# 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*

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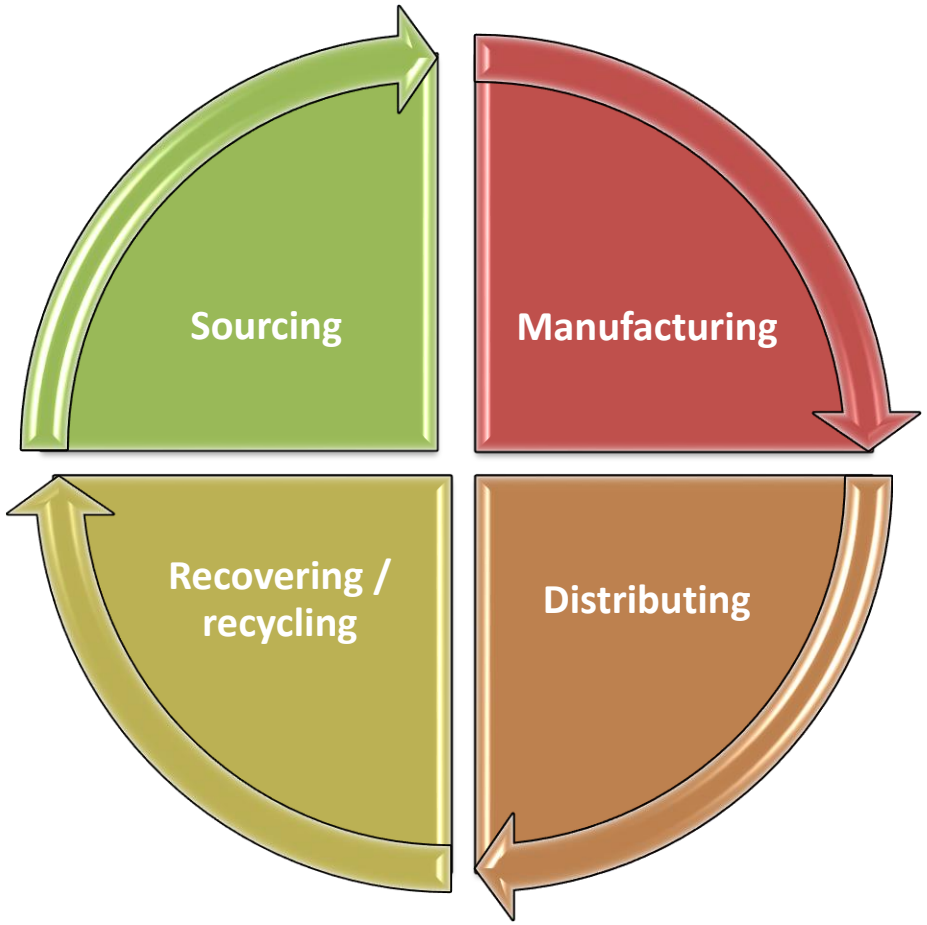
RadoNorm
Managing risks from radon and NORM

NuTeC
Nucleair Technologisch Centrum

This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 900009.

# 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



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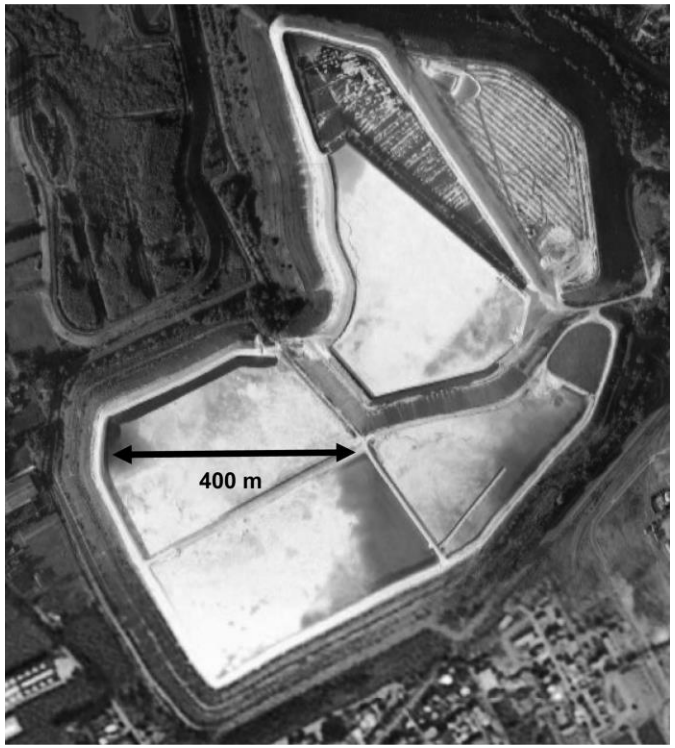
# Recovering / recycling of by-products from NORM related industries

- 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 %






Wang et al. Separation and Purification Technology, 108 (2013) 96–102

IAEA (2013), Safety report series 78

Paridaens and Vanmarcke, Health Physics, 95, 4 (2008), 413-424

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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



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# Bauxite residue - chemical / mineralogical properties

