Environmental and health aspects of coal and biomass co-combustion ashes

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ABSTRACT
Co-combustion is an important aspect of power generation from coal in the Netherlands and becomes increasingly important in the rest of Europe as well. To study these aspects several ashes have been sampled for many years under different firing conditions in test series, mostly at power plants. These ashes were analyzed and its properties assessed. Occupational health aspects discussed in this paper include respirable quartz, Cr(VI) and exposure to heavy metals and organics. The environmental aspects discussed in this paper include leaching, and composition with respect to PAH's, dioxins, other organics and heavy metals. Fly ash must be utilized in the Netherlands since landfill is prohibited. Fly ashes can be utilized as a building material for which insulation measures are to be applied. It is shown in this paper that co-combustion does not negatively influence occupational health and environmental aspects of fly ash. Coal and co-combustion ashes do not classify as hazardous waste according to the European Waste Catalogue. Ashes have been registered according to the newly introduced European REACH regulation as a substance without any hazard classification.

1 INTRODUCTION

The Dutch government promotes co-combustion of biomass or other secondary fuels to reduce the CO_2 emissions. An agreement was made between the Dutch government and the electricity producing companies for reducing the CO_2-emissions. It has been practiced in Netherlands for over fifteen years now and co-firing rates of 25% on thermal heat input are common practice nowadays. It is important that the environmental and occupational safety and health aspects of fly ash are not negatively influenced by co-combustion. A good understanding of the effects is therefore necessary.

Occupational health aspects concern, amongst others, respirable quartz, hexavalent chromium and heavy metals. If inhaled, quartz can cause silicosis. When workers are exposed to fly ash, for example when it is utilized in cement, Cr(VI) can cause allergic reactions. In addition, Cr(VI) is more toxic than Cr(III) and carcinogenic. Threshold Limit Values (TLV's) exist for most heavy metals, e.g. since they are carcinogenic like As, Be,

Cd, Co, Cr(VI) and Ni or toxic in another way. The co-firing ashes therefore need to be assessed against those values.

Since ashes are utilized as construction material, e.g. as cement replacement, it has to comply with limit values of the Dutch Soil Quality Decree. These limit values are leaching values for heavy metals and in case of unbound applications also composition limits for PAH's. In addition the presence of dioxins is measured, since these are also known to be toxic to the soil environment as well as for humans.

Co-firing ashes have to be evaluated according to the European List of Waste. This is to check that co-firing ashes are not classified as hazardous waste. Classification is done based on the concentrations of toxic elements.

In Netherlands there is a landfill ban for fly ashes and ashes are utilized in construction industry. The product is also registered as a product under the European regulation for chemicals (REACH). Therefore it is important to check composition of toxic metals as well as aquatic toxicity.

2 SAMPLING METHODS AND MEASUREMENTS

Research has been done on the effect of direct co-combustion in over 40 test series, mostly at power stations. In these test series secondary fuels were co-combusted in proportions up to 50% by dry mass. During most of these tests relationships have been established between fuel composition on the one hand and the composition of residues and flue gases on the other hand. For many (trace) elements complete mass balance studies have been performed by measuring the composition and flow of all in- and outgoing streams of the power station (see Figure 1).

For several samples obtained, including ashes, environmental and health properties were studied. Typical measurements carried out on ashes (and method) include Particle Size Distribution (laser granulometry), respirable quartz (SEM), Cr(VI) content (X-ray absorption fine structures, XAFS), macro composition, e.g. Al_2O_3, SiO_2, CaO, Fe_2O_3 (ICP or XRF), heavy metals, e.g. As, Cd, Cu, Ni, Pb, Se, Sn, Zn (ICP-AES, ICP-MS), mercury (CVAFS), anions, e.g. F, Cl, Br (IC), leaching (batch and column test), PAH's, dioxins, other organics (GC-MS), aquatic toxicity (OECD algae and daphnia tests).

KEMA has developed a model that calculates the composition of the ash and the emission into the air as a function of fuel and plant data. The model is called the KEMA TRACE MODEL®. Not only the total elemental composition of the ash is calculated, but also the composition of the inhalable fraction of the ash, the order of magnitude of the leached elements and the radioactivity. The composition of the inhalable fraction of the ash is needed for the judgement of the health properties of the ash. The model is used by the Dutch power plants to predict the influence of co-combustion on ash quality and emissions. The model is accepted by the Dutch authorities and used in environmental

impact studies and permit applications, as well as for reporting annual emissions of trace elements.

