BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE
Leuven 5-7 October 2015
STUDY OF THE REUSABILITY OF Bauxit Residue
in Clay-Based Building Materials
(from a radiological point of view: gamma dose, exhalation, leachability)

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Red mud (Bauxite residue)

Bauxite refining in Hungary (1943)
- Huge amount of BR (~50 Mt) deposited in reservoirs
  Environment impact → Strong reason for reusing, recycling

Ecological disaster
- 2010, Ajka, Hungary: 800,000 m³ flood

The possibility of reuse has great importance in Hungary and in PE-RRI
- Concrete bricks additives
- Disadvantage: poor static and mechanical properties, leachable amount is high, radium emanation is not blocked

Pathway of by-product reuse

By-product

Characterization

Test products

Survey

Reuse of by-products

Pottery

Indoor inbuilt

Outdoor inbuilt

Compressed brick
Radionuclide content in NORMs

Natural radioisotope content
Th-232, K-40, U-238, (Ra-226)

Health risk
Rn exhalation
Rn-222 and Progenies
Internal exposure

Gamma-dose
Th-232, K-40, Ra-226
and their progenies
External exposure

Emanation
Internal structure

Leaching
Toxic & radioactive compounds
Internal exposure
The European COST network ‘NORM4BUILDING’

- Stimulate the **reuse of NORM** residues in **new tailor-made sustainable construction materials**

- Considering the **exposure to external gamma radiation** and the resulting **indoor air quality**.

8-9/10/2015 Workshop + round table (Leuven)
@Campusbibliotheek Arenberg

More information at:
[www.norm4building.org](http://www.norm4building.org)
Screening

**Gamma-dose** (Ra-226, Th-232, K-40)

- I-index

\[ I = \frac{C_{Ra-226}}{300} + \frac{C_{Th-232}}{200} + \frac{C_{K-40}}{3000} \]

Radon exhalation is a problematic issue. Radon exhalation greatly depends on the structure. The investigation of possibilities to reduce exhalation capacity are very important.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dose criterion (mSv y^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used in bulk amounts (concrete, brick, etc.)</td>
<td>(I \leq 1.0)</td>
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<tr>
<td>Superficial or with restricted use (tile, etc.)</td>
<td>(I \leq 6.0)</td>
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Radon „anomalies” in case of inbuilt NORM origin bottom ash (coal)

Anomalies in dwellings where the Ra-226 were high the radon concentration was relatively low and opposite

Two bottom ash samples where the $^{226}$Ra conc. was similar

“A”: $2526 \pm 86$ Bq kg$^{-1}$, “B”: $2568 \pm 92$ Bq kg$^{-1}$

Big difference in emanation and exhalation capacity

Different firing temperature was used in coal power plants

Great influence of temperature on internal structure
Great possibility to reduce exhalation capacity
Measurements and methods
Sampling

- 27 clay samples were taken
- 16 BM factories from every region of Hungary
- BR reservoir I-X (Ajka)
- 68 samples from 1-2 m depths

Gamma spectrometry

- Drying, milling, storage in Marinelli vessels
- Instrument: ORTEC GMX40-76 HPGe detector
- Data collection: Tennelec PCA-MR 8196 MCA
- Measurement time: 80 000s

Gamma spectrometry

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Rn/Tn exhalation and emanation

- Accumulation chamber technique
- Short accumulation period
  - 12-48 hours for Rn
  - Rn exhalation and emanation can be measured simultaneously
- Any kind of radon monitor can be used
  - Sensitivity depends on radon monitor
- Sample → grain, spherical, powders, etc.
  - thickness < 4 - 5 mm
Leaching studies

MSZ-21470-50: Hungarian standard for the measurement of toxic elements, heavy metals and chrome(IV) in soil

The Tessier sequential extraction is a 5 step process

- **Water soluble fraction**: 5.0 g sample, 50 cm³ distilled water, 1 min shaking, 24 h waiting, 2 h shaking
- **Plant available fraction**: Lakanen-Erviö solution EDTA-ammonium-hydroxide-acetic acid puffer solution, 5.0 g sample, 50 cm³ diluted solution, 1 h shaking
- **Total digestion by HNO₃+H₂O₂**: 0.5 g sample, 6 ml 65% HNO₃, 2 ml 30% H₂O₂, microwave, 10 min to 200°C, 20 min at 200°C
- **Total digestion by HNO₃+HCl**: 0.5 g sample, 9 ml cc. HCl, 3 ml cc. HNO₃, microwave, 10 min to 200°C, 15 min at 200°C

