Ash Utilisation 2012

Wood ash as raw material for Portland cement

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Outline

- Norwegian Bioenergy goals – ash production
- Portland cement
- Traditional use of ash in concrete - pozzolan
- Wood ash as raw material for Portland cement
- Ash preferences
- Significance of constituents
- Does ash contain carbonate?
- Conclusion

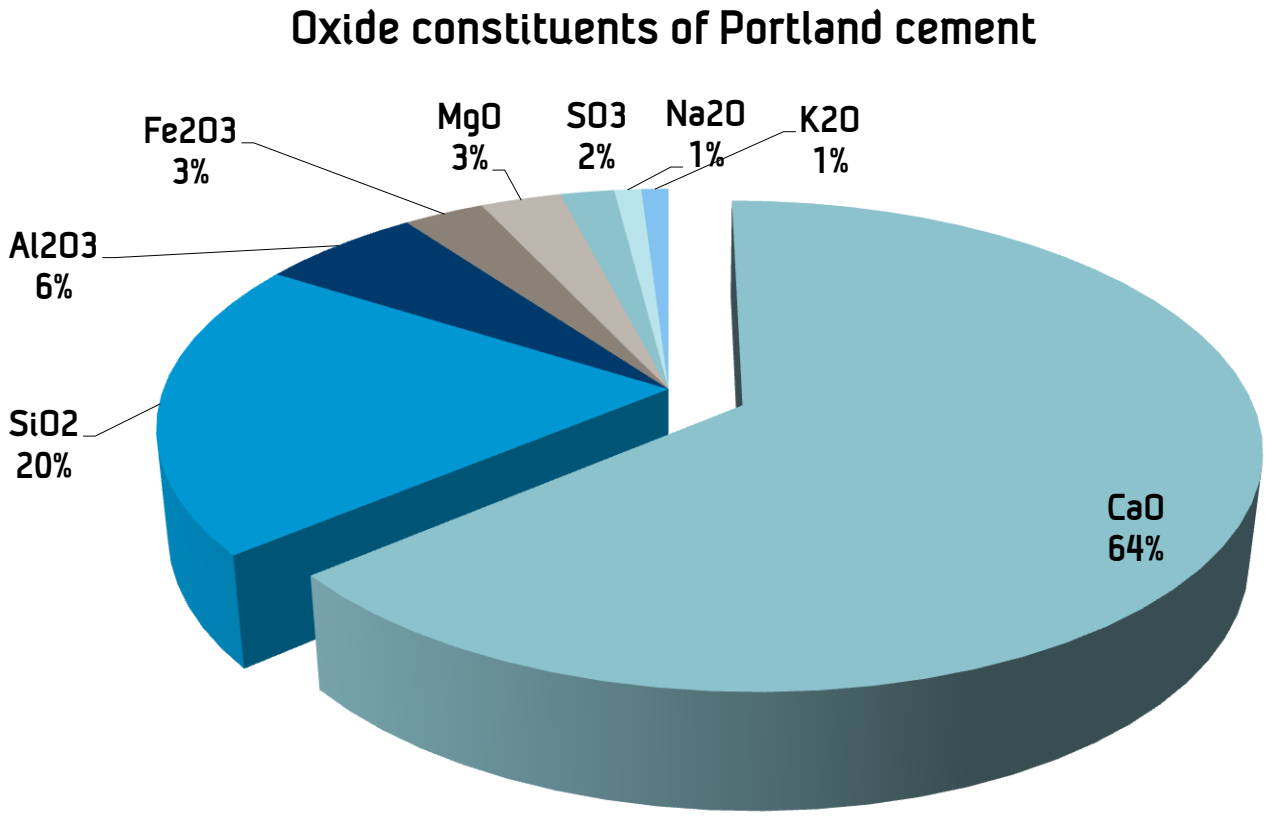
Norwegian Bioenergy Goals

- Total Norwegian biomass resources (2003): 55 TWh, of which 16 TWh is utilized as energy.
- Norwegian goal: 14 TWh increase by 2020
- A rough estimate of ash production: 70 000 tons per year
- Much of this ash will be rich in calcium - possible raw matedrial for Portland cement production

