A STUDY ON THE CHEMISTRY OF ASH FRACTIONS FROM MSW INCINERATION

*S. Arvelakis, F.J. Frandsen, M. Pomeroy and K. Dam-Johansen,
1CHEC research group, Department of Chemical Engineering, Danish Technical University, (DTU), Lyngby 2800, Denmark. Tel:+45 45252835, Fax:+45 45882258, 2Materials Science and Technology Department, University of Limerick, Limerick, Ireland. Tel:+35361202200, Fax:+353331693 Email: stylianos.arvelakis@ul.ie

Abstract
In this work, a methodology for analysis and characterization of different ash fractions (bottom ash, 2-3rd pass ash, super-heater ash, economizer ash and filter ash) generated from the incineration of MSW in a grate firing plant is presented. The methodology is shown to provide detailed information regarding the chemical composition and the main characteristics of the generated fly and bottom ash that could provide valuable information concerning the handling of ash-related problems, (slagging, fouling, corrosion), and also ash disposal problems. Comparison of the results obtained with results from corrosion studies with MSW ash showed that the sampling point and the sampling procedure significantly affect the results obtained.

Keywords: ash, leaching, MSW, incineration

1. Introduction
Ash-related problems in the form of fouling, slagging, corrosion and erosion comprise one of the biggest obstacles towards the safe, economical and environmental friendly utilization of a large variety of biomass and waste fuels, (straws, hulls, MSW, sewage sludge), for heat and power production via thermochemical conversion methods.

In specific, the ash fractions investigated appeared to be rich in alkali metals, chlorine and sulphur, usually in very reactive forms such as simple inorganic salts, (KCl, NaCl), inorganic grains finely dispersed in the organic structure of these materials or as cations associated with the organic structure of the materials.

During thermal treatment, the inorganic part undergoes a number of transformations forming gases, liquids and solids that can react further or re-condense on the cooler surfaces of the furnace or on the heat transfer surfaces forming ash deposits. These deposits may continue to grow with time since they usually create a sticky surface layer that increases the capture efficiency of the deposit, while they increase corrosion, slagging and fouling effects and may inhibit the heat transfer to the steam cycle. [1-5]

Furthermore, in the case of municipal solid waste (MSW) incineration plants, the deposition and the corrosion processes can be also affected by the presence of heavy metals such as zinc and lead in the forms of chlorides and sulphates. These compounds have very low melting points, e.g. 290°C for ZnCl₂, 501°C for PbCl₂ and 680°C for ZnSO₄, and they may also interact with compounds such as the KCl and the alkali metal sulphates present in large amounts in the ash material deposited after MSW incineration. This leads to the formation of molten phases with even lower melting points compared to the pure salts, i.e., 250°C for the ZnCl₂/KCl (48/52%wt.) mixture accelerating significantly the deposition and the corrosion processes. [6-11]

The presence of large amounts of heavy metals (Zn, Pb, Cu, etc.) and also alkali chlorides and sulphates in the ash formed during the MSW...
incineration apart from their contribution in the ash-related problems also constitute a significant problem regarding the treatment and disposal of the generated ash material in an economical and environmentally friendly way.\[12-29\]

As a result, ash analysis and characterization methods have become more important as a tool in order to predict the behavior of the ash during the thermal treatment of the specific biomass and waste materials but also the reactivity of the final ash material during its disposal in landfill areas or its use as base material for construction purposes.\[14,15,22,27\]

This leads to the need of developing advanced techniques and methodologies regarding both the design and operation of the conversion systems in order to minimize the ash-related problems and the treatment of the ash material after the thermal treatment stage.

2. Materials and methods

Four different ash samples from the Svendborg MSW incineration plant appearing in Figure 1 were studied in this work. The MSW incineration plant consists of a Velund mass burn furnace with a fully integrated natural circulation steam boiler. The ash samples consisted of 2-3rd pass ash, super-heater ash, economizer ash and finally ash collected from the electrostatic filters of the plant. The specific ash samples were encoded as Fly ash 2, Fly ash 3, Fly ash 4 and Fly ash 5 respectively. The ash sampling was done by entering the plant during its shut-down period and collecting ash material from the different parts.

The applied methodology includes the fractionation of the ash material in two different fractions a water-soluble that contains the majority of the inorganic salts deposited on the surface of the ash particles, and a water non-soluble fraction containing mainly the initially formed ash particles and any water non-soluble inorganic salts e.g. CaSO₄. The analysis and characterization of the resulted fractions is performed using a variety of analytical techniques and methods such as ICP, SEM-EDX, XRD and STA.

