# Electrochemical upgrading of different ashes for use in production of bricks

**Chen, Wan**

*Publication date:*
2017

*Document Version*
Publisher's PDF, also known as Version of record

# Electrochemical upgrading of different ashes for use in production of bricks


Wan Chen

PhD Thesis

Department of Civil Engineering
2017

DTU Civil Engineering Report 380

DTU Civil Engineering
Department of Civil Engineering

# Electrochemical upgrading of different ashes for use in production of bricks

**PhD Thesis, 2017**

by

**Wan Chen**

Department of Civil Engineering
Technical University of Denmark

# Preface

The thesis “Electrochemical upgrading of different ashes for use in production of bricks” covers the research work that has been conducted from December 2012 to March 2017.

The task cannot be finished without the help from my supervisor Lisbeth M. Ottosen; co-supervisors Pernille E. Jensen, Gunvor M. Kirkelund and Jacob W. Schmidt; our lab technicians Ebba Cederberg Schnell, Malene Grønvold, Sabrina June Hvid and Natasja Rudbæk Eggertsen; and my PhD fellows Annemette Kappel, Barbora Krejcirikova, Bente Højlund Hansen, Ida Maria Gieysztor Bertelsen, Raimon Pares Viader and Zhaoyu Zhang. I would like to express my deep appreciation of all their help and support during my PhD study at the Technical University of Denmark, not only in the research work but also to make me feel at home.

First and foremost, I would like to express my sincere thanks to my supervisor, Prof. Lisbeth M. Ottosen, for her guidance and mentorship throughout my study. I am very lucky to have worked with her, and I have derived much benefit from her knowledge and good advices. Her encouragement, constant support, patience, kindness and understanding have always accompanied me during my PhD. In addition, I owe my gratitude to my co-supervisors for their encouragement, help and discussions regarding problems.

Part of the research work was conducted at the University of Aveiro (Portugal) under the supervision of Célia Maria Dias Ferreira. I would like to give my special thanks to her, for her valuable suggestions and help during my stay in Portugal. Thanks are also due to Rui Miguel Teixeira Novais and Marinélia de Neto Capela at the University of Aveiro for their help with my lab work.

My family and friends play an indispensable part in my life, always standing behind me, providing me assistance and support in times of trouble. I would like to thank my parents and my parents-in-law, for supporting me and taking the responsibility to take care of my son, Zimai Liu, and thank my husband for his unconditional commitment, love, dedication and compromise. Last but not least, my sincere thanks go to my best friend Ana Rita Ferreira for her encouragement and trust.

Denmark, March, 2017

Wan Chen

# Supervisors

**Lisbeth M. Ottosen**, Professor and Head of Section, Section of Arctic Engineering and Sustainable Solutions, Department of Civil Engineering, Technical University of Denmark

**Pernille E. Jensen**, Associate Professor, Section of Arctic Engineering and Sustainable Solutions, Department of Civil Engineering, Technical University of Denmark

**Gunvor M. Kirkelund**, Associate Professor, Head of Studies, Nordic Master in Cold Climate Engineering, Section of Arctic Engineering and Sustainable Solutions, Department of Civil Engineering, Technical University of Denmark

**Jacob W. Schmidt**, Associate Professor, Section for Building Design, Department of Civil Engineering, Technical University of Denmark

# Abstract

This PhD work deals with the upgrading and use of two kinds of ashes, bioash from co-combustion of wood/straw and fly ash from municipal solid waste incineration (MSWI), in the production of bricks. The overall aim is to use these secondary resources prior to natural resources, and by the upgrading to reduce adverse environmental effects caused by the brick making process and at the same time to have a high material quality of the bricks.

Two Danish bioashes from co-combustion of straw and wood were studied. They were collected from Enstedværket and Vordingborg Kraftvarme A/S, both combined heat and power plants. The bioashes had Cd concentrations of 9.0-9.7 mg/kg TS, which exceeds the limiting value of 5 mg/kg TS for the ash for agriculture purposes. The use of the ashes directly in brick production results in a loss of plant nutrients, mainly potassium. Potassium is generally present in the water-soluble fraction, which is in practice already being recovered from e.g. straw ash for use as fertilizer by water leaching and other chemical treatments to precipitate dissolved heavy metals prior to use. The scope of this PhD work is on using the water washed ash as resource.

The water washed bioashes had a Cd concentration varying between 20 and 67 mg/kg TS. The enrichment of other heavy metals, such as As, Cr, Ni, Pb and Zn, was also observed due to the high ash dissolution ranging from 75% to 88% of the initial mass. Considering the enrichment effect of water washing on heavy metals, recycling of the washed bioashes is problematic from an environmental point of view. Removal of heavy metals from the washed ashes was carried out by electrodialytic remediation (EDR). The results showed that the Cd bound in the two studied bioashes was EDR extractable. After 10-14 days electrodialytic extraction, the Cd concentration in both the raw and the washed ashes originating from Enstedværket CHP was reduced to below 2 mg/kg (with removal rate >95%); and, after 7 days EDR, the Cd concentration in the washed bioash originating from Vordingborg CHP was reduced from 63.7 to 21.4 mg/kg TS. Pb had a removal rate ranging between 12% and 67% from the Enstedværket CHP ash, which shows that Pb in the bioashes was harder to remove than Cd. A two-compartment electrodialytic cell with anode placed in the ash suspension was tested and facilitated the extraction of Pb by creating a faster acidification process. The results showed that prewash with water before EDR stabilized the ash properties, and the removal of Cl resulted in good separation of e.g. Cd, Pb and Ni by hindering the formation of chlorine complexes. The XRD analysis showed that the ashes from Enstedværket CHP underwent dramatic changes in the main mineral compositions: from KCl and $K_2SO_4$ in the raw ashes, to quartz and carbonates and sulfates after water washing, and finally to mainly quartz in the ashes after EDR treatment.

In relation to the use of the treated bioashes in the production of bricks at sintering temperature 1000 °C, substituting 25% clay in the small brick pellets (~2 g) with the washing-EDR treated bioashes resulted in pellets with higher porosity, higher water absorption, and less total

shrinkage compared to the pure clay pellets. The water absorption of the pellets increased with increasing ash content, but decreased with increasing sintering temperature. Increasing sintering temperature also led to the decrease in porosity and the increase in bulk density. In addition, by increasing sintering temperature the leaching of heavy metals from the fired pellets containing bioash, in particular As and Cr, could also be minimized to a level that allows the clay pellets to be reused or landfilled as nonhazardous waste at the end of service life. The bricks also had good material qualities. For instance, when fired at 1100 °C for 1 h, the pellets with 25% treated fly ash from Enstedværket CHP met the water absorption requirement for building bricks in accordance with ASTM C62-13a. When fired at 1100 °C, the pellets with 20% treated ash from Vordingborg CHP showed acceptable leaching of heavy metals such as As, Cd, Cr, Ni, Pb and Zn, allowing the bricks to be used in construction work. The use of the bioashes in the production of clay bricks is technically possible, after being treated first by water washing to extract plant nutrients, and then by EDR to extract easily mobilized Cd and the mobile fraction of other heavy metals to lower the leaching to acceptable low levels.

The recycling of MSWI fly ash faces challenges from technical, legislative, environmental and economical aspects. Thus, identifying options allowing use of the resources retained in the ash is necessary. Direct use of MSWI fly ash in the production of bricks leads to air pollution (e.g. the emission of volatile heavy metals) and the loss of metal resources (e.g. Zn), and also causes heavy metal leaching from the bricks themselves.

Zn was the metal with the highest concentration in the MSWI fly ash studied, followed by Pb. Water washing was also applied to remove the soluble salts in the MSWI fly ash in the present work. Approximately 19% of the ash was dissolved in water. It was found that Pb and Zn had relatively higher concentrations in the leachate after washing than the other heavy metals, probably due to the presence of chlorine complexes of Pb and Zn in the ash.

The raw MSWI fly ash and the washed ash were alkaline; whereas EDR could lower pH to the acidic range, resulting in elevated leaching of Cd and Zn after EDR. At same time, the Cr leaching could be reduced, which was related to the pH and redox potential of the treated ash. Up to 59% of Zn and 6% of Pb were extracted by EDR for 7-12 days compared to less than 0.6% extraction by water washing. However, the extraction of Cr was generally low, because Cr was strongly bound in the ash. The major fraction of Cr remained bound in the ash even after different EDR treatments including one, two and three step treatments, involving ash suspension alkalization by the cathode reaction and acidification by the anode reaction and/or water splitting. The Cr extraction rate was improved by combining different electrodialytic cells to achieve first acidification (especially to pH below 4) and then alkalinity generation. The improvement was mainly due to the combined extraction of Cr(III) at low/oxidizing condition

(e.g. anode reaction taking place in the ash suspension) and extraction of Cr(VI) at high pH/reducing condition (e.g. cathode reaction taking place in the ash suspension).

Thermal treatment was conducted on the pure EDR-treated ash at 1000 °C for 1 h. The results showed that during thermal treatment the slightly acidic to neutral ashes (pH 5-6.5) were re-alkalized. The thermal treatment reduced the leaching of most heavy metals by solidification, and possibly also by evaporation; however, the leaching of As and Cr were still problematic and did not meet the limiting values for the ash being reused in construction work. It was found that the removal of Ca by EDR resulted in a decrease in the leaching of Cr after thermal treatment, but an increase in As leaching. However, minimizing leaching from the thermally treated ash (especially of Cr) could be obtained when optimizing the combined water washing and EDR prior to the thermal treatment. In addition, the evaporation of especially Pb during thermal treatment was significantly reduced by water washing and EDR pre-treatment.

Handmade bricks (50 mm × 50 mm × 50 mm) incorporating the MSWI fly ash treated after water washing and EDR, had higher porosity, lower compressive strength and higher soluble salts content compared to the 100% clay brick when sintered at 1000 °C for 6 h. Still the washing-EDR treatment significantly improved the properties of the fired fly ash-clay bricks compared to the properties of the bricks incorporating the untreated ash. The results indicated that the MSWI fly ash could be fit for the studied clay replacement at low substitution ratio i.e. 5%, as the bricks with this substitution met the technical requirements for bricks (properties: weight loss during firing 11.3%; density 1.63 g/cm$^3$; apparent porosity 41%; water absorption 25.5%; and compressive strength 8 N/mm$^2$). The leaching of heavy metals from all the bricks with ash content up to 20% sintered at 1000 °C for 6 h met the requirement for landfilling as mineral waste. Even better was that the fly ash-clay brick with 5% ash content might be reused in construction work at the end of service life as the heavy metal leaching was low enough to allow this, and thus these bricks could be reused directly. Even though washing-EDR treatment reduced the Cr leaching from the fired bricks compared to that from the bricks with the untreated ash, the fine fraction in the ash was shown to significantly contribute to the leaching of Cr. Thus, fractionation of the treated MSWI fly ash was beneficial to its recycling in particular of the less toxic fraction.

# Resume

I denne PhD afhandling udvikles tekniske løsninger til opgradering af to typer asker, en fra biomasseforbrænding og en fra affaldsforbrænding, til anvendelse i teglproduktion. Formålet er at kunne producere teglsten som både er miljømæssigt forsvarlige at anvende og som har materialeegenskaber af høj kvalitet, når disse opgraderede asker anvendes som sekundære ressourcer i produktion af tegl.

To danske bio-asker fra samforbrænding af halm og træ er undersøgt. Askerne var fra Enstedværket og Vordingborg Kraftvarme A/S, begge er kombinerede varme- og kraftværker. Askerne havde en koncentration af Cd på 9.0-9.7 mg/kg TS, hvilket overskrider grænseværdien på 5 mg/kg TS som er gældende for samfyringsaske fra halm og træ, der kan anvendes til landbrugsmæssige formål. Anvendes bio-askerne direkte i murstensproduktion, vil det resultere i et tab af de næringsstoffer som findes i askerne, primært Kalium. I bio-asker findes kalium hovedsagelig i vandopløselige salte, og kan i praksis allerede udvindes fra f.eks. halmaske. K ekstraheres og anvendes som gødning ved at vaske asken med vand, mens tungmetallerne fældes kemisk. Dette projekt fokuserer på at anvende den vaskede askefraktion som ny ressource.

Cadmium koncentration i de vaskede asker var mellem 20 og 67 mg/kg TS. En opkoncentrering af andre tungmetaller i asken efter vask blev ligeledes observeret pga. askens høje vandopløselighed, som var i størrelsesordenen hhv. 75 % og 88 % af den oprindelige masse. Fjernelse af tungmetaller fra de vaskede asker blev udført ved elektrodialytisk rensning (EDR). Resultaterne viste, at Cd kunne ekstraheres vha. EDR, således at den ønskede lave koncentration var opnået. Efter 10-14 dages EDR var koncentrationen af Cd i både de uvaskede og vaskede asker fra Enstedværket reduceret til under 2 mg/kg (med en rensningsgrad > 95 %). Efter 7 dages EDR var koncentrationen af Cd i den vaskede aske fra Vordingborg Kraftvarme reduceret fra 63.7 til 21.4 mg/kg TS. En rensningsgrad mellem 12 % og 67 % for Pb for askerne fra Enstedværket indikerer, at Pb var sværere at mobilisere sammenlignet med Cd. Resultaterne indikerede generelt at askens egenskaber stabiliseredes, når asken blev vasket, samt at fjernelsen af Cl formentlig resulterede i en god separation under EDR af bl.a. Cd, Pb og Ni ved at forhindre dannelse af klorforbindelser. XRD-analysen viste, at askerne fra Enstedværket undergik betydelige ændringer i mineralsammensætningen; fra overvejende KCl og $K_2SO_4$ i de ubehandlede asker, til kvarts og karbonater og sulfater efter vask; og endeligt til primært kvarts i askerne efter EDR behandlingen.

De vaskede og efterfølgende EDR behandlede bioasker blev testet som erstatning for ler i teglproduktionen. Små murstensprøver (~2g) sintret ved 1000°C og fremstillet af 25 % substitution af ler med vasket og EDR behandlet bioaske, resulterede i højere porøsitet, højere vandabsorption og mindre totalt svind sammenlignet med små murstensprøver af rent ler. Vandabsorptionen af teglprøver steg med stigende askeindhold, men faldt med stigende sintringstemperatur. Stigende sintringstemperatur førte også til et fald i porøsiteten samt en stigning a bulk densiteten. Ved at øge sintringstemperaturen var det også muligt at minimere udvaskningen af tungmetaller fra de brændte teglprøver indeholdende bioaske, såsom især As og Cr, til et niveau så det er muligt at genanvende asken i teglproduktion. Teglprøver brændt ved 1100 °C i 1 time med 25 % behandlet aske fra Enstedværket viste f.eks. at disse kunne opfylde kravene for mursten beskrevet i ASTM standard C62-13a. Murstensprøverne med 20 % behandlet aske fra Vordingborg Kraftvarme brændt ved 1100 °C viste acceptable mængder af tungmetaller såsom As, Cr, Cd, Ni, Pb og Zn i forhold til at blive anvendt i byggematerialer. Genanvendelse af bioasker i produktionen af mursten er teknisk set mulig efter askerne er behandlet, ved at kombinere vask af askerne for at ekstrahere kalium, og derefter EDR for at fjerne tungmetaller.

Genanvendelse af flyveaske fra affaldsforbrænding (affaldsaske) møder både tekniske, lovgivningsmæssige, miljømæssige og økonomiske udfordringer, hvorfor det er vigtigt at identificere mulige anvendelser for de ressourcer som affaldsaskerne indeholder. Direkte anvendelse af affaldsaske i produktionen af tegl leder til luftforurening pga. fordampningen af ustabile tungmetaller under produktionen af teglstenene, tab af metalliske ressources som f.eks. Zn, og uacceptabel udvaskning af tungmetaller fra tegl pga. tilsvarende højt tungmetalindhold i affaldsaskerne.

Zink og bly er de tungmetaller med den højeste koncentration i den undersøgte affaldsasker. Vask af affaldsasken med vand blev anvendt til at fjerne opløselige salte. Omkring 19 % af asken var vandopløselig. Der blev fundet en højere koncentration af Zn og Pb i skyllevandet end af de andre målte tungmetaller, hvilket formentlig er pga. klorkomplekserne af Pb og Zn i asken.

Den rå og den vaskede affaldsaske var begge basiske, hvorimod EDR behandling af den vaskede affaldsaske kunne sænke pH'en fra basisk til sur. Dette medførte en øget udvaskning af Cd og Zn. Udvaskning af Cr kunne reduceres, hvilket var relateret til pH og redoxpotentialet af den behandlede aske. Op til 59 % af Zn og 6 % af Pb blev fjernet ved EDR i 7-12 dage. Til sammenligning blev under 0.6 % af disse metaller fjernet fra affaldsasken kun ved vask. Generelt var fjernelsen af Cr lav, eftersom den var stærk bundet i asken. Den største fraktion af Cr forblev bundet i asken selv efter forskellige EDR behandlinger såsom en-, to- og tretrinsbehandlinger, som involverede basedannelse i askesuspension ved katodereaktionen og

forsuring af suspensionen ved anodereaktionen. Ekstraktionsgraden af Cr steg ved at kombinere forskellige EDR celler for først at opnå en forsuring (specielt til en pH under 4) og dernæst ved at øge pH ved basedannelse. Forbedringen var primært relateret til den kombinerede udtrækning af Cr(III) ved lav pH/oxiderende forhold (f.eks. når anodereaktionen sker i askesuspensionen) og udtrækningen af Cr(VI) ved høj pH/reducerende forhold (f.eks. når katodereaktionen sker i askesuspensionen).

Termiske behandlinger af EDR-behandlede affaldsasker ved 1000°C i 1 time viste, at affaldsasker med pH 5-6.5 blev re-alkaliseret under EDR-behandlingen. Den termiske behandling reducerede udvaskningen af de fleste tungmetaller ved sintring og muligvis også ved fordampning. Dog var udvaskningen af As og Cr stadig problematisk høj og mødte ikke grænseværdierne for mulig genanvendelse i byggematerialer. Det blev vist, at fjernelsen af Ca ved EDR resulterede i et fald i udvaskningen af Cr efter termisk behandling, men en stigning af udvaskningen af As. En lavere udvaskning, specielt for Cr, kunne opnås med vask, elektrodialytisk separation og termisk behandling. Ydermere var fordampning af særligt Pb under den termiske behandling betydelig reduceret ved kombination af vask og EDR behandling.

Små mursten (50 mm × 50 mm × 50 mm) med inkorporering af affaldsaske, som var behandlet med en kombination af vask og EDR, havde højere porøsitet, lavere trykstyrke og højere indhold af opløselige salte i forhold til en mursten bestående af 100 % ler. Dette selv om vask og EDR behandlingerne forbedrede egenskaberne af den termisk behandlede flyveaske anvendt i mursten i forhold til mursten indeholdende ubehandlet aske brændt ved 1000°C i 6 time. Udvaskningen af tungmetaller fra mursten, indeholdende optil 20% affaldsaske sintret ved 1000 °C i 6 timer, overholdt grænseværdierne for deponi som mineralsk affald. Murstenene med 5 % askeindhold var egnede som byggemateriale, da tungmetaludvaskningen var lav nok til dette, og de tekniske egenskaber var gode. Selv om vask og EDR behandling reducerede Cr udvaskningen fra mursten i forhold til mursten med rå affaldsflyveaske, viste det sig, at Cr udvaskningen fra den fine fraktion af affaldsasken var høj. Derfor vil en fraktionering af den behandlede affaldsaske være gavnlig for at øge genanvendelsespotentialet.

# Contents


1. Introduction and background *1*

2. Electrodialytic remediation of fly ash from co-combustion of wood and straw *27*

3. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash *39*

4. A comparative study on electrodialytically treated bioash and MSWI APC-residue for use in bricks *53*

5. Incorporation of EDR-treated ash from co-combustion of straw and wood chips into clay pellets – leaching of heavy metals *71*

6. Recycling of MSWI fly ash in clay bricks – effect of washing and electrodialytic treatment *85*

7. Electrodialytic extraction of Cr from washed MSWI fly ash by changing pH and redox conditions *111*

8. Additional note to Chapter 7 – As extraction *145*

9. Conclusions *151*

# Chapter 1

*Introduction and background*

# Introduction and background

As the title of this thesis says, this Ph.D project covers two main tasks, upgrading the studied ashes and utilizing the upgraded ashes in the production of bricks.

***Why is it important to upgrade the ash residues?***

The ash residues studied are residual waste from the waste-to-energy sectors after recovery of heat and power from biomass and municipal solid waste, namely bioash and MSWI fly ash. These ashes, the hazardous in particular, are usually excluded from recycling in society and are regarded as residual waste in the context of circular economy (Figure 1). At present, controlled landfilling or backfilling in mines is the most common way to dispose these unrecyclable ashes. The ashes do, however, contain resources, which are lost in this current practice. The bio fly ash (from wood and straw combustion), for instance, contains plant nutrients, and the MSWI fly ash contains metals, which are becoming scarce. Moreover, the ash particles themselves might be recovered as a secondary material resource. Therefore, investigation on upgrading ash residues attempting to recover elemental resources and to detoxify the ash itself is believed to be of importance in transforming the ash from a residue, for which the current option is landfill, to useful resources, which could go back into the materials circle in a circular economy.

***Why are the ashes utilized in the production of bricks?***

There are no implemented environmentally safe applications for hazardous bioashes and MSWI fly ash, though quite intensive research has been conducted. Use in ceramic bricks is one of the research areas, by taking advantage of the $SiO_2$-$Al_2O_3$-CaO system in the ashes. Sintering is critical to brick production, and it is also important in thermal treatment of ashes. Thermal treatment is one of the three main groups of techniques under development for MSWI fly ash treatment; the two others being separation/extraction and solidification/stabilization. Sintering of MSWI ash generally lowers the leaching of heavy metals, but this is often not the

case for As and Cr. Thus the question appears if acceptable leaching levels can be obtained for all heavy metals in case the ash is pretreated before the sintering? The response and the utilization of the ashes after different upgrading processes prior to thermal treatment in ceramic bricks appears to be a knowledge gap to fill. Understanding the pretreatment(s) and the following thermal treatment is important to convert the toxic ashes to resources for the production of sintered clay-ash bricks.


Figure 1. Simplified model of the circular economy. (Source: European Parliament)

## 1. Bioash

Denmark has committed itself to reducing the greenhouse gas emission to share the European Union goal, by 20% by 2020 compared to 2005 (European Parliament and the Council of the European Union, 2009). In addition, the Danish government has set the goal of making Denmark independent of fossil fuel by 2035 in electricity and heat supply, and phasing out of fossil fuel in its whole energy system (electricity, heat, industry and transport) by 2050 (THE DANISH GOVERNMENT, 2011). The share of renewable energy must increase to meet the goals. Figure 2 shows the development of the shares (historical and projected) of different renewable energy sources in primary energy consumption in Denmark from 2000 to 2020. A significant increase in use of biomass is foreseen in Figure 2. Accordingly, conversion from

coal to biomass (mainly wood) has been promoted in power plants, and the conversion is undergoing in many plants these years (ENERGINET, 2017).

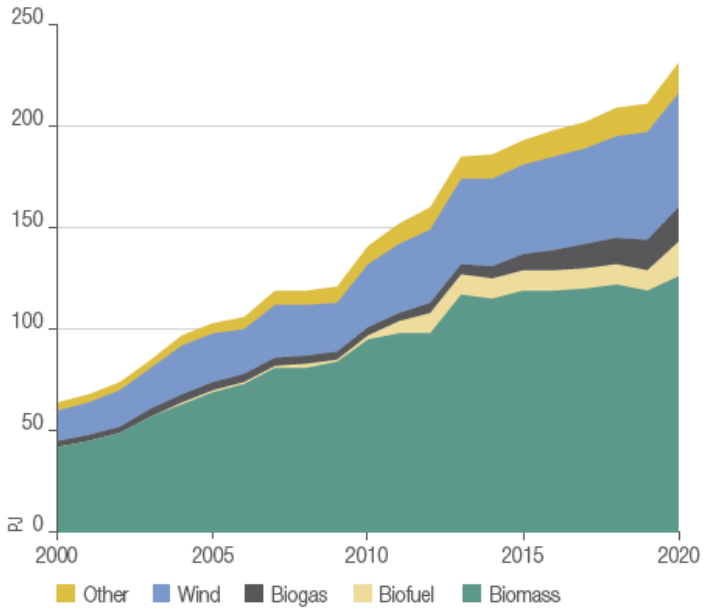


Figure 2. Renewable energy in primary energy consumption 2000-2020. (Danmark. Regeringen., 2011)

Bioashes (from wood and straw) generated from biomass power plants contain plant nutrients, but also heavy metals (especially Cd (Reijnders, 2005)). The heavy metal content (Hg, Pb, Ni, Cr and Cd) plays a decisive role in the application of bioashes for agricultural purposes as fertilizer. In Denmark, bioash can be spread on land field, but only if the heavy metal contents fulfill the limits (as shown in Table 1) regulated in Danish Decree BEK nr 818 (2008). Currently, bio fly ashes are most commonly stored in waste deposits.

Unlike coal fly ash being valued in concrete production, biomass fly ash exceeding the limits in Table 1 does not have any identified beneficial use, and is thus a waste challenge. On the other hand, the high alkali and chloride content and the low alumina content in bioashes do not fulfill the standards for their recycling in concrete (Dodson, 2011). Researchers have studied the use of bioashes for application in ceramics, suggesting that bioashes such as rice husk ash (Sutas et al., 2012), sugarcane bagasse ash (Kazmi et al., 2016) and wood ash (Eliche-Quesada

et al., 2017) could be used as substitute for clay in the production of bricks, and that rice straw ash could be used as silica source in the production of glass ceramics (Ruangtaweep et al., 2013). Accordingly, the bioashes studied in the present work from co-combustion of straw and wood may be used to produce clay-based ceramics such as bricks.

The direct use of bioashes in brick production, however, results in a loss of plant nutrients, mainly potassium. Potassium is mainly present in the water-soluble fraction, which in practice can be recovered from e.g. straw ash for use as fertilizer by water leaching and other chemical treatment to precipitate unwanted heavy metals already dissolved in the liquid fertilizer (Nikolaisen et al., 2008). The bioashes after potassium extraction may be recycled in bricks, but the concentration of heavy metals in the bioashes can cause concern to their recycling. Thus, extracting heavy metals from the bioashes after potassium recovery, is necessary, before the ashes can be used in the brick production in an environmentally safe way.

Table 1. Limiting concentrations of heavy metals in bioash for agricultural purposes. (BEK nr 818, 2008)

| Heavy metal | Limit (mg/kg TS) |
|---|---|
| Hg | 0.8 |
| Pb | |
| - general | 120 |
| - for wood ash used in forestry | 250 |
| Ni | 60 |
| Cr | 100 |
| Cd | |
| - for straw ash and mixed straw and wood ash | 5 |
| - for wood ash | 20 |

## 2. MSWI fly ash

As an alternative to landfilling, recycling, composting and incinerating of waste have gradually played an increasingly important role in waste management in EU. It can be seen from Figure 3 that in 2014 the landfill rate of waste in 9 of the given countries was more than 60%. In the countries with landfill rate less than 10%, the waste recycling rate (including composting and digestion) varied between 37% and 64%. The incineration rate in Denmark (54%) was twice the average rate in EU in 2014.

Waste-to-energy (especially referring to incineration) plays three important roles in residual waste management: reduction in the amount of waste going to landfills, production of energy from residual waste and reduction in greenhouse gas emissions from combustion of fossil fuels. However, waste incineration is foreseen to play a less important role in the future, because we must recycle more and incinerate less according to the resource strategy 'Denmark without waste', where the targets for recycling have been set: recycling 50% of household waste by 2022 (22% in 2013); energy recovery from 25% of garden waste by 2018 (4% in 2013); recycling 70% of paper, cardboard, glass, metal and plastics packaging from the service sector by 2018 (53% in 2013); recycling 60% of organic waste for biogas production by 2018 (about 17% in 2013); and more recycling from waste electronic equipment, shredder waste and construction and demolition waste.

Even though waste incineration is decreasing in Denmark in the years to come, it will still be the option for the non-reusable waste fractions, and thus landfilling or backfilling with these ashes from incinerators continuously means a substantial loss of resources found in the MSWI ash.

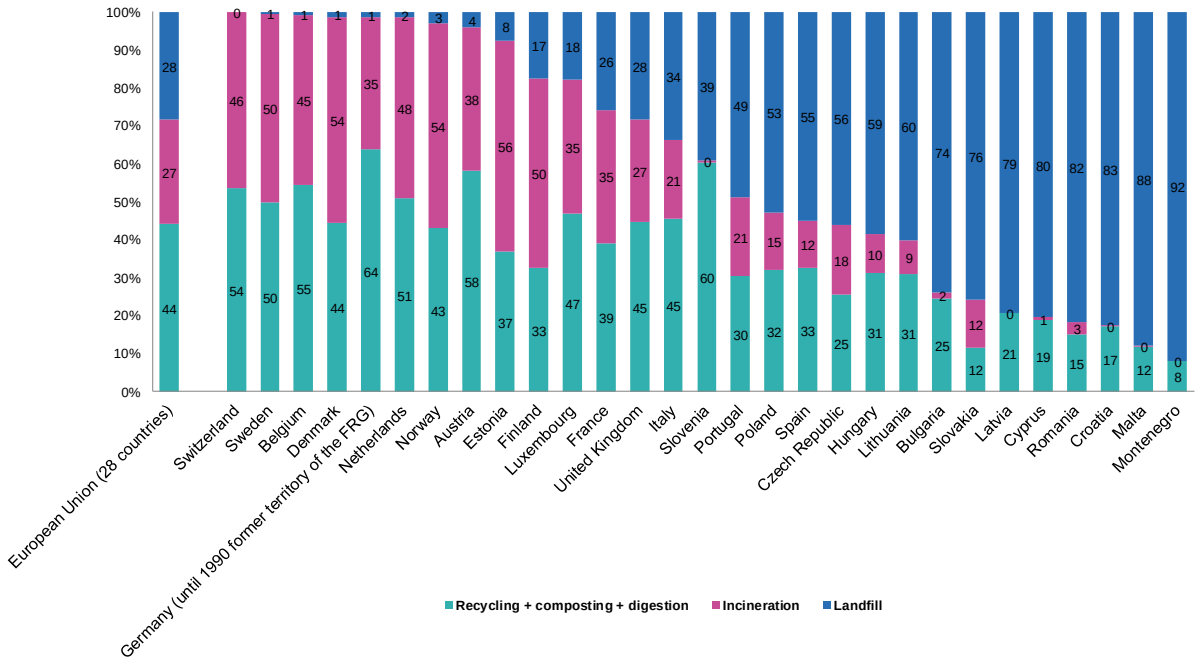


Figure 3. Municipal waste treatment in 2014 (data source: EUROSTAT [env_wasmun]).

Recycling of MSWI fly ash is motivated by the expensive fee for ash disposal due to the legislative requirements (Zacco et al., 2014) and by the goal to reduce the depletion of natural resources (Margallo et al., 2015). In general, MSWI fly ash is landfilled after stabilization, but such handling always means a potential for emissions of toxic substances to the environment. In some cases, MSWI fly ash or air pollution control (APC) residues are utilized; for instance, the Danish MSWI fly ashes and APC residues are currently exported to Norway and Germany for utilization in waste acid neutralization and salt mine backfilling. This practice, however, means a loss of potential resources, which could be used in the production of new materials.

Margallo et al. (2015) reviewed the options for handling of MSWI residues, both bottom and fly ashes. They noted that the MSWI residues mainly consist of oxides (CaO, $SiO_2$ and $Al_2O_3$) with high content of toxic metals, in particular lead and zinc. Both Margallo et al. (2015) and Ferreira et al. (2003) gave overviews of the possible applications of MSWI fly ash, such as in construction materials (concrete, cement and ceramics), as absorbent, as well as for geotechnical purposes (road pavement and embankment). According to Margallo et al. (2015), the use of MSWI fly ash is less common than the use of MSWI bottom ash, such as in the production of building ceramics. This is due to the content of soluble salts and volatile components, which can cause problems during the manufacturing process. High chloride content increases the evaporation of heavy metals (e.g. Cd and Pb) (Jakob et al., 1996) and causes emissions to the environment in case no flue gas purification system is applied at the brickwork. The chlorides also have the negative effect on the produced bricks, as it may cause cracks on the surface of the ash-clay bricks (Zhang et al., 2011).

As Margallo et al. (2015) stated, the use of MSWI fly ash in the production of fired clay bricks is not common. There are a limited number of studies (Belmonte et al., 2016; Lee et al., 2009; Lin, 2006; Zhang & He, 2013; Zhang et al., 2011) *(5 publications since 2006 found using the keywords 'MSWI ash; clay brick' in the Scopus database)* on the incorporation of MSWI fly ash in clay bricks. Lin (2006) stated that MSWI slag, which was produced by melting the

MSWI fly ash at 1400 °C for 30 min, was suitable for the partial replacement of clay in bricks. The melting process has been applied in practical operation at full-scale melting plants of MSW incinerator residues in Japan (Sakai and Hiraoka, 2000). MSWI slag addition of up to 40% into the bricks (optimal temperature 800 °C, firing for 6 h, molding under 60 kg/cm$^2$ of pressure to form 50mm(L)×25mm(W)×50mm(H) bars) led to similar compressive strength to that of normal clay bricks, which was very promising. Zhang et al. (2011) did not pre-treat the MSWI fly ash, but mixed the ash directly with red ceramic clay, feldspar and gang sand (one kind of aggregates) to make bricks by press molding. They found that the optimal condition for incorporating the MSWI fly ash into brick was: 20% MSWI fly ash, 60% red ceramic clay, 10% feldspar and 10% gang sand in the raw material mixture by weight; and sintering temperature 950 °C. Even though, as is described by Lin (2006) and Zhang et al. (2011), the mechanical/technical properties of MSWI fly ash-clay brick can meet the requirements of different building materials, the recycling of MSWI fly ash is still challenged by legislative and environmental issues (e.g. leaching and radiation).

MSWI fly ash is a hazardous material, and the recycling of hazardous materials is questionable considering the existing regulatory constraints. According to Waste Framework Directive 2008/98/EC (European Commission, 2008), hazardous compounds are encouraged to be separated from the waste streams to be used as resources; and care should be taken in the management of hazardous wastes in order to achieve environmentally sound management. Some excerpts of the articles in Waste Framework Directive 2008/98/EC related to end-of-waste status and hazardous waste (European Commission, 2008) are shown as follows:

*Article 6 point 1*: *'Certain specified waste shall cease to be waste within the meaning of point (1) of Article 3 when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions: (a) the substance or object is commonly used for specific purposes; (b) a market or demand exists for such a substance or object; (c) the substance or object fulfils the technical requirements for*

*the specific purposes and meets the existing legislation and standards applicable to products; and (d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.'*

*Article 7 point 4*: *'The reclassification of hazardous waste as non-hazardous waste may not be achieved by diluting or mixing the waste with the aim of lowering the initial concentrations of hazardous substances to a level below the thresholds for defining waste as hazardous.'*

*Article 18 point 2*: *'Member states may allow mixing provided that: (a) the mixing operation is carried out by an establishment or undertaking which has obtained a permit from the competent authority; (b) the adverse impact of the waste management on human health and the environment is not increases; and (c) the mixing operation conforms to best available techniques.'*

Thus removal/recovery of toxic substances from MSWI fly ash may result in an ash product, which subsequently can be mixed into clay for utilization in brick production from a legislative point of view.

Besides technical, legislative and environmental challenges when treating MSWI fly ash, there is also a challenge from the economical aspect. Huang et al. (2016) conducted life-cycle assessment (LCA) and cost-benefit analysis (CBA) to evaluate the environmental and cost impacts of four different applications of (water-washed) MSWI fly ash: landfill after stabilization/solidification, reuse as part of raw material in a cement kiln, reuse in brick and reuse as a substitute alkali reagent in the Waelz process (a process for recovering Zn from typically electric arc furnace (EAF) ash). The environmental impacts were divided into four categories: human health, ecosystem quality, climate change and resources. The cost analysis only included that for energy, personnel and other operating expenditure. By doing both LCA and CBA analysis, Huang et al. (2016) found that MSWI fly ash landfill after stabilization/solidification had the highest integrated environmental and cost impacts; whereas

the use as alkaline in the Waelz process had the lowest. In relation to the two options related to construction materials, use in bricks had lower integrated impacts compared to use in cement production, even though the brick making process is highly energy-consuming. Amongst all the selected environmental impacts, air pollution related to the furnace emission was found to account for 57% of the total impact from the option concerning brickmaking.

Even though the reuse of MSWI fly ash faces challenges from technical, legislative and environmental and economical aspects, research is highly important on identifying options, which allow the use of the resources retained in the ash, in order to lead these ashes back into the materials cycle (Figure 1) rather than being residual waste. Investigations are necessary on detoxifying the ash, recovering potential resources from the ash, and simultaneously dealing with the content of soluble salts, heavy metals and volatile components in the ash before being reused in bricks or other materials.

## 3. Heavy metal extraction

Most heavy metals are extractable at low acidic pH. Therefore, acidic chemical solutions, such as HCl, nitrilotriacetic acid and ethylenediaminetetraacetate (EDTA) (Hong et al., 2000), have been studied to extract heavy metals from MSWI fly ashes. However, the residual extractant on the ash and the toxicity of the extractant are some of the biggest concerns as to chemical extraction. The extractant left on the ash needs to be treated and/or removed. In this regard, electrodialytic remediation (EDR) was chosen in the present work, which achieves heavy metal extraction and separation but does not introduce new chemical compounds or elements into the ash during treatment.

Different electrodialytic remediation (EDR) methods have been developed at the Technical University of Denmark since the 1990s. The methods have been applied for remediation of heavy metal polluted soils (Ottosen et al., 1997), mine tailings (Hansen et al., 2005), harbour sediment (Nystrøm et al., 2006), ash residues and wastewater sludge (Ottosen

et al., 2007) etc.. This electrodialytic technique can either be applied alone or in combination with pre-treatment methods, such as water washing (Pedersen, 2003) and (wet) sieving (Jensen et al., 2007). A stirring EDR system, where the material to be treated is suspended in water or an extractant solution during the treatment, was found to be more stable than a static system (treating materials in humid/wet-satuated state without stirring) in the treatment of ash residues (Pedersen, 2003). The high dissolution of ash samples causes operational problems such as poor electrical contact between ash and membranes in the static system, and this problem was solved by suspending the ash. To achieve heavy metals simultaneous extraction and separation from ash suspension, an electric direct current is applied to the EDR cell used for ash treatment, and in electric field mobile heavy metals in the suspension consequently migrate towards either the anode or cathode through ion exchange membranes.

*Different EDR setups*. Lab-scale electrodialytic cells used for ash treatment can have two (Fig. 4a and b), three (Fig. 4c) or five (Fig. 4d) compartments. A two compartment (2C) cell has an anode and a cathode compartment separated by a cation exchange membrane, as is illustrated in Figure 4a. The distilled water-ash suspension to be treated is placed in the anode compartment (Kirkelund et al., 2015). A two compartment cell can also have an anode and a cathode compartment separated by an anion exchange membrane (Figure 4b), and this cell is used later in this study. A three-compartment (3C) cell (Figure 4c) has an anode compartment, a center compartment and a cathode compartment separated by a pair of cation and anion exchange membranes. The anode and cathode compartments contain electrolyte solutions, and the ash suspension to be treated is placed in the center compartment. The three-compartment cell is the one most often chosen. A five-compartment cell has two separate electrode compartments, two electrolyte compartments plus one ash-suspension compartment (Figure 4d). In the five-compartment cell the electrode processes are separated from the electrolyte solutions so e.g. chloride will not reach the anode where toxic chlorine gasses could be produced and the heavy metal cations are prevented from electroprecipitating at the cathode.

When electricity is passed through an electrodialytic cell, water is electrolyzed to hydrogen ions and oxygen at the anode and to hydroxyl ions and hydrogen at the cathode. The current is carried by ions, which either are in the suspension originally or which are produced as the ash dissolves during EDR. The cations electromigrate towards the cathode end, and anions to the anode end.

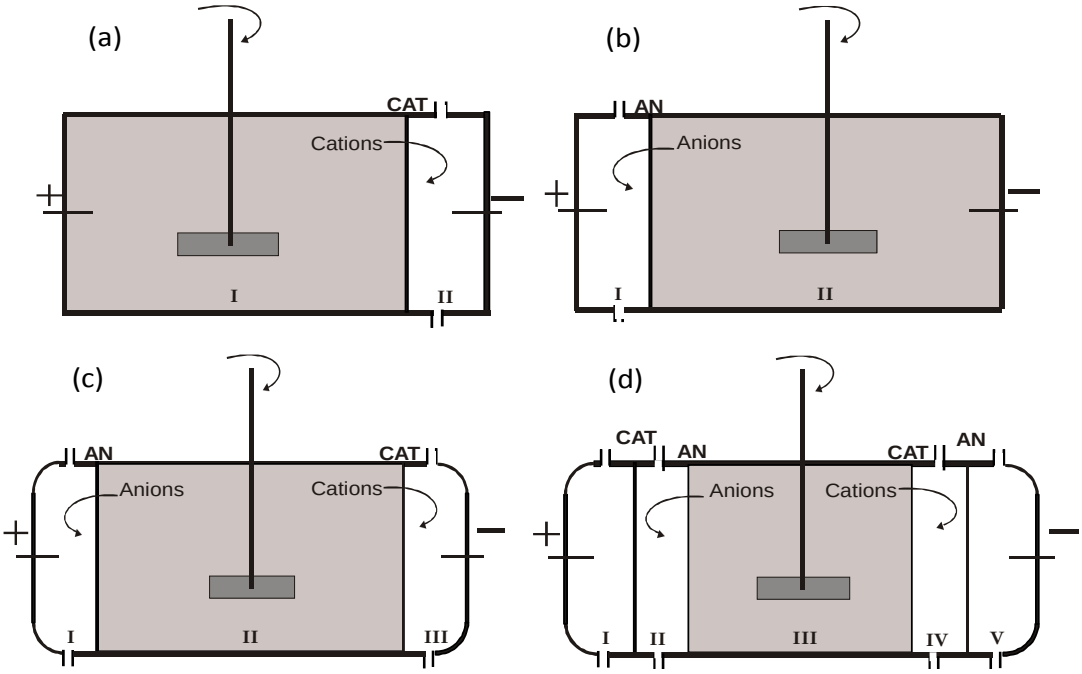


Figure 4. Setups of electrodialytic cells. (AN: anion exchange membrane; CAT: cation exchange membrane).

### *3.1. Bioash*

Investigations of EDR treatment of both straw ash and wood ash have been carried out, with special focus on Cd extraction (Ottosen et al., 2007; Pedersen, 2003). Migration of Cd to either anolyte or catholyte during EDR is mainly associated with prevalent Cd-Cl complexes: anionic species ($CdCl_3^-$ and $CdCl_4^{2-}$), cationic species ($CdCl^+$ and $Cd^{2+}$) and uncharged species ($CdCl_2$), in the solution of the ash suspension. The Cl concentration in the ash is thus determining the distribution between different valence states of the Cd-Cl species. Pedersen (2003) proved that prewashing was beneficial for electrodialytic treatment of wood combustion fly ash, which contained a high amount of soluble salts. However, heavy metal extraction from bioash or prewashed bioash has only been studied using three-compartment EDR setup. Considering the depletion of chloride from the ash during prewashing, the chloride complexes

are not significant when EDR treating the washed ash. Instead cationic Cd species are prevailing in the solution. Moreover, as Cd is most soluble at acidic pH, the two-compartment electrodialytic cell is probably a good option. Thus this option is investigated in the present study, taking advantage of the faster acidification of ash suspension.

### *3.2. MSWI fly ash*

EDR has also been investigated to treat MSWI fly ash, e.g. by Ferreira et al. (2004), Pedersen et al. (2005), Ottosen et al. (2006) , Jensen et al. (2015) and Kirkelund et al. (2015). Table 2 presents the previous researches on EDR extraction of heavy metals and chloride from the MSWI fly ashes collected from the same incineration plant as in the present study. The works presented in Table 2 cover the application of different electrodialytic cells and the treatment of ash suspension with or without using enhancement agent. In addition to lab-scale tests, an ion-exchange membrane system has been tested in pilot scale on the treatment of MSWI air pollution control (APC) residues (Jensen et al., 2014). As aforementioned in subsection 2, soluble salts and heavy metals are main concerns related to air pollutant emission during firing (mainly volatile elements e.g. Cd, Pb and Zn (Sun et al., 2011)) and heavy metal leaching from sintered clay-ash ceramics (mainly As and Cr (Belmonte et al., 2016)). It can be seen from Table 2 that EDR is capable of extracting heavy metals from MSWI fly ash. The extraction rate varies among different elements; and the extraction rate differs for the same element in the same ash depending on the conditions of the EDR treatment including treatment time, EDR setup, current density, and liquid-to-solid ratio of the ash suspension. As for volatile elements, the extraction rates of Cd and Zn were higher than Pb (Kirkelund et al., 2015; Pedersen et al., 2005); as for Cr, its extraction was low unless using assisting agent and/or prolonging the duration of treatment.

After extraction/recovery of heavy metals from MSWI fly ash, the use of the treated ash is an important aspect to be taken into consideration. The investigations on using EDR treated

MSWI fly ash in brick production were carried out in the present study. Recycling of EDR treated MSWI fly ash may benefit from low heavy metal leaching or from total concentration. Reducing heavy metal leaching and extracting more heavy metals are pointed out because it is a difficult task to balance the two. Lab-scale experiments conducted by Kirkelund et al. (2015) showed that approaching a low leaching of e.g. Cd, Cu, Pb and Zn was conditional to pH above 8. On the other hand, to extract most heavy metals (e.g. Cr, Cd, Zn, Pb and Cu), a higher mobility in MSWI fly ash is seen at acidic pH, and to some extent at alkaline pH based on the results from chemical extraction (using $HNO_3$ as extractant) (Pedersen, 2002). Mobility of the problematic elements is critical to EDR treatment. A higher extraction percentage is achieved by lowering the pH of the ash suspension, but at the same time the leaching of some heavy metals from the treated acidic ash is still high after the treatment at acidic pH. The pH of the ash suspension at the end of EDR treatment has correlations with both heavy metal extraction and heavy metal leaching from the treated ash, and the final pH of ash suspension can be controlled by varying the duration of EDR treatment or by changing between cells (Figure 4).

In relation to lowering the pH of ash suspension, the two-compartment electrodialytic cell (Figure 4a) reduces the pH of ash suspension faster than the three-compartment cell (Kirkelund et al., 2015). The two-compartment cell (Figure 4a) was not efficient in Cl removal from raw MSWI fly ash (Kirkelund et al., 2015), but it has not been investigated on treating pre-washed MSWI fly ash, where the idea is to wash out the major part of the chlorides prior to EDR both to improve the heavy metal removal and to prevent the production of chlorine gasses.

Considering the presence of oxyanion forming elements in MSWI fly ash such as As and Cr (Cornelis et al., 2008), a three-compartment electrodialytic treatment could be used as post-treatment after a two-compartment electrodialytic treatment. In addtion, the mobility of As and Cr is both pH and oxidation-reduction potential dependent. Creation of different pH and oxidation-reduction potential ranges in the ash suspension taking advantage of both anode and cathode reactions was thus conducted in the present work to study the extraction of As and Cr.

Table 2. Selected results on extraction of heavy metals and chloride by electrodialytic remediation.

| Reference | Experimental design | Extraction |
|---|---|---|
| Pedersen et al. (2005) | five-compartment cell<br>two pairs of anion and cation exchange membranes<br>suspension state<br>assisting agent: 0.25M ammonium citrate solution<br>0.8 mA/cm$^2$<br>5 – 70 days<br>L/S 6.5 | 70 days extraction:<br>86% Cd<br>20% Pb<br>62% Zn<br>81% Cu<br>44% Cr |
| Ottosen et al. (2006) | three-compartment cell<br>one pair of anion and cation exchange membranes<br>suspension state<br>0.8 mA/cm$^2$<br>15 days<br>L/S 6 10 and 15 | the highest extraction:<br>41% Pb<br>90% Cu<br>>98% Cl |
| Kirkelund et al. (2015) | two- (2C) and three-compartment (3C) cell<br>suspension state<br>0.1 and 1 mA/cm$^2$<br>3/7/14 days<br>L/S 3.5 | 14 days and 1 mA/cm$^2$ extraction:<br>3C/ 2C<br>61% / 56% Cd<br>1.1% / 3.8% Cr<br>3.3% / 15% Cu<br>2.5% / 0.5% Pb<br>53% / 4.6% Zn |

## 4. Ash stabilization in sintered clay bricks

Sintering treatment has been reported to be capable of stabilizing MSWI fly ash (Chou et al., 2009). Low heavy metal leaching from both sintered bioash-clay brick (Eliche-Quesada, Felipe-Sesé, Moreno-Molina, Franco, & Infantes-Molina, 2016) and MSWI fly ash-clay brick (Zhang et al., 2011) has been observed. This section provides background information about sintering and what happens when firing clay. The major results from literature on research using bioash and MSWI fly ash as resource in clay bricks are outlined.

### *4.1. Clay brick firing*

Clay is one of the basic raw materials used in making clay-based ceramic products. Clay contains hydrated aluminum silicates resulting from the weathering of rocks. There are a variety of clay minerals, such as kaolinite, pyrophyllite and montmorillonite (Richerson, 2005). When

clay minerals encounter water, the formed clay-water compositions exhibit plasticity, which is important in the shaping process of clay products. Moreover, the shape of clay products can be maintained during drying and firing. Besides minerals, clay also contains fluxes (e.g. feldspar), which fuse over temperature thus leading to dense, strong products without losing the shape.

Firing is the key process for making bricks. If improperly fired, the brick could be unqualified, such as place brick, one kind of bricks which are not fully burned and have low strength and poor durability, and crozzle, another kind of bricks, which are overfired, having a crisp knocking sound, high strength and good durability, but easy to deform (Zhang, 2011).

Table 3 summarizes what can happen at important temperatures during the firing of clay, including burn-off of organic matters, decomposition of carbonates in clay, dehydration, decomposition of clay minerals or metal oxides, and sintering.

Silica is a key compound in clay. The most important silica is quartz. Quartz inversion during firing bricks is an important process. Both displacive and reconstructive transformation occur between $SiO_2$ polymorphs. The quartz inversion at 573°C between $\alpha$-quartz and $\beta$-quartz is displacive phase transformation, which means the composition of the parent phase does not change, but rather only the crystal structure. Because no long-range atomic migration and movement is required, the displacive transformation (e.g. the transformation between $\alpha$-cristobalite and $\beta$-cristobalite at 200-270°C) is rapid and cannot be restrained from occurring (Richerson, 2005). Temperature change can also initiate reconstructive transformations between quartz, tridymite and cristobalite. During reconstructive transformation, chemical bonds in the crystal structure are broken and reformed. In comparison to the rapid reversible transitions between $\alpha$-quartz and $\beta$-quartz or between $\alpha$-cristobalite and $\beta$-cristobalite, the reconstructive transformation, e.g. from quartz to tridymite, is very sluggish (Richerson, 2005). Displacive transformation is accompanied by substantial volume change. When heated, $\alpha$-quartz changes to $\beta$-quartz with a volume expansion of about 1.6%. When cooled, $\beta$-cristobalite changes to $\alpha$-cristobalite with a sudden

volume shrinkage. Therefore, temperature increase and decrease in clay brick production must be slow, to avoid the crack formation caused by the transformations between the $SiO_2$ polymorphs.

