Introduction

Recently, waste incineration has been a preferred alternative in hazardous waste and sewage sludge management in developed countries since landfilling became more difficult to site due to high costs, diminishing land availability, more strict regulations, and frequent public opposition to establishing new landfills [1]. The substantial reduction of volume of waste and the generation of usable energy during combustion are the most important advantages of waste incineration [2, 3]. However, the control of gas emissions and solid residues (e.g., bottom ash, fly ash, filter cake) produced following the incineration processes are the major problems encountered in today’s waste incineration practices. Therefore, research on waste incineration and its threats to human health have been attracted by researchers. In the last 25 years, many studies have been carried out in order to characterize the emissions of hazardous waste incineration plants. Along with the emissions, in recent years, the organic and heavy metal contents of wastes have become an important research subject [4].

During combustion, the chlorine present in wastes reacts with heavy metals to generate metal chlorides that are more volatile than metal oxides. Therefore, toxic metal compounds may widely present in gas emissions and fly ash [5].

The flue gas in the incineration plants may include a variety of instable combustion products such as chlorinated organic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and adsorbable organic halogens (AOXs). In incineration plants, chlorinated aromatics are observed in different...
temperature ranges [6]. Chlorinated organic compounds generally penetrate the environment through water chlorination, combustion processes and the forest industry [7]. Orginally bounded absorbable halogens are very stable in nature and may aggregate in the food chain [8]. In the abbreviation of AOX, X stands for a halogen, i.e. chlorine, bromine and iodine [9]. Since the AOXs can easily dissolve in water, in most of the studies usually the AOXs dissolved in water are analyzed [8, 10].

Although incineration technology has for a long time been used for the removal of domestic and hazardous wastes in the world, it is a new subject in Turkey. The first and only waste incineration plant of Turkey, Izmit Hazardous and Clinical Waste Incineration Plant (IZAYDAS), is located in the province of Kocaeli, the most industrialized area in Turkey. The IZAYDAS has been in use since 1997 and currently is operated by the Metropolitan Municipality of Kocaeli.

The objective of this study is to evaluate the AOX content, heavy metal content (Pb, Cd, Cr(VI), Cu, Ni, Hg, As(III), Zn), and the concentrations of Cl\(^-\), CN\(^-\), SO\(_4\)\(^{2-}\) in bottom ash, fly ash and filter cake produced from the IZAYDAS. The samples were collected from time-to-time when enough amounts were obtained. While the bottom ash samples were collected approximately once per week, the samples of fly ash and filter cake were collected approximately every three and two weeks, respectively.

**Presentation of the IZAYDAS Incineration Plant**

The IZAYDAS is located in an 800,000 m\(^2\) area, 32,000 m\(^2\) of which is used as a combustion plant and the rest has a landfill area constructed for both municipal and hazardous waste storage.

Although the IZAYDAS is constructed to incinerate a total capacity of 35,000 tons of waste per year, the plant is usually operated at 80% of its capacity due mainly to the lack of waste. Various industrial wastes including plastic and rubber wastes, cosmetics wastes, used lubricants and oil residues, waste paint, and clinical wastes are combusted in the plant. Explosives, radioactive material, and slaughterhouse wastes are not accepted by the plant. Analysis of all waste transferred to the plant is done with respect to the appearance, smell, density, oil, water and sludge content, halogen amount, sulfur amount, and calorific value. All of the analysis is carried out in a laboratory located within the plant according to the criteria mentioned in the Hazardous Waste Control Act of Turkey (HWCA) [11].

The IZAYDAS consists of five main parts, i.e. a waste storage area, a rotary kiln, a post-combustion chamber, vapor and energy production systems, and ash collection systems. The process flow scheme of the plant is shown in Fig. 1. After the wastes are accepted to the plant according to laboratory analyses, they are transferred to the...
intermediate storage area and stored based on their physical and chemical characteristics. Then a waste menu is prepared according to the plant’s incineration conditions determined during the trial burning processes. A typical composition of waste menu is presented in Fig. 2.

