Blast-furnace-slag geopolymers as catalysts and adsorbents in water treatment

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Blast-furnace-slag geopolymers

Co-authors: Dr. Anne Heponiemi, Dr. Janne Pesonen, Dr. Sari Tuomikoski, Dr. Hanna Runtti, Dr. Tero Luukkonen, Dr. Tao Hu, M.Sc. Arne van Damme
What are geopolymers?

Joseph Davidovits in 1970’s: Geopolymers are mineral polymers resulting from geochemical reactions.

Amorphous, three-dimensional, inorganic materials, consisting of aluminosilicate framework (most commonly):

- alkali-activated aluminosilicates
- can be a prepared material that contains SiO₂ and Al₂O₃, for example from industrial by-products such as fly ashes

Uses in the following fields, for example:

- Low CO₂ producing binders (in contrast to portland cement from CaCO₃)
- Fire resistant materials
- Composites
- Waste stabilization and encapsulation
- Wastewater treatment
- Catalyst support
Preparation of geopolymers

- Geopolymers were synthesized by mixing blast-furnace-slag (BFS) with 50 wt% NaOH solution at different BFS/NaOH ratios.
- Pastes were poured into molds and they were allowed to consolidate first at 60 °C for 24h and then at room temperature for 6 days.
- Geopolymers were crushed, sieved to a particle size of 0.5-2 mm and washed with distilled water.
- Stability is essential when using industrial by-products, and it was tested at elevated temperatures and pressures before the use.
Stability of geopolymer catalysts

- Stability is essential when using industrial by-products, and it was tested at elevated temperatures and pressures before catalytic tests.
- Sequential leaching experiments

1 g of material + 40 ml deionized water, shaking 16 h at 25 °C

Filtration → Water soluble

40 ml 0.1 M CH₂COOH, shaking 16 h at 25 °C

Filtration → Exchangeable

40 ml 0.1 M HONH₂Cl, shaking 16 h at 25 °C

Filtration → Easily reduced

10 ml 30 % H₂O₂, evaporation
10 ml 30 % H₂O₂, evaporation
50 ml 1 M CH₃COONH₄, shaking 16 h at 25 °C

Filtration → Oxidizable

20 ml HF, shaking 8 h at 25 °C, evaporation
20 ml HF + 20 ml 65 % HNO₃, shaking 6 h at 25 °C, evaporation
20 ml 30 % HCl, shaking 6 h at 25 °C

Filtration → Residual

BFS
Adsorbents
Sorption of Cs, Ca, Cd, Sr, Co, Pb, Cu, Zn, Cr, Ni, As, Sb, \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), cationic dyes

Photocatalysts
Degradation of recalcitrant organic compounds with UV

Membranes & filters
Physical size-exclusion and adsorption

Stabilization/solidification
of concentrated wastewaters, sludges, and other water treatment residues

Other uses
pH buffers, antimicrobial filters, carrier media for fixed-film bioreactors

Ref. Luukkonen et al. (2017) Application of geopolymers in water and wastewater treatment (submitted)
Blast-furnace-slag geopolymers as adsorbents

Co-authors: Dr. Anne Heponiemi, Dr. Janne Pesonen, Dr. Sari Tuomikoski, Dr. Hanna Runtti, Dr. Tero Luukkonen, Dr. Tao Hu, M.Sc. Arne van Damme
**Hanna Runtti, PhD thesis, 2016


Sulphate removal over barium-modified blast-furnace-slag geopolymer

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Adsorption experiments

<table>
<thead>
<tr>
<th>Composition [%]</th>
<th>BFS</th>
<th>BFS-GP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>8.42</td>
<td>5.87</td>
</tr>
<tr>
<td>SiO₂</td>
<td>27.20</td>
<td>25.81</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>CaO</td>
<td>38.47</td>
<td>29.87</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.78</td>
<td>0.71</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.28</td>
<td>1.04</td>
</tr>
<tr>
<td>MgO</td>
<td>9.39</td>
<td>6.38</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.76</td>
<td>2.66</td>
</tr>
<tr>
<td>Mn</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.03</td>
<td>8.00</td>
</tr>
<tr>
<td>LOI</td>
<td>0.46</td>
<td>12.92</td>
</tr>
</tbody>
</table>

