

Health aspects of coal fly ash

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SUMMARY

Employees of coal-fired power stations and people living nearby as well as those involved in the shipment and processing of coal fly ash can be exposed to coal fly ash (pulverised fuel ash or "PFA"). An extensive research program was carried out in order to map such exposure and its effects. Particle size distribution, chemical composition, quartz, radioactivity, emission factors and fugitive dust modelling were studied.

PFA is a combustion aerosol, which means that the elements which volatilise during combustion are found mostly on the outside of the particles. Particle size is thus dependent on the concentration of these elements. Occupational limits (TLV's or PELs) generally refer to the inhalable fraction (PM₅₀). Based on more than twenty years of research at Dutch coal-fired power stations, it appears that there exists a relationship, the so called RE factor, between fuel composition and ash composition. For all the elements studied RE factors have been determined: for the total PFA, as well as for the inhalable PFA and the respirable PFA. This relationship is incorporated in the KEMA Trace Model[®], which also enables the ash composition in case of co-combustion to be calculated.

The occupational threshold values for nuisance dust apply for PFA. This has been determined using the KEMA Dust Assessment Methodology (KEMA-DAM[®]). In this methodology PFA is interpreted as a mixture of components. The exposure of each individual component is calculated assuming the maximum allowable exposure of inhalable nuisance dust. If the concentration of each individual (trace) element is less than half of its allowed TLV and the concentration of each potential carcinogenic component is less than 0.1%, then the PFA can be regarded as a nuisance dust. So far all the PFA produced, including through co-firing up to 10% (m/m), easily meets this standard.

INTRODUCTION

The policy in the Netherlands is for power stations to produce residues that can be used as (building) products or as raw materials for making (building) products, rather than producing waste. It is therefore of vital importance that the quality of the ash be controlled. In the Netherlands coal from all over the world is fired, besides which it is general practise that biomass or other secondary fuels is co-fired. These factors require an enhanced alertness for the ash quality, which is monitored by the Vliegassunie organization. A relatively constant ash quality is obtained by blending the coal: normally five different lots of coal are involved.

Ash quality is of great consequence for the following three items: a) the technical quality (in order to meet the specifications for the various applications), b) the environmental quality (in order to meet Dutch environmental requirements) and c) the health and safety quality (in order to meet legal requirements in the field of occupational exposure). Each item is equally important, because ash quality must comply with all three.

Based on more than twenty years of measurements ¹⁾, KEMA has developed a model which makes it possible to predict the elemental composition of ash as a function of the fuel composition; the KEMA Trace Model[®]. Moreover KEMA has built up databases, based on own measurements, with composition of coals from all over the world and various type of secondary fuels. This makes it possible to predict the elemental composition of ash without carrying out a single measurement.

This paper will deal with ash quality with respect to health and safety aspects.

OCCUPATIONAL HEALTH AND SAFETY ASPECTS OF PULVERISED FUEL ASH

The most important route for exposure to pulverised fuel ash is inhalation. People involved in the production and processing of pulverised fuel ash can be exposed via this route. Measurements indicate that, under normal operating conditions, concentrations of inhalable pulverised fuel ash associated with occupational exposure in power stations vary between 0.1 and 7 milligrams per cubic metre, while concentrations of respirable pulverised fuel ash associated with such exposure are between 0.1 and 2.3 milligrams per cubic metre. During maintenance or in the event of an accident, individuals may be exposed to higher concentrations. Under such circumstances, breathing equipment will be worn.

A great deal of research has been conducted into the health implications of working with pulverised fuel ash. Data from cell test systems and animal experiments indicates that normal levels of exposure (i.e. exposure to levels below the limit for nuisance inhalable substances) are not likely to have any significant health implications. The results of epidemiological research confirm this conclusion.

KEMA has developed the KEMA DAM (Dust Assessment Methodology) ²⁾, a tool which makes it possible to easily determine whether Threshold Limited Values (TLVs) set by the Dutch health authorities for macro-elements and trace elements in ash are likely to

be exceeded in the event of exposure to pulverised fuel ash dust. KEMA DAM is used as a means of risk assessment.