| Composition (% wt.) | Krivenko et al., 2017. [81] (Ukraine) | Do et al., 2019. [84] (South Korea) | Hairi et al., 2015. [79] (Canada) | Hu et al., 2019. [80] (China) | Cardenia et al., 2018. [85] (Greece) | Koshy et al., 2019. [86] (China) | Lemougna et al., 2017. [53] (China) | Pérez-Villarejo et al., 2012. [87] (Spain) | Borra et al., 2015. [88] (Greece) | Agrawal et al., 2021 [89] (India) |
|---|---|---|---|---|---|---|---|---|---|---|
| $Fe_2O_3$ | 48.6 | 22.21 | 38.92 | 33.88 | 42.34 | 41.0 | 33.99 | 39.23 | 44.60 | 36.8 |
| $Al_2O_3$ | 12.9 | 19.87 | 22.12 | 17.89 | 16.25 | 21.8 | 18.47 | 19.80 | 23.60 | 22.07 |
| $SiO_2$ | 4.8 | 15.12 | 10.52 | 19.43 | 6.97 | 11.0 | 9.39 | 8.77 | 10.20 | 11.81 |
| $Na_2O$ | - | 14.92 | 6.82 | 12.18 | 3.83 | 8.0 | 5.11 | 5.02 | 2.50 | 10.21 |
| CaO | 10.1 | 7.1 | 1.36 | 2.66 | 11.64 | 1.6 | 14.19 | 4.54 | 11.20 | 1.62 |
| $TiO_2$ | 5.3 | 5.24 | 7.61 | 0.72 | 4.27 | 7.0 | 5.42 | 10.09 | 5.70 | 15.6 |
| $SO_3$ | - | 0.72 | 0.59 | - | - | 0.5 | - | - | - | - |
| MgO | - | 0.37 | 0.10 | 0.10 | - | 0.1 | 0.32 | 0.07 | - | - |
| $K_2O$ | - | 0.11 | 0.55 | 0.37 | - | 0.1 | 0.10 | 0.14 | - | - |
| $Cr_2O_3$ | - | - | - | - | - | - | - | - | - | - |
| $ZrO_2$ | - | - | - | - | - | - | - | - | - | - |
| $SO_2$ | - | - | - | - | - | - | 0.33 | - | - | - |
| MnO | - | - | 0.02 | - | - | - | 0.09 | - | - | - |
| $P_2O_5$ | - | - | 0.21 | - | - | 0.2 | - | - | - | - |
| Others | 2.5 | - | - | - | 2.04 | - | - | - | - | - |
| Loss of ignition | - | 13.68 | 10.51 | 12.84 | 36.912.66 | 8.7 | - | - | - | - |

Several minerals' forms

25–27 wt% hematite
25–28 wt% goethite
4.5–6.5 wt% rutile and anatase ($TiO_2$)
15–17 wt% hydrogarnets
6–7 wt% sodium aluminosilicate hydrate
2.5–3.0 wt% calcite

hematite ($Fe_2O_3$),
goethite (-FeOOH),
$TiO_2$ in the anatase polymorph,
gibbsite (-$Al(OH)_3$),
sodium aluminosilicate hydrate
boehmite (-AlOOH),
quartz (SiO2),

**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

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

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

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# 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)



REVIEW: Silveira et al., Sustainability, 13 (2021) 12741
REVIEW: Lu et al., Bulletin of Environmental Contamination and Toxicology (2022), published online

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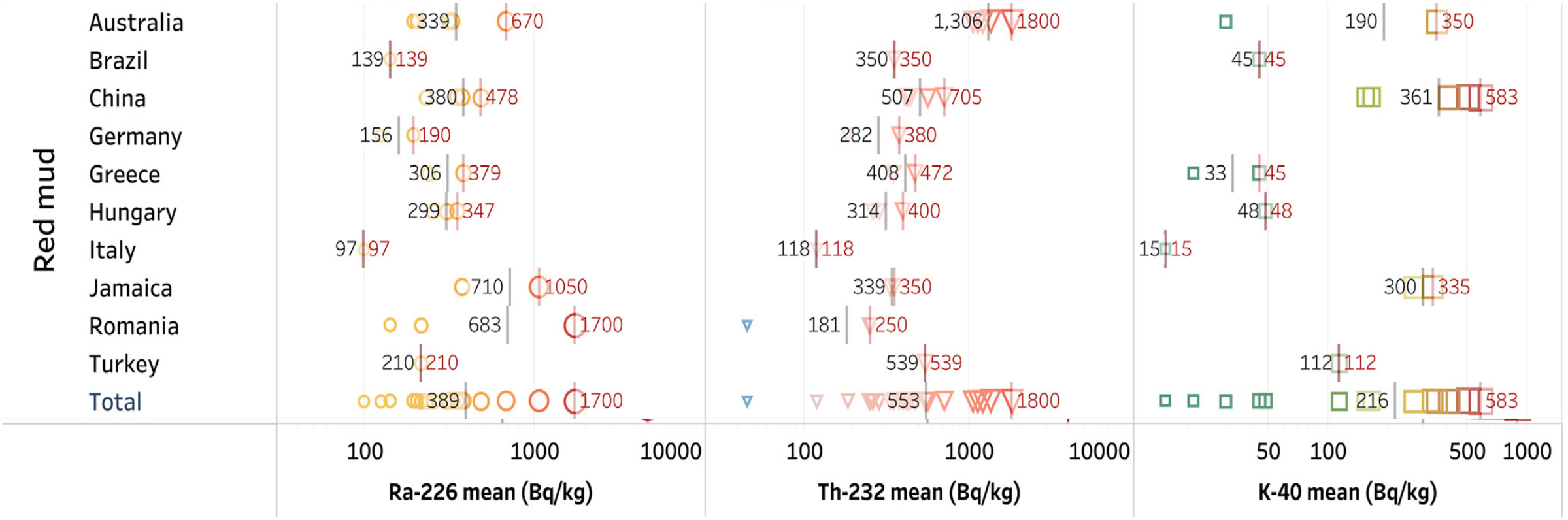
# Bauxite residue - activity concentration






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

# Phosphogypsum (PG) - chemical / mineralogical properties

| (wt %) | | PG IAEA | |
|---|---|---|---|
| CaO | | 39.5 | |
| $SO_3$ | | 56.5 | |
| $SiO_2$ | 0,5 | 1.0 | 18 |
| $F^-$ | 0,1 | 1.2 | 1.8 |
| $P_2O_5$ | - | 1.5 | |
| $Al_2O_3$ | | 0.2 | |
| 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 originaly present in phosphate rocks | | |

Gypsum: **$CaSO_4 \cdot 2H_2O$**

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)

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



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

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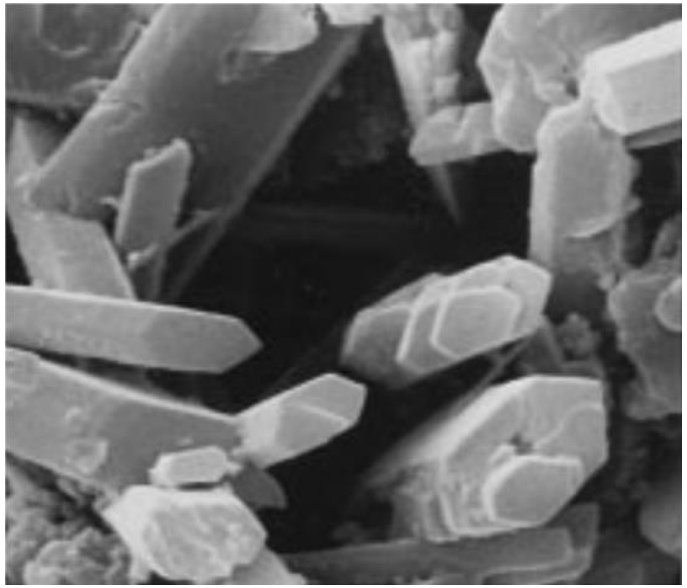
# Phosphogypsum - physico-chemical properties

