Roll pelletizing of ash - Cost efficient handling and improved ash product quality with accelerated carbonation

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Abstract – Roll pelletizing of ash has in earlier studies, [1] and [2], shown to be a cost efficient method to prepare ash from the combustion of forest biomass for recycling of minerals and acid-neutralizing lime components back to forest. Roll pelletizing is an automatized method requiring fewer manhours and allowing for fewer handling steps, and claiming less land area for the ash preparations compared with other techniques, for example self-hardened ash. Roll pelletizing can become an even more efficient technique when accelerated carbonation is being integrated with the automatized preparation of the ash product. In our laboratory study we showed for the first time that bottom ash from a biomass-fired boiler can be roll pelletized. The effect on mineralogy, pH, conductivity, acid neutralization capacity and leaching properties were shown to improve hardening of ash products treated with accelerated carbonation for 10 minutes or 24 hours at 50 ºC in humid atmosphere.

Keywords: Forest fertilization, roll pelletizing, hardening, carbonation, bottom ash

INTRODUCTION

Swedish authorities recommend [3] recycling of ash from combustion of forest biomass back to the forest with the purpose of maintaining a productive forest in order to minimize natural acidification of soil from natural growing of trees and in former times the high deposits of acid rain. It has also been discussed whether the need to compensate the slow depletion of basic cations that will occur as a result from harvesting branches, tree tops and roots. The ash products to be recycled have to meet certain requirements. There are minimum and maximum limits for macro and micro nutrient elements as well as for heavy metals. There are also requirements that the ash product shall be hardened to an acceptable degree. Effects from ash recycling on soil water, soil, flora and fauna from ash recycling have been described in many scientific studies [*e.g*. ref. in 4].

Roll pelletizing of ash has in earlier studies, [1] and [2], shown to be a cost efficient method to prepare ash from the combustion of forest biomass for recycling of basic cations and acid-neutralizing lime components back to forest. Roll pelletizing is an automatized method requiring fewer manhours and allowing for fewer handling steps, and claiming less land area for the ash preparations compared with other techniques, for example self-hardened ash. The method has been used in industrial scale at two board mills and one district heating plant in Sweden. Roll pelletizing (patented by Gert Nordström) requires an ash rich in oxides (most often CaO and MgO) with low content of unburnt organic matter that is well mixed with correct amount of water (the proportions depend on the individual ash) during a correct energy input with a forced batch mixer [5], [6].

A roll pelletized ash products normally show a high quality with slow leaching patterns and with no expected negative effects to soil or soil water [7] neither on clear-cut areas or closed forest areas.

Several more recent interesting scientific studies [8], [9], [10] and also [11] and [12] describe findings on factors influencing the chemistry of hardening and especially factors that accelerate carbonation of ash. Carbonation is of main importance in the hardening process of an ash product. Roll pelletizing can become an even more efficient technique if the hardening step is being accelerated and automatized so that an outdoor hardening period (normally between a month and a year) is omitted altogether. The aim with our project is a ready-hardened ash product that can be transported and used as fertilizer immediately after production without any unnecessary storage and re-loadings.

When fresh dry ash is wetted the following chemical reaction occurs.

$$CaO \text{ (calcium oxide)} + H_2O \text{ (water)} \rightarrow Ca(OH)_2 \text{ (calcium hydroxide)} + \text{heat} \quad (1)$$

Under the influence of carbon dioxide (CO_2), normally from air but here actively added as a moist gas, the carbonation of the ash will occur:

$$Ca(OH)_2 + CO_2 \text{ (carbon dioxide)} \rightarrow CaCO_3 \text{ (calcium carbonate)} + H_2O \quad (2)$$

The formed calcium carbonate is less chemically reactive and thus less hazardous than calcium oxide and calcium hydroxide to soil, soil water, flora and micro fauna. If the water is added unevenly or in too small amounts the ash product will carbonate unevenly and will like not meet quality requirements measured as pH or salt effects on water, and become dusty and with a high tendency to form big ash lumps difficult to spread. A high quality ash product shows a slow leaching pattern which only is obtained with a well carbonated ash product.

