GEOPOLYMERISATION POTENTIAL OF METALLURGICAL SLAGS AND PLASMA TREATED APC RESIDUES

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- Geopolymers from FeNi slag
- Geopolymers from lead slag
- Geopolymers from plasma treated APC residues
- Conclusion
Geopolymers from FeNi slag

FeNi slag

- Electric arc slag is produced at LARCO S.A. ferronickel plant in Greece
- Annual slag production reaches 1,700,000 t; cement industry uses 450,000 t
- Slags are currently disposed of on surface heaps or under the sea
- Slag was dried and crushed (-120 μm and d<sub>50</sub>: -12 μm) to increase surface area

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th></th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>43.83</td>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.07</td>
<td>C</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>32.74</td>
<td>MgO</td>
<td>2.76</td>
<td>Ni</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8.32</td>
<td>Mn&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.44</td>
<td>Co</td>
</tr>
<tr>
<td>CaO</td>
<td>3.73</td>
<td>S</td>
<td>0.18</td>
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</table>
Geopolymers from FeNi slag
Synthesis

- Pulverised slag + Activating solution
  - Na$_2$SiO$_3$ + KOH pellets + water
  - Homogeneous paste

- The paste was cast in moulds (5 cm edge)
- Specimens were pre-cured at room temperature for 2 days before heated at 80 °C for 48 hours
- Aging took place for 7 days at room temperature
Geopolymers from FeNi slag

Tests

- Long term durability:
  - immersion in distilled, seawater, acid rain and 0.05N HCl solutions for a max period of 8 months
  - pH, Eh, EC and metal ion concentration were monitored monthly
  - weekly freeze-thaw cycles (-15 and +60 °C) and high temperature heating up to 800 °C

- Compressive strength was measured using an MTS 1600 load frame

- Elucidation of geopolymerisation mechanisms by analytical techniques (XRD, SEM, FTIR, TG)
Evolution of the compressive strength of geopolymers immersed in various solutions or subjected to freeze-thaw cycles over 8 months
Geopolymers from FeNi slag
Results and discussion

Evolution of the compressive strength of geopolymers vs. temperature

8 M KOH, 8% Na$_2$SiO$_3$ - 2d, 80 °C, 48 h, 7 d
Geopolymers from FeNi slag
Results and discussion

pH vs. time when geopolymers are immersed in various solutions

Dissolution of Mn, Fe, Ca, Ni, Mg, Cr, Na, K, Al and Si (mg/L) when geopolymers are immersed in 0.05N HCl solution
Geopolymers from FeNi slag
Results and discussion

XRD patterns of geopolymers subjected to high temperature heating (P80, P200 and P800 heated at 80, 200, 800 °C, respectively)

Geopolymers from FeNi slag
Results and discussion

Slag-glass geopolymer 50% w/w

G: glass grains
S: slag grains
B: geopolymeric gel

Potassium
Iron
Silicon
Aluminum
Geopolymers from FeNi slag
Results and discussion

Infrared absorption bands identification of bonds

- Asymmetric stretching vibration T-O-Si (T:Si or Al) [950-1200 cm\(^{-1}\)]
- In plane Si-O bending and Al-O linkages [460-465 cm\(^{-1}\)]
- Atmospheric carbonation or/and Na\(_2\)CO\(_3\) [1410-1570 cm\(^{-1}\)]

FTIR spectra of slag, glass and G80 glass-based geopolymer, SG80 slag-glass geopolymer
Geopolymers from lead slag
Introduction

- Production of lead slag:
  - Oxidation in autoclave
  - Lead concentrate → Oxidised lead concentrate → Melting
  - Lead
  - Lead slag

- Fly ash is also used in order to compensate the small amount of Si-, Al-source in lead slag

- Production of fly ash:
  - Lignite → Combustion
  - Solid wastes
  - Gaseous wastes
  - Energy
  - Bottom ash
  - Fly ash
Geopolymers from lead slag
Materials

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>PbO</th>
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<tr>
<td><strong>Slag</strong></td>
<td>21.58</td>
<td>1.71</td>
<td>35.9</td>
<td>2.78</td>
<td>0.2</td>
<td>15.83</td>
<td>0.3</td>
<td>8.3</td>
<td>13.4</td>
</tr>
<tr>
<td><strong>Fly ash</strong></td>
<td>51.4</td>
<td>23.5</td>
<td>7.73</td>
<td>9.21</td>
<td>1.69</td>
<td>0.89</td>
<td>1.45</td>
<td>2.66</td>
<td>-</td>
</tr>
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</table>

- **Slag** composition:
  - Litharge, PbO
  - Wustite, FeO
  - Sodium aluminium silicate, Na₆Al₄Si₄O₁₇
  - Magnetite, Fe₃O₄
  - Sodium zinc silicate, Na₂ZnSiO₄

