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## AEROSOLS FROM THERMAL SPRAYING OPERATIONS WITH MATERIALS CONTAINING CHROMIUM AND NICKEL

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### Introduction

Thermal spraying is a technique for coating objects with a surface protective layer. The material which is to be deposited is heated by either an oxygen-acetylene flame, an electric arc or in a plasma. The heated material is brought to the object by either the expanded gas (flame spraying and plasma spraying) or by using a jet of compressed air (flame spraying and electric arc spraying).

Chromium and nickel are among the most toxic metals used in thermal spraying materials (Norseth, 1980). Several compounds of these metals have been shown to be carcinogenic. For chromium the oxidation state is of a major importance. Cr(VI)-compounds have much higher health hazard potential than Cr(III)-compounds. For Cr(VI)-compounds water solubility is also a parameter of considerable interest. Indications exist that the less soluble compounds are those of highest carcinogenicity.

Five common methods of thermal spraying with materials containing chromium and nickel were characterized regarding the particle size distribution, the elemental composition, the oxidation state of chromium and a measure of the solubility of chromium.

### Sampling

The spraying and the sampling of aerosols were performed in a room sealed off from other activities in a workshop.

Techniques for "total" sampling and respirable sampling were utilized in the present work. Three types of samplers were used: 1) a multi-filter sampler for total and respirable fractions, 2) a modified Battelle impactor and 3) a sampler with two parallel filters prepared for transmission electron microscopy studies.

The multi-filter sampler consists of four filters (Millipore GSWP, 37 mm diameter, 0.22  $\mu\text{m}$  pore size), two of them with pre-collectors (cyclone pre-collector; Casella Personal Sampler) (A and B) and two without (C and D). A cylindrical common inlet with a length of 300 mm and a diameter of 50 mm was used. The inner surface was of aluminium, electrically grounded. The air flow through each filter was 1.9 l/min. The sampler was intended to give samples for a) gravimetric determination of the ratio between respirable and total fraction, b) analysis of the elemental composition of particles in the two fractions and c) determination of the oxidation state of chromium. The multi-filter sampler was designed for sampling a large fraction of the total aerosol. The upper limit of particle size depends mainly on the sedimentation rate in the inlet tube. The sampler collects 50 % of the particles with a 35  $\mu\text{m}$  aerodynamic diameter and particles larger than 50  $\mu\text{m}$  are not collected. The mean of the  $M_A/M_B$ - and  $M_C/M_D$ -ratios, where  $M_A$ ,  $M_B$ ,  $M_C$  and  $M_D$  denote the gravimetrically determined mass of particles collected on the filters, were  $1.04 \pm 0.10$  and  $0.97 \pm 0.14$  respectively for 25 collections.

A modified Battelle impactor (Mitchell and Pilcher) was used for determining the particle size distribution within the respirable fraction.

For studying individual particles with transmission electron microscopy, a double filter sampler was used for particle collection.

The samplers were placed 50 to 150 cm above and 50 to 100 cm behind the spraying object with the inlets facing downwards during sampling. The distance between the nozzle of the spray-gun and the object were between 5 and 20 cm. Five collections with each sampler were performed for each spraying method.

### Analytical methods

Gravimetric analysis was applied to the filters from the multi-filter sampler by using a Sartorius balance with 1  $\mu\text{g}$  precision and accuracy. Particle Induced X-ray Emission analysis (PIXE) was used for elemental analysis (Malmqvist *et al.*). One of the respirable and one of the total samples (B and D) from the multi-filter sampler were washed in distilled water buffered to pH 7.4. A procedure for analysis of chromium described by Bohgard *et al.* (1979) including PIXE, ESCA and spectrophotometry with DPC and spectrophotometry with DPC reagent was used. In the present study AAS, with Perkin-Elmer 403, was used as complement to the procedure for determining the total fraction of soluble chromium. Knowledge about the structure of individual particles is essential for evaluating the results from ESCA, since the results from ESCA are valid only for a thin surface layer (~2 nm) of the sample. Transmission electron microscopy was used to study individual particles before and after washing.

### Results

The relative abundancies of the major metals in the aerosols agree with the relative abundancies in the spraying materials. The lower concentrations of the metals in the fume relative to the materials can be explained by the fact that the fumes consist of metal oxides while the spraying materials consist of alloys of the metals. The differences in metal concentrations between the total and the respirable fraction are below 10 %. When the same spraying material was used for different methods minor differences in metal composition were seen.

Two modes of particles categorized according to aerodynamic diameter can be seen. The respirable fraction consists of 40 - 90 % of the particle mass in the total fraction as defined in this study. The mass median aerodynamic diameter was below 0.5  $\mu\text{m}$  for the respirable fraction. The methods flame spraying with powder and electric arc spraying give higher percentages in the respirable fraction than the other methods. Figure 1 shows the particle size distribution for one of the methods of fine particles. Significant differences between the methods occur, but for all the five methods the finest particles dominate the mass of the respirable fraction. The mass median aerodynamic diameters of the respirable fractions are below 0.5  $\mu\text{m}$ .

