Geopolymers based on different types of slags. Comparison in terms of reactivity and mechanical properties developed.

M.A. Gómez-Casero, L. Pérez-Villarejo, P.J. Sánchez-Soto, D. Eliche-Quesada

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INTRODUCTION

Portland cement manufacture

- Industrial waste
- Ashes
- Slags
- Natural sources

Alkali-activated materials
Geopolymers

Good results

Material used
Depends on
Mechanical strength and Durability

- Industrial waste
- Ashes
- Slags
- Natural sources

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Universidad de Jaén
INTRODUCTION

Slags as precursor

Several origin

- Ground granulated blast furnace slag (black steel slag)
- Secondary metallurgical slag (white slag)
- Basic oxygen furnace slag
- Other slags

(Lancellotti et al, 2021)

In this work

Main chemical components

- BSS: CaO, SiO$_2$ and Fe$_2$O$_3$
- CS: FeO, Fe$_2$O$_3$

Black Steel slag (BSS) & Copper slag (CS)
MATERIALS AND METHODS

RAW MATERIALS

- Black Steel slag (BSS)
- Copper slag (CS)

From

- Siderúrgica Sevillana S.A. (Sevilla, Spain)
- Atlantic Copper Fundición and Refinería (Huelva, Spain)

Graph:

- BSS: $D_{50} = 8.7 \, \mu m$
- CS: $D_{50} = 30.5 \, \mu m$

Volume (%) vs. Particle size (μm)
MATERIALS AND METHODS

RAW MATERIALS

XRD

SEM

<table>
<thead>
<tr>
<th>Precursor</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>LOI</th>
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<tr>
<td>BSS</td>
<td>17.29</td>
<td>10.71</td>
<td>24.16</td>
<td>30.89</td>
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MATERIALS AND METHODS

RAW MATERIALS

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SEM
MATERIALS AND METHODS

RAW MATERIALS

XRF

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<td>0.00</td>
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MATERIALS AND METHODS

MANUFACTURE OF BINDERS

Precursor

Activator solution

<table>
<thead>
<tr>
<th>KOH molar ratio</th>
<th>Ms</th>
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<tr>
<td>5M</td>
<td>1.70</td>
</tr>
<tr>
<td>8M</td>
<td>1.38</td>
</tr>
<tr>
<td>12M</td>
<td>1.17</td>
</tr>
<tr>
<td>15M</td>
<td>1.08</td>
</tr>
</tbody>
</table>

65% $\text{K}_2\text{SiO}_3$ + 35% KOH

KOH molar ratio $\text{Ms}$

20 °C – 90 % RH

Climatic chamber

7, 28 and 90 days
RESULTS AND DISCUSSION

MECHANICAL STRENGTH

Compressive strength

BSS

Age of curing

Compressive strength (MPa)

1d 7d 28d 90 d

BSS-5M BSS-8M BSS-12M BSS-15M

CS

Age of curing

Compressive strength (MPa)

1d 7d 28d 90 d

CS-5M CS-8M CS-12M CS-15M
RESULTS AND DISCUSSION

MECHANICAL STRENGTH

Compressive strength

BSS

Age of curing

1d 7d 28d 90 d

Compressive strength (MPa)

CS

Age of curing

1d 7d 28d 90 d

Compressive strength (MPa)
RESULTS AND DISCUSSION

MECHANICAL STRENGTH

Flexural strength

BSS
Age of curing

Flexural strength (MPa)

10
8
6
4
2
0

BSS-5M BSS-8M BSS-12M BSS-15M

1d 7d 28d 90d

CS
Age of curing

Flexural strength (MPa)

10
8
6
4
2
0

CS-5M CS-8M CS-12M CS-15M

1d 7d 28d 90d
RESULTS AND DISCUSSION

MECHANICAL STRENGTH

Flexural strength

BSS

Age of curing

1d  7d  28d  90d

Flexural strength (MPa)

CS

Age of curing

1d  7d  28d  90d

Flexural strength (MPa)
## RESULTS AND DISCUSSION

### PHYSICAL PROPERTIES

#### BSS

<table>
<thead>
<tr>
<th>Age</th>
<th>BSS-5M</th>
<th>BSS-8M</th>
<th>BSS-12M</th>
<th>BSS-15M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>1719 ± 17.8</td>
<td>1739 ± 22.7</td>
<td>1700 ± 14.0</td>
<td>1702 ± 5.4</td>
</tr>
<tr>
<td>7d</td>
<td>1784 ± 17.9</td>
<td>1836 ± 24.0</td>
<td>1734 ± 11.7</td>
<td>1742 ± 5.1</td>
</tr>
<tr>
<td>28d</td>
<td>1828 ± 9.1</td>
<td>1884 ± 25.3</td>
<td>1781 ± 15.5</td>
<td>1769 ± 14.7</td>
</tr>
<tr>
<td>90d</td>
<td>1865 ± 15.5</td>
<td>1914 ± 19.3</td>
<td>1854 ± 51.2</td>
<td>1784 ± 13.9</td>
</tr>
</tbody>
</table>

