Potential Alternative Utilization of Manganese Nodules

Ng. Hong VU
Utilization of leaching residues as sorbents

**Reductive leaching:**
- 90 °C, l/s = 10:1, ~ 20g SO$_2$/l, ~ 100g H$_2$SO$_4$/l, 60 min

**Sorbents preparation:**
- A1: original leaching residue
- A2/Cl: A1 activated in 10% vol. HCl
- A2/N: A1 activated in 10% vol. HNO$_3$
- A3/1: A1 thermally activated at 250 °C, 8 h
- A3/Cl: A2/Cl thermally activated at 250 °C, 8 h
- A4/Cl: A2/Cl mechanically activated in a mill at 600 rpm, 30 min
- A5/Fe$^{II}$: precipitation of Fe$^{II}$ on A1, 24 h, FeSO$_4$ under N$_2$
- A5/Fe$^{III}$: precipitation of Fe$^{III}$ on A1, 24 h, Fe(NO$_3$)$_3$, NaOH
- A5/Al$^{III}$: precipitation of Fe$^{III}$ on A1, 24 h, AlCl$_3$, NaOH

**Sorption tests:**
- 0.1g of a sorbent, 50 mL, 100 mg/L of a selected meta
Utilization of leaching residues as sorbents

Results:

Chemical composition of sorbents [%]

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Sr</th>
<th>Ba</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.89</td>
<td>0.41</td>
<td>5.95</td>
<td>38.71</td>
<td>1.10</td>
<td>0.03</td>
<td>2.39</td>
<td>1.42</td>
<td>0.67</td>
<td>1.66</td>
<td>0.29</td>
<td>3.60</td>
<td>0.24</td>
</tr>
<tr>
<td>A2/N</td>
<td>1.06</td>
<td>0.42</td>
<td>6.73</td>
<td>41.87</td>
<td>0.92</td>
<td>0.03</td>
<td>2.48</td>
<td>1.34</td>
<td>0.63</td>
<td>1.74</td>
<td>0.15</td>
<td>3.62</td>
<td>0.14</td>
</tr>
<tr>
<td>A2/Cl</td>
<td>0.87</td>
<td>0.53</td>
<td>6.28</td>
<td>40.24</td>
<td>0.62</td>
<td>0.03</td>
<td>2.36</td>
<td>1.29</td>
<td>0.52</td>
<td>1.51</td>
<td>0.14</td>
<td>4.12</td>
<td>0.16</td>
</tr>
<tr>
<td>A3/1</td>
<td>0.91</td>
<td>0.42</td>
<td>6.01</td>
<td>40.30</td>
<td>1.14</td>
<td>0.04</td>
<td>2.50</td>
<td>1.35</td>
<td>0.69</td>
<td>1.72</td>
<td>0.30</td>
<td>4.01</td>
<td>0.29</td>
</tr>
<tr>
<td>A3/Cl</td>
<td>0.88</td>
<td>0.53</td>
<td>6.19</td>
<td>40.18</td>
<td>0.62</td>
<td>0.03</td>
<td>2.41</td>
<td>1.28</td>
<td>0.53</td>
<td>1.52</td>
<td>0.14</td>
<td>4.14</td>
<td>0.15</td>
</tr>
<tr>
<td>A4/Cl</td>
<td>0.88</td>
<td>0.50</td>
<td>6.15</td>
<td>41.04</td>
<td>0.54</td>
<td>0.03</td>
<td>2.34</td>
<td>1.28</td>
<td>0.52</td>
<td>1.50</td>
<td>0.15</td>
<td>3.50</td>
<td>0.15</td>
</tr>
<tr>
<td>A5/FeII</td>
<td>1.00</td>
<td>0.45</td>
<td>6.33</td>
<td>39.16</td>
<td>1.43</td>
<td>0.03</td>
<td>2.37</td>
<td>1.40</td>
<td>0.64</td>
<td>3.07</td>
<td>0.27</td>
<td>3.95</td>
<td>0.25</td>
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<tr>
<td>A5/FeIII</td>
<td>1.01</td>
<td>0.45</td>
<td>6.17</td>
<td>39.73</td>
<td>0.89</td>
<td>0.02</td>
<td>2.48</td>
<td>1.39</td>
<td>0.66</td>
<td>4.89</td>
<td>0.18</td>
<td>3.23</td>
<td>0.14</td>
</tr>
<tr>
<td>A5/AlIII</td>
<td>0.67</td>
<td>0.23</td>
<td>13.77</td>
<td>27.78</td>
<td>0.68</td>
<td>0.79</td>
<td>3.21</td>
<td>1.14</td>
<td>0.46</td>
<td>1.18</td>
<td>0.09</td>
<td>2.06</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Utilization of leaching residues as sorbents