I. **Exchangeable fraction**
   - 40 cm³ 1M MgCl₂ adjusted to pH 7, 1 h constant agitation

II. **Carbonate bound fraction**
   - 40 cm³ 1M NaOAc, adjusted to pH 5 with acetic acid, 5 h constant agitation

III. **Fe- and Mn-oxide bound fraction**
   - 80 cm³ 0.04M NH₄OH+HCl in 25% acetic acid, 93±3°C 5 h with occasional agitation

IV. **Oxidable fraction**
   - 15 cm³ 0.02M HNO₃, and 25 cm³ 30% H₂O₂ adjusted to pH 2 with HNO₃, 85±2°C 2 h
   - 15 cm³ 30% H₂O₂, adjusted to pH 2 with HNO₃, 85±2°C 2 h, wait for it to cool
   - 15 cm³ 3.2M NH₄OAc in 20% HNO₃, adjust to 100 ml with Millipore water 30 minute agitation

V. **Residue**
   - Total microwave digestion 0.5 g sample, 3 cm³ cc. HCl, 1 cm³ cc. HNO₃, microwave, 10 min to 200°C, 15 min at 200°C
Results
### Radionuclide content of clays & BR, Mixing ratio

#### Clays

<table>
<thead>
<tr>
<th>Activity Concentration [Bq/kg]</th>
<th>I-index</th>
</tr>
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<tr>
<td>Ra-226 ± Th-232 ± K-40 ±</td>
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<table>
<thead>
<tr>
<th>AVG</th>
<th>Min</th>
<th>Max</th>
</tr>
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<tbody>
<tr>
<td>37</td>
<td>16</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>40</td>
<td>31</td>
<td>49</td>
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<tr>
<td>9</td>
<td>7</td>
<td>11</td>
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<tr>
<td>803</td>
<td>534</td>
<td>1127</td>
</tr>
<tr>
<td>37</td>
<td>16</td>
<td>105</td>
</tr>
<tr>
<td>0.59</td>
<td>0.40</td>
<td>0.81</td>
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</table>

#### BR

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<tr>
<th>AVG</th>
<th>Min</th>
<th>Max</th>
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<tr>
<td>289</td>
<td>152</td>
<td>435</td>
</tr>
<tr>
<td>31</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>255</td>
<td>129</td>
<td>314</td>
</tr>
<tr>
<td>25</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>110</td>
<td>17</td>
<td>360</td>
</tr>
<tr>
<td>12</td>
<td>29</td>
<td>40</td>
</tr>
<tr>
<td>2.28</td>
<td>1.25</td>
<td>3.04</td>
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</table>

#### Maximum BR content [%]

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>IV</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
</tr>
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<tbody>
<tr>
<td>Min</td>
<td>13.6</td>
<td>11.5</td>
<td>11.9</td>
<td>12.3</td>
<td>12.7</td>
<td>11.7</td>
<td>11.6</td>
</tr>
<tr>
<td>Max</td>
<td>32.7</td>
<td>28.6</td>
<td>29.3</td>
<td>30.2</td>
<td>31.0</td>
<td>29.0</td>
<td>28.7</td>
</tr>
<tr>
<td>AVG</td>
<td>24.7</td>
<td>21.4</td>
<td>21.9</td>
<td>22.7</td>
<td>23.3</td>
<td>21.7</td>
<td>21.5</td>
</tr>
</tbody>
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Effect of heat treatment on emanation and exhalation

- Heat-treatment reduces emanation and exhalation rate
- Brick production → 800-1000°C
- Emanation and exhalation under 5-10% of initial above 700-800°C
- Effective mitigation technique
- Allows e.g. NORM additives in building material production
- Thoron exhalation characteristic was investigated in case of mixed samples
- Same characteristic was found

References:
Internal structure vs. Emanation in case of BR

- Despite of total porosity increased the emanation decreases
- Strong correlation
  - between emanation factor and nanopores (1.7-300 nm)
  - That pore size range responsible for emanation!
- The nano structure is cardinal
- Porous building materials can be produced with low nanoporosity!!!

Preliminary results of leaching survey

The MSZ-21470-50 Hungarian standard

- The results indicate that while the directly water soluble fraction is relatively small, with the changing of pH or red-ox potential a considerable amount of the red mud’s uranium content becomes available for leaching.

- 26% of the uranium content in BR is available for plants, so it can get into the food-chain.

Tessier-method

- The majority of the leachable uranium is bound to the iron- and manganese-oxide bound fraction.
Thank You

Merci

Gracias

Danke

KamSahHamida

Saham

Mulsimmes

CámOn

Spacibo

TananaVaga

Blessings

Peace

Thank you

Gracies

Faaamindit

Dakujem

TerimaKasih

Rahmat

NajisTuke

Hvala

Arigato

TeiKi

Merci

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