#### CS

<table>
<thead>
<tr>
<th>Age</th>
<th>CS-5M</th>
<th>CS-8M</th>
<th>CS-12M</th>
<th>CS-15M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>2670 ± 10.8</td>
<td>2677 ± 15.3</td>
<td>2742 ± 8.9</td>
<td>2716 ± 15.7</td>
</tr>
<tr>
<td>7d</td>
<td>2675 ± 26.3</td>
<td>2682 ± 4.6</td>
<td>2742 ± 7.2</td>
<td>2723 ± 11.3</td>
</tr>
<tr>
<td>28d</td>
<td>2696 ± 10.8</td>
<td>2707 ± 36.3</td>
<td>2744 ± 9.3</td>
<td>2728 ± 10.3</td>
</tr>
<tr>
<td>90d</td>
<td>2700 ± 27.7</td>
<td>2714 ± 12.2</td>
<td>2749 ± 17.4</td>
<td>2740 ± 12.7</td>
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</table>

### Water Absorption (%)

#### BSS

<table>
<thead>
<tr>
<th>Age</th>
<th>BSS-5M</th>
<th>BSS-8M</th>
<th>BSS-12M</th>
<th>BSS-15M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>22.93 ± 0.4</td>
<td>24.15 ± 0.5</td>
<td>22.59 ± 0.7</td>
<td>20.66 ± 0.2</td>
</tr>
<tr>
<td>7d</td>
<td>18.89 ± 0.6</td>
<td>23.01 ± 0.4</td>
<td>21.16 ± 1.3</td>
<td>19.25 ± 0.1</td>
</tr>
<tr>
<td>28d</td>
<td>17.51 ± 0.2</td>
<td>18.67 ± 0.9</td>
<td>18.43 ± 0.7</td>
<td>18.41 ± 0.1</td>
</tr>
<tr>
<td>90d</td>
<td>16.82 ± 0.5</td>
<td>14.80 ± 0.3</td>
<td>16.68 ± 0.4</td>
<td>16.66 ± 0.7</td>
</tr>
</tbody>
</table>

#### CS

<table>
<thead>
<tr>
<th>Age</th>
<th>CS-5M</th>
<th>CS-8M</th>
<th>CS-12M</th>
<th>CS-15M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>7.77 ± 0.1</td>
<td>8.11 ± 0.3</td>
<td>6.86 ± 0.2</td>
<td>6.98 ± 0.2</td>
</tr>
<tr>
<td>7d</td>
<td>7.58 ± 0.3</td>
<td>7.56 ± 0.1</td>
<td>6.67 ± 0.1</td>
<td>6.83 ± 0.1</td>
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<tr>
<td>28d</td>
<td>7.41 ± 0.2</td>
<td>6.93 ± 0.4</td>
<td>6.56 ± 0.1</td>
<td>6.54 ± 0.2</td>
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<tr>
<td>90d</td>
<td>7.15 ± 0.4</td>
<td>6.80 ± 0.1</td>
<td>6.36 ± 0.1</td>
<td>7.18 ± 0.3</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

**BSS**

- BSS-15M-90d
- BSS-15M-28d
- BSS-15M-8h
- BSS-12M-90d
- BSS-12M-28d
- BSS-12M-8h
- BSS-8M-90d
- BSS-8M-28d
- BSS-8M-8h
- BSS-5M-90d
- BSS-5M-28d
- BSS-5M-8h

**CS**

- SAC-15M-90d
- SAC-15M-28d
- SAC-15M-8h
- SAC-12M-28d
- SAC-12M-8h
- SAC-8M-90d
- SAC-8M-28d
- SAC-8M-8h
- SAC-5M-90d
- SAC-5M-28d
- SAC-5M-8h
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

Band centred at 962-945 cm\(^{-1}\):
Si-O-T bonds (T is Si or Al)
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