**Results:**

**Mineralogical composition of the sorbent A1**

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>SemiQuant [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-046-1045</td>
<td>Quartz, syn</td>
<td>SiO$_2$</td>
<td>19</td>
</tr>
<tr>
<td>00-005-0448</td>
<td>Barite</td>
<td>BaSO$_4$</td>
<td>5</td>
</tr>
<tr>
<td>04-007-5092</td>
<td>Albite</td>
<td>NaAlSi$_3$O$_8$</td>
<td>32</td>
</tr>
<tr>
<td>01-086-0438</td>
<td>Orthoclase</td>
<td>K(AlSi$_3$O$_8$)</td>
<td>11</td>
</tr>
<tr>
<td>01-073-9865</td>
<td>Muscovite 2M1, ferrian</td>
<td>$K_{0.92}Na_{0.08}Al_{1.78}Fe_{0.22}Mg_0.1(Al_{0.83}Si_{3.17}O_{10})(OH)_{1.56}O_2$</td>
<td>28</td>
</tr>
<tr>
<td>04-011-5452</td>
<td>Dickite 2M1</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>5</td>
</tr>
</tbody>
</table>
Utilization of leaching residues as sorbents

Results:

Specific surface of sorbents, measured by BET [m²/g] and their moisture

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface</td>
<td>234</td>
<td>227</td>
<td>229</td>
<td>220</td>
<td>211</td>
<td>216</td>
<td>274</td>
<td>253</td>
<td>298</td>
</tr>
<tr>
<td>Moisture</td>
<td>6.07</td>
<td>5.13</td>
<td>5.52</td>
<td>2.15</td>
<td>2.30</td>
<td>8.78</td>
<td>2.42</td>
<td>2.80</td>
<td>3.22</td>
</tr>
</tbody>
</table>
Utilization of leaching residues as sorbents

Results:

Effect of pH on the adsorption of Pb onto adsorbents: 200rpm, 8h
Utilization of leaching residues as sorbents

**Results:**

Dependence of the Pb uptake on adsorption time: 200rpm, pH 5.05
Utilization of leaching residues as sorbents

Results:

Effect of pH on the adsorption of Cd onto adsorbents: 200rpm, 8h
Utilization of leaching residues as sorbents

Results:

Dependence of the Cd uptake on adsorption time: 200rpm, pH 6.0
Utilization of leaching residues as sorbents

Results:

Effect of pH on the adsorption of Cu onto adsorbents: 200rpm, 8h
Utilization of leaching residues as sorbents

Results:

Dependence of the Cu uptake on adsorption time: 200rpm, pH 4
Utilization of leaching residues as sorbents

Results:

Effect of pH on the adsorption of Ni onto adsorbents: 200rpm, 8h
Utilization of leaching residues as sorbents

Results:

Dependence of the Ni uptake on adsorption time: 200rpm, pH 5.5
Utilization of leaching residues as sorbents

Results:

Effect of pH on the adsorption of Co onto adsorbents: 200rpm, 8h
Utilization of leaching residues as sorbents

Results:

Dependence of the Co uptake on adsorption time: 200rpm, pH 5
Utilization of leaching residues as sorbents

Results:

Dependence of the As uptake on adsorption time: 250rpm, pH 7.0
Utilization of leaching residues as sorbents

Results:

