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Peak exposures to main components of ash and gaseous diesel exhausts in closed and open ash loading stations at biomass-fuelled power plants

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HIGHLIGHTS

Health risks caused by crystalline silica compounds were found in FA and BA.

Air concentrations of dust, SiO₂, Cr, Mn, Ni and nitric NO were high during loading.

Synergistic health effects on upper and lower respiratory system are possible.

Technical measures and PPEs are essential for the safe loading of ash.
ABSTRACT

Fly and bottom ashes are collected at power plants to reduce the environmental effects of energy production. However, handling the ashes causes health problems for operators, maintenance workers and truck drivers at the power plants. Hence, we evaluated ash loaders’ peak inhalation exposures to the chemical components of ash and diesel exhausts in open and closed ash loading stations at biomass-fuelled combined heat and power plants. We also carried out chemical and morphological analyses of the ashes to evaluate their health hazard potential in order to find practical technical measures to reduce workers’ exposure. On the basis of X-ray diffraction analyses, the main respirable crystalline ash compounds were SiO$_2$, CaSO$_4$, CaO, Ca$_2$Al$_2$SiO$_7$, NaCl and Ca$_3$Al$_2$O$_6$ in the fly ashes and SiO$_2$, KAlSi$_3$O$_8$, NaAlSi$_3$O$_8$, and Ca$_2$Al$_2$SiO$_7$ in the bottom ashes. The short-term exposure levels of respirable crystalline silica, inhalable inorganic dust, Cr, Mn, Ni and nitric oxide exceeded their Finnish eight hours occupational exposure limit values in the closed ash loading station. According to our observations, more attention should be paid to the ash-moistening process, the use of tank trucks instead of open cassette flatbed trucks, and the sealing of the loading line from the silo to the truck which would prevent spreading the ash into the air. The idling time of diesel trucks should also be limited, and ash loading stations should be equipped with exhaust gas ventilators. If working conditions make it impossible to keep to the OEL values, workers must use respirators and protect their eyes and skin.

Keywords: Peak exposures, chemical components of ash, morphology of ash, diesel exhausts, ash loading
1. INTRODUCTION

Fly and bottom ashes are collected at power plants to reduce the environmental effect of energy production. In general, combustion technology and the flue gas cleaning system determine the basic characteristics of ashes and form the basis of ash management. The properties and therefore behaviour of ashes are also highly dependent on the fuels used and the prevailing combustion conditions. The coarser bottom ash is collected from the bottom of a combustion chamber and fine fly ash is separated from flue gases by electrostatic precipitators or fabric filters. The fly ash fraction is largest in fluidised bed boilers, usually 80–90% of the total generated ash. Fly ash can be unloaded from ash silos in either moistened or dry form, depending on how it is to be delivered and its end use. The moistening of ash effectively diminishes ash dusting. Biomass ashes that are used as forest fertilizers are usually unloaded and transferred in dry form, and moistened in a separate granulation process by an entrepreneur.

The handling of ashes poses problems for operators and maintenance workers in power plants such as their high exposures to inhalable dust and metals (Jumpponen et al. 2014). The loading of ashes causes peak exposures for truck drivers and the workers who recycle the ashes. Bottom and fly ash contains many inorganic chemical agents such as heavy metals and crystalline silica, to which workers may be exposed. Fine fly ash particles are mainly formed from alkali metal compounds, for example the alkali salts of potassium, sodium sulphates, chlorides and carbonates (Bølling et al. 2009). In addition to alkali salts, the coarse particle fraction includes Ca, Mg, Al, Fe and several other metals in the form of oxides, silicates, carbonates, sulphates and phosphates, depending on the fuel used and possible additives used in the combustion processes (Tissari et al. 2008, Sippula et al. 2009a, Sippula et al., 2009b).

