

Safety Reports Series

No. 76

Radiation Protection and NORM Residue Management in the Titanium Dioxide and Related Industries



IAEA

International Atomic Energy Agency

IAEA SAFETY STANDARDS AND RELATED PUBLICATIONS

IAEA SAFETY STANDARDS

Under the terms of Article III of its Statute, the IAEA is authorized to establish or adopt standards of safety for protection of health and minimization of danger to life and property, and to provide for the application of these standards.

The publications by means of which the IAEA establishes standards are issued in the **IAEA Safety Standards Series**. This series covers nuclear safety, radiation safety, transport safety and waste safety. The publication categories in the series are **Safety Fundamentals**, **Safety Requirements** and **Safety Guides**.

Information on the IAEA's safety standards programme is available at the IAEA Internet site

<http://www-ns.iaea.org/standards/>

The site provides the texts in English of published and draft safety standards. The texts of safety standards issued in Arabic, Chinese, French, Russian and Spanish, the IAEA Safety Glossary and a status report for safety standards under development are also available. For further information, please contact the IAEA at PO Box 100, 1400 Vienna, Austria.

All users of IAEA safety standards are invited to inform the IAEA of experience in their use (e.g. as a basis for national regulations, for safety reviews and for training courses) for the purpose of ensuring that they continue to meet users' needs. Information may be provided via the IAEA Internet site or by post, as above, or by email to Official.Mail@iaea.org.

RELATED PUBLICATIONS

The IAEA provides for the application of the standards and, under the terms of Articles III and VIII.C of its Statute, makes available and fosters the exchange of information relating to peaceful nuclear activities and serves as an intermediary among its Member States for this purpose.

Reports on safety and protection in nuclear activities are issued as **Safety Reports**, which provide practical examples and detailed methods that can be used in support of the safety standards.

Other safety related IAEA publications are issued as **Radiological Assessment Reports**, the International Nuclear Safety Group's **INSAG Reports**, **Technical Reports** and **TECDOCs**. The IAEA also issues reports on radiological accidents, training manuals and practical manuals, and other special safety related publications.

Security related publications are issued in the **IAEA Nuclear Security Series**.

The **IAEA Nuclear Energy Series** consists of reports designed to encourage and assist research on, and development and practical application of, nuclear energy for peaceful uses. The information is presented in guides, reports on the status of technology and advances, and best practices for peaceful uses of nuclear energy. The series complements the IAEA's safety standards, and provides detailed guidance, experience, good practices and examples in the areas of nuclear power, the nuclear fuel cycle, radioactive waste management and decommissioning.

RADIATION PROTECTION AND
NORM RESIDUE MANAGEMENT
IN THE TITANIUM DIOXIDE AND
RELATED INDUSTRIES

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN	GHANA	NIGERIA
ALBANIA	GREECE	NORWAY
ALGERIA	GUATEMALA	OMAN
ANGOLA	HAITI	PAKISTAN
ARGENTINA	HOLY SEE	PALAU
ARMENIA	HONDURAS	PANAMA
AUSTRALIA	HUNGARY	PAPUA NEW GUINEA
AUSTRIA	ICELAND	PARAGUAY
AZERBAIJAN	INDIA	PERU
BAHRAIN	INDONESIA	PHILIPPINES
BANGLADESH	IRAN, ISLAMIC REPUBLIC OF	POLAND
BELARUS	IRAQ	PORTUGAL
BELGIUM	IRELAND	QATAR
BELIZE	ISRAEL	REPUBLIC OF MOLDOVA
BENIN	ITALY	ROMANIA
BOLIVIA	JAMAICA	RUSSIAN FEDERATION
BOSNIA AND HERZEGOVINA	JAPAN	SAUDI ARABIA
BOTSWANA	JORDAN	SENEGAL
BRAZIL	KAZAKHSTAN	SERBIA
BULGARIA	KENYA	SEYCHELLES
BURKINA FASO	KOREA, REPUBLIC OF	SIERRA LEONE
BURUNDI	KUWAIT	SINGAPORE
CAMBODIA	KYRGYZSTAN	SLOVAKIA
CAMEROON	LAO PEOPLE'S DEMOCRATIC REPUBLIC	SLOVENIA
CANADA	LATVIA	SOUTH AFRICA
CENTRAL AFRICAN REPUBLIC	LEBANON	SPAIN
CHAD	LESOTHO	SRI LANKA
CHILE	LIBERIA	SUDAN
CHINA	LIBYA	SWEDEN
COLOMBIA	LIECHTENSTEIN	SWITZERLAND
CONGO	LITHUANIA	SYRIAN ARAB REPUBLIC
COSTA RICA	LUXEMBOURG	TAJIKISTAN
CÔTE D'IVOIRE	MADAGASCAR	THAILAND
CROATIA	MALAWI	THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
CUBA	MALAYSIA	TUNISIA
CYPRUS	MALI	TURKEY
CZECH REPUBLIC	MALTA	UGANDA
DEMOCRATIC REPUBLIC OF THE CONGO	MARSHALL ISLANDS	UKRAINE
DENMARK	MAURITANIA	UNITED ARAB EMIRATES
DOMINICA	MAURITIUS	UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
DOMINICAN REPUBLIC	MEXICO	UNITED REPUBLIC OF TANZANIA
ECUADOR	MONACO	UNITED STATES OF AMERICA
EGYPT	MONGOLIA	URUGUAY
EL SALVADOR	MONTENEGRO	UZBEKISTAN
ERITREA	MOROCCO	VENEZUELA
ESTONIA	MOZAMBIQUE	VIETNAM
ETHIOPIA	MYANMAR	YEMEN
FINLAND	NAMIBIA	ZAMBIA
FRANCE	NEPAL	ZIMBABWE
GABON	NETHERLANDS	
GEORGIA	NEW ZEALAND	
GERMANY	NICARAGUA	
	NIGER	

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

SAFETY REPORTS SERIES No. 76

**RADIATION PROTECTION AND
NORM RESIDUE MANAGEMENT
IN THE TITANIUM DIOXIDE AND
RELATED INDUSTRIES**

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2012

COPYRIGHT NOTICE

All IAEA scientific and technical publications are protected by the terms of the Universal Copyright Convention as adopted in 1952 (Berne) and as revised in 1972 (Paris). The copyright has since been extended by the World Intellectual Property Organization (Geneva) to include electronic and virtual intellectual property. Permission to use whole or parts of texts contained in IAEA publications in printed or electronic form must be obtained and is usually subject to royalty agreements. Proposals for non-commercial reproductions and translations are welcomed and considered on a case-by-case basis. Enquiries should be addressed to the IAEA Publishing Section at:

Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
<http://www.iaea.org/books>

© IAEA, 2012

Printed by the IAEA in Austria
August 2012
STI/PUB/1568

IAEA Library Cataloguing in Publication Data

Radiation protection and NORM residue management in the titanium dioxide and related industries. — Vienna : International Atomic Energy Agency, 2012.

p. ; 24 cm. — (Safety reports series, ISSN 1020-6450 ; no. 76)

STI/PUB/1568

ISBN 978-92-0-132110-7

Includes bibliographical references.

1. Radiation sources — Safety measures. 2. Mineral industries — Safety measures. 3. Titanium dioxide. I. International Atomic Energy Agency. II. Series.

IAEAL

12-00752

FOREWORD

The Fundamental Safety Principles (IAEA Safety Standards Series No. SF-1), together with Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards (IAEA Safety Standards Series No. GSR Part 3 (Interim)), set out the principles and basic requirements for radiation protection and safety applicable to all activities involving radiation exposure, including exposure to natural sources of radiation. The Safety Guides on Occupational Radiation Protection in the Mining and Processing of Raw Materials (IAEA Safety Standards Series No. RS-G-1.6) and Management of Radioactive Waste from the Mining and Milling of Ores (IAEA Safety Standards Series No. WS-G-1.2) provide guidance on the control of exposure of workers and members of the public to naturally occurring radioactive material (NORM) in industrial activities involving the exploitation of minerals. This guidance applies irrespective of whether the minerals are exploited for their radioactivity content. The titanium dioxide and related industries constitute one of several industry sectors for which the radioactivity content of the minerals and raw materials involved is too small to be of commercial value but is large enough to warrant consideration by the regulatory body concerning the possible need to control exposures of workers and members of the public.

This Safety Report has been developed as part of the IAEA's programme to provide for the application of its safety standards in the field of radiation, transport and waste safety. It is a compilation of detailed information on the processes and materials involved in the titanium dioxide and related industries and on the radiological considerations that need to be taken into account by the regulatory body when determining the nature and extent of radiation protection measures to be taken. This is consistent with the graded approach to regulation, in terms of which the application of the requirements of the safety standards is commensurate with the characteristics of the practice or source and with the magnitude and likelihood of the exposures.

This Safety Report was drafted in four consultants meetings held between March 2004 and December 2011. The IAEA acknowledges the contributions made by G.S. McNulty and D. Fillion, as well as the input and assistance provided by the Titanium Dioxide Manufacturers Association (a sector group of the European Chemical Industry Council (CEFIC)). The IAEA officers responsible for this report were D.G. Wymer and P.P. Haridasan of the Division of Radiation, Transport and Waste Safety.

CONTENTS

1.	INTRODUCTION	1
1.1.	Background	1
1.2.	Objective	2
1.3.	Scope	2
1.4.	Structure	3
2.	OVERVIEW OF THE TITANIUM DIOXIDE AND RELATED INDUSTRIES	4
2.1.	Sources of titanium	4
2.2.	Titanium mineral feedstocks and main process routes	5
2.3.	Titanium products	10
2.3.1.	Titanium dioxide	10
2.3.2.	Titanium metal and other titanium-containing products	11
3.	GENERAL RADIATION PROTECTION CONSIDERATIONS ...	13
3.1.	Application of the standards to industrial activities involving exposure to natural sources	13
3.1.1.	Scope of regulation	13
3.1.2.	Graded approach to regulation	13
3.1.3.	Applicability of the Transport Regulations to material in transport	16
3.2.	Exposure to gamma radiation	20
3.3.	Exposure to radionuclides in inhaled dust particles	20
3.3.1.	Particle size	20
3.3.2.	Monitoring techniques for workers	21
3.3.3.	Calculation of effective dose	24
4.	FEEDSTOCKS FOR THE PRODUCTION OF TITANIUM DIOXIDE AND OTHER TITANIUM-CONTAINING PRODUCTS	28
4.1.	Feedstock characteristics	28
4.2.	Ilmenite upgrading processes	30

4.2.1.	Production of synthetic rutile	30
4.2.2.	Production of upgraded ilmenite	32
4.2.3.	Management of residues	35
4.2.4.	Radionuclide activity concentrations	36
4.3.	Occupational exposure	39
4.3.1.	Exposure pathways	39
4.3.2.	Exposure levels	40
4.3.3.	Effective dose	41
4.4.	Public exposure	45
4.5.	Regulatory considerations	45
5.	PRODUCTION OF TITANIUM DIOXIDE BY THE SULPHATE PROCESS	46
5.1.	Process description	46
5.1.1.	Main process	46
5.1.2.	Generation of by-products	50
5.1.3.	Management of waste	53
5.2.	Radionuclide activity concentrations	55
5.2.1.	Migration of radioactive species	55
5.2.2.	Activity concentrations in process materials	56
5.3.	Occupational exposure	62
5.3.1.	Exposure levels	62
5.3.2.	Effective dose	66
5.3.3.	Measures to reduce doses	69
5.4.	Public exposure	71
5.5.	Regulatory considerations	73
5.5.1.	Normal plant operation	73
5.5.2.	Maintenance and decontamination of equipment	73
5.5.3.	Process material falling outside the scope of regulatory control of practices	73
5.5.4.	Digester residue	74
5.5.5.	Applicability of the Transport Regulations	74
6.	PRODUCTION OF TITANIUM DIOXIDE PIGMENT AND TITANIUM METAL BY THE CHLORIDE PROCESS	75
6.1.	Process description	75
6.1.1.	Production of titanium dioxide pigment	75
6.1.2.	Production of titanium metal	80