The procedure includes the following steps:

- 250g of each ash fraction are being leached using 1l hot distilled water (T 70-75°C), under continuous mechanical stirring for 1h,
- The solution is filtrated through a 45μm filter under vacuum and the leachate is kept,
- Portions of the leached ash (2-3g), and of the leachate (100ml, 200ml), are kept for further analysis and characterization,
- The remaining washing water is also kept for total water soluble salts determination at the end of the procedure,
- Then the material is dried in an evaporation furnace at 110°C and the mass loss corresponding to the extracted salts is calculated,
- The procedure is repeated for 6 times following the same conditions. Following this procedure a number of seven ash and six salt samples were formed after the leaching treatment of each ash fraction.
- The first part of the leachate (200ml), from the six washing series is evaporated in a drying furnace at temperatures below 150°C and the remaining salts are collected, weighed, mixed, homogenized and used for STA, XRD and SEM-EDX analyses,
- The second part of the leachate (100ml), can be used for the determination of anions, (Cl, SO₄, etc.), and cations, (K, Na, etc.), using ion chromatography techniques,
- The ash material from the six washing series is dried in an evaporating furnace at 110°C, followed by carbon burnout at 550°C in a muffle furnace. The resulting material is also used for further analysis and characterization using STA, ICP, XRD and SEM-EDX methods.

3. Results and discussion

3.1 Leaching treatment

The amounts of water-soluble salts present in the various ash samples show large variations depending on the location of the ash sampling. Fly ash 2 that is sampled in a high temperature region of the furnace (2-3rd pass) contains small amounts of salts accounting for 9.6%w.b. of the total sample mass. The amounts of the water-soluble salts in the other three ash samples that were sampled downstream of the furnace at lower
temperatures are higher accounting for almost 30\%w.b. of the total mass of the respective initial samples.

The leaching treatment appears to remove the majority of the water-soluble salts in most of the cases during the first three leaching stages, while the removal rate seems to follow a second-power pattern. Approximately 90\%w.b. of the water-soluble salts is removed during the first three leaching stages from the fly ash samples. In all cases the first leaching stage shows to remove more than the 60\%w.b. of the total amount of the water-soluble salts.

All the leached ash samples were heated in a muffle furnace at 550\°C in order to eliminate any organic matter present before used for further analysis and characterization. The produced results show that all the fly ash samples show to contain low amounts of organic matter in the range of 2-5\%w.b.

3.2 Characterization of ash and salt samples using various (ICP, SEM-EDX, XRD and STA) techniques

3.2.1 Chemical characterization of ash fractions using ICP-OES

Table 1 presents the results from the chemical analysis of the four fly ash samples analyzed using the ICP-OES method. The ash samples sampled downstream of the combustion chamber (Fly ash 3,4 and 5), contain mainly alkali metals, calcium and silicon in almost equal concentrations. Other elements such as Mg, Fe, P, Al, Ti and Pb were also found to be present in small amounts and in almost equal concentrations in these specific ash samples. In addition, the presence of elements such as sulphur and chlorine was also significant, while the concentrations varied among the different ash samples with the Fly ash 3 and 4 samples showing high concentrations of sulphur varying from 21-27\%w.b., and low to medium, 2.4-6.4\%w.b., concentrations of chlorine respectively. The Fly ash 5 sample shows high concentrations of chlorine reaching almost 16\%w.b. and medium of sulphur in the area of 10\%w.b. A similar distribution among the different ash samples is seen also in the case of zinc. Zinc concentrations appear to be similar in the case of the Fly ash 4 and 5 samples, while the zinc amount in the case of the Fly ash 3 sample is seen to be the half.

Fly ash 2 sample is mainly enriched in silicon, calcium and aluminium, the concentrations of elements such as Mg, Fe and Ti are higher compared to the previous ash samples, while the amounts of alkali metals, zinc and lead are significantly lower now. The amounts of chlorine and sulphur are also seen to be low but at the same levels with some of the other samples such as the Fly ash 4 for sulphur and Fly ash 3 for chlorine. The results from the characterization of the fly ash samples resulting after the end of the leaching process show that chlorine is the only element that is almost totally removed in all cases. The concentrations of alkali metals are reduced by almost 90\%w.b. in Fly ash 3, 4 and 5, showing that these elements are present mainly in the form of water-soluble salts and only in small amounts participate to the formation of silicates. Sulphur is reduced by almost 30\%w.b. in Fly ash 3 and 4, while it is slightly increased in Fly ash 5. The concentrations of all the other elements show an increase from 20-60\%w.b. with silicon, calcium and sulphur forming the main matrix of these ash samples.

The expulsion of alkali metals and sulphur from Fly ash 2 is limited since only the 60\%w.b. of the alkali metals and the 6.5\%w.b. of sulphur are removed during the leaching process. The observed increase in the concentrations of the other elements is also limited below 12\%w.b. for all the major elements, while it shows to be higher in the case of the trace elements such as zinc, copper and lead that show an increase from 16-28\%w.b. respectively. This shows that the specific ash particles consist mainly of aluminosilicates. The higher temperatures prevailing in the specific reactor area do not favor the deposition of alkali metals and also calcium salts to the surface of the ash particles as in the case of the Fly ash 3, 4 and 5 samples.

