

Conversion and leaching characteristics of ashes during outdoor storage – results of laboratory tests

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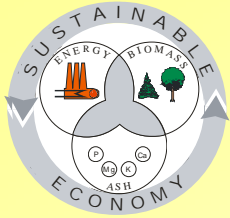
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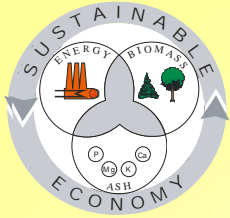


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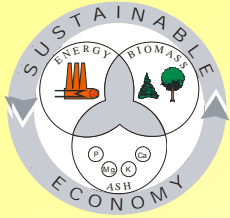


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Background (I)

- Nutrient rich and rather heavy metal poor wood ash fractions (bottom and coarse fly ash) are used for fertilizing and soil improvement purposes in Austria and several European countries.
- The main share of the ash is often produced during the winter season but ash application usually takes place during warmer periods
→ a logistic concept with intermediate storage sites is necessary.
- Wood ash contains up to 50% (w/w, d.b.) of CaO , so the addition of water facilitates the formation of Ca(OH)_2 and further with airborne CO_2 the formation of CaCO_3 (carbonatization).
- This process changes the chemical and physical properties of the ash and leads to self-hardening. Practical experience from Sweden shows that by adding a specific amount of water the carbonatization process can be improved.

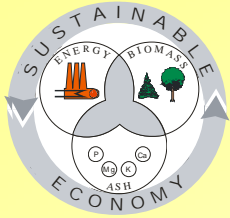


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Background (II)

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

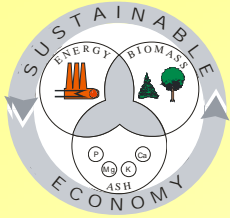


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Goals

- **Improvement of ash logistics**
- **Evaluation of the evolution of chemical and physical properties of wood ashes during storage.**
- **Evaluation of the ecological impacts of outdoor wood ashes storage**
- **Preparation of guidelines for the proper intermediate ash storage**



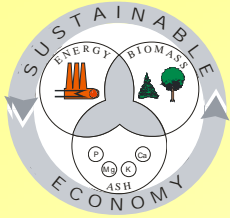
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Methodology General

The research and development activities follow a two-step-approach:

- Performance of laboratory tests with ash samples from different combustion technologies (fluidized and fixed bed combustion) over 16 weeks
 - The goal was 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. The results of these tests will be presented here.
- Performance of field tests with ash from different combustion technologies over 6 months.
 - During these tests, leachate from the storage sites was sampled and analyzed in regular intervals. In addition, the ashes stored were also sampled and analyzed regularly. The evaluation of the results of the outdoor storage test is currently underway and will not be discussed here.



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Methodology Laboratory tests (I)

➤ Selection of wood ash samples

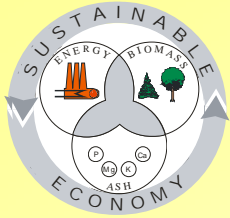
- Bottom ash and a mixture of bottom ash and coarse fly ash (mixture of economiser, air pre-heater and cyclone fly ash) from a grate furnace (GF)
- Boiler fly ash from a bubbling fluidised bed boiler (BFBB)
- Fine bottom ash from a circulating fluidised bed boiler (CFBB)

➤ Investigation of the alteration of physical and chemical properties of the wood ash fractions selected over a period of 16 weeks, applying different storage conditions:

- Dry
- Wet with two different water mixing rates, open storage
- In addition, two ash fractions were also stored wet under absence of air

➤ Determination of the particle size distribution of the original samples

➤ Determination of the chemical composition and CaO-content of the original samples



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Methodology Laboratory tests (II)

- **Measurement and analysis of the following parameters of the original and all stored samples after 1, 2, 4, 8 and 16 week(s) of storage:**
 - Carbonatization rate by measuring the total inorganic carbon content (TIC)
 - pH-level, electric conductivity and the water content
 - Chemical composition of the leachate
- **Determination of crystalline components by XRD-analysis of the original samples and after 8 weeks of storage**
- **Simulation of rainfall by regularly wetting the wet samples with a water sprayer**
- **Continuous measurement of the temperature and the humidity in the storage room**