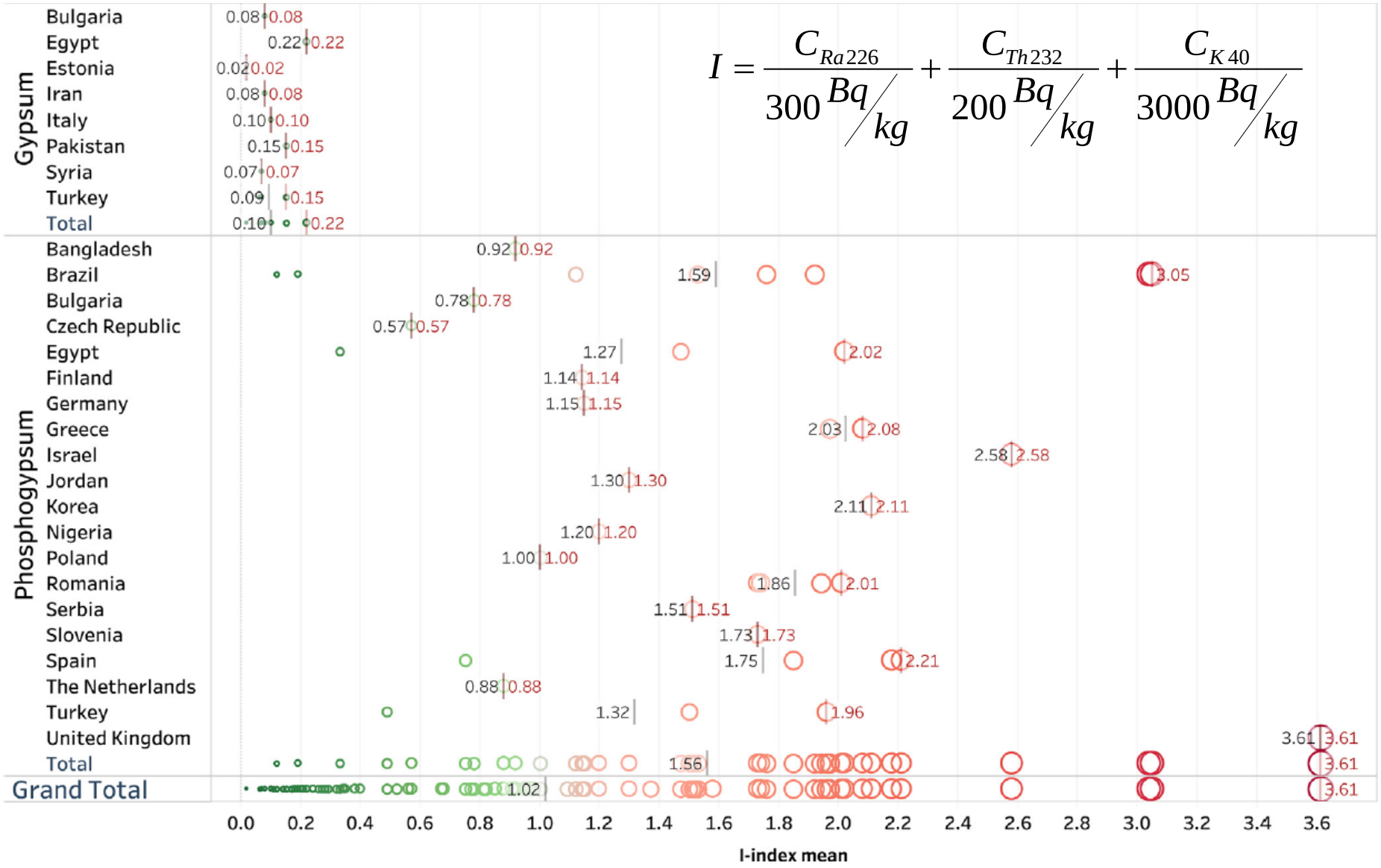


- **Silt-sized gypsum crystals**
  - **Morphology** depends on:
    - Source of the phosphate rock,
    - Reaction conditions in the acid attack
- **Large total specific surface area ➔ high reactivity** (dissolves more rapidly than natural gypsum)
- **Density, permeability and strength** influenced by:
  - 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 ↓



Schroeyers et al., book 'Naturally Occuring Radioactive materials in construction', Woodhead Publishing (2017)