Table 3. Important temperatures and the corresponding events that happen when firing clay.

| | **Temperature, °C** | **Event** |
|---|---|---|
| *Heating* | [1]100 | Complete evaporation of water below 100°C |
| | [1]300 - 800 | Complete burning off carbonaceous materials. Trapping unburned carbonaceous and sulfides would cause bloating and black coring. |
| | [1]480-700 | Driving off chemical water |
| | [1]573 | Quartz inversion from an alpha (α) crystal structure to a beta (β) crystal structure |
| | [1]800 - 900 | Sintering begins. |
| | [2]1005 - 1145 | Earthenware vitrification range |
| | [1]1100 - 1200 | • Clay converts to glass.<br>• Chemical reactions: Forming mullite *($Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$), where x (0.17~0.59) refers to the number of oxygen vacancies per average unit cell)* and cristobalite (two types of silica). |
| | [1]1200 | End of earthenware (red clay) range |
| *Cooling* | [1]573 | Quartz inversion from a beta (β) crystal structure to an alpha (α) crystal structure |
| | [1]220 | Cristobalite shrinks . |

[1](The American Ceramic Society, 2017)

[2](Peterson, 2017)

Sintering begins at temperatures 800-900 °C (Table 3). It is also referred to as densification, which is a critical process to produce strong bricks. During sintering, bricks are subjected to physical changes such as particle rearrangement, neck formation, grain growth and volume shrinkage, which lead to adjacent particles integration and reduction in porosity (Richerson, 2005). Sintering mechanisms include solid-state, liquid-state, viscous-flow sintering, given in Table 4, as well as reaction sintering which achieves densification by chemical reaction (Valenzuela, 2005). During a sintering process e.g. for making clay-brick, all the mechanisms can be involved to achieve densification, depending on the composition and the firing temperature. All the physical and chemical changes, during the period of brick heating

and cooling (Table 3), should be well controlled in order to produce bricks of high quality, and avoid problems such as cracking, bloating, warpage and overfiring.

Table 4. Sintering mechanisms. (De Jonghe and Rahaman, 2003; Richerson, 2005; Valenzuela, 2005)

| **Type of sintering** | **Material transport mechanism** | **Driving Energy** | **Condition** |
|---|---|---|---|
| Solid-state | diffusion | differences in free energy or chemical potential | No liquid; heating to 0.5-0.9 of the melting point of the original solid mixture |
| Liquid-state | viscous flow, diffusion | capillary pressure, surface tension | A small amount of liquid |
| Viscous-flow /vitrification | viscous flow | capillary pressure, surface tension | Amorphous/glassy particles; conversion ≥20% of the original solid mixture to liquid |

*4.2. Clay-ash brick*

The quality and the sintering level of bricks can be revealed by the properties of bricks, such as density, shrinkage, compressive strength, porosity and water absorption. Incorporating bioash or MSWI fly ash causes changes to the properties of bricks.

*Clay-bioash brick*. Sutas et al. (2012) examined the bulk density, compressive strength and water absorption of the clay bricks containing rice husk ash at replacement levels of 2%, 4%, 6%, 8% and 10% by weight. They found that after sintering at a temperature of about 700 °C for 7 days, adding 2 wt.% of the rice husk ash gave the best brick properties: 6.2 MPa of compressive strength, 1.68 g/cm$^3$ of density and 15.2% of water absorption. In addition, with increasing bioash content, the compressive strength and bulk density of the bricks decreased, whereas water absorption increased. The same effect of increasing ash content on compressive strength, water absorption and porosity was observed by Eliche-Quesada et al. (2017) and Kazmi et al. (2016) when incorporating sugarcane bagasse ash and wood ash in clay bricks. Eliche-Quesada et al. (2017) compared the properties of the bricks made from two kinds of bioashes: rice husk ash and wood ash. They found that the bricks with 20 wt.% wood ash fired

at 1000 °C (compared to 900 °C) fulfilled the technical properties for bricks, and a higher content of fluxing oxides in wood ash helped the sintering of the bricks with addition of wood ash. In contrast, rice husk ash contained a higher amount of organic matters and irregularly shaped particles, causing higher porosity, which allowed only 10% replacement level in the clay bricks. In relation to the use of bioash in bricks, the degree of sintering plays an important role in the property of the bricks. According to Eliche-Quesada et al. (2017), heavy metals in bioash can be stabilized in clay bricks by proper sintering.

*MSWI fly ash-clay brick*. Recycling and stabilization of MSWI fly ash in bricks was possible either by mixing it with red ceramic clay, feldspar and gang sand (Zhang et al., 2011), or by melting it into slag prior to use in bricks (Lin, 2006). However, Belmonte et al. (2016) found that the clay-based MSWI fly ash (untreated, washed and EDR treated) bricks (containing ash 20% or 40%; shaped by pressing at 47 MPa; fired at 1000 °C for 1 h) had high open porosities, higher water absorption and swelling during firing. In addition, the problematic leaching of As and Cr from the fired clay-ash discs was observed by Belmonte et al. (2016) . In relation to MSWI fly ash, Belmonte et al. (2016) emphasized the importance of upgrading MSWI fly ash to meet the requirement for recycling; and in relation to clay-ash bricks, optimising the clay-MSWI fly ash mixtures and firing scheme is recommended for stabilization and immobilization of heavy metals into bricks. Though EDR treated MSWI fly ash has been tested by Belmonte et al. (2016) to make clay-based bricks, pretreatment/upgrading of the ashes by EDR may affect the recycling possibility in the production of bricks, in terms of technical properties of the brick material, and environmental impact (e.g. evaporation and leaching). Thus a detailed investigation is needed to understand and clarify the effect of the upgrading processes such as water washing and EDR on the thermal behavior of heavy metals. In the present study, the response of the MSWI fly ash, after a series of upgrading processes, to sintering was investigated. This will help to evaluate and predict the result from the use of the upgraded ashes in bricks. In addition, as the content and mobility of heavy metals differ between the particles

with different sizes (De Boom and Degrez, 2015), a fractionation of the MSWI fly ash was also performed in the present work.

## 5. Scope of project

In the present project, two kinds of bioashes were included in the investigation: one was collected from Enstedværket CHP plant (DONG Energy, Denmark), and another one from Vordingborg CHP plant (Denmark). One MSWI fly ash collected from Vestforbrænding waste incineration plant (Glostrup, Denmark) was included in the investigation.

The present study integrated ash upgrading with utilization. In the upgrading phase, the extraction of elements out of the ashes especially focused on soluble salts, cadmium and lead from the bioashes; and soluble salts, arsenic, chromium, lead and zinc from the MSWI fly ash.

In the utilization phase for thermal treatment, the thermal behavior of As, Cr, Pb and Zn was analyzed in terms of evaporation and leaching for pure MSWI fly ash sintering. The study of the clay-ash pellets (bioash and MSWI fly ash)/brick-cubic (only MSWI fly ash) included both the technical properties such as density, porosity, water absorption and compressive strength, and the environmental properties with special focus on the leaching of heavy metals.

## 6. Structure of thesis

To fulfill Task I of this project - upgrading the studied ashes - three techniques (*water washing (A), electrodialytic remediation (B),* and *sieving (C)*) as well as *their combinations (A+B and A+C+B)* were investigated before the thermal treatment (Task II). To fulfill Task II - utilizing the upgraded ashes in the production of bricks - two approaches were used: *pure ash sintering (D)* and *ash sintering with clay in pellet/brick-cubic form (E).* Table 5 outlines the techniques. By investigating the pure ash sintering (D), the comparison of the thermal behavior was drawn between the ashes untreated or upgraded in different ways in Task I, aiming at screening possible upgrading processes of the ashes for utilization in bricks. Small brick samples (pellets) and brick blocks (Approach E) were made in Task II to study their properties

when incorporating the treated ashes. If for example an ash went through A+C+B+E, it means the ash was orderly upgraded by washing, sieving and EDR, before used in making clay-ash bricks. Accordingly, A+B+D means the ash was washed and EDR treated prior to thermal treatment without the presence of clay, and so forth.

Table 5. Approaches to upgrade ash (Task I) and to study the ash utilization in bricks (Task II).

| Task | Approach (in the order of appearance) | Aim |
|---|---|---|
| I | washing (A) | to remove/recycle water soluble fraction |
| | electrodialytic remediation (B) | to achieve simultaneous resource recovery and detoxification (heavy metal extraction and separation) |
| | sieving (C) | to increase the possibility for MSWI fly ash recycling |
| | A+B | combining water washing and EDR |
| | A+C+B | combining the three techniques |
| II | thermal treatment of pure ash (D) | to study the thermal behavior of pure ash |
| | thermal treatment in clay mix (E) | to study the effect of ash addition in clay bricks |

The structure of this thesis is shown in Table 6. The thesis consists of 9 chapters, grouped into two main parts: one providing the upgrading of the ashes (Chapter 2, 3, 7 and 8) and another providing the reuse of the ashes in fired clay bricks (Chapter 4, 5 and 6).

Table 6. Structure of thesis.

| **Chapter** | **Idea** (Table 5) | **Aim** |
|---|---|---|
| *2. Electrodialytic remediation of fly ash from co-combustion of wood and straw* | A+B | • Bioash upgrading |
| *3. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash* | A+B+D<br>A+D<br>D | • MSWI fly ash upgrading<br>• Thermal behavior study of pure ash |
| *4. A comparative study on electrodialytically treated bioash and MSWI APC-residue for use in bricks* | A+B+E<br>B+E | • Preliminary clay-ash brick study in pellet form<br>• Identify the problems related to clay-based ash bricks, e.g. leaching of As and Cr from fired clay-MSWI fly ash bricks |
| *5. Incorporation of EDR-treated ash from co-combustion of straw and wood chips into clay pellets – leaching of heavy metals* | A+B+E | • Clay based bioash brick study in pellet form<br>• Understand the relationship between leaching of heavy metals (especially Cr) from fired pellets and the degree of densification |
| *6. Recycling of MSWI fly ash in clay bricks - effect of washing and electrodialytic treatment* | A+B+E | • Clay based MSWI fly ash brick study in cubic-block form<br>• Study the compressive strength of the bricks which could not be measured in pellet form<br>• Study the leaching of heavy metals from fired bricks<br>• Comparison between EDR treated and raw ash to figure out the effect of EDR treatment on the properties of the fired bricks |

| | | |
|---|---|---|
| *7. Electrodialytic extraction of Cr from washed MSWI fly ash by changing pH and redox conditions* | A+C+B | • EDR extraction of Cr from MSWI fly ash was low.<br>• Mobility of Cr is pH and redox potential dependent.<br>• Preliminary study on fractionation of ash |
| *8. Additional note to Chapter 7* | A+C+B<br>A+C+B+E<br>C+E | • EDR extraction of As<br>• Mobility of As<br>• Preliminary study on using fractionated ash in making brick pellets |
| *9. Conclusions* | - | - |

**References**


BEK nr 818. (2008). Bekendtgørelse om anvendelse af bioaske til jordbrugsformål (Bioaskebekendtgørelsen).

Belmonte, L. J., Ottosen, L. M., Kirkelund, G. M., Jensen, P. E., & Vestbø, A. P. (2016). Screening of heavy metal containing waste types for use as raw material in Arctic clay-based bricks. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-016-8040-z

Chou, S. Y., Lo, S. L., Hsieh, C. H., & Chen, C. L. (2009). Sintering of MSWI fly ash by microwave energy. *Journal of Hazardous Materials*, *163*(1), 357–362. https://doi.org/10.1016/j.jhazmat.2008.06.100

Cornelis, G., Johnson, C. A., Gerven, T. Van, & Vandecasteele, C. (2008). Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Applied Geochemistry*, *23*(5), 955–976. https://doi.org/10.1016/j.apgeochem.2008.02.001

Danmark. Regeringen. (2011). *Energy Strategy 2050: From Coal, Oil and Gas to Green Energy: Summary*. Danish Government.

De Boom, A., & Degrez, M. (2015). Combining sieving and washing, a way to treat MSWI boiler fly ash. *Waste Management*, *39*, 179–188. https://doi.org/10.1016/j.wasman.2015.01.040

De Jonghe, L. C., & Rahaman, M. N. (2003). Sintering of Ceramics. *Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties*. https://doi.org/10.1016/B978-012654640-8/50006-7

Dodson, J. (2011). *Wheat straw ash and its use as a silica source*. Retrieved from http://etheses.whiterose.ac.uk/1931/

Eliche-Quesada, D., Felipe-Sese, M. A., Lopez-Perez, J. A., & Infantes-Molina, A. (2017). Characterization and evaluation of rice husk ash and wood ash in sustainable clay matrix bricks. *Ceramics International*, *43*(1), 463–475. https://doi.org/10.1016/j.ceramint.2016.09.181

Eliche-Quesada, D., Felipe-Sesé, M. A., Moreno-Molina, A. J., Franco, F., & Infantes-Molina, A. (2016). Investigation of using bottom or fly pine-olive pruning ash to produce environmental friendly ceramic materials. *Applied Clay Science*, *135*, 333–346. https://doi.org/10.1016/j.clay.2016.10.015

ENERGINET. (2017). Biomass. Retrieved January 30, 2017, from http://www.energinet.dk/EN/KLIMA-OG-MILJOE/Miljoerapportering/VE-produktion/Sider/Biomasse.aspx

European Commission. (2008). DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 November 2008 on waste and repealing certain Directives. *Official Journal of the European Union*.

European Parliament and the Council of the European Union. (2009). Decision No 406/2009/EC of the European Parliament and of the Council of 23 April 2009 on the effort of Member States to reduce their greenhouse gas emissions to meet the Community's greenhouse gas emission reduction commitments up to 2020. *oJ L 140*, 136–148. https://doi.org/10.3000/17252555.L_2009.140.eng

Ferreira, C., Ribeiro, A. B., & Ottosen, L. M. (2004). Treatment of MSW fly ashes using the electrodialytic remediation technique. *Waste Management and the Environment II*.

Ferreira, C., Ribeiro, A., & Ottosen, L. (2003). Possible applications for municipal solid waste fly ash. *Journal of Hazardous Materials*, *96*(2–3), 201–216. https://doi.org/10.1016/S0304-3894(02)00201-7

Hansen, H. K., Rojo, A., & Ottosen, L. M. (2005). Electrodialytic remediation of copper mine tailings. *Journal of Hazardous Materials*, *117*(2), 179–183. https://doi.org/10.1016/j.proeng.2012.09.042

Hong, K. J., Tokunaga, S., & Kajiuchi, T. (2000). Extraction of heavy metals from MSW incinerator fly ashes by chelating agents, *B75*, 57–73.
Huang, T. Y., Chiueh, P. T., & Lo, S. L. (2016). Life-cycle environmental and cost impacts of reusing fly ash. *Resources, Conservation and Recycling*. https://doi.org/10.1016/j.resconrec.2016.07.001
Jakob, A., Stucki, S., & Struis, R. P. W. J. (1996). Complete heavy metal removal from fly ash by heat treatment: Influence of chlorides on evaporation rates. *Environmental Science and Technology*, *30*(11), 3275–3283. https://doi.org/10.1021/es960059z
Jensen, P. E., Kirkelund, G. M., Ferreira, C., & Ottosen, L. M. (2014). Pilot scale electrodialytic treatment of MSWI APC residue to decrease leaching of toxic metals and salts. In *13th Symposium on Electrokinetic Remediation*.
Jensen, P. E., Kirkelund, G. M., Pedersen, K. B., Dias-Ferreira, C., & Ottosen, L. M. (2015). Electrodialytic upgrading of three different municipal solid waste incineration residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and SO4. *Electrochimica Acta*, *181*, 167–178. https://doi.org/10.1016/j.electacta.2015.06.012
Jensen, P. E., Ottosen, L. M., & Ferreira, C. (2007). Electrodialytic remediation of soil fines (<63 um) in suspension-Influence of current strength and L/S. *Electrochimica Acta*, *52*(10 SPEC. ISS.), 3412–3419. https://doi.org/10.1016/j.electacta.2006.03.116
Kazmi, S. M. S., Abbas, S., Saleem, M. A., Munir, M. J., & Khitab, A. (2016). Manufacturing of sustainable clay bricks: Utilization of waste sugarcane bagasse and rice husk ashes. *Construction and Building Materials*, *120*, 29–41. https://doi.org/10.1016/j.conbuildmat.2016.05.084
Kirkelund, G. M., Magro, C., Guedes, P., Jensen, P. E., Ribeiro, A. B., & Ottosen, L. M. (2015). Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension - Test of a new two compartment experimental cell. *Electrochimica Acta*, *181*, 73–81. https://doi.org/10.1016/j.electacta.2015.03.192
Lee, W. K., Kim, T. E., & Yoo, Y. S. (2009). Compressive Strength of Brick Made from Waste Materials. *Materials Science Forum*, *620–622*, 639–642. https://doi.org/10.4028/www.scientific.net/MSF.620-622.639
Lin, K. L. (2006). Feasibility study of using brick made from municipal solid waste incinerator fly ash slag. *Journal of Hazardous Materials*, *137*(3), 1810–1816. https://doi.org/10.1016/j.jhazmat.2006.05.027
Margallo, M., Taddei, M. B. M., Hernández-Pellón, A., Aldaco, R., & Irabien, Á. (2015). Environmental sustainability assessment of the management of municipal solid waste incineration residues: A review of the current situation. *Clean Technologies and Environmental Policy*, *17*(5), 1333–1353. https://doi.org/10.1007/s10098-015-0961-6
Nikolaisen, L., Hinge, J., Christensen, I., Dahl, J., Jensen, P. A., Birkmose, T. S., Sander, B., & Kristensen, O. (2008). Utilization of Ash Fractions from Alternative Biofuels used in Power Plants.
Nystrøm, G. M., Pedersen, A. J., Ottosen, L. M., & Villumsen, A. (2006). The use of desorbing agents in electrodialytic remediation of harbour sediment. *Science of the Total Environment*, *357*(1), 25–37. https://doi.org/10.1016/j.scitotenv.2005.04.040
Ottosen, L. M., Hansen, H. K., Laursen, S., & Villumsen, A. (1997). Electrodialytic remediation of soil polluted with copper from wood preservation industry. *Environmental Science and Technology*, *31*(6), 1711–1715. https://doi.org/10.1021/es9605883
Ottosen, L. M., Lima, A. T., Pedersen, A. J., & Ribeiro, A. B. (2006). Electrodialytic extraction of Cu, Pb and Cl from municipal solid waste incineration fly ash suspended in water. *Journal of Chemical Technology and Biotechnology*, *81*(4), 553–559. https://doi.org/10.1002/jctb.1424
Ottosen, L. M., Pedersen, A. J., Hansen, H. K., & Ribeiro, A. B. (2007). Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method. *Electrochimica Acta*, *52*(10), 3420–3426.
Pedersen, A. J. (2002). Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash. *Journal of Hazardous Materials*, *95*(1–2), 185–198. https://doi.org/10.1016/S0304-3894(02)00138-3
Pedersen, A. J. (2003). Characterization and electrodialytic treatment of wood combustion fly ash for the removal of cadmium. *Biomass and Bioenergy*, *25*(4), 447–458. https://doi.org/10.1016/S0961-9534(03)00051-5
Pedersen, A. J., Ottosen, L. M., & Villumsen, A. (2005). Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent. *Journal of Hazardous Materials*, *122*(1–2), 103–109. https://doi.org/10.1016/j.jhazmat.2005.03.019
Peterson, B. E. (2017). How Temperature Changes Clay. Retrieved February 12, 2017, from http://pottery.about.com/od/temperatureandmaturation/tp/tempclay.htm
Reijnders, L. (2005). Disposal, uses and treatments of combustion ashes: A review. *Resources, Conservation and Recycling*, *43*(3), 313–336. https://doi.org/10.1016/j.resconrec.2004.06.007
Richerson, D. W. (2005). *Modern ceramic engineering: properties, processing, and use in design.* CRC press.
Ruangtaweep, Y., Srisittipokakun, N., Boonin, K., Yasaka, P., & Kaewkhao, J. (2013). Characterization of Rice

Straw Ash and Utilization in Glass Production. In *Advanced Materials Research* (Vol. 748, pp. 304–308). Trans Tech Publ.
Sakai, S., & Hiraoka, M. (2000). Municipal solid waste incinerator residue recycling by thermal processes. *Waste Management*, *20*(2–3), 249–258. https://doi.org/http://dx.doi.org/10.1016/S0956-053X(99)00315-3
Sun, C. J., Li, M. G., Gau, S. H., Wang, Y. H., & Jan, Y. L. (2011). Improving the mechanical characteristics and restraining heavy metal evaporation from sintered municipal solid waste incinerator fly ash by wet milling. *Journal of Hazardous Materials*, *195*, 281–290. https://doi.org/10.1016/j.jhazmat.2011.08.040
Sutas, J., Mana, A., & Pitak, L. (2012). Effect of rice husk and rice husk ash to properties of bricks. *Procedia Engineering*, *32*, 1061–1067. https://doi.org/10.1016/j.proeng.2012.02.055
THE DANISH GOVERNMENT. (2011). OUR FUTURE ENERGY, (November).
The American Ceramic Society. (2017). KILN FIRING CHART. Retrieved February 12, 2017, from http://www.ceramicartdaily.net/PMI/KilnFiringChart.pdf
Valenzuela, R. (2005). *Magnetic ceramics* (Vol. 4). Cambridge University Press.
Zacco, A., Borgese, L., Gianoncelli, A., Struis, R. P. W. J., Depero, L. E., & Bontempi, E. (2014). Review of fly ash inertisation treatments and recycling. *Environmental Chemistry Letters*, *12*(1), 153–175. https://doi.org/10.1007/s10311-014-0454-6
Zhang, H. (2011). Wall and Roof Materials. In *Building materials in civil engineering*. Elsevier. https://doi.org/10.1016/B978-1-84569-955-0.50007-4
Zhang, H. Y., & He, H. H. (2013). Characterization of Microstructure of FA Ceramic Brick Using SEM. *Advanced Materials Research*, *849*, 283–286. https://doi.org/10.4028/www.scientific.net/AMR.849.283
Zhang, H., Zhao, Y., & Qi, J. (2011). Utilization of municipal solid waste incineration (MSWI) fly ash in ceramic brick: Product characterization and environmental toxicity. *Waste Management*, *31*(2), 331–341. https://doi.org/10.1016/j.wasman.2010.10.017

# Chapter 2

## *Electrodialytic remediation of fly ash from co-combustion of wood and straw*

Published in Eletrochimica Acta

Electrochimica Acta 181 (2015) 208–216

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Electrodialytic remediation of fly ash from co-combustion of wood and straw

Wan Chen *, Pernille E. Jensen, Lisbeth M. Ottosen, Gunvor M. Kirkelund

*Department of Civil Engineering, Technical University of Denmark, Denmark*

ARTICLE INFO

*Article history:*
Received 25 December 2014
Received in revised form 13 April 2015
Accepted 14 April 2015
Available online 17 April 2015

*Keywords:*
Electrodialytic remediation
Straw and wood
Fly ash
Heavy metals

ABSTRACT

The heavy metal content in fly ash from biomass combustion, such as straw, wood and sludge, often needs reducing before the ash can be used as fertilizer for agricultural land or as a component in the production of construction materials. In this study, fly ash from a boiler fueled with wood chips and straw was treated either by electrodialytic remediation (EDR) directly or by a combination of EDR and pre-wash with distilled water to investigate the possibilities of reducing the heavy metal content and reusing nutrients as fertilizer and bulk material in construction materials. Different experimental set-ups were tested for EDR treatment primarily of Cd and Pb as well as of Cu and Zn. Elemental contents such as K, P and Ni were compared in ash samples before and after treatment. The results showed that pre-washing caused an increase in total concentrations of most heavy metals because the highly soluble fraction, mainly KCl and $K_2SO_4$, was removed. After EDR treatment, the Cd concentration was reduced to below 2 mg kg$^{-1}$ in all ash samples with high and stable average removal of above 95%, no matter how high the initial concentration was. The amount of Pb removed varied from 12% to 67%. Even though Pb was extracted from the ash samples, its concentrations in the treated ash samples were elevated due to the ash dissolution, except in the case of pre-washed ash treated in a two-compartment EDR cell, where the mass of Pb removed was the highest with a final concentration of about 100 mg kg$^{-1}$. The two-compartment EDR cell probably performed better due to a fast acidification process. In addition, this process was less energy-consuming. However, the fast acidification did in turn affect the leaching property of the treated ash, such as As and Ni, exceeding the limiting concentrations. The EDR/pre-wash-EDR treated ash mainly contained quartz, and the X-ray diffraction (XRD) peaks of K salts had disappeared. This shows that the potassium fertilizer potential was lost in the treated ashes, but the quartz mineral is beneficial in construction materials, such as ceramics. The K fertilizer could be recovered from the water after pre-washing and also from the catholyte through chemical operations, including a separation step.



## 1. Introduction

The European Union's renewable energy target and climate and energy policies have driven the increasing use of renewable energy resources in heat and power production [1]. Field crop residues, such as straw, are one source of agricultural biomass fuels, which are generally cheap in price and abundant in quantity and are, therefore, increasingly being used for energy production. However, pure straw combustion has slagging and fouling problems in boilers because of the high ash content and the high content of chlorine and potassium. Co-combustion of straw with other fuels, such as coal and forest (woody) fuels, can ease the problem by diluting the elements that form straw ash [2]. The main ash-forming elements are: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si and Cl [3]. Straw has a high ash content in the range of 4–7%, whereas wood chips have a relatively low ash content of less than 2% [4]. By incorporating Ca-rich wood in straw combustion, Ca-rich particles can be deposited in the straw-based K-silicate melt to form silicates and oxides (e.g. CaO) of high melting points, thus changing the elemental composition of the bottom ash and reducing slagging propensity [2]. In Denmark, co-combustion of straw and wood chips has been implemented in some bio-fueled power plants.

The main by-products generated in the co-combustion of wood and straw are bottom and fly ashes. This type of bio-ash usually contains plant nutrients (K and P) which have value as fertilizers [5,6]. The bottom ash can normally be spread on agricultural fields, thus using the fertilizer value directly [7]. In Denmark, the fly ash

* Corresponding author. Tel.: +4545251816.
*E-mail address:* wach@byg.dtu.dk (W. Chen).

http://dx.doi.org/10.1016/j.electacta.2015.04.083
0013-4686/

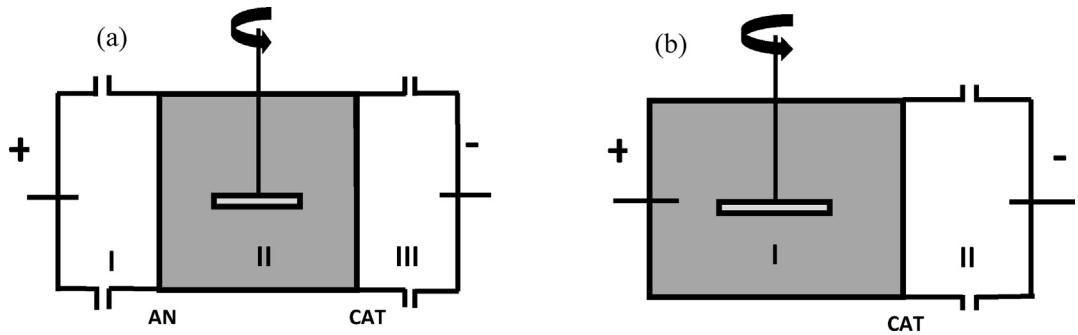


**Fig. 1.** The schematic drawing of the types of EDR cells used in the experiments. Anion exchange membrane = AN; cation exchange membrane = CAT.

cannot be used in this way because the heavy metal content (especially Cd [8]) often exceeds the maximum limit value of 5 mg Cd $kg^{-1}$ TS (total solid) in the Danish regulation "Bioaskebekendtgørelsen" [9] for use of bio-ash on agricultural land. This study, therefore, focuses on using the resources in fly ash from wood and straw co-combustion.

EDR (electrodialytic remediation) is a method of removing heavy metals from particulate materials. It was originally developed for remediation of contaminated soils in a stationary, humid state [10], and later developed towards the treatment of fine particulate materials in suspension [11]. In the electric field, mobile ions in the suspension will electromigrate to electrode compartments through anionic or cationic ion exchange membranes, thus achieving a separation of ions from the suspension. The reduction and oxidation of water at the electrodes are the primary reactions occurring in the EDR system [12]. The half reactions are: (1) cathode reaction $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$, and (2) anode reaction $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$. Removing Cd from biomass combustion fly ash in a three- or five-compartment EDR setup was reported in [5,10,13–15], and EDR turned out to be successful. Not only heavy metals but also other mobile element ions, such as K and P, are removed from ash suspensions during EDR. Later a two-compartment cell setup was developed for extraction of P from wastewater sludge. In the two-compartment cell, an ash-water suspension is directly acidified from the anode reaction as the anode is placed in the suspension. In this study, the focus is on the separation of nutrient elements and heavy metals for the recovery of the nutrients in an environmentally usable form. If the nutrients recovered can be used on agricultural fields, they will give additional economic value and replace a part of the commercial potash K fertilizer with a recently reported sale price of about US $310 per tonne [16]. The reuse of treated ash residue will also give an economic benefit, as disposal of the ashes is expensive in many countries. However, a few studies have reported results related to the possible management of EDR-treated ash residue according to the ash properties [17–19].

In this study, co-combustion fly ash from a boiler fueled with wood chips and straw was treated either by EDR or by a pre-wash/EDR combination to lower the heavy metal content in the ash. We tested a two-compartment EDR cell for the first time to treat such co-combustion ash and compared it with the three-compartment cell regarding heavy metal removal. We investigated the influence of the water pre-wash on EDR treatment. This is relevant to industries using water to wash out nutrients (mainly K) from bio-ashes, to offer an alternative technique to handle the ash residues by reducing the heavy metal content. In line with a zero-waste concept, a possible reuse of the detoxified fly ash residue for construction purposes was discussed. Since the fly ash studied contained plant nutrients, how the nutrients could be recovered during EDR or the pre-wash/EDR combination was discussed.

## 2. Experimental

### 2.1. Materials

Two straw/wood co-combustion fly ash (FA) samples from Enstedværket Power Plant (Denmark) were used in this study. The FAs were sampled on different days and were named EFA-1 and EFA-2. After being washed with distilled water in three stages at the total liquid-to-solid (L/S) ratio of 15 l/kg, i.e. 5 l/kg in each, the fly ash samples were named WEFA-1 and WEFA-2, respectively. The wet ash samples were dried at 105 °C for 24 h for further use in the experimental work. The dry mass recovered from the pre-washing step was directly used to calculate the content of soluble compounds.

### 2.2. Experiments

The EDR cells illustrated in Fig. 1 were used in this study. They were different in configuration, i.e. three-compartment (Fig. 1a) and two-compartment (Fig. 1b). In relation to conventional EDR for e.g. water treatment, compartment II in Fig. 1a and compartment I in Fig. 1b were demineralization compartments, where the ash-water suspension was placed. The remaining compartments where the electrodes were placed, were concentration compartments filled with circulating electrolytes (a 0.01 M $NaNO_3$ solution with a pH of 2 adjusted by $HNO_3$). In the setup illustrated in Fig. 1b, the anode was directly placed in the ash suspension. The cells were cylindrical with an inner diameter of 8 cm and made from polymethyl methacrylate. The compartment for ash suspension was 10 cm long and the length of the other compartments was 5 cm.

**Table 1**
EDR conditions.

| Experiment no. | Sample | Current/mA | Compartment | Duration/d | Charge/C |
|---|---|---|---|---|---|
| E1 | EFA-1 | 50 | 3 | 14 | 60480 |
| E2 | WEFA-1 | 50 (Day 1) to 10 | 3 | ~67 | 60480 |
| E3 | EFA-2 | 50 | 3 | 10 | 43200 |
| E4 | WEFA-2 | 10 | 3 | 70 | 60480 |
| E5 | WEFA-2 | 40 | 3 | 10 | 34560 |
| E6 | WEFA-2 | 40 | 2 | 10 | 34560 |

Table 1 gives the experimental conditions for the EDR experiments conducted. The L/S ratio was set at 7 (350 ml distilled water/50 g dry ash) according to the experience of Ottosen et al. [10] with respect to straw or wood ash EDR treatment. The constant current density was planned to be the same in all experiments, but in experiment E2 with WEFA-1 the voltage between the two working electrodes reached the maximum output voltage of the power supply on day 1, so it was decided to decrease the current from 50 mA to 10 mA from day 2. The experiments were designed to obtain the effect of stable/low current density (e.g. experiments E2 and E4), different current densities (e.g. experiments E4 and E5), and EDR cells (e.g. experiments E5 and E6) on the treatment. The repeatability of EDR treatment of the raw ash is found in experiments E1 and E3. Details regarding the practical application of EDR in the laboratory experiments are as follows.

- Stirring. A plastic flap mounted on a glass stick was placed inside the ash suspension. The glass stick was fixed into an overhead 'lab egg' stirrer.
- Electrolyte circulation. Pumps were used to keep the electrolytes circulating in electrode compartments. The volume of electrolyte in each compartment was 500 ml.
- Power supply. A DC power supply (HP E3612A) maintained the constant output current and monitored the development of voltage between the two working electrodes.
- Measurements and control during the experiment. The conductivity and pH of the ash suspension and the voltage between the working electrodes were measured once per day. The pH changes in electrolytes induced by electrode reactions were monitored during the experiment, and the pH was manually controlled at between 1 and 2 by adding $HNO_3$ and/or NaOH solutions. Water flux [13] occurred during the experiments, especially in three-compartment cells; this was diminished by adjusting the pumping rate.

### 2.3. Analysis

Water content was measured as the weight loss during drying at 105 °C for 24 h and calculated by ((initial ash mass–dry ash mass)/initial ash mass; %). The content of organic matter was determined as the weight loss on ignition (LOI) at 550 °C for 1 h.

The dry ashes were manually grinded prior to the following analyses. Elemental analysis according to Danish Standard DS259 [20]: the concentrations of Cd, Cu, K, P, Pb and Zn were determined after acid digestion, where 1.0 g of dry ash in 20.0 ml of 1:1 $HNO_3$ was autoclaved at a pressure of 200 kPa at 120 °C for 30 min. The digested ash solution was vacuum filtered through a 0.45 μm filter. Finally, the filtrate was diluted to 100.0 ml for elemental analysis by ICP-OES (Varian 720-ES, Software version: 1.1.0). A series of at least three replicates (number of replicates: N) was made. All concentrations are expressed on a dry mass basis.

The $pH_{H2O}$ was measured in distilled water at a L/S ratio of 5. Radiometer analytical pH electrode was used for pH determination after 1 h of agitation of the ash suspension.

The chloride content was extracted by distilled water for 16 h at a L/S ratio of 5. After agitation, the ash suspension was filtered through a 0.45 μm filter. The concentration of chloride in the filtrate was determined by volumetric titration with standard silver nitrate solution.

The crystalline phases were studied by X-ray diffraction (XRD, 2θ Cu Kα, 40 mA, 45 kV) using a PANalytical Xpert Pro diffractometer.

Leaching tests were conducted referring to the principle in DS/EN 12457-1 [21]. The L/S ratio was 2. The suspension was agitated for 24 h and then vacuum filtrated through a 0.45 μm filter. Concentrated $HNO_3$ was added to the filtrate for the purpose of preserving the sample before the determination of elemental concentrations by ICP-OES.

## 3. Results

### 3.1. Ash characterization

EFA-1 and EFA-2 were very similar in their general properties such as pH, conductivity, water content, LOI and chloride concentration (Table 2). The slight differences could be explained by the variation in straw/wood ash fractions on the dates of ash sampling. Straw ash normally has a slightly acidic to neutral pH and high content of chloride and soluble salts, while wood ash is alkaline due to the presence of alkaline oxides (e.g. CaO) and has

**Table 2**
Properties of the ashes studied (mean values and standard deviation of N replicates; nd = not determined).

| Ash samples<br>Initial concentration ($c_i$) | | EFA-1<br>E1<br>(N = 5) | WEFA-1<br>E2<br>(N = 3) | EFA-2<br>E3 (N = 5) | WEFA-2<br>E4, E5, E6 (N = 4) | Reference<br>Straw ash ([5]/[7]) | Reference<br>Wood ash<br>[5] | Reference<br>Prewashed straw ash [5] |
|---|---|---|---|---|---|---|---|---|
| Major element | Ca | 20.2 ± 0.5 | 105.0 ± 0.2 | 31.3 ± 0.3 | 122.3 ± 1.1 | 2.7/3.7 | 113 | 12.1 |
| ($g\,kg^{-1}$ TS) | K | 373.1 ± 4.8 | 40.2 ± 0.4 | 371.8 ± 4.3 | 35.7 ± 0.3 | 485/nd | 323 | 291 |
| | P | 10.7 ± 0.2 | 44.7 ± 0.1 | 12.1 ± 0.1 | 48.0 ± 0.5 | nd | nd | nd |
| Trace element | As | 8.1 ± 0.9 | 24.4 ± 0.2 | 8.6 ± 0.9 | 17.1 ± 0.8 | nd | nd | nd |
| ($mg\,kg^{-1}$ TS) | Cd | 9.0 ± 0.2 | 31.8 ± 0.3 | 9.3 ± 0.2 | 19.6 ± 0.4 | 18/11.3 | 12.1 | 64 |
| | Cr | 5.0 ± 2.7 | 17.7 ± 0.4 | 5.5 ± 0.4 | 19.1 ± 0.5 | nd/13.5 | nd | nd |
| | Cu | 44.8 ± 0.6 | 253.6 ± 1.4 | 49.0 ± 0.5 | 186 ± 3 | 79/81 | 303 | 370 |
| | Ni | 1.0 ± 0.2 | 6.6 ± 0.4 | 3.0 ± 0.6 | 9.6 ± 0.3 | 15/nd | 77 | 35.3 |
| | Pb | 27.2 ± 0.9 | 192.8 ± 2.9 | 35.0 ± 0.4 | 135 ± 3 | 93/nd | 102 | 194 |
| | Zn | 1013 ± 14 | 8008 ± 67 | 1089 ± 10 | 4960 ± 36 | 572/nd | 800 | 1271 |
| pH($H_2O$) | | 7.4 ± 0.2 | 9.4 ± 0.0 | 7.4 ± 0.0 | 9.9 ±0.0 | 5.5($pH_{KCl}$)/5.9 | 13.3 ($pH_{KCl}$) | 5.7($pH_{KCl}$) |
| Conductivity ($mS\,cm^{-1}$) | | 98.1 ± 0.8 | 11.3 ± 0.6 | 109.5 ± 2.8 | 1.8 ±0.0 | | | |
| Water content (%) | | 0.2 | 78.5 | 0.2 | 71.3 | 0.4/1.2 | 0.4 | 87.5 |
| Chloride content (%) | | 23.9 | 0.1 | 22.7 | 0.1 | 20/21 | 3.2 | 2.8 |
| LOI (%) | | 2.4 ± 0.03 | nd | 2.5 ± 0.2 | 7.3 ± 0.3 | 8.0/nd | 2.2 | 9.0 |
| Ash recovery after washing (%) | | | 17 | | 25 | | | |
| Main minerals | | KCl, $K_2SO_4$ | Quartz, $CaCO_3$, $CaSO_4$ | | | | | |

low dissolution and chloride content [22]. The EFAs studied inherited the most characteristics of straw ash, because straw was the dominating fuel in the combustion process. The average consumption of straw in the power plant takes about 80% of the total consumption of straw and wood chips [23]. The water solubilities of EFAs were high at 83% and 75%, respectively. The high content of K in the wash water together with the remarkable decrease in chloride concentration in the ash from about 23% to 0.1% and the XRD result of EFA-1 (Table 2) suggested that the most easily soluble salts washed out were KCl and $K_2SO_4$. The peaks of K and Cl disappeared from the XRD pattern after washing. Washing caused an increase in pH of WEFAs to above 9.4. The species of $CaCO_3$ and $CaSO_4$ detected in the pre-washed EFA can explain the increase in pH.

Compared with the limiting values for bio-ash as fertilizer regulated in [9], i.e. maximum 5 mg Cd $kg^{-1}$ TS, 100 mg Cr $kg^{-1}$ TS, 60 mg Ni $kg^{-1}$ TS and 120 mg Pb $kg^{-1}$ TS, Cd was the main problematic heavy metal in EFAs (9 mg $kg^{-1}$) prohibiting their spread on agricultural land (Table 2). The heavy metal contents in WEFAs were all higher than in the original EFAs, as were Ca and P but not K, which supports the proposition that a large proportion of K in EFAs was water-soluble. The water solubility of P might be low, and the enrichment of Ca is believed to be due to the precipitation of Ca on the ash particles in the form of $CaSO_4$ and $CaCO_3$ (Table 2) during washing. Besides Cd, the concentration of Pb in WEFAs was elevated to a problematic level, i.e. higher than 135 mg $kg^{-1}$ TS. Therefore, the target elements in our EDR experiments were the

**Table 3**
Mass balances (%) of each element in the experiments. The K value was not given in E3 due to the leaking problem with the circulating pipeline at the end of treatment, which especially had a great impact on the mass balance of K, but a less impact on the other elements with relatively low concentrations.

| No. | K | P | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|
| E1 | 94 | 99 | 91 | 124 | 94 | 110 |
| E2 | 108 | 89 | 102 | 114 | 96 | 92 |
| E3 | - | 95 | 106 | 138 | 122 | 110 |
| E4 | 95 | 80 | 100 | 97 | 91 | 86 |
| E5 | 102 | 82 | 105 | 102 | 94 | 94 |
| E6 | 87 | 78 | 93 | 105 | 83 | 92 |

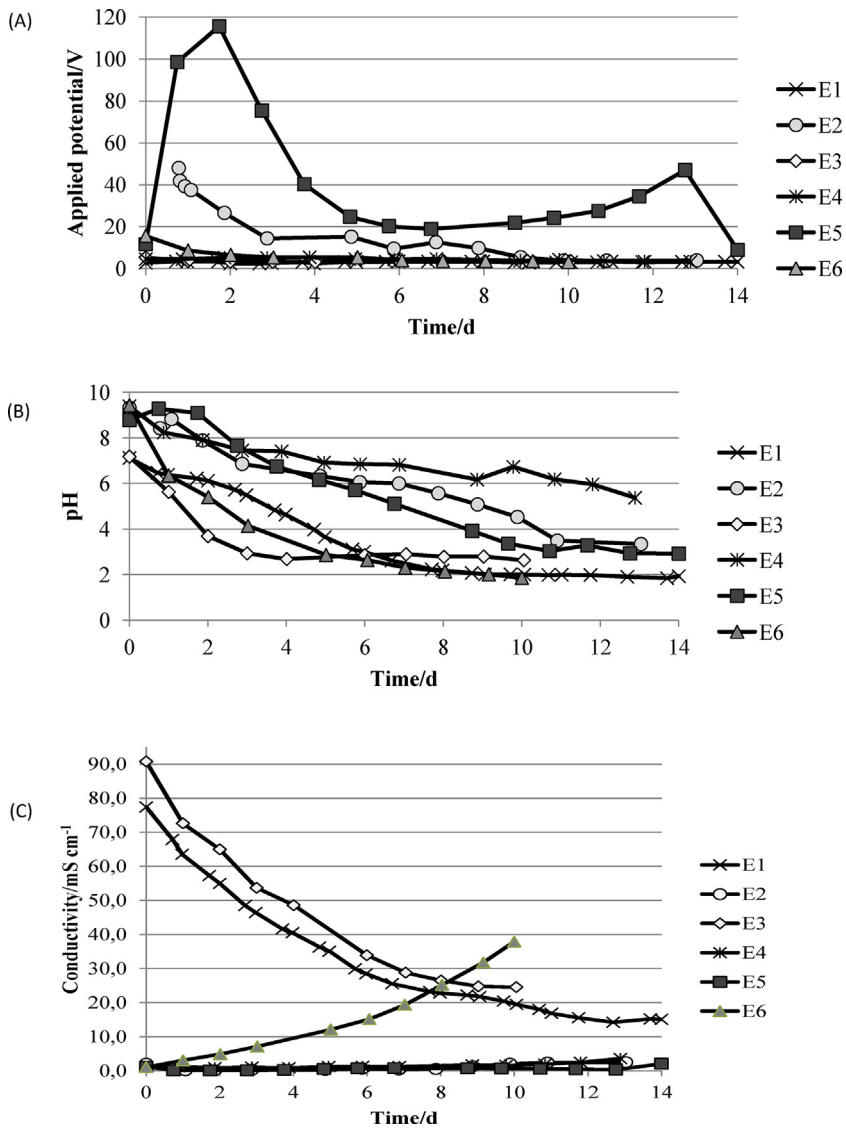


**Fig. 2.** Development of voltage between the working electrodes (A), development of pH (B) and conductivity (C) of the ash suspensions within the first 14 days of EDR treatment. In this period of time the changes were considered significant.

**Table 4**
Overall results of treatment: $c_f$ for final concentration (mean values and standard deviation based on N measurements; na. = not analyzed).

| Final concentration $c_f$ in experiments (parallel test N=3) | | EFA-1 E1 | WEFA-1 E2 | EFA-2 E3 | WEFA-2 E4 | WEFA-2 E5 | WEFA-2 E6 |
|---|---|---|---|---|---|---|---|
| Major element ($g\,kg^{-1}$ TS) | Ca | 6.5 ± 0.1 | 8.4 ± 0.1 | 7.5 ± 0.1 | 9.3 ± 0.2 | 17.7 ± 0.1 | 7.6 ± 0.1 |
| | K | 13.6 ± 0.1 | 8.7 ± 0.2 | 15.4 ± 0.2 | 9.6 ± 0.2 | 12.4 ± 0.1 | 10.7 ± 0.2 |
| | P | 3.5 ± 0.0 | 6.3 ± 0.1 | 5.3 ± 0.0 | 8.6 ± 0.2 | 7.5 ± 0.0 | 4.5 ± 0.1 |
| Trace element ($mg\,kg^{-1}$ TS) | As | 1.6 ± 2.2 | 2.8 ± 1.0 | 1.8 ± 2.5 | 4.0 ± 0.6 | 2.0 ± 0.5 | 2.8 ± 2.1 |
| | Cd | 1.06 ± 0.03 | 1.6 ± 0.3 | 0.99 ± 0.03 | 1.07 ± 0.13 | 1.6 ± 0.1 | 0.65 ± 0.21 |
| | Cr | 21.3 ± 0.6 | 19.5 ± 1.1 | 22.1 ± 0.4 | 19.8 ± 0.6 | 19.6 ± 0.4 | 14.2 ± 0.3 |
| | Cu | 25.7 ± 0.2 | 71.6 ± 1.5 | 39 ± 1 | 56 ± 1 | 70 ± 1 | 48 ± 1 |
| | Ni | 3.6 ± 0.4 | 3.8 ± 0.3 | 9.4 ± 0.3 | 8.0 ± 0.1 | 7.7 ± 0.2 | 7.8 ± 0.4 |
| | Pb | 47.8 ± 0.7 | 210.4 ± 4.8 | 100 ± 1 | 139 ± 2 | 168 ± 1 | 102 ± 1 |
| | Zn | 100 ± 1 | 260 ± 10 | 224 ± 2 | 234 ± 4 | 300 ± 4 | 166 ± 3 |
| pH_ash suspension | initial | 6.47 | 9.32 | 7.18 | 8.79 | 9.39 | 9.44 |
| | final | 1.93 | 1.93 | 2.79 | 1.96 | 2.92 | 1.86 |
| Ash recovery (%) | | 19 | 75 | 18 | 73 | 71 | 71 |
| pH_ash after treatment | | na. | na. | na. | 5.37 | 6.92 | 5.97 |
| Energy consumption ($Wh\,g^{-1}$) | | 1.03 | Unstable current | 0.84 | 1.02 | 8.42 | 1.06 |
| Removal efficiency (%) | Cd | 98 | 96 | 98 | 96 | 94 | 98 |
| | Pb (mass removed) | 67 (0.91mg) | 18 (1.21mg) | 48 (0.83mg) | 25 (1.69mg) | 12 (0.82mg) | 47 (3.16mg) |
| | Cu | 89 | 79 | 85 | 78 | 73 | 82 |
| | Zn | 98 | 98 | 96 | 97 | 96 | 98 |
| | K | 99 | 84 | 99 | 80 | 75 | 79 |
| | P | 94 | 89 | 92 | 87 | 89 | 93 |

problematic Cd and Pb, but Cu and Zn were also included since Cu can be problematic in wood ash and Zn had relatively higher concentrations in the samples studied.

### 3.2. EDR experiments

#### 3.2.1. Mass balances

Mass balance ($mass_{out}/mass_{in}$, %) shows the relationship between the total mass output of a contaminating element from the whole EDR system (compartments, electrodes and membranes) after treatment and its initial mass input from the ash. The values given in Table 3 are not exactly 100%, mainly due to the unhomogeneous nature of the ash samples. The mass balances of the four target elements are acceptable referring to [24], and varied between 78% and 138% with an average of 108%.

#### 3.2.2. Voltage, pH and conductivity

Significant changes in pH and conductivity of the ash suspensions, and in voltage between the working electrodes were seen within the first 14 days of EDR treatment, as shown in Fig. 2.

Low and stable voltage (2.8–5.3 V) was seen throughout the experiments E1 and E3 (Fig. 2A) due to the high content of easily soluble salts resulting in high conductivity of the raw ash suspensions (Fig. 2C). During these two experiments, the conductivity of the suspensions decreased as ions were electromigrating into the electrode compartments, but the conductivity never limited the flow of current. The conductivity decreased faster during the first week of experiment than after. This can be explained by the acidification of ash suspension (Fig. 2B) where the $H^+$ ions and subsequent ash dissolution added to the overall conductivity.

The voltage in experiment E2 with pre-washed ash, on the other hand, increased to the maximum output of the power supply during the first day when the same current, i.e. 50 mA, was applied. The conductivity of such a pre-washed ash suspension was too low to maintain this high current after washing the soluble parts out. The current was changed to 10 mA so as to maintain a constant applied current. This was an appropriate current for treatment of pre-washed ash as the voltage varied no more than ±2 V from the average value of 4 V as seen in experiment E4. After day 14, the voltage in experiments E2 and E4 showed very weak fluctuations around 2.5 V, and the pH of their ash suspensions kept decreasing till a steady state was reached at pH around 1.90, but the conductivity slowly increased to 30 $mS\,cm^{-1}$ in the end. Unlike E4, experiment E5 showed considerable variation in voltage from 9 V to 116 V within 10 days. The current applied, 40 mA, seemed too high for treatment of the low conductive pre-washed ash in a three-compartment EDR cell compared with that in experiment E4. The dramatic increase in voltage in experiment E5 within two days was probably due to the extensive ion-concentration polarization at the membrane surfaces and, very important, the high resistance of the ash suspension. Experiment E6 had a different voltage development pattern from experiment E5 despite the same current applied. Instead of initially increasing and then decreasing, the voltage kept decreasing from about 16 V to 3 V. The pre-washed ash suspension had very low initial conductivity, but the fast acidification from the anode reaction in experiment E6 caused an increase in conductivity throughout the experiment. The pH decreased accordingly. The comparison between experiments E5 and E6 shows that a faster decrease in pH and increase in conductivity in a two-compartment cell can be achieved than in a three-compartment cell at the same current density.

#### 3.2.3. Changes in ash composition during treatment

In general, the concentrations of selected heavy metals in the ash samples decreased after EDR treatment except Ni in

**Table 5**
Leaching properties.

| ($\mu g\,dm^{-3}$) | Se | As | Ba | Cd | $Cr_{tot}$ | Cu | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Limiting value | 30 | 50 | 4000 | 40 | 500 | 2000 | 1000 | 70 | 100 | 1500 |
| Raw EFA-2 | 393 | 2321 | 131 | 2864 | 28 | 42 | 77 | 2.3 | <2 | 364 |
| Treated ash in E5 | <2 | 41 | 112 | <2 | 2 | <2 | 52 | 147 | <2 | 53 |
| Treated ash in E6 | 97 | 92 | 89 | 2 | 4.7 | <2 | 493 | 227 | <2 | 243 |

experiments E1 and E3, and Cr and Pb in experiments E1 to E5, by comparing the initial (Table 2) with the final (Table 4) concentrations. Both experiments E1 and E3 were used for treatment of EFAs, so the lower content of Ni in raw ash compared with the amount of ash dissolved during EDR treatment explained the increase in Ni. No increase in Cr and Pb concentrations was seen in experiment E6, although it was seen in the other experiments, which suggested that the two-compartment cell generally gave a better removal of heavy metals than the three-compartment cell. Compared with experiment E5, the enhanced removal of Pb and Cr in experiment E6 is probably associated with the faster pH decrease in the two-compartment cell (Fig. 2B). All the selected elements were within the limiting concentrations for spreading on agricultural land after treatment in experiment E6.