There are no significant differences (< 5 %) in metal composition between different particle size fractions.

There are significant differences in the Cr(VI)-concentration in the respirable and the total fractions. The concentration of Cr(VI) seems to depend on both spraying method and spraying material. The analyses of the soluble part of Cr(VI) were performed within four hours after washing the filters. There is, however, a risk of loss due to the reduction of Cr(VI) to Cr(III). The systematically higher values obtained from the AAS analysis relative to the DPC analysis may not be significant because of the reduction of Cr(VI) to Cr(III) by other constituents of the aerosol acting as reduction agents during the washing procedure, and the time elapse between washing and analysis. Hence the soluble fraction of chromium may consist entirely of Cr(VI).

The differences between the concentrations of Cr(VI) in the total and respirable part of the aerosols and the determined mass ratios between respirable and total fractions, indicate that the soluble part of Cr(VI) is mainly in the respirable fraction for all methods. The ESCA-results from unwashed samples do not show significant differences between the total and the respirable fraction. Assuming spherical particles, the total particle area of the respirable fraction exceeds 99 % of the total aerosol area according to the determined particle size distributions. Hence by using ESCA, for the spraying methods studied, the respirable fraction dominates the particle area and hence the material analyzed by ESCA. After washing Cr(VI) was still detected for four of the spraying methods.

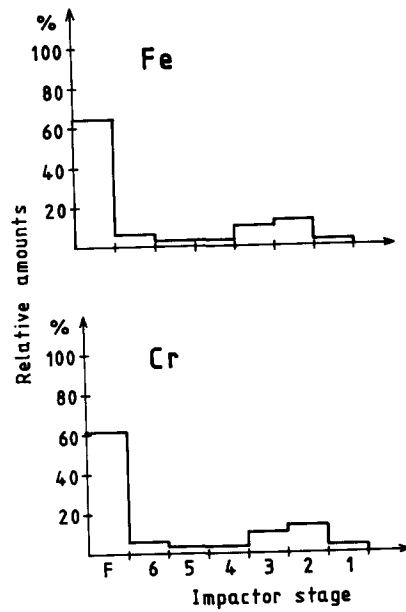


Figure 1: Example of distributions of Fe and Cr in different particle size A fractions from impactor measurements. Stage 1 was used as a pre-collector stage collecting particles with aerodynamic diameter larger than  $8 \mu\text{m}$ . On the stages 2, 3, 4, 5, 6 and the filter (F) are the fractions with aerodynamic diameters  $D$ ;  $8 \geq D \geq 4$ ,  $4 \geq D \geq 2$ ,  $2 \geq D \geq 1$ ,  $1 \geq D \geq 0.5$ ,  $0.5 \geq D \geq 0.25$  and  $D \geq 0.25 \mu\text{m}$  respectively.

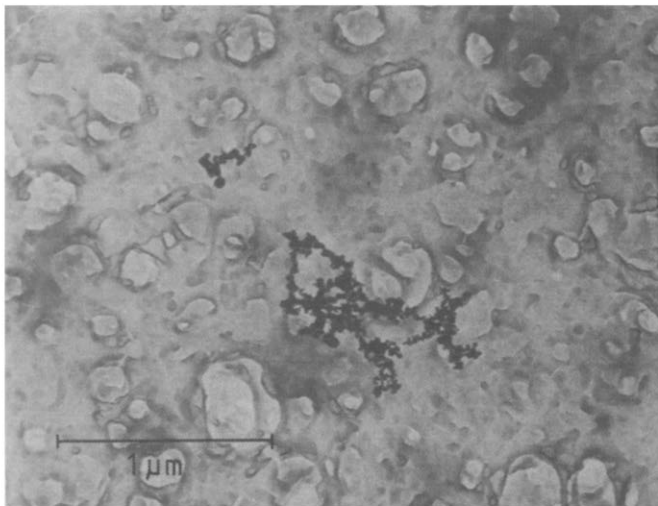


Figure 2: Transmission electron micrographs of an aggregate of primary particles.

Individual particles have been studied with transmission electron microscopy. Generally two classes of particles can be seen; coarser spherical particles and finer particles being aggregates of small (0.005 - 0.05  $\mu\text{m}$ ) primary particles. Figure 2 shows a micrograph of an aggregate. The number of aggregates always dominate over the number of spherical particles in the micrographs. ESCA is valid for 20 to 80 % of the volume of the particles in figure 2. The observations further support the assumption made above that the total particle area of the respirable fraction exceeds 99 % of the total aerosol area.

### Conclusion

The characterization procedure used in this study has been shown to give detailed data about the aerosol emission from methods of thermal spraying. The sampling and analytical techniques used give results of high significance for parameters of considerable interest in health effect assessments and for toxicological and epidemiological studies.

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