Opportunities for Novel Residue-Based Products in the Bothnian Arc Steel and Paper Industries – a Pragmatic Approach in Forest Soil Amendment

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Pulp, Paper and Steel Industry Residues in the Bothnian Arc Region

Evident availability of large, relatively stable solid residue streams:

- Iron and steel production slags (cementitious characteristics & alkalinity)
- Pulp and paper residues (alkalinity, reactive fibrous content & pozzolanic characteristics)

-> Possibilities for novel, non-thermal residue-based product?
- Taking into account not only the alkaline nature of pulping residuals but also the respective fibrous and cementitious characteristics of paper and steelmaking residues

Matrix strength properties

Fibre reinforced cement products
Encapsulation/ solidification
Soil amendment/ amelioration

Matrix leaching and individual particle size
Soil amendment/amelioration

- Use of wood raw material removes important nutrients (e.g. Ca, Mg, Na, K) from forest ecosystems, thus decreasing soil buffering capacity and promoting soil acidity.

- Residue-based amendment products could promote sustainable resource management by recycling these residues back to forest ecosystems and by promoting "immediate" increases of soil pH.

- By integration of various residues into a solid matrix, an alkaline shock effect could be avoided and the physical break-down of the respective matrix could be controlled.

Steel industry slags
Cementitious properties of slags (Raahe) and fly ash (Oulu)

Replacing 1 part of fine-grained, inert silica sand with slag/fly ash (with reference to rapid cement).

While maintaining an equivalent w/c – ratio.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference 1</th>
<th>Reference 2</th>
<th>GBFS5001</th>
<th>DS5001</th>
<th>CSS501</th>
<th>SL550ESP</th>
<th>FA501</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>rapid cement</td>
<td>rapid cement</td>
<td>50/50 GBFS and rapid cement</td>
<td>50/50 cement</td>
<td>50/50 steel slag and rapid cement</td>
<td>50/50 steel slag and rapid cement</td>
<td>50/50 fly ash and rapid cement</td>
</tr>
<tr>
<td>Binder/filler</td>
<td>2.5/1.7</td>
<td>2.0/1.6</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Water/binder</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Glenium 51 super-plasticizer from BASF used in SL5501ESP formulation to enhance workability of the matrix (0.006% of binder mass with a dry matter content of 35%).

Slag milling in a cylindrical ball mill:
- batch sizes of app. 10 kg
- ball charge of 100 kg
- milling times of nearly 7.5 hours (app. 20,000 revolutions).
Cementitious properties of slags (Raahe) and fly ash (Oulu)

Particle size determination:
- measured with a laser diffractioner
- sample sizes of app. 10 mg
- substantial uncertainty

<table>
<thead>
<tr>
<th>Variable</th>
<th>GBFS</th>
<th>DSS</th>
<th>CSS</th>
<th>SLS</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean particle size (µm)</td>
<td>9.0</td>
<td>11.3</td>
<td>5.8</td>
<td>7.6</td>
<td>58.4</td>
</tr>
<tr>
<td>D₁₀</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>5.7</td>
</tr>
<tr>
<td>D₅₀</td>
<td>4.5</td>
<td>3.1</td>
<td>2.2</td>
<td>2.3</td>
<td>34.2</td>
</tr>
<tr>
<td>D₉₀</td>
<td>23.6</td>
<td>27.1</td>
<td>15.3</td>
<td>17.3</td>
<td>135.0</td>
</tr>
</tbody>
</table>

Mean particle size for slags 9.0-11.3 µm, 58.4 µm for fly ash.

GBFS = granulated blast furnace slag.
DSS = desulphurisation slag.
CSS = steel slag.
SLS = steel lube slag.
FA = fly ash.

jv-kuona = SLS
lentotuhka = fly ash
masuunikuona = GBFS
teräskuona = CSS
rikinpointokuona = DSS
Cementitious properties of slags (Raahe) and fly ash (Oulu)

Curing conditions: room temperature, 95 % relative humidity.

Testing dates: 3, 7 and 28 days.

Zwick RK 250/50 loading machine with a pre-load of 50 N and a loading rate of 3 mm/min.
Cementitious properties of slags (Raahe) and fly ash (Oulu)

Compression strength comparison

![Compression strength comparison graph]

Cementitious properties of slags (Raahe) and fly ash (Oulu)

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Granulated blast furnace slag</th>
<th>Desulfurization slags</th>
<th>Converter steel slag</th>
<th>Steel一分钟 slag</th>
<th>Ordinary Portland Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>35.7</td>
<td>35.1</td>
<td>47.9</td>
<td>41.4</td>
<td>41.1</td>
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<tr>
<td>SiO₂</td>
<td>35.3</td>
<td>39.3</td>
<td>12.0</td>
<td>14.0</td>
<td>14.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.9</td>
<td>2.4</td>
<td>2.5</td>
<td>28.0</td>
<td>28.5</td>
</tr>
<tr>
<td>MgO</td>
<td>11.3</td>
<td>1.5</td>
<td>1.6</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>0.10</td>
<td>16.4</td>
<td>16.6</td>
<td>3.66</td>
<td>3.3</td>
</tr>
<tr>
<td>S</td>
<td>1.35</td>
<td>2.0</td>
<td>0.1</td>
<td>0.23</td>
<td>0.2</td>
</tr>
<tr>
<td>Ti</td>
<td>1.25</td>
<td>0.89</td>
<td>0.64</td>
<td>0.85</td>
<td>0.8</td>
</tr>
<tr>
<td>P</td>
<td>0.05</td>
<td>0.56</td>
<td>0.56</td>
<td>0.035</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Main chemical oxidic contents of Raahe slags and general Ordinary Portland Cement, % XRF (Ruukki 2009; Virola & Raivio 2000).
Soil amendment

Incorporated residues:
- green liquor dregs and lime waste as alkaline components
- paper mill sludge as reactive aggregate
- fly ash and GBFS or CSS as binder material

Source: Nurmesniemi et al., 2009.