The composition of the inhalable fraction of PFA is calculated using the KEMA TRACE MODEL. Further assessment using KEMA Dust Assessment Methodology (KEMA DAM) indicates that exposure to all macro-elements and trace elements is well below relevant Threshold Limited Values (TLVs) set by the Dutch health authorities, provided that the concentration of inhalable pulverised fuel ash does not exceed 10 milligrams per cubic metre.

In this methodology PFA is interpreted as a mixture of components. The exposure of each individual component is calculated assuming the maximum allowable exposure of inhalable nuisance dust. If the concentration of each individual (trace) element is less than half of its allowed TLV and the concentration of each potential carcinogenic component is below 0.1%, then the PFA can be regarded as a nuisance dust. So far all the PFA produced, including co-firing up to 10% (m/m), easily meets this standard.

The applied research and this risk estimation indicate that there is no reason to regard pulverised fuel ash as a “harmful” dust as opposed to a “nuisance” dust. No increased health risk is involved as long as the requirements laid down for nuisance dust in the occupational environment are met. This means that the standards for nuisance dust should be applied.

Some specific compounds in PFA, will be discussed in the next sections.

PARTICLE SIZE DISTRIBUTION OF OF PULVERISED FUEL ASH

The particle size distribution in pulverised fuel ash has been determined on the basis of internationally accepted differentiation between an inhalable fraction (PM_{50}) (consisting of larger particles), a fine fraction (PM_{10}) and a respirable fraction (PM_4). In order to assess the implications for high-risk groups, such as small children and CNSLD sufferers, an additional very fine fraction was also defined ($PM_{2.5}$).

The proportions of the mass accounted for by inhalable particulate material (PM_{50}), fine particulate material (PM_{10}), respirable particulate material (PM_4) and very fine particulate material ($PM_{2.5}$) average 55 per cent, 20 per cent, 5 per cent and 1 per cent, respectively.

Ten per cent of the mass of pulverised fuel ash is accounted for by particles of less than 4.5 micrometres in diameter (± 0.2 micrometres). Fifty per cent of the mass consists of particles of less than 21.4 micrometres (± 3.2 micrometres). Particles of less than 90.4 micrometres (± 10.8 micrometres) make up 90 per cent of the mass. The diameters are expressed as their geometric or projected diameters.

THE ROLE OF QUARTZ IN COAL AND IN PULVERISED FUEL ASH AND HUMAN EXPOSURE

Exposure to quartz can lead to “black lung” or more precisely, pneumoconiosis or silicosis. Especially the malignant condition progressive massive fibrosis (PMF) is serious. For PMF to occur, a number of limiting conditions need to be met. The particulate material containing the quartz must be respirable (i.e. sufficiently fine that it is able to penetrate deep into the lungs). The surface of the material is also very important, since it is believed that surface radicals act as the trigger. Surface radicals are found mainly on freshly created surfaces and their formation can be inhibited by weathering/ageing and by the presence of other substances, such as aluminium and some forms of iron. As well as causing silicosis, it is recently known that quartz is a human carcinogen at concentrations above a certain threshold.

Since quartz is found in coal and pulverised fuel ash, it is important to know the concentrations in which it is present and whether its presence can cause fibrosis or cancer.

In Dutch power stations, when coal is fired, approximately 50 per cent of the quartz is vitrified. This vitreous material is one of the main components of pulverised fuel ash. The remainder of the quartz finds its way into the pulverised fuel ash in non-vitreous form. Most of this quartz is found in the non-respirable fraction of the ash; the respirable fraction contains only about 1 per cent of the quartz.

In absolute terms, quartz accounted for roughly 0,1 per cent of the respirable fraction of the pulverised fuel ash samples tested. Between 60 and 86 per cent of this quartz was embedded in the ash particles and therefore not available at the surface. Thus, only a very small amount of the quartz is biologically available³⁾.