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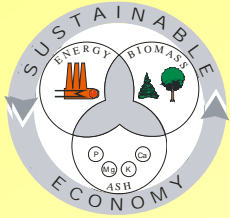
Methodology Laboratory tests (III)

➤ Storage conditions for the lab-scale storage tests:

Ash fraction	Combustion type	Fuel	Dry sample	Water content, water mixing rate		Storage of wet samples
				Water content, mixing rate 1 [wt%, w.b.]	Water content, mixing rate 2 [wt%, w.b.]	
Bottom ash	Grate furnace	bark and wood chips	yes	16.7	27.0	open and airtight
Mixture of bottom & coarse fly ash	Grate furnace	bark and wood chips	yes	16.7	27.0	open
Boiler fly ash	BFBB	wood chips	yes	15.3	21.9	open and airtight
Fine bottom ash	CFCB	forest residues	yes	17.4	-	open

➤ The water mixing rates were based on experiences from Sweden, results of preliminary test and the potential reactions that might occur if biomass ashes are mixed with water:

- Water demand for the formation of hydroxides (based on the content of Ca and Mg)
- Water demand for the formation of ettringite based on the Al and S contents
- Water demand for the formation of gypsum, if any S remains after the formation of ettringite

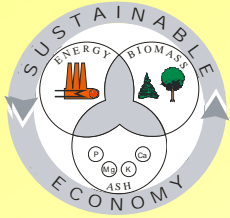


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Test layout Laboratory tests





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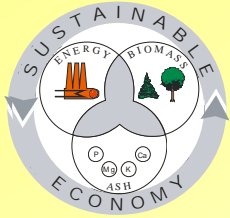
Results Laboratory tests (I)

Formation of new components

- The main reaction over the first 16 weeks is the hydration of CaO with H_2O to form Ca(OH)_2 . The carbonatization of Ca(OH)_2 with CO_2 to CaCO_3 plays only a minor role.
- Ettringite and gypsum were not formed because of the low S-contents of the ash samples used in the test (between 0.06 and 0.3 wt%).

Mass increase due to water uptake

- Significant mass increase for all samples within the first week → mass increase is mainly driven by the reaction of CaO with H_2O to form Ca(OH)_2 , a rapid and exothermal reaction.
- Higher mass increase (between 8 and 16 wt% (d.b.) for ashes from grate furnaces compared to ashes from fluidized bed boilers (between 2 to 6 wt%, d.b.) due to the higher CaO content of ashes from grate furnaces.