The first objective of our current study was to evaluate whether bottom ash from biomass-fired boiler with inclined grate can be roll pelletized. This has never been evaluated earlier. In earlier studies only well-combusted fly ash with low content of organic matter and with no slag, like fly ash from circulated fluidized bed (CFB) and bubbling fluidized bed (BFB) boilers, have been roll pelletized with excellent results. The second objective of our study was to evaluate the impact of carbon dioxide treatment of freshly rolled pellets in laboratory scale. A third, subordinate, objective was method development for analysis of leaching behavior comparable with natural forest conditions.

MATERIAL AND METHODS

Ashes (Tab. 1) were thoroughly mixed in a food processor in the laboratory and immediately pelletized in a bench scale hand driven roll pelletizer. Roll pelletizing requires a well tried-out ash recipe. Ten recipes were tried-out in our pre-study (Tab. 2).

Table 1. *Ashes, from forest biomass-fired boilers, used in the study.*

Type of boiler	Type of ash	Ash code
Inclined grate boiler, 55 MW heat, 23 MW electricity	Bottom ash, wet ash removal	GB-B
As above	ESP[1] fly ash, dry	GB-ESP
Circulating Fluidized Bed (CFB), 75 MW heat and 43 MW electricity	ESP fly ash, dry	CFB-ESP
Rebuild steam power plant with Axon cyclone boiler and plane grate, 30 t/h	ESP fly ash, dry	Axon-ESP

[1]*Electrostatically precipitated*

Table 2. *Obtained ash recipes after testing in bench scale roll pelletizer [g DS]. Recipe nine was selected for the carbonation tests.*

Raw material	1	2	3	4	5	6	7	8	9	10
GB-B	-	-	330	180	168	-	200	100	140	150
GB-ESP	-	-	670	730	682	500	800	400	290	310
CFB-ESP	-	1000	-	90	150	-	-	-	70	40
Water	200	300	400	400	400	160	250	230	155	145
CaO	200	-	-	-	-	-	100	200	-	-
Anox-ESP	1000	-	-	-	-	-	-	-	-	-
Visual result of pellets	Hard and good	Hard and good	No good, very friable	No good, very friable	No good, very friable	No good, very friable	No good, very friable	No good, very friable	Hard and good	Hard and good

As mentioned, one objective of this study was to evaluate whether bottom ash from a grate boiler was possible to use for roll pelletizing. This study showed that this was possible, so it was then decided to continue with the next step in our study and try the interesting carbon dioxide treatment to evaluate accelerate carbonation for a selected ash pellet recipe containing bottom ash. Recipe 9 was selected prior recipe 10 due to lower total content of organic matter (though still rather high).

The fresh ash pellets with recipe 9 were treated (Tab. 3) with moist carbon dioxide gas ($CO_{2\,(g)}$) in a laboratory oven for 10 minutes (9B) and for 24 hours (9C), respectively. The carbon dioxide treatments were compared with no CO_2 treatment (9A) and also with 30 days outdoor-under-roof-treatment (9D). Samples of pellets 9A-9D were then chemically analyzed.

Table 3. *Carbon dioxide treatments of roll pelletized ash recipe 9 containing bottom ash from a grate boiler.*

Treatment code	Treatment
9A	No carbon dioxide treatment
9B	10 minutes CO_2-tmt at 50 ºC in humid atmosphere
9C	24 hours CO_2-tmt at 50 ºC in humid atmosphere
9D	30 days outdoor-under-roof-treatment. No CO_2-tmt.

High content of unburnt organic matter was measured since it is known to interfere with agglomeration of ashes. The Swedish Forest Agency (*Skogsstyrelsen)* [3] has provided recommendations on laboratory tests on ash products to be spread in the forests for pH and electric conductivity (EC) to ensure that highly chemically reactive ashes are not spread and do not cause corrosive damages or salt effects to flora and fauna of the forest or leaching of nutrients from soil or other soil water effects. The Agency also has provided recommendations on minimum and maximum content of elements in ash products (Tab. 4). The recommended tests were done in our study.

Crystalline compounds and minerals were quantitatively determined in ash raw materials and pellets with x-ray powder diffraction (XRD) with a Siemens D5000 powder diffractometer and primary radiation Cu-Kα (1.54 Å) was supplied by a conventional X-ray tube. Outgoing radiation intensity was detected with a scintillation detector as a function of the angle of incidence. Present compounds were identified by comparison with data in the data base from the Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 release 2010, 2010, Philadelphia, USA. An unhardened ash product normally has a high content of chemically unreacted oxides, and a well hardened ash product normally has only traces of oxides or hydroxides and a high content of carbonates.

