this study offers only minimal support to the hypothesis that maternal hair levels around 10 ug/g are associated with deficiencies in childhood neurological development.

The most extensive data set currently available is that of Kjellstrom *et al.*[12] who selected 73 New Zealand children whose mothers had the highest hair Hg levels during pregnancy, out of a cohort of some 11,000 births. These cases were matched with 164 controls whose mothers had lower hair Hg levels during pregnancy. The analysis then seeks to determine to what extent maternal hair Hg levels may predict the children's IQ at ages 6-7. We performed screening analyses that found 3 low IQ outliers; after removing these points, we found a marginally significant relationship (p=0.08) between WISC-R full-scale IQ and the log of average maternal hair Hg during pregnancy:

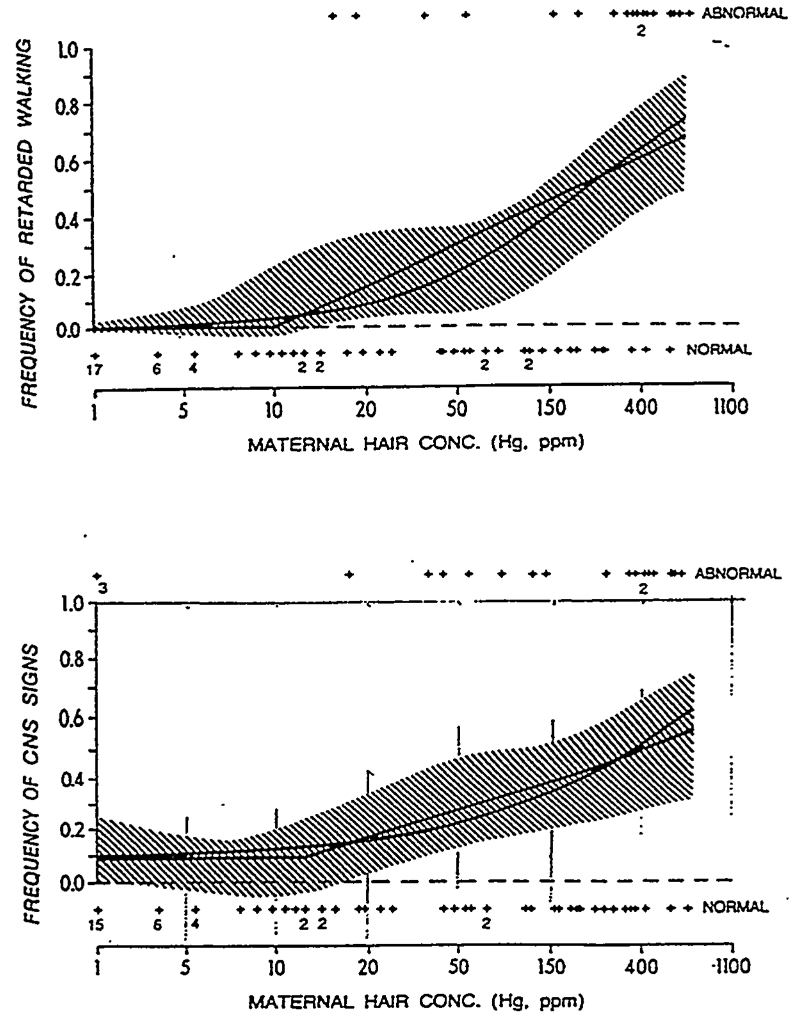

Figure 5. Exposure-response functions for the Iraqi data on prenatal exposures.[15] (a) late walking. (b) central nervous system signs. The solid lines are logit and hockey-stick fits; the shaded area represents 95% confidence limits from nonparametric smoothing analysis (reproduced with permission).

$$IQ = 0.33\ (\text{years in NZ}) + 0.37\ (\text{child's age}) - 4.7\ (\log[Hg]) + \text{dummy variables for island of origin.} \quad [2]$$

Similar regressions using the fish consumption index instead of log(Hg) were run; the fish consumption variable never achieved a p (significance) level below 0.25. An analysis of possible thresholds in the IQ exposure-response function suggested threshold values anywhere from 4-10 ug/g average maternal Hair Hg. The report of Lipfert[19] provides more details on the reanalysis of the New Zealand data.

Some of the problems with this study include the methods used to select "cases" (exposure rather than outcome), the lack of data on social class, and the possibility of postnatal exposures including exposures to other neurotoxins. Use of only the highest 0.7% of the hair Hg observations to define "cases" may place undue importance on whatever spurious high observations that may have been included. Nevertheless, the New Zealand data imply that average maternal hair Hg levels above about 3-10 ug/g (4.5-15 ug/g as peak hair levels, based on a factor of 1.5 to convert from average hair Hg to peak Hg levels during pregnancy, as suggested by Kjellstrom *et al.*[12]) may carry the risk of a small decrement in the mental development of the offspring, as typically measured by IQ.

Although each of these studies has certain flaws, they all support the onset of children's neurological effects at average maternal hair levels around 10 ug/g. The curve-fits to the Iraqi data by Cox *et al.*[17] seem to provide the best basis for quantitative risk assessment.

ESTIMATED HEALTH RISKS

Adults

The risk analysis simulations were performed for 5000 trials, intended to represent a hypothetical population of 5000 who derive a substantial portion of their fish diet from local waters. We then compare their risks with and without additional Hg deposition into these waters from a nearby coal-fired power plant. We examine the 99th percentiles of these exposure distributions; the statistics would become unreliable for probabilities further out on the "tail." All of the body burden predictions fell well short of the paresthesia threshold of 0.75 mg/kg (Figure 4). The 99th percentile body burden was 0.01 mg/kg for the baseline and was approximately doubled by deposition from the hypothetical power plant. These values are almost two orders of magnitude below the onset of adult paresthesia observed in Iraq.

Prenatal Exposures

The analysis of congenital health risks proceeds from the same simulations used for adults; no changes in diet or body weight were assumed for pregnant females. All of the exposure-response information on congenital effects was keyed to maternal hair concentrations. Fortunately, we have observations on the distributions of hair Hg to judge the acceptability of the simulated hair Hg distributions.

The simulations predicted average MeHg hair concentrations of 4.5 and 8.1 ug/g at the 99% level, for baseline and impact cases, respectively. We also noted that the baseline difference according to whether (predatory) fresh-water fish is consumed is larger than the effect of the hypothetical power plant. Estimates of the probability of neurological effects due to prenatal exposure may be made by combining the probabilities of exposure and the probability of effects. Using the data tabulated by Cox et al.[17] at a peak maternal hair level of 5 ug/g, we estimated overall risk probabilities of 0.0002 to 0.0004 for the baseline case and 0.0008 to 0.0017 for the impact case. These risk estimates depend somewhat on the intersection point between exposure and response that is selected for evaluation, as well as on the type of curve-fit used to extrapolate the original exposure-response data. The predicted congenital risks are about an order of magnitude higher than the predicted adult paresthesia risks based on similar extrapolations.

CONCLUSIONS

We conclude from this assessment that neurological health risks to adults in the United States from eating fish containing methylmercury are trivial, with or without the local effects of coal combustion. The margins of safety for congenital risks are lower, but this portion of the analysis is compromised by uncertainties in the indices of exposure used (maternal hair concentrations). We also conclude that, given the many elements in such risk assessment and the opportunities for error, it is essential to compare predictions with observations as a form of "reality check."

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Emissions of air toxics from coal combustion: measurement and control

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ABSTRACT

Since coal contains virtually all the elements, combustion of coal is a potential source of many trace elements and organic compounds to the atmosphere. Accurate measurement and monitoring of air toxics are required to determine contributions to ambient air pollution, to provide emission factors for inventory calculations and to determine whether control technologies are required.

It has been estimated that coal combustion may be responsible for over 35% of Hg emissions and around 20% of Sb emissions to the atmosphere globally. Between 5 and 20% of global emissions of Cr, Cu, Ni, Se, Sn, Tl and Zn may also arise from coal combustion. Coal combustion is only an important source of complex organic compounds if combustion systems are inefficient.

These values for emissions of trace species are estimates based upon the best available data. The wide variation in the composition of different coals, differing combustion conditions and pollution control equipment make it difficult to estimate emission values with any accuracy. More accurate estimates may be available once sampling and analysis techniques for stack emissions have been optimised and standardised. Measurement techniques for trace emissions are still under development and few countries have published any official guidelines. Methods for the measurement of trace emissions are specified by law only in the USA, and those which apply to trace emissions are still subject to review.

Currently there are no widely available control technologies designed specifically for the removal of the low concentrations of trace elements and organic compounds from coal-fired power stations. Existing legislation for the control of particulate emissions effectively controls emissions of the majority of trace elements and some organic compounds. However, elements and organic compounds which remain in the vapour phase pass through such devices largely uncontrolled. Flue gas desulphurisation technologies may efficiently capture many of the remaining vapour phase pollutants. Over 90% of the halogens, 70% of the Hg and 40-50% of the B and Se may be captured by FGD systems. However, an integrated approach to pollution control requires that reductions in air emissions do not increase pollution from solid or liquid wastes.

In future, emissions of trace elements and organic compounds may be subject to stringent emission limits. This may pose two problems;

- new, more efficient or more specific flue gas cleaning systems will have to be designed, and
- methods for sampling and analysis of trace emissions must be defined which can provide the required accuracy and reliability.

INTRODUCTION

Combustion of coal is a potential source of emissions of many trace elements and organic compounds to the atmosphere. Some of these are toxic to animals and man or may become so by interacting with other pollutants. It is important that emissions of toxic air pollutants from sources such as coal combustion are measured and, if necessary, controlled in order to limit any environmental effects. Increasing concern about the effects of trace pollutants in the environment may lead to the introduction of emission standards for some of these species. If such emission standards are adopted they must be supported by commercially available equipment which can measure and monitor the emissions with enough accuracy to ensure compliance.

Several reviews have been published by IEA Coal Research on emissions from coal combustion. These include the halogens (Sloss, 1992), trace elements (Clarke and Sloss, 1992), and organic compounds (Sloss and Smith, 1993). A complementary report has also been published on sampling and analysis of emissions of these compounds from coal-fired power station stacks (Sloss and Gardner, 1994). This paper draws together the conclusions from these reports.

EMISSIONS OF AIR TOXICS

Various estimates have been published which attempt to evaluate coal combustion as a source of total global air toxic emissions, from both human activities and natural sources. Data from Nriagu and Pacyna (1988) indicate the importance of coal as a source of some trace elements on a global scale. For example, coal combustion is a significant source of Hg emissions to the atmosphere, accounting for up to 38% of total emissions. Coal combustion may also be responsible up to 21% of Sb emissions, around 18% of Ni and Se emissions and 15% of Cr emissions. Less specifically, it has been suggested that energy production from all fossil fuels is the largest single source of Hg (38%), Ni (52%), Sn (64%) and V (74%) emissions and the second largest global source of Sb (21%), Cd (9%), Se (23%) and Tl (22%) (Nriagu, 1990).

In Europe, human activities are thought to account for up to 90% of Hg emissions to the atmosphere (Hellner and Lövgren, 1990). In the USA, coal-fired power plants are reported to be responsible for between 15 and 20% of the total national Hg emissions to the atmosphere (EPRI, 1994*).

With respect to emissions of organic compounds, including non-methane volatile organic compounds (NMVOC) and polycyclic aromatic hydrocarbons (PAH), coal combustion does not appear to be a major source on a global scale. In a review of global emissions of NMVOC by Piccot and others (1992), emissions from coal combustion were not significant enough for it to be included as a source. Major sources of NMVOC on a global scale included fuel wood utilisation (20%), savanna burning (16%) and petrol preparation, transport and use (16%).

Combustion sources, including coal combustion, incineration and agricultural burning, account for over 90% of the atmospheric concentrations of polycyclic aromatic hydrocarbons (PAH) (Hutzinger and Reischl, 1991). However, in a review of PAH emissions in the Norway, Sweden and the USA, Baek and others (1991) concluded that coal combustion for power generation contributed less than 5% of total PAH emissions. Industrial processes, including coke plants, were responsible for up to 69% of emissions and residential heating, using coal and other fuels, gave rise to another 36%. These estimates are for emissions of all unspecified PAH. However, emissions of individual PAH compounds may be more specific to individual sources. Data on emissions of individual PAH compounds are rarely available.

The values cited above are examples of emission inventories calculated for air toxics. The large number of air toxics and their possible sources, both natural and from human activities, make estimation of such global and regional budgets difficult. Emissions from coal combustion are commonly calculated by multiplying the amounts of coal used in coal-fired power stations by emission factors. These emission factors are estimated from what is known about the average concentration of the air toxic or air toxic precursor in coal and/or from measured emissions of air toxics from representative sources. Accurate values for total amounts of coal combusted may be available. However, the wide variation in the composition of coals, in combustion conditions, and in pollution control equipment need to be taken into account when estimating emission factors. Furthermore, many of the techniques used for the measurement of emissions of trace species, and thus for the estimation of emission factors, are still under development and are known to have serious limitations. Estimates for global and even regional emissions of trace species from most sources can therefore be considered as no more than educated guesses.

LEGISLATION

Concern over the emissions of air toxics from all sources and their potential effects in the environment has lead to the introduction of legislative controls at several levels.

The North Sea Convention of March 1990 produced an international agreement signed by Belgium, Denmark, France, Germany, the Netherlands, Norway, Sweden, Switzerland, the UK and the Commission of the European Communities. The Convention listed As, Cu, Cr, Ni and Zn as priority pollutants and stipulated that emissions of these elements to the atmosphere must be reduced by at least 50% by 1999 (compared with 1985 values). Emissions of Cd, Hg and Pb must be cut by 70% in the same time period (Weiderkehr, 1991). The same convention also specified a target reduction of 70% for dioxin emissions to the air in the same time period.

Although NMVOC are also limited by a UNECE agreement, it is unlikely that controls will be necessary from utilities using coal since the contribution from these source to total emissions of NMVOC is virtually negligible (Sloss and Smith, 1993).

National legislation specific to the emission of individual trace elements or organic species is not common and has only been specified in Austria, Germany and certain states in Australia (AHC, 1992; Maier, 1990; Nilsson, 1991). This legislation is summarised in Table 2. As some of this legislation deals with classes of compounds rather than individual air toxics, the inaccuracy associated with the measurement of each individual species is increased when total emissions of each species have to be added together.

The 1990 US Clean Air Act requires the evaluation of emissions of several trace elements and organic species with a view to the possible introduction of relevant legislation in the future. It is unclear whether such legislation will apply specifically to power stations (Chow and others, 1990). Legislation for power stations is also being considered in Canada and the Netherlands.

Although no specific emission standards apply in Sweden, electrical utilities are required to fit best available technologies. These include particulate controls and FGD processes and therefore result in a substantial reduction in the emissions of most trace elements and some organic compounds. Reductions in emissions of air toxics are therefore likely to occur in most countries where efficiency is promoted and best available control technologies are required. In addition to these requirements, most countries have ambient air quality criteria for some air toxic species (Clarke and Sloss, 1992).

It is interesting to note that countries such as Austria and Australia have emission standards for trace pollutants but no standards for their sampling and analysis whereas countries such as Japan, the UK and, for the moment, the USA, have standards for sampling and analysis but no emission emission standards for trace species. Emission standards are becoming more stringent and, in the future, it is likely that emission limits for air toxics will be introduced more widely for sources such as coal-fired power plants. However, emission standards are worthless if the emission concentrations they specify cannot be measured accurately and on a regular basis by operators and regulatory authorities.

MEASUREMENT OF EMISSIONS

Sampling and analysis techniques for the measurement of trace species at the concentrations emitted from coal-fired power plants are still under development. Countries such as Germany, Japan and the UK have published guidelines for sampling and analysis of some trace pollutants. In the USA, the methods are specified by law within the Code of Federal Regulations. However, many of these methods are known to have inherent problems and are still subject to review.

The majority of sampling techniques are based, initially, on the separation of gases from particles. Particles of a pre-determined minimum size may be collected on filters, in cyclones or in cascade impactors. The particles collected in such systems may be weighed and analysed to provide data on trace emissions which are non-volatile. However, each of these techniques are known to have problems:

- filters are liable to clogging, may irreversibly adsorb some air toxics, and may contain background contamination which interferes with analyses (Meij and others, 1989; Dams, 1992).
- cyclones may suffer from pressure drop problems and samples may be affected by the collection of sulphuric acid mist within the cyclones (Maxwell and others, 1993).
- cascade impactors suffer from the association of particles with the impactor walls, particle bounce and particle "blow-off", all of which results in incorrect particle-size distribution data (Masterson and Barnert-Wiemer, 1987).

Particle collection systems may also be used to remove particles from the flue gas so that gaseous species may be studied separately. Although some gaseous species may be analysed directly by analytical instruments, such instruments are rarely portable. Samples are more commonly transported to the laboratory for analysis. Gases may be kept in the gas phase if they are sampled into inert chambers such as Tedlar bags. However, it is not known whether air toxic species such as organic compounds continue to react within such chambers. More commonly gaseous species are captured in solid or liquid phases where they are more stable. Some vapour-phase species may be reduced to liquid form simply by condensation in cooled chambers. Other species are captured in a series of impinger bottles containing solutions which selectively solubilise the species of interest. Various impinger solutions are available and some examples are listed in Table 1.

Commercially available solid resins such as XAD or Tenax can be used to capture organic species in a relatively stable form. Activated carbon can be used to capture both organic compounds and volatile trace metals such as Hg. Although solid sorbents have the advantage of allowing volatile species to be trapped and transported in a stable form, some have problems with background contamination and decomposition products (Sloss and Gardner, 1994).

Many different types of sampling system are available. As mentioned earlier, some are specified by law or by national guidelines. However, there is no general agreement over which technique is the most suitable. Comparisons of different techniques have been performed with respect to their suitability for use with air toxics, for example for dioxins (Coleman, 1993) or Hg (Nott and others, 1994). However, since there is no definitive way of determining the actual concentration of trace pollutant in flue gases, it is not possible to identify which technique produces the most accurate result.

The primary aim of any sampling system is to obtain a sample which is representative of the flue gas. This depends not only upon suitable sampling equipment but also the way in which the equipment is used, the selection of an appropriate sampling location or locations, the timing of sampling, and the collection of enough samples to reflect any variation within the flue. Therefore, the skill of the crew performing the sampling is probably the variable which is most important to control.

Analytical systems are normally instruments which are highly automated if not computer controlled. The areas where errors arise in such systems are due to either miss-preparation of samples, miss-calibration or poor operation of the system, or miss-interpretation of the results, all of which are under operator control (Sloss and Gardner, 1994).

Hence, the greatest source of error in both sampling and analysis systems may be the human operator. Variation due to different levels of skill between operators should be minmised. In countries where sampling and analysis methods are specified, measurement crews are required to adhere to strict protocols and to adhere to well-defined quality control and quality assurance procedures. In addition to this, the USA is planning to introduce accreditation schemes which all measurement personnel must pass.

Measurement techniques are designed to produce a single final result to represent the concentration of an air toxic species in the flue gas. This value may be used to estimate an emission factor. However, the use of such values for emission calculations must take into account the following limitations:

- sampling and analysis techniques are not at the stage where they are accurate enough to produce a single value which would be considered representative; and
- from what is already known of the behaviour of air toxics in coal-fired systems, emissions of air toxics are never constant, they vary with coal type, combustion conditions, pollution control systems and even depend on the concentration of other pollutants within the flue gas with which they may react.

If single emission values are inappropriate, how then are emissions to be presented? Ideally concentrations should be presented as an average value accompanied by a confidence range showing the full range of values into which the actual concentrations may fall. If legislation is ever introduced specifically for any air toxic species, continuous emissions monitoring will be required to ensure compliance. Continuous emissions monitors produce virtually real-time data, avoiding transport and handling errors, and providing true representation of air toxic concentrations over time. Continuous emissions monitors are not currently available for air toxics. However, many systems, such as those based on FTIR, are under development (Sloss and Gardner, 1994).

EFFECTS OF EMISSION CONTROL TECHNOLOGIES

Currently there are no widely available control technologies designed specifically for the removal or trace elements or organic compounds from coal-fired power stations. However, technologies for the removal of particulates, such as electrostatic precipitators (ESP) and fabric filters, and control technologies for SO_x and NO_x, may affect emissions of air toxics.

Particulate control systems capture any pollutants which are associated with the particles retained. The capture of individual air toxics thus depends upon their volatility. Most trace elements are not especially volatile and are captured efficiently by particulate controls, for example only 2% of Cd in the flue gases passes ESP uncaptured. However, B and Se are slightly more volatile and between 20 and 30% of these elements may pass uncaptured. Since Hg is even more volatile, between 70 and 80% remains in the flue gas beyond particulate controls. Unless lime or a similar sorbent has been used in the boiler, virtually all the halogen gases pass through particulate controls (Clarke and Sloss, 1992; Sloss, 1992).

The volatility of organic compounds is usually temperature dependent, hence capture efficiencies vary greatly between pollution control systems. Although some organic compounds associated with particulates will be captured, it would seem that, at the temperatures of most particulate control systems (<200°C), organic compounds are generally still in the vapour phase and thus escape in the flue gases (Sloss and Smith, 1993).

There is increasing concern that the temperatures and other conditions found in ESP may be ideal for the production of dioxins and furans. Although this has been proven in waste incineration systems operating at higher temperatures (>240°C) (Dickson and others, 1992), no evidence has been published for this effect in coal-fired power stations.

Wet and dry flue gas desulphurisation (FGD) systems, required in many countries to remove SO_x, incidentally remove some other air toxics. For example, Figure 1 shows the average removal of volatile elements in wet-lime FGD systems in the Netherlands. Various studies have shown removal efficiencies from the flue gas of 30-50% for Hg and 60-75% for Se by wet scrubbers. The overall removal of Hg in various spray dry scrubber systems varies from 35% to 85%. Reductions of over 90% for all the halogens have been achieved in both FGD systems. However, it is important to note that the sorbents used in such systems may be a source of some trace elements to combustion systems (Clarke and Sloss, 1992; Sloss, 1992). The capture of organic compounds in FGD systems is not well documented but, in general, depends on the volatility and also the solubility of the individual compounds (Sloss and Smith, 1993).