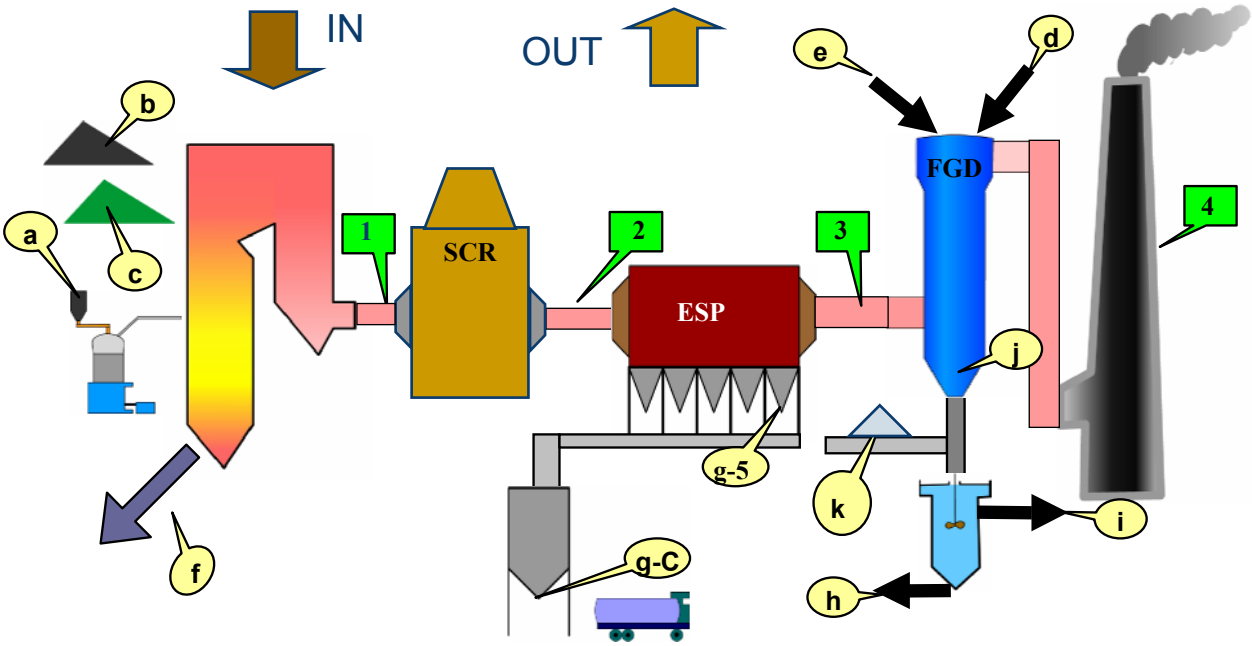

Figure 1 Measurement samples and sampling points at a mass balance campaign. 1,2: before and after deNOx, 3: after ESP and 4: in stack. a) indirectly co-fired fuel, b) coal, c) biomass, d) lime, e) process water, f) bottom ash, g-C) ESP ash (collection tank), g-x) ESP ash (hopper x), h) waste water treatment sludge, i) waste water treatment effluent j) FGD sludge, k) gypsum

When composition and properties of ashes are known in detail, an extensive evaluation against several regulations and technical guidelines can be carried out to check for compliance.

3 OCCUPATIONAL HEALTH ASPECTS

3.1 Respirable quartz

Quartz is of interest because it can have an adverse effect on human health, if inhaled, such as “black lung” or more precisely pneumoconiosis or silicosis. Especially the malignant condition progressive massive fibrosis (PMF) is serious. In relation to the development of silicoses 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.

Since quartz is found in coal and pulverized fuel ash, it is important to know the concentrations in which it is present and whether its presence can cause PMF. Therefore extensive measurements of α-quartz in ashes of 100% coal firing and of co-combustion were performed with Scanning Electron Microscopy (SEM). From the SEM-results the share of respirable α -quartz in coal ashes was determined with a special developed computer program, called KEMPHASE. With this technique an automatic distinction is made between several size fractions and between free α-quartz particles and α -quartz that is enclosed in fly ash particles.

It was found that in absolute terms, quartz accounted for roughly 0.1 per cent of the respirable fraction of the pulverized fuel ash samples tested. The main part 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 available [1].

The results of the study confirm that pulverized fuel ash of the kind produced at power stations 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 total-quartz found in pulverized fuel ash.

