

OPERATIONAL PROTOCOL

Industrial sector: *TiO₂ pigment production*

Class or type of practice or critical scenario: *management and maintenance of titanium dioxide pigment production plants*

Version 2.0

This protocol has been developed within the framework of the research project (BRIC2019 ID30) «Operational protocols and calculation methodologies for the implementation of the new radiation protection legislation, transposing Directive 2013/59/Euratom, in NORM industrial sectors characterized by significant radiological impact»

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Operational Protocol Structure

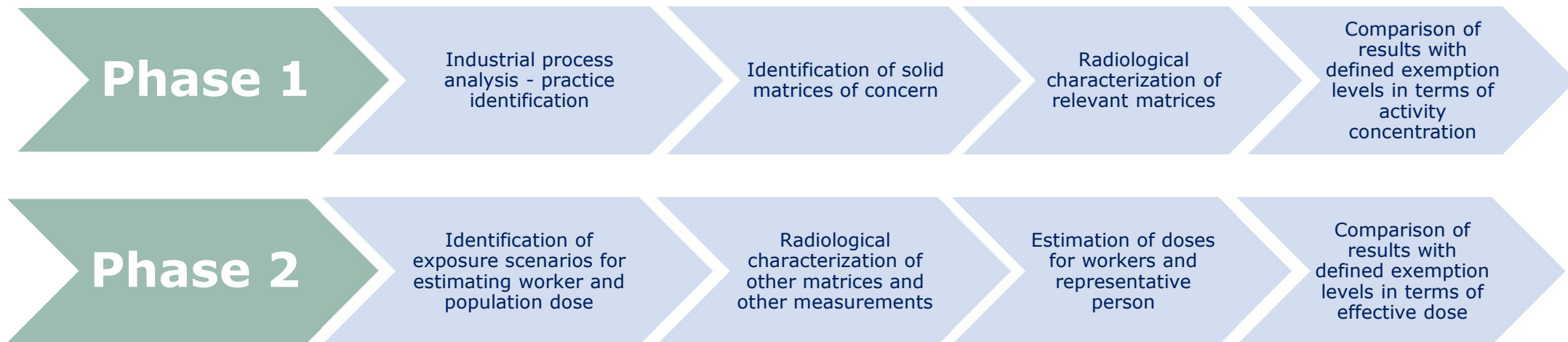
The present operational protocol consists of:

- a general description of the activities to be carried out in **Phases 1** and **Phase 2** for the development of the operational protocol;
- a summary of main matrices of interest for the industrial sector under consideration;
- a scheme of exposure scenarios and matrices of interest for the assessment of occupational exposure and exposure of the representative person (*);
- 2 tables concerning the matrices to be sampled, indicating the radionuclides to be determined and the most appropriate analytical method (**Phase 1**);
- 2 tables concerning the methodologies for dose assessment for workers and for the representative person (**Phase 2**);
- 1 table concerning additional matrices and analyses required to complete the dose assessment (**Phase 2**).
- Tables notes are provided at the end of this protocol.

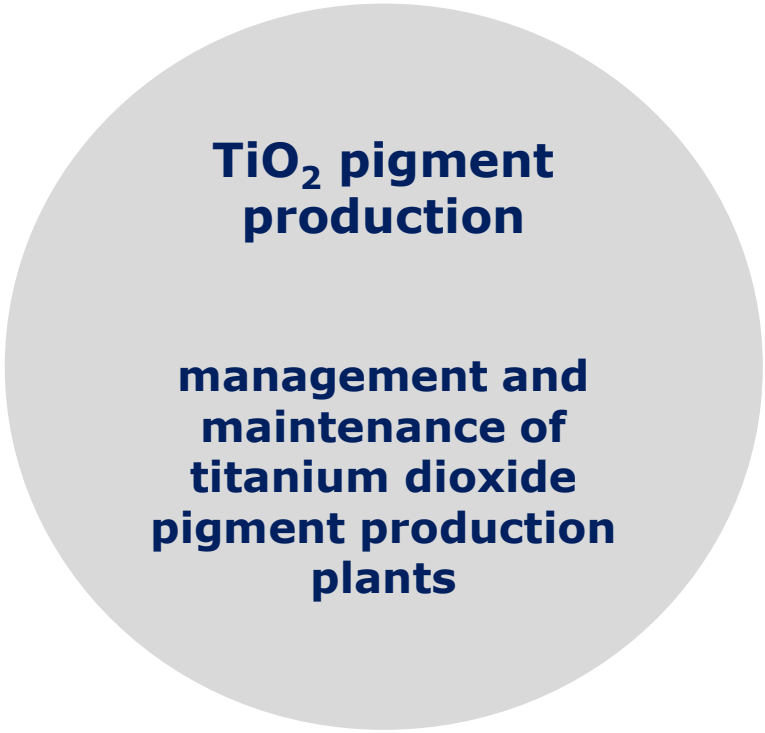
For the estimation of radon exposure in workplaces, please refer to the specific protocol.