An XRD analysis was made on the ash treated in experiment E1, and here the main crystalline phase detected was quartz, which is normally acid-insoluble (except in HF). This could support the hypothesis that $SiO_2$ is the main crystalline residue after EDR treatment.

Leaching properties of the ashes treated in experiments E5 and E6 were given in Table 5. Compared with the values obtained from EFA-2, the leachability of all the listed elements (except Ni) was reduced after washing and EDR treatment.

### 3.2.4. Elemental distribution

Fig. 3 shows the distributions of Cd, Cu, Zn, Pb, P and K in the whole EDR system. In general, the cationic species, such as Cd, Cu, Pb, Zn and K, were primarily transported to the cathode end, and the anionic species, such as $PO_4^{3-}$, primarily migrated to the anode end. The outcome of experiment E5 was the best with respect to a good elemental distribution and separation as the content of heavy metals in filtrate from the ash suspension was very low. The filtrate and anolyte with low heavy metal content may be used as a source for P fertilizer. It is likely that the properties of pre-washed ash, such as less solubility and alkaline pH, were related to the special performance of experiment E5. The $CaCO_3$ content in the pre-washed ash implied higher buffering capacity to the acidification process, and washing may convert heavy metal compounds into

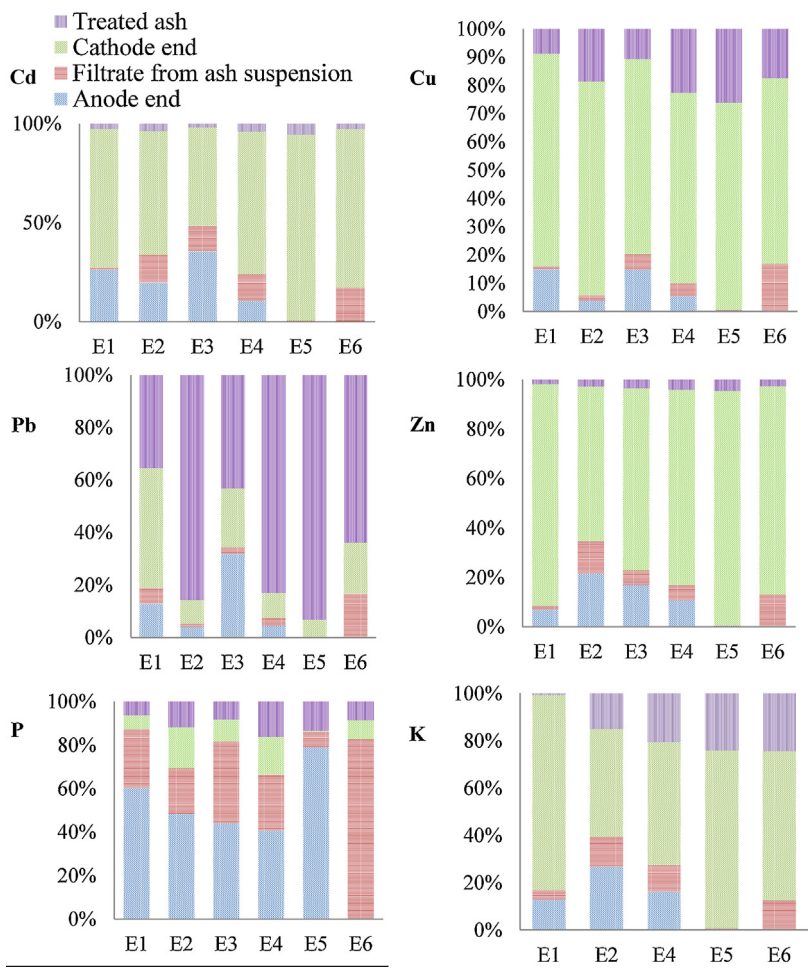


**Fig. 3.** Distribution of elements in the electrodialytic cell after remediation. Anode end includes element at the anode, in the anion-exchange membrane and in the anolyte. Cathode end includes the element at the cathode, in the cation-exchange membrane and in the catholyte. Elements in the treated ash were measured on dry basis. Due to the bad mass balance of K resulting from pump leaking, the distribution of K in E3 was not given.

less reactive forms [25], resulting in almost unchanged conductivity which may suggest that there was a balance between the release and removal of mobile ions.

*3.2.5. Energy consumption*

The equation, $E = \int VIdt/W$ [26], was used to estimate the energy consumptions in the EDR experiments, where E is the power consumption per gram ash ($Wh\,g^{-1}$); V, voltage between working electrodes (V); I, current (A); t, duration (h); W, the mass of ash (g). Comparing experiment E5 with E6, a lower energy consumption (Table 4) was seen in the latter due to the rapid increase in conductivity (Fig. 2C). At the same time, the concentrations of heavy metals obtained in E6 using a two-compartment cell were the lowest, so the energy efficiency was the highest in this setup.

## 4. Discussion

*4.1. Overall removal*

The operational parameters in EDR (current density, L/S and duration of treatment) affect the outcome of remediation, and a delicate balance must be maintained to obtain the most efficient treatment [11]. In the present study, extending the duration from 10 to 14 days did not have a great impact on the removal of Cd from raw ashes in the three-compartment EDR cell (experiments E1 and E3), so the remediation could be conducted in less than 10 days under the same conditions. The duration between 10 and 14 days, on the other hand, affected the removal of Cu, Pb and Zn, and the results (Table 4) imply that a longer duration can reduce the content of Pb and Cu; this has also been seen in EDR treatment of contaminated soils [27,28]. The goal of remediation, therefore, determines the duration. Where Cd is the only target element, the duration is relatively short, but if Pb is a target element as well, the duration must be significantly longer. When comparing the overall results, it can be found that EDR treatment of unwashed ash gave better results than the treatment of pre-washed ash in the three-compartment cell in terms of heavy metal content in the ash after treatment and energy consumption of the treatment.

EDR treatment of straw and/or wood ashes within 14 days has shown great potential. Previous experiments were conducted in the three/five-compartment cell on straw or wood ash separately [5,10,14,22]. Ottosen et al. [10] conducted EDR experiments for 14 days at the current density of $0.8\,mA\,cm^{-2}$ (corresponding to approximately 40 mA), and achieved removal of Cd of 75% and 45% from straw ash and wood ash, respectively. The corresponding Pb removals were 66% and 33%. Kirkelund et al. [5] treated a straw fly ash and a pre-washed straw ash with high initial Cd concentrations of 18 and $64\,mg\,kg^{-1}$ TS, respectively. They achieved a Cd concentration below $2\,mg\,kg^{-1}$ TS in the raw straw fly ash after treatment at a L/S ratio of 7 and a current of 40 mA (equivalent to the current density of $0.8\,mA\,cm^{-2}$) for 14 days. At the same current density and duration, a decrease in Cd concentration in the pre-washed ash was gained of between 3.5 and $2\,mg\,kg^{-1}$ TS when the L/S ratio varied from 7 to 13.

In summary, EDR can be used not only as a method for direct fly ash treatment, but also as a post-treatment method after pre-treatment by washing. This is consistent with the finding in [24]. Our study also suggests that the sudden increase in current density as a result of very low conductivity of the ash suspension is not preferable in the extraction of some metals even when the same charges passed. For example, the removal efficiencies of Pb were 18% in experiment E2 where the voltage reached high levels, and 25% in experiment E4 with low initial current and stable voltage throughout the experiment (Table 4). Thus it is advisable to determine the optimal current density at laboratory scale before scaling up the process. The type of EDR cells should be selected according to the aim of treatment and properties of the materials.

*4.2. Removal of Cd, Pb, Cu and Zn*

Calculating the removal efficiency of Cd (as the total mass difference in the ash before and after treatment divided by the total initial mass of Cd), a quite stable and high level of efficiency in the removal of Cd was seen under all the experimental conditions (Table 4). The removal efficiencies are in the order: E1 = E3 = E6 > E4 = E2 > E5. Compared with the removal efficiencies reported in [10], the values in our study were high and more than 94% of Cd was removed. The final Cd concentration of below $2\,mg\,kg^{-1}$ was obtained in both this study and [10]. The majority of the Cd ions electromigrated to the cathode compartment (Fig. 3), but they were also found in the anode compartment in four of the experiments, i.e. E1–E4 (maximum about 30%). Removal of Cd ion towards the anode was described in [10] and [14] in detail. It can be concluded that many different Cd complexes can form when ash is suspended, and they can be positive ($Cd^{2+}$ and $CdCl^{+}$), negative ($CdCl_3^{-}$ and $CdCl_4^{2-}$) or neutral ($CdCl_2$). Hansen et al. [14] pointed out that Cd was mainly removed as $CdCl_4^{2-}$ at the beginning of remediation, and with the decrease in Cl content and pH, Cd is present as $Cd^{2+}$. As the percentages of Cd in anolyte were the highest in experiments E1 and E3, negatively charged chloride complexes in the raw ashes may be an explanation. In experiments E2 and E4, other anionic Cd complexes must be prevalent. Experiment E5 showed another pattern, where about 95% of Cd was found at the cathode end and about 5% was left in the ash. The ash used in this experiment was water-washed, which resulted in a very low chloride content (0.1%, Table 2) in the ash. Thus the formation of negatively charged Cd-Cl complexes will not occur to an extent of any importance to EDR. The major difference between experiment E5 and the other two experiments E2 and E4 for treatment of pre-washed ash is a higher current applied in E5. The pattern of separation of Cd from the ash in E5 shows that the formation of negatively charged Cd complexes is less at higher current, which again may imply that the removal rate is faster than the kinetics for such complexes to form. Thus optimization of the current is crucial to the outcome of treatment also from this point of view.

Pb can be transported to both the cathode and the anode compartment (Fig. 3). The same behaviour was shown by Ottosen et al. [10] where chloride complexes were proposed to explain the removal of Pb to the anode end; this may also explain the distribution pattern of Pb in experiment E5. In [10], the removal efficiencies of Pb were 33% and 66% from the wood ash and straw ash, respectively. In our study, the removal efficiency varied from 12% to 67%. The low removal efficiency does not, however, reflect the small amount of mass removed (Table 4). Pb removal efficiencies (highest percentage) are in the order of E1 > E3 > E6 > E4 > E2 > E5, and the mass of Pb removed is in the order E6 > E4 > E2 > E1 > E3 > E5. The removal efficiency and mass removed were in the same pattern for EFAs (E1 > E3) and WEFAs (E6 > E4 > E2 > E5). The low Pb concentration in raw ashes explained the higher removal efficiency even when a lower mass removed. The two-compartment cell setup used in experiment E6 had a great advantage in treatment of WEFAs, even at the same current density as in experiment E5 but with the lowest charge passed. Stable current improved the removal efficiency of Pb from WEFAs. A high current density seemed not to be competitive (E5 against E4) for the removal of Pb from WEFAs in three-compartment cell, as exemplified in experiment E5 having the lowest removal in both efficiency and mass. It could be concluded that a longer duration of treatment, faster decrease in pH and

stable current favour efficient Pb removal, and the properties of the material also influence the outcome of EDR treatment.

Unlike Cd and Pb, which were problematic in the ashes studied, there are no limiting values for Cu and Zn in [9] for bio-ash spread as fertilizer, but their concentrations in the ashes before treatment were relatively high and their concentrations were also affected by EDR treatment. During EDR the removal was sufficient for the concentrations not to increase as a result of ash dissolution. The results showed that the contents of Cu and Zn in the treated ashes were lower than 75 mg $kg^{-1}$ TS and 300 mg $kg^{-1}$ TS, respectively, with average removal efficiencies of 81% and 97%, respectively.

### 4.3. Washing and EDR

EDR can be used for post-treatment of water-washed ashes. By including EDR, heavy metals can be removed, valuable metals or nutrients may be further recovered, and the residue after remediation may be reused, therefore reducing the amount of waste for landfill and avoiding tax-related disposal. Challenges are faced in the application of the pre-wash/EDR combination, including how to deal with the wash water.

Pre-wash results in ash wash water. The elemental contents in the wash water after washing EFA-2 were measured. The analyses showed that the water contained about 26 g $dm^{-3}$ of K, 363 mg $dm^{-3}$ of P, 195 mg $dm^{-3}$ of Ca, 0.4 mg $dm^{-3}$ of Cd, 0.1 mg $dm^{-3}$ of Cu, 0.03 mg $dm^{-3}$ of Pb and 3 mg $dm^{-3}$ of Zn. The pre-washing greatly transferred the easily soluble contents into water, mainly K, and the K-rich water could be used as K fertilizer. But as irrigation water for agriculture, care should be taken of the heavy metal content in the wash water, because heavy metals can accumulate in soils, be taken up by crops and, therefore, affect crop growth. The recommended maximum concentrations of Cd, Cu, Pb and Zn in irrigation water are 0.01, 0.20, 5.0 and 2.0 mg $dm^{-3}$, respectively, when a water application rate is not more than 10000 $m^3$ per hectare per year [29]. They can be toxic to crops at different levels. For example, in nutrient solutions 0.1 mg $dm^{-3}$ Cd is toxic to beans, beets and turnips, and 0.1∼1.0 mg $dm^{-3}$ Cu can be harmful to many plants [29]. Cd concentration in our wash water was 40 times higher than the recommended concentration. Zn also exceeded the recommended value. As a result, the washing process has to be optimized in the operational parameters to meet the requirements for irrigation water, for example the L/S ratio, or a separation step is needed to remove the heavy metals, especially Cd, from the wash water.

To optimize the washing process, the experience from DongEnergy, which has a pilot plant to produce liquid K fertilizer from straw fly ash, can be used for reference. In their process, the L/S ratio is controlled to maintain a high K content in the water in order to transform it into liquid K fertilizer, and the pH of the water is adjusted to between 9 and 10 by adding NaOH or HCl to minimize the heavy metal content [30]. Electrodialytic treatment could be an option for the removal of heavy metals from the wash water.

EDR treatment results in electrolytes containing heavy metals and some plant nutrients as well as filtrate from ash suspension and the treated ash. The separation of heavy metals and nutrients from electrolytes could be achieved by chemical precipitation, and filtrate could have fertilizer potential (for example, the P concentrated filtrate in experiment E6), even though the P concentration was reduced in the treated ash. Where the recovery from these solutions is not feasible, reuse of the liquids in the EDR process is the preferred option.

### 4.4. Possible use of treated ash

Both this and the previous study showed successful Cd removal by EDR from pre-washed bio-ashes. The selection of EDR cell composition and operational conditions need to be optimized during laboratory studies relating to both the economic and technical aspects. For example, lower energy consumption and shorter treatment time may be achieved using two-compartment EDR cell, but leaching of some heavy metals may pose problems (Table 5). For example, the fast acidification in experiment E6 affected the leaching property of the treated ash, where As, Se and Ni exceeded the limiting concentrations (Table 5) for possible reuse of waste materials in the construction industry [31]. Ni needed attention when the ashes were treated in three-compartment cell. The leaching of Ni and As was higher from the ash in experiment E6 than in experiment E5, probably because the lower pH resulted in a chemical environment favouring formation of soluble Ni and As during an accelerated dissolution of ash. The soluble Ni and As present in filtrate attached to the particle surface, leached out again into water. The fractions of Ni and As found in filtrate and treated ash in experiments E5 and E6 could support the explanation: $(\text{filtrate/ash})_{E6}$: $(\text{filtrate/ash})_{E5}$ = (33%/39%): (1%/60%) for Ni with mass balances of 148% and 95% in E6 and E5, respectively; $(\text{filtrate/ash})_{E6}$: $(\text{filtrate/ash})_{E5}$ = (25%/14%): (1%/8%) for As with mass balances of 86% and 101% in E6 and E5, respectively. However, experiments should be done to get more data to optimize the treatment in respect to leaching properties of toxic elements.

This study showed that the EDR-treated ashes had low fertilizer value, especially due to the dramatic reduction in K content according to the elemental measurement and the disappearance of KCl peaks in the XRD pattern. Only a few works can be found on the nutrient content of EDR-treated bio-ashes. Lima et al. [7] discussed whether the ash, if spread on agricultural land after treatment, could mainly have qualities for soil amendment due to the acidic pH and low fertilizer value. A more attractive possibility of reuse is in the production of construction materials. Biomass fly ash has been studied quite extensively as a secondary construction raw material, such as partly replacing cement in the production of concrete/mortar [22,32] or clay in brick production [33,34]. The advantages of this kind of reuse are reducing $CO_2$ emission, saving natural materials, reducing energy consumption in building material production and decreasing need for landfilling.

When bio-ashes are used for part substitution of clay in bricks, a problem may occur with the soluble salts causing efflorescence in fired bricks. Ash washing and EDR have an advantage in this sense in the removal of soluble salts such as chlorides and sulfates. Compared with the limiting elemental concentrations for ashes used in construction materials in category 1 [31] (maximum 20 mg As $kg^{-1}$ TS, 0.5 mg Cd $kg^{-1}$ TS, 500 mg Cr $kg^{-1}$ TS, 500 mg Cu $kg^{-1}$ TS, 30 mg Ni $kg^{-1}$ TS, 40 mg Pb $kg^{-1}$ TS and 500 mg Zn $kg^{-1}$ TS), the raw ashes exceeded in Cd and Zn, the pre-washed ashes exceeded in As, Cd, Pb and Zn, and all of the EDR-treated ashes exceeded in Cd and Pb. The preliminary study by Chen et al. [17] about the application of EDR-treated bio-ash in clay brick production showed that it is promising to use the EDR-treated straw and wood co-combustion fly ash as a clay substitute, since the ash contained mainly $SiO_2$. In addition, the bricks made from municipal solid waste incineration residues, which are more toxic than the co-combustion fly ash, had low leaching with regards to Cd and Pb. The metals Cd and Pb probably cause a limited problem, but a comprehensive study of the application of the ashes studied is needed in order to assess their use in the brick sintering process.

## 5. Conclusions

The problem with the Cd concentration exceeding limiting values in fly ash from co-combustion of straw and wood chips can be solved by EDR, as a concentration lower than 2 mg $kg^{-1}$ TS can be obtained. The method is efficient in extracting other heavy

metals as well, such as Pb, Cu, and Zn. A water-washing process stabilizes the ash properties by removing easily soluble salts, mainly potassium and chloride, where chlorides could form complexes with heavy metals such as Cd, Pb and Ni hindering good separation during EDR. Placing the anode directly in the ash suspension (two-compartment cell) gave a faster acidification process, facilitating Cd and Pb extraction from the pre-washed ash with a lower energy consumption than in the traditional three-compartment cell, but the leaching-related problem was found in the ash after treatment.

K and P are two nutrient elements in the ash that can be used as fertilizer. K can be recovered by water-washing the raw ash since most of K is water-soluble, and the heavy metal content in the liquid fertilizer could be controlled by adjusting the liquid-to-solid ratio and pH of the solution. K was found primarily located at the cathode end of the EDR system, co-existing with other heavy metal cations. A feasible way to separate K could be by chemical precipitation of these heavy metals at alkaline pH. The P concentration was lower than K in the ashes studied, and P is primarily transported to the anode compartment. In the two-compartment cell P was well separated from the mobilized heavy metals, as P remained in the filtrate from the ash suspension and the heavy metals were removed into catholyte.

The XRD analysis showed that the ashes studied underwent dramatic changes in the main mineral compositions: from KCl and $K_2SO_4$ in the raw ashes, to quartz and calcium carbonates and sulfates after water-washing, finally to mainly quartz in the ashes after EDR treatment. These transformations in ash mineralogy together with the elemental analyses (K removal rate $\geq$ 75% and highest 99% when treating the raw ashes; P removal rate > 85%) further indicate that the fertilizer value of the treated ashes has decreased greatly. Other applications, such as in ceramics or in construction materials where quartz is normally involved, could possibly be an option for reuse of the treated ashes.

## Acknowledgments

The reported work was financially supported by the Department of Civil Engineering at the Technical University of Denmark.

## References

[1] P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresource technology 83 (2002) 37–46.
[2] D. Nordgren, H. Hedman, N. Padban, D. Boström, M. Öhman, Ash transformations in pulverised fuel co-combustion of straw and woody biomass, Fuel processing technology 105 (2013) 52–58.
[3] J. Werkelin, B.-J. Skrifvars, M. Zevenhoven, B. Holmbom, M. Hupa, Chemical forms of ash-forming elements in woody biomass fuels, Fuel 89 (2010) 481–493.
[4] J. Koppejan, S. Van Loo. The handbook of biomass combustion and co-firing, Routledge (2012).
[5] G.M. Kirkelund, A.J. Damoe, L.M. Ottosen, Electrodialytic removal of Cd from biomass combustion fly ash suspensions, Journal of Hazardous Materials 250–251 (2013) 212–219.
[6] M.-L. Sander, O. Andrén, Ash from cereal and rape straw used for heat production: liming effect and contents of plant nutrients and heavy metals, Water, air, and soil pollution 93 (1997) 93–108.
[7] A.T. Lima, L.M. Ottosen, A.B. Ribeiro, Electroremediation of straw and co-combustion ash under acidic conditions, Journal of hazardous materials 161 (2009) 1003–1009.
[8] L.M. Ottosen, I.V. Kristensen, A.J. Pedersen, H.K. Hansen, A. Villumsem, A.B. Ribeiro, Electrodialytic removal of heavy metals from different solid waste products, SEPARATION SCIENCE AND TECHNOLOGY 38 (2003) 1269–1289.
[9] BEK nr 818, Bekendtgørelse om anvendelse af bioaske til jordbrugsformål (Bioaskebekendtgørelsen), Miljøministeriet, (2008) (In Danish).
[10] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method, electrochimica acta 52 (2007) 3420–3426.
[11] P.E. Jensen, L.M. Ottosen, B. Allard, Electrodialytic versus acid extraction of heavy metals from soil washing residue, Electrochimica Acta 86 (2012) 115–123.
[12] A. Ribeiro, J. Rodríguez-Maroto, E. Mateus, E. Velizarova, L.M. Ottosen, Modeling of electrodialytic and dialytic removal of Cr, Cu and As from CCA-treated wood chips, Chemosphere 66 (2007) 1716–1726.
[13] A.T. Lima, L.M. Ottosen, A.B. Ribeiro, H.K. Hansen, Electrodialytic removal of Cd from straw ash in a pilot plant, Journal of Environmental Science and Health Part A 43 (2008) 844–851.
[14] H.K. Hansen, L.M. Ottosen, A. Villumsen, Electrodialytic removal of cadmium from straw combustion fly ash, Journal of Chemical Technology and Biotechnology 79 (2004) 789–794.
[15] A.J. Pedersen, Characterization and electrodialytic treatment of wood combustion fly ash for the removal of cadmium, Biomass and Bioenergy 25 (2003) 447–458.
[16] Scotiabank Commodity Price Index, www.scotiabank.com, September 29 (2014).
[17] W. Chen, L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, J.W. Schmidt, A comparative study on electrodialytically treated bio-ash and MSWI APC-residue for use in bricks, 5th International Conference on Engineering for Waste and Biomass Valorisation, Mines d'Albi, Rio de Janeiro, Brazil, 2014.
[18] G.M. Kirkelund, M.R. Geiker, P.E. Jensen, Electrodialytically treated MSWI APC residue as substitute for cement in mortar, Nordic Concrete Research (2014) 1–16.
[19] G.M. Kirkelund, M.R. Geiker, P.E. Jensen, Feasability test of electrodialytically upgraded MSWI APC residue utilization in mortar, Proceedings Papers 3rd International Conference on Engineering for Waste and Biomass Valorisation (2010) .
[20] DS 259, Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry in flame (2003).
[21] DS/EN 12457-1, Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges, part 1: One stage batch test at a liquid to solid ratio of 2l/kg for materials with high solid content and with particle size below 4mm (without or with size reduction) (2002).
[22] A. Lima, L.M. Ottosen, A.B. Ribeiro, Assessing fly ash treatment: remediation and stabilization of heavy metals, Journal of environmental management 95 (2012) S110–S115.
[23] J. Staal, DONG Energy Power plans and experience in Biomass, https://www.essent.eu/content/Images/90684_04_DONG%20plans%20in%20biomass_Jesper%20Staal.pdf.
[24] P.E. Jensen, L.M. Ottosen, B. Allard, Electrodialytic versus acid extraction of heavy metals from soil washing residue, Electrochimica Acta . 86 (2012) .
[25] T. Mangialardi, Disposal of MSWI fly ash through a combined washing-immobilisation process, JOURNAL OF HAZARDOUS MATERIALS 98 (2003) 225–240.
[26] T.R. Sun, L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, Electrodialytic remediation of suspended soil–Comparison of two different soil fractions, Journal of hazardous materials 203 (2012) 229–235.
[27] L.M. Ottosen, P.E. Jensen, H.K. Hansen, A.B. Ribeiro, B. Allard, Electrodialytic Remediation of Soil Slurry-Removal of Cu, Cr, and As, Separation Science and Technology 44 (2009) 2245–2268.
[28] P.E. Jensen, L.M. Ottosen, C. Ferreira, A. Villumsen, Kinetics of electrodialytic extraction of Pb and soil cations from a slurry of contaminated soil fines, JOURNAL OF HAZARDOUS MATERIALS 138 (2006) 493–499.
[29] R.S. Ayers, D.W. Westcot, Water quality for agriculture, FAO, Rome, 1985.
[30] L. Nikolaisen, J. Hinge, I. Christensen, J. Dahl, P. Arendt Jensen, T. Søndergaard Birkmose, B. Sander, O. Kristensen, R.E. Danish Technological Inst, Utilization of ash fractions from alternative biofuels used in power plants (2008).
[31] BEK nr 1662, Danish Ministry of the Environment, Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald (21/12/2010) (in Danish).
[32] S. Wang, L. Baxter, Fly ash and concrete, Concrete Producer, Concrete Prod 24 (2006) 48–49.
[33] M. Elwan, M. Attriss, A. Mahmoud, S. Salem, Characterization of rice straw ash and its use in clay bricks, Interceram 57 (2008) 19–25.
[34] C. Bories, M.-E. Borredon, E. Vedrenne, G. Vilarem, Development of eco-friendly porous fired clay bricks using pore-forming agents: A review, Journal of Environmental Management 143 (2014) 186–196.

# Chapter 3

## *Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash*

Accepted in Waste Management

Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

# Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash

Wan Chen *, Gunvor M. Kirkelund, Pernille E. Jensen, Lisbeth M. Ottosen

*Department of Civil Engineering, Technical University of Denmark, Denmark*

ARTICLE INFO

*Article history:*
Received 6 March 2017
Revised 26 May 2017
Accepted 11 July 2017
Available online xxxx

*Keywords:*
Fly ash
Electrokinetic remediation
Heavy metals
Thermal stability
Trace elements
Sequential extraction

ABSTRACT

To reduce heavy metal leaching and stabilize municipal solid waste incineration (MSWI) fly ash, different methods and combination of methods were tested: water washing, electrodialytic separation and thermal treatment at 1000 °C. A comparison of heavy metal concentration and leaching levels of As, Cr, Pb and Zn for the different untreated and treated ashes was made. The results showed that minimizing leaching to meet the limiting values of the all the studied heavy metals can be obtained at the same time by combining water washing, electrodialytic separation and thermal treatment. The ash subjected to this combination had lower Cr than the ash solely subjected to thermal treatment or subjected to water washing prior to thermal treatment. The electrodialytic separation (EDS) of the washed ash lowered pH from alkaline to acidic, which resulted in elevated leaching of Cd and Zn, while the Cr leaching was reduced. Up to 58.6% of Zn and 5.5% of Pb were extracted by EDS compared to less than 0.6% extraction by water washing. During thermal treatment of the EDS treated ash, the ash was re-alkalized. Due to solidification and possibly evaporation, most heavy elements left in the thermally treated ash were stabilized and immobilized. However, leaching of As and/or Cr was still problematic and did not meet the limit value for the thermally treated ash being recycled in construction work. The removal of Ca and decomposition of Ca oxides and minerals during EDS was linked to the leaching patterns of As and Cr after thermal treatment.



## 1. Introduction

Incineration of municipal solid waste (MSWI) generates hazardous residues including fly ash. MSWI fly ash contains carcinogenic substances, such as heavy metals and organic compounds (dioxins, furans, PCBs, VOCs and PAHs) (Allsopp et al., 2001). The carcinogenic substances need to be stabilized or removed before the ash being disposed of or potentially recycled as resources.

Thermal treatment can stabilize MSWI fly ash, form stable phases and chemical bonds taking advantage of the $SiO_2$-$Al_2O_3$-CaO system in the ash, and decompose hazardous organics depending on the treatment temperature, such as dioxins at around 1400 °C (Sakai and Hiraoka, 2000). The ash generally shows less leaching of heavy metals after thermal treatment than before treatment. However, one of the main obstacles related to the thermal stabilization of MSWI fly ash and the recycling of the resulting thermally treated ash could be the leaching of Cr, which may increase caused by thermal treatment for both raw MSWI fly ash (Zhang et al., 2010) and the pretreated fly ash (e.g. water-washed (Wang et al., 2001a)). The temperature of thermal treatment, dwelling time and gaseous atmosphere influence the Cr leaching: In an oxygen-containing atmosphere, the oxidation of Cr(III) to more soluble Cr(VI) is the main factor for the increased Cr leaching (Wang et al., 2001b), and this oxidizing process can be accelerated in the presence of a high content of CaO in the ash (Hu et al., 2013a).

Another main concern of thermal treatment of MSWI fly ash is that, volatile heavy metals can be removed from the ash during this treatment, turning into air pollutants. In addition to applying flue gas treatment systems, suppressing and reducing the evaporation of heavy metals is the basis for controlling air pollutant emission during the thermal treatment of MSWI fly ash. The evaporation and release of heavy metals into the flue gas is related to the chloride content in the MSWI fly ash. Tian et al. (2009) found that copper-chloride species ($CuCl_2$ and $CuCl_2{\cdot}2H_2O$) dominated the Cu speciation in the secondary fly ashes generated from the thermal treatment of MSWI fly ash at 1000, 1150 and 1250 °C by X-ray absorption spectroscopy analysis; whereas, Cu was mainly in the form of CuO and $CuSO_4{\cdot}5H_2O$ in the initial ash. In addition, Jakob et al. (1996) noted that chlorides in MSWI fly ash could increase the evaporation of Cd, Pb and Zn. The removal of chlorides

* Corresponding author.
*E-mail address:* wach@byg.dtu.dk (W. Chen).

http://dx.doi.org/10.1016/j.wasman.2017.07.011
0956-053X/© 2017 Elsevier Ltd. All rights reserved.

and the easily soluble alkali and alkaline metal oxides from MSWI fly ash can improve the thermal stability of Cr, Cd, Cu, Pb and Zn and suppress evaporation, as found by Wang et al. (2001a), when the ash was subjected to water washing (removing more than 95% Cl) prior to thermal treatment at 600–900 °C. Ho et al. (2008) reported similar evaporation inhibition effects on Cd, Cu and Zn by water washing of MSWI fly ash prior to thermal treatment.

Water washing affects the ash characteristics and thus influences the fate of heavy metals in the thermal treatment, and so would the other MSWI fly ash treatment methods such as electrodialytic separation (EDS). In EDS, MSWI fly ash is treated in suspension in an electric DC field (Ferreira et al., 2005). Electromigration of mobile ions from the ash suspension toward either the anode or cathode under application of the electric field separates the mobile heavy metals from the suspended MSWI fly ash. Ion exchange membranes separate the electrode compartments from the ash suspension. The ash properties are changing during EDS in terms of pH, conductivity, the content and mobility of heavy metals (and other elements), the content of organic compounds, and mineralogy (Chen et al., 2015; Dias-Ferreira et al., 2016; Jensen et al., 2015; Kirkelund et al., 2015). However, EDS as pretreatment prior to thermal treatment has not been studied yet in dealing with MSWI fly ash; thus the effect of EDS treatment on the thermal behavior of heavy metals such as leaching and volatility needs to be investigated.

Compared to the direct EDS treatment of MSWI fly ash, the combination of washing and EDS avoids the generation of toxic chlorine gas ($Cl_2$) during EDS. In addition, this combination could reduce the energy consumption during EDS by reducing the transport of immediately soluble salts. Moreover, the heavy metals (e.g. Cd, Cu, Pb and Zn) were left in the strongly bound and residual phases in the ash after the combined washing and EDS treatment, as found by Ferreira et al. (2008).

Accordingly, the present study was designed to investigate the use of a combination of methods (i.e. treatment steps: water washing, EDS and thermal treatment (sintering at 1000 °C)) for MSWI fly ash stabilization, aiming to upgrade MSWI fly ash to a resource with acceptable heavy metal leaching levels for recycling in the applications involving sintering or firing (e.g. the production of ceramics/glass), and at the same time suppress the volatility of the heavy metals in the ash. Changes in ash characteristics, focusing on As, Cr, Pb and Zn concentrations and leachability, were investigated after each treatment step. Under different conditions for water washing and EDS, the thermal behavior of As, Cr, Pb and Zn in terms of volatility and leachability were tested and compared. The EDS treatment was conducted mainly using a 2-comparment cell (Kirkelund et al., 2015) to achieve the accelerating acidification in the ash-water suspension.

## 2. Materials and methods

### 2.1. Materials

The MSWI fly ash studied originated from a municipal solid waste incineration plant, I/S Vestforbrænding (VF) in Glostrup, Denmark, with a total incineration capacity of 600,000 t/year. At VF, 15,000 tons of APC residues, including fly ash are produced annually, and the residues are currently exported and used for filling of previous mines. The fly ash sample was collected after the electrostatic precipitator before the neutralization of the acidic components by the wet scrubber process. The ash was sieved in the lab, and the fraction passing the 1-mm sieve was preserved in a closed bucket. The ash as received smaller than 1 mm is termed Ref. The ash underwent different treatments in series: water washing, EDS and thermal treatment as shown in Table 1. To distinguish the ashes after each treatment step, a roman number is linked to the name of the different treatments: (I) washing, (II) EDS and (III) thermal treatment. The treated ash samples are named A, B and C as referring to the differences in the washing procedures (Table 1): L:S 2, 5 and 3 × 5; and the following Latin numbers distinguish different EDS treatments: For example, ash B1-II is the ash washed at L:S 5 and treated with EDS in a 2 compartment setup (2C) for 3 days, and ash C2-III is the ash washed at L:S 3 × 5, treated thermally in addition to EDS. Apart from the Ref and C1 samples, all samples were washed followed by EDS and finally thermal treatment. C1 was treated by washing and thermal treatment only. The pH, mass loss, leaching and total heavy metal content was measured after each step.

### 2.2. Ash treatment processes

*Step I - Washing procedure of the raw ash Ref*: Three different liquid-to-solid (L:S) ratios of (A) 2, (B) 5 or (C) 3 × 5 distilled water/kg ash were used to remove the easily soluble components in the ash. The washing was vigorous by turning the bottle end-over-end for 5 min with 60 rotations per minute. After the one-step washing procedure the ash suspension was filtrated through a 12–15 μm filter. The ash was dried at 105 °C for 24 h, and following crushed by hand in a mortar to pass a 1 mm sieve. The L:S 3 × 5 was a 3 steps procedure with L:S of 5 for each. Between the three steps, the ash suspension was allowed to sediment to ease liquid and solid separation, and the supernatant fraction was decanted through the same filter used for ash collection after the third step. The filtrates were collected for elemental analysis after a secondary filtration (0.45 μm filter): As, Cr, Pb and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian 720-ES, Software version: 1.1.0), and $Cl^-$ by ionic chromatography (IC).

*Step II - EDS treatment* of washed samples: The conditions for EDS treatment are given in Table 1. The variables included L:S ratio of washing pretreatment, time of EDS treatment and setup of EDS cell, which could affect the outcome of EDS treatment such as the removal efficiency of heavy metals from the ash. Two different EDS setups were used (Fig. 1). In the two-compartment (2C) cell (Fig. 1a) the anode was placed directly in the ash suspension (washed ash + distilled water). In the three-compartment (2–3C) cell (Fig. 1b) the anode was first placed in the ash suspension (as in a 2C cell) and later the anode was moved to the anode compartment, where after the experiment continued as a 3C setup. The ash suspensions contained 100 g washed ash and 350 mL distilled water. In the electrode compartments the electrodes were immersed in an electrolyte solution (0.01 M $NaNO_3$ with pH 2), which was recirculated by pumps. The pH of the anolytes and catholytes were adjusted at least once a day to be between 1 and 2 with 1M NaOH or 1:1 $HNO_3$. The pH and electrical conductivity of the ash suspension were also measured at least once a day. A constant

**Table 1**
Overview of the treatment processes and the names of the samples after each step. In general, the washed ashes were named as A-I (A1-I), B-I (general designation of B1-I and B2/3-I) and C-I (general designation of C1-I and C2-I).

| | As received or washed (Step I) | EDS (Step II) | Thermal treatment (Step III) |
|---|---|---|---|
| Ref | Ash as received | – | × (Ref-III) |
| A | Washed, L:S 2 (A1-I) | A1: 2C, 7 days (A1-II) | × (A1-III) |
| B | Washed, L:S 5 (B1-I) | B1: 2C, 3 days (B1-II) | × (B1-III) |
| | Washed, L:S 5 (B2/3-I) | B2: 2C, 7 days (B2-II) | × (B2-III) |
| | Washed, L:S 5 (B2/3-I) | B3: 2C + 3C, 7 + 5 days (B3-II) | × (B3-III) |
| C | Washed, L:S 3 × 5 (C1-I) | C1: – | × (C1-III) |
| | Washed, L:S 3 × 5 (C2-I) | C2: 2C, 7 days (C2-II) | × (C2-III) |



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

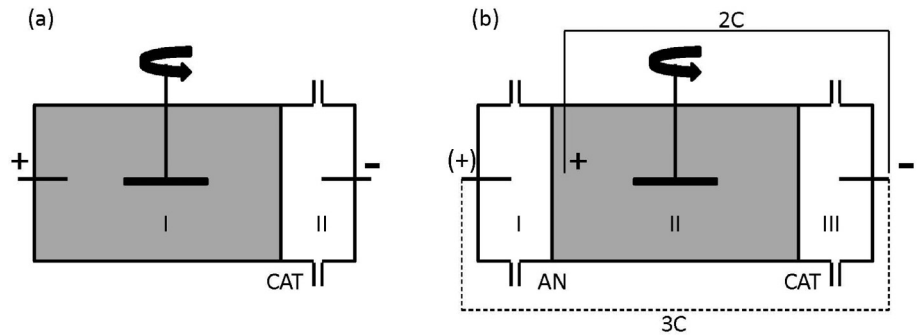


**Fig. 1.** Experimental setups: (a) two-compartment cell (2C); (b) three-compartment cell used for 2-step EDS treatment in Experiment B3: first 2C, effective two compartment cell by current passing through the anode in the ash suspension and the cathode; and then 3C, effective three compartment cell by current passing through the two electrodes in electrolyte solutions (dotted route). AN, anion exchange membrane; CAT, cation exchange membrane.

current of 50 mA was applied to the electrodes in all experiments. The ash suspension after EDS was filtrated. The filtrate was collected for elemental analysis after concentrated nitric acid digestion followed by a secondary filtration (0.45 μm filter). The remaining ash on the filter was dried at 105 °C for 24 h for further analysis. The other liquid samples collected after EDS, including electrolytes and acidic solutions for electrodes cleaning, were ready for elemental analysis after filtered through a 0.45 μm filter.

*Step III - Thermal treatment (sintering):* The ash, 17–20 g was placed in crucible and fired at 1000 °C for 1 h. The fired ash was hand-crushed for analysis using a mortar and pestle after cooling down to room temperature in a desiccator.

### 2.3. Characterization of ash samples

The water content of the Ref ash was determined after drying at 105 °C for 24 h, and calculated as wet based i.e. $\left(\frac{\text{mass}_{\text{wet}}-\text{mass}_{\text{dry}}}{\text{mass}_{\text{wet}}} \times 100\right)$. Particle size distribution was found in a Malvern Mastersizer 2000 particle size analyzer. Organic matter content was measured as mass loss at 550 °C for 1 h. Ash pH was measured with a Radiometer Analytical pH electrode in 1 M KCl solution at L:S of 2.5 after 1 h of agitation. The electric conductivity was determined in distilled water extract of L:S 2.5 with a Radiometer Analytic electrode. The determination of ash solubility in water followed the same procedure as the washing at L:S 3 × 5, and the weight loss in percentages between initial ash and the recovered ash after washing was calculated as the solubility.

The As, Cr, Pb and Zn concentrations of the ash samples were determined after two different digestion methods (a) $HNO_3$ digestion according to Danish Standard DS 259 (2003) and (b) $HNO_3$-HCl-HF acid digestion according to EPA method 3052 (USEPA, 1995). For (a) the $HNO_3$ digestion, 1 g (three or five replicates) of dry ash suspended in 20 mL of 1:1 $HNO_3$ was digested at 200 kPa at 120 °C for 30 min in an autoclave. For (b) the microwave assisted $HNO_3$-HCl-HF digestion had 2 steps: 0.25 g (in duplicate) ash sample suspended in 6 mL of 65% $HNO_3$, 2 mL of 37% HCl, and 2 mL of 40% HF in the digestion vessel, and digested at ~180 °C for 15 min (5 min at 1200 W plus 10 min at 1400 W). Following, the samples allowed cooling before the second digestion using 12 mL of 10% $H_3BO_3$ solution at ~160 °C for 15 min at 1400 W. After digestion, the samples were filtered through a 0.45 μm filter and diluted to (a) 100 mL and (b) 50 mL. The concentrations were measured by ICP-OES, except for Cr digested by method (b), which was measured by inductively coupled plasma mass spectrometry (ICP-MS). All concentrations are expressed on a dry mass basis.

The pH-desorption curves (Pedersen, 2002) for the Ref and the ash washed at L:S (B) 5 and (C) 3 × 5 were made by measuring the concentrations of heavy metals in the leachates of ash suspensions at L:S 25 (1g/25 mL) (in duplicate) in distilled water and $HNO_3$: (0.01 M, 0.05 M, 0.1 M, 0.2 M, 0.3 M, and 0.5 M) after shaking the suspension for one week.

Sequential extraction was made in duplicate with 0.5 g dried ash samples. Sequential extraction was performed after the method described by BCR (Quevauviller et al., 1994). This three step sequential extraction includes: Step 1 (exchangeable and carbonate): acetic acid extraction at L:S of 40 (water and acid soluble, exchangeable fraction), Step 2 (reducible): hydroxylammonium chloride extraction at L:S of 40 (reducible fraction, bound to Fe/Mn oxides) and Step 3 (oxidisable): 2-step hydrogen peroxide attack (20 + 5 mL)/ammonium acetate extraction at L:S of 50 (oxidisable fraction; bound to organic matter and sulphides). A horizontal shaker was used to keep the ash in continuous suspension during the extractions. In this study, an extra step, Step 4 (residual), was added to the method, to measure the residual phase in the ash: this was done by the method from DS 259 (2003).

A leaching test was conducted at L:S of 2 according to DS/EN 12457-1 (2002). The ash was suspended in distilled water and the suspension was agitated in a closed vial for 24 h and vacuum filtered through a 0.45 μm filter. The pH and the oxidation-reduction potential (ORP) was measured with MC3051Pt-9 combined redox electrode in the leachate. The ORP was expressed as Eh (ORP + 210 mV, where 210 mV is the reference potential of an Ag/AgCl reference electrode with 3M electrolyte solution at 20–30 °C). The concentrations of As, Cr, Pb and Zn in the leachate were analyzed by ICP-OES without any pretreatment but concentrated nitric acid preservation. The analysis of the fired ash samples included heavy metal concentrations (3 replicates) and leaching (1 sample).

## 3. Results and discussion

The Ref ash was alkaline (pH 12.2) with low water content (0.4 ± 0.1%) and organic matter content (1.7 ± 0.1%). Generally, MSWI fly ash is alkaline, with pH between 10 and 12 or even higher (like in this case) (He et al., 2016; Wang et al., 2016). The presence of alkali metal and alkaline earth metal oxides, mostly CaO, contribute to the high alkalinity of MSWI fly ashes (Lam et al., 2010). The organic matter content was identical to the number found by Ottosen et al. (2006). About 57% (volume percentage) of the Ref ash had a size from 0.05 to 2 mm in diameter, with the $D_{50}$ value of 73 ± 2 μm. De Boom and Degrez (2012) compared the size distributions of MSWI fly ashes collected at the furnace ($D_{50}$ 117 ± 7 μm), the boiler ($D_{50}$ 240 ± 6 μm) and the electrostatic precipitator (ESP) ($D_{50}$ 55 ± 2 μm). Thus the average particle size of the Ref ash is in accordance with that found for other furnace ashes (De



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

Boom and Degrez, 2012). In addition, the solubility of Ref was 19.0 ± 0.4%.

The heavy metal concentrations of the Ref and treated ash samples are shown in Fig. 2 for the two digestion methods. The concentrations of the heavy metals were generally observed lower when digestion was made by (a) $HNO_3$ compared to (b) the microwave assisted digestion with $HNO_3$, HCl and HF. This is as expected, since method (b) is a total destruction of the sample, whereas not all mineral phases are destructed by method (a). In the actual samples, the As concentrations determined after digestion (b) were 1.1–1.7 times higher than determined after (a), while 2.6–6.4 times for Cr, 0.9–4.5 times for Pb, and 0.9–2.3 times for Zn. The thermally treated ashes were observed to have a greater difference in Pb and Zn concentration between the two digestion methods than the other ash samples. This was probably due to the fixation of Pb and Zn in siliceous solid phases, which are not digestible by $HNO_3$. The major concentration difference measured after the two digestion methods was for Cr, and in many cases the concentration found after digestion by method (b) was three times higher than after (a). This reveals that Cr was bound in the phases not digestible in $HNO_3$ to a higher extent than the other three heavy metals. The range of total concentrations of heavy elements in MSWI fly ashes from waste incineration from different countries were reported in IAWG (1997): 37–320 mg/kg for As, 140–1100 mg/kg for Cr, 5300–26,000 mg/kg for Pb and 9000–70,000 mg/kg for Zn, without specifying which digestion methods were used. The MSWI fly ash of the present study had concentrations of the heavy metals falling within these ranges.

The differences in heavy metal concentrations between each treatment step are influenced by the total ash mass loss during each treatment step (Table 2) as well as by the removal of heavy metals during the treatments. The inhomogeneous nature of the fly ash must also be taken into account, and is illustrated by the error bars for the Ref samples in Fig. 2.

The ash properties changed after each treatment step, in terms of pH, heavy metal concentration, oxidization-reduction potential,

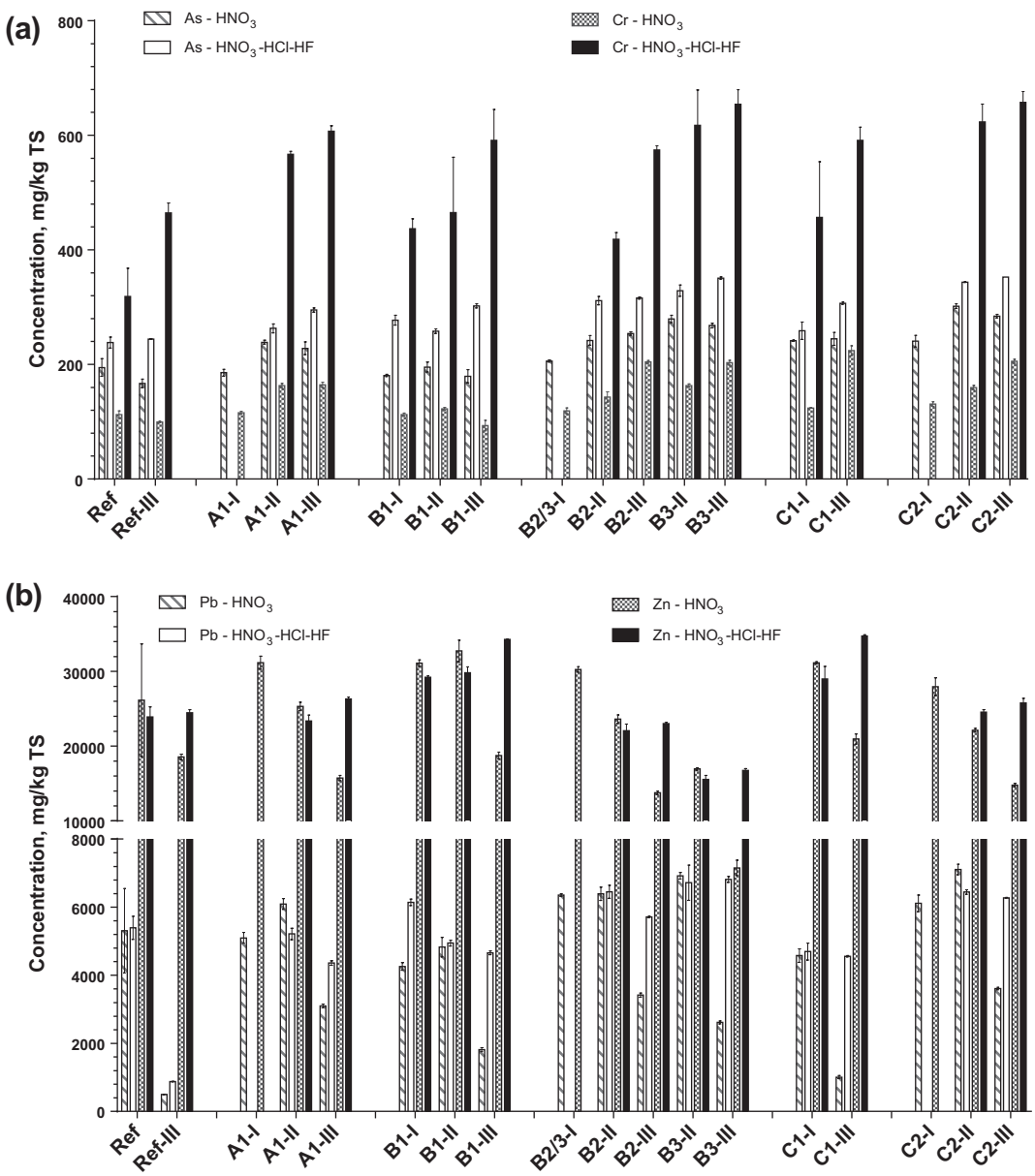


**Fig. 2.** Total concentrations (mg/kg total day solid) of the heavy metals in the ash samples: (a) results for As and Cr; and (b) results for Pb and Zn.



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

**Table 2**
Mass loss (%) for each treatment step.

| | As received or washed (Step I) | EDS (Step II) | Thermal treatment (Step III) |
|---|---|---|---|
| Ref | – | – | 5.2 |
| A | 8 | A1: 15 | 6.5 |
| B | 14 | B1: 7.3 | 7.3 |
| | | B2: 15 | 4.5 |
| | | B3: 21 | 5.2 |
| C | 19 | C1:– | 6.7 |
| | | C2: 14 | 4.5 |

leaching of heavy metals, and the chemical speciation and bonding pattern of the heavy metals. In the following, the changes caused by each treatment step are discussed separately.

### 3.1. Washing in water

In general, the heavy metal concentration in the ash (Fig. 2) increased during washing, as the soluble salts were removed from the total mass. Heavy metals were also removed during the washing. The concentrations of Pb and Zn in the water after washing were quite high, probably due to their soluble chlorine complexes (Jiao et al., 2016), other soluble species such as $K_4PbO_4$ (Ottosen et al., 2006), and their amphoteric properties (Wang et al., 2001a). The repeated washings at L:S 5 from 1 time to 3 times significantly increased the extracted mass of Pb and Zn (Table 3). On the contrary, the repeated washings did not influence Cr and As (the As and Cr mass washed at L:S 5 was found higher after 1 washing than 3, but this relates to the heterogeneous nature of the ash initially).