3.2.2 SEM-EDX analysis of various salt and ash fractions

A number of both the ash and the salt samples, produced in the different stages of the leaching process, were characterized using the SEM-EDX technique. The characterized samples included initial untreated ash material from all the ash samples as well as samples produced after the completion of the leaching process. The study also included the ash and salt samples resulting from the six-stage leaching treatment of Fly ash 5. In addition, portions of the Fly ash 5 initial untreated sample before the carbon burnout stage were kept and also analyzed here. For each sample 10-15 point and area EDX analyses were performed and the results were averaged to give the results presented in Tables 2-4.
which was not in the form of deposits. This during MSW incineration have shown that zinc had been done by taking parts of the ash combustion chamber. [7,8,11] However, in indicates that the formation of zinc chloride different areas of the MSW incinerator, but deposits on the tubes. In our case the sampling probably takes place over time in the deposits parts of the incinerator downstream the stage shows that zinc is not present on the ash 5 sample after the carbon burnout stage though the difference in the case of the sample after the carbon burnout stage is smaller. As the leaching progresses the amounts of silica and alumina in the particles of the produced samples are increasing, while the amounts of alkali metals decreasing. The majority of the ash particles have an aluminosilicate structure that is mainly complemented by alkali metals, zinc calcium and sulphur. Low amounts of elements such as iron, phosphorus, magnesium and titanium are also present. These samples have also been seen to contain a large number of particles where Ca and S are present in large amounts most likely in the form of calcium sulphate. The presence of such particles is seen to slightly reduce as the leaching treatment progresses.

The analysis of the final sample after the six-stage leaching treatment of the Fly ash 5 shows that leaching has successfully achieved to extract the salts from the surface of the ash particles as it is seen in Table 2 and Figure 2c. The salt layers observed on the surface of the ash particles in Figure 3a have been removed as it is seen in Figure 2c disclosing the main structure of the ash particles. Table 2 shows that substantial amounts of sodium and zinc have been incorporated in this structure, while the amounts of potassium detected are marginal. Many particles are seen to contain large amounts of calcium and sulphur and also medium amounts of sodium and zinc as the main coating layer most likely in the form of sulphates due to the oxidative conditions prevailing in the MSW incineration plant.

Table 3 and Figure 4 present the results from the SEM-EDX analysis of the different salt samples from the six-stage leaching treatment of the Fly ash 5. The analysis of these samples shows that the majority of alkali metals and chlorine in the ash particles are removed during the first two stages of the leaching process. After the 3rd leaching stage the leached salts contain mainly calcium and sulphur. Since pure calcium sulphate is insoluble in water the formation of mixed alkali and calcium sulphates must be
responsible for the extraction of the calcium sulphate salts. [6,31] The random presence of elements such as zinc, magnesium silicon and aluminium in some of the samples is attributed mainly to ash impurities passing the filter during the filtering of the leachate.

A comparison among the results from the ICP-OES and the SEM-EDX methods regarding the composition of the various ash samples analysed shows that the SEM-EDX method tends to overestimate the amounts of most of the elements calcium, zinc, magnesium, sodium, aluminium, and iron, while underestimates the amounts of elements such as the silicon, phosphorus, titanium, and in some cases also potassium compared with the results from the ICP-OES method. This is attributed to the fact that SEM-EDX determines the concentrations of the elements present on the surface of the ash particles and is highly sensitive to the morphology and type of the particle. Nevertheless, SEM-EDX seems to provide good estimates regarding the concentrations of the main elements in the ash particles in a significantly cheaper and faster way compared to the ICP-OES method. It also provides useful information regarding the distribution of the elements forming the ash particles and their possible chemical form. However, relative experience with both techniques and their limitations is necessary when interpreting the results.

3.2.3 XRD analysis of various ash fractions

A large part of the ash samples were seen to be amorphous resulting in a large background signal during the XRD analysis. All the ash samples had the same basic aluminosilicate structure. The main crystalline compounds detected include SiO₂, Al₂O₃, as well as silicates such as K₂Si₃O₈, Na₂SiO₃, Ca₂SiO₄, K₂CaSiO₄, Zn₂SiO₄ and also traces of PbSiO₃. Aluminosilicates were also detected, together with a layer of inorganic salts, carbonates and oxides deposited on the surface of the ash particles.