Combustion modifications for NO_x control may lead to increased concentrations of unburned carbon in flue gases. It is not clear to what extent this unburnt carbon may affect the distribution and behaviour of air toxics. NO_x control systems do not appear to reduce or increase trace or minor element emissions. Although emissions of most organic compounds do not appear to be affected significantly by such systems, it has been reported that oxidative catalysts used in NO_x control may also oxidise, and thus destroy, dioxins and furans (Achyra and others, 1991).

SPECIFIC CONTROL OF AIR TOXICS

There is currently no requirement for the specific removal or abatement of air toxics from the flue gases of coal-fired power stations. However, in the future, legislation on air toxics emissions is likely to become more stringent. Some specific technologies for the capture of air toxics are already under development and some are commercially available for use on waste incineration units. Concentrations of the more harmful air toxics, such as Hg and dioxins, may be several orders of magnitude higher in flue gas emissions from waste incinerators than from coal-fired power plants.

Work has already been started in several countries to reduce emissions of air toxics from waste incinerators. Some of the technologies used in waste incinerators may be applicable, with modification, to coal-fired units (Clarke and Sloss, 1992).

Sorbents which are available for the removal of heavy metals, such as Hg, from flue gases, include those based on activated carbon, zeolites, siliceous materials, alumina, and calcium compounds. However, the use of some of these in coal-fired power stations may be limited due to low operating temperatures, harmful secondary effects and the high cost of some sorbents (Mojtahedi and Mroueh, 1989). Activated carbon is also being tested at pilot scale in coal-fired systems for the specific adsorption of organic vapours from flue gases (Makansi and others, 1992). Sorbents for air toxics removal may be used in two ways:

- direct injection as powder for in situ removal: or
- the flue gases may be passed through a fixed filter or fluidised bed of sorbent.

Further research is required to assess the application of such systems for use in power stations. In addition, consideration must be given to the potential disposal problem of sorbents with elevated concentrations of pollutants.

A novel process, based on the exposure of flue gases to pulsed and direct-current corona discharges, is also being investigated for the decomposition of organic compounds such as benzene, toluene and phenol (Belousova and others, 1992).

CONCLUSIONS

Coal combustion is an important source of some trace elements and organic compounds to the environment.

Existing legislation for the control of particulate emissions effectively controls emissions of the majority of trace elements and some organic compounds. However, elements and organic compounds which remain in the vapour phase pass through such devices uncontrolled. Flue gas desulphurisation technologies may efficiently capture many of the remaining vapour phase pollutants. Over 90% of the halogens, 70% of the Hg and 40-50% of the B and Se may be captured by this means. In future, emissions of some trace elements and organic compounds may require the implementation of more efficient or more specific flue gas cleaning systems.

Perhaps the most important priority for both regulatory authorities and plant operators should be the development and standardisation of sampling and analysis techniques for the measurement of trace emissions. Sampling and analysis techniques are vital for:

- studying the behaviour of air toxics in coal-fired power plants;
- estimation of emission factors for use in calculation emission inventories;
- studying the effects of pollution control equipment and to investigate new technologies for the control of air toxics; and
- ensuring compliance of sources with any emission standards which are introduced.

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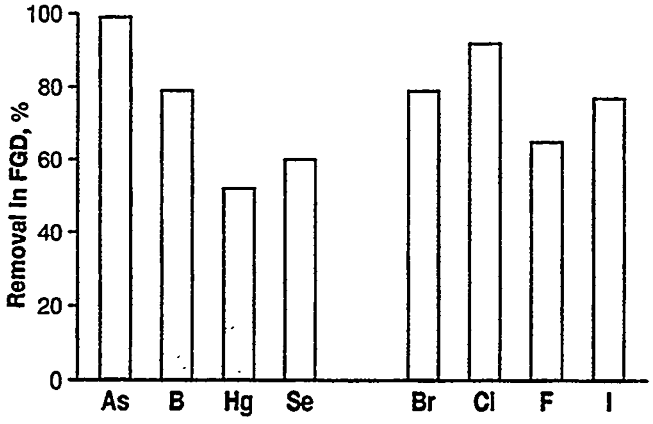

Figure 1 Average removal of volatile elements in wet-lime FGD systems in the Netherlands (Meij, 1992)

Table 1 Impinger solutions for the extraction of various trace species

Target Species	Impinger solution(s)	Reference
HCl	distilled water	Environment Canada, 1989a
HCl	hydrogen peroxide then sodium hydroxide	Jackson and King, 1993
HCl	sodium hydroxide	Vesterinen, 1994
HCl HBr HF Cl_2 Br_2	sulphuric acid then sodium hydroxide	US EPA Method 26
HF	sodium hydroxide	Jackson and King, 1993
Hg Cd	potassium permanganate in sulphuric acid	US EPA Method 101A
Hg Cd	nitric acid	Jackson and King, 1993
Hg (species)	deionised water then nitric acid/hydrogen peroxide then potassium permanganate/sulphuric acid	DeVito and others (1993)
Hg	hydrogen peroxide	Meij, 1991 (review)
Hg	ammonium persulphate with/without silver nitrate	Meij, 1991 (review)
Hg	potassium dichromate in nitric acid	Meij, 1991 (review)
Hg	iodine chloride	Meij, 1991 (review)
Pb	nitric acid	US EPA Method 12
trace elements	nitric acid	Gemmill and others, 1991
trace elements	hydrogen peroxide then potassium permanganate in sulphuric acid	Meij and others, 1984
trace elements	nitric acid/hydrogen peroxide then potassium permanganate in sulphuric acid	US EPA Method 29

Table 2 National Legislation for air toxic emissions from coal-fired power plants

Country	Air toxic	Limit, mg/m^3
Australia	As, Cd, Hg, Ni, Pb, Sb, V	Varies between States and Territories
Austria	Cr, Pb, Zn As, Co, Ni Cd and Hg	2.0 (total of all three) 0.5 (total of all three) 0.05 (total separately)
Germany	Inorganic dust	
Category I	Cd, Hg, Tl	0.2 (total of all three)
Category II	As, Co, Ni, Se, Te	1.0 (total of all three)
Category III	Cr, Cu, Mn, Pb, Pd, Pt, Sb, Sn, V	5.0 (total of all three)
Organic substances		
Category I		20 (total)
Category II		100 (total)
Category III		150 (total)
Carcinogenic substances		
Category I	(including BaP)	0.1 (total)
Category II	As, Co etc	1.0 (total)
Category III	hydrazine etc	5.0 (total)
Planned legislation	Canada, the Netherlands, the USA	

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COAL-WATER SLURRY REBURNING FOR NO_x EMISSIONS CONTROL

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ABSTRACT

The Energy and Environmental Research Corporation (EER) has designed, installed and tested several natural gas reburning systems for NO_x control. Coal reburning has also been studied by EER and demonstrated by others. Coal-Water Slurry(CWS) reburning offers the potential to significantly lower the cost of NO_x control. This paper describes the retrofit application of coal-water slurry as a reburn fuel on a pulverized coal fired utility boiler. A comparative analysis is provided with respect to boiler performance and combustion efficiency between the proposed (CWS) reburn fuel and the demonstrated natural gas / coal reburn fuels. An economic evaluation of the capital and operating cost of a typical utility boiler is also presented.

INTRODUCTION

This paper assesses natural gas(GAS), pulverized coal (PC) and coal water slurry (CWS), as reburn fuels for a generic 500 MWe coal fired boiler. Reburning is an in-furnace combustion modification process for reducing NO_x emissions which has been extensively studied over the last 20 years and has been successfully retrofitted to all types of boilers (wall, tangential and cyclone). The reburning technology is particularly significant for cyclone fired units because of difficulties in retrofitting other types of in-furnace NO_x control techniques.

REBURNING TECHNOLOGY

The reburn process can be divided into three zones: a primary combustion zone, a sub-stoichiometric reburn zone, and a burnout or overfire air zone. The characteristics of each zone can be summarized as follows:

- Primary Zone: The heat released in the primary combustion zone usually accounts for 80-100 percent of the total heat release. Suitable residence time and excess air (10 to 15%) are provided to minimize the unburned primary fuel entering the reburning zone.

- Reburning Zone: The remaining 0 to 20 percent of the heat is added by injection of the reburning fuel into the reburning zone to create fuel rich conditions. The reburn zone overall stoichiometric air is lowered to approximately 0.9. In this environment, the NO_x from the primary combustion zone reacts with hydrocarbon fragments, carbon monoxide and hydrogen which are formed during the partial oxidation of the reburning fuel. A substantial portion of the nitrogen oxide species are converted to diatomic nitrogen (N_2). Flue gas recirculation (FGR) may be used with the GAS and PC reburn systems to provide for penetration of the fuel across the furnace. For the CWS case, flue gas recirculation is not required. The momentum provided by the slurry and atomizing air is sufficient to provide the fuel penetration required for proper dispersion throughout the reburn zone.

- Burnout Zone: In the final zone, air is supplied to maintain the normal boiler overall excess air conditions (15 to 20 % excess air) while to oxidizing the remaining reburn fuel in the flue gas to complete the combustion process.

The retrofit equipment must be designed to be compatible with the existing furnace which requires a site specific analysis. Flow modeling studies are undertaken to simulate aerodynamic mixing of the injected reburning streams and burnout air streams with the bulk flue gas. EER's numerical computer models are also used to predict NO_x reduction and thermal performance during reburn system operation.

PERFORMANCE ANALYSIS

An evaluation was performed to assess the effect of reburn fuel type on utility boiler performance. The use of coal-water slurry as a reburn fuel was compared to pulverized coal and natural gas. This analysis was based on the measured performance of a 170 MWe wall fired unit on which EER is currently demonstrating long-term gas reburn operation. Although this analysis was not performed on a specific 500 MWe cyclone unit, the analysis does provide a view of the relative impact of reburn fuel characteristics on boiler performance. For this study, an EER two-dimensional computational model was used.

Four cases were examined: 1) a baseline case with no reburn fuel, 2) a natural gas (GAS) reburn case, 3) a pulverized coal (PC) reburn case, and 4) a coal water slurry (CWS) reburn case. The representative fuel analyses and higher heating values for fuels used in the modeling study are given in Table 1. Table 2 is a summary of the key parameters and mass flow rates at 100% load for the four cases. This study assumes that the baseline coal is the same parent coal used for the PC case and the CWS case.

TABLE 1 FUEL ANALYSES

Natural Gas		Baseline/Pulverized Coal		Coal Water Slurry	
Composition	Vol% (dry)	Proximate Analysis	Wt%	Proximate Analysis	Wt%
CH_4	82.8	Fixed Carbon	42.3	Fixed Carbon	32.6
C_2H_6	6.0	Volatile Matter	33.2	Volatile Matter	25.6
C_3H_8	1.8	Moisture	14.8	Moisture	33.3
CO_2	2.2	Ash	9.7	Ash	7.5
N_2	7.2				
Specific Gravity:		Ultimate Analysis	Wt%	Ultimate Analysis	Wt%
0.6535		Carbon	58.3	Carbon	44.9
		Hydrogen	4.0	Hydrogen	3.1
		Oxygen	11.6	Oxygen	9.0
		Nitrogen	1.2	Nitrogen	0.9
		Sulfur	0.4	Sulfur	0.3
		Ash	9.7	Ash	7.5
		Moisture	14.8	Moisture	34.3
Higher Heating Value:		Higher Heating Value:		Higher Heating Value:	
982 Btu/scf		10,116 Btu/lb		7,801 Btu/lb	

TABLE 2 SUMMARY OF KEY PARAMETERS

	Case 1	Case 2	Case 3	Case 4
Parameters	Baseline	GAS Reburn	PC Reburn	CWS Reburn
% of Heat Input:				
Coal/Reburn Fuel	100/0	82/18	80/20	80/20
Stoichiometric Ratio:				
Burner Level	1.17	1.10	1.12	1.12
Reburn Fuel Level	1.17	0.90	0.90	0.90
Furnace Exit	1.17	1.17	1.17	1.17
Fuel Flow (lb/s):				
Coal Burner	41.03	33.73	32.83	32.83
Reburn Fuel	0	3.99	8.20	10.65
FGR (lb/s):				
Reburn Zone	0	13.76	12.52	0
Air Flow (lb/s):				
Coal Burner	365.21	283.20	280.62	280.62
OverFire Air	0	83.73	84.59	84.59
Total Mass In (lb/s): (including FGR)	406.24	418.41	418.76	408.69

TABLE 3. IMPACTS OF REBURN FUEL TYPE ON BOILER PERFORMANCE

Case Number	Case 1	Case 2	Case 3	Case 4
Case Definition	Baseline	GAS Reburn	FPC Reburn	CWS Reburn
Exit Gas Temp. (°F):				
ReHeat (rear)	1304	1318	1315	1302
Primary SuperHeat	753	762	759	751
Economizer	712	717	717	710
Air Preheater	314	318	316	316
Steam Flow (lb/s):				
Main Steam	314.4	312.2	318.1	317.7
ReHeat Steam	258.7	258.9	261.6	260.6
Attemperation Flow (lb/s):				
SuperHeat	6.13	12.66	7.98	4.53
ReHeat	1.59	3.64	1.58	0.77
Water/Steam Temp. (°F):				
Economizer Inlet	487	487	487	487
Economizer Outlet	499	501	499	499
Primary SH Inlet	636	636	636	636
Primary SH Outlet	798	820	807	796
Sec. SH Attemperator Outlet	777	775	780	780
Sec. SH Outlet	985	985	985	985
RH Attemperator Outlet	638	625	638	643
RH Outlet	1002	1002	1002	1002
Heat Absorption (MMBtu/hr):				
Furnace	720.2	697.7	723.6	731.2
Economizer	16.7	18.1	17.4	17.2
Primary Super Heat	231.1	242.5	240.2	233.2
Secondary Super Heat	161.5	163.0	161.2	159.6
ReHeat	181.3	187.8	183.3	180.0
Unburned Carbon in Ash (%)	2.67	4.89	5.77	6.09

Boiler Performance and Carbon Burnout

The predicted impacts of the reburn system, operated with various reburn fuels, on boiler performance are shown in Table 3. The variation of the backpass gas temperature caused by different reburn fuels is insignificant. The attemperation flows for the PC and CWS reburn fuels are lower than that of the GAS reburn case since more heat is absorbed by the furnace walls and less heat becomes available in the convective sections for the coal reburn fuels.

The CWS reburn fuel is conservatively projected to yield the highest carbon loss in the fly ash among the three reburn fuels studied due to its water content. CWS has never been tested as a reburn fuel at full scale. EER has developed a new atomizing nozzle, the VEERjet™, which gives superior CWS atomization compared to conventionally available dual fluid nozzles. Improved atomization and good fuel dispersion could increase the rate of coal combustion thereby reducing the predicted carbon loss in the ash.

Boiler Efficiencies Table 4 displays the impacts of reburn fuel upon the boiler thermal efficiency, based upon the ASME heat loss method. Evaluation of boiler performance showed that all three fuels should perform similarly. Based on a computer modeling simulation of the three reburn fuels, the boiler efficiency for the baseline case was 86.9%, for GAS reburn 85.8%, for PC reburn 86.4% and for CWS reburn 85.7%. Both the natural gas and CWS reburn fuels result in an efficiency loss of about one percent lower than the baseline. The increased heat loss due to H_2O generated from the combustion of H_2 is the main cause of efficiency loss for the reburn gas while the heat losses due to fuel moisture and unburned fixed carbon in ash are slightly more significant for the CWS reburn case. Using coal as a reburn fuel results only in about one-half per cent drop in efficiency. This is due primarily to increased carbon loss in the fly ash. Among the three types of reburn fuels presented, the results show that coal reburn has the smallest effect on boiler thermal efficiency. However, to determine the impact on net power available for sale for each of these three reburn fuels, based on identical fuel heat input rates, auxiliary power use will have to be accounted for as well.

Table 4 IMPACTS OF REBURN FUEL TYPE ON BOILER EFFICIENCY*

Case Number	Case 1	Case 2	Case 3	Case 4
Case Definition	Baseline	GAS Reburn	PC Reburn	CWS Reburn
Heat Loss (%):				
Due to Dry Gas	5.12	5.07	5.17	5.13
Due to Moisture in Fuel	1.70	1.38	1.70	2.37
Due to H_20 from Fuel H_2	4.15	5.39	4.16	4.15
Due to Combustible in Ash	0.38	0.60	0.88	0.91
Due to Radiation	0.22	0.22	0.22	0.22
Unmeasured Losses	1.50	1.50	1.50	1.50
Total Heat Losses	13.07	14.16	13.63	14.28
Boiler Efficiency (%)	86.93	85.84	86.37	85.72

* Based on ASME Heat Loss Method at Full Load

TEST DATA

A series of pilot scale reburn tests utilizing CWS were performed by EER. These tests were funded by Electric Power Research Institute - Upgraded Coal Interest Group (EPRI-UCIG). The reburn tests were performed on EER's 800,000 Btu/hr Boiler Simulator Facility (BSF) located in Santa Ana, California. The BSF was configured to simulate full scale utility boiler conditions. This test unit has been used to characterize GAS reburn and PC reburn in the past.

A primary objective of the experiments was to obtain parametric coal-water slurry reburning data which could be used for comparison with dry pulverized coal and natural gas reburning results. The tests were designed to characterize the main parameters known to control reburn performance. Test parameters and the range over which each parameter was varied were as follows:

Coal type: Kentucky or Pennsylvania
Coal grind: Nominal (70% < 200 mesh) or fine (70% < 325 mesh)
Coal form: Coal-water slurry, dry pulverized coal
SR_2: 0.8 - 1.05
Reburn zone residence time: 400 - 1000 ms
Baseline NO_X: 400 - 1300 ppm
Atomization medium: Air or Nitrogen
Injection temperature: 2600 - 2700°F

Reburn performance as a function of the major test parameters can be summarized as follows: Fine grind (70% < 325 mesh) performed slightly better than nominal grind (70% < 200 mesh), most likely due to an earlier release of volatiles with the fine grind. Performance was generally similar for CWS and PC. At short residence time, PC performed slightly better than CWS, but this is attributed to CWS droplet ballistics rather than chemical differences between the systems. The optimum SR_2 was found to be in the range of 0.85 - 0.88 with nitrogen atomization (simulating flue gas) and 0.80 - 0.85 with air atomization.

In summary, the variables found to most strongly influence NO_X reduction were reburn zone residence time and initial NO_X concentration. Maximum NO_X reduction obtained during any CWS reburn test was 63% with fine grind CWS at the test condition of 1000 ms residence time, 1300 ppm initial NO_X, and reburn zone stoichiometry of 0.85, with both air and nitrogen atomization. When compared under constant conditions, CWS reburning was found to give approximately 8 percentage points less NO_X reduction than natural gas reburning. Based on fuel preparation and handling requirements, and achievable NO_X reduction, the tests confirm that CWS reburning is technically viable as a NO_X control technology.

SYSTEM CAPITAL AND OPERATING COST ANALYSIS

Economic analyses were preformed for a 500 MWe cyclone fired boiler with a capacity factor of 75%. The assumed cost for auxiliary power requirements was $0.03/kWhr and for primary fuel (coal) was $1.00/ MMBtu.

In the the economic analyses the capital and operating cost for natural gas, pulverized coal and coal-water slurry reburning were compared. The three cases studied are assumed to have identical overfire air systems. The equipment required for handling the three reburn fuels are all different due to the physical properties of the fuels. Gas reburn is the least capital intensive of the reburn systems, followed by coal water slurry. Pulverized coal reburn, because of the pulverizer and relatively large coal pipes required, is the most costly reburn system from an capital installation perspective.

Natural Gas Reburn System

The capital cost for the natural gas system was based on natural gas being available at the plant site. The natural gas reburn system installation includes 300 feet of buried natural gas piping from a metering station to the powerhouse. The system includes natural gas reburn injectors, piping, controls and control modifications, and electrical equipment.

The overfire air system includes the OFA nozzles and the tubewall penetrations. It also includes ductwork from the windbox to the nozzles, valves and two flow meters, one to each sides of the furnace. No OFA booster fan is required due to the high static pressure available from the combustion air supply to the cyclones.

The GAS reburn system will be the simplest to operate and maintain. The projected capital and operating costs for the natural gas reburn case are shown in Table 5. For the operating cost projections it was assumed that the cost differential between natural gas and coal was $2.10/MM Btu. The total plant investment is projected at $8.8 million, with an incremental operating cost increase of $14.3 million per year over baseline operation.

Pulverized Coal Reburn System

The capital cost for the pulverized coal reburn case was based on utilizing the existing coal receiving and handling system. The pulverized coal reburn system includes the addition of a new coal bunker, feeders, pulverizers with a dynamic classifier, coal reburn injectors, piping, controls and control modifications, and electrical equipment.

TABLE 5

Natural Gas Reburn

500 MWe Unit

Total Plant Investment

Category	Cost
Equipment/ Construction	$5,744,562
Engineering/ Project Management / Startup	$1,602,612
Freight / Taxes / Permits	$284,310
Subtotal	$7,631,484
Project Contingency	$1,137,091
Total Plant Investment (TPI)	$8,768,575

Natural Gas Reburn

500 MWe Unit

Projected Incremental Operating Costs*

	Annual Use	Cost/Unit	Cost/ Yr
Raw Material:			
Natural Gas	5,913,000 MM Btu	$2.10 /MM Btu	$12,417,300
Coal **	328,500 MM Btu	$1.00 /MM Btu	$328,500
Utilities:			
Electricity	8,760 kWhr	$0.03 /kWhr	$263
Fixed Charges: (@ 12% of TPI)			$1,052,229
Labor:			
Maintenance @ 60% of 2% of TPI			$105,223
Supervision @ 20% of Maint. Labor			$21,045
Supplies:			
Maintenance @ 40% of 2% of TPI			$70,149
Admin. and Gen. Ovhd. (60% of total labor):			$75,760
Insurance and Taxes (2.7% of TPI):			$236,752
Total Operating Costs			$14,307,220

*75% Capacity factor with 18% fuel as reburn
**adder for decrease in boiler effiency of 1%
Note:
Natural gas assumed delivered at $3.10/MM Btu; coal cost at $1.00/MM Btu
Auxiliary power cost assumed at $0.03/kWhr
Assumed no incremental operating labor

The overfire air system includes the OFA nozzles and the tubewall penetrations. It also includes ductwork from the windbox to the nozzles, valves and two flow meters, one to each set of injectors to two sides of the furnace.

