

MILJÖRIKTIG ANVÄNDNING AV ASKOR

880

Långsamupplösande askpellets

Maryam Mahmoudkhani och Hans Theliander



Långsamupplösande askpellets
- en jämförande studie av olika alternativ

Slow dissolving bio-fuel ash pellets
- A comparison of different alternatives

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Q4-139
Långsamupplösande askpellets

VÄRMEFORSK Service AB
101 53 STOCKHOLM · Tel 08-677 25 80
Oktober 2004
ISSN 0282-3772

Abstract

Within this project, the feasibility of controlling the leaching properties of bio-fuel ashes was studied. Different methods were applied to treat bio-fuel ash. The influence of different treatment method on leaching properties of both easily soluble substances and substances with limited solubility was investigated. The results indicate that depending on the chemical composition and crystalline structure of bio-fuel ash, treatment techniques influence the leaching properties of bio-fuel ash differently.

Sammanfattning

Eftersom biobränsle bland annat är koldioxidneutralt kan dessa anses vara miljövänliga för alla typer av energibehov, exempelvis för uppvärmning och fjärrvärme. Vidare är tillgången ofta lokal (låga transportkostnader) och även kostnaden låg för biobränsle, vilket är fördelaktigt jämfört med kol och olja.

Biobränsleaskan innehåller höga halter basiska salter, men även låga halter av vissa toxiska ämnen. De toxiska ämnena begränsar användbarheten av askan, men halterna är inte högre än att askan vanligtvis kan användas som pH-höjande gödningsmedel i sura skogar. För att få en långtidseffekt i skogen, behöver dock askan behandlas. Även askans hanterbarhet (dammning) behöver förbättras under behandlingen.

Syftet med detta arbete är att utvärdera några olika möjliga behandlingsmetoder som kan användas för att kontrollera lakningskaraktistiken av alkaliska substanser från pelletaska. Inom ramen för projektet har våtbehandling och värmebehandling av biobränsleaska studerats. Undersökningen omfattar hur olika behandlingsmetoder påverkas fysikaliska egenskaper, till exempel hållfastighet, och lakningskaraktistik, till exempel lakningshastighet av lösliga substanser från pellets av biobränsleaska.

Biobränsleaskor från två olika pannor undersöktes: flygaska från en rosterpanna, ASH A, och aska från en cirkulerande fluidiserad bäddpanna, ASH B. Sammansättningen hos biobränslet som användes i rosterpannan är enligt följande: vedflis (barrved) ~50, sågspån ~17, bark ~18 och salix ~15 vikt-%. Sammansättningen hos biobränsle som användes i den andra pannan (cirkulerande fluidiserande bäddpannan) är: ved flis (barrved) ~82, sågspån ~1, bark ~16 och fiberslam ~1 vikt-%.

Den kemiska sammansättningen hos ASH A och ASH B analyserades med "Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)" och "Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)". Innehållet av Si och Al i ASH B var högre på grund av att kiselsand användes som bäddmaterial i den fluidiserade bäddpannan. En jämförelse av Ca och K halterna i ASH A och ASH B visar att ASH B innehåller mindre mängd Ca och K. Halten av Mg och P är ungefär samma i båda fallen. ASH B innehåller högre halt av natrium. Många av spårämnehalterna i ASH B var lägre än i ASH A, till exempel Cd, Ba och As. Orsaken till att

kadmiumhalten i ASH A var hög beror troligtvis på av förekomsten av salix i biobränsle som användes i rosterpannan.

För att underlätta transport och spridning av askan, måste den vara i aggregerad form, antingen pellet (dvs. sammanpressad aska i form av ex.v. en cylinder) eller granuler (dvs. en nära sfärisk partikel som formats genom att lager på lager byggs upp till en partikel). Pelletering medför att askan får en stabil och tät matris, vilket innebär en minskad masstransports- och reaktionsarea. Pelletering av ASH A var svår, vilket antagligen berodde på ett visst sotinnehåll. Detta innebar att det fanns många sprickor på ytan av pelletarna, vilka utgjorde brottanvisningar. Även elektrostatiska egenskaper och densitet hos askan var ett problem vid tillverkning av pelletar från ASH A. Inga av dessa problem uppträdde när ASH B behandlades. Den specifika ytarean minskade med ca 50% då pellets producerades.

Tre behandlingsmetoder undersöktes; självhärdning, värmebehandling och härdning med tillsatts av ett bindningsmaterial.

Då självhärdningsmetoden användes blandades askan med avjonat vatten (viktförhållandet 2.5:1) och hölls vid rumstemperatur under tiden för härdningsreaktionen, ca sex dagar. Efter dessa sex dagar tillverkades pelletar av den självhärdade askan.

Värmebehandlingsmetoden innebar att den pelleterade askan värmdes upp i en elektrisk ugn till 800°C och 850°C, atmosfären i ugnen utgjordes av koldioxid för att förhindra kalcinering av karbonatsalter. Uppehållstiden var tre timmar.

Härdning med bindningsmaterial innebar tillsats av en kaliumsilikatlösning, tre olika koncentrationsnivåer undersöktes. Härdningen sker genom att kaliumsilikatet binder samman askpartiklarna som därmed blir mindre löslig. Reaktionerna som sker liknar de reaktioner som sker då cement härdas. Efter behandling pressas materialet till pellets.

Resultaten från denna undersökning visar att askan beter sig olika då de behandlas med de olika metoderna. Resultatet av hållfasthetsmätningarna visade för ASH B att självhärdande pelletar hade starkast struktur, medan för ASH A var de värmebehandlade pelletarna starkast.

En viktig egenskap för materialet är dess lakningsegenskaper, det är väsentligt att salterna löses upp i lagom takt. Det är flera fysikaliska och kemiska materialegenskaper som påverkar upplösningshastigheten. I

tidigare undersökningar har vi funnit att den specifika ytarean mätt enligt B.E.T.-metoden väl speglar de fysikaliska egenskaperna, vilket torde bero på att det är från denna yta som upplösningen främst sker. Resultaten från denna undersökning visar att den specifika ytarean främst påverkades då pelleten värmebehandlades, de andra metoderna visade ingen större påverkan, vilket gäller för båda askorna i denna undersökning. Att påverkan sker vid värmebehandling kan förklaras med att sintring av materialet sker vid de aktuella temperaturerna.

När det gällde partiklarnas specifika yta gav de två olika askorna något olika resultat: För ASH A minskades specifika yta mer under värmebehandling än för ASH B. Det är viktigt att komma ihåg att den kemiska sammansättningen hos askan har en avgörande betydelse för lakningshastigheten, vilket innebär att specifika yta endast är jämförbar för kemiskt lika material. Det går exempelvis inte att jämföra ett material som huvudsakligen består av kalciumkarbonat med ett som huvudsakligen består av kalciumoxid. Den senare släcks då den kommer i kontakt med vatten och den bildade kalciumhydroxiden löses upp mycket fortare än kalciumoxiden.

En viktig effekt av värmebehandlingen av ASH A var att dess innehåll av vissa toxiska ämnen minskade radikalt: Arsenikkoncentrationen minskade med hela 90 %, kadmiumkoncentrationen med 32 % och kromkoncentrationen med 27 %.

Materialens lakningsegenskaper studerades i en modifierad kolontestutrustning i vilken lakningsstudier genomfördes vid konstant pH och temperatur. Detta är en typ av vad vi kan kalla "accelererade lakningstester", vilket innebär att sex dagars experiment innebär en mycket längre tidsperiod i skogsmark. Hur mycket längre vet vi inte ännu, men vissa indikationer ger vid hand att sex dagar i den accelererade testtriggen motsvarar en tidsperiod som är längre än 1 år i skogen.

Resultaten från lakningstesterna visade för ASH A att självhärdning gav en något ökad lakningshastighet jämfört med obehandlad pelleterad aska, skillnaden var emellertid mycket liten. Däremot gav temperaturbehandling en rejäl minskning, vad beträffar lakningshastigheten, vidare gav en högre behandlingstemperatur (mer sintrat material) en lägre lakningshastighet. Detta gäller lösliga kalium-/natriumsalter såväl som kalciumsalter. Det visade sig även att en rejäl dosering av kaliumsilikat minskade lakningshastigheten för såväl kalium som kalcium. Mängden tillsatt kaliumsilikat var emellertid så hög att det sannolikt inte är ekonomiskt försvarbart.

För ASH B var resultaten mer svårtolkade och förvånande: Ingen av de utnyttjade metoderna kunde minska lakningshastigheten i någon väsentlig grad, i vissa fall skedde till och med en ökning av lakningshastigheten. Orsaken till detta har vi inte kunnat utröna under föreliggande arbete.

I syfte att kunna beskriva lakningshastigheten i mer generella termer har matematiska modeller utvecklats. Dessa modeller är baserade på masstransport och kemisk reaktionskinetik. Reaktionshastighets- och diffusionsparametrar bestämdes genom att anpassa modellerna till de experimentella resultaten. När det gäller modellen för kalium visade det sig att det hastighetsbestämmande steget är masstransport i pelleten. Denna modell har god anpassning över hela koncentrationsområdet och kan användas för långa tider. När det gäller kalcium är situationen inte riktigt lika rättfram, här är mekanismerna pH-beroende samt att hänsyn måste tas till såväl masstransport som kemisk reaktion. Modellerna som utvecklats ger emellertid en god anpassning till experimentella data.

Nyckelorden: bio-aska, behandling, materialkaraktärisering, kontrollerad lakning.

Summary

Bio-fuel combustion is considered as an environmentally friendly way of providing energy for various purposes, e.g. process heat and district heating. One important reason is that it is carbon dioxide neutral. Biofuels are, often, locally available with lower costs compared with fossil fuels.

Bio-fuel ash is highly alkaline and it may contain some toxic elements. However, the amount of toxic elements is not too high and most ash can safely be used as neutralizer in acidified forests. In order to provide long-term effect, it is necessary to treat the ash in terms of lowering the leaching rate of alkaline substances as well as lowering the level of toxic elements prior to use it as neutralizer/fertilizer in acidified forests.

Wet treatment and thermal treatment of wood ash has been studied in earlier works. The focus of this project, however, is to evaluate different treatment techniques that are possible to be applied in order to control the leaching properties of alkaline substances from ash pellets. To do so, the influence of different treatment techniques on the physical characteristics, e.g. strength, and leaching properties, e.g. leaching rates of soluble substances, of bio-fuel ash pellets was investigated. Bio-fuel ashes from two different combustion boilers were investigated: fly ash from a grate-fired combustion boiler, ASH A, and ash from a circulating fluidized bed combustion boiler, ASH B. The bio-fuel used in the grate-fired combustion boiler consisted of: wood chips (softwood) ~50 wt %, sawdust ~17 wt %, bark ~18 wt % and Salix ~15 wt %. The bio-fuel used in the circulating fluidized bed combustion boiler consisted of: wood chips (softwood) ~82 wt %, bark ~16 wt %, saw dust ~1 wt % and sludge from water treatment / fibre sludge ~1 wt %.

The chemical compositions of ASH A and ASH B were measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) methods. The content of silicon (Si) and aluminium (Al) in ASH B was higher, which was due to the fact that sand was used as bed material during combustion in fluidized bed boiler. Comparing calcium (Ca) and potassium (K) content of ASH A with ASH B, it was found that ASH B contained less Ca and K. The content of Mg and P in ASH A and ASH B was about the same. Most of the trace elements content of ASH B was lower than in ASH A, e.g. cadmium (Cd), barium (Ba), and arsenic (As). The cadmium content in ASH A was high, this is probably due to presence of salix in bio-fuel used in the grate-fired combustion boiler.

