Research perspectives for embedding NORM in the circular economy

Wouter Schroeyers

10th International Symposium on Naturally Occurring Radioactive Material (NORM X) 9th -13th May 2022
Circular economy

▪ Consumption/use:
  ▪ Minimizing waste via suitable design of products, processes and business models
  ▪ Rethinking energy and resource intensive products and processes
  ▪ Reducing use and consumption of materials
  ▪ Controling finite stocks, preserving and regenerating natural systems
Recovering / recycling of by-products from NORM related industries

- Aluminium production
  - Total stockpile of **bauxite residue** (red mud) in the world: **4 billion tons** (2015)
    - Annual production: 150 million tons
  - Recycling rate < 5%

- Phosphate industry
  - Total amount of **phosphogypsum** produced worldwide: **6 billion tonnes** (up to 2006)
    - Annual production: >160 million tonnes (IAEA, 2013)
  - Recycling rate < 5 %


IAEA (2013), Safety report series 78
Paridaens and Vanmarcke, Health Physics, 95, 4 (2008), 413-424
Outline

1. Residues & their properties

2. State of the art in applied research
   a) Application as construction material
   b) Source of raw materials

3. Socio-economic research on non-technical barriers

4. Conclusions
Bauxite residue - chemical / mineralogical properties

Mixture of compounds:
- Initially present in original bauxite ore
- Generated during Bayer cycle

Organic compounds:
- Vegetable and organic substances in bauxite/overburden
- Modifiers or flocculants added in process,
  - Mainly carbohydrates, alcohols, phenols, and sodium salts of polybasic and hydroxy acids

Challenges in standardizing processes to develop a red mud recycle route

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Krivenko et al. 2017 [81] (Ukraine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>48.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>10.1</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>53.3</td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.2</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>2.5</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>-</td>
</tr>
</tbody>
</table>

Several minerals' forms:
- 25–27 wt% hematite
- 25–28 wt% goethite
- 4.5–6.5 wt% rutile and anatase (TiO₂)
- 15–17 wt% hydrogarnets
- 6–7 wt% sodium aluminosilicate hydrate
- 2.5–3.0 wt% calcite
- Hematite (Fe₂O₃), goethite (-FeOOH), TiO₂ in the anatase polymorph, gibbsite (-Al(OH)₃), sodium aluminosilicate hydrate boehmite (-AlOOH), quartz (SiO₂).
### Bauxite residue - physico-chemical properties

- Fresh untreated red mud: high alkalinity pH 11 – 13

- Red mud: **extremely fine** (e.g. particle size distribution, 95 % volume < 44μm)
  - Strongly affects **rheological properties**, (possible applications)
Bauxite residue activity concentration

Red mud

Australia
Brazil
China
Germany
Greece
Hungary
Italy
Jamaica
Romania
Turkey
Total

Ra-226 mean (Bq/kg)

Th-232 mean (Bq/kg)

K-40 mean (Bq/kg)

Schroeyers et al., Construction and building materials, 159 (2018), 755-767
### Phosphogypsum (PG) - Chemical / Mineralogical Properties

<table>
<thead>
<tr>
<th>(wt %)</th>
<th>PG IAEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>39.5</td>
</tr>
<tr>
<td>SO₃</td>
<td>56.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.0</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.1</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Acidic</td>
<td>-high content in phosphoric, sulfuric, hydrofluosilicic acids</td>
</tr>
<tr>
<td>Trace metal(loid)s</td>
<td>High concentrations (e.g. As)</td>
</tr>
<tr>
<td>Radionuclides</td>
<td>Ra-226 and Po-210</td>
</tr>
<tr>
<td>Nitrates</td>
<td>High concentrations</td>
</tr>
<tr>
<td>REE</td>
<td>70-85 % of REE originally present in phosphate rocks</td>
</tr>
</tbody>
</table>

Gypsum: \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)