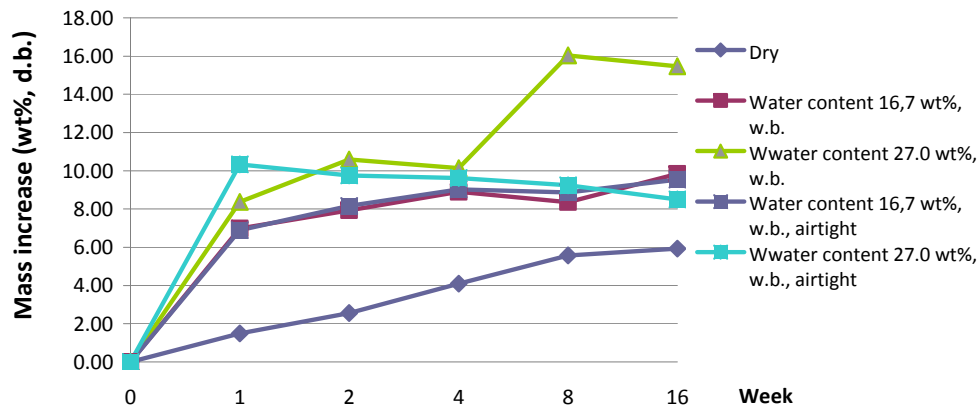


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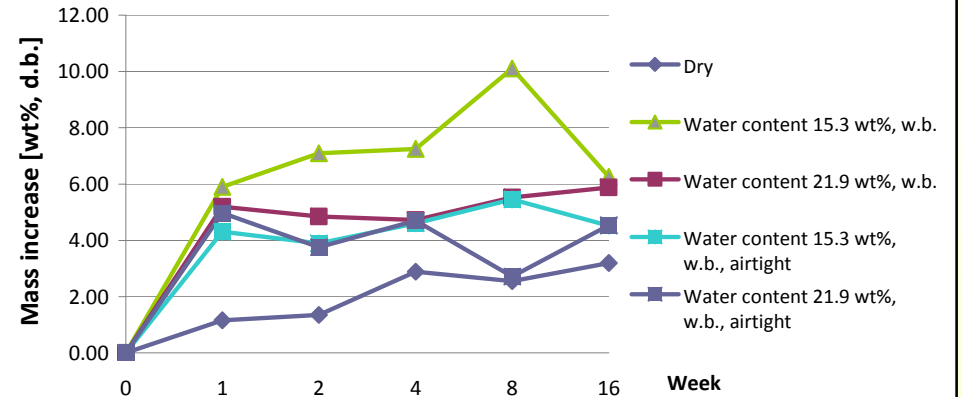


Results Laboratory tests (II)

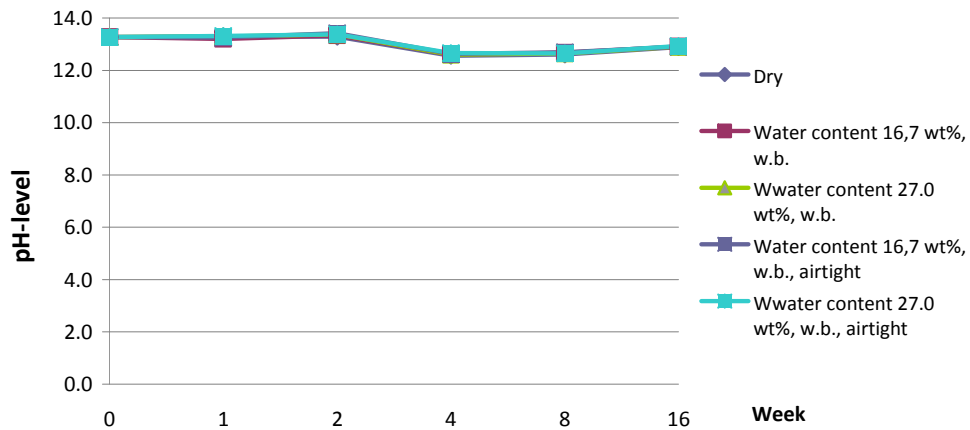
Bottom ash grate furnace, mass increase



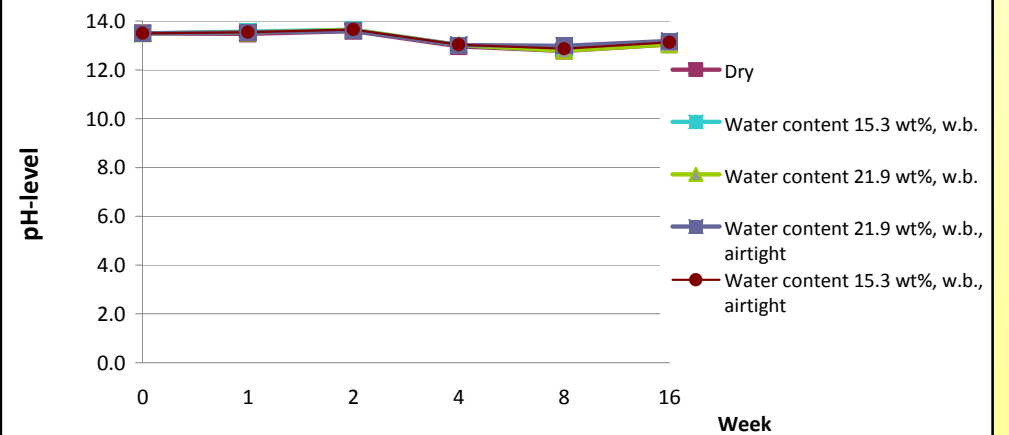
Boiler fly ash bubbling fluidized bed boiler, mass increase