To make it easy to transport and spread, ash must be aggregated by either pelletization (i.e. forming a particle by compression)/granulation (i.e. forming a particle by adding layer by layer), which forms stable and dense particles with a small mass transfer area and reaction surface. Forming ash pellets from ASH A was difficult due to presence of some soot/char which hindered binding particles to a dense pellet. Therefore, there were several cracks on pellets which made them fall apart. The other problem with ASH A was the electrostatic property and the low density of it, which made it difficult to put it into the die (a device used for forming pellets). None of these difficulties were found for ASH B. When ashes were pelletized, the specific surface area was found to be lowered by about 50 %.

Three treatment techniques were investigated: self-hardening, thermal treatment and hardening by addition of binding material.

In the self-hardening technique, ash was mixed with de-ionized water with a weight ratio of 2.5:1 and stored at room temperature for ~6 days, during which the hardening reactions occurred. The pellets were then formed of self-hardened ash.

In thermal treatment method, ash pellets were exposed to the thermal treatment in an electrical furnace by three hours at temperatures of 800°C and 850°C in carbon dioxide atmosphere. Carbon dioxide was used to prevent calcination of carbonate salts.

In hardening with binding material, potassium silicate solution was added into ash to bind the ash particles together and transform ash to a less soluble and denser matrix due to reactions similar to cement hardening reactions. Three different concentration of potassium silicate were tested. The hardened ash was then pelletized.

The results show that ash materials behaved differently when treated by different techniques. The results of the strength measurement of ash pellets showed that self-hardened ASH B pellets had the strongest structure; while the strength of thermal treated ASH A was the highest among the other treated pellets.

Pore structure of ashes was investigated by measuring the B.E.T. surface area which is a measure of the size of the surface area of agglomerates and crystals within pellet structure. This is an important measurement showing the available surface area of the solid material from which material can be dissolved. This surface area should be minimized in order to lower the leaching rate. The results showed that thermal treatment has

the largest influence on minimizing the specific surface area characteristics of ASH A and ASH B pellets. This can be explained by the sintering phenomena which occur at high temperature. However, the thermal treatment was found to be more pronounced for ASH A in term of lowering the specific surface area. Therefore, it should be kept in mind that there may be an interaction between treatment method and the properties of the ash (chemical as well as physical properties).

An important effect of thermal treatment of ASH A pellets was lowering of the cadmium and arsenic content due to vaporization at high temperature. Arsenic content was lowered by 90-, cadmium content by 32- and chromium by 27 wt%.

The leaching properties of ash pellets were investigated by applying a modified column test method (pH-static experiments). It should also be pointed out that the leaching test in this study is an accelerated leaching test and the amount of potassium and calcium leached out during six days experiments in this study, may be leached out during much longer time in forests (order of years).

The results of self-hardened ASH A pellets showed a slightly increase in leaching rates of both potassium and calcium compared with non-treated ash pellets. However, the leaching rate of potassium and calcium from thermal treated ASH A were lowered, the higher the temperature is during the thermal treatment (more sintered particles), the lower leaching rates of potassium and calcium. On the other hand, the results of potassium and calcium leaching from hardened ASH A pellets showed that large amount of added potassium silicate could lower the leaching rates of both potassium and calcium. However, from an economical viewpoint, it is not beneficial to add larger amount of potassium silicate in order to lower the leaching rates.

Results from all treatment techniques applied on ASH B pellets, showed that none of those techniques could lower the leaching rate of soluble potassium and calcium from ash pellets.

To be able to make a general description for the leaching rates of potassium and calcium, a mathematical model was developed. The model was based on mass transport and chemical reaction kinetics. In our earlier studies, it was found that the rate-determining step in leaching of potassium was mass transport within the pellets. Therefore, to describe the leaching rate of potassium the model was based on the diffusional mass transfer of potassium ions that were leached out from ash pellets. This model can well describe the leaching of easily soluble substances, K

and Na, from the pellets. The model gives a good estimation of long term leaching rate of Na/K. However, the leaching of calcium was found to be dependent on pH. Therefore, to interpret the leaching rate of calcium, the reaction kinetics, involved in dissolution of calcium compounds, was considered. The numerical values of reaction rate constants and diffusion coefficients are indications of how easily the calcium and potassium are leached out. The values of diffusion coefficients and kinetic rate constants were calculated by fitting the corresponded models to the experimental data.

Keyword: bio-fuel ash, treatment, material characterization, controlled leaching.

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1 Background

Bio-material becomes more and more important as fuel in heat and power plants. The main combustion methods used for solid fuels are fluidized bed combustion techniques, the grate firing and the pulverized fuel firing. During the combustion process the organic matrix of the fuel is consumed and the inorganic species are liberated in form of ash and transformed into more or less crystalline inorganic compounds. The main constituents in the bio-fuel ash are calcium (Ca), potassium (K), sodium (Na), sulphur (S), magnesium (Mg) and phosphorus (P), which imply that the economic value is quite low even if the residues have been treated. However, Ca, K and P, are plant nutrients that should be recycled to forest or agricultural soils, thus closing the mineral material fluxes of the overall energy production process.

A potential problem with recycling wood ash is that it causes a rapid increase in the pH and ion concentration on the surfaces of the vegetation and in the upper soil horizon². The problem is that besides easily soluble nutrients, ash also contains heavy metals: cadmium (Cd), as an example, poses a risk to the use of wood ash on soils. This is especially important in cases when cadmium accumulating species such as *Salix* are used as fuel. *Salix* is an interesting short rotation crop and has been seen to extract and accumulate cadmium from soils ¹⁴. Therefore, treatment of the ash is necessary in order to modify the properties of the material (lowering dissolution rate and minimizing heavy metal content) and to make it easy to transport to and spread in the forest.

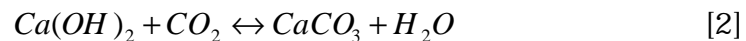
Today most of the bio-fuel ash from heat and power plants end up as landfills; however some bio-fuel ash is used as a neutralizer or fertilizer on an industrial scale. A total of 240,000 tons (dry matter)/year has been reported for ashes only from the Swedish pulp and paper industry, 75% of this ends up as landfill and 25% becomes construction material. The other alternatives for the management of ashes that can be found in the literature are ¹:

- a. Filling material in road banks
- b. Sealing material for landfill areas
- c. Raw material for concrete

1.1 Description of the research area

To make it easy to transport and spread, ash must be aggregated by either pelletization or granulation. Pelletization makes a stable and dense matrix of ash and forms large agglomerates from the ash particles. Therefore, mass transfer area and reaction surface decrease.

To circumvent the rapid increase in the pH on the surface of the vegetation, the ash is currently treated by self-hardening before recycling. This method is mainly applicable to biofuel ash, in which the major content of calcium in ash is as calcium oxide, which reacts with water and forms calcium hydroxide, reaction [1]. Calcium hydroxide reacts further with carbonate ions, originating from absorbed carbon dioxide from the surrounding air, and forms calcium carbonate, reaction [2] ³.



Reaction [1] is a rapid, exothermic process involving inter-particle bond formation. The newly formed compound forms bridges between particles and thus creates an agglomeration of the material. The reaction step following reaction [1] is a carbonation of the calcium hydroxide resulting in formation of calcium carbonate, reaction [2]. The carbonation of calcium hydroxide requires the presence of water phase in which the reactants, calcium hydroxide and carbon dioxide, can be dissolved and transported ³. The calcium carbonate thus formed, precipitates from the solution and creates a product layer on the ash surface and in the pores ³. Calcium carbonate has considerably lower solubility than calcium oxide and calcium hydroxide. Therefore, the carbonation of the ash is an important step in the stabilization process.

Wet treatment of bio-fuel ash has been studied earlier⁴, in which ash is washed and dissolved partially with a solvent such as water or an acid to reduce the risk for contamination of the environment by removing soluble compounds from ash. However, this method does not seem to be effective for treatment of bio-fuel ashes that are going to be spread on forest soils, due to removal of potassium.

Thermal treatment process has several advantages over the self-hardening technique. One is that it is possible to control the quality of the product (the dissolution rate) by changing the conditions in the thermal treatment

step. Another is that most of the heavy metals can be separated from the product in the thermal treatment step. In the earlier studies, thermal treatment of ash has been suggested as an effective method to separate substances like Zn, Pb, Cd etc ⁵. Economical and technical evaluation of thermal treatment of ash has been investigated earlier ⁵. However, the quality of thermal treated ash is very important to decide for which purpose it is going to be used, e.g. construction material. Therefore, studies with leaching tests are necessary to clarify this issue.

1.2 The purpose of the research assignment and its role within the research area

The aim of this project is to evaluate the treatment techniques that are possible to be applied in order to control the leaching properties of alkaline substances from ash pellets. To do so, the influence of different treatment techniques on the physical characteristics, e.g. strength, and leaching properties, e.g. leaching rates of soluble substances, of bio-fuel ash pellets was investigated. From a chemical point of view, there is an obvious difference between the salts for which the dissolution can be described as a dissolution reaction (e.g. alkali salts) and the dissolution of salts where the dissolution rate and equilibrium are strongly affected by the presence of other species, e.g. calcium carbonate is affected by the concentration of H^+ -ions. In the latter, the dissolution kinetics also depends on the diffusion of reactant (H^+) from soil layer to reaction zone, which is not the case for the alkali salts. This fact indicates that there may be a difference in the leaching mechanism in the two cases. This has, however, not been investigated, thoroughly, earlier. This work has, therefore, been focused on leaching mechanism and the factors affecting the leaching rate of different substances from bio-fuel ash pellets.

2 Combustion process

Currently there are several combustion techniques that are widely used for the combustion of bio-fuel. The two most common are: i) grate-fired combustion (GFC) and ii) circulating fluidized bed (CFB) combustion. The most traditional combustion technique is using a grate-fired combustion boiler. This technique is high temperature technique commonly operating at temperatures exceeding 1100°C , whereas fluidized bed combustion operates at much lower temperatures, usually around 850°C . Ashes from both types were studied in this project.

2.1 Grate-fired combustion boiler

In a grate-fired combustion boiler, mechanical stokers are used to feed the fuel onto a grate within the furnace and to remove ash residue. A simplified sketch of a GFC boiler is shown in figure 1. Spreader stoker firing provides an excellent way to burn bio-fuels. As the name indicate, the spreader stoker projects fuel into the furnace over the fire with a uniform spreading action, permitting suspension burning of the fine fuel particles. The heavier pieces, which cannot be supported in the gas flow, fall to the grate for combustion in a thin, fast-burning bed. The continuous-ash-discharge travelling grate has no interruptions for removing ashes and because of the thin, fast-burning fuel bed and this design, increases average burning rates.

