FORMATION AND EMISSION OF FINE PARTICLES FROM TWO DANISH PULVERISED COAL FIRED POWER PLANTS

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ABSTRACT

Measuring campaigns at two Danish pulverised coal fired power plants has been performed. The power plants are equipped with the same type og flue gas cleaning devices. The concentrations and chemical compositions of the formed particles were similar for the two plants. The measurements were performed simultaneously at three locations including both total dust measurements and fine particle characterisation with low pressure impactors and scanning mobility particle sizers. The size distribution of the particles formed during the combustion is clearly bimodal and the fine particles (< 1   m) account for less than 1 % w/w of the total dust concentration. The fine particles are formed by condensation of vaporised species and show significant enrichment of several trace elements. Less than 0.5 % w/w of the total particle mass penetrate the electrostatic precipitators. The fine particles have penetrations of 4-6 % w/w clearly indicating the difficulties accompanied with the removal of fine particles from the flue gas, in good agreement with the theory for electrostatic precipitator performance. The flue gas desulfurisation plants have very little effect on the fine particles which easily penetrate the plants. Almost all particles emitted from the stacks are smaller than 10   m and the fine particles account for 19-38 % w/w of the total emitted mass.

1 INTRODUCTION

Several investigations have shown that elevated levels of fine particulate matter in the ambient air causes an increase in respiratory symptoms, cardiopulmonary disease and mortality [1,2,3,4]. In 1997, based on that knowledge the US EPA proposed a new standard for the levels of fine particulate matter in ambient air. This so called $PM_{2.5}$ standard dictates limits for the concentration of particles in the ambient air with an aerodynamic diameter less than 2.5 microns at 15 g/m^3 on an annual basis [5].
In 1998 a Danish investigation sponsored by the Department of Energy and in cooperation with FLS miljø a/s, Risø National Laboratory, The Technical University of Denmark and the power companies ELSAM a/s and ENERGI E2 was initiated to investigate the formation and emissions of fine particles from Danish power plants using different fuels (coal, biomass and Orimulsion).
In the following the results from field measurements at two pulverised coal fired power plants will be presented and compared. Both Avedøre Power Plant and Nordjylland Power Plant deliver power and district heating to the Danish consumers. Key figures for the two power plants are shown in table 1.

Table 1 *Features of the two power plants investigated with emphasis on units influencing the particles in the flue gas. (DC = Direct Current)*

	Avedøre power plant	Nordjylland power plant
Electric power generation	250 MW	380 MW
District heating	330 MW	420 MW
Boiler construction	Boxer formation in four rows (Deutsche Babcock)	Tangential firing in four rows (FLS miljø a/s, BWE)
Burners	16 Low NOx	16 Low NOx (BWE)
DeNOx	High dust deNOx (Haldor Topsøe / FLS miljø a/s)	High dust deNOx (Haldor Topsøe / FLS miljø a/s)
Electrostatic Precipitator	Four sections, two DC and two intermitting DC (FLS-miljø a/s)	Four sections, DC with pulses (FLS-miljø a/s)
DeSOx	Single loop wet limestone absorber (FLS-miljø a/s)	Single loop wet limestone absorber (FLS-miljø a/s)

The bituminous coals burned during the measuring campaigns at the two power plants were similar in chemical composition.
The measurements were performed simultaneously at three locations on the plant (figure 1): at the inlet to the electrostatic precipitator, at the outlet of the electrostatic precipitator and in the stack. Data from these three positions give information about the formation of particles in the boiler, the electrostatic precipitator efficiency, the impact on particle characteristics of the flue gas desulfurisation plant and the emissions from the stack.

2 PARTICLE CHARACTERISATION

The total dust concentration was measured at all three locations with isokinetic sampling with precyclone and depth filter or plane filter depending on the dust concentration and traversing in the flue duct was performed if space allowed it.

The fine particles in the flue gas were characterised with a Berner-type low pressure cascade impactor (Hauke) and a Scanning Mobility Particle Sizer (TSI Inc.).