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

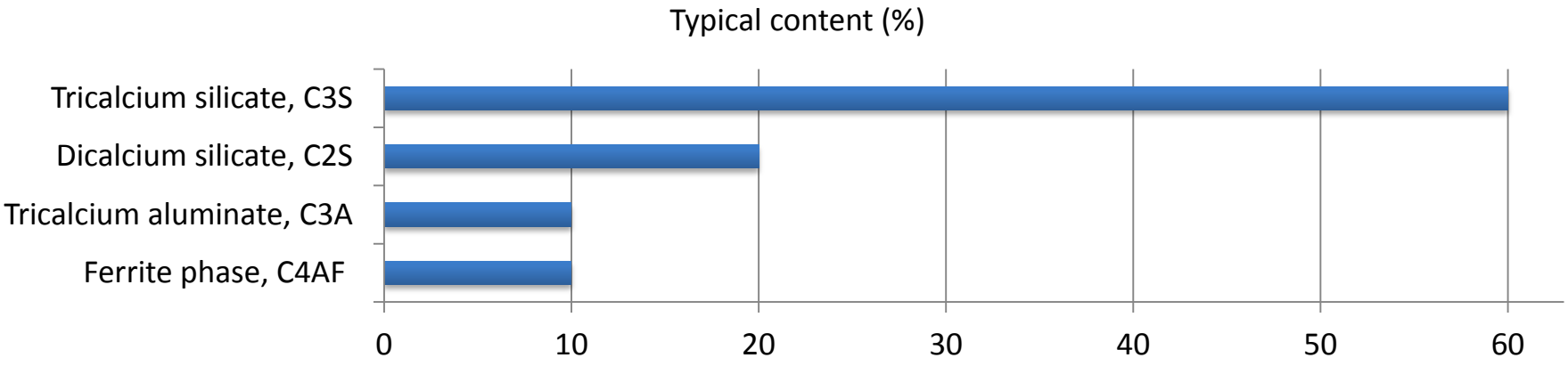
Portland cement constituents

- Cement clinker
- Gypsum (2-3% as SO_3)



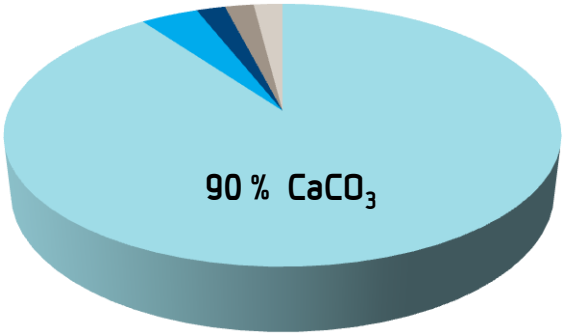
Portland cement mineralogy – major phases

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



Cement raw materials and fuel

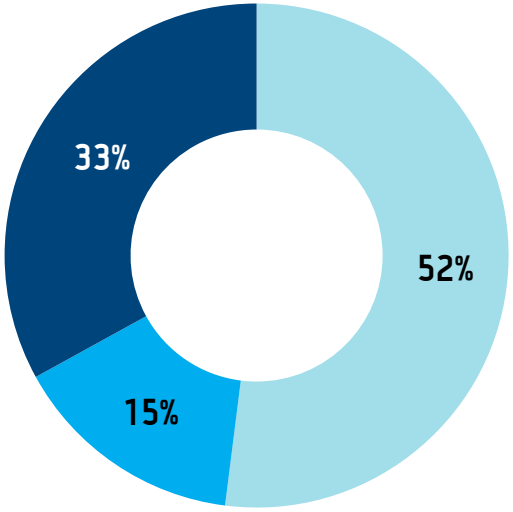
Portland cement raw materials



Limestone, CaCO3
Quartz, SiO2
Burnt shale (Si, Al, Fe)
Bauxite (Al-hydroxide)
Iron oxide (Fe2O3)

Process fuel mix at Norcem Brevik

Fossil fuel (coal, petrol coke)
Alternative fossil fuel (waste oil and solvents)
Biomass (animal meal, wood residue)



