

Reactivity and Leaching of Wood Ash Pellets Dehydrated by Hot Air and Flue Gas

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Abstract: Companies that generate a large amount of wood ash will need an industrial process to agglomerate the ash and lower its reactivity, because untreated ash is a dust hazard for workers and is difficult to spread evenly on forest soil. In addition, untreated ash can cause burning damage to vegetation owing to its alkalinity and rapid release of salts. Production of large amounts of wood ash agglomerates demands an effective dehydration process. The reactivity and release of inorganic constituents from wood ash pellets dehydrated at room temperature using hot air and flue gas was investigated. Our results imply that flue gas-treated pellets have significantly lower reactivity in terms of pH and electrical conductivity, and release less Ca^{2+} and more Mg^{2+} compared to pellets dried at room temperature or in hot air. Ash pellets dehydrated in hot air are very reactive, and release more Ca^{2+} than pellets dried in other ways. The formation of syngenite during the flue-gas treatment decreases K^+ release from the ash pellets.

Keywords: Wood ash, ash pellet, leaching, dehydration, carbonation, reactivity.

INTRODUCTION

The recycling of ash from wood combustion back to the forest floor has been suggested as a method of closing the cycle for non-combustible matter, i.e., mineral nutrients. However, practical handling of ash materials may involve a considerable dust source. Newly generated, untreated wood ash can also have an adverse effect the ground vegetation from burning damage owing to its reactivity [1, 2], along with an increase in soil respiration and microbial activity [3, 4]. Therefore, it is necessary to pre-treat the ash to lower its reactivity. The purpose of pre-treatment is to facilitate the practical management of the ash, to decrease dust formation, and to prolong the decomposition time of ash particles. Ideally, the rate of decomposition of the recycled ash particles should match that of the natural decomposition of forest residues, such as needles, leaves, and branches. It is possible to process hydrated ash to form small spherical granules by granulation, or to press a hydrated ash mixture into pellets in a pelletizer. It is also possible to “self-harden” hydrated wood ash in a pile outdoors over the period of a year; then the ash is crushed and sieved. The crushed ash agglomerates are then spread in a forest. The drawbacks of this method are that it requires space, it is time consuming, and it creates dust problems during the handling operations.

HYDRATION AND CARBONATION

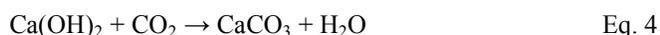
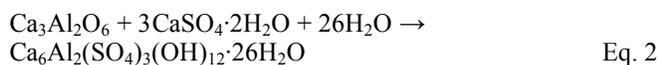
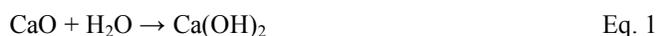
The crystalline phases observed in untreated wood ash include, among others, calcium oxide (CaO), calcite (CaCO_3), portlandite (Ca(OH)_2), anhydrite (CaSO_4), and larnite (Ca_2SiO_4) [5-8]. However, calcium oxide and portlandite are the main constituents of untreated fresh wood ash, with as much as 30 wt%. This is responsible for the

most important reactions during the hydration and carbonation of ash materials. Hydration of CaO is a rapid and exothermic reaction that forms portlandite, Ca(OH)_2 , (Eq. 1), which precipitates in a crystalline form. The formation of other hydration minerals, e.g., ettringite (Eq. 2) and gypsum (Eq. 3), is also possible, depending on the origin and the properties of the ash, and on whether additives have been used. Ettringite is the phase that crystallizes during the hydration of tricalcium aluminate (the main crystalline phase of cements) when sulphate ions are present. As well, it is the main hydrated phase in many other cementitious materials [9]. The formation of ettringite in wood ash depends on the aluminum content of the ash (as Al_2O_3) exceeding the sulphur content, with the ash pore solution having $\text{pH} > 11$ [10]. The formation of gypsum from anhydrite occurs if the conditions for ettringite formation are not suitable [6]. The hydration reactions are followed by a carbonation process, where portlandite reacts with available (atmospheric) CO_2 to form calcium carbonate, CaCO_3 (Eq. 4). This process is a liquid-phase reaction of carbon dioxide with aqueous hydroxide and cations to produce carbonates [11]. The formation of other carbonate phases is also possible. For example, Steenari and Lindqvist [6] observed $\text{CaAl}_2(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ in biofuel ashes. The former product was suggested to be the result of a reaction of ettringite with CO_2 .