3.3 Cr(VI) share of total chromium

Recently, chromium speciation in co-combustion ash has been studied by Stam *et al*. [2] using a combination of XAFS spectroscopy and thermodynamic equilibrium calculations. Also leaching results and Relative Enrichment (RE) factors were taken into account. RE-factors describe the behavior of elements that end up in the ash, where a higher RE-factor for a specific element indicates more enrichment of that element in the ash compared to the original fuel. In [2] it is stated that the influence of co-firing on Cr speciation is very dependent on the type of fuel. Cr(VI) share of total Cr in the investigated fly ash samples from both coal and co-firing average around 7% of the total chromium. An exception is the specific case of co-firing 7-28% wood, exhibiting Cr(VI) shares of 12 – 16% of the total Cr-content. This compares to values of US coal ash found by Huffman *et al.* [3] of less than 5% as well as measurements by Galbreath and Zygarlicke [4] showing less than 6% and Huggins *et al.* [5] of US and world traded coal ash of less than 5%. Huggins *et al.* [5] found higher shares in coal ash from an Israeli power station (10 and 19%). Higher Cr(VI) shares were also found in coal ash resulting from western US coals by Shoji *et al*. [6] (9 – 26%) and by [4] (up to 43%). The referred observations all result from XAFS measurements, which is a direct method for measurement at the solid state, i.e. it does not require dissolution in water which potentially causes reactions and hence uncertainty.

Although the Cr(VI) levels are measurable with XAFS, the chemical form is in many cases less straightforward (as well as the formation process). Availability leaching tests show that not in all cases all hexavalent chromium is leachable: unleachable fractions vary from 0 up to 75%. The RE factors show that Cr is volatile to a minor extent (volatilization depends on the extent of organic binding of Cr in the fuel) and

thermodynamic equilibrium calculations show that chromium oxides are stable only at a very high temperature (>1500 °C). It is believed that Cr(VI) formation occurs as follows. It is formed at this high temperature in the gas phase as $CrO_3(g)$ (depending on the local oxygen content). It is then stabilized by reacting at the surface of ash particles forming chromates with BaO, CaO, MgO, K_2O, Na_2O or FeO (having different water solubility's). The higher Cr(VI) content in wood co-combustion ash can be explained in this way by the higher free lime (CaO) content in wood. Indeed a correlation was found.

3.4 Heavy metals and TLV's

KEMA has developed a methodology in order to judge the ashes. The KEMA Dust Assessment Methodology (KEMA-DAM®) is a methodology to detect, through simple judgement, whether in case of exposure to fly ash dust the TLVs (Threshold Limited Value) and/or health limit values of certain substances in the dust can be exceeded. The TLV-value of a substance is the maximally accepted concentration of a gas, vapour, fume or of a dust-formed agent in the air at one's workplace. When determining the air limit value the principle that, even upon repeated exposure and even during long working periods, this concentration should, in general and, obviously, keeping the level of knowledge on this in mind, not harm the employees' and their offspring's health, is used as often as possible.

The KEMA-DAM® was primarily set up to deal with inorganic substances. The TLVs sometimes refer to elements, but mostly to compounds. In the latter case the chemical form or speciation for the element in question has to be known. In order to get more insight into the chemical form of the elements in coal fly ash, a research program was started, consisting of (a) a literature search, (b) thermodynamic calculations by the FACTSage-model and (c) speciation measurements.

The TLVs refer to the inhalable fraction of the substances. The concentrations in the inhalable fraction of the ash are calculated by the KEMA TRACE MODEL®. The KEMA-DAM® procedure is applied to the calculated coal fly ash composition at co-combustion in proportions of 10%, 30% and 50% by dry mass of five selected secondary fuels. It appears that up to 50% co-combustion of paper sludge, sewage sludge, residual wood, chicken manure and RDF of average composition does not lead to individual occupational exposure limits being exceeded at an inhalable coal fly ash dust exposure of 10 mg/m^3. The sum of the average concentrations of the potential carcinogenic trace elements As, Be, Cd, Co, Cr(VI) and Ni in total coal fly ash amounts in all cases to less than 40% of the limit value for carcinogenic components and mixtures of 1000 mg/kg. It is concluded the co-combustion ashes produced in the Netherlands could be assigned as "nuisance dust". The calculations revealed that co-combustion of pet cokes is limited because of increased concentrations of vanadium. For this reason pet cokes are not co-combusted in the Netherlands. Also the co-combustion of sewage sludge is restricted in the Netherlands because of limitations for mercury emission into the air.

