Conversion and leaching characteristics of biomass ashes during outdoor storage

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Introduction and objectives
In recent years, the promotion of energy production from biomass in Austria and the European Union has led to a strong increase in the amount of combustion residues, i.e. ashes. Finding ways to utilize these ashes in an environmentally and economically efficient manner is thus an important goal throughout Europe.

The utilization of the nutrient rich and rather heavy metal poor wood ash fractions (bottom and coarse fly ash) for fertilizing and soil improvement purposes is already implemented in Austria and several European countries (Sweden, Finland and Germany to name a few). The utilization path, however, implicates logistic challenges for many biomass plant operators, since the main part of the ash is often produced during the winter season whereas ash application usually takes place during warmer periods. Therefore, a logistic concept considering intermediate storage sites is necessary. As the ash has to be stored for several months, it seems reasonable to take advantage of the storage period and facilitate the self-hardening process by adding water [1]. The most important reaction of the hardening process is the transformation of CaO to Ca(OH)2 and further into CaCO3 which lowers the calcium leaching rate significantly and leads to a reduction of the pH-level. Alkaline shock effects on ground vegetation can thus be prevented.

In December 2009, a 4-year R&D-project was initiated in Austria with the focus on the development of innovative strategies of ash utilization in order to promote increased ash utilization. The improvement of ash logistics with a detailed investigation of intermediate outdoor storage of wood ashes in order to provide biomass plant operators with guidelines for proper intermediate ash storage is one of the main topics of this project.

Background
The intermediate outdoor storage of wood ash is especially relevant if the wood ash shall be used as a fertilizing and liming agent in agriculture and forestry. Usually the main part of the ash is often produced during the winter season whereas ash application on agricultural and forest soils is not allowed before spring. Since the storage capacities at biomass plants are limited, the ash produced during winter needs to be stored on storage areas outside the biomass plant premises.

If possible, the storage area should be located close to the agricultural or forest areas where the ash application is planned, in order to reduce transport routes and thus minimizing the lag time between filling of the spreading device and ash application [1].

Due to the chemical composition of wood ash, which contains up to up to 50 % mass fraction of CaO in the dry material, the addition of water facilitates the formation of Ca(OH)2 and further with airborne CO2 the formation of CaCO3 (carbonatation). This process changes the chemical and physical properties of the ash and leads to self-hardening. Practical experience from Sweden [1, 2, 3, 4], where self-hardenning is recommended for biomass ash utilization in forests since it reduces the pH-level (negative effects on ground vegetation caused by alkali burn can be prevented) as well as the dust formation of biomass ashes, shows that by adding a specific amount of water the carbonatation process can be improved. The carbonatation of biomass ashes also leads to a reduced leaching of Ca, thus a longer lasting liming effect of the ash can be achieved.

However, intermediate outdoor storage of ashes is only reasonable, if negative ecological effects like dust formation and leaching of heavy metals and other hazardous compounds can be avoided. Therefore, a detailed investigation of the ecological effects of intermediate outdoor storage is necessary. In addition, the optimum water mixing rates for self-hardening shall be determined.

Methodology
The research and development activities followed a three-step-approach:

1. Performance of laboratory tests with ash samples from different combustion technologies (fluidized and fixed bed combustion) over 16 weeks in order to determine the changes of the
ash quality and the leaching behavior depending on the duration of the storage and the amount of water added to the ash (performed 2010).

2. Performance of field tests with ashes from the same combustion technologies over 6 months. During the tests, leachate from the storage sites was sampled and analyzed in regular intervals. In addition, the ash itself was sampled and analyzed regularly (performed 2011).

3. Performance of additional laboratory tests with bottom ash from a grate furnace and coarse fly ash from a fluidized bed furnace over 16 weeks in order to determine the optimal water mixing rate for the ageing of ashes during storage (performed 2013).

The storage conditions applied in the respective tests are shown in Table 1.