The $Cl^-$ concentration was high in the water from the washing process, showing a high concentration of soluble Cl-salts in the Ref (Table 3). Ottosen et al. (2006) reported a water-extractable Cl content in a MSWI fly ash collected from the same incineration plant of 12.4% per weight of the ash (L:S 40). The extractable Cl in the present study amounted to 3.7% of the total ash mass at L:S 2 increasing to 4.1% at L:S 5 (Table 3). When increasing the washing procedure to 3 steps the extracted Cl increased to 4.8%, revealing that the extraction of Cl is dependent on the water volume used.

### 3.2. Electrodialytic separation

The mass balances for the heavy metals are calculated as the total amount in the different parts of the EDS cell after treatment divided by the initial amount in the ash before treatment. The mass balances ranged from 92% to 121% based on $HNO_3$ ash digestion and from 75% to 132% based on $HNO_3$-HCl-HF ash digestion in the EDS experiments, which is considered acceptable due to the heterogeneity of the MSWI fly ash.

In general, the Zn concentration was reduced by EDS, and the reduction increased with increasing duration (B1-II to B2-II) (Fig. 2). The Zn concentration decreased further when the 2C–3C setup was used (B3-II). The concentrations of Pb, As and Cr generally increased during EDS. The removal of heavy elements was pH-dependent. Fig. 3 shows pH and conductivity in the ash suspension during the EDS experiments. The pH of the ash suspension (Fig. 3a) decreased as the result of electrolysis at the anode, and there was no clear effect from of L:S ratio from the preceding washing. The conductivity in the ash suspension was on the other hand highly dependent on the washing procedure, as the conductivity decreased with increasing volume of water used for the washing, and this effect was only equalized after one week of EDS. Shifting from 2C to 3C (experiment B3), the pH of the suspension continued decreasing after a short rebound (due to the removal of hydrogen ions into the catholyte (Ottosen et al., 2014)), and the conductivity decreased followed by an increase.

The desorption of the heavy metals from the raw and washed ashes was highly pH dependent, and water washing had no overall influence on the desorption pattern in the investigated pH interval (Fig. 4). The acidification process during EDS also enhanced the mobilization of the heavy metals. The heavy metal desorption curves at Fig. 4 suggest that: As, Cr, Pb, and Zn leach very little in the alkaline to neutral region until a certain pH is reached in the acidic region, where the leaching increases sharply with decreasing pH.

The heavy metal removal during the EDS experiments is shown in Table 4. The removal efficiency was calculated as the sum of the mass on electrodes (except the anode in the ash suspension), in electrolytes and membranes divided by the sum of the abovementioned three and on the stirring stick, in the ash after treatment and in the filtrate of the ash suspension. The removal percentages were Zn $\gg$ Pb > As, Cr; less than 0.5% Cr was removed, whereas up to 59% Zn was removed. Table 4 shows that: (a) with the same treatment time (experiments A1, B2 and C2), increasing L:S ratio in the water washing improved the removal efficiency of Pb and Zn. On the contrary, the increasing L:S did not improve the removal efficiency of As and Cr; (b) at the same washing L:S (experiments B1 and B2), increasing EDS duration increased the removal efficiency of As, Pb and Zn, with the highest increase seen for Zn; and (c) continuing the EDS treatment by shifting from 2C to 3C (experiments B2 and B3) increased the removal efficiency of all four heavy metals.

A detailed distribution of the mobilized heavy metals in experiments B2 and B3 is illustrated in Table 5. In the 2C step the anode was placed directly in the suspension, and the ash suspension acted as anolyte. With the generation of acid at the anode, the ash dissolves. Only the cations (mostly cationic Zn according to Table 5) could be separated from the ash suspension into catholyte during 2C. The anion forming elements such as As and Cr (Cornelis et al., 2008) remained in the liquid phase of the ash suspension when mobilized. During the 3C step, both cations and anions electromigrated to the electrolytes. Most of the desorbed As and Cr was transported into the anolyte, whereas Pb and Zn into the catholyte.

The leachability of Pb from MSWI fly ash could be very low at a pH below 3.4, controlled by species such as chloropyromorphite (Van Herck et al., 2000). As and Cr desorption/adsorption depends on both pH and redox potential. As can exist in forms of As(V) and As(III) in MSWI ash residue, and Cr in forms of Cr(III) and Cr(VI) (Cornelis et al., 2008). In the 2C setup, the anode process in the ash suspension resulted in an acidic environment with a high redox potential. Under such conditions, the dominating speciation of As and Cr was expected to be As(V) and Cr(VI), respectively. Their anionic species electromigrated to the anolyte during 3C treatment, probably mainly as $H_2AsO_4^-$ and $HCrO_4^-$. Since Cr(VI) has high adsorption at low pH, its desorption was suppressed during treatment, which explains the low removal rate. On the other

**Table 3**
Heavy metals and Cl extracted during washing calculated as $[(C * V)/m_0]$, where C is the concentration in the water, V the volume of the water and $m_0$ the mass of ash before washing.

| | A (L:S 2) | B (L:S 5) | C (L:S 3 × 5) |
|---|---|---|---|
| As (μg/kg) | 11 | 136 ± 0.2 | Not detected |
| Cr (μg/kg) | 150 | 1430 ± 89 | 1380 ± 27 |
| Pb (mg/kg) | 11.1 | 11.3 ± 0.8 | 56.6 ± 3.9 |
| Zn (mg/kg) | 1.8 | 19.9 ± 0.2 | 25.1 ± 2.9 |
| Cl (g/kg) | 37.3 | 40.8 ± 1.5 | 48.4 ± 2.5 |



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

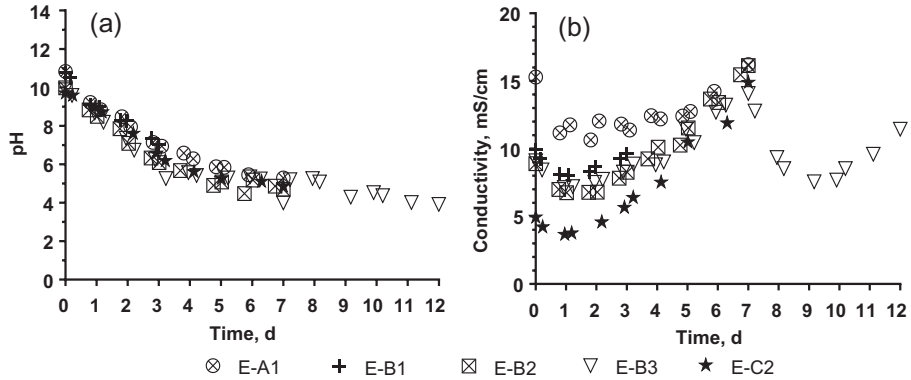


**Fig. 3.** EDS experiments: (a) pH and (b) electric conductivity vs. time in the ash suspension.

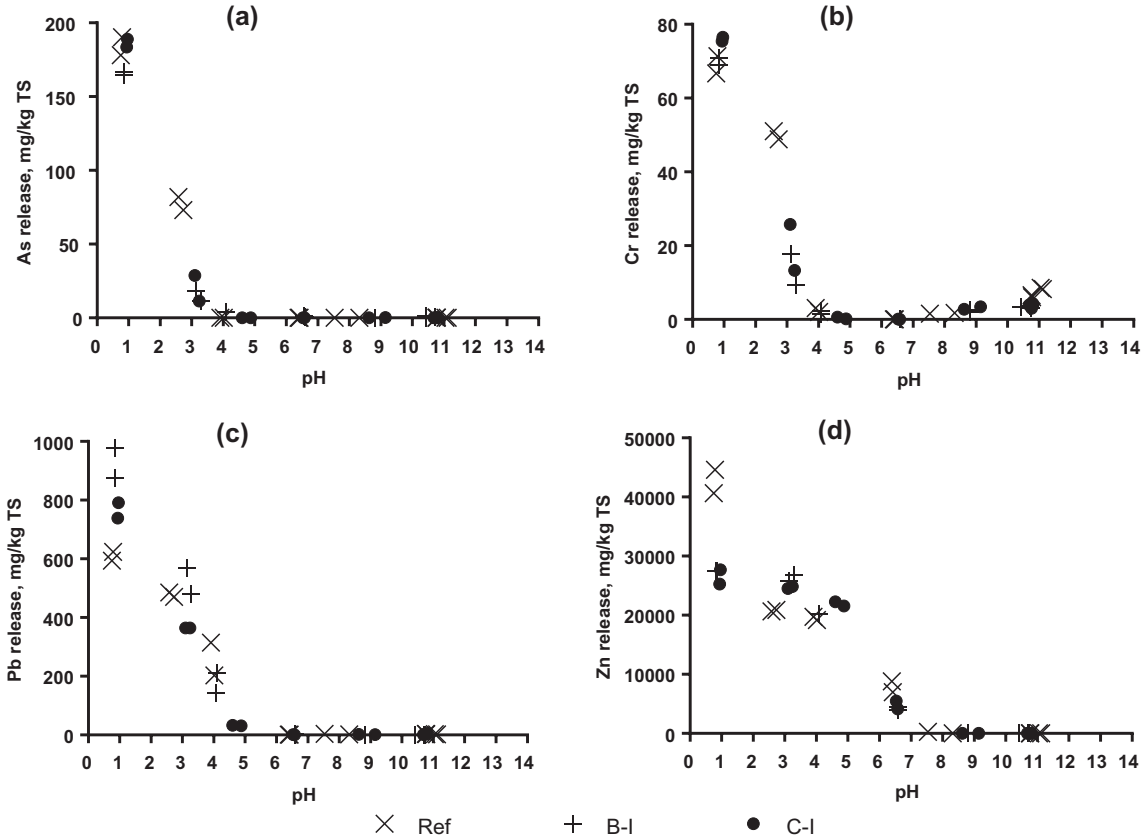


**Fig. 4.** The dependence of each element in the raw Ref ash and the washed ashes B-1 and C-I available for release (mg/kg TS) into nitric acid solutions with different pH values: (a), As; (b), Cr; (c), Pb; (d), Zn.

**Table 4**
Heavy metal removal efficiencies by EDS treatment (based on ash digested using $HNO_3$ / $HNO_3$-HCl-HF).

| Total removal, % | Ash pH before treatment | As | Cr | Pb | Zn | Ash pH after treatment |
|---|---|---|---|---|---|---|
| E-A1 | 10.8 | 0.2 | 0.5/0.1 | 1.0/1.2 | 22.1/23.4 | 6.5 |
| E-B1 | 10.2 | 0.05/0.04 | 0.4/0.1 | 0.3 | 0.6/0.7 | 8.4 |
| E-B2 | 10.2 | 0.2 | 0.2/0.1 | 1.0 | 34.2/35.6 | 6.3 |
| E-B3 | 10.2 | 0.5/0.4 | 1.5/0.4 | 5.4/5.5 | 56.7/58.6 | 5.1 |
| E-C2 | 10.6 | 0.04 | 0.3/0.1 | 1.5/1.6 | 35.8/33.6 | 6.5 |

hand, the pH rebound after shifting to 3C (resulting in almost the same pH in the ash suspension after 2C and 2C–3C) could slightly increase the Cr(VI) desorption. Cr(III) is cationic, but mainly dominates in the leachate at pH lower than 4 (Guertin et al., 2016). Thus, further decreasing the pH of the ash suspension might increase the Cr removal.



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

**Table 5**
The distribution of the elements in the EDS system.

| | As E-B2 | As E-B3 | Cr E-B2 | Cr E-B3 | Pb E-B2 | Pb E-B3 | Zn E-B2 | Zn E-B3 |
|---|---|---|---|---|---|---|---|---|
| Cathode end, mg | 0.05 | 0.02 | 0.03 | 0.05 | 6.6 | 27 | 1163 | 1897 |
| Anode end (3C), mg | – | 0.1 | – | 0.15 | – | 4.3 | – | 31 |
| Filtrate + anode (2C) in ash suspension, mg | 1.03 | 0.1 | 0.1 | 0.08 | 77 | 3.9 | 222 | 127 |
| Ash ($HNO_3$-HCl-HF digestion), mg | 27 | 26 | 36 | 49 | 549 | 534 | 1878 | 1235 |

### 3.3. Thermal treatment

Thermal treatment has by some researchers been investigated as a dry process to achieve heavy metal removal from MSWI fly ash for recovery of the valuable heavy elements and conversion of the fly ash to a non-hazardous material for recycling. For example, these works used chlorinated additives during the thermal treatment in order to enhance the volatility of the heavy elements (Chan, 1997). Other researchers suggest to reduce the chlorides and sulfates volatilization during the thermal process by prewashing or other pre-treatment to remove soluble chlorides and sulfates and/or stabilize the volatile metals; for example Chou et al. (2008) addressed that washing as pretreatment can effectively reduce the leaching of Pb from thermally co-treated MSWI ash residues and also reduce the emission of PAHs in the gas phase.

In the present study, the thermal treatment resulted in an increase in ash pH (Ref 9.9; B3-III 8.4; C2-III 8.6; B1-III 9.3). The formation of alkaline oxides by thermal decomposition was responsible for the pH increase. Zhang et al. (2010) studied thermal behavior of a MSWI fly ash by differential temperature analysis (DTA) and thermogravimetric analysis (TGA). They observed the removal of physical adsorptive/hydrate/constitutional water at temperature below 500 °C, the decomposition of $Ca(OH)_2$, $CaCO_3$, $CaSO_4$ and chlorides at temperature between 531 °C and 1241 °C, and the burning of organic matters at temperature between 481 °C and 531 °C. They detected e.g. CaO in the thermally treated MSWI fly ash by X-ray diffraction, which explains the pH increase by thermal composition.

The concentrations of As, Cr and Zn (based on the $HNO_3$ + HCl + HF digestion) in the sintered ashes increased in comparison to those in the ashes before sintering (Fig. 2), which was associated with the weight loss of the ashes. On the contrary, the Pb concentration decreased. The decrease in Pb concentrations in the sintered ashes is most likely caused by Pb evaporation. Both Pb and Zn are volatile metals. Pb is highly volatile, whereas Zn has medium to low volatility (Wang et al., 2001a).

The volatility of heavy elements can be estimated as the mass loss (L) for each element in percentage during sintering by $L\% = \frac{c_{in} * m_{in} - c_{out} * m_{out}}{c_{in} * m_{in}} * 100$, where c [mg/kg] and m [kg] are the concentration of the element and the mass either of the ash input (in) or the ash output (out) for the sintering. The L% values are compared in Table 6. For As and Zn, the mass losses were all less than about ±12%. By far, the highest mass loss was found for Pb during sintering of the Ref ash. Treatment of the Ref ash by water washing or combined water washing and EDS decreased the evaporation Pb significantly. Similarly, Wang et al. (2001a) reported water washing decreased the evaporation of Pb, and enhanced the stability heavy elements in the washed ash. This decrease is linked to the removal of chlorides during the washing.

Belevi and Langmeier (2000) did laboratory thermal treatment (below 1100 °C) with synthetic and bottom ash samples to determine the element behavior in municipal solid waste incinerators. They found that physical and chemical conditions in furnace, such as temperature, redox condition and chlorine content, affected evaporation of the elements in the samples. However, it is not the physical and chemical conditions but the entrainment in the furnace that primarily affected the transfer of e.g. Cr into the gaseous phase.

According to Table 6, the volatility of Cr was generally low in the present ashes. The results, however, showed an increase in Cr mass during sintering of the Ref and B2-II ashes. This cannot be the case. Accordingly, the recovery rate of chromium by $HNO_3$-HCl-HF digestion could affect the Cr volatility calculation. Chen and Ma (2001) observed low Cr recovery (66–77%) in standard reference materials using the microwave aqua regia (3:1, v/v, HCl to $HNO_3$) + HF digestion. Chromium recovery can be higher than 140% by $HNO_3$-HCl-HF digestion; Andersen and Kisser (2004) compared the recovery rate of Cr in different Si-matrices (including coal fly ash, waste incineration ash, sludge, sediment and soil) by digestion with different acid mixtures, and they showed that the Cr recovery rate varied with Si-matrices as well as digestion methods.

A good Cr recovery could be obtained if Cr was in a relatively labile form, because aqua regia + HF could be inefficient in dissolving some insoluble Cr minerals, as stated by Chen and Ma (2001). In Ref, the Cr concentration might be underestimated due to less labile Cr content. Instead, the Cr mass was more mobile and more easily extracted in the sintered ash due to the oxidation of Cr(III) to easily soluble Cr(VI). The difference in Cr mass between pre and post sintering was reduced when washing and EDS treatment were applied. The Cr behavior during re-sintering of MSWI fly ash has not to the best of our knowledge been reported previously, whereas other heavy elements have been reported quite extensively. Sakai and Hiraoka (2000) reported a mass balance of Cr of 140% in a melting process of MSWI ashes (including bottom and fly ash), and they stated that Cr indicated a high transfer rate into slag. Wang et al. (2001a) e.g. only reported Cr concentrations in the raw ashes, but not in the thermally treated ashes. It might be that the missing reporting on Cr volatilization is due to the difficulties in its mass balances similarly to those shown in Table 6.

**Table 6**
The mass loss (volatility) in percentages for each element induced by thermal treatment.

| Input<br>Output | Ref<br>Ref-III | A1-II<br>A1-III | B1-II<br>B1-III | B2-II<br>B2-III | B3-II<br>B3-III | C1-I<br>C1-III | C2-II<br>C2-III |
|---|---|---|---|---|---|---|---|
| As, % | 3 | −5 | −9 | 3 | −1 | −11 | 2 |
| Cr, % | −48 | 0 | −7 | −25 | 6 | −8 | 3 |
| Pb, % | 85 | 22 | 13 | 15 | 4 | 9 | 7 |
| Zn, % | 3 | −5 | −7 | 0 | −2 | −12 | 0 |



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

### 3.4. Leaching of heavy metals

Fig. 5 gives an overview of the heavy metal leaching from the ash samples before and after each treatment. The leaching is plotted against the leachate pH as the leaching is generally expected to be pH dependent (supported by the findings in Fig. 4). There are no general limiting values for such ashes, and to evaluate the leaching, comparison was made to three different limiting values: landfill for hazardous waste (Class FA1) and landfill for mineral waste (Class MA1) both according to Danish Decree BEK nr 252 (2009) and for reuse of waste for construction work category 3 (C3) according to BEK nr 1414 (2015). Fig. 6 shows the chemical speciation in the ashes by sequential extraction. The results from Figs. 5 and 6 are discussed for each element below.

#### 3.4.1. As and Cr

All As concentrations in the leaching tests were below the limit for ash landfilled as mineral waste (MA1) and no leaching was detected from samples B-I and B1-II. Expect from samples Ref, B2-III, B3-III and C1-III, the leaching of As also met the requirement for ash being used for construction work C3.

It was possible to decrease the As leaching by washing and EDS, compared to the leaching from Ref (Fig. 5). Thermal treatment remobilized As in the ashes treated by washing and EDS (e.g. the leaching B3-III > B3-II, B2-III > B2-II, and C2-III > C2-II according to Fig. 5). The effects from the treatments on the leaching of As were not solely related to the changes in ash pH, but also the changes in the As speciation in the ash, since for instance both of the samples B1-II (Table 4) and B3-III had the same ash pH of 8.4, but they had different leaching levels of As: undetectable for the former and the highest among all the samples for the latter.

Fig. 6 shows that water washing did not significantly change the As speciation in the ash, and the two major fractions both in the Ref and the washed ashes were the oxidisable and residual phases. EDS caused a slight increase in the two first phases of the sequential extraction (exchangeable and carbonate, and reducible). The thermal treatment of the EDS treated ashes with acidic pH values (A1-II, B2-II, B3-II and C2-II), on the other hand, significantly changed the speciation so the reducible phase had the highest concentration. The increase in the reducible fraction of As during thermal treatment has previously been reported by González-Corrochano et al. (2012) when making lightweight aggregates with 75% contaminated mine soil and 25% fly ash from a thermal power plant. They addressed that thermal treatment could destroy the As associated mineral or solid phase in the residual fraction, and thus translocate into other fractions (mainly to reducible and oxidisable fractions in the present study).

Contrary to expectations that high leaching is related to high concentration of the heavy metal found in the exchangeable and carbonate fraction, the Ref ash had a low As concentration in the exchangeable and carbonate fraction and almost the highest leaching, whereas the EDS treated ashes had a high concentration in the exchangeable and carbonate fraction, but lower leaching than the Ref. When the Ref sample was fired without any other treatment (Ref-III) the fraction of As in the exchangeable and carbonate bound phases increased significantly compared to Ref before firing, and to the highest level of all (Fig. 6). An additional trend was an increased reducible fraction during the thermal treatment. Thus, the previous treatments strongly influenced the speciation after firing. Since the residual fraction in sequential extraction was determined by $HNO_3$ digestion the residual fraction of As might be larger than what is shown in Fig. 6 (in accordance to the findings from Fig. 2 where $HNO_3$ digestion resulted in lower concentrations than digestion in the three acids).

An increase in Cr leaching after thermal treatment has been reported in many studies (e.g. Hu et al., 2013b; Wang et al., 2001b), due to the oxidation of insoluble trivalent chromium to its soluble hexavalent state, for example $Cr_2O_3$ to $CrO_4^{2-}$. Similarly,

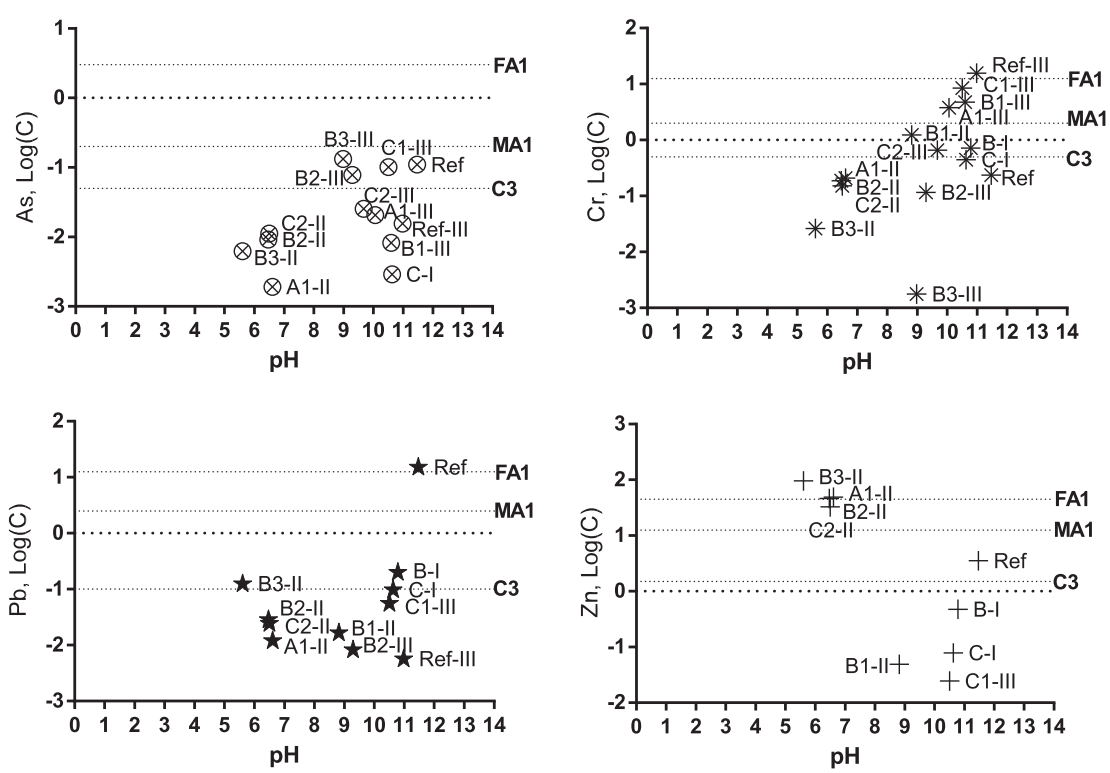


**Fig. 5.** Summary of the results from the leaching test of the untreated and treated ashes at L/S 2, where C [mg/l] is the concentration of each element in the leachate, in order to assess the environmental impact according to Danish regulations for landfill (FA1 and MA1) and recycling (C3).



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

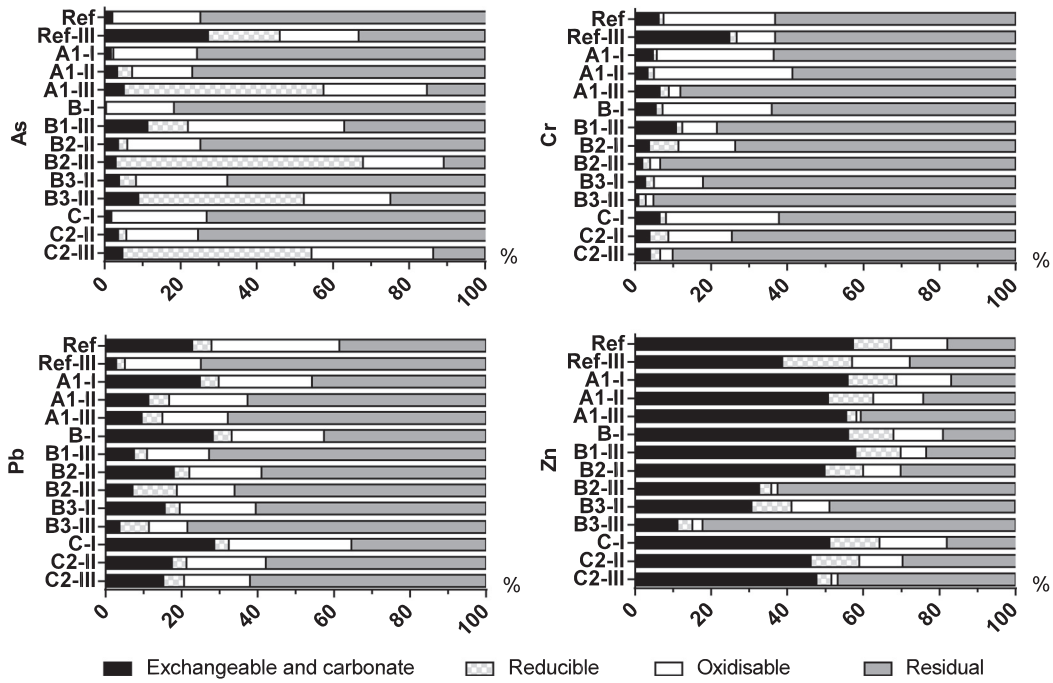


**Fig. 6.** Chemical speciation gained from sequential extraction procedure.

sintering the Ref ash resulted in increased Cr leaching. In fact, leaching from Ref-III (Fig. 5) was higher than from all other samples in the investigation (equivalent to above 80% of the exchangeable and carbonate fraction leached out, Fig. 7), and it was also higher than all the limiting values used for comparison in this work. Similar to As, the highest Cr leaching was found at the alkaline pH, though there was no clear relation between pH and leaching. The increase in EDS duration from 3 days (B1-II) to 12 days (B3-II) caused an ash pH decrease from 8.4 to 5.1, leading to a decrease in Cr leaching (to less than 10% of the exchangeable and carbonate fraction, Fig. 7). This is as expected from Fig. 4b, which showed the lowest release of Cr at slightly acidic pH. Another explanation could be the removal of Cr(VI) with no or little mobilization of Cr(III). The slowly desorbed Cr(III) might be oxidized to Cr(VI) at the 2C step, but it was further extracted to the anolyte at the following 3C step. Firing of the EDS treated ashes increased pH to the alkaline range again and the increase in Cr leaching induced by thermal treatment was generally suppressed by water washing and EDS pretreatment.

The Cr speciation determined by sequential extraction (Fig. 6) showed that the residual fraction dominated in all the samples. Similar to As, the Cr concentration in the exchangeable and carbonate fraction increased after firing the Ref sample. Oxidisable Cr decreased during firing of all samples. On the contrary to As, the residual Cr did not decrease during thermal treatment, but increased, especially when the ash was first water washed and then EDS treated. The ashes B2-II, B3-II and C2-II had increased concentrations in the residual and reducible fractions. The thermal treatment reduced the oxidisable Cr, which suggested that the oxidation of Cr containing complexes occurred, transferring the Cr into the residual fraction. B3-III had the largest proportion of Cr in the residual fraction and smallest in exchangeable and carbonate fraction (Fig. 6), and this ash had the lowest Cr leaching among all the fired samples (Fig. 5).

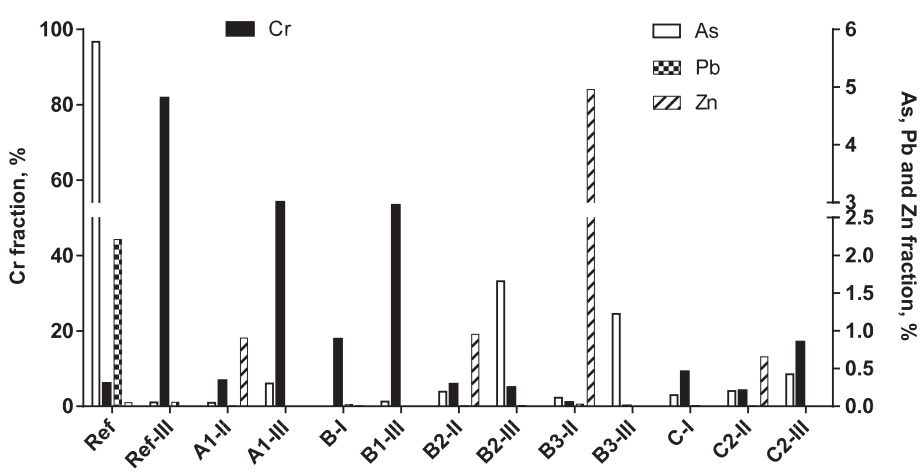


**Fig. 7.** Comparison of leaching to exchangeable/carbonate ratios for the samples. Fraction (%) was calculated by the amount (mg/kg) of the element leached out from the ash divided by the amount (mg/kg) of the element found in the form of exchangeable and carbonate by sequential extraction.



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

According to Cornelis et al. (2008), the leachability of As and Cr in general is highly dependent on the redox state of the leaching system (e.g. ash into water) as well as pH. The leachate of the Ref ash had Eh-pH values of 186 mV-11.3, the washed ash B-I 213 mV-11.1, and the ash samples from the EDS experiments: B1-II 413-8.8, B2-II 508-6.8, C2-II 507-6.7, A1-II 512-6.6, and B3-II 539-5.5. The ORP (=Eh-210 mV) of the raw ash (Ref) was negative, indicating slightly reducing conditions and the washing increased the ORP to a slightly oxidized state. Compared with washing, EDS highly increased the ORP of the ash, which was associated with the oxidation reactions at the anode directly placed in the ash suspension during 2C EDS. The EDS treatment time had a higher effect than the L:S ratios in the washing procedure on the redox potential of the leachates from the EDS-treated ashes. The longer duration of EDS, the higher the ORP was in the leachate.

By integrating the Eh-pH points got in the present study into the Eh-pH diagram for As presented in Cornelis et al. (2008), the dominating species of As in the leachate in the present study was most likely As(V) ($HAsO_4^{2-}$ for Ref, B and B1-II; and $H_2AsO_4^-$ for A1-II, B2-II, B3-II and C2-II). Referring to the sequential extraction pattern of As (Fig. 6), the reducible As greatly increased and, besides the oxidation-reduction reaction in the ash during thermal treatment, the release of As(V) from the residual fraction might happen as well.

For Cr, a similar way of comparing the measured Eh-pH conditions in the present study to the Eh-pH reported by Cornelis et al. (2008) showed that the expected dominating species in the leachate in the present study were the anion $CrO_4^{2-}$ for the raw ash Ref, B-I and B1-II, but the cation $Cr(OH)_2^+$ for the ashes B2-II, C2-II and A1-II and the cation $CrOH^{2+}$ for B3-II. In general, Cr(VI) is more soluble than Cr(III), and the presence of Cr(VI) mainly accounts for the Cr leaching from alkaline wastes, such as MSWI ash (Cornelis et al., 2008). However, when the ashes were treated by EDS for 7 days or more, Cr(III) instead of Cr(VI) dominated in the leachates according to the before-mentioned Eh-pH analysis, which might indicate the possibility of Cr(VI) extraction by EDS, and might also indicate that Cr(VI) was not generated by oxidation of Cr(III) or by transferring Cr(VI) from the residual fraction to the less hard bound fractions. Ribeiro et al. (1997) showed mobilization of Cr from the higher steps of sequential extraction to the soluble and exchangeable phase in soil during electrodialytic soil remediation, which is on the contrary to what was seen in the present investigation. Considering that during the longest EDS experiments (e.g. B3-II) the percentage of Cr in the exchangeable and carbonate fraction in the MSWI ash decreased (Fig. 6) and that the Cr removal was so low (Table 4), this Cr must have been transformed to the other three fractions (reducible/oxidisable/residual) of the sequential extraction. The difference between EDS of soil and ash clearly shows the difference in Cr speciation in these two media.

The order of As leaching from the fired ashes was B3-III > C1-III > B2-III > C2-III > A1-III > Ref-III > B1-III, and the order of Cr leaching Ref-III > C1-III > B1-III > A1-III > C2-III > B2-III > B3-III (Fig. 5). It is noticed that B3-III, B2-III, C2-III and A1-III showed a reverse order when comparing the As and Cr leaching, and these fired ash samples originated from the EDS-treated ashes with pH lower than 7. According to Cornelis et al. (2008), the solubility of oxyanions in solution is associated with their metalates and formation of complexes with Ca-containing minerals (e.g. ettringite and calcite). The leaching of Ca from the fired ashes were in the order of B3-III (710 mg/l) > B2-III (510 mg/l) > C2-III (500 mg/l) > A1-III (480 mg/l), and it is likely that the more water-leachable Ca in the fired samples, the more As and the less Cr leached out from the ash. Increased leaching of As (except from Ref to Ref-III here) has rarely been reported for thermally treated MSWI fly ash. Goetz et al. (1995) compared the As mobility of thermally treated contaminated soil samples with low and high lime content. They found that the mobility of As increased after thermal treatment at both low and high lime content, but the increase was more significant at low lime content. This is in line with the As leaching behavior from our study, and it suggests that the relation between As and Ca-speciation cannot be overlooked during thermal treatment. Hu et al. (2013a) found that during a thermal process, CaO played a significant role in the oxidation of $Cr_2O_3$ in MSWI fly ash to Cr(VI), which led to a sharply increase in Cr leaching. They showed that an adjustment of the ratio of CaO and total of silicon and aluminum oxides in the fly ash inhibited the leaching of Cr from thermally treated MSWI fly ash. This shows that the leachability of Cr is highly dependent on the composition of the ash itself. In the case of our study, reactions with Ca could explain the lower Cr leaching and increased As leaching if e.g. $CaCrO_4$ and $Ca_3(AsO_4)_2$ were the dominating species controlling the leaching of Cr and As. In this case lower Cr leaching and higher As leaching would be expected (Flora, 2014). Firstly, the decrease in pH to neutral and slightly acidic ash pH during EDS is expected to influence the Ca leaching from the subsequent fired samples, as the lower the pH was after EDS, the higher the Ca leaching was after thermal treatment. Secondly, removal of Ca into the cathode compartment at acid pH during EDS may result in less Ca available for formation of As-Ca or Cr-Ca complexes. Lastly, the decrease in Cr leaching and increase in As leaching is possibly due to the acidification of the ash during EDS, which changed the $CaO$-$Al_2O_3$-$SiO_2$ composition and thus limited the possibility to form leachable $CaCrO_4$. Kirkelund et al. (2014) showed that during EDS the concentrations of Ca, Na and K (given in oxide form analyzed by X-ray fluorescence) decreased while Al and Si concentrations increased in an MSWI APC residue. Less Ca available for forming soluble $CaCrO_4$ and stable $Ca_3(AsO_4)_2$ during the thermal treatment due to the EDS pretreatment might explain the findings in the present work.

### 3.4.2. Pb and Zn

The Zn leaching (Fig. 5) was low at alkaline pH even though the total concentration of Zn was by far the highest of the four investigated heavy metals (Fig. 2). No Zn leaching was detected from samples Ref-III, A1-III, B1-III, B2-III, B3-III and C2-III. The Zn leaching increased after the EDS step, probably due to the decreased pH. After washing and thermal treatment, the Zn leaching was below all the three limiting values (Fig. 5). All the three treatment steps reduced the less hard bound Zn fractions (exchangeable, carbonate, reducible and oxidisable), and increased the residual fraction (Fig. 6), especially in the case of B3-III which went through the longest EDS duration and had the highest removal efficiency (58.6%).

The leaching of Pb (Fig. 5) was around the limit C3 for reuse in construction work from all samples, except from the Ref ash. No Pb leaching was detected from the samples A1-III, B1-III, B3-III and C2-III. The high Pb leaching from the Ref ash was probably related to its chloride complexes in the ash. Chou et al. (2009) found that thermal treatment could change the distribution patterns of Pb to more stable states, therefore reducing the leaching. This is consistent with our findings about the chemical speciation of Pb in the fired samples (Fig. 6). The three treatment steps gradually decreased the exchangeable and carbonate fraction of Pb in the ash and increased Pb in the residual fraction.

## 3.5. Overall assessment of the combined treatments

The purpose of combining the three treatments was to stabilize the studied MSWI fly ash. Neither the raw MSWI fly ash (Ref) nor the thermally treated raw ash (Ref-III) met the requirements for controlled landfill as hazardous waste in Class FA1, because the leaching of Pb and Cr exceeded the limiting values. Washing alone



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

reduced the heavy metal leaching to meet the limit values for landfill as mineral waste or for reuse in construction work, but after thermal treatment the washed ash (C1-III) still had a high leaching of Cr. EDS showed potential in extracting the heavy metals from the washed ashes especially for Zn, but the pH decrease of the ash after EDS generally increased the leaching of Zn to a concentration higher than the limit for hazardous landfill (FA1). Thermal treatment, as a post-treatment method after EDS, showed great potential to lower the leaching of Zn and Pb. In addition, the pH decrease caused by EDS suppressed the leaching of Cr from the subsequently thermally treated ash (e.g. C2-III and B2-III), which was lower than the Cr leaching from the sintered-washed ash (C1-III). Notably, the firing of the ash washed at L:S 5 (1 or 3 times) followed by EDS-treated for 7 days (e.g. sample C2-III) could meet the leaching limits of As, Cr, Pb and Zn for mineral waste (Class MA1).

## 4. Conclusion

MSWI fly ash is a highly instable product, and leaching of heavy metals makes handling difficult. Thermal treatment of MSWI fly ash emitted air pollutants and resulted in a residue having high leaching of Cr, which limits the application of MSWI fly ash in e.g. bricks or lightweight aggregates, where high temperature is applied.

MSWI fly ash treatment such as water washing and the combination of washing and electrodialytic treatment, affected the thermal behavior of As, Cr, Pb and Zn in the post thermal treatment in terms of heavy metal evaporation and leaching. Washing, EDS and thermal treatment all influenced the ash matrix, but in different ways. These changes influenced the heavy metal speciation in the ash as revealed by sequential extraction.

The combination of water washing, EDS and thermal treatment (e.g. sintering) stabilized the studied MSWI fly ash, and lowered the evaporation level, especially of Pb, during thermal treatment. EDS decreased the leaching of Cr from the afterwards thermally treated ash, which was lower than the Cr leaching from the sintered-washed ash. The change in ash pH, the removal of chloride, the decomposition of CaO, the removal of heavy metals and their changed chemical speciation during treatment were related to the leaching of Cr. Ca is important to especially As and Cr leaching levels from the fired ash. Removal of Ca by EDS resulted in an inhibited leaching of Cr after thermal treatment, but an increased As leaching. The study shows that minimizing leaching of all the studied heavy metals can be obtained at the same time after thermal treatment (e.g. the treated ash named C2-III which had a leaching level close to that for recycling).

## Acknowledgments

This study was financially supported by the Department of Civil Engineering at the Technical University of Denmark.

## References

Allsopp, M., Costner, P., Johnston, P., 2001. Incineration and human health. State of knowledge of the impacts of waste incinerators on human health. Environ. Sci. Pollut. Res. 8 (2), 141–145.

Andersen, K.J., Kisser, M.I., 2004. Digestion of Solid Matrices-Desk Study Horizontal. Eurofins A/A, Denmark.

BEK nr 1414, 2015. Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald. Retrieved from <https://www.retsinformation.dk/Forms/R0710.aspx?id = 134831>.

BEK nr 252, 2009. Bekendtgørelse om deponeringsanlæg.

Belevi, H., Langmeier, M., 2000. Factors determining the element behavior in municipal solid waste incinerators. 2. Laboratory experiments. Environ. Sci. Technol. 34 (12), 2507–2512. http://dx.doi.org/10.1021/es991079e.

Chan, C.C.-Y., 1997. Behaviour of Metals in MSW Incinerator Fly Ash during Roasting with Chlorinating Agents. National Library of Canada = Bibliothèque nationale du Canada.

Chen, M., Ma, L.Q., 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. Soil Sci. Soc. Am. J. 65 (2), 491–499. http://dx.doi.org/10.2136/sssaj2001.652491x.

Chen, W., Jensen, P.E., Ottosen, L.M., Kirkelund, G.M., 2015. Electrodialytic remediation of fly ash from co-combustion of wood and straw. Electrochim. Acta 181, 208–216. http://dx.doi.org/10.1016/j.electacta.2015.04.083.

Chou, J.D., Wey, M.Y., Chang, S.H., 2008. Emission of Pb and PAHs from thermally co-treated MSWI fly ash and bottom ash process. J. Hazard. Mater. 150 (1), 27–36. http://dx.doi.org/10.1016/j.jhazmat.2007.04.041.

Chou, J.D., Wey, M.Y., Chang, S.H., 2009. Evaluation of the distribution patterns of Pb, Cu and Cd from MSWI fly ash during thermal treatment by sequential extraction procedure. J. Hazard. Mater. 162 (2–3), 1000–1006. http://dx.doi.org/10.1016/j.jhazmat.2008.05.155.

Cornelis, G., Johnson, C.A., Van Gerven, T., Vandecasteele, C., 2008. Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: a review. Appl. Geochem. 23 (5), 955–976. http://dx.doi.org/10.1016/j.apgeochem.2008.02.001.

De Boom, A., Degrez, M., 2012. Belgian MSWI fly ashes and APC residues: a characterisation study. Waste Manage. 32 (6), 1163–1170. http://dx.doi.org/10.1016/j.wasman.2011.12.017.

Dias-Ferreira, C., Kirkelund, G.M., Jensen, P.E., 2016. The influence of electrodialytic remediation on dioxin (PCDD/PCDF) levels in fly ash and air pollution control residues. Chemosphere 148, 380–387. http://dx.doi.org/10.1016/j.chemosphere.2016.01.061.

DS/EN 12457-1, 2002. Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction).

DS 259, 2003. Vandundersøgelse – Bestemmelse af metaller i vand, jord, slam og sedimenter – Almene principper og retningslinjer for bestemmelse ved atomabsorptionsspektrofotometri i flamme.

Ferreira, C.D., Jensen, P., Ottosen, L., Ribeiro, A., 2008. Preliminary treatment of MSW fly ash as a way of improving electrodialytic remediation. J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng. 43 (8), 837–843. http://dx.doi.org/10.1080/10934520801974319.

Ferreira, C., Jensen, P., Ottosen, L., Ribeiro, A., 2005. Removal of selected heavy metals from MSW fly ash by the electrodialytic process. Eng. Geol. 77 (3–4 SPEC. ISS.), 339–347. http://dx.doi.org/10.1016/j.enggeo.2004.07.024.

Flora, S.J.S., 2014. Handbook of Arsenic Toxicology. Academic Press.

Goetz, D., Holz, C., Meyenburg, G., 1995. Influence of thermal treatment on the mobility of arsenic, chromium and vanadium in soils. In: Contaminated Soil'95. Springer, pp. 1215–1216.

González-Corrochano, B., Alonso-Azcárate, J., Rodas, M., 2012. Effect of thermal treatment on the retention of chemical elements in the structure of lightweight aggregates manufactured from contaminated mine soil and fly ash. Constr. Build. Mater. 35, 497–507. http://dx.doi.org/10.1016/j.conbuildmat.2012.04.061.

Guertin, J., Jacobs, J.A., Avakian, C.P., 2016. Chromium (VI) Handbook. CRC Press.

He, X.H., Zhu, S.J., Jiann-Yang, H., 2016. Physical and Chemical Properties of MSWI Fly ash. In: Characterization of Minerals, Metals, and Materials. Springer International Publishing, pp. 451–459, doi: http://dx.doi.org/10.1007/978-3-319-48210-1_56.

Ho, H.C., Chow, J.D., Gau, S.H., 2008. Thermal mobility of heavy metals in municipal solid waste incinerator fly ash (MSWIFA). Environ. Eng. Sci. 25 (5), 649–656. http://dx.doi.org/10.1089/ees.2007.0043.

Hu, H., Luo, G., Liu, H., Qiao, Y., Xu, M., Yao, H., 2013b. Fate of chromium during thermal treatment of municipal solid waste incineration (MSWI) fly ash. Proc. Combust. Inst. 34 (2), 2795–2801. http://dx.doi.org/10.1016/j.proci.2012.06.181.

Hu, H.Y., Liu, H., Shen, W.Q., Luo, G.Q., Li, A.J., Lu, Z.L., Yao, H., 2013a. Comparison of CaO's effect on the fate of heavy metals during thermal treatment of two typical types of MSWI fly ashes in China. Chemosphere 93 (4), 590–596. http://dx.doi.org/10.1016/j.chemosphere.2013.05.077.

IAWG, 1997. Municipal Solid Waste Incinerator Residues, vol. 67. Elsevier.

Jakob, A., Stucki, S., Struis, R.P.W.J., 1996. Complete heavy metal removal from fly ash by heat treatment: influence of chlorides on evaporation rates. Environ. Sci. Technol. 30 (11), 3275–3283. http://dx.doi.org/10.1021/es960059z.

Jensen, P.E., Kirkelund, G.M., Pedersen, K.B., Dias-Ferreira, C., Ottosen, L.M., 2015. Electrodialytic upgrading of three different municipal solid waste incineration residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and $SO_4$. Electrochim. Acta 181, 167–178. http://dx.doi.org/10.1016/j.electacta.2015.06.012.

Jiao, F., Zhang, L., Dong, Z., Namioka, T., Yamada, N., Ninomiya, Y., 2016. Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior. Fuel Process. Technol. 152, 108–115. http://dx.doi.org/10.1016/j.fuproc.2016.06.013.

Kirkelund, G.M., Geiker, M.R., Jensen, P.E., 2014. Electrodialytically treated MSWI APC residue as substitute for cement in mortar. Nordic Concr. Res. 49, 1–16.

Kirkelund, G.M., Magro, C., Guedes, P., Jensen, P.E., Ribeiro, A.B., Ottosen, L.M., 2015. Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension – test of a new two compartment experimental cell. Electrochim. Acta 181, 73–81. http://dx.doi.org/10.1016/j.electacta.2015.03.192.



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

Lam, C.H.K., Ip, A.W.M., Barford, J.P., McKay, G., 2010. Use of incineration MSW ash: a review. Sustainability 2 (7), 1943–1968. http://dx.doi.org/10.3390/su2071943.

Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., 2014. Two step electrodialytic remediation of soil suspension for simultaneous removal of As and Cu. In: Proceedings of the13th Symposium on Electrokinetic Remediation, pp. 156–157.

Ottosen, L.M., Lima, A.T., Pedersen, A.J., Ribeiro, A.B., 2006. Electrodialytic extraction of Cu, Pb and Cl from municipal solid waste incineration fly ash suspended in water. J. Chem. Technol. Biotechnol. 81 (4), 553–559. http://dx.doi.org/10.1002/jctb.1424.

Pedersen, A.J., 2002. Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash. J. Hazard. Mater. 95 (1–2), 185–198. http://dx.doi.org/10.1016/S0304-3894(02)00138-3.

Quevauviller, P., Rauret, G., Muntau, H., Ure, A.M., Rubio, R., López-Sánchez, J.F., Fiedler, H.D., Griepink, B., 1994. Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments. Fresenius' J. Anal. Chem. 349 (12), 808–814. http://dx.doi.org/10.1007/BF00323110.

Ribeiro, A., Villumsen, A., Jensen, B., Refega, A., Vieira Silva, J.M., 1997. Redistribution of Cu, Cr and As in a Portuguese polluted soil during electrokinetic remediation. Colloques de l'INRA (France).

Sakai, S., Hiraoka, M., 2000. Municipal solid waste incinerator residue recycling by thermal processes. Waste Manage. 20 (2–3), 249–258. http://dx.doi.org/10.1016/S0956-053X(99)00315-3.

Tian, S., Yu, M., Wang, W., Wang, Q., Wu, Z., 2009. Investigating the speciation of copper in secondary fly ash by X-ray absorption spectroscopy. Environ. Sci. Technol. 43 (24), 9084–9088. http://dx.doi.org/10.1021/es902039x.

USEPA, E.P.A., 1995. Method 3052: Microwave assisted acid digestion of siliceous and organically based matrices. Test Methods for Evaluating Solid Waste.

Van Herck, P., Van Der Bruggen, B., Vogels, G., Vandecasteele, C., 2000. Application of computer modelling to predict the leaching behaviour of heavy metals from MSWI fly ash and comparison with a sequential extraction method. Waste Manage. 20 (2–3), 203–210. http://dx.doi.org/10.1016/S0956-053X(99)00321-9.

Wang, K.S., Chiang, K.Y., Lin, K.L., Sun, C.J., 2001a. Effects of a water-extraction process on heavy metal behavior in municipal solid waste incinerator fly ash. Hydrometallurgy 62 (2), 73–81. http://dx.doi.org/10.1016/S0304-386X(01)00186-4.

Wang, K.S., Sun, C.J., Liu, C.Y., 2001b. Effects of the type of sintering atmosphere on the chromium leachability of thermal-treated municipal solid waste incinerator fly ash. Waste Manage. 21 (1), 85–91. http://dx.doi.org/10.1016/S0956-053X(00)00041-6.

Wang, L., Chen, Q., Jamro, I.A., Li, R., Li, Y., Li, S., Luan, J., 2016. Geochemical modeling and assessment of leaching from carbonated municipal solid waste incinerator (MSWI) fly ash. Environ. Sci. Pollut. Res. Int. 23 (12), 12107–12119. http://dx.doi.org/10.1007/s11356-016-6320-2.

Zhang, H.Y., Zhao, Y.C., Qi, J.Y., 2010. Thermal characterization of fly ash from one municipal solid waste incinerator (MSWI) in Shanghai. Process Saf. Environ. Prot. 88 (4), 269–275. http://dx.doi.org/10.1016/j.psep.2010.03.004.



Please cite this article in press as: Chen, W., et al. Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.07.011

# Chapter 4

## *A comparative study on electrodialytically treated bioash and MSWI APC-residue for use in bricks*

Conference paper

# A COMPARATIVE STUDY ON ELECTRODIALYTICALLY TREATED BIO-ASH AND MSWI APC-RESIDUE FOR USE IN BRICKS

W. CHEN*, L. M. OTTOSEN, P. E. JENSEN, G. M. KIRKELUND and J. W. SCHMIDT
Department of Civil Engineering, Technical University of Denmark, Denmark.
*Corresponding author: e-mail wach@byg.dtu.dk, telephone + 4545251816

**Keywords**: fly ash, clay brick, sintering, heavy metal, electrokinetics

## Abstract

Two main electrodialytically treated particulate residues: co-combusted straw and wood fly ash (TSWFA) and municipal solid waste incineration (MSWI) air pollution control residue (TMAPC), were considered for partly clay replacement (up to 25 %) in brick production. Another washed MSWI fly ash (WMFA) was also studied to compare with TMAPC. They had the main difference in calcite content.

Brick pellets containing maximum 25 % ash were shaped by pressing and fired at temperatures ≤ 1100 $^0$C. The sintering properties of the materials were determined, including weight loss, shrinkage, vacuum water absorption, apparent porosity and bulk density. The heavy metal leaching from the pellets containing TMAPC and WMFA was also investigated.