The IZAYDAS is designed to incinerate a maximum 4,100 kg of waste per hour. The main control parameters for the incineration process are the calorific value of wastes, minimum incineration temperature and halogen contents of wastes. In the IZAYDAS, in order to meet the legal standards of gas emissions, the maximum concentrations of halogens in the waste menu are pre-determined as 4% of chlorine, 5% of iodine, bromine and fluorine, 1% of phosphorus, and 1% of heavy metals. In order to maintain the optimum incineration temperature, the daily waste menu is enriched by fuel oil. When the temperature of the rotary kiln reaches 425-450°C, the rotation around the axis starts automatically and the rotation speed is adjusted with respect to the amount and characteristics of the waste. Although the rotation speed is chosen as 5-8 rotations/hour, if necessary, it may be increased up to 30 rotations/hour. The main reason for this rotation is the radial mixture of wastes and the enrichment of wastes with air. In order to maintain complete combustion and necessary air enrichment, secondary air is also provided from a bunker using suction fans. In the rotary furnace, 8% of oxygen is automatically maintained. The clinker output is 120-150 minutes period to incinerate the wastes transferred to the rotary furnace at 900-1150°C. Therefore, the wastes are completely exposed to rotary kiln heat in every stage. Following the first stage of incineration, approximately 15% of waste and unburned clinkers are transferred to a container by a wet clinker conveyor, and then stored at the ash silo for analyses.

Ash collected in the wastewater tank is first transferred to the economizer section from the vaporization section by the wet clinker conveyor, and then stored at the ash silo for analyses.

The temperature of the flue gas leaving the waste heating boiler reduces to approximately 180-200°C. The dust particles are removed by an electrostatic filter unit where effective dust separation takes place with a minimum 99% efficiency. The dust trapped at the electrostatic filter is carried to the ash silo by the conveyor and collected in impermeable bags for further evaluation.

The gas leaving the electrostatic filter is washed out in the venturi scrubber unit using water and 10% of concentrated lime solution under a reverse flow. In this unit, the halogen compounds along with the heavy metals are trapped. Following this unit, the flue gas passes through the lime spray scrubber in which neutralization, oxidization and absorption take place. The primary aim of this unit is to remove SO$_2$; however, the remaining halogen compounds and heavy metals are also removed from the flue gas.

The wastewater coming from the entire air pollution control unit within the plant is transferred to the physical and chemical wastewater treatment unit. Here, the wastewater is treated by adding 15% dilute solution of trimerkaptopriazin-Na (TMT-15), 45% dilute solution of FeCl$_3$, 0.1% solution of polyelectrolyte, and 10% of lime solution. After the effluent is treated in the dissolved air flotation (DAF) tank, it is transferred to the municipal wastewater treatment plant of Kocaeli for final treatment and disposal.

The sludge taken from the DAF tank is sent to the filter press unit, where it is dewatered and turned into filter press cake. The filter press cake is also stored for further evaluation similar to the other solid residues.

The treated flue gas having a temperature of 50-58°C is discharged by the stack (65 m in length and 1.2 m in diameter) to the atmosphere using a suction fan. The plant also has an on-line flue gas analysis room where particle, HCl, HF, NO$_x$, SO$_x$, CO, CO$_2$, O$_2$, humidity and TOC are analyzed frequently using Fourier Transform Infra Red (FTIR), Flame Ionization Detection (FID) and particle measurement equipment.

Following laboratory measurements, solid residues are managed according to the requirements indicated by the HWCA [11]. If the standards are not met, they are re-incinerated.

Materials and Methods

The samples are collected from bottom ash, fly ash, and filter press cake in order to determine the concentrations of AOX, Pb, Cd, Cr(VI), Cu, Ni, Hg, As(III), Zn, Cl$^-$, CN$^-$, and SO$_4^{2-}$.

Samples of bottom ash, fly ash and filter cake were taken according to TS 12090 and ICS 13.03.10. For each group, 2 kg of sample was taken, dried for 24 h at 105°C, and homogenized by mixing.
The AOX is determined in the leachate by preparing eluate for solid residues. The eluate samples are prepared following the method of DIN 38414-S4. The AOX amount is determined by AD-2000 Adsorption Module and DX-2000 Organic Halogen Analysis Module according to DIN 38409 method. All of the measurements are carried out in the certified laboratory located in IZAYDAS plant.

The following procedure is followed:
- The percentage of the solid matter is determined.
- Particle dimensions bigger than 10 mm are broken up.
- Samples equivalent to 100 g of solid matter are weighed.
- The sample is shaken in a 2 l jar of 1 l pure water at room temperature for 24 hours.
- The undissolved part is separated by filtration using a 0.45 µm filter.