**Table 1: Storage conditions applied in the individual storage tests**

<table>
<thead>
<tr>
<th>Ashes investigated</th>
<th>Storage period</th>
<th>Sampling</th>
<th>Water mixing rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st laboratory tests</td>
<td>16 weeks</td>
<td>24 weeks</td>
<td>2nd laboratory tests</td>
</tr>
<tr>
<td>Storage conditions</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
<td>Sprinkling with water at the beginning of the tests, regular wetting of the samples with a water sprayer</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
</tr>
<tr>
<td>Ashes investigated</td>
<td>2 piles per ash, each pile was sprinkled with water corresponding to 40 mm/m² of rainfall at the beginning of the storage period. Natural rainfall during storage</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
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<td>Ashes investigated</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
<td>Collection and sampling of leachate and rainwater</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
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</tr>
<tr>
<td>Ashes investigated</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
<td>After 1, 2, 4, 8, 12, 16, 20 and 24 weeks, sampling of the outside layer and the inner zone; Collection and sampling of leachate and rainwater as a reference</td>
<td>Ashes 1) to 3) were delivered dry, ash-4) was delivered in wet condition (24% water mass fraction), wet basis.</td>
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</tr>
</tbody>
</table>

**Laboratory tests**

The purpose of the laboratory tests performed in 2010 was the investigation of the conversion and leaching behavior of different wood ash fractions (bottom ash and mixture of bottom ash and coarse fly ash from a grate furnace (GF) fired with bark and wood chips, boiler fly ash from a bubbling fluidized bed furnace (BFBF) fired with wood chips, fine bottom ash from a circulating fluidized bed furnace (CFBF) fired with forest residues under different storage conditions (dry/wet, open or in absence of air). The results of the laboratory tests shall also be used to pre-evaluate the ecological impact of ash storage (leaching behavior) as well as its impact on the quality of the ash stored (self-hardening) and provide the basis for the design of the outdoor storage tests which were performed from April to October 2011.

At the beginning of the storage test the four ash fractions selected (original samples) were physically (particle size distribution) and chemically (water mass fraction, CaO mass fraction, TIC mass fraction, pH-level, electrical conductivity, chemical composition, leaching ratio of major elements as well as heavy metals), characterized.

In detail, the following elements were analyzed in the solid matter: Si, Ca, Mg, K, Na, P, Al, Fe, Mn, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn, S, Cl. The following elements were analyzed in the leachate: Cr (VI), Cl, S, Si, Ca, Mg, K, Na, P, Al, Fe, Mn, Cu, Zn, Co, Mo, Ni, Cr, Pb and Cd.

In addition, the main crystalline components were analyzed using X-ray diffraction. For each ash fraction dry and wet samples were stored over a period of 16 weeks. The amount of water added was estimated based on the experience of earlier tests performed in Sweden (the amount of water required for hardening was estimated based on the content of CaO and other components that may take up water) as well as on the results of preliminary tests performed prior to the lab-test. Based on these findings two different water mixing rates were defined for the two ash fractions from the grate furnace and the boiler fly ash from the BFBF. Since the content of CaO and other components that can form hydrates of the fine bottom ash from a CFBF is due to the dilution with bed material (SiO₂) very low, only one water mixing rate was determined. In order to avoid the drying of the wet samples, water was added regularly over the storage period. In addition, for two ash fractions (bottom ash from a GF and boiler fly ash from a BFBF) also airtight samples were prepared in order to investigate the storage behavior of wood ashes in absence of air i.e. CO₂.
Over the storage period of 16 weeks, 5 sampling dates (after 1, 2, 4, 8 and 16 weeks of storage) were selected. For each sampling date, a total set of ash samples was prepared. Each sample was stored in a plastic box (capacity approx. 5 l) and weighed. On each sampling date, one set of samples was weighed again, collected and analyzed (except for the particle size distribution, the CaO mass fraction, the chemical composition of the solid matter and X-ray diffraction, all the samples were subject to the same analyses like the original samples). After analysis the samples were not used for later sampling dates. This way, the evolution of the individual parameters analyzed over time could be observed. Moreover, the samples collected after 8 weeks storage were also subject to X-ray diffraction analysis in order to evaluate the changes in the crystalline components during storage. Besides the chemical analysis, a comprehensive photo documentation of the samples was performed and the climatic conditions in the storage room (rel. humidity and temperature) were monitored.