6.2. Radionuclide activity concentrations	82
6.2.1. Migration of radioactive species	82
6.2.2. Activity concentrations in process materials	83
6.3. Occupational exposure	83
6.3.1. Exposure levels	86
6.3.2. Effective dose	87
6.3.3. Measures to reduce doses	90
6.4. Public exposure	90
6.5. Regulatory considerations	91
APPENDIX: THORIUM AND URANIUM DECAY SERIES	93
REFERENCES	95
ANNEX I: MINING AND BENEFICIATION OF HEAVY MINERAL SAND	99
ANNEX II: MANAGEMENT OF RESIDUES FROM SYNTHETIC RUTILE PRODUCTION	103
CONTRIBUTORS TO DRAFTING AND REVIEW	105

1. INTRODUCTION

1.1. BACKGROUND

Titanium dioxide (TiO_2) was first identified from mineralogical studies more than 200 years ago, but it was not until the early 20th century that the technology was available for its production and use as a pigment, initially in Norway and the United States of America. The material gained rapid acceptance as a replacement for toxic, lead based pigments, and its use has become widespread since the 1940s. Its high light scattering efficiency enables it to have extremely high hiding power. That property, combined with its chemical inertness, durability, dispersibility and non-toxicity, makes it a critical ingredient in products such as coatings, plastics and paper. The annual world consumption of titanium dioxide pigment is close to 6 million t. Much smaller quantities of titaniferous feedstocks are used to manufacture other products such as titanium metal and welding electrodes.

Titanium minerals and the various process feedstocks derived from them contain radionuclides of natural origin in the ^{232}Th and ^{238}U decay series. The radionuclide activity concentrations are moderately elevated above those in normal rocks and soil. During processing, the radionuclides may become mobilized and migrate to dusts, scales and other process residues, leading to the possibility of radionuclide activity concentrations higher than those in the relevant feedstock mineral. Isotopes of radium in particular may become concentrated in scales. Titanium dioxide and other titanium-containing products are essentially free of radioactivity.

The radioactivity content of the feedstocks and process residues is not significant enough to be of any commercial value, but creates a possible need to control exposures of workers and members of the public in accordance with the IAEA safety standards, in particular the Fundamental Safety Principles [1], Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards (the BSS) [2], the Regulations for the Safe Transport of Radioactive Material (the Transport Regulations) [3] and relevant Safety Guides [4, 5]. In some process materials, the activity concentrations of radionuclides in the ^{232}Th decay series (and to a lesser extent the ^{238}U series) are such that, in terms of the BSS [2], these materials would be considered for inclusion within the scope of regulation, as naturally occurring radioactive material (NORM) — further information on the criteria for regulatory control is given in the Safety Guide on Application of the Concepts of Exclusion, Exemption and Clearance [6].

The Safety Report on Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials [7] confirms that the

titanium dioxide and related industries constitute one of several minerals-related industry sectors likely to warrant radiation protection measures through the system of regulatory control for practices. This Safety Report emphasizes the particular relevance of the graded approach to the regulation of practices to ensure that any radiation protection measures applied to the industrial processes involved and to the management of NORM residues arising from those processes are commensurate with the characteristics of the operation and with the magnitude and likelihood of the exposures. This implies the need for a thorough understanding of all the processes, the process materials, the associated radiological risks to workers and members of the public, and the practicalities of any protective measures that might need to be considered.

1.2. OBJECTIVE

The objective of this Safety Report is to provide detailed information that will assist regulatory bodies in implementing a graded regulatory approach to the protection of workers and members of the public against exposures associated with the titanium dioxide and related industries. This information will also serve as the basis for creating a common understanding between regulatory bodies and other stakeholders — such as operators, workers and their representatives, and health, safety and environmental professionals — of the radiological aspects of the various processes involved and the ways in which these aspects can be addressed appropriately and effectively.

1.3. SCOPE

This report provides detailed information on the titanium dioxide and related industries, including the processes involved, the management of NORM residues arising from such processes, the radiological characteristics of the various process materials (feedstocks, intermediate products, final products, by-products and residues), the exposure pathways to workers and members of the public, the exposure levels, the annual effective doses likely to be received and examples of good practice with respect to monitoring techniques and practical measures to reduce doses.

For each major step in the production process, the report includes an assessment of the regulatory implications for radiation protection, the management of radioactive waste and the transport of material, in terms of the standards. Particular attention is given to the extent to which existing occupational, health and safety (OHS) regulation or environmental protection

regulation may be effective in avoiding or minimizing the need for additional, more specific regulatory measures for the control of radiation exposure.

While some of the information provided in this report has been obtained from published literature, most of the information has been obtained from company data contributed by industry experts engaged in the drafting of the report. Although an attempt has been made to include all available information of relevance, data in some areas are still lacking. In such areas, further investigations may be necessary.

Most commercially exploited titanium minerals are obtained from deposits of heavy mineral sands¹. The radiological aspects associated with the mining of these sands and the processes by which the various heavy minerals of commercial interest, including titanium-bearing minerals, are concentrated and separated are addressed in another Safety Report [8]. For this reason, such operations are not included within the scope of this report but a brief overview is provided in Annex I. The report focuses on commercial processes only and does not cover new processes under development for the upgrading of feedstocks and for the production of titanium dioxide and titanium metal.

1.4. STRUCTURE

This report contains six sections, including this Introduction. Section 2 provides a general overview of the titanium dioxide and related industries. This overview describes the sources of titanium worldwide; the raw and upgraded feedstocks involved; the various titanium based products and their commercial applications; and the basic processes used for the production of titanium dioxide pigment and titanium metal, including the generation of by-products. Section 3 summarizes the application of the standards to industrial activities involving exposure to natural sources, including the application of the IAEA Transport Regulations to material in transport. Section 4 addresses the radiological aspects of the various titanium-bearing feedstocks and of the processes for upgrading them, as well as the regulatory considerations involved. Sections 5 and 6 cover the production of titanium dioxide by the so-called sulphate process and chloride process, respectively. Each of these two sections includes a description of the process; the generation and use of by-products; the generation and management of effluents and waste; the migration of radionuclides from the feedstocks to the

¹ Heavy minerals are normally defined as those with densities exceeding 3000 kg/m³. The heavy minerals of commercial importance are zircon, the titanium-bearing minerals ilmenite, rutile and leucosene, and the rare-earth-bearing minerals monazite and xenotime.

various residues and by-products; information on occupational and public exposures; and regulatory considerations. Section 6 also covers the production of titanium metal from the intermediate product titanium tetrachloride (TiCl_4). Details of the radionuclides in the ^{232}Th and ^{238}U decay series are provided in the Appendix to this publication. The report concludes with two annexes: the first provides a brief summary of the mining and beneficiation of titanium-bearing heavy mineral sand (which is dealt with in more detail in another Safety Report [8]), while the second provides an example of the management of residues from the production of synthetic rutile.

2. OVERVIEW OF THE TITANIUM DIOXIDE AND RELATED INDUSTRIES

2.1. SOURCES OF TITANIUM

Titanium is the ninth most abundant element in the Earth's crust and the fourth most abundant metal of major industrial importance after aluminium, iron and magnesium. Its occurrence in nature is usually in chemical combination with oxygen and iron. The key commercial titanium minerals are:

- (a) Ilmenite, a mixed oxide of titanium and iron (FeTiO_3 or $\text{FeO} \cdot \text{TiO}_2$ with an equivalent TiO_2 content of 34–69%);²
- (b) Rutile (93–96.5% TiO_2);
- (c) Leucoxene ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ with a TiO_2 content of 70–90%)³.

Information on titanium mineral reserves is presented in Table 1 and details of worldwide mining output are given in Table 2. Nearly two thirds of the worldwide production of titanium minerals comes from just four countries: Australia, South Africa, Canada and China. More than 90% of titanium mineral production is in the form of ilmenite. Roughly three quarters of this is ilmenite sand, a component of heavy mineral sand, while the remainder is ilmenite rock

² Throughout this report, mineral concentrations expressed as percentages refer to mass concentrations.

³ Leucoxene is sometimes referred to as 'weathered ilmenite'. The weathering process increases the titanium dioxide content of the ilmenite.

TABLE 1. RESERVES OF TITANIUM MINERALS, BY COUNTRY [9]

	Reserves, expressed as contained TiO ₂ (kt)			Contribution to world total (%)
	Ilmenite	Rutile	Total	
China	200 000	— ^a	200 000	28.9
Australia	100 000	18 000	118 000	17.0
India	85 000	7 400	92 400	13.3
South Africa	63 000	8 300	71 300	10.3
Brazil	43 000	1 200	44 200	6.4
Madagascar	40 000	—	40 000	5.8
Norway	37 000	—	37 000	5.3
Canada	31 000	—	31 000	4.5
Mozambique	16 000	480	16 480	2.4
Ukraine	5 900	2 500	8 400	1.2
Sierra Leone	—	3 800	3 800	0.5
United States of America	2 000	400	2 400	0.3
Vietnam	1 600	—	1 600	0.2
Other countries	26 000	400	26 400	3.8
World totals, rounded	650 000	42 000	693 000	100

^a —: not reported.

originating from Canada and Norway. Leucoxene (produced in Australia) accounts for a mere 1% of world production of titanium mineral concentrate.

2.2. TITANIUM MINERAL FEEDSTOCKS AND MAIN PROCESS ROUTES

All of the titanium minerals described in Section 2.1 are used directly as feedstocks for the production of titanium dioxide pigments and other titanium

TABLE 2. PRODUCTION OF TITANIUM MINERALS, BY COUNTRY^a

	Production, expressed as contained TiO ₂ (2010) [9]			Production, expressed as titanium mineral concentrate (2008) [10]				
	Quantity (kt)		Contribution to world total (%)	Quantity (kt)		Contribution to world total (%)		
	Ilmenite	Rutile		Ilmenite	Rutile		Total	
Australia	1 070	280	1 350	21.3	2 042	325	2 525 ^b	19.5
South Africa	1 120	130	1 250	19.7	2 176	132	2 308	17.9
Canada	700	0	700	11.0	2 600	0	2 600	20.1
China	600	0	600	9.5	1 000	0	1 000	7.7
India	420	20	440	6.9	730 ^c	22 ^c	752 ^c	5.8
Vietnam	410	0	410	6.5	700	0.5	700.5	5.4
Ukraine	300	57	357	5.6	600	100	700	5.4
Mozambique	350	2	352	5.6	328.875	32.985	361.86	2.8
Norway	320	0	320	5.1	915	0	915	7.1
United States of America	200 ^d	— ^d	200	3.2	400 ^d	— ^d	400	3.1
Madagascar	150	6	156	2.5	0	0	0	0
Sierra Leone	0	67	67	1.1	17.26	78.91	96.17	0.7

TABLE 2. PRODUCTION OF TITANIUM MINERALS, BY COUNTRY^a (cont.)