(*) representative person: the individual receiving a dose that is representative of the more highly exposed individuals in the population, excluding those individuals having extreme or rare habits.

General graded methodological approach



Summary of the matrices present in the production cycle

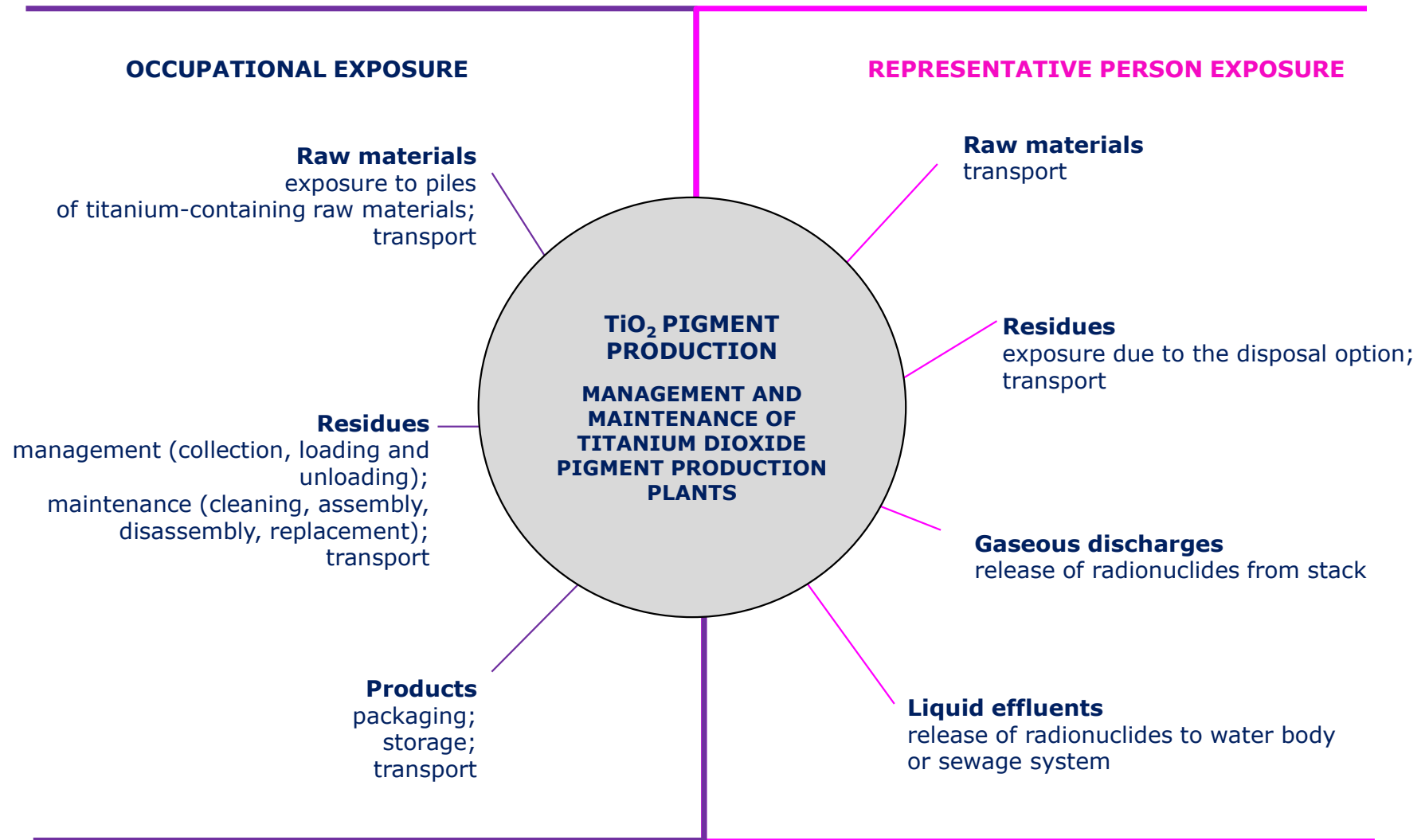


TiO₂ pigment production

**management and
maintenance of
titanium dioxide
pigment production
plants**

- **Raw materials**
titanium-containing raw materials of natural origin,
titanium-containing raw materials of non-natural origin,
other materials containing naturally occurring radionuclides
- **Residues**
abatement dust, processing waste, sludges, spent filter
material, scales, plant components, spent process materials,
wastes and by-products
- **Liquid effluents**
discharge into water body or sewer
- **Gaseous discharges**
release from stack
- **Products**
titanium dioxide pigment, copperas (iron sulfate)

Exposure scenarios and matrices of interest in case of TiO₂ pigment production



Phase 1



TABLE I: MATRICES OF INTEREST AND RADIOLOGICAL CHARACTERIZATION

Matrix Category	Type of Matrix	Matrix Description	Analytical Method	Radionuclides
Raw material	titanium-containing raw materials of natural origin (1)	ilmenite	gamma spectrometry	K-40, decay chains of U-238 and Th-232
	titanium-containing raw materials of non-natural origin	titaniferous slag		K-40, decay chain segments of U-238 and Th-232
	other materials containing naturally occurring radionuclides (1)			K-40, K-40, decay chains of U-238 and Th-232 or decay chain segments of U-238 and Th-232
Residue (4)	abatement dust	from stack related to grinding processes (2)	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
		from stack related to thermal processes (3)	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			alpha spectrometry	Po-210
		from other stacks	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
	by-product	tionite (3)	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			alpha spectrometry	Po-210
	by-product	red gypsum	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
	sludges	sludge from on-site wastewater treatment		
		sludge from wastewater collection sump		

Phase 1



TABLE I: MATRICES OF INTEREST AND RADIOLOGICAL CHARACTERIZATION (cont.)

Matrix Category	Type of Matrix	Matrix Description	Analytical Method	Radionuclides
Residue (3,4)	spent filter material	activated carbon filters	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			alpha spectrometry	Po-210