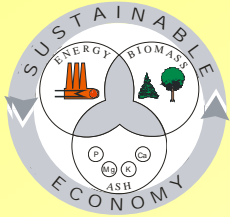


Bottom ash grate furnace, pH-level



Boiler fly ash bubbling fluidized bed boiler, pH-level





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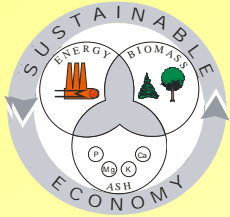
Results Laboratory tests (III)

Evolution of the pH-level and the electric conductivity

- The pH-level decreased by about 0.5 points after 4 weeks storage independent of ash type and storage conditions (wet or dry, open or airtight)
- The electric conductivity showed a small increase over 16 weeks of storage for all wet ashes (exception: fine bottom ash from the CFCB). The dry ash samples showed no or only a small increase.

Leaching behavior & ecological impact

- Decrease of the Ca and Mg leaching rates and increase of the K and Na leaching rates for all wet samples over time.
- Most of the dry samples showed the same trend but with smaller changes.
→ results correspond to findings from Swedish research projects
- Some parameters (e.g. Ba, Cr, Cr(VI), pH-level) exceed the limiting values of the Austrian Landfill Ordinance → for a more detailed ecological evaluation the results of the outdoor storage test have to be considered



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Results Laboratory tests (IV)