Fig. 3. Total SO₄²⁻ removal percent (left, solid lines) and total adsorbed amount (right, dashed lines) versus initial pH on the sorption of SO₄²⁻ from mine effluent. Sorbent dosage: 5 g L⁻¹, contact time: 24 h, temperature: 22–23 °C, adsorbate: mine effluent (C₀, SO₄²⁻: ~850–870 mg L⁻¹).
Fig. 4. Effect of the initial concentration on the sorption of $\text{SO}_4^{2-}$ on Ba-BFS-GP from model solution. Initial pH: 7–8, sorbent dosage: 5 g L$^{-1}$, contact time: 24 h, temperature: 22–23°C.
Adsorption isotherms

\[ q_e = \frac{q_{m1} b_{L1} C_e}{1 + b_{L1} C_e} + \frac{q_{m2} b_{L2} C_e}{1 + b_{L2} C_e} \]

\[ q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \]

\[ q_e = \frac{q_{m}(b_{S} C_e)^{n_s}}{1 + (b_{S} C_e)^{n_s}} \]

\[ q_e = \frac{q_{Th} K_{Th} C_e}{\left[1 + (K_{Th} C_e)^{Th}\right]^\frac{1}{Th}} \]

Fig. 6. Bi-Langmuir, Sips, Redlich-Peterson and Toth isotherms of SO₄²⁻ sorption on Ba-BFS-GP. (a) Model solution: \( C_0 (SO_4^{2-}) \): 100–1800 mg L⁻¹, sorbent dose: 5 g L⁻¹. (b) Mine effluent: \( C_0 (SO_4^{2-}) \): 865 mg L⁻¹, sorbent dose: 1.3–15 g L⁻¹. Initial pH was 7–8, contact time 24 h and temperature 22–23°C.
Adsorption kinetics

Fig. 8. a) Pseudo-first-order kinetic, b) pseudo-second-order kinetic and c) Elovich model plots of $\text{SO}_4^{2-}$ sorption on Ba-BFS-GP. α: Model $\text{SO}_4^{2-}$ solution ($C_0$, $\text{SO}_4^{2-}$: 1100 mg L$^{-1}$). □: Mine effluent ($C_0$, $\text{SO}_4^{2-}$: 853 mg L$^{-1}$). Initial pH: 7–8, sorbent dosage: 5 g L$^{-1}$, contact time: 24 h, temperature: 22–23°C.
## Adsorption capacity - Comparison

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Capacity $q$ (mg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coir pith carbon</td>
<td>0.06$^a$</td>
</tr>
<tr>
<td>Iron sand</td>
<td>1.15$^b$ (12 mmol g$^{-1}$)</td>
</tr>
<tr>
<td>Feldspar</td>
<td>0.275$^a$</td>
</tr>
<tr>
<td>Pulp and paper waste</td>
<td>2.786$^b$ (29 mmol g$^{-1}$)</td>
</tr>
<tr>
<td>Surfactant-modified palygorskite</td>
<td>3.24$^b$</td>
</tr>
<tr>
<td>ZnCl$_2$ activated coir pith carbon</td>
<td>4.9$^a$</td>
</tr>
<tr>
<td>Surfactant-modified clinoptilolite</td>
<td>$\sim 7.0^a$</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>7.7$^a$</td>
</tr>
<tr>
<td>Surfactant modified coir pith</td>
<td>8.76$^a$</td>
</tr>
<tr>
<td>Raw rice straw</td>
<td>11.68$^a$</td>
</tr>
<tr>
<td>Flotation fines</td>
<td>21.23$^b$ (221 mmol g$^{-1}$)</td>
</tr>
<tr>
<td>Limestone</td>
<td>23.7$^a$</td>
</tr>
<tr>
<td>Filter sand</td>
<td>25.07$^b$ (261 mmol g$^{-1}$)</td>
</tr>
<tr>
<td>Alkali-treated fly ash</td>
<td>43.0$^a$</td>
</tr>
<tr>
<td>Ba-modified zeolite</td>
<td>64.10$^a$ (1.33 meq g$^{-1}$)</td>
</tr>
<tr>
<td>Epichlorohydrin and trimethylamine modified rice straw</td>
<td>74.76$^a$</td>
</tr>
<tr>
<td>poly($m$-phenylenediamine)</td>
<td>108.5$^a$</td>
</tr>
<tr>
<td><strong>Ba-modified blast-furnace-slag geopolymer</strong></td>
<td><strong>119.0$^b$</strong></td>
</tr>
<tr>
<td>Chitin-based shrimp shells</td>
<td>156.0$^a$</td>
</tr>
</tbody>
</table>

$^a$ Langmuir maximum sorption capacity, $q_{m,calc}$.

