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SPRAY DRY SCRUBBING OF SECONDARY POLLUTANTS FROM COAL BURNING

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ABSTRACT

A two-year test program has been conducted on a lime based spray dry scrubber treating all the flue gas from a 150 MW coal fired boiler. The flue gas cleaning (FGC) system consists of an ESP followed by a spray dryer and a fabric filter system. Measured data focusing on the fate of particulates, 10 trace metals $HCl/HF/SO_3/NO_x$ and polyorganic matters (POM) were analyzed in light of the potential for pollution control. A large number of measurements of the flue gas dust load were made to enable the estimation of the removal of particulates and trace elements enriched in fine particles. The concentration of ten trace metals (ie. As, Pb, Cd, Co, Cu, Cr, Mn, Ni, V and Zn) were measured in 7 streams of solids entering and exiting the boiler and the FGC system. This was done in order to outline the fate of the trace metals entering the system. The enrichment pattern of metals in fine particles was shown to be different when comparing the dust laden flue gas exiting the ESP with the flue gas exiting the fabric filter system. The problem area is pertinent with respect to emission levels as well as with respect to the impact of precollection of fly ash on the carry over of metals to the dry end product. The removal of hydrochloric acid was determined when burning mixtures of British, Polish and Russian coals. The measurements covered inlet concentrations from below 10 to above 100 ppm HCl. The removal efficiency was shown to be constant up to about 25 ppm HCl, after which the removal increased strongly with inlet concentration. The behavior may be a result of an autocatalytic mechanism. The measured concentrations of HF varied from 2 to 7 ppm. The outlet levels were in most cases below the detection level. Individual data points indicate up to greater than 85 percent removal of HF. SO_3 was measured by means of controlled condensation and by using the isopropanol method. A considerable descrepancy between the two methods was observed. Attempts were made to identify 130 different POM species ahead of the flue gas cleaning system, as well as downstream from the fabric filter system. In addition, Ames' test was applied on particulates and gaseous species collected from the flue gases, for identification of mutagenic species. As anticipated for a PF boiler, very low or non-detectable levels were seen.

INTRODUCTION

Spray dry scrubbing is a proven concept for SO_2 control on coal fired boilers burning low sulfur coals. When comparing the spray dry scrubbers installed around the world during the past 5 years, only superficial differences in operating features are revealed. Most systems use a lime slurry to spray cool the flue gas from a boiler and subsequently the dried solids are captured in a downstream particulate collection device. This leads to a certain removal of SO_2 in the spray dryer and the particulate collection device.

Besides SO_2, the flue gas obtained from a coal fired boiler will contain a number of secondary pollutants such as particulates and trace elements. It is of great concern to control the emission of these species to a desirable degree as well. The study described in this paper was undertaken to investigate the potential for removing the following secondary pollutants in a full scale spray dry process:

o fly ash and trace metals
o acidic species such as HCl, HF, SO_3, and NO_x
o polyorganic matters (POM)

Besides measuring POM by direct sampling and by subsequently making chemical analyzes, samples from various streams were also subjected to Ames' test for identification of mutagenic species.

Considerable experience of most of the above described species exists what concerns equipment such as particulate collection devices and wet scrubbers. The present study was focused on features imposed by a spray dryer.

PLANT DESCRIPTION

In 1981, Southern Sweden Power Supply (Sydkraft) decided to retrofit a spray dry process on an old coal fired boiler at the Öresund Power Station in Malmö (Sweden). Due to a number of reasons, such as the result of the Swedish referendum in 1980 on nuclear power, it was felt that the time had come to achieve more experience with modern flue gas desulfurization (FGD) tehnology. Swedish utilities have no experience with real large coal fired

power stations, and consequently, they have no experience with large scale FGD. However, wet scrubbers have been used on oilfired boilers and at paper mills for more than 15 years in Sweden.

The boiler is a wall-fired Steinmüller construction with nine Peabody burners. Coal is supplied via three grinders at a designed rate of 25 ton/h. The boiler can deliver 55 and 70 MW with coal and oil burning, respectively. During the design of the FGD system, a decision was taken to convert the boiler for heat production. The existing turbine was originally designed in such a way that it did not enable bypass conversion. Instead, a full pressure direct-condenser was installed. During the period from the construction in 1958, the boiler had only been in operation for 50 000 h, but it had experienced more than 2000 start-ups. Because the considerable age of the boiler, a number of actions were taken as follows:
o New control equipment were installed and a new control room was constructed
o A large part of the boiler refractory was replaced
o A modern water filled ash discharger was installed at the bottom of the boiler
o Twin steam coolers were installed between the first and second superheaters.
A data sheet including design features of the boiler and the FGD system is displayed in Table 1.

TABLE 1
DESIGN DATA FOR BOILER UNIT 15
AND FGD UNIT 15 AT THE ÖRESUND POWER STATION

Reconstructed boiler
  Rating: 150 MW$_{th}$
  Steam rate: 180 ton/h (396 000 lb/h)
  Steam pressure: 7.0 MPa (1015 psi)
  Steam temperature: 500 °C (932 F)

Flue gas desulfurization system
  Flue gas flow rate: 270 000 Nm^3/h (160 000 scfm)
  Inlet flue gas temperature: 125-150 °C (257-302 F)
  Coal sulfur: 1.5 percent
  Sulfur emission: 0.05 g S/MJ (0.24 lb SO$_2$/10^6 Btu)
  Particulate emission: 30 mg/Nm^3 (0.013 grains/scf)

Fabric filter
  Type: High ratio, pulse jet cleaning
  Air-to-cloth ratio: 0.023 m/s (4.0 ft/min)
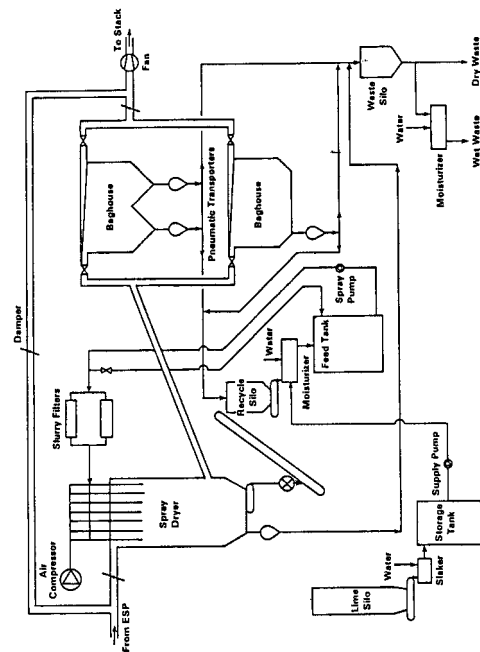 Pressure drop: 1200 Pa (4.6 in. H$_2$O)

Figure 1. Flow sheet of the spray dry scrubber at the Öresund Power Station.