The XRD analysis of Fly ash 2 shows that the surface layers of the untreated initial sample contain compounds such as NaCl, CaCO₃, CaSO₄ and ZnSO₄ as well as mixed salts such as K₂Ca₃(SO₄)₃, (Na,K)₂SO₄ and KNaCO₃. The analysis of the leached sample shows the presence of mainly simple salts such as CaSO₄, ZnSO₄ and CaCO₃, while there is no indication regarding the presence of alkali chlorides. The amounts of mixed salts were found to reduce as was indicated by their weaker signal.

The XRD results for untreated Fly ash 3 gives a very strong signal for alkali chlorides and oxides. Heavy metal oxides such as PbO and ZnO as well as salts such as CaSO₄, Na₂SO₄, K₂CO₃, and Na₂Ca(SO₄)₂ also gave a strong detection signal. Mixed alkali sulphates such as (K,Na)₂SO₄ were seen to give a weak detection signal. Strong signals for alkali and heavy metal (Zn, Pb) oxides and also of CaSO₄ were detected in the XRD analysis of leached Fly ash 3. There was no detection signal for alkali chlorides as well as for the mixed alkali and calcium sulphate salts, which were effectively removed during the leaching treatment.

Alkali chlorides, simple alkali and calcium sulphates in combination with mixed alkali and alkali-calcium sulphates were also found to be the main crystalline compounds detected on the ash particles for untreated Fly ash 4. ZnO gave also a weak detection signal but there was no signal for alkali oxides as in the case of the untreated Fly ash 3. The XRD analysis of the leached sample shows that apart from the aluminosilicate structure the crystalline phases detected are mainly CaSO₄ and heavy metal oxides such as ZnO and PbO.

The XRD analysis of untreated Fly ash 5 shows that the main crystalline compounds found on the top of the silicate particles are alkali chlorides, CaSO₄, mixed alkali and alkali-calcium sulphates as well as heavy metal oxides such as ZnO and PbO. Leaching shows to remove as in the previous cases all the alkali chlorides as well as the mixed sulphates from the Fly ash 5. CaSO₄ and the heavy metal oxides remain as the main crystalline phases on the top of the silicates.

3.2.4 Simultaneous thermal analysis (STA) of various ash and salt fractions

Figure 5 presents the results from the STA tests performed using the salt samples extracted during the 1, 3 and 4 stages of the leaching treatment of Fly ash 5 as well as using the total extracted salt material.

All the salt samples present an endothermic peak as well as a mass loss below 200°C due to water evaporation. In Figure 5a a small endothermic peak is shown at 382.3°C in the DSC curve for salt 1. A similar larger endothermic peak is seen to start at 539°C and to end at 647°C. These peaks are not accompanied by a simultaneous mass loss and are attributed to the melting of the salt 1 sample. As it has been shown in previous
studies the presence of mixed alkali and alkali-calcium chlorides and sulphates can lead to melting points in the temperature area the specific endothermic peaks are now observed. [31] The XRD analysis performed on the specific ash sample has verified the presence of such inorganic salt mixtures on the surface of the ash particles. A large endothermic peak starts at 700°C and ends at 1153°C with intermediate peaks at 804.7°C, 902.1°C and 1142°C. A large mass loss of 94%w.b. corresponding mainly to alkali chloride evaporation, and to a smaller extent to the evaporation of sulphates, and to alkali carbonates dissociation is also seen there. The produced results correlate well with the results from the SEM-EDX analysis according to which more than 78%w.b. of the salt particles was alkali chlorides.

Figure 5b presents the results for salt 3. As it is seen from the DSC curve two consecutive endothermic peaks are present at 521°C and 604°C corresponding mainly to the melting of alkali and alkali-calcium chlorides and sulphates mixtures. A large endothermic process starts at 912°C as it is seen from the DSC curve and ends at 1437°C accompanied by a mass loss of 70%w.b. This large endothermic area can be divided in two smaller areas. The first starting at 912°C and ending at 1159°C accompanied by a mass loss of 44%w.b. presents two peaks at 1035°C and 1097°C and is attributed mainly to the evaporation of chlorides and mixed alkali, alkali-calcium sulphates, as well as to the partial dissociation of carbonates. The second sub-area starting at 1221°C and finishing at 1437°C with peaks at 1221°C and 1300°C and a mass loss of 25.7%w.b. is attributed mainly to the dissociation of carbonates and calcium sulphate and the production of SO₃ as it has also been seen in a previous study. [31]

The STA analysis of the total salts extracted during the six-stage leaching treatment of Fly ash 5 is presented in Figure 5d. Both the DSC and the TGA curves show large similarities with the curves produced during the STA tests with the salt samples 1,3 and 4. The DSC curve shows a melting peak at 598°C as in the case of the previous salt samples. A large endothermic peak starts at 685°C and ends at 1086°C accompanied by a mass loss of almost 65%w.b. mainly due to the evaporation of alkali chlorides. A narrow endothermic peak is present in the temperature segment 1086-1230°C, in combination with a mass loss of almost 27%w.b. due to the evaporation of mixed alkali and alkali-calcium sulphates and the dissociation of carbonates. Finally, a small endothermic peak is present at 1403°C as well as a small mass loss of 1.5%w.b. that is attributed to calcium sulphate dissociation.