# Phosphogypsum <-> gypsum - activity concentration index




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



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

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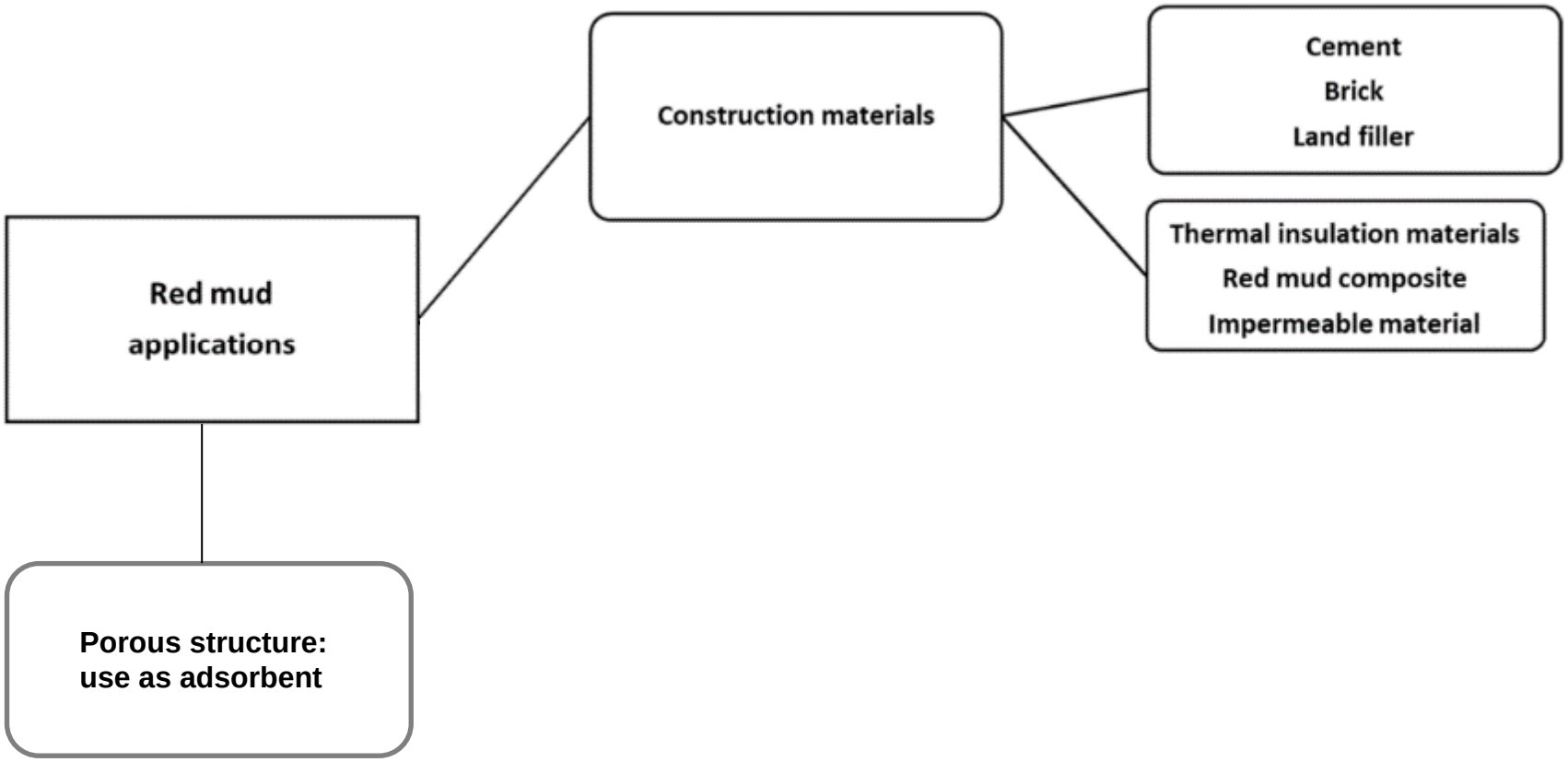
# Bauxite residue - important research/application areas






REVIEW: Samal, Materials, 14 (2021), 2211

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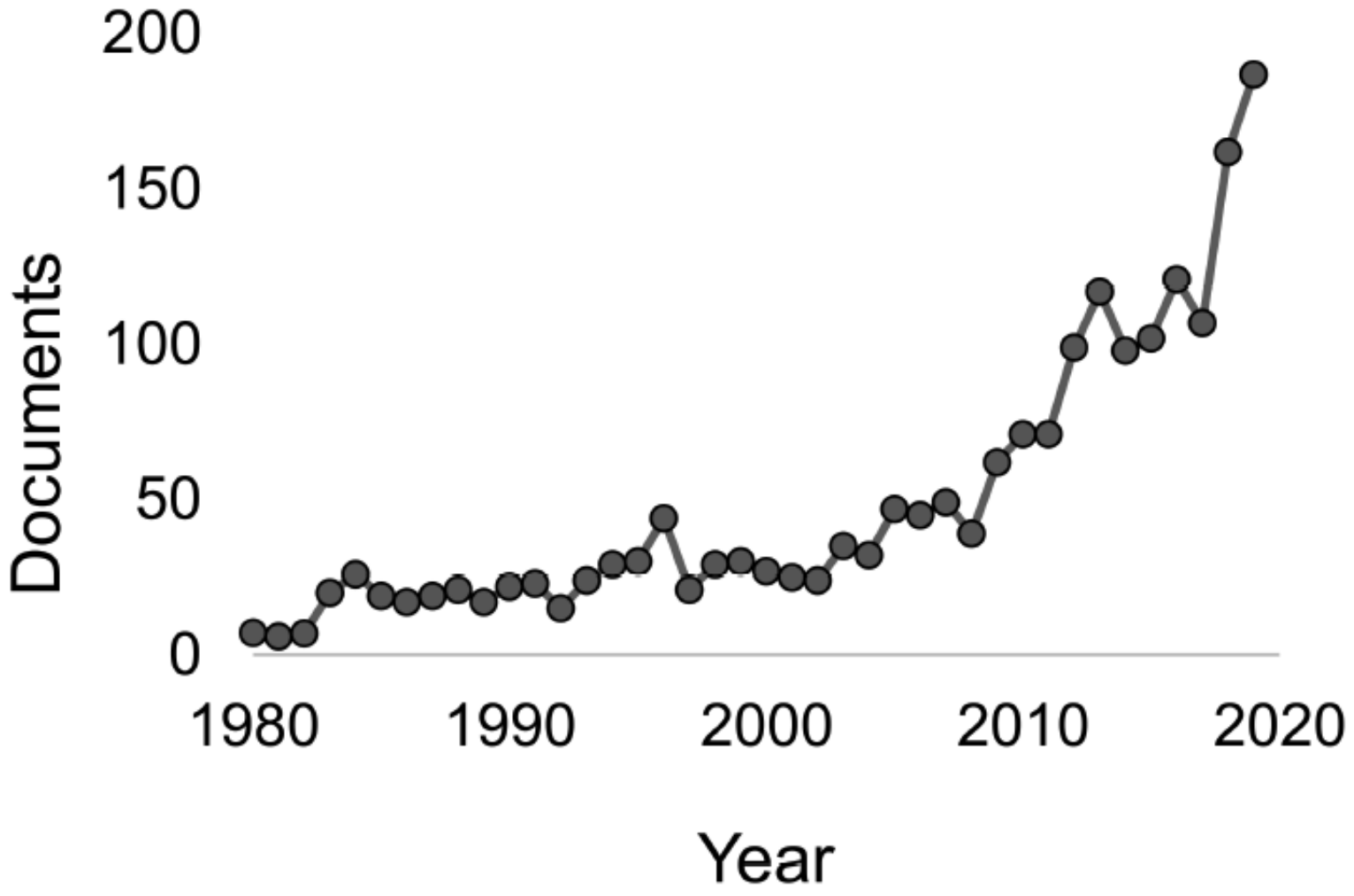
# Number of papers in area **phosphogypsum** research