Acid neutralization capacity (ANC; unit: mole H^+/kg DS ash) is an important characteristic for an ash product intended to compensate for natural acidification of soil and soil water and to be a good so-called “vitalizing fertilizer” (in Swedish *vitaliseringsgödselmedel*). In other words, the ANC can also be described as a measure of the liming effect. A well hardened ash product shall compensate for the natural acidification with the same rate as it appears, *i.e.* the ANC of the ash product should be exerted slowly. 60 years of leaching is a good aim for Swedish forestry. Roll pelletized ash has in earlier studies [1] been shown to display low leaching rates. Today there is no standard method to describe the ANC of a well hardened ash product. A test method was developed by Sundin [13] and was further developed by Larsson & Westling [14] and further by IVL [1]. We learned that pH should be kept constant to have the test period short. pH 4 is chosen to simulate acid spruce and pine forest soils. In the current study, the ANC is measured with a modified version of the pH stat test SIS-CEN/TS 14429:2005 where L/S was 100 and pH was held constant with nitric acid at 4. The pellets were not pounded prior to analyzing but the whole pellets were placed in an acid washed fine-meshed net to avoid contact with the magnetic stirrer; alternatively a platform shaker could also have been used. The ANC was followed during five days.

RESULTS AND DISCUSSION

It was not possible to agglomerate the ashes from the grate boiler, neither the bottom ash alone (GB-B) nor in an ash mixture with the grate boiler fly ash (GB-ESP) and not with GB-ESP only (Tab. 2; recipes 3-8). A well burnt CFB ash (Tab. 4) had to be mixed in with the grate boiler ashes to obtain a hard and good ash pellet (recipes 9 and 10). Reasons for the agglomeration problems with a grate boiler ash are believed to come from high content of unburnt organic matter and low content of reactive oxides due to the wet ash removal system or aged ashes. Recipe 9 had between 7.5 and 11.3 % unburnt organic matter (Tab. 5) which is high but was possible to agglomerate and gave good but not excellent pellet quality. 9B and 9C pellets gave a high pH (12.0 – 13.1) when added into water [3]. The 9C pellets had hardened rather well and had an electric conductivity (EC) value (Tab. 5) well below the limits recommended by the Swedish Forest Agency (Tab.6).

Both the ash product (recipe 9) and the raw materials fulfilled (with minor exceptions) the threshold values for important elements established by the Swedish Forest Agency (Tab. 4).

Table 4. *Content of macro and micro plant nutrients and heavy metals (g and mg/kg DS) in ash raw materials (grate boiler bottom ash, grate boiler fly ash, CFB boiler fly ash) and ash pellets (recipe 9) compared with threshold values recommended by the Swedish Forest Agency.*

	Unit	GB-B wet untreated	GB-ESP dry untreated	CFB-ESP	Pellets 9	Inaccuracy of measurement	Limits by Sw. Forest Agency* 2008
Water		50.5 %	0.5 %	0.2 %		± 10 %	-
Organic matter*		14.5 %	6.5 %	0.1 %		± 10 %	-
Calcium Ca	g/kg DS	123	221	216	188.3	± 30 %	≥ 125
Magnesium Mg	g/kg DS	15.4	22.1	24	19.9	± 25 %	≥ 15
Potassium K	g/kg DS	51.4	80.4	64	61.7	± 25 %	≥ 30
Phosphorous P	g/kg DS	10.3	19.1	15	14.6	± 20 %	≥ 7
Boron B	mg/kg DS	100	290	288	140	± 20 %	≤ 800
Cupper Cu	mg/kg DS	120	150	79	180	± 20 %	≤ 400
Zink Zn	mg/kg DS	500	4 700	1084	3000	± 25 %	500 – 7 000
Arsenic As	mg/kg DS	4.2	13	3	7.8	± 25 %	≤ 30
Lead Pb	mg/kg DS	120	170	65	120	± 20 %	≤ 300
Cadmium Cd	mg/kg DS	2.1	38	15	25	± 30 %	≤ 30
Chromium Cr	mg/kg DS	77	73	69	120	± 25 %	≤ 100
Mercury Hg	mg/kg DS	< 0.046	0.58	0.18	0.36	± 25 %	≤ 3
Nickel Ni	mg/kg DS	39	40	31	61	± 35 %	≤ 70
Vanadinium V	mg/kg DS	32	28	22	32	± 25 %	≤ 70
PAH, carcinogenic	µg/kg DS			< 0.18	18.53		-