During production of cement mortars, the water:cement ratio is critical, in that sufficient moisture must be present for carbonation to occur rapidly, but there must not be too much, as it could fill any pores and impede the diffusion of CO_2 into the sample [12]. Similarly, the hydration of wood ash is a critical moment during the manufacturing of wood ash agglomerates [13], both in terms of the physical formation of agglomerates and the chemical reactions on the addition of water. Too much water hinders the physical formation of agglomerates (i.e., the mixture becomes a slurry), and too little water impedes the adherence of the particles during dehydration. The required range of water addition is narrow,

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as demonstrated by Svantesson [13]. The addition of 2-4 litres of water to 250-300 kg of a saturated batch of ash results in a mixture that is too wet. In turn, the chemical reactions decrease the reactivity of ash materials by lowering their electrical conductivity, pH, and dissolution kinetics. In addition, the mechanical strength of the material is enhanced.



Water is liberated during carbonation and becomes available for any non-reacted material. In a manner similar to Portland cement, the ash material undergoes chemical changes during the course of time and “ages”. The carbonation of cement matrices has a significant physical effect on the mass transport properties of these materials through a narrowing of the pore structure due to the increase in solid volume (11%-12%) expected when portlandite is converted to calcium carbonate [11]. The carbonation of cement and concrete is not desirable because it causes a cracking of the structures and a reduction in strength. However, in the context of wood ash recycling, at least a partial carbonation is desirable to decrease the material reactivity and to slow down its dissolution kinetics.

ACCELERATED CARBONATION

Accelerated carbonation using gas containing CO_2 at a concentration between 5% and 100% is used in cement chemistry [12, 14] and in research into residues from municipal solid waste incineration (MSWI) [15, 16] to fix the time of testing. The CO_2 source used can be either pure CO_2 gas or any other CO_2 -rich gas, such as the flue gas from incineration [16]. The approximate concentration of CO_2 in air is 0.035%, and the carbonation depth of structural concretes occurs at the rate of 1 cm per year [11]. It has been shown that the carbonation of cementitious materials, such as MSWI fly ash, occurs in minutes when exposed to high concentrations of CO_2 [16].

To ensure effective agglomeration, it is necessary to dehydrate ash products rapidly, as this enables immediate packing and distribution. Very little research has been carried out on the influence of dehydration methods on the chemical properties of wood ash agglomerates with respect to their reactivity and the release of inorganic constituents. There have been examples of drying biofuels using flue gas [17, 18], and the utilization of hot air and flue gas to dehydrate ash has been discussed in the literature [13]. We found only a single report concerning treatment of wood ash products with different drying media in a literature search. The results of Holmberg *et al.* [19] imply that the calcite content is higher and the portlandite and arcanite $\text{K}_2(\text{SO}_4)$ content slightly lower in wood ash granules treated using flue gas (11 -16 vol.% CO_2) from sawdust combustion compared to those dried using only hot air. In addition, flue-gas drying did not affect the chemical composition of the granules, and only changes in their mineralogy were observed. However, no leaching test results were presented.

SCOPE AND OBJECTIVES

In this paper, the reactivity and the leaching of wood ash pellets dehydrated using four different methods are compared. The aim was to produce ash pellets with as low reactivity as possible in terms of the pH, EC, and release of constituents upon first contact with water.

MATERIALS AND METHODOLOGY

Ash pellets were produced in industrial roll-pelletizing equipment by mixing 100 kg (fresh weight) of fly ash from a 40 MW pulverized wood-fired boiler with 50 kg of dolomite powder (as a binder and adds Mg and Ca to the mixture) and 50 kg of water. The paste was then pressed and cut into pellets. Directly after pelletizing, the pellets were subjected to the following dehydration treatments:

- 1) **Room temperature** (Sample D20): 20 °C in the laboratory, in a 5 cm -thick layer of ash pellets.
- 2) **Hot air** (Sample D60): 60 °C, fan-forced air (3000 m³ h⁻¹), in an oven for 120 min, in an 8–10 cm -thick layer of ash pellets.
- 3) **Hot air** (Sample D130): 130 °C, in an oven for 10 min, in a 5 cm -thick layer of ash pellets.
- 4) **Flue gas** (Sample DF): flue gas from the combustion of pulverized wood in a 40 MW boiler (DF): ~ 130 °C, 10–15 % CO_2 and H_2O . The ash pellets were exposed perpendicular to the flue gas flow in a chimney, for a period of 10 min in stainless steel net bags.

After dehydration, all the pellet samples were stored in open vessels in the laboratory. After a period of 75 d, the ash pellets were subjected to two different laboratory leaching tests: a compliance test and a reactivity test. All equipment was rinsed with 0.1 M nitric acid before the leaching experiments were performed. The pellet samples were fractionated into the size interval 4–8 mm using a stainless steel mesh. The leaching tests were performed on five replicates for each sample.