	Production, expressed as contained TiO ₂ (2010) [9]			Production, expressed as titanium mineral concentrate (2008) [10]				
	Quantity (kt)		Contribution to world total (%)	Quantity (kt)		Contribution to world total (%)		
	Ilmenite	Rutile		Ilmenite	Rutile		Total	
Sri Lanka	40	12	52	0.8	56.824	3.405	60.229	0.5
Brazil	43	3	46	0.7	130	3	133	1.0
Republic of Korea	0	0	0	0	226.069	0	226.069	1.7
Egypt	0	0	0	0	88	0	88	0.7
Malaysia	0	0	0	0	36.779	1.834	38.613	0.3
Kazakhstan					16 ^d	— ^d	16	0.1
Other countries	35	0	35	0.6	0	0	0	0
World totals, rounded	5 800	580	6 300	100	12 100	700	12 900 ^b	100

^a Figures in italics are estimated.

^b Includes 158 kt leucoxene.

^c Year ended 31 March 2009.

^d Ilmenite and rutile production not quantified separately; total production taken to be ilmenite.

products. In addition, ilmenite, because of its relatively low content of titanium dioxide equivalent, is frequently processed into higher grade feedstocks instead of being used directly. These upgraded feedstocks comprise synthetic rutile, SREP⁴ and upgraded ilmenite (UGI), a generic term referring to both titanium slag and upgraded slag. The feedstocks, upgraded or otherwise, are processed via one of two routes: the sulphate process route and the chloride process route. A simplified, schematic representation of the various processes and products associated with the titanium dioxide and related industries, including an indication of which processes are within the scope of this Safety Report, is given in Fig. 1.

The sulphate process route accounts for about 45% of pigment production and involves the use of sulphuric acid to separate the titanium dioxide from the other components of the mineral concentrate. The chloride process route accounts for the remaining 55% of production and involves the use of gaseous chlorine to produce TiCl_4 , which is then converted to titanium dioxide by oxidation. The choice of process route and of specific processes depends on local conditions such as the market situation, the environmental management situation in terms of its implications for waste disposal, the economic situation (for instance, the costs of power and chemicals) and the availability of technology. The nature of the local avenues available for waste disposal is a major determinant of the types of processes and feedstock used. The availability of commercial outlets for by-products derived from feedstock components other than titanium dioxide strongly influences the feedstock choice and the environmental management strategy at each production site.

The grade of feedstock is determined by its content of titanium dioxide equivalent. The majority of chloride process plants require feedstocks of relatively high grade, while sulphate process plants can be operated with feedstocks of lower grade. Ilmenite sand is used directly as a feedstock for pigment manufacture via either the sulphate or the chloride process route. Rutile and leucoxene are used directly as feedstocks for the manufacture of titanium dioxide pigments via the chloride process route. Of the upgraded feedstocks, synthetic rutile, SREP and upgraded slag are used only in the chloride process route. Titanium slag is used in either process route (see Fig. 1) and is accordingly referred to as 'sulphate slag' or 'chloride slag', as appropriate. The estimated proportions of each type of feedstock used are shown in Fig. 2.

⁴ The term 'SREP' (an acronym for 'synthetic rutile enhancement process') is used to denote a higher grade form of synthetic rutile.

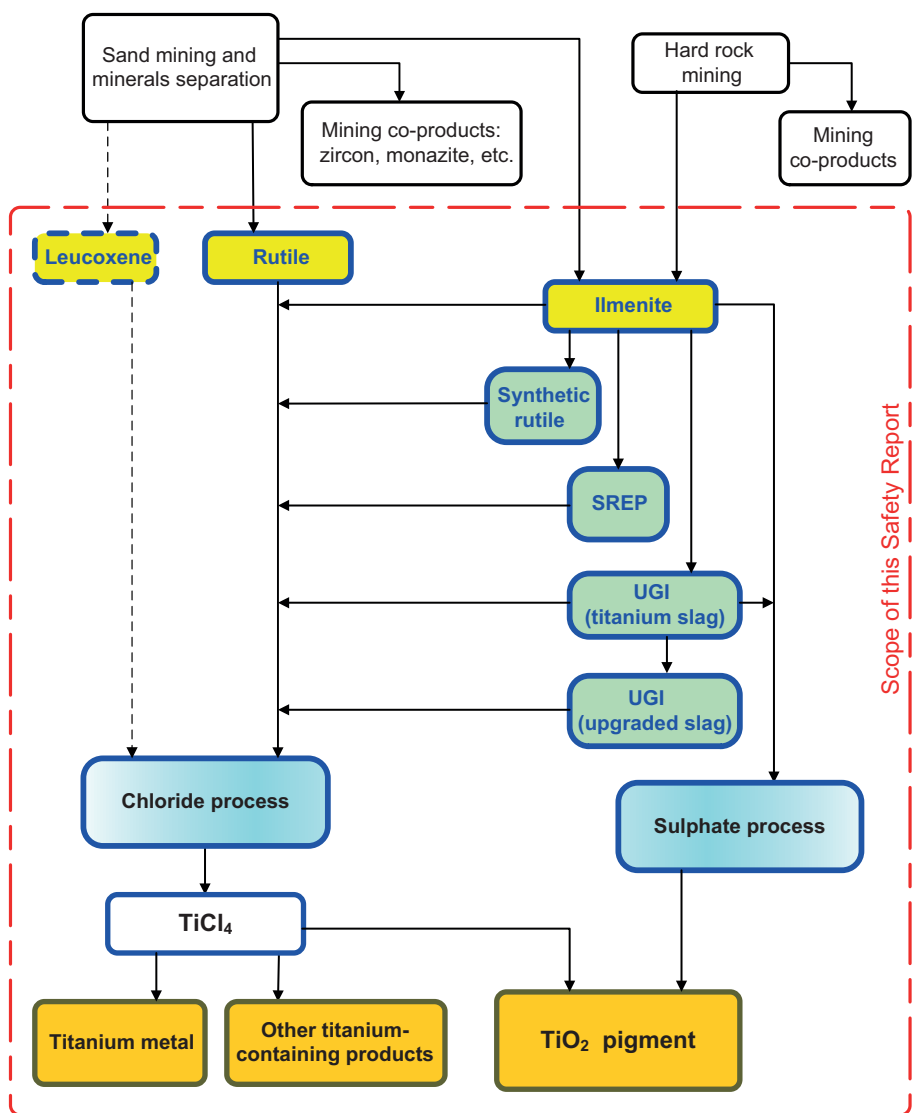


FIG. 1. Processes and products associated with the titanium dioxide and related industries. (The dashed lines associated with leucoxene reflect the very small contribution of this mineral to total production. SREP — synthetic rutile enhancement process; UGI — upgraded ilmenite.)

The need for whiteness and brightness of titanium dioxide pigment requires that the product be made to a high degree of purity. All titaniferous feedstocks contain components that must be removed to obtain a pigment product that satisfies market requirements with respect to whiteness, brightness and purity.

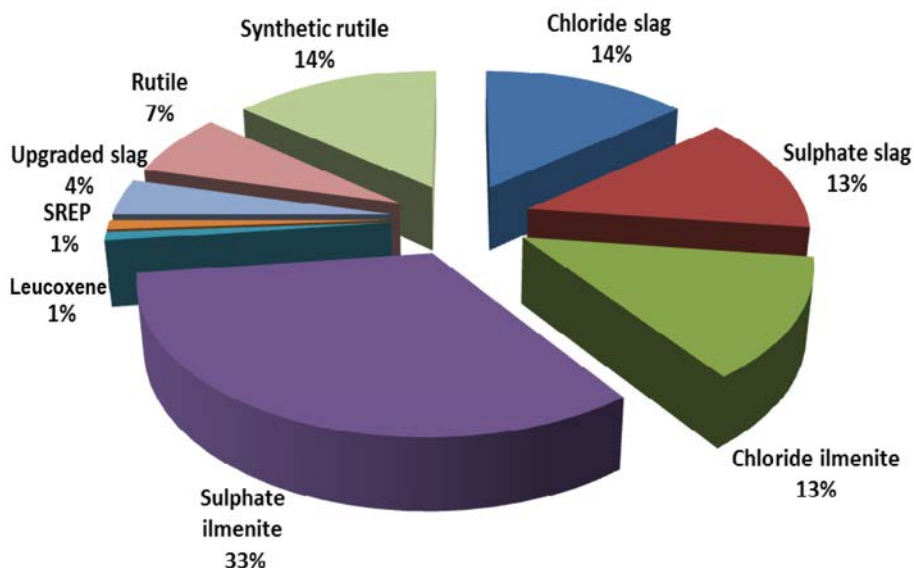


FIG. 2. Proportions of feedstocks used in the manufacture of titanium dioxide pigments. SREP — synthetic rutile enhancement process.

Conversion of these components into by-products with beneficial uses is an integral part of the TiO_2 manufacturing process to ensure the full utilization of the raw material resource and to avoid or minimize the generation of process wastes. The range of by-products produced is dependent on the feedstock and the process route. The major by-products associated with the sulphate process route are gypsum, iron sulphates, sulphuric acid, digester residue and iron oxide, while those associated with the chloride process route are iron chloride, hydrochloric acid and neutralized iron oxides, hydroxides or carbonates.

2.3. TITANIUM PRODUCTS

2.3.1. Titanium dioxide

Titanium dioxide has a very high refractive index of 2.4. This, together with its high reflectivity and excellent opacifying properties, causes it to be the most widely used white pigment for a variety of applications including paints and coatings, plastics, paper, ceramic glazes, printing inks, food and toothpaste. It is also used as a pigment and thickener in cosmetics (ultraviolet (UV) blockers, make-up and skin care products) and as a tattoo pigment. A breakdown of the

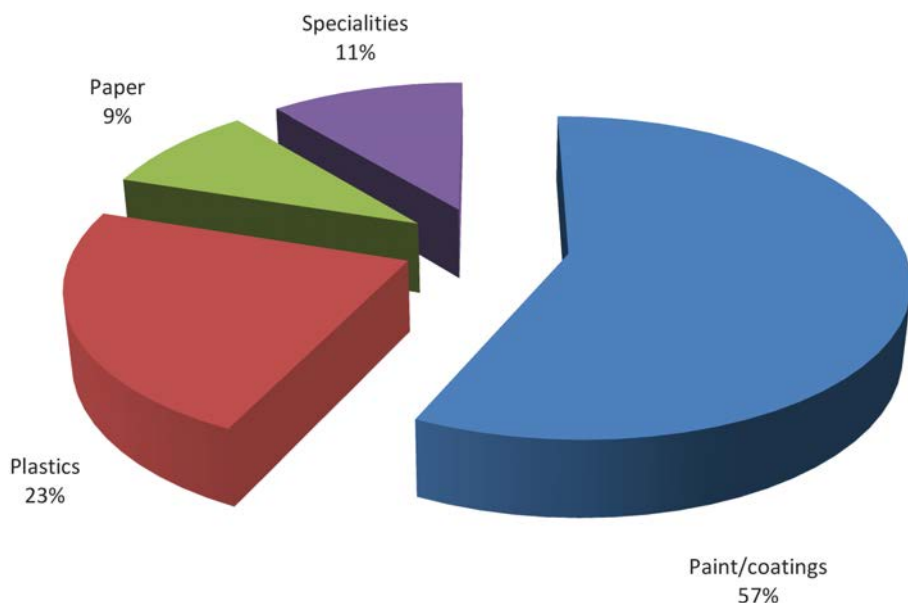


FIG. 3. Applications of titanium dioxide pigments.

main titanium dioxide pigment applications is shown in Fig. 3. The suitability of titanium dioxide for different uses is dictated by its particle size and final treatment. The annual worldwide production of titanium dioxide pigments is close to 6 million t, accounting for the consumption of approximately 95% of all titaniferous feedstocks.