*Recommendation in final ash product ready for spreading in forest

Table 5. *Samples of ash pellets with recipe 9 were analyzed for water content, organic matter and according to recommendations by the Swedish Forest Agency [3, annex 2] for pH and electric conductivity.*

Sample	Water content [%]	Unburnt organic matter [%]	pH**	Electric conductivity** [mS/m]
9A.1	26.9	9.3	12.9	3510[1]
9A.2	-	9.4	13.0	3610[2]
9A.3	-	-	13.0	3580[2]
9B.1	24.5	7.9	13.0	2790[3]
9B.2	-	7.5	12.9	2720[3]
9B.3	-	-	13.1	2690[3]
9C.1	2.1	10.5	12.0	2000[3]
9C.2	-	10.5	12.0	2010[3]
9C.3	-	-	12.0	1975[3]
9D.1	11.4	11.2	13.1	2770[4]
9D.2	-	11.3	13.1	3230[4]
9D.3	-	-	13.1	3270[4]

[1]pH and electric conductivity (EC) was measured 26 days after pelletizing
[2]pH and EC was measured 18 days after pelletizing
[3]pH and EC was measured 34 days after pelletizing
[4]pH and EC was measured 67 days after pelletizing

Table 6. *Maximum limits for electric conductivity (EC) from recycled ash products to be spread in forest as recommended by the Swedish Forest Agency [3; annex 2].*

Ash dose (ton DS / hectare)	EC limit [mS/m]
Clearcut forest area	2 400
2 – 3	2 800
1 – 2	3 200
< 1	3 600

Ash pellets with high quality are well carbonated, *i.e.* the reactive oxides are chemically transformed to carbonates primarily the mineral calcite ($CaCO_3$) or other slow leaching minerals like ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$). This can be seen directly with the X-ray analysis and should be verified with slow leaching properties in the ANC test, and low pH and EC effects when pellets are added to water.

The 9D treated pellets showed a rather poor quality (Tab. 5, Tab. 7) despite the long storage period prior to analyze (67 days). Some of the reasons for this could be the high content of organic matter and probably low oxide content prior pelletizing. It is interesting to see that the 9C pellets had improved properties and had carbonated to a higher degree which is shown from the pH, EC and ANC (Fig. 1, Tab. 8) values and also confirmed with the presence of only traces of calcium hydroxide (Tab. 7) and the highest calcite concentration (Fig. 2) shown with the X-ray powder diffraction analysis.

Table 7. *Determined chemical compounds with X-ray powder diffraction analysis.*

Mineral	GB-ESP	CFB-ESP	9A	9B	9C	9D
$CaCO_3$	S	S	S	S	S	S
$Ca(OH)_2$	W	W	W	Tr	Tr	M
Ettringit	-	-	W	W	-	Tr
SiO_2	M	M	M	M	M	M
K_2SO_4	M	-	M	M	W	W
KCl	Tr	Tr	Tr	-	Tr	-
Fe_2O_3	-	-	W	W	Tr	-
Ca_2SiO_4	W	W	W	W	W	W
$CaSO_4*0.62H_2O$	-	Tr	W	W	M	-
$KAlSi_3O_8$ (feldspar)	-	M	-	-	-	-
K silicate	-	-	-	-	-	present
CaO	M	Tr	-	-	-	-

Strong (S); Medium (M); Weak (W); Traces (Tr)