The PC reburn system will be the most complicated to operate and maintain. The projected capital and operating costs for the fine pulverized coal reburn case is shown in Table 6. The cost of coal to the PC system was assumed to be identical to the current cost of coal being delivered to the plant. The total plant investment is projected at $17.4 million, with an incremental operating cost increase of $3.4 million per year over baseline operation.

Coal Water Slurry Reburn System

The capital cost for the coal water slurry reburn case was patterned after EER's experience with CWS co-firing at Penelec's Seward Plant. The study CWS reburn system includes a CWS storage tank with mixer, two progressive cavity pumps, two 300 hp air compressors, strainers, a slurry flow meter, CWS dual fluid atomizing nozzles, slurry piping, controls and control modifications, and electrical equipment.

The overfire air system will include the OFA nozzles and the tubewall penetrations. Also included will be ductwork from the windbox to the nozzles, valves and two flow meters, one to each set of injectors to two sides of the furnace.

The CWS reburn system will be less complicated to operate and maintain than the PC coal reburn system, but more complicated than the GAS reburn system. The projected capital and operating costs for the CWS reburn case are shown in Table 7. The cost of coal delivered to the power plant was assumed to be $1.00/MM Btu. The cost of the coal water slurry fuel could range from $0.60 to $0.80/MM Btu; conservatively the delivered price was set at $0.75/MM Btu. Based on a current assumed coal delivery cost of $1/MM Btu, the CWS would be $0.25/MM Btu less than the current coal cost. The total plant investment is projected at $10.2 million, with an incremental operating cost increase of $990,000 per year over baseline operation.

Economic analysis were performed to determine the effect of CWS cost on the incremental cost of operation. Case 2 was for a CWS cost of $1.00/MM Btu which had a incremental cost of $2.3 million and a cost per ton of NO_x reduced of $154. Case 3 was for a CWS cost of $0.50/MM Btu which had a incremental savings of $300,000 and a savings per ton of NO_x reduced of $23. Case 4 was for a CWS cost of $0.57/MM Btu which had a zero incremental cost therefore a zero cost per ton of NO_x reduction. The CWS option has the best potential for providing low cost NOx control.

TABLE 6

Coal Reburn

500 MWe Unit

Total Plant Investment

Category	Cost
Equipment/ Construction	$11,288,414
Engineering/ Project Management / Startup	$3,175,382
Freight / Taxes / Permits	$657,072
Subtotal	$15,120,868
Project Contingency	$2,253,009
Total Plant Investment (TPI)	$17,373,877

Coal Reburn

500 MWe Unit

Projected Incremental Operating Costs*

	Annual Use	Cost/Unit	Cost/ Yr
Raw Material:			
Coal	6,570,000 MM Btu	$0.00 /MM Btu	$0
Coal**	197,100 MM Btu	$1.00 /MM Btu	$197,100
Utilities:			
Electricity	3,233,504 kWhr	$0.03 /kWhr	$97,005
Fixed Charges:			
(@ 12% of TPI)			$2,084,865
Labor:			
Maintenance @ 60% of 2% of TPI			$208,487
Supervision @ 20% of Maint. Labor			$41,697
Supplies:			
Maintenance @ 40% of 2% of TPI			$138,991
Admin. and Gen. Ovhd. (60% of total labor):			$150,110
Insurance and Taxes (2.7% of TPI):			$469,095
Total Operating Costs			$3,387,350

*75% Capacity factor with 20% fuel as reburn
**adder for decrease in boiler effiency of .56%
Note:
Coal for reburn assumed identical to primary coal, cost of $1.00/MM Btu
Auxiliary power cost assumed at $0.03/kWhr
Assumed no incremental operating labor

TABLE 7

Coal Water Slurry Reburn
500 MWe Unit
Total Plant Investment

Category	Cost
Equipment/ Construction	$6,693,435
Engineering/ Project Management / Startup	$1,870,239
Freight / Taxes / Permits	$342,225
Subtotal	$8,905,899
Project Contingency	$1,326,979
Total Plant Investment (TPI)	$10,232,878

Coal Water Slurry Reburn
500 MWe Unit
Projected Incremental Operating Costs*

	Annual Use	Cost/Unit	Cost/ Yr
Raw Material:			
Coal	4,927,500 MM Btu	($0.25) /MM Btu	($1,231,875)
Coal**	394,200 MM Btu	$0.75 /MM Btu	$295,650
Utilities:			
Electricity	3,429,474 kWhr	$0.03 /kWhr	$102,884
Fixed Charges:			
(@ 12% of TPI)			$1,227,945
Labor:			
Maintenance @ 60% of 2% of TPI			$122,795
Supervision @ 20% of Maint. Labor			$24,559
Supplies:			
Maintenance @ 40% of 2% of TPI			$81,863
Admin. and Gen. Ovhd. (60% of total labor):			$88,412
Insurance and Taxes (2.7% of TPI):			$276,288
Total Operating Costs			$988,521

*75% Capacity factor with 20% fuel as reburn
**adder for decrease in boiler effiency of 1.2%
Note:
Coal water slurry from ponds at $0.75/MM Btu w/ primary coal at $1.00/MM Btu
Auxiliary power cost assumed at $0.03/kWhr
Assumed no incremental operating labor

CONCLUSIONS

Table 8 summarizes the results of the economic analyses. Based on preliminary capital and operating cost projections, coal water slurry clearly appears to be the most economic reburn fuel choice. A baseline emission rate of 1.7 lb of NO_x/MM Btu was used for this paper. The cost of NOx removal, based on a 54% reduction from baseline for natural gas and 51% for the PC and CWS is CWS at $66/ton, PC at $225/ton and GAS at $896/ton, respectively. The projected total plant investment and annual operating costs for the three reburn fuels are shown below. The annual operating costs shown are projected incremental costs over and above current baseline operation.

Table 8 COST SUMMARY

Reburn Fuel:	GAS	PC	CWS
Total Plant Investment:	$8.8 Million	$17.4 Million	$10.2 Million
Annual Operating Cost:	$14.3 Million	$3.4 Million	$0.99 Million
Annual NOx Reduction: (Tons/yr)	15,965	15,078	15,078
NOx Reduction Cost: ($/ton)	$896	$225	$66

Dry Injection of Carboxylic Acid Salts and Waste Plastics for Dual SO_2-NO_x Emission Control

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Abstract

The in-boiler injection of calcium/magnesium carboxylic acid salts for dual SO_2-NO_x reduction becomes more economically attractive if the relatively expensive sorbents can be supplemented by less expensive hydrocarbons for NO_x control. Excellent SO_2-NO_x reductions of 85 - 90% were obtained by dry-injection of a blend consisting of pulverized carboxylic acid salts and poly(ethylene). This warrants a more thorough investigation of replacing part of the expensive carboxylic acid by organic wastes that would otherwise be landfilled.

INTRODUCTION AND LITERATURE REVIEW

Aliphatic carboxylic acid salts of Ca and Mg, e.g., calcium magnesium acetate (CMA), calcium formate (CF) and calcium propionate (CP), are effective agents for in-boiler simultaneous removal of SO_2 and NO_x emitted from the combustion of coal. Over 90% removal of these pollutants has been obtained by dry-injecting CMA in laboratory-scale experiments at temperatures near 1000°C in gases containing 3% O_2, 12% CO_2, 2000 ppm SO_2 and 1000 ppm NO in N_2 at a molar Ca/S ratio of 2 for a nominal 1 second residence time (Steciak, et al., 1995a). Common thermodynamic and chemical kinetics windows wherein the dual reaction mechanisms are effective were identified by temperatures between 950 and 1150°C, residence time of at least 1 second, and bulk equivalence ratio, ϕ, between 1.1 and 1.3. The fuel-rich reaction zone was followed by a fuel-lean after-fire air zone, wherein occurs the oxidation of a) CO to CO_2; b) unburned HCs to CO_2 and water; and c) NH_3 back to NO_x; and the continued sulfation of Ca to $CaSO_4$.

Previous work exploring dual SO_2-NO_x reduction quantified the contribution of Mg to SO_2 reduction by CMA (Steciak, et al., 1995a). It further showed that substantial amounts of $CaCO_3$ remain in the residues due to the incomplete decomposition of $CaCO_3$ to CaO – leading to the direct sulfation of $CaCO_3$, and that the sulfation kinetics of the residues were bounded between those of pure CaO and pure $CaCO_3$ (Steciak, et al., 1995a, b).

Commercially available carboxylic acid salts are expensive due to the cost of manufacturing the organic acid from natural gas. The total cost can be reduced if the amount of the carboxylic acid salts that are injected into the furnace is reduced and is supplemented by less costly organics, such as waste plastics, to keep the injection zone in the furnace fuel-rich ($\phi > 1.0$). This substitution will be feasible as long as the necessary amount of alkali earth metal (Ca and Mg) is introduced to remove SO_2.

The direct use of plastics – which would need to be finely shredded or pulverized – would divert material from landfills. Even the inadvertent presence of chlorinated hydrocarbons, e.g., poly(vinyl chloride), may be tolerable because of the affinity of Ca for Cl to form $CaCl_2$[1] in the fuel-lean after-fire air zone (Dougherty, et al., 1993).

For these reasons, experiments were undertaken to explore the effectiveness of blends of carboxylic acid salts with different amounts of poly(ethylene), a polymer found in quantity in the municipal waste stream [2]. The advantage associated with the custom-blended compounds is the ability to deliver to a particular furnace, with its characteristic SO_2 and NO_x concentrations, a single injection point of compounds that have been optimized for the most efficient simultaneous removal of SO_2-NO_x.

Greene, et al. (1985) injected secondary fuels (various pulverized coals and propane) for NO_x reduction and calcium-based sorbents (mainly $CaCO_3$) for SO_2 control. They concluded that the optimum location for sorbent injection was with the after-fire air because of increased reactivity of the calcined stone at 1000 - 1100°C (gas temperature at the location of after-fire air injection) compared to stone reactivity at 1400°C (gas temperature at the secondary fuel injection location). In our approach, the dual SO_2-NO_x reduction can occur at the same temperature which is a few hundred degrees centigrade lower than the usual in-boiler secondary-fuel injection temperature for NO_x reduction in a "reburning" scheme (Wendt, et al., (1973)). Hence, loss of stone reactivity due to sintering at high temperatures is avoided and the simplicity of a single injection point is maintained – provided that one uses a secondary fuel that decomposes easily at the lower injection temperature; e.g., poly(ethylene) is a good candidate while pulverized coal is not. Incomplete sorbent calcination at injection temperatures below 1100°C and the lower rate of CaO sulfation at these temperatures are not detrimental because of the direct sulfation of $CaCO_3$ (Steciak, et al., 1995a, b; Tullin, et al., 1989; Snow, et al., 1988) and the sulfation of Mg if it is present in the stone.

Supplementing the carboxylic acid salts with external hydrocarbons for NO_x control resulted in improved SO_2 concentration reduction as the equivalence ratio increased, a trend that was opposite to that obtained elsewhere when ϕ increased because additional hydrocarbons were bound (interior) to the salts (Steciak, et al., 1995b). However, the present trend was consistent with the small but measurable improvement of H_2S capture by calcitic limestone as ϕ increased when both the sorbent and H_2S were injected with secondary fuel (Greene, et al., 1985).

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[1] $CaO + 2\ H\text{-}C + C\text{-}Cl + 4\ O_2 \longrightarrow CaCl_2 + 4\ CO_2 + H_2O$

[2] 8 million tons of poly(ethylene) were discarded in 1990 (Krieth, 1991). Examples of poly(ethylene) wastes abound, e.g., milk jugs, grocery bags, etc.

EXPERIMENTAL APPARATUS

The apparatus used was the same as that described in detail previously (Steciak, et al., 1994a, b, 1995a, b). Basically, the bench-scale drop-tube furnace consisted of an isothermal high temperature zone followed by a quenching zone wherein the temperature dropped at a rate of at least 350°C/sec (Figure 1). A capped stainless steel tube with end perforations facilitated the introduction of after-fire air at the end of the isothermal zone. All of the experiments described herein were conducted with dry-injected sorbents and solid hydrocarbon powders with a nominal residence time of 1 s in the isothermal zone. The sorbents were conducted pneumatically through a water-cooled injector to the beginning of the isothermal zone. For all experiments, the background gas partial pressures were 12% CO_2, 3% O_2, 2000 ppm SO_2 and 1000 ppm NO, balanced in N_2. Although NO alone was introduced to the furnace, the total NO_x ($NO + NO_2$) was monitored at the furnace exhaust by a chemilluminescent analyzer. Other species monitored at the furnace exhaust were SO_2 (UV analyzer), CO (IR detection), and CO_2 (IR detection). The removal efficiencies of SO_2 and NO_x were deduced by comparing inlet and outlet gas concentrations.

EXPERIMENTAL RESULTS AND DISCUSSION

Our goal was to determine the most efficient dual SO_2-NO_x reduction 'blend' of carboxylic acid salts and waste plastics. Poly(ethylene) was chosen in this work because it is found in abundance in the municipal waste stream. Poly(ethylene) particles below ≈ 200 μm in nominal size were injected in the reported experiments. Upon calcination, unreacted CF and CP crystals of a nominal 50μm size formed cenospheres of the same order-of-magnitude.

Ca Utilization and SO_2 Concentration Reduction by Blends of CF or CP and Poly(ethylene)

Calcium utilizations[3] of $\approx$ 60% were achieved by injecting blends of CF or CP and poly(ethylene) in the furnace at 1000 - 1100°C, $\phi \approx 1.8$, Ca/S molar ratio ≈ 1.3, and C/Ca between 10 and 15 (or 10 - 15 moles of [-CH_2-] per mole of Ca). The results are plotted in Figure 2.

The data in Figure 2 indicate that Ca utilization - and hence SO_2 concentration reduction - tends to *increase* as ϕ increases.

This trend is the opposite of that obtained elsewhere (Steciak, et al., 1995b) by calcium carboxylic acid salts wherein ϕ was increased by using salts with increasing amounts of hydrocarbons bonded to Ca, i.e., CF, CA and CP. In agreement with the

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[3] Utilization is the fraction of Ca that reacts with SO_2.

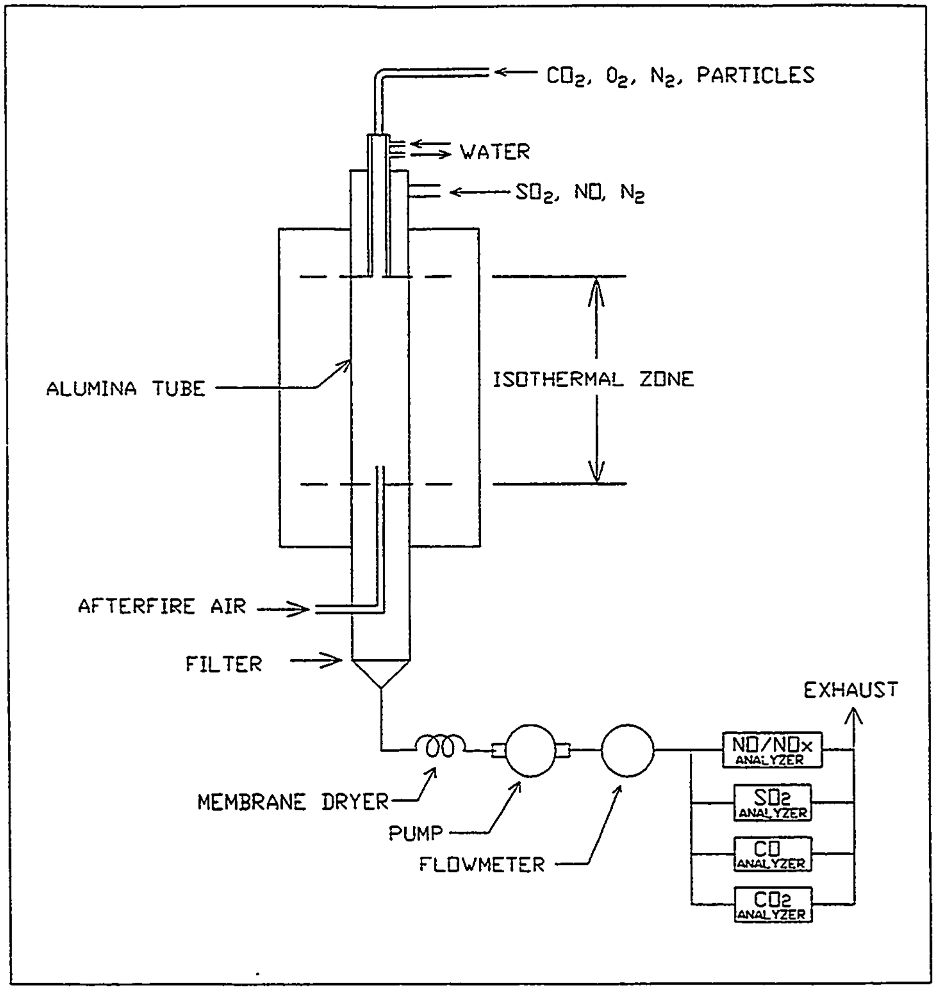

Figure 1: Experimental Apparatus

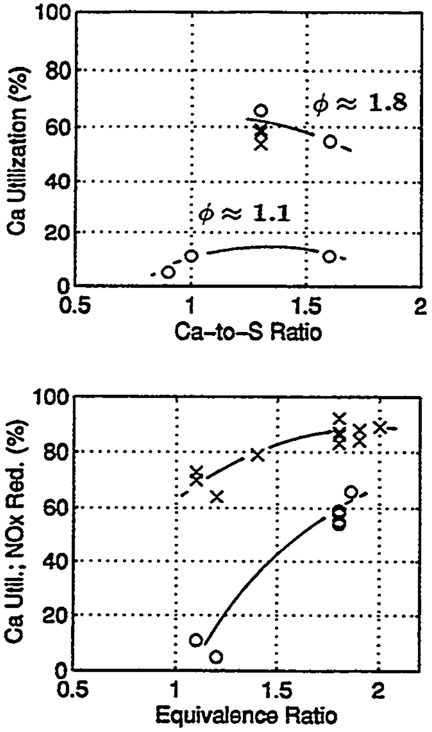

Figure 2: SO_2-NO_x concentration reduction by blends of CF or CP and PE at gas temperatures between 1000 - 1000°C. a) Ca utilization vs. Ca/S ratio for $\phi \approx 1.1$ and 1.8. o - CF; x - CP. b) Ca utilization and NO_x concentration reduction vs. ϕ. o - Ca utilization; x - NO_x reduction (%).

present trend, Greene, et al. (1985) also observed a small but measurable *improvement* of H_2S capture from 12% to 18% by calcitic limestone as ϕ increased from 0.9 to 1.4 when both the sorbent and H_2S were injected with the secondary fuel at Ca/S=1. A physical explanation of why these opposite trends occur may rest on the ease of decomposition of the hydrocarbons.

When most of the organic was imbedded within the injected sorbent particles and bonded to the salt, local fuel-rich clouds enveloped the particles as the organic components gasified. As the fraction of organic within the particle increased, longer times were needed for gasification and subsequent diffusion of SO_2 to the calcined residues for heterogeneous sulfation.

When most of the organic was available outside the salt particle and decomposed separately, as for the experiments listed in Table I and plotted in Figure 2, diffusion of SO_2 to the calcined residue was not hindered by an envelope cloud of gasifying hydrocarbons.

Ca sulfation under fuel-rich conditions and mild furnace temperatures may explain the role of the organic in SO_2 removal observed by Steciak, et al. (1995a). Precalcined CMA (i.e., devoid of organic) was injected at (Ca+Mg)/S=6 and 750°C and failed to remove more than 10% of SO_2. Injection of the precalcined CMA in combination with sucrose, to achieve ϕ=1.3, caused the same amount of SO_2 reduction as that obtained by raw CMA injected at the same (Ca+Mg)/S and ϕ.

Nearly 100% reduction of SO_2 was obtained herein by a blend of CP and poly(ethylene) at 1000°C at a Ca/S=2.2, ϕ=2.0 and C/Ca = 12, as listed in Table I. The addition of after-fire air had no effect on SO_2 reduction.

Results obtained by Greene, et al., in experiments using combinations of different sorbents and secondary fuels showed sulfur captures of 15% or 22% using calcitic limestone at a Ca/S molar ratio of 2 and propane as the secondary fuel. The difference in SO_2 capture was due to the location of the sorbent injection. A 15% SO_2 capture was obtained when the sorbent was injected with the secondary fuel at a location in their furnace where the gas temperature was ≈ 1400°C, whereas the 22% SO_2 capture occurred when the sorbent was injected with the after-fire air where the gas temperature was ≈ 1170°C. The difference in SO_2 capture was attributed to loss of stone reactivity at the higher injection temperature caused by sintering. The ϕ of the secondary fuel injection zone in that study was 1.1 and the residence times in the fuel-rich and after-fire zones were 0.4 sec. and ≈1 sec., respectively. The fuel-rich zone was not isothermal, but had a cooling rate of 575°C/s (the cooling rate of the after-fire zone was less than 200°C/s).