In more specialized applications, titanium dioxide, usually in ultrafine form, acts as a photocatalyst when exposed to UV radiation (and, when doped with nitrogen ions, to normal lamp light). It is thus added to paints, cements, windows, tiles and other products for its sterilizing, deodorizing and anti-fouling properties, and is used for the detoxification of wastewater. Exposure to UV radiation also causes it to become increasingly hydrophilic, allowing it to be used for anti-fogging coatings and self-cleaning windows. The high refractive index of titanium dioxide makes it an excellent optical coating for dielectric mirrors.

2.3.2. Titanium metal and other titanium-containing products

The production of titanium metal and of titanium-containing welding electrodes each account for the consumption of about 3% of all titaniferous feedstocks. The chloride process route involving titanium tetrachloride is generally used for these products. The commercial production of titanium

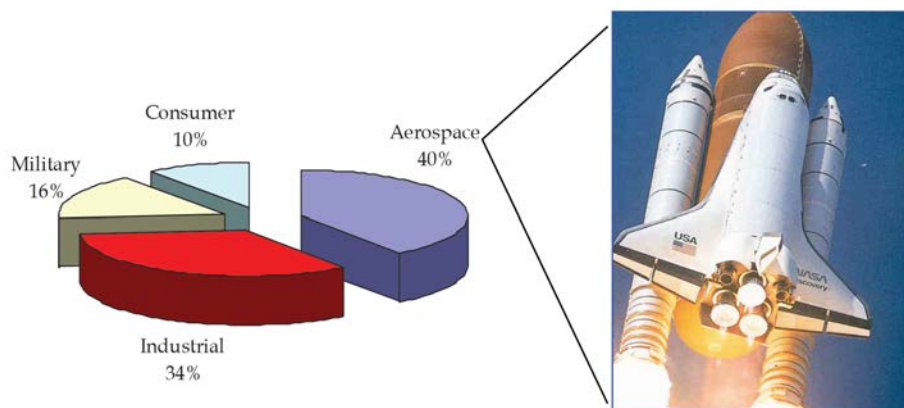


FIG. 4. Applications of titanium metal.

tetrachloride as an intermediate product in its own right accounts for less than 0.3% of total feedstock consumption. The need for high levels of purity restricts titanium metal producers to the use of high grade feedstocks. Most metal producers operate their own chloride process plants using rutile, synthetic rutile or upgraded slag as a feedstock, while a few producers purchase titanium tetrachloride from chloride process pigment plants and further purify it before conversion to titanium metal.⁵

At present, about 125 000 t of titanium sponge are produced per year and sold, either as sponge of different purity grades and particle sizes, or as ingot (melted sponge with or without special alloying elements). Figure 4 shows the major areas of application for titanium metal products. They are used primarily in the commercial aerospace industry, in industrial and military applications, and for consumer products such as golf clubs and watches.

The commercial uses of titanium tetrachloride include catalysts for the production of polymers such as polyethylene and polypropylene, glass and metal treatments, pharmaceutical products, titanium chemicals and food applications. It is also used as a source of seed nuclei in the sulphate pigment process and as an intermediate product in the manufacture of titanium metal.

⁵ The figure of 3% of feedstock material quoted for the production of titanium metal does not include the relatively small amount of titanium metal made from titanium tetrachloride purchased as a commercial intermediate product.

3. GENERAL RADIATION PROTECTION CONSIDERATIONS

3.1. APPLICATION OF THE STANDARDS TO INDUSTRIAL ACTIVITIES INVOLVING EXPOSURE TO NATURAL SOURCES

3.1.1. Scope of regulation

Paragraph 3.4 of the BSS [2] states that exposure due to natural sources is generally considered as an existing exposure situation, meaning that the exposure does not fall within the scope of regulation in terms of the requirements for planned exposure situations. However, some industrial activities giving rise to exposure to natural sources have the characteristics of practices, and para. 3.4 of the BSS makes provision for the requirements for planned exposure situations to apply in such cases, depending principally on the activity concentrations of radionuclides of natural origin in the material giving rise to the exposure (in this case, any of the process materials involved). The requirements for planned exposure situations apply if the activity concentration of any radionuclide in the uranium or thorium decay chains is greater than 1 Bq/g or the activity concentration of ^{40}K is greater than 10 Bq/g. As a result of this criterion, the titanium dioxide and related industries are identified in Ref. [7] as being among those industrial activities that are likely to be subject to the requirements for planned exposure situations.

3.1.2. Graded approach to regulation

Where the activity concentration values specified in Section 3.1.1 are exceeded, a graded approach to regulation as a practice is adopted in accordance with para. 3.6 of the BSS [2]. The application of the graded approach to the regulation of operations involving exposure to NORM is described in Refs [4, 7] and is summarized in Sections 3.1.2.1–3.1.2.3.

3.1.2.1. Initial assessment

An initial assessment is made of the process, the materials involved and the associated exposures. For industries engaged in the processing of NORM, the exposure pathways to workers and members of the public that are most likely to require consideration are those involving external exposure to gamma radiation emitted from process material and internal exposure via the inhalation of radionuclides in dust. Consideration of internal exposure via the inhalation of

^{220}Rn and/or ^{222}Rn emitted from process material (leading to exposure to the short lived progeny of these radionuclides) may also be necessary during the exploitation of certain minerals. Internal exposure via ingestion is unlikely to require consideration under normal operational circumstances.

The assessment of the effective dose received by an individual involves summing the personal dose equivalent from external exposure to gamma radiation in a specified period and the committed equivalent dose or committed effective dose, as appropriate, from intakes of radionuclides in the same period. The assessment method is described in more detail in Ref. [4].

3.1.2.2. Regulatory options

The four basic options open to the regulatory body, in ascending order of degree of control, are as follows:

- (1) The regulatory body may decide that the optimum regulatory option is not to apply regulatory requirements to the legal person responsible for the material. The mechanism for giving effect to such a decision could take the form of an exemption. For exposure to NORM, the exemption criterion given in the BSS [2] is a dose of the order of 1 mSv per year. The background to this criterion is given in Ref. [11], which concludes that exemption is likely to be the optimum option if the material does not give rise to an annual effective dose received by a worker exceeding about 1–2 mSv (this being a small fraction of the occupational dose limit), bearing in mind that the dose received by a member of the public in such circumstances is likely to be lower by at least an order of magnitude [7].
- (2) Where the regulatory body has determined that exemption is not the optimum option, the minimum requirement is for the legal person to formally submit a notification to the regulatory body of the intention to carry out the practice. As in the case of a decision to grant an exemption, this is an appropriate option when the maximum annual effective dose is a small fraction of the applicable dose limit, but it provides the added reassurance that the regulatory body remains informed of all such practices.
- (3) Where the level of exposure to NORM is such that neither exemption nor the minimum regulatory requirement of notification is the optimum regulatory option, the regulatory body may decide that the legal person has to meet additional (but limited) obligations to ensure that exposed individuals are adequately protected. These obligations would typically involve measures to keep exposures under review and to ensure that the working conditions are such that exposures remain moderate, with little

likelihood of doses approaching or exceeding the dose limit.⁶ The mechanism for imposing such obligations on the legal person is the granting of an authorization in the form of a registration [4].

- (4) Where an acceptable level of protection can only be ensured through the enforcement of more stringent exposure control measures, an authorization in the form of a licence may be required [4]. This is the highest level of the graded approach to regulation, and its use for practices involving exposure to NORM is likely to be limited to operations involving substantial quantities of material with very high radionuclide activity concentrations.

3.1.2.3. Control measures for authorized practices

A detailed account of the control measures that may be appropriate for authorized practices involving work with minerals and raw materials is given in Refs [4, 5]. In terms of the graded approach to regulation, the nature and extent of such measures will be commensurate with type of practice and the levels of exposure, but will generally entail the establishment of some form of radiation protection programme with suitable provisions for monitoring and dose assessment at a more detailed level than in the initial assessment referred to in Section 3.1.2.1.

Specific radiological measures in the workplace such as control of the occupancy period or even shielding may sometimes be appropriate to minimize external exposure to NORM. Materials with relatively low activity concentrations give rise to modest gamma dose rates (typically no more than a few microsieverts per hour), even on contact. In such cases, discouraging access, for example, by storing materials in mostly unoccupied areas, may be sufficient. In areas containing materials with relatively high activity concentrations, physical barriers and warning signs may be necessary.

Exposure to airborne dust is likely to be controlled already in many workplaces through general OHS regulations. Control of the air quality for the purpose of minimizing dust levels may also help to reduce radon and thoron concentrations. Therefore, the extent to which existing OHS control measures are effective in minimizing workers' radiation exposure is something that the regulatory body would first need to establish before deciding to impose additional control measures for purely radiological reasons. In some workplaces, existing OHS control measures alone may provide sufficient protection against internal

⁶ For situations in which workers are exposed to gamma radiation and radionuclides in inhaled dust, Ref. [11] states that "Control, if considered necessary, would include the use of methods to suppress or contain any airborne dusts and general radiological supervision".

exposure. In other workplaces, additional control measures specifically for radiation protection purposes may become necessary for achieving compliance with the standards. Engineered controls are the favoured option, with working procedures and, finally, protective respiratory equipment being considered only where further engineering controls are not effective or practicable.

Complete containment of material is often impractical, especially where large quantities of low activity concentration materials are involved, but spills and the spread of materials outside the area are often of no radiological significance unless substantial and persistent airborne dust levels result. Prevention of resuspension of dust is therefore likely to be the most effective approach. Specific measures to control surface contamination only become meaningful where materials with higher activity concentrations are present.

Worker awareness and training are particularly important for supporting the introduction of local rules and for creating an understanding of the precautions embodied in such rules. Individual employee work practices may exacerbate dust generation and, in some cases, may completely negate the effect of any engineering controls installed. There may be deficiencies in the way in which equipment maintenance tasks are undertaken, implying the need for periodic review to determine if improvements are possible. The general standard of housekeeping and spillage control also needs to be kept under regular review. Even where the materials being handled have a low activity concentration, a reasonable standard of housekeeping may be necessary to ensure that dust resuspension is adequately controlled.

3.1.3. Applicability of the Transport Regulations to material in transport

3.1.3.1. Basic criteria

The safety requirements for material in transport are set out in the Transport Regulations [3]. The transport of material, in its natural or processed state, associated with the titanium dioxide and related industries may or may not fall within the scope of the Transport Regulations, depending on the activity concentration of the material. The Transport Regulations apply only if the activity concentration of the material exceeds ten times the activity concentration for

exempt material.⁷ For individual radionuclides of natural origin, the activity concentrations for exempt material are shown in Table 3.