Field tests
The purpose of the field tests performed in 2011 was the investigation of the conversion and leaching behaviour of different wood ash fractions under outdoor conditions. Three (bottom ash and mixture of bottom ash and coarse fly ash from grate furnace as well as coarse fly ash from a bubbling fluidized bed furnace) of the 4 ashes used in the laboratory tests were also used in the outdoor storage tests. These three fractions were delivered in dry condition to the storage site. In addition, bottom ash from a grate furnace (fired with bark) with a wet ash removal system was used, which was delivered with a water mass fraction of 24% (wet basis). Each of the four ash fractions was stored in three piles (about 2 tons of ash per pile), respectively. Each pile was equipped with a separate leachate collecting system. In addition a similar system was installed and left empty in order to collect rainfall. An overview of the storage area is given in Figure 1.

Figure 1: Overview over the storage area for the field test
At the beginning of the storage test the four ash fractions selected (original samples) were physically (particle size distribution) and chemically (water mass fraction, CaO mass fraction, TIC mass fraction, pH-level, electrical conductivity, chemical composition, leaching ratio of major elements as well as heavy metals), characterized (see description of the laboratory tests for details regarding elements analyzed). In addition, the main crystalline components were analyzed using X-ray diffraction. At the beginning of the tests each pile was sprinkled in order to avoid wind-blown dispersal of dust. The amount of water added was equal to rainfall of 40 mm/m². The initial water mass fractions (wet basis) of the ashes were between 0.5 and 2.5% for the dry ashes and about 24% for the wet ash. After that no water other than the natural rainfall (some 250 mm/m² over 24 weeks) was added during storage.

Over the storage period of 24 weeks, 8 sampling dates (after 1, 2, 4, 8, 12, 16, 20 and 24 weeks of storage) were selected. On each sampling date, two samples (one sample of the outside layer and one drill core sample of the inner zone of the pile) were taken from each pile and analyzed for water mass fraction, TIC mass fraction, pH-level and electrical conductivity. In addition, the leaching ratio of major elements and heavy metals was analysed after 2, 8 and 24 weeks. This way, the evolution of the individual parameters analyzed over time could be observed. Moreover, the samples collected after 8 and 24 weeks storage were also subject to X-ray diffraction analysis in order to evaluate the changes in the crystalline components during storage. The leachates collected at the site from each pile were also sampled after 1, 2, 4, 8, 12, 16, 20, and 24 weeks and analyzed on Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, V, W, Zn, pH, EC, DOC (dissolved organic carbon), BrO₃⁻, Cl⁻, F⁻, NO₂⁻, NO₃⁻ and SO₄²⁻.
Formation of new components
wet basis; inorganic carbon; w.b. circulating fluidised bed furnace

Explanations:
Table
The chemical composition of the ashes used in the storage tests are shown in Table 2. Besides the chemical analysis, a comprehensive photo documentation of the samples was performed in order to evaluate the changes in the crystalline components during storage.

Two different ash fractions (bottom ash from a grate furnace and coarse fly ash from a bubbling fluidized bed boiler) were stored dry and with three different water mixing rates. The bottom ash featured a Ca mass fraction of 14.0% (dry basis), leading to a water mass fraction from 4.5 to 7.3% (wet basis). The original samples were analyzed on the same parameters as the original samples of the first laboratory storage tests. Over the storage period of 16 weeks, 4 sampling dates (after 1, 4, 8 and 16 weeks of storage) were selected. The procedure regarding sample preparation, storage and sampling was similar to the first laboratory test. Except for the particle size distribution, the CaO mass fraction, the chemical composition of the solid matter and X-ray diffraction, all the samples were subject to the same analyses like the original samples. After analysis the samples were not used for later sampling dates. This way, the evolution of the individual parameters analyzed over time could be observed. Moreover, the samples collected after 8 and 16 weeks storage were also subject to X-ray diffraction analysis in order to evaluate the changes in the crystalline components during storage.