Depending upon rock source and efficiency of wet process

Traces of unreacted phosphate rock and organic matter

Process waters trapped in interstices of mineral particles (sometimes low quality of sulfuric acid)

1-2 wt% REE in igneous phosphate rocks (much richer than sedimentary)

Solid phase e.g. alkali fluorosilicates, fluorides, quartz, and feldspars

REVIEW: Canovas et al., Journal of Cleaner Production, 174 (2018) 678-690
Phosphogypsum - physico-chemical properties

- **Silt-sized gypsum crystals**
  - Morphology depends on:
    - Source of the phosphate rock,
    - Reaction conditions in the acid attack

- Large total specific surface area → high reactivity (dissolves more rapidly than natural gypsum)

- **Density, permeability and strength** influenced by:
  - Characteristics source rock and reaction process
  - Method of deposition
  - Age, location, and depth within the PG stack
    - With age and depth within the stack:
      Density and strength ↑ Water content & permeability ↓

### Phosphogypsum <-> gypsum - activity concentration index

$$I = \frac{C_{Ra226}}{300 \, Bq/kg} + \frac{C_{Th232}}{200 \, Bq/kg} + \frac{C_{K40}}{3000 \, Bq/kg}$$

<table>
<thead>
<tr>
<th>Gypsum</th>
<th>$C_{Ra226}$</th>
<th>$C_{Th232}$</th>
<th>$C_{K40}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulgaria</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Egypt</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estonia</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iran</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pakistan</td>
<td>0.15</td>
<td></td>
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<tr>
<td>Syria</td>
<td>0.07</td>
<td></td>
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</tr>
<tr>
<td>Turkey</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bangladesh</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brazil</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulgaria</td>
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<tr>
<td>Czech Republic</td>
<td>0.78</td>
<td></td>
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</tr>
<tr>
<td>Egypt</td>
<td>1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>1.27</td>
<td></td>
<td></td>
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<tr>
<td>Germany</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
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<td>Greece</td>
<td>1.30</td>
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<td></td>
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<tr>
<td>Israel</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jordan</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Korea</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nigeria</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poland</td>
<td>1.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Romania</td>
<td>1.00</td>
<td></td>
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</tr>
<tr>
<td>Serbia</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slovenia</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>1.51</td>
<td></td>
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</tr>
<tr>
<td>Spain</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Netherlands</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turkey</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Schroeyers et al., Construction and building materials, 159 (2018), 755-767
Outline

1. Residues & their properties

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Bauxite residue - important research/application areas

- Porous structure: use as adsorbent

- Red mud applications

- Construction materials
  - Cement
  - Brick
  - Land filler
  - Thermal insulation materials
    - Red mud composite
    - Impermeable material
Number of papers in area phosphogypsum research

REVIEW: Chernysh et al., Appl. Sci., 11 (2021), 1575
Main subjects of interest in phosphogypsum research (1975-2017)

REVIEW: Canovas et al., Journal of Cleaner Production, 174 (2018) 678-690
Bauxite residue as construction material

- Technically successful applications in research papers:
  - Cement & concretes, bricks, tiles, land filler, thermal insulation, impermeable material...

- High temperature treatments (below melting point metal):
  - Calcination (remove impurities)
  - Sintering (weld together small particles of metals);
    - Usually improves: stability, heat resistance and thermal insulation properties
  - Come with an (energy) cost

- Material substituted by red mud = very available and cheap
  - Any negative characteristic = obstacle for use

- Strong alkalinity
  - Health and safety aspects, adverse impact on properties?

REVIEW: Silveira et al., Sustainability, 13 (2021) 12741
Babisk et al., Journal of materials research and technology, 9, 2 (2020) 2186-2195
Use of by-product in Alkali Activated Materials (AAMs)

Alkali Activated Materials:

- **Source material** = $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$
- **Activator** = Alkaline solution
  - mainly alkali-hydroxide/silicate

**Bauxite residue**

**Fly ash**

**Slags**

**Phosphogypsum**

**Siliciumdioxide waste**

From NORM related industries

Circular economy
Alkali Activated Materials (AAMs): enabling multiple cycles of use

Youssef et al., SN Appl. Sci., 1 (2019) 1252
Bauxite residue as precursor for alkali activated materials

Alkali activated materials
- Source material: red mud + fly ash, GGBFS, silica fume, metakaolin, ...