Comparison of maximum As(V) adsorption capacities of different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial pH</th>
<th>Concentration range (mg L$^{-1}$)</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanohydrous Fe-Ti mixed oxide</td>
<td>7</td>
<td>5 - 150</td>
<td>14.3</td>
<td>(Gupta and Ghosh 2009)</td>
</tr>
<tr>
<td>TiO$_2$ nanoparticle</td>
<td>7.6</td>
<td>5 - 90</td>
<td>20.53</td>
<td>(Nabi 2009)</td>
</tr>
<tr>
<td>Crystalline hydrous Fe$_2$O$_3$</td>
<td>3-4</td>
<td>50 - 250</td>
<td>25</td>
<td>(Manna et al. 2003)</td>
</tr>
<tr>
<td>Nanostructure Fe(III)-Zr(IV) bimetal mixed oxide (NHZO)</td>
<td>7</td>
<td>5 - 150</td>
<td>9.36</td>
<td>(Gupta et al. 2009)</td>
</tr>
<tr>
<td>CuO nanoparticles</td>
<td>8</td>
<td>0.1 - 100</td>
<td>22.6</td>
<td>(Martinson and Reddy 2009)</td>
</tr>
<tr>
<td>Nanostructured akaganeite</td>
<td>7.5</td>
<td>5 - 20</td>
<td>1.80</td>
<td>(Deliyanni et al. 2003)</td>
</tr>
<tr>
<td>Fe–Zr binary oxide</td>
<td>7.0</td>
<td>5 - 40</td>
<td>46.1</td>
<td>(Ren et al. 2011)</td>
</tr>
<tr>
<td>Al$_2$O$_3$ /Fe(OH)$_3$</td>
<td>7.2</td>
<td>7.5 - 135</td>
<td>36.7</td>
<td>(Hlavay and Polyák 2005)</td>
</tr>
<tr>
<td>CuO nanoparticles</td>
<td>8.0</td>
<td>0.1 - 100</td>
<td>22.6</td>
<td>(Martinson 2009)</td>
</tr>
<tr>
<td>A$_5$/Fe$^{II}$</td>
<td>7.0</td>
<td>100</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>A$_5$/Fe$^{III}$</td>
<td>7.0</td>
<td>100</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>A$_5$/Al$^+$</td>
<td>7.0</td>
<td>100</td>
<td>28.1</td>
<td></td>
</tr>
</tbody>
</table>

Present work
Conclusions:

- Prepared adsorbents are effective in a fast removal of Pb and Cd.
- Chemical and mechanochemical (milling) activation generally increased the maximum adsorption capacity.
- The activated sorbents can be used to remove Cu, Ni and Co from aqueous solution.
- Nanostructured sorbents were proved to be effective for arsenic removal. Especially the adsorbent A5/AIII based on nanoparticles of Al(OH)₃ can be considered one of the best materials for an effective arsenic removal at low cost.

Using leaching residues to treat waste water in hydrometallurgical plants
Nodules and Metals for E-mobility - **LITHIUM**

3 millions tones of nodules

400 tones of lithium metal

2,500 tones of Li$_2$CO$_3$

1% of the Li world production

37,5 millions USD
LITHIUM – a key raw material for modern technologies

Li consumption is usually divided to Chemical and Technical

- Metal (6%)
- Glass (9%)
- Glass ceramics (12%)
- Ceramics (14%)
- Lubricants (8%)
- Primary batteries (2%)
- Polymers (5%)
- Air treatment (5%)
- Aluminium alloys (1%)

Main factor for increased Li consumption is Rechargeable batteries with 29%.
LITHIUM – a key raw material for modern technologies

2001
Many years ago, lithium was used in a variety of industrial purposes.

2015
Today, the major use by far is batteries.

And in the future?

2025
The battery market alone will be almost 2x bigger than the entire lithium market today.
LITHIUM – a key raw material for modern technologies

<table>
<thead>
<tr>
<th>Lithium demand and UBS’ forecasts (thousand tonnes per annum LCE*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batteries</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>01</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

Demand CAGR 2015-25
Batteries 24.6%
Ceramics & glass 4%
Total 17%

SOURCE: UBS
LITHIUM – a key raw material for modern technologies

Price development of main marketable lithium compounds
LITHIUM – a key raw material for modern technologies

Global Salt Lakes – ranked by lithium brine grade

- Chile
- Argentina
- Bolivia
- USA
- China
LITHIUM – a key raw material for modern technologies

Lithium minerals
LITHIUM – a many junior miners want to join the league of big
1 t of zinnwaldite concentrate – 100 USD
1 t of spodumene concentrate – 550 USD
New approaches needed for recovering Li at low concentration

Direct usage of manganese nodules to recover Li
Nodules and Metals for E-mobility - LITHIUM

Titration curves for pH_{pZc} determination

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The point of zero charge $\text{pH}_{\text{pZC}}$

The dependence of the Li sorption capacity of the nodules on pH

Li sorption kinetics of the untreated nodules, pH 4

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Desorption kinetics of Li from nodules, pH 1.2

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Another solution – a new nano-adsorbent

Synthesis of functionalized magnetic silicon-based nano-adsorbents
Nodules and Metals for E-mobility - LITHIUM

Another solution – a new nano-adsorbent

Schematic representation cycle of functionalized magnetic silicon-based nano-adsorbents process for metal recovery from leach solutions.
Thank you