NO_x Concentration Reduction by Blends of CF or CP and Poly(ethylene)

Nearly 100% reduction of NO_x in the isothermal zone was obtained by a blend of CP and poly(ethylene), the first entry in Table I. The addition of after-fire air lowered NO_2

Table I. SO_2-NO_x Reduction by Blends of CF or CP and Poly(ethylene) at 1000-1100°C

Salt	Zone	C/Ca	Ca/S	Iso. Zone ϕ	SO_2 Red. (%)	Ca Util. (%)	NO_x Red. (%)
CP	Isotherm.	12	2.2	2.0	98	45+	97
CP	After-fire	12	2.2	2.0	98	45+	89
CP	After-fire	10	1.3	1.8	77	59	83
CP	After-fire	10	1.3	1.8	75	58	87
CP	After-fire	10	1.3	1.8	70	54	92
CF	After-fire	6	1.6	1.1	17	11	70
CF	After-fire	10	1.0	1.1	11	11	73
CF	After-fire	12	0.9	1.2	5	5	64
CF	After-fire	12	1.6	1.8	88	55	86
CF	After-fire	15	1.3	1.8	86	66	84

Note: All data at ≈ 1 s residence time in isothermal zone.

reduction to 89%, suggesting that NH_3 or HCN products from the fuel-rich reaction zone might have been oxidized back to NO_x.

When blends of CF or CP and PE were injected, the NO_x concentration reduction (Figure 2b) *increased* as ϕ of the isothermal zone increased. This was consistent with the trend obtained by calcium carboxylic acid salts wherein ϕ was increased by using salts with increasing amounts of hydrocarbons bonded to Ca (Steciak, et al., 1995b), i.e., CF, CA and CP. While some NO_x reduction reactions are known to be catalyzed by CaO (Steciak, et al. (1994a)), most selective and non-selective reactions occur in the gas phase and would not be affected by diffusion through local fuel-rich clouds. The trend of improving NO_x reduction with increasing ϕ in Figure 2b was the opposite of that observed by Greene, et al. (1985). The explanation for the difference may lie in the significant difference in gas temperature between the experiments of Greene, et al. (1985) and the ones conducted herein (Figure 2; 1400 vs. 1000 °C, respectively). The lower temperature reactions may allow for the selective reduction of NO by NH_3 formed during the fuel-rich decomposition of the organics. Some NH_3 was measured in the isothermal reaction zone during NO_x reduction by CP (Steciak, et al. (1994a)) and nearly all of it oxidized to NO_x in the after-fire oxidizing zone.

The excellent SO_2-NO_x reduction demonstrated by the introduction of blends of carboxylic acid salts and waste poly(ethylene) in a furnace is very promising and warrants the full investigation of blends of different carboxylic acid salts and other waste plastics.

CONCLUSIONS AND RECOMMENDATIONS

1. Application of the carboxylic acid salts for dual SO_2-NO_x reduction could become competitive if the expensive carboxylic acids are supplemented with less expensive hydrocarbons such as waste plastics.

2. The reduction of SO_2 by combinations of calcium carboxylic acid salts and hydrocarbon supplements injected into the reaction zone increased as ϕ increased from 1.1 to 2. This trend opposed that found previously by Steciak, et al. (1995b) wherein the reduction of SO_2 by carbon carboxylic acid salts decreased as ϕ increased. The physical explanation may rest on the ease of decomposition of the hydrocarbons.

   When most of the organic was bonded within the salt, local volatile clouds that could be extremely fuel-rich enveloped the particles as the organic components gasified and opposed the diffusion of SO_2 to the particle. When most of the organic was introduced externally to the salt and decomposed separately, diffusion of SO_2 to the calcined residue was not hindered by an envelope cloud of gasifying hydrocarbons.

3. The reduction of NO_x by calcium carboxylic acid salts increased as ϕ increased from 1.1 to 2 regardless of whether the increase in ϕ was due to an increase in hydrocarbons bonded to the Ca or injected alongside Ca into the reaction zone. This trend suggests that - at the temperature range of these experiments (1000 - 1100°C) - selective reduction of NO could have occurred by amine radicals that were produced in the fuel-rich zone as the hydrocarbons decomposed. This selective reduction would be in addition to the non-selective reduction of NO_x by HC radicals.

4. Excellent SO_2-NO_x reduction was obtained by dry-injected blends of CF or CP and poly(ethylene). Further investigation of carboxylic acid salt-plastic blends is warranted.

5. Dual SO_2-NO_x reduction by combinations of wet-sprayed carboxylic acid salts and different supplemental plastics will be investigated in the future. Wet-spraying achieves high Ca utilization for efficient SO_2 removal (Steciak, et al., 1994b). The use of waste plastics as sacrificial hydrocarbons for the reduction of NO_x diverts significant amounts of material from landfills. The presence of Ca in the reaction zone may also remove any existing Cl, a decomposition product of chlorinated hydrocarbons, in the form of $CaCl_2$. The combination of wet-sprayed carboxylic acid salts and waste plastics may be the most economical and advantageous scheme for SO_2-NO_x reduction, providing that the cost of the carboxylic acid salts can be significantly reduced and the plastics can be shredded or pulverized to facilitate quick decomposition in the reaction zone.

ACKNOWLEGEMENTS

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Development Activities and Commercial Status of the Moving Bed Copper Oxide Desulfurization/Denitrification Process, *Joseph N. Darguzas, David G. Sloat and William R. Bullock, Sargent & Lundy; Henry Pennline, U.S. Department of Energy; Peter Steiner, Foster Wheeler Development Corp.; and Anthony Litka, Tecogen; USA*

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Adsorption Behavior of Polyanion Additives and Coal-Water Mixture Properties

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ABSTRACT

A new method for the determination of CWM additives, such as naphthalenesulfonate-formaldehyde condensate (NSF), polystyrenesulfonate (PSS), and polyisoprenesulfonate (PIPS), have been developed with the aid of an ion-selective electrode (Poly-ISE). By use of the method, adsorption of the CWM additives on coal in CWM has been studied. Adsorption isotherms of the additives describe that NSF is more adsorbed on coal than PSS and PIPS. However, NSF is inferior to PSS and PIPS in terms of attaining high coal concentration in CWM. Time-course of the adsorption of PSS on coal is favorably monitored by the Poly-ISE. The properties of CWM, such as fluidity and storage stability, are discussed with adsorption behavior of the additives.

INTRODUCTION

Coal-water mixture (CWM) which is composed of powdery coal and water is an attractive utilization of coal and one of the most promising alternatives for heavy oil.[1-3] The characteristics of CWM are its fluidity and long time stability without sedimentation. The addition of appropriate surfactants into CWM as solid dispersants is essential in order to attain such characteristics of CWM.

For such additives, polyelectrolyte surfactants (polyanion surfactants), such as naphthalenesulfonate-formaldehyde condensate (NSF), polystyrenesulfonate (PSS), and polyisoprenesulfonate (PIPS), have been most frequently utilized (Fig. 1). The adsorption

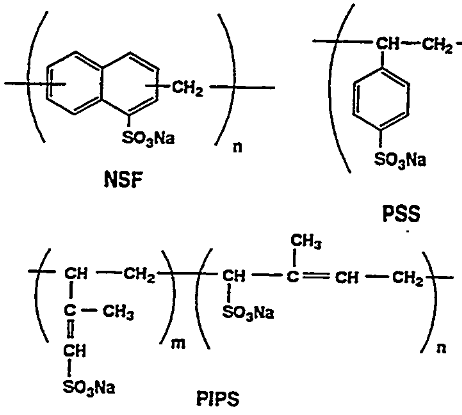

Fig. 1 CWM additives

behavior of these additives on coal has not been clarified well yet. So far, concentration of the additives in the CWM aqueous phase has been mainly analyzed by spectrophotometric methods.[4-7] However, such methods are often disturbed by the presence of various contaminants elutriating from coal and that of ultra-fine coal particles which cannot be removed by filtration.

The cost of the additives comprises a considerable part of the total cost of CWM. The clarification of the additive distribution in CWM is important from the view point of lowering the amount of additives. On the other hand, rapid determination of the CWM additives should be necessary for process control in practical CWM operation.

We have developed an ion-selective electrode (ISE) which responds to the polyanion additives in the aqueous phase of CWM.[8-10] By use of the polyanion responsive ISE (Poly-ISE), adsorption behavior of the CWM additives in CWM has been studied. CWMs have been prepared from various brands of coals. For these CWMs, the CWM properties, such as fluidity (viscosity) and storage stability, have been examined. Relationship between the CWM properties and the adsorption behavior will be discussed.

EXPERIMENTAL

Preparation of Poly-ISE

A polymeric solvent membrane electrode which responds to polyanion species was prepared in a similar manner to that described in our previous paper.[8] A diphosphonium salt, hexamethylenebis(trioctylphosphonium) dibromide, was used as a sensing material for polyanions. A mixture of poly(vinyl chloride) (PVC; 0.4 g), dioctyl phthalate (1.0 g), and the diphosphonium salt (0.2 g) was dissolved in 10 mL of tetrahydrofuran (THF). The THF solution was poured onto a flat Petri dish and THF was allowed to evaporate slowly at room temperature. A piece of the PVC membrane was attached to a Denki Kagaku Keiki (DKK, Musashino, Japan) number 7900 electrode body. A portion of an aqueous solution containing 10 mM KCl was used as an internal solution of the electrode. The electrode was conditioned by soaking in a 100 mg/L solution of a polyanion for one or two days. Thus, the Poly-ISE was prepared.

Potentiometric Measurements with ISE

Potentiometric measurements with the Poly-ISE were carried out at 24-26 °C with a voltage meter (DKK PHL-40), a double junction Ag-AgCl reference electrode (DKK number 4083), and a magnetic stirrer to agitate the sample solution. The electrode cell was Ag-AgCl/10 mM KCl/PVC membrane/sample solution/10 mM KCl/3 M KCl/Ag-AgCl.

Adsorption Isotherm of Additives

Sodium salts of polyanion additives, NSF ($\overline{M}_w$ = ca. 1,900), PSS ($\overline{M}_w$ = ca. 1.6×10^4), and PIPS (1: $\overline{M}_w$ = ca. 2.0×10^4; 2: $\overline{M}_w$ = ca. 3.3×10^4) were donated by Kao Corporation, Lion Corporation, and Japan Synthetic Rubber Co., Ltd., respectively. Three coals A, B, and C listed in Table 1 were used. The coals were pulverized by dry grinding in a ball mill. The particle size was adjusted by blending coals under 74 μm and 74-125 μm in weight ratio 80:20. Average particle sizes of coals A, B, and C were 17.8 μm, 16.3 μm, and 14.9 μm, respectively. An aqueous solution (20 mL) containing a set amount (0.02-0.1 g) of additive was shaken with 10 g of powdery coal in a stoppered centrifuge tube (50 mL) with a reciprocal shaker (100 strokes/min) for 24 h in an air-conditioned room (24-26 °C). The powdery coal was removed by centrifugation and the supernatant was filtered with a Millipore filter (pore size 0.45 μm). A portion of the filtrate (0.5 mL) was diluted to 50 mL. Sodium sulfate (20 mM) was added to the solution as a supporting electrolyte. Concentration of the polyanion additive in the resulting solution was measured by the Poly-ISE.

Preparation of CWM (Dry Grinding Method)

Table 1 Analysis of Coals

Coal[a)]	Proximate (%)[b)]					Ultimate (%)					
	IM	Ash	VM	FC	FR	C	H	N	S	O	O/C
A	3.7	13.9	32.0	54.3	1.70	80.9	5.3	1.5	0.6	11.7	0.145
B	3.3	10.3	33.5	56.3	1.68	81.1	5.1	1.2	0.3	12.3	0.152
C	6.0	13.8	40.9	45.4	1.11	76.3	5.8	1.3	0.6	16.0	0.209
D	1.8	6.6	20.6	71.0	3.45	89.8	4.8	1.9	0.6	2.9	0.024
E	1.7	12.7	20.3	65.3	3.22	89.2	4.9	1.8	0.6	3.5	0.029
F	2.6	9.0	29.5	58.9	2.00	86.4	5.4	2.2	0.8	5.2	0.045
G	3.4	8.5	32.3	55.8	1.72	84.2	5.4	1.7	0.4	8.3	0.074
H	3.2	8.8	32.5	55.5	1.71	84.1	5.5	1.8	0.5	8.1	0.072

a) All of the coals are from Australia except for B (China).

b) IM: Inherent moisture; VM: Volatile matter; FC: Fixed carbon; FR: Fuel ratio.

For coals A, B, and C, powdery coal which was prepared in a similar manner to above was slowly added into an aqueous solution containing a CWM additive by use of a mixer with four blades (1,000 rpm; 20 min; Tokushu Kikakogyo HV-M). Then the mixture was further stirred (4,000 rpm) for 10 min to prepare a CWM which composition was coal (52-71 wt%), water (47.5-28.5 wt%), and an additive (0.5 wt%).

Preparation of CWM (Wet Grinding Method)

Five coals D, E, F, G, and H listed in Table 1 were used. CWMs were prepared by the wet grinding method.[4] Coal (1,000 g, dry base) which had been passed through a sieve of 3.35 mm mesh, water, and PSS were placed in a ball mill. Added amounts of water and PSS (*W* (g) and *P*(g), respectively) were determined by the following equations. *C* (g) is the added amount of coal which contains inherent water.

$$C = \frac{1000}{1-(c_w/100)} \quad (1) \qquad P = \frac{1000}{c/100} \times \frac{a}{100} \quad (2)$$

$$W = \frac{1000}{c/100} - C - P \quad (3)$$

c_w: water concentration in coal (wt%)
c: coal concentration (wt%/CWM)
a: PSS concentration (wt%/CWM)

The mixture was pulverized until a portion of coal which passed through a sieve of 74 μm mesh became 80-83 wt%. After pulverization, a slurry was obtained and the slurry was sieved by a sieve of 1 mm mesh to remove coarse particles. An appropriate amount of water was added to the slurry, and the resulting slurry was stirred by the mixer with four blades (4,000 rpm) for 10 min to prepare a CWM which had a variation in coal concentration. The precise coal concentration was determined by a weight loss during the heat of CWM in an electric oven (108 ± 2 °C). Average particle sizes of coals D, E, F, G, and H were 16.7 μm, 16.9 μm, 18.6 μm, 18.4 μm, and 19.8 μm, respectively. The determination of PSS concentration in the CWM aqueous phase was performed in a similar manner to that in the adsorption isotherm experiments described above.

Apparent Viscosity of CWM

Apparent viscosity of CWM was measured by a rheometer with a coaxial rotating cylinder (Haake Rotovisco RV2). The shear history was as follows: shear rate 0→150 s^{-1} (3 min), 150 s^{-1} (3 min), 150→0 s^{-1} (3 min). The apparent viscosity was obtained from shear stress at 100 s^{-1} on the downward curve.

Storage Stability of CWM

In order to evaluate the storage stability of CWM, the "slurry discharge test" was performed according to a literature.[4] A CWM (200 g) were stored in a 350 mL polystyrene bottle for a given period. The bottle was inclined for 10 min at an angle of 60° above a sieve of 1 mm mesh which was placed on a beaker. A portion of the slurry passed through the sieve was defined as the "discharged slurry".

RESULTS AND DISCUSSION

Determination of CWM Additive by Poly-ISE

A dicationic liquid anion-exchanger, hexamethylenebis(trioctylphosphonium) dibromide, was incorporated into a solvent polymeric membrane in which PVC was the polymer and dioctyl phthalate was the membrane solvent. By use of the Poly-ISE, we have measured potentiometric responses for three polystyrenesulfonates which are used for the standard material of gel-permeation chromatography (GPC-PSS). These GPC-PSSs have very narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n < 1.2$). As shown in Fig. 2, a GPC-PSS which has a molecular weight of 1,800 provides a linear response ranging from 10 to 1,000 mg/L. However, the Poly-ISE does not show good responses for GPC-PSSs which have higher molecular weights (8,000 and 35,000).

When a mixture of the same amounts of three GPC-PSSs which have molecular weights of 1,800, 8,000, and 35,000 (MIX) was measured, a linear response ranging from 10 to 1,000 mg/L was obtained. Therefore, it is found that the response of the Poly-ISE depends upon not only the average molecular weight of polyanions but also their molecular weight distribution.

The PSS for CWM has a wide molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = ca. 3.6). As shown in Fig. 3a, the PSS provides a linear response ranging from 10 to 2,000 mg/L, although the PSS has a high average molecular weight ($\overline{M}_w$ = ca. 1.6×10^4). PIPS-1 for CWM, which also has a high average molecular weight (ca. 2.0×10^4) and quite wide molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = ca. 1.8), gives a good response as well (Fig. 3c).

When one measures the concentration of polyanion additives in the CWM aqueous phase, the following problems should be encountered: i) various colored contaminants elutriate from coal particles, ii) even after filtration ultra-fine coal particles are still left, and iii) amount of the contaminants and the coal particles which are present in the CWM aqueous phase depends upon the added amount of additive. Especially for spectrophotometric determinations, these are essential problems. In order to confirm that these problems do not affect the determination by the

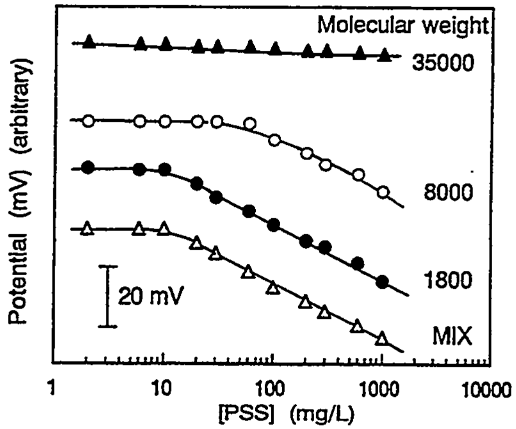

Fig. 2 Potential response of Poly-ISE to GPC standard PSSs
MIX: Mixture of three GPC-PSSs whose molecular weights are 1,800, 8,000, and 35,000.

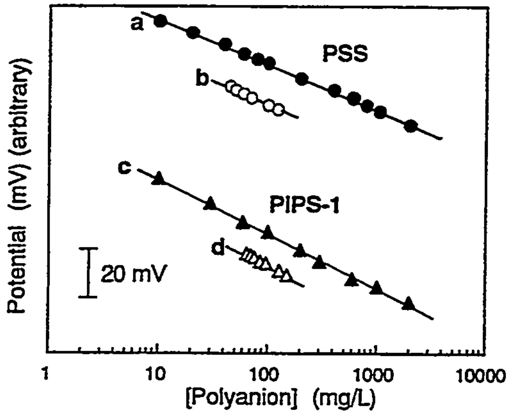

Fig. 3 Response of the Poly-ISE to polyanions
a: Response to PSS
b: Standard addition method for PSS
c: Response to PIPS-1
d: Standard addition method for PIPS-1

Poly-ISE, the standard addition method was performed for the CWM aqueous phase which was separated by centrifugation and filtration. The results for PSS and PIPS-1 are indicated in Figs. 3b and 3d, respectively. These plots give the same slope of linear response that the calibration curves (Figs. 3a and 3c) do. Consequently, it is proved that the Poly-ISE enables us to favorably determine the CWM additives in the aqueous phase of CWM.

Adsorption Isotherm of CWM Additives

Adsorption isotherms of the CWM additives (NSF, PSS, PIPS-1, and PIPS-2) were investigated. Powdery coal, water, and an additive were placed in a centrifuge tube and shaken. After equilibrium the aqueous phase was separated and analyzed by the Poly-ISE. In Fig. 4 is shown adsorption isotherms for the additives. These isotherms are plots of the amount of equilibrium adsorption (log x/m) against the equilibrium concentration in the aqueous phase (log C). Three brands of coals, A, B, and C, were examined. For all three coals, NSF gives the largest adsorption among the four additives, which may be attributed to lipophilicity of NSF.

CWMs which utilize NSF, PSS, PIPS-1, and PIPS-2 as additives were prepared from powdery coals (A, B, and C) (the dry grinding method). Apparent viscosities of these CWMs were measured by a rheometer when the coal concentration of CWM was changed (Fig. 5). For all coals, the CWM viscosity drastically increases as the coal concentration is raised. The "achievable coal concentration (ACC)" is defined as the coal concentration of CWM where the CWM viscosity becomes 1.0 Pa·s. The ACC values for coals A, B, and C are recorded in Table 2. Although NSF provides the largest adsorption on coal, NSF-CWMs do not exhibit high ACC values. Compared with PSS- and PIPS-1-CWMs, the ACC values for NSF-CWMs are lower by 2-3 wt% for coals A and B. PIPS-1 which has a molecular weight of ca. 2.0 X 10^4 is superior to PIPS-2 ($\overline{M}_w$ = ca. 3.3 X 10^4). Consequently, it is proved that PSS and PIPS-1 are good for CWM additives.

Time-Course of Adsorption of PSS on Coal

CWMs were prepared from five brands of coals D, E, F, G, and H via the wet grinding method by use of PSS as an additive. In Fig. 6 is shown time-course of the PSS adsorption when various concentrations of PSS are initially added. It is found that time-course of the adsorption of PSS on coal is favorably monitored by the Poly-ISE. For the wet grinding method, PSS is initially added with coal and water in a ball mill. Therefore, even immediately after the preparation of CWM, the additive is considerably adsorbed on coal. The PSS adsorption further proceeds gradually while CWMs are stored.