The low pressure cascade impactor (LPI) classifies the fine particles based on their aerodynamic properties. The LPI consists of ten consecutive stages on each of which a specific size interval of particles are deposited as the gas passes through the impactor

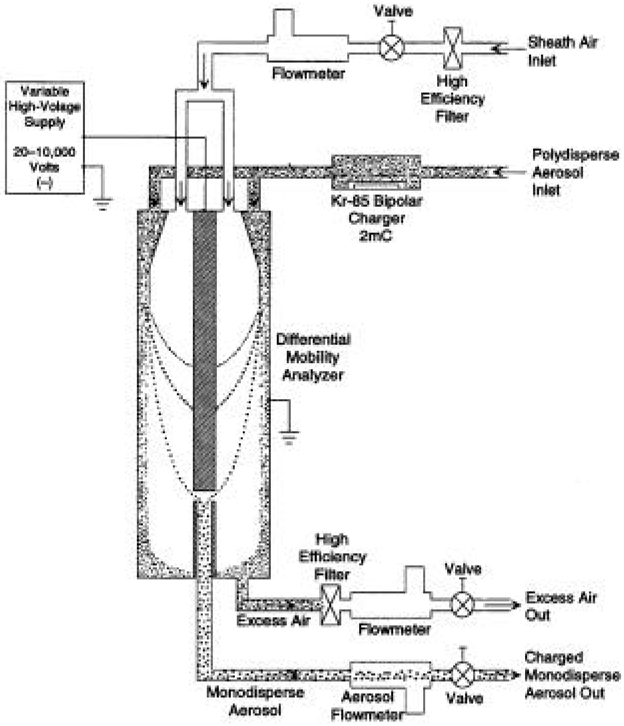
On each stage the sampled gas is drawn through a number of small nozzles giving the gas a high linear velocity. An impaction plate is placed a short distance below the nozzles forcing the gas to make a 90°turn and leave the stage. Particles having too much inertia will be deposited on a thin alumina foil, covered with a thin film of vacuum grease to avoid particle bounce. Particles with sufficiently low inertia will follow the gas to the next stage where the gas velocity in the nozzles is increased and/or the pressure on the stage is decreased thereby collecting particles with less inertia. By reducing the pressure and increasing the nozzle velocity particles in the size interval 0.04 m - 12 m can be classified by the low pressure cascade impactor, giving a mass-based discrete size distribution.

The Scanning Mobility Particle Sizer (SMPS) classifies the fine particles by their electrical mobility i.e. the ability of a charged particle to move in an electrical field. The SMPS system consists of a Differential Mobility Analyser (DMA 3071, TSI Inc), a Condensation Particle Counter (CPC 3022, TSI Inc) and a laptop that controls the DMA and the CPC. In the DMA the particles acquire electrical charge by passing the particle laden gas through a Kr^{85} neutralizer (see figure 2).

The gas is introduced to the electrical grounded outer wall of the DMA’s classifying column upon which a negative electrical field is applied on the centre rod of the column. Sheath air is supplied to the classifying column between the centre rod and the particle laden gas in order to keep the particle laden gas close to the outer wall as both sheath air and particle laden gas moves down the column towards the exit. Positively charged particles will move from the outer wall towards the centre rod and only particles with a specific mobility are extracted through the narrow slit in the centre rod close to the exit of the DMA enter the CPC to be counted.

In the CPC the classified particles from the DMA passes through a heated saturator unit where the gas is saturated with n-butanol. The gas then passes through a condenser where the n-butanol becomes supersaturated and condenses on the existing particles which quickly grows to ~1 m and passes through an optical device that counts each particle.

By scanning the electrical field strength in the DMA and compare the field strength with the particle number concentration measured with the CPC a number based size distribution in the size range 0.013 - ~ .800 m can be calculated.



0.1 Particle sampling

The sampling of the fine particles depends on the sample location and the problems and solutions concerning particle sampling on the three locations will be explained below.

Upstream of the electrostatic precipitator the mass fraction of fine particles is very small compared to the total dust concentration and care should be taken not to overload the impactor and SMPS with coarse particles. Even so the fine particle concentration is high and dilution of the fine particles is needed in order not to overload the impactor and SMPS.