Influence of water mixing rates on chemical and physical properties

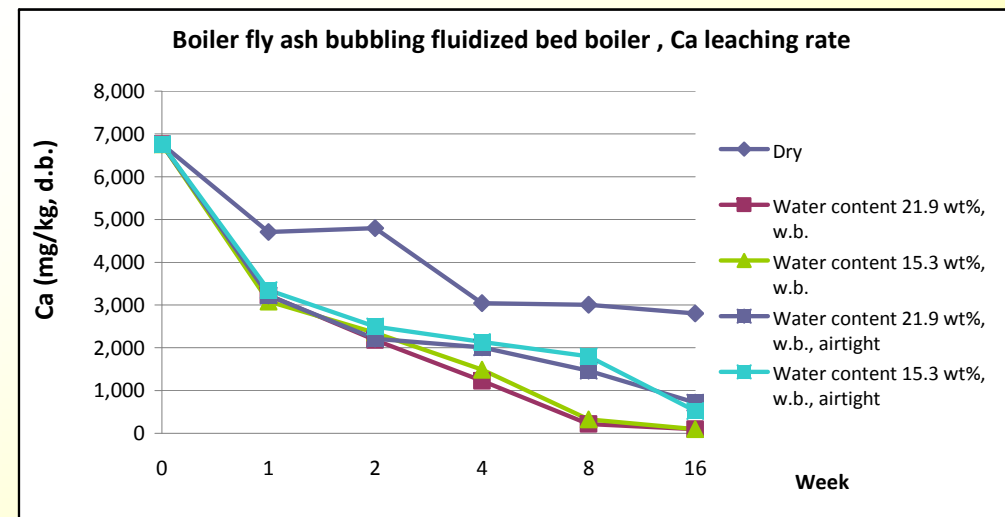
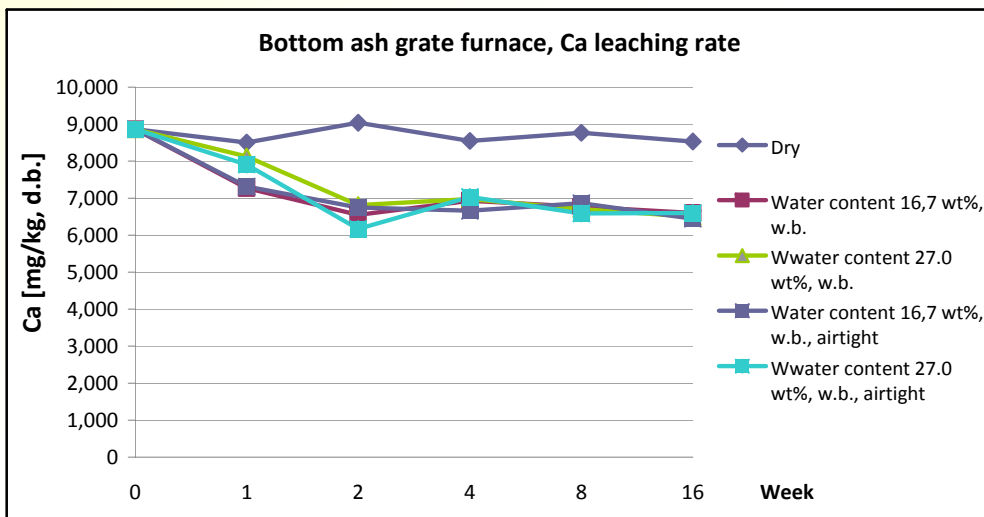
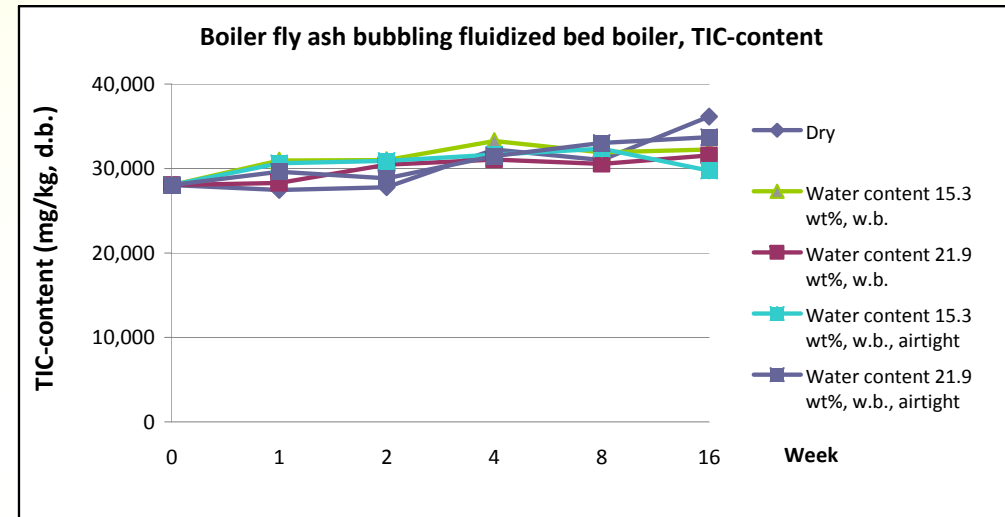
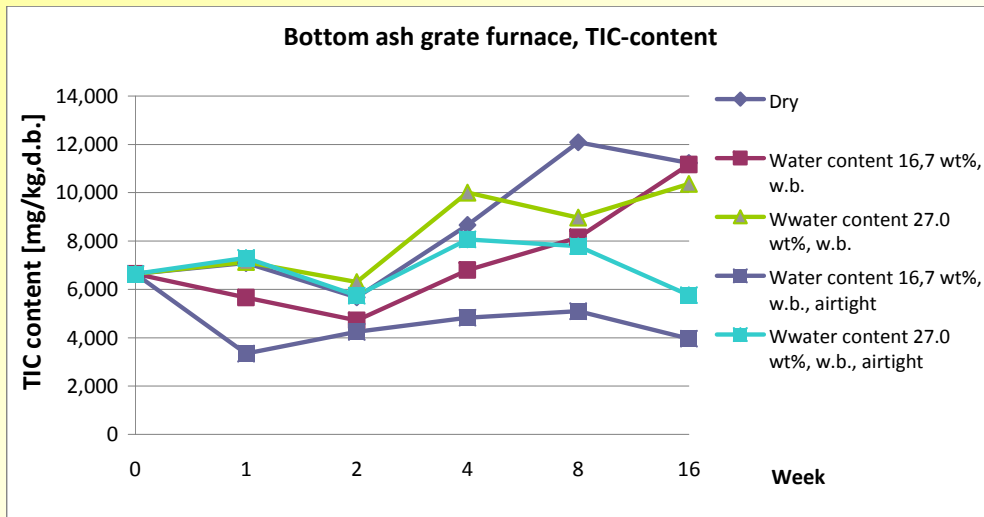
- No significant effects of different water mixing rates or open and airtight storage on the mass increase nor the leaching behavior. Wet samples show higher mass increase compared to dry samples.
- Significant difference between dry and wet samples for the leaching rates of Ca, K and Na.
- As expected, no dust formation was observed when handling the wet samples, while the handling of dry samples raised a lot of dust.

