COMPRESSIVE STRENGTH AND LEACHING BEHAVIOR OF MORTARS WITH BIOMASS ASH

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Biomass ash in construction: Environmental Sustainability

- Biomass is the only renewable resource that can easily be converted to satisfy all energy sectors.

- In 2012, biomass and waste accounted for about two-thirds of all renewable energy consumption in the EU.

- In 2014, the European Commission published a report which includes information on current and planned EU actions to maximize the benefits of using biomass while avoiding negative impacts on the environment.
For combustion relevant raw materials

Raw materials, which are considered to be most relevant for the energetic utilization by the interviewed actors in the partner countries (n=38, multiple answers were possible)
Compared to wood, herbaceous plants show some unfavorable fuel properties, that can affect the combustion process either in a technical or an ecological way.

Technical problems can, for example, be due to the presence of chlorine, sulphur, potassium, nitrogen, magnesium, and/or calcium that can cause corrosion, and even slagging problems in the combustion boiler-plant and consequently reduce the useful life of the combustion equipment.

Other chemical components, such as heavy metals in the ash can result in excessive pollutant emissions or remain in the ash, leading to challenges in the disposal.

Ash, therefore, should undergo a broad and critical assessment before being disposed, with the aim to provide an option for beneficial use in construction materials.
WCSA Biomass ash heavy metals content

Heavy metal contents of WCSA compared to the published heavy metal data of coniferous wood and crop of grain straw

| Element     | Data for Corn Plant | Published data for comparison (Hartmann et al. 2000) |
|-------------|---------------------|-----------------------------------------------------|
|             | Corn, wholeplant [mg/kg d.b.] | coniferous wood [mg/kg d.b.] | grain straw [mg/kg d.b.] |
| Chrome      | 4,85                | 4,50                   | 4,62 |
| Cobalt      | 0,23                | 0,35                   | 0,14 |
| Copper      | 6,08                | 3,45                   | 2,21 |
| Manganese   | 46,25               | 344,70                 | 22,00 |
| Molybdenum  | 2,53                | 1,12                   | 0,38 |
| Nickel      | 0,62                | 4,23                   | 0,69 |
| Zinc        | 50,08               | 37,64                  | 9,42 |
Exclusion of available raw materials from the list of the 5 most relevant biomasses is based on the following reasons:

- some products do not reach interesting or significant amount available for energy purposes;
- there are biomasses which are too much spread on the territory and difficult or expensive to collect;
- some materials show difficulties in harvesting operation.

| Raw material                  | Biomass availability                      | Equipment availability of harvesting technologies | Other application of the biomass                      | Product distribution on the region                      |
|-------------------------------|-------------------------------------------|---------------------------------------------------|------------------------------------------------------|--------------------------------------------------------|
| Vine prunings                 | *Several Italian regions have significant amounts* | *There are some machines, allowing the harvesting and collection* | *The pruning is used as fertilizer* | *In general, spread in large amount on territorial districts* |
| Straw                         | *Very large amounts*                       | *Widely used and available*                       | *Animal feed*                                       | *Spread over a large parts of the country*             |
| Corn stalks                   | *Large amounts*                            | *Widely used and available*                       | *The product is used as fertilizer*                 | *Spread over a large parts of the North Italy*         |
| Residues from viniculture     | *The availability depends on the regions*  | *There are no particular needs*                   | *None in particular*                                | *Concentrated in plants for the processing of raw materials* |
| Residues from the olive processing industry | *The availability depends on the regions* | *There are no particular needs*                   | *None in particular*                                | *Concentrated in plants for the processing of raw materials* |
Biomass fuel properties of corn cobs and stalks

|                 | Corn cobs       | Corn stalks     |
|-----------------|-----------------|-----------------|
| **Net calorific value [MJ/kg dm]** | 16.5            | 16.6-17.5       |
| **Ash content [wt.-% dm]**         | 1-3             | 11-17           |
| **Water content [wt.-%]**           | 6-7             | 15-18           |
| **Ash softening temperature [°C]**  | 1,100           | 1250            |
| **N [wt.-% dm]**                    | 0.4-0.9         | 0.7-0.9         |
| **S [wt.-% dm]**                    | 0.03            | 0.08-0.1        |
| **Cl [wt.-% dm]**                   | 0.02            | n.a.            |
## Main ash forming elements

| Kind of biomass         | Al  mg/kg (d.m.) | Ca  mg/kg (d.m.) | Fe  mg/kg (d.m.) | K   mg/kg (d.m.) | Mg  mg/kg (d.m.) | Na  mg/kg (d.m.) | Si  mg/kg (d.m.) |
|-------------------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------|
| straw                   | 60-130           | 2900-3300        | 120              | 7100-10000       | 630-1030         | 100-120          | 9000-10300      |
| Corn cobs               | 60               | 400              | 70               | 8500             | 200              | <50              | 1100            |
| Corn stalks             | 140              | 7390             | 680              | 8100             | 500              | 800              | 14200           |
| Cereal spinning         | 700              | 2050-5000        | 500              | 1340-5380        | 1170-1400        | 300              | 28100           |
Cultivation in Italy 1.1 million hectares

Production 10.6 mln tons

Biomass is intended for incineration

≈ 160000 ton/year

≈ 0.4 % cement use Per year

It provides 10% ash
The hydration behavior of OPC in the presence of biomass ash needs to be assessed as a suitable material for mechanical properties and environmental impact.