Bottom ash consists mainly of the coarse fraction of particulate matter, and is partially the same matter as coarse fly ash, which originates from the mineral matter present in the fuel (van Loo & Koppejan 2008). Thus, the typical bottom ash components in biomass combustion processes are, for
example, Ca, Mg, Fe, Mn, and Al, in the form of silicates, phosphates, carbonates, and sulphates (Tissari et al. 2008). Awareness of the composition of the ash provides valuable information for workers’ occupational risk assessments. In addition, the composition of the ash might also indicate its potential to dissolve into the sweat and gastric fluids of workers, causing dermal and oral exposure to heavy metals (Pöykiö et al. 2012). Earlier studies have found maintenance workers’ potential inhalation exposure to be very high. During ash removal or maintenance tasks in biomass- and recycled fuel-fired power plants, the average air concentrations of Mn, Al, As and Pb have been found to be over or very close to occupational exposure limit values (OEL) (Jumpponen et al. 2014). Reported health effects after simultaneous exposure to multiple metals have varied from irritation of the upper respiratory tract to damage to the central nervous system, resulting in mutagenic effects (Shukla and Singhal 1984, Mani et al. 2007, Celic et al. 2007, Garcon et al. 2007, Halatek et al. 2009, Walton 2011). In addition, ash loaders might be exposed to respirable crystalline silica originating from soil contaminated stumps and from the sand of fluidized bed boilers. Exposure to respirable crystalline silica can cause silicosis. Silicosis is normally associated with long-term exposure, but symptoms of acute silicosis may also develop shortly after exposure to high concentrations. Silicotic workers may be at a higher risk of lung cancer than workers who do not have silicosis (Kreiss and Zhen 1996, Miller et al. 1998, NIOSH 2002). Due to above mentioned findings, the International Agency for Research on Cancer (IARC) has classified respirable crystalline silica as carcinogenic to humans (WHO 1997). Strong epidemiological evidence also supports the association between long-term exposure to crystalline silica and severe health effects, e.g. chronic obstructive pulmonary diseases (COPD), cardiovascular disease and rheumatoid arthritis (Chen et al. 2012, Calvert et al. 2003, Preller et al. 2010, Sauni et al. 2012, Zhou et al. 2012, Hochgatterer et al. 2013).

Idling of trucks during the ash loading process may also expose workers to components of diesel exhaust such as nitric oxide, nitrogen dioxide, carbon monoxide and fine soot (elemental carbon).
diesel engine exhausts as carcinogenic to humans (Group 1) on the basis of sufficient evidence that
exposure is associated with an increased risk of lung cancer (IARC 2012). Exposure to diesel
exhausts can also cause inflammation of the lungs, which may aggravate chronic respiratory
symptoms and increase the frequency and intensity of asthma attacks. Nitrogen oxides on the other
hand can damage lung tissue, lower the body's resistance to respiratory infection and worsen
chronic lung diseases such as asthma (Sydbom et al. 2001). As in the case of crystalline silica, high
short-term exposures to diesel exhausts also seem to induce more alterations in lung tissues than

This study evaluated ash loaders' rarely studied possible inhalation peak exposures to the chemical
components of ash and diesel exhausts in open and closed ash loading stations at biomass-fired
power plants. By combining several chemical and morphological analyses of the ashes, we
determined the major chemical compounds and trace metals in the ashes, and evaluated their
potential to expose workers through the inhalation system. Ashes' potential to dissolve into the
saliva or gastric fluids and thus cause exposure through the dermal and oral exposure routes were
also discussed. The final goal of the study was to find the best practices for reducing workers’
exposure in ash loading stations.

2. MATERIALS AND METHODS

2.1 Sampling procedures

Air and material samples were collected from three Finnish combined heat and power (CHP) plants.
All the plants were bubbling fluidized bed boilers (BFB), and their power capacities varied from 75
to 200 MW_{fuel}. New Power Plant A used 100% of wood fuels. For example, forest chips, used
wood, whole tree chips, wood industry residues, and fly ashes were collected using a bag filter. Old
Power Plant B was fuelled by wood fuels together with bark, milled peat and waste water sludge,
and ESP was used for fly ash separation. Solid recovered fuel (SRF) and bark, together with wastewater sludge, were combusted in old Plant C, which had an ESP and a wet scrubber for flue gas cleaning. Plants A and C used elemental sulphur as an additive to control the corrosion, fouling and air emissions.