In the AOX device, organic halogens adsorbed on active carbon are determined in the water consisting of halogens such as Cl, Br, and I that have more than 10 µg/l and organic carbon that dissolved less than 10 mg/l. The organic matters in water are adsorbed in the active carbon and acidified with nitric acid. Later, it is washed with sodium nitrate solution to remove the inorganic parts of the halogens on active carbon. The active carbon charged after this process is incinerated under oxygen flow. The halogens in the organic halogen compounds react with hydrogen and pass through the titration container and are measured with the microcalometric method.

The concentration of heavy metals in bottom ash, fly ash, and filter cake were determined using Inductively Coupled Plasma Atomic emission Spectroscopy (ICP/AES) (Spectra) located at the IZAYDAS Laboratory. The method of DIN 38406-E22 was followed and the results were expressed on weight basis (weight of metal to total dry weight of sample). Before the ICP/AES analysis, 3 g samples of each group were digested in 50 ml of HNO₃:HCl mixture at 3:1 by volume for 24 h.

The concentration of Cl⁻ is measured by using an Ion Chromatography (IC) (Dionex) Device according to the method of DIN 38405-D20. The measurements of CN⁻ and SO₄²⁻ were carried out using a Genesys Spectrophotometer (Spectronic).

## Results and Discussion

The results are presented in Table 1. The level of AOX in bottom ash was higher than that in fly ash and filter cake. This is due mainly to incomplete combustion. It should be noted that the samples were not collected at the same time since the residues were collected as they were available. The complete mixture of the wastes in the bunker affects the compounds of the menu since almost half of the incineration menu is carried out in the bunker. In cases of incomplete incineration, organic and inorganic compounds are generated and inorganic halogenated compounds are observed [12]. Organic halogenated compounds can be found in bottom ash in different temperature ranges [6]. In the bottom ash, most of the high molecular organic halogenated compounds precipitate in solid form. The reason for AOX in the filter cake is the treatment of the wastewater generated during the flue gas treatment where heavy metals were transferred into compounds that hardly dissolve in water. During this treatment, since the dilute solution (45%) of FeCl₃ is added for flocculation, the concentration of Cl⁻ in the filter cake increases. Moreover, as the AOXs are adsorbable

<table>
<thead>
<tr>
<th>Parameters (mg/l)</th>
<th>Bottom Ash</th>
<th>Fly Ash</th>
<th>Filter Cake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ranges</td>
<td>Means</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>AOX</td>
<td>0.014 – 1.879</td>
<td>0.404</td>
<td>0.59</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.021 – 0.132</td>
<td>0.064</td>
<td>0.031</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.0009 – 0.04</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>&lt;0.007 – 0.685</td>
<td>0.052</td>
<td>0.159</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.002 – 0.4718</td>
<td>0.1057</td>
<td>0.128</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.0037 – 0.3848</td>
<td>0.0474</td>
<td>0.088</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.0048 – 0.0598</td>
<td>0.0134</td>
<td>0.014</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0031 – 1.511</td>
<td>0.1975</td>
<td>0.359</td>
</tr>
<tr>
<td>As (III)</td>
<td>&lt;0.0276 – 0.031</td>
<td>0.029</td>
<td>0.002</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>70 – 380</td>
<td>177.86</td>
<td>98.15</td>
</tr>
<tr>
<td>CN⁻</td>
<td>0.0019 – 0.059</td>
<td>0.011</td>
<td>0.016</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1320 – 2040</td>
<td>1676</td>
<td>216.82</td>
</tr>
</tbody>
</table>
organic halogens that can dissolve in water, little amount of it aggregates in the cake [9]. The AOXs can also be found in the smoke generated from the furnace and fly ash [13]. The more halogen-containing wastes incinerated, the more AOX is formed in the fly ash. Nevertheless, the halogens may help ClO₂ generation during the incineration process. The amount of AOX may be decreased when ClO₂ is formed. Hence, the amount of AOX is less in fly ash than that in bottom ash. In addition, the volatile forms are either held on particular matters or get through the stack as emission. The detailed presentation of AOX content of solid residues produced from the IZAYDAS can be found elsewhere [14].

The concentrations of most of the heavy metals (Pb, Cd, Cu, Ni, Hg, Zn), Cl⁻, CN⁻, and SO₄²⁻ are much higher in fly ash than that in bottom ash or filter cake. The only two exceptions are Cr(VI) and As(III). While the Cr(VI) concentration is higher in bottom ash, the As(III) concentration is higher in filter cake. Pb is volatilized at temperatures higher than 600°C. At 1000°C of temperature, Pb is combined with Cl⁻ and/or CN⁻, and PbCl₂ and/or Pb(CN)₂ is produced. At temperatures higher than 1000°C, it is possible to produce PbO. Later, PbO may be combined with SO₂ to produce PbSO₄ or PbSO₃ [15]. Since the dissolutions of PbCl₂ and Pb(CN)₂ in water are low, they are usually deposited in fly ash [16].