Soil amendment

Objective was to produce a solid matrix with sufficient mechanical properties combined to liming and buffering ability and possible nutrient contents.

<table>
<thead>
<tr>
<th>Element</th>
<th>BFSFA15</th>
<th>CSSFA15</th>
<th>BFSFA10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td>GBFS 15, FA 15</td>
<td>CSS 15, FA 15</td>
<td>GBFS 7.5, FA 7.5</td>
</tr>
<tr>
<td>Fibre material</td>
<td>ECO-fibre 30</td>
<td>ECO-fibre 30</td>
<td>ECO-fibre 45</td>
</tr>
<tr>
<td>Reactive alkali</td>
<td>GLD 10, lime waste 30</td>
<td>GLD 10, lime waste 30</td>
<td>GLD 10, lime waste 30</td>
</tr>
<tr>
<td>Water/binder</td>
<td>1.125</td>
<td>1.125</td>
<td>1.125</td>
</tr>
</tbody>
</table>

Mixing ratios of various elements expressed in dry weight percentages prior to water addition, except for ECO-fibre which has a dry solids content of app. 25 percent (Kuokkanen et al., 2008).

GBFS = granulated blast furnace slag.
FA = fly ash.
CSS = converter steel slag.
GLD = green liquor dregs.
Soil amendment

Superior mechanical performance with BFSFA10 (lowest binder quantity & highest fibre content)

- ability of ECO-fibre to promote GBFS hydration by providing hydration water or by chemical activation?

Sufficient mechanical performance for soil amendment purposes?

Cross-sectional images.
Soil amendment

Physiochemical properties, total element and easily available nutrient concentrations and leaching characteristics of produced formulations analysed by Suomen Ympäristöpalvelu Oy.

Physiochemical properties of produced formulations.

Neutralising (35.8-38.6 % as Ca-eq. d.w.) and reactivity (33.3-38.0% as Ca-eq. d.w.) values, with supporting high pH values (12.9-13.0) indicate liming abilities comparable to commercial ground limestone products.

Precipitation of most likely Ca(OH)$_2$ due to abundant Ca-content and slag hydration.

Total element concentrations (in mg/kg) of produced formulations.

Total concentrations of cadmium (Cd) exceeded respective Finnish statutory limit values set for fertilisers used in agriculture (MMM 2007).

The total concentration of chromium (Cr) in CSS formulation exceeded respective Finnish statutory limit value set for fertilisers used in agriculture and forestry (MMM 2007). Soluble Cr(VI) not determined.

Total concentrations determined by microwave digestion with a mixture of HNO$_3$ and HCl (USEPA 3051).
Soil amendment

Leaching characteristics of produced formulations.

Leaching procedure = a two-stage batch test (SFS-EN 12457-3) + three-stage sequential BCR test.

Only app. 72 mg/kg (from 370 mg/kg) of Cr was attained during the leaching procedure.

However, substantial BCR (III) Cd (1.9, 2.3 and 2.3 mg/kg) recovery could restrict the use of produced formulations in agricultural amendment (limit value 1.5 mg/kg).

Recovery percentages of individual elements.

Less than a fifth of total Cr content is likely to become mobile in conditions normally found in nature. Respective Cd recoveries 74-83 %.

Availability of the remaining Cr content (app. 80 %) would require total decomposition of the respective lattice.

Recovery percentage = (sum of individual leaching fractions / total concentration)·100 %.
Conclusions

• Mechanical strength of produced formulations appear to be sufficient for soil amendment purposes (mechanical application methods).

• Liming effect value ($NV = 35.8-38.6\%$), in addition to corresponding high pH values ($12.9-13.0$), indicate liming and buffering capacities comparable to commercial ground limestone products.

• Total concentrations of cadmium ($Cd; 2.8-3.3\, mg/kg$) in all formulations exceeded respective Finnish statutory limit values ($1.5\, mg/kg$) set for fertilisers used in agriculture.

• Total concentration of chromium ($Cr; 370\, mg/kg$) in CSS formulation exceeded respective limit values ($300\, mg/kg$) set for fertilisers used in agriculture and forestry (of which over $80\%$ is not likely to become mobile in conditions normally found in nature).

• Concentrations of Ca, K, Mg and Na and concentrations of Cu, Mn and Zn were higher than organic and mineral soil contents normally found in the Ostrobothnia region of Northern Finland (Nurmesniemi et al. 2009).

Further research

• Heavy metals availability due to weathering (over long periods of time). Ability of the pellet concept to hinder alkaline shock effect (physical decomposition of the matrix).

• In-situ field test: bioavailability of macro- and micronutrients, physiochemical impacts on soil and hence on plant growth.

• Life Cycle Assessment (LCA) to provide quantitative information on the "environmental benefits" of such a beneficial use of residues in soil amendment.

• Collaboration with fertiliser manufacturers and small to medium-sized companies.
Thank you for your kind attention.

References