4 ENVIRONMENTAL ASPECTS

4.1 Decree on soil quality

On 1 July 2008, the Dutch Decree on Soil Quality (DSQ) came into force for application of building materials. This Decree replaced the Building Materials Decree (BMD) which was installed in 1995 The DSQ decree gives limit values for the composition and the leaching behaviour of building materials. Demands are set for unbound as well as bound application of the product. For more than ten years, many leaching test have been performed on the ashes produced at coal-firing and co-combustion. Table 2 gives an example of the results.

Table 1 Example of leaching of co-combustion ashes as a percentage of limit values for unbound application according to the Dutch Decree on Soil Quality

	Bottom ash		PFA	
insulation	without	with	without	with
	%	%	%	%
Cl	28	2	6	< 0.5
As	11	5	4	2
Ba	< 0.5	< 0.5	52	11
Br	< 0.5	< 0.5	12	7
Cd	2	1	2	1
Co	5	1	< 0.5	< 0.5
Cr	4	< 0.5	70	6
Cu	12	1	< 0.5	< 0.5
F	2	< 0.5	13	< 0.5
Hg	2	< 0.5	2	< 0.5
Mo	6	< 0.5	267	18
Ni	21	4	2	< 0.5
Pb	1	< 0.5	< 0.5	< 0.5
Sb	15	3	14	3
Se	34	2	84	4
Sn	3	1	1	< 0.5
V	1	< 0.5	30	3
Zn	3	1	1	< 0.5
SO_4	6	1	112	10

From the results it is shown that all the bottom ashes produced in the Netherlands fulfil the demands for unbound application without insulation of the Dutch DSQ. This means

that unbound application of the bottom ashes is allowed without any further precautions. The leaching of the PFA is higher and as a result the PFA produced in general is categorized as a building material for which insulation measures are to be applied when the PFA is used in unbound applications. This means that unbound application of PFA as a building material is allowed for most of the ashes produced, but that precautions have to be made to prevent contact of the ashes with ground- and rainwater. In rare cases, for some specific PFA-ash samples the leaching of Se appeared to be critical with regard to the limit value.

Furthermore leaching tests have been performed on concrete in which 30% of cement is replaced by co-combustion fly ash. The tests were performed on concrete cubes by the so-called diffusion test (NEN 7375) according to the Dutch guideline BRL 2505. Test have been performed for many different co-combustion fly ashes in co-combustion percentages up to 21% (m/m). The results show that the leaching of all concrete cubes is well below the limit values of the Dutch Building Materials Decree (up to July 2008) and the limit values of the Decree on Soil Quality. This means that the application of Dutch co-combustion fly ash in concrete fulfils the leaching demands.

4.1.2 PAH's, dioxins and other organics

Incomplete combustion of fossil fuels and waste can lead to the formation polycyclic aromatic hydrocarbons (PAH) and dioxins (PCDD) and furans (PCDF). There are 210 different types of dioxin, of which a ‘congeneric’ group of seventeen are toxic (‘dirty seventeen’). Measurements have been performed on these 17 dioxins and on a group of 16 PAH-components (the EPA-list) of which five are (suspected) carcinogenic.

Large-scale combustion of fossil fuels, as in power stations, in general results in very low levels of PAH and dioxins. This is mainly because combustion in modern coal-fired power stations is virtually complete. Furthermore, SO_2 appears to inhibit dioxin formation.

Measured concentrations of dioxins and furans in Dutch pulverized fuel ash and bottom ash appeared to be low and mostly below detection limit. On average the summarized concentration of dioxins/furans in ashes amounts to less than 2 pg TEQ/g. This value is 30 times lower than the limit value for application of soil in or on the ground according to the Dutch Decree on Soil Quality and 500 times lower than the intervention value for soil.

Concentrations of PAH in ashes are also (very) low. In many samples none of the 16 EPA-PAHs is demonstrated above the detection limit. The average upper-bound concentration of the 16 PAH components amounts to less than 1 mg/kg. There is no indication that PAH and dioxin/furan concentrations in co-combustion ashes are increased because of co-combustion of secondary fuels.

For people working with fly ash under normal conditions (meeting the requirements for exposure to nuisance dust), the levels of dioxin exposure attributable to the exposure to

pulverized fuel ash are low. The daily intake as a result of this exposure is negligible in relation to WHO-guidelines and to the background daily dioxin intake, which mainly is associated with the consumption of food.