Air samples were taken from stationary sampling sites near workers’ working areas from open and closed ash loading stations. Material fly ashes were taken from ash silos, depending on the sampling possibilities at the power plants. Bottom ashes were sampled from the bottom ash containers of the power plants.

2.2 Procedure for fly and bottom ash sample sieving

The material samples were sieved for the analyses, to remove particles larger than the respirable fraction (<10 µm), in order to reflect better health effects of ashes during inhalation. Bottom ash (BA) samples were first sieved with a 4 mm sieve to remove the biggest particles. Sample (BA) A was not analysed, because it consisted entirely of the large particle size class. All fly ash (FA) and bottom ash samples were then sieved using a 45 µm sieve (Retsch AS200 sieving machine with metal wire sieves) and further with a 10 µm sieve (HK Technologies Ultrasonic sieving machine with stainless steel/nickel wire sieves).

2.3 Determination of the mineral and morphological composition of the ash

X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance (Cu Kα source, 40 kV, 40 mA) with a Lynx Eye 1D detector. The diffraction was measured between 2θ angles of 5 and 80°, with a step size of 0.02°. The crystalline compounds were identified using the PDF-4+ 2014 crystallography database. The observed compounds were classified into three categories on the basis of the comparison of the measured XRD data and the reference diffractogram found in the database.
The minimum requirement for a compound to be assigned into the category of possible compounds was that its constituent elements were observed in the ICP-MS/IC analyses, and that the reference diffractogram did not contradict the measured data. In addition, for a compound to be considered probable, at least one of the main peaks of the reference had to have a corresponding distinct peak in the XRD data that could not be explained by the main compounds. Finally, to be considered a main compound, the main peaks of the reference had to be coincident with some of the main peaks of the measured data.

We used a scanning electron microscope (SEM Zeiss Sigma HDVP), operated at 3–10 kV with an energy dispersive microscope (EDS Thermo Noran, 60 mm²) to study the morphology and chemical composition of the ashes. One fly ash sample (FA) B and one bottom ash sample (BA) B were analysed. The samples were placed on stubs (AGG301 SEM Specimen Stubs, Zeiss Instruments) using graphite glue.

2.4 Determination of total element concentrations in the ash

Chemical compositions were analysed using inductively coupled mass spectrometry (ICP-MS) and ion chromatography (IC). Metals and other elements were analysed using ICP-MS (Agilent Technologies 7700) according to standard EN ISO 17294-2. Prior to analyses, the samples were digested using microwaves according to EN 15297, with HNO₃ and HF. Anions (Br-, Cl-, NO₃-, SO₄²-, F-, PO₄³-) were analysed with IC (Metrohm Compact 882 ICplus with column Metrosep a SUPP5-150/4.0) according to standard EN ISO 10304-1/2. The samples were prepared by eluting with NaOH and Na₂CO₃ in an ultrasonic treatment. The studied heavy metals were the same as those mentioned in the directive on industrial emissions 2010/75/EU. In addition to these, Zn was included in the analysis, due to its known toxic effects (Uski et al. 2015).
2.5 Air sampling methods

Inhalable dust samples were collected in a Millipore filter (25 mm AAWP, pore size 0.8 µm, Merck Millipore), using an IOM sampler (SKC) at a calibrated flow rate of 2.0 L min⁻¹, and using direct reading instrument Split 2 (SKC). After the inhalable dust collection, filters were gravimetrically analysed, and the results of direct reading instruments were corrected gravimetrically. Respirable crystalline silica was sampled in a Millipore filter (37 mm AAWP, pore size 0.8 µm, Merck Millipore) using a GS-3 cyclone (SKC) at a calibrated flow rate of 2.75 L min⁻¹. We performed further crystalline silica analysis of the respirable dust samples using the FT-IR technique (NIOSH 1994). Direct reading instruments X-am 5600, X-am 7000 and Pac 7000 (Dräger) were used to measure concentrations of carbon monoxide (CO), nitric oxide (NO) and nitrogen dioxide (NO₂). We recorded the measured data on data loggers, and the recorded values represented the average values of sampling intervals from 10 seconds to 1 minute. The gas monitor sensors for CO, NO and NO₂ were calibrated using calibrating gases (AGA) with known concentrations.