$^b$ Experimental maximum sorption capacity.

Adsorption capacities for sulphate removal

Excellent capacity for Ba-modified BFS!

Mechanisms of removal: adsorption combined with precipitation
Highly efficient sulphate sorbent for mine water treatment was developed.

Ba-modified blast-furnace slag geopolymer showed sorption capacity up to 119 mg/g.

Extremely low sulphate concentrations were achieved (< 2 mg/l)

Sorption could be described by the Sips isotherm and the pseudo-second-order model.
Research article

Simultaneous removal of Ni(II), As(III), and Sb(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers

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d University of Jyväskyla, Kokkola University Consortium Chydenius, Unit of Applied Chemistry, Talonpajankatu 28, FI-67100 Kokkola, Finland
Preparation of geopolymer adsorbents

alkaline solution + metakaolin = 1.3 : 1 (w/w)

- Mixing (15 min), vibration (30 s), consolidation (3 d, 22°C)
- Drying at 105°C
- Washing

Crushing

Metakaolin geopolymer

Sieving: 63 μm–125 μm, 0.5–1.0 mm or 2–8 mm

10 M NaOH : sodium silicate
= 1 : 1 (w/w), 24 h standing before use
Characterization

Table 3
Specific surface area, average pore width, and pore volumes of blast-furnace slag (BFS), blast-furnace-slag geopolymer (BFS-GP), metakaolin (MK) and metakaolin geopolymer (MK-GP).

<table>
<thead>
<tr>
<th></th>
<th>BFS</th>
<th>BFS-GP</th>
<th>MK</th>
<th>MK-GP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area [m²/g]</td>
<td>2.79</td>
<td>64.5</td>
<td>11.5</td>
<td>22.4</td>
</tr>
<tr>
<td>Average pore width [nm]</td>
<td>12.7</td>
<td>5.93</td>
<td>18.17</td>
<td>30.97</td>
</tr>
<tr>
<td>Macro- and mesopore volume [cm³/g]</td>
<td>0.008</td>
<td>0.070</td>
<td>0.047</td>
<td>0.165</td>
</tr>
<tr>
<td>Micropore volume [cm³/g]</td>
<td>0.001</td>
<td>0.025</td>
<td>0.005</td>
<td>0.008</td>
</tr>
</tbody>
</table>

a = macropores: \( d_0 > 50 \) nm, mesopores: \( 2 \) nm \( \leq d_0 \leq 50 \) nm.

b = micropores: \( d_0 < 2 \) nm.
Adsorption experiments

Fig. 7. Effect of contact time on the simultaneous removal of Ni (○), As (●), and Sb (□): a) blast-furnace slag, b) blast-furnace-slag geopolymer, c) metakaolin, and d) metakaolin geopolymer.
# Adsorption kinetics