Eluates from the reactivity test were analysed for pH and EC using a Metrohm 744 pH Meter and a Jenway 4510 Conductivity Meter, respectively. Eluates from the compliance tests were conserved in concentrated nitric acid before analysis of the concentration of Na, Ca, K, Mg, Mn, Al, Fe, P, and Zn. The analysis was carried out using inductively coupled plasma mass spectrometry, ICP-MS Perkin Elmer, Optima 3300 DV. The inorganic element content in the pellet samples was analysed at Acme Analytical Laboratories Ltd, Canada, employing a multi-acid digestion and inductively coupled plasma emission spectrometry (ICP-ES) and ICP-MS. The mineralogical composition was examined using X-ray diffraction (XRD), Siemens D5000, employing the data DIFFRAC PLUS evaluation programme and the on-line JCPDS database (PDF-4) located at the Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg, Sweden.

Ash pellets (length = 10mm, diameter = 5 mm) were also produced manually from the ash by pressing wet ash paste

through a plexiglass matrix. Before pellet production, the ash was ignited at 550 °C for a period of two hours to reduce the amount of organic matter. One fraction of the pellets was then subjected to flue gas for a period of 10 min, and another fraction of ash pellets was subjected to hot air (130 °C) in an oven for a period of 10 min, similar to the industrially produced pellets described above. The mineralogy of the untreated ash and pellets dehydrated using hot air and flue gas was determined using XRD as described above.

Compliance Test EN12457-4

The compliance test was used to determine whether the waste complied with specific reference values. The test is a single-stage batch test that is relatively rapid to perform, and assumes that a chemical equilibrium or a semi-equilibrium is achieved between the liquid and solid phases in the time period of the test. Compliance tests are also suitable for comparing properties of different materials. The material to be leached is placed in water in bottles, and agitated for a period of 24 h, and then the eluate is analyzed. We performed our compliance tests with some modifications to this procedure: a test portion of 80 g rather than 90 g was subjected to leaching, and the L:S ratio was modified to L:S

= 5 (the same L:S ratio as in the Swedish Forest Agency SFA reactivity test) instead of L:S = 10. A horizontal platform shaker, with a reciprocating motion at 140 rpm was used in the tests instead of an end-over-end tumbler.

The SFA Reactivity Test

This reactivity test was developed by the SFA [20]. Its purpose is to determine the chemical reactivity of a wood ash product before spreading. Ash is placed in a flask of water (L:S = 5) along with a magnetic stirrer, and the mixture is stirred for a period of 1 h (at 600 rpm). The eluate is then analyzed. The pH is measured directly in the eluate and the electrical conductivity of the eluate is measured after separation of the solid residue after filtering (Munktell filter paper No. 3). The dry substance of the ash pellets was determined according to the Swedish Standard SS 02 81 13.

Data Analysis

Differences in the reactivity and leaching behavior between the pellets dehydrated using different methods were investigated using a Partial least squares regression (PLSR) technique, using the leached amounts as the X variables and the dummy variables indicating the chosen drying technique

Table 1. Average Concentration of Analytes in Industrially Produced Wood Ash Pellets Dehydrated Using Different Methods. (Standard Deviation is Given in Parentheses)

%	Room Temp.	Hot Air (60 °C) 120 min	Hot Air (130 °C)10min	Flue Gas 10 min
C (inorg.)	20.8 (0.23)	19.9 (0.70)	20.7 (0.53)	20.8 (0.56)
Ca	17.1 (0.36)	17.3 (0.24)	17.3 (0.33)	17.3 (0.26)
Mg	6.77 (0.091)	6.91 (0.13)	6.83 (0.30)	6.87 (0.15)
K	3.97 (0.18)	3.96 (0.046)	3.99 (0.046)	4.08 (0.18)
S	1.6 (0.0020)	1.6 (0.017)	1.6 (0.010)	1.6 (0.066)
Fe	0.437 (0.055)	0.387 (0.0058)	0.387 (0.015)	0.390 (0.010)
Al	0.343 (0.0058)	0.347 (0.015)	0.353 (0.0058)	0.343 (0.012)
P	0.296 (0.0061)	0.299 (0.0025)	0.308 (0.0076)	0.313 (0.0070)
Na	0.223 (0.0087)	0.225 (0.0064)	0.227 (0.0068)	0.229 (0.0061)
H ₂ O	0.93 (0.99)	1.2 (0.59)	0.75 (0.66)	1.2 (0.43)
mgkg ⁻¹				
Mn	4800 (92)	4840 (19)	4900 (16)	5010 (150)
Sr	800 (6.8)	796 (13)	802 (13)	834 (9.8)
Zn	425 (11)	426 (2.7)	428 (5.0)	433 (12)
B	164 (1.5)	177 (8.6)	177 (4.6)	173 (9.1)
Ba	79 (1.7)	85 (2.1)	91 (4.7)	95 (7.6)
Cu	70 (0.81)	69 (0.9)	70 (1.1)	72 (2.4)
Pb	27 (0.82)	26 (0.42)	27 (1.5)	26 (1.1)
Cr	29 (11)	22 (1.7)	22 (1.0)	21 (0.42)
Ni	15 (7.0)	11 (7.0)	11 (0.57)	12 (0.50)
As	1.5 (0.2)	1.1 (0.15)	1.0 (0.058)	1.3 (0.21)
Cd	6.6 (0.074)	6.6 (0.13)	6.7 (0.19)	7.0 (0.28)
V	6.3 (0.58)	6.7 (0.58)	6.7 (0.58)	5.7 (0.58)
Mo	2.0 (1.3)	1.0 (0.023)	1.0 (0.042)	1.0 (0.021)
Co	23 (0.44)	24 (0.53)	23 (0.21)	24 (1.1)

