REVALORISATION OF RESIDUES IN THE SCOPE OF THE CIRCULAR ECONOMY

Case study from the Titanium Dioxide Industry

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• **Reuse** of residues generated in industrial processes — solution to simultaneously address environmental issues and development of new products that meet performance and durability expected requirements.

• In 2019, Brazil produced 145 million tons of titanium concentrate (equivalent to 90 million tons of TiO$_2$), corresponding to 1.2% of the world production.

• Brazil is the largest producer of TiO$_2$ in Latin America.
Common titanium-containing minerals are ilmenite, anatase, rutile and titaniferous slag. The proportion of titanium concentrates from ilmenite and rutile in Brazil is around 96% and 4%, respectively.

In Brazil, the main reserves of ilmenite are located in Mataracá.

One great challenge for Brazil is the viability of using anatase resources in Minas Gerais and Goiás, allowing Brazil to reach the world's largest reserves.

Tronox Pigmentos do Brasil is responsible for more than 90% of the national production of processed titanium.
Production of TiO$_2$ in Brazil

The production of titanium dioxide through the sulfate route produces approximately 60,000 tons of TiO$_2$ annually, generating 30,000 tons of waste, known as UOW (unreacted ore waste), which is disposed off in industrial landfills.

Mean concentration of $^{238}$U, $^{226}$Ra, $^{210}$Pb, $^{232}$Th, $^{228}$Ra and $^{40}$K (Bq/kg) in ilmenite and UOW residue

<table>
<thead>
<tr>
<th>Sample</th>
<th>U-238</th>
<th>Ra-226</th>
<th>Pb-210</th>
<th>Th-232</th>
<th>Ra-228</th>
<th>K-40</th>
</tr>
</thead>
<tbody>
<tr>
<td>ilmenite</td>
<td>207</td>
<td>275</td>
<td>267</td>
<td>1016</td>
<td>796</td>
<td>&lt; 7</td>
</tr>
<tr>
<td>UOW</td>
<td>538</td>
<td>1103</td>
<td>960</td>
<td>400</td>
<td>2906</td>
<td>119</td>
</tr>
</tbody>
</table>

Diagram of the TiO$_2$ production process
The standard CNEN-NN-4.01 – “Requirements of Safety and Radiation Protection for NORM mining and milling facilities” establishes a regulatory approach based on total activity concentration.
According to this standard, the TiO$_2$ production is classified as category I due to the presence of 50,000 Bq/g in the filters of the Liquor production.

<table>
<thead>
<tr>
<th>Category</th>
<th>Total activity concentration</th>
<th>Documents required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category III</td>
<td>&lt; 100 Bq/g</td>
<td>Basic information</td>
</tr>
<tr>
<td>Category II</td>
<td>≤ 500 Bq/g, ≥100 Bq/g</td>
<td>Basic information, Occupational Radiological Protection Plan; Environmental Radiological Monitoring Plan; Radioactive Waste Management Plan; and Preliminary Radiological Decommissioning Plan</td>
</tr>
<tr>
<td>Category I</td>
<td>&gt; 500 Bq/g</td>
<td>Basic information, Radiation Safety Analysis Report (SAR)</td>
</tr>
</tbody>
</table>
The policy of stacking, regarding the indefinite containment of waste as the best option, is now under pressure on reasons of cost, safety, and environmental impact and because it erroneously defines a reusable material as a waste, for which there are increasingly stringent controls on disposal.
There is an overall trend worldwide towards greater recycling or re-use of NORM residues and their use as co-products. This is being driven by a growing recognition that the amounts of NORM disposed off as waste need to be minimized and by sustainability considerations such as concern for the depletion of non-renewable resources and the environmental protection legislation increasingly restrictive...
To minimize the environmental impact of the amount of UOW deposited, it is necessary to provide alternatives for the safe re-use, transforming this residue in a co-product.

Several successful attempts in applying the sustainable approach to the TiO$_2$ industry showed that UOW residue can be recycled into useful co-products.

UOW has physicochemical characteristics favourable to its use as building material and cement components, since it can degrade organic compounds and NOx gases adhered to its surface, reducing atmospheric pollution, providing greater durability to the final product due to its self-cleaning capacity.

A consistent regulatory approach to NORM waste management is needed to comply with this new approach.
The Standard CNEN NN 8.01 establishes general criteria and basic requirements for safety and radiological protection related to the management of radioactive waste with low and medium levels of radiation.

However, NORM tailings containing natural radionuclides in the form of mineral raw materials, natural or industrialized, with radionuclides of the uranium and thorium series in quantities exceeding 1 ton are excluded from this Standard.
CNEN's Regulatory Position 3.01/001:2011 establishes the criteria for exclusion, exemption and clearance from the application of radiation protection requirements.

However, cases of quantities exceeding 1 ton of natural or technologically enhanced radioactive materials or deposit of sterile, or mining tailings are excluded from this Standard.
In conclusion, the management of NORM residues is not specifically regulated by any available CNEN standard and is subject to specific case-by-case CNEN decision.

The use of UOW in the manufacture of construction materials is only possible if the concentration of radionuclide activity in the product (mortar) presents values below exemption levels (10 Bq/g) and the annual doses to individuals of the public (IP) and individuals occupationally exposed (IOE) are below 0.3 mSv and 1 mSv, respectively.

To comply with these regulations, the UOW should be used mixed with other materials already used in civil construction, such as sand, lime and cement.
• This paper aims at evaluating the radiological occupational exposure of using UOW in a pilot production of industrialized coating mortar.