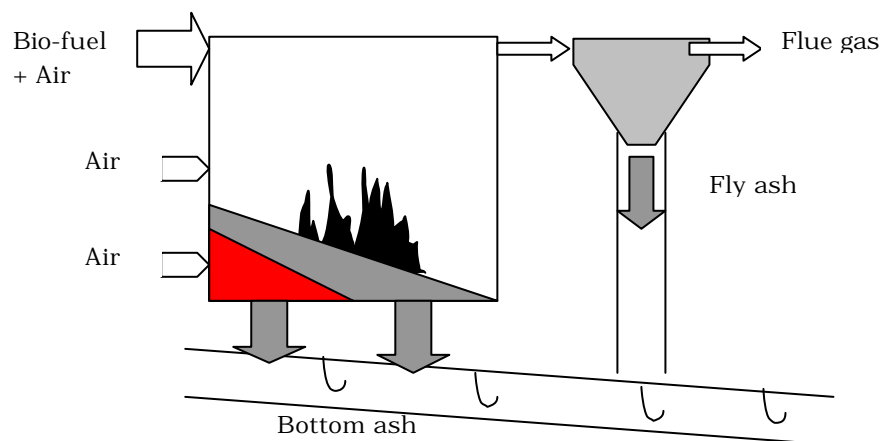


Figure 1: Grate-fired combustion boiler

2.2 Circulating fluidized bed combustion boiler

In a circulating fluidized bed boiler, the fuel is fed into the lower bed. A simplified sketch of CFB boiler is shown in figure 2. A portion of air, primary air, is introduced through the bottom of the bed. The bed material normally consists of fuel, limestone/sand and ash. In the presence of fluidizing air, the fuel quickly and uniformly mixes under the turbulent environment and behave like a fluid. The secondary air flow is introduced at the top of the lower, dense bed. The fluidizing air elutriates the particles through the combustion chamber to the U-beam separators at the furnace exit. The captured solids, including any unburned carbon and unutilized carbon oxide, are re-injected directly back into the combustion chamber without passing through an external recirculation. This internal solids circulation provides longer residence time for fuel, resulting in good combustion. Off-gas and ash are then separated and ash is circulated into the combustion chamber. Some ash is discharged at this step to avoid the overloading of ash in the bed.

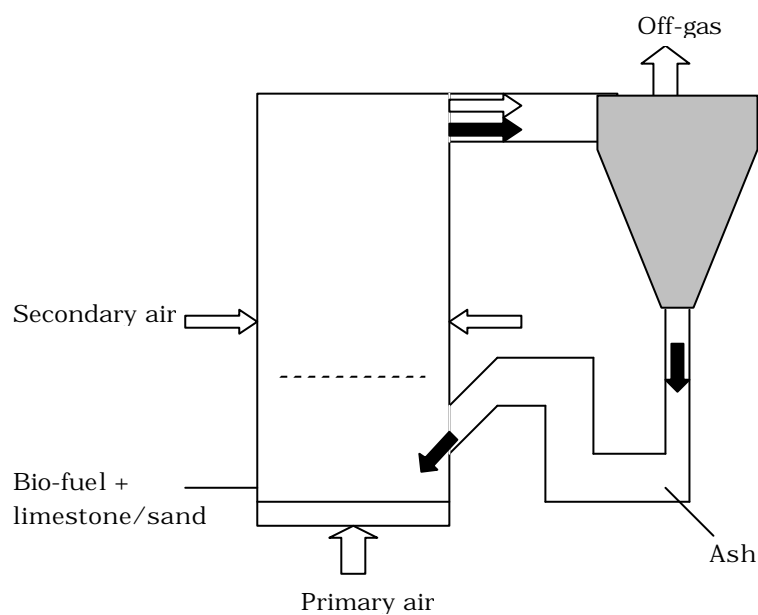


Figure 2: Circulating fluidized bed combustion boiler

2.3 Ash

The main part of ash, in this study, originates from the combustion of bio-fuel (mainly wood chips and bark). During combustion, most of the inorganic macro- and micro-nutrients and trace elements are retained in

ash. Wood ash consists of mineralogical part and char/soot, the latter caused by incomplete combustion.

The composition of the ash depends on several factors, e.g. the tree species, the soil conditions where the tree has grown, the combustion technique, the combustion temperature, and the method used when removing the ash from the boiler. Since combustion in a fluidized bed boiler is carried out in an inert bed consisting of sand/limestone, part of constituents of this material is added to the ash residues.

Some elements, particularly potassium and sodium, are volatilized at high combustion temperatures, thereby lowering their content in the bottom ash. The alkali metals and alkaline earth elements in wood ash are present mainly in the form of oxides, hydroxides, and carbonates, such as potassium oxide, calcium oxide, potassium carbonate and calcium carbonate. Biofuel ash may contain some toxic elements, which in some cases; the concentration can exceed the maximum recommended level issued by the Swedish National Forestry Board. Generally, bark contains a higher concentration of heavy metals than wood chips, thus the amount of bark may determine the level of heavy metals in ash.

3 Ash samples studied in this project

Bio-fuel ashes from two different combustion boilers were investigated: fly ash from a grate-fired combustion boiler, ASH A, and ash from a circulating fluidized bed combustion boiler, ASH B.

The bio-fuel used in the grate-fired combustion boiler consisted of: wood chips (softwood) ~50%, sawdust ~17%, bark ~18% and Salix ~15%, weight percents.

The bio-fuel used in the circulating fluidized bed combustion boiler consisted of: wood chips (softwood) ~82%, bark ~16%, saw dust ~1% and sludge from water treatment / fibre sludge ~1%, weight percents.

4 Experiments

This section deals mainly with the methodology of the experimental work developed and used in this project to investigate how different treatment methods influence the physical and leaching properties of ashes. It is also discussed the methodology to study the leaching mechanism of various elements from ash in aqueous media. Ash pellets were characterized by means of physical structure and strength. A number of leaching experiments in acidic solution were carried out on ash pellets and the influence of treatment techniques on physical structure of ash pellets and on the leaching properties of alkaline substances was investigated.

4.1 Treatment techniques

Three different techniques studied in this study, are: i) self-hardening, ii) thermal treatment, iii) hardening with binding material.

In the self-hardening technique, ash was mixed with de-ionized water with a weight ratio of 2.5:1 and stored at room temperature for about 6 days, during which, the hardening reactions occurred, see section 1.1. The pellets were then made of hardened ash.

In thermal treatment method, ash pellets were exposed to the thermal treatment in an electrical furnace from “Naberthem”, figure 3. The furnace heating up period was one hour and the sintering proceeded by three hours at temperatures of 800°C and 850°C for pellets in carbon dioxide atmosphere. Carbon dioxide was used to prevent calcination of carbonate salts.



Figure 3: “Naberthem” furnace for thermal treatment

In hardening with binding material, potassium silicate solution was added into ash to bind the particles together and transform ash to less soluble and denser matrix due to reactions similar to cement hardening reactions. Generally, potassium silicate solutions are prepared by dissolving potassium silicate glass in hot water. Potassium silicate glass is a colourless super-cooled melt of potassium carbonate and silicate sand. Although potassium silicate has properties and uses similar to those of sodium silicates, certain differences offer advantages in different uses, forming a basis for selecting potassium silicate in place of sodium silicate. One advantage is that it is potassium that is added to ash and not sodium. Potassium is an important nutrient which migrates quickly down to the lower level of soils after it is leached. Therefore, addition of potassium silicate increases the amount of potassium in ash pellets. The other advantage is that potassium silicate is not as sticky and tacky as sodium silicate, which makes it to be easier to use and handle.

In hardening with potassium silicate solution technique, three different weight ratios based on potassium content in ash, 30%, 16% and 1%, added to ash and the mixture was stored at room temperature for about 6 days to be hardened and then it was pelletized.

4.2 Pelletization

Cylindrical ash pellets were formed using a hydraulic hand press. The formed pellets weighed 1.3 ± 0.1 g and had a diameter of 10 mm and a length of 8.5mm, see figure 4. Forming ash pellets from ASH A was difficult due to presence of some soot/char which hindered binding particles to a dense pellet. Therefore, there were several cracks on pellets which made them fall apart. The other problem with ASH A was the electrostatic property and the low density of it which made it difficult to put it into the die (a device used for forming pellets). None of these difficulties were found for ASH B.

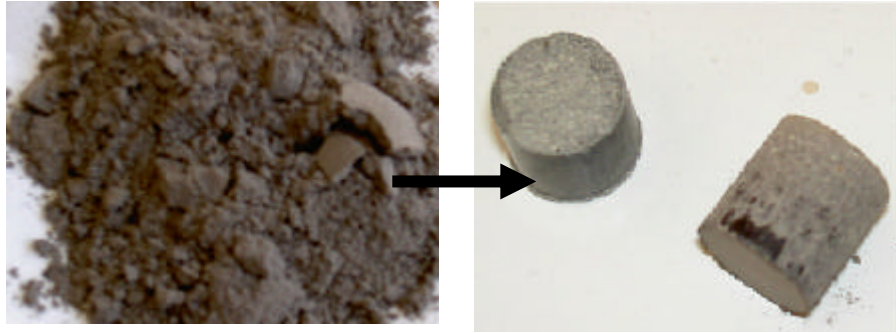


Figure 4: Ash pellets

4.3 Characterization method

Formed pellets were then characterized by means of strength, pore structure and leaching properties. This section deals with the experimental equipments used to measure characteristics of ash pellets both physically and chemically.

4.3.1 Strength measurements

The compression strength of the pellets was measured with equipment from “Etewe” called a “*Granulat Strength Testing Unit*”, figure 5. The strength was measured as the mechanical stress needed to break the pellet: the stress was calculated as the force divided by the cross-sectional area of the pellet. The force was measured with a strain gauge and the cross-sectional area is based on the measured diameter. The strength of the aggregates is an important measure in order to evaluate if and how the material can be transported and spread in the forest.

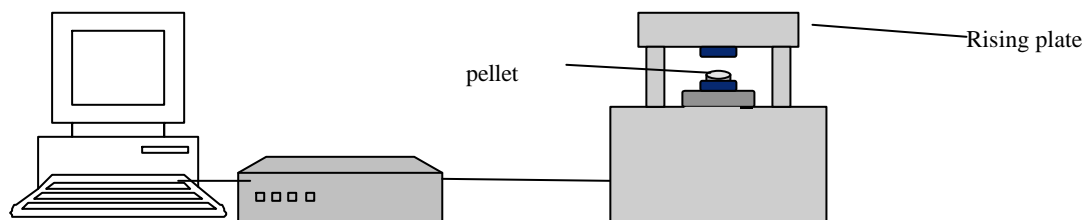


Figure 5: strength measurement equipment

4.3.2 Pore structure

The physical characteristics of pellets with significant influence on dissolution rate are; size of pellet, porosity, pore size distribution, size of agglomerate and crystal size. Porosity, pore size and pore size distribution are evaluated by many different methods.