The water absorption of the pellets increased as the addition of TSWFA and TMAPC increased, and it decreased as the sintering temperature increased. The total shrinkage decreased significantly due to the addition of the ashes. The results showed that brick pellets sintered at 1100 $^0$C with 25 % TSWFA addition, or at 1000 $^0$C with 5 % TMAPC met the water absorption requirement for Grade MW building bricks in ASTM C62 − 13a. Cr from TMAPC and WMFA, posed the major leaching problem among the heavy metals.

The results indicate that the treated fly ash from co-combusted straw and wood can be used in making clay bricks. The relatively high amount of calcite in TMAPC seemed to retard its use into yellow clay. This explains the different sintering behaviors of TMAPC and WMFA in this study.

## 1- INTRODUCTION

Clay, a non-renewable natural resource, is the major raw material for clay brick production. When mixed with water, clay minerals, e.g. hydrous aluminum silicates, show plasticity and formability. During firing at high temperatures, $SiO_2$ and $Al_2O_3$ in clay react to form brick network. Meanwhile, fusing occurs owing to the network modifiers (e.g. $K_2O$ and $Na_2O$), and then bricks shrink and become dense and strong, possessing long durability. Such behaviors make clay born for ceramics. However, the ban of using solid clay bricks has been set in China [1, 2], for the main reasons to prevent farmland destruction, to reduce the energy consumption [3], and to reduce gas emission during firing clay bricks. New and sustainable building materials have been encouraged, and will be the inevitable trend of development. Commonly, additives are blended to modify clay compositions in order to produce different bricks for example in color and porosity, and to improve the properties, such as strength and chemical resistance [4]. The additives can be pure chemicals (e.g. $BaCO_3$), natural resources (e.g. sand to lower shrinkage) and even wastes.

Waste is generated continuously in high amounts, and requires proper management methods. Using particulate waste products as clay substitute has the following advantages: (1) to utilize the waste as secondary resources and landfill less; (2) to save clay. The waste recycling situation in fired clay bricks was reviewed in [5]. It reveals that replacing clay with waste (e.g. limestone dust, wood dust, fly ash and sludge) is promising and has positive effects on the materials' sintering behavior. In most cases in [5] covering the reuse of sludge, vegetal matters, grass, sawdust and combustion, porosity of the fired bricks increased, and density decreased, which could improve the insulation property of bricks [6], and reduce transport costs. Water absorption increased due to the increase in open pores, which could reduce the brick durability when too much water penetrates into brick. Fly ash is a by-product from waste incineration. The $SiO_2$, $Al_2O_3$ and CaO contents in fly ash are attractive as a clay substitute [7]. However, the high heavy metal content retards its application to some extent. Municipal solid waste incineration fly ash is highly toxic [8], and straw and wood fly ash contains a relatively high amount of Cd [9]. To avoid heath issues and ensure social acceptance, it would be preferential to remove these heavy metals before using the ash in construction materials.

There are techniques investigated to treat contaminated ash, such as washing treatment [10], thermal treatment [11], acid extraction and precipitation, and combination of water washing and electrokinetic stabilization [8, 9, 12, 13]. Washing removes easily soluble compounds in ash. It is a simple method that can be applied as an early-stage treatment, which could be followed by e.g. sintering to produce aggregates [14]. In comparison to the ash prior to washing, the washed ash shows significant reduction in soluble salts (e.g. alkaline chlorides), and could be enriched in some heavy metals [15]. Heavy metal dissolution is however also happening to some extent [16]. The ash application would benefit from the washing process, such as the most favorable aspects in reducing the heavy metal leaching [16], and improving the chemical and mechanical properties of the sintered products [15].

Electrodialytic remediation (EDR) is a method developed to reduce heavy metals in ash through electromigration in an applied electric field [8, 9, 12, 13, 17, 18]. The important functions of EDR are: (1) decreasing metal solubility, e.g. Ba, Cr and Pb [18]; (2) reducing heavy metal and salt leaching to some extent [12]; and (3) removing heavy metals, such as Cd, Cu, Pb and Zn [8, 9]. The combination of water washing and EDR can minimize the ash

dissolution and reduce the heavy metal leachability [8].

The aim of this study was to investigate the effect of partly replacing clay with electrodialytically treated ash in clay brick production on the sintering behavior. Laboratory clay brick pellets were made to find out how the clay substitution affects the sintering behavior in terms of weight loss, shrinkage, vacuum water absorption, apparent porosity and bulk density. The heavy metal leaching was also investigated.

## 2- MATERIALS AND METHODS

### Materials

Four raw materials (clay, two EDR treated ash, and washed MSWI fly ash) were used:

(1) The clay was collected from a brickwork for the production of yellow bricks. Pure clay has plate-like structure, but the clay used in this study did not show this structure, so it suggests impurities in the clay. The yellow colour of the brick is caused from the mass of CaO being at least 3 times higher than the mass of $Fe_2O_3$ in the original clay.

(2) EDR *Treated* co-combusted *Straw* and *Wood Fly Ash* (TSWFA): the ash originated from Enstedværket CHP plant (Dong Energy, Denmark). The raw ash was prewashed in distilled water prior to the treatment in a 3-compartment EDR cell.

(3) Water-*Washed MSWI Fly Ash* (WMFA): the raw fly ash, which originated from a municipal waste incinerator in Denmark (REFA), was washed in the same way as prewashing the raw ash in (2).

(4) *Treated MSWI Air Pollution Control* (TMAPC) residue: the raw residue was also collected from REFA. It included flue gas cleaning products formed upon injection of ammonia and slaked lime ($Ca(OH)_2$), while MSWI fly ash in (3) included only flue gas cleaning products formed upon injection of ammonia, taken out before lime injection. The residue was ED treated, and the process is reported in Kirkelund et al. [12]. During the treatment, the mobile fraction of heavy metals and the major part of soluble salts were removed in the electrodialytic stack.

### Treatment experiment

Figure 1 shows the principle of electrodialytic remediation. The water-washed fly ash was suspended in water, and placed in the demineralization compartment (compartment II). Compartment I and III are electrode compartments, containing circulated electrolyte (0.01M $NaNO_3$ solution with pH 2 adjusted by $HNO_3$) during the experiment. Upon the electric field, mobile ions in the ash electromigrate to the concentration compartments through the ion exchange membranes, therefore achieving the extraction of ions from the ash suspension. The ash was treated for 66 days with liquid to solid ratio (L/S) of 7 at the current of 10 mA.

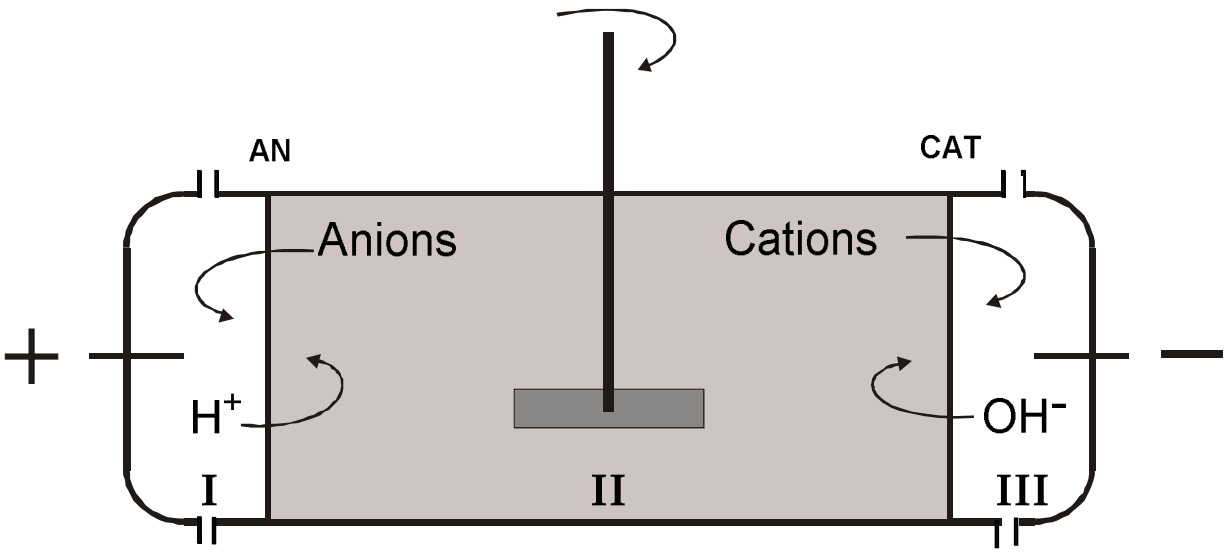


*Figure 1: The princple of EDR treatment and the schematic drawing of a 3-compartment EDR cell. AN - Anion exchange membrane, and CAT - cation exchange membrane.*

## Analytical

The analytical methods are shown in Table 1.

| Material | Elemental content | Atterberg test | $CaCO_3$ | XRD | pH |
|---|---|---|---|---|---|
| Ashes | √ | | | √ | √ |
| Clay | | √ | √ | √ | |

*Table 1: Material characterization methods.*

Elemental content determination by acid digestion according to Danish standard DS 259 [19]: 1 g of dry ash was digested by 20 ml (1:1) $HNO_3$ under the pressure of 200 kPa (120 $^0$C) for 30 min. After digestion the sample was vacuum filtered through a 45 µm filter and diluted to 100 ml. Series of at least three replicates were made. The heavy metal concentration was measured by ICP-OES (Varian 720-ES, Software version: 1.1.0).

Atterberg test: Liquid limit ($w_L$,%) and plastic limit ($w_P$,%) were determined according to DS/CEN ISO/TS 17892 – (part 6 [20], 12 [21]). Using 76 g of fall-cone the liquid limit was measured. The difference between liquid and plastic limit is the plasticity index ($I_P$ or PI).

$CaCO_3$ content: Using the Scheibler-method the $CO_2$ generated from clay reacting with 10 % HCl was measured volumetrically. Before this, a standard curve ($V_{CO2}$ vs $m_{CaCO3}$) was plotted using pure $CaCO_3$. A corresponding $CaCO_3$ content therefore can be found in the standard curve based on the measured $CO_2$ volume from clay. The same measurement was not conducted on the ash samples due to the presence of reactive compounds that could release gas when encountering HCl.

X-ray diffraction (XRD, 2θ Cu Kα, 40 mA, 45 kV): The crystalline phases were studied using PANalytical X'pert Pro diffractometer.

Using a combined Radiometer pH electrode, $pH_{H2O}$ was measured in the L/S of 5 after 1 h of agitation.

## Preparation and testing of brick pellet specimens

All the materials (ash and clay) were manually grinded to fine particles before accurately mixed under different proportions (maximum 25 % ash), and distilled water was added into the mixture. The water contents in the wet clay and the wet clay-ash mixtures were 15 % and 20 - 22 %, respectively. The processes involved are shown in Figure 2.

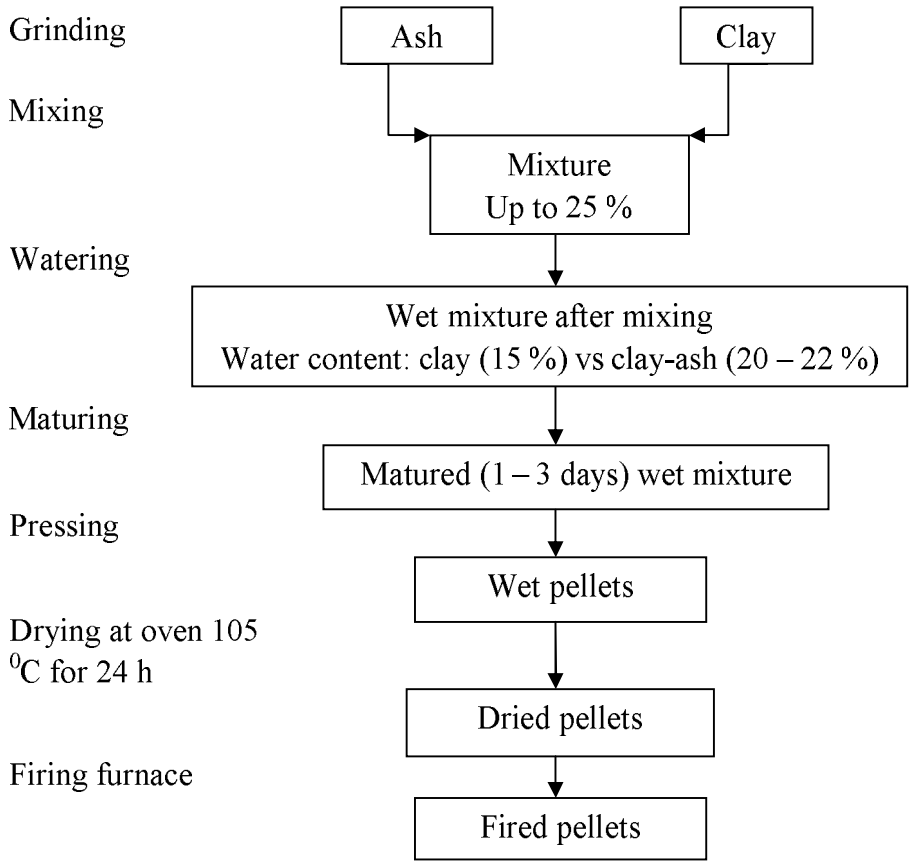


*Figure 2: Brick pellet making processes.*

The preliminary test method in [22] was adopted in the study. The wet pellets were made under the pressure around 47.0 ± 0.5 MPa by a man-made press die (Figure 3). The pellet press die was made from stainless steel. It consists of 5 main components, as detailed in Figure 3. The base of the press die and the piston (part 2) support frame is a whole unit. Part 3 and part 4 make a material holder. Part 3 is the base for the holder, and the wet pellet stands on it. In the pressing process, an external pressure is applied to the top of the piston. Part 5 was designed to aid the removal of wet pellets from the material holder. The wet pellets were dried at 105 $^0$C for one day, and the diameter and weight were measured on the dried specimens. Every dry pellet had a total weight of around 2.0 ± 0.1 g with a diameter of 20.00 ± 0.09 mm. Then they were ready for sintering at a furnace.

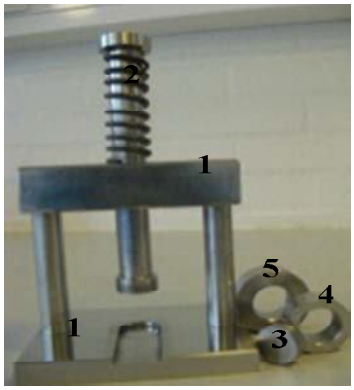


*Figure 3: Press die.*

The pellets were fired in a laboratory furnace. The heating and cooling profile for the furnace is presented in Figure 4. The heating rate was calculated with the assumption that the relation between temperature and time is linear in every 10 minutes time interval. It took about 2.5 h to reach 1000 $^0$C, and the heating rate gradually reduced from 12.6 $^0$C/min to 0. This heating rate was faster than in the typical Hoffman furnace [1]. The dwell time at sintering temperature (1000 $^0$C) was 1 hour, and when the time was up, the furnace was turned off and the pellets cooled down naturally in the furnace, which took about 20 hour down to around 100 $^0$C.

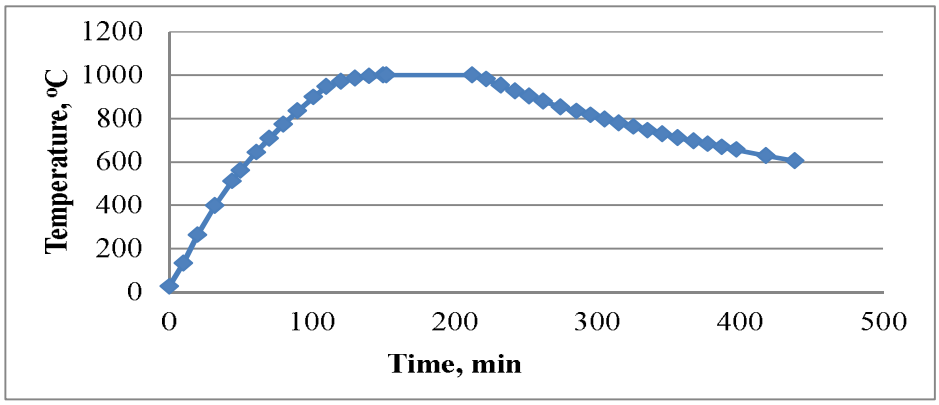


*Figure 4: Corresponding heating and cooling profile versus time in the furnace.*

The overall information about fired pellets and tests are summarized in Table 2.

| Fired pellet | 1000 $^0$C | 1050 $^0$C | 1075 $^0$C | 1100 $^0$C | Leaching |
|---|---|---|---|---|---|
| Control (100% clay) | 5 | | | | |
| 95 % clay- 5 % TMAPC | 5 | | | | x |
| 85 % clay- 15 % TMAPC | 5 | 2 | | | x |
| 75 % clay- 25 % TMAPC | 4 | 2 | 2 | | x |
| 75 % clay- 25 % TSWFA | 5 | 3 | | 3 | |
| 75 % clay- 25 % WMFA | 5 | | | | x |

*Table 2: Test frame with pellet numbers.*

Fired pellets were characterized by the following main properties, linear firing shrinkage in diameter, the weight loss, vacuum water absorption, apparent porosity, and bulk density. DS/EN ISO 10545-3:1997 [23] was referred to determine the vacuum water absorption, apparent porosity and bulk density at the same time. However, the vacuum process was modified and done according to LBM-Prøvemetode 2 (Fugtparametre, porosity and density) [24], as follows: (1) pump 3 hour to reach vacuum; (2) stop the pump and let pellets stay in water under pressure for 1 hour; (3) the pellets were in water for 24 hour at normal pressure, and then the pellets were ready for further measurement of saturated mass in air, and suspended mass in water.

The linear drying and firing shrinkage based on diameter were determined by the diameter difference between wet and dry pellet, and the difference between dry and fired pellet, respectively. Weight loss was determined by loss on ignition.

Leaching tests were done on the fired pellets made from MSWI ash, according to DS/EN 12457-3 [25], with slight modifications. The liquid (distilled water) to solid (crushed fired pellet ash) (L/S) ratio was 2. The suspension was agitated for 16 hour prior to vacuum filtration through a 45 µm filter. Concentrated $HNO_3$ was added to the leachate to preserve samples (0.1ml/10ml sample). The heavy metals, As, Ba, Cd, $Cr_{tot}$, Cu, Mn, Ni, Pb and Zn, in the leachate was measured on ICP-OES.

3- RESULTS AND DISCUSSION

## *Clay characterization*

The Atterberg results are summarized in Table 3. The liquid limit and plastic limit for the clay were 27 % and 15% respectively. In comparison to the optimal values for good brick-making clays (Table 3), the clay is suitable for making good quality bricks.

Due to the insufficient TSWFA mass left after the EDR treatment, the washed SWFA (WSWFA) was used for Atterberg test as a reference for TSWFA. The liquid limit, plastic limit and plasticity index for the clay mixed with 25 % WSWFA are also presented in Table 3.

| Properties | Clay | 75 % Clay – 25 % WSWFA | Optimal value [26] |
|---|---|---|---|
| Natural water content (%) | 17.4 | | |
| Liquid limit (%) | 27 | 30 | 30-35 |
| Plastic limit (%) | 15 | 21 | 12-22 |
| Plasticity index (%) | 12 | 9 | 7-18 |

*Table 3: Results from Atterberg test.*

The amount of water used in the mixing and shaping process was determined based on the plastic limit of the clay and of the clay-WSWFA mixture. The amount of water for shaping clay-ash mixture was therefore larger than that in pure clay. After adding WSWFA, the plastic and liquid limit increased compared to that of clay, and the plasticity index decreased from 12 to 9 %. The same trend is seen in [27] by substituting clay with sludge. The plastic limit is a good indicator of optimum moisture content (OMC) for compaction to attain maximum density [28]. In [27], the difference between plastic limits and the determined OMCs was

within 3% in absolute terms when PI≤18%, and the results may suggest that the OMC is much more close to $W_p$ when PI is around 15 – 13 %. So 20 - 22 wt-% water was added to the clay-ash mixture in the shaping process, based on the observed relation between OMC and $W_p$. The shaping water content was kept the same in both TSWFA and T/WMSWI ash for comparison.

The clay minerals bring about the occurrence of plasticity in the clay-water system. The XRD measurement showed that the clay contained the following minerals: quartz ($SiO_2$), illite (potassium aluminium silicate hydroxide), dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$) and feldspar minerals (microcline intermediate and albite ordered). The alkaline oxides in e.g. feldspar act as fluxes to reduce the sintering temperature. The content of calcium carbonate in the clay was about 19% (equivalent to 10.64% of CaO). The carbonates decompose during sintering accompanied with pore formation in brick due to gas release.

## *Ash characterization*

The elemental contents in the ash samples are presented in Table 4. The three ash was in category 3 according to the Danish limiting concentrations for heavy metals for application in construction industries [29]. Cd and Pb in TSWFA were beyond the range, but the Cd concentration had been changed from 31.8 ± 0.3 mg/kg TS in the washed ash to 1.6 ± 0.3 mg/kg TS after EDR treatment. Pb was also removed from the ash, but the mass of removed Pb was far lower than that of ash dissolved during the EDR treatment, so the Pb concentration was elevated and enriched in the final ash. The ash dissolution can also explain the high amount of heavy metals in TMAPC, although a significant amount of heavy metal had been removed during EDR treatment. The raw APC-residue contained high amount of easily soluble salts, and the solubility before ED-stack treatment reported in [8] was 35.2 ± 0.4 %. Thus the dominant mass loss was pronounced during treatment.

WMFA was hazardous, and had lower Ca concentration as expected. The water washing process resulted in lowering the soluble salts concentration (e.g. easily soluble chlorides, sulphates, potassium and sodium) [10, 30-32], and immobilizing some of the heavy metals therefore lowering leaching [8, 32], although some heavy metal concentrations were enriched in the washed ash. Given ash dissolution observed in both washing and EDR, WMFA could be used to compare with TMAPC, in order to study the different sintering behaviours of these two ash induced by adding $Ca(OH)_2$.

| | Element | TSWFA | TMAPC | WMFA | Category-3 [29] |
|---|---|---|---|---|---|
| pH($H_2O$) | | < 6 | 12.50 | 11.17 | |
| Bulk element (g/kgTS) | Al | 2.8 ± 0.0 | 11.7 ± 0.3 | 31 ± 0 | |
| | Ca | 8.4 ± 0.1 | 406 ± 6 | 182 ± 1 | |
| | Fe | 6 ± 0 | 4.5 ± 0.0 | 15.5 ± 0.4 | |
| | K | 8.7 ± 0.2 | 4.2 ± 0.1 | 7.4 ± 0.3 | |
| | P | 6.3 ± 0.1 | 3.1 ± 0.1 | 8.5 ± 0.1 | |
| | Si[1] | 0.3 ± 0.0 | 0.3 ± 0.1 | 0.2 ± 0.0 | |
| Trace element (mg/kgTS) | As | 2.8 ± 1.0 | 188 ± 3 | 128 ± 7 | > 20 |
| | Cd | 1.6 ± 0.3 | 197 ± 4 | 108 ± 1 | > 0.5 |
| | Cr | 19.5 ± 1.1 | 108 ± 3 | 216 ± 3 | > 500 |
| | Cu | 71.6 ± 1.5 | 876 ± 13 | 1427 ± 2 | > 500 |
| | Ni | 3.8 ± 0.3 | 50 ± 0.1 | 94 ± 2 | > 30 |
| | Pb | 210.4 ± 4.8 | 4516 ± 88 | 9239 ± 26 | > 40 |
| | Zn | 260 ± 10 | 26131 ± 400 | 44060 ± 156 | > 500 |

[1] *Si is digestion-insufficient by $HNO_3$, so the concentration was expected to be lower than the total concentration determined by HF digestion. [33]*

*Table 4: Elemental compositions (mean of three measurements ± standard deviation) in the studied ash samples compared with the limiting concentrations in category 3 in Danish legislation for possible reuse of waste materials in the construction industry [29].*

The mineral phases in the ashes are listed in Table 5. TSWFA differed from the MSWI ashes, and this has to do with the different constituents in the fuels, from which the ashes originated, and the different combustion techniques used. TSWFA mainly contained $SiO_2$ and plagioclase feldspar minerals, while MSWI ashes had high amount of carbonates and sulphates. They were primarily in form of calcite and anhydrite. Moreover, alkaline chlorides, such as sylvite and halite, existed in TMAPC. The occurrence of α-cristobalite and α-$SiO_2$ in TSWFA was because of the high calcination temperature [34] on the grate typically in the range 1000 – 1200 $^0$C [35]. It is noteworthy that by introducing the ashes into the host material (e.g. clay), the mineralogy in the raw material would change, so would the mineralogy structure in the final sintered products [36]. Amorphous phases, which are ultrafine and highly reactive due to high specific surface area [34], were detected in all the three ash.

| TSWFA | TMAPC | WMFA |
|---|---|---|
| α-Cristobalite | anhydrite | anhydrite |
| albite calcian | bassanite | bassanite |
| quartz | calcite | calcite |
| rutile | gehlenite | gehlenite |
| | halite | quartz |
| | quartz | rutile |
| | sylvite | |
| amorphous phases | amorphous phases | amorphous phases |

*Table 5: XRD determined mineral phases in the ashes.*

## *Properties of sintered brick pellets*

The overall results of weight loss on ignition, shrinkage, waster absorption, bulk density and apparent porosity are shown in Table 6.

| | Temp. $^0$C | LOI % | Firing Shrinkage % | Water absorption % | Bulk density g/cm$^3$ | Apparent porosity % | Drying shrinkage % |
|---|---|---|---|---|---|---|---|
| 25% TSWFA | 1000 | 12.7 | 0.5 | 27.6 | 1.53 | 42.1 | <0.2 |
| | 1050 | 12.9 | 0.7 | 27.2 | 1.53 | 41.6 | |
| | 1100 | 13.0 | 5.4 | 15.4 | 1.82 | 28.0 | |
| 25% TMAPC | 1000 | 14.7 | 0.4 | 29.3 | 1.52 | 44.6 | 0.1~0.2 |
| | 1050 | 14.7 | 0.4 | 29.3 | 1.53 | 44.8 | |
| | 1075 | 14.7 | 1.0 | 28.3 | 1.54 | 43.5 | |
| 15% TMAPC | 1000 | 13.5 | 1.2 | 23.6 | 1.68 | 39.7 | 0.3 |
| | 1050 | 13.9 | 1.3 | 23.9 | 1.66 | 39.7 | |
| 5% TMAPC | 1000 | 12.8 | 0.7 | 19.7 | 1.80 | 35.4 | 0.1 |
| Control | 1000 | 12.1 | 0.2 | 20.9 | 1.77 | 37.0 | 2.6 |
| 25% WMFA | 1000 | 10.7 | 0.2 | 19.6 | 1.79 | 35.0 | n.d. |

*Table 6: Overall results from pellets test. 'n.d.' - not determined.*

The LOI increased slightly when introducing TSWFA and TMAPC into clay. The results may indicate that LOI increases slightly as the sintering temperature and the clay substitution level increase, exemplified by the pellets with 25 % TSWFA addition (12.7 - 13.0 % at temperatures 1000 - 1100 $^0$C), and the substitution levels with TMAPC (0 - 25 % with corresponding LOI 12.1 - 14.7 %). This could be interpreted by the decomposition of the organic and inorganic materials from the clay and the ashes. The small LOI variation with temperature up to 1075 $^0$C in the pellets containing 25 % TMAPC may indicate that the main decomposition process has been finished at 1000 $^0$C. The compounds, e.g. sulfates, which decompose at higher temperature than 1000 $^0$C, may be still in the brick, but not incorporated into brick network. Weng et al. [27] and Karaman et al. [37] reported the weight loss for a normal clay brick is 15%. With the ash addition, this criterion was not exceeded.

The drying and firing shrinkage degree in bricks can be considered as a factor for quality control. To avoid cracking, the drying shrinkage should not be too high, normally $\leq 7$ % [26]. It is also important when it comes to determining the size of molds for making bricks with wanted dimensions. The linear drying shrinkage was 2.6 % in the control, and it decreased to less than 0.3 % through adding TSWFA and TMAPC up to 25 %. Compared to clay, ash is generally plastic limited [36] and coarser [36, 38], and thus the reduction in drying shrinkage was believed to be due to the reduction in the clay fine particle proportion in the pellets. Taking TSWFA, the burned bar-shaped straw fibers could retard the brick shrinkage when water was removed. The firing shrinkage determines the stability of the bricks in kiln, and should normally be below 8 % [26]. All the pellets exhibited small firing shrinkage, i.e. well below 8 %. The firing shrinkage increased in general as firing temperature increased, and the increase in vitrification degree was most probably responsible for this. The highest total shrinkage from wet to fired pellets was in the control.

Water absorption, which affects the brick durability, has close relation to porosity, which reveals the brick internal structure. The lower the open porosity, the lower the water penetration of brick, and therefore the higher the brick durability and resistance to environmental damage [39]. Substituting clay with 25 % TSWFA and TMAPC resulted in the increase in apparent porosity of sintered pellets at 1000 $^0$C from 37 to higher than 42 %. The dominant pore-forming mechanisms in TSWFA and TMAPC seemed to be different: burn-off of carbon in the former, and decomposition of carbonates in the latter according to our mineralogy study. The apparent porosity increased as the substitution level increased, and it decreased as the sintering temperature increased. The substitution level of 5 % TMAPC was an exception, where the porosity decreased compared to that in the control. The variation of water absorption was in accordance with that of apparent porosity. The absorption ranged from 19.6 to 29.3 %. According to ASTM C62-13a [40] in terms of water absorption, bricks containing 25 % TSWFA sintered at 1100 $^0$C may be used for building brick under severe weathering, and bricks containing 5 % TMAPC sintered at 1000 $^0$C could be suitable for building brick under moderate weathering (Grade MW).

TSWFA and TMAPC had the same impact on the sintering properties in terms of shrinkage, mass loss, water absorption and apparent porosity, so did they in bulk density. Bulk density is generally inversely proportional to apparent porosity. Hence, the pellets containing 25 % TSWFA sintered at 1100 $^0$C were the densest, followed by the ones containing 5 % TMAPC sintered at 1000 $^0$C. WMFA from the same source of the raw APC had opposite effects on the pellets properties, such as decrease in mass loss, water absorption and porosity, and increase in density. This may indicate the lime injection made a big difference on the properties of WMFA and TMAPC, as exemplified by the different mineral phases.

CaO in the raw material could damage the brick products, e.g. 'lime blowing' in the most severe case. Commonly, CaO is in the form of calcite in materials, and the particle size should be fine enough (< 0.5 mm) to avoid 'lime blowing' [41]. CaO takes a significant share in MSWI ashes compared to that in clay. The CaO content was especially high in the studied raw APC-residue (64.4 %), and in the ED treated APC-residue (40.6 %) [42]. However, straw and wood fly ash contained mainly $SiO_2$. This could explain the lower substitution level (~ 5 %) of TMAPC, and the moderate level (~ 25 %) of TSWFA in the yellow clay brick pellets. Attentions also need to be paid on the role of $SO_3$ in TMAPC on the clay brick production. According to [42], the amount of $SO_3$ in ED treated APC-residue could be as high as 12.5 %. $SO_3$ content should be as low as possible. According to DS/EN 771-1 [43], active soluble salts content in bricks, which are intended for use with limited protection against water penetration, shall be declared in terms of $K^+$, $Na^+$ and $Mg^{2+}$. Their sulfates in the fired bricks, which may originate from the ashes, may lead to efflorescence [44].

Lower clay substitution level with TMAPC, for example lower than 5 %, seemed to help the sintering process, considering the increase in density, the decrease in water absorption, and thus the improved durability of bricks. The reduction of density with higher ash content could however be beneficial to reduce the transport cost and improve thermal insulation. FA is probably better than APC in terms of slight influence on clay sintering properties even with 25 % addition, so it could be recovered not to mix with sorbent (e.g. slaked lime) at the waste incineration plants, or only use FA for construction materials, e.g. as in semidry flue gas cleaning systems.

## Heavy metal leaching

The pellets with TMAPC and WMFA addition fired at 1000 $^0$C were studied on the leaching behavior. Table 7 shows the results. For those pellets containing TMAPC, Pb and Cr were most problematic compared to category 3 in Table 7. Cr leaching from the fired pellets was far above the limit value in the three studied substitution levels, and the oxidation of $Cr^{3+}$ to $Cr^{6+}$ during firing, which is more soluble and toxic, is supposed to be the main reason. For the pellets with 5 % TMAPC and 25 % WMFA addition, which met Grade MW (moderate weathering) in water absorption i.e. 22 % in average, Pb content in the leachate was little, but Ni was slightly above 70 μg/L in the former and As was above 50 μg/L in the latter. Cr level in both cases was exceeded. Sintering at optimum conditions, i.e. optimum raw material proportions and sintering temperature, can reduce the heavy metal leaching [45], so finding the optimum conditions is necessary in further studies, and a further understanding of the Cr behavior would enhance the MSWI ash's application potential.

| | **Leaching (μg/L)** | **As** | **Ba** | **Cd** | **$Cr_{tot}$** | **Cu** | **Mn** | **Ni** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|
| Limit | Category-3 [29] | 50 | 4000 | 40 | 500 | 2000 | 1000 | 70 | 100 | 1500 |
| TMA PC | 5 % - FB | 35 | 128 | 0 | 1834 | 5 | 5 | 94 | 9 | 0 |
| | 15 % - FB | 30 | 333 | 0 | 3029 | 18 | 1 | 42 | 419 | 240 |
| | 25 % - GB | 34 | 386 | 0 | 229 | 389 | 2 | 14 | 195 | 572 |
| | 25 % - FB | 28 | 242 | 0 | 4589 | 14 | 1 | 0 | 949 | 61 |
| WMF A | 25 % - GB | 39 | 159 | 0 | 1027 | 171 | 1 | 17 | 30 | 5 |
| | 25 % - FB | 92 | 145 | 0 | 3052 | 6 | 3 | 37 | 0 | 0 |

*Table 7: Leaching properties of pellets made from TMAPC and WMFA. FB- fired brick pellet; GB- green brick pellet.*

## 4- CONCLUSIONS

The treated biomass ashes, i.e. the fly ash from co-combustion of straw and wood chips and the MSWI APC-residue are pore-forming agents leading to increase in porosity. The dominating pore-forming mechanisms probably differ: the burn-off of carbon fibers in the former, and the decomposition of carbonates in the latter.

Treated straw and wood fly ash can be used in the production of clay bricks. Brick pellets sintered at 1100 $^0$C with 25 % clay substitution have the average water absorption of 15.4 % that meets the requirement for Grade SW building bricks in ASTM C62 − 13a. Low clay replacement with APC-residue, e.g. 5 %, seems to be beneficial to form glassy phases during vitrification. The pellets containing 5 % TMAPC sintered at 1000 $^0$C could be suitable for building brick under moderate weathering (Grade MW). Moreover, the leaching of Pb is low, while Cr leaching poses a main problem. Too much CaO and $SO_3$ content in the raw materials are deleterious to produce good quality clay bricks, so care must be exercised in finding the optimal clay and ash proportions. WMFA, whose raw ash was the source of the raw APC, has opposite effect on the pellets properties compared with TMAPC. This may indicate the lime injection made a big difference on the properties of WMFA and TMAPC. It could be advantageous to take FA out before APC as in semidry flue gas cleaning systems.

Using the bio ash in clay bricks is promising, with advantages of utilizing waste as secondary resources, reducing the burden on landfill, and less extracting natural resources. Further studies are needed to test the mechanical properties of the bricks in addition to screening the optimal conditions. Efforts are needed to remedy the Cr problem.

REFERENCES

[1] Garcia-Ubaque, C.A., Gonzalez-Haessig, A., Vaca-Bohorquez, M.L.: Ceramic bricks made from municipal solid waste incineration-derived clay and ashes: a quality study. Ingenieria E Investigacion, 33(2), 36-41 (2013)
[2] Xu, L.L., Guo, W., Wang, T., Yang, N.R.: Study on fired bricks with replacing clay by fly ash in high volume ratio. Construction and Building Materials, 19(3), 243-247 (2005)
[3] Zhang, B.: Consideration of improving earthquake resistant capacity of earth buildings. Advanced materials research, 243, 1199-1202 (2011)
[4] Clay modifiers. Brick and Clay Record, 135(4), 30-41 (1959)
[5] Kadir, A.A., Sarani, N.A.: An overview of wastes recycling in fired clay bricks. International Journal of Integrated Engineering, 4(2), 53-69 (2012)
[6] Koronthalyova, O., Matiasovsky, P.: Pore structure and thermal conductivity of burnt clay bricks. in Proceedings of meeting of the Thermophysical Society, Kocovce (2007)
[7] Zhang, H.Y., Zhao, Y.C., Qi, J.Y.: Utilization of municipal solid waste incineration (MSWI) fly ash in ceramic brick: Product characterization and environmental toxicity. Waste Management, 31(2), 331-341 (2011)
[8] Jensen, P.E., Ferreira, C.M.D., Hansen, H.K., Rype, J.U., Ottosen, L.M., Villumsen, A.: Electroremediation of air pollution control residues in a continuous reactor. Journal of applied electrochemistry, 40(6), 1173-1181 (2010)
[9] Ottosen, L.M., Pedersen, A.J., Hansen, H.K., Ribeiro, A.B.: Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method. Electrochimica Acta, 52(10), 3420-3426 (2007)
[10]Wang, Q.H., Yang, J., Wang, Q., Wu, T.J.: Effects of water-washing pretreatment on bioleaching of heavy metals from municipal solid waste incinerator fly ash. Journal of hazardous materials, 162(2), 812-818 (2009)
[11]Jakob, A., Stucki, S., Struis, R.P.W.J.: Complete heavy metal removal from fly ash by heat treatment: influence of chlorides on evaporation rates. Environmental science & technology, 30(11), 3275-3283 (1996)
[12]Kirkelund, G.M., Jensen, P.E., Villumsenet, A., Ottosen, L.M.: Test of electrodialytic upgrading of MSWI APC residue in pilot scale: focus on reduced metal and salt leaching. Journal of applied electrochemistry, 40(6), 1049-1060 (2010)
[13]Ferreira, C., Jensen, P.E., Ottosen, L.M., Ribeiro A.B.: Removal of selected heavy metals from MSW fly ash by the electrodialytic process. Engineering Geology, 77(3–4), 339-347 (2005)
[14]Tan, W.F., Wang, L.A., Huang, C., Liu, Y.Y., Green, J.E., Newport, D., Green, T.: Utilization of municipal solid waste incineration fly ash in lightweight aggregates. Journal of Central South University of Technology, 19(3), 835-841 (2012)
[15]Mangialardi, T.: Sintering of MSW fly ash for reuse as a concrete aggregate. Journal of Hazardous Materials, 87(1), 225-239 (2001)
[16]Gau, S.H., Wu, C.W., Sun, C.J.: Washing pretreatment to improve the quality during the regeneration of MSWI fly ash. in The 3rd International Conference on Waste Management and Technology, Beijing, China (2008)
[17]Hansen, H.K., Ottosen, L.M., Villumsen, A.: Electrodialytic removal of cadmium from straw combustion fly ash. Journal of Chemical Technology and Biotechnology, 79(7), 789-794 (2004)
[18]Kirkelund, G.M., Jensen, P.E., Ottosen, L.M.: Electrodialytic extraction of heavy metals from Greenlandic MSWI fly ash as a function of remediation time and L/S ratio. in ISCORD 2013: Planning for Sustainable Cold Regions: Proceedings of the 10th

International Symposium on Cold Regions Development, June 2-5, 2013, Anchorage, Alaska. ASCE Publications (2013)
[19]DS 259: Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry in flame, (2003)
[20]DS/CEN ISO/TS 17892-6: Geoteknisk undersøgelse og prøvning - Laboratorieprøvning af jord - Del 6: Faldkegleprøvning, (2004)
[21]DS/CEN ISO/TS 17892-12: Geoteknisk undersøgelse og prøvning - Laboratorieprøvning af jord - Del 12: Bestemmelse af Atterberg-grænser, (2004)
[22]Torres, P., Fernandes, H.R., Olhero, S., Ferreira, J.M.F.: Incorporation of wastes from granite rock cutting and polishing industries to produce roof tiles. Journal of the European Ceramic Society, 29(1), 23-30 (2009)
[23]DS/EN ISO 10545-3: Keramiske fliser. Del 3: Bestemmelse af vandabsorption, åben porøsitet, synlig relativ densitet og volumendensitet, (1997)
[24]LBM-Prøvemetode 2: Fugtparametre, porøsitet og densitet. 290390 CBN :sl. (In Danish)
[25]DS/EN 12457-3: Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction), (2002)
[26]Office, I.L., Organisation, U.N.I.D., ILO., UNIDO.: Small-scale brickmaking (1984)
[27]Weng, C.H., Lin, D.F., Chiang, P.C.: Utilization of sludge as brick materials. Advances in Environmental Research, 7(3), 679-685 (2003)
[28]TxDOT: Test Procedure for laboratory compaction characteristics and moisture-density relationship of subgrade, embankment soils, and backfill material, TxDOT Designation: Tex-114-E, (2011)
[29]Danish Ministry of the Environment: Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald BEK nr 1662 af 21/12/2010 (in Danish)
[30]Zhu, F., Takaoka, M., Oshita, K., Kitajima, Y., Inada, Y., Morisawa, S., Tsuno, H.: Chlorides behavior in raw fly ash washing experiments. Journal of hazardous materials, 178(1), 547-552 (2010)
[31]Colangelo, F., Cioffi, R., Montagnaro, F., Santoro, L.: Soluble salt removal from MSWI fly ash and its stabilization for safer disposal and recovery as road basement material. Waste management, 32(6), 1179-1185 (2012)
[32]Zheng, L., Wang, C.W., Wang, W., Shi, Y.C., Gao, X.B.: Immobilization of MSWI fly ash through geopolymerization: effects of water-wash. Waste management, 31(2), 311-317 (2011)
[33]Skibsted, G., Ottosen, L.M., Jensen, P.E., Elektorowicz, M.: Long-term electrodialytic soil remediation - Soil weathering. Appendix A in PhD-thesis 2013
[34]Chandrasekhar, S., Satyanarayana, K.G., Pramada, P.N., Raghavan, P.: Review processing, properties and applications of reactive silica from rice husk—an overview. Journal of Materials Science, 38(15), 3159-3168 (2003)
[35]Jensen, P.A., Hansen, S.B., Flemming, J.F., Wu, H., Glarborg, P., Sander, B., Wadenback, J.: Danish Experiences with Deposit Probe Measurements in Grate and Pulverized Fuel Biomass Power Boilers. in 20th European Biomass Conference and exhibition.
[36]Başpınar, M.S., Kahraman, E., Görhan, G., Demir, I.: Production of fired construction brick from high sulfate-containing fly ash with boric acid addition. Waste Management & Research, 28(1), 4-10 (2010)
[37]Karaman, S., Ersahin, S., Gunal, H.: Firing temperature and firing time influence on mechanical and physical properties of clay bricks. Journal of scientific and industrial research, 65(2), 153 (2006)

[38]Chandler, A.J., Eighmy, T.T., Hartlen, J., Hjelmar, O., Kosson, D.S., Sawell, S.E., van der Sloot, H.A., Vehlow, J.: Municipal solid waste incinerator residues. Elsevier (1997)
[39]Shih, P.H., Wu, Z.Z., Chiang, H.L.: Characteristics of bricks made from waste steel slag. Waste Management, 24(10), 1043-1047 (2004)
[40]ASTM C62 − 13a: Standard Specification for Building Brick (Solid Masonry Units Made From Clay or Shale)
[41]Elert, K., Cultrone, G., Navarro, C.R., Pardo, E.S.: Durability of bricks used in the conservation of historic buildings — influence of composition and microstructure. Journal of Cultural Heritage, 4(2), 91-99 (2003)
[42]Kirkelund, G.M., Geiker, M.R., Jensen, P.E.: Electrodialytically Treated MSWI APC Residue as Substitute for Cement in Mortar, accepted in Nordic Concrete Research
[43]DS EN 771-1 Specification for masonry units : Part 1: Clay masonry units, (2011)
[44]Brocken, H., Nijland, T.G.: White efflorescence on brick masonry and concrete masonry blocks, with special emphasis on sulfate efflorescence on concrete blocks. Construction and Building Materials, 18(5), 315-323 (2004)
[45]Bethanis, S., Cheeseman, C.R., Sollars, C.J.: Effect of sintering temperature on the properties and leaching of incinerator bottom ash. Waste Management & Research, 22(4), 255-264 (2004)

# Chapter 5

*Incorporation of EDR-treated ash from co-combustion of straw and wood chips into clay pellets – leaching of heavy metals*

# Incorporation of EDR-treated ash from co-combustion of straw and wood chips into clay pellets – leaching of heavy metals


## Abstract

This chapter reports additional experimental work on the use of bioash from co-combustion of straw and wood chips in the production of bricks to the investigation conducted in Chapter 4. In this additional work, the clay was sieved to remove the particles greater than 1 mm in diameter. Approximately 88% (by weight) of the bioash studied was water-extractable. Prior to use as a substitute for clay, the bioash was treated by combining water washing to remove water soluble constituents and electrodialytic remediation to separate heavy metals. As for making pellets, the resulting treated bioash was used to replace clay at the replacement level of 2%, 5%, 10% and 20%. The temperatures for sintering the clay-bioash pellets were 1050 °C, 1075 °C and 1100 °C. After sintering at these temperatures for one hour, the properties of the pellets were studied, with a special focus on the leaching of heavy metals, which was not investigated in Chapter 4. Selected material properties (weight loss on firing, apparent porosity, vacuum water absorption and bulk density) were also discussed. The results showed that the leaching of Cr from the fired clay-bioash pellets containing 2%, 5% and 20% of ash can be reduced below the limit for use in construction work by elevating sintering temperature from 1050 °C to 1075 °C. Increasing the sintering temperature to 1100 °C further reduced the leaching of Cr. As the leaching of heavy metals can be lowered to an acceptable level, incorporating the washing-EDR treated bioash from co-combustion of straw and wood chips into clay pellets for construction use is technically possible.

## 1. Raw materials

### *1.1. Clay*

The clay (denoted as C) used in this chapter was the same as the one used in Chapter 4, which originated from Wienerberger Denmark, one producer of bricks. However, different from Chapter 4, the clay used in the present study was first grinded by ring mill for 30 seconds, and afterwards sieved to remove particles greater than 1 mm in diameter (d50: 24±4 μm; d90: 388±32 μm).

The plastic properties of the clay are given in Table 1 together with the unsieved clay from Chapter 4. The difference in particle size distribution was believed to account for the big difference in the liquid limit of the clay. White (1949) found that the Atterberg limits of clay minerals increased with decreasing particle size, which is consistent with what we observed here. The two methods for determination of liquid limit, Casagrande method and fall-cone test, could also contribute to the difference in the liquid limit, but to what extent, is unclear based on current knowledge. They could give similar liquid limit results such as in pure clays (Christaras, 1991). On the other hand, Casagrande method could give slightly lower liquid limits in illitic and kaolinitic clays than those obtained from the fall-cone test (Spagnoli, 2012). In addition, the consistency of soil samples (i.e. intermediate plasticity or high plasticity) might also affect the differences in liquid limit between the two methods (Hrubesova et al., 2016). Thus there is no overall comparison.

Table 1. Atterberg limits of clay.

| **Property** | **% (< 1mm)** | **% (Chapter 4) without sieving** |
|---|---|---|
| Natural water content | 17.95±0.03 (wet-based) / 21.9±0.04 (dry-based) | 17.4 (wet-based) |
| Plastic limit | 17.4 | 15 |
| Liquid limit | 40.96 (Casagrande cup) | 27 (fall-cone) |
| Plasticity index | 23.5 | 12 |

*1.2. Ash from co-combustion of straw and wood chips*

The bioash, named 'V', was collected from Vordingborg CHP plant in Denmark. It is the residue after co-firing of straw and wood chips. The physical-chemical composition and leaching properties of the ash as received are given in Table 2. The ash cannot be used as fertilizer for agricultural purposes, because the concentration of Cd exceeded the limit (9.7>5 mg/kg TS). Danish Decree BEK nr 1414 (BEK nr 1414, 2015) regulates the rules on the use of residues and soil for building and construction work in order to reduce the amount of waste to be landfilled or incinerated, and to reduce taw material consumption. In accordance with Danish regulation BEK nr 1414, the ash however cannot be used for construction work, because the concentrations of As, Cd, Cr, Ni, Pb and Zn in the leachate from the ash were higher than the maximum limits for residues in Category 3 which may be used for roads, paths, trenches, foundations and floors: 50 μgAs/l, 40 μgCd/l, 500 μgCr/l, 70 μgNi/l, 100 μgPb/l and 1500 μgZn/l. Thus, ash upgrading is necessary for recycling purpose.

Water washing (three steps, L/S 5 each) combined with EDR was performed on the ash, as same as in Chapter 4, but the duration of EDR treatment differed, which was 7 days in the present study while 10 days in Chapter 4. The ash suspension (50 g washed ash / 350 ml distilled water) was treated at the current density of 0.5 mA/cm$^2$ (i.e. 25±0.02 mA) in a three-compartment electrodialytic cell illustrated in Figure 1. In total three EDR experiments were carried out to get the treated ash for use for making clay pellets.

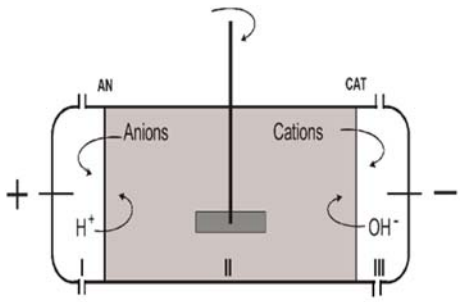


Figure 1. Sketch of a three compartment EDR cell. AN: anion exchange membrane. CAT: cation exchange membrane.

Approximately 88% of the ash were dissolved during washing, resulting in the enriched concentrations of Cd, Cr, Ni, Pb and Zn in the washed ash (Table 2). The concentration of As on the contrary decreased. This might reveal that a significant amount of As in the studied bioash was in the water extractable fraction. Properties such as pH, electric conductivity and leaching (L/S 2) could not be determined for the washed ash, because the water used for extraction (L/S 2.5 or 2) in the determination of pH, conductivity and leaching was absorbed by the washed ash. Yeboah et al. (2014) observed the presence of large fibrous, woody chars/remnants in the biomass ash from combustion of mill waste, logging, or urban wood waste. The high water absorption capacity of the washed ash in the present study may be due to the existence of similar porous carbonaceous particles and/or biomass char in the ash.

The pH of the ash suspension decreased from 7.3 to 4.8±0.1 at the end of EDR treatment, and the electric conductivity decreased to < 112 µS/cm. Approximately 20-24% of the washed ash were dissolved during EDR. Seven days treatment reduced the concentrations of As, Cd, Cr, Ni and Zn in the ash, but not Pb. This is consistent with the findings in Chen et al. (2015). Removal of Pb was relatively slower than that of e.g. Cd and Zn. Unlike the ash used in Chen et al. (2015) which was very fine, the ash used in here was much coarser. The origin of the bioash affects the optimal conditions for EDR treatment, such as current density, duration of treatment and liquid to solid ratio of ash suspension. For instance, in the present case, the concentration of Cd in the EDR treated ash (Table 2) was still above 20 mg/kg TS after 7 days treatment, and it indicated a requirement of a longer treatment time to reduce Cd concentration. On the other hand, EDR works well in Cd extraction from bioash in general (Ottosen et al., 2007).