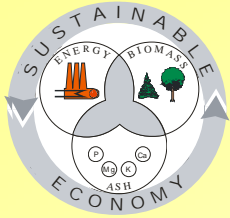


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Results Laboratory tests (V)





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Results Laboratory tests (VI)

Carbonatization

- Rather low grade of carbonatization of most of the ash samples. Some samples didn't show any significant TIC increase at all.
- No clear correlation between carbonatization and water mixing rate or open and airtight storage → dry samples show comparable or even higher carbonatization rates than wet samples.

Optimum water mixing rate

- Dry ash samples showed significant TIC-content increase while some wet samples did not → were the water mixing rates applied too high?
- Compared to the water added, the water consumption during storage was significantly lower → another indication for too high water mixing rates

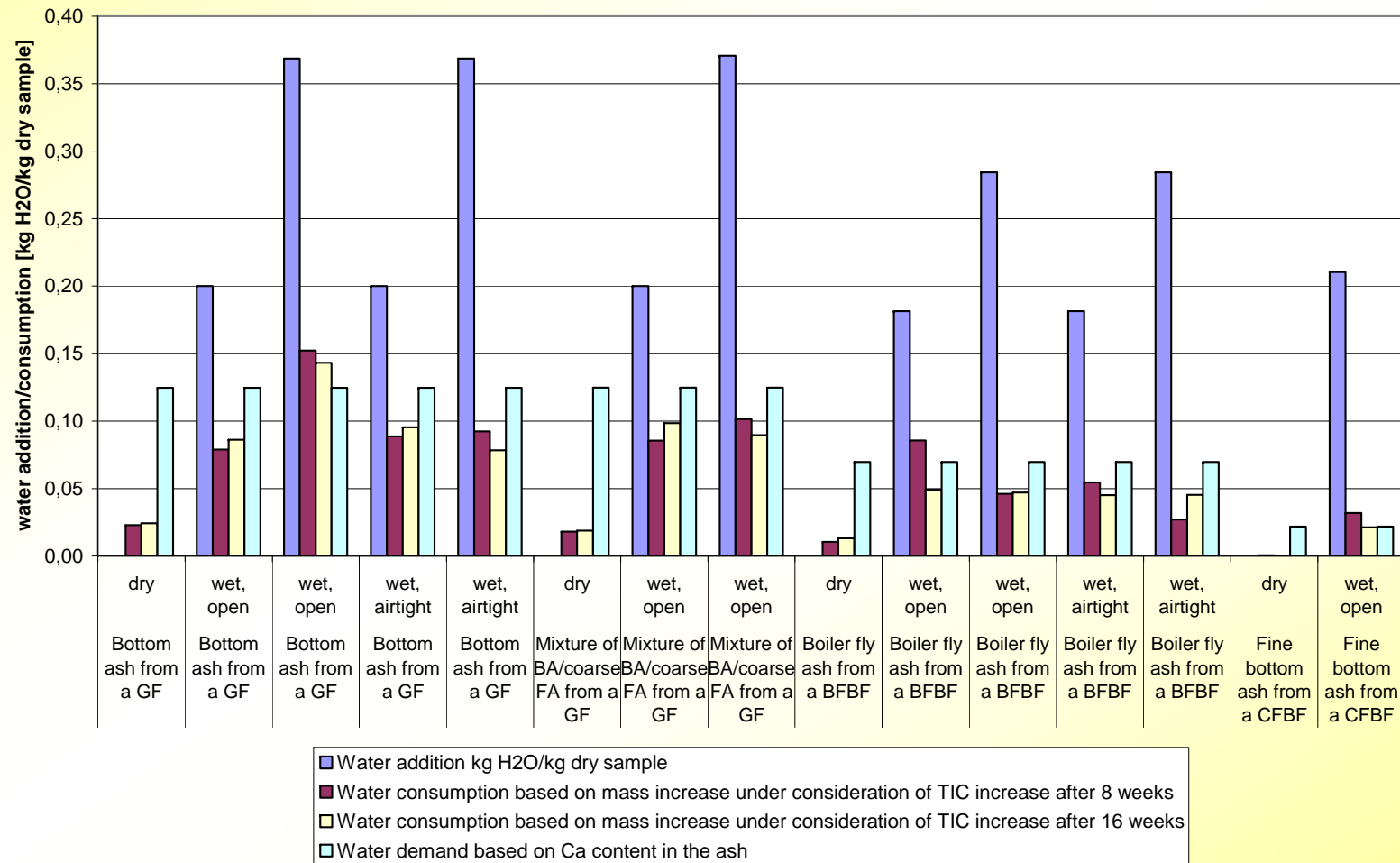


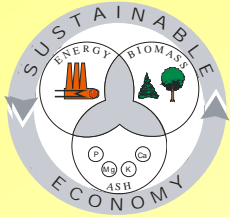
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Results Laboratory tests (VII)

➤ Optimum water mixing rate (continued)





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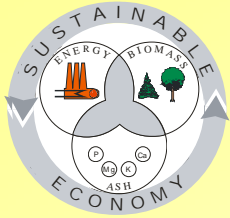


Summary & Conclusions (I)

- The main reaction observed during the 16 weeks storage test was the formation of Ca(OH)_2 from CaO and water.
- The overall increase of the TIC-content of all ash samples was rather low → carbonatization of Ca(OH)_2 with CO_2 to form CaCO_3 played only a minor role during the 16 weeks storage period.
- The water consumption during storage was 50 to 85% lower than the water added at the beginning of the test → probably too much water was added, which might be the reason for the rather low carbonatization rates during storage.

The analysis of the Ca content and the water consumption during the storage test indicates that the Ca content is a suitable parameter to determine the optimum water mixing rate.