Table 2 Achievable coal concentration (ACC) for coals A, B, and C

Coal	ACC (wt%/CWM)			
	NSF	PSS	PIPS-1	PIPS-2
A	63.6	65.3	66.5	63.9
B	67.5	70.6	68.7	66.7
C	54.6	55.3	56.7	56.7

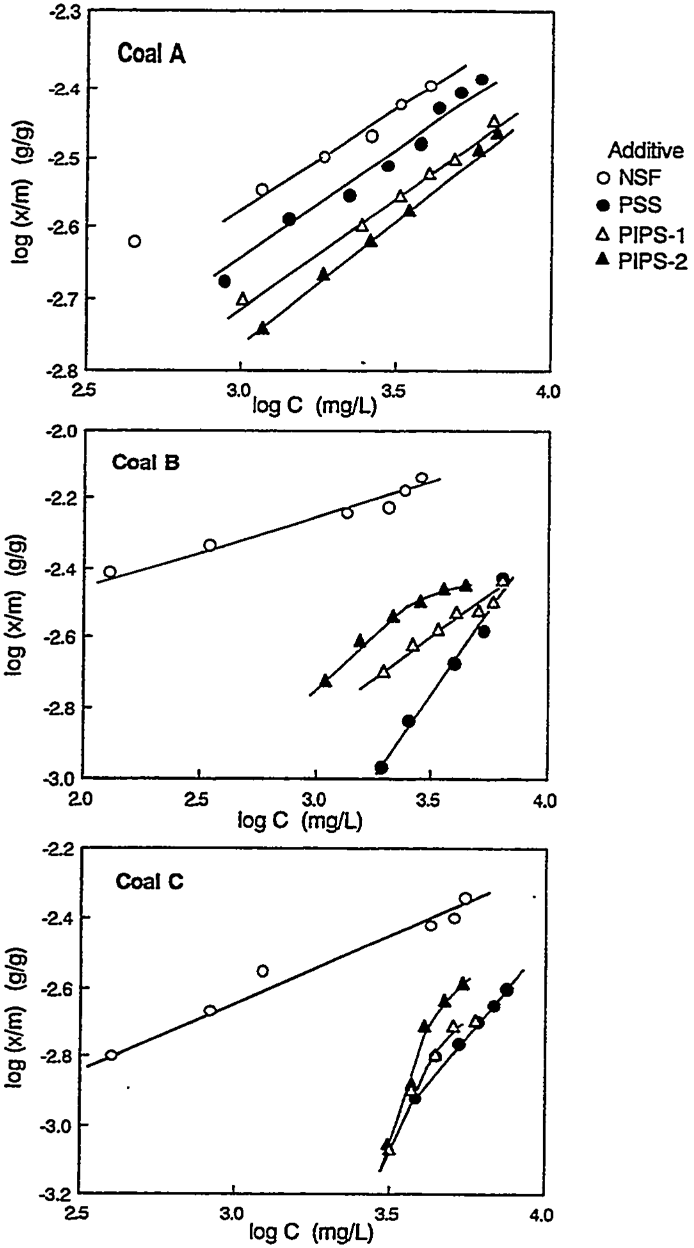

Fig. 4 Adsorption isotherms of CWM additives

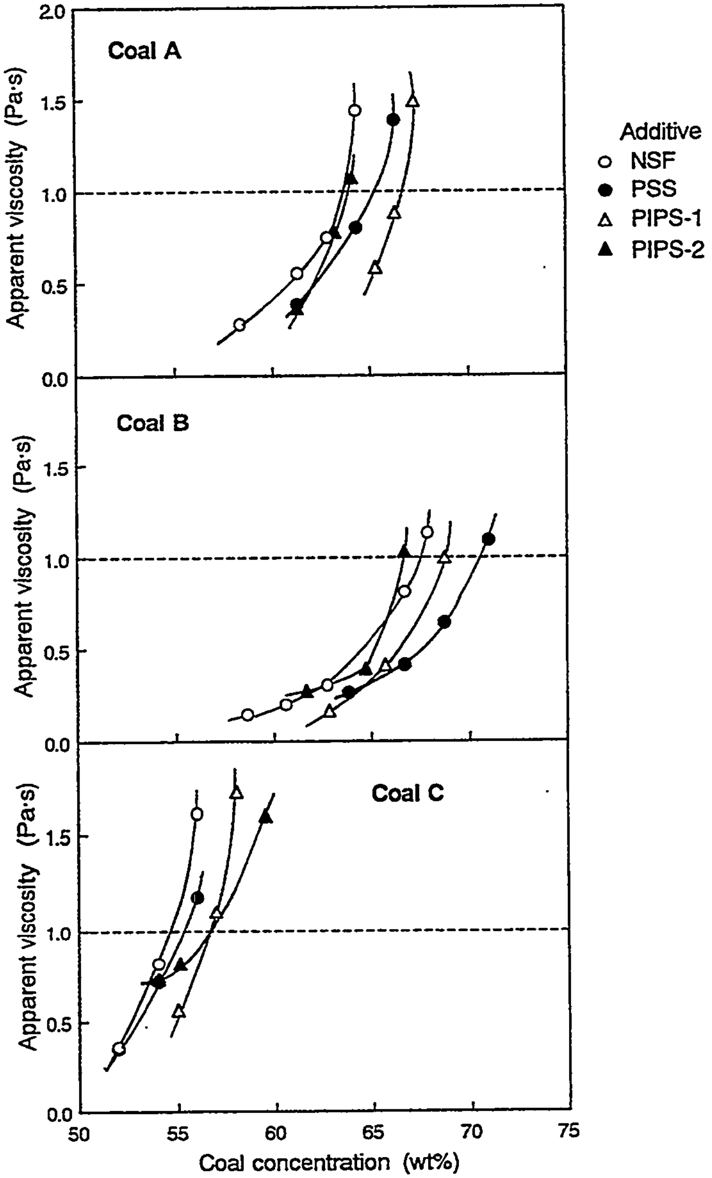

Fig. 5 Plot of CWM viscosity against coal concentration

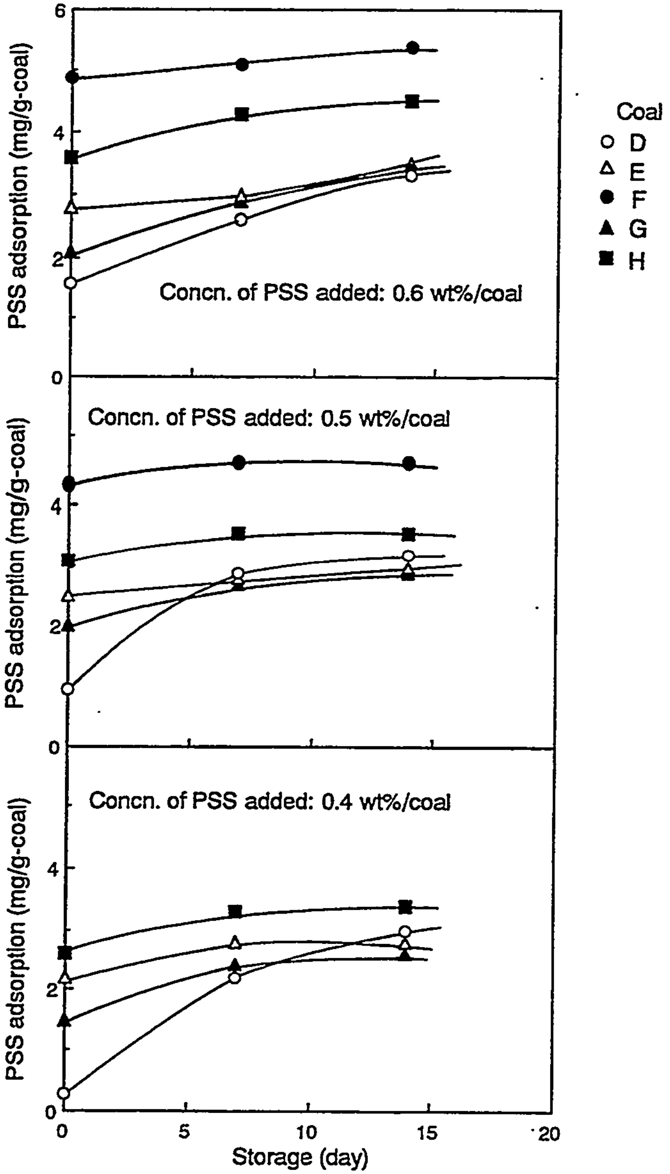

Fig. 6 Time-course of PSS adsorption on coal in CWM

Storage Stability of CWM

Storage stabilities of CWMs prepared from the five brands of coals via the wet grinding method were evaluated by the slurry discharge test.[4] CWMs which have more discharged slurry are better in terms of flowability after storage.[4] In Fig. 7 is shown the amount of discharged slurry after 7 days and 14 days storages. When coal F which shows the largest adsorption of PSS among the five coals (see Fig. 6) is used, the amount of discharged slurry for the CWM is less than 1 wt% after storage, which means that the CWM has very bad storage stability. A CWM from coal D which shows considerably small PSS adsorption provides 19 wt% discharged slurry after 14 days storage. CWMs from coals E, G, and H, which give 75-85 wt% discharged slurry after 14 days storage, are quite good in terms of storage stability..

Plots of the CWM viscosity against the coal concentration are shown in Fig. 8. The ACC value decreases when coal is varied D > E > G ≈ F > H which almost parallels the fuel ratio of coal (Table 1). Thus, when more lipophilic coals are used, the coal concentration in CWM can be more raised. However, CWMs which show high ACC values are not necessarily good in terms of storage stability (e. g., CWM from coal D). This would be due to small adsorption of PSS on coal D as shown in Fig. 6.

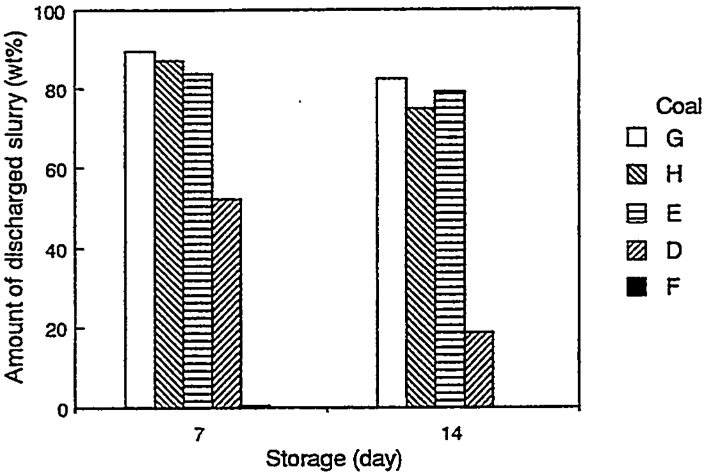

Fig. 7 Amount of discahrged slurry after storage

Concn. of PSS added: 0.5 wt%/CWM

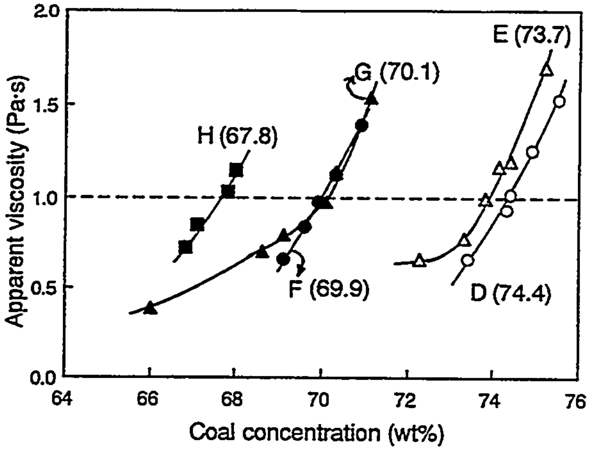

Fig. 8 Plot of CWM viscosity against coal concentration
Concn. of PSS added: 0.5 wt%/CWM
ACC values (wt%) are indicated in parentheses.

CONCLUSION

An ion-selective electrode (Poly-ISE) which responds to polyanion species, such as NSF, PSS, and PIPS, has been developed. By use of the Poly-ISE, adsoption behavior of the CWM additives in CWM has been studied. Although the adsorptions of PSS and PIPS-1 are smaller than that of NSF, the former additives are superior to the latter in terms of attaining high ACC values. The additive (PSS) is considerably adsorbed immediately after the preparation of CWM by the wet grinding method, and the adsorption further proceeds gradually during the storage. The CWM properties, such as fluidity and storage stability, are rationalized in terms of lipophilicity of coal and adsorption behavior of the additive.

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BRIQUETTING OF COAL WITH ROLLER PRESSES.

AN IMPORTANT TECHNOLOGY FOR THE PRODUCTION OF COAL BASED COMPLIANCE FUEL

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1. ABSTRACT:

This will be the third of a series of papers at this Conference discussing the briquetting of coal.

While the first presentation in 1993 [1] covered the historical and technical fundamentals, equipment designs, as well as traditional and contemporary applications, the second paper in 1994 [2] looked at briquetting as an upgrading process for different types of coal.

This year's Conference theme is: "1995 - The year of Compliance". Therefore, the paper will show that briquetting plays an important, often critical role in the production of coal based compliance fuel.

After summarizing present clean coal technologies and the characteristics of coal based compliance fuels resulting from such processes the beneficial and economical application of modern roller presses is being discussed.

2. INTRODUCTION:

The National Coal Council (NCC), a private, nonprofit advisory body, chartered under the Federal Advisory Committee Act, was asked in June of 1993 by the Clinton Administration's new Secretary of Energy to review certain aspects of the U.S. Department of Energy's Clean Coal Technology (CCT) Program and to recommend future directions. The NCC's response is a report entitled *"Clean Coal Technology for Sustainable Development"* [3]. As an introduction to this paper some citations from this report will be presented:

The first states that "coal is the fuel used most widely to generate electricity in the United States" (as well as in many other areas of the world, the Author) "and it will remain critically important for the foreseeable future". Another reports that the US "coal reserves represent over 200 years of energy supply, while natural gas has approximately 50 years of recoverable resources (according to the National Petroleum Council) at current rates of consumption". Worldwide similar relationships exist making coal much more abundantly available than natural gas. Therefore, the NCC report asks if, as a response to the Clean Air Acts of the USA and other Nations, it is really prudent to use natural gas as a primary electricity production fuel, particularly when natural gas is a very efficient end-use fuel for water and home heating achieving upward of 95% efficiency while reaching only approximately 50% efficiency in its most effective electric generation application. Natural gas is also a valuable feed stock for a variety of chemical products.

The NCC report concludes that "we need to take action now to ensure that coal will play its proper role in the future fuel portfolio of this nation" and points to the U.S. Department of

Energy's Clean Coal Technology (CCT) Program, initiated in 1986, and the endorsement of its intent in the language of the Energy Policy Act (EPACT) of 1992. This legislation identifies a number of energy goals which already are part of the CCT Program, including:

- Achieving greater efficiencies in the conversion of coal to useful energy.
- Achieving control of sulfur oxides, oxides of nitrogen, air toxics, solid and liquid wastes, greenhouse gases, or other emissions resulting from coal use.
- Promoting the export and transfer of U.S. clean coal technologies and services to developing countries and countries making the transition to free market economies.

The first of these goals refers to power plant and boiler technology. The second requires identification and/or production of so-called compliance fuels. Since there are only a limited number of natural compliance coals, clean coal technologies must convert non-compliance coals into compliance fuels. Such coal based fuels can be gaseous, liquid, or solid.

Solid compliance fuels from coal, whether natural or processed, are particulate in nature. To reduce the amount of compounds in coal which will cause pollution during combustion, conventional methods of mineral processing are modified to fit the particular needs of coal cleaning and upgrading. Most of these methods require particle size reduction by crushing and grinding to the so-called "liberation size"; when this fineness is reached each individual particle contains only one compound so that suitable separation methods, such as flotation, heavy media separation, jigging, selective agglomeration, etc., will yield a "concentrate" of clean coal and a waste in which all objectionable compounds are held. Another method of upgrading coal is to carry-out a mild gasification during which the polluting volatiles are removed; since this process is accellerated if the particles are small, offering a large surface area, the resulting char or semi-char particles are finely divided, more or less porous particulates.

Many of the natural compliance coals, for example from the Powder River Basin (PRB) in the Western USA, contain large amounts of moisture. The authors of a paper presented at an earlier conference of the Coal & Slurry Technology Association [4] showed the impact of moisture on boiler capacity and efficiency. They stated that "there is a 4% difference in boiler efficiency because of moisture differences between Eastern and PRB coals. In addition, 30% more coal must be transported to the power plant to deliver an equivalent calorific value". However, after drying, PRB coal becomes a powder.

Upgraded, coal based compliance fuel, whether produced by processing or simply drying, that has become a finely divided particulate solid could be burned on the spot to produce electricity or converted to a coal/water slurry and transported in pipelines. However, there are a number of restrictions to the building of power lines or pipelines to distant consumers. The preferred method of transportation in the USA, railroads, which are established in a large scale and accepted by the utilities, can not be used because railcars and handling facilities on both sides are not designed to accept fine particulate solids. Also such materials exhibit a pronounced tendency of selfignition.

As stated in earlier papers [1, 2, 4, 5] briquetting with roller presses can modify the product characteristics such that acceptable handling and transportation characteristics result and railroads can be used for large scale bulk transportation.

After establishing technologies for the production of coal based particulate fuels using the above mentioned methods, including briquetting, the export and transfer of these technologies and of services can be accomplished as stipulated by EPACT creating jobs and widespread commercial deployment.

3. REQUIREMENTS ON ROLLER PRESSES FOR CLEAN COAL TECHNOLOGIES:

A panel during last year's (1994) conference addressed "Coal Fines Utilization". The author of this paper pointed to briquetting as an important technology for the size enlargement of coal fines and, ultimately, the production of valuable coal products. In response, the panel and several persons in the audience highlighted limitations and problems of certain coal briquetting facilities in the past. Because of time constraints it was not possible to refute these opinions.

Most of the concerns were related to the cost of briquetting with all three cost components, i.e. investment, operating, and maintenance, cited as unacceptably high. This is true for most of the "conventional" coal briquetting facilities. History shows [1] that, after a brief period during the first half of the 19th century when a small number of large briquettes was produced in punch presses from coal fines and even peat as a fuel for steam engines, the roller press was invented to form small, high quality, mostly pillow or egg shaped briquettes as premium fuel for domestic use and some smaller industrial applications.

The characteristics of these plants are that bituminous coal fines with a high calorific value were, and in some few cases still are, converted into a consumer product. The briquetting plants were small and competed for consumer acceptance by producing briquettes with extremely high quality including "pleasing" shapes which sometimes included identifying marks (Figure 1). Since these briquettes were sold in small quantities to the consumer they commanded high price and large profit margins. Plant sizes were in the range of a few hundred thousand tons per year with some smaller than 100,000 t/y and, in the heydays of coal briquetting in Europe, a few as large as 1.5 Million t/y. In the beginning, individual roller presses briquetted less than 10 t/h and later typical machine capacities were in the range of 30 t/h (Figure 2). Maintenance was frequent, involving the press manufacturer for remachining the molds on the replaceable rings (Figure 3) to guarantee flawless briquette shapes, sometimes including identifying marks as mentioned above, and its cost was easily absorbed.

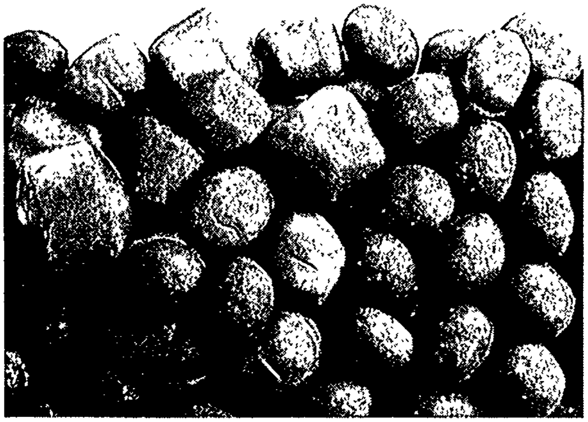

Figure 1: Photograph showing high quality briquettes from bituminous coal and a binder produced in roller presses.

Obviously, requirements on roller presses for use with clean coal technologies are quite different. For one, the product is no consumer product but a bulk commodity for consumption by large power stations. Secondly, the product must be moved with mass handling and transportation equipment over long distances often including several transfer points. Thirdly, while quality is a concern, the "briquettes" must not nearly have the same characteristics as the traditional consumer product. And finally, the cost of briquetting must be as low as possible; this includes that the product must be handleable and transportable using the same facilities presently used for raw coal so that no new investments are necessary in this area.

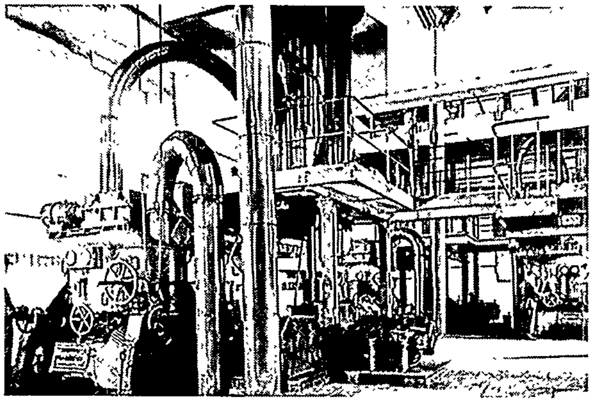

Figure 2: View of a conventional coal briquetting plant showing roller presses with capacities of approx. 30 t/h (courtesy KÖPPERN).

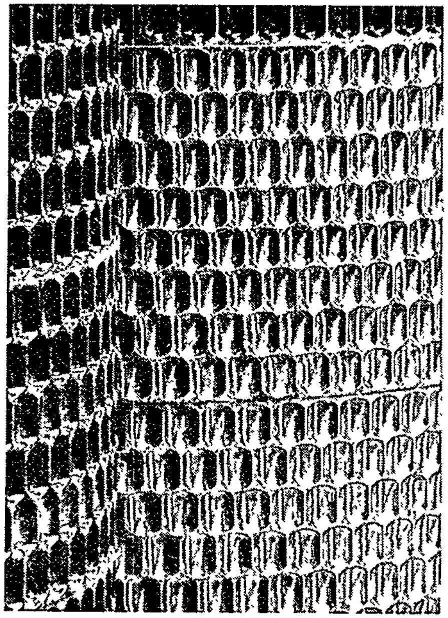

Figure 3:
Replacement press rings for coal briquetting stacked-up at the facility of a roller press manufacturer waiting for reinstallation (courtesy KÖPPERN).

