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STUDY OF COMBUSTION ORIGINATED ASH PARTICLES

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INTRODUCTION

We are engaged in a study of the ash produced by combustion of lignite in a 750-MW power station. The aim is to follow the transport of elements with $Z > 16$ from the mine, through: a) the combustion process, b) emission to the atmosphere or c) deposition in a land fill, d) transport in the environment and e) subsequent uptake by animals and humans. The resulting data will be used to estimate potential adverse impact on human health caused by operation of the power station.

The power station of interest is located 2 km to the east of the village of Gyöngyös-Visonta which is approximately 80 km to the northeast of Budapest. It has a maximum generating capacity of 750 MW. The station (Hungarian Electricity Board, 1991) burns 15,000 tons of lignite each day. Most of the lignite is obtained from a large open-pit mine situated about 5 km from the power plant. It is transported to the plant and the resulting ash is returned to the mine pit in a slurry form for disposal. The typical ash content of the lignite is about 20 % (Civin, 1993) so that the total production of ash is roughly 3000 tons/day. The ash is removed from the exhaust by an electrostatic filter system, but approximately 1-2 % of the ash consists of fine particles which are not removed by the filter system and escape into the atmosphere producing a particulate density of 50 mg/m³.

The particles contain toxic elements such as Pb, Cr, and As. Consideration of the fate of the ash particles is thus of importance for assessment of the environmental hazards posed by operation of the power plant. The amounts of toxic materials are relatively large: For concentrations of the order of 100 ppm, total production of an element such as lead is around 100 tons per year which is high enough to be of concern.

The initial measurements (Rausch et al., 1993, Török et al., 1993a, Tuniz et al., 1992) have characterized the ash using neutron activation analysis, inductively-coupled plasma-emission spectrometry (ICP-AES), electron microscopy, electron probe energy-dispersive x-ray microscopy, synchrotron radiation x-ray emission (SRIXE), and synchrotron x-ray absorption near-edge spectroscopy (XANES), etc. Some of the SRIXE measurements have investigated individual particles with sizes as small as 2 μm . The XANES work helps to delineate the chemical state of these elements which is important for assessment of their toxicity.

This initial work (Tuniz et al., 1994) investigated elemental concentrations in bulk samples of fly ash and determined the oxidation states of Cr and As in samples from Gyöngyös-Visonta and other Hungarian power plants. The measurements showed that the oxidation state for both elements was shifted to a slightly higher state compared to Cr^{3+} and As^{3+} . There was no evidence for the existence of Cr^{6+} which is the most toxic oxidation state for Cr.

In the present work, we extend the measurements to samples taken from the land-fill site close to the power plant and then consider a simple model calculation of the transport of materials through the atmosphere. This calculation uses a 3-dimensional mesoscale model to find the wind and pressure profiles over the region surrounding the power plant. Application of the model then makes possible estimates of the transport and deposition of the combustion particles as a function of particle size and distance from the source. It is expected that the atmospheric transport will be the important mechanism at large distances from the power station.

EXPERIMENTAL PROCEDURES

Samples for the present investigation were taken from the land-fill site to the north of the power station. In previous work by Török et al. (1993a) ash samples were obtained from the filters used in the electrostatic precipitation system at the power station. Here, the samples were taken from the land-fill site in order to ascertain whether the conditions following deposition had brought about changes in the sample elemental concentrations or oxidation states. The samples were taken at 200 m, 1 km and 2 km from the power plant at depths a few centimeters from the surface. The material is representative of recent deposits acted upon by atmospheric conditions only.

Sample analysis was carried out using both electron beam and x-ray beam methods. Results of scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) work carried out in Budapest will be reported in a separate communication (Török et al., 1993b). The x-ray work was carried out at the Brookhaven National Synchrotron Light Source X26 beamline. The characteristics of the beam line have been described by Sutton et al. (1994). Measurements were made with beams down to about 5 μm in size. The minimum detection limit is around 1 part per million by weight for the samples investigated with this beam size. Measurements of the energy spectra were made with white beams of x rays from the NSLS. These conditions gave high detection efficiency for most elements in the periodic table. A channel-cut silicon (111) monochromator was used to produce the beams used for the XANES measurements. In order to obtain sufficient beam intensity for measurements on samples with concentrations of Cr around 100 ppm or less the beam size was increased to the order of 100 μm .

Figure 1. SRIXE spectra obtained from bulk samples of soil taken near the village of Markaz which is located approximately 2 km north of the power station exhaust stack.

EXPERIMENTAL RESULTS

XANES measurements were carried out in fluorescence mode. A spectrum obtained from a bulk land-fill sample from Markaz is shown in Figure 1. Cr is clearly visible in this spectrum by monochromatic excitation at 60 eV energy above absorption edge. The concentration of Cr is below 100 $\mu\text{g/g}$.