In the work area directly underneath the E-filter, the measured stationary respirable atmospheric quartz concentrations under normal stationary conditions average 0,0005 milligrams per cubic metre. That is less than 1 per cent of the Dutch TLV for quartz, which is 0,075 milligrams per cubic metre.

All the research undertaken, including epidemiological, *in vivo* and *in vitro* studies, indicates that quartz in pulverised fuel ash does not have the same effect on humans or animals as pure quartz or some substances containing quartz and does not constitute a fibrogenic risk. However, exposure to respirable pulverised fuel ash in concentrations of more than 5 milligrams per cubic metre can result in functional impairment of the lungs and respiratory complaints. At even higher concentrations, there is a risk of chronic bronchitis. However, these effects are what one would expect from any particulate material (nuisance dust); they are not specific to pulverised fuel ash and are certainly not attributable directly to the presence of quartz in the ash.

The absence of the effects normally associated with quartz is attributable to the fact that the quartz in pulverised fuel ash is mainly enclosed within vitreous material. This has been established by electron microscopy of roughly eleven thousand cross-cut pulverised fuel ash particles. Moreover, it appears that quartz loses its fibrogenic

properties when heated to temperatures of more than 1200 °C. All pulverised fuel ash particles undergo heating in excess of this level.

The Dutch Health Council's Expert Committee on Occupational Standards assumes that inhaled quartz particles can cause lung fibrosis, leading to the development of tumours, as a result of prolonged irritation of the lung tissue. Since pulverised fuel ash does not have any of the effects normally associated with quartz, it is highly unlikely that the quartz in pulverised fuel ash is carcinogenic.

It can be concluded that pulverised fuel ash of the kind produced at power stations firing pulverised coal in the Netherlands does not have any of the effects (e.g. silicosis) normally associated with quartz. Hence, the TLVs for quartz are not appropriate for the quartz found in pulverised fuel ash.

CHROMIUM VI

Chromium is found in the environment in various forms, the most significant and stable being the trivalent form (Cr(III)) and the hexavalent form (Cr(VI)). Chromium (III) is essential for human health, the minimum daily requirement being estimated at between 30 and 130 nanograms per kilo bodyweight per day. Too much chromium can be harmful, however, since chromium (III) is fairly cytotoxic. Chromium (VI) is not only cytotoxic for the lungs and kidneys, but it is also a genotoxic carcinogen. When assessing the risks associated with chromium, two standards are therefore usually applied: one for chromium (VI) and one for other chromium compounds, including chromium (III) compounds.

The status of chromium (VI) as a carcinogen derives mainly from its ability to cause lung cancer. Consequently, inhalation is the most significant exposure route.

It is not easy to determine the concentration of chromium (VI) in the atmosphere or in solid particulate material. Only in recent years have methods for doing so been developed, yielding a better picture of the presence of chromium (VI) in solid samples.

Tests on pulverised fuel ash from Dutch power stations have shown that chromium (VI) accounts for 4 to 9 per cent of all chromium in the ash, with the average being 6 per cent. For the purpose of calculating exposure, it is therefore assumed that no more than 10 per cent of the chromium in the ash is chromium (VI). In absolute terms, the concentration of chromium (VI) in pulverised fuel ash is low, averaging about 13 milligrams per kilo. Leaching of this chromium has been tested under two sets of conditions. Under mild conditions, roughly 1 per cent of all chromium present leached out during a column test conducted in a laboratory environment. Under more extreme conditions simulated for an availability test, roughly 5 per cent leached out. All the leached chromium was initially hexavalent. However, after leaching, the chromium reacted with iron compounds and other substances, thereby forming insoluble chromium (III) compounds.

The concentrations of chromium (VI) to which power station personnel could theoretically be exposed are low compared with the maximum acceptable concentrations (TLVs) set for chromium (VI). If it is assumed that the maximum concentration of airborne pulverised

fuel ash to which personnel are liable to be exposed is 10 milligrams per cubic metre of air (i.e. the TLV for nuisance inhalable particulate material), the corresponding chromium (VI) exposure is just 0.5 per cent of the TLV for chromium (VI). In practice, personnel working at or near the storage facility will on average be exposed to a concentration equal to 0.003 per cent of the TLV. In the event of an accident leading to the short-term release of ash, the burden would be six per cent of the TLV.