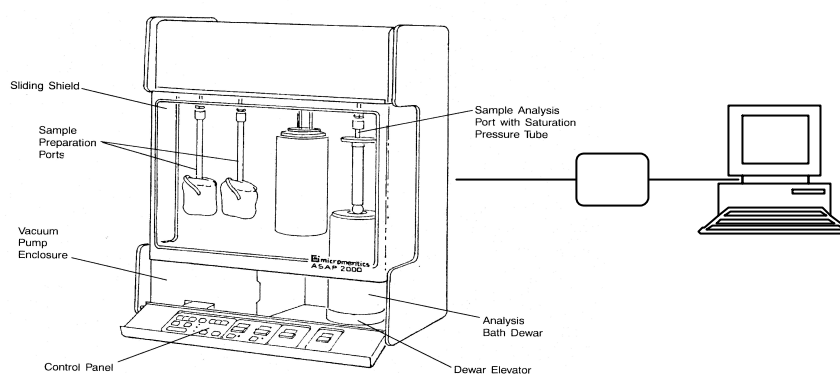


Figure 6: Specific surface area measurement

Mercury porosimetry and gas adsorption methods are commonly used. Mercury porosimetry can be applied to evaluate pore sizes from 1 mm to nanometers in diameter. Gas adsorption methods are applied to evaluate micropores (and partly mesopores) up to 200nm diameter. The later technique is non-destructive, safe and clean compared with mercury porosimetry. Size of agglomerate and crystal size, however, are often difficult to evaluate, but they can be characterized as a group by measuring the specific surface area, according to B.E.T. (*Brunauer-Emmet-Teller*) method. This method is the most common method of surface area calculation based on gas adsorption-desorption. In this study, the specific surface area of the samples was determined by measuring the nitrogen adsorbed on the samples in a “*Micromeritics ASAP 2010*”, which consists of an analyzer, a control module to enter analysis and report options, and an interface controller, which controls the analysis, figure 6.

4.3.3 Leaching properties

Within this study, long-term pH-static experiments for leaching pellets were performed. In a pH-stat experiment, acid is added to the reaction mixture to ensure that the pH is maintained at a predetermined value. A modified column test method has been used in this study, in which a single pellet is studied at a constant pH and temperature, Figure 7. By using this type of equipment, it is possible to make a more accurate evaluation than with a common column test or shaking test, because the risk of channelling in a column test is avoided and the pH is kept constant, which is not the case in shaking and batch tests.

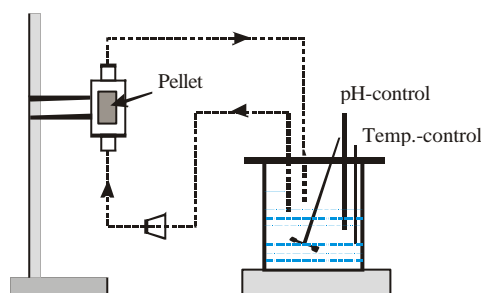


Figure 7: Experimental set-up for leaching tests

A pellet with known composition and physical properties was placed in a column. The inner volume of the column was 2.5 times the volume of a single pellet, i.e. the total free path for the flow was 1.5 times the volume of the pellet. The acidic solution of nitric acid was pumped upwards through the column with a constant flow rate of 90 ml/min. This flow rate provided a short residence time for the solution in the column (<1 s) i.e. the liquid media surrounding the pellet had a virtually constant pH.

A few leaching tests were performed using a weak acidic solution which simulated the soil solution. A normal soil solution of the top layer of the soil is very complex with a broad range of organic components that are derived from the degradation of organic matter. Both high molecular weight (HMW) and low molecular weight (LMW) acids are present in soil solution. In many investigations they are all lumped together and called dissolved organic carbon (DOC). However, there is reason to believe that the LMW acids are more active than the high molecular weight acids despite the fact that their concentration is lower. The LMW most commonly identified in soil solutions are citric, oxalic, shikimic, acetic, fumaric and formic acid. Among these acids, citric acid was chosen based on the fact that it is found in quite "high" concentrations in most of the

investigated soil profiles. Such simulated soil solution prepared by addition of citric acid to lithium chloride and the pH adjusted to 5.5 by addition of nitric acid.

A *Titroline alpha titration device* monitored and controlled the pH continuously. The acidic solution was allowed to circulate through the column for 6 days. Two replicates were used for each test. In this study, the pH level of 5.5 was considered to represent the acidified soil in the C horizon of the ABC soil (see figure 8). Samples were taken regularly and analyzed for metal ions using atomic absorption spectroscopy.

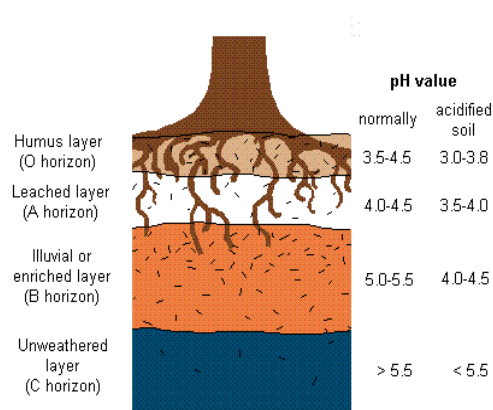


Figure 8: Typical pH values in podzol soils ⁷

4.3.4 Mineralogical characteristics

The mineralogy of ash refers to crystalline and amorphous phases. In order to investigate the different compounds present in the ash pellets, X-ray diffractometry was performed using a “D5000 Siemens X-Ray diffractometry”.

5 Theoretical study of leaching rate

In this chapter, the expressions and models used to theoretically describe the experimental data are presented. The first part describes the diffusive mass transfer model of leaching easily soluble species, e.g. potassium, from the pelletized material. In the second part, the focus is on modeling the leaching rate of limited soluble species, e.g. calcium. The influence of physical structure, i.e. the porosity of the pelletized material as well as pH, on the leaching behaviour of species is investigated.

5.1 Leaching rate model for potassium and sodium compounds

No thorough evaluation of the leaching mechanism (i.e. the mass transport mechanism and the kinetics of dissolution reaction) for easily soluble elements was found in the literature. However, some studies on the long-term leaching behaviour of solid waste from municipal solid waste incineration have been performed, in which, the leaching behaviour of easily soluble and less soluble elements were investigated to follow a diffusional mechanism according to *Fick's law* ⁸.

In a diffusional mass transfer model, two parameters characterize the intensity and dynamic of the leaching: initial leachable concentration and the effective diffusion coefficient, D_{eff} , of the species in the porous medium. The latter is highly influenced by the pore structure parameters, i.e. porosity.

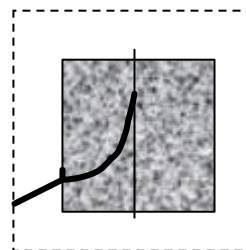


Figure 9: concentration profile

In this project, a diffusional mass transfer model was fitted to experimental data of K-leaching using the numerical software MATLAB version 6.5 in order to determine the values of the fitted parameter, D_{eff} . In the model, concentration profiles shown in figure 9, are described by a diffusional flux for the concentration profile within the pellet and a convective mass transfer for the outer concentration profile. Detailed model description can be found in our earlier study ⁹.

5.1.1 Estimation of mass transfer coefficient

To be able to calculate the outer mass transfer rate, the overall mass transfer coefficient needs to be calculated. To calculate overall mass transfer coefficient, empirical expressions were used for different hydrodynamics regime of flow around a single cylinder¹⁰. The hydrodynamic regime through which mass transfer takes place is divided into three regions, frontal, lateral and wake regions. The following empirical expressions were used for lateral and wake mass transfer, respectively:

$$Sh_l = \frac{k_l D_p}{D_{AB}} = 1.6 \left(\text{Re} \, Sc \left(\frac{D_e}{L} \right) j(a) \right)^{1/3} \quad [3]$$

where

$$j(a) = \frac{(1-a)}{a} \left[\frac{0.5 - \frac{a^2}{(1-a^2)} \ln\left(\frac{1}{a}\right)}{\frac{(1+a^2)}{(1-a^2)} \ln\left(\frac{1}{a}\right) - 1} \right] \quad [4]$$

$$Sh_w = \frac{k_w D_p}{D_{AB}} = 3.25 \text{Re}^{0.17} Sc^{1/3} \quad [5]$$

The expression for frontal mass transfer reported in literature, cannot describe the frontal mass transfer from pellets studied in our work due to different experimental set-up. Therefore, it was only the expressions for wake and lateral mass transfer that were applied for calculation of mass transfer coefficient at these regions, in this study.

The overall mass transfer coefficient is then calculated by:

$$K_{ovr} = \frac{k_f A_f + k_l A_l + k_w A_w}{A_f + A_l + A_w} \quad [6]$$

where k_l is calculated from Equation [3], k_w from Equation [5] and k_f is the frontal mass transfer coefficient, which is calculated by fitting the model to experimental data.

The diffusional model was then fitted to experimental data to calculate the values of effective diffusion coefficient for each pellet.

5.2 Leaching rate model for calcium compounds

Calcium and magnesium salts have a limited solubility in the chemical context of pores (calcium mainly presents in its carbonate/silicate form). In this case, a heterogeneous reaction was assumed to describe leaching rate of the limited soluble species. This model is based on the assumption that leaching Ca^{2+} and Mg^{2+} from the pellet is accomplished by a surface reaction on the pellet surface and the transfer of ions from the surface to the bulk and vice versa, i.e. the diffusive mass transport within the pellet has been neglected, see figure 10b.

5.2.1 Heterogeneous dissolution mechanism

One way to describe the dissolution of a solid material can be a heterogeneous reaction mechanism that depends on mass transfer and surface reaction. Mass transfer depends on physical factors like fluid flow and viscosity, while the reaction depends largely on chemistry and kinetics. When the bulk of the solution next to the solid is continuously renewed, the active chemical can be transported to the solid surface very quickly. For a porous solid matrix, the active chemical may diffuse into the pores and then react with the solid particles. The reaction zone then moves into the solid matrix see figure 10a.

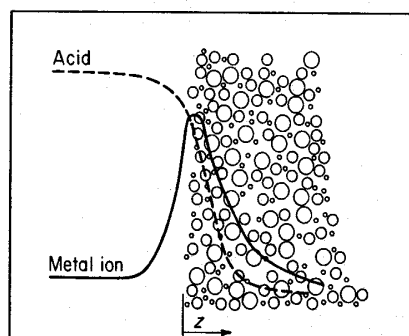


Figure 10a: Reaction zone within porous material

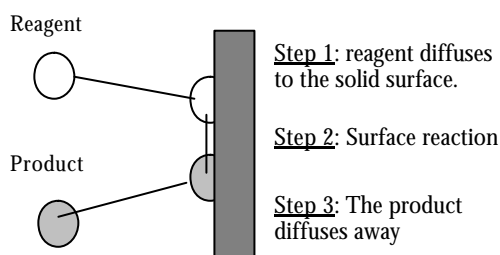


Figure 10b: Heterogeneous chemical reaction

When the reaction at the surface is much faster than the diffusion within the pores, the latter can be neglected. Therefore, it is only the surface reaction that may be considered, see figure 10b. In this case, the reagent is moving toward the surface, where it reacts, and the product ions are quickly swept back into the bulk solution, because the diffusion path is very short. To determine

the overall dissolution rate, the rate of both the mass transfer and the surface reaction steps, must be calculated.

5.2.2 Reactant mass transfer model

Since hydrogen ions are consumed by the reaction [9], there will be a concentration profile between the liquid bulk and the surface of the solid material. Thus the transport of hydrogen ions from the bulk to the surface can be described by:

$$N_{H^+} = K_{H^+} (C_{H_b^+} - C_{H_{surface}^+}) \quad [7]$$

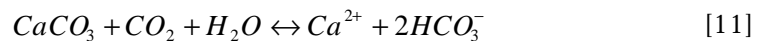
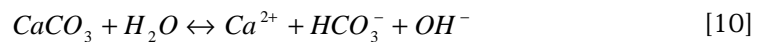
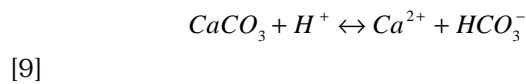
where N_{H^+} signifies the transport rate and is in moles per area per time and K_{H^+} represents the overall mass transfer coefficient, Equation [6]. If the transport of hydrogen ions is the rate-determining step in overall reaction rate, the overall leaching rate at steady-state equals the diffusion flux:

$$r_{overall} A = \frac{\partial m_{Ca^{2+}}}{\partial t} = K_{H^+} A (C_{H_b^+} - C_{H_{surface}^+}) \quad [8]$$

where A denotes to overall transfer area of pellet and $m_{Ca^{2+}}$ refers to moles of leached Ca^{2+} ion. If the reactions is assumed to be fast at the surface, $C_{H^+,surface}$ is approaching zero.