The selected vendor of the installed spray dry FGD system was Fläkt. The plant was originally designed for a 2000 h test and development program. Consequently, limited redundancy was applied as what equipment such as pumps and compressors concern. In addition, very limited space was available between the existing electrostatic precipitator (ESP) and the stack. A very tight retrofit with complicated duct work layout was thus obtained. Although the plant was originally installed as a test unit, it is now utilized on a commercial basis. Figure 1 shows a schematic diagram of the layout and the components of the plant. Flue gas treated by the ESP, enters the spray dryer at the top, where a lime slurry is atomized by means of dual fluid nozzles. The flue gas is cooled down to a desired temperature due to the evaporation of the water content of the slurry. Simultaneously, SO$_2$ reacts with lime dissolved in the droplets, to produce mainly calcium sulfite. Some of the solids are collected in the spray dryer. However, most of the dried solids pass via the dryer to be collected on the fabric filter, where removal of SO$_2$ continues as the flue gas passes through the filter caked with partly unreacted lime. Milk of lime slurry is prepared by mixing lime and water in a slaker, and subsequently dumping the obtained slurry of hydrated lime into a storage tank. Feed slurry is obtained by mixing lime slurry, water and recycled dry solids in a moisturizer, and subsequently dumping the mixture into a feed tank. Feed slurry is continuously pumped to the top of the spray dryer, and enters the dryer through a number of nozzles.

Solids on the bottom of the spray dryer are returned to a silo by a scrape conveyor. However, most of the dry product is taken care of by a pneumatic system. The product is collected in a number of dust pots, and blown intermittently through a pipe system back to the recycle silo or, when a bleed is required, it is blown to the waste silo. The dry product in the waste silo is loaded on trucks by first adding water. Optionally, dry loading is feasible. At present, dumping at nearby disposal areas is practiced. However, comprehensive development programs to recover dry product for reuse are underway. Various options such as filler for road construction are under consideration.

Since the plant was installed as a test unit, it was extensively equipped with instruments and measuring devices. In addition to the process and control computer, two desk computors have been used for sampling of various parameters.

SCOPE OF TEST PROGRAM

Table 2 summarizes the tasks included in the overall test program for the spray dry scrubber. Part of the results from task 4 will be presented in this paper. In order to enable the calculation of material balances for trace elements as well as to outline the impact of operating conditions on the secondary emissions, information from task 1 was utilized. This information includes data such as flow rates of various streams. The overall test program was started late in the fall of 1983 and completed in the spring of 1985. Some complementary measurments were done late in the spring of 1986.

The following coal types were tested: Russian coal (0.3 % S), Polish coals (0.5-0.8 % S), British coals (1.1-1.5 % S) and North American coal (1.7 % S). Properties such as heating value and ash content of the coals varied slightly. Actual ash contents ranged from about 8 to 12 percent. The chlorine content was highest for the Brithish coal (0.5 % Cl), and lowest for the Russian coal. During most of the trials, mixtures of the different coals and plain Polish coals were fired. The number of tests on each Task 4 species will be given under each section, along with pertinent operating conditions.

TABLE 2
OVERALL FGD TEST PROGRAM

Task 1: Evaluation
  o component and equipment performance/failure mechanisms
  o sampling procedures/compliance tests
  o impact of design and operating parameters on SO$_2$-removal

Task 2: Process development
  o sorbent chemistry/additives

Task 3: Byproduct recovery
  o disposal/recovery options

Task 4: Secondary emissions
  o removal of fly ash, trace metals (ie. As, Pb, Cd, Co, Cu, Cr, Mn, Ni, V, Zn), acidic species (ie. HCl, HF, SO$_2$, NO$_x$), polyorganic matters (130 POM species), mutagenic species

FLY ASH AND PARTICULATES

The ESP is designed for removal of 95 percent of the fly ash ahead of the FGD system. When the flue gases enter the FGD system, particles are added to the flue gas in the form of slaked lime and recycle material. This leads to a considerable increase of the dust load in the spray dryer. The major reason of having a downstream fabric filter system is thus to remove unreacted as well as consumed lime from the flue gas. The objective of measuring the dust level ahead of and downstream from the FGD system was to establish the removal of fly ash over the system. In addition, the dust samples were also used to analyze the concentration of dust born trace metals. The sampling equipment was of standard type, with heated sampling probes and filter holders. The probes and filter holders were blasted and pickled with acid before each test. Flue gas samples were withdrawn isokinetically via 5 holes on each side of the FGD system, by screening a matrix of 30 positions within the flue gas duct. A total of 16 tests were done; each test was extended over a period of time of 2 to 4 hours.

Table 3 summarizes the results from the first nine tests (test period I). Various coal blends were burned under almost full load in all tests. The spray dryer was operated at about 20 °C (36 F) above the saturation point; the flue gas inlet temperature was 125-135 °C (257-275 F). The concentration of the feed slurry to the spray nozzles was kept at around 25 weight percent solids, yielding the concentration of particulates in the spray dryer as indicated by the table. The removal of fly ash by the ESP varied for the different coal types according to an expected pattern, except for test 5; a much higher removal was anticipated for British coal than for Russian coal. It should be pointed out that the ESP removal includes the fraction of ash discharged as bottom ash in the boiler.

The concentration of particulates downstream from the FGD system varied considerably. This variation was due to operating problems with one of the fabric filters during the first test period. For instance, during test 3, the automatic cleaning cycle was not working properly. Furthermore, foreign metal pieces were found in the dust pot, partly blocking the discharging of the dry product. These problems did upset the operation considerably. After tests 5 and 6, repectively, it was established that some bags had come lose and plugged the hopper. Surprisingly, the emission levels of particles were still low with some bags missing.