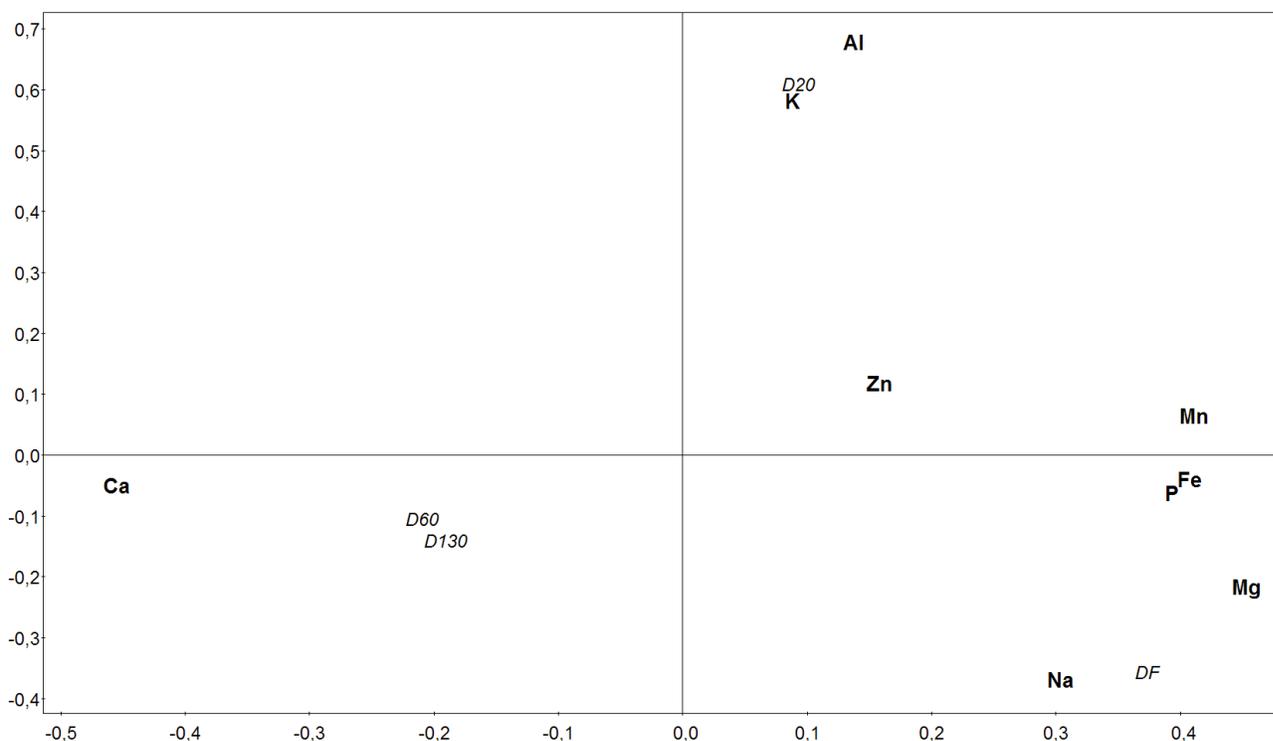


Fig. (1). Loadings from partial least squares regression of the leached percentage from industrially produced pellets with respect to the different dehydration methods used. Pellets dehydrated at room temperature (D20), using hot air (D60 and D130), and flue gas (DF). The x and y axes denote $w*c1$ and $w*c2$, respectively.

were the Y-variables. The significance of the observed differences was tested using the Tukey HSD post hoc test at the $P < 0.05$ level.