5.2.3 Surface reaction rate model

The major component in lime mud, hardened-ash and other solid residues is calcium carbonate. A number of studies have been conducted on calcite particle dissolution kinetics. The most important chemical reaction involved in dissolution mechanism of calcite, are:



A general equation for the dissolution rate based on reactions [9], [10] and [11] is expressed as ¹¹:

$$r_c = k_1 a_{H^+,s} + k_2 a_{H_2CO_3,s} + k_3 - k_4 a_{Ca^{2+},s} a_{CO_3^{2-},s} \quad [12]$$

where k_1 , k_2 , k_3 , and k_4 are the chemical rate constants and $a_{i,s}$ refers to the activity of the i^{th} aqueous species adjacent to the calcite surface. Detailed description in greater details is presented in our earlier study ¹⁰. In this project, a combined mass transfer and kinetic model for 5.5 pH level, was investigated to describe Ca-leaching rate from pellets.

5.2.4 Combined kinetic and reactant mass transfer model

To investigate the kinetic of calcium carbonate dissolution at pH level of about 5.5, a combined mass transfer and surface reaction kinetic was investigated. Reactions [9] and [10] are considered to be dominated in the dissolution mechanism.

$$r_{\text{overall}} A = (K_{H^+} A C_{H_b^+}) + (k_w A_{\text{act}}) \quad [13]$$

The first term in equation [13] describes the mass transfer of hydrogen ions, while the second term describes the kinetic of reaction [10]. It should be noted that in equation (13), A signifies the superficial mass transfer area, while A_{act} represents the active surface area for reaction, which is dependent to specific surface area and physical structure of pellets ¹⁰.

6 Results and discussion

In this chapter, the results from experimental work and the modeling are presented.

6.1 Chemical composition of ashes

Table 1 shows the analytical results of chemical composition of ASH A and ASH B, which were measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) methods.

The variation of composition of ASH A and ASH B is significant. For simplification in comparison, the results of chemical composition of ashes were normalized against calcium oxide content, as the major macro-element in both ASH A and ASH B. The higher content of Si and Al in ASH B is, probably, due to presence of sand that was used as bed material during combustion. Generally, sand contains a high content of Si and Al.

Calcium as the major element in ashes is one of the most significant alkaline components. Potassium, being an essential nutrient for trees, is also one of the most important components in bio-fuel ash. Comparing calcium (Ca) and potassium (K) content of ASH A with ASH B, it can be seen that ASH B contains less Ca and K. Magnesium (Mg) is a secondary macronutrient for the trees. Magnesium is the central atom of the chlorophyll molecule and is therefore important in photosynthesis. The content of Mg in both ASH A and ASH B is about the same.

The high level of sodium in ASH B is probably due to presence of water treatment plant/fibre sludge in the bio-fuel used, i.e. sodium content in sludge varies between 370-1460 mg/kg.

In addition to Ca, K, Mg and Na, phosphorous is also an important plant nutrient. The content of phosphorous is both ashes is about the same.

Most of the trace element contents of ASH B are lower than in ASH A, e.g. cadmium (Cd), barium (Ba), and arsenic (As). The cadmium content in ASH A is high, which is probably due to presence of salix in bio-fuel used in the grate-fired combustion boiler. However, in some cases, e.g. chromium (Cr) and lead (Pb), the concentration in ASH B is higher than in ASH A, which may be due to circulation of ash into the combustion chamber. It should be noted that the maximum cadmium and arsenic levels in bio-fuel ash

which is going to be recycled to forest soils, recommended by the Swedish National Forestry Board, is 30 and 20 mg/kg, respectively ⁶. The cadmium and arsenic levels of ASH A, studied in this project, exceed the issued limitation. Therefore, it is necessary to apply a suitable treatment technique, especially in case of ASH A, to reduce the toxic substances and it is necessary to monitor the quality of ash prior to recycling into the forests.

Table 1: Chemical composition of bio-fuel ashes

	ASH A	ASH B	Normalized	ASH A	ASH B
DC, %	99.5	100	DC, %	99.5	100
SiO ₂ , %DC	4.56	28	SiO ₂ / CaO	0.107	1.120
Al ₂ O ₃ , %DC	0.764	21.2	Al ₂ O ₃ / CaO	0.018	0.848
CaO, %DC	42.8	25	CaO / CaO	1.000	1.000
Fe ₂ O ₃ , %DC	0.376	3.52	Fe ₂ O ₃ / CaO	0.009	0.141
K ₂ O, %DC	13.8	4.43	K ₂ O / CaO	0.324	0.177
MgO, %DC	4.22	3	MgO / CaO	0.100	0.120
MnO, %DC	1.28	1.2	MnO / CaO	0.030	0.048
Na ₂ O, %DC	0.347	1.84	Na ₂ O / CaO	0.008	0.074
P ₂ O ₅ , %DC	3.75	2.29	P ₂ O ₅ / CaO	0.088	0.092
TiO ₂ , %DC	0.03	0.25	TiO ₂ / CaO	0.0007	0.010
Sum	71.9	90.7	Sum	1.680	3.628
LOI, %DC	21	2.8	LOI / CaO	0.490	0.112
As, mg/kg	32.6	14.1	As / CaO, mg/kg/%	0.762	0.564
Ba, mg/kg	2210	1650	Ba / CaO, mg/kg/%	51.63	66
Be, mg/kg	<0.6	2.7	Be / CaO, mg/kg/%	<0.014	0.108
Cd, mg/kg	45.1	7.5	Cd / CaO, mg/kg/%	1.054	0.300
Co, mg/kg	11	8.7	Co / CaO, mg/kg/%	0.257	0.348
Cr, mg/kg	20.3	95.4	Cr / CaO, mg/kg/%	0.474	3.816
Cu, mg/kg	130	258	Cu / CaO, mg/kg/%	3.037	10.32
Hg, mg/kg	<0.1	0.1	Hg / CaO, mg/kg/%	<0.002	0.004
La, mg/kg	<6	29.3	La / CaO, mg/kg/%	<0.140	1.172
Mo, mg/kg	<6	13.9	Mo / CaO, mg/kg/%	<0.140	0.556
Nb, mg/kg	<6	<6	Nb / CaO, mg/kg/%	<0.140	<0.240
Ni, mg/kg	24.8	34.9	Ni / CaO, mg/kg/%	0.580	1.396
Pb, mg/kg	40.5	129	Pb / CaO, mg/kg/%	0.946	5.160
S, mg/kg	19100	15200	S / CaO, mg/kg/%	446	608
Sc, mg/kg	<1	4	Sc / CaO, mg/kg/%	<0.023	0.160
Sn, mg/kg	<20	<20	Sn / CaO, mg/kg/%	<0.467	<0.8
Sr, mg/kg	867	667	Sr / CaO, mg/kg/%	20	27
V, mg/kg	8	36.2	V / CaO, mg/kg/%	0.187	1.448
W, mg/kg	<60	<60	W / CaO, mg/kg/%	<1.4	<2.4
Y, mg/kg	2.39	15.8	Y / CaO, mg/kg/%	0.056	0.632
Zn, mg/kg	4350	1900	Zn / CaO, mg/kg/%	102	76
Zr, mg/kg	9.9	325	Zr / CaO, mg/kg/%	0.231	13

6.2 Influence of treatment techniques on strength of ash pellets

Table 2 shows the results of strength measurements of ash pellets treated in different ways. The results of both ASH A and ASH B pellets are shown in Table 2. Mean values were calculated for each set of experimental conditions. As the results show, treatment technique has a significant influence on strength characteristics.

It should be kept in mind that there may be an interaction between treatment method and the properties of the ash (chemical as well as physical properties). Very little, is, however, known about this interaction.

Table 2: Strength property of ash pellets

ASH A	Strength, MPa	ASH B	Strength, MPa
Non-treated ash pellet	3.5 ± 0.05	Non-treated ash pellet	0.6 ± 0.15
Self-hardened pellet	0.66	Self-hardened pellet	3.3 ± 0.16
Thermal treated at 800°C, in CO ₂	4.4 ± 0.4	Thermal treated at 800°C, in CO ₂	1.2 ± 0.14
Thermal treated at 850°C, in CO ₂	5.18 ± 0.02	Thermal treated at 850°C, in CO ₂	1.5 ± 0.5
Hardened with K-Si solution, 30% K, w/w	1.42 ± 0.1	Hardened with K-Si solution, 30% K, w/w	NM
Hardened with K-Si solution, 16% K, w/w	NM	Hardened with K-Si solution, 16% K, w/w	NM
Hardened with K-Si solution, 1% K, w/w	2.1 ± 0.4	Hardened with K-Si solution, 1% K, w/w	2.5 ± 0.2

NM: Not-measured

The two investigated ashes behave different in some respects, i.e. thermal treatment could modify the strength property of ASH A, while self-hardening had the most significant effect on strength property for ASH B pellets. This may possibly be explained by chemical structure of constituents in ASH B. Due to high concentration of silica and aluminium in ASH B, most of the components might be bound to a silicate aluminates network. This silicate aluminates network was, also, detected using X-ray diffractometry analysis. Therefore, by making any treatment, this structure may be deformed. The lattice deformation may make the pellet become weaker and have a low strength property. It should also be pointed out that pellets with a weak structure may have potential problems; i.e. they may collapse easily and make a large available surface area for dissolution of alkaline metals. Therefore, it can be concluded that

depending on the chemical composition of ash, different treatment techniques may be applied in order to make a strong network structure for pellets.

6.3 Influence of treatment techniques on pore structure of ash pellets

Treatment techniques influence other physical characteristic of pellets. In this study, this was investigated by measuring the B.E.T. surface area which is a measure of size of agglomerates and crystals within pellet structure. This is an important measurement of how available surface area of agglomerates can be minimized and consequently the leaching properties of some elements can be controlled. Table 3 shows the results of specific surface area measurements for both ASH A and ASH B pellets treated in different ways. As the results show, the influence of different treatment techniques is significant in term of specific surface area. It has been shown that pelletization without any other treatment can reduce the specific surface area of the pellet by about 50%.