The STA analysis of Fly ash 2 salts is presented in Figure 6a. The DSC curve shows a small endothermic peak accompanied by a mass loss of almost 15%w.b. at 253°C. This peak could be associated with the melting and evaporation of mixed alkali-zinc chlorides, as it has also been suggested by others.[7,8,11] A large melting process is seen in the temperature segment 498-587°C with peaks at 519°C and 560°C. A large endothermic process is seen in the temperature segment 700-1445°C in the DSC curve accompanied by a mass loss of almost 85.82%w.b. as it is seen in the TGA curve. The mass loss takes place in two stages from 700-1160°C and from 1160-1445°C. In the first stage endothermic peaks are seen at 873°C as well as a double peak at 1103-1118°C, while the mass loss reaches 47.43%w.b. mainly due to the evaporation of alkali chlorides and sulphates and the partial dissociation of carbonates. In the second stage peaks are present at 1334°C and 1379°C and the mass loss is 38.39%w.b.. This mass loss is attributed to the evaporation of mixed alkali-calcium sulphates as well as to the dissociation of alkali carbonates and calcium sulphate.

The STA results of the total salts extracted during the leaching of Fly ash 3 are shown in Figure 6b. The DSC curve shows a small endothermic peak at 246°C accompanied by a very low mass loss of 0.5%w/w that could be attributed to the evaporation of zinc chloride/alkali chloride mixtures. Two melting peaks are seen at 460°C and 518°C due to the melting of the complex salt mixture. A large
endothermic peak is seen in the temperature segment 873-1470°C accompanied by a mass loss of almost 85%w.b. The mass loss takes place in two stages as it was also seen in the previous STA tests. The first stage starts at 873°C and ends at 1206°C with a mass of 21%w.b. mainly due to the evaporation of alkali chlorides and sulphates and the partial dissociation of carbonates. The second stage at the temperature segment 1206-1470°C leads to a mass loss of almost 64%w.b. that is attributed to the evaporation of alkali-calcium sulphates and the formation of SO₃, K₂O and CO₂ due to the dissociation of calcium sulphate and alkali carbonates. [31] Figure 6c presents the STA analysis of the total salts extracted during the leaching of the Fly ash 4 ash sample. The DSC curve shows a small endothermic peak at 245°C accompanied by a low mass loss <0.5%w.b. that can be attributed to the melting and evaporation of a zinc chloride/alkali chloride mixture as in the case of the Fly ash 3 salt sample. Three melting peaks at 364.4°C, 459°C and 496°C correspond to the melting of the specific salt sample. A large endothermic process is observed in the temperature segment 800-1460°C accompanied by a mass loss of 92%w.b. The endothermic process is divided into two stages. The first stage is present in the temperature segment 800-1200°C where a peak is observed at 1156°C and is accompanied by a mass loss of 23%w.b.. The second stage starts at 1200°C and ends at 1460°C with peaks at 1232°C and 1391°C and a mass loss of 69%w.b. The mass loss is attributed to the evaporation of alkali chlorides and sulphates and the partial dissociation of carbonates during the first stage of the endothermic process and to the evaporation of alkali-calcium sulphates as well as to the total dissociation of alkali carbonates and calcium sulphate during the second stage of the process.

4. Conclusions

The main findings of this work can be summarized as follows:

Leaching proved to be a low cost and easily adopted technique in order to remove the alkali salts from the surface of the fly and bottom ash particles produced during the MSW incineration. The applied process will ensure the complete removal of the water-soluble salts after a three-stage process.

The applied methodology provides a very detailed characterization of the ash material sampled from different parts of an MSW incinerator. All the applied techniques show to produce compatible results and their simultaneous use allows the successful identification of the various compounds participating to the formation of ash particles.

The fly ash samples are composed of two different parts. The ash particles have basically an aluminosilicate structure as seen from the XRD and SEM EDX analyses. These aluminosilicate particles are covered with layers of mainly alkali and calcium salts, such as chlorides, carbonates and sulfates. The presence of heavy metals mainly as oxides and sulphates as well as silicates was also identified. The amount of salt deposition on the surface of the ash particles was increasing as the temperature was dropping on the various sampling points allowing compounds with lower evaporation points to condense on the surface of the ash particles. The various inorganic salts and oxides have been seen to interact forming new mixed compounds with melting points significantly lower compared to those of the pure compounds. As a result molten phases may form at very low temperatures, as it was seen from the STA tests, which is believed to significantly accelerate the corrosion and deposition rates.