• Since the UOW presents a significant concentration of natural radionuclides, its reuse in the production of coating mortar may result in exposition of IOE, as well as of people living in dwellings where the mortar has been used.
To evaluate the radiological exposure of using UOW in a pilot production of coating mortar, this study was divided in four steps, comprising:

- coating mortar processing phase,
- application phase,
- use phase,
- decommissioning phase.

It is important to emphasize that although these four steps represent the full cycle of manufacturing of mortar, the coating mortar processing and decommissioning phases involve exposition of IOE; whereas the application and use steps involve exposition of IP.
The production of UOW and its disposal in stacks were considered as part of the processing of ilmenite to obtain TiO₂, therefore were not included in this study. The starting point for the pilot production of coating mortar was the collection of UOW from the stack.

The radiometric survey in the area of the deposition of UOW was evaluated by using a Geiger-Muller. The mean value measured was 0.38 µSv/h (0.08 mSv/y). This dose is below the limit of 1 mSv/y, for IOE.
The radiometric survey of the working area and internal dosimetry of IOE in the production of coating mortar were evaluated. The weighing, bagging and transportation of the mortar bags to the palletizing area were done automatically.

The internal dosimetry due to inhalation was carried out by measuring the respirable particulate, with dust particle size distribution represented by AMAD standard of 5 µm, and by measuring the total alpha emission with a gas flow proportional detector. The internal dosimetry was measured for three workers and the doses below 0.75 mSv/y.
The radiometric survey of the working area was evaluated by using a Geiger-Muller. The mean exposition rate was 0.07 μSv/h (0.6 mSv/y).

The doses obtained for the IOE involved in the production of coating mortar are far below the limit of 1 mSv/y established in the standard CNEN-NN-4.01.
Radiological characterization of mortar components

For the radiological characterization of the mortar components, the concentration of natural radionuclides was determined in the samples of UOW, lime, sand, cement, and in the prepared mortar with various proportions of the UOW residue.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U-238 (Bq/kg)</th>
<th>Ra-226 (Bq/kg)</th>
<th>Pb-210 (Bq/kg)</th>
<th>Th-232 (Bq/kg)</th>
<th>Ra-228 (Bq/kg)</th>
<th>K-40 (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOW</td>
<td>538±103</td>
<td>1103±115</td>
<td>960±166</td>
<td>400±82</td>
<td>2906±262</td>
<td>119±50</td>
</tr>
<tr>
<td>lime</td>
<td>10±3</td>
<td>11±1</td>
<td>10±1</td>
<td>1.7±0.2</td>
<td>5.2±0.4</td>
<td>22±4</td>
</tr>
<tr>
<td>sand</td>
<td>8.6±3.2</td>
<td>3.3±0.7</td>
<td>5.0±1.1</td>
<td>2.6±1.0</td>
<td>2.4±0.5</td>
<td>15±9</td>
</tr>
<tr>
<td>cement</td>
<td>39±9</td>
<td>50±3</td>
<td>54±14</td>
<td>14±3</td>
<td>12±2</td>
<td>215±28</td>
</tr>
<tr>
<td>Mortar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% UOW</td>
<td>17±4</td>
<td>19±1</td>
<td>15±3</td>
<td>12±3</td>
<td>26±2</td>
<td>11±2</td>
</tr>
<tr>
<td>10% UOW</td>
<td>21±2</td>
<td>26±2</td>
<td>19±5</td>
<td>15±7</td>
<td>45±3</td>
<td>15±6</td>
</tr>
<tr>
<td>15% UOW</td>
<td>24±4</td>
<td>33±2</td>
<td>24±4</td>
<td>18±5</td>
<td>66±5</td>
<td>16±6</td>
</tr>
</tbody>
</table>

The total activity concentration of the UOW residue was 5.9 Bq/g, below the limit of 10 Bq/g established in the standard CNEN-NN-4.01 – Requirements of Safety and Radiation Protection for mining and milling facilities.
The external dosimetry of the IP who applied the coating mortar in the room was considered negligible, since the radiometric survey in the room before the application of the coating mortar gave results similar to the local background.

Besides, the mortar application process took only two days, which was not enough time for the dosimeter (TLD) detect any variation.
The results obtained for the Rn concentration before and after the application of the coating mortar were 72±11 Bq.m\(^{-3}\) and 71±25 Bq.m\(^{-3}\), respectively. The results are of the same order of magnitude, compatible with the concentration of radon in indoor environments and below the values recommended by ICRP and WHO (300 and 100 Bq.m\(^{-3}\), respectively).

The external gamma exposure measured using a TLD was always less than 0.1 mSv.y\(^{-1}\).
After three months of monitoring the mortar plaster was removed and transported to the final deposition site. The expected duration for the mortar removal was 8 hours, therefore, it was not possible to perform the external dosimetry. The internal dosimetry was performed, since during the removal of the plaster there was particulate emission. The internal dose was 1.0 mSv/y.

The dose due to the transportation to the final deposition site was below 0.46 mSv/y.
The viability of re-utilization of UOW residue in the production of coating mortar was analyzed.

The evaluation of the radiological exposure of the IOE and IP involved in the collection of UOW from the stack, transport, preparation of the coating mortar and final disposition showed that doses were below the limits of 1 mSv and 0.3 mSv per year established in the standard CNEN-NN-4.01.

The radiological impact of such practice can be considered negligible.

The re-utilization of UOW as component of coating mortar in Brazil meets the needs of the circular economy, delivering the Sustainable Development Goals.
The implementation of such practice in Brazil was only feasible and successful due to the partnership of important stakeholders:

- the titanium dioxide industry
- the Academia to provide scientific evidence that the practice will not cause any additional risk to the population
- the Regulatory Agency to provide that the adequate regulation is implemented.
Thank you for your attention