RESULTS

General Composition of Wood Ash Pellets

The elemental composition of the ash pellets was uniform in all four cases. The main constituents of the pellets were Ca, Mg, and K as 17%, 7% and 4 % (db), respectively (Table 1). Powdered dolomite was used as the binder in 33% by weight of fly ash for pelletization, and this altered the composition of the ash by adding Ca, Mg and Si to the mixture, and lowering the concentration of many other elements, e.g., phosphorus, because of dilution. Consequently, the concentrations of trace elements, such as Cd, V, Mo and As were moderate. The content of inorganic carbon was high, at 20 -21% (db), depending on the presence of dolomite. The moisture content of the pellet samples ranged from 0.75% to 1.2%.

Leaching of Elements

Leaching tests were performed on five replicates for each sample of the industrially produced pellets and the reproducibility of the test procedure was verified as being good. The PLSR process resulted in two principal components describing 56% of the variation in the Y variables, 80% of the variation in the X variables, and with a predictive ability of 50% ($R^2Y = 0.56$, $R^2X = 0.80$, and $Q^2 = 0.50$). There were general differences in the leaching behavior between the ash pellets that had been dehydrated

using different methods, indicated by the high Q^2 value, and shown by the clear separation between the corresponding points in the loading plot (Fig. 1). Leaching from pellets dehydrated using hot air was uniform, regardless of temperature. Both the hot-air treatments produced pellets with a significantly higher release of Ca (Fig. 1; Table 2) compared to the pellets subjected to other treatments: they released twice as much Ca than the room-temperature dried pellets did and eight times more than the flue-gas treated pellets. There was a significantly higher release of K and Al from the pellets dehydrated at room temperature (Sample D20) compared to the other samples (Fig. 1; Table 2). The flue-gas treated pellets released significantly less Ca and more Mg compared to the pellets treated using other drying methods (Fig. 1; Table 2). The release of Mn, P, Fe, and Zn from all pellet types was insignificant.

pH and EC

There were also significant differences in the reactivity in terms of pH and EC between the pellet types. The pH in flue-gas treated pellets was up to two units lower compared to pellets dehydrated using hot air and room temperature. The hot-air dehydrated pellets had the highest EC (2020-2070 mSm^{-1} ; Table 2), with Sample D20 having an intermediate EC (1700 mSm^{-1}), and Sample DF the lowest EC (1590 mSm^{-1}).

Mineralogy

The crystalline compounds present in untreated fly ash are: calcite ($CaCO_3$), sylvite (KCl), quartz (SiO_2), arcanite (K_2SO_4), halite ($NaCl$) and apthitalite ($K_3Na(SO_4)_2$). In addition,

Table 2. Concentration of Released Elements (in mg L⁻¹), pH, and Electrical Conductivity (EC) of Industrially Produced Ash Pellets Dehydrated using Different Methods. (Standard Deviation is Given in Parentheses)

Compliance test, L/S 5	Room temp.	% Leached	Hot Air (60°C) 120 min	% leached	Hot Air (130 °C) 10 min	% Leached	Flue Gas 10 min	% Leached
K	7000 (120)	88	6690 (140)	85	6740 (82)	85	6724 (89)	82
Na	284 (5.5)	64	282 (4.5)	63	290 (10)	64	302 (4.5)	66
Ca	194 (8.9)	0.57	438 (24)	1.3	404 (50)	1.2	56.4 (2.9)	0.16
Mg	0.490 (0.18)	0.0036	0.134 (0.029)	0.00097	0.106 (0.017)	0.00078	1.56 (0.38)	0.011
Al	0.174 (0.03)	0.025	0.058 (0.024)	0.0084	0.056 (0.015)	0.0079	0.07 (0.025)	0.010
Mn	0.062 (0.033)	0.0065	0.024 (0.0055)	0.0002	0.014 (0.0089)	0.0014	0.088 (0.025)	0.0088
P	0.034 (0.023)	0.0057	0.012 (0.013)	0.0020	0.0080 (0.013)	0.0013	0.066 (0.023)	0.011
Fe	0.024 (0.017)	0.0027	0.0020 (0.0045)	0.00031	0.0020	0.00026	0.050 (0.025)	0.00064
Zn	0.0020 (0.0045)	0.0024	*	*	*	*	0.0020 (0.0045)	0.0023
Reactivity test, L/S 5								
pH	12.3 (0.10)		13.1 (0.065)		13.5 (0.0085)		11.4 (0.12)	
EC mS/m	1700 (49)		2070 (30)		2020 (53)		1590 (43)	

* Below the limit of detection.

syngenite (K₂Ca(SO₄)₂) was also present in both the flue-gas and hot-air treated pellets (manually produced pellets). The mineralogy of the industrially produced pellets was the same in all samples: dolomite (CaMg(CO₃)₂), calcite, quartz, and arcanite were observed in all samples (Fig. 2).