Table 2. The physical-chemical composition and leaching properties of the ash before and after treatment. EC= electric conductivity. N, number of replicates.

| Property | As-received | Washed | EDR-treated |
|---|---|---|---|
| pH($H_2O$) (N=3) | 6.1±0.2 | | |
| EC, mS/cm (N=3) | 95±10 | | |
| Carbonate content, % (N=3) | 2.0±0.1 | | |
| LOI 550 / 950 °C, % (N=3) | 4.4±0.1/82±7 | | |
| *Heavy metal concentration, mg/kg TS (N=5 (as-received)/3(washed/EDR-treated )* | | | |
| As | 6.6±0.6 | 3.2±0.1 | 1.3±0.3 |
| Cd | **9.7±0.3** | 63.7±1.8 | 21.4±0.4 |
| Cr | 2.1±0.4 | 10.8±0.1 | 5.6±0.5 |
| Ni | 1.2±0.4 | 3.9±0.4 | 2.3±0.3 |
| Pb | 48±1 | 372±13 | **409±36** |
| Zn | 535±19 | 3924±107 | 310±19 |
| *Concentration in leachate from leaching test at L/S 2 (N=3)* | | | |
| pH | 6.6±0.5 | Could not be determined | |
| As (mg/l) | 3.8±0.5 | | |
| Cd (mg/l) | 1.9±0.1 | | |
| Cr (µg/l) | 514±11 | | |
| Ni (µg/l) | 563±52 | | |
| Pb (mg/l) | 2.6±0.4 | | |
| Zn (mg/l) | 10.2±0.5 | | |

## 2. Pellet Making and characterization

The overall process for making the pellets was the same as in Chapter 4. There were also some differences:

- Pressing pressure: reduced from 47 MPa to10 MPa to check the performance of the pellets shaped at a lower pressure.
- Sintering temperature: including 1075 °C and excluding 1000 °C to sinter the pellets at the temperatures 1050°C (T1), 1075°C (T2) and 1100°C (T3) (having a narrower interval of 25 °C than 50 °C applied in Chapter 4). The time for pellets staying at each sintering temperature was still 1 hour.
- The formulae (F, i.e. different clay-bioash mixtures) for tests are given in Table 3, which aimed to examine the effect of the ash content on the properties of the pellets.

The characterization of the fired pellets was conducted as the same as in Chapter 4, including weight loss (i.e. loss on ignition in Chapter 4) during the whole pellet firing process, apparent porosity, vacuum water absorption and bulk density. The heavy metal leaching test

was conducted on the crushed pellets. The leachates were collected after 24 h distilled water extraction at L/S 2 according to DS/EN 12457-1 (DS/EN 12457-1, 2002), and then filtered through a 0.45-µm filter prior to concentration determination. The pH of the leachates was measured. The concentrations of As, Ba, Ca, Cd, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se and Zn were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES).

Table 3: Formula (F) for brick making.

| **wt.%** | **F1** | **F2** | **F3** | **F4** |
|---|---|---|---|---|
| Clay (C) | 98 | 95 | 90 | 80 |
| V | 2 | 5 | 10 | 20 |
| T, °C | T1, T2 | T1, T2 | T1, T2, T3 | T1, T2, T3 |

## 3. Properties of fired pellets

Figure 2 shows the appearance of the fired pellets. Both ash content and sintering temperature influenced the color of the pellets. As can be seen from the pellets fired at 1050 °C, 20% ash content bleached the color out of the pellets in comparison to 5% ash content. Increasing sintering temperature to 1075 °C also resulted in the pellets with a lighter color. The diluted clay content and the reactions between clay minerals and ash particles contributed to the color change. The size of the pellets sintered at 1100 °C was smaller than that of the pellets fired at the other two temperatures, which indicated a great shrinkage of the pellets happened at 1100 °C. Obvious shrinkage together with the darker color of the pellets indicated that the sintering temperature 1100 °C was too high. At such a high sintering temperature, crozzle, one kind of unqualified bricks, could be produced.

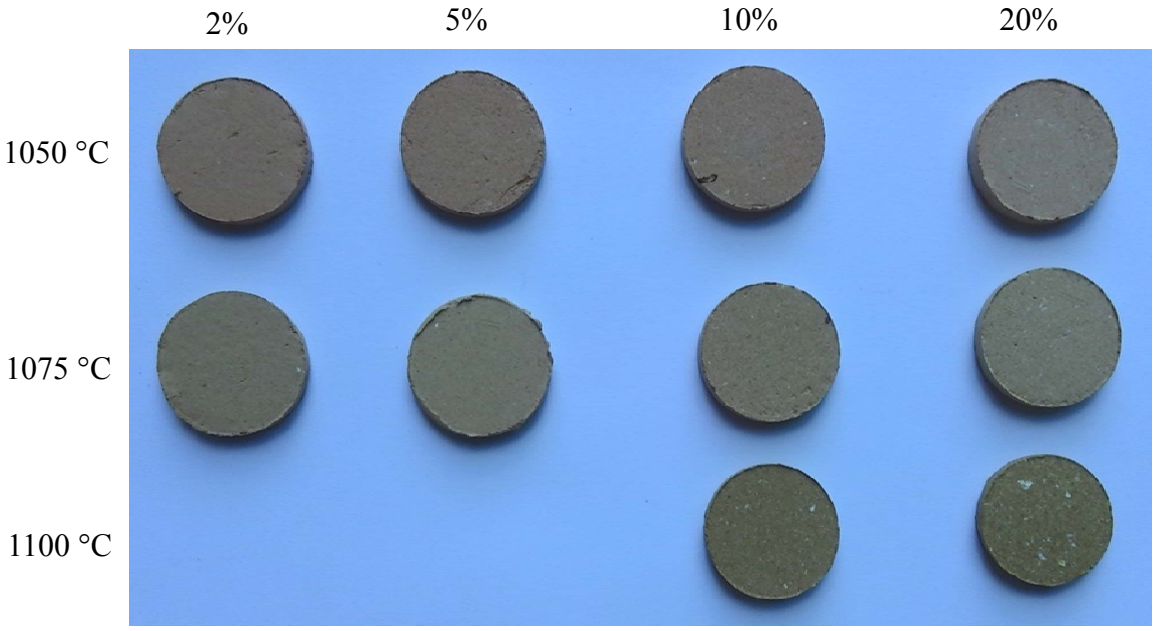


Figure 2. The appearance of the pellets having different ash contents and fired at different temperatures.

Figure 3 shows the weight loss of the pellets during firing, the vacuum water absorption, the apparent porosity and the bulk density of the fired pellets. The weight loss during firing was related to the development of porosity and the densification level of the brick (Lin, 2006). The weight loss (Fig. 3a) of the clay-bioash pellets was between 11.7% and 18.6%, and increased with increasing the ash content. Compared to the weight loss for a normal clay brick 15% (Lin, 2006), substituting the washing-EDR treated bioash for clay up to 10% exhibited weight loss less than 15% when the pellets were fired at 1050 ° C and 1075 °C. The corresponding water absorption (Fig. 3b) and bulk density (Fig. 3c) of the pellets (ash content ≤10%, firing temperature 1050 ℃ and 1075 °C) were 15%~30% and 1.5-1.9 g/cm$^3$, respectively. In accordance with ASTM C62-13 (ASTM C62-13a, 2013), water absorption of the pellets with 2% and 5% ash content may be used under moderate weathering (maximum water absorption 22%) or severe weathering (maximum water absorption 17%). If neglecting weathering conditions i.e. for indoor use, the pellets with ash ≤10% could be used for structural and nonstructural purpose. Making pellets at the lab scale differs from making bricks in industrial production; and the material properties can also vary among different

kinds of bricks (e.g. pressed, handmade and extruded). Thus, the specific applications of the clay bricks containing the studied bioash are not assigned. But it must be stated that, firing weight loss, water absorption and apparent porosity increased with increasing ash content; and the clay-bioash pellets had low bulk densities. It is noted that the clay-bioash bricks had high porosities, which might not only related to the decomposition of the components in the ash and clay but also the high amount of silica in the ash (Kazmi et al., 2016). The pellets sintered at 1100 °C had the lowest water absorption, apparent porosity and the highest density, which indicated that a significant amount of liquid-phase presented during sintering, therefore increasing the level of densification by filling the voids.

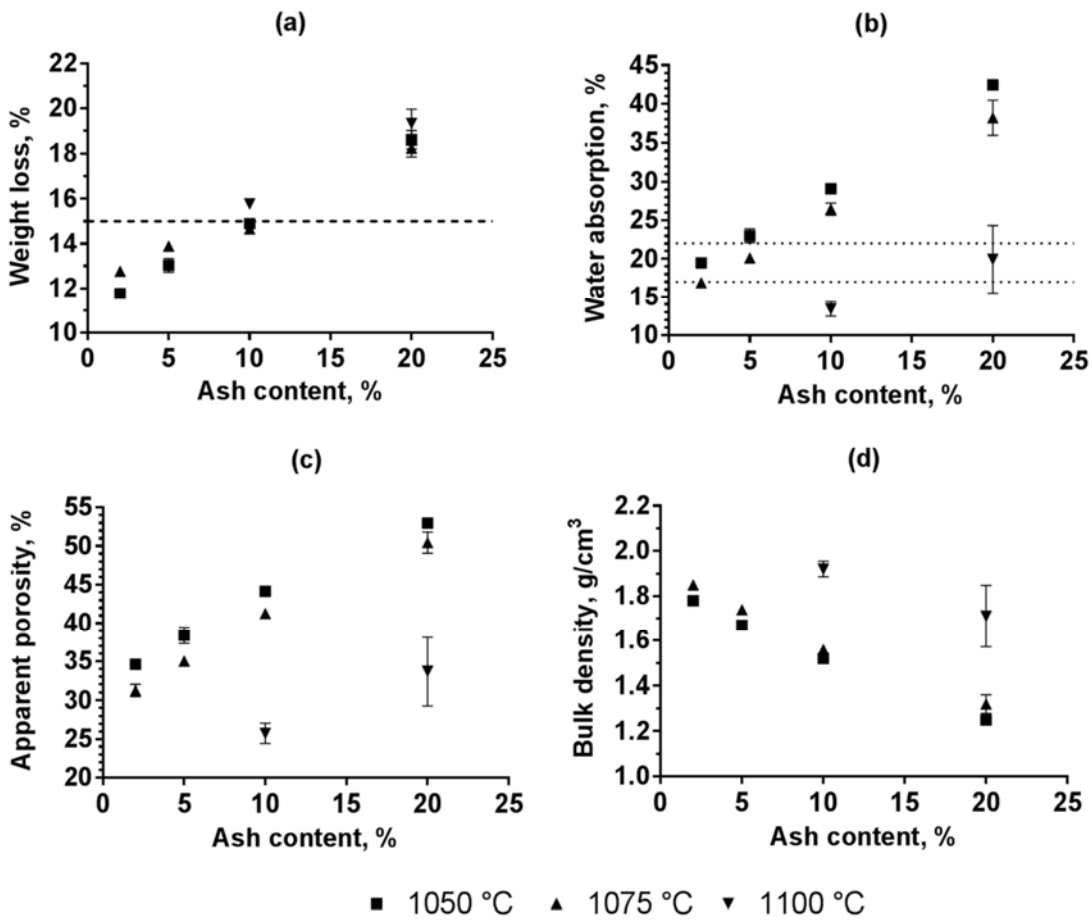


Figure 3. Weight loss(a) of the clay-ash pellets during firing, water absorption (b), apparent porosity (c) and bulk density (d) of the fired pellets.

Tables 4 and 5 give the leaching of major elements and trace elements from the fired pellets. Little variation in pH of the leachates was observed with increasing ash content or firing temperature. In comparison to the limits in C3, the leaching of Cr exceeded the limit in particular from the pellets sintered at 1050 °C. However, the Cr leaching was reduced to fulfill the limit by increasing sintering temperature (i.e. increasing densification of the pellets) to 1075 °C and further reduced at 1100 °C. The leaching results (Tables 4 and 5) suggested that the clay-bioash pellets sintered at 1075 °C and 1100 °C, as waste in Category 3, could be reused for construction purpose. Moreover, it can be seen from Table 6 that, all the pellets fulfilled the leaching limits for landfill as mineral waste, suggesting that incorporating the bioash into fired clay pellets is also beneficial to stabilize the bioash. The high sintering temperature was likely related to the low content of fluxing materials and higher content of silica in the treated bioash after washing and electrodialytic treatment.

It is noteworthy that the leaching of trace elements such as As, Cd, Cr, Ni, Pb and Zn from the fired pellets was much lower than the leaching from the as-received ash. Treatment by washing and EDR, dilution of the concentrations of the trace elements with clay, evaporation during sintering and incorporation into pellets matrix were responsible for the decrease in leaching of trace elements from the fired clay-bioash pellets.

Table 4. Leaching of major elements from fired pellets at L/S 2. 'n.d.' = not determined.

| Temp. | Pellet | pH-leachate | Na, mg/l | K, mg/l | Ca, mg/l | Mg, µg/l |
|---|---|---|---|---|---|---|
| 1050 °C | 2V98C | 11.4 | 21 | 23 | 160 | 92 |
| | 5V95C | 11.3 | 18 | 19 | 169 | 122 |
| | 10V90C | 11.4 | 18 | 18 | 191 | 105 |
| | 20V80C | 11.3 | 19 | 20 | 242 | 115 |
| 1075 °C | 2V98C | 11.2 | 11 | 11 | 119 | 167 |
| | 5V95C | 11.2 | 11 | 9.7 | 118 | 187 |
| | 10V90C | 11.5 | 10 | 9.6 | 209 | 130 |
| | 20V80C | 11.2 | 7.1 | 7.2 | 159 | 245 |
| 1100 °C | 10V90C | 11.4 | n.d. | 4.1 | 127 | n.d. |
| | 20V80C | 11.3 | n.d. | 4.3 | 100 | n.d. |
| [1]limit | C3 | | 100 – 1500 | | | |

[1] C3: Category 3 for the reuse of contaminated waste for geotechnical purposes, mainly for roads, paths, gravel foundations and floors, according to Danish regulation BEK 1414 (BEK nr 1414, 2015).

Table 5: Leaching of trace elements, µg/l in leachate, from fired pellets at L/S 2. '<'= not detected.

| Temp. | Pellet | As | Ba | Cd | Cr | Cu | Mn | Ni | Pb | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1050 °C | 2V98C | 6.8 | 21 | < | **811** | 7.4 | 22 | < | 35 | < | 4.7 |
| | 5V95C | 12 | 16 | 0.9 | **762** | 6.3 | 24 | 6.3 | 35 | < | 2.6 |
| | 10V90C | 16 | 17 | < | **848** | 6.5 | 21 | 6.3 | 41 | < | 2.0 |
| | 20V80C | 13 | 19 | < | **1218** | 5.7 | 17 | < | 41 | **128** | < |
| 1075 °C | 2V98C | 35 | 5.2 | 0.4 | 389 | 7.4 | 0.8 | 1.9 | < | 15 | < |
| | 5V95C | 32 | 4.9 | 0.5 | 391 | 10 | 1.2 | 2.7 | < | 13 | < |
| | 10V90C | 32 | 14 | 0.5 | **716** | 8.7 | 2.6 | 0.9 | < | 11 | < |
| | 20V80C | 31 | 11 | 0.4 | 399 | 8.2 | 4.2 | 1.4 | < | 11 | < |
| 1100 °C | 10V90C | 24 | 15 | < | 236 | 5.0 | < | < | 20 | 14 | 21 |
| | 20V80C | 24 | 24 | < | 201 | 4.5 | < | < | 17 | 23 | < |
| [1] Max. limit | C3 | 50 | 4000 | 40 | 500 | 2000 | 1000 | 70 | 100 | 30 | 1500 |

Table 6: Leaching of trace elements, mg/kg dry ash, from fired pellets at L/S 2. '<'= not detected.

| Temp. | Pellet | As | Ba | Cd | Cr | Cu | Mo | Ni | Pb | Sb | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1050 °C | 2V98C | 0.01 | 0.04 | < | 1.6 | 0.01 | 0.8 | < | 0.07 | 0.02 | < | 0.009 |
| | 5V95C | 0.02 | 0.03 | 0.002 | 1.5 | 0.01 | 1.3 | 0.01 | 0.07 | < | < | 0.005 |
| | 10V90C | 0.03 | 0.03 | < | 1.7 | 0.01 | 2.1 | 0.01 | 0.08 | 0.02 | < | 0.004 |
| | 20V80C | 0.03 | 0.04 | < | 2.4 | 0.01 | 3.9 | < | 0.08 | < | 0.26 | < |
| 1075 °C | 2V98C | 0.07 | 0.01 | 0.001 | 0.8 | 0.01 | 0.6 | 0.004 | < | 0.02 | 0.03 | < |
| | 5V95C | 0.06 | 0.01 | 0.001 | 0.8 | 0.02 | 0.9 | 0.01 | < | < | 0.02 | < |
| | 10V90C | 0.06 | 0.03 | 0.001 | 1.4 | 0.02 | 1.8 | 0.002 | < | < | 0.02 | < |
| | 20V80C | 0.06 | 0.02 | 0.001 | 0.8 | 0.02 | 2.5 | 0.003 | < | 0.05 | 0.02 | < |
| 1100 °C | 10V90C | 0.05 | 0.03 | < | 0.5 | 0.01 | 0.7 | < | 0.04 | < | 0.03 | 0.042 |
| | 20V80C | 0.05 | 0.05 | < | 0.4 | 0.01 | 1.0 | < | 0.03 | < | 0.05 | < |
| [2]Landfill limit | [1]MA1 | 0.4 | 30 | 0.6 | 4.0 | 25 | 5.0 | 5.0 | 5.0 | 0.2 | 0.3 | 25 |

[2] Limits leaching from landfill waste in coastal landfills for mineral waste in Class MA1 according to Danish regulation BEK nr. 252 (BEK nr 252, 2009).

## 4. Conclusions

(1) Reuse of the bioash from co-combustion of straw and wood chips in the production of clay brick is technically possible. It is also profitable by reducing the consumption of natural resources, and by cutting off the tax-related expenses for waste disposal.

(2) Pretreatment such as water washing and electrodialytic remediation can remove the soluble salts and heavy metals from the bioash.

(3) In relation to leaching properties, the clay-bioash pellets could be landfilled as non-hazardous waste in granular form; and especially the ones sintered at 1075 °C and 1100 °C could be reused for construction work.

(4) High sintering temperature, such as 1075 °C, is beneficial for controlling the leaching of heavy metals by increasing the densification degree of the pellets. But higher sintering temperature means more energy consumption.

(5) The properties of the pellets incorporating 2%, 5% and 10% the washing-EDR treated ash sintered at 1075 °C were: bulk density 1.9–1.6 g/cm$^3$, apparent porosity 31.2–41.3% (ash acting as a pore-forming agent), and water absorption 16.9– 26.4%.

(6) Conditions could be recommended for making clay-bioash pellets: ratio of ash replacement up to 10% and sintering temperature ≤1075 °C. The sintering temperature 1075 °C could be reduced in industrial production because of the well-designed firing process.

**References**


ASTM C62-13a. (2013). Standard Specification for Building Brick (Solid Masonry Units Made From Clay or Shale). https://doi.org/10.1520/C0652-12A.

BEK nr 1414. Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald (2015). Retrieved from https://www.retsinformation.dk/Forms/R0710.aspx?id=134831

BEK nr 252. Bekendtgørelse om deponeringsanlæg (2009).

Chen, W., Jensen, P. E., Ottosen, L. M., & Kirkelund, G. M. (2015). Electrodialytic remediation of fly ash from co-combustion of wood and straw. *Electrochimica Acta*, *181*, 208–216. https://doi.org/10.1016/j.electacta.2015.04.083

Christaras, B. (1991). A comparison of the Casagrande and fall cone penetrometer methods for liquid limit determination in marls from Crete, Greece. *Engineering Geology*, *31*(2), 131–142.

DS/EN 12457-1. (2002). Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 L/kg for materials with high solid content and with particle size below 4mm (without or with size reduction).

Hrubesova, E., Lunackova, B., & Brodzki, O. (2016). Comparison of liquid limit of soils resulted from casagrande test and modificated cone penetrometer methodology. *Procedia Engineering*, *142*, 363–369. https://doi.org/10.1016/j.proeng.2016.02.063

Kazmi, S. M. S., Abbas, S., Saleem, M. A., Munir, M. J., & Khitab, A. (2016). Manufacturing of sustainable clay bricks: Utilization of waste sugarcane bagasse and rice husk ashes. *Construction and Building Materials*, *120*, 29–41. https://doi.org/10.1016/j.conbuildmat.2016.05.084

Lin, K. L. (2006). Feasibility study of using brick made from municipal solid waste incinerator fly ash slag. *Journal of Hazardous Materials*, *137*(3), 1810–1816. https://doi.org/10.1016/j.jhazmat.2006.05.027

Ottosen, L. M., Pedersen, A. J., Hansen, H. K., & Ribeiro, A. B. (2007). Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method. *Electrochimica Acta*, *52*(10), 3420–3426.

Spagnoli, G. (2012). Comparison between Casagrande and drop-cone methods to calculate liquid limit for pure clay. *Canadian Journal of Soil Science*, *92*(6), 859–864. https://doi.org/10.4141/cjss2012-011

White, W. A. (1949). Atterberg plastic limits of clay minerals. *Report of Investigations No. 144.*

Yeboah, N. N. N., Shearer, C. R., Burns, S. E., & Kurtis, K. E. (2014). Characterization of biomass and high carbon content coal ash for productive reuse applications. *Fuel*, *116*(March 2015), 438–447. https://doi.org/10.1016/j.fuel.2013.08.030

# Chapter 6

## *Recycling of MSWI fly ash in clay bricks – effect of washing and electrodialytic treatment*

A short version submitted to the conference WASTES : Solutions, Treatments and Opportunities 2017 .

# Recycling of MSWI fly ash in clay bricks

# – effect of washing and electrodialytic treatment

Wan Chen[1], C. Dias-Ferreira[2,3], E. Klupsch[1], G.M. Kirkelund[1], P.E. Jensen[1], L.M. Ottosen[1]

[1]*Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark.*
[2]*Materials and Ceramic Engineering Department, CICECO, University of Aveiro, Campus Universitario de Santiago, Aveiro, Portugal*
[3] *Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture, Polytechnic Institute of Coimbra, Bencanta 3045-601 Coimbra, Portugal*

## Abstract

The feasibility of incorporation of MSWI fly ash into sintered clay bricks was studied. Clay is still commonly used in Denmark and many other countries for production of building bricks. The MSWI fly ash was pre-treated by a combination of water washing and electrodialytic remediation before being used in bricks in order to remove soluble salts and lower the soluble content of heavy metals. MSWI fly ash-clay bricks with 5%, 10% and 20% ash substitution levels, were handmade and fired at 1000 °C for 6 h. The fired fly ash-clay bricks had higher porosity and lower compressive strength, compared with the 100% clay brick, even though the washing-electrodialysis treatment improved the properties of the fired fly ash-clay bricks. This study indicates that fired MSWI fly ash-clay bricks with 5% treated ash might be used as building materials and, at the end of their service life, they might be reused again in construction work, as the heavy metal leaching was low enough to allow this.

## 1. Introduction

Fly ash generated from municipal solid waste incineration (MSWI) is a hazardous material. In 2000, approximately 25 Mt/year (estimated) of fly ash was generated by burning municipal solid waste in the USA, Japan and the European Union (Reijnders, 2005). MSWI fly ash is hazardous due to the content of heavy metals and organic pollutants, and the leachability of these inorganic and organic pollutants. In Denmark, MSWI fly ash is currently exported to Norway for waste acid neutralization and to Germany for salt mines backfilling (Astrup, 2008).

As regards the treatment of MSWI fly ash, there are techniques such as washing by water or acid (Mangialardi, 2003), chemical stabilization (Zhao et al., 2002), thermal treatment (Park and Heo, 2002) as well as electrodialytic remediation (Ferreira et al., 2005; Kirkelund et al., 2015; Pedersen et al., 2005). In electrodialytic remediation (EDR), an electric DC field is applied to an ash-water suspension and mobile heavy metals in the suspended MSWI fly ash electromigrate toward either the anode or cathode through ion exchange membranes, therefore achieving simultaneous heavy metal extraction and separation from the suspension. Ferreira et al. (2008) combined washing pre-treatment with EDR, and observed that the combination of washing and EDR was successful in reducing the environmental risk of the MSWI fly ash since the metals (Cd, Cu, Pb and Zn) were mainly found in the strongly bonded and residual phases after the treatment.

MSWI fly ash can be used as raw material for construction materials and for geotechnical applications (Ferreira et al., 2003). Recycling fly ash conserves natural resources, eliminates waste streams, and provides zero-cost raw material (Ferreira et al., 2003). In terms of the production of building ceramics, MSWI fly ash showed potential of being a substitute for clay in brick production (Lin, 2006; Zhang et al., 2011). However, MSWI fly ash is less commonly used in the production of building ceramics than MSWI bottom ash, due to its content in soluble salts and

volatile components (Margallo et al., 2015). In this regard, electrodialytically treated MSWI fly ash could be more suitable than the raw ash for incorporation in bricks, because soluble salts (mainly chlorides) and volatile heavy metals such as Pb are extracted from the ash during the electrodialytic treatment (Chen et al., 2017; Kirkelund et al., 2015).

Given that electrodialytically treated MSWI fly ash has not yet been studied in clay brick production, fired fly ash-clay bricks with different EDR-treated ash contents (5%, 10% and 20%) were made in the present study and characterized in terms of water absorption, density, open porosity, compressive strength and leaching of heavy metals. These bricks were further compared with 100% clay bricks and with bricks made from raw MSWI fly ash (not electrodialytic treated) at 20% substitution rate. The feasibility of incorporation of electrodialytically treated MSWI fly ash in production of sintered clay brick was investigated.

## 2. Materials and methods

### *2.1. Materials*

The materials used for the production of bricks were:

(1) *The clay sample (C)* was purchased from Wienerberger, Helsinge, Denmark, a manufacturer of bricks. It was dried at 105 °C for 24 h. The dried clay was grinded by dry ring milling for 60 seconds prior to use.

(2) *MSWI fly ash (R)* originated from a municipal solid waste incineration plant, I/S Vestforbrænding (VF) in Glostrup, Denmark. The fly ash sample was collected after the electrostatic precipitator before the neutralization of the acidic components by the wet scrubber process.

(3) *EDR-treated washed MSWI fly ash (T)* was obtained by first water washing the raw MSWI fly ash R (3-step washing at L/S 2.5 for each) and then treating the washed ash by electrodialytic remediation (EDR). The electrodialytic cell was cuboid-shaped and had two compartments, i.e. anode (length× width × height = 37.5 cm × 5.5 cm /6 cm to membrane × 27.5 cm) and cathode compartment (length× width × height = 37.5 cm × 2.5 cm/ 3cm to membrane × 27.5 cm), separated by a cation exchange membrane (effective area 500 $cm^2$). As illustrated in Fig. 1, the washed fly ash-water suspension (1kg ash into 15 l distilled water) was feed continuously into the anode compartment of the cell at a speed of 5 l/min, and recirculated in the system. An electrolyte solution (5 l of 0.01 M $NaNO_3$ with pH 2) was recirculated in the cathode compartment. The pH of the electrolyte solution was controlled twice a day to maintain pH ~2 by adding 1:1 $HNO_3$ solution. The duration of the electrodialytic treatment was 7 days at room temperature. A constant direct current of 250 mA was applied.

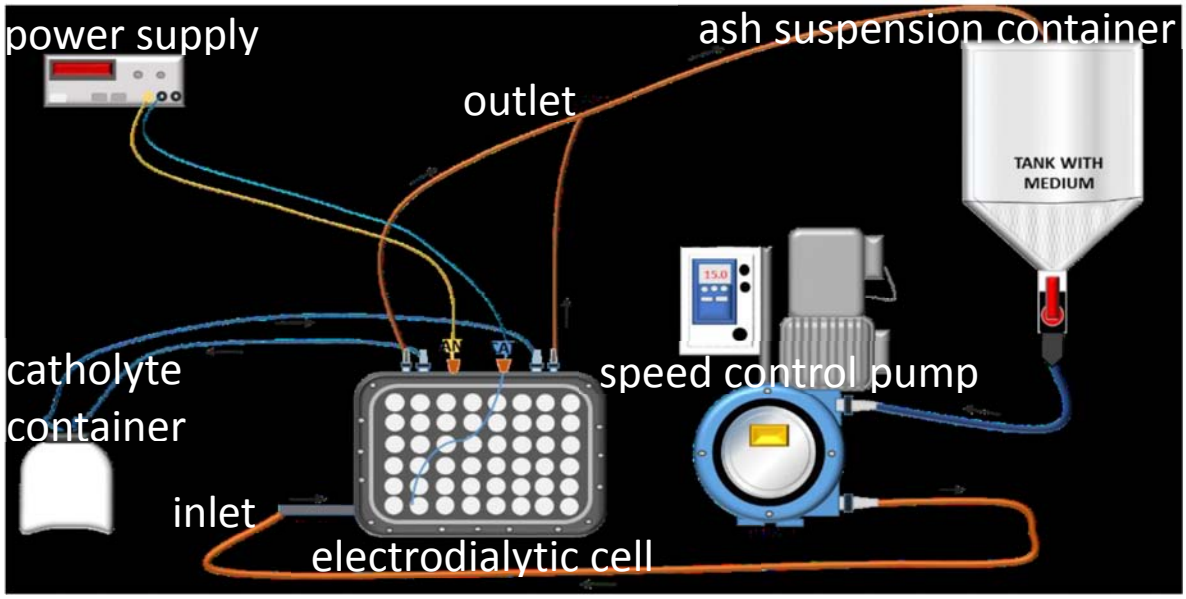


Figure 1: Flowsheet of the EDR treatment.

*2.2. Characterization of raw materials*

*Heavy metal concentrations* of the ash samples were determined by $HNO_3$ digestion according to Danish Standard DS 259 (2003). For $HNO_3$ digestion, 1 g (three or five replicates) of dry ash suspended in 20 ml of 1:1 $HNO_3$ was digested at 200 kPa at 120 °C for 30 min in an autoclave. After digestion, the samples were filtered through a 0.45-μm filter and diluted to 100 ml. The concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian 720-ES, Software version: 1.1.0). All concentrations are expressed on a dry mass basis.

*Particles size distribution* was measured using a Malvern Mastersizer 2000 particle size analyser. *Morphology* of the ash samples was revealed by scanning electron microscope (SEM) imaging. Images were captured using a large field detector (LFD) under the accelerating voltage of 20 kV. The *crystalline phases* of the ash samples were studied by X-ray diffraction using PANalytical X'pert Pro diffractometer. Scans were made in 2θ mode, using Cu Kα radiation with an operating current of 40 mA and voltage of 45 kV.

*2.3. Brick making*

The bricks were handmade. Referring to the processes reported in Arabia (1988) and Lin (2006), the overall process was designed, including:

(a) Mixing of raw materials (Table 1) with water (water content of green brick 23-26 wt.%) in a blender attempting to get a homogenised mixture;

(b) Hand moulding into 5cm×5cm×5cm brick blocks;

(c) Drying the wet bricks first at 40 °C for 24 h and subsequently at 105 °C for 24 h;

(d) Firing: The heating rate was 10 °C/min. The temperature was first maintained at 200 °C for 999 min (the maximum built in the heating program of the oven) to make sure that water was

sufficiently removed from the unfired ‘green’ bricks, and then increased to the sintering temperature 1000 °C and kept for 6 h ; and

(e) Cooling: After sintering, the bricks were allowed to cool down naturally in the furnace to room temperature.

Table 1: The ratios of the raw materials by weight used for brick-making.

| Brick name | Clay (wt.%) | Raw ash (wt.%) | Treated ash (wt.%) |
|---|---|---|---|
| C | 100 | | |
| R20 | 80 | 20 | |
| T5 | 95 | | 5 |
| T10 | 90 | | 10 |
| T20 | 80 | | 20 |

*2.4. Characterization of fired bricks*

The vacuum water absorption, apparent porosity and bulk density were determined at the same time according to DS/EN ISO 10545-3 (1997), but some modifications were made in terms of vacuum residence time and the period of water-soaking in order to sufficiently fill the open pores with water. The vacuum process was done as follows: (1) pump 3 hours to reach vacuum; (2) stop the pump and let pellets stay in water under pressure for 1 hour; (3) the pellets were in water for 24 hours at normal pressure, and then the pellets were ready for further measurement of saturated mass in air, and suspended mass in water.

Firing weight loss, %, is the mass difference between the fired brick and the green brick before sintering.

Compressive strength analysis without mortar joints was performed (Shimadzu AG-A/AG-25TA).

Soluble salts content (Na, K, Ca, Mg) (DS/EN 772-5, 2016): One hour distilled water extraction at liquid-to-solid ratio of 10 was performed on the crushed fired brick (< 125 μm). The concentrations of Na, K, Ca and Mg were determined in the eluent after filtration through a 0.45 μm filter.

Two leaching tests were conducted: tank leaching test according to NEN 7345 and batch leaching test according to DS/EN 12457-1 (2002) and DS/EN 12457-2 (2002), respectively. In the tank leaching test for monoliths, the fired bricks were immersed in acidified distilled water (pH 4 adjusted by nitric acid). The volume of the acidified water was five times that of the brick. Total number of days to run the tank leaching test was 64 days. The leachate samples were collected after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. The acidified water for extraction was renewed when the samples were collected. For the batch leaching test, the fired bricks were crushed into granules with particle size less than 4 mm. The leachates were collected after 24-h agitated extraction using distilled water at liquid-to-solid ratios 2 and 10. Using Radiometer Analytical pH electrode, the pH value was determined in the leachate samples collected from both tank and batch leaching tests. Afterwards, the leachates were filtered through a 0.45 μm filter for elemental analyses of the filtrate. The concentrations of As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn in the leachates were analyzed by ICP-OES.

## 3. Results and discussion

### *3.1. Characteristics of raw materials*

The same type of clay has been used in Chen et al. (2014). The clay is named yellow clay due to a high $CaCO_3$ content (22±0.2%), and the colour of the bricks made from this kind of clay is commonly yellow. The liquid limit and plastic limit for the clay were 27% and 15%, respectively (Chen et al., 2014). Clay minerals exhibit plasticity. Quartz, illite, dolomite, calcite and feldspar

minerals (microcline and albite) were detected in the clay sample. It had good plasticity and is used for commercial bricks production. Because the ash residues were non-plastic, the clay acted as a good binder to make clay-ash bricks.

Table 2 compares the heavy metal concentrations before and after the washing-EDR treatment. Reduction in As, Cd, Pb and Zn concentration was obtained after treatment. Chen et al. (2017) also observed the reduction in Zn concentration after washing and EDR treatment, but not in Pb. The disagreement in concentration change between the present study and Chen et al. (2017) was due to the difference in EDR setup and experimental conditions for both washing and EDR treatment. As for EDR, the setup illustrated in Fig. 1 differs from the small lab-scale setups used in Chen et al. (2017) in terms of dimensions, and thus also in terms of the ash treatment capacity. Another difference in EDR treatment is the liquid to solid (L:S) ratio of the ash suspension, which in the present work was 15 to ensure the flow of the ash suspension in the tubes, whereas the L:S ratio was 3.5 in Chen et al. (2017). Regardless of the differences between this and previous works, generally speaking, it is better to have reduced heavy metal concentrations in the treated MSWI fly ash (if possible) because when raw fly ash is incorporated into clay bricks they emit heavy metals and toxic organic pollutants during firing, greatly contributing to air pollution (Huang et al., 2016). These emissions are associated with the chemical speciation of volatile heavy metals in the ash, especially the chloride species which seemingly increase the volatilization of heavy metals (Chen et al., 2017). In Chen et al. (2017), a reduction in the volatilization of Pb from more than 80% down to less than 20% was seen when electrodialytic treated ash was fired at 1000 °C for 1 h, as opposed to raw ash. Considering the slightly reduced concentrations of the electrodialytically treated ash (Table 2) and the previous finding by Chen et al. (2017) referred above, it is expected

that the electrodialytic treatment of the MSWI fly ash used in this work might reduce the emission of volatile metals during firing.

Table 2: trace elements in the MSWI fly ash compared to clay, mg/kg TS.

| | **Raw MSWI fly ash** | **Treated ash** | **Clay** |
|---|---|---|---|
| pH | 11.7±0.1 | 9.7±0 | - |
| Conductivity, mS/cm | 61±3 | 3.0±0.1 | - |
| As | 195±15 | 172±7 | 1.9±0.2 |
| Cd | 144±6 | 106±3 | 0.28±0.06 |
| Cr | 113±6 | 119±3 | 25±3 |
| Cu | 680±29 | 713±26 | 14±1 |
| Ni | 44±2 | 45±1 | 15±0.4 |
| Pb | 5 309±1241 | 4 386±144 | 13±5 |
| Zn | 26 149±7533 | 19 137±449 | 65±28 |

Figure 2 shows the morphology of the ash samples. The raw ash particles were built into a fluffy phase of small crystals. After treatment components making up the fluffy phase were removed. Fig. 3 presents the results from the XRD analysis of the ash samples. The mineral phases of anhydrite ($CaSO_4$), calcite ($CaCO_3$) and quartz ($SiO_2$) were detected in the ash samples both before and after treatment. Hallite (NaCl) and sylvite (KCl) were detected in the raw fly ash, whereas gypsum ($CaSO_4 \cdot H_2O$) was detected in the treated ash. The results indicated that the treatment mainly removed the alkaline metal chlorides. In addition, the ash particles were irregular in shape as can be seen in Fig. 2, probably depending on the composition of the ash particles. For instance, according to Keppert et al. (2015) the carbon particles are bar-shaped, whereas siliceous particles were spherical; both shapes can be easily identified in the treated ash (Fig. 2, right). Different shapes could also be linked to the different heavy metal mineral phases. In general, the ash particles were bigger than the clay particles according to the particle size distribution given in Fig. 4.

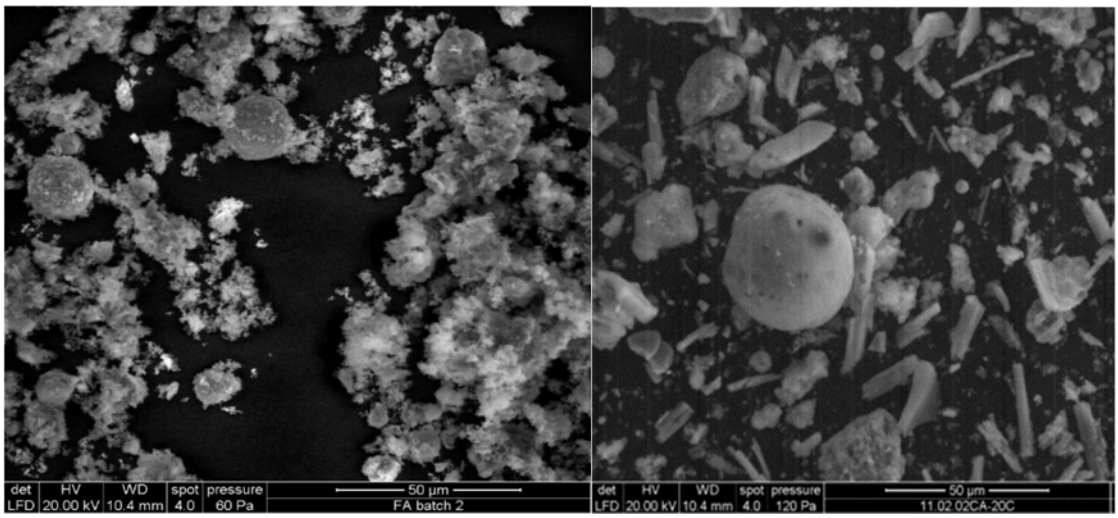


Figure 2: Microstructure of the ash samples: left, the raw MSWI fly ash; right, the treated fly ash by combined water washing and EDR.

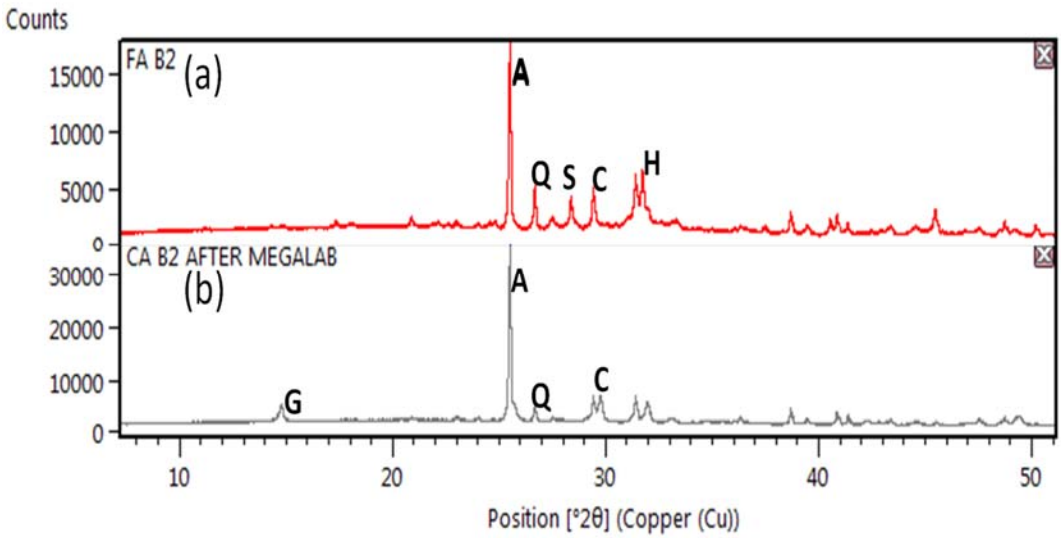


Figure 3: Mineralogy of the ash samples: (a) raw ash; and (b) treated ash. A-anhydrite, C-calcite, G-gypsum, H-hallite, S-sylvite, Q-quartz.

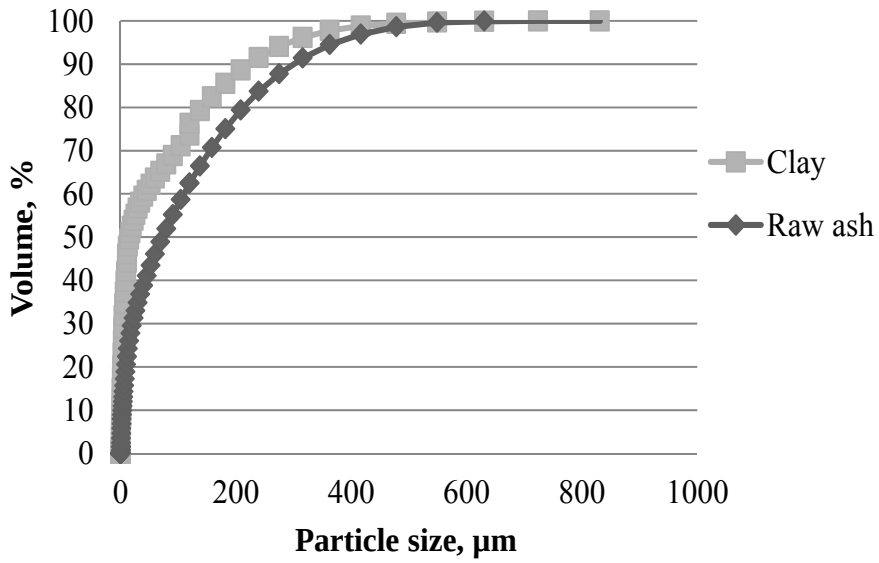

Figure 4: Particle size distribution of clay and raw MSWI fly ash.

*3.2. Physical properties of fired bricks*

3.2.1 Appearance

The fired bricks (Fıgure 5) all exhibited yellow-based colours, but were different in the shades of yellow. The shade became increasingly lighter with increasing ash content, and the lightest was the brick with untreated ash (R20). It is also observed that only in the case of brick R20 the surface was fluffy, and particles peeled off from the surface, which was most likely ascribed to the presence of a high content of soluble salts in the untreated MSWI fly ash. Manual preparation of the green bricks caused irregular surfaces, as appeared in the fired bricks.

Figure 5: The appearance of the fired bricks. Notes: C – 100% clay, T5 – 5% treated MSWI fly ash; T10 - 10% treated MSWI fly ash, T20 - 20% treated MSWI fly ash; R20 – 20% raw (not treated) MSWI fly ash.

*3.2.2. Soluble salts content*

Danish standard DS/EN 771-1:2011+A1:2015 (2015) regulates the requirements for active soluble salts content in clay masonry units, because soluble salts are related to the efflorescence when the brickwork is drying out after water exposure. Clay bricks are defined by three categories: (1) Category S0 bricks: there is no requirement for soluble salts content. Bricks are intended for use in situations where a complete protection against water penetration is provided (e.g. thick layer of suitable render, cladding, inner leaf of a cavity wall, internal walls); (2) Category S1 bricks: 0.17% (equivalent to g/l in here) for the sum of $Na^+$ and $K^+$, and 0.08% for $Mg^{2+}$; and (3) Category S2 bricks: 0.06% for the sum of $Na^+$ and $K^+$, and 0.03 g/l for $Mg^{2+}$. In addition, more than 0.3% of soluble calcium salts and more than 0.5% of soluble sulphate salts are also considered to be a high soluble salt content level (Maybery-Thomas and Charlett, 2013). Given the limits described, it is interesting to see how the fly ash-clay bricks performed against clay-bricks. Table 3 presents the results of the soluble salts tests that highlight this comparison. The soluble Na, K, Ca and Mg increased with increasing MSWI fly ash content in the bricks, except in the case of the bricks with

5% treated ash. The highest soluble salts content was in R20 (20% untreated MSWI fly ash), which indicated the highest risk of efflorescence. Bricks with up to 10% of treated fly ash obtained the best classification in this parameter (category S2).

Table 3: Soluble salts content *(DS/EN 772-5, 2016)* in eluates from the fired bricks, in ***mg/l***.

| | **Na** | **K** | **Ca** | **Mg** | **Category** |
|---|---|---|---|---|---|
| C | 6.5±0.4 | 7.8±0.6 | 22±0.5 | 0.5±0.0 | S2 |
| T5 | 5.6±1.4 | 7.2±2.0 | 83±8 | 0.5±0.1 | S2 |
| T10 | 14±5 | 12±3 | 187±9 | 1.0±0.1 | S2 |
| T20 | 69±10 | 90±20 | 259±23 | 1.1±0.1 | S1 |
| R20 | 272±40 | 209±12 | 292±9 | 1.0±0.1 | S0 |

*3.2.3. Mineralogy*

Figure 6 shows the XRD patterns of the fired bricks. Quartz, anorthite, augite, microcline, mullite and wollastonite were detected in all the bricks. Quartz is commonly the most abundant phase in fired clay bricks. The formation of wollastonite, feldspar (e.g. anorthitic) and augite has been observed in the fired bricks made from calcareous clay sintered at temperature above 950 °C (Cultrone et al., 2004; Jordán et al., 1999). Mullite can also be formed in the bricks made from calcareous clay (Cultrone et al., 2004). Bricks T5 and C had the same mineral compounds. A new phase, cordierite, was detected in the bricks with ash content greater than 5 wt.%. The characteristic peaks of cordierite became more obvious with increasing ash content. Notably, the presence of cordierite was also observed by Zhang et al. (2011) in the fired bricks made from MSWI fly ash (20% by mass), red ceramic clay (60%), feldspar (10%) and gang sand (10%). The bricks T20 and R20 presented the same mineral phases, which indicates that the ash treatment did not significantly affect the mineralogy of the fired bricks. The minerals detected in the fly ash samples such as $CaCO_3$ and $CaSO_4$ decomposed during firing, and thus the peaks in the XRD patterns disappeared after firing.

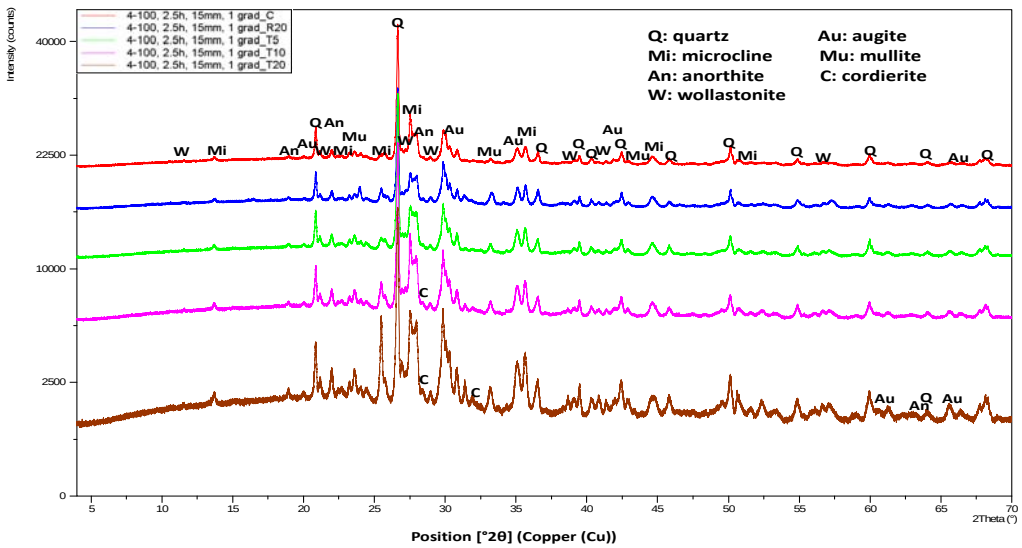


Figure 6: Mineralogy of the fired bricks.

*3.2.4. Bulk density, water absorption and apparent porosity*

Sintering is a densification process. Through different sintering mechanisms such as reaction sintering, solid-state and liquid-state sintering, the ash particles and clay particles bond together. The sintering process is accompanied by shrinkage of the component. It was observed that total shrinkage during drying and firing was less than 8% for each of the bricks.

The weight loss (Fig. 7a) during firing was less than 15% (value for a normal clay brick (Lin, 2006)) for all the bricks. The addition of 20 wt.% the treated MSWI fly ash in the bricks slightly reduced the weight loss, but the addition of 20% the raw ash slightly increased the weight loss. Loss on ignition is closely correlated to burn-off of the organic matter and decomposition of carbonates in the clay-ash mixture; however, dehydration of clay minerals or metal oxides, loss of volatile salts, or loss of inorganic carbon in minerals also contribute to loss on ignition (Heiri et al., 2001). The volatile salts (e.g. chlorides) and $CaCO_3$ in the raw MSWI fly ash probably resulted in the increase in weight loss. Whereas, the treatment (water washing and electrodialytic remediation) reduced the chlorides content and transformed $CaCO_3$ partially to gypsum in the ash.

Moreover, Chen et al. (2017) observed a reduction in volatility of heavy metals (e.g. Pb) in the same MSWI fly ash after combined water washing and electrodialytic treatment. These changes in ash composition after treatment as well as the lowest clay content in bricks T20 were possibly related to the reduction in weight loss during firing.

The bulk density of the bricks (Fig. 7b) varied from 1.44 to 1.65 g/cm$^3$, which is lower than the bulk density of normal clay bricks (1.8-2.0 g/cm$^3$) (Lin, 2006). With increasing ash content the bulk density of the fired bricks decreased. However, the lowest density of the bricks was still believed to be acceptable, in comparison to *London Stock bricks*, one type of handmade bricks commonly made from yellow clay having bulk density of about 1.39 g/cm$^3$ (Domone and Illston, 2010).

Moreover, the bricks T20, with 20% treated ash, had a higher bulk density than the bricks R20, with 20% raw ash. Considering a brick as a bi-phase material i.e. air-phase in pores embedded in solid phases, a higher density indicates a smaller amount of air-phase in the brick, i.e. lower porosity. The measured apparent porosity of the fired bricks (Fig. 7c) was inversely proportional to the bulk density (Fig. 7b).