		other emission filtration systems (e.g. bag filters)	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			gamma spectrometry, spettrometria gamma ND in situ	K-40, decay chain segments of U-238 and Th-232
		Moore filter cloths	alpha spectrometry	Po-210
			gamma spectrometry, in situ nd gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
	scales (5)	residues from the maintenance of plant components	gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			alpha spectrometry	Po-210
	plant components	fittings, valves, pipes...	gamma spectrometry, in situ nd gamma spectrometry	K-40, decay chain segments of U-238 and Th-232

Phase 1



**TABLE II: VERIFICATION OF THE COMPLIANCE WITH EXEMPTION AND CLEARANCE LEVELS
(art. 22 and Annex. 2 of Legislative Decree 101/2020)**

Matrix Category	Type of Matrix	Matrix Description	Destination	Exemption and clearance levels
Raw material	titanium-containing raw materials of natural origin (1)	ilmenite	-	Table II-2
	titanium-containing raw materials of non natural origin (1)	titaniferous slag	-	Table II-2, except for Pb-210; Po-210 = 5 kBq/kg
	other materials containing naturally occurring radionuclides (1)		-	Table II-2; exception for Pb-210; Po-210 = 5 kBq/kg
Residue	abatement dust	from stack related to grinding processes	clearance – reuse	Table II-2, except for Pb-210; Po-210 = 5 kBq/kg In case of reuse for road construction and for disposal in landfill : Annex II, Section II, paragraph 4, item 4)
		from stack related to thermal processes		
		from other stacks		
	by-product	tionite		

Phase 1

Fase 1

Industrial process
analysis - practice
identification

Identification of
solid matrices of
interest

Radiological
characterization of
matrices of interest

**Comparison of
results with defined
exemption levels in
terms of activity
concentration**

**TABLE II: VERIFICATION OF THE COMPLIANCE WITH EXEMPTION AND CLEARANCE LEVELS
(art. 22 and Annex. 2 of Legislative Decree 101/2020) - cont.**

Matrix Category	Type of Matrix	Matrix Description	Destination	Exemption and clearance levels
Residue	by-product	red gypsum	clearance – reuse	Table II-2, except for Pb-210; Po-210 = 5 kBq/kg In case of reuse for road construction and for disposal in landfill : Annex II, Section II, paragraph 4, item 4
	sludges	sludge from on-site wastewater treatment		
		sludge from wastewater collection sump		
	spent filter material	activated carbon filters		
		other emission filtration systems (e.g. bag filters)		
		Moore filter cloths		
		other filter cloths (e.g. Moretti, filter press cloths, Fundabac)		
	scales	residues from the maintenance of plant components		
	plant components	fittings, valves, pipes...		