DISCUSSION

A rapid dehydration process increases the effectiveness of the production of ash pellets. It is favorable, in that the ash is also carbonated, because carbonation decreases the ash reactivity with regard to the pH and EC, and prolongs the leaching of cations such as Ca from the ash matrix.

Composition – Contamination

The composition of the pellets subjected to different dehydration techniques was surprisingly uniform (Table 1). Dehydration during 10 minutes in the flue gas in the chimney seemed not to have contaminated the ash pellets. The only significant difference in the composition of the pellet samples was in the phosphorus content in the flue-gas treated pellets. This difference is positive, although small (Table 1) and was probably due to the inherent variation in the material's composition.

Compounds present in the flue gas may contaminate the material being dried, for example, with Si, Al and Fe when drying bio-fuels in flue gas [21], and a given level of contamination does occur in ash material over the course of time. In our study, 10 minutes was not long enough to allow a detectable degree of contamination to occur. The flue gas from the boiler passed an electrical precipitator before emission to the atmosphere, and its composition was dependent on the running conditions of the boiler. The current tests were performed at an intermediate load with a high oxygen level (Table 4).

The elemental content in the pellets agree with results from earlier studies on ash from the same boiler [19]. A

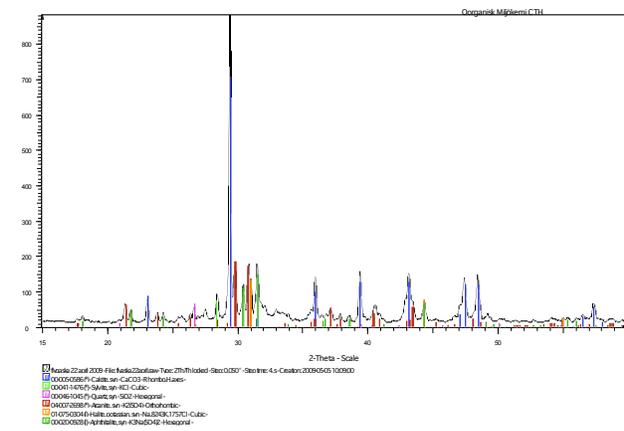
common phosphorus content of wood ash is 1-2% [6] and the mean value of 0.3% is low. In Sweden, the quality of the ash formed is subjective rather than based on the type, and fertilizers using mixed ash from different fuel types is allowed if quality requirements are met [22]. Compared to the recommended SFA values (Table 3), the P and Zn content was not sufficient for recycling purposes. However, dolomite adds Ca and Mg to the mixture, and dilutes the concentrations of potentially ecotoxic trace metals, such as Cd, As, and Ni. Consequently, levels of these metals of concern were very low. For comparison, up to 200 mgkg⁻¹ of Cd in birch and spruce ash has been determined in other studies [23]. With regard to the mineralogy of the flue-gas treated pellets, our results differ from the data of Holmberg *et al.* [19] in that no portlandite was found in the ash materials in this study.

Leaching

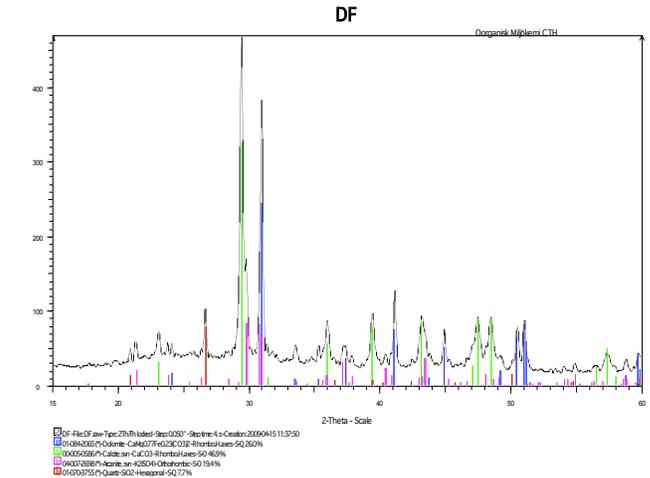
Factors that influence the leaching of inorganic constituents from ash materials are: the particle size distribution, test duration, pH, the L:S ratio, and the temperature. It is on the first contact with water that the highest concentration of elements is released from the ash material. This can give rise to the so-called "salt effect" on forest soil, and should be avoided. The release of S, Cl, Na, and K from salts and related compounds in ash is generally a rapid process, and leaching of metals, such as Pb, Zn, and Cu is commonly suppressed until the pH of the ash is decreased substantially.

The industrially produced pellet samples were stored in the laboratory for a period of 75 d before the leaching tests were performed. These pellets were exposed to air in 5 cm-thick layers in open vessels.