Table 3: B.E.T. Specific surface area of ash pellets

ASH A		B.E.T. m ² /g	ASH B		B.E.T. m ² /g
Non-pelletized ash		19.74	Non-pelletized ash		NM
Non-treated ash pellet		9.42	Non-treated ash pellet		8.6 ± 0.02
Self-hardened pellet		8.3 ± 0.04	Self-hardened pellet		16 ± 0.02
Thermal treated at 800°C, in CO ₂		0.15 ± 0.00	Thermal treated at 800°C, in CO ₂		3.3 ± 0.01
Thermal treated at 850°C, in CO ₂		0.06 ± 0.00	Thermal treated at 850°C, in CO ₂		4 ± 0.14
Hardened with K-Si solution, 30% K, w/w		14.48 ± 0.2	Hardened with K-Si solution, 30% K, w/w		NM
Hardened with K-Si solution, 16% K, w/w		NM	Hardened with K-Si solution, 16% K, w/w		NM
Hardened with K-Si solution, 1% K, w/w		7.46 ± 0.1	Hardened with K-Si solution, 1% K, w/w		14.5 ± 0.02

NM: Not-measured

Thermal treatment has the largest influence on minimizing the specific surface area characteristics of both ASH A and ASH B pellets. This can be explained by the sintering phenomena which occur at high temperature. During sintering, the particles are merged together and the total pore volume is decreased. After sintering, the particles and agglomerates

become significantly harder and stronger. For each material, the level of atomic motion can be related to melting temperature. Therefore, there is no single best sintering temperature appropriate for all materials. The smaller specific surface area for ASH A pellets compared with ASH B pellets might be due to different material in the chemical structure.

6.4 Influence of thermal treatment on trace elements minimization

An example of a bio-fuel with a high content of heavy metals is salix. Salix may contain a high content of cadmium¹⁴, which can be an explanation for high concentration of cadmium in ASH A studied in this project. The results show that thermal treatment of ASH A pellets can minimize the cadmium and arsenic content due to vaporization at high temperature. The compositional analysis of ASH A pellets before and after thermal treatment showed a significant decrease in arsenic, cadmium and chromic content. Arsenic content lowered by 90 %, cadmium content by 32 % and chromium by 27 %, weight percent. This minimization is due to high vapour pressure at high temperature. Vapour pressure of inorganic substance is calculated by the expression ¹³:

$$\log P = A + \frac{B}{T} + C \log T + DT^2 + ET^2 \quad [14]$$

where the constants vary for each substance, T is the temperature in K. If calculating vapour pressure of arsenic, cadmium and chromium using equation [14] at the same temperature, the vapour pressure of arsenic is higher than cadmium and chromium has the lowest vapour pressure. This may explain why the separation of arsenic is the most effective among the other two elements.

6.5 Influence of treatment techniques on leaching rate of potassium and calcium from ASH A pellets

From the results of leaching experiment, it was found that potassium has different leaching behaviour than calcium. Potassium was almost completely leached out from ASH A pellets within the period of time investigated, but calcium was partly leached out.

In order to investigate the influence of different treatment techniques on the leaching rate of potassium and calcium, seven experimental series were carried out on ASH A pellets in strong acidic solution (nitric acid).

6.5.1 Thermal treatment

Figures 11 and 12 show the decrease in leaching of potassium ions for ash pellets, which were exposed to thermal treatment compared with non-treated ash pellets. It should be noted that all experimental data of leaching of calcium and potassium are presented as the leached mass of calcium/potassium ions per initial mass of calcium/potassium in the pellets.

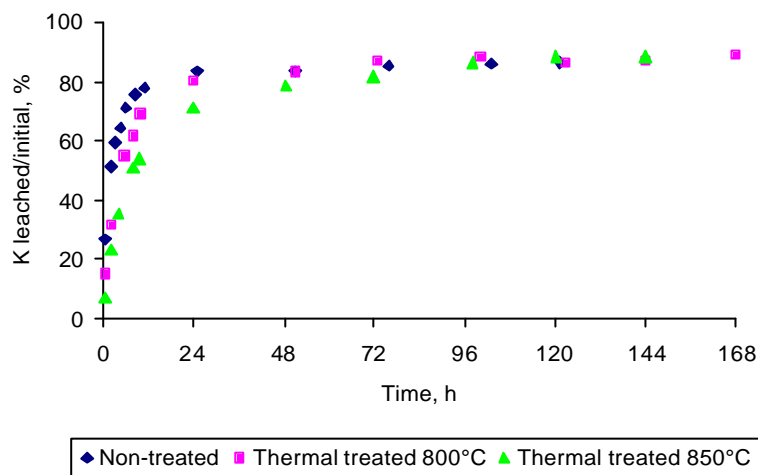


Figure 11: K-leaching data from ASH A pellets

As figures 11 and 12 show the higher the temperature is during the thermal treatment, the lower leaching rate of potassium. This may be explained by sintering that occurs during the heat treatment and decreases the porosity and, thus, the available surface area.

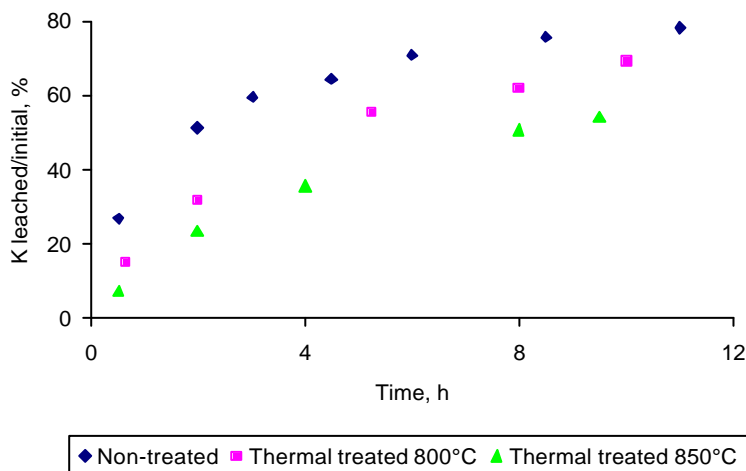


Figure 12: K-leaching data from ASH A pellets

Figure 13 shows the lowering of leaching rate of calcium. In figure 13, the thermal treated ash pellets are compared with the non-treated ash pellets. A significant influence of thermal treated on leaching rate of calcium can be seen. This can be explained by recarbonation of calcium oxide content of ash into calcium carbonate during thermal treatment. Calcium carbonate has lower solubility than calcium hydroxide; therefore, the leaching rate of calcium lowers from thermal treated ash pellet. Another explanation is the sintering phenomena that makes a more stable and dense structure of agglomerates during the treatment.

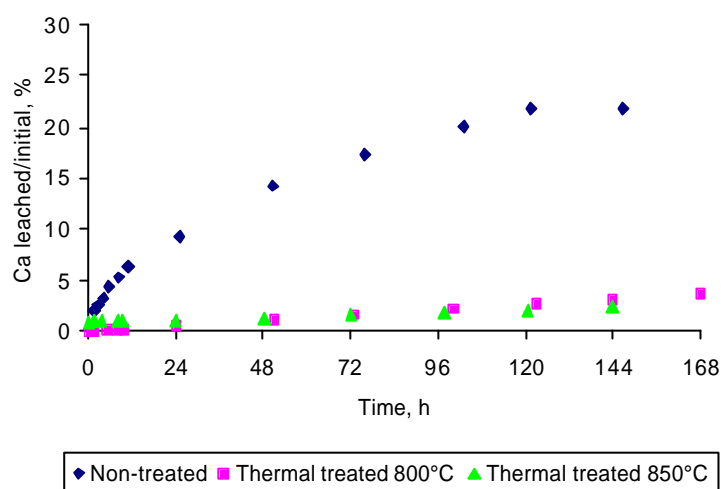


Figure 13: Ca-leaching data from ASH A pellets

6.5.2 Hardening with different concentration of binding material

ASH A pellets were treated by addition of binding material, potassium silicate solution. Three different concentration of potassium added to ash pellets which corresponded to 30%, 16% and 1% of weight fraction of initial potassium content of ash. The results of potassium and calcium leaching from bound ash pellet together with potassium silicate solution are shown in figures 14 and 15.

As the results show, large amount of added potassium silicate can lower the leaching rates of both potassium and calcium, while the small amount of added potassium solution (corresponds to 1 % of initial potassium in ash) enhances the leaching rate of potassium and calcium. This may be explained by slaking of calcium oxide to calcium hydroxide due to reaction

with water in the potassium silicate solution. Slaking of calcium oxide increases the available surface area, and therefore, the leaching of potassium and calcium increase.

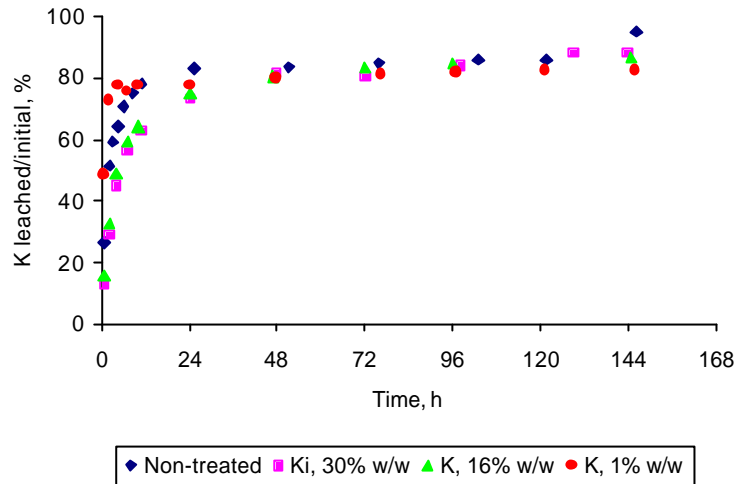


Figure 14: K-leaching data from ASH A pellets

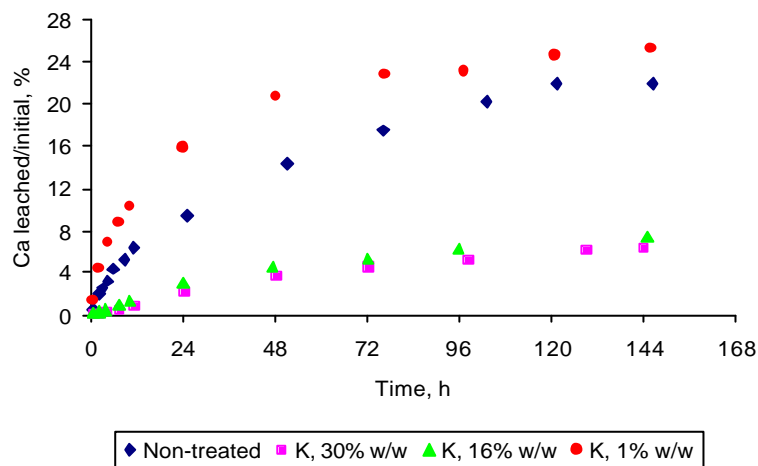


Figure 15: Ca-leaching data from ASH A pellets

However, from an economical point of view, it is not beneficial to add larger amount of potassium silicate in order to lower the leaching rates.

6.5.3 Self-hardening

ASH A was self-hardened by addition of about 25% (weight fraction) de-ionized water and stored at room temperature for about six days and then pelletized. The results of potassium and calcium leaching rates are shown

in figure 16 and 17. The results show a slightly increase in leaching rates of both potassium and calcium.