- **Fly ash** composition:
  - Quartz, SiO₂
  - Gehlenite, Ca₂Al₂SiO₇
  - Magnetite, Fe₃O₄
  - Anorthite, CaAl₂Si₂O₈
  - Anhydrite, CaSO₄

**Slag size distribution**:
- d₁₀ = 4.6 μm
- d₅₀ = 37.1 μm
- d₉₀ = 116.3 μm

**Fly ash size distribution**:
- d₁₀ = 0.5 μm
- d₅₀ = 4.4 μm
- d₉₀ = 32.2 μm
Geopolymers from lead slag

Sample preparation

<table>
<thead>
<tr>
<th>Materials</th>
<th>GRINDING</th>
<th>MIXING</th>
<th>CASTING</th>
<th>CURING</th>
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<tr>
<td>SS</td>
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<td></td>
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</tr>
<tr>
<td>SH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Slag</th>
<th>S/W</th>
<th>Si/Al</th>
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</thead>
<tbody>
<tr>
<td>28.2</td>
<td>25.4</td>
<td>20.8</td>
</tr>
<tr>
<td>GL51</td>
<td>48.9</td>
<td>51.1</td>
</tr>
<tr>
<td>GL70</td>
<td>29.8</td>
<td>70.2</td>
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<tr>
<td>GL86</td>
<td>13.8</td>
<td>86.2</td>
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<table>
<thead>
<tr>
<th>S/W</th>
<th>Si/Al</th>
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<tbody>
<tr>
<td>3.59</td>
<td>5.04</td>
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<tr>
<td>4.31</td>
<td>5.97</td>
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<tr>
<td>5.19</td>
<td>7.63</td>
</tr>
<tr>
<td>6.31</td>
<td>11.3</td>
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Geopolymers from lead slag
Results and discussion: Crystalline phases

Fly ash

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<thead>
<tr>
<th>Phase</th>
<th>Before</th>
<th>After</th>
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<tbody>
<tr>
<td>Anorthite</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Gehlenite</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Quartz</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>Calcite</td>
<td>N</td>
<td>Y</td>
</tr>
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</table>

Slag

<table>
<thead>
<tr>
<th>Phase</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litharge</td>
<td>Y</td>
<td>traces</td>
</tr>
<tr>
<td>Wüstite</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Sodium aluminium silicate</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Sodium zinc silicate</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Sodium lead carbonate hydrate</td>
<td></td>
<td>(after storing)</td>
</tr>
</tbody>
</table>

Qu-quartz, An-anorthite, Ma-magnetite, Ge-gehlenite
Ca-calcite, Li-litharge, SAS-sodium aluminium silicate
Wu-wuestite, SZS-sodium zinc silicate, Pb-lead
Geopolymers from lead slag
Results and discussion: Bonds characteristics

- The sharpening and shifting of the main band for the geopolymer with 100% fly ash, attributed to asymmetric stretching vibrations of Si – O – Si and Al – O – Si, indicates the formation of the aluminosilicate gel
- When only lead slag was used, the FTIR pattern of the geopolymers produced appears almost identical to the raw material
- For specimens produced using both fly ash and lead slag as the percent of slag in the body increases, the IR patterns resemble more the 100% slag geopolymer
Geopolymers from lead slag
Results and discussion: physical properties

![Graphs showing the relationship between slag wt.% and physical properties such as compressive strength, flexural strength, bulk density, and water absorption.](image-url)
Geopolymers from lead slag

Results and discussion: Microstructure

GLS51

GLS70

GLS51

GLS70
Geopolymers from lead slag
Results and discussion: Leaching

**Decreased leaching**

- Pb (ppm)
- Al (ppm)
- Na (ppm)
- Si (ppm)

**Increased leaching**

- Pb (ppm)
- Al (ppm)
- Na (ppm)
- Si (ppm)
Geopolymers from plasma treated APC residues

APC residues

- Hazardous waste from cleaning gaseous emissions
- Mixture of lime, fly ash and carbon
  - Fine particles removed by high efficiency filters
- Issues with APC residues are:
  - Heavy metals
  - High alkalinity
  - High soluble salt content, particularly leachable chloride (Cl⁻)

SELCHP Energy from Waste facility, London
Geopolymers from plasma treated APC residues
APC residue plasma derived glass

- DC plasma treatment of APC residues blended with $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ → Volume reduction ~70–75%
- Amorphous aluminosilicate glass
- Dark green colour
- Inert material

Research aim: Use APC glass as raw material for geopolymer’s production
Geopolymers from plasma treated APC residues

Preparation of geopolymers

1. Preparation of activating solutions:
   - Water
   - Alkali Source (NaOH)
   - Silicate Source (Sodium silicate solution)

