Research perspectives for embedding NORM in the circular economy

Wouter Schroeyers
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
  - Controlling 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%

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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

<table>
<thead>
<tr>
<th>Composition (% wt.)</th>
<th>Krivenko et al., 2017 [81] (Ukraine)</th>
<th>Do et al., 2019 [84] (South Korea)</th>
<th>Hairi et al., 2018 [80] (Canada)</th>
<th>Hu et al., 2018 [82] (China)</th>
<th>Cardenia et al., 2018 [83] (Greece)</th>
<th>Koshly et al., 2019 [86] (China)</th>
<th>Lemoungna et al., 2017 [85] (China)</th>
<th>Pérez-Villarreal et al., 2012 [87] (Spain)</th>
<th>Berra et al., 2015 [88] (Greece)</th>
<th>Agrawal et al., 2021 [89] (India)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>48.6</td>
<td>22.21</td>
<td>38.92</td>
<td>33.88</td>
<td>42.34</td>
<td>41.0</td>
<td>33.99</td>
<td>39.23</td>
<td>44.60</td>
<td>36.8</td>
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<tr>
<td>Al₂O₃</td>
<td>12.9</td>
<td>19.87</td>
<td>22.12</td>
<td>17.89</td>
<td>18.25</td>
<td>21.8</td>
<td>18.47</td>
<td>19.80</td>
<td>23.60</td>
<td>22.07</td>
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<tr>
<td>SiO₂</td>
<td>4.8</td>
<td>15.12</td>
<td>10.52</td>
<td>19.43</td>
<td>6.97</td>
<td>11.0</td>
<td>9.39</td>
<td>8.77</td>
<td>10.20</td>
<td>13.81</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6.6</td>
<td>14.92</td>
<td>6.62</td>
<td>12.18</td>
<td>3.83</td>
<td>8.0</td>
<td>5.11</td>
<td>5.02</td>
<td>2.90</td>
<td>10.21</td>
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<tr>
<td>CaO</td>
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<td>7.1</td>
<td>1.36</td>
<td>2.66</td>
<td>11.64</td>
<td>1.6</td>
<td>14.19</td>
<td>4.54</td>
<td>11.20</td>
<td>1.62</td>
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<tr>
<td>TiO₂</td>
<td>6.3</td>
<td>5.24</td>
<td>7.61</td>
<td>0.72</td>
<td>4.27</td>
<td>7.0</td>
<td>5.42</td>
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<td>5.70</td>
<td>13.6</td>
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<tr>
<td>SO₃</td>
<td>-</td>
<td>0.72</td>
<td>-</td>
<td>0.59</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MgO</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
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<tr>
<td>ZrO₂</td>
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<tr>
<td>SO₄</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>0.21</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Others</td>
<td>2.5</td>
<td>13.68</td>
<td>10.51</td>
<td>13.68</td>
<td>36.912.66</td>
<td>8.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

Several minerals’ forms:
- Hematite (Fe₂O₃),
- Goethite (-FeOOH),
- Rutile and anatase (TiO₂),
- Hydrogarnet,
- Sodium aluminosilicate hydrate,
- Calcite (CaCO₃),
- Gypsum (CaSO₄·2H₂O),
- Quartz (SiO₂),
- Mica (K₃Al₂Si₃O₁₀(OH)₂),
- Bauxite (Al₂O₃·H₂O)

**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**

**REVIEW:** Silveira et al. Sustainability 2021, 13, 12741, https://doi.org/10.3390/su1322127
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>Component</th>
<th>PG IAEA</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>39.5</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Acidic**

- High content in phosphoric, sulfuric, hydrofluosilicic acids

**Trace metal(loid)s**

- High concentrations (e.g. As)

**Radionuclides**

- Ra-226 and Po-210

**Nitrates**

- High concentrations

**REE**

- 70-85 % of REE originally present in phosphate rocks

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**Gypsum:** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

**Depending upon rock source and efficiency 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)

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

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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 $\leftrightarrow$ gypsum - activity concentration index

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

<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>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Egypt</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Estonia</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Iran</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Italy</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Pakistan</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Syria</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Turkey</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Total</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

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

![Graph showing the number of papers in phosphogypsum research over the years from 1980 to 2020. The number of papers increases significantly from 2010 onwards.]

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

![Bar chart showing publications in phosphogypsum research]

- **Management**: 500 publications
- **Agriculture**: 400 publications
- **Pollution treatment**: 200 publications
- **Building**: 300 publications
- **Mineral Resources**: 100 publications
- **CO₂ sequestration**: 50 publications

**Source:** 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?
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

- Bauxite residue
- Fly ash
- Slags
- Phosphogypsum
- Siliciumdioxide waste

**Aluminosilicate polymer**

From NORM related industries

mainly alkali-hydroxide/silicate

**Circular economy**

REVIEW: Hertel & Pontikes, Journal of Cleaner Production 258 (2020) 120610
Nodehi & Taghvaee, Circular Economy and Sustainability, 2 (2022) 165–196
Alkali Activated Materials (AAMs): enabling multiple cycles of use

Formulate Geopolymer based on waste materials for construction.

Waste bricks

Alkaline activation

Geopolymer bricks

Strength (MPa)

Formulations

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 ➔ 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>Australia</th>
<th>Brazil</th>
<th>China</th>
<th>Greece</th>
<th>Hungary</th>
<th>Italy</th>
<th>Jamaica</th>
<th>Turkey</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.92</td>
<td>2.23</td>
<td>3.92</td>
<td>2.84</td>
<td>2.90</td>
<td>3.92</td>
<td>3.43</td>
<td>3.43</td>
</tr>
</tbody>
</table>

**AAM**

- AAM containing red mud as partial replacement of cement and aggregates
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

REVIEW: Rashad, Journal of Cleaner Production 166 (2017) 732-743
REVIEW: Chernysh et al., Appl. Sci. 11 (2021) 1575
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

Activating solution + Alkali activated materials (AAMs)

T, t Curing

Phosphogypsum → Ettringite binders

NaOH, KOH, Na$_2$SiO$_3$/NaOH

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 (heterogenity)?
- 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

REVIEW: Rashad, Journal of Cleaner Production, 166 (2017) 732-743
REVIEW: Chernysh et al., Appl. Sci., 11 (2021) 1575
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Extraction from bauxite residue

- **Fe₂O₃ (35-60 wt%):** use in steel metallurgy
  - Problem: large sodium content prohibits the use of blast furnaces (evaporation Na₂O at high T → attacks ceramic refractory bricks)
  - Options to not introduce bauxite residue in existing process but design a dedicated process (e.g. Electric arc furnace carbothermic smelting: convert bauxite residue 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 Al₂O₃
  - Sintering processes designed to achieve higher aluminium recovery
  - Titanium recovery via leaching with H₂SO₄

- **Rare earth elements 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 HNO₃, Dilute H₂SO₄, 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 $\text{H}_2\text{SO}_4$ (ambient temperature, s/l ratio 1:10)
  - Leaching efficiency increased via gravity flow of $\text{H}_2\text{SO}_4$ through PG column
  - Enhanced $\text{H}_2\text{SO}_4$ leaching via **mechanical activation** of PG (example: ball milling, stirring)
  - Higher leaching efficiencies with $\text{HNO}_3$ (or mixtures of $\text{HNO}_3$ and $\text{Ca(NO}_3)_2$)

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

- **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 → different solutions

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