4.2 European Waste Catalogue

In January 2001 the European Commission has adopted a decision in order to come to a harmonized list of hazardous and non hazardous waste, the European Waste Catalogue (EWC). The EWC includes an annex with a list of about 800 wastes. The different types of waste in the list are fully defined by the six-digit code for the waste. Any waste considered as a hazardous waste obtains a code that is marked with an asterisk (*).

Ashes produced at 100% coal-firing are defined as non-hazardous waste in the EWC. For co-combustion ashes, a classification has to be established in order to decide whether it can be treated as hazardous or non-hazardous waste. This classification is based on the chemical composition of the ashes and limit values for several classes of hazard properties. If the ashes contain hazardous components above one of the limit values, the EWC-codes are marked with an asterisk, i.e. considered as a hazardous waste. If the concentrations are below the limit values, the ashes get the same EWC-code as ashes from 100% coal-firing and are considered as "non-hazardous waste".

The hazard properties can be divided into:
- physical-chemical properties (categories H1 - H3)
- health aspects (categories H4 - H11)
- environmental properties (categories H12 - H14)

For the categories H1, H2, H9, H12, H13 and H14 there are as yet no limit values available, so that at this time these categories cannot be included in the evaluation. More detailed content for these categories is being investigated within the EU.

For several by-products produced at several Dutch power plants it was determined whether the by-products of co-combustion earn the qualification “hazardous” or “non-hazardous” waste. In practice this means that the composition of the ash has to be known in detail: speciation and concentration. The composition of the elements is measured by extensive analyses or calculated. The speciation of the elements is established in the same way as discussed above. The concentration of each compound as present in the ash was compared to the appropriate limit as mentioned in the EWC and given above.

For all categories, the weight percentages of dangerous components in the evaluated co-combustion ashes fall (far) below the limit values listed in the EWC. This means that the co-combustion ashes evaluated are qualified as non-hazardous.

5 Eco-toxicity and REACH

The bio-availability of compounds present in solid waste is dominated by the water-soluble part. Water is the prevailing mechanism for transport in the environment and intake in the organisms. The bio-availability of a material depends therefore on its leaching behavior rather than on its chemical composition. So a leaching test is the appropriate first step for a bioassay. Several eco-toxicity tests have been carried out on by-products from 100% coal firing and co-combustion. The test were performed on eluates of a leaching test at Liquid to Solid ratio of 10 liter/kg with bioassays daphnia, thamno and algae and luminescent bacteria (microtox) and at the by-products itself with different plant material.

A comparison was made of measured eco-toxicity for co-combustion ash, a MSWI-bottom ash (INC), treated wood (WOO) and a clean soil sample (SOI). From the results it is shown that the toxicity of the tested samples decreases in the order WOO > INC > PFA > SOI. The relative high toxicity of the preserved wood sample seems to be caused mainly by a very high amount of copper in the sample and the eluate. The amount of leachable copper is determining in this and not the total amount of copper in the sample. The amount of copper leached out of ash samples is always low.

