Wood ash as raw material for Portland cement

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Abstract – The Norwegian goal for increasing the energy production from biomass, leads to the roughly estimated production of 70 000 metric tons bio ash per year. Bio ashes from coniferous wood have a chemical composition close to Portland cement clinker, making it interesting to evaluate the possibility of utilising such ashes as raw material for cement manufacturing. This is a valid way of stretching the plant's calcium resources and utilize all parts of the bio mass. The CaO in the ashes will replace limestone ($CaCO_3$) in the feed stock, thus reducing the cement plants overall CO_2 emission, directly as well as indirectly by reducing the energy demanding calcining.

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Keywords: Wood ash, Portland Cement manufacturing, CO_2 emission.

INTRODUCTION

This work is part of the CenBio - Bioenergy Innovation Centre - one of the eight Norwegian Centres for Environment-friendly Energy Research (in Norwegian: FME - Forskningssentre for miljøvennlig energi). The centre is co-funded by the Research Council of Norway, a number of industrial partners and the participating research institutions.

The Norwegian goal for increasing the energy production from biomass, leads to the production of about 70 000 metric tons bio ash per year, roughly estimated.

The Portland cement production at Heidelberg Norcem Brevik amounts to about 1.4 Mt (million metric tons) per year.[1] The main source of calcium is calcium carbonate, $CaCO_3$, mostly in the form of limestone. The making of cement involves calcining if the limestone, which leads to emission of CO_2 corresponding to about 79 wt% CO_2 of the amount of CaO produced, or about 50 % of the total cement clinker mass. 60 % of the total amount of CO_2 emitted from the manufacturing of cement clinker originates from the calcining of $CaCO_3$, while the remaining originates from the fuel.

Replacing some of the limestone with Ca-rich bio wood ashes would be an efficient way of reducing the plant's CO_2 emission, both directly and indirectly by reducing energy demand by avoiding the endothermic calcining process involved.

NORWEGIAN GOALS

Biomass energy potential

Total biomass resources extracted from agriculture and forestry in Norway amounts to about 55 TWh[2]. Of this, 16 TWh is utilised as energy, while the rest is lumber, wood processing, food, and fodder. Annually, about 40 TWh of forest biomass are left unused. Productive forests make up about 90 % of the total wood biomass. Of the remaining, non-productive forest makes up 8%, while other areas are only 2%.

The Norwegian goal is to increase the annual energy production from biomass to 14 TWh by 2020.[3] Since the bulk of the biomass is made up by productive forest, the energy potential from biomass growing outside productive forests is estimated to only 1 TWh, the remaining 13 TWh then will have to come from productive forest.

Some of this, 4–6 TWh, could come from left behind biomass, from branches/tops (25%) and roots/stumps (25%) that are left on the site. The remaining 7–9 TWh then would have to come from new forest.

The energy yield from wood biomass is estimated to 5.3 kWh per kg dry mass. Provided the goals are reached, the growth of 14 TWh sums up to roughly 2.6 Mt dry wood biomass annually.

Bio ash production

The biomass ash content varies widely. For wood fuel, the ash content varies from < 1% to 8 % depending of which part of the tree and combustion technology, see Table 1. The analyses reported in the table are from ash from combustion at 550°C, hence the ashes could contain come carbonates, possibly making the tabulated values for wood ash a bit higher than expected from a power plant. Assuming 2.5 % ash content (wood+bark), the potential ash yield of 2.6 Mt wood biomass is roughly 70 000 metric tons per year.

Table 1 Fuel-specific ash content of biomass fuels. Ash content given in wt% (dry base), measured according to ISO 1171-1981 at 550°C.[4]

Biomass fuel	Ash content (wt%)
Bark	5.0 – 8.0
Woodchips with bark (forest)	1.0 – 2.5
Woodchips without bark (industrial)	0.8 – 1.4
Sawdust	0.5 – 1.1
Waste wood	3.0 – 12.0
Straw and cereals	4.0 – 12.0

MANUFACTURING OF PORTLAND CEMENT

Portland cement constituents

Portland cement consists of cement clinker, gypsum (3-4 % as SO_3), and optionally pozzolanic fly ash (FA) from bituminous coal fired power plants (Norcem Standardsement FA contains 20% FA).