3.1.3.2. Mixtures of radionuclides

For mixtures of radionuclides, the activity concentration for exempt material is:

$$X_m = \frac{1}{\sum_i \frac{f(i)}{X(i)}} \quad (1)$$

where

X_m is the activity concentration for exempt material;

$f(i)$ is the fraction of activity concentration of radionuclide i in the mixture;

$X(i)$ is the activity concentration for exempt material for radionuclide i ;

and the condition for application of the Transport Regulations (see Section 3.1.3.1) is:

$$\sum_i x(i) > 10X_m \quad (2)$$

where $x(i)$ is the activity concentration of radionuclide i in the mixture.

Combining Eqs (1) and (2) and making the substitution:

$$f(i) = \frac{x(i)}{\sum_i x(i)}$$

⁷ This activity concentration criterion applies only to material containing radionuclides of natural origin that either is in its natural state or has been processed only for purposes other than for the extraction of the radionuclides, and that is not intended to be processed for the use of these radionuclides.

TABLE 3. ACTIVITY CONCENTRATIONS FOR EXEMPT MATERIAL IN TRANSPORT

	Activity concentration (Bq/g)	Progeny included in secular equilibrium
<i>Th-232 decay series</i>		
Th _{nat} (Th-232)	1	Ra-228, Ac-228, Th-228, Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Th-232	10	None
Ra-228	10	Ac-228
Th-228	1	Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Ra-224	10	Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
<i>U-238 decay series</i>		
U _{nat} (U-238)	1	Th-234, Pa-234m, U-234, Th-230, Ra-226, Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
U-238	10	Th-234, Pa-234m
Th-234	1000	Pa-234m
U-234	10, 100 ^a	None
Th-230	1	None
Ra-226	10	Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
Pb-210	10	Bi-210, Po-210
Po-210	10	None
K-40	100	None

^a The applicable value depends on the chemical form of the material.

gives the condition for application of the Transport Regulations as:

$$\sum_i \frac{x(i)}{X(i)} > 10 \quad (3)$$

3.1.3.3. *Material with decay chains in equilibrium*

For material in which the radionuclides in each decay series are (or are deemed to be) in equilibrium, the values of activity concentration for exempt material for U_{nat} , Th_{nat} and ^{40}K (see Table 3) can be used to derive the condition for application of the Transport Regulations, with the progeny of ^{238}U and ^{232}Th automatically being taken into account. Equation (3) then becomes:

$$\frac{x(U_{\text{nat}})}{1} + \frac{x(Th_{\text{nat}})}{1} + \frac{x(^{40}\text{K})}{100} > 10 \quad (4)$$

For materials that are not particularly rich in potassium, Eq. (4) can be approximated to:

$$x(U_{\text{nat}}) + x(Th_{\text{nat}}) > 10 \quad (5)$$

3.1.3.4. *Material with decay chain segments in equilibrium*

The available data on the radionuclide composition of the material may indicate that equilibrium conditions do not prevail throughout the decay chains but that it may be possible to treat the material as a mixture of decay chain segments, each of which can be assumed to be in equilibrium. In such cases, however, the available data and/or the information in Table 3 may not always be sufficiently detailed to determine unequivocally whether the Transport Regulations apply, in which case, a conservative estimate may have to be made by assigning the highest individual radionuclide activity concentration in each decay chain or chain segment to all radionuclides in that decay chain or chain segment. Further information on how to proceed when insufficient data are available on individual radionuclide activity concentrations is given in Ref. [3].

3.2. EXPOSURE TO GAMMA RADIATION

The main radionuclides contributing to gamma exposure are ^{228}Ac , ^{212}Pb and ^{208}Tl from the ^{232}Th decay series and ^{214}Pb and ^{214}Bi from the ^{238}U decay series. The highest gamma energy (2614 keV) is associated with ^{208}Tl . In the titanium dioxide and related industries, as in many other NORM industries, exposure to gamma radiation arises mainly from accumulations of mineral concentrates or residues. Dose rates are generally highest near process tanks, piping, filters and large material stockpiles. For workers, workplace monitoring or individual monitoring techniques, or a combination of both, are used.

3.3. EXPOSURE TO RADIONUCLIDES IN INHALED DUST PARTICLES

Airborne dust particles arise from the resuspension of contamination on floors and other surfaces, releases from processing operations and the conveying of minerals. For inhalation of such particles by workers in the titanium dioxide and related industries, exposure to radionuclides in both the thorium and uranium decay series is of concern for radiation protection. The quantity of inhalable dust produced in low temperature processes, and thus the severity of the dust inhalation hazard, is limited because most particles finer than 75 μm have already been removed during the initial mineral sands separation process (see Annex I). In situations where the radionuclide activity concentrations in the materials being handled are moderate, it is important to recognize that the silica content of the airborne dust is likely to be of greater concern for occupational health than the radionuclide content.

3.3.1. Particle size

In the absence of particle size information specific to the workplace concerned, an activity median aerodynamic diameter (AMAD) of 5 μm is normally recommended for airborne dust in the workplace [12], and this could be an appropriate value to use in any initial assessment (see Section 3.1.2.1). However, when subsequently performing a more detailed assessment (see Section 3.1.2.3), measurements may indicate that in some workplaces, a higher AMAD such as 10 μm may be more appropriate.

Where high temperature processes are involved, some radionuclides, notably ^{210}Pb and ^{210}Po , can become volatilized in the furnace fume⁸, and an AMAD of $1\text{ }\mu\text{m}$ is normally recommended in situations where this fume contaminates the air in the workplace (in the area around the furnace, for example). In some high temperature processes, however, a higher AMAD may be appropriate, and the best approach is therefore to determine the particle size distribution for the particular workplace concerned.

3.3.2. Monitoring techniques for workers

In the titanium dioxide and related industries, as with other NORM industries, routine determination of intakes of radionuclides by workers is, in most cases, achieved using techniques based on air sampling. This approach is consistent with the findings of an investigation into monitoring strategies and methods for optimization of internal exposures of workers exposed to NORM, carried out for the European Commission [13]. One of the conclusions of that investigation was that “[a]ir sampling, rather than biological sampling (or whole body counting) is the best way of assessing doses and providing ALARA [as low as reasonably achievable] information.”

Guidance on the use of techniques based on air sampling for the monitoring of workers is given in Ref. [4]. Such techniques involve the drawing of air through a filter to capture the dust particles, which are then analysed by measuring the activities of alpha emitting radionuclides in the thorium and uranium decay series. The use of gross alpha activity measurements to determine the intake is subject to the following considerations:

- (a) In materials that have not been chemically processed, the equilibrium of the thorium and uranium decay chains is unlikely to be significantly disturbed, allowing equilibrium to be generally assumed for freshly generated airborne dust particles. However, as discussed in the annex to Ref. [4], some thoron and radon may have escaped from the dust particles when they are analysed in the laboratory after a delay of some days. The resulting depletion of thoron and radon leads to a corresponding depletion of short lived thoron or radon progeny. For minerals with extremely low thoron and radon emanation coefficients, such as the heavy minerals zircon and monazite, 100% retention of thoron and radon can be assumed. On this basis, 1 Bq of ^{232}Th captured on the filter corresponds to 6 Bq of measured

⁸ The term ‘fume’ in this context denotes the vapour and/or suspended fine dust particles released from a high temperature industrial process.

gross alpha activity, while 1 Bq of ^{238}U corresponds to 8.32 Bq of measured gross alpha activity. For other minerals, the retention can be expected to be in the range of 50–100%, and it would seem reasonable to assume 75% retention as being typical. On this basis, 1 Bq of ^{232}Th captured on the filter corresponds to 5.25 Bq of measured gross alpha activity, while 1 Bq of ^{238}U corresponds to 7.54 Bq of measured gross alpha activity.

- (b) In materials that have been subject to chemical or thermal processing, equilibrium conditions in the airborne dust particles can no longer be assumed, and the analysis may have to include the measurement of certain individual decay progeny.

Two basic types of air sampling technique are in use: stationary air sampling (also known as workplace or static air sampling), in which the sampling device remains at a fixed location in the workplace, and personal air sampling, in which the sampling device is attached to the worker in a position such that the air sample is reasonably representative of the air breathed by the worker. The use of stationary air sampling is generally less preferred for dose assessment purposes because the air that is sampled may not be representative of the air breathed by the worker. It is noted in Ref. [13] that the use of stationary air sampling can result in dust inhalation doses being significantly underestimated, sometimes by several orders of magnitude, particularly in workplaces where the resuspension of dust by worker activities is a significant factor. On the other hand, stationary air sampling may result in a significant overestimation of the dose if the worker is not continuously stationed in a dusty area.

Because of difficulties in applying personal air sampling to every exposed worker all of the time, monitoring strategies usually involve the assignment of workers to work categories that reflect the general nature and scope of the work activities. In many workplace situations involving exposure to dust containing radionuclides of natural origin, such exposure is not uniform within a work category, since a worker may, during the course of the work shift, spend time in different exposure environments. A further complication arises in accounting for the wearing of respiratory protective equipment.

Air sampling equipment and techniques have been reviewed in terms of their applicability to radiation protection in workplaces involving exposure to radionuclides in airborne dust [13]. Some of the findings of that review are summarized in the following:

- (i) Air samplers are designed to follow a specific particle size sampling convention based on industrial hygiene sampling criteria and therefore typically underestimate the true ambient aerosol and thus the activity inhaled. The degree of underestimation depends on the AMAD and

geometric standard deviation (GSD) of the ambient aerosol and on the type of sampler used. A correction factor can be applied to minimize the degree of underestimation of the airborne activity concentration, but this does not remove all of the uncertainty because the AMAD and GSD vary with location, time and circumstances of dust production and can therefore never be known precisely.

- (ii) The aerosol particle size distribution also has a significant effect on the dose coefficient, leading to an additional source of uncertainty when assessing the effective dose due to inhalation of particles. The dependence of the dose coefficient on AMAD is particularly strong for particles of lung solubility class S. When assessing the effective dose, it is important to select a sampler with an efficiency that follows as closely as possible the AMAD dependency of the relevant dose coefficients.
- (iii) Knowledge of the lung absorption class is important because it is needed for determining not only the most appropriate dose coefficient but also the type of sampler that best minimizes the errors arising from an incomplete knowledge of the particle size distribution.
- (iv) The preferred type of sampling for minimizing dose assessment errors is inhalable sampling for particles in lung absorption class F and thoracic sampling for particles in lung absorption classes M and S. While particles of class M or S are likely to be encountered in many NORM industries, it is pointed out that thoracic samplers are currently not as widely available as inhalable samplers and often are not suitable for alpha counting owing to the dust particles being collected on foam rather than flat filters.
- (v) Where the particle size distribution is not known, the assignment of an AMAD of 5 μm has been found to reasonably minimize errors in assessing the effective dose, whatever the true value of AMAD, sampling type, radionuclide and lung class.⁹ The assignment of a GSD of 2.5 is recommended by the International Commission on Radiological Protection (ICRP) for aerosols with an AMAD above 1 μm when the actual value is unknown [14]. Sampling efficiency correction factors, as referred to in (i), for a GSD of 2.5 are shown in Table 4.

The activity inhaled by workers, as determined from alpha counting of dust samples collected on filters, may be underestimated if there is significant alpha particle self-absorption in large particles or in multilayers or agglomerates of smaller particles deposited on the filter. Dust loadings on filters may, in such

⁹ The measurement of the AMAD requires specialized equipment such as a cascade impactor.