The concentration was too low to make measurements on individual particles feasible. As a result, the XANES measurements were done using a beam of about 100 μm . The results of the XANES measurements are shown in Figure 2. In this figure curves are

Figure 2. XANES spectrum for chromium taken on the land-fill sample from the village of Markaz

given for Cr standards with oxidation states of 3+ and 6+ as well as for three specimens taken at 200 m (Markaz 1), at 1km (Markaz 2) specimen and at 2 km from the power station (Markaz 3). The results for each of the three specimens shows that the oxidation state is shifted slightly above the 3+ state, but the lack of any preedge peak shows that the 6+ state is not present. The results of a XANES measurement obtained from analysis of a sample collected from the stack scrubber system is also shown in Figure 2 (Electrofilter). It can be seen that the oxidation state for all the samples is about the same.

RESULTS OF TRANSPORT MODEL CALCULATIONS

A program for calculating the wind profiles over the polluted area was developed. The model was combined with a simple transport model to calculate deposition values under different meteorological situations.

This 3-dimensional wind model solves the Navier-Stokes equations and the continuity equation for the wind and pressure over an area of approximately 50 km length in both directions. The program uses the finite element method with linear elements to discretise these partial differential equations and the non-linear discrete system is solved by Newtonian and conjugate gradient iterations.

The geostrophic wind and the terrain configurations represent the main effect on the wind-pressure field. The model has been applied to the Mátra mountain range in Hungary, where the largest Hungarian lignite burning power station is located at Gyöngyös-Visonta.

Figure 3 shows the wind profiles calculated 150 m high above the ground. The geostrophic wind speed is 3 m/s, and its direction is 30 degrees (0 degree is North wind). The stack and the largest town (Gyöngyös) near to it are noted on the map. This result shows that this stack is located in a region where the wind-field is unstable, and in meteorological situation like this, the pollution values will significantly differ from the Gaussian approximation. This suggests that it is necessary to upgrade the transport model using finite-element technology to solve the diffusion equation in three dimensions.

As a first approximation the transport and deposition of solid particles was calculated with the Rimpuff 4 model (Mikkelsen et al., 1984), which uses spherical 'puffs' to approximate the transport of pollutants. Figure 4. shows the total deposition in g/m² during 90 minutes of emission using the calculated wind profiles (shown on Figure 3). The same model can be used to estimate deposition values for any particle size > 10 µm. However, since it is known (Török et al., 1993a) that the ash particles with small sizes have relatively high concentrations of Cr, As, and Pb it will be necessary to give more consideration to the human health hazards caused by exposure to the estimated concentration levels at these distances. For example, in the proximity of the stack the concentration level will be about 5000 ng/m³ for elements contained in the ash at the 100 ppm level. This value is above the maximum permissible air quality concentration - 700 ng/m³ (Hungarian Standard, 1993). These concentrations can also be compared to background concentration levels reported (Bozó et al., 1992, Bozó, 1993, Molnár et al., 1993) to be of the order of a few ng/m³.

DISCUSSION AND CONCLUSIONS

The present results are considered in conjunction with the conclusions from our previous experiments that bear on combustion originated particles. The previous work

Figure 3. Wind profiles calculated for a height 150 m from the ground. Locations of the power station exhaust stack and nearby town of Gyöngyös are indicated.

Figure 4. Deposition values during 90 minutes of emission calculated using the program RIMPUFF. The particle size is $50 \mu\text{m}$, the emission rate is 10^3 g/s .

showed that high concentrations of toxic elements were carried by ash particles a few μm in size. It was demonstrated that XANES can be used for chemical speciation of ash

deposited on scrubbing filters and even for single particles when the concentration levels are high (more than 100 ppm). This work has been extended to include measurements on specimens taken from the near-surface region of the ash dump-site at the power plant. Results here show that there are high concentrations of the toxic elements in the earth at that point and that, in the case of Cr, there is no indication of change of oxidation state as a result of the disposal process and that there is no evidence found for substantial concentrations of the toxic 6+ charge state.

In order to fully evaluate the environmental impact different approaches need to be implemented. A more detailed examination of the toxic element distribution in the land fill needs to be done as a function of depth below the surface. Soluble material in the land fill will be mainly transported by the leaching action of rain and ground water. Thus toxic elements could be taken up by growing vegetation or ingested by humans in the drinking water. Experiments to measure the uptake in vegetation are now in progress (Török, 1993b). The transport of airborne ash has been examined theoretically in the present work. It indicates that appreciable concentrations of toxic elements could exist in the air at substantial distances from the power station. It appears that a more detailed experimental investigation of the concentrations in the air are important to carry out in the future.

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