The cement clinker constituents are hydraulic, and react with water to form solid hydroxides which constitute the binder in concrete. The gypsum is added to prevent flash setting of the cement. The fly ash acts as a pozzolan, i.e. it forms a secondary binder phase by reacting with $Ca(OH)_2$ formed by the clinker hydraulic reactions.

The typical composition of Portland clinker is shown in Table 2 (oxide composition) and Table 3 (major phases). The clinker contains four major phases which in cement nomenclature are called alite, belite, aluminate and ferrite.

Table 2 Typical oxide composition of Portland clinker (Kjellsen)[5]

Oxide	Typical composition range (wt%)
CaO	60-67
SiO_2	17-24
Al_2O_3	4-7
Fe_2O_3	1.5-5
MgO	1-5
SO_3	0.5-3.5
K_2O+ Na_2O	0.2-1.5

Table 3 The four major phases in Portland Clinker.[5]

Phase	Mineralogical term	Cement chemical notion	Shortened cement chemical notion	Typical content (%)
Tricalcium silicate	Alite	$3CaO·SiO_2$	C_3S	50 - 65
Dicalcium silicate	Belite	$2CaO·SiO_2$	C_2S	15 - 25
Tricalcium aluminate	Aluminate	$3CaO·Al_2O_3$	C_3A	5 - 15
Tetracalcium aluminoferrite	Ferrite	$4CaO·Al_2O_3·Fe_2O_3$	C_4AF	5 - 15

Raw materials in cement production

The main raw material component is limestone ($CaCO_3$), which make up typically 90% or more of the raw meal. In addition small amounts of quartz (SiO_2), burnt shale (Si, Al, Fe), bauxite (Al-hydroxide) and iron oxide (Fe_2O_3) are added. The origin of the minor constituent materials may vary between cement plants depending on local availability.

Fuel

The fuel mix at Heidelberg Norcem Brevik consists of a mix of fossil fuel, alternative fossil fuels and biomass as shown in Table 4. Part of the waste derived fuel is declared CO_2 neutral (biomass). The plant already uses wood residue fuel. The CO_2 emission associated with cement production origins primarily from combustion of the fuels in the kiln system and from the calcination of the limestone.

Table 4 Fuel mix applied at Norcem Brevik (as % of the supplied energy)[5]

Fuel type	%
Fossil fuel (e.g. coal, petroleum coke)	52
Alternative fossil fuel (e.g. waste oil and solvents)	15
Biomass (e.g. animal meal, wood residue)	33

Emissions

The by far largest contributor to the emissions is CO_2, making up more than 680 kg CO_2 per metric ton cement produced[6], of which 60% origins from the calcining of limestone.

Ashes in Portland cement

Traditionally, fly ash from bituminous (black) coal fired power plants has been mixed into Portland cement as pozzolans. A pozzolan can be described as a material which can be activated to act cementitious in the presence of Portland cement. Typically silica (SiO_2) in the ash reacts with $Ca(OH)_2$ formed by the hydration of cement, forming stable hydration products adding to the concrete stength. Also the presence of alkalis acts to activate the silica. One of the reasons the pozzolanic reaction is considered beneficial is that it causes the reduction of free $Ca(OH)_2$ in the concrete matrix. Coal fly ash has sufficient content of silica to react as a pozzolan (Table 5). Norcem has two cement types containing fly ash, Standardsement FA and Anleggsement FA, both containing 20% fly ash.

The general idea behind the use of wood ash as raw material for clinker production is its high content of calcium. The ashes then become part of the clinker. Wood ashes are low in SiO_2 and high in CaO, making them suitable as cement raw material rather than pozzolans, replacing $CaCO_3$ in the cement raw meal.

Bio ash as raw material for clinker production

The composition of Portland cement clinker is shown together with the composition of birch and spruce bottom ashes in Table 5. Bottom ashes are enhanced in non-volatile elements like calcium. Especially the spruce ash resembles the Portland cement clinker in being rich in CaO, thus being suitable to replace $CaCO_3$ in the raw meal.

The Heidelberg Norcem Brevik plant processes about 1.6 Mt raw materials per year. Thus, by introducing the entire production of about 70 000 tons of wood bio ash into the stream, the ash will make up less than 5% of the total - perhaps significantly less, since much of the ashes are preferably recycled to the soil. Since the ash will only be a minor constituent, the exact chemical resemblance of ash compared to cement clinker is not critical.