Besides the chemical analysis, a comprehensive photo documentation of the samples was performed and the climatic conditions in the storage room (rel. humidity, temperature, rainfall) were monitored.

**Additional laboratory tests**

The purpose of the additional laboratory tests performed in 2013 was the determination of the optimal water mixing rate for ash ageing during storage. The general test layout was similar to the layout of the first laboratory test. Two different ash fractions (bottom ash from a grate furnace and coarse fly ash from a bubbling fluidized bed boiler) were stored dry and with three different water mixing rates. The water mixing rate was calculated based on the theoretical water demand under the assumption that all of the Ca is bound as CaO in the ash at the beginning of the storage test. In addition, water mixing rates 25% higher and 25% lower were also applied. The bottom ash featured a Ca mass fraction of 31.7% (dry basis), leading to a water mass fraction from 9.7 to 15.1% (wet basis), and the coarse fly ash featured a Ca mass fraction of 14.0% (dry basis), leading to a water mass fraction from 4.5 to 7.3% (wet basis).

**Ashes used in the storage tests**
The chemical composition of the ashes used in the storage tests are shown in Table 2.

**Table 2:** Chemical composition of the ashes used in the individual storage tests

<table>
<thead>
<tr>
<th>Mass fraction in solid phase</th>
<th>1st lab storage tests</th>
<th>Field storage tests</th>
<th>2nd lab storage tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bottom ash from a GF</td>
<td>Boiler fly ash from a BFBF</td>
<td>Bottom ash from a GF</td>
</tr>
<tr>
<td>Water mass fraction [%] w.b.</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>pH value</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>TOC (mg/kg) d.b.</td>
<td>&lt; 500</td>
<td>2,340</td>
<td>6,290</td>
</tr>
<tr>
<td>TIC (mg/kg) d.b.</td>
<td>3,300</td>
<td>4,540</td>
<td>24,300</td>
</tr>
<tr>
<td>Cl (mg/kg) d.b.</td>
<td>96</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Na (mg/kg) d.b.</td>
<td>630</td>
<td>1,317</td>
<td>2,740</td>
</tr>
<tr>
<td>Ca (mg/kg) d.b.</td>
<td>277,000</td>
<td>277,400</td>
<td>155,000</td>
</tr>
<tr>
<td>K (mg/kg) d.b.</td>
<td>412,000</td>
<td>42,520</td>
<td>63,200</td>
</tr>
<tr>
<td>Mg (mg/kg) d.b.</td>
<td>44,400</td>
<td>45,190</td>
<td>11,700</td>
</tr>
<tr>
<td>Si (mg/kg) d.b.</td>
<td>4,786</td>
<td>4,786</td>
<td>3,150</td>
</tr>
<tr>
<td>Al (mg/kg) d.b.</td>
<td>117,000</td>
<td>118,089</td>
<td>215,000</td>
</tr>
<tr>
<td>Fe (mg/kg) d.b.</td>
<td>1,5</td>
<td>1,5</td>
<td>1,5</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>4,1</td>
<td>4,1</td>
<td>4,1</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Cr (%)</td>
<td>192.0</td>
<td>196.4</td>
<td>20.0</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>87</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>114.0</td>
<td>116.4</td>
<td>76.1</td>
</tr>
<tr>
<td>Ni (%)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Pb (%)</td>
<td>57</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>Zn (%)</td>
<td>54.7</td>
<td>55.7</td>
<td>15.1</td>
</tr>
<tr>
<td>Co (%)</td>
<td>94.0</td>
<td>381.9</td>
<td>198.0</td>
</tr>
</tbody>
</table>

All of the ashes used meet the limiting values of the Austrian Guideline for proper utilization of biomass ashes in agricultural and forest soils [6].