An Italian law protocol, designed to assess the environmental impact for a biomass ash reuse, is based on a leaching test to be performed, both on the ash as such or in the form of its reuse (such as in concrete), in the range of pH of the leaching, which is presumed to be actual field work of the form recovered in different environmental exposure conditions.

In the present research, this leaching protocol was applied to the cement-based specimens, mortar cubes, containing wood, corn stover, corn cob ash (WCSA) as supplementary cementitious material that was used as a binder replacement for the use in concrete production.
GOALS

 micro-structural & mechanical behavior, and metal analysis of leachate obtained from mortars made with various percentages of wood, corn stover, corn cob ash (WCSA, 0%, 10%, 20 and 30%).

 Relationships between environmental leaching parameters and mechanical properties
MIND MAP METHODOLOGY

WOOD, CORN STOVER AND COB ASH

CHEMICAL AND PHYSICAL CHARACTERISATION
- SEM ASH ANALYSIS
- EDXA ASH ANALYSIS

PRISMATIC MORTARS SPECIMEN
- COMPRESSIVE STRENGTH
- FLEXURAL STRENGTH

LEACHING TESTS ON MORTARS AND PASTES
- LEACHATE EVALUATION
- INORGANIC IONS RELEASE
- HEAVY METALS RELEASE
### ASH CHARACTERIZATION

#### Table 2. Main Oxides Composition from EDXA Analysis of WCSA

| Units | Na  | Mg  | Al  | Si  | P   | S   | Cl  | K   | Ca  | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| %     | 5.62| 3.96| 8.20| 39.94| 3.31| 6.03| 2.63| 7.09| 16.52| 5.02|

Ca = 4%; Al = 22%; Fe = 0.73%; Si = 58%.

|       | CEM 32,5R | WCSA |
|-------|------------|------|
| HM    | 1.7-2.3    | 0.31 |
| SR    | 1.9-3.2    | 3.02 |
Scanning electron micrograph of WCSA particles
MORTAR SPECIMEN PREPARATION

CEM II / A-L 32,5 R

36 prismatic specimens
- length = 160 mm
- height ≈ 40 mm
- width = 40 mm

Two series of specimen:
- w/cm=0.42
- w/cm=0.5
Table 3. Mixture proportions of mortars. Two series of specimen: s/cm=0.42 and w/cm=0.5

| WCSA % | Water (ml) | CEM II/A-L 32,5R | Ash (g) | Sand (g) | w/cm |
|--------|------------|-------------------|---------|----------|------|
| 0      | 189        | 450               | 0       | 1350     | 0.42 |
| 10%    | 193        | 405               | 54      | 1350     | 0.42 |
| 20%    | 197        | 360               | 108     | 1350     | 0.42 |
| 30%    | 200        | 315               | 152     | 1350     | 0.42 |

| WCSA % | Water (ml) | CEM II/A-L 32,5R | Ash (g) | Sand (g) | w/cm |
|--------|------------|-------------------|---------|----------|------|
| 0      | 227        | 450               | 0       | 1426     | 0.5  |
| 10%    | 244        | 405               | 45.2    | 1426     | 0.5  |
| 20%    | 262        | 360               | 90.4    | 1426     | 0.5  |
| 30%    | 280        | 315               | 135.5   | 1426     | 0.5  |

Table 4. Workability of mixtures

| WCSA % | w/cm | Average diameter (cm) | w/cm | Average diameter (cm) |
|--------|------|-----------------------|------|-----------------------|
| 0      | 0.42 | 13                    | 0.5  | 14                    |
| 10     | 0.42 | 13                    | 0.5  | 16                    |
| 20     | 0.42 | 13                    | 0.5  | 18                    |
| 30     | 0.42 | 13                    | 0.5  | 19                    |
Table 5. Compressive strength development (MPa)

| Age, days | Control | 10 % | 20 % | 30 % |
|-----------|---------|------|------|------|
| 3         | 28.0    | 26.4 | 26.6 | 23.3 |
| 7         | 32.5    | 35.0 | 32.3 | 25.6 |
| 28        | 38.4    | 38.8 | 36.7 | 37.2 |
| 56        | 38.7    | 40.0 | 37.2 | 37.3 |

| Age, days | Control | 10 % | 20 % | 30 % |
|-----------|---------|------|------|------|
| 3         | 22.0    | 17.8 | 14.6 | 14.9 |
| 7         | 27.4    | 21.3 | 17.6 | 19.4 |
| 28        | 30.6    | 27.9 | 25.2 | 26.7 |
| 56        | 31.4    | 28.2 | 25.7 | 27.6 |

The compressive strength (MPa) and maturity (M) of mortar have been related by the following equation where $a_1$ and $b_1$ are constants.