Table 5. Typical constituents of birch and spruce bottom ashes from Southern Norway (Reimann et al)[7] compared to Portland cement and and bituminous coal fly ash.[8]

Component	Portland cement clinker	Spruce ash	Birch ash	Bituminous coal fly-ash
SiO_2	17 – 24	-	-	20-60
Al_2O_3	4 – 7	-	-	5-35
Fe_2O_3	1.5 – 5	0-1	0-1	10-40
CaO	60 – 67	60	34	1-12
MgO	1 – 5	9	14	0-5
SO_3	0.5 – 3.5	11	12	0-4
Na_2O	0.2 – 1.5	1	1	0-4
K_2O	0.2 – 1.5	16	26	0-3
P_2O_5				0-5

The action of the wood ash is largely to replace limestone ($CaCO_3$) in the raw meal with CaO from the wood ash, an efficient way of reducing the overall CO_2 emission from the cement plant.

The calcining of $CaCO_3$ emits 44 wt% CO_2 of the starting mass, or 79 wt% CO_2 of the amount of CaO produced. The overall CO_2 emission amounts to about 50 % of the total clinker mass produced. This includes the extra amount of fuel needed for the decomposition of the CO_2:

$CaCO_3$ (s) = CaO (s) + CO_2 (g), ΔH_{rx} = 167 kJ/mol, P_{CO2} = 1 bar at 860 °C[9] Eq. 1

At Norcem, about 60% of the total CO_2 emission originates from the calcining of $CaCO_3$, while the remaining part originates from the fuel[10]. Thus replacing limestone with ash will also reduce the energy consumption of the plant. The overall effect may not be very large, but seen from an ash utilization point of view, this is a very efficient way of reducing the carbon footprint.

Ash preferences

Since the wood ash content of the cement feed stock will be less than five percent, the ash composition does not have to match the clinker composition accurately. The most important factors are high Ca content and low amounts of undesirable elements in the cement. A more detailed view of relevant elements in different ashes are provided by Vassiliev et al and shown in Table 6.

Table 6 Chemical ash composition of some types of wood and woody biomass, based of high temperature gas analyses, normalised to 100 % (from Vassiliev et al[11])

Biomass group, sub-group and variety	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2
Birch bark	4.38	69.1	8.99	4.13	0.55	5.92	2.24	2.75	1.85	0.13
Pine bark	9.20	56.8	7.78	5.02	7.20	6.19	2.79	2.83	1.97	0.19
Pine Chips	68.2	7.89	4.51	1.56	7.04	2.43	5.45	1.19	1.20	0.55
Pine pruning	7.76	44.10	22.32	5.73	2.75	11.33	1.25	4.18	0.42	0.17
Spruce bark	6.13	72.4	7.22	2.69	0.68	4.97	1.90	1.88	2.02	0.12
Spruce wood	49.3	17.2	9.60	1.90	9.40	1.10	8.30	2.60	0.50	0.10

An examination of the different elements' significance for the cement is as follows:

Major constituents - calcium, silicon, aluminium and iron

Data for spruce and pine show that Ca is concentrated mainly in the bark, the wood having lower values. Tree tops and branches are comparatively rich in bark, and therefore rich in Ca (Pine pruning). However spruce wood is rich in the other main clinker constituents, Si, Al and Fe, and the alkali contents are acceptable for Portland cement production.

Magnesium

The MgO content of Portland cements is typically less than one per cent. Too high MgO content can lead to strength loss of the concrete, but this can be avoided by sufficiently rapid cooling of the clinker.[12]

The Mg content of wood ashes is in the range of a few per cent, which will result in only a small contribution to the total amount of about 0.2% MgO.

Alkali content

The alkali content (Na_2O+K_2O) of cements typically range from 0.2 to 1.5 %. Too high alkali contents might lead to alkali-silica reaction (ASR), where an expanding gel forms in concrete exposed to constant moisture. The gel has a disruptive effect on the concrete, and can lead to serious problems in aged structures. It is the total alkali content which is important.[13] Also, the free SiO_2 content and aggregate properties play a role, so no definite alkali limit can be stated. The alkalis are also linked to the sulphates, as they are present as Na_2SO_4 and K_2SO_4 in the clinker.

Spruce ashes contains about 9-10% alkalis, which when diluted in the total feed stock will contribute with maximum 0.5 % alkalis to the clinker. This seems to be acceptable values, even the three times higher value of K_2O found in straw ash is not disqualifying.