A sampling probe based on the ejector principle is used for the extraction of flue gases with high fine particle concentration. Hot particle-free pressurized air is expanded at the tip of a capillary tube, thereby withdrawing and diluting a gas sample from the tube which extends into the flue gas.

The dilution ratio of the ejector probe is determined by simultaneously measuring and logging the CO_2-concentration in the flue gas and in the diluted gas. Dilution ratios between 15 and 100 can be applied by changing the dilution air flow and the inner diameter of the capillary tube. More information about the ejector probe can be found in [6].

The coarse particles in the flue gas overloads the instruments and should therefore be excluded from the flue gas sampling. This is done by placing the tip of the ejector probe perpendicular to the direction of the flue gas flow. The perpendicular sampling acts as an one-stage impactor and the 50% cut diameter can be calculated with knowledge of the linear velocities of the flue gas and sampled gas respectively. A cut diameter at 2-3 m is preferable at the location upstream of the electrostatic precipitator but a compromise must be made concerning the dilution ratio and cut diameter.

At the precipitator outlet the amount of condensable gaseous sulfuric acid (or SO_3) can be comparable to the fine particle mass concentration and therefore the gaseous sulfuric acid is removed from the flue gas before cooling to room temperature which is the temperature where the SMPS-system operates. The sulfuric acid removal is done by passing the sampled flue gas through an in-stack sulfuric acid denuder which consists of a manifold of ceramic porous tubes impregnated with potassium carbonate. The sulfuric acid will diffuse to the tube walls and react with the potassium carbonate to form potassium sulfate thereby immobilizing the sulfuric acid. The sulfuric acid denuder is designed to have minimal particle loss and SMPS-measurements have confirmed that.

The particle concentration after the precipitator is so low that dilution of the flue gas is not necessary. The flue gas for the impactor sampling is either kept well above the dew point and sampled directly (Nordjylland Power Plant) or the flue gas is dried and the impactor measurements are performed at room temperature (Avedøre Power Plant). The flue gas sample for the SMPS is always dried since the SMPS-measurements are performed at room temperature. Diffusion dryers packed with molecular sieves are used for removing the gaseous water from the sampled gas. The diffusion driers are tubes with porous walls which enables the gaseous water to penetrate the wall and physically be bounded to the surfaces of the molecular sieves placed in a packed bed behind the tube walls.

In the stack the amount of coarse particles is generally low compared to the fine particles and the impactor is used in-stack fitted with an adjustable tip which enables isokinetic sampling with the impactor. The impactor is preheated to the stack temperature in order to avoid condensation during start up and sampling.

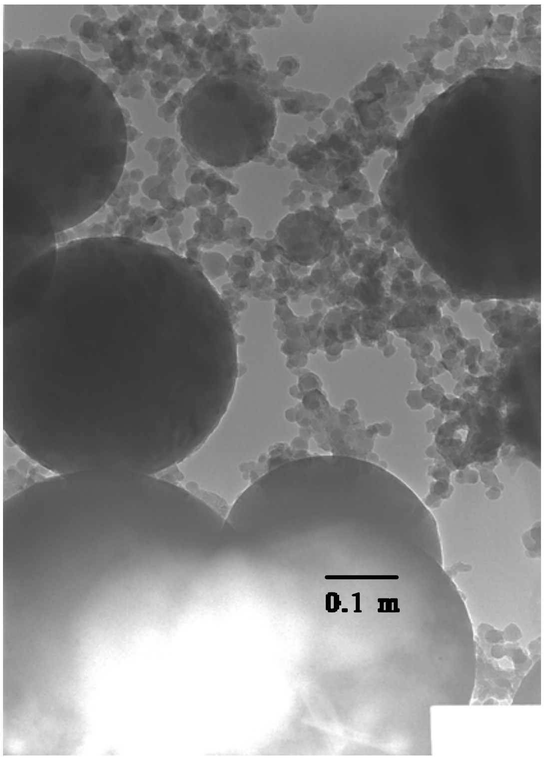
Besides total dust and fine particle measurements, samples of the fuel, bottom ash and ash from different sections in the electrostatic precipitator were also taken for subsequent wet chemical analysis. Most elements were analysed with ICP-AES and Pb was measured with GF-AAS.
Chemical analysis was also performed on the small amounts of particles deposited on the alumina foils in the impactor, giving a size dependent chemical composition of the sampled particles. Due to the low sample amounts wet chemical analysis is not possible and the chemical analysis was performed with the semi-quantitative EDX-method.