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

Radiological characterization of other matrices and other measurements

Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE III: WORKERS – IDENTIFICATION OF EXPOSURE SCENARIOS, DOSE ASSESSMENT AND EXEMPTION LEVELS IN TERMS OF EFFECTIVE DOSE

Matrix Category	Type of Matrix	Matrix Description	Exposure scenarios	Exposure pathways	Exemption level (effective dose)
Raw material	titanium-containing raw materials of natural origin	ilmenite	transport, piles of raw materials	external irradiation, inhalation, ingestion, radon (9)	1 mSv/year
	titanium-containing raw materials of non-natural origin	titaniferous slag			
	other materials containing naturally occurring radionuclides	zircon beads			
Product (6)	titanium dioxide pigment		packaging; storage; transport	external irradiation, inhalation, ingestion, radon (9)	
	copperas (iron sulfate)				
Residue	by-product	tionite	transport, management (8)	external irradiation, inhalation, ingestion, radon (9)	
	by-product	red gypsum			
	scales (5)	residues from the maintenance of plant components	maintenance (8), management (7), transport		

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

Radiological characterization of other matrices and other measurements

Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE III: WORKERS – IDENTIFICATION OF EXPOSURE SCENARIOS, DOSE ASSESSMENT AND EXEMPTION LEVELS IN TERMS OF EFFECTIVE DOSE

Matrix Category	Type of Matrix	Matrix Description	Exposure scenarios	Exposure pathways	Exemption level (effective dose)
Residue	abatement dust	from stack related to grinding processes	transport, management (6)	external irradiation, inhalation, ingestion, radon (9)	1 mSv/year
		from stack related to thermal processes			
		from other stacks			
	sludges	sludge from on-site wastewater treatment	transport, management (6)	external irradiation, radon (9)	
		sludge from wastewater collection sump			
	spent filter material	activated carbon filters (2)	maintenance (7), replacement, management (6), transport	external irradiation, inhalation, ingestion, radon (9)	
		other emission filtration systems (e.g. bag filters)			
		Moore filter cloths (2)			
		other filter cloths (e.g. Moretti, filter press cloths, Fundabac)			
	plant components	fittings, valves, pipes...	maintenance (7), replacement, management (6), transport	external irradiation, radon (9)	
	processing waste	zircon beads	replacement, management (6), transport	external irradiation, inhalation, ingestion, radon (9)	

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

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Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE IV: REPRESENTATIVE PERSON – IDENTIFICATION OF EXPOSURE SCENARIOS, DOSE ASSESSMENT AND EXEMPTION LEVELS IN TERMS OF EFFECTIVE DOSE

Matrix Category	Type of Matrix	Matrix Description	Exposure scenarios	Exposure pathways	Exemption level (effective dose)
Raw material	titanium-containing raw materials of natural origin	ilmenite	transport	external irradiation, inhalation	0.3 mSv/year
	titanium-containing raw materials of non natural origin	titaniferous slag			
	other materials containing naturally occurring radionuclides	zircon beads			
Discharge (10)	atmospheric discharge	atmospheric emissions from stacks	release of radionuclides from stacks	external irradiation, inhalation, ingestion (13)	
	liquid effluent	discharge to water body or to sewer system	release of radionuclides to water body or sewage system		
Residue	abatement dust	from stack related to grinding processes	it depends on residue destination (11,12), transport	external irradiation, inhalation, radon	
		from stack related to thermal processes			
		from other stacks			

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

Radiological characterization of other matrices and other measurements

Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE IV: REPRESENTATIVE PERSON – IDENTIFICATION OF EXPOSURE SCENARIOS, DOSE ASSESSMENT AND EXEMPTION LEVELS IN TERMS OF EFFECTIVE DOSE – cont.