4. DESIGN OF MODERN ROLLER PRESSES FOR CLEAN COAL TECHNOLOGIES:

After the sharp decline in the 1960s of conventional coal briquetting, which produced an excessively polluting fuel, three new applications of coal briquetting evolved:

4.1 Smokeless Fuel.
4.2 Form Coke.
4.3 Compliance Fuel.

4.1 Smokeless Fuel:

To overcome the main problem of conventional coal briquettes, beginning in approx. the 1960s, research started in Europe, particularly England, and Japan to develop "smokeless" coal briquettes. As a result of fundamental studies into and evaluations of briquetting of coal at the British National Coal Board's Coal Research Establishment (NCB/CRE) a book on Roll Pressing was published in 1976 [6].

Smokeless Fuel was to become again a consumer product with all the requirements mentioned above, including excellent physical quality and pleasing appearance. The latter motivated one producer in England to dip the briquettes into a special gold bronze during curing to replace the "dirty black coal look".

Although a number of processes were developed which were either based on cold cure binders [7] or on hot briquetting, the abundant availability of clean, cheap energy did not let this technology grow as originally anticipated. The few plants built and operated were small using low capacity roller presses. Some included a new feature, the "hinged" frame which allows quick exchange of rollers (Figure 4) so that the frequently required remachining can be carried- out with a minimum of downtime (see also below, 4.3). The machine in Figure 4 also features large roller diameter, which results in better forming characteristics in the longer nip area, and cooling required for hot briquetting.

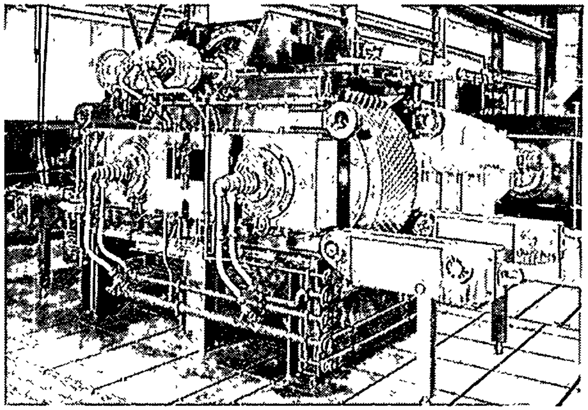

Figure 4: Modern, small capacity roller press built for a smokeless fuel producer in England (courtesy KÖPPERN).

4.2 Form Coke:

Also in the late 1950s and early 1960s a number of companies and organizations around the world began working on the development of so-called form coke processes [5]. These activities followed in the wake of an unprecedented growth in steel production and forecasts predicting a continuing steep increase. At the same time, fears came up that coking coal reserves may soon be insufficient to satisfy the demand and a growing awareness of the need for a better protection of the environment became a topic of much concern. Therefore, the goals of all developments in this field were:

- A coke product that would perform as well as or better than conventional coke.
- A process that permits use of a wide range of either coking or non-coking coals and produces a consistently uniform coke.
- A process that meets present and future environmental laws.
- A process that delivers a coke product at essentially the same cost as that from conventional coke making while meeting the above requirements.

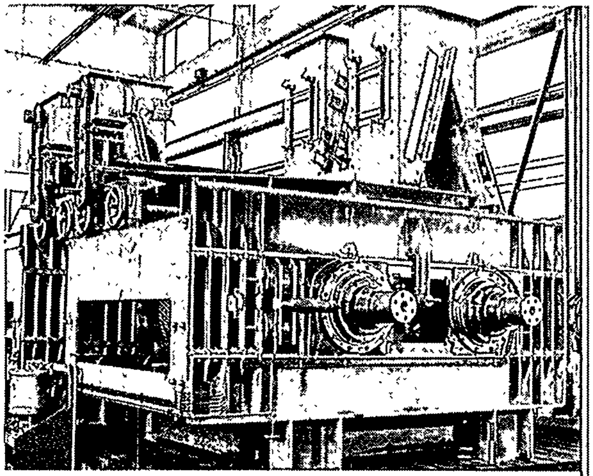

Figure 5:
Large roller press with a capacity of up to 120 t/h of coal briquettes with a binder for the SUMICOAL partial briquetting process (courtesy KÖPPERN).

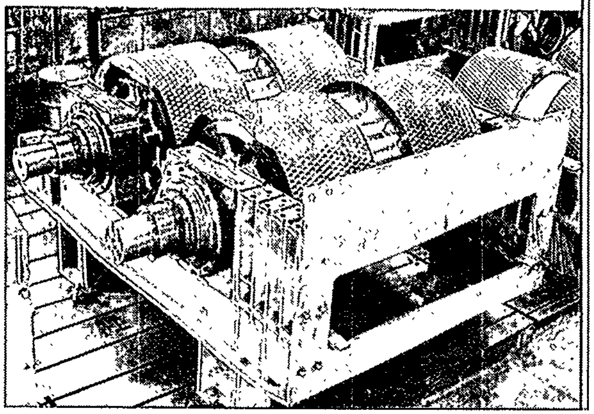

Figure 6:
Roller press of Figure 5 with its top removed for roller maintenance (courtesy KÖPPERN).

Although the pilot work using roller presses was carried-out with small conventional equipment, it became obvious that the economical and environmentally safe production of this new bulk commodity required large facilities. Several such plants were in advanced planning stages, e.g. U.S. Steel, Gary Works, IN, 1.5 Million t/y, when new coking coal reserves were discovered and a fundamental technological change began in the steel industry with a move away from the blast furnace, the major consumer of coke. Therefore, the only larger applications also using high capacity roller presses are plants in Japan and South-Africa [5]. Beginning in 1974, KÖPPERN of Germany supplied a total of 12 machines for the *SUMICOAL* partial briquetting process of coke oven charges. Each of these machines (Figure 5) is rated for a capacity of up to 120 t/h [5]. Because a binder is added for briquetting, relatively low forces are required and wear is moderate. When the rollers must be removed for maintenance, the top part of the press, including feeder, is removed (Figure 6) providing access to the roller sets.

4.3 Compliance Fuel:

As compared with the two previous technologies, the briquetting of compliance fuel must yield a bulk commodity with much higher production rate and lower conversion cost. While in the above two cases well shaped briquettes were required or preferred, compliance fuel must meet the size criteria of coal for power plant which is, for example, 0 to 50 mm (approx. 0 to 2 inches) with only a small amount of "dust", a characteristic which is not defined [8] but represents a subjective "requirement" for "safe" loading and handling.

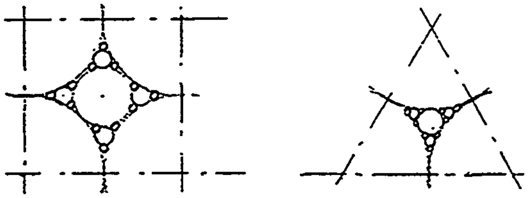

Figure 7: Two models with spherical particles depicting sizes for theoretically densest packing.

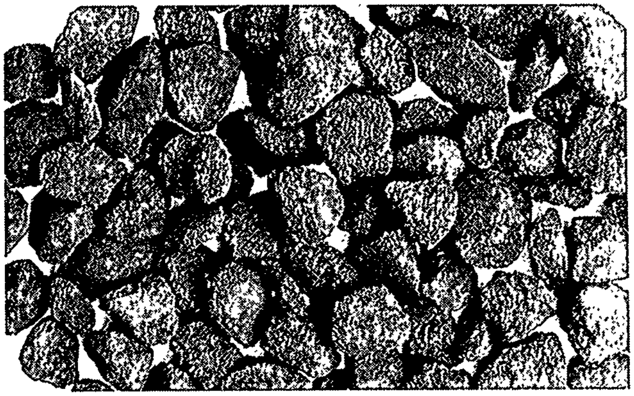

Figure 8: Screened product after the sizing (calibration) of briquetted coal

Coal for power plants is transported in bulk in large trucks, railroad hopper cars, unit trains, barges, and seagoing vessels. Because, particularly in the case of railroad cars, the volume of the load is predetermined by the existing car design, the unit mass of a new, briquetted product in t/m^3 or lbs/ft^3 must be similar to that of raw coal to guarantee delivery of the same amount. Monosized particles, such as clean briquettes do not pack densely because large voids form between them similar to the situation encountered in regular cubic or orthorhombic packings. As shown in two models (Figure 7) smaller particles can fill these voids and increase the unit bulk mass. Therefore, it is desirable for the production of this bulk commodity to obtain partially broken briquettes or to pass briquettes through special "calibration" equipment. As shown in Figure 8 the screened product after calibration is similar to regular screened coal and, in reality, also contains a considerable amount of finer material which fills the interparticle voids and increases the bulk density as indicated by the models of Figure 7.

Depending on the nature of the finely divided particulate compliance fuel, briquetting can be accomplished binderless or with a binder. The major difference between the two briquetting technologies is the specific force in kN/cm roller width, which is high for binderless briquetting (approx. 40 - 60 kN/cm) and low if binders are used (approx. 20 - 30 kN/cm). Consequently, the throughput capacitiy of a machine briquetting coal with binder is approx. two to three times as high as that of binderless briquetting.

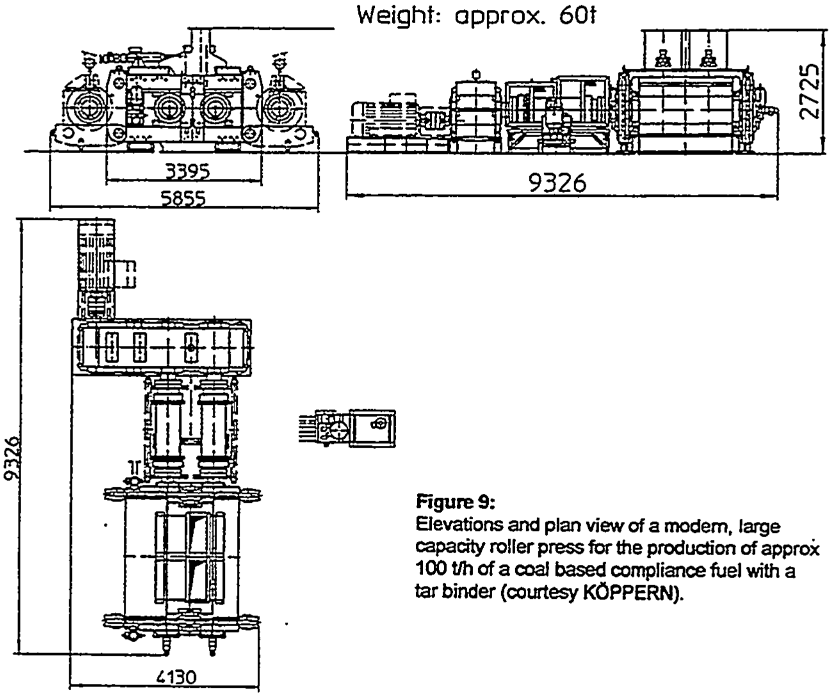

Figure 9:
Elevations and plan view of a modern, large capacity roller press for the production of approx 100 t/h of a coal based compliance fuel with a tar binder (courtesy KÖPPERN).

Figure 9 represents elevations and a plan view of a modern roller press for the briquetting of approx. 100 t/h of a coal-based compliance fuel including a tar binder. Contrary to the design shown in Figures 5 and 6, -although the feeders, rollers, and drives are similar-, the frame features the hinged design as depicted in Figure 4. This allows a much simpler and faster exchange of rollers when wear requires maintenance of the pressing tools thus increasing availability and decreasing maintenance costs. A roller press for binderless briquetting would be narrower, only have one pair of rollers and one feed chute per machine and, therefore, only yield approx. half the production rate at twice the specific pressing force. While the product size distribution from a process using binder must be adjusted in a calibrator to result in a densly packing mass as described above, the briquettes from binderless compaction are so "imperfectly formed" that no additional sizing step is required.

5. CONCLUSIONS

Conventional coal briquetting and the production of smokeless fuels were designed to yield consumer products with high quality, pleasing appearance, and high profit margins. Therefore, small production units were preferred and theoretically economical but the abundant availability of clean, cheap energy did not favor the continued use of a fuel with a relatively troublesome application.

Form coke technologies, on the other hand, required large plant capacities together with well shaped products. After extensive demonstrations in pilot plants, large roller presses were designed and installed to meet these requirements; however, when a rather unexpected change in major steel making techniques occured the justification for further development was lost.

The private and legislative drive for the development and use of Clean Coal Technologies opens another opportunity for the briquetting of coal based fuels with roller presses, Since now the objective is to produce a boiler fuel, briquetting plants are only economical if the units are large and the conversion costs, which are greatly influenced by the need for maintenance, are low. Since the product from such plants does not require to be of particularly high quality but must be handleable and transportable in bulk, whereby similar conditions are accepted as presently experienced with bulk coal [9], modern high capacity equipment is available to fulfill these requirements including easy maintenance.

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MASS FLOW MEASUREMENT OF PULVERIZED COAL

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BACKGROUND

Despite of the national and international agreements for limitation of carbon monoxide emissions, the use of coal in energy production will inevitably increase both in industrial and developing countries. For example in 1990 the share of coal in electricity production was 39% and according to estimtes its share will stay fairly stable at 40% in 2010 and 38% in 2020. The forecasted absolute growth numbers of coal use are 63% in 2010 and 87% in 2020 compared to 1990. According to the International Energy Agency (IEA Coal Reseach Profiles, January 1992) the world coal use in power stations will increase by over 80.000 tons a day during the 1990s'.

When burning coal, several harmful enviromental gases are formed, the most harmful being carbon dioxide and oxides of sulphur and nitrogen. Technically speaking the amount of the gases mentioned can be reduced to acceptable levels, the problem being the costs of the reduction. The reduction of carbon dioxide is not economically solved while the reduction of sulphur and nitrogen oxides are on the level of economic acceptance.

There are over 150 methods available to reduce sulphur oxides from flue gases. However, only a couple of these methods are in practical use. Sulphur oxides can also be reduced by using advanced burning technologies, which allow the capture of of sulphur of the fuel during combustion process (e.g. fluidized combustion technology).

Nitric oxides can be reduced either during the process of their formation, i.e. while burning the fuel, or by handling flue gases. In general, reduction of nitric oxides is far more difficult and expensive than reduction of sulphur oxides.

Reduction of nitric oxides during combustion of pulverized coal is succesful when so called Low NOx burners are used. The problem with these burners is that the combustion air to fuel ratio should be known and kept in very narrow limits, which means that the air flow to the burners should be adjusted. Today measurement technology of air flow is well known and reliable. However, there is no continuously working measurement instrument to measure the mass flow of coal to the burners. This is confirmed e.g. in the market analysis made in spring 1994 in Finland by a company called Cerntech Oy.

Knowing the problems with Low NOx burners we started to think about the possibilities of measurement of pulverized coal mass flow. Some years ago we made some trials with laser technology to measure the coal concentration in carrier pipes. The principle was to measure the concentration of coal via absorption of laser light. Because of the very strong absorption by coal dust it was necessary to install so called "light tubes" into the carrier pipe for the purpose of shortening the light path (acceptable absorption needs a light path of only abt. 3" in length). Even in the case of ceramic light tubes the erosion was terrible; their life time was only two weeks. At that time the velocity measurement problem was not solved.

Now there is a PCT patent application which covers e.g. measurement of mass flow of pulverized coal. A prototype made according to the patent application has been tested in the Laboratory for Emission Measurement and Reduction Technology of Lappeenranta University of Technology where circumstances close to those in real coal carrier pipes of boilers can be achieved. According to our test results it is assumed that the planned measurement arrangement and instrument can be applied to the existing boilers.

MEASUREMENT PRINCIPLE

Figure 1 shows the basic principle of the measurement. Coal concentration is measured by a well known and reliable radioactive method (absorption of beta radiation). Velocity is measured by marking of the flow, the possible marking methods are mentioned at the bottom of Figure 1. The easiest and cheapest marking method is the dilution of the flow, i.e. creating an air bubble in the flow. When the bubble crosses the combination of radiation source and radiation detector, it is recorded by the electronics of the meter. In the case of two radiation source+detector systems quite accurate velocity can be measured by measuring the retention time in path b. A simpler and cheaper method is shown in Figure 2; because the air bubble is formed in some tens of milliseconds it can be assumed that this arrangement will be good enough for practical measurements (this arrangement corresponds to the measurement of retention time in path a shown in Figure 1). It must be remembered that in most cases the information of relative mass flow is enough for adjustment of air flow (remember that one pulverizer feeds all burners in one burner level of the boiler).

The mass flow can now be calculated simply by multiplying the concentration by velocity and by the cross section area of the pipe. It must be pointed out that in practical coal carrier pipes the velocity profiles of the flow are similar and that the flow is a plug flow the boundary layer thickness being abt. 1% of the radius of the pipe.

In our laboratory tests the air bubbles were formed by feeding air into the dust flow via four ports according to Figure 3.

There are even written claims that the coal pulver flows in some cases in a form of "rope" in the pipe. We have not found this phenomenom yet. In the eventual case of rope formation the measurement arrangement shown in Figure 4 should be used. In this case we use two or three radiation sources and strip-formed detectors. This kind of detector must be developed (they are easily developed; the problem being only money). In Figure 4 it can be seen that the cross section area of the pipe covered by radiation is large enough for really exact concentration measurement. This kind of measurement arrangement is called "advanced".

As mentioned before, the radiation source is a beta source, i.e. electron source. In our arrangement the transmitted electrons collide with a plastic scintillator plate, which transforms the collision energy into UV light, which is detected by a photomultiplier tube. In the future a semiconductor detector will be more probably used.

Both the radiation source and the detection system are flushed with purge air to avoid erosion of the protection foils of the source and detector. This arrangement has worked well - there are no signs of erosion at all.

TEST RESULTS

The tests were carried out in the Laboratory for Emission Measurement and Reduction Technology of our University (see the scheme in Figure 5). Pulverized coal was "real" coal from a power plant. In the first stage the coal was fed by a screw feeder but afterwards a new lock feeder was constructed, because the capacity of the screw feeder was too low.

In Figure 6 the output signals of the meter are shown at a constant feeding rate. In the figure the expression "counts" means counts from the photomultiplier tube and "time" the collecting time of the pulses. It is clearly seen that the lock feeder especially gives uneven concentration, which is clearly understood knowing the operation principle of the feeder.

In the Figure 7 the effect of coal concentration variation on the meter output signal can be seen. It accurately follows the theoretically calculated dependence, the confidence limits being only a small percentage. This is exact enough for practical purposes. In practice the concentration is abt. 500 g/m^3 (abt. 220 grains/cu ft).

It was expected that in our test arrangement the air purge (bubble formation) causes a thickening effect instead of dilution, because the pressure drop in the system is too low. Thus the purge air pulse lowers the air velocity between the air fan and purge air feeding ports, which causes thickening of the coal-air mixture before the purge air feeding points. After closing the air ports the thick mixture enters the radiation source+detector combination, which can be clearly seen in the readings of the meter (see Figure 8). In the real pipe this kind of phenomenom is not possible - there must be dilution of the flow.

NEXT STEPS

In the near future one meter will be installed in a coal feed tube of a boiler. If - and when - it works really, three other pipes will be equipped with the meters. The boiler is equipped with four corner burners. In this case we will see the advantages of the measurement.

ADVANTAGES OF THE MASS FLOW MEASUREMENT

The advantages of the measurement can be listed as follows:

1. Reduction of nitrogen oxides during combustion due to correct combustion air to fuel ratio (the correct ratio allows achievement of the minimum combustion temperature of the flame)
2. Increased life time of the NOx converter catalysts due to decreased NOx concentration of incoming gases
3. Increase of thermal efficiency of the boiler due to uniform distribution of combustion air for every burner
4. Decrease of carbon content of fly ash, which increases the possibilities of economical use of the ash
5. Decrease in fouling, slagging and reducing corrosion of the upper part and superheaters of the boiler
6. Better possibilities to fulfill the legislative levels of NOx concentration (e.g. ECE directives)
7. It is a powerful tool for pulverizer condition control (in case of damaged balls or bowls a "puff" can be seen by the meter)
8. It gives easy possibilities to retrofit old boilers with Low NOx burners
9. **No mechanical parts inside the coal carrier pipe; no erosion problems**

As an example a calculation of the economical and technical aspects are given in App. 1 and App. 2.

Appendicies:
Figures 1...8 (5 pages)
App. 1 (2 pages)
App. 2 (1 page)

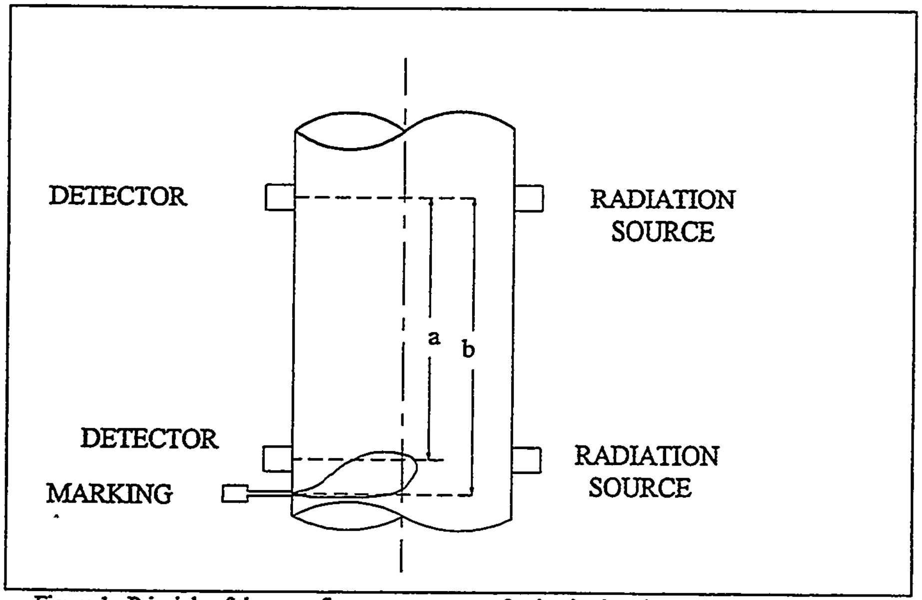

Figure 1. Principle of the mass flow measurement of pulverized coal.