To prevent further bags and bag cages from coming lose, new top ring reinforcements and cage holders were installed. Furthermore, when inspecting the baghouse, some imperfect weldings were seen which probably had caused a small leakage of particles. After proper adjustments, 7 new tests were done (test period II). The results have been summarized in Figure 2. All measurements were carried out when burning Polish coal at full load. Steam

TABLE 3

CONCENTRATION OF PARTICULATES DURING TEST PERIOD I

Test	1	2	3(a)	4	5(b)	6(b)	7	8	9
Coal blend(c)	60% B	>90%R	>90%R	60%B	>90%R	>90%P	>90%P	>90%P	>90%P
Concentration of particulates (mg/Nm³ and grains/scf, respectively)									
Coal ash	{7600 / 3.3}	{10800 / 4.7}	{10400 / 4.5}	{8500 / 3.7}	{8500 / 3.7}	{10300 / 4.5}	{10100 / 4.4}	{10200 / 4.5}	{9700 / 4.2}
After ESP	{72 / 0.031}	{270 / 0.12}	{420 / 0.18}	{79 / 0.035}	{319 / 0.14}	{78 / 0.034}	{92 / 0.040}	{84 / 0.037}	{143 / 0.062}
In FGD	{12300 / 5.4}	{13100 / 5.7}	{12900 / 5.6}	{10800 / 4.7}	{10100 / 4.4}	{11200 / 4.9}	{10300 / 4.5}	{8700 / 3.8}	{8900 / 3.9}
After FGD	{30 / 0.013}	{<5 / <0.002}	{207 / 0.090}	{5 / 0.002}	{82 / 0.036}	{184 / 0.080}	{22 / 0.010}	{9 / 0.004}	{0.7 / 0.0003}
Removal of particulates (percent)									
ESP	99.1	97.5	96.0	99.1	96.2	99.2	99.1	99.2	98.5
FGD	58	>98	51	94	74	<0	77	89	49
Total	99.6	>99.9	98.0	>99.9	99.0	98.2	99.8	>99.9	>99.9

(a) problems with automatic cleaning cycle of fabric filter
(b) lose bags found in the lower section of the fabric filter system
(c) B=British; R=Russian; P=Polish

soot blowing was applied to some extent during all tests. As can be seen from the figure the conditions did not vary substantially; the shaded areas represent the ranges covered by the measured data. Furthermore, the emission level after the FGD system did not exceed 1.9 mg/Nm³ (0.00083 grams/scf). Average values of particle concentrations, as well as average values of the removal efficiencies have been given in the figure. The data indicate 99.98 percent overall removal of particles on an average.

Essential conclusions from the tests may be summarized as follows:

o   No apparent correlation between coal type and emission level of particulates downstream from the FGD system was seen.

o   Extremely low emission levels, ie. below 2 mg/Nm³ (<0.001 grains/scf) may be obtained on a continuous basis, if the fabric filter system is adjusted properly.

o   The emission level does not increase to above unreasonable levels if bag failure occurs.

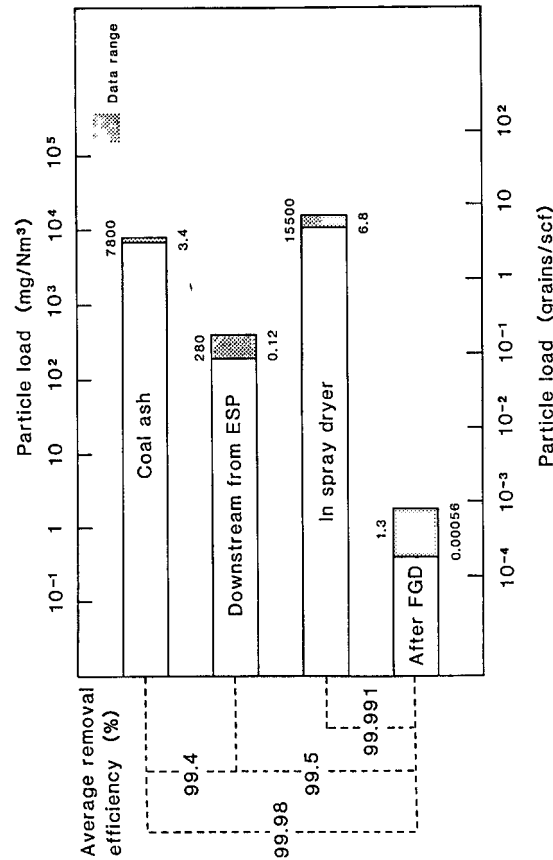o   No apparent correlation between inlet dust load, including recycle material, and emission level was seen.

Average removal efficiency (%)

Particle load (mg/Nm³): 10^{-1} 1 10 10^2 10^3 10^4 10^5

Coal ash — 7800
99.4 — 3.4
Downstream from ESP — 280
99.5 / 99.98 — 0.12
In spray dryer — 15500
99.991 — 6.8
After FGD — 1.3 — 0.00056

Data range

Particle load (grains/scf): 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10 10^2

Figure 2. Concentration of particles, based on 7 tests (test period II).

TRACE METALS

Trace metals originate from the coal and the lime used for flue gas desulfurization. The fate of the trace metals depends mainly on the efficiency of particulate collection devices; trace metals may be found in the bottom ash of the boiler, in the fly ash removed by the ESP, in the dry end product from the FGD system as well as in the flue gas exiting the fabric filter system. The objective of the tests was to study the fate of 10 trace metals and to outline the potential for control of the emission rate from the spray dry system. Figure 3 shows a simplified flow sheet of the boiler and FGD system in which case streams subjected to trace metal determinations are indicated. A total of 7 tests on trace metals were done, corresponding to test period II described previously.