2.6 Calculated results

The direct reading instruments’ results (Split 2) regarding inhalable dust were corrected by weighing their filter before and after sampling, to determine the right gravimetric factor for the collected dust. The gravimetrically corrected inhalable dust results and the elemental metal results from the analysis of material fly ash samples were used as the basic values in the conversion of inhalable dust results to the variation results of the metal concentrations. The gravimetrically corrected inhalable dust results of the direct reading instrument [mg m⁻³] were multiplied by the results of the elemental metal concentration [µg mg⁻¹]. The concentration variation of crystalline silica was also calculated from the gravimetrically corrected results of inhalable dust. The corrected results were multiplied by the parallel measured percentage of crystalline silica concentration (0.2%) in inhalable dust measured from the same stationary sampling site.
3. RESULTS AND DISCUSSION

3.1 Chemical composition and structure of ash particles.

Both fly and bottom ash samples contained Ca, Si and Al as their main components. Bottom ashes contained more Si and Al than the fly ashes (Figure 1). The main source of Si is likely to have been the bedsand of the boiler. Both the bottom and fly ashes of Power Plant A and C’s ashes were rich in $\text{SO}_4^{2-}$, but Power Plant B’s ashes were not. The difference is obviously because elemental sulphur is added to the combustion process in Power plants A and C. The main heavy metal components were Mn and Zn in all of the studied ashes, which is in agreement with earlier studies (Alakangas 2016, Sippula et al. 2009). Power Plant B’s fly ashes contained considerably more Cr and Ni than other ash samples, while Power Plant C’s ashes contained more Cd, Cu, Pb and Sb, probably due to the use of SRF fuel (Figure 2). The fly ashes generally contained more Cd, Pb, Tl, Sb and As than the bottom ashes (Figure 2), which is consistent, as these species are known to volatilize and enrich in the fly ash particle fraction of biomass combustion processes (Sippula 2009b). It has been reported that the measured metals V, Cr, and Zn obtain the highest potential to dissolve into sweat fluid leading to their higher potential for dermal exposure (Pöykiö et al. 2012). In addition, the measured Cu, Co, and Zn have been reported to have the highest potential to dissolve into gastric fluid, leading to their higher risk via oral exposure (Pöykiö et al. 2012).

3.1.1 Morphology and crystallographic structure of fly ash particles

The fine particles existed on the surfaces of the coarser particles. The shapes of the particles varied from coarser spheres to fine fibres (Figure 3a and b). Figure 3c shows an example of the SEM-EDS analysis of fly ash Sample B. The largest particles contained O, Al, Si and Ca, the particle on the left O, Al, Si, K and Na, and the middle area of the agglomerate Si and O, and Ca, O, Al and S. These observations partly agree with the coal combustion fly ash analysis results of Kutchko et al.
(2006), who also found Si, Al, Fe, Ca and O in various compounds when analysed by EDS. They concluded that fly ashes consisted of mostly alumino-silicate spheres as well as iron-containing spheres, and that Ca is not associated with Si or Al. In contrast, in our samples, Ca in the spherical particle seemed to be associated with Al, Si and O.

The XRD analyses indicated that the main Ca-containing compounds in fly ashes were CaSO$_4$, CaO and probably also Ca$_2$Al$_2$SiO$_7$ and Ca$_3$Al$_2$O$_6$ (Table 1), which is in agreement with Enestam et al. (2011), Vassilev et al. (2013) and Fernandez-Turiel et al. (2004). The fly ashes from Power Plants A and C had the highest concentrations of Ca, and were predominantly in the form of CaSO$_4$ and CaO. Si was found to mainly exist as SiO$_2$ (Table 1), most likely originating mainly from the bedsand.

As regards alkali metals, Na was mainly found as NaCl, while no crystalline K-containing compounds could be unambiguously identified (Table 1). The most thermodynamically favoured potassium compounds in the fine fly ashes of biomass combustion are usually potassium sulphates and chlorides (Sippula 2010), which most likely exist in amorphous form in the samples, and were therefore not seen with XRD. We identified ZnSiO$_4$, ZnO and ZnAl$_2$O$_4$ as possible zinc species, which means that zinc may exist mainly as poorly water soluble species in the ashes. However, K$_2$Zn$_2$(SO$_4$)$_3$, which is a water soluble salt, fits the spectrum in Power Plant A and C’s fly ashes, probably because these plants use sulphur additives.