Water absorption affects the durability of bricks. Fig. 7d exhibits the water absorption values of the fired bricks, ranging between 24.5% and 33.7%. Most common burnt clay bricks, including common bricks and facing bricks, have water absorption between 12% and 26% (Maybery-Thomas and Charlett, 2013), whereas, *London Stock handmade bricks* can have water absorption varying from 22% to 37% (Domone and Illston, 2010). The water absorption of bricks C and T5 was thus within the range for common burnt clay bricks. All the fired bricks were within the water absorption range of London stock bricks. Water absorption is closely related to the porosity of the bricks. The apparent porosity (Fig. 7c) was higher than 40% for all the bricks. The water porosity

of fired clay bricks can be higher than 40% (volume %), depending on the type of the bricks, such as 19-42% for handmade facing bricks, and 36-50% for London Stock bricks (Domone and Illston, 2010). Air trapped in the component and low compaction during hand-making of bricks, and gaseous phase generation and release during firing could contribute to the generation of voids. The high porosity indicated that the liquid-phase formation during sintering at 1000 °C for 6 h was insufficient to fill the pore space. In addition, the presence of carbonates in the studied clay played an indispensable role in the development of porosity.

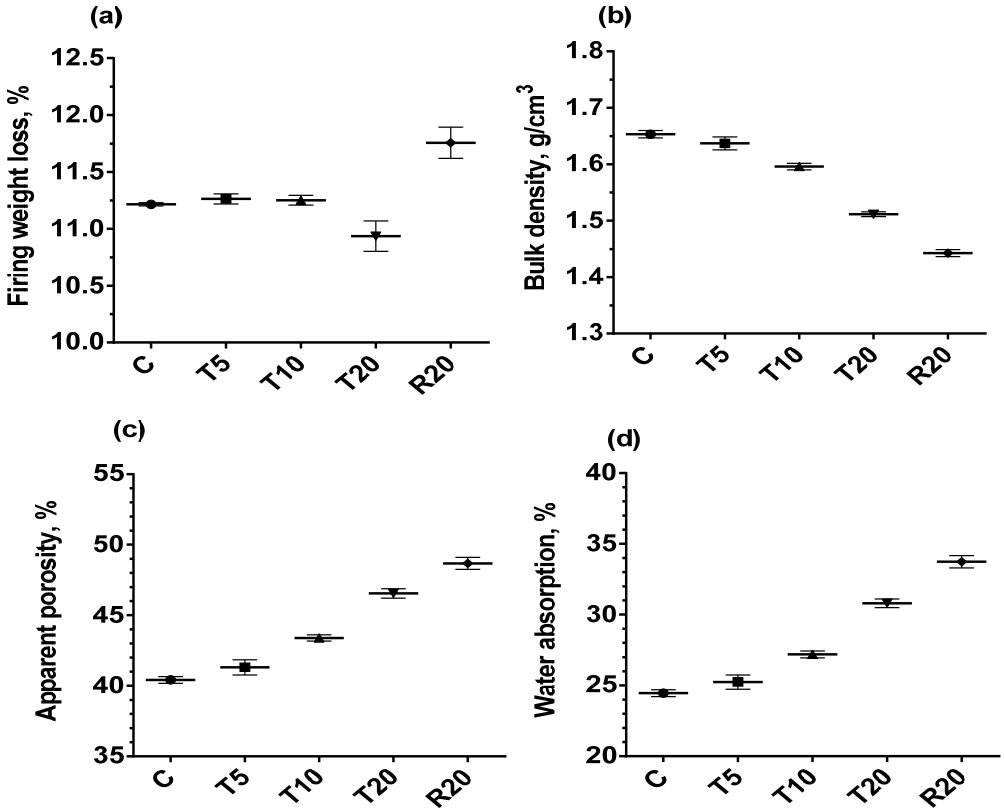


Figure 7: Results of loss on ignition, bulk density, apparent porosity and water absorption.

*3.2.5. Compressive strength*

The compressive strength measures the resistance to crushing. Clay bricks are commercially available with compressive strengths ranging from less than 10 N/mm$^2$ for a soft mud brick to

more than 200 N/mm$^2$ for an engineering brick (Domone and Illston, 2010). The compressive strength of London Stock bricks can range from 5 N/mm$^2$ to 20 N/mm$^2$ (Domone and Illston, 2010).

Fig. 8 shows the compressive strength results. Only the 100% clay bricks met the minimum compressive strength requirement for clay masonry units regulated in DS/EN 771-1:2011+A1:2015 (2015), i.e. 9 N/mm$^2$ for Group 2 bricks which have formed voids greater than 25% but not more than 50% (the range that the studied bricks fell into). Making the bricks by hand was believed to be responsible for the significant deviation between the measured values. It can be seen from Fig. 8 that with increasing ash content, the compressive strength of the fired bricks decreased. The bricks with 20% the raw fly ash had lower compressive strengths than the bricks with 20% treated fly ash. The function of the washing-EDR treatment is worthy to be affirmed. Compared to the untreated fly ash, the treated ash did improve the compressive strength of the bricks with the same substitution rate.

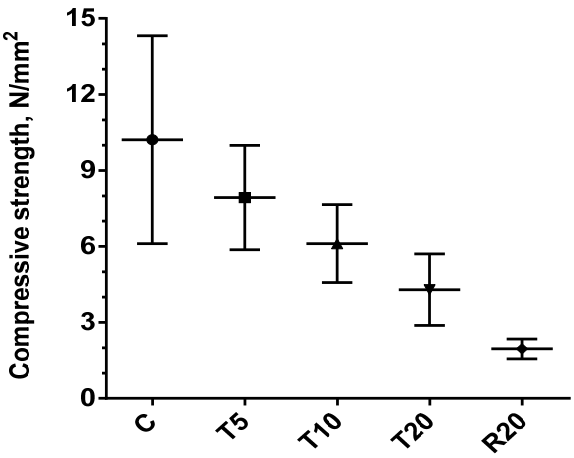


Figure 8: compressive strength

*3.3. Environmental properties of fired bricks*

Heating during firing causes decomposition (such as water, sulphates, carbonates and organic matters), state change (quartz transformation and densification), and volatilization of pollutants in

the MSWI fly ash. However, the leaching of the pollutants from the brick matrix can potentially influence the environment negatively once the brick is used in construction work.

To assess these potential environmental impacts, tank leaching tests were performed on the fired bricks. This type of tests simulate the leaching properties of pollutants during the service-life of brick (Quijorna et al., 2012). The results of the tank leaching test according to NEN 7345 over 64 days are shown in Table 4. The limiting values regulated in Dutch building material decree (BMD) used in Quijorna et al. (2012) were also used in here for comparison. Even though compared to pure clay bricks, the clay-ash bricks had higher release of heavy metals into water, none of the heavy metals released from the fired clay-ash bricks failed to meet the limits. With increasing the addition of the treated fly ash, the release of almost all the heavy metals, except Cd, increased. With 20% ash addition, the release of As, Ba and Mo was higher from the bricks with treated ash than from those with untreated ash. Whereas, the rest elements, i.e. Cd, Cr, Cu, Ni, Pb and Zn, released more from the bricks made from untreated ash.

Batch leaching tests evaluate the disposal of bricks at the end of their service life by means of landfill (Quijorna et al., 2012). The results of the leachability of heavy metals and anions from the fired bricks are presented in Tables 5 and 6. The addition of both untreated and treated MSWI fly ash decreased the pH of the leachates by less than one pH unit compared to the pH of the leachate from control clay bricks C. However, the ash content had very little influence on the pH of leachate. The leaching of As, Cr and Mo increased with increasing ash content. They are classified as oxy-anionic forming elements (Cornelis et al., 2008). In a previous work, Chen et al. (2014) conducted leaching test on fired pellets containing 25% washed MSWI fly ash and 75% clay at L/S 2. It was found out that the leaching of Cr increased dramatically after sintering, in comparison to green pellets. The present study shows that the treatment of the raw ash by washing

and EDR reduces leaching, especially of Cr, from the fired bricks at both L/S 2 and 10. A relatively lower Cr leaching was also observed by Chen et al. (2017) from the thermally treated pure ash after water washing and EDR treatment than from the thermally treated pure raw ash. The mobility of Cr after thermal treatment is believed to be related to the content of Ca and the chemical speciation of Ca in the ash (Chen et al., 2017; Hu et al., 2013). It is observed from Table 5 and 6 that leaching of heavy metals meets the limits for landfill of mineral waste in Class MA1, which means the demolished fired bricks after utilization could be landfilled as mineral waste.

Danish Decree BEK nr 1414 (2015) regulates the requirements for waste being used in construction work. This decree defines the residues that can be used in construction work in three categories according to the level of heavy metal concentration and leaching of heavy metals based on leaching test DS/EN 12457-1 (2002). Category 3 is the least stringent category, having the higher limits and fewer applications amongst the three categories. Category 3 does not restrict the upper limits of heavy metal concentration, but instead the upper limits of heavy metal leaching in eluent: 50 µg As/l, 4000 µg Ba/l, 40 µg Cd/l, 500 µg Cr/l, 2000 µg Cu/l, 70 µg Ni/l, 100 µg Pb/l, and 1500 µg Zn/l. Table 5 lists the results of leachability of the heavy metals in mg/kg TS, which is numerically twice the values, in mg/l, of the heavy metal concentrations in eluent. Accordingly, compared to the doubled values of the above mentioned limits in the unit of mg/l, it can be seen that As exceeded the limit (equivalent to 0.1 mg/kg TS) in the case of T10, T20 and R20, whereas Cr (equivalent to 1 mg/kg TS) only in the case of R20. The other heavy metals' leaching was far below the limits. Bricks T5 were the only ones with incorporated fly ash, which met the requirements of Category 3. Therefore, 'demolished' T5 bricks might be reused again in construction work such as paths and foundations, whereas demolished T10, T20 and R20 bricks could only be landfilled as mineral waste.

Table 4: Total leachability, in mg/m$^2$, of the heavy metals from the fired bricks determined by tank leaching test (NEN 7345). (Assumption, the surface area was constant, 0.015 m$^2$).

| | As | Ba | Cd | Cr | Cu | Ni | Mo | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| **C** | 2.1 | 0.06 | 0.15 | 2.1 | 0.56 | 0.79 | 3.5 | 0.8 | 0.59 |
| **T5** | 2.8±0.7 | 3.2±0.01 | 0.14±0.07 | 2.49±0.03 | 0.92±0.06 | 1.43±0.08 | 5.05±0.22 | 1.19±0.53 | 2.33±0.48 |
| **T10** | 3.73±0.79 | 8.67±0.90 | 0.20±0.15 | 4.26±0.16 | 1.16±0.41 | 1.51±0.01 | 25.89±21.42 | 2.40±1.03 | 6.82±1.48 |
| **T20** | 9.01±2.91 | 11.26±1.58 | 0.15±0.15 | 16.44±3.12 | 1.49±0.18 | 2.00±0.25 | 42.17±1.93 | 1.90±2.69 | 8.05±5.98 |
| **R20** | 5.5 | 10.7 | 0.25 | 32 | 1.83 | 2.34 | 25.4 | 2.79 | 18 |
| **BMD** | 435 | 6300 | 12 | 1500 | 540 | 525 | 150 | 1275 | 2100 |

Table 5: Leaching from the fired bricks, in mg/kg TS, by leaching test at 2 l/kg (DS/EN 12457-1). MA1, limits of leaching from landfill waste in coastal landfills for mineral waste in Class MA1 according to Danish Decree BEK nr. 252.

| | pH | As | Ba | Cd | Cr | Cu | Mo | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **C** | 11.1 | 0.10 | 0.01 | <d.l. | 0.43 | 0.017 | 0.40 | 0.05 | <d.l. | 0.002 |
| **T5** | 10.5 | 0.06 | 0.11 | <d.l. | 0.27 | 0.022 | 0.55 | 0.02 | 0.007 | 0.001 |
| **T10** | 10.5 | 0.11 | 0.33 | <d.l. | 0.35 | 0.01 | 0.91 | 0.02 | <d.l. | 0.002 |
| **T20** | 10.3 | 0.19 | 0.23 | <d.l. | 0.95 | 0.01 | 3.55 | 0.04 | <d.l. | 0.003 |
| **R20** | 10.5 | 0.20 | 0.23 | <d.l. | 1.95 | 0.02 | 2.61 | 0.03 | <d.l. | 0.003 |
| **MA1** | | 0.40 | 30 | 0.60 | 4 | 25 | 5 | 5 | 5 | 25 |

Table 6: Leaching from the fired bricks, in mg/kg TS, by leaching test at 10 l/kg (DS/EN 12457-2).

| | pH | As | Ba | Cd | Cr | Cu | Mo | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **C** | 11.0 | 0.16 | 0.02 | 0.002 | 0.46 | 0.08 | 0.34 | 0.09 | 0.03 | 0.01 |
| **T5** | 10.5 | 0.10 | 0.16 | 0.004 | 0.27 | 0.02 | 0.54 | 0.03 | 0.03 | 0.01 |
| **T10** | 10.4 | 0.29 | 0.87 | 0.005 | 0.38 | 0.07 | 0.93 | 0.07 | <d.l. | 0.01 |
| **T20** | 10.2 | 0.74 | 1.98 | 0.003 | 1.16 | 0.03 | 3.69 | 0.06 | <d.l. | 0.01 |
| **R20** | 10.2 | 0.52 | 1.06 | <d.l. | 2.00 | 0.06 | 2.73 | 0.05 | 0.02 | 0.01 |
| **MA1** | | 2 | 100 | 1.0 | 10 | 50 | 10 | 10 | 10 | 50 |

## 4. Conclusions

(1) The incorporation of MSWI fly ash in clay bricks reduced the compressive strength of the bricks, and increased the soluble salts content, which can cause efflorescence.

(2) Treatment of the MSWI fly ash by washing and EDR reduced the soluble salts content in the fired fly ash-clay bricks containing the treated ash, and reduced by half the Cr leaching compared to that from the bricks with the untreated ash.

(3) Environmental impact of the fly ash-clay bricks was analyzed. Tank leaching test showed that the leaching of heavy metals did not exceed the limiting values from the building materials. Batch leaching test revealed that the fired clay-ash bricks met the limits for waste landfill as mineral waste at the end of service life. On the contrary, the 'demolished' bricks with 5% treated fly ash might be reused again in construction work as the heavy metal leaching was low enough to allow this.

## References


Arabia, S. (1988). Effect of rice husk ash on the properties of bricks made from fired lateritic soil-clay mix, 222–227.

Astrup, T. F. (2008). Management of APC residues from W-t-E Plants - An overview of management options and treatment methods.

BEK nr 1414. Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald (2015). Retrieved from https://www.retsinformation.dk/Forms/R0710.aspx?id=134831

Chen, W., Kirkelund, G. M., Jensen, P. E., & Ottosen, L. M. (2017). Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management. https://doi.org/10.1016/j.wasman.2017.07.011

Chen, W., Ottosen, L. M., Jensen, P. E., Kirkelund, G. M., & Schmidt, J. W. (2014). A comparative study on electrodialytically treated bio-ash and MSWI APC-residue for use in bricks. *Proceedings of the 5th International Conference on Engineering for Waste and Biomass Valorization (wasteeng2014).*

Cornelis, G., Johnson, C. A., Gerven, T. Van, & Vandecasteele, C. (2008). Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Applied Geochemistry*, *23*(5), 955–976. https://doi.org/10.1016/j.apgeochem.2008.02.001

Cultrone, G., Sebastián, E., Elert, K., de la Torre, M. J., Cazalla, O., & Rodriguez-Navarro, C. (2004). Influence of mineralogy and firing temperature on the porosity of bricks. *Journal of the European Ceramic Society*, *24*(3), 547–564. https://doi.org/10.1016/S0955-2219(03)00249-8

Domone, P., & Illston, J. (2010). *Construction materials: their nature and behaviour*. CRC Press.

DS/EN 12457-1. (2002). Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 I/kg for materials with high solid content and with particle size below 4mm (without or with size reduction).
DS/EN 12457-2. (2002). Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 I/kg for materials with particle size below 4mm (without or with size reduction).
DS/EN 771-1:2011+A1:2015. (2015). Specification for masonry units – Part 1: Clay masonry units.
DS/EN 772-5. (2016). Methods of test for masonry units – Part 5: Determination of the active soluble salts content of clay masonry units.
DS/EN ISO 10545-3. Keramiske fliser – Del 3 : Bestemmelse af vandabsorption , åben porøsitet , synlig relativ densitet og volumendensitet (1997).
DS 259. (2003). Vandundersøgelse – Bestemmelse af metaller i vand, jord, slam og sedimenter – Almene principper og retningslinjer for bestemmelse ved atomabsorptionsspektrofotometri i flamme.
Eikelboom, R. T., Ruwiel, E., & Goumans, J. J. J. M. (2000). The building materials decree: an example of a dutch regulation based on the potential impact of materials on the environment. *Waste Management Series*, *1*(C), 963–974. https://doi.org/10.1016/S0713-2743(00)80104-X
Ferreira, C. D., Jensen, P., Ottosen, L., & Ribeiro, A. (2008). Preliminary treatment of MSW fly ash as a way of improving electrodialytic remediation. *Journal of Environmental Science and Health. Part A, Toxic/hazardous Substances & Environmental Engineering*, *43*(8), 837–843. https://doi.org/10.1080/10934520801974319
Ferreira, C., Ribeiro, A., & Ottosen, L. (2003). Possible applications for municipal solid waste fly ash. *Journal of Hazardous Materials*, *96*(2–3), 201–216. https://doi.org/10.1016/S0304-3894(02)00201-7
Ferreira, C., Ribeiro, A., & Ottosen, L. (2005). Effect of Major Constituents of MSW Fly Ash During Electrodialytic Remediation of Heavy Metals. *Separation Science and Technology*, *40*(10), 2007–2019. https://doi.org/10.1081/SS-200068412
Heiri, O., Lotter, A. F., & Lemcke, G. (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, *25*(1), 101–110.
Hu, H. Y., Liu, H., Shen, W. Q., Luo, G. Q., Li, A. J., Lu, Z. L., & Yao, H. (2013). Comparison of CaO's effect on the fate of heavy metals during thermal treatment of two typical types of MSWI fly ashes in China. *Chemosphere*, *93*(4), 590–596. https://doi.org/10.1016/j.chemosphere.2013.05.077
Huang, T. Y., Chiueh, P. T., & Lo, S. L. (2016). Life-cycle environmental and cost impacts of reusing fly ash. *Resources, Conservation and Recycling*. https://doi.org/10.1016/j.resconrec.2016.07.001
Jordán, M. M., Boix, A., Sanfeliu, T., & De La Fuente, C. (1999). Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles. *Applied Clay Science*, *14*(4), 225–234. https://doi.org/10.1016/S0169-1317(98)00052-0
Keppert, M., Siddique, J. A., Pavlik, Z., & Cerny, R. (2015). Wet-Treated MSWI Fly Ash Used as Supplementary Cementitious Material. *Advances in Materials Science and Engineering*. https://doi.org/10.1155/2015/842807
Kirkelund, G. M., Magro, C., Guedes, P., Jensen, P. E., Ribeiro, A. B., & Ottosen, L. M. (2015). Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension - Test of a new two compartment experimental cell. *Electrochimica Acta*, *181*, 73–81. https://doi.org/10.1016/j.electacta.2015.03.192
Lin, K. L. (2006). Feasibility study of using brick made from municipal solid waste incinerator fly ash slag. *Journal of Hazardous Materials*, *137*(3), 1810–1816. https://doi.org/10.1016/j.jhazmat.2006.05.027
Mangialardi, T. (2003). Disposal of MSWI fly ash through a combined washing-immobilisation process. *Journal of Hazardous Materials*, *98*(1–3), 225–240. https://doi.org/10.1016/S0304-3894(02)00359-X

Margallo, M., Taddei, M. B. M., Hernández-Pellón, A., Aldaco, R., & Irabien, Á. (2015). Environmental sustainability assessment of the management of municipal solid waste incineration residues: A review of the current situation. *Clean Technologies and Environmental Policy*, *17*(5), 1333–1353. https://doi.org/10.1007/s10098-015-0961-6

Maybery-Thomas, C., & Charlett, A. J. (2013). *Fundamental Building Technology*. *Fundamental Building Technology*. Taylor and Francis.

Park, Y. J., & Heo, J. (2002). Vitrification of fly ash from municipal solid waste incinerator. *Journal of Hazardous Materials*, *91*(1), 83–93. https://doi.org/10.1016/S0304-3894(01)00362-4

Pedersen, A. J., Ottosen, L. M., & Villumsen, A. (2005). Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent. *Journal of Hazardous Materials*, *122*(1–2), 103–109. https://doi.org/10.1016/j.jhazmat.2005.03.019

Quijorna, N., Coz, A., Andres, A., & Cheeseman, C. (2012). Recycling of Waelz slag and waste foundry sand in red clay bricks. *Resources, Conservation and Recycling*, *65*, 1–10. https://doi.org/10.1016/j.resconrec.2012.05.004

Reijnders, L. (2005). Disposal, uses and treatments of combustion ashes: A review. *Resources, Conservation and Recycling*, *43*(3), 313–336. https://doi.org/10.1016/j.resconrec.2004.06.007

Zhang, H., Zhao, Y., & Qi, J. (2011). Utilization of municipal solid waste incineration (MSWI) fly ash in ceramic brick: Product characterization and environmental toxicity. *Waste Management*, *31*(2), 331–341. https://doi.org/10.1016/j.wasman.2010.10.017

Zhao, Y. C., Song, L. J., & Li, G. J. (2002). Chemical stabilization of MSW incinerator fly ashes. *Journal of Hazardous Materials*, *95*(1–2), 47–63. https://doi.org/10.1016/S0304-3894(02)00002-X

# Chapter 7

## *Electrodialytic extraction of Cr from washed MSWI fly ash by changing pH and redox conditions*

Submitted

# Electrodialytic extraction of Cr from washed MSWI fly ash by changing pH and redox conditions

Wan Chen, Gunvor M. Kirkelund, Pernille E. Jensen, Lisbeth M. Ottosen

*Department of Civil Engineering, Technical University of Denmark, Lyngby, 2800, Denmark*

Key words: Fly ash, Chromium, Electrochemical, Electrokinetic remediation, Waste incineration, Sieving

**Abstract**

Many studies have shown that electrodialytic separation (EDS) of Cr from different ashes is limited unless using assisting agents. This investigation focuses on the possibility for extracting Cr from MSWI fly ash by controlling and changing the pH and redox conditions. The conditions were changed through different designs of EDS setups, which were combined in series. Two different two-compartment and one three-compartment electrodialytic cells were used. The experiments were designed into single, two and three steps. The two and three steps were achieved either by shifting working electrode pairs or by changing electrodialytic cells. Prior to the electrodialytic treatment, the MSWI fly ash was water washed and dry sieved as pre-treatment. The water washed ash was fractionated into two fractions with a 50 µm sieve. The Cr was strongly bound in the ash and the major fraction remained bound after the different treatments. The Cr extraction was less than 28% even after applying two or three steps treatment, however this is an improvement from the single step treatments which extracted maximum 3.1%. The highest extraction was obtained by combined extraction of Cr(III) at low pH/oxidizing conditions, followed by and extraction of Cr(VI) at high pH/reducing conditions. In addition, it was found that the leaching of Cr from the treated ashes with acidic pH was lower than from those with alkaline pH. After the three-step treatment, the leaching

of Cr from the coarse fraction (> 50 μm) was much lower than from the fine fraction (≤ 50 μm) or the un-sieved ash. As for the coarse fraction, two/three step treatment reduced the leaching of Cr compared to the single step treatment in the same pH range (either acidic or alkaline).

## 1. Introduction

### *1.1. Application of electrochemical process in Cr treatment*

Chromium is widely used for industrial purposes, such as for chrome plating, dyes and pigments, leather tanning and wood preserving (Owlad et al., 2009). The resulting chromium-containing products and their producing processes, thus, become a great source for chromium-containing waste (solid and liquid) generation. Hexavalent chromium, amongst the different chromium oxidation states, is highly toxic and carcinogenic. Many research initiatives have accordingly been carried out to find methods to treat Cr(VI) containing waste to prevent spreading the hazard to the environment.

Hawley et al. (2004) reviewed the treatment technologies for hexavalent chromium, and classified them into three groups: (I) reduction of toxicity, (II) destruction and removal, and (III) containment. Owlad et al. (2009) reviewed the removal techniques for hexavalent chromium contaminated water and wastewater. Electrokinetics / electrochemical treatment, as one of the Cr treatment technologies mentioned in both aforementioned reviews, has been investigated for remediation of chromium contaminated soil (Reddy et al., 1999), chromium solution regeneration by oxidizing trivalent chromium to hexavalent chromium (Phillips and Swink, 1989), chrome plating rinse wastewater treatment and recovery (Frenzel, 2005), and solid ash residues such as municipal solid waste incineration (MSWI) fly ash (Kirkelund et al., 2015).

#### *1.1.1. Treatment of aqueous solution*

Membrane electrolysis is one of the electrokinetic techniques for chromic acid treatment and recovery from plating waste solutions generated in chromium plating industry (Frenzel, 2005). As stated by Frenzel (2005), there are two approaches for chromium recovery by membrane electrolysis. One approach is to use a cation exchange membrane to separate the two compartments (anode compartment and cathode compartment) of the electrolysis cell. The waste solution is placed in the anode compartment. Cr(III) is oxidized in the anode compartment to Cr(VI), regenerating chromium plating solution. Cationic impurities migrate to the cathode compartment, increasing the purity of the plating solution. Another approach is to use an anion exchange membrane to separate the two compartments. The chromium acid containing rinse wastewater is placed in the cathode compartment. Anionic Cr(VI) ions migrate to the anode compartment through the anion exchange membrane, and thus concentrate in the anode compartment. Different from membrane electrolysis, electrodialysis uses a three-compartment cell. Both anion and cation exchange membranes are used. The rinse wastewater is placed in the central compartment between the two membranes. The migration of Cr(VI) to the anode compartment and the migration of cations to the cathode compartment take place simultaneously. By doing so, both the rinse water and the chromic acid are regenerated (Frenzel, 2005).

### *1.1.2. Treatment of solid waste – MSWI fly ash*

As an incinerator ash residue, MSWI fly ash is hazardous, and contains carcinogenic heavy metals such as chromium. The circular economy strategy encourages keeping materials at their highest utility and value, and recycling the valuable materials from waste (The Ellen MacArthur Foundation, 2012). Although MSWI fly ash is toxic, recycling and reuse of metals (e.g. full-scale Zn recovery in Switzerland (Purgar et al., 2016)) (Dodson et al., 2012; Funari et al., 2016) and the ash itself (Ferreira et al., 2003; Pan et al., 2008) have caught great attentions by researchers.

Electrodialytic remediation (EDS) has been developed to treat hazardous materials such as MSWI fly ash (Jensen et al., 2015; Kirkelund et al., 2015). In the EDS techniques, electrodialytic cells with two or more compartments are used. The two-compartment EDS cell is in the overall principle similar to the setup used in membrane electrolysis as mentioned in subsection 1.1.1. A two compartment (2C) cell has an anode and a cathode compartment separated by a cation exchange membrane, as illustrated in Fig. 1a. The distilled water-ash suspension to be treated is placed in the anode compartment (as anolyte) (Chen et al., 2015; Kirkelund et al., 2015). Theoretically, like membrane electrolysis, a two compartment cell can also have an anode and a cathode compartment separated by an anion exchange membrane, as depicted in Fig. 1b. However, this kind of setup is not commonly seen in MSWI fly ash treatment, and with good reason: most of heavy metals (such as Cd, Zn) are mobilized to the highest extent at low pH values in mainly cationic form. A three-compartment (3C) cell for MSWI treatment (Fig. 1c) has an anode compartment, a center compartment and a cathode compartment separated by a pair of cation and anion exchange membranes. The anode and cathode compartment contains electrolyte solutions, and the ash suspension to be treated is placed in the center compartment (Chen et al., 2015; Kirkelund et al., 2015).

When electricity is passed through an electrodialytic cell, water is electrolyzed to hydrogen ions and oxygen at the anode and to hydroxyl ions and hydrogen at the cathode. The current is carried by ions, which either are in the suspension originally or which are released as the ash dissolves during the process as a result of the changing equilibrium conditions. The cations are electromigrating towards the cathode end and anions to the anode end. There are different options on where to place the working electrodes in electrokinetic remediation. As stated in Virkutyte et al. (2002), in order to gain the most efficient results some researchers placed the electrode directly into e.g. the wet soil, whereas most researchers place the electrodes in electrolytes. As to MSWI fly ash

treatment, placing the anode in the ash suspension or placing both anode and cathode in electrolyte has been reported (Kirkelund et al., 2015; Pedersen et al., 2005). Both ways intend to extract heavy metals at a condition with decreasing pH.

Electromigration of charged, mobile Cr ions in the ash suspension is the main process of transporting Cr out from the ash suspension during the electrodialytic extraction. Studies (Ferreira et al., 2004; Pedersen, 2002; Pedersen et al., 2005) have demonstrated the possibility of Cr extraction from MSWI fly ash by EDS. In terms of Cr removal, there are several features learned from the previous studies. (1) The type of ash and final pH of the treated ash determines the Cr removal. According to Ferreira et al. (2004), the extraction of Cr is relatively easier from MSWI fly ash than from MSWI air pollution control residue, and the acidification during electrodialytic separation enhances Cr extraction efficiency. (2) Adding assisting agents, such as ammonium citrate, could improve Cr extraction from 5% (only water without assisting agent) to 20% in a 14-day treatment of a MSWI fly ash (Pedersen, 2002). (3) The duration of the electrodialytic treatment influences the Cr extraction according to Pedersen et al. (2005). They found that the Cr extraction efficiency reached around 20% after 14 days of remediation using ammonium citrate solution as assisting agent which was subsequently increased to 44% after 70 days of electrodialytic remediation. (4) Most of the removed Cr was transported to the anode compartment (Kirkelund et al., 2015; Pedersen, 2002), most likely by electromigration of chromate ions and other negatively charged compounds. (5) Previous work has primarily focused on single-step electrodialytic remediation of MSWI fly ash using 2-compartment (Fig. 1a) (Chen et al., 2017; Kirkelund et al., 2015) or 3-compartment EDS cell (Fig. 1c) (Ferreira et al., 2004; Kirkelund et al., 2015; Pedersen et al., 2005). Membrane electrolysis, adopting the same principle as the setup illustrated in Fig. 1b has been applied for chromic acid recovery, but has not commonly seen for MSWI fly ash treatment yet based on literature study. (6) In most cases without using assisting agents the extraction of Cr was

low compared to that of other heavy metals such as Cd, Cu and Zn. The extraction of 1.1-4.5% of Cr as compared to 3.3-15% of Cu, 1.1-61% of Cd, 1.5-53% of Zn removal was obtained in Kirkelund et al. (2015) after the MSWI fly ash was treated both using 2C (with cation exchange membrane) and 3C EDS cells under the conditions: the suspension water-to-ash ratio (L:S) of 3.5; current density of 0.1 and 1 mA/cm$^2$; 14 days treatment. Chen et al. (2017) treated the same MSWI fly ash as used in the present study through single step 2C EDS treatment and two-step 2C+3C EDS treatment. A slight increase in Cr extraction was observed by introducing the second treatment step (effective 3C), but the extraction rate was still less than 1.5% under the conditions: the L:S of 3.5; current density of 1 mA/cm$^2$; 3-12 days treatment.

*1.2. Cr speciation and predominant redox states in MSWI ash residues*

The valence of Cr can vary from -2 to +6. However, trivalent and hexavalent Cr are the two prevalent and stable Cr species in alkaline solid waste such as MSWI residues (Cornelis et al., 2008; Jiao et al., 2016). Cr is mainly in the oxidation state Cr(III), ascribed partially to the resistance of Cr(III) to oxidation and partially to the reduction of Cr(VI) to Cr(III) in the flue gas in the presence of reducing agents such as $SO_2$ (Cornelis et al., 2008). Hu et al. (2013) analyzed total Cr concentration and the Cr(VI) concentration in five MSWI fly ashes collected from five different incinerators in China using $HNO_3$-HF-$HClO_4$ digestion. They found that the concentration of Cr(VI) was low (varying from 0.48 to 17.42 mg/kg) in comparison to that of the total Cr (varying from 127 to 175 mg/kg); and Cr(VI) as a percentage of the total Cr was 0.4 wt.% - 11.5 wt.%. Other fly ashes, coal fly ash and ash from co-firing coal and wood, have similarly been reported to have a Cr(VI) concentration of 7% of the total Cr in average (Stam et al., 2011) or < 5% (Izquierdo and Querol, 2012). However, the Cr(VI) concentration could vary depending on the type of fuel, Cr evaporation, oxidation and interaction with other constituents in the ash (Stam et al., 2011).

As aforementioned, Cr in the MSWI fly ash was believed to be mainly in the oxidation state Cr(III), but Cr(VI) is the major concern in terms of leaching, because of its high solubility at alkaline pH, high toxicity and carcinogenicity. Forms of Cr(VI) identified in MSWI residue are $K_2CrO_4$ (solubility 629 g/l at 20 °C), $CaCrO_4$, $BaCrO_4$ (2.6 mg/l at 20 °C), $PbCrO_4$ ( 0.17 mg/l at 20 °C) and $Ba(S,Cr)O_4$ solid solution (Cornelis et al., 2008). Cr(III) has a low solubility compared to Cr(VI) in alkaline wastes, such as MSWI ash residues, metallurgical residues and fossil fuel combustion fly ash (Cornelis et al., 2008). Cr(III) has soluble forms such as $CrCl_3$ and $Cr_2(SO_4)_3$ as well as insoluble forms such as $Cr_2O_3$ and $FeCr_2O_4$ (Hu et al., 2013; Kirk et al., 2002). Lima et al. (2008) suggested that Cr was mainly present as oxides in the MSWI fly ash and might have low affinity to chloride. Jiao et al. (2016) examined the chemical speciation of Cr by sequential extraction in a MSWI fly ash collected from a MSW incineration plant in Aichi-ken, Japan. About 7% Cr was found in the water soluble fraction (about 2.4%)/exchangeable fraction (<2%)/carbonate fraction, and about 15% in the reducible fraction, less than 5% in the oxidizable fraction and more than 70% in the residual fraction. Chen et al. (2017) found similar chemical speciation patterns of Cr in the MSWI fly ash used in the present study, except in the reducible and oxidizable fraction; about 29% of oxidizable Cr was determined in the fly ash. Knowledge on the complex speciation of Cr(III) and Cr(VI) in MSWI fly ash is crucial in order to understand the mobility and migration of Cr during EDS.

### *1.3. Mobility of Cr*

The pH conditions during EDS play an important role in the mobilization of heavy metals as well as the charge of the mobile ions. Most of the metals form soluble cations at acidic conditions (e.g. $Zn^{2+}$), but amphoteric metals (e.g. Pb and Zn) can also form soluble hydroxides at alkaline conditions (e.g. $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$). However, the presence of soluble species for oxyanion

forming elements such as Cr is pH and redox potential dependent (e.g. Eh-pH diagram) (Cornelis et al., 2008), which indicates Cr can be mobilized and leach out over a large pH range. The leaching behavior of oxyanion forming elements has increasingly caught the attention due to their high solubility and high concentrations in leachates (Cornelis et al., 2008).

Normally, MSWI fly ash is alkaline (Cornelis et al., 2008). During EDS treatment, the alkaline MSWI fly ash suspension will be gradually acidified by using setup-a (Fig. 1a) and setup-c (Fig. 1c). As the pH of the ash suspension changes from alkaline to acidic, the change in Cr speciation is also expected to take place. Likewise, change in Cr mobility and speciation might occur when the ash suspension is alkalized by using setup-b (Fig. 1b). Hence, using different EDS setups might lead to different heavy metals extraction rates based on Cr mobility and speciation at different pH.

### *1.4. Aim and structure of present study*

Washing reduces the current needed to move soluble salts ions such as chloride ions and reduces the negative effect of the soluble salts (Ca, Cl, Na and K) on the leaching and mobility of heavy metals from the ash suspension (Nagib and Inoue, 2000). In addition washing suppress the generation of toxic chlorine gas at the anode during the EDS treatment.

Boom and Degrez (2015) combined sieving with washing for treatment of MSWI ash residues because of the difference in contaminants content (finest > coarsest). They found that after three washing steps the coarse fraction met the leaching limits to landfill for non-hazardous materials, thus achieving the valorization the coarse fractions from MSWI fly ash. Therefore, how the coarse and fine fractions behaved during EDS treatment was also investigated.

The aim of the present study was to investigate the possibility for chromium extraction from MSWI fly ash under different pH and redox potential conditions without using any assisting agents. Different pH and redox conditions were generated using different combinations of the 2C and 3C

electrodialytic cell setups. For instance, an oxidizing environment was generated when the fly ash suspension was placed in the anode compartment (Fig. 1a). While, the setup illustrated in Fig. 1b was used to investigate the feasibility to extract Cr at high alkaline and reducing conditions due to water electrolysis at the cathode in the ash suspension. The Cr extraction was compared between different EDS combinations: one step treatment with either acidification or alkalization in ash suspension; two-step treatment combining both acidification and alkalization in the ash suspension; three-step treatment involving all the three electrodialytic cells shown in Fig. 1.

## 2. Material and methods

### *2.1. MSWI fly ash and pretreatment*

The MSWI fly ash studied was sampled from the Vestforbrænding MSW incineration plant located in Glostrup, Denmark. The fly ash sample was collected after the electrostatic precipitator before the neutralization of the acidic components by the wet scrubber process. The MSWI fly ash sample was sieved in the laboratory to remove the few particles exceeding 1 mm.

The ash was washed in distilled water at L:S 5 for 5 minutes. The suspension was filtered (12-15 µm filter) and the ash on the filter paper was dried at 105 °C for 24 h. A part of the washed ash was used in the EDS experiments and another part fractionated by dry sieving using a 50 µm sieve.

### *2.2. EDS treatment*

Three different electrodialytic cells (Fig. 1), were used in the present lab-scale study. The colored compartment (Fig. 1 a/b: compartment I; c: compartment II) marks where the ash suspension was placed during the treatment. The overall experimental design is outlined in Table 1. Each experiment was named based on the ash sample treated (i.e. C - coarse fraction; or F - fine fraction; or W - the whole washed ash) together with the setup(s) arranged in the order of use (e.g. b

– single step treatment using the cell 1b; a-b/b-a – treatment involving two kinds of setups in the order of a and b or in reverse order; and so forth). The experiments were made in three phases:

*Phase I* (C-a, C-b and F-a): Single step treatments comparing cell a and b, as well as treatment of coarse and fine fraction in setup-a.

*Phase II* (C-a-b and C-b-a): The two setups used in Phase I were combined in two-step processes. The two-step process was achieved by shifting electrodes in a three compartment cell (Fig. 1c). There were four electrodes in the three compartment cell, two in the ash suspension and one in each of the electrolytes as illustrated in Fig. 2. Connecting the electrode in the cathode compartment (separated from the suspension by a cation exchange membrane) and the electrode in the opposite side of the ash suspension with power supply, a two compartment cell as in Fig. 1a was formed. Connecting the other two electrodes resulted in a cell as Fig. 1b.

*Phase III* (C-a-c-b, F-a-c-b and W-a-c-b): Extension of the two-step treatment to three-steps by including treatment in a three-compartment cell (Fig. 1c). The same order was used in all three experiments in this phase, but the ash treated varied. A new cell was used for each step in the experiments F-a-c-b and W-a-c-b meaning that the suspension was transferred from one cell to the other. The treatment was pH controlled at the first two steps (e.g. 2C+3C: C-a-c). The first step was terminated at ash suspension pH of about 4. The second step was stopped at pH ~2.

In each experiment, 50.0 g ash was suspended in 350 ml distilled water. Platinum coated titanium bar electrodes with a diameter of ~2 mm were used. The electrolyte solutions in the electrode compartments were 0.01 M $NaNO_3$. Electrolyte solution (500 ml per electrolyte compartment per step) was kept circulating in the electrolyte compartment(s) during treatment. The experiments were conducted at a constant current at 50 mA for setup-a and 25 mA for setups-b and -c. The pH and electric conductivity of the ash suspension was measured at least once a day. The pH of the electrolytes was adjusted to between 1 and 2 for setups-a and -c and to between 10 and 11

for the steps involving setup-b by 1:1 $HNO_3$ or 6 M NaOH, respectively. The electrolytes were renewed between each shift in cell.

*2.3. Ash characterization*

The concentration of Cr in the ash was determined according to Danish Standard DS 259 by $HNO_3$ digestion. One gram of dry ash and 20 ml of 1:1 $HNO_3$ was autoclaved at 200 kPa at 120 °C for 30 min. After digestion, the samples were vacuum filtered through a 0.45 µm filter. The Cr concentration was measured in the filtrate by ICP-OES (Varian 720-ES, Software version: 1.1.0). Series of three replicates were made. All concentrations are expressed on a dry mass basis.

The pH of the ash was measured with a Radiometer Analytical pH electrode in 1 M KCl solution at L:S of 2.5 after 1 hour.

The buffer capacity of the two ash fractions was analyzed in accordance to Reddy et al. (1999) by adding concentrated HCl into the ash-distilled water suspension (20 g and 300 ml distilled water) every 30 minutes after agitation. The pH of the suspension was measured between each acid addition, until the pH was between 1 and 2.

Leaching (triplicate for C-a-b and C-b-a; duplicate for C-a, F-a, C-b and W-a-c-b; one sample for C-a-c-b and F-a-c-b) of the treated ash samples was measured at L:S 2 (20 ml deionized water / 10 g ash) according to DS/EN 12457-1(DS/EN 12457-1, 2002). The ash and distilled water mixture was agitated for 24 h and vacuum filtered through a 0.45 µm filter. The pH was measured with a Radiometer Analytical pH electrode and the oxidation-reduction potential (ORP) was measured with MC3051Pt-9 combined redox electrode in the leachate. The ORP was expressed as Eh (ORP+210 mV, where 210 mV is the reference potential of an Ag/AgCl reference electrode with 3M electrolyte solution at 20-30 °C). The concentration of Cr in the leachate was analyzed by ICP-OES.

**3. Results**

*3.1. Characterization of ash*

The total Cr concentration by $HNO_3$ digestion in the ash as received was 113±6 mg/kg (as shown in Table 2) and, after washing in water, the concentration decreased to 112±3 mg/kg.

The mass distribution in the washed ash was 42% fine (≤ 50 µm) and 58% coarse fraction. The fly ash as-received had a pH of 12.2. After washing, the pH of ash decreased to 10.2 (coarse fraction: 10.5; fine fraction: 10.3). Fig. 3 shows the buffer capacity of the two fractions. The fine fraction had a higher buffering capacity than the coarse fraction. Also the Cr concentration after washing was different in the coarse and the fine fraction. Table 2 shows the Cr concentration in the ash sample used for each of the experiments, and the concentration in the coarse fraction ranged from 114-120 mg/kg and the fine fraction from 155-158 mg/kg.

The leaching of Cr from the untreated ash was 0.47 mg/kg (equals to 0.24 mg/l in the leachate), but the leaching increased after washing (Table 2). Cr is an oxy-anion forming element. Its leachability depends on the chemical (such as mineralogy, pH and redox potential) and physical (such as particle size, porosity and hydraulic conductivity) interactions between the sample and the leaching medium (Sabbas et al., 2003). Changes in pH and Eh of the leachates, for instance, affected Cr leaching. As shown in Table 2, the ash as received ash water leaching system had negative ORP (-24 mV, equivalent to Eh 186 mV), indicating a reducing environment. Whereas, washing increased the ORP to an oxidizing environment. The Cr leaching from the untreated ash was lower than the limiting values e.g. 0.5 mg/l for waste to be used in geotechnical construction work (Category 3) (BEK nr 1414, 2015).

*3.2. Changes in pH and conductivity in ash suspension during EDS*

Fig. 4a shows the pH changes during the treatments. The setup-a (Fig. 1a) led to the fastest pH decrease. The setup-c was used only in the three-step treatment after setup-a. Compared to setup-a, setup-c caused a relatively slow acidification.

When controlling pH of the ash suspension during the treatment, the time taken to reach the set pH value was not only affected by the electrodialytic cell setup used, but also by the buffering capacity of the ash treated (Fig 3). For example, to reach pH 2 in the coarse washed fraction was faster (21.5 days) compared to the ash as received and the fine washed fraction (both 23 days). Contrarily, using setup-b, a strong pH increase was seen in the ash suspension due to the production of $OH^-$ from electrolysis at the cathode in the suspension here.

The electric conductivity of the ash suspension during EDS is shown in Fig. 4b. When the ash suspension was treated in setup-a, the electric conductivity decreased about the first day, followed by a strong increase. This kind of pattern for conductivity change using setup-a was seen when the setup was used individually (e.g. C-a and F-a), or in the first/second steps of the combined EDS treatment (e.g. W-a-c-b and C-b-a). When the ash suspension treated using setup-a was subsequently placed in a desalination compartment of setup-c, the conductivity decreased first (probably due to the migration of $H^+$) and increased afterwards related to ash dissolution at acidic pH. When the ash suspension was first treated using setup-b (C-b and C-b-a), the conductivity also increased, and here it is a result of the strong alkalinity of the suspension. However, if setup-b was used as post-treatment after setup-a and setup-c, the conductivity of the ash suspension decreased. This was because the suspension prior to setup-b was acidic, and when placing the cathode in the suspension, the acid was neutralized and the conductivity subsequently decreased. Also precipitation of ions may occur, when pH increased. The conductivity seemingly stabilized or even increased when the pH of the ash suspension was higher than 10.5, as observed in e.g. experiment C-a-b.

*3.3. Cr extraction*

Table 2 summarizes the mass balance (%), mass loss of the ashes during the treatment, Cr extraction efficiency, Cr leaching from the ash after treatment, and Cr concentrations in the ashes

before and after treatment. The Cr mass balance describes the difference between Cr mass in the whole EDS system at the end of treatment in comparison with the Cr input from the ash initially. The mass balances were between 90% and 109%, which is acceptable, taking into account the heterogeneous nature of MSWI fly ash.

The total Cr extraction varied from 0.4% to 27.5%. Only the Cr found in the separate electrode compartments (in electrolytes (anolyte/catholyte), on anode/cathode and in the anion/cation exchange membranes) was considered as extracted. The Cr in the liquid phase of the suspension is thus not regarded as extracted in this work. The order of extraction percentage was: W-a-c-b > C-a-b > C-a-c-b > F-a-c-b > C-b-a > C-a > C-b > F-a.

This order reveals that:

(1) Combining the setups (Phase II and III) gave higher extractions than a single cell treatment (Phase I).

(2) The extraction of Cr from the coarse fraction was relatively easier than from the fine fraction, seen from the two experiments which were directly comparable (C-a-c-b > F-a-c-b and C-a > F-a).

(3) Combining setup-a and setup-b resulted in a significantly higher extraction when using setup-a first (C-a-b >> C-b-a).

(4) Setup-c did not enhance the Cr extraction when used as a third step between setup-a and -b as C-a-b > C-a-c-b. Still the combination setup a-c-b gave the highest extraction of all, and this was obtained when treating the ash as received (W-a-c-b).

Even though Cr was extracted during the experiments, the Cr concentration in the ashes generally increased during treatment (Table 2), except in experiment C-b and C-a-c-b. The increase was because the Cr containing particles were dissolved to a lower extent than the ash in total. The ash mass loss calculated as $\left(\left(1 - \frac{mass\ of\ the\ dry\ ash\ after\ EDR}{mass\ of\ the\ day\ ash\ before\ EDR}\right) \times 100\%\right)$ is shown in Table 2. The mass loss was between 3 and 53%, where the highest mass losses were obtained in the experiments

of Phase III, and the far lowest (3%) was obtained in experiment C-b, where the ash was alkaline all through the treatment, and also the lowest extraction was obtained. There is a tendency for higher mass loss in the experiments with fine fraction compared to the corresponding experiments with the coarse fraction: F-a > C-a and F-a-c-b > C-a-c-b.

*3.4. Cr leaching after treatment*

The leaching of Cr from the ash after the EDS experiments, as well as pH and Eh in the leachates are seen in Table 2. The two experiments in Phase II showed that the leaching from C-a-b > C-b-a, which is most likely related to the final pH of the leachate (9.9 and 5.3, respectively). Chen et al. (2017) reported pH dependent desorption for Cr from an ash from the same plant as the present, and showed, that the desorption was almost non-measurable around pH 5.3 but about 3% at pH around 10.4. The leaching from the two experiments in Phase I, C-a and F-a, further confirmed a lower Cr leaching at acidic pH around 5.2/5.8. For the three step treatments in Phase III, the order of leaching was F-a-c-b > W-a-c-b (average) > C-a-c-b and the pH of the leachates were 7.5, 9.1, and 8.7, respectively. In the pH range from 7.5 to 9.1 a slight increase in Cr desorption with increasing pH was previously observed (Chen et al., 2017), and thus the leaching order was not likely to be determined by pH in this range but rather by the fact the leaching was lowest from the coarse fraction in general. Overall, the Cr leaching was in the order of F-a-c-b > W-a-c-b > C-b > C-a-b > untreated > C-a-c-b > F-a > C-a > C-b-a. The redox potential (Eh) of the leachates from the experiments using setup-b as the last step (i.e. F-a-c-b, W-a-c-b, C-b, C-a-b and C-a-c-b) ranged from 400 mV to 450 mV. According to the Eh-pH diagram for Cr (Cornelis et al., 2008), the dominating soluble Cr species at 25 °C in water at Eh 400-450 mV in the pH range of 7.5-10.7 is Cr(VI) in the form of $CrO_4^{2-}$. Whereas, the dominating soluble Cr species is Cr(III) in the form of $CrOH^{2+}$ at Eh 520-680 mV in the pH range of 5.2-5.8 for the experiments using setup-a as the last step.

## 4. Discussion

### *4.1. Effect of electrodialytic setups on extraction of chromium*

Fig. 5a shows the distribution of Cr in the EDS system at the end of treatment. In comparison to the Cr remaining in the ash, the proportion removed was low (the highest total extraction was 27.5%, Table 2). Fig. 5b gives the amount of Cr removed at each treatment step in the three-step EDS experiments in Phase III. C-a-c-b is not included in Fig. 5b, because the removal in the three steps could not be separated as the shift in treatment step was achieved by shifting working electrodes in the same cell. Cr extraction largely took place at the second and the third step, and between these two steps, the third step had the highest extraction.

The pH and redox conditions in the steps of the experiments in Phase III are shown in Table 3. The most likely ionic species of Cr in the ash suspension are also shown in Table 3. These are found by combining the geochemistry of Cr in terms of Eh-pH (redox potential – pH) diagram for the Cr-O-H system and for the Cr-$O_2$-water system (Jacobs and Testa, 2005) with the conditions of each treatment step. Below each treatment step is discussed separately:

*Two compartment cell, setup-a*

Setup-a is designed for the extraction of cations. According to Table 3, Cr(III) is the main source for cationic Cr species. The mobility and leachability of Cr from MSWI fly ash is solubility-controlled (Li et al., 2016). However, the solubility of Cr(III) is less than Cr(VI) (Cornelis et al., 2008). The low release of Cr in is probably linked to a general low solubility at pH above 4 (Chen et al., 2017). The redox potential in the ash suspension is increasing (Chen et al., 2017) and Cr dissolved in the suspension at pH between 4 and 10.7 could be anionic Cr(VI) (e.g. $CrO_4^{2-}$ and $HCrO_4^-$), anionic Cr(III) in form of $Cr(OH)_4^-$ and cationic chromium hydroxide ($Cr(OH)_2^+$ and $CrOH^{2+}$). The Cr which electromigrated to the cathode compartment, must have been Cr(III) as

Cr(VI) does not form cationic species. During the treatment in setup-a, Cr(VI) could dissolve in the ash suspension, but due to the lack of anion separation, it remained in the ash suspension (Chen et al., 2017; Kirkelund et al., 2015).

Cr was detected on the anode, which had been placed in the ash suspension. The amount of Cr detected on the anode in ash suspension corresponded to 2% - 86% of the total amount of Cr dissolved in the liquid phase of suspension. Especially for experiment F-a, the Cr precipitated on the anode was higher than the total Cr removed to the electrolyte. Electrode deposition on application of a DC electric field can be due to electrophoretic deposition (moving species: solid particles) and electrolytic deposition (moving species: ions) (Besra & Liu, 2007). Cr might be adsorbed onto the anode and/or co-precipitated with e.g. Pb and Fe, which were also found on the anode in the present work.