The total mass flow rates of the streams indicated by A through F in the figure, were determined by computerized and manuel sampling, and by appropriate calculations. The concentration of trace metals of the various solid was determined by atomic absorption spectrophotometry. Coal samples were taken from the pneumatic coal feeders downstream from the grinders by means of a vacuum sampler. Fly ash was taken from the pneumatic dust pots under the ESP. A simplification was made by not taking samples of bottom ash from the boiler, and instead considering the fly ash as representing all the ash produced. Samples of dry end product was taken from a dust pot under one of the fabric filters. Samples were taken at least two times during each 2 to 4 hour test. Finally, the samples of particles taken from the flue gas, according to the previous section were also used.
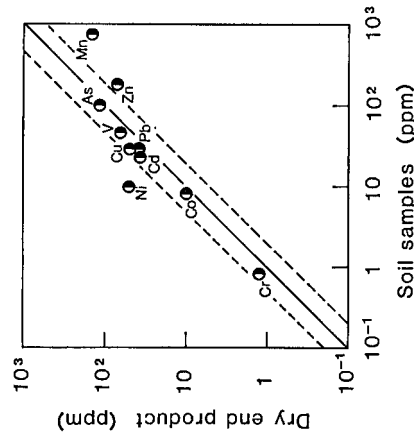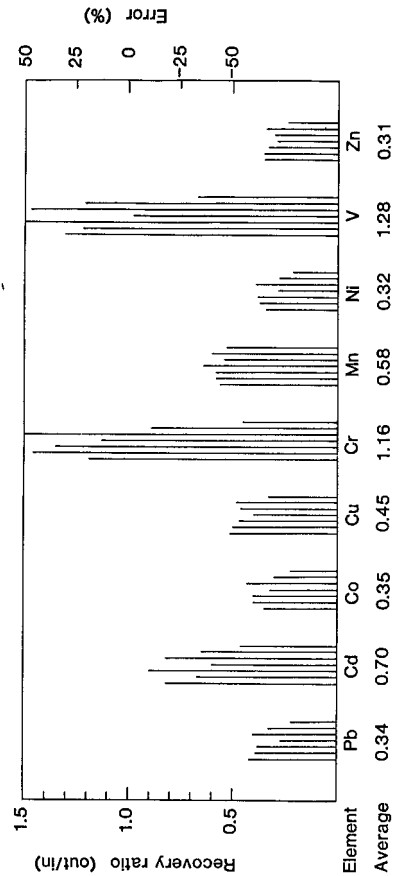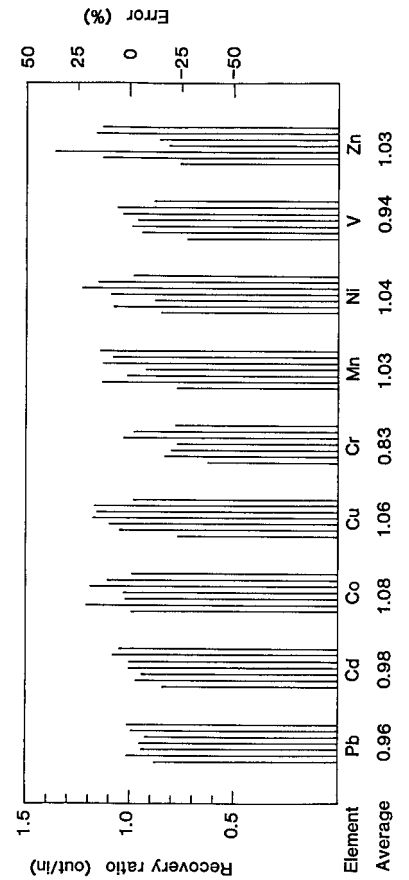
Concentrations

Most of the trace metals occurring in the flue gas can be found mainly in the particles. One exception is mercury, which occurs as a gaseous species. The contribution of trace metals to the system is dominated by the coal. This is mainly a cause of the large mass flow of coal. Average values of the contribution from the lime are shown in Table 3. The figures indicate values around one or a few percent, with the exception of Cd which originates to more than 10 percent from the lime. The problem area is of practical importance. One of the arguments for designing spray dry scrubbers with an ESP to precollect fly ash, is to prevent carry over of trace metals to the dry end product. This would enable the production of an end product with comparatively low levels of trace metals. However, the argument requires that the concentration of trace metals is considerably higher in the fly ash than the concentration in the lime used for desulfurization.

To give a picture of the concentration of trace metals in the dry end product, 5 soil samples were taken at different locations for comparison. Figure 4 shows the average values of the trace metal concentrations in the dry end product as a function of the average values from the soil samples. The broken lines correspond to a deviation of a factor of 2 and 0.5, respectively. Surprisingly enough, data for most of the trace metals fall within the area confined by these two lines. Soil and dry end product thus show similar concentration levels. The largest deviations are seen for nickel (Ni) and manganese (Mn); a factor 5 in each direction. Most of the trace metals fall within the range from 10 to 100 ppm; considering all metals, the range is extended from 1 to 1000 ppm.

Material balances

Material balance calculations were done for nine of the trace metals for each individual test. The mass flow rates of trace metals were used to estimate recovery ratios for two different systems. The recovery ratio is defined as the total flow of a species leaving a system, divided by the total flow of the same species entering the system. For the boiler and the ESP, this can be expressed as: out/in = (B+C)/A; similar for the FGD system: out/in = (E+D)/(F+C). Here A through F are explained by Figure 3. The estimated recovery out/in = (E+D)/(F+C).

TABLE 3

AVERAGE CONCENTRATION OF TRACE METALS IN LIME AND COAL, RESPECTIVELY,
AND PERCENTAGE CONTRIBUTION OF TRACE METALS BY LIME, BASED ON 7 TESTS

Element	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn	
Coal	21	0.20	6.3	21	78	140	16	15	44	(ppm, dry basis)
Slaked lime	64	3.5	18	14	11	150	28	23	19	(ppm, dry basis)
Contribution from lime	2.3	12.2	2.2	0.51	1.1	0.85	1.3	1.1	0.34	(percent)

Coal (A) → Boiler → Fly ash (B) → ESP → Flue gas after ESP (C) → FGD → Flue gas after FGD (E); Slaked lime (F); Dry end product (D)

Figure 3. Simplified schematic diagram indicating major streams containing trace metals.

Figure 4. Trace metal concentrations in dry end product (96 percent precollection of fly ash) as a function of the concentration of the metals in soil. Average data points based on 5 samples.


Element	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn
Average	0.34	0.70	0.35	0.45	1.16	0.58	0.32	1.28	0.31

Figure 5. Recovery ratio of trace metals for the boiler/ESP system.

Element	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn
Average	0.96	0.98	1.08	1.06	0.83	1.03	1.04	0.94	1.03

Figure 6. Recovery ratio of trace metals for the FGD system.

Since all data reveal much greater than 50 percent removal of trace metals, the following relations were used for the boiler/ESP system and the FGD system: $(1-C/A)\cdot100$, respectively $(1-E/C)\cdot100$. Data for 7 tests have been summarized in Table 4 for each trace metal; only the lowest, the highest and the average values have been given. Considering the average values for the ESP, cadmium is removed to the least extent (91.0 percent), while manganese is removed to more than 98 percent. The remaining part of the trace metals are in most cases removed to more than 99 percent on an average in FGD system. Considering each individual test, the lowest measured overall removal was 99.5 percent. However, in many cases efficiencies greater than 99.99 percent were seen.

Enrichment

It is generally known that most trace metals have a tendency to attain a higher concentration the smaller the particles are. Thus, trace metals may be enriched in the fraction of particles not removed by a particulate collection device, since large particles are most easy to remove. The problem area is very complicated. Data are available in the literature for ESP:s, fabric filters, wet scrubbers and cyclones, eg. Bolton (2), Laevitt (3), Ensor (4,5), Evers (6), Jahnig (7), Klein (8), Meserole (9), Nader (10), Ondov (11,12), Cowherd (13), etc. It is very difficult to find a consistent pattern from available literature data. Obviously, aspects such as ash/particle properties may be of great importance. The discrepancy in data may also reflect the extreme difficulty in obtaining accurate information, due to inherent problems with sampling and chemical analyses. In addition, attempts were not made to close the material balances in many studies. However, there are some tendencies indicated. Most studies reveal a positive enrichment. Most studies do not show extremely large enrichments of metals such as manganese, cobalt and copper; the enrichment may in general be larger for lead and cadmium. It should be added that the data investigated comprised such collection devices showing less than 99.5 percent removal of particulates.