TABLE 4. SAMPLING EFFICIENCY CORRECTION FACTORS FOR ESTIMATING THE AIRBORNE ACTIVITY CONCENTRATION OF PARTICLES WITH A GEOMETRIC STANDARD DEVIATION OF 2.5 [13]

AMAD (μm)	Correction factor		
	Inhalable sampler	Thoracic sampler	Respirable sampler
1	1.04	1.05	1.11
5	1.18	1.41	2.5
10	1.31	2.1	5.6

Note: AMAD — activity median aerodynamic diameter.

cases, need to be restricted accordingly (see, for example, Ref. [15]). Various types of filter medium and sampling cassette are available. Where the dust concentration is relatively low (say, about 1–2 mg/m³) and sampling is undertaken over a 4–6 h period, the choice of filter medium and cassette is not likely to be critical. However, where the dust concentration is relatively high (more than about 3 mg/m³) and the sampling is undertaken for a period of 8 h or more, the selection of equipment requires more careful consideration. For some types of filter medium, such as polyvinyl chloride, part of the sample may be lost as a result of dust not fully adhering to the surface. For some types of monitoring cassette, the dust may adhere to the inside wall, requiring it to be removed by washing and added to the material collected on the filter prior to radiometric analysis.

3.3.3. Calculation of effective dose

Dose coefficients (values of committed effective dose per unit intake of activity) for inhalation of radionuclides by workers and members of the public are specified in a database compiled by the ICRP [16]. The values are based on the model for the respiratory tract described in Ref. [14]. The dose coefficients for workers quoted in Ref. [16] cover a wide range of AMADs. Most of the values for AMADs of 1 and 5 μm also appear in table III-2A in Schedule III of the BSS [2]. The dose coefficients for members of the public are specified in Ref. [16] for a default AMAD of 1 μm and also appear in table III-2E in Schedule III of the BSS [2].

3.3.3.1. Dose coefficients for low solubility dust particles

It is pointed out in Ref. [13] that in most NORM industries, the radioactive components of the material involved, and thus of their aerosol particles, are contained within a matrix of non-radioactive elements and their compounds. These matrices determine the solubility of the particles, and it is therefore appropriate to choose the same lung absorption class for all the radionuclides contained within them. It is further pointed out that many of these materials are resistant to all but the most vigorous forms of chemical attack and that their dust particles are obviously lung absorption class S. This is said to apply to heavy mineral sands, including rutile, and to radium rich process scales, including those encountered in both the chloride and sulphate process routes for titanium dioxide pigment production.

Inhalation dose coefficients applicable to workers in industrial operations involving low solubility airborne dust particles are given in Table 5. The coefficients relate to lung absorption class S to the extent possible and cover all radionuclides with significant dose contributions. In the few instances where a value for class S is not available, the value given is that corresponding to the next fastest lung absorption class for which information is available.¹⁰ Most of the values in Table 5 are taken from Ref. [16]. In some cases (denoted by figures in italics), values for lung absorption class S are not available from this source and data are quoted instead from the results of other calculations [13, 17] based similarly on the ICRP respiratory tract model described in Ref. [14].

Many assessments of worker doses reported for NORM industries are based on the inhalation dose coefficients given in table III-2A in Schedule III of the BSS [2] for AMADs of 1 or 5 μm , since these coefficients have been agreed upon by international consensus as providing the basis for regulation in accordance with the standards. However, the BSS do not provide coefficients for ^{228}Ra , ^{224}Ra , ^{226}Ra , ^{210}Pb and ^{210}Po in lung absorption class S, with the result that, for low solubility particles, the coefficients for class M (or F in the case of ^{210}Pb) have to be used instead. In addition, the dose coefficients for ^{228}Th given in the BSS are different from those incorporated into the ICRP database [16] and given in Table 5. For particles with decay progeny in equilibrium and a ^{232}Th activity concentration twice that of ^{238}U (typical of titanium minerals), the total inhalation dose will be underestimated by 10% if the BSS dose coefficients are used instead of those in Table 5. Considering the many uncertainties associated with any dose assessment of this nature, this degree of underestimation is unimportant.

¹⁰ The use of dose coefficients for lung absorption classes other than class S in these few instances may lead to some underestimation of the dose.

TABLE 5. RADIONUCLIDE SPECIFIC INHALATION DOSE COEFFICIENTS FOR WORKERS (LOW SOLUBILITY DUST PARTICLES)

	Dose coefficient for specified AMAD ($\mu\text{Sv/Bq}$) ^a				
	0.3 μm	1 μm	3 μm	5 μm	10 μm
<i>Thorium decay series</i>					
Th-232	32	23	17	12	8.1
Ra-228	3.3 (M)	<i>15</i>	<i>14</i>	<i>11</i>	<i>7.1</i>
Th-228	45	37	33	25	18
Ra-224	3.3 (M)	2.9 (M)	3.1 (M)	2.8	1.3 (M)
Series in equilibrium ^b	83.6	77.9	67.1	50.8	34.5
<i>Uranium decay series</i>					
U-238	10	7.3	7.2	5.7	3.5
U-234	12	8.5	8.6	6.8	4.1
Th-230	18	13	10	7.2	5.2
Ra-226	4.4 (M)	8.7	8.7	<i>6.9</i>	<i>4.2</i>
Pb-210	0.76 (F)	5.2	5.3	4.3	2.7
Po-210	3.9 (M)	3.9	3.5	2.7	<i>1.7</i>
Ac-227 (from U-235 series) ^c	88	66	52	47	27
Series in equilibrium ^{b,c}	53.1	49.6	45.7	35.8	22.6

Note: AMAD — activity median aerodynamic diameter.

- ^a The dose coefficients quoted are those corresponding to lung absorption class S, except where specified in parentheses as M or F. Values shown in italics are taken from Ref. [13] (rounded to two significant figures) or, in the case of ²²⁴Ra, from Ref. [17]. All other values are taken from Ref. [16].
- ^b The values refer to the dose per unit activity of the parent radionuclide.
- ^c The natural abundance of U-235 is 0.711%, resulting in an activity concentration in natural uranium of 0.046 relative to that of U-238. Consequently, the relative contributions to the inhalation dose from the U-235 decay series radionuclides are insignificant except for that from Ac-227. The dose coefficient for Ac-227 is multiplied by 0.046 in calculating the dose coefficient for the full series.

Consequently, the use of BSS dose coefficients instead of those given in Table 5 can be considered acceptable for dose assessment purposes.

The derivation of the dose coefficients for ^{226}Ra specified in the ICRP database [16], the BSS [2] and Table 5 is based on the assumption that ^{222}Rn produced in the respiratory tract does not have the same biokinetic behaviour as its parent ^{226}Ra , but rather is removed to the environment at a rate of 100/d (see annex B of Ref. [18]). Should the removal rate be lower than 100/d, the use of these dose coefficients would, by implication, result in the dose being underestimated. In an extreme (and highly unlikely) situation of zero radon removal from the respiratory tract, calculations based on data reported in Ref. [13] suggest that the degree of underestimation could be about 18% for typical dust particles in titanium mineral processing operations.

3.3.3.2. *Dose coefficients for ^{210}Pb and ^{210}Po in the furnace fume and precipitator dust*

In high temperature processes, the volatile radionuclides ^{210}Pb and ^{210}Po are likely to be removed from the original mineral matrix. When assessing doses arising from the inhalation of furnace fume and precipitator dust, the most appropriate lung absorption class needs to be determined experimentally because lung absorption class S cannot automatically be assumed. Dose coefficients for ^{210}Pb and ^{210}Po in lung absorption classes M and F are given in Table 6.

TABLE 6. INHALATION DOSE COEFFICIENTS FOR WORKERS (^{210}Pb , ^{210}Po)

Lung absorption class		Dose coefficient ($\mu\text{Sv/Bq}$)		Ref.
		1 μm AMAD	5 μm AMAD	
Pb-210	F	0.89	1.1	[2, 16]
	M	1.0	0.74	[13]
Po-210	F	0.60	0.71	[2, 16]
	M	3.0	2.2	[2, 16]

Note: AMAD — activity median aerodynamic diameter.

4. FEEDSTOCKS FOR THE PRODUCTION OF TITANIUM DIOXIDE AND OTHER TITANIUM-CONTAINING PRODUCTS

4.1. FEEDSTOCK CHARACTERISTICS

Titanium minerals used directly as feedstocks (ilmenite sand, rutile and leucoxene) have contents of titanium dioxide equivalent ranging from 45% upwards. The particle sizes of such feedstocks are in the range of 55–300 μm . Ilmenite rock has a lower content of titanium dioxide equivalent and is used mainly for the production of UGI. The thorium and uranium concentrations vary considerably from one mineral to another, but evidence suggests, as expected, that the thorium and uranium decay chains are in equilibrium. Further details are shown in Table 7. Values of radioactivity content outside the ranges given in the table can be found (see examples in the footnotes to the table), but are not representative of normal commercial production.

Upgraded feedstocks have contents of titanium dioxide equivalent ranging from 78% upwards and, with the exception of synthetic rutile, have lower radioactivity levels than those of the ilmenite from which they are derived. Further details are shown in Table 8. Again, values of radioactivity content

TABLE 7. COMPOSITION OF TITANIUM MINERALS

	TiO ₂ content (%)	Radioactivity content				Ref.
		Th-232 decay series		U-238 decay series		
		Thorium (ppm)	Radionuclide activity concentration (Bq/g)	Uranium (ppm)	Radionuclide activity concentration (Bq/g)	
Ilmenite sand	45–69	10–500	0.04–2	2–30 ^a	0.03–0.4 ^a	[19–25]
Ilmenite rock	34–45	0.3	0.001	0.1	0.001	[19]
Rutile	93–96.5	15–90 ^b	0.06–0.4 ^b	<10–60	<0.1–0.7	[20–23]
Leucoxene	70–90	80–700	0.3–3	20–60	0.2–0.8	[21, 22]

Note: Data were obtained from suppliers' feedstock specifications and material safety data sheets. Radioactivity data were, in addition, obtained from the reference sources indicated.

^a The use of a feedstock with a U-238 concentration of 1.5 Bq/g (120 ppm uranium) and a Ra-226 concentration of 2.3 Bq/g was reported in 1993 [20].

^b Non-typical concentrations of up to 350 ppm thorium, that is, 1.4 Bq/g Th-232 (and, by assumption, Ra-228), are reported in Refs [21, 22].

TABLE 8. COMPOSITION OF UPGRADED FEEDSTOCKS

	TiO ₂ content (%)	Particle size (µm)	Radioactivity content					
			Thorium decay series			Uranium decay series		
			Thorium (ppm)	Activity concentration (Bq/g)		Uranium (ppm)	Activity concentration (Bq/g)	
				Th-232	Ra-228		U-238	Ra-226
Synthetic rutile [21, 22]	88–94	75–300	35–480	0.1–1.9	0.1–1.9	7–60	0.09–0.7	0.09–0.7
SREP	93.5–95.5	90–300	40–90	0.16–0.37	0.5–1 ^a	3–15	0.04–0.15	<0.2
<i>UGI</i>								
Chloride slag	85–90	55–850	0.2–225 ^b	0.001–0.91 ^b	<0.1 ^c	0.2–20 ^b	0.002–0.25 ^b	<0.08 ^c
Sulphate slag	78–86	— ^d	0.2–30	0.001–0.12	<0.1	0.2–6	0.002–0.08	<0.08
Upgraded slag	93–95	55–850	0.2	0.001	<0.025	0.2	0.002	<0.002

Note: Data were obtained from suppliers' feedstock specifications and material safety data sheets. Radioactivity data for synthetic rutile were, in addition, obtained from Refs [21, 22]. SREP — synthetic rutile enhancement process; UGI — upgraded ilmenite.