- Other reactions also described in literature, like the formation of gypsum or ettringite, were not observed due to the low S content in the ashes used in the test.

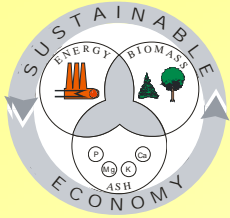


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Summary & Conclusions (II)

- During storage, a slight decrease of the pH-level and a small increase of the electric conductivity were observed.
- The Ca and Mg leaching rates decrease over time while the K and Na leaching rates increase → similar to storage tests performed in Sweden.
- Since Ca, Mg and K are valuable nutrients and the pH-level as well as the electric conductivity are relevant ecological parameters, their evolution over time determines the value of the stored ash.
- Regarding the ecological impact of ash storage, the results of the leaching tests show that for some parameters the limiting values of the Austrian Landfill Ordinance are exceeded for certain landfill types.



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Outlook

- The evaluation of the results of the outdoor storage test performed between April and October 2011 will provide further information regarding the
 - leaching behavior of the ashes over time to evaluate the ecological impact (effects on soil and ground water) of outdoor ash storage, and
 - the optimum storage conditions required to receive ashes as valuable as possible at the end of the storage period.
- Further research will focus on the determination of the optimum water mixing rate. Based on the results of the laboratory and field tests performed so far, additional lab-scale storage tests with optimized water mixing rates are planned in 2012.
- The results of these investigations shall provide the basis for the definition of framework conditions for economically and ecologically feasible intermediate ash storage in practice in the future.



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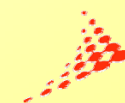
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