The enrichments obtained for the present tests are shown in Table 5, which summarizes average values for 7 tests (test period II). Here, the enrichment has been defined as the actual metal concentration of flue gas borne particles, divided by mean value of the concentration of all solids exiting a system. First, if the metals are ranked according to increasing enrichment, a different pattern is obtained for the FGD system, when compared to the boiler/ESP system. Second, the dust load is more than 100 times larger downstream from the FGD than the dust load downstream from the ESP; however, the enrichment factor for the FGD system is still only substantially higher for five metals (Cu, Cr, Mn, Ni and Zn), when compared to the ESP. In fact, for some element a substantially lower enrichment can be seen.

Two shortcomings have to be pointed out with respect to the data given in Table 5. As discussed previously, the recovery ratio was not acceptable for most of the metals when considering the boiler/ESP system. Furthermore, since the dust load downstream from the FGD system was extremely low, substantial errors may be introduce due to the difficulty

TABLE 4

REMOVAL EFFICIENCIES OF TRACE METALS;
LOWEST, HIGHEST AND AVERAGE VALUES, RESPECTIVELY, BASED ON 7 TESTS

Element	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn	Dust
Boiler and ESP										
lowest	94.9	89.5	96.3	94.4	91.6	98.0	96.0	87.4	95.1	94.7
average	95.7	91.0	97.0	96.1	93.1	98.3	96.8	92.6	96.4	96.4
highest	97.0	93.7	97.8	97.2	94.3	98.8	97.6	94.0	97.6	97.5
FGD system(a)										
lowest	99.89	98.92	99.47	99.13	90.31	98.80	94.44	99.82	95.80	99.1
average	99.93	99.44	99.82	99.37	96.52	99.39	96.48	99.89	97.77	99.5
highest	99.98	99.69	99.97	X	99.52	99.85	98.54	99.98	99.99	99.9
Total										
lowest	X(b)	99.90	99.99	99.93	99.45	99.99	99.68	99.98	99.86	99.98
average	X	99.95	X	99.97	99.74	99.99	99.90	99.99	99.96	99.98
highest	X	99.98	X	99.96	99.96	X	99.96	X	X	X

(a) Based on data downstream from ESP
(b) X means > 99.99 percent removal efficiency

ratios are shown in Figure 5 and 6. As can be seen, the recovery ratio is poor for most of the trace metals. The exact cause for this has not been identified. However, there are several potential causes. First, samples were not taken from the bottom ash due to extreme difficulties; a discrepancy of trace metal concentrations when comparing bottom ash and fly ash leads to an error. This has also been shown to be the case (1). However, it can not explain the whole discrepancy in the recovery ratios. Second, there were only sampling devices on 3 of the 12 dust pots under the ESP. Although the 3 dust pots represent all positions in flow direction, this shortcoming may not be overlooked. It is anticipated that most trace metals are enriched in small particles. Thus, the trace metal concentration may vary from one dust pot to another. In essence, the sampling procedure used did not consider if there were any variations in metal concentrations perpendicular to the flow direction. Third, the amount fly ash pneumatically transmitted by each pot was not known exactly. The mixed samples used for analyses in connection with each test may not have represented the true composition of the fly ash. From the facts given avove, it may be aliged that the discrepancy in recovery ratios for the boiler/ESP system most likely is due to the difficulty in taking appropriate fly ash samples.

Turning to the recovery ratio for the FGD system, Figure 6, it can be seen that the agreement is excellent. There are deviations up to 38 percent for individual tests. However, the average deviation for all recovery ratios is only about 6 percent. Furthermore, the deviation for the mean value of the sum of all recovery ratios is only -0.4 percent. From this it may be deduced that one of the reasons for failing in closing a material balance is the lack of enough of data points. However, Figure 5 shows that there are other reasons as well.

As an example, the flow rates of cadmium (Cd) have been given in Figure 7. The bar representing the emission is actually too small to be seen in the diagram. As can be seen, about 30 to 50 percent of the cadmium content of the dry end product is due to carry over of fly ash.

Removal efficiency

The removal efficiency of trace metals has been estimated for both the boiler/ESP system and for the FGD system. It should be pointed out that the calculated removal for the FGD system has been based on the flow rate of trace elements entering the system by recycle system has been based on the flow rate of trace metals are introduced into the spray dryer by recycle not removed in the ESP. Since trace metals are introduced into the spray dryer by recycle material and lime, the actual capacity for removal of trace metals is much higher than the data presented here. However, the estimated removal efficiencies based on the definition used here, reflect what fractions of trace metals that are removed when comparing to operation without an FGD system. It can also be established that the three parameters: trace metal enrichment, particulate removal and trace metal removal are uncoupled, because an independent flow of trace metals is introduced by added lime. For instance, if the removal efficiency of a certain trace metal is greater than the removal efficiency of particulates, it may still be that the trace metal is enriched in the particulates exiting the FGD system.
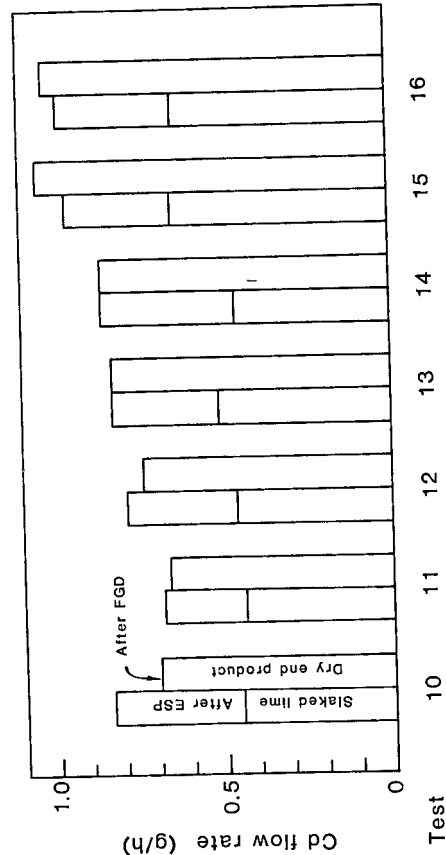

Figure 7. Flow rates of cadmium.