**Results and discussion**

Formation of new components
The results of both laboratory tests and the field test showed that the self-hardening process over the first 16 weeks of storage is mainly driven by the hydration of CaO with water to Ca(OH)₂, while the carbonatation of Ca(OH)₂ with CO₂ to CaCO₃ plays only a minor role. Only the outside layers of the
piles of bottom ashes and the mixture of bottom ashes und coarse fly ashes from grate furnaces showed a significant increase of the TIC mass fraction (dry basis) over 24 weeks outdoor storage. Most of the hydration reaction took place within the first week of storage, since after week 1 only a minor increase in the mass of the samples could be observed for most of the samples investigated during the laboratory tests (the change of the mass of the piles during the field test was not possible). The formation of Mg(OH)$_2$ from MgO and H$_2$O could not be observed in significant amounts. In addition, the formation of ettringite or gypsum was not observed in significant amounts. This was expected, since the ash fractions used in the laboratory storage tests featured rather low S mass fractions (between 0.06 and 0.3%, dry basis).

**Mass increase due to water uptake**

All of the samples analyzed during the two laboratory tests showed a mass increase over the storage period. The main share of the mass increase was observed within the first week, which is a strong indication that the mass increase is mainly driven by the reaction of CaO with H$_2$O to form Ca(OH)$_2$. The overall increase of the dry mass amounts to 8 to 16% (dry basis) for ashes from grate ashes and 2 to 6% (dry basis) for ashes from fluidized bed boilers over a 16 weeks storage period. The higher mass increase of the ashes from grate furnaces can be linked with the higher CaO content of these ashes compared to the ashes from the bubbling and circulating fluidized bed furnaces.

**Evolution of the pH-level and the electric conductivity**

During both laboratory storage tests, the pH-level slightly decreased after 4 to 8 weeks storage independent of ash type and storage conditions (wet or dry). Thereafter, the pH-level remained rather constant (first laboratory tests with higher water mass fractions) or rose again up to the initial pH-level (second laboratory tests with lower water mass fractions) until the end of the test period after 16 weeks. The pH-values at the end of the storage period were around or slightly below 13.0 for the two ash fractions from the GF and the boiler fly ash from the BFBF. The pH-level of the ash from the CFBF was around 12.0 after 16 weeks. Regarding the initial water content of the ash samples, no significant differences in the evolution of the pH-level was observed between different water contents and between wet and dry samples.

The results from the field test showed significant differences between the outside layer and the inner zone. The pH-level of the outside layer decreased by 1 to more than 2 points and reached values between 12 (ashes from GF) and 10.3 (coarse fly ash from a BFBF). The pH-levels of the inner zone showed only small decreases over the 24 weeks storage with pH-levels around 12.5 at the end of the 24 weeks storage period.

The electrical conductivity (EC), on the contrary, showed a small increase over 16 weeks of storage during the first laboratory storage test for all wet ashes except the fine bottom ash from the CFCF, which didn’t show a clear trend over 16 weeks. The dry samples of the bottom ash and the mixture of bottom ash and coarse fly ash remained rather constant, the dry sample of the boiler fly ash from a BFBF showed a slight increase in the EC. During the second laboratory storage tests, where the ashes featured lower water mass fractions compared to the first laboratory storage test, the EC decreased over time.

Similar to the pH-level, the evolution of the electrical conductivity over time showed significant differences between the outside layer and the inner zone of the piles. The EC of the outside layer significantly decreased over the 24 weeks storage period, while the EC of the inner zone showed a small increase (bottom ash from a grate furnace) or remained rather constant (all other ashes investigated).

**Leaching behaviour and ecological impact**

The results of the leaching tests showed for both laboratory tests a decrease of the Ca and Mg leaching rates and an increase of the K and Na leaching rates for all wet samples over time compared to the original samples at the beginning of the storage test. Most of the dry samples showed the same trend but with smaller changes. These results correspond to findings from Swedish research projects performed earlier [2, 3]. However, a significant difference between the magnitude of the increase of the K leaching rate was observed between the first and second laboratory storage tests. While the leaching rate of K increased by 150% (coarse fly ash from a BFBF) to 400% (bottom ash from a GF) in the first lab test with ashes with higher water mass fractions, the K leaching rate only increased by 50% (coarse fly ash from a BFBF) to 80% (bottom ash from a GF) in the second lab test with ashes with the lower water mass fractions.

