One-part geopolymers from spent filtering earths using alternative activators from waste glass. An example of circular economy

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Introduction

High energy consumption

High consumption of mineral resources

High emissions of gases, mainly carbon dioxide (5-7 % CO₂)

Cement is one of the most widely used building materials.

- Low Price, economical material
- Versatile
- Ability to harden under water

CEMENT PORTLAND PRODUCTION
Cement industry more environmentally friendly

More sustainable alternative cements

Alkaline-activated cements or geopolymer cements

- Low environmental impact: reduce CO\textsubscript{2} emissions
- No High temperatures in manufacturing
- Good mechanical properties
- High chemical attack resistance
Alkaline activation binders

**PRECURSOR**
ALUMINOSILICATES (with high or low calcium contents)

Metakaolin
Calcined clays

**ALKALINE ACTIVATOR**

Chemical Reaction

**ALKALINE ACTIVATED CEMENTS OR GEOPOLYMERS**

Alkaline hidroxides
Alkaline silicates

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### Commercial activators: Problems-Challenges

<table>
<thead>
<tr>
<th>Geopolymers</th>
<th>Emissions (kg CO₂/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash, slag</td>
<td></td>
</tr>
<tr>
<td>Sodium hidroxides</td>
<td></td>
</tr>
<tr>
<td>SODIUM SILICATES</td>
<td></td>
</tr>
<tr>
<td>Coarse aggregates</td>
<td></td>
</tr>
<tr>
<td>Fine aggregates</td>
<td></td>
</tr>
<tr>
<td>Additions</td>
<td></td>
</tr>
<tr>
<td>Dosage</td>
<td></td>
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<tr>
<td>Curing</td>
<td></td>
</tr>
<tr>
<td>Transport</td>
<td></td>
</tr>
<tr>
<td>Commissioning</td>
<td></td>
</tr>
</tbody>
</table>

- **TOTAL 320**
- **TOTAL 354**

<table>
<thead>
<tr>
<th>OPC Concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEMENT</td>
</tr>
<tr>
<td>Coarse aggregates</td>
</tr>
<tr>
<td>Fine aggregates</td>
</tr>
<tr>
<td>Additions</td>
</tr>
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</tr>
</tbody>
</table>

- **OPC**

Need to look for alternative activators to commercial alkaline silicates in order to produce near-zero carbon footprint cements.
Alternative activators. Solutions-Proposals

Silica-based alternative activators

Alkaline hydroxide

+ Silica-rich raw material

\[ 2\text{NaOH} + \text{SiO}_2 \xrightarrow{\text{\(\Delta\)}} \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \]

Alkaline silicate
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**Objective**

The **activation** of spent filtering earth from the oil refining industry (SFE) by the **use of alternative activators** made from **waste glass** (WG) with different dosages of **alkali** to obtain **geopolymer cements** with near **zero carbon footprint**.
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Filtering earths are widely used in the agri-food industry with the problem that the end-of-life material is a useless waste.

Inorganic fraction of SFE obtained by calcination at 700 °C
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**RAW MATERIAL: SPENT FILTERING EARTHS (SFE)**

**XRF ANALYSIS**

- 84.29% SiO₂
- 5.87% Al₂O₃
- 0.96% CaO

**XRD ANALYSIS**

- C: Cristobalite_96-900-8230
- Q: Quartz_96-901-3322
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**SYNTHESIS OF ALTERNATIVE SOLID ACTIVATOR**

1. Adding water and Mixing
   - 20.0 g

2. Heat treatment
   - 3h - 300 ºC
   - (Rate 10 ºC/min)

3. Ground in a ball mill
   - 100 g

**Chemical Composition**

- 77.5 % Na₂O
- 73.9 % SiO₂

**NaOH**
- 36.4 g
- 99 % Purity

**Waste glass (WG)**
- Ground and sieved under 0.063 mm

**Mol Ratio**

\[ M_s = \frac{\text{mol SiO}_2}{\text{mol Na}_2O} = 1 \]
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**XRD study**

[Image of XRD study graph showing intensity (a.u.) vs. 2θ (°) with peaks labeled as Sodium silicate for ASA and WG samples.]
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Manufacture of the geopolymers cements

- SFE
- planetary mixer
- Water
- Cured a 20 °C, 28 days

- ASA
- moulds
- punching table
- SFE-10
- SFE-20
- SFE-30
- SFE-SS-20

60 strokes
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### Manufacture of the geopolymers cements