REVIEW: Chernysh et al.,, Appl. Sci., 11 (2021), 1575



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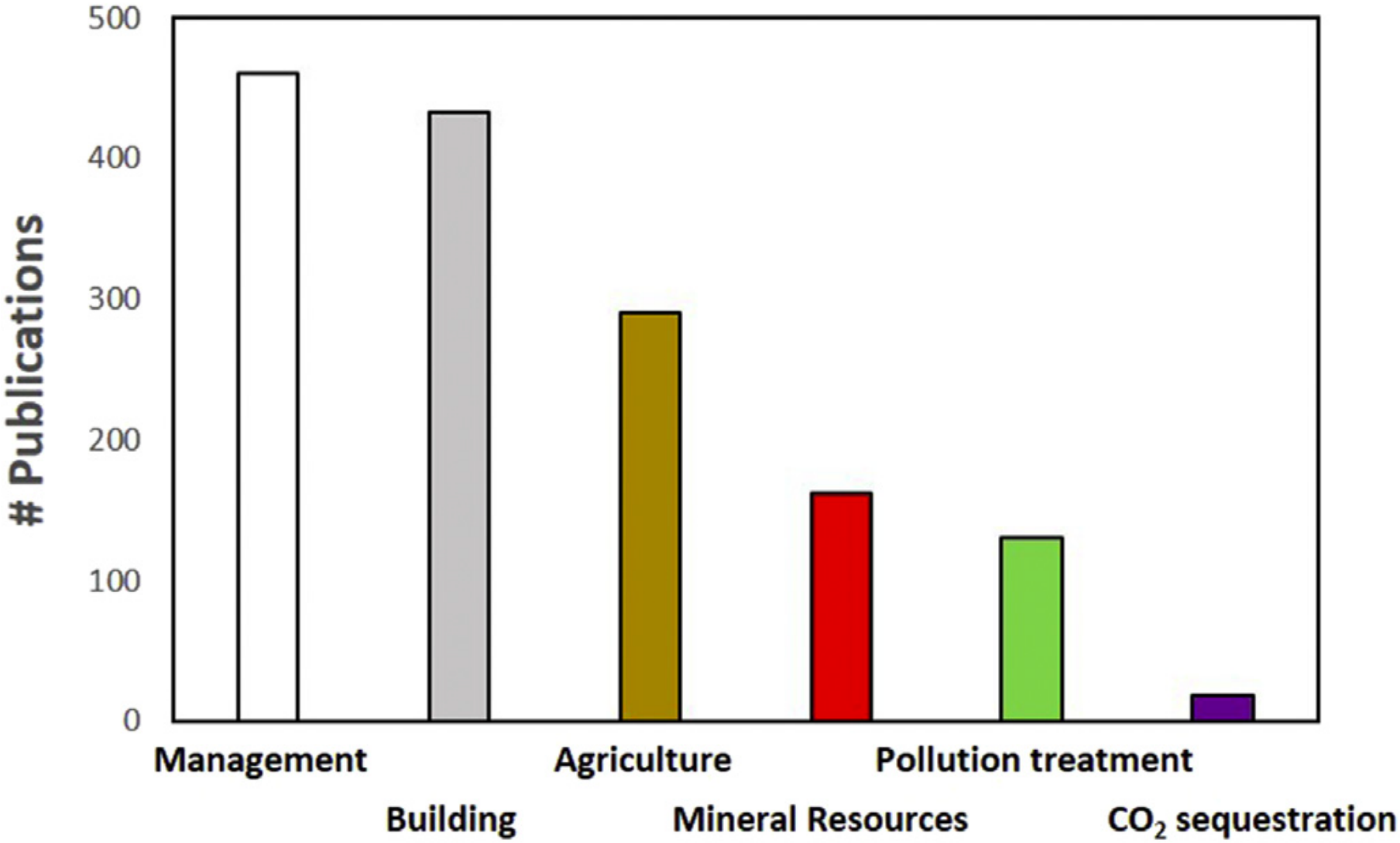
# Main subjects of interest in **phosphogypsum** research (1975-2017)




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



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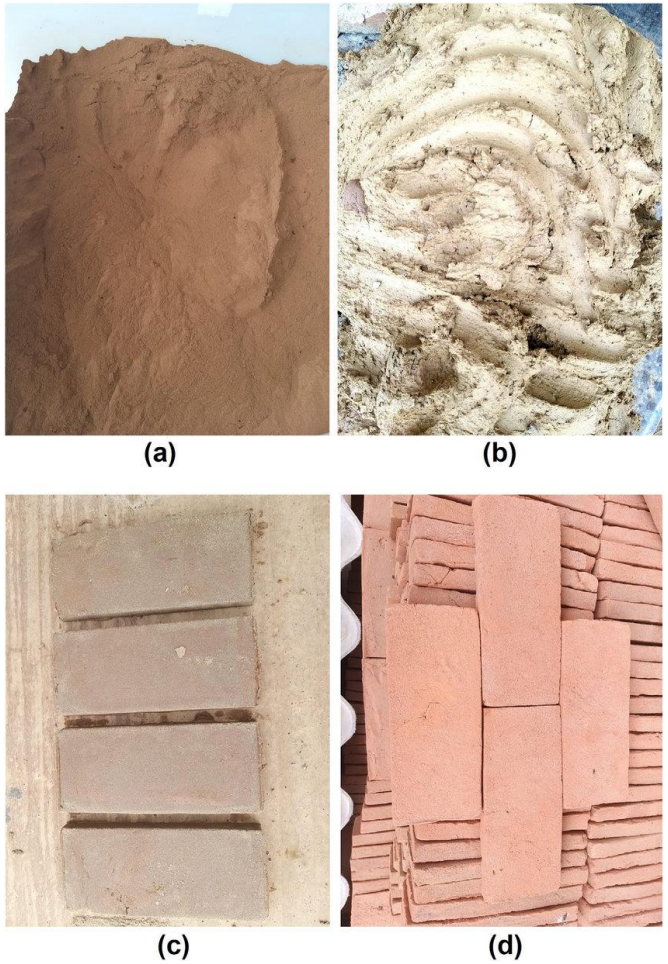
# **Bauxite residue** as construction material