The leaching rate of Ca observed during the field storage tests showed comparable trends compared to the lab tests. Similar to the evolution of the pH-level and the EC, the Ca leaching rates measured for the samples from the outside layer of the piles were lower compared to the samples taken from the inner zone of the piles. The Mg leaching rates were for all samples very low or below the detection
limit of the analysis method applied, so no clear trend could be observed. The K and Na leaching rates of the samples taken from the field test showed the same behaviour over the storage period. The parallel evolution of the leaching rates of K and Na were observed for all samples at all three tests, so it is obvious that the leaching behaviours of K and Na follow the same mechanisms, which were described in [2] and [3]. However, compared to the trend observed at the laboratory tests, the increase of the leaching rates of K and Na was only moderate or even negligible. Like for the Ca leaching rates, the K and Na leaching rates observed in the samples form the outside layer of the piles were lower compared to the leaching rates measured for samples from the inner zone of the piles.

The contents of Cr and Cr(VI) in the leachate showed for both laboratory tests an increasing trend over the storage period, while the Cr and Cr(VI) leaching rates of the samples taken from the field test remained rather constant. The leaching rates of Ba showed an influence of the water mass fraction in the ashes. While the Ba leaching rates of the samples taken from the first laboratory test (ashes with rather high water mass fractions) showed no clear trend, the Ba leaching rates of the samples taken from the second laboratory test (ashes with low water mass fractions) showed a significant decrease over the 16 weeks storage time. The samples taken from the field test, which also featured a rather low water mass fraction, also showed decreasing Ba leaching rates over the storage period. The leaching behaviour of other elements did not show a clear trend over time (Cl, S) or could not be determined in detail (Al, As, Cd, Co, Cu, Fe, Mn, Mo, Ni, P, Pb, Si, V, Zn) since the content of these elements in the leachates was below the detection limit of the analysis methods applied.

Regarding the ecological impact of ash storage, the results of the leaching tests from the ash samples show that for some parameters (especially Ba, the pH-level and the electric conductivity, but for some samples also Cr and Cr VI) the limiting values of the Austrian Landfill Ordinance are exceeded for certain landfill types.

For a more comprehensive evaluation the results of the analysis of the leachate collected during the outdoor storage test have to be considered. The results were compared with the limiting values of different Austrian ordinances and European directives (ordinance/directive for drinking water, ordinances for waste water and leachate from landfills). Compared to the collected rainwater, the leachate from the ash fractions which were delivered in dry condition to the storage site partly exceeded the limiting values for As, SO$_4^{2-}$ and pH-level (drinking water ordinance/directive only) as well as B, Cr, NO$_2^-$ and electrical conductivity (waste water and leachate ordinances). The leachates from these three ash fractions collected at the end of the storage period all featured values below the limiting values of the drinking water ordinance/directive.

The leachate collected from the three piles with wet bottom ash from a grate furnace featured values for Na and SO$_4^{2-}$ (drinking water guideline only) as well as As, B, Cr, P, Pb, pH-level, EC and NO$_2^-$ (waste water and leachate guidelines) which exceeded existing limiting values. At the end of the storage period, still some limiting values were exceeded. Obviously, the handling and storage of the ash at the biomass combustion plant in wet condition increases the solubility of several elements and anions.

In order to avoid any ecological impact the ashes should either be stored on landfills (in designated separated areas) or covered with air permeable but water impermeable membranes (similar to those used during composting).

**Influence of water mixing rates on physical properties**

Regarding the physical properties the ashes from the grate furnace showed a significant impact of the water mixing rate on the hardness of the stored samples. Based on the results of the two laboratory tests the samples with the higher water mixing rates (water mass fractions 20% to 27%, wet material) were quite difficult to break up after storage, while ashes with lower water mixing rates (water mass fractions 10 to 15%, wet material) could be easily broken up and remained in a rather flowable form. As a consequence, ashes stored with low water mixing rates need no other processing than screening (in order to provide the ash in a spreadable particle size below 1.5 cm) after storage.