RADIOACTIVE ASPECTS

The earth's crust contains natural radionuclides. These radionuclides are naturally radioactive substances present since the formation of the earth; they have a very long half-life and are consequently still in existence. The three main natural radioactive substances are uranium, thorium and potassium-40 (^{40}K). Each of the first two substances is associated with numerous radionuclides forming a decay series: radioactive daughter products formed by the decay of uranium ^{238}U and thorium ^{232}Th . These radioactive daughters include radium (^{226}Ra) and the radioactive inert gases radon (^{222}Rn) and thoron (^{220}Rn).

Because radioactive substances are found throughout the earth's crust, a certain amount of radioactive radiation occurs naturally. This is known as background radiation. Substances extracted from the earth's crust, including sand, clay, flint, marble, granite and coal, also contain radioactive material. The use of such substances – in construction, for example, or in power generation – can result in the concentration of radiation, so that levels exceed natural background radiation levels. When coal is burnt, the radioactive materials are left behind in the ash, which consequently has a raised concentration of radioactivity per unit weight. Working with such ash can therefore increase one's background radiation level.

Every year, everyone in the Netherlands is exposed to an average of 2 mSv of radiation from natural sources. Various human activities increase the level of exposure to roughly 2.5 mSv.

The occupational radiation exposure limit is 1 mSv per year. If someone working at a power station spent all his/her working time (1800 hours a year) within twenty-five metres of a pulverised fuel ash store, he would be exposed to 0.016 mSv of radiation per year. This is 1.6 per cent of the maximum permitted level of exposure. Most of this radiation would be external; internal radiation associated with the inhalation of pulverised fuel ash would be negligible.

DIOXINS

Incomplete combustion of fossil fuels and waste can lead to the production of hydrocarbons. Under certain circumstances, some of the hydrogen atoms in these hydrocarbons can be replaced by atoms of chlorine, fluorine or bromine to form substances called dioxins. There are 210 different types of dioxin, of which a 'congeneric' group of seventeen, the so-called 'dirty seventeen', are toxic.

Pulverised fuel ash contains very little dioxin: less than 1 picogram FTEQ per gram. The dioxin 2,3,7,8-TCDD, which is highly toxic to humans and animals, was not found in any of the pulverised fuel ashes analysed. Calculations indicate that, for people working at or living near coal-fired power stations, the levels of dioxin exposure attributable to the airborne dispersal of pulverised fuel ash and stack-emitted flue gases are low. Exposure is negligible in relation to the background dioxin burden (between <0.1 per cent and 0.00004 per cent). Some 80 per cent of the background dioxin burden is associated with the consumption of food (mainly animal fats).

POLYCYCLIC AROMATIC HYDROCARBONS

Incomplete combustion of fossil fuels and waste results in the formation of soot and tar. These materials contain various organic compounds (hydrocarbons), including polycyclic aromatic hydrocarbons (PAHs). Some PAHs are known to have carcinogenic properties, while others do not. When considering the health issues associated with pulverised fuel ash and other airborne particulate materials, it is therefore important to distinguish between carcinogenic and non-carcinogenic PAHs.

No PAHs were detected in pulverised fuel ash. However, since the possibility cannot be excluded that PAHs are present in the ash in non-detectable concentrations, exposure calculations were made, assuming an overall concentration of carcinogenic PAHs right on the detection limit (0.07 mg•kg⁻¹). On the basis of this and other pessimistic assumptions, it was calculated that a person working at or near an ash storage facility would be exposed to less than 5 picograms of carcinogenic PAHs per cubic metre. This is less than 1 per cent of the maximum acceptable concentration in ambient air. Even assuming exposure to pulverised fuel ash in a concentration equal to the maximum acceptable concentration in ambient air, these PAHs-levels would not be exceeded.

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