- Technically succesfull 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 sustituted 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

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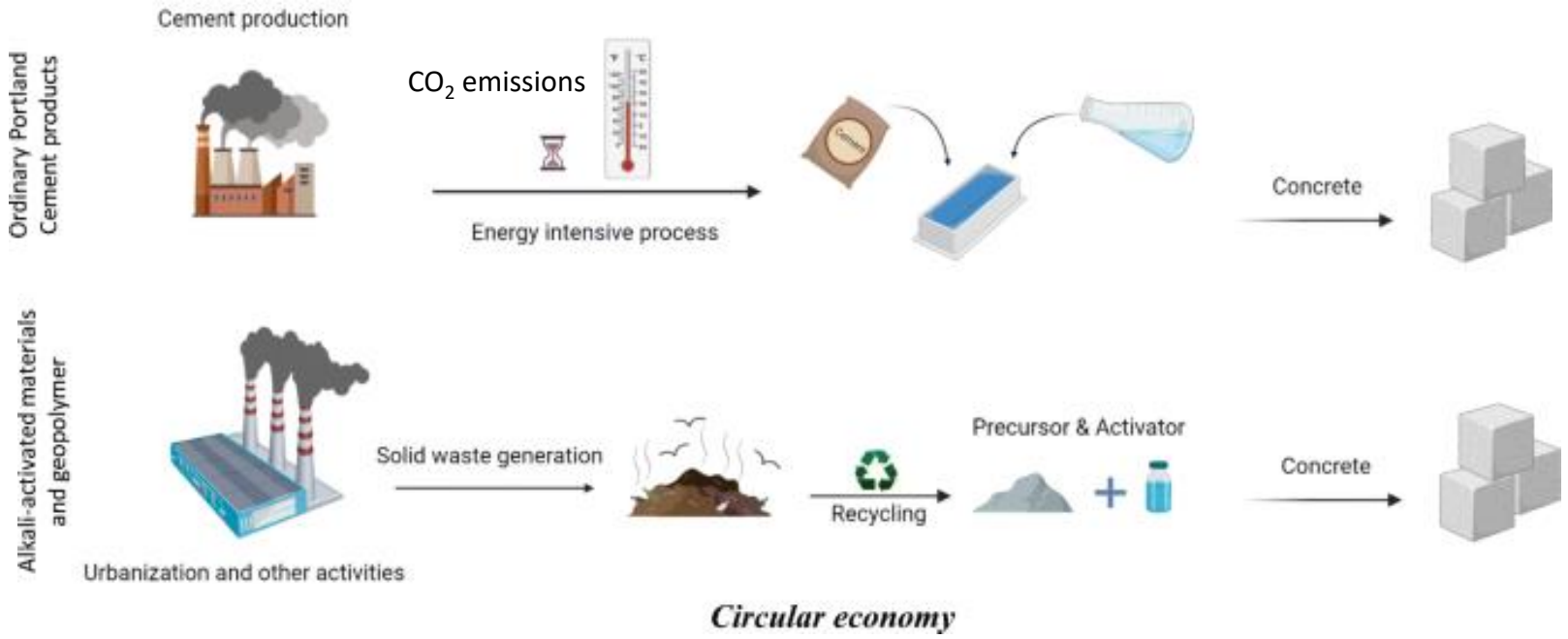
# Use of by-product in Alkali Activated Materials (AAMs)




## Alkali Activated Materials:

Source material = **$SiO_2$ and $Al_2O_3$**

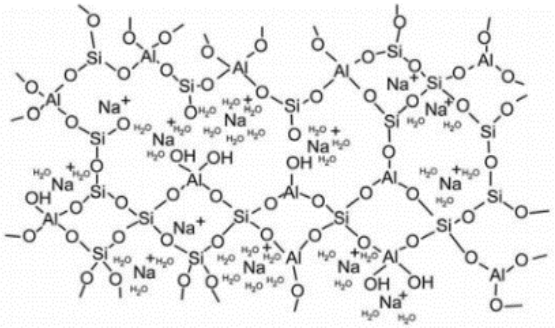
***Bauxite residue***
***Fly ash***
***Slags***
***Phosphogypsum***
*Siliciumdioxide waste*

From NORM related industries

Activator = Alkaline solution

mainly alkali-hydroxide/silicate

Aluminosilicate polymer





REVIEW: Hertel & Pontikes, Journal of Cleaner Production 258 (2020) 120610
Nodehi & Taghvaee, Circular Economy and Sustainability, 2 (2022) 165–196