No significant differences in terms of hardness were observed between the boiler fly ash samples from the bubbling fluidized bed furnace with different water mixing rates (water mass fractions 4.5 to 22%, wet material). All of the samples were difficult to break up after storage, so milling of the ashes is necessary before application on agricultural or forest soils.

The ashes from the CFBB showed no significant hardening in the first laboratory storage tests. This is due to the very low CaO content in the ash, which is caused by the dilution with the bed material of the furnace (SiO$_2$).

The field test showed quite similar results. The piles of wet bottom ash from a grate furnace (initial water mass fraction 24%) became rather hard over time and were difficult to sample (even with a sample driller), while the piles of the other ashes, which were only sprinkled at the beginning of the storage test and featured lower water mass fractions during storage could be sampled rather easily.
As expected, no dust formation was observed when handling the wet samples, while the handling of dry samples raised a lot of dust.

**Carbonatation and optimal water admixing rates**

An interesting result of the first laboratory test was the rather low grade of carbonatation of most of the ash samples. After 16 weeks of storage the dry as well as the open stored wet samples of the bottom ash from a grate furnace featured a TIC mass fraction of 1 to 1.1% (dry basis), with the dry sample showing a slightly higher TIC mass fraction than the wet samples, while the TIC mass fraction of the airtight samples remained at the level of the original sample (0.4 to 0.6 %, d.b.). The open stored samples of a mixture of bottom and coarse fly ash had similar TIC mass fractions after 16 weeks of storage (1.1%, d.b., for the dry sample and 1.3 %, d.b., for the wet samples), compared to an initial TIC mass fraction of 0.6% (d.b.).

The TIC mass fraction of the original boiler fly ash sample from a BFBF was significantly higher compared to the ash samples from the grate furnace (2.8 %, d.b.). This can be attributed to the lower combustion temperatures in BFBF (800 to 850°C) compared to grate furnaces 950 to 1,000°C. The relative increase of the TIC mass fraction during the storage period, however, was significantly lower. Surprisingly, the dry samples showed the highest TIC mass fraction after 16 weeks of storage (3.6 %, d.b.), while the open stored wet samples featured TIC mass fractions at around 3.2 % (d.b.). The wet sample with an initial water mass fraction of 21.9 wt% (wet basis) featured a TIC mass fraction of 3.4% (d.b.), while the samples with a water mass fraction of 15.3% (w.b.) showed the lowest TIC mass fraction (3.0%, d.b.).

Due to the dilution with bed material the initial TIC mass fraction of the fine bottom ash sample from a CFBB was very low (0.03%, d.b.). The TIC mass fraction at the end of the storage period increased significantly, but the TIC-content still remained low (0.05%, d.b., for the dry sample, 0.15%, d.b., for the wet sample). The fact that all dry ash samples showed a significant increase in the TIC mass fraction while some wet samples did not might be an indication that the water mixing rates applied were probably too high to allow the contact of CO\(_2\) with Ca(OH)\(_2\) on the surface of the ash particles. Another indication that the water mixing rates applied in the first laboratory storage test were too high gives the comparison of the water added at the beginning of the storage test and the water consumption during storage, calculated based on the mass increase under consideration of the increase of the TIC mass fraction, shown in Figure 2.

![Figure 2](image-url)  
Figure 2: Comparison of water added at the beginning and water reacted during storage with the water demand based on the total Ca content in the ash

As shown in Figure 2, the water reaction rates for all wet samples are significantly lower than the amount of water added at the beginning of the storage period so it is quite likely that the initial water
addition was too high. This indication was also reconfirmed by the results of the field storage tests which showed a significant increase of the TIC mass fractions over time (relative increase by up to 250%) in the outside layers of the piles of the ashes from grate furnaces, which featured water mass fractions of around 5% (wet basis).