Matrix Category	Type of Matrix	Matrix Description	Exposure scenarios	Exposure pathways	Exemption level (effective dose)
Residue	by-product	tionite	it depends on residue destination (11,12), transport	external irradiation, inhalation, radon (9), ingestion	0.3 mSv/year
	by-product	red gypsum			
	sludges	sludge from on-site wastewater treatment			
		sludge from wastewater collection sump			
	spent filter material	activated carbon filters			
		other emission filtration systems (e.g. bag filters)			
		Moore filter cloths			
		other filter cloths (e.g. Moretti, filter press cloths, Fundabac)			
	scales	maintenance residues from plant components			
	plant components	fittings, valves, pipes...			
	processing waste	zircon beads			

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

Radiological characterization of other matrices and other measurements

Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE V: RADIOLOGICAL CHARACTERIZATION OF OTHER MATRICES OF INTEREST AND FIELD MEASUREMENTS

Matrix Category	Type of Matrix	Matrix Description	Analytical technique	Radionuclides
Discharge	Atmospheric discharge	atmospheric emissions from stacks (14)	gamma spectrometry	K-40, decay chains of U-238 and Th-232
			alpha spectrometry	Po-210
	liquid effluent	wash water from the dust scrubber	liquid scintillation (16)	total alpha and total beta activity concentration
		discharge from internal wastewater treatment plant	ICP/MS gamma spectrometry alpha spectrometry	uranium concentration, K-40, decay chains of U-238 and Th-232, Po-210
Water (15)	incoming water	seawater, industrial water, etc.	liquid scintillation (16) ICP/MS gamma spectrometry alpha spectrometry	total alpha and total beta activity concentration uranium concentration, K-40, decay chains of U-238 and Th-232, Po-210

Phase 2

Phase2

Identification of exposure scenarios for estimating worker and population dose

Radiological characterization of other matrices and other measurements

Estimation of doses for workers and representative person

Comparison of results with defined exemption levels in terms of effective dose

TABLE V: RADIOLOGICAL CHARACTERIZATION OF OTHER MATRICES OF INTEREST AND FIELD MEASUREMENTS

Matrix Category	Type of Matrix	Matrix Description	Analytical technique	Radionuclides
Raw material	other materials containing naturally occurring radionuclides	zircon beads	dose rate	
Residue	plant components	fittings, valves, pipes...	dose rate	
	spent process materials	zircon beads	dose rate	
Product	titanium dioxide pigment		gamma spectrometry	K-40, decay chain segments of U-238 and Th-232
			alpha spectrometry	Po-210
	copperas (iron sulfate)		gamma spectrometry	K-40, decay chain segments of U-238 and Th-232

NOTE ALLE TABELLE

1. Radioactive equilibrium within the U-238 and Th-232 decay chains can be assumed a priori for raw materials of natural origin.
2. In the absence of high-temperature thermal processes, the activity concentration in abatement dusts generated from grinding operations can be assumed to be equal to that of the milled materials.
3. Volatilization of Po-210 and Pb-210 can occur during high-temperature thermal processes, meaning that alpha spectrometry may be required for the matrices involved in such processes for complete radiological characterization.
4. The undertaking can choose not to perform the measurement of Po-210 activity concentration through alpha spectrometry on all “Matrices” of the same “Type of Matrix”: in such cases, the choice must be justified, and the assessment of Po-210 can be performed based on the detected concentrations of Pb-210 and the involved processes that originated the residue.
5. The activity concentration of radionuclides must be referred to the mass of the scales themselves.
6. In the estimation of the effective dose to workers, operations involving products such as finishing processes, packaging, storage, and transport must also be considered, i.e. all processes involving exposure of workers prior to the commercialization of the products.
7. The management of residues includes collection, loading and unloading operations...
8. Maintenance includes cleaning, assembly, disassembly operations, etc.
9. For radon exposure, please refer to the dedicated protocol.
10. The estimation of the effective dose to the representative person due to the discharges can be calculated using simplified models (Radiation Protection n.135, Volumes 1 and 2) or more sophisticated models.
11. In the estimation of the effective dose to the representative person resulting from exposure to residues, the specific destination of each residue must be considered.

NOTES TO THE TABLES

12. Among all residues, only those with an activity concentration exceeding the exemption /clearance levels shall be considered in the effective dose estimates for the representative person.
13. It refers to the ingestion through the food chain.
14. For airborne effluents, the activity concentration of radionuclides can be estimated, using appropriate assumption, from the activity concentrations measured in the abatement dust from stacks.
15. The measurement of activity concentration in the water entering the plant is required if the activity measured in the liquid effluent is higher than the Minimum Detectable Activity (MDA).
16. In the characterization of incoming water and liquid effluents, if the total alpha activity concentration is $< 0.1 \text{ Bq/L}$ and the total beta activity concentration is $< 0.5 \text{ Bq/L}$, no further analyses are necessary.