3.1.2 Morphology and crystallographic structure of bottom ash particles

The fine particles existed on the surfaces of coarser particles, as in the fly ashes (Figure 3f and 3e). The coarse particles in Figure 3d and 3e were probably SiO$_2$. In Figure 3f, the particle on the right side of the picture contained Cr, Fe and Ni, and is probably stainless steel, originating from, for example, fuel crushing processes.
Similar to fly ashes, Si was found to exist mainly as SiO$_2$ in the bottom ashes. Other main Si compounds were KAlSi$_3$O$_8$ and NaAlSi$_3$O$_8$ (Table 1). All these three compounds were also found by Lindström et al. (2010) and Gilbe et al. (2008) in bottom ashes from the combustion of woody biomass pellets. Power Plant B bottom ash contained more KAlSi$_3$O$_8$ and NaAlSi$_3$O$_8$ than Power Plant C bottom ash. In the bottom ashes, Ca$_2$Al$_2$SiO$_7$ were the main Ca-containing component. K was found to exist mainly in KAlSi$_3$O$_8$ and in small amounts probably also in K$_2$Ca$_2$(SO$_4$)$_3$ and K$_2$MgSiO$_4$ (Table 1). The total zinc concentration was small in the bottom ash samples, which meant that the identification of crystalline Zn species was challenging. On the basis of the XRD data, the presence of Zn$_2$SiO$_4$ and K$_2$ZnCl$_4$ is unlikely. However, the existence of ZnAl$_2$O$_4$, Zn(OH)$_2$ and ZnO cannot be excluded. Nevertheless, interestingly, it seems that Zn does not exist predominantly as ZnO, which is thermodynamically its most probable form (Tissari et al., 2015).

3.2 Variation of inhalable inorganic dust concentrations in closed and open ash loading stations

We evaluated truck drivers’ and operators’ short-term exposures to inhalable dust, respirable crystalline silica and the component of diesel exhaust from stationary sampling sites. The loading process took place in both closed and open loading stations. The measured variations of inhalable inorganic dust concentrations in the closed and open ash loading stations in the ash loaders’ working area are shown in Figure 4. The highest short-term inhalable dust levels were over 10 times higher than the Finnish OEL$_{8h}$ value (10 mg m$^{-3}$) for inhalable inorganic dust in the closed ash loading station when ash was loaded onto the open cassette flatbed of the truck (Ministry of Social Affairs 2014). Due to the high portion of fine particles in the fly ash, the precipitation of inhalable particles lasted 75 minutes after the ash loading process ended, and only then did these dust concentrations achieve the level of 10% of the OEL$_{8h}$ value (Fig. 4 A). Similar concentrations have been found in ash removal and maintenance work tasks, in which the median concentration of inhalable dust has been 33 mg/m$^3$ and 120 mg/m$^3$ (Jumpponen et. al., 2014). Wojtczak et al. (1989)
also found that the mean concentrations of respirable dust exceeded their hygienic standard value in
64% of all measured thermoelectric power stations.

The measured concentrations were lower in the open ash loading station. The highest short-term
level was over 1.7 times higher than the OEL\textsubscript{8h} value for inorganic dust (Fig. 4 B), when loaded
onto the flatbed of the truck. In the open ash loading station, wind effect seemed to reduce inhalable
dust concentrations. Occupational problems seemed to be more evident in the closed ash loading
stations, and due to this, we decided to focus our detailed studies on these stations.