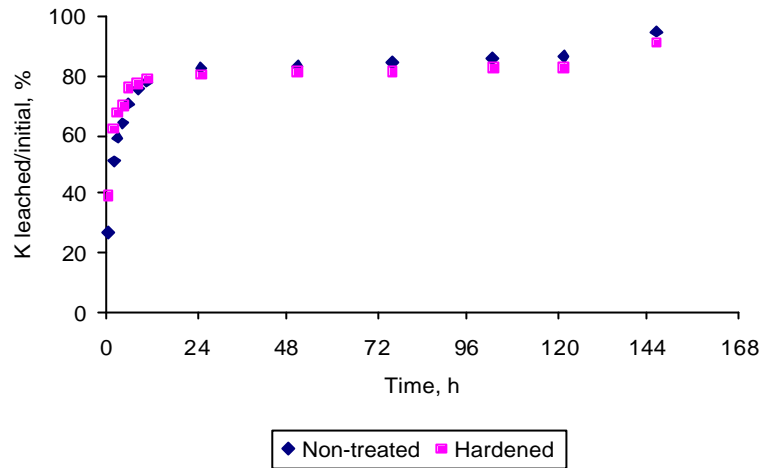


Figure 16: K-leaching data from ASH A pellets

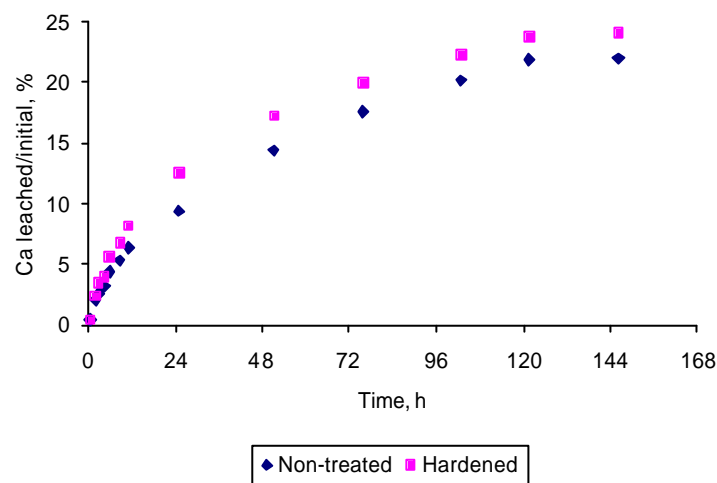


Figure 17: Ca-leaching data from ASH A pellets

6.6 Leaching tests in weak acid solution

Figures 18 and 19 show the leaching rates of potassium and calcium, respectively, for ASH A pellets treated at 800°C in carbon dioxide. The leaching experiments were performed in weak acidic solution, which could simulate the soil acid solution.

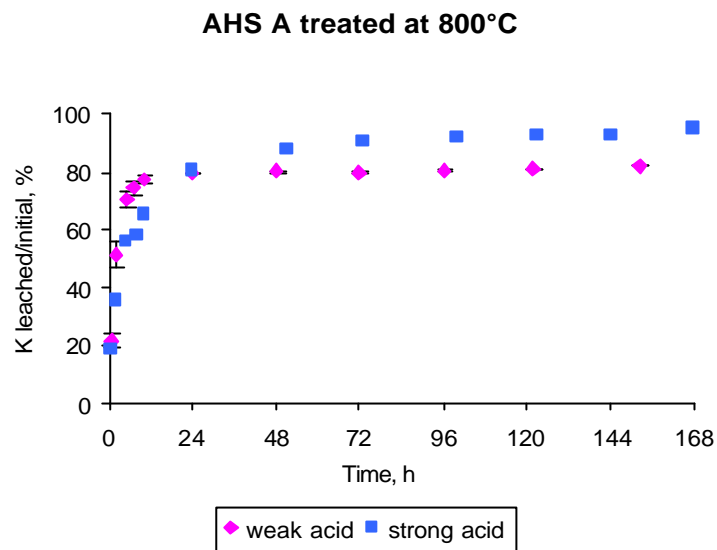


Figure 18: K-leaching data

Figure 18 shows that the leaching rate of potassium in both strong and weak acidic solution is about the same. It can also be seen that the amount of soluble potassium decreases by about 10 % when performing the leaching tests in weak acidic solution.

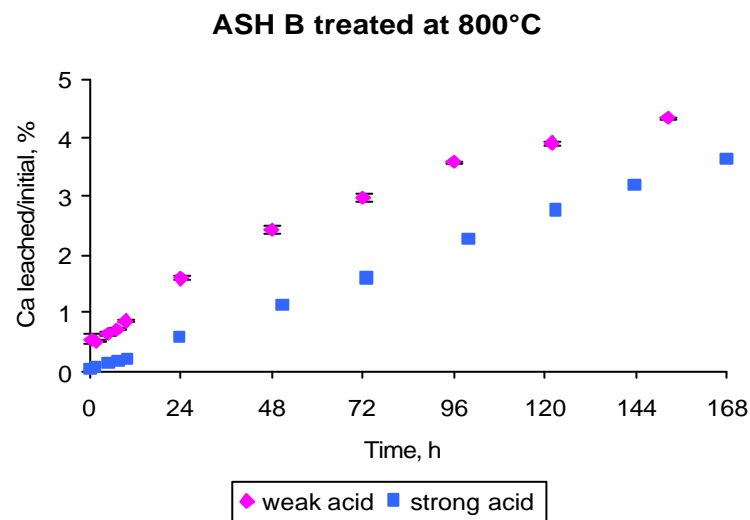


Figure 19: Ca-leaching data

The result of calcium leaching rate in weak acidic solution shows a fast dissolution just at the beginning and afterward it is higher than the leaching rate obtained in strong acidic solution. This higher leaching rate might be due to different dissolution mechanism or due to possible formation of some big calcium and citric acid chelate groups, which leach

out easier due to the larger driving force. However, more investigation needs to be done to understand the phenomena of leaching for both potassium and calcium in weak acid solution.

6.7 Influence of treatment techniques on leaching rates of potassium and calcium from ASH B pellets

In order to investigate the influence of different treatment techniques on the leaching rate of potassium from ASH B, five experimental series were carried out. The higher concentration of binding material (30 and 16%) was not examined, simply, because the cost will be far too high compared to the effect.

6.7.1 Thermal treatment

ASH B pellet were exposed to thermal treatments at 800°C and 850°C in carbon dioxide atmosphere. The results of potassium leaching rate from thermal treated and non/treated ASH B pellets are shown in figure 20.

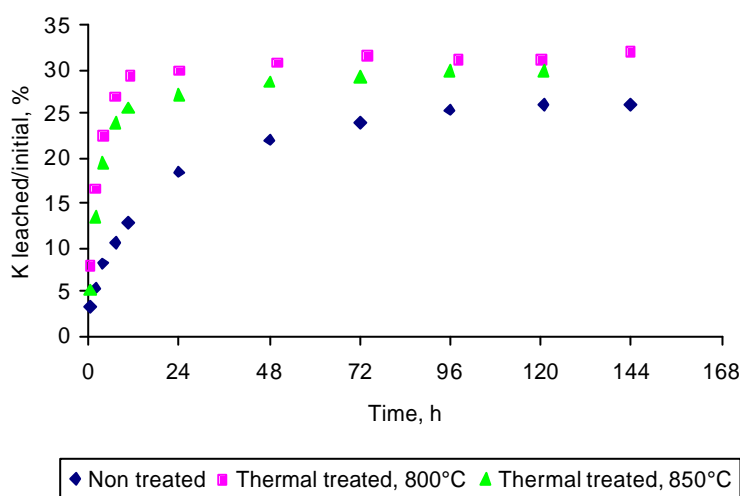


Figure 20: K-leaching data from ASH B pellets

It can be seen that thermal treatment has an inverse effect on leaching rate of potassium while it was expected that thermal treatment could lower the rate. It should be pointed out that ASH B has different chemical composition compared to ASH A, i.e. it consists of more silica and aluminium due to presence of sand and silicate material and therefore, the crystalline structure of material is different from ASH A. Therefore,

the higher leaching rate of potassium from ASH B might be explained by the difference in chemical composition and structure of ASH B. Another possible explanation can be the deformation of possible silicate matrix that potassium can be bound to it, and therefore, the lattice deformation cause a higher dissolution and leaching rate. However, this explanation should be studied more in detail.

Figure 21 shows that no significant influence on leaching rate of calcium can be achieved by thermal treatment. However, a slightly lower leaching rate of calcium from thermal treated ash pellets was obtained during the first 24 hours of leaching tests. X-ray diffractometry results showed that there is some calcium oxide in the non-treated ash. This can explain the slightly higher rate of calcium leaching from non-treated ash, while no calcium oxide was detected in ash pellets after the thermal treatment.

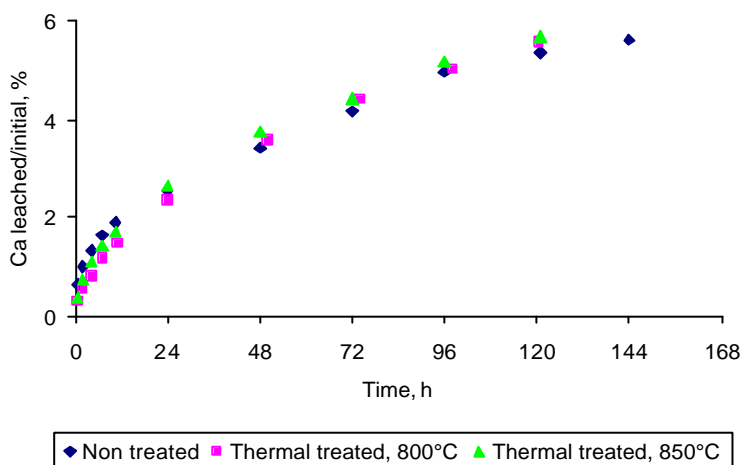


Figure 21: Ca-leaching data from ASH B pellets

6.7.2 Hardening with binding material

Potassium leaching tests results show that potassium content of ash pellets becomes more soluble by adding binding material to ash pellets, figure 22. The results of leaching tests show almost no difference in terms of calcium leaching rates for treated ash pellets compared with non-treated, figure 23.

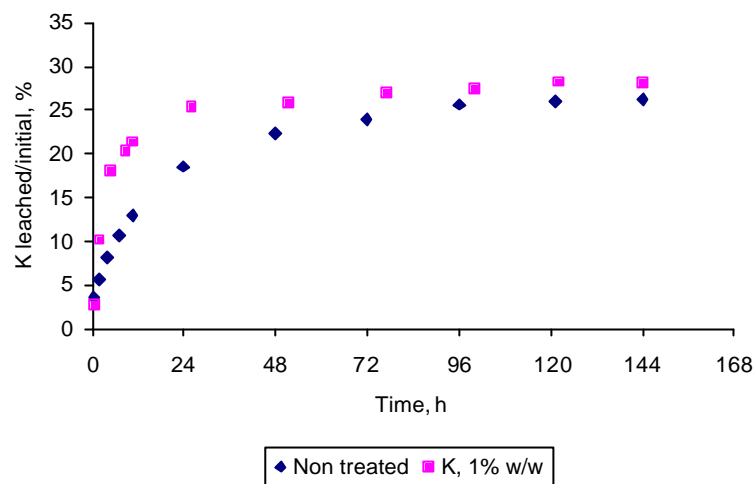


Figure 22: K-leaching data from ASH B pellets

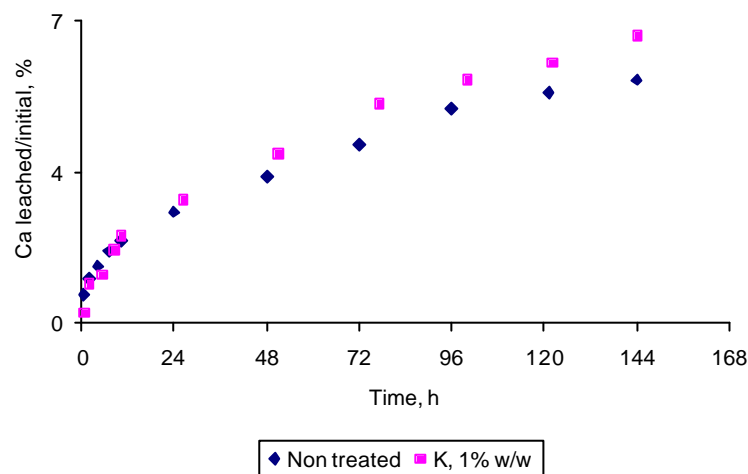


Figure 23: Ca-leaching data from ASH B pellets

6.7.3 Self-hardening

Figure 24 and 25 show the leaching rates of potassium and calcium from self-hardened pellet which are compared with non-treated ash pellets. Self-hardened ash pellets have higher leaching rate of potassium compared with non-treated ash pellet. This may be explained due to higher available surface area, i.e. B.E.T. of self-hardened ASH B pellet is about two times larger of B.E.T. of non-treated ASH B pellet. However, the calcium leaching was lowered during the first 48 hours for self-hardened ASH B pellet and after that time, it followed the same trend as non-treated ASH B pellet. Carbonation during hardening may explain this lowering in leaching rate of calcium.