TABLE 5

THE FACTOR BY WHICH TRACE ELEMENTS ARE ENRICHED IN FLUE GAS BORNE PARTICULATES
EXITING THE ESP AND THE FGD SYSTEM, RESPECTIVELY

Element	As	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn
Enrichment after ESP	-	1.3	3.0	0.9	1.2	2.2	0.5	1.0	2.5	1.1
Enrichment after FGD	0.51	0.28	3.3	0.98	8.1	36	3.8	22	0.87	10

In determining low amounts of the metals. This is shown by Figure 8, in which the concentration of trace metals in flue gas dust after the fabric filter has been plotted as a function of the metal concentration in the dry end product obtained from the FGD system. The figure shows the comparatively large range covered by each metal. Furthermore, the negative enrichment is clearly seen; data points below the straight line. However, no correlation of particles varied fivefold downstream from the fabric filter. However, no correlation was found between the enrichment factor and the dust load.

Table 6 shows the calcium concentration of the flue gas borne particulates. The fly ash can be seen to contain 0.9 to 1.8 percent by weight, which does not represent a substantial variation. However, the particles leaving the fabric filter by the flue gas, in general contain no calcium, but a concentration as high as 21 percent can be seen for test 10. At first glance, it may be anticipated that the sample obtained is very similar
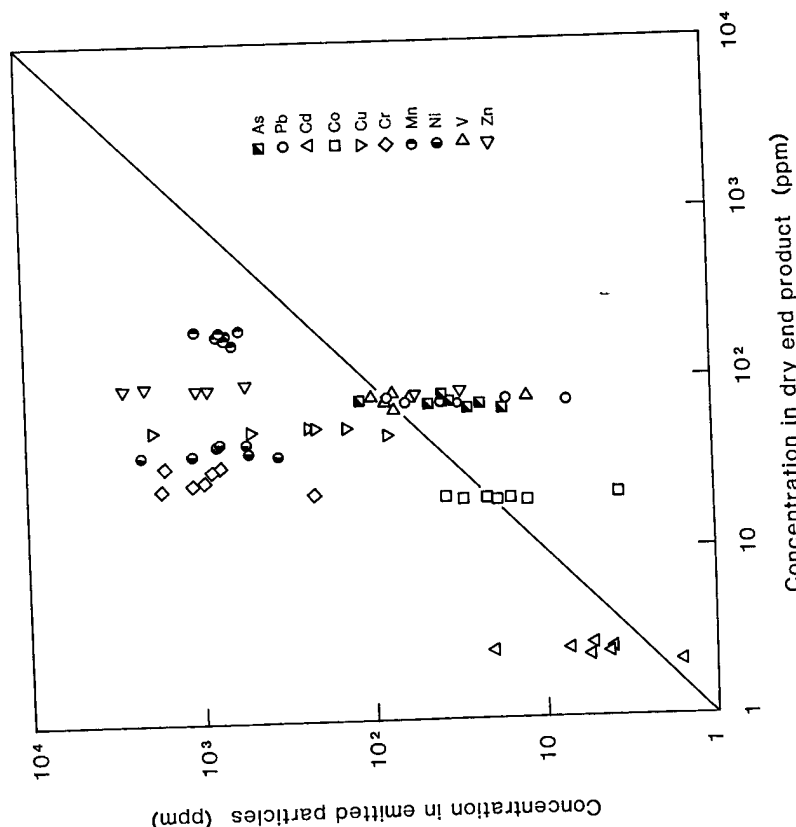

Figure 8. The concentration of trace metals in flue gas borne dust downstream from the FGD system and in the dry end product respectively.
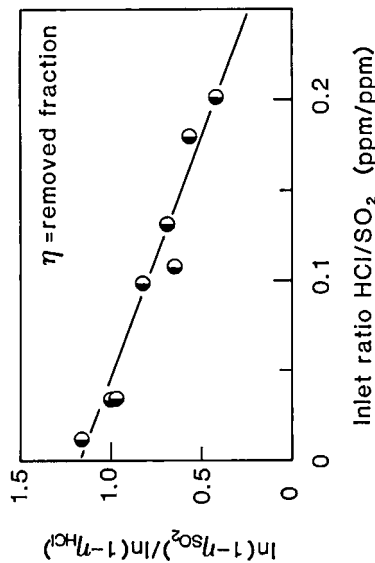
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to the dry end product. However, when looking into the trace metal concentrations, it can clearly be established that this is not the case. When comparing the individual tests, there is a tendency of that high calcium concentration leads to high concentrations of As, Hg and Cr, and low concentrations of Cu, Ni and Zn, while Pb, Cd, Co, Mn, and V follow no pattern. These observation may indicate theat there may be particles of three different properties leaving the fabric filter with the flue gas. First, particles with a composition similar to the dry end product may be emitted during, eg. bag failure. Second, particles with an enrichment pattern according to Table 5 may be obtained. Third, the enrichment pattern may be altered somewhat for high calcium concentrations as described above.

TABLE 6

CONCENTRATION OF CALCIUM IN FLUE GAS BORNE
PARTICULATES (PERCENT BY WEIGHT)

Test	10	11	12	13	14	15	16
Fly ash after ESP	1.2	0.9	1.0	1.0	1.8	1.0	1.1
Particulates after FGD	21	2.3	2.4	0	0	0	0

Carry over to dry end product

The pattern for carry over of trace metals from the ESP to the dry end product is more complicated. First, there is a dilution effect that increases with decreasing degree of precollection of fly ash; ie. the amount of dry end product increases with decreasing precollection. Second, depending on the fly ash concentration of trace metals, there will be a certain contribution of trace metals. Here, the enrichment factor plays an important role. Table 7 shows how the dry end product concentration of trace metals changes if the degree of precollection of fly ash is changed. In the case of complete precollection, the metal concentration drops considerably. However, this state is hard to achieve in practice. If all fly ash is allowed to mix with the end product, 0 % precollection, the situation becomes more complicated. The ranges indicated in the tabel correspond to the uncertainty due to discrepancies in the recovery ratios for the boiler/ESP system. As can be seen, no precollection may be beneficial for maintaining a low concentration of some trace metals. It is now possible to classify the trace metals into different groups with respect to the benefits from precollection:

o precollection is always beneficial: Cr, Mn
o precollection is probably beneficial: Cu, Ni, Zn, V
o precollection may or may not be beneficial: Pb, Co
o precollection is a drawback (except for 100 %): Cd

Conclusions

Some conclusions may be summarized as follows:

o The overall removal of trace metals varied from 99.74 % (Cr) to greater than 99.99 % (Pb, Cd) on an avarage
o The FGD system removal of Pb, Co, Cr, V is better than the FGD system removal of particulates
o The enrichment factor for particulates emitted from the FGD system varied from 0.28 (Pb) to 36 (Cr). The pattern is different for the ESP
o Particulates with three different characteristic properties are emitted from the FGD system