$$MPa = \frac{M}{a_1 \times M + b_1}$$
MATURITY – INDEX
COMPRESSION STRENGTH RELATIONSHIP

\[ f_{MAX} = \frac{M}{(M \cdot a_1) + b_1} \]

\[ M = T \cdot (10 + °C) \]
Table 6  Equation 1 parameters

\( w/cm=0.42 \)

| Sample ash% | 1/b1 (\text{-}) | 1/a1 (MPa) |
|-------------|----------------|------------|
| 0           | 0.047          | 39.1       |
| 10          | 0.036          | 41.4       |
| 20          | 0.036          | 40.3       |
| 30          | 0.022          | 38.6       |

\( w/cm=0.5 \)

| Sample ash% | 1/b1 (\text{-}) | 1/a1 (MPa) |
|-------------|----------------|------------|
| 0           | 0.031          | 31.9       |
| 10          | 0.022          | 27.4       |
| 20          | 0.014          | 25.1       |
| 30          | 0.013          | 28.6       |

![Graph showing the relationship between f-ash (%) and f_{max} (MPa)](image-url)
RELATIVE STRENGTH EVOLUTION

Hydration rate decreases increasing the amount of ash

w/cm=0.42

w/cm=0.5
The calcium ions mass release follows the same progress as compressive strength in relation to the amount of ash present.

\[
\text{w/cm} = 0.42 \\
\text{w/cm} = 0.5
\]
Table 7. Cumulated heavy metals (mg/l) in the leaching solution.

| %WCS A | Ba    | Cr    | Cu    | Ni    | Pb    | V     | Zn    |
|--------|-------|-------|-------|-------|-------|-------|-------|
| 0      | 0.087 | 0.008 | 0.042 | 0.004 | 0.003 | 0.008 | 0.128 |
| 10     | 0.082 | 0.007 | 0.008 | 0.002 | 0.002 | 0.011 | 0.113 |
| 20     | 0.049 | 0.005 | 0.009 | 0.005 | 0.001 | 0.007 | 0.386 |
| 30     | 0.285 | 0.006 | 0.013 | 0.004 | 0.001 | 0.015 | 0.001 |
| 0      | 0.272 | 0.008 | 0.019 | 0.003 | 0.002 | 0.012 | 0.001 |
| 10     | 0.079 | 0.026 | 0.037 | 0.007 | 0.005 | 0.026 | 0.116 |
| 20     | 0.034 | 0.011 | 0.015 | 0.006 | 0.002 | 0.026 | 0.001 |
| 30     | 0.143 | 0.008 | 0.011 | 0.008 | 0.003 | 0.010 | 0.298 |
| ref. limit | 1.0 | 0.05 | 0.05 | 0.01 | 0.05 | 0.25 | 3.0 |
Table 8. Equation 1 leaching parameters

| (w/cm=0.42) Ash % | 1/b1 | 1/a1 (meq Ca) | (w/cm=0.5) Ash % | 1/b1 | 1/a1 (meq Ca) |
|-------------------|------|---------------|-------------------|------|---------------|
| 0                 | 0.094| 10.58         | 0                 | 0.049| 20.31         |
| 10                | 0.073| 13.61         | 10                | 0.062| 16.04         |
| 20                | 0.124| 8.06          | 20                | 0.075| 13.23         |
| 30                | 0.183| 5.45          | 30                | 0.074| 13.41         |

**Strength (MPa) Vs WCSA %**

**mEq Calcium release Vs WCSA**
Strength estimation model incorporating ash, cement, calcium released and w/cm.

\[
f_{\text{MAX}} = 437,857 + 0,793279Ca - 0,397104g_{\text{water}} - 0,73823g_{\text{cem}} - 0,576116g_{\text{ash}}
\]

Independent Variables:
- \(C_a\) amount of Calcium ions released,
- \(g_{\text{water}}\) amount of water used,
- \(g_{\text{cem}}\) amount of cem,
- \(g_{\text{ash}}\) amount of ash
Leaching-strength estimation model incorporating ash, cement, and w/cm.

\[ Ca = \frac{f_{MAX}}{0.793279} - 0.5 \cdot g_{water} + 0.93 \cdot g_{cem} + 0.73 \cdot g_{ash} - 552 \]

Independent Variables:
- \( C_a \) amount of Calcium ions released,
- \( g_{water} \) amount of water used,
- \( g_{cem} \) amount of cem,
- \( g_{ash} \) amount of ash
CONCLUSIONS

- The WCSA examined is characterized by high amounts of Silicium (39%), calcium (16%), and potassium ions (7%) not different from many other biomass ash.

- For the constant w/cm ratio of 0.42, the compressive strength of prismatic mortars specimens, obtained with WCSA up to 20% as a partial replacement of cement, show a small increase, without losing workability.

- However, at higher w/cm a clear performance decrease has been observed.
CONCLUSIONS

- The pore solution given by the leaching tests of WCSA specimens are characterized by high concentration of Calcium and Potassium ions indicating a notable alteration of the pore water chemistry.

- This change has been attributed either to the particular composition of the WCSA examined or to the cement hydration delay as indicated by the kinetics values obtained from the diffusion model adopted.

- In conclusion, it is believed that with additional studies, the use of WCSA, can be put to good use in construction with environmental sustainability.