3.3 Variations of heavy metal and crystalline silica concentrations in the air in closed ash loading
stations

Figure 5 (A-D) show the calculated metal concentrations during the loading of moistened ash in the
closed loading station at Power Plant B. The short-term levels of Cr (Fig. 5A), Mn (Fig. 5B) and Ni
(Fig. 5A) exceeded their OEL\textsubscript{8h} value during ash loading (Ministry of Social Affairs and Health
2014). The highest short-term concentrations of As (Fig. 5D), Co (Fig. 5C), Pb (Fig. 5C), Zn (Fig.
5B) and Cd (Fig. 5D) were 68%, 30%, 7.8%, 3.9%, and 1.5% of their OEL\textsubscript{8h} values, respectively,
during the loading of ash. In other studies of maintenance and ash removal workers, the most
occupationally important metals have also been Al, Mn, Pb and Cd (Liu et. al. 2005, Jumpponen et
al. 2014). As described in Figure 2, the elementary results from different power plants varied
greatly. Our calculated example from Power Plant B represented the worst exposure situation as
regards Co, Cr, Ni and V of all power plants, but the calculated short-term concentrations of the
other metals were higher in other power plants. For example, Pb concentrations in the fly ash of
Power Plant C were almost 40 times higher than those in Power Plant B (figure 2).

Figure 6A shows the variation of calculated respirable crystalline silica concentrations. The highest
short-term respirable crystalline silica concentration levels were over 4.5 times higher than the
Finnish OEL\textsubscript{8h} value (0.05 mg m\textsuperscript{-3}) in the closed ash loading station (Ministry of Social Affairs and
Health 2014). The precipitation of respirable crystalline silica lasted 47 minutes after the end of the ash loading process, and only then did the inhalable dust concentrations achieve the level of 10% of the OEL_{8h} value in the ash loaders’ working area (Fig. 6A). Earlier studies of maintenance and ash removal workers have found average concentrations of respirable crystalline silica to vary from 0.2 mg/m^3 to 0.5 mg m^{-3}, which are equal to the short-term exposure levels in the present study (Jumpponen et al. 2014).

3.4 Variation of the component concentrations of diesel-exhaust in the air in closed ash loading stations

Figure 6 (B-D) shows the variation of nitric oxide concentration during the loading of moistened ash in the closed ash loading station, when the diesel engine of the truck was idling during loading. The highest short-term nitric oxide (Fig. 6B), carbon monoxide (Fig. 6C), and nitrogen dioxide (Fig. 6D) concentrations were 160%, 87% and 27% of their OEL_{8h} values, respectively (Ministry of Social Affairs and Health 2014). Nitric oxide concentrations decreased to the level of 10% of the OEL_{8h} value within 15 minutes after ash loading ended (Fig. 6B).

4. CONCLUSION

The main Si compound observed with XRD was crystalline SiO_2, which probably originated from the bedsand or impurities of crushed fuel. The other main crystalline compounds observed by XRD were CaSO_4, CaO, Ca_2Al_2SiO_7, NaCl and Ca_3Al_2O_6 in the fly ashes, and KAISi_3O_8, NaAlSi_3O_8 and Ca_2Al_2SiO_7 in the bottom ashes. According to the literature, all these are typical compounds of biomass combustion ashes. Mn and Zn were the main heavy metals, which are typical for woody biomass fuels. In addition to these, in the SRF co-firing plant, a relatively high concentration of Cu was found in the ashes. The fly ashes generally contained more Cd and Pb, and also some more Sb and As, than the bottom ashes, which is consistent with the fact that these species are known to volatilize and
increase in the fly ash particle fraction in biomass combustion processes. The ashes from the power plant co-firing SRF contained more As, Cd, Co, Cu, Pb, Sb and Zn than the other ashes. The effect of sulphur addition was observed as existence of crystalline CaSO$_4$ in the fly ashes. In addition, according to XRD analyses, Zn possibly existed in K$_2$Zn$_2$(SO$_4$)$_3$ in the fly ashes of the power plants that used sulphur addition, while without sulphur addition, several zinc oxide compounds were possible. However, due to the relatively small amount of Zn in the samples, these compounds cannot be confirmed without further study. Nevertheless, interestingly, it seems that Zn does not exist predominantly as ZnO (Tissari et al., 2015). We can thus conclude that zinc may exist in both well water soluble and in hardly water soluble forms in the ashes. In general, the size, shape and surface structure of ash particles affect their health-related properties. The attachment of the fine particles to the surfaces of the coarse particles might also be of particular importance, because this largely affects the dispersion and lung deposition of the ashes that are suspended in the air.