TABLE 7

CHANGE IN CONCENTRATION OF TRACE METALS IN THE DRY END PRODUCT WHEN ALTERING THE STATE OF
PRECOLLECTION BY THE ESP; NO PRECOLLECTION AND COMPLETE PRECOLLECTION, RESPECTIVELY, AS
COMPARED TO THE BASE CASE OF 96 % PRECOLLECTION OF FLY ASH

Element	Pb	Cd	Co	Cu	Cr	Mn	Ni	V	Zn
Measured concentration (ppm) 96 % precollection	75	24	20	52	28	196	41	79	92
Anticipated change (factor) 100 % precollection	0.7	0.6	0.4	0.1	0.2	0.3	0.3	0.1	0.1
0 % precollection	0.8-2.2	0.5-0.8	0.9-2.5	1.4-3.2	22-25	3-6	1-3	1.5-1.9	1-4

Figure 10. Interdependency of SO_2 and HCl removal

with increased inlet concentration of HCl, since the product content of calcium chloride increases with the latter parameter.

Figure 10 shows that there is an apparent interdependency between the overall removal efficiency of SO_2 and the overall removal efficiency of HCl. The data have been plotted as a function of inlet HCl/SO_2 ratio, and it can be seen that an increase in this ratio has a larger impact on the HCl removal than on the SO_2 removal. No obvious explanation of Figure 10 has been derived.

Hydrofluoric acid

Data for hydrofluoric acid were obtained during the same time as the HCl tests were done. The results of the HF measurements have been summarized in Table 8. In many of the cases, the concentration was below or just above the detection level. The interpretation should thus be done with considerable care. However, at least 50 percent were removed in all cases; the highest removal obtained was greater than 85 percent.

TABLE 8

CONCENTRATION OF HF (ppm)

Test	1	2	3	4	5	6	7	8
After ESP	4	6	2	2	2	7	7	4
After FGD	<1	<1	<1	<1	<1	<1	2	2

Sulfur trioxide

A total of 22 flue gas samples were taken to determine the concentration of sulfur trioxide in the flue gas. Ten of the samples were withdrawn ahead of the spray dryer and the remaining were taken downstream from the fabric filter. The sampling time ranged from 1/2 to 1 hour, and during each sampling period, part of the flue gas was lead to a condenser maintained at 75 °C (167 F); the remaining flow was lead to train of sampling bottles with an acidic isopropanol solution. Hence, sulfur trioxide was determined by the controlled condensation method and by the isopropanol method simultaneously, in order to enable a comparison of the two methods.

The operating conditions for the spray dry scrubber were as follows over the two day test period:

o Inlet concentration of SO_2: 400 ppm
o Outlet concentration of SO_2: 120 ppm
o Stoichiometric ratio: 0.7
o Flue gas inlet temperature: 130 °C (266 F)
o Approach to the adiabatic saturation point: 20 °C (36 F)
o Recirculation: mixed slurry controlled at 25 solids

ACIDIC SPECIES

Flue gas samples were taken ahead of the spray dryer as well as downstream from the fabric filter, in order to determine the concentration of hydrochloric acid (HCl), hydrofluoric acid (HF), sulfur trioxide (SO_3) and nitrogen oxides (NO_x). A train of absorption bottles was used to absorb HCl and HF in a sodium hydroxide solution. Chloride and fluoride ions were determined by titration and ion selective electrode respectively. SO_3 was measured simultaneously by controlled condensation and by absorption in isopropanol, respectively; sulfate ion was analyzed by ion chromatography. Oxides of nitrogen were continuously recorded by chemiluminescent instruments.

Hydrochloric acid

A total of 8 samples were taken to determine HCl ahead as well as downstream from the FGD system when burning mixtures at British, Polish and Russian coals. Each sample was extended over a time period of 2 to 4 hours. The chlorine content of the individual coals varied two orders of magnitude, with a maximum level of 0.5 percent Cl by weight for the British coal. Obtained inlet flue gas concentrations of HCl ranged from 7.6 to 127 ppm.

The operating conditions of the spray dry were approximately as follows:

o Inlet concentration of SO_2: 200-850 ppm
o Stoichiometric ratio: 0.7±1.3
o Flue gas inlet temperature: 125-135 °C (257-275 F)
o Approach to the adiabatic saturation point: 20 °C (36 F)
o Recirculation: 25 % solids in feed slurry (set point)
o Precollection of fly ash: 96 %

Virtually all operating conditions are constant, except for the SO_2 concentration and the stoichiometric ratio. Based on the fact that the solubility of HCl is much greater than the solubility of SO_2, one may argue that the removal of HCl in the spray dryer is less sensitive to the stoichiometric ratio than SO_2. Therefore, the measured data have been plotted simply as the outlet concentration as a function of the inlet concentration, as shown in Figure 9. The left straight line corresponds to a removal efficiency of 59 percent. When the inlet concentration increases above 25 ppm, the removal starts to increase considerably. At 127 ppm HCl inlet concentration, the removal efficiency is 97 percent. The consequence of this behavior is that the outlet concentration never exceeds 10 ppm.

The observed phenomenon may be explained by an autocatalytic effect. When hydrochloric acid reacts with lime, the product is calcium chloride. This species is strongly deliquescent if it is allowed to keep its water of hydration. Thus the calcium chloride leads to an increase in the water holding properties of the reaction products. This may include an extended drying time as well as an increase in the equilibrium moisture content. It is well established that the moisture holding properties is of importance for SO_2 capture, and the same thing may be anticipated for HCl. As a consequence, the reactivity increases
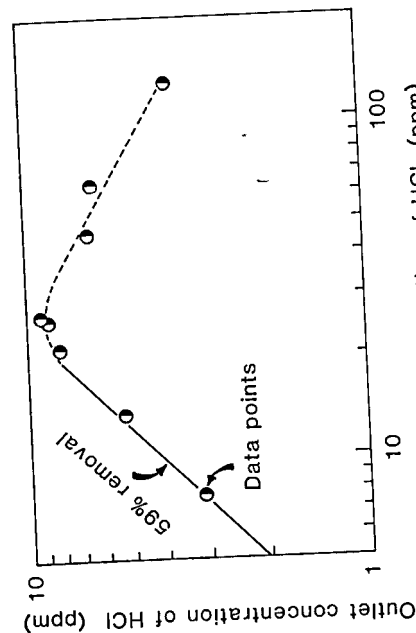

Figure 9. The flue gas outlet concentration of HCl as a function of the flue gas inlet concentration of HCl.