The alkali content is typically controlled in the clinker burning process by bleeding off high-alkali dust from the kiln system.

Sulphates

Sulphate act to bind alkalis in the clinker as Na_2SO_4 and K_2SO_4. Due to kiln process reasons, it is desireable to have an alkali to sulphate molar ratio of about 1. Too little sulphate might lead to alkali clogging effects, while excess sulphate may lead to low melting eutectics based on alkali- and calcium sulphates – which also increases the clogging risk.[14] SO_3 has roughly the same molar weight as the alkalis (Na_2O, K_2O), making the desired amounts of sulphates in bio ashes not higher than the alkali content.

Reported ash data show less than 2 % SO_3 in wood ashes, which is about the same amount as found in the remaining feed stock.

Phosphorus

High phosphorous content in the cement clinker will affect the hydraulic properties. 0.3 wt% P_2O_5 in C_2S will prolong the setting time by about 20 minutes, which is within the normal range present in cements.[15] Higher amounts of P_2O_5 may lead to stabilisation of the C_2S phase during burning, thus inhibiting the formation of C_3S, the main hydraulic phase in Portland cement, which ultimately leads to slower build-up of strength in the concrete.

The phosphorous present in pine chips and bark ash is about 1.5% and 5%, respectively, while the values for spruce are 1.9% and 2.7% (Table 6). Other Norwegian bio energy plants have reported the amounts of 1-2%.[16] The contribution from 5% bio ash in the feed stock then should be limited to max 0.15%, which is well below the considered limits.

Heavy metals

Concrete is frequently used to demobilize heavy metals, so in general, a modest level of heavy metals present in Portland cement is not regarded a problem.

Reported levels of heavy metals in bottom and fly ashes from pine bark and wood from Haraldsen,[17] plus data from Norwegian bioenergy plants,[18] show that the only heavy metals that might require attention are cadmium and zinc contained in some fly ashes. Bottom ashes seem to never reach significant levels of Cd and Zn, compared to what is present in Portland cement.

In general, the compounds of heavy metals like cadmium, mercury and lead are volatile, and tend to concentrate in fly ashes.

Does the ash contain carbonate?

The equilibrium pressure of CO_2 in Eq.1 reaches one bar at 860 °C. Hence there is a risk that wood ashes from fluidized bed (FB) combustors might contain $CaCO_3$, since FB combustors operate at temperatures lower than 900 °C, which might be too low to ensure proper decomposing of the carbonate. The reaction is endothermic, and considerable excess temperatures may be needed to decompose $CaCO_3$ at short residence times.

Grate boilers operate on a temperature scale in the range of 1000 to 1200°C, with several minutes residence time on the grate, which should be sufficient to ensure a substantial decomposing of the carbonate present in the bottom ash.

The CO_2 concentration of the ash also depends on the storing of the ash, at moist conditions CaO will start to pick up CO_2 from the air or flue gas, forming $CaCO_3$.

Van Loo et al[19] assessed the carbonate concentration in mixtures of bottom ash and cyclone fly-ash from bark and wood chips to be in the range of 3.2 to 4.0 %. A.T. Lima et al[20] have characterized Danish fly ash from bio and municipal waste, danish bio-ash from straw combustion, Avedøre (ST), and ash from co-combustion of wood and oil, Avedøre Unit 2 (CW), both collected by electrostatic precipitators, ESP. The analyses show a carbonate content in the ashes of 12-13 %.

From the cement manufacturer's point of view, an ash low in carbonate is an extra argument for using it as a raw material. Using a proper composed wood ash with calcium present as carbonate ($CaCO_3$) is a valid way to stretch the plants calcium resources and utilize all parts of the bio mass. However if the bio ash calcium exists as oxide (CaO), an additional gain is obtained by directly reducing the plant's CO_2 emissions.

CONCLUSION

Bio ashes from coniferous wood have a chemical composition close to Portland cement clinker, making it interesting to evaluate the possibility of utilising them as raw material for cement manufacturing. This is a valid way of stretching the plants calcium resources and utilize all parts of the bio mass. The CaO in the ashes will replace limestone ($CaCO_3$) in the feed stock, thus reducing the cement plants overall CO_2 emission, both directly and indirectly due to reduction of the energy demanding calcining step.

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