BSS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSS-15M-90d</td>
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<tr>
<td>BSS-15M-28d</td>
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<tr>
<td>BSS-15M-8h</td>
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<tr>
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<tr>
<td>BSS-12M-28d</td>
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<tr>
<td>BSS-12M-8h</td>
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<tr>
<td>BSS-8M-90d</td>
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<tr>
<td>BSS-8M-28d</td>
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</tr>
<tr>
<td>BSS-8M-8h</td>
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<tr>
<td>BSS-5M-90d</td>
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</tr>
<tr>
<td>BSS-5M-28d</td>
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<tr>
<td>BSS-5M-8h</td>
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CS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber (cm⁻¹)</th>
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<tr>
<td>SAC-15M-28d</td>
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<td>SAC-12M-8h</td>
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<td>SAC-5M-8h</td>
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Bands centred at 3000 and 1650 cm⁻¹: O-H bonds

Intensity (a.u.)

Wavenumber (cm⁻¹)
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

BSS

- BSS-15M-90d
- BSS-15M-28d
- BSS-15M-8h
- BSS-12M-90d
- BSS-12M-28d
- BSS-12M-8h
- BSS-8M-90d
- BSS-8M-28d
- BSS-8M-8h
- BSS-5M-90d
- BSS-5M-28d
- BSS-5M-8h

CS

- SAC-15M-90d
- SAC-15M-28d
- SAC-15M-8h
- SAC-12M-28d
- SAC-12M-28d
- SAC-12M-8h
- SAC-8M-90d
- SAC-8M-28d
- SAC-8M-8h
- SAC-5M-90d
- SAC-5M-28d
- SAC-5M-8h

1442 cm⁻¹: Associated to C-O bonds of Carbonates (CaCO₃)
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

BSS

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<th>BSS-15M-90d</th>
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<td></td>
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CS

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<td></td>
<td>SAC-8M-90d</td>
<td>SAC-8M-28d</td>
<td>SAC-8M-8h</td>
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Band in 875 cm⁻¹: C-O-C bond or Si-O-Fe bond
RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

**BSS**
- BSS-15M-90d
- BSS-15M-28d
- BSS-15M-8h
- BSS-12M-90d
- BSS-12M-28d
- BSS-12M-8h
- BSS-8M-90d
- BSS-8M-28d
- BSS-8M-8h
- BSS-5M-90d
- BSS-5M-28d
- BSS-5M-8h

**CS**
- SAC-15M-90d
- SAC-15M-28d
- SAC-15M-8h
- SAC-12M-90d
- SAC-12M-28d
- SAC-12M-8h
- SAC-8M-90d
- SAC-8M-28d
- SAC-8M-8h

Band in 670 cm\(^{-1}\): C-H bond
RESULTS AND DISCUSSION

XRD

BSS

CS

+ Wustite
° Larinite
× Gehlenite
• Mn₃O₄

+ Fayalite
× Magnetite
RESULTS AND DISCUSSION

XRD

BSS

+ Wuestite
° Larinite
x Gehlenite
• Mn₃O₄

CS

+ Fayalite
x Magnetite

Intensity (a.u.)
2 theta (°)
5 15 25 35 45 55

Intensity (a.u.)
2 theta (°)
5 15 25 35 45 55
RESULTS AND DISCUSSION

SEM-EDX

**BSS**

- BSS 8M
- BSS 12M

**CS**

- CS 8M
- CS 12M

Spectra:

1. Spectrum 1
2. Spectrum 2
3. Spectrum 3
4. Spectrum 4
RESULTS AND DISCUSSION

SEM-EDX

BSS

- C-A-S-H gel predominate
- Microcrash: high molar ratio
- Porous appear when molar ratio is increased.
RESULTS AND DISCUSSION

SEM-EDX

- K-A-S-H gel formed
- Less porous present in the matrix
- Less molar concentration used, more unreacted particles were found, obtaining a lower strength structure.
CONCLUSIONS

• Two different materials were obtained: alkali-activated cement with BSS (C-A-S-H gel and in lower amount geopolymeric K-A-S-H gel) and geopolymers with CS (K-S-H gel).

• The highest strength at 90 days was performed by CS with any molar concentration of KOH. The reason could be higher amount of silica and lower (FeO+CaO)/SiO$_2$ molar ratio.

• Optimal activator different for each precursor:
  • BSS: best activator was using 35% 8M KOH and 65% Silicate.
  • CS found best activator with 35% 12M KOH and 65% Silicate.

• CS performed better physical properties than BSS, although real density of raw materials are close.

• Both precursors could be used as alternative material to Portland cement. Valuing these wastes could reduce greenhouse gases emission and avoid their disposal in landfills. Although better approach could be performed with CS, due to the development of high resistances.
THANK YOU

ACKNOWLEDGEMENTS:

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