At temperatures of 600-1000°C, CdCl₂ may be produced under the HCl existence. At temperatures lower than 600°C, CdSO₄ may be produced if SO₂ exists. However, at temperatures higher than 1000°C, it may be in the form of CdO [15]. On the other hand, Cd²⁺ is deposited in fly ash as when the wastes are combusted at elevated temperatures [17]. Since some amount of Cl⁻ exists in the system, CdCl₂ may be dissolved in liquid and later dissociated to Cd²⁺ and 2Cl⁻. Hence, it is likely that Cd²⁺ might be present in filter cake. Although Cr(VI) is considered as a non-volatile element, it may be semi-volatile at temperatures higher than 1100°C. Cr(VI) is generally measured in higher amounts in fly ash than that in bottom ash and filter cake [17]. In this study, due to the low Cr(VI) content of waste combusted at the plant, the Cr(VI) content measured is generally low. Cu might be in the form of CuO at low temperatures. On the other hand, it forms CuSO₄ and CuCl₂ at 500-650°C and 800°C, respectively. Moreover, Cu is a semi-volatile element and it is deposited mostly in fly ash [15]. While CuCl₂ dissolves in water, CuCN does not and it might be deposited in fly ash. Although NiCl₂ is hardly dissolved in liquid, it is oxidized after loosing Cl⁻ when it is heated. If it is in the form of NiCl₂·6H₂O, its solubility is high. On the other hand, if it is in the form of Ni(CN)₂·7H₂O, it loses water at 200°C and even dissociate at higher temperatures. It is possible to form [Ni(CN)₄]²⁻ or Ni(CO₃)₂ that are dangerous compounds. While NiO and NiSO₄ may form at temperatures below 900°C, it is likely to form Ni(OH)₂ and NiCl₂ at temperatures higher than 900°C. As noted by other researchers, Ni is deposited in fly ash rather than bottom ash or filter cake [17]. Since Hg is a volatile element, it is oxidized at temperatures lower than 600°C and forms HgCl₂ if there is HCl in the system. HgCl₂ cannot dissolve in water and it is deposited in fly ash. Under the SO₂ existence, it is possible to form HgSO₄ [15]. If Hg(CN)₂ is formed, it may not dissolve in water; however, it dissociates to Hg²⁺ and 2CN⁻ at 400°C. As reported by earlier studies, Zn is found mostly in fly ash following incineration [16]. The amount of Zn in fly ash depends on the waste menu combusted in the plant. As(III) is easily volatilized at 500°C or higher temperatures. At 400-800°C, it is possible to form AsCl₃ [15] and it easily dissociates to As³⁺ and 3Cl⁻ at the filter cake. However, in this study, the levels of As are generally low due to the low As content of raw waste incinerated at the plant.

If the results are compared with the Standard Limits presented in Table 2, in bottom ash, all of the mean concentrations are within or lower than the limits of Criteria II. Moreover, the concentration ranges of all of the parameters are within or lower than the limits of Criteria II except Hg²⁺ and SO₄²⁻ that are within the limits of Criteria III. Therefore, the concentration of Hg²⁺ and SO₄²⁻ in bottom ash must be reduced before deposition in non-hazardous waste landfills. Otherwise, bottom ash must be deposited in hazardous waste landfills having specially constructed cells.

On the other hand, the concentrations of Pb, Cd, Cu, Ni, Hg, Zn, Cl⁻ and SO₄²⁻ in fly ash exceed the upper limits of Criteria III. Hence, the fly ash should be considered as hazardous waste.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Criteria I* (mg/l)</th>
<th>Criteria II+ (mg/l)</th>
<th>Criteria III§ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>≤0.05</td>
<td>0.05 – 1</td>
<td>&lt;1 – 5</td>
</tr>
<tr>
<td>Cd</td>
<td>≤0.004</td>
<td>0.004 – 0.1</td>
<td>&lt;0.1 – 0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>≤0.05</td>
<td>0.05 – 1</td>
<td>&lt;1 – 7</td>
</tr>
<tr>
<td>Cu</td>
<td>≤0.2</td>
<td>0.2 – 5</td>
<td>&lt;5 – 10</td>
</tr>
<tr>
<td>Ni</td>
<td>≤0.0</td>
<td>0.04 – 1</td>
<td>&lt;1 – 4</td>
</tr>
<tr>
<td>Hg</td>
<td>≤0.001</td>
<td>0.001 – 0.02</td>
<td>&lt;0.02 – 0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>≤0.4</td>
<td>0.4 – 5</td>
<td>&lt;5 – 20</td>
</tr>
<tr>
<td>As</td>
<td>≤0.05</td>
<td>0.05 – 0.2</td>
<td>&lt;0.2 – 2.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>≤80</td>
<td>80 – 1500</td>
<td>&lt;1500 – 2500</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>≤100</td>
<td>100 – 2000</td>
<td>&lt;2000 – 5000</td>
</tr>
</tbody>
</table>