Comparison of the produced results with previous studies on the corrosion of metals using ash deposits from MSW incineration have shown that the composition of the ash shows to be different. Zinc/Lead chlorides that have been seen to be present in large amounts in the deposits found in downstream areas of the incinerators e.g. super-heaters were not present in any of the fly ash samples collected from the MSW incinerator. This is attributed to the different sampling procedure applied in our case and it shows that the formation of heavy metal chlorides takes place mainly in the deposits through further reactions with the other ash constituents.

Zinc and lead appeared mainly as oxides, sulphates as well as in the form of silicates in all the ash samples.

The produced results can be used in combination with the results obtained from the corrosion studies using ash deposits in order to provide a better understanding of the mechanisms responsible for the formation of the ash deposits and the transformations occurring during this process. This is expected to assist in the development of new protection methods and reduce the deposition and corrosion problems.
Power plant operators could use the applied methodology in order to extract fast and accurate information regarding the composition of the ash and the ash deposits formed during the MSW incineration, which will assist them to develop new tools and strategies regarding the control of ash deposition and corrosion problems.

References

“Elemental characterization of coal ash and its leachates using sequential extraction techniques”
1995;192:2:265.
sulfur and high-sulfur coal sources: Partitioning of carbon and trace elements with particle size”
[25] Eighmy TT, Eusden JDJR, Krzanowski JE, Domingo DS, Stampflii D, Martin JR, Erickson PM.
“Comprehensive approach toward understanding element speciation and leaching behavior in
municipal solid waste incineration electrostatic precipitator ash” Environ. Sci. Technol.
J. “An international perspective on the characterisation and management of residues from MSW
[27] Nugteren HW, Jansen-Jurcovicova M, Scarlett B. “Improvement of environmental quality of coal
fly ash by applying forced leaching” Fuel 2001;80:873.
[28] Camerani MC, Somogyi A, Drakopoulos M, Steenari B-M. “Synchrotron radiation induced mu-X-
ray fluorescence spectroscopy on municipal solid waste fly ashes” Spectrochimica Acta Part B
2001;56:8:1355.
[29] Mudd GM, Kodikara J. “Field studies of the leachability of aged brown coal ash” Journal of
Hazardous Materials 2000;76:2;159.
[30] Ollanders B, Steenari B-M. “Characterization of ashes from wood and straw” Biomass and
Bioenergy 1995;8:105.
[31] Arvelakis S, Jensen P-A, Dam-Johansen K. “Simultaneous thermal analysis (STA) on high alkali
Table 1: Chemical composition of various ash samples using the ICP-OES analysis method % w.b.

<table>
<thead>
<tr>
<th>Samples</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>P₂O₅</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>CuO</th>
<th>PbO</th>
<th>ZnO</th>
<th>S₀₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash 2. Initial</td>
<td>2.83</td>
<td>2.86</td>
<td>3.34</td>
<td>9.82</td>
<td>27.43</td>
<td>3.28</td>
<td>10.96</td>
<td>28.93</td>
<td>2.17</td>
<td>0.09</td>
<td>0.04</td>
<td>1.50</td>
<td>11.50</td>
</tr>
<tr>
<td>Flyash 2. Final</td>
<td>2.60</td>
<td>2.60</td>
<td>3.33</td>
<td>9.82</td>
<td>27.43</td>
<td>3.33</td>
<td>10.96</td>
<td>28.93</td>
<td>2.17</td>
<td>0.09</td>
<td>0.04</td>
<td>1.50</td>
<td>11.50</td>
</tr>
<tr>
<td>Difference %</td>
<td>-63.33</td>
<td>-63.33</td>
<td>-6.00</td>
<td>-6.00</td>
<td>-2.00</td>
<td>-0.06</td>
<td>-1.00</td>
<td>-1.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
</tr>
<tr>
<td>Flyash 3. Initial</td>
<td>8.68</td>
<td>7.28</td>
<td>16.52</td>
<td>2.00</td>
<td>2.00</td>
<td>2.75</td>
<td>5.48</td>
<td>15.21</td>
<td>1.28</td>
<td>0.09</td>
<td>0.04</td>
<td>1.50</td>
<td>11.50</td>
</tr>
<tr>
<td>Flyash 3. Final</td>
<td>1.06</td>
<td>1.24</td>
<td>26.46</td>
<td>3.33</td>
<td>3.33</td>
<td>11.54</td>
<td>5.47</td>
<td>8.33</td>
<td>23.08</td>
<td>21.25</td>
<td>0.07</td>
<td>0.04</td>
<td>1.50</td>
</tr>
<tr>
<td>Difference %</td>
<td>-86.81</td>
<td>-86.81</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Flyash 4. Initial</td>
<td>9.16</td>
<td>6.74</td>
<td>16.94</td>
<td>2.17</td>
<td>2.17</td>
<td>2.75</td>
<td>5.48</td>
<td>15.21</td>
<td>1.28</td>
<td>0.09</td>
<td>0.04</td>
<td>1.50</td>
<td>11.50</td>
</tr>
<tr>
<td>Flyash 4. Final</td>
<td>1.02</td>
<td>1.01</td>
<td>24.08</td>
<td>2.83</td>
<td>2.83</td>
<td>11.54</td>
<td>5.47</td>
<td>8.33</td>
<td>23.08</td>
<td>21.25</td>
<td>0.07</td>
<td>0.04</td>
<td>1.50</td>
</tr>
<tr>
<td>Difference %</td>
<td>-88.82</td>
<td>-88.82</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Flyash 5. Initial</td>
<td>10.72</td>
<td>8.28</td>
<td>17.08</td>
<td>2.17</td>
<td>2.17</td>
<td>2.75</td>
<td>5.48</td>
<td>15.21</td>
<td>1.28</td>
<td>0.09</td>
<td>0.04</td>
<td>1.50</td>
<td>11.50</td>
</tr>
<tr>
<td>Flyash 5. Final</td>
<td>1.11</td>
<td>1.21</td>
<td>24.24</td>
<td>2.83</td>
<td>2.83</td>
<td>11.54</td>
<td>5.47</td>
<td>8.33</td>
<td>23.08</td>
<td>21.25</td>
<td>0.07</td>
<td>0.04</td>
<td>1.50</td>
</tr>
<tr>
<td>Difference %</td>
<td>-98.9</td>
<td>-98.9</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
</tr>
</tbody>
</table>