^a Non-typical concentrations of up to 1.3 Bq/g can be found.

^b The majority is in the range of 0.2–30 ppm thorium (0.001–0.12 Bq/g Th-232) and 0.2–6 ppm uranium (0.002–0.08 Bq/g U-238).

^c Non-typical concentrations of 0.40–0.47 Bq/g Ra-228 and 0.30–0.34 Bq/g Ra-226 are reported for chloride slag used by one titanium metal producer [26].

^d The size varies from less than 50 µm to 'lump' size. More than 10% of the material may be less than 50 µm.

outside the ranges given in the table can be found (see examples in the footnotes to the table), but are not representative of normal commercial production.

Industrial operators frequently use blends of feedstocks to control the many constituents that determine product quality, process economics and residue management approach. A consequence of such blending is that the higher radionuclide concentrations found in some of the feedstocks used in the production process become moderated.

4.2. ILMENITE UPGRADING PROCESSES

4.2.1. Production of synthetic rutile

Synthetic rutile is produced in several countries, including Australia, China (Taiwan), India and Malaysia. Two basic processes are used, the Becher process and the Benilite process.

4.2.1.1. *The Becher process*

This process was developed around 1960 in Australia (the largest producer of synthetic rutile) and continues to be used in several plants in that country and elsewhere. A schematic representation of the process is shown in Fig. 5. Ilmenite is reacted with coal in a rotary iron reduction kiln at about 1100°C, along with other additives such as sulphur compounds to assist with the subsequent removal of impurities. The burning of the coal in the oxygen deficient atmosphere of the kiln generates carbon monoxide, which penetrates the cracks and pores in the ilmenite mineral grains and reacts with the iron oxide to form metallic iron and carbon dioxide. Unreacted carbon monoxide and other combustible volatile materials from the coal are burned in an afterburning chamber and the gas is cooled for cleaning before release. The 'reduced ilmenite' product of the kiln is cooled and then screened to remove the kiln discharge oversize, which includes coal char and sintered reduced ilmenite lumps. A magnetic separator recovers the iron-containing reduced ilmenite lumps and other iron-containing (magnetic) materials for crushing and feeding back to the screening step of the process. The coal char may be returned to the kiln, thus improving the energy efficiency of the process. Alternatively, the kiln discharge oversize may be disposed of as waste.

The fine reduced ilmenite is passed through a magnetic separator to remove the non-magnetic fines. The reduced ilmenite is then aerated in the presence of ammonium chloride while in the form of a slurry. This causes reoxidation of the iron in a very rapid rusting process. The ammonium chloride acts as a catalyst to

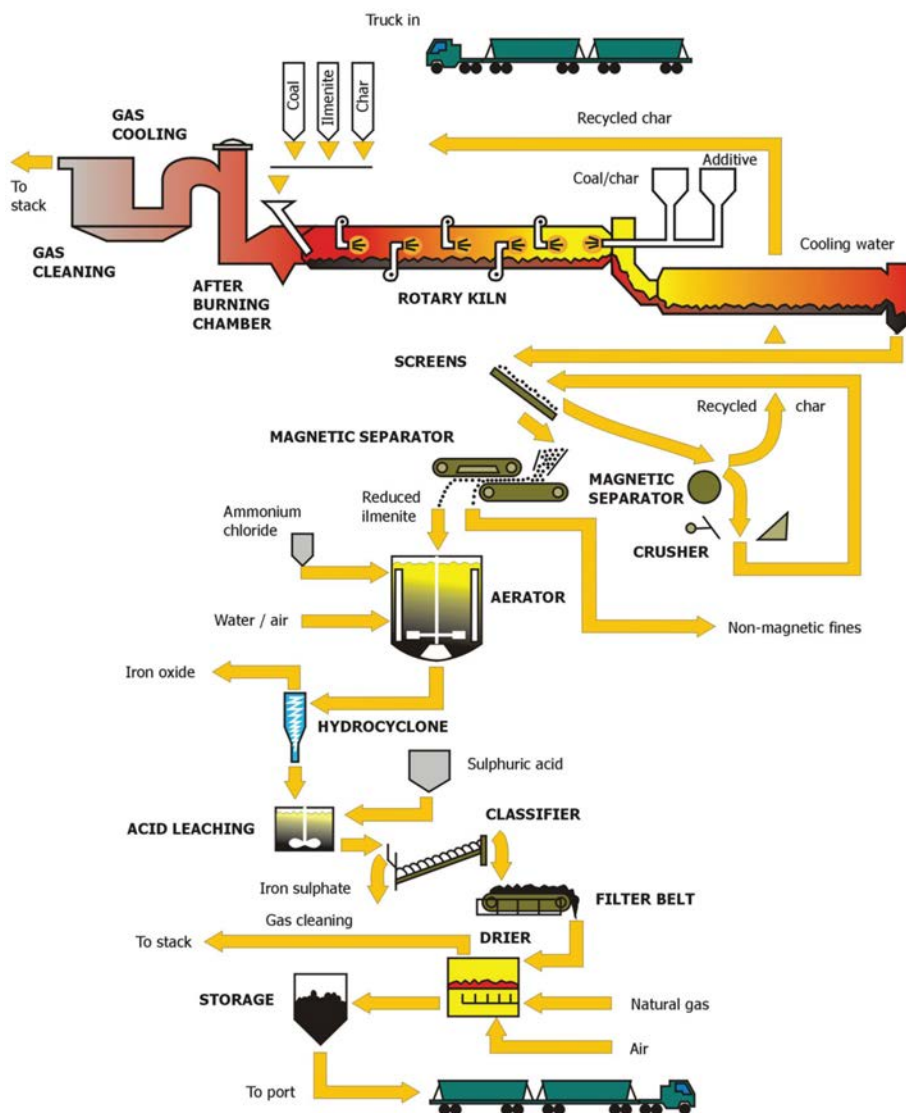


FIG. 5. The Becher synthetic rutile process.

accelerate the corrosion of the iron and prevents iron oxide from precipitating inside the titanium mineral grains. The fine iron oxide particles precipitate from the slurry and are separated from the coarser titanium dioxide grains in a hydrocyclone. A mild sulphuric acid treatment leaches the remaining iron oxide

and other impurities such as manganese. The leached synthetic rutile product, after drying, has a titanium dioxide content of 88–93%.

4.2.1.2. The Benilite process

This process, which is used, for instance, in Malaysia and India, is shown schematically in Fig. 6. The process involves the roasting of ilmenite for 6 h in a rotary iron reduction kiln at 800°C, in a similar fashion to the Becher process, followed by a multistage hydrochloric acid leach under pressure with a cycle period of 12 h or more to remove soluble iron and other impurities. The leached product is calcined¹¹ to produce synthetic rutile with a typical titanium dioxide content of 92–94%. The residual iron chloride solution is heated to 800°C in a hypopyrolysis reactor to produce hydrochloric acid, which is fed back into the leaching process, and an iron oxide residue.

4.2.1.3. The synthetic rutile enhancement process

A modification of the Becher process, known as the SREP, involves the addition of a flux at the thermal treatment stage. During this stage, the radionuclides migrate to the flux. Subsequent leaching of the treated reduced ilmenite results in a higher grade synthetic rutile product (SREP) with a lower concentration of radioactivity.

4.2.2. Production of upgraded ilmenite

Countries in which ilmenite is upgraded to UGI in the form of titanium slag include Canada, China, Norway, the Russian Federation, South Africa and Vietnam. Titanium slag production begins with the high temperature smelting of rock ilmenite or sand ilmenite with coal. Slag and iron are produced from the smelting operation. The iron is further processed to produce pig iron, steel or metal powders. The slag particle size is then adjusted to meet the specifications for chloride slag or sulphate slag as appropriate. Chloride slag is usually crushed and classified to produce a limited size range with relatively few fines. Sulphate slag is normally only crudely crushed with a front end loader or equivalent equipment because further grinding takes place during subsequent processing via

¹¹ Calcining is a process in which a material is heated to a high temperature without fusing, so that hydrates, carbonates or other compounds are decomposed and the volatile material expelled.

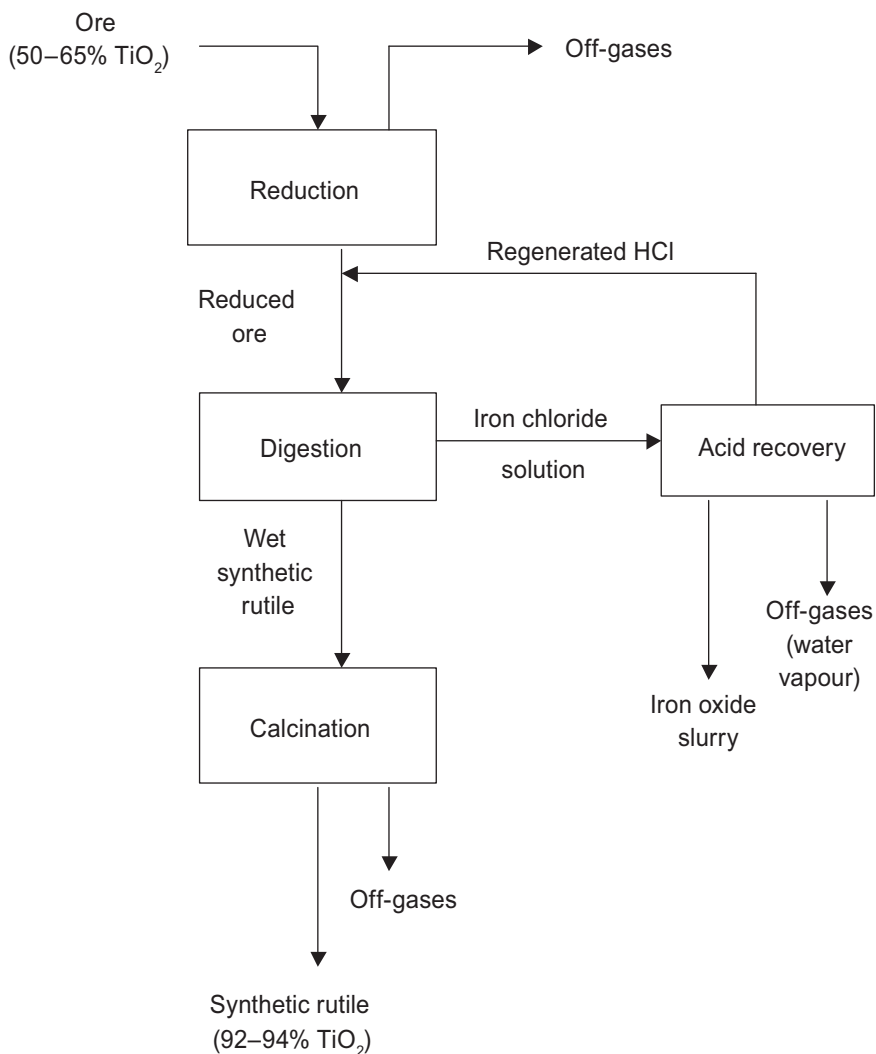


FIG. 6. The Benilite synthetic rutile process.

the sulphate route — water sprays are used to suppress dust during handling for transport, and the contained moisture is typically 2–4%. A diagram of the process is shown in Fig. 7.