*If the concentrations are below these limits, wastes are considered as inert and can be deposited along with municipal wastes in municipal waste landfills.

+ If the concentrations are within these limits, wastes are considered non-hazardous and must be deposited in special cells (monoliths) in municipal waste landfills.

§ If the concentrations are within or higher than these limits, wastes are considered hazardous. If the concentrations are within the limits, the wastes must be deposited in hazardous waste landfills. If the concentrations are higher than the upper limits, wastes cannot be deposited in any way. They must be incinerated or treated to reduce the concentrations before disposal.
a hazardous waste, and it must be treated before deposition. Otherwise it must be re-incinerated.

It can be seen that all of the parameters measured in filter cake are below the limits of Criteria iii. Therefore, it can be concluded that filter cake is not considered a hazardous waste and can be deposited in specially constructed cells in landfills. In addition, the concentrations of Cd, Cu, and Ni are below the limits of Criteria ii.

As seen in Table 2, the mean concentrations of Zn and Cu in fly ash are higher than the other parameters. These high concentrations result from the waste menu combusted during the incineration process. As indicated in an earlier study conducted in IZAYDAS [18], the Zn and Cu contents of waste (especially wastes in solid form) are the highest among other parameters. Therefore, the content of Pb, Cd, Cu, Ni, Hg, and Zn of waste menu should be decreased before incineration if the fly ash residues are planned to be deposited in landfills. Figure 3 also shows that the AOX levels are higher in the bottom ash than in both the fly ash and filter cake. This was also reported by a previous study [14]. On the other hand, fly ash is more contaminated by the other parameters measured in this study than bottom ash or filter cake. The only exceptions are Cr(VI) and As(III) that are higher in bottom ash and filter cake, respectively.

**Conclusions**

1. Solid residues out of hazardous waste incinerators may contain certain chemicals at high levels despite the incinerator’s state-of-the-art technology. This is due mainly to the difficulties of the combustion of solids. Although the temperatures and residence time inside the kiln are suitable for complete combustion, cold points and pyrolytic conditions could occur locally, and may cause the formation of products of incomplete combustion (PICs).

2. The bottom ash can be considered as a non-hazardous waste if it is treated by means of reduction of Hg^{2+} and SO_{4}^{2-} contents. After treatment, it may be deposited in special solid waste landfills having special cells. Otherwise, it must be only deposited in hazardous waste landfills.

3. Fly ash is classified as a hazardous waste due to high content of soluble metals including Pb, Cd, Cu, Ni, Hg and Zn in leachates. The concentrations of SO_{4}^{2-} were also high due to the soluble metal sulfates. Therefore, it should be concluded that fly ash must be utilized as a hazardous waste. It must be treated in order to reduce the metal content before final deposition in landfills or re-incinerated.

4. Filter cake is not considered a hazardous waste and can be deposited in specially constructed cells in landfills.

5. The AOX levels are higher in the bottom ash than in both the fly ash and filter cake. This is mainly due to incomplete combustion.

6. Although heavy metals (especially As and Cd) are volatilized at elevated temperatures, they may return to solid form at cold regions at the process flow. If the concentration of HCl increases, trace elements would generally produce compounds in gas form. On the other hand, condensed compounds will usually form in the presence of SO_{2}.

**Acknowledgments**

The authors thank the personnel of the Chemical Analysis Laboratory at IZAYDAS for their contribution.

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9. MULLER G. Sense or no-sense of the sum parameter for water soluble “absorbable organic halogens” (AOX) and “adsorbed organic halogens” (AOX-S18) for assessment of organohalogenes in sludges and sediments. Chemosphere 52, 371, 2003.