Copyright © 2005 by ASME
Table 2: SEM-EDX Analysis of the Fly ash 5 sample ash fractions % w.b.

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>ZnO</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>Cl</th>
<th>CuO</th>
<th>PbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial 1</td>
<td>15.1</td>
<td>19.52</td>
<td>12.06</td>
<td>8.04</td>
<td>0.00</td>
<td>3.94</td>
<td>1.77</td>
<td>0.70</td>
<td>1.05</td>
<td>0.57</td>
<td>10.21</td>
<td>18.76</td>
<td>0.86</td>
<td>0.00</td>
</tr>
<tr>
<td>Initial 2</td>
<td>8.49</td>
<td>12.23</td>
<td>15.52</td>
<td>16.34</td>
<td>2.91</td>
<td>8.41</td>
<td>5.24</td>
<td>1.46</td>
<td>1.28</td>
<td>0.00</td>
<td>13.36</td>
<td>10.86</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample 1</td>
<td>2.57</td>
<td>7.77</td>
<td>13.89</td>
<td>28.04</td>
<td>3.89</td>
<td>7.42</td>
<td>5.03</td>
<td>1.92</td>
<td>1.26</td>
<td>1.63</td>
<td>23.50</td>
<td>2.14</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.40</td>
<td>8.88</td>
<td>16.59</td>
<td>26.54</td>
<td>2.95</td>
<td>9.67</td>
<td>7.62</td>
<td>3.40</td>
<td>1.69</td>
<td>0.99</td>
<td>19.20</td>
<td>0.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.46</td>
<td>7.90</td>
<td>11.71</td>
<td>29.83</td>
<td>3.67</td>
<td>15.39</td>
<td>8.51</td>
<td>2.73</td>
<td>1.28</td>
<td>3.32</td>
<td>15.03</td>
<td>0.12</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample 4</td>
<td>1.47</td>
<td>10.94</td>
<td>15.68</td>
<td>19.33</td>
<td>3.94</td>
<td>24.23</td>
<td>7.31</td>
<td>2.08</td>
<td>2.64</td>
<td>0.00</td>
<td>12.10</td>
<td>0.18</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sample 5</td>
<td>6.27</td>
<td>7.05</td>
<td>8.19</td>
<td>6.41</td>
<td>1.00</td>
<td>34.95</td>
<td>30.53</td>
<td>2.69</td>
<td>1.37</td>
<td>0.00</td>
<td>1.44</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Final area 1</td>
<td>3.74</td>
<td>13.88</td>
<td>17.14</td>
<td>13.31</td>
<td>2.83</td>
<td>20.56</td>
<td>20.78</td>
<td>1.55</td>
<td>1.73</td>
<td>0.00</td>
<td>4.48</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Final area 2</td>
<td>0.28</td>
<td>11.48</td>
<td>13.46</td>
<td>25.34</td>
<td>3.81</td>
<td>6.94</td>
<td>5.36</td>
<td>1.59</td>
<td>1.55</td>
<td>0.50</td>
<td>28.44</td>
<td>0.13</td>
<td>1.06</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3: SEM-EDX Analysis of the salt samples resulting during the leaching of the Fly ash 5 ash sample % w.b.