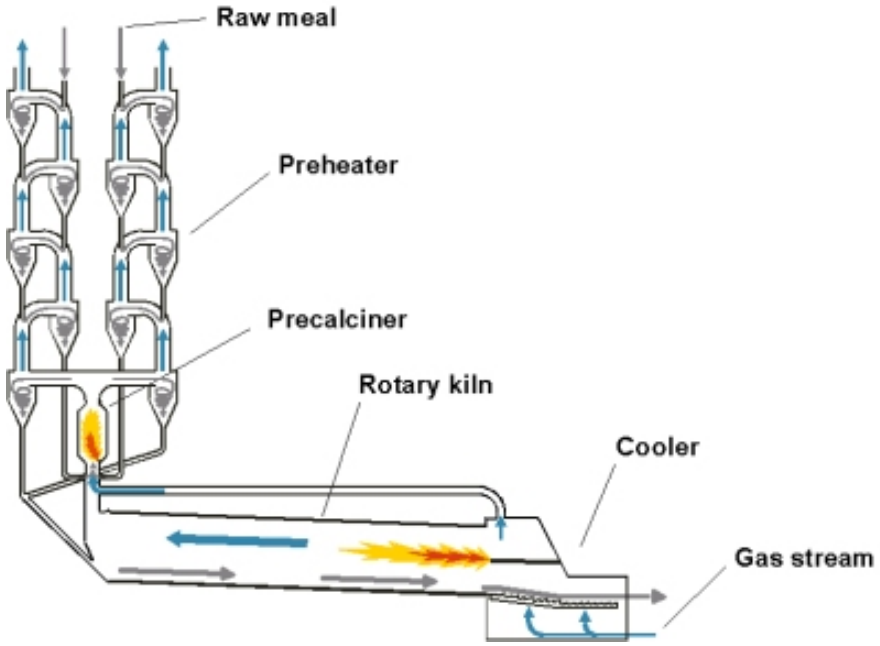
Manufacturing process - emissions

Process

- The raw meal is preheated and calcined counter current the firing exhaust.
- Max temperature ca 1450 °C
- Rapid cooling of cement clinker.
- Heidelberg Norcem Brevik: 1.4 Mt/y

Emissions

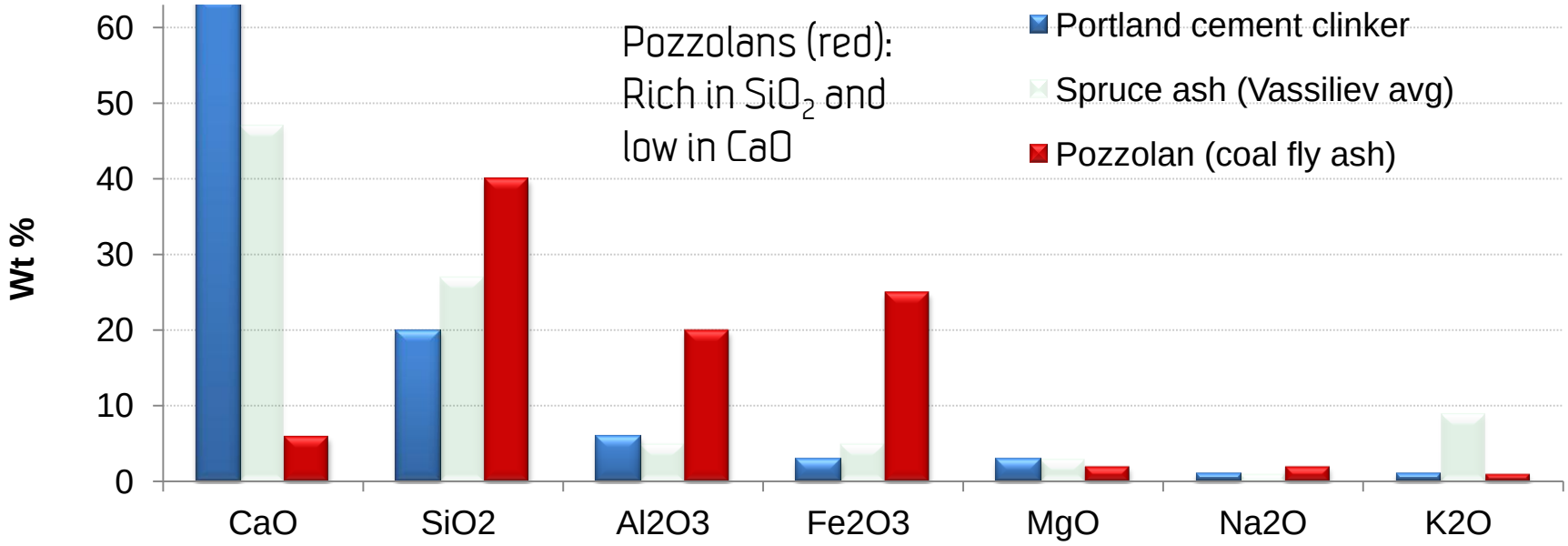
- CO_2 emission is about 700 kg CO_2 per metric ton cement produced
- 60% of the CO_2 origins from the calcining of limestone, the remaining from fuel.