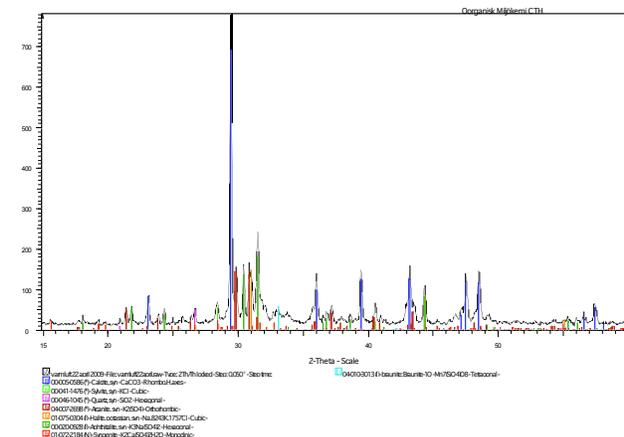
The results from both laboratory leaching tests imply that chemical hardening had occurred in different ways in the pellets that were dehydrated using different methods. Hot-air dehydrated pellets had a high pH and EC, which suggests



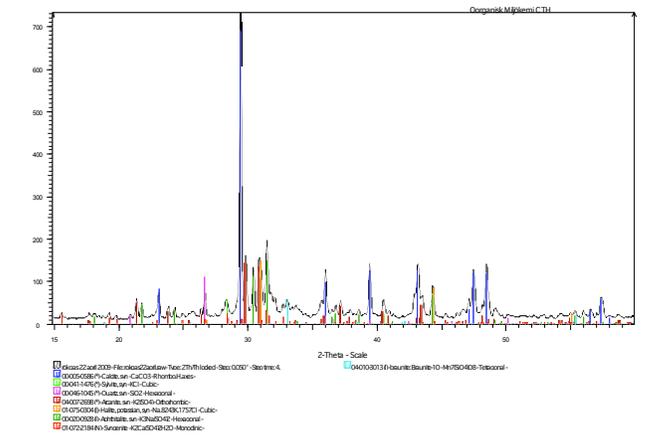
Untreated fly ash



Industrially produced pellets of ash and dolomite, flue-gas treated



Manually produced pellets of ash, dehydrated in hot air



Manually produced pellets of ash, flue-gas treated

Fig. (2). Mineralogy of untreated ash and pellets.

that a main part of the Ca is still present as the hydroxide, which is much more soluble compared to the carbonate. However this was not confirmed by the XRD data. For comparison, the solubility of $\text{Ca}(\text{OH})_2$ and CaCO_3 is 1.6 and $0.0066 \text{ gL}^{-1} \text{ H}_2\text{O}$, respectively. Dehydration was similarly efficient at both 60 and 130°C since both pellets had $\text{pH} > 13$ and conductivity $> 2000 \text{ mS/m}$. For comparison, the pH and EC of fresh, untreated wood ash is 13 and $4500 - 6400 \text{ mS/m}$, respectively [24]. Pellets dehydrated at room temperature were moist during a longer period of time compared to the hot-air dehydrated pellets, allowing for a longer reaction time (Table 2). Their reactivity was intermediate compared to the hot-air and flue-gas treated pellets.

The greatest change was observed in the properties of the flue-gas treated pellets, since the pH decreased by two units compared to the hot-air treated pellets, and the conductivity also decreased significantly. A 10 min exposure time for flue gas (containing app. 9% CO_2) was long enough to achieve a significant reduction of the ash reactivity. Similar results were obtained by Li *et al.* [15] and Zhang *et al.* [25]: accelerated carbonation (up to 100% CO_2) lowered the MSWI ash pH by several units. Treatment times varied from 3 to 10 h although for Li *et al.*, this was up to 3 d, and

elsewhere, Jianguo *et al.* [16] concluded that 90% of the reaction takes place in the first 20 min when carbonating MSWI fly ash for a period of 5 min, followed by 2 h rotation in bottles, in which the gas was composed of 10 -100% CO_2 .

It is also possible that the temperature influences the rate of hydration and carbonation of wood ash. For example, the rate of tricalcium silicate hydration in Portland cement increases with increasing temperature [26]. It has also been shown that after the addition of water, coal ash with a high Ca content had a rapid carbonation rate at $200 - 230^\circ\text{C}$ [27].

The compliance test results support the results from the reactivity tests, and also suggest that chemical hardening had occurred in the different grades in the pellet materials, because the element release patterns differed between the samples (Table 2, Fig. 1). In general, the release of Ca is suppressed when the pH exceeds 12. However, difference in Ca leaching was significant. The release of Ca from the flue-gas treated pellets was almost eight times lower than that of the pellets dehydrated in hot air (Table 2), and the pellets dehydrated at room temperature released half as much Ca as the hot-air treated pellets did.