<table>
<thead>
<tr>
<th>Sample</th>
<th>SFE (g)</th>
<th>Alternative solid activator (g)</th>
<th>Sodium hydroxide (NaOH) (g)</th>
<th>Sodium silicate (Na$_2$SiO$_3$) (g)</th>
<th>Water</th>
<th>Na$_2$O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFE-10</td>
<td>300</td>
<td>72.6</td>
<td>-</td>
<td>-</td>
<td>280.9</td>
<td>10</td>
</tr>
<tr>
<td>SFE-20</td>
<td>300</td>
<td>145.1</td>
<td>-</td>
<td>-</td>
<td>291.8</td>
<td>20</td>
</tr>
<tr>
<td>SFE-30</td>
<td>300</td>
<td>217.7</td>
<td>-</td>
<td>-</td>
<td>302.6</td>
<td>30</td>
</tr>
<tr>
<td>SFE-SS-20</td>
<td>300</td>
<td>-</td>
<td>55.66</td>
<td>199.2</td>
<td>176.7</td>
<td>20</td>
</tr>
</tbody>
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**Bulk density**

- Increase of BD with increasing alkali dosage from 10 to 20% of Na$_2$O.
- Increase up to 30% produced cements with a lower BD.
- Commercial silicate results in specimens with lower BD than obtained with ASA.

A more compact microstructure is obtained due to a higher advance in the geopolymerisation reaction when ASA is used.
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**Water absorption**

- WA is very high with the addition of 10 % Na₂O.
- The addition of 20 % Na₂O resulted in a significant reduction of WA up to 13 %, with a slight increase with the addition of 30 % and when commercial activator is used.

It is observed that the open porosity of the cement is reduced with the use of 20 % Na₂O because the capillary pores are gradually filled by the formation of amorphous reaction products.
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**Flexural and compressive strength**

- Poor mechanical properties are obtained at an alkali dosage of 10 %

10 % amount of the ASA is insufficient to activate the pozzolanic reactivity of the SFE, resulting in many unactivated SFE particles.
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**Flexural and compressive strength**

- Increasing alkali dosage up to 20%, the compressive and flexural strength shows a significant improvement.

Increase in the geopolymerisation reaction, leading to the formation of more geopolymer gel, resulting in a denser matrix.
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**Flexural and compressive strength**

- Higher alkali dosage (30% Na₂O) is unfavourable for the mechanical properties of the SFE

Less amorphous gel possibly due to the rapid formation of oligomers covering the surface, decreasing the degree of reaction
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- The mechanical properties of the geopolymers using the ASA are superior to those obtained for the commercial activator.
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**XRD**

Shift of the halo in the geopolymers tower lower values of 2θ

Formation of an alkaline aluminosilicate gel (N-A-S-H gel), the main reaction product.

C: Cristobalite
Q: Quartz
Z: zeolite

Intensity (a.u.)

2 theta (°)
The appearance of new zeolite-type diffraction peaks which is a crystalline phase from the formation of the geopolymer gel.

C: Cristobalite
Q: Quartz
Z: zeolite
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FTIR

Asymmetric vibrations generated by the T-O-T bonds (where T is Si or Al)

This band shifts towards lower wavenumbers in geopolymers indicating the formation of sodium aluminosilicate gel.
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Bands attributed to the presence of \textbf{carbonates}.

\textbf{Water adsorbed on the hydration products.}

- SFE-SS-20
- SFE-30
- SFE-20
- SFE-10
- SFE

Absorbance (a.u.)

Wavenumber (cm$^{-1}$)
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Conclusions

ASA can be used in the manufacture of SFE cements.

The dosage of the alternative alkaline activator has a significant influence on the physical and mechanical properties of geopolymers using SFE as a precursor.

At a low alkali dosage of 10 % Na$_2$O and a high dosage of 30 % Na$_2$O, SFE geopolymers show a low amount of amorphous reaction products, high porosity and poor flexural and compressive strength.

The optimal amount of alkali (20 % Na$_2$O) promotes the geopolymerisation reaction resulting in a denser structure with lower porosity improving the mechanical properties of SFE geopolymers.

One-part activation of SFE using an solid alternative activator made from glass and sodium hydroxide results in geopolymers with higher mechanical properties than two-part activation using a sodium silicate and sodium hydroxide solution as a commercial activator.
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Thank you very much for your attention!

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