Traditional use of ash - pozzolan

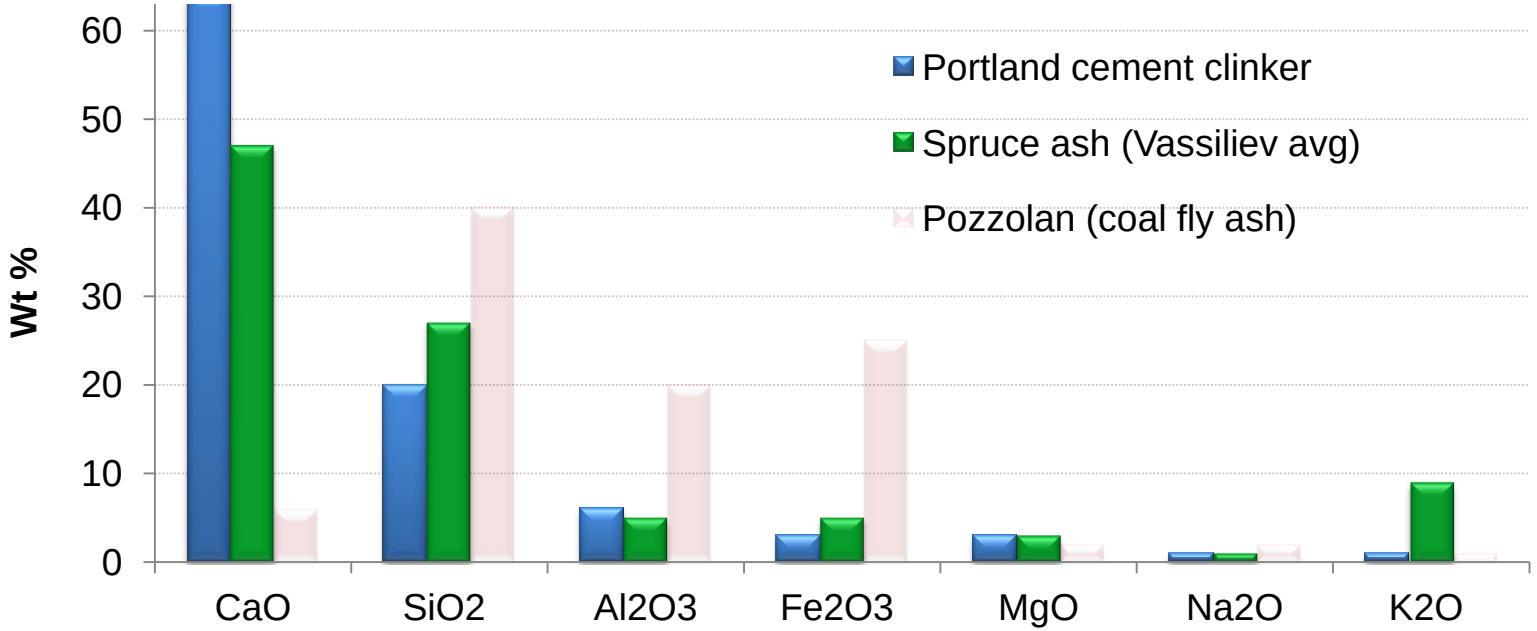
- Hydration of C_3S : $2\ C_3S + 6\ H_2O = C_3S_2H_3 + 3\ Ca(OH)_2$
- Hydrolyzed SiO_2 in the pozzolan "feeds on" the $Ca(OH)_2$:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow CaH_2SiO_4 \cdot 2\ H_2O$$



Wood ash as raw material for cement production

- General idea : High content of calcium in the ashes – possible cement raw material.
- Limestone ($CaCO_3$) in the raw meal is replaced with CaO from the wood ash
  - CO_2 emission is reduced significantly.