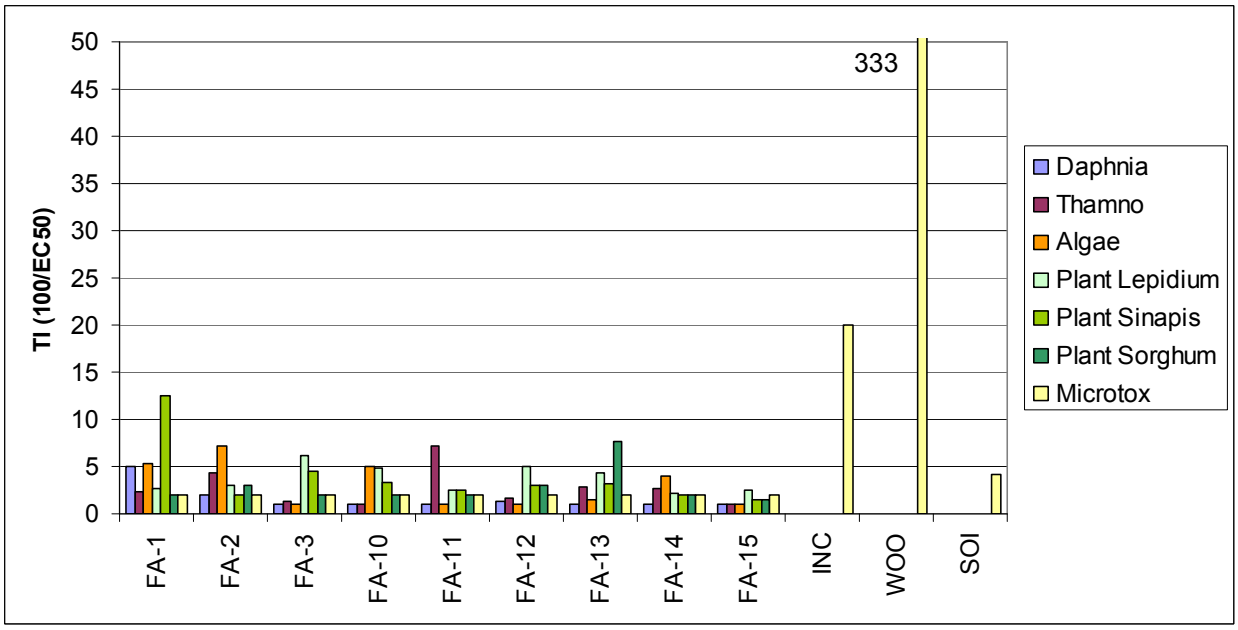

Figure 2 Results of eco-toxicity tests on fly ash (FA) from 100% coal firing (FA 1-3) and co-combustion (FA 10-15) compared with waste incineration bottom ash (INC), treated wood (WOO) and soil (SOI)

Figure 2 shows the results of the ashes as well as the samples INC, WOO and SOI used for comparison. The toxicity is expressed as the Toxicity Index which is defined as TI50= 100 / EC50, where EC 50 is the concentration or dilution where 50 % effect is

observed. Note that all values of 1 and 2 represent a detection limit caused by minimal dilutions required in the method. The TI of the wood sample was 333, so the column in the figure was cut-off.

From the results it is concluded that there is no difference in eco-toxicity between ashes from 100% coal-firing and co-combustion ashes. Also for bottom ashes there was no difference between the measured toxicity of 100% coal ashes and co-combustion ashes. In general the eco-toxicity of bottom ashes is lower compared to PFA.

In 2007 the European REACH-regulation (Registration, Evaluation and Authorisation of Chemicals) came into force. As by-products of coal-fired power plants are utilized in the building industry, they are placed on the market and therefore they are subject to the REACH obligations. This means that these by-products have to be registered at the European Chemicals Agency. This registration requires information on the physical, toxicological and ecotoxicological properties and potential risks of the substances.

In 2010 the European industry has prepared lead dossiers for the registration of ashes (siliceous ashes, calcareous ashes and bottom ashes) and flue gas desulfurisation gypsum under the REACH regulation for registration of substances [7]. Based on all studies as collected by industry, including the studies presented in this paper, the by-products were defined as being non-hazardous. This classification was done according to the regulation for Classification, Labeling and Packaging (CLP), the EU implementation of the United Nations' Globally Harmonised System (GHS). Co-firing ashes comply with the REACH dossier for ashes as long as sameness with ashes as defined in the dossier can be demonstrated, i.e. they have similar composition and no hazardous properties. European energy companies have submitted their individual dossiers successfully before 1 December 2010, which was the registration deadline for substances produced or imported over 1000 ton per year.

6 CONCLUSIONS

The applied research indicates that there is no reason to regard co-combustion ash dust as harmful. No increased health risk will be caught under circumstances, which generally meet the requirements laid down for nuisance dust in the occupational environment. This means that the standards for nuisance dust can be applied. This holds for all the co-combustion ashes tested so far with co-combustion percentages up to 40% on a dry mass base.

Large-scale combustion of fuels in power stations results in very low levels of PAH and dioxins in by-products and in emitted flue gasses. There is no indication that PAH and dioxin/furan concentrations in co-combustion ashes are increased because of co-combustion of secondary fuels.

Pulverized fuel ash produced at power stations in the Netherlands does not have any of the effects normally associated with quartz. Hence, the TLVs for quartz are not

appropriate for the total-quartz found in pulverized fuel ash. Only a very small amount of the quartz in PFA is biologically available.

Based on the leaching behavior of fly ashes in general it is categorized as a building material for which insulation measures are to be applied when the PFA is used in unbound applications.

An extensive study on by-products of coal-fired plants shows that co-combustion ashes as produced in the Netherlands are considered “non-dangerous substances”, according to the European Waste Catalogue.

Toxicity measurements revealed no difference between the eco-toxicity of ashes from 100% coal firing and ashes of co-combustion as produced in the Netherlands. Ashes and flue gas desulfurisation gypsum are registered in the EU under REACH as being non-hazardous substances without any labeling for aquatic toxicity.

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