The two methods yielded quite different results. Considering the isopropanol method, no significant change in SO_2 concentration was seen across the FGD system. Actual measured values ranged from 2 to 12 ppm SO_3. From the chemical analyses of the absorption solutions, it was observed that the concentration of sulfate ranged from 21 to 27 ppm, for all sample bottles in the train as well as for all tests. The gas sample volume varied up to fivefold from one test to another, and the volume of absorption solution varied two-fold. Hence, the apparent range of SO_3 concentration is merely a direct cause of differences in sampling conditions. Actually, it can be shown that the apparent SO_3 concentration is proportional to the ratio of the absorption solution volume and the gas sample volume. The high concentrations obtained can be derived from the SO_2 in the flue gas. Since SO_2 is somewhat soluble in the isopropanol, some extent of oxidation may be anticipated. However, the degree of oxidation is independent of the flue gas concentration of SO_2. It seems that the oxidation is inhibited when the sulfate level reaches about 24 ppm. This may not be attributed to the production of hydrogen ion, because the starting solution contains excess of hydrogen ion. The problem of SO_2 oxidation in connection with the isopropanol method is a well known phenomenon, and has been discussed previously, eg. Jaworowski and Mack (14).

The controlled condensation method yielded 1 to 3 orders of magnitude lower concentration of SO_3, depending on were the samples were taken. The measured data have been summarized in Figure 11. The concentration ahead of the spray dryer varied from 0.14 to 0.44 ppm SO_3 with an average of 0.24 ppm SO_3. This latter figure corresponds to an acid point of about 97 °C (207 F), which should be compared to the actual temperature of 130 °C (266 F). The concentration after the fabric filter was very low. The actual amount of SO_3 captured in the condenser, corresponded to the contamination of sulfate in the solution used to wash the condenser. Hence, the actual concentration was less than the data points inserted in the diagram. Taking the average values, the removal was seen to be greater than 95 percent SO_3.

Oxides of nitrogen

Four-hour-mean values of the NO_x ($NO+NO_2$) concentration was determined for various coal types. The concentration ahead of the FGD systems ranged from 300 to 500 ppm NO_x. As anticipated, no removal was seen. The expected concentration downstreams from the FGD system with no removal, was actually measured within 10 percent error.

POLYORGANIC MATTERS

Flue gas samples were taken during three tests for identification of larger hydrocarbons. The samples were cooled and passed through beds of an adsorbent, ie. XAD-2. After treatment by extraction of the adsorbent, hydrocarbons were identified by gas chromatography. A total of 130 different polyorganic species (POM) were tried to be identified, including a large number of cyclic compounds. However, as anticipated for a coal pulver fired
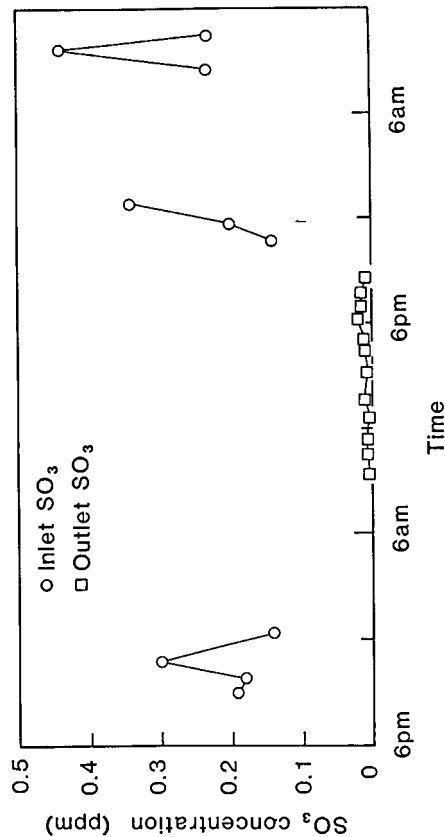

Figure 11. The flue gas concentration of SO_3 before and after the FGD system, respectively.

boiler, very low concentrations were seen. In fact, only harmless bicyclic compounds were identified. The concentrations obtained were in the following ranges:

o Naphthalene: 0-54 µg/Nm^3 (0-2.4·10^5 grains/scf)
o 1-Methylnaphthalene: 0-0.9 µg/Nm^3 (0-4·10^{-7} grains/scf)
o 2-Methylnaphthalene: 0-0.6 µg/Nm^3 (0-3·10^{-7} grains/scf)

Furthermore, no conclusion concerning the removal efficiency of these species can be drawn from the tests.

During one test, samples of flue gas were withdrawn on both sides of the FGD system to collect particles and water vapor by condensation besides adsorption on XAD-2. Furthermore, product samples were taken during the test, ie. fly ash and dry end product from the FGD system. All samples and the collected fractions from the flue gas were subjected to Ames' test for identification of mutagenic species.

All samples were subjected to Soxhlet extraction, and further prepared as described elsewhere (15). The samples were exposed to different strains of Salmonella Thyphimurium to determine the number of revertants for each sample. The three strains used have been described by Ames (16). The procedure was repeated in the presence of microsomalenzymes from rat liver to detect promutagens, ie. mutagenic species produced by metabolic activity.

The results have been summarized in Table 9, expressed as number of revertants per MJ fuel; for conversion to Btu, divide the figures by 1000. The table shows that mutagenic species primarily can be found in the samples obtained by adsorption. Furthermore, it is indicated that the activity drops considerably as the flue gas passes the FGD system. However, there seems to be no activity in the products, ie. fly ash and dry end product. The fact that the number of revertants is larger in the absence of rat liver enzymes indicates that it is not POM that generate the revertants. It may instead be nitrated POM or radioactive species. The fact that XAD-2 compounds dominate, makes the latter option less likely. Finally, as a comparison, it can be mentioned that measured data from diesel engines indicate 50 000 revertants per MJ (17).

TABLE 9

NUMBER OF REVERTANTS PER MJ FUEL

Strains	TA 97		TA 98		TA 100	
Rat liver enzymes	yes	no	yes	no	yes	no
Products						
Fly ash from ESP	0	0	0	0	0	100
FGD end product	0	0	0	0	0	0
Flue gas after ESP						
Particulates	0	180	0	0	0	0
XAD-2 adsorbed	180	240	0	0	360	800
Condensate	0	0	0	0	0	0
Flue gas after FGD						
Particulates	0	0	0	0	0	0
XAD-2 adsorbed	0	410	0	0	225	500
Condensate	0	0	0	0	0	0

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Spray Dryer Absorption Applications for High Sulfur Coal

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