A process for further upgrading of slag is carried out in Quebec, Canada, using sized slag produced from locally mined rock ilmenite. A diagram of the

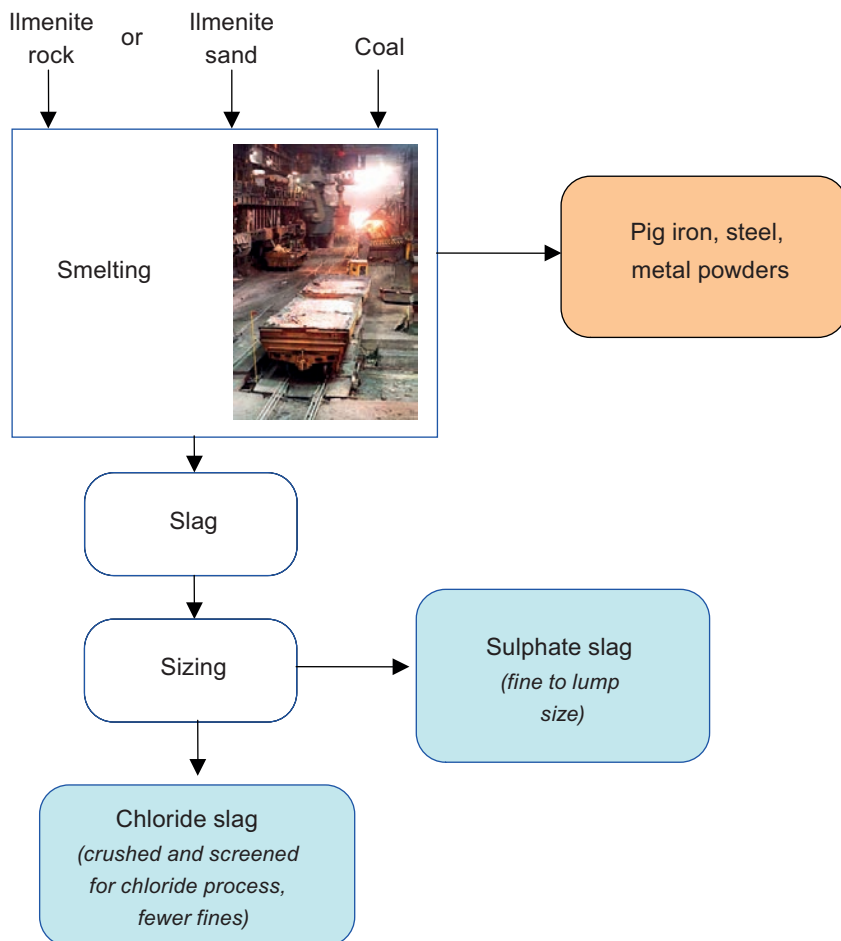


FIG. 7. The upgraded ilmenite production process for titanium slag.

process is shown in Fig. 8. The slag, known as Sorels[®], is thermally treated to achieve the desired modification of the structure so that iron, magnesium, calcium and other impurities can be readily leached out. The treated slag is cooled under controlled conditions and stored in readiness for leaching with hydrochloric acid. The leached product is separated from the spent acid liquor, and the recovered spent acid is pumped to the acid regeneration plant, while the leached solid is conveyed to the calcining stage. The acid regeneration plant converts the metal chlorides into gaseous hydrochloric acid and solid metal oxides, which are collected for disposal. The regenerated vapour is condensed and recirculated to the leaching section. After leaching, the upgraded slag product

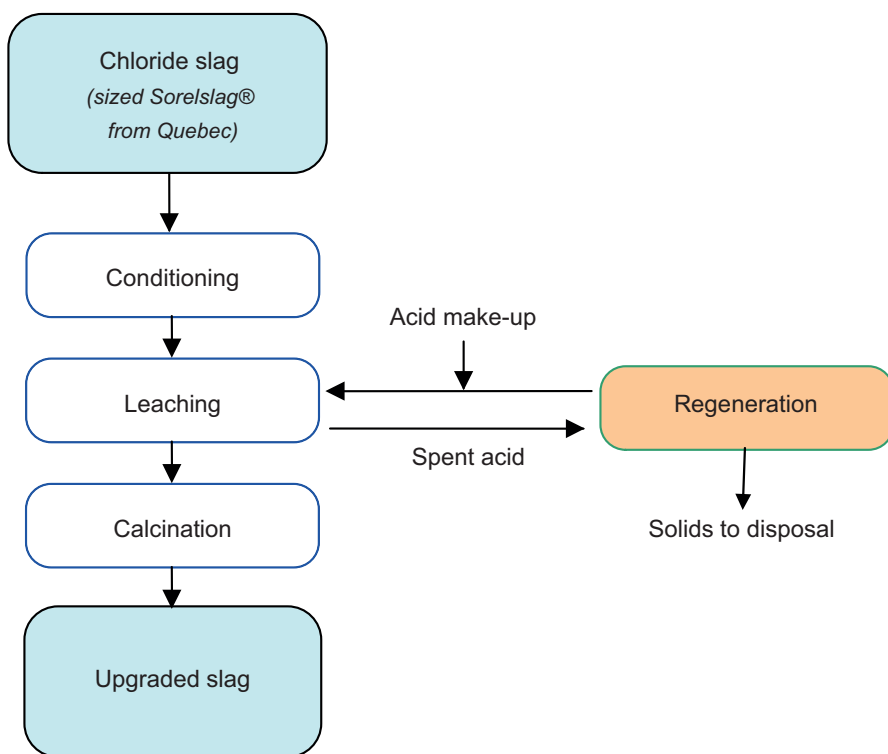


FIG. 8. The upgraded ilmenite production process for upgraded slag as carried out in Quebec, Canada.

(UGS) is calcined to remove any traces of water and residual metal chlorides, and stored in silos prior to shipment to customers.

4.2.3. Management of residues

Two of the residues from the Becher process may be used as by-products:

- (i) Solids precipitated as gypsum during the neutralization with lime of spent acid from the leaching step (known as neutralized acid effluent solids) may be used in a variety of applications, including use as a slow-release sulphur fertilizer and soil conditioner.
- (ii) Kiln discharge oversize from the screening of the reduced ilmenite, where not recycled to the process, may be used as a road base.

Alternatively, these residues, along with the other residues from the process (iron oxide, kiln scrubber solids, non-magnetic fines from the magnetic separator,

inert solids from the plant dust extraction system and very small quantities of scales) are disposed of as waste in engineered surface containment facilities.¹² The management of residues from the production, via the Becher process, of synthetic rutile in Australia, the main producer of this type of upgraded feedstock, is described in Annex II.

In the Benilite process, the main residue is iron oxide slurry. Operations in Malaysia are reported to produce 30 000 t/a of this residue, which is disposed of in surface containment facilities [27].

The production of slag generates dust from the smelting operation, while the upgraded slag process generates solid metal oxides. Both are disposed of as waste in surface containment facilities.

When mineral sands separation processes (see Annex I) are carried out at the same location as the subsequent chemical processes for upgrading of ilmenite, the waste streams are sometimes combined for purposes of disposal.

4.2.4. Radionuclide activity concentrations

During the various thermal and chemical processing steps, the radionuclides introduced via the ilmenite will tend to migrate selectively into various process streams according to their individual chemical and physical properties. Consequently, the radionuclide concentrations will change and equilibrium will be disturbed, as illustrated by the following general examples:

- (a) During smelting operations, the oxygen potential is such that long lived radionuclides contained in the ilmenite, such as the isotopes of thorium, uranium and radium, form refractory compounds (stable oxides) and migrate to the slag.
- (b) Dust entrained in the furnace fume from high temperature processes contains volatile radionuclides, notably ²¹⁰Po and ²¹⁰Pb. Such dust may also contain small amounts of uranium and thorium. The activity concentrations of these radionuclides may be elevated, particularly if the dust is repeatedly recycled back to the process to recover components of value.
- (c) During hydrometallurgical processing, radionuclides such as the isotopes of thorium and uranium will be more easily leached than others such as the isotopes of radium.

¹² Iron oxide, the main process residue, representing typically 40% of the ilmenite content, could potentially be used as a by-product; however, to date, no commercial application has been identified.

- (d) Under certain process conditions, radium isotopes may dissolve in aqueous systems and then precipitate and become concentrated within process scales, which may therefore exhibit elevated radionuclide concentrations. However, the quantities of such scales containing elevated concentrations of activity are very small.

In the Becher process, usually only a small proportion of the thorium and uranium content (typically 15%) is removed from the process stream via the residues, with the majority passing through to the synthetic rutile product. However, depending on the extent and nature of the leaching processes used, greater proportions of thorium, uranium and other decay chain elements (up to about 50%) may sometimes be removed. The quantity of synthetic rutile produced is typically 60% of that of the ilmenite from which it is derived. Thus, considering the mass balance and the radionuclide balance together, the radionuclide activity concentrations in the product may be higher or lower than the corresponding ilmenite values. The iron oxide solids that become separated from the ilmenite represent about 40% of the total process throughput, but contain only a small part of the total radioactivity. Their activity concentrations are therefore much less than that of the ilmenite and far below 1 Bq/g. There is no significant enrichment of radionuclides in the non-magnetic fines and the neutralized acid effluent solids, and their activity concentrations are generally also below 1 Bq/g. Radium becomes mobilized in aqueous systems during the process and, depending on the specific process conditions, can precipitate into process scales at elevated concentrations, but the quantities of such scales are very small.

In the Benilite process, radioactive elements such as thorium, uranium, radium, lead and polonium become dissolved in the hydrochloric acid. These generally end up in the iron oxide residue from the regeneration of hydrochloric acid from iron chloride, although the high process temperature creates the potential for accumulation of volatile radionuclides such as ^{210}Pb and ^{210}Po in the off-gas system. The distribution of ^{232}Th and ^{228}Ra in various process samples obtained from plants in India is shown in Table 9 [28].

In the SREP, which is designed specifically to minimize the radioactivity in the SREP product, most of the thorium and uranium in the ilmenite dissolves in the sulphuric acid and is then precipitated with the neutralized acid effluent solids. Small portions of the radioactivity end up in the other process residues. The dissolution process results in the selective mobilization of radionuclides and consequently the radionuclides in the SREP product are not in equilibrium. A typical distribution of radionuclides in the synthetic rutile enhanced process is shown in Table 10.

TABLE 9. DISTRIBUTION OF RADIONUCLIDES IN THE BENILITE PROCESS

	Proportion of the total activity (%)		Activity concentration (Bq/g)			
			Th-232		Ra-228	
	Th-232	Ra-228	Range	Mean	Range	Mean
Ilmenite	100	100	0.23–0.86	0.57	0.21–0.69	0.51
Iron oxide waste	76.6	45.0	0.75–1.20	1.02	0.40–0.71	0.58
Synthetic rutile product	18.4	9.2	0.11–0.23	0.19	0.08–0.15	0.09
Liquid effluent	5.0	45.8	—	—	—	—

TABLE 10. DISTRIBUTION OF RADIONUCLIDES IN THE SYNTHETIC RUTILE ENHANCEