



REVALORISATION OF RESIDUES IN THE SCOPE OF THE CIRCULAR ECONOMY

Case study from the Titanium Dioxide Industry

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Introduction

- 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 TiO₂), corresponding to 1.2% of the world production.
- Brazil is the largest producer of TiO₂ in Latin America.

Main reserves of ilmenite, anatase and rutile



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.

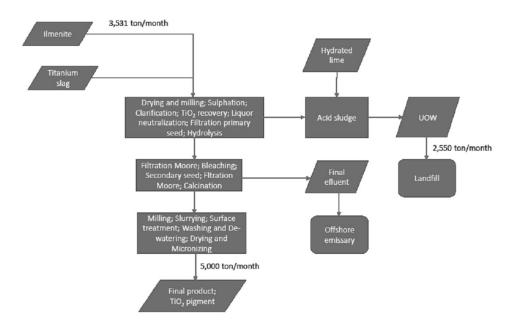
In Brazil, the main reserves of ilmenite are located in Mataracá.

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 TiO₂ in Brazil

Diagram of the TiO₂ production process



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

Sample	U-238	Ra-226	Pb-210	Th-232	Ra-228	K-40
ilmenite	207	275	267	1016	796	< 7
UOW	538	1103	960	400	2906	119

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.

Brazilian Regulation concerning NORM

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. REQUISITOS DE SEGURANÇA E PROTEÇÃO RADIOLÓGICA PARA INSTALAÇÕES MÍNERO-INDUSTRIAIS

> Resolução CNEN 28/04 Publicação: DOU 06.01.2005

Retificação: DOU 26.05.2005

Resolução CNEN 208/16 Publicação: DOU 26.12.2016

Comissão Nacional Comissão Nacional MINISTÉRIO DA CIÊNCIA, TECNOLOGIA, INOVAÇÕES E COMUNICAÇÕES

Norma CNEN NN 4.01 Resolução CNEN 208/16 Dezembro / 2016

Brazilian Regulation concerning NORM

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.

	Facility classification and documents required according to CNEN-NN-4.01				
	Category	Total activity concentration	Documents required		
	Category III	< 100 Bq/g	Basic information		
	Category II	≤ 500 Bq/g ≥100 Bq/g	Basic information Occupational Radiological Protection Plan; Environmental Radiological Monitoring Plan; Radioactive Waste Management Plan; and Preliminary Radiological Decommissioning Plan		
	Category I	> 500 Bq/g	Basic information Radiation Safety Analysis Report (SAR)		

Circular economy: a new pathway to sustainability

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.



Circular economy: a new pathway to sustainability

...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... Management of NORM Residues

IAEA-TECDOC-1712

IAEA

Revalorization of NORM residue in the TiO₂ production

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 TiO₂ 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.

Regulatory approach to shift from "NORM waste" to "NORM co-product"

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.



Norma CNEN NE 6.05 Publicação: DOU 17.12.1985

Resolução CNEN 167/14 Publicação: DOU 15.05.2014



Ministério da Ciência, Tecnologia e Inovação

Norma CNEN NN 8.01 solução CNEN 167/14

Regulatory approach to shift from "NORM waste" to "NORM co-product"

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.

POSIÇÃO REGULATÓRIA-3.01/001-2011 CRITÉRIOS DE EXCLUSÃO, ISENÇÃO E DISPENSA DE REQUISITOS DE PROTEÇÃO RADIOLÓGICA

1. REQUISITO DA NORMA SOB INTERPRETAÇÃO

Esta Posição Regulatória refere-se aos requisitos da Norma CNEN-NN-3.01 "Diretrizes Básicas de Proteção Radiológica" expressos nas subseções $1.2.5, 5.3.6 \times 5.3.7$, relacionados, respectivamente, aos critérios de exclusão, isenção e dispensa da aplicação de requisitos de proteção radiológica.

2. AVALIAÇÃO DO REQUISITO

Os crátérios de exclusão, isanção e dispensa contidos, respectivamente, nas subseções 1.2.5, 5.3.6 e 5.3.7 da Norma CNEN-NN-3.01 "Diretrizes Básicas de Proteção Radiológica" devem ser estabelecidos pela CNEN.

3. INTERPRETAÇÃO DO REQUISITO

3.1 EXCLUSÃO

3.1.1 A exclusão se aplica a quaisquer exposições cuja intensidade ou probabilidade de ocorrência não possa ser reduzida por ações de proteção radiológica, ou naqueles casos que a CNEN vise a considear exclusãos do seu controle.

3.1.2 Considera-se, desde já, exposições excluidas aquelas devidas à presença de K-40 no corpo, à radiação cósmica na superfície da terra ou às concentrações não alteradas de radiouncilidos naturais excitentes em praticamente todos os materiais ou matérias primas.

3.2 ISENÇÃO

3.2.1 A isenção se aplica a práticas e fontes associadas a práticas que, em função dos baixos niveis de radiação envolvidos, atendam aos critérios de isenção e/ou niveis de isenção estabelecidos nesta Posição Regulatória.

3.2.2 A isenção não se aplica a práticas que não sejam justificadas.

3.2.3 Os princípios gerais para a isenção são:

 a) o risco individual associado à radiação, em função de práticas ou fontes isentas é irrelevante (deve ser suficientemente baixo de forma a estar relacionado a danos radiológicos relevantes);

b) o impacto radiológico coletivo das práticas e fontes isentas deve ser suficientemente baino de forma a nôn necessitar o cumprimento de requisitos de proteção radiológica, nas circumstâncias existentes; e

c) as práticas e fontes isentas devem ser inerentemente seguras, com probabilidade irrelevante de cenários que levem a uma não conformidade com os principios (a) e (b).

3.2.4 Práticas ou fontes associadas a práticas podem ser isentas quando se enquadrarem nos seguintes critérios, em todas as situações razoáveis previstas: a) a dose sefetiva seperada, a ser recebida por qualquer individuo do público devido àquela

prática ou fonte, seja inferior ou da ordem de $10 \ \mu$ Sv em qualquer período de um ano; e b) a doce efetiva coletiva em qualquer ano de condução da prática não seja superior a 1 pescoa.Sv; a menos que uma avaliação de otimização da proteção radiolópica ou da

relevância social demonstre que a isenção é a solução ótima para aquela prática. 3.2.5 Fontes de radiação estarão isentas da aplicação de requisitos de proteção radiológica quando atenderem aos segurintes critérios específicos:

Posição Regulatória-3.01/001:2011

Regulatory approach to shift from "NORM waste" to "NORM co-product"

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.

Objective

- 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.

Methodology

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.

Exposition due to collecting UOW from the stack

The production of UOW and its disposal in stacks were considered as part of the processing of ilmenite to obtain TiO_2 , 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 μ Sv/h (0.08 mSv/y). This dose is below the limit of **1mSv/y**, for IOE.

Exposition due to the production of coating mortar

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 μ m, 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.

Exposition due to the production of coating mortar



The radiometric survey of the working area was evaluated by using a Geiger-Muller. The mean exposition rate was 0.07μ Sv/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.

Mean concentration of ²³⁸ U, ²²⁶ Ra, ²¹⁰ Pb, ²³² Th, ²²⁸ Ra and ⁴⁰ K (Bq/kg) in the components of mortar and mortar blended with UOW residue										
Sample	U-238	Ra-226	Pb-210	Th-232	Ra-228	K-40				
UOW	538±103	1103±115	960±166	400±82	2906±262	119±50				
lime	10±3	11±1	10±1	1.7±0.2	5.2±0.4	22±4				
sand	8.6±3.2	3.3±0.7	5.0±1.1	2.6±1.0	2.4±0.5	15±9				
cement	39±9	50±3	54±14	14±3	12±2	215±28				
Mortar										
5% UOW	17±4	19±1	15±3	12±3	26±2	11±2				
10% UOW	21±2	26±2	19±5	15±7	45±3	15±6				
15% UOW	24±4	33±2	24±4	18±5	66±5	16±6				

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.

Measurement of the background prior to the application of the coating mortar



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.

Measurement of radon and external gamma exposition before and after the application of the coating mortar



Dosimeters CR-39 and TLD installation before and after the application of the mortar

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.

Evaluation of the exposition due to the demolition, transportation and final deposition

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.

Conclusion

- 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 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.

Final message

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