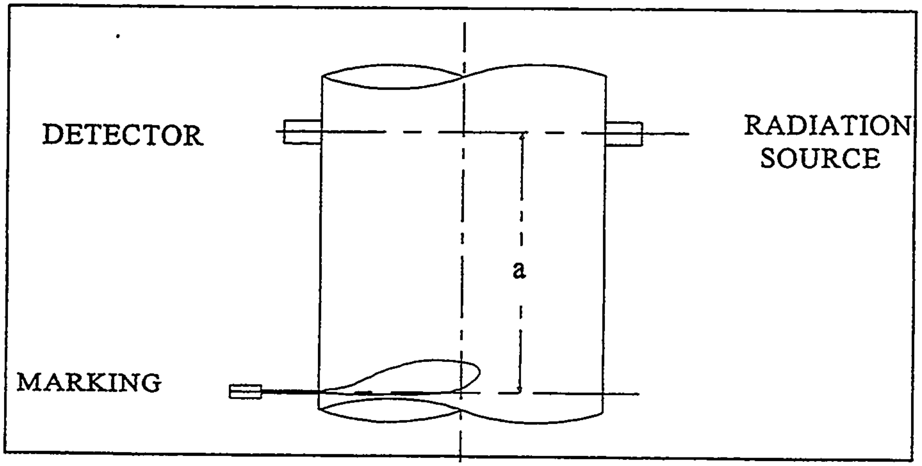

Figure 2. Simplified method for measuring the coal dust mass flow.

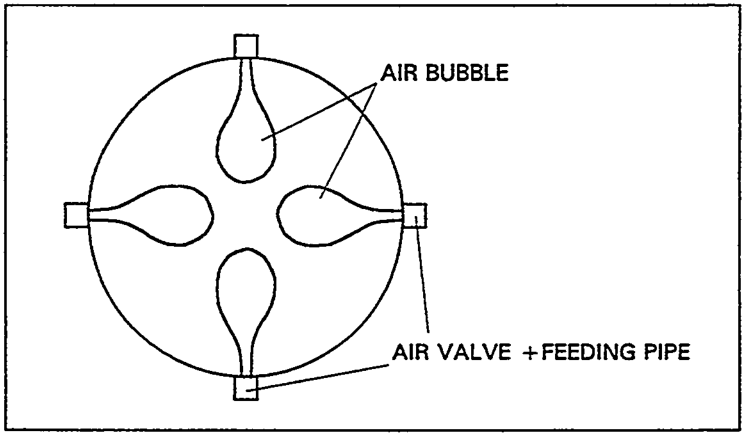

Figure 3. Forming of air bubbles

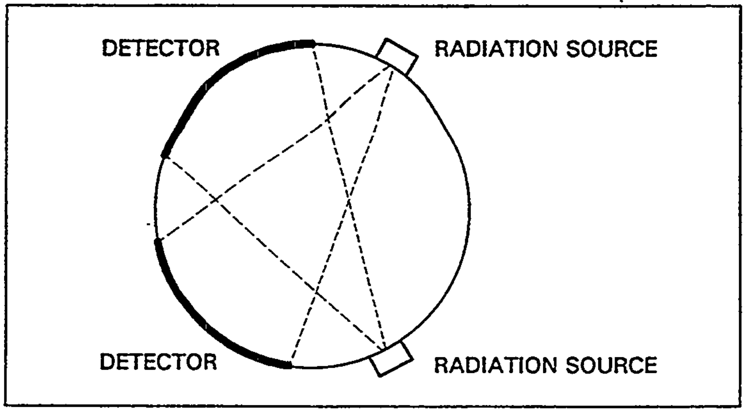

Figure 4. Advanced measurement arrangement

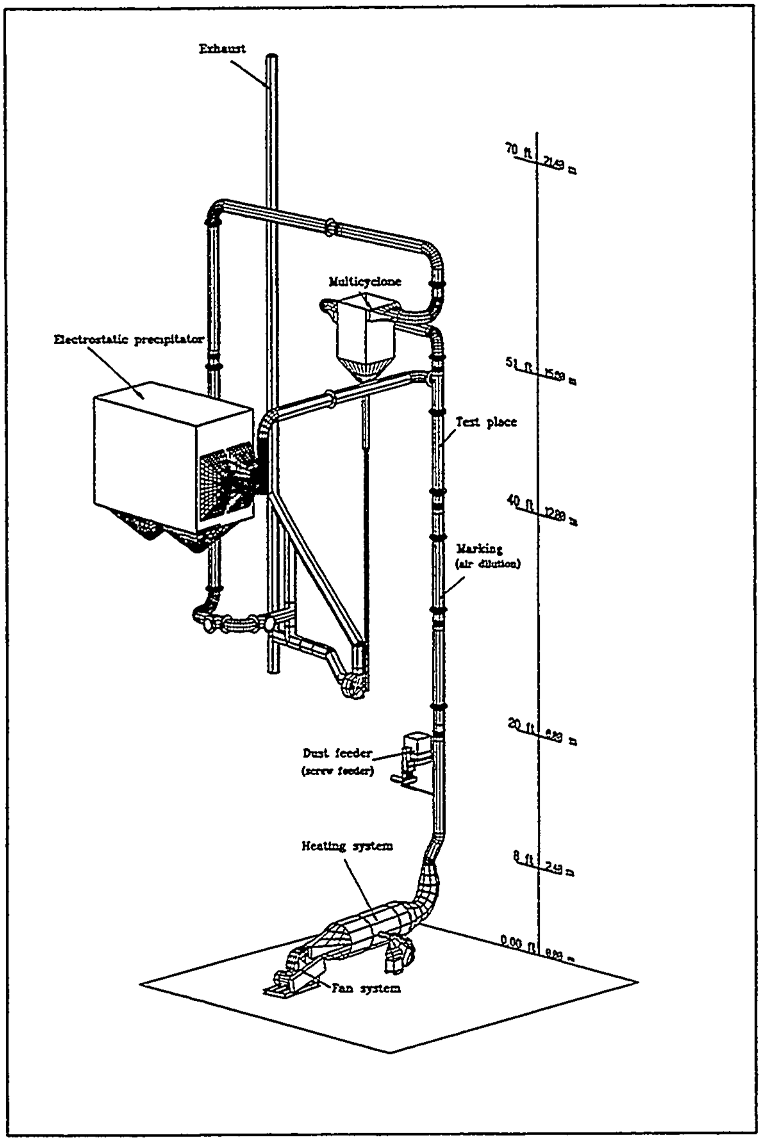

Figure 5. Schematic drawing of test arrangement

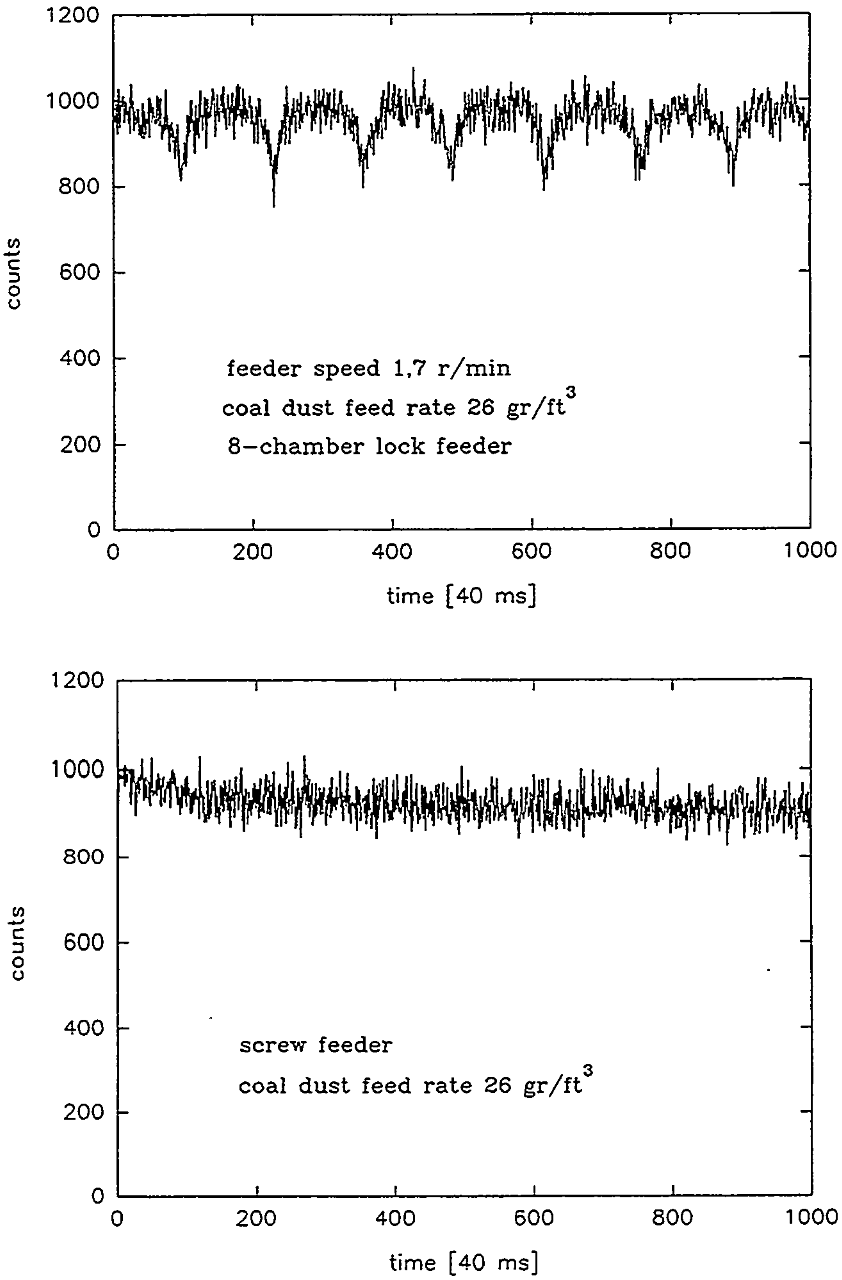

Figure 6. Examples of the output signals from the meter

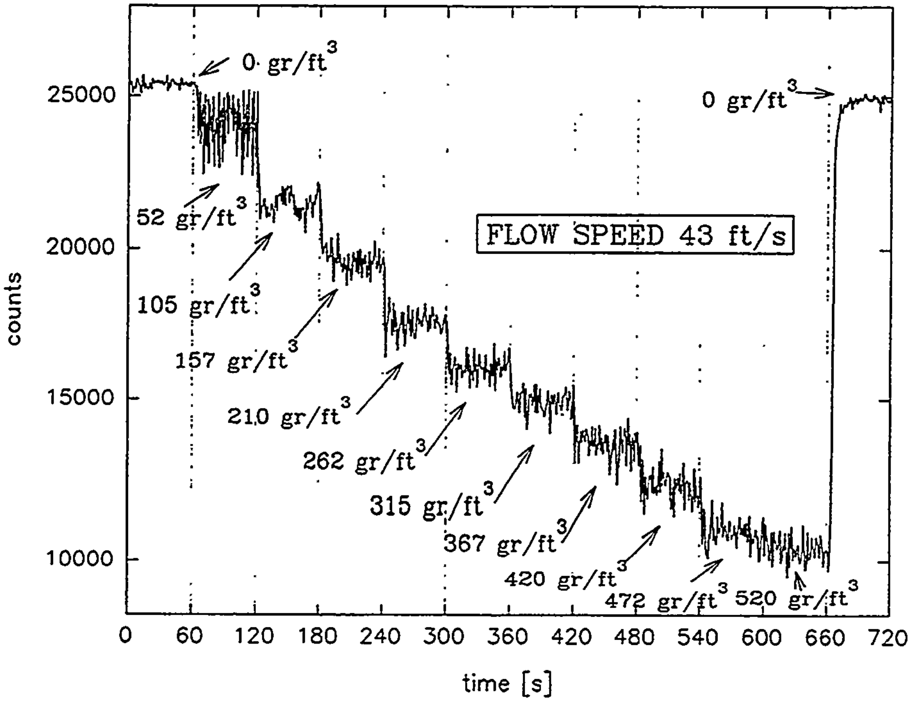

Figure 7. Effect of coal concentration variation on the output signal

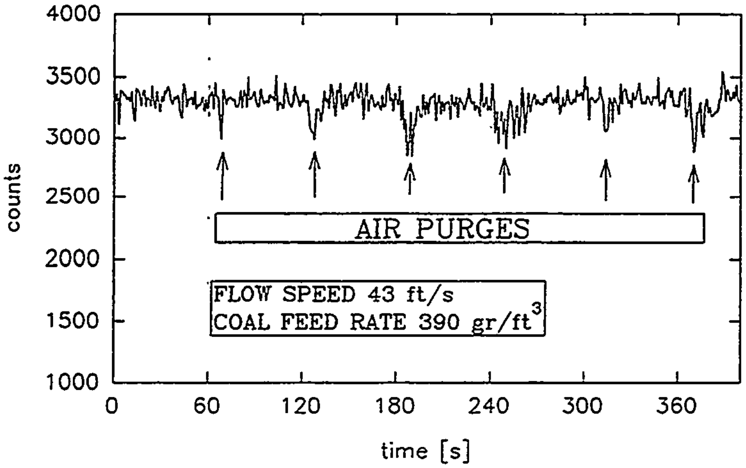

Figure 8. Effect of air purge on the meter output signal

MASS FLOW MEASUREMENT OF PULVERIZED COAL
ECONOMICAL AND TECHNICAL ASPECTS

ASSUMED INPUT DATA FOR EVALUATION

In the following the burning process **for one burner** is examined. The capital and variable costs and their dependence on some process parameters are shown. The basic assumptions for the calculations are:

* diameter of the carrier pipe of pulverized coal	15.7 in
* coal concentration in the carrier pipe	220 gr/ft^3
* velocity of the coal/air mixture in the pipe	82 ft/s
* lower heating value of the coal	26 MJ/kg
* ash concentration of the coal	12 %
* peak load utilization time of the burner	6.000 h/a
* electricity generation efficiency of the power plant	35 %
* energy price of the coal in Finland (at coast) 1993/XII (Ministry of Trade and Industry; Energy Review 1/1994)	7,84 $/MJ 40 FIM/MJ
* SCR NOx reduction plant investment cost is 80 /kWe, of which 40 % for catalysts; effective service time of catalysts is supposed to be 3 years, so the annual investment cost for catalysts is (Chemical Engineering/January 1994)	10,7 $/kWe,a 54,4 FIM/kWe,a
* ammonia price	0,088 $/lb 0,45 FIM/lb

SOME PARAMETERS CALCULATED FOR THE BURNER

* heat output of the burners	40MWth
-corresponds to electricity output	14 Mwe
* coal mass burned during one year	34.000 t/a
* heat energy released theoretically in the burning process during one year	246.000 Mwh 884.000 GJ
* ash mass into the boiler during one year	4.080 t/a
* 1 % unburned coal in the ash corresponds to yearly energy (calculated according to lower heating value of pure coal 33,73 MJ/kg)	1.380 GJ/a 382 MWh/a

ECONOMICAL AND TECHNICAL EFFECTS

Effect Of Unburned Coal In The Ash

* calculated on the basis of the energy price of the coal 1 % of unburned corresponds to energy savings of	3.000 $/a 15.300 FIM/a

Effect Of The Reduction Of Nitrogen Oxide Concentration

Assuming that the concentration of nitrogen oxides reduces **20 % from the initial value of 150 mg/MJ ,ie. 30 mg/MJ,** the economical effects can be calculated as follows:

* ammonia economy calculated on stoichiometric reaction ratio of nitrogen monoxide/ammonia	1.880 $/a 9.600 FIM/a
* annual cost savings of catalysts assuming the effective service time of the catalysts proportional to the nitrogen oxide concentration of incoming gas	29.800 $/a 152.300 FIM/a

Other Saving Potentials

Other saving potentials which can be achieved by using the mass flow metering system, should be estimated case by case. The use of the measuring system allows to influence positively on the following phenomena:

- * fouling and slagging of the boiler furnace walls
- * corrosion of the boiler furnace tubes due to unwanted reducing atmosphere
- * uneven steam temperature distribution after superheaters
- * heat transfer

ADDITIONAL INFORMATION

The Finnish Govemement has decided (winter 1991) the highest permissible nitrogen oxide concentration limits as follows:

* existing plants; heat output over 100 MW , plants equipped with burners:	
- wall firing	230 mg/MJ
- corner firing	180 mg/MJ
* new plants; heat output over 150 MW	50 mg/MJ

In the light of above mentioned figures the nitrogen oxide reduction target 30 mg/MJ is a moderate and realistic value; in the practice higher reduction values should and must be reached.

Measured nitrogen oxide values in boilers without any reduction measures vary from hundreds to over one thousand of mg/MJ; even if the boiler is equipped with Low-NOx burners the concentration limit of 150 mg/MJ is difficult to achieve.

APPENDIX TO THE PAPER "MASS FLOW MEASUREMENT OF PULVERIZED COAL. ECONOMICAL AND TECHNICAL ASPECTS" FROM 07.08.1994.

In the "Chemical Engineering"/January 1994, page 29 there is a table, where it is shown that in the year 1995 North America's NOx control equipment renevue forecast as it regards to burners, is abt. M$ 306. If we assume the price of one burner being 0,3 M$, this means that in North America there will be installed abt. 1.020 burners in 1995.

If we take into account that the use of coal in North America is abt. 22% of the clobal use, in the world there should be installed abt. 4.600 burners. Of course most of these burners should be the Low-NOx ones, but due to lack of money of the developing countries this can not be reality. But still it seems that there is a big market waiting.

SPONTANEOUS IGNITION OF COAL IN PRESSURISED LOCK-HOPPERS; SAFETY ASPECTS

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SUMMARY

Coal, as well as other fuels, have a tendency to produce heat through oxidation and consequently, to ignite spontaneously during storage. The risk of spontaneous ignition increases, in particular, if the temperature of the fuel is higher than normally at the start of storage, for example, due to drying or grinding processes.

The temperature of self-ignition is reduced sharply by pressure rise. On the other hand, this temperature can be increased by inertisation. The ignition tendency is dependent, in addition to the fuel type, on the shape of the store and, in particular, on the amount of the fuel.

The tendency of coal to spontaneous ignition was studied with the pressurised dynamic research equipment in the Energy Production Technologies Unit of VTT Energy (one of nine Research Institutes of the Technical Research Centre of Finland). It is possible to study spontaneous ignition even at 100 bar pressure with this equipment. Results of tests carried out with granular coal (D_{50} = 0.95 mm) and pulverised coal (55 % <200 mesh) at normal 1 bar pressure and 25 bar pressure will be discussed in the paper. The measurement results were extrapolated to full-scale storage bins and hence can be applied directly to cases in practice. Self-ignition determinations were also carried out for different biofuels, like forest residue and straw.

The results indicated that the coal ignited at much lower temperature than the wood fuels. The coal ignites at much lower temperature at 25 bar pressure in pressurised plants, for example, in lock-hoppers, than at normal atmospheric pressure. Typical values are the results extrapolated for a bin of 21 m^3, in which the granular coal ignites spontaneously at 25 bar pressure already at <40 °C. By inertising with flue gas of 5 vol% oxygen content the self-ignition temperature can be increased to an about 5 °C higher level than by pressurising with air. The corresponding value for forest residue at 25 bar pressure was about 120 °C (O_2 = 21 %), and when inertising with flue gas (O_2 = 3 %) the self-ignition temperature can be increased close to 140 °C. Respectively, pulverised coal ignited spontaneously at about 65 °C at atmospheric pressure, when extrapolated to the bin size of 21 m^3.

The results can be utilised in dimensioning fuel bins, in selecting and designing preventive safety systems, and in monitoring and controlling processes.

INTRODUCTION

The thermal processes (combustion, gasification, pyrolysis) applied today require almost without exception a homogeneous fuel and hence a fairly exhaustive pretreatment. Coal is usually sufficiently homogeneous, while the heterogeneity is a general characteristic of biomasses. All fuels require a pretreatment of some kind, which usually includes drying, crushing, grinding and sieving, and in all these stages the inhomogeneity and dusting of biomasses hamper their easy and safe treatment. Knowledge of safety-technical characteristics of coal and biomasses is of crucial significance for the preparation of safety systems and instructions, and for the assessment of explosion and fire hazards.

The aim of the project is to measure and assess safety factors related to pressurized feeding of different fuels. Self-ignition characteristics of forest residue chips, coal and straw are measured in ambient and pressurized conditions. The effect of different types of inert gas on self-ignition temperatures at different pressures have also been studied.

SELF-IGNITION TESTS

Treatment of Test Materials

The particle size of forest residue was rather coarse and the materials were, therefore, milled by a disc refiner two times to obtain a sufficiently fine particle size for a homogeneous mixture suitable for the tests. The particle size of forest residue chips ,coal and straw are shown in Figure 1. Other characteristics and chemical composition of the fuels are presented in Table 1.

The self-ignition temperature is affected by the volume weight of biomass in practice. As there was no exact value of bulk density in practice available, the volume weight was determined with a laboratory method generally used by machine manufacturers for bulk material when dimensioning equipment if no other value of volume weight is available. The method has been presented in [1].

The volume weight measurements were carried out with a 500 cm^3 vessel as shown in Figure 2 by filling the vessel to the brim through the funnel, by dropping the vessel to its base with 3 mm amplitude 1 000 ± 50 times and by measuring the change in volume. This operation was repeated so many times that the difference of two consecutive measurements is < 50 cm^3. The final loaded volume weight is calculated from this last volume. Results of volume weight measurements for some fuels are presented in Table 2.

Results obtained with this method have been compared with volume weight measurements carried out for peat in a 5.4 m^3 bin at the Laboratory of Fuel and Process Technology of VTT in 1986 [2], which indicated fairly similar results.