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>ZnO</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>SO$_3$</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts 1</td>
<td>26.63</td>
<td>16.10</td>
<td>8.00</td>
<td>0.65</td>
<td>3.39</td>
<td>0.52</td>
<td>1.53</td>
<td>2.40</td>
<td>33.95</td>
</tr>
<tr>
<td>Salts 2</td>
<td>25.12</td>
<td>16.09</td>
<td>0.00</td>
<td>7.44</td>
<td>1.62</td>
<td>0.00</td>
<td>0.86</td>
<td>6.41</td>
<td>34.37</td>
</tr>
<tr>
<td>Salts 3</td>
<td>0.45</td>
<td>nd</td>
<td>nd</td>
<td>41.77</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>53.53</td>
<td>2.79</td>
</tr>
<tr>
<td>Salts 4</td>
<td>1.38</td>
<td>2.68</td>
<td>nd</td>
<td>45.80</td>
<td>nd</td>
<td>nd</td>
<td>0.82</td>
<td>40.00</td>
<td>7.43</td>
</tr>
<tr>
<td>Salts 5</td>
<td>0.57</td>
<td>nd</td>
<td>nd</td>
<td>42.59</td>
<td>nd</td>
<td>0.19</td>
<td>0.43</td>
<td>55.37</td>
<td>0.54</td>
</tr>
<tr>
<td>Salts 6</td>
<td>1.50</td>
<td>nd</td>
<td>nd</td>
<td>40.62</td>
<td>nd</td>
<td>nd</td>
<td>2.68</td>
<td>53.67</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 4: SEM-EDX Analysis of various ash samples before and after the leaching treatment % w.b.

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>ZnO</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>Cl</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash 2. Initial</td>
<td>3.10</td>
<td>5.26</td>
<td>3.33</td>
<td>34.29</td>
<td>3.46</td>
<td>16.41</td>
<td>12.51</td>
<td>3.66</td>
<td>1.15</td>
<td>1.04</td>
<td>11.90</td>
<td>2.64</td>
<td>0.00</td>
</tr>
<tr>
<td>Fly ash 2. Final</td>
<td>0.96</td>
<td>1.48</td>
<td>3.93</td>
<td>40.20</td>
<td>3.83</td>
<td>14.40</td>
<td>8.50</td>
<td>3.87</td>
<td>1.09</td>
<td>2.33</td>
<td>15.54</td>
<td>0.49</td>
<td>3.16</td>
</tr>
<tr>
<td>Fly ash 3. Initial</td>
<td>5.50</td>
<td>7.81</td>
<td>8.16</td>
<td>25.92</td>
<td>3.23</td>
<td>10.61</td>
<td>6.59</td>
<td>2.61</td>
<td>1.66</td>
<td>1.78</td>
<td>22.65</td>
<td>2.38</td>
<td>0.00</td>
</tr>
<tr>
<td>Fly ash 3. Final</td>
<td>0.88</td>
<td>5.78</td>
<td>9.68</td>
<td>28.26</td>
<td>3.42</td>
<td>9.19</td>
<td>5.55</td>
<td>1.74</td>
<td>1.65</td>
<td>1.10</td>
<td>32.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fly ash 4. Initial</td>
<td>6.94</td>
<td>12.32</td>
<td>11.68</td>
<td>19.07</td>
<td>2.67</td>
<td>12.60</td>
<td>6.81</td>
<td>1.79</td>
<td>1.63</td>
<td>2.21</td>
<td>15.49</td>
<td>4.72</td>
<td>0.00</td>
</tr>
<tr>
<td>Fly ash 4. Final</td>
<td>0.79</td>
<td>9.26</td>
<td>16.38</td>
<td>23.31</td>
<td>2.13</td>
<td>10.54</td>
<td>7.25</td>
<td>2.95</td>
<td>2.14</td>
<td>1.94</td>
<td>21.80</td>
<td>0.00</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Fig. 1: Schematic diagram of the Svendborg MSW Incineration plant.

Fig. 2: SEM Morphology of the particles of various ash fractions resulted from the leaching of the Fly ash 5 ash sample: a) Initial 1, b) Initial 2, c) Final
Fig. 3: SEM-EDX analysis of the various ash fractions resulted during the leaching of the Fly ash 5 ash sample.

Fig. 4: SEM-EDX analysis of the various salt fractions resulted during the leaching of the Fly ash 5 ash sample.
Fig. 5: STA of various salt samples extracted during the six-stage leaching treatment of the Fly ash 5 ash sample: a) Salts 1, b) Salts 3, c) Salts 4, d) Total salts

Fig. 6: STA of various salt samples resulting after the six-stage leaching treatment of the various ash samples: a) Fly ash 2 salts, b) Fly ash 3 salts, c) Fly ash 4 salts