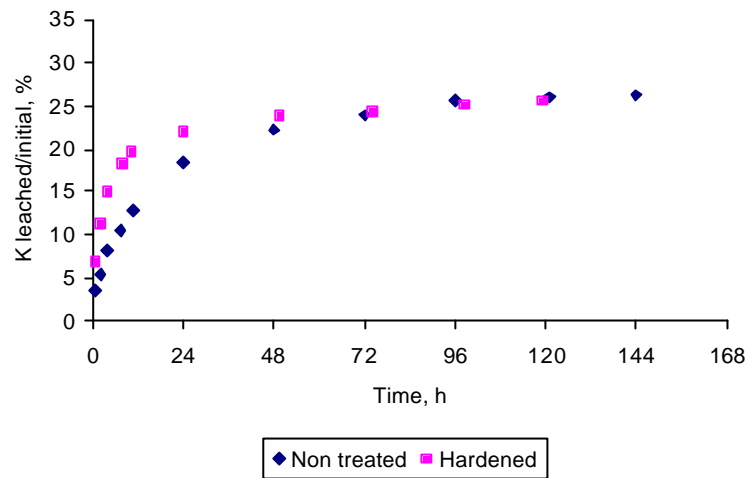


Figure 24: K-leaching data from ASH B pellets

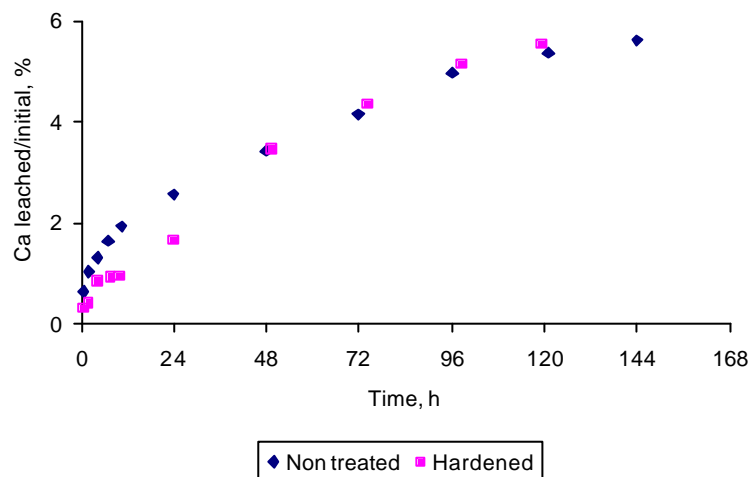


Figure 25: Ca-leaching data from ASH B pellets

6.8 Fitting potassium leaching rate model to experimental data

The mathematical model describing the potassium leaching rate was discussed in section 5.1. The result of fitting the model to experimental data is shown in figure 26 for some ash pellets. The solid lines represent the model and the symbols are experimental data. It can be seen that the model describes different trends of leaching rates well, both slow and steep slope. The effective diffusion coefficients of potassium ions, obtained from experimental data of potassium leaching rates, are given in Table 4.

Table 4: Calculated effective diffusion coefficient of potassium ions

Pellet	ASH A non-treated	ASH A treated at 850°C, CO ₂	ASH B non-treated	ASH B treated at 850°C, CO ₂
D _{eff} , m ² /s	13.4 · 10 ⁻¹¹	2.7 · 10 ⁻¹¹	1.8 · 10 ⁻¹¹	14.8 · 10 ⁻¹¹

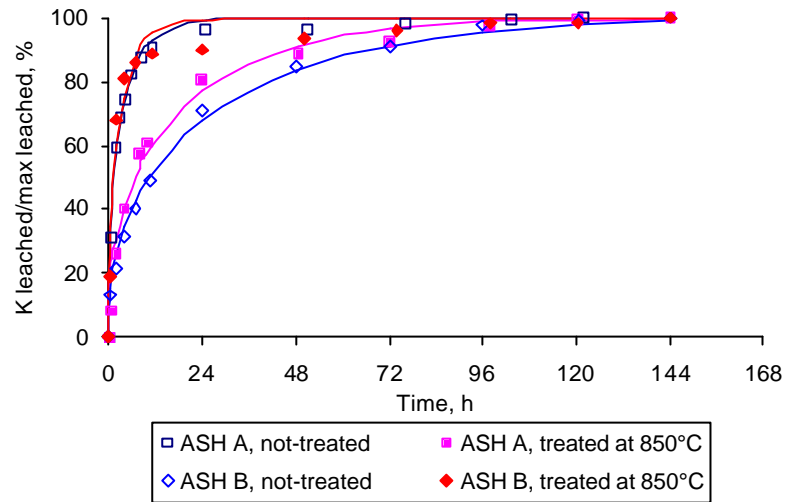


Figure 26: Fitting the potassium leaching rate model to experimental data

Computed effective diffusion coefficients are an indication of how easily the potassium ions are leached out, i.e. the smaller the value for effective diffusion coefficient is, more difficult to leach out.

6.9 Fitting calcium leaching rate model to experimental data

The combined reactant mass transfer and surface reaction kinetic model discussed in section 5.2.4, was fitted to experimental leaching data for ash pellets. In this work, the overall mass transfer coefficient, K_{ovr} , and the reaction rate constant, k_w , were determined when the model was fitted to experimental data. Figure 27 shows an example of how the combined mass transfer and kinetic model can describe the experimental leaching data of calcium. The solid lines represent the model and the symbols represent the experimental data. The fitted parameter of reaction rate constants, k_w is given in Table 5.

Table 5: Reaction rate constants

Pellet	ASH A, non-treated	ASH A, treated at 800°, CO ₂	AHS B, treated by K-Si addition	ASH B, treated at 800°C, CO ₂
$k_w, \text{ mol m}^{-2} \text{ s}^{-1}$	$1.7 \cdot 10^{-6}$	$1.9 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$	$1.96 \cdot 10^{-7}$

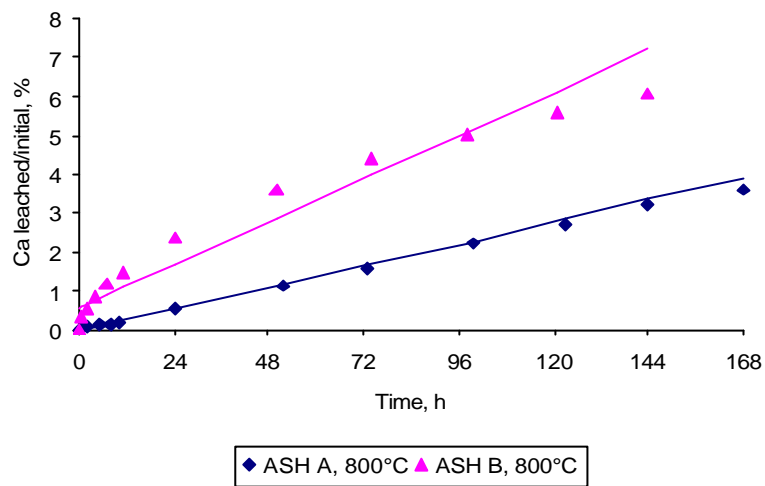


Figure 27: Modeling of calcium leaching rate

7 Recommendations and applications

In order to control the leaching of substances, ash agglomerates should be transformed into a stable and dense matrix. This is done via pelletization. The pelletized bio-fuel ash materials are not only easy to be handled, but also may have a slower leaching time due to the smaller available surface area.

In addition to pelletization, applying different treatment techniques can influence leaching characteristics of pelletized ash. To evaluate this, controlled leaching experiments need to be done. It should also be pointed out that the leaching test, performed in this study, is an accelerated leaching experiments and the amount of potassium and calcium leached out during six days experiments in this study, may be leached out during much longer (order of years) time in the forest.

The results of this study indicate that depending on chemical composition of ash material, treatment techniques may have a different influence on physical and chemical properties. Thermal treatment can be applied to lower the leaching rate of the components from ASH A, while it influences ASH B properties diversely. A positive aspect of thermal treatment is the minimization of cadmium and arsenic content.

It can also be concluded that self-hardening of ASH B can be applied as a technique to lower the calcium leaching rate of ash pellets, partly.

Since the leaching mechanism of soluble components, e.g. potassium, and limited soluble components, e.g. calcium, differ; it should be understood to be able to estimate the leaching rate. To predict the leaching rate of potassium mathematical modeling can be used based on the diffusional mass transfer of potassium ions that are leaching out from ash pellets. This model gives good estimation of prediction of leaching rate of potassium and sodium in long term. The numerical value of effective diffusion coefficient of potassium ions, can be correlated to the physical characteristics of pellets, i.e. the lower leaching rate may be achieved for pellets with smaller porosity. This depends on chemical composition of ash.

However, to interpret the leaching rate of calcium, the kinetic of reactions involved in dissolution of calcium compounds should be considered. The numerical values of reaction rate constant can also be an indication of how easily the calcium is leached out.

8 Suggestions for continued research

Within this project, the influence of three treatment methods on properties of ashes was studied. Self-hardening, addition of binding material and thermal treatment was evaluated as different alternatives. One can also study the influence of other alternative methods to lower the leaching rate of soluble components. Methods such as addition of cement to ash as binding material or thermal treatment of the mixture of binding material, e.g. potassium silicate, and ash and even thermal treatment of the mixture of ash and cement can be interesting to evaluate.

It is also valuable to study how the removal efficiency of heavy metals is modified as the temperature during the thermal treatment increases. However, it should be noticed that the temperature can not be so high, even though that at higher temperature the removal efficiencies of some heavy metals are higher¹². Therefore, the calcination reaction should be monitored in order to avoid the decomposition of calcium carbonate at higher temperature.

To develop the leaching model, correlations of porosity and leaching rate would be interesting to take into account. However, it should be noticed that porosity is a time dependent variable and it can not be considered as a constant parameter. This fact should be considered when correlating leaching rate to physical structure.

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