As far as oxidation of Cr(III) is concerned, electrolytic techniques have been reported to regenerate hexavalent chromium in a solution. By placing the spent chromium solution to be regenerated in an anode compartment, the oxidation of Cr(III) to Cr(VI) occurred (Phillips and Swink, 1989). Sabbas et al. (2003) indicated that in an alkaline environment Cr(III) may be rapidly oxidized by atmospheric oxygen to Cr(VI); however, high values of the redox potential are required. Frenzel (2005) addressed that the anodic oxidation of Cr(III) is also dependent on the electrode material. To have high electrode potentials, the anode material must have a high over potential for the oxygen evolution reaction (Simonsson, 1997). Lead dioxide anodes have been extensively used in oxidation at high potential such as in Soboroff et al. (1982). The efficiency of anodic oxidation of Cr(III) to Cr(VI) though seems unstable (Soboroff et al., 1982). The acceptance of two-compartment membrane electrolysis in plating businesses has been hindered, probably because of a lack of operational stability and efficiency (Frenzel, 2005). Even though Soboroff et al. (1982) found that the anodic oxidation was relatively independent of membrane type and current density,

the current density 0.1 A/dm$^2$ used in the present study was significantly lower than in Soboroff et al. (1982), who used 2.15 A/dm$^2$. The possibility and extend of oxidation of Cr(III) to Cr(VI) also depend on the reactive mineralogy of the material, the pH and the form and solubility of Cr(III) related to oxidation, according to James et al. (1997). In summary, it must be said, that oxidation of Cr(III) to Cr(VI) in the MSWI suspension is possible, but to which extent it happens, is difficult to foresee on basis on current knowledge.

*Three compartment cell, setup-c*

The three-compartment cell (setup-c) allows extraction of both anions and cations. During the use of this setup, pH decreased from 4 to 2. At pH below 4, $Cr^{3+}$ was believed to be the dominating soluble Cr species in water system according to the Eh-pH diagram (Cornelis et al., 2008), which is thus considered the major cation migrating to the catholyte compartment in the present work. Fig. 5b shows that at this treatment step most of the Cr was extracted to the catholyte compartment, which indicated that the dissolution of Cr(III) dominated the Cr dissolution from the ash.

Cr(VI) is expected to have low mobility under acidic conditions, which is reflected in the limited transport to the anode compartment (Fig. 5b). The ratio of $HCrO_4^-$ to $CrO_4^{2-}$ is a function of pH (Hawley et al., 2004), and at pH between 2 and 4, Cr(VI) was believed to be prevailingly in the form of $HCrO_4^-$.

Kirkelund et al. (2010) conducted electrodialytic remediation experiments on raw and carbonated MSWI -APC residue using an electrodialysis (ED) stack (no electrodes in ash suspension) for 4-21.15 hours. They suggested that the shift from Cr(III) to Cr(VI) during ED treatment might account for the slight increase in Cr leaching from the treated residues (Kirkelund et al., 2014). Jensen et al. (2012) pointed out that the oxidation of Cr(III) using a three-compartment cell to treat suspended sludge after soil washing could be hard, due to the high kinetic stability of Cr(III). The oxidation of Cr(III) to easily soluble Cr(VI) does increase Cr leaching, but the overall

chemical speciation of Cr should be considered as well. Another explanation could be that the slow extraction rate of Cr during EDS (Pedersen et al., 2005) led to incomplete extraction of soluble Cr(VI) over the treatment period, and then the Cr(VI) remaining in the ash leached out again at the alkaline conditions that favor Cr(VI) desorption. In Kirkelund et al. (2010) the finial pH of the APC residue suspension after the experiment was between 9.9 and 12.4, which could support the release of Cr(VI) due to desorption.

*Two compartment cell, setup-b*

In setup-b the cathode was placed directly in the ash suspension, and this setup was designed for extraction of anions. When using setup-b directly for treatment of the MSWI fly ash, pH remains high as expected. The extraction of Cr was very low when setup-b was used as first step of the treatment (C-b and C-b-a). However, it was seen that the combination with setup-a followed by setup-b (in experiment C-a-b) resulted in a more efficient chromium extraction. This resulted from the ash dissolution at low pH values, which exposed more Cr to the liquid phase or to the surface of the particles. As the pH of the ash suspension increased fast in setup-b, the adsorbed Cr(VI) would be able to desorb and electromigrate to the anolyte. The cathode reaction generated $OH^-$ in the ash suspension, and the precipitation Cr(III) as $Cr(OH)_3$ could occur.

A similar setup as setup-b has been used for chromic acid recovery using an anion exchange membrane (Frenzel, 2005). In this chromic acid recovery process, the waste solution containing chromic acid generated from chromium plating industry was placed in the cathode compartment. Chromate anions electromigrate from the waste water towards the anode through the anion exchange membrane. In the anode compartment chromic acid is formed by protons generated at the anode. The difference from this acid recovery process and the present experiment, was that the anolyte was controlled at pH around 10 in the present study, avoiding a great pH difference between the anolyte and the ash suspension.

In experiment C-a-b, Cr primarily electromigrated to the anode compartment, whereas to the cathode compartment in C-a-c-b. This shows that including setup-c in the treatment made a difference in Cr extraction. The majority of Cr found in the anolyte in experiment C-a-b might be related to the lower desorption of Cr(III) and longer treatment in the pH increasing period using setup-b. Experiment C-a-c-b had a long duration for reducing the pH of the ash suspension from 4 to 2, during which more Cr(III) in form of $Cr^{3+}$ could be dissolved in the suspension. If oxidation happened at the first step of experiment C-a-c-b, the oxidized Cr(VI) might be reduced back to Cr(III) at the second step, therefore contributing to the electromigration to the catholyte. Castillo et al. (2008) treated a Cr(VI) contaminated soil (not suspension but static state) using a three-compartment electrodialytic cell under constant-voltage conditions for 7-14 days, and the results showed that over 90% of the Cr removed was found in the anolyte and less than 10% in the catholyte. The migration of Cr towards the catholyte was suggested to be associated with the reduction of Cr(VI) in the soil by reducing agents (e.g. clay minerals and iron oxides) at low pH. Accordingly, the Cr(VI) in the ash suspension might be reduced to Cr(III) by reducing agents in the MSWI fly ash such as organic matter, $Fe^0$/Fe(II) and $Al^0$ at pH 2-4. Short duration at step 3 possibly resulted in less Cr(VI) desorption and extraction.

The presence of the cathode reaction in the ash suspension is believed to create a reducing environment, which might reduce Cr(VI) to Cr(III). However, this reduction reaction was not mentioned for example in the case of chromic acid recovery in Frenzel (2005). Chromate ions can be reduced in acidic solutions, having a pH of above three, having excess acid to complete the reaction with reducing agents such as sulfur dioxide, sodium disulfide and ferrous sulfate (Vaughan, 1994). The conditions formed by setup-b did not seemingly favor Cr(VI) reduction, such as the alkaline pH. The presence of reducing agents depended on the composition in the ash. Treating a MSWI fly ash is believed to be more complicated than treating an aqueous waste solution, due to

the complicated element matrix in ash. It is known that Cr(VI) reduction commonly needs $H^+$, and if it occurred, it could be only at the anion exchange membrane or membrane-ash interface where $H^+$ can be generated by water splitting at the anion exchange membrane (Simons, 1985). The Cr(VI) reduction rate and its electromigration rate can also affect the reduction efficiency of Cr(VI) in the ash suspension.

Larger deposits on the cathode in the ash suspension than on the anode when it was placed in the ash suspension was seen. Electrophoretic deposition (EPD) or reduction of metal ions were probably responsible for the cathodic deposition. EPD was likely, as the cathode was wrapped by particles, which could partially dissolve in strong nitric acid. The particles, which did not dissolve had a “jelly like” consistency and this consistency of the particles remained after acid digestion left in the 1:1 nitric acid solution. According to Besra and Liu (2007), the principal driving force for electrophoretic deposition is the charge on the particle and the electrophoretic mobility of the particles in the solvent in electric field. Convection caused by stirring might also contribute to the electrophoresis of colloidal particles. Electrolysis deposition accounted for the disposition of ionic species on the cathode. The Cr found on the cathode corresponded to 11%-77% of the total amount of Cr dissolved in the liquid phase of suspension in the experiments. Experiment C-b exhibited a higher amount of Cr deposited on the cathode than the total Cr removed to the anolyte.

*4.2. Overall assessment*

Pretreatment of the ash by water washing removed the soluble salts from the ash, as well as the easily soluble Cr. The desorption of Cr(III) from the washed ash was enhanced as pH decreased from alkaline to acidic. The desorbed Cr(III) electromigrated to the catholyte end. Due to the low solubility of Cr(III), the Cr extraction rate was low. When the treatment was stopped at pH 4 using a 2C electrodialytic cell with the anode placed in the ash suspension and then shifted

to a three-compartment cell, the Cr(III) dissolution increased, resulting in more Cr migration to the catholyte than to the anolyte end. The Cr(VI) would be desorbed with increasing pH and extracted to the anolyte end using a two-compartment cell with the cathode in the ash suspension.

Besides electromigration, other processes such as electrolysis, diffusion (e.g. in C-a-b, C-b-a and C-a-c-b), convection, adsorption/desorption and precipitation/dissolution were involved in the treatment. The EDS treatment not only changed the pH of the ash but also the redox potential. The oxidation-reduction reactions between Cr(III) and Cr(VI) are complicated, and may occur during the treatment, but the kinetics in general is believed to be slow (Hawley et al., 2004).

Even though the amount of Cr extracted was improved, the extraction rate was not higher than 27.5%. Chromium leaching from the three-step treated washed ash was not reduced to a low level. Only the treated coarse fraction had a leaching of Cr within the limiting value for mineral waste landfill. The change in pH and redox potential caused by EDS significantly changed the properties of the ash. A huge difference has been seen in the Eh and pH of the leachate from as-received ash and the ash (containing the fine fraction) treated by the three-step EDS. The redox potential of the leachate changing from negative to positive was believed to influence the ash leaching property. Solubility of Cr in the MSWI fly ash in solution relies on the presence of Ca, Ba and Pb metalates, surface adsorption (e.g. to Fe and Al oxides), and formation of solid solution with e.g. ettrigite (Cornelis et al., 2008). Fruchter et al. (1990) analyzed pore fluids and leachates from a large coal fly ash field lysimeter. They indicated that solid solution appeared to play an important role in controlling the concentration of Cr in the pore fluids and leachates. Accordingly, the Cr-containing metalate precipitation and Cr solid solution might also change due to the EDS treatment. In summary, EDS treatment can be used to control the ash properties under different pH and redox conditions.

Treated ash W and F (in particular with alkaline pH) met the Cr leaching limit for landfill as hazardous material, whereas the coarse fraction met the limit for mineral waste landfill in accordance with Danish regulation BEK nr 252 (BEK nr 252, 2009). Fractionation might be a way to reduce the quantity of the MSWI fly ash that needs to be landfilled.

## 5. Conclusion

Three electrodialytic cells were investigated, being used individually and/or in series, in order to increase the knowledge on Cr speciation under different conditions and the feasibility for Cr extraction from MSWI fly ash. Each kind of cell and each combination of the cells created different pH and redox conditions. The Cr extraction rate was improved by combining the electrodialytic cells to achieve first acidification (especially to pH below 4) and then alkalinity generation. This improvement in Cr extraction is related to the different properties of the oxidation states of Cr, trivalent and hexavalent. Acidification enhanced the desorption of Cr(III) especially with pH below 4 and led to primary electromigration of Cr(III) to the catholyte end. A fast re-alkalization of the acidified ash increased the desorption of chromium, and thus increased the extraction. Direct alkalization of the ash did not result in a better extraction than when the ash was first acidified and then alkalized; and this might indicate that besides pH, the co-existence of chromium with the other ions or particles affected the extraction. As the leaching from the coarse and fine fraction of the washed fly ash differed, with the lowest leaching from the coarsest fraction, size separation might ease handling of this fraction of the ash. In conclusion it must be stated, that Cr is strongly bound in the MSWI fly ash, and the major fraction is not influenced by the prevailing pH and redox conditions in the suspension (in the time span of few days).

## Acknowledgments

This work was financially supported by the Department of Civil Engineering at the Technical University of Denmark.

BEK nr 1414. Bekendtgørelse om anvendelse af restprodukter og jord til bygge- og anlægsarbejder og om anvendelse af sorteret, uforurenet bygge- og anlægsaffald (2015). Retrieved from https://www.retsinformation.dk/Forms/R0710.aspx?id=134831

BEK nr 252. Bekendtgørelse om deponeringsanlæg (2009).

Besra, L., & Liu, M. (2007). A review on fundamentals and applications of electrophoretic deposition (EPD). *Progress in Materials Science*, *52*(1), 1–61. https://doi.org/10.1016/j.pmatsci.2006.07.001

Chen, W., Jensen, P. E., Ottosen, L. M., & Kirkelund, G. M. (2015). Electrodialytic remediation of fly ash from co-combustion of wood and straw. *Electrochimica Acta*, *181*, 208–216. https://doi.org/10.1016/j.electacta.2015.04.083

Chen, W., Kirkelund, G. M., Jensen, P. E., & Ottosen, L. M. (2017). Comparison of different MSWI fly ash treatment processes on the thermal behavior of As, Cr, Pb and Zn in the ash. Waste Management. https://doi.org/10.1016/j.wasman.2017.07.011

Cornelis, G., Johnson, C. A., Gerven, T. Van, & Vandecasteele, C. (2008). Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Applied Geochemistry*, *23*(5), 955–976. https://doi.org/10.1016/j.apgeochem.2008.02.001

De Boom, A., & Degrez, M. (2015). Combining sieving and washing, a way to treat MSWI boiler fly ash. *Waste Management*, *39*, 179–188. https://doi.org/10.1016/j.wasman.2015.01.040

Dodson, J. R., Hunt, A. J., Parker, H. L., Yang, Y., & Clark, J. H. (2012). Chemical Engineering and Processing : Process Intensification Elemental sustainability : Towards the total recovery of scarce metals. *Chemical Engineering & Processing: Process Intensification*, *51*, 69–78. https://doi.org/10.1016/j.cep.2011.09.008

DS/EN 12457-1. (2002). Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 L/kg for materials with high solid content and with particle size below 4mm (without or with size reduction).

Ferreira, C., Ribeiro, A. B., & Ottosen, L. M. (2004). Treatment of MSW fly ashes using the electrodialytic remediation technique. *Waste Management and the Environment II*.

Ferreira, C., Ribeiro, A., & Ottosen, L. (2003). Possible applications for municipal solid waste fly ash. *Journal of Hazardous Materials*, *96*(2–3), 201–216. https://doi.org/10.1016/S0304-3894(02)00201-7

Frenzel, I. (2005). *Waste minimization in chromium plating industry*.

Fruchter, J. S., Rai, D., & Zachara, J. M. (1990). Identification of solubility-controlling solid phases in a large fly ash field lysimeter. *Environmental Science and Technology*, *24*(8), 1173–1179. https://doi.org/10.1021/es00078a004

Funari, V., Nadeem, S., Bokhari, H., Vigliotti, L., Meisel, T., & Braga, R. (2016). The rare earth elements in municipal solid waste incinerators ash and promising tools for their prospecting Cooling tank Convey or. *Journal of Hazardous Materials*, *301*, 471–479. https://doi.org/10.1016/j.jhazmat.2015.09.015

Hawley, E. L., Deeb, R. A., Kavanaugh, M. C., & G, J. J. R. (2004). *Treatment Technologies for Chromium(VI). Chromium (VI) Handbook*. https://doi.org/10.1002/chin.200614270

Hu, H., Luo, G., Liu, H., Qiao, Y., Xu, M., & Yao, H. (2013). Fate of chromium during thermal treatment of municipal solid waste incineration (MSWI) fly ash. *Proceedings of the Combustion Institute*, *34*(2), 2795–2801. https://doi.org/10.1016/j.proci.2012.06.181

Izquierdo, M., & Querol, X. (2012). Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology*, *94*, 54–66. https://doi.org/10.1016/j.coal.2011.10.006

Jacobs, J., & Testa, S. (2005). Overview of chromium (VI) in the environment: background and history. *Chromium (VI) Handbook*, (Vi), 1–22. https://doi.org/doi:10.1201/9780203487969.ch1

James, B. R., Petura, J. C., Vitale, R. J., Mussoline, G. R. (1997). Oxidation - reduction chemistry of chromium : Relevance to the regulation and remediation of chromate - contaminated soils.

Jensen, P. E., Kirkelund, G. M., Pedersen, K. B., Dias-Ferreira, C., & Ottosen, L. M. (2015). Electrodialytic upgrading of three different municipal solid waste incineration residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and SO4. *Electrochimica Acta*, *181*, 167–178. https://doi.org/10.1016/j.electacta.2015.06.012

Jensen, P. E., Ottosen, L. M., & Allard, B. (2012). Electrodialytic versus acid extraction of heavy metals from soil washing residue. *Electrochimica Acta*, *86*, 115–123. https://doi.org/10.1016/j.electacta.2012.07.002

Jiao, F., Zhang, L., Dong, Z., Namioka, T., Yamada, N., & Ninomiya, Y. (2016). Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior. *Fuel Processing Technology*, *152*, 108–115. https://doi.org/10.1016/j.fuproc.2016.06.013

Kirk, D. W., Chan, C. C. Y., & Marsh, H. (2002). Chromium behavior during thermal treatment of MSW fly ash. *Journal of Hazardous Materials*, *90*(1), 39–49. https://doi.org/10.1016/S0304-3894(01)00328-4

Kirkelund, G. M., Geiker, M. R., & Jensen, P. E. (2014). Electrodialytically treated MSWI APC residue as substitute for cement in mortar. *Nordic Concrete Research*, (49), 1–16.

Kirkelund, G. M., Jensen, P. E., Villumsen, A., & Ottosen, L. M. (2010). Test of electrodialytic upgrading of MSWI APC residue in pilot scale: Focus on reduced metal and salt leaching. *Journal of Applied Electrochemistry*, *40*(6), 1049–1060. https://doi.org/10.1007/s10800-009-0059-0

Kirkelund, G. M., Magro, C., Guedes, P., Jensen, P. E., Ribeiro, A. B., & Ottosen, L. M. (2015). Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension - Test of a new two compartment experimental cell. *Electrochimica Acta*, *181*, 73–81. https://doi.org/10.1016/j.electacta.2015.03.192

Li, J. shan, Xue, Q., Wang, P., Wang, H. qing, & Zhang, T. ting. (2016). Evaluation of leaching characteristics of heavy metals from municipal solid waste incineration fly ash by up-flow percolation column tests. *Environmental Earth Sciences*, *75*, 714. https://doi.org/10.1007/s12665-015-4772-1

Lima, A. T., Ottosen, L. M., Pedersen, A. J., & Ribeiro, A. B. (2008). Characterization of fly ash from bio and municipal waste. *Biomass and Bioenergy*, *32*(3), 277–282. https://doi.org/10.1016/j.biombioe.2007.09.005

Nagib, S., & Inoue, K. (2000). Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. *Hydrometallurgy*, *56*(3), 269–292. https://doi.org/10.1016/S0304-386X(00)00073-6

Nieto Castillo, A. M., Soriano, J. J., & García-Delgado, R. A. (2008). Changes in chromium distribution during the electrodialytic remediation of a Cr (VI)-contaminated soil. *Environmental Geochemistry and Health*, *30*(2), 153–157. https://doi.org/10.1007/s10653-008-9137-1

Owlad, M., Aroua, M. K., Daud, W. A. W., & Baroutian, S. (2009). Removal of hexavalent chromium-contaminated water and wastewater: A review. *Water, Air, and Soil Pollution*, *200*(1–4), 59–77. https://doi.org/10.1007/s11270-008-9893-7

Pan, J. R., Huang, C., Kuo, J. J., & Lin, S. H. (2008). Recycling MSWI bottom and fly ash as raw materials for Portland cement. *Waste Management*, *28*(7), 1113–1118. https://doi.org/10.1016/j.wasman.2007.04.009

Pedersen, A. J. (2002). Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash. *Journal of Hazardous Materials*, *95*(1–2), 185–198. https://doi.org/10.1016/S0304-3894(02)00138-3

Pedersen, A. J., Ottosen, L. M., & Villumsen, A. (2005). Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent. *Journal of Hazardous Materials*, *122*(1–2), 103–109. https://doi.org/10.1016/j.jhazmat.2005.03.019

Phillips, P. M., & Swink, B. J. (1989). Ulllted States Patent, *2*(12). Retrieved from ww.google.com/patents/US6099288w

Purgar, A., Winter, F., Blasenbauer, D., Hartmann, S., Fellner, J., Lederer, J., & Rechberger, H. (2016). Main drivers for integrating zinc recovery from fly ashes into the Viennese waste incineration cluster. *Fuel Processing Technology*, *141*, 243–248. https://doi.org/10.1016/j.fuproc.2015.10.003

Reddy, K. R., Donahue, M., Saichek, R. E., & Sasaoka, R. (1999). Preliminary Assessment of Electrokinetic Remediation of Soil and Sludge Contaminated with Mixed Waste. *Journal of the Air and Waste Management Association*, *49*(7), 823–830. https://doi.org/10.1080/10473289.1999.10463849

Sabbas, T., Polettini, A., Pomi, R., Astrup, T., Hjelmar, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R., Lechner, P. (2003). Management of municipal solid waste incineration residues. *Waste Management*, *23*(1), 61–88. https://doi.org/10.1016/S0956-053X(02)00161-7

Simons, R. (1985). Water splitting in ion exchange membranes. *Electrochimica Acta*, *30*(3), 275–282. https://doi.org/10.1016/0013-4686(85)80184-5

Simonsson, D. (1997). Electrochemistry for a Cleaner Environment. *Chemical Society Reviews*, *26*(3), 181–189. https://doi.org/10.1039/cs9972600181

Soboroff, D. M., Troyer, J. D., & Cochran, A. A. (1982). REGENERATION OF WASTE METALLURGICAL PROCESS LIQUOR.

Stam, A. F., Meij, R., Winkel, H. Te, Van Eijk, R. J., Huggins, F. E., & Brem, G. (2011). Chromium speciation in coal and biomass co-combustion products. *Environmental Science and Technology*, *45*(6), 2450–2456. https://doi.org/10.1021/es103361g

The Ellen MacArthur Foundation. (2012). Towards a Circular Economy - Economic and Business Rationale for an Accelerated Transition. *Greener Management International*, 97. https://doi.org/2012-04-03

Vaughan, D. J. (1994). Electrodialytic oxydation-reduction of metals.

Virkutyte, J., Sillanpää, M., & Latostenmaa, P. (2002). Electrokinetic soil remediation - Critical overview. *Science of the Total Environment*, *289*(1–3), 97–121. https://doi.org/10.1016/S0048-9697(01)01027-0

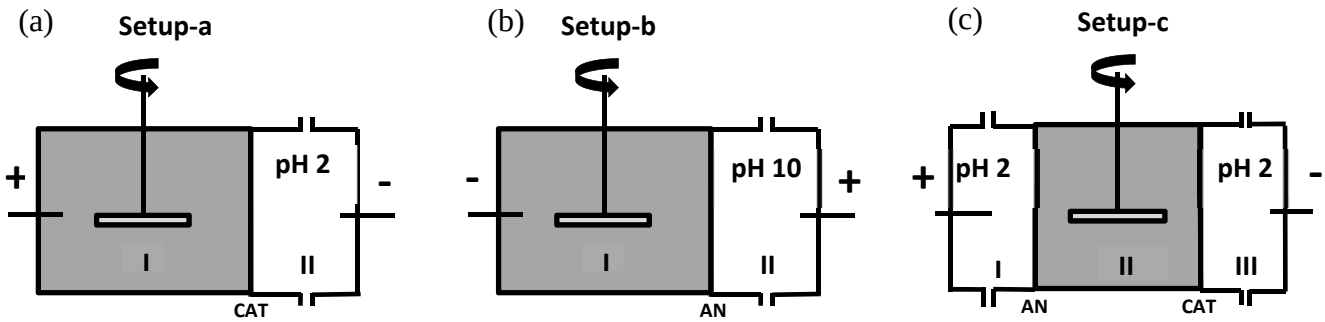


Figure 1: setups of electrodialytic cells. (AN - anion exchange membrane; CAT - cation exchange membrane; number of compartment - I, II and III).

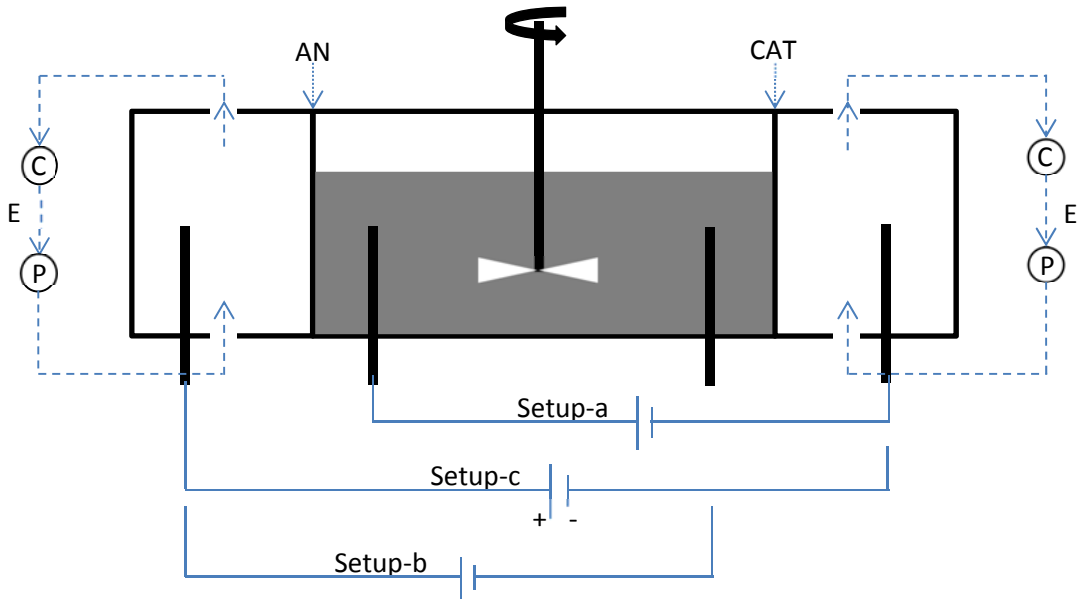


Figure 2: The experimental setup used. Ion exchange membranes: anion (AN) and cation (CAT). E: electrolyte. C: container. P: pump.

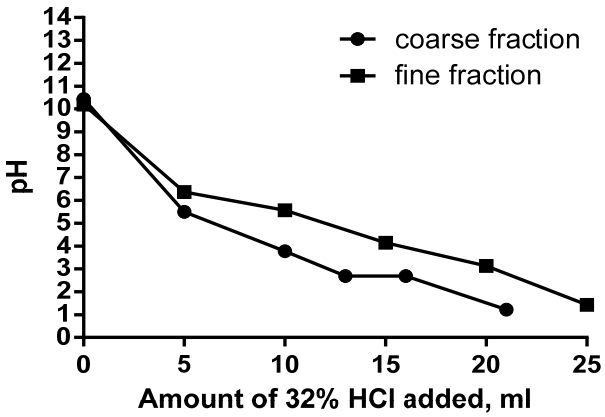


Figure 3: The buffer capacity of the washed fly ash: fine fraction and coarse fraction.

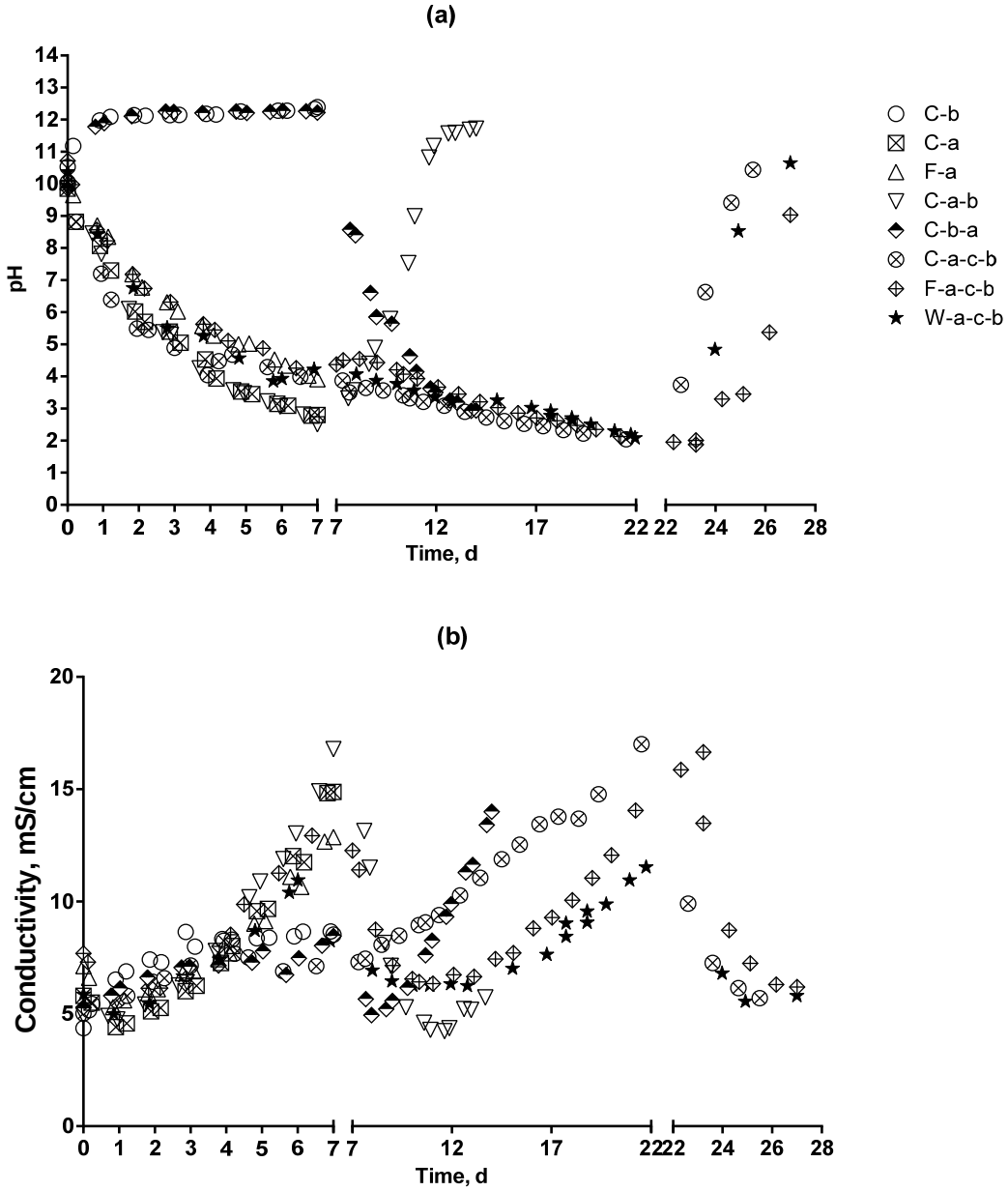


Figure 4: Development of pH and electric conductivity in ash suspension.

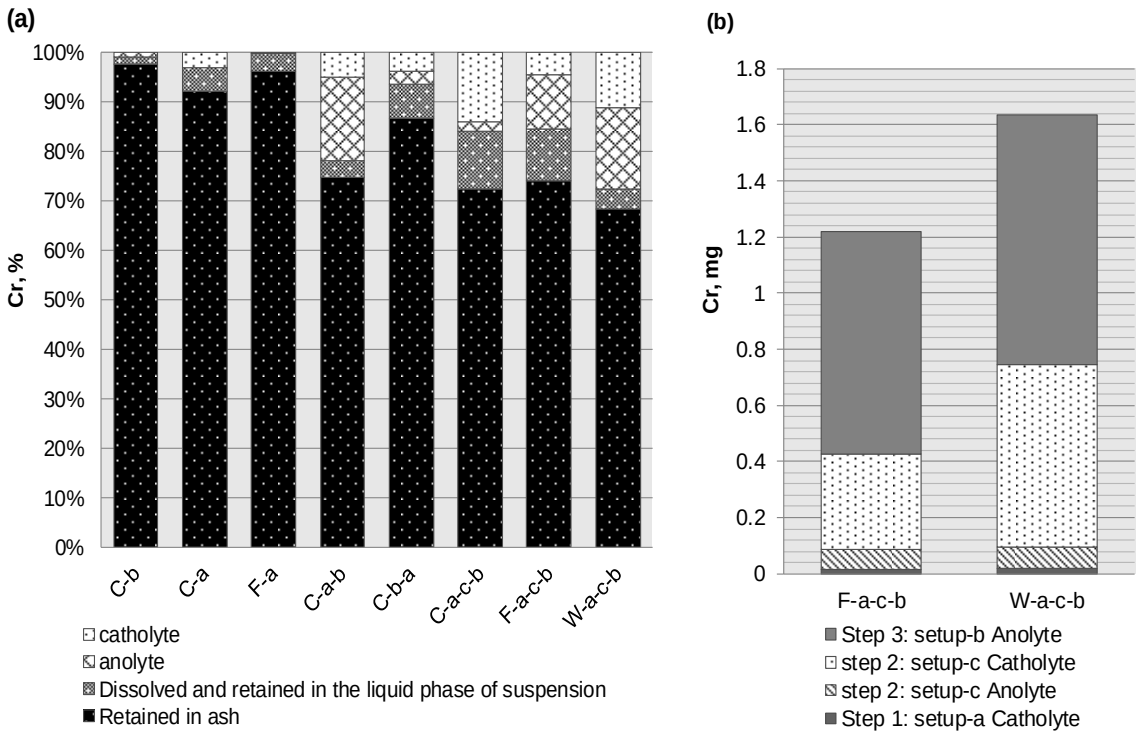


Figure 5: Chromium extraction and transport during EDS treatment. (a) Distribution of Cr, in %, in the EDS cell at the end of the experiment: where Cr dissolved and retained in liquid solution includes electrodes in ash suspension (assumption: ionic Cr species moved and deposited on electrodes), stirring, solvent (water); and (b) Contribution of each treatment step to the total extracted mass.

Table 1: The experimental design (coarse fraction C >50 µm; fine fraction F; and W unsieved ash)

| | **Experiment (fraction – setup)** | **Setup-a (time/day)** | **Setup-c (time/day)** | **Setup-b (time/day)** |
|---|---|---|---|---|
| Phase I | C-b | - | - | 7 |
| | C-a | 7 | - | - |
| | F-a | 7 | - | - |
| Phase II | C-a-b | 7 | - | 7 |
| | C-b-a | 7 | - | 7 |
| Phase III | C-a-c-b | 3.9 (till pH 4) | 17.6 (till pH 2.04) | 4 |
| | F-a-c-b | 7 (till pH 4.4) | 16.2 (till pH 2.01) | 4 |
| | W-a-c-b | 6 (till pH 3.9) | 17 (till pH 2.08) | 4 |

Table 2: The mass balance, mass loss and extraction efficiency of Cr from the experiments, the Cr concentration before and after treatment, and the leaching of Cr from the ash after treatment. Limiting leaching values for comparison: mineral waste class 0 (MA0) 0.36 mg/kg TS; mineral waste class 1 (MA1) 4.0 mg/kg TS; hazardous waste class 2 (FA2) 12 mg/kg TS. (n.d. = not determined; blank space = irrelevant parameter)

| | **Exp.** | **Mass balance %** | **Extraction %** | **Mass loss %** | **pH ash** | **pH leachate** | **Eh leachate mV** | **Leaching mg/kg TS** | **Concentration mg/kg TS** before treatment | after treatment |
|---|---|---|---|---|---|---|---|---|---|---|
| Untreated | | | | | 12.2 | 11.5 | 186 | 0.47 | 113±6 | |
| Washed | | | | | 10.2 | 10.8 | 213 | 1.44 | 112±3 | |
| EDS-treated | | | | | | | | | | |
| Phase I | C-b | 96 | 0.91 | 3 | 10.8 | 10.7 | 399 | 1.66±0.27 | 114±2 | 111±2 |
| | C-a | 90 | 3.1 | 24 | 4.3 | 5.2 | 682 | 0.12±0.01 | 115±1 | 125±5 |
| | F-a | 109 | 0.4 | 26 | 5.3 | 5.8 | 658 | 0.15±0.03 | 155±2 | 219±0.8 |
| Phase II | C-a-b | 100 | 21.9 | 30 | 10.4 | 9.9 | 424 | 1.01±0.47 | 114±2 | 121±0.8 |
| | C-b-a | 98 | 6.6 | 32 | 4.1 | 5.3 | 521 | 0.04±0.04 | 114±2 | 143±2 |
| Phase III | C-a-c-b | 90 | 16.0 | 34 | n.d. | 8.7 | 409 | 0.30 | 120±5 | 118±5 |
| | F-a-c-b | 98 | 15.5 | 53 | n.d. | 7.5 | 453 | 8.67 | 158±9 | 245±6 |
| | W-a-c-b | 105 | 27.5 | 50 | n.d. | 9.1 | 430 | 7.57±5.47 | 112±3 | 162±8 |

Table 3: Experimental conditions and possible ionic Cr species for each setup in the three-step treatment. The underlined ionic mononuclear species could migrate to electrolyte(s) for the corresponding setup. The species in brackets is pH dependent such as the interaction between $CrO_4^{2-}$ and $HCrO_4^-$.

| | **pH** | **Eh change** | **Ionic Cr** (Jacobs and Testa, 2005; Cornelis et al., 2008) | | **Interface** | |
|---|---|---|---|---|---|---|
| | | | cation | anion | ash and membrane | ash and electrode |
| Setup-a | acidification<br>4<pH<10.7/10.4 | increasing | $\underline{Cr(OH)_2^+}$<br>$\underline{CrOH^{2+}}$ | $CrO_4^{2-}$<br>$HCrO_4^-$<br>$Cr(OH)_4^-$ | CAT | anodic |
| Setup-c | 2<pH<4 | possibly slightly increasing<br>(Chen et al., 2017) | $\underline{Cr^{3+}}$<br>$\underline{(CrOH^{2+})}$ | $\underline{HCrO_4^-}$<br>$\underline{(CrO_4^{2-})}$ | AN<br>CAT | no |
| Setup-b | alkalization<br>2<pH<9/10.7 | reducing | $Cr^{3+}$<br>$CrOH^{2+}$<br>$Cr(OH)_2^+$ | $\underline{CrO_4^{2-}}$<br>$\underline{(HCrO_4^-)}$<br>$\underline{Cr(OH)_4^-}$ | AN | cathodic |

# Chapter 8

## *Additional note to Chapter 7 – As extraction*

# Additional Note to Chapter 7

# - As extraction

The results of arsenic extraction in the experiments in Chapter 7 are included into this supplement. Besides chromium, arsenic is another heavy metal that has low extraction rate by EDR from MSWI fly ash.

Arsenic allows forming oxidation states such as negative charged arsine, unchanged arsenic, arsenite and arsenate. Those arsenic species which are mobile and charged have a chance of being separated from an ash suspension through ion exchange membranes during EDR. As for MSWI ash, trivalent and pentavalent arsenic are typically present in such ash (Cornelis et al., 2008).

The existence of arsenic in solution is typically in the form of oxyanions rather than cations in hydrometallurgical processes (Nazari et al., 2016). The species of As in a solution are pH and redox potential dependent. Generally in an As-$H_2O$ system at 25 °C, pentavalent arsenic is more stable than trivalent arsenic at high redox potential. At pH below 2, both oxidation states of arsenic form unchanged species, $H_3AsO_3$ and$H_3AsO_4$. With increasing pH i.e. increasing the concentration of hydroxyl ions, $H_3AsO_4$ first deprotonates at pH above 2, forming $H_2AsO_4^-$ up to pH ~6 and further forming $HAsO_4^{2-}$ up to pH 11. Whereas, the deprotonation of $H_3AsO_3$ initiates at pH above 9, appearing as $H_2AsO_3^-$ up to pH 12 (Nazari et al., 2016).

## Main results

*Extraction of As during EDR*

As can be seen from Figure 1a, the extraction of arsenic out of the ash suspensions (i.e. to catholyte and anolyte) mainly took place in the three-step experiments C-a-c-b, F-a-c-b and W-a-c-b. In addition, more arsenic was extracted into the anolyte than into the catholyte. As is shown in

Figure 1b, the second treatment step amongst the three where a three-compartment cell was used, remarkably contributed to the migration of As to the anolyte. The migration to the catholyte also increased at the second treatment step (Fig. 1b). During the second treatment step, $H_2AsO_4^-$ might predominate the ionic As species in the suspensions in the experiments F-a-c-b and W-a-c-b, because the suspensions had pH between 2 and 4 and redox potential which was believed not to be low after the first treatment step that created an oxidizing environment in the suspensions. Another observation was on the dissolution of arsenic into the liquid phase of the suspension (Fig. 1a). The remaining As in the liquid phase was quite high which might be associated with the extraction rate of As through the membranes. The extraction rate through the membranes might have been low due to the presence of uncharged As species and/or the interaction of As with e.g. Fe/Al oxides (Cornelis et al., 2008).

Table 1 summarizes the extraction rates of As in all the experiments. The experiment W-a-c-b resulted in the highest extraction, followed by F-a-c-b. Despite exhibiting different extraction rates, the concentration of As in the ash after treatment was enriched, except in C-b. The arsenic leaching from the treated ashes fulfilled the limit for landfilling as mineral waste, except from the fine ash fraction treated in the experiment F-a-c-b which met the limit for landfilling as hazardous waste. The difference in As leaching between the two ash fractions might suggest that fractionation treatment could increase the possibility for reusing the MSWI fly ash, in particular the coarse fraction with a lower leaching value.

*As leaching from fired pellets*

Leaching of heavy metals is one of the main concerns with regard to the reuse of MSWI fly ash in the production of clay bricks. The clay pellets containing 10 wt.% and 20 wt.% the treated ashes from the experiments C-a-c-b and F-a-c-b were made following the same way as in Chapter 5. The pellets were fired at 1000 °C for 1 h. The leaching results given in Table 2 reveal that the three-

step EDR treatment reduced the leaching of both As and Cr from the pellets incorporating 10 wt.% the fine fraction of the ash (Pellet II vs Pellet III). Moreover, both As and Cr leaching were found the lowest from the pellets incorporating the coarse fraction of the ash (Table 2, Pellet I), which might further emphasize the benefit of fractionation on the management of the MSWI fly ash.

**References**


BEK nr 252. Bekendtgørelse om deponeringsanlæg (2009).

Cornelis, G., Johnson, C. A., Gerven, T. Van, & Vandecasteele, C. (2008). Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Applied Geochemistry*, *23*(5), 955–976. https://doi.org/10.1016/j.apgeochem.2008.02.001

Nazari, A. M., Radzinski, R., & Ghahreman, A. (2016). Hydrometallurgy Review of arsenic metallurgy : Treatment of arsenical minerals and the immobilization of arsenic. *Hydrometallurgy*. https://doi.org/10.1016/j.hydromet.2016.10.011


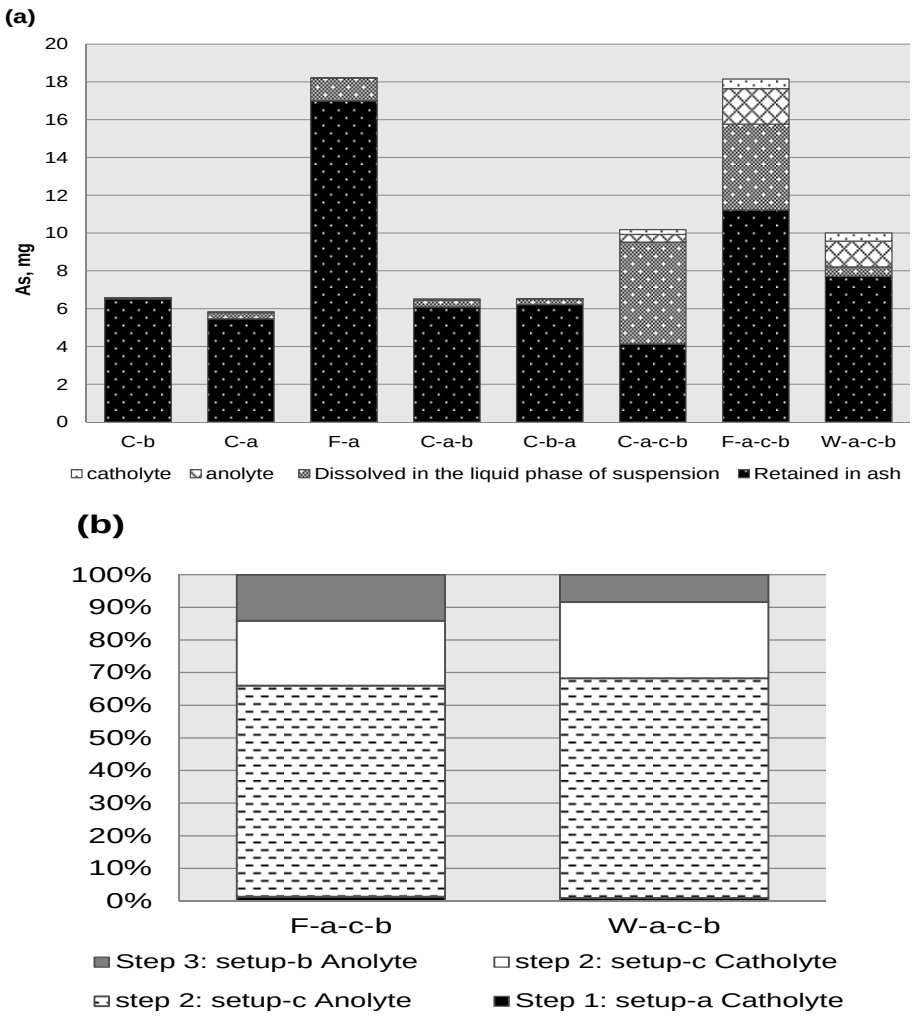


Figure 1. Arsenic extraction and transport during EDS treatment. (a) Distribution of the total mass of As in the EDS cell at the end of the experiment: where As dissolved in liquid solution includes electrodes in ash suspension (assumption: ionic As species moved and deposited on electrodes), stirring, solvent (water); and (b) Contribution of each treatment step to the total extraction.

Table 1. The mass balance, mass loss and extraction efficiency of As from the experiments, the As concentration before and after treatment, and the leaching of As from the ash after treatment. Limiting leaching values for comparison: mineral waste class 0 (MA0) 0.082mg/kg TS; mineral waste class 1 (MA1) 0.40 mg/kg TS; hazardous waste class 2 (FA2) 6.0 mg/kg TS (BEK nr 252, 2009). (n.d. = not determined; blank space = irrelevant parameter; d.l. = detection limit)

| | **Exp.** | **Mass balance%** | **Extraction %** | **Mass loss %** | **pH ash** | **Leaching mg/kg TS** | **Concentration mg/kg TS** | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | before treatment | after treatment |
| As-received | | | | | 12.2 | 0.22 | 195±15 | |
| Washed | | | | | 10.2 | < d.l. | 181±2 | |
| EDS-treated | | | | | | | | |
| Phase I | C-b | 94 | 0.25 | 3 | 10.8 | 0.16±0.04 | 140±9 | 135±4 |
| | C-a | 82 | 0.96 | 24 | 4.3 | 0.19±0.01 | 143±3 | 144±7 |
| | F-a | 103 | 0.1 | 26 | 5.3 | 0.20±0.02 | 355±2 | 462±7 |
| Phase II | C-a-b | 91 | 1.2 | 30 | 10.4 | 0.10±0.07 | 140±9 | 171±1 |
| | C-b-a | 93 | 0.7 | 32 | 4.1 | 0.12±0.05 | 140±9 | 182±4 |
| Phase III | C-a-c-b | 205[1] | 6.5 | 34 | n.d. | 0.06 | 99±9 | 125±5 |
| | F-a-c-b | 91 | 13.2 | 53 | n.d. | 0.78 | 394±6 | 472±5 |
| | W-a-c-b | 110 | 18 | 50 | n.d. | 0.27±0.09 | 181±2 | 307±11 |

[1]The mass balance for As in experiment C-a-c-b was not acceptable for some unknown reasons.

Table 2. Leaching of As and Cr from fired clay-ash pellets.

| **Pellet** | **Ash content** | **pH** | **ORP, mV** | **As, mg/kg TS** | **Cr, mg/kg TS** |
|---|---|---|---|---|---|
| I | 20wt.% C-a-c-b | 10.1 | 206 | **0.022** | **1.58** |
| II | 10% untreated ash <50 µm | 10.2 | 194 | 0.167 | 3.95 |
| III | 10% F-a-c-b | 10.2 | 150 | 0.031 | 3.39 |
| IV | 20% F-a-c-b | 10.9 | 137 | 0.024 | 4.78 |

# Chapter 9

*Conclusions*

# Conclusions

This study shows that the upgraded bioashes from co-combustion of straw and wood chips by water washing followed by EDR can be used in the production of bricks in both regarding technical and environmental issues. Easily soluble salts in the bioashes, mainly potassium and chloride, are washed out with water. Subsequently, the elevated concentration of heavy metals, such as Cd and Zn, in the washed bioashes can be reduced by EDR (e.g. to below 2 mg/kg TS for Cd). Even though Pb is to some extent extracted by EDR, the concentration in the ash may increase after this treatment; however, the Pb leaching from the treated ash was low. After water washing and EDR treatment, quartz appeared to be the main crystalline phase in the ash. Incorporation of the treated bioashes in clay bricks led to an increase in apparent porosity, water absorption and weight loss of the bricks during firing, with increasing substitution level (up to 20%). By increasing the sintering temperature from 1050 °C to 1075 °C, the apparent porosity and water absorption of the clay-bioash bricks decreased, as well as the leaching of Cr, which was associated with the increase in sintering degree of the bricks. The sintering temperature 1075 °C was found as the optimum at the present lab-scale pellet-test.

The MSWI fly ash might be incorporated into clay bricks at a low level (5%) after upgrading by water washing and EDR, based on both technical properties and heavy metal leaching results. Water washing and EDR resulted in removal of soluble chlorides and heavy metals, which was shown to lower the effect of evaporation of heavy metals during the firing of the untreated MSWI fly ash. In relation to leaching properties of thermally treated raw ash or fired MSWI fly ash-clay bricks, the leaching of e.g. Cd, Pb and Zn were low; whereas the As and Cr leaching increased compared to the values prior to thermal treatment. The water washing and EDR treatment reduced the leaching of Cr from both the thermally treated raw ash and the fired fly ash-clay bricks. However, only the fly ash-

clay brick with 5% ash content (properties: weight loss during firing 11.3%; density 1.63 g/cm$^3$; apparent porosity 41%; water absorption 25.5%; and compressive strength 8 N/mm$^2$) might be reused again in construction work at the end of service life in regards to the leaching properties. It must here be stated that the upgrading processes i.e. water washing and EDR are promising in minimizing the leaching of Cr from the fired MSWI fly ash-clay bricks. To increase the incorporation level of the MSWI fly ash in brick, further study is recommended to include fractionation as one upgrading step based on the observation that the fine fraction of the ash contributed significantly to the leaching of As and Cr from the fired brick pellets.

In conclusion, this work shows that it is technically possible to upgrade both ash types investigated from waste products to possible resources for the production of clay bricks.

As long as municipal solid waste (MSW) and biomass are being used to produce heat and power, ash residues will continue to be produced. The present PhD study raises the possibility that fly ashes from combustion of MSW and straw/wood might be upgraded by electrochemical technique to secondary resources for the production of clay bricks.

**DTU Civil Engineering**
Technical University of Denmark

Brovej, Bygning 118
2800 Kongens Lyngby

www.byg.dtu.dk

ISBN 9788778774750
ISSN 1601-2917