Advantages:
- Important cost = activator \(\rightarrow\) lower due to high NaOH content of red mud
- Good adsorption of heavy metals

Research challenges:
- Durability needs more in-depth investigation before utilisation
- Heterogeneity (origin, treatment process, properties vary in time...)
- Need for proper code standards and regulation for various applications
- Role of iron in structure needs further clarification
- Reinforced alkali activated materials: Corrosion? Bond and structural behaviour?
I-index AAM containing *bauxite residue*

<table>
<thead>
<tr>
<th>kg/m³</th>
<th>Cement</th>
<th>Red mud</th>
<th>Aggregates</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference concrete</td>
<td>400</td>
<td>1850</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Alkali activated concrete containing red mud</td>
<td>1800</td>
<td>450</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

**Red Mud**

<table>
<thead>
<tr>
<th>Country</th>
<th>AAM (kg/m³)</th>
<th>Reference concrete (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>Brazil</td>
<td>2,23</td>
<td>2,23</td>
</tr>
<tr>
<td>China</td>
<td>3.92</td>
<td>3.92</td>
</tr>
<tr>
<td>Greece</td>
<td>3.07</td>
<td>3.63</td>
</tr>
<tr>
<td>Hungary</td>
<td>2.34</td>
<td>2.68</td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jamaica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turkey</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**AAM**

<table>
<thead>
<tr>
<th>AAM (kg/m³)</th>
<th>Reference concrete (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>0.77</td>
</tr>
<tr>
<td>0.77</td>
<td>1.76</td>
</tr>
<tr>
<td>1.76</td>
<td>3.03</td>
</tr>
<tr>
<td>3.96</td>
<td>2.81</td>
</tr>
<tr>
<td>2.81</td>
<td>2.18</td>
</tr>
<tr>
<td>2.66</td>
<td>2.66</td>
</tr>
</tbody>
</table>

AAM containing red mud as partial replacement of cement and aggregates

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Schroeyers et al., Construction and building materials, 159 (2018), 755-767
Phosphogypsum <-> natural gypsum as construction material

- PG in cement, mortars, concretes & bricks:
  (cement substitution or replacing natural sand for mortar)
  - Impurities -> purification step required, increasing costs
    - Washing (tap water, milk of lime, sulphuric acid) => water use, waste water (facility)
    - Calcination => thermal resources
  - Lower density (<- sand, cement) => benefit for producing lightweight bricks/plaster
  - Declination in workability of concrete mixtures => requires using chemical admixtures
  - Reduction mechanical strength (cement, mortars, concretes & bricks)
    => solved by calcinated PG and increase curing temperature to improve strength
  - Delay in the setting time => use as retarder agent

- Negative effects on drying shrinkage and soundness expansion (stability of cement after setting, crack formation) => more study required, major defects that could limit wide use
- Chemical, abrasion, freeze/thaw and fire resistance
- Thermal conductivity => needs more study
Phosphogypsum as construction material

- New research options
  - Adding (mineral or glass) **fibers** can improve flexural strength, freeze/thaw, anti-impact work and water resistance.
  