Wood ash as raw material for cement production cntd.

- The Heidelberg Norcem Brevik plant processes about 1.6 Mt raw materials per year.
- Thus, 70 000 tons of wood bio ash makes up < 5% of the total.
- Since the ash will only be a minor constituent, the exact chemical composition regarding minor constituents is not critical.
- The calcining of $CaCO_3$ emits 79 % CO_2 of the CaO produced, plus the energy needed to the for the decomposition of the CO_2:

$CaCO_3\,(s) = CaO\,(s) + CO_2\,(g)$, $\Delta H_{rx} = 167$ kJ/mol, $P_{CO2} = 1$ bar at 860 °C

Ash preferences – significance of constituents

- Low ash fraction – exact composition not crucial – provided the ash is rich in Ca.
- Major constituents – Ca, Si, Al, Fe:
  - Ca tend to concentrate in the bark – parts of the tree rich in bark (tops and branches?) preferred.
  - Si might be high in some ashes. Easy to correct by reducing quartz in the raw meal.
  - Al, Fe is acceptable for cement production.

Composition of some wood and woody biomass ashes (Vassiliev et al)

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	4.4	69.1	9.0	4.1	0.6	5.9	2.2	2.8	1.9	0.1
Pine bark	9.2	56.8	7.8	5.0	7.2	6.2	2.8	2.8	2.0	0.2
Pine Chips	68.2	7.9	4.5	1.6	7.0	2.4	5.5	1.2	1.2	0.6
Pine pruning	7.8	44.1	22.3	5.7	2.8	11.3	1.3	4.2	0.4	0.2
Spruce bark	6.1	72.4	7.2	2.7	0.7	5.0	1.9	1.9	2.0	0.1
Spruce wood	49.3	17.2	9.6	1.9	9.4	1.1	8.3	2.6	0.5	0.1

Significance of constituents

- Mg:
  - Typical values in Portland cement <2 %.
  - Too high values can lead to concrete strength loss – the effect can be controlled by rapid cooling.
  - Worst case scenario is about 0.2 % contribution by from the ash.
- Na, K:
  - Typical cement values 0.2 to 1.5 %. Controllable by bleeding off alkali vapours.
  - No specific limit, dependent of SO_3 which forms stable alkali sulphates. Too high values may cause alkali-silica reaction (ASR), causing the expansion and cracking of the concrete.
  - Worst case scenario is about 0.5 % contribution by from the ash.
- Sulphate:
  - Linked to the alkali content of the cement - desired alkali:sulphate molar ratio is about 1.
  - Act to bind alkalis in the clinker as Na_2SO_4 and K_2SO_4.
  - Ashes typically contains less than 2 % SO_3 in wood ashes, which is about the same amount as in cement feed stock

Significance of constituents cntd.

- Phosphorus:
  - Typical values in Portland cement 0.3 wt% P_2O_5.
  - Too high values prolong setting times - stabilisation of the less reactive C_2S phase during burning.
  - Worst case scenario is 0.15%, contribution from ash.
- Heavy metals:
  - Concrete is frequently used to demobilize heavy metals, so in general a modest level of heavy metals is not a problem.
  - Reported levels show that the only heavy metals that might require attention are cadmium and zinc contained in some fly ashes. Bottom ashes are generally OK.

Does the ash contain calcium carbonate?

- $CaCO_3$ = CaO + CO_2 (g)
  - P_{CO2} = 1 bar at 860 °C
  - ΔH_{rx} = 167 kJ/mol,
  - In practice, the reaction needs excess temperatures to speed up.
- Fluidised bed combustors can operate at temperatures ~ 900 °C
  - ➢ Risk that wood ashes from fluidized bed (FB) combustors might contain $CaCO_3$
- If Ca is present as carbonate rather than oxide, the value of the ashes are rediced for the cement manufacturer.

Conclusion

- Norwegian bioenergy goals may produce roughly 70 000 tons wood ash per year.
- Bottom ashes from wood bio plants have a composition resembling Portland cement, making them interesting as raw material.
- Portland cement feed stock consists of about 90% limestone (mainly calcium carbonate) – some of this can be replaced by calcium oxide from the ashes, reducing corresponding CO_2 emission and energy needed for the calcination.
- Wood bottom ashes contain no components in concentration harmful to cement.

Thank you for your attention!