3 RESULTS

0.1 Formation of fine and coarse particles

Size distributions of particles formed during pulverised fuel combustion are typically bimodal and the two distributions have very different formation mechanisms. [7,8,9]
The coarse particles are formed when the temperatures in the burning coal particle is sufficiently high to melt the mineral inclusions in the coal matrix. These mineral inclusions coalesce during burnout of the char particle to form a large spherical particles. When the flue gas cools the spheres will harden to spherical glass-like coarse particles. [7,8,10]
The fine particles are formed when species evaporated during the char burnout reach supersaturation due to either cooling or chemical reactions and condense on already existing particles or form new primary particles by nucleation. Newly formed primary particles are very small and produced in vast amounts. The high concentration causes the particles to collide and the relatively low temperature at that time will only allow a partial fusion of particles to agglomerates each consisting of a number of primary particles.[7,10,11]

The TEM-picture in figure 3 clearly shows that two mechanisms are responsible for the formation of particles during pulverised coal combustion as both coarse spherical particles and fine agglomerates are seen.
The size distributions at the precipitator inlet are also bimodal. The size distribution of the fine particles have a mean geometric diameter of 0.06 m and accounts for less than 1% of the total dust concentration. The coarse size distribution have a mean diameter between 10 and 20 m.



EDX-analysis on the deposited particles on the ten stages of the impactor clearly shows a difference in chemical composition between the fine and coarse particles. The coarse particles are mainly composed of Si, Al and Fe and although the fine particles also are composed of Si, Al and Fe the amounts are smaller and the fine particles are enriched in S and Ca and to some extent Ba and V.

A further study of the enrichment of elements on the fine particles was performed by sampling adequate amounts of particles smaller and larger than 2.5 m and using wet chemical analysis (ICP-AES and GF-AAS) on the two types of samples. Comparison of the composition of the fine and coarse particles showed that S, Zn, Cu, V, Ba, P, Ni, Be and Pb are enriched on the fine particles.

These results are in good agreement with previously published results: McElroy et al. found that As, Zn, Hg, Ba, Ni and Cs were enriched on the fine particles [9] and Kauppinen and Pakkanen found that S, Ca, V, Cu, Sr, Cd and Pb were enriched on the fine particles [12].

The enrichment on the small particles can be explained by a condensation mechanism in which evaporated species condense as the flue gas cools down after the combustion. Condensation occurs mainly on small particles and for fine particles it is theoretically found that a D_p^{-1} dependence exist for the bulk concentration of condensed species [10].

0.2 Particle removal in the electrostatic precipitator

Both power plants are fitted with the same type of electrostatic precipitators to remove dust from the flue gas. In the electrostatic precipitator electric charges are applied to the particles and the charged particles are separated from the flue gas by electrostatic forces. Theory predicts that particles in the size range 0.1-1 m are difficult to remove in electrostatic precipitators due to inefficient charging of these particles. [13]

The two electrostatic precipitators efficiently removes the coarse particles with penetrations less than 0.5 % w/w (> 99.5 % removal efficiency).

As predicted by the theory the fine particles are more difficult to remove showing penetrations which are larger by more than an order of magnitude.

0.3 Particle removal in the flue gas desulfurisation plant

The two power plants are equipped with similar flue gas desulfurisation plants (se table 1)
In the flue gas desulfurisation plant the flue gas is brought into contact with a falling film of a limestone slurry. The SO_2 in the flue gas then diffuses into the liquid phase where it is oxidized and hydrolysed and with reaction with Ca^{2+} forms gypsum. Particles have very low diffusivities compared to gases and it is expected that the fine particles easily penetrate the flue gas desulfurisation plant.
That is true for the flue gas desulfurisation plants at Avedøre and Nordjylland power plant. A large fraction (50-80 % w/w) of the coarse particles are removed in the desulfurisation plant, most likely due to inertial removal.