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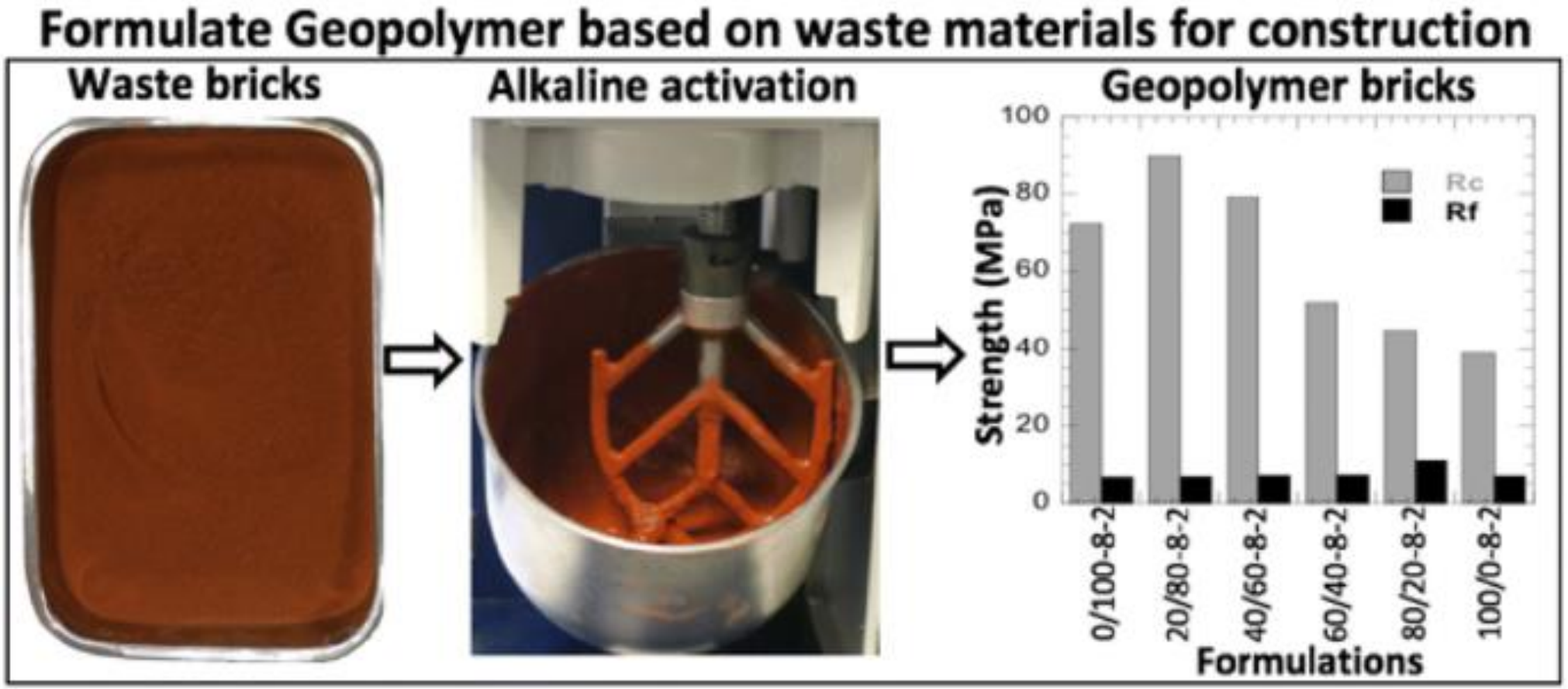
# Alkali Activated Materials (AAMs): enabling **multiple cycles** of use






Youssef *et al., SN Appl. Sci.,* **1** (2019) 1252

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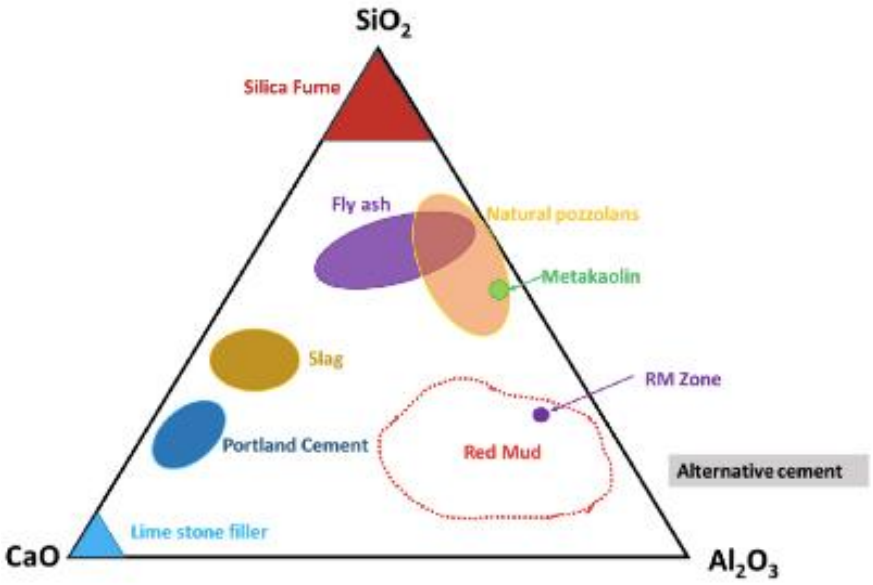
# **Bauxite residue** as precursor for alkali activated materials




## 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?


REVIEW: Kumar et al. Construction and Building Materials 302 (2021) 124170

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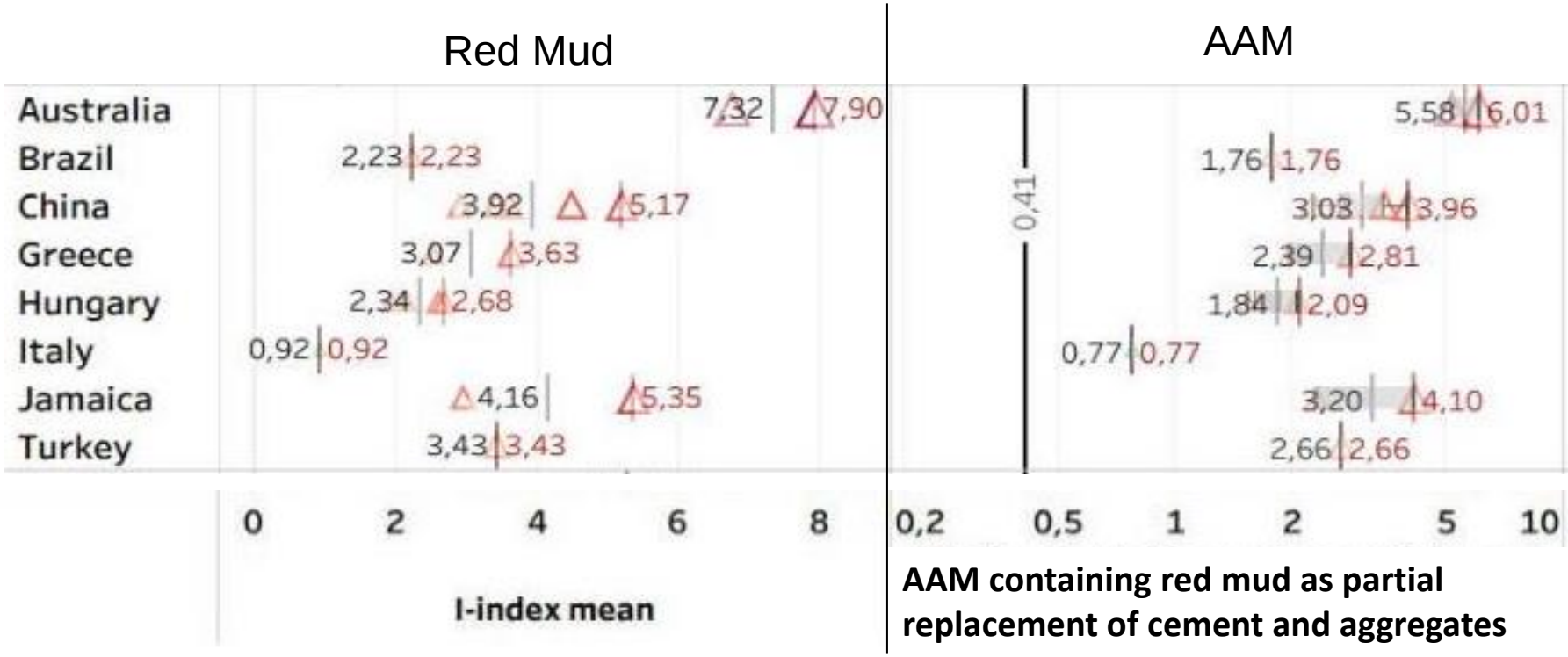
# I-index AAM containing **bauxite residue**