During ash loading in a closed ash loading station, the short-term exposure levels of respirable crystalline silica, inhalable inorganic dust, Cr, Mn, Ni and nitric oxide exceeded their eight hour occupational exposure limit values. Because most of these chemical agents affect ash loaders’ upper and lower respiratory systems, it is possible that they have synergist or at least additive health effects on workers’ respiratory systems. Moreover, it has been reported that especially high short-term exposure to diesel exhausts and respirable crystalline silica also initiate alterations in respiratory systems. These findings show that high levels of measured ash loaders’ exposure might cause health problems for unprotected workers. It is essential to cut their high short exposure levels and to find suitable technical measures to do this. According to our experience, open ash loading stations are better from the workers’ point of view, but in the future, biofuel-fired power plants will be situated near residential areas, setting stricter requirements for ash handling at power plants. So from an environmental point of view, closed ash loading stations will be more preferable in future. In closed ash loading stations, more attention should be paid to the moistening process of ash, to
prevent it spreading. One possible technical solution could be to use tank trucks instead of open conventional cassette flatbed trucks; this would make it much easier to prevent ash spreading. The loading line from silo to the truck should be equipped with local ventilators, which remove dust immediately from where it originates. Efficient general ventilation of the loading stations would ensure that the concentration of exposure agents in the hall decreases more efficiently after the loading process. The best way to reduce components’ concentrations in diesel exhausts would be to limit the idling time of diesel trucks during the ash loading process. Another possible technical measure would be to equip ash loading stations with exhaust gas ventilators, which are connected to the truck’s exhaust pipes. If it is not possible to reduce the particular concentrations of the aforementioned exposure agents to under OEL values, workers should use respirators that are equipped with at least FFP3 filters. To prevent skin and eye disorders, and exposure through the gastro-intestinal route, workers must ensure skin and eye protection and pay attention to their personal hygiene, due to possible dermal exposure to Cr, Mn, Ni, and the high pH of ash.

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REFERENCES


EN 15297:2011. Solid biofuels - Determination of minor elements As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn.


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<td>CaSO₄</td>
<td>K₂Na₂(SO₄)₂</td>
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<tr>
<td>Al</td>
<td>FA</td>
<td>Ca₂Al₂SiO₇, Ca₃Al₂O₆</td>
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<td>Fe₂O₃</td>
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FIGURE CAPTIONS:

Figure 1. Chemical composition of samples (FA=fly ash, BA=bottom ash and letters A, B and C describe different power plants) (* amount of Si is semi-quantitative)

Figure 2. Heavy metal composition of samples (FA=fly ash, BA=bottom ash, and letters A, B and C describe different power plants). 1 µg/mg = 1000 mg kg⁻¹.

Figure 3. SEM images of fly ash sample (FA) B (a-c) and bottom ash sample (BA) B (d-f)

Figure 4. Variation of inhalable inorganic dust concentration during ash loading in closed (A) and open ash loading stations (B). Finnish OEL₈₈ value for inhalable inorganic dust is 10 mg m⁻³.

Figure 5. Variation of calculated inhalable heavy metal concentrations during ash loading in closed ash loading stations. Finnish OEL₈₈ values for inhalable Cr, Ni, Mn, Zn, Co, Pb, As and Cd are 500, 50, 20, 2000, 20 and 100 µg m⁻³, respectively.

Figure 6. Concentration variation of crystalline silica (A) and diesel exhaust components (B-D) in closed ash loading station at Power Plant B. Finnish OEL₈₈ values for respirable crystalline silica, nitric oxide, nitrogen dioxide and carbon monoxide are 0.05 mg m⁻³, 25 ppm, 3 ppm, and 30 ppm, respectively.
A

Inorganic dust concentration, mg m\(^{-3}\)

B

Inorganic dust concentration, mg m\(^{-3}\)


A

Crystalline silica concentration, mg m$^{-3}$

B

Nitric oxide concentration, ppm

C

Nitrogen dioxide concentration, ppm

D

Carbon monoxide concentration, ppm

Nitric oxide concentration, ppm