Table 3. Swedish Threshold Values for Constituents and the Limit Values for the Electrical Conductivity (EC) in Ash Intended for Recycling on Forest Soils

% (DW)	Minimum	Maximum
Ca	12.5	
Mg	1.5	
K	3	
P	0.7	
mgkg ⁻¹ (DW)		
B		800
Cu		400
Zn	500	7000
As		30
Pb		300
Cd		30
Cr		100
Hg		3
Ni		70
V		70

Dose Tons of Ash (DW) Per Hectare	Limit Value EC mSm ⁻¹
Clear-cut forest	2400
2 -3	2800
1 -2	3200
<1	3600

Source SFA (2008).

Table 4. Composition and Properties of the Flue Gas from the Combustion of Sawdust During the Experimental Dehydration of Wood Ash Pellets

Variable	Value
Boiler load (MW)	24
Flue gas torrent (m ³ n/h)	35516
Flue gas temperature (°C)	129
O ₂ (vol%)	7
CO ₂ (vol%)	12
CO mg/nm ³ at 6% O ₂	133
H ₂ O (vol%)	9
Dust mg/nm ³ at 6% O ₂	0.11
NOx mgMJ ⁻¹	52

Potassium and Na had the highest leaching rates. In general, the release of K and Na is not affected by carbonation, as they are readily soluble species bound as sulphates and chlorides, and are leached from all types of ash

on contact with water. The exception is the K that is bound in alkaline feldspars, which is practically insoluble. Steenari *et al.* [28] observed that the release rate of K did not decrease on curing, and nearly 80% from wood ash agglomerates was released during the first leaching step with L:S =16. In contrast, Li *et al.* [15] observed a reduced release of Cl and SO₄ from carbonated MSWI fly ash. This is of particular interest in that our results also suggest that flue-gas treatment leads to a decrease in K leaching. Calcite, sylvite, quartz, arcanite, halite, and apthitalite are the mineral phases present in both untreated ash and pellets treated with hot air or flue gas. An additional secondary mineral phase was present in the manually produced pellets: syngenite (K₂Ca(SO₄)₂H₂O). Earlier studies confirm that K is present as arcanite and syngenite in this ash, and that the only K-containing secondary mineral in this ash is syngenite [7]. The solubilities of sylvite, arcanite, and syngenite are 238, 120 and 2.5 g/L H₂O, respectively, and so the formation of syngenite could have a positive effect and temporarily slow down the kinetics of K release from ash materials. The release of K in forest ecosystems is generally a very rapid process compared to P and other cations, such as Ca. When cement is stored in paper sacks under high humidity conditions, the formation of lumps can occur owing to the formation of syngenite, because syngenite acts as an effective binder of the dry cement particles [29]. Most of the K had leached out from the pellets that were dehydrated at room temperature.

Most of the Mg originates from powdered dolomite rock and its parent mineral, dolomite (MgCa(CO₃)₂). The leaching of Mg is insignificant in the early stages and for low L:S ratios. The observed differences in the leached amounts of Mg were dependent on the pH, and thus are a consequence of the different degrees of carbonation. Only small amounts of Mn, Al, Cu, Fe, P, and Zn were released from the pellets, in agreement with earlier studies [8]. At high pH levels, calcium binds with P in calcium phosphate compounds that have a low solubility, and becomes more mobile when the pH decreases below pH =8 [30].

CONCLUSIONS

A flue-gas treatment offers a route to the rapid drying of ash pellets. A time of 10 min appears to be short enough such that there is only a limited contamination from the flue gas. The flue-gas treatment resulted in pellets with the lowest reactivity in terms of their pH and electrical conductivity. In addition, the flue-gas treated pellets released significantly less Ca, but more Mg compared to pellets treated using other methods. Our results suggest that the formation of syngenite in the K rich ash material leads to suppressed K leaching in the flue-gas treated pellets. The reactivity of the pellets dehydrated at room temperature was higher than that of flue-gas treated pellets, but was lower than hot-air treated pellets. Moderate pH and EC values are important during spreading of wood ash to hinder adverse effects on ground vegetation.

EXTENSIONS AND FUTURE WORK

Further studies should be undertaken to determine whether the flue-gas treatment time could be decreased further. In addition, the treatment time should be extended to evaluate the risk of contamination from flue gas. All contaminants captured by the ash particles from the flue gas

will be spread onto forest soil and extensive contamination should be avoided. It is also important to measure the particle size distribution and brittleness in pellets dehydrated using different methods to evaluate the formation of dust during handling and spreading. Dust is unhealthy and increases the risk of occupational diseases. Therefore the durability of carbonated ash particles is another urgent issue to study.

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