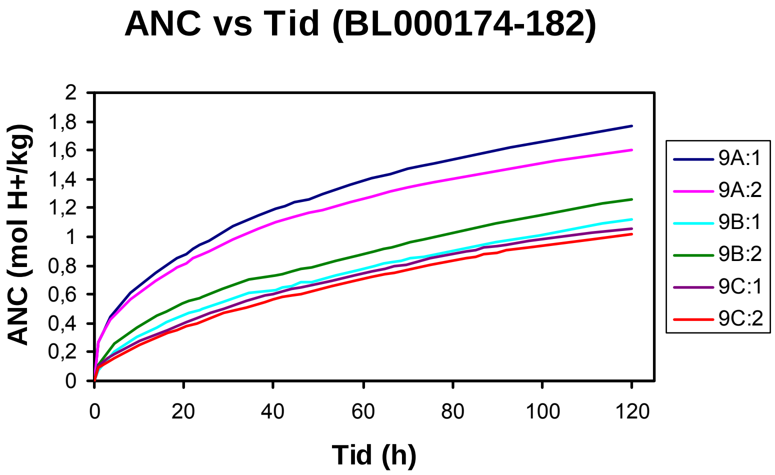

Figure 1. *The accumulated acid neutralization capacity, ANC [mole H+/ kd DS ash product], over time (Swedish* tid*). Five days with a constant pH of 4, L/S 100 (SIS-CEN/TS 14429:2005 Annex B:2).*

Table 8. *The accumulated acid neutralization capacity, ANC [mole H+/ kd DS ash product], after five days leaching with L/S 100 and pH 4 (SIS-CEN/TS 14429:2005 Annex B:2).*

	9.A1	9.A2	9.B1	9.B2	9.C1	9.C2
ANC mole H^+/kg DS	1.8	1.6	1.1	1.2	1.1	1.0

The accumulated ANC was in earlier studies [1], with well hardened ash products, 3 mole H^+/kg DS ash after 30 days leaching tests (leaching water was changed once a day) and the control lime had an ANC of 10 mole H^+/kg after the same time period. The accumulated ANC graph in our current study was slowly decreasing over time (Fig. 1) but the graph did not level out in five days. This means that the ash product still has acid neutralization capacity (which is favorable) and that the test should have had to continue more days to obtain the total acid neutralization capacity for this ash product.

Pellets 9A (without CO_2 treatment) had a more rapid acid neutralization capacity (Fig. 1) than 9B and 9D. This means that carbon dioxide treated pellets 9B and 9D had hardened to a higher degree and would have neutralized soil acidification under a longer period if spread in the forest which is better from an environmental point of view.

9B and 9C treated pellets obtained an ANC between 1.0 and 1.2 after five days (Tab. 8) and with the IVL method [1] well hardened ash pellets obtained the corresponding ANC in 10-17 days (N.B. the methods were slightly different so the results are not absolutely comparable.)

Potassium, an important plant nutrient and known to leach easily, is also easy leachable in the analyzed 9A-9C. Approximately 50 % of total potassium content had leached into the pH 4 water in 24 hours independent of the degree of hardening. This means for example that these ash products should not be stored outdoors without roof or other protection from rain. Earlier studies [1] indicate that well hardened ash pellets was not as sensible to leaching as these pellets containing bottom ash from grate boiler.

The carbon dioxide treatments 9B and 9C contributed to a substantial reduction of the leaching of calcium. Only 3-4 % of total calcium leached from the carbon dioxide treated pellets in 24 hours in water in the pH stat test compared with 6-7 % of calcium that leached from the untreated 9A pellets. As another comparison, 77-78 % of total calcium leached from the untreated unpelletized bottom and fly ash in 24 hours in water at pH 4. This indicates that the carbonation contributes substantial to a decrease in leaching of calcium.