| kg/m³ | Cement | Red mud | Aggregates | Water |
|---|---|---|---|---|
| Reference concrete | 400 | | 1850 | 150 |
| Alkali activated concrete containing red mud | | 1800 | 450 | 150 |




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



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



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

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# 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



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# **Phosphogypsum** as construction material

- New research options

Fly ash

Blast furnace slag

**Phosphogypsum**

**Activating solution**

***NaOH***
***KOH***
**$Na_2SiO_3$/NaOH**

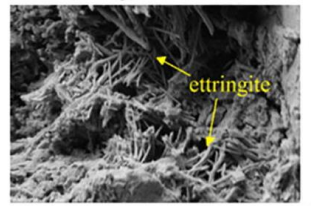
T, t

Curing

**Alkali activated materials (AAMs)**

**Ettringite binders**

$H_2O$






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

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# **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 vallue**

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**

- **$Fe_2O_3$ (35-60 wt%) :** use in steel metallurgy
  - Problem: **large sodium content prohibits the use of blast furnaces**
    (evaporation $Na_2O$ 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 $Al_2O_3$
  - **Sintering** processes designed to achieve higher **aluminium recovery**
  - **Titanium** recovery via leaching with $H_2SO_4$

- **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 $HNO_3$, Dilute $H_2SO_4$, HCl)
  - Majority elements (Fe) cannot be leached under same experimental conditions


REVIEW: Binnemans et al., Journal of Cleaner Production, 99 (2015) 17-38

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# Extraction of REE from **phosphogypsum**

- Leaching by **aqueous solutions**
  - **50 % REE** recovered with 0.1-0.5 M **$H_2SO_4$** (ambient temperature, s/l ratio 1:10)
  - Leaching efficiency increased via gravity flow of $H_2SO_4$ through **PG column**
  - Enhanced $H_2SO_4$ leaching via **mechanical activation** of PG (exemple ball milling, stirring)
  - Higher leaching efficiencies with **$HNO_3$** (or mixtures of $HNO_3$ and $Ca(NO_3)_2$)
- 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)


REVIEW: Binnemans et al., Journal of Cleaner Production, 99 (2015) 17-38

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# Extraction of REE from **phosphogypsum**

- purification of phosphogypsum
  - Select suitable solvent for leaching (previously used: dilute $H_2SO_4$ 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


REVIEW: Binnemans et al., Journal of Cleaner Production, 99 (2015) 17-38

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# Studying the **societal challenges** related to the use of NORM in building materials

RadoNorm
Managing risks from radon and NORM

Work Package 6

- **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



This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 900009.

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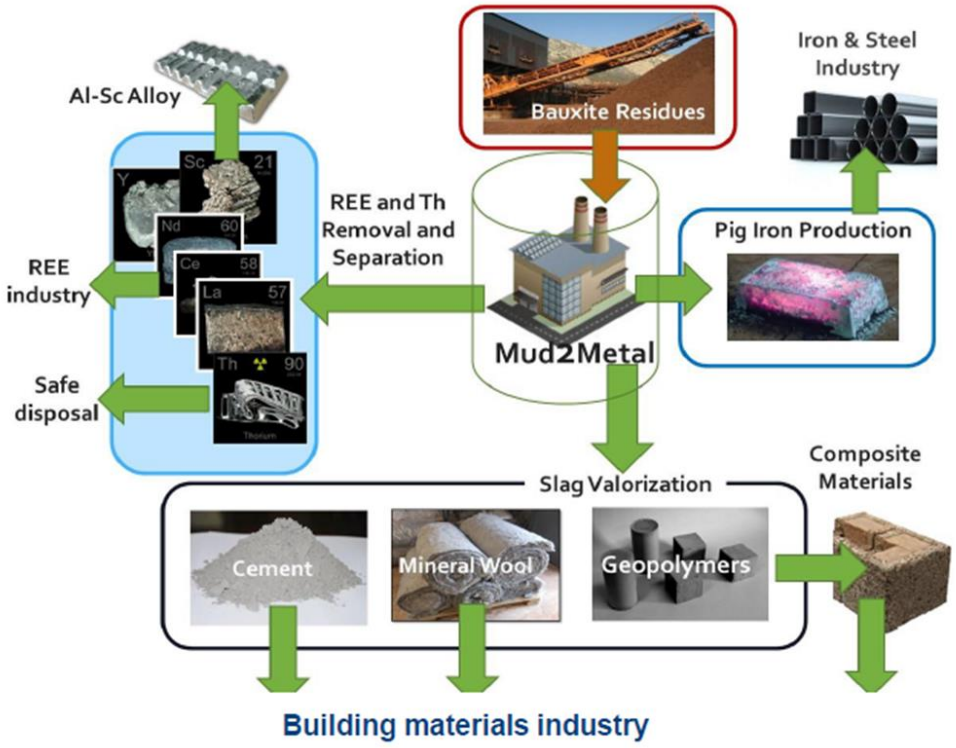
# Perspectives for embedding NORM in the circular economy




- **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 save disposal

- **Embrace the local differences**:
  different materials → different solutions

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



Pontikes, Mineral Recycling forum, 14-15 March (2016)

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