<table>
<thead>
<tr>
<th></th>
<th>MK</th>
<th>MK-GP</th>
<th>BFS</th>
<th>BFS-GP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Ni</td>
<td>Sb</td>
<td>As</td>
</tr>
<tr>
<td><strong>q_e [mg/g]</strong></td>
<td>0.014</td>
<td>0.269</td>
<td>0.068</td>
<td>0.008</td>
</tr>
<tr>
<td><strong>k_1 [1/min]</strong></td>
<td>0.005</td>
<td>0.002</td>
<td>0.007</td>
<td>0.058</td>
</tr>
<tr>
<td><strong>q_{calc} [mg/g]</strong></td>
<td>0.0089</td>
<td>0.243</td>
<td>0.023</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>R^2</strong></td>
<td>0.673</td>
<td>0.992</td>
<td>0.693</td>
<td>0.175</td>
</tr>
<tr>
<td><strong>k_2 [g/(mg min)]</strong></td>
<td>3.137</td>
<td>0.025</td>
<td>1.996</td>
<td>-13.911</td>
</tr>
<tr>
<td><strong>q_{calc} [mg/g]</strong></td>
<td>0.014</td>
<td>0.28</td>
<td>0.069</td>
<td>0.008</td>
</tr>
<tr>
<td><strong>R^2</strong></td>
<td>0.987</td>
<td>0.912</td>
<td>0.999</td>
<td>0.997</td>
</tr>
<tr>
<td><strong>β [g/mg]</strong></td>
<td>476.19</td>
<td>33.11</td>
<td>256.4</td>
<td>1250</td>
</tr>
<tr>
<td><strong>Elovich equation</strong></td>
<td><strong>u_0 [mg/(g min)]</strong></td>
<td>0.003</td>
<td>0.011</td>
<td>88.13</td>
</tr>
<tr>
<td></td>
<td>0.669</td>
<td>0.755</td>
<td>0.675</td>
<td>0.292</td>
</tr>
</tbody>
</table>

MK = metakaolin, MK-GP = metakaolin geopolymer, BFS = blast furnace slag and BFS-GP = blast furnace slag geopolymer.
Conclusions

- Specific surface area and pore volumes of blast furnace slag and metakaolin increased as a result of geopolymer formation.

- Geopolymerization of blast furnace slag increased removal capacity of Ni, As and Sb from 0.33 mg/g, 0.18 mg/g and 0.06 mg/g to 4.42 mg/g, 0.52 mg/g and 0.34 mg/g, respectively.

- Blast furnace slag geopolymer proved out to be more effective in Ni, As and Sb removal than metakaolin or metakaolin geopolymer.

- The relatively low removal capacities are probably a result of competition between adsorbates and other water matrix (real mine effluent) related inhibitive effects.

- The results indicate that blast furnace slag could a feasible metal and metalloid sorbent with one utilization prospect in the mining industry.
Blast-furnace-slag geopolymers as catalysts

Co-authors: Dr. Anne Heponiemi, Dr. Janne Pesonen, Dr. Sari Tuomikoski, Dr. Hanna Runtti, Dr. Tero Luukkonen, Dr. Tao Hu, M.Sc. Arne van Damme
Characterization of geopolymer catalysts

- Surface area was higher in samples containing more amount of NaOH
- Hydrotalcite was the main crystalline phase in geopolymer samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area [m²/g]</th>
<th>Pore volume [cm³/g]</th>
<th>Average pore width [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS</td>
<td>2.79</td>
<td>0.009</td>
<td>12.7</td>
</tr>
<tr>
<td>BFS30</td>
<td>27.3</td>
<td>0.162</td>
<td>23.7</td>
</tr>
<tr>
<td>BFS25</td>
<td>23.7</td>
<td>0.119</td>
<td>20.1</td>
</tr>
<tr>
<td>BFS20</td>
<td>14.8</td>
<td>0.083</td>
<td>22.4</td>
</tr>
<tr>
<td>BFS17.5</td>
<td>13.2</td>
<td>0.062</td>
<td>18.8</td>
</tr>
</tbody>
</table>

X-ray diffractogram of prepared geopolymers. #: hydrotalcite, *: calcium silicate hydrate

The infrared spectrum for blast-furnace-slag and two geopolymer catalysts at 1400-400 cm⁻¹.
Catalytic conversion of BPA

- The catalytic activity of prepared geopolymers was tested in the catalytic wet peroxide oxidation of bisphenol A (BPA) aqueous solution.

- Reaction conditions:
  - $C$ (BPA) = 60mg/L
  - reaction temperature 50°C
  - atmospheric pressure,
  - $H_2O_2$ concentration 1.5 g/L
  - catalyst load 2 g/L
  - reaction time 3 h

- All prepared geopolymers were active in the removal of BPA.
Conclusions

‒ Novel, low-cost, geopolymer-based materials for adsorption and catalytic applications were successfully developed from industrial by-product, blast-furnace-slag (BFS)

‒ All prepared geopolymers were active in the removal of BPA from aqueous solution (max removal around 50%)

‒ Further plans:
  ➢ Modification of geopolymers in order to get higher surface area
  ➢ Addition of active metal to the samples

Thank you for your kind attention!
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