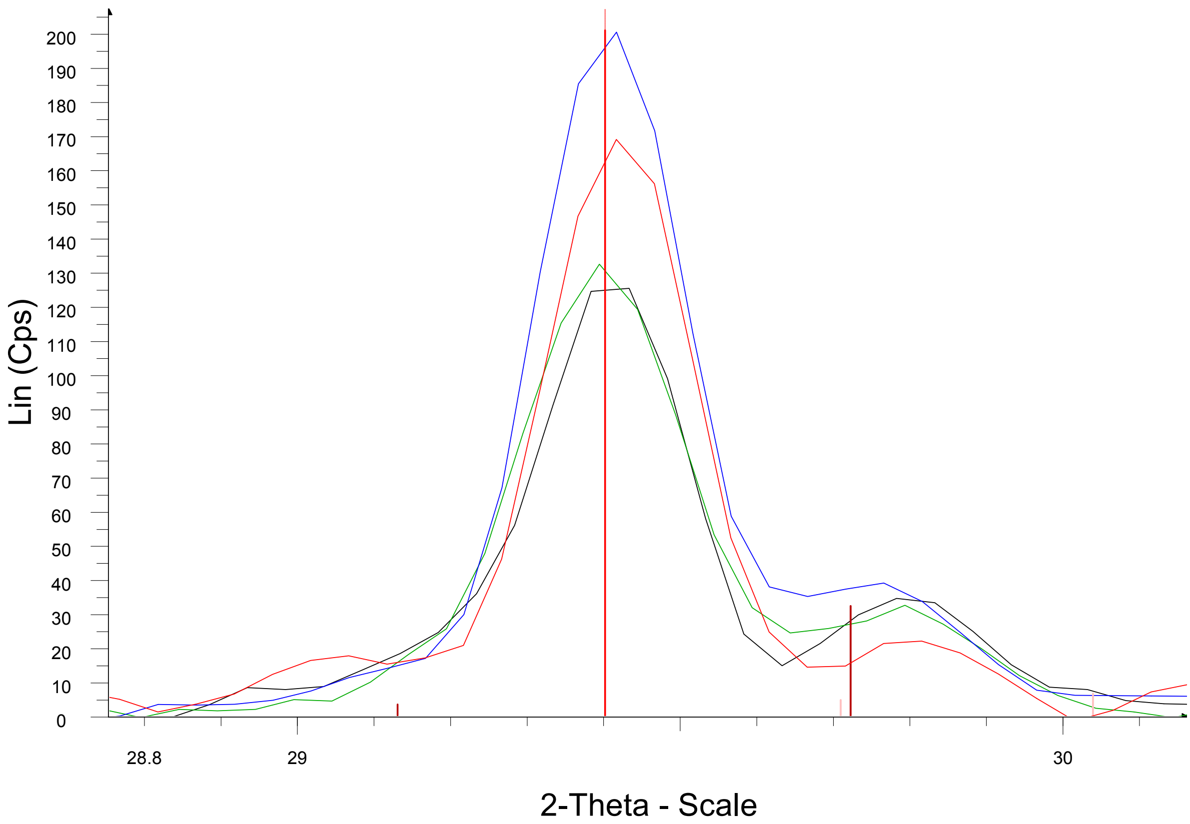

Figure 2. *Content of calcium carbonate, $CaCO_3$, in form of the mineral calcite, in four ash pellet samples: 9A (black; lowest content), 9B (green), 9C (blue: highest content), 9D (read graph). Ash recipe 9 is described in Tab. 2 and the treatments A-D are described in Tab. 3.*

SOME CONCLUSIONS

Roll pelletizing and accelerated carbonation of forest biomass ash have been studied and the work has led to the following conclusions.

- Bottom ash from an inclined grate boiler was possible to roll pelletize if the ash was mixed with a well combusted CFB fly ash. (Wearing damages on rolls in the roll pelletizer due to presence of slags was not evaluated in this study.)
- Carbon dioxide treatment was shown to improve ash quality and shorten the hardening time.
- Combustion of forest biomass in a grate boiler needs to be optimized and well controlled if the ashes should be pelletized. Content of unburnt organic matter should be well below 10 % and the slag formation minimized.
- Only fresh and dry ash should be used for pelletizing. Ash that earlier have been in to contact with water or moist air prior to pelletizing will lose its ability to agglomerate and harden well.
- Rain will likely cause leasing of easy leachable nutrients like potassium. The analyzed pellets in our study (recipe 9 with grate boiler bottom ash) did not carbonate to such an extent that the ready pellets could be stored without roof or under other protection from rain.
- The acid neutralization capacity of the ash product was analyzed with a modification of the pH stat test SIS-CEN/TS 14429:2005 Annex B:2 with L/S 100 and pH kept constant at 4. Pellets were kept as produced without pounding. This method seems to be a good choice being a quicker method and less laborious than earlier tested methods but should have been conducted in our case more than five days since the accumulated ANC graph did not level out in only five days.

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