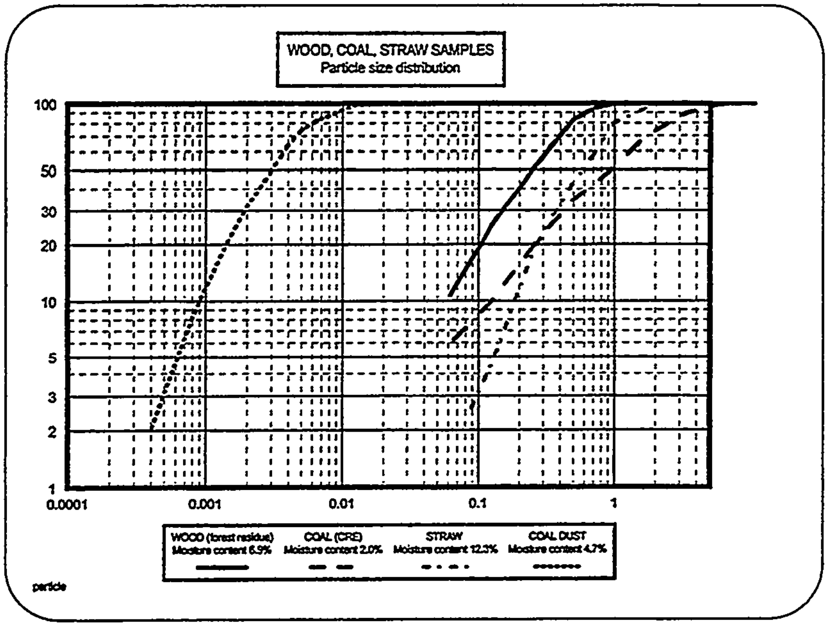

Figure 1. Particle size of forest residue (milled), straw and coal used in ignition tests.

Table 1. Characteristics of forest residue chips compared with those of some other biomass fuels used in ignition tests.

	Coal dust	Coal	Forest residue	Straw (dried)
Particle size, D50, mm	0.074	~0.95	0.22	<3
Moisture content, %	4.7	3.9	6.9	11.6
Ash content, % of dry matter	19.3	16.2	2.6	4.7
Volatiles, % of dry matter	30.8	31.9	78.8	77.7
C content, % of dry matter	60.7	63.4	53.1	47.3
H content, % of dry matter	4.4	4.0	5.9	5.8
N content, % of dry matter	1.3	1.1	0.3	0.6
O content (by difference), %	6.8	8.5	38.1	41.6
S content (total)	2.0	1.6	-	
Chlorine	<0.10	0.21	-	

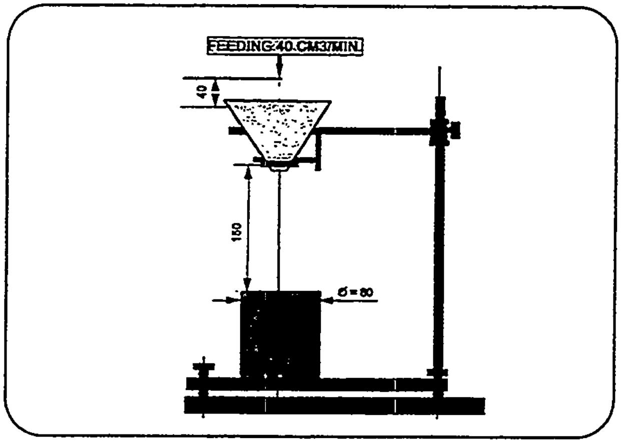

Figure 2. Measuring equipment of volume weight (FEM) [1].

Table 2. Results of volume weight measurements for fuels.

Fuel	Density kg/m^3 (loose)	Density kg/m^3 (compacted)
Forest residue /coarse	196.5	238.3
Forest residue / fine	216.8	273.8
Saw dust	253.9	274.1
Coal d_{50}=0.95mm	840.3	910.9
Coal dust d_{50}=0.03 mm	503.8	762.1
Straw (<3mm,dried)	67.4	91.3

General

In the statistics on dust explosions in coal and peat plants in Germany, the ignition source has often, in more than 20 % of explosions, been self-ignited fuel. The most common ignition sources are presented in Table 3.

When storing and handling biomass and other fuels, the tendency to spontaneous ignition and the temperature required for ignition should be known. Primarily four factors contribute to spontaneous ignition:

1. oxidation tendency
2. ambient temperature
3. amount and characteristics of the material
4. shape of the storage bin.

Table 3. The proportion of different ignition sources in coal and peat dust explosions [5].

Ignition source	% of cases
Self-ignition	20.5
Smouldering	15.4
Hot surface	12.8
Fire	12.8
Mechanical sparks	5.1
Mechanical heating	5.1
Welding (flame. sparks. etc.)	2.6
Electrical tools (cable lamps)	2.6
Unknown. or not given	12.8
Other	10.3

Changes in the oxidation tendency of the material also affect its tendency to spontaneous ignition. The ambient temperature and the amount and form of the stored material are of significance, as heat generation typically occurs in proportion to volume and heat losses occur through the surface. As the volume increases according to the third power and the surface area according to the second one, there is a critical amount of material in which the generated heat is able to escape through the surface relatively quickly to prevent the temperature within the material from reaching the ignition point. The prevailing pressure also affects the tendency to spontaneous ignition via oxidation and heat transfer.

Materials consisting of combustible substances always heat spontaneously to some extent due to exothermic reactions. These materials have no exact self-ignition temperature, but self-ignition is dependent i.a. on the amount of the material. The self-ignition temperature is defined in this case as the temperature, at which the heat amount produced by oxidation per time unit and, on the other hand, the heat efficiency transferring from the outer surfaces of the material to the surroundings and their derivatives with regard to temperature are equal. The temperature dependence of reaction rate is usually very highly unlinear. Consequently, if the temperature exceeds the self-ignition temperature, the heat yield is greater than the heat losses, and as a result the reactions are accelerated further by the temperature rise. The temperature continues to rise until a new stationary state, i.e. combustion temperature, is reached.

Theoretical Background

The theory of spontaneous combustion has been discussed by Bowes [3] and Beever [4]. It has been found that the critical boundary of conditions between safe and unsafe storage of a material can be indicated by the equation:

$$\ln \frac{\delta_c \cdot T_c^2}{r^2} = M - \frac{N}{T_c} \qquad (1)$$

where T_c = ambient temperature, K
r = characteristic dimension (e.g., radius of a cylindric bin)
δ_c = Frank Kamenitskii parameter depending on geometries
M and N =constants of the material.

Equation (1) describes critical conditions - if the temperature is higher than T_c and/or if the size of the storage bin is larger than r, ignition will take place. If the temperature is lower than T_o or the size smaller than r, the storage bin is safe. The value of the parameter δ_c is available from the literature [4] and the parameters M and N have to be determined experimentally.

The principle of isothermal test methods is to establish constants M and N in the laboratory so that T_c can be predicted for a given r for a known geometry in the practical case, or vice versa. This is done by finding the critical ambient temperature T_c for the ignition of at least three relatively small samples of material in the laboratory. Equation (1) can be used to extract M and N by linear extrapolation, and when δ_c and r for the practical situation have been substituted into the equation T_c can be deducted.

To define the self-ignition temperature of the material, it is necessary to know the rate of reactions, and also the heat conductance λ, amount and shape of the material. In small material amounts, the heat transfer coefficient α also affects the heat losses in the boundary surface between the material and its surroundings, while in larger amounts, the cooling efficiency is often determined by the heat conductance of the material itself.

Determination of Spontaneous Ignition

Spontaneous ignition is usually studied on at least three samples of different volumes to be able to extrapolate the results for larger amounts. The samples are usually small, or else the time required by the tests would be too long. In small samples, the temperature changes quickly and hence the determinations can be carried out rapidly, although the accuracy is poor. The sample can be of any shape; however, cylindrical ones (according to bin shape) are most often used.

The following method is used at VTT Energy for determining spontaneous ignition at an elevated pressure. The principle of the equipment is shown in Figure 3.

A cylindrical fuel sample is placed in a metal mesh vessel and then into an autoclave, which is pressurized (maximum 10 MPa), and the desired gas composition is fed in. Prior to feed, the temperature of the gas is raised to that of the autoclave to secure a steady temperature around the sample. The gaseous atmosphere is dynamic, as the gas flows slowly through the autoclave and the composition of the gaseous atmosphere is nearly constant. The temperature of the sample is raised stepwise. The sample is kept at each temperature stage a sufficiently long time (usually from one to several hours) to monitor whether the ambient temperature is sufficiently high for spontaneous ignition. The temperatures of the midpoint and of one end

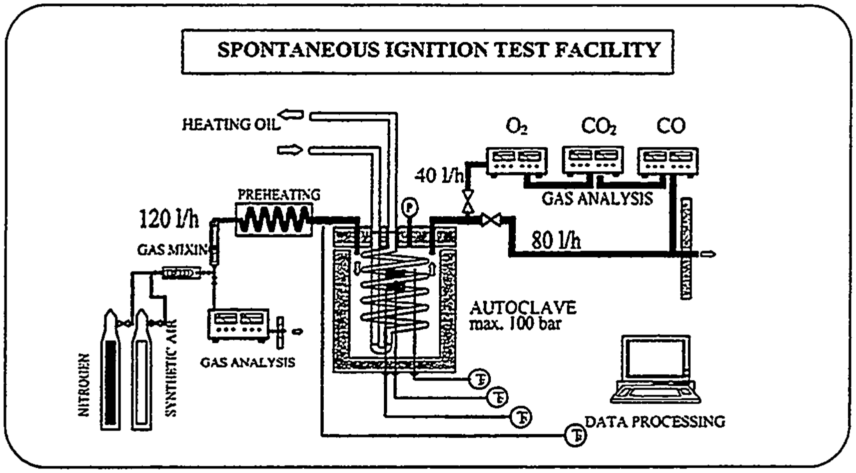

Figure 3. Schematic of test equipment for spontaneous ignition in pressurized and inertized atmosphere.

of the sample as well as the temperature of the gas, are recorded. The temperature of the gas volume near the sample at the moment of spontaneous ignition is given as the result of the determination.

The composition of the inlet and outlet gas is measured with continuously operating gas analyzers to control the stability of the gaseous atmosphere. and also to record the moment of Nitrogen is typically used as an inert gas to dilute the oxygen concentration below ignition limits except for the use of special gases, such as flue gas for inerting. The temperatures and gas analyses are recorded automatically by a data logger. The sample is changed rather often, depending on the temperature level, irrespective of whether it is ignited or not. The ignition characteristics can change, if the same sample is kept at the elevated temperature too long.

If the fuel is conveyed hot to the store (lock hopper), fo example, direct from the drying process, it has an increased tendency to self-ignition already at a lower temperature than usually. This tendency is determined by calculating the heat conductance of the fuel at normal operating temperature and by extrapolating these values for the full-scale storage bins. In addition to the heat transfer factor mentioned above, the heat capacity of the fuel also affects the time required for self-ignition.

Results

The ignition temperatures were determined both using a normal oxygen content of air and different inert gases with a reduced oxygen content. Two kinds of flue gases were used as inert gases, instead of the normal nitrogen dilution applied earlier.

1) Dry flue gas from gas fired boiler (O_2 = 3 % ; CO_2=19% ;N_2=78%)
2) Dry combustion flue gas (O_2=5% ; CO_2=15.5% ; N_2=79.5%)

The tests were carried out both at atmospheric and elevated pressures with samples of about 50, 100 and 400 cm³. The net-structured sample baskets were cylindric, the height being equal to the diameter. Figures 4 and 5 show examples of output obtained in a test carried out with coal at 1 and at 25 bar. The essential results are shown in Table 4 and in Figures 6 - 8. These results also include an extrapolation for one bigger bin volume /diameter (D = 3 m). The accuracy of the measured self-ignition temperature was about 5 °C in these experiments.

Figure 6 shows self-ignition temperatures at various initial pressures and at 4 and 21 % oxygen content (nitrogen dilution) for a 400 cm³ forest residue sample (= the largest sample size used in the tests).

Table 4. Ignition temperatures for different fuels.

V = 21 m³, D = 3 m *(Calculated)*	Fuel	Pressure bar	Sample size cm³	Ignition °C	(O_2) %
109.2	Forest residue	25	50	162	21
	Forest residue	25	100	158	21
	Forest residue	25	400	152.5	21
134.8	Forest residue	25	50	185.4	3
	Forest residue	25	100	182.7	3
	Forest residue	25	400	176.5	3
37.7	Coal	25	50	141.7	5
	Coal	25	100	133.0	5
	Coal	25	400	120.3	5
30.6	Coal	25	50	120.0	21
	Coal	25	100	110.9	21
	Coal	25	400	102.3	21
66.1	Coal dust	1	50	132.5	21
	Coal dust	1	100	125.9	21
	Coal dust	1	400	120.3	21

In Figure 7, a calculatory extrapolation to bin size 21 m³ has been made on the basis of the results obtained for the measured three sample sizes (forest residue) It can be concluded that the effect of pressure as a factor reducing ignition temperature is a little smaller than that purely for the sample of 400 cm³. Self-ignition in the bin of 21 m³ is shown, calculatory scaled , with the different oxygen content in the bin.

The extrapolated self-ignition temperatures for the 21 m³ bin as a function of oxygen content are presented in Figure 8.

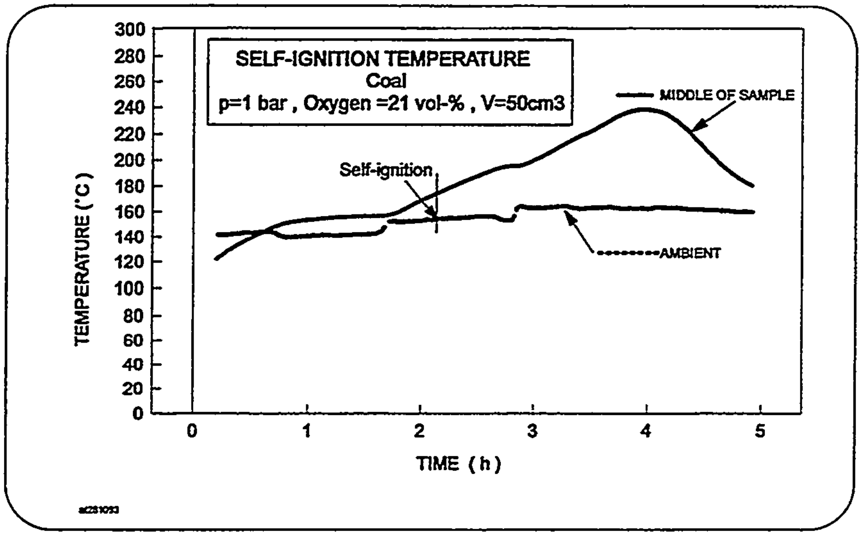

Figure 4. Development of temperatures in a test with spontaneous ignition of coal when the sample ignited (p = 1 bar).

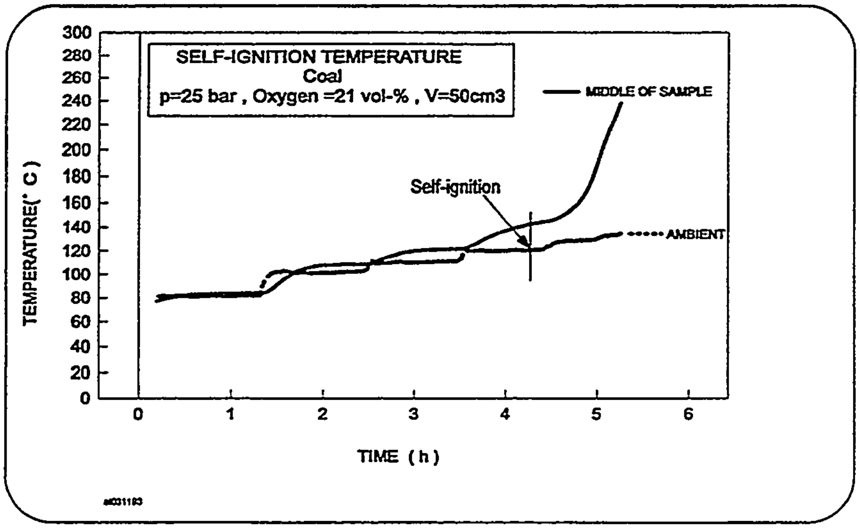

Figure 5.Development of temperatures in a test with spontaneous ignition of coal when the sample ignited (p = 25 bar).

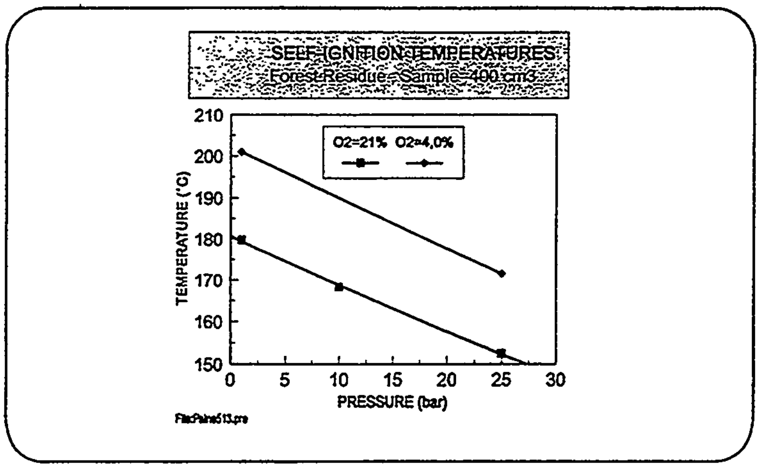

Figure 6. Self-ignition temperatures of coal as a function of oxygen content and pressure (sample 400 cm³).

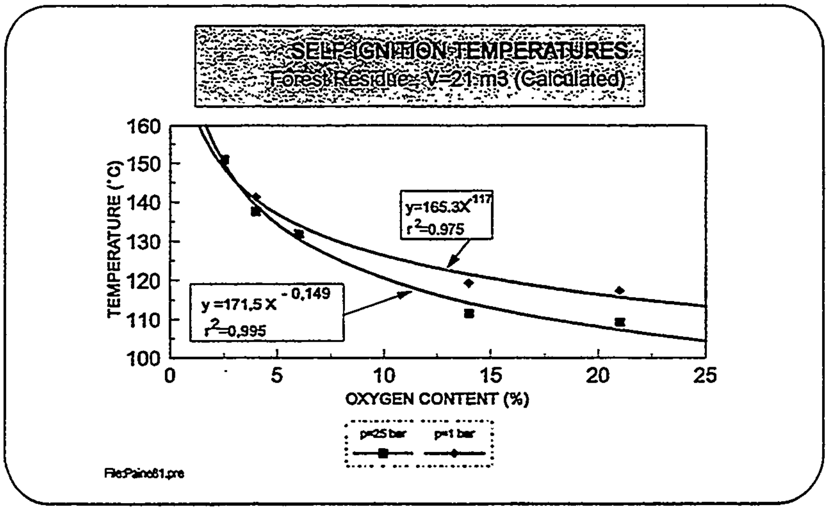

Figure 7. Self-ignition temperature extrapolated to the bin size (21 m³) at different pressures and with different oxygen contents.

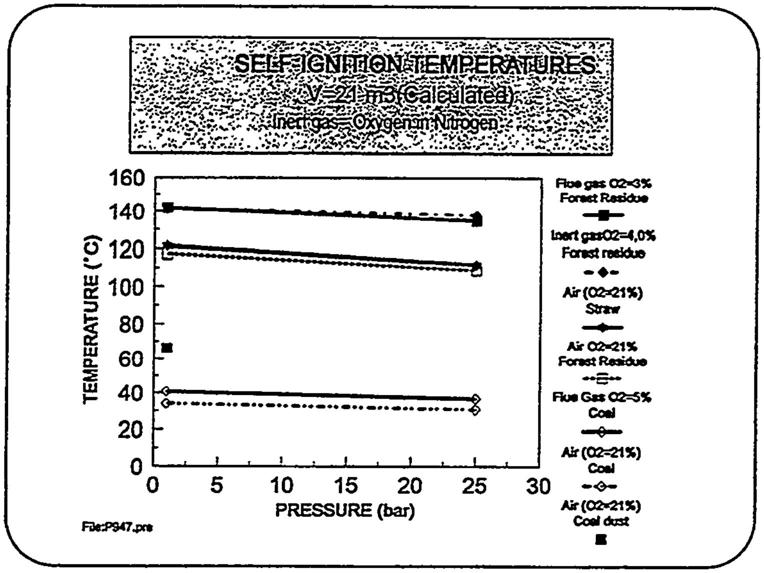

Figure 8. Self-ignition temperatures ($V = 21\ m^3$) of different fuels with different oxygen contents and at different pressures.

CONCLUSIONS

Small samples ignite quickly at elevated pressure (10 and 25 bar), and also at low oxygen contents (usually within 2 - 4 hours), while spontaneous ignition of larger samples may take several days. The reduction of the oxygen content can result in an increase in the ignition temperature. The increase of pressure from 1 to 25 bar resulted in lower spontaneous ignition temperatures. It should be borne in mind that in practice with large amounts of materials, spontaneous ignition temperatures may be much lower than these measured test values, and differences between materials are quite significant. The coal seemed to ignite in large (extrapolated) volumes at significantly lower temperatures than the biomasses do, although the self-ignition temperatures of small samples in separate tests were not especially low. However, as the volume increases, the self-ignition temperatures of coals are reduced to much lower values than those of the biomasses. In the coal tests, inertization also seemed to contribute much lesser to the rise of self-ignition temperature than in the biomass tests. Due to compactness the actual oxygen content in the core of the sample may be low due to poor diffusion of gases into the sample. The self-ignition temperature and ignition time are also affected, for example, by the initial temperature, heat conductivity (storage compactness of fuel), and insulation or heating level of the store.

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