0.4 Emissions from the stack

Comparison between the total dust measurements and the impactor results shows that practically all the emitted particles from the two plant have diameters less than 10 m. The size distribution is still bimodal but the size distribution of the coarse particles is highly reduced both in concentration and mean diameter compared to the distribution at the precipitator inlet.
The fine particles (i.e. particles with diameter less than 1 m) account for 19-38 % w/w of the emitted particles.

4 CONCLUSIONS

The measurements at the two coal fired power plant have shown good agreement with the theories of the formation and removal of fine particles during combustion and flue gas cleaning.
Although less than 1 % w/w of the total particles formed belong to the fine fraction this fraction increases as the flue gas passes through the electrostatic precipitator and flue gas desulfurisation plant and accounts for 19-38 % w/w of the emissions from the stack significantly increasing the importance of the fine particles formed during the combustion.
Enrichment of the fine particles by several trace elements was observed.

5 ACKNOWLEDGMENTS

The project is supported by the Danish Department of Energy (EFP-98), Elkraft System and Eltra.

6 REFERENCES

1 Anderson, H.R., Ponce de Leon, A., Bland, J.M., Bower, J.S., Strachan, D.P. "*Air pollution and daily mortality in London: 1987-92* " B.M.J 312, pp 665-669 (1996)

2 Dockery, D.W., Pope III, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris jr, B.G., Speizer, F.E. "An association between air pollution and mortality in six U.S. cities" The New England journal of Medicine, vol 329, no. 24, pp 1753-1759 (1993)

3 Pope III, C.A., Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E., Heath Jr., C.W. "*Particualte Air Pollutions as a Predictor of Mortality in a Prospective Study of U.S. Adults*" Am. J. Respir. Crit. Care. Med. vol 151, pp 669-674 (1995).

4 Schwartz, J. "*Health effects of air pollution from fraffic: ozone and particulate matter*" Chapter 6 in "*Health at the crossroads, transport policy and urban health*", edited by Fletcher, T., McMichael, A.J. London School of Hygiene & Tropical Medicine, London U.K.
John Wiley and Sons, Baffins Lane, Chichester, West Sussex PO 191 UD, England (1997)

5 US EPA "*EPA's Revised Particulate Matter Standards*", July 17, 1997. Standard found from the US EPA net-site http://ttnwww.rtpnc.epa.gov/naaqsfin/pmfact.html

6 Nielsen, M.T. "*Field Measurements of Combustion Aerosols*" Ph.D.thesis from the Department of Chemical Engineering, The Technical University of Denmark, (2001).

7 Flagan, R.C. "*Submicron particles from coal combustion*", 17.th symposium on combustion, The Combustion Inst., Pittsburg, PA. pp 97-104. (1979)

8 Desrosiers, R.E., Riehl, J.W., Ulrich, G.D., Chiu, A.S. "*Submicron fly-ash formation in coal-fired boilers*", 17.th symposium on combustion, The Combustion Inst., Pittsburg, PA. pp 1395-1403. (1979)

9 McElroy, M.W., Carr, R.C., Ensor, D.S., Markowski, G.R. "*Size Distribution of Fine Particles from Coal Combustion*", Science, 1. January 1982, volume 215, pp13-19

10 Flagan, R.C., Friedlander, S.K. "*Particle formation in pulverized coal combustion -a review*" Chapter 2 in "Recent developments in Aerosol Science", edited by Shaw, D.T., Wiley, New York (1978).

11 Taylor, D.D, Flagan, R.C. "*The Influence of Combustor Operation on Fine Particles from Coal Combustion*", Aerosol Science and Technology, volume 1, pp 103-117 (1982)

12 Kauppinen, E.I., Pakkanen, T.A. "*Coal Combustion Aerosols: A Field Study*", Environ. Sci. Technol., vol 24, pp 1811-1818 (1990)

13 Flagan, R.C., Seinfeld, J.H. "*Fundamentals of air pollution engineering*", Prentice Hall Inc., New Jersey (1988)

7 BIOGRAPHY

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