2. Preparation of mix:
   - APC glass (SiO$_2$ = 41.1%, CaO = 32.6%, Al$_2$O$_3$ = 14.8%)

3. Mixing for 10min
4. Casting in rectangular moulds
5. Curing in the moulds for 24hr
6. Samples ready for further curing

80x25x25 mm
(Compressive strength sample 40x25x25 mm)
Geopolymers from plasma treated APC residues

Results and discussion

- Strong and dense geopolymers over a wide range of S/L ratios

- Process highly affected by:
  - Particle size distribution of APC glass:
    - Fine particles improve early compressive strength
    - Broad particle size distribution of APC glass powder improves later strengths
  - NaOH concentration in the activating solution:
    - [NaOH] up to 10M → High strength geopolymers
Geopolymers from plasma treated APC residues
Results and discussion

- Optimum APC glass geopolymer’s composition:
  - Si/Al = 2.6
  - S/L = 3.4
  - [NaOH] = 6M in the activating solution

- Properties of APC glass geopolymers:
  - Very high strength (110 MPa @ 28 days)
  - High density (2300 kg/m³)
  - Low porosity and water absorption
  - No leaching of heavy metals
  - High acid resistance
  - High freeze-thaw resistance

- Not a pure geopolymer
Geopolymers from plasma treated APC residues
Composite microstructure of APC glass geopolymers

- Material resembles a particle reinforced composite
- Geopolymer-glass composite
- Unreacted APC glass have a strengthening and toughening effect

Crack deflection mechanism
Geopolymers from plasma treated APC residues
Binder phase characterisation

- APC glass geopolymer contains both geopolymer gel incorporating calcium and hydration products.

- High compressive strength can be attributed to:
  - Calcium present in the material.
  - Microstructure with the unreacted APC glass particles acting as rigid inclusions.

- Similarities with both metakaolin and GGBFS geopolymers.
Geopolymers from plasma treated APC residues

Potential applications

- Properties similar or better than concrete, cement geopolymer and some types of tiles

- Potential applications:
  - Replacement of cement or concrete in non-structural applications (eg. Pre-cast products, paving blocks)
  - Tile production
  - Hazardous and toxic waste management (Further research)

- Further testing is required for commercial applications
Geopolymers from plasma treated APC residues

Carbon footprint

- Carbon footprint assessment based on Greenhouse Gas Protocol
- Comparison with similar material prepared with Portland cement

Plasma process:
- Higher energy consumption than alternative APC residues management options
- Proven technology which maximises resource efficiency

DC plasma process on-site WtE plant:
- On-site solution for APC residues
- Minimises carbon footprint of process (renewable energy used)
- Economically attractive. Cost of process independent of energy price variations
Geopolymers from plasma treated APC residues

Carbon footprint

- CF of APC glass geopolymer and PC material is affected:
  - Additional materials used
  - Milling (if required)

- Reuse of APC glass in geopolymers → Savings in use of natural resources

Reuse of APC glass in geopolymers helps to mitigate climate change as CO2 emissions are significantly lower compared to Portland cement use.
Conclusions
Geopolymers from FeNi slag

Conclusion

- Geopolymerisation potential of low Ca FeNi slags (high compressive strength ~60 MPa is seen for optimum Si/Al ratio)
- Geopolymers exhibit very good behaviour in various aggressive environments, over a period of 8 months
  - sustain temperature variations between -15 & 60 °C
  - immersion in distilled water does not practically affect strength
  - immersion in seawater, acid rain or 0.05N HCl solutions decreases strength gradually but still remains above 30 MPa after 8 months
- Analytical techniques (XRD, SEM, FTIR, TG) may be used to elucidate mechanisms involved
Geopolymers from lead slag

Conclusion

- Geopolymers can be made from 100% fly ash, 100% lead slag and mixtures of them.
- The main change occurring after geopolymerisation revealed by XRD and IR is that litharge and calcium sulphate dissolve and a new amorphous aluminosilicate gel phase is formed.
- The system of larger particles originating from lead slag in a geopolymeric matrix mainly derived from fly ash, behaves as a composite structure, where the larger particle act as rigid inclusions and contribute in crack deflection during crack propagation.
Geopolymers from plasma treated APC residues

Conclusion

- Plasma treated APC residues is a raw material suitable for geopolymers’ production
- Formed amorphous, high strength geopolymer-glass composites
- Unreacted APC glass particles are embedded in the binder phase and provide reinforcement
- The binder phase contains both geopolymer gel incorporating calcium and hydration products
- Existence of both phases contributes to the excellent properties of the material
- Carbon footprint of APC glass geopolymers is ~12% lower than similar products from Portland cement