As shown in Figure 2, the water reaction rates for all wet samples are significantly lower than the amount of water added at the beginning of the storage period so it is quite likely that the initial water addition was too high. Figure 2 also shows the theoretical water demand under the assumption that all of the Ca is bound as CaO in the ash at the beginning of the storage test. The theoretical water demand based on the Ca content is quite close to the water consumption calculated based on the test results. Therefore, the water demand for the second laboratory storage test was based on the Ca content.

The lower water mass fractions at the second laboratory storage test led to an increase of the TIC mass fraction by almost 190% (from 0.39% to 1.13%) in the wet bottom ash samples from a GF. The TIC mass fraction of the dry bottom ash sample increased by about 100% (from 0.39 to 0.80%). However, the TIC mass fraction of the coarse fly ash from the BFBF showed no increase over the 16 weeks storage period. The results indicate that for ashes from grate furnaces the carbonatation can be enhanced by addition of moderate amounts of water at the beginning of the storage period.

Conclusions and recommendations

Conclusions
The results of the storage tests show that the main reaction during storage, at least over the first 16 weeks, is the formation of Ca(OH)$_2$ from CaO and water. The overall increase of the TIC-content of all ash samples was rather low so the carbonatation of Ca(OH)$_2$ with CO$_2$ to form CaCO$_3$ played only a minor role during the first 16 to 24 weeks storage period. Carbonation can be enhanced by addition of moderate amounts of water. The optimal water admixing rate can be determined based on the Ca mass fraction of the ash (dry basis) under the assumption that all of the Ca is bound as CaO in the ash at the beginning of the storage test. Ashes from grate furnaces remain, if the optimal water mixing rate is applied, in a rather flowable condition during storage, so they need no other processing than screening (in order to provide the ash in a spreadable particle size below 1.5 cm) after storage. Ashes from bubbling fluidized bed furnaces, however, were difficult to break up after storage, so milling of the ashes is necessary before application on agricultural or forest soils.

The evaluation of the leaching behaviour of the ashes stored showed that the leaching of Ca and Mg decreases and the leaching of K and Na increases over storage time. The results of the outdoor storage test showed significant differences between the outside layer of the piles and the area inside the piles in terms of the trends of pH-level, electric conductivity, carbonate content as well as leaching rates for Ca and K over the storage period, while the outside layer showed generally lower values except for the carbonate content, which was higher in the outside layer. Generally, the ashes from grate furnaces (bottom ash and mixtures of bottom ash and coarse fly ash) featured a stronger and more positive change of physical and chemical properties compared to ashes from fluidised bed furnaces (bottom ash and coarse fly ash).

Recommendations
Based on the experience gathered from the storage tests the following recommendations for intermediate ash storage can be given:

- The ageing of ashes (facilitated by adding water) during outdoor storage can be recommended for ashes from grate furnaces, while a pre-treatment of ashes from fluidised bed furnaces with water does not show significant positive effects during storage other than minimized dust formation.
- A minimum storage time of 8 to 12 weeks is recommended if a reduction of the solubility of Ca and a reduction of the pH-level and the electric conductivity is desired.
- In order to enable a thorough ash ageing, the ash piles should be turned several times.
- The addition of water during storage is only necessary after longer dry periods (> 4 weeks) in order to avoid dust formation.
- Ashes can be stored in landfills or, if the specific permits are available, on designated sites at the biomass plant or farms. If the ashes are not stored in landfills, the ashes (after mixing them with water) should be covered with air permeable but water impermeable membranes (similar to those used during composting) in order to avoid undesirable leachates during ash storage.
- After storage, the ashes should be screened in order to provide a spreadable particle size (< 1.5 cm) for application.
• The long-term liming effect (due to the reduction of the solubility of Ca) of aged ashes is especially useful for the utilization on grasslands and forests. These recommendations shall provide the basis for the definition of framework conditions for economically and ecologically feasible intermediate ash storage in practice in the future.

**Literature**