  - Adding **superplasticizers** (enhance strength, decline the water absorption) or **NaOH** (enhance strength; decline setting time)

REVIEW: Rashad, Journal of Cleaner Production, 166 (2017) 732-743
Phosphogypsum as construction material

- New research options

Fly ash + Phosphogypsum + Activating solution + Alkali activated materials (AAMs)

Blast furnace slag

Activating solution: NaOH, KOH, Na$_2$SiO$_3$/NaOH

Curing: $T$, $t$

Ettringite binders

H$_2$O

Gijbels et al., Science of the total environment, 660 (2019) 1098-1107
Gijbels et al., Cement and Concrete Research 128 (2020) 105954
Phosphogypsum as construction material

- Using it as a filling material?
- Adding costs (via pre-treatment)?
- Adding radionuclides?
- Adding complexity (heterogeneity)?
- Most applications use only low amounts?
- Perception of companies and end users?

Search for added value

Not only mitigating the contaminations/costs of PG disposal
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Extraction from bauxite residue

- **Fe$_2$O$_3$ (35-60 wt%)**: use in steel metallurgy
  - Problem: **large sodium content prohibits the use of blast furnaces**
    - (evaporation Na$_2$O at high T → attacks ceramic refractory bricks)
  - Design a **dedicated process**?
    - (e.g. Electric arc furnace carbothermic smelting: convert in pig iron and mineral wool)

- (remaining) **Aluminium and Titanium**
  - Problem: **high silica content** → Bayer process: precipitation **aluminosilicates**, loss of up to 20 wt% of Al$_2$O$_3$
  - **Sintering** processes designed to achieve higher **aluminium recovery**
  - **Titanium** recovery via leaching with H$_2$SO$_4$

- **Rare earth elements (REE) recovery**: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, etc.
  - Leaching with diluted mineral acids (0.5 M HNO$_3$, Dilute H$_2$SO$_4$, HCl)
  - Majority elements (Fe) cannot be leached under same experimental conditions
Extraction of REE from phosphogypsum

- Leaching by aqueous solutions
  - 50% REE recovered with 0.1-0.5 M H₂SO₄ (ambient temperature, s/l ratio 1:10)
  - Leaching efficiency increased via gravity flow of H₂SO₄ through PG column
  - Enhanced H₂SO₄ leaching via mechanical activation of PG (example ball milling, stirring)
  - Higher leaching efficiencies with HNO₃ (or mixtures of HNO₃ and Ca(NO₃)₂)

- Leaching by organic solvents
  - Leach metals and radionuclides from PG with organic extraction agents
    (e.g. tributylphosphate) dissolved in kerosene \( \rightarrow \) 69.9% REE removal

- REE recovery via:
  - Selective precipitation
    (from aqueous phase via using oxalic acid)
  - Solvent extraction
    (e.g. from aqueous phase via dibutylbutylphosphonate in xylene)
Extraction of REE from phosphogypsum

- purification of phosphogypsum
  - Select suitable solvent for leaching (previously used: dilute H$_2$SO$_4$ or 10-20% aqueous ammonia solutions)
    - Remove fluorides, phosphates and water-soluble sodium compounds
    - Simultaneous dissolution/extraction of rare-earth
    - Remove radionuclides → **concentrate in specific fraction** but a volume reduction and land reclamation is realized

- Valorizing residue as construction material
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Studying the **societal challenges** related to the use of NORM in building materials

- **Perceptions, concerns, acceptance and decision-making processes** of:
  - ‘Intermediate’ actors
    (producers of concrete, potentially using large quantities of these cementitious binders)
  - ‘End-users’
    (those constructing/using buildings in which such concrete might be used).

- **Use of NORM in cement**
  (Belgium, Slovenia and Czech Republic)

- **Exploratory and semi-structured interviews**

Presentation @ NORM X: Nazanin Love, PhD student UHasselt – SCK CEN
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Perspectives for embedding NORM in the circular economy

- **Pre-treatment = extraction**
  - = preparing remaining residues for entering the circular economy

- Recovery of valuable materials & reduction of intrinsic environmental risk
- Metal recovery can be viable if solution is provided for residue
- Radionuclides are in many research scenario’s concentrated in remaining fraction for safe disposal

- **Embrace the local differences:** different materials $\rightarrow$ different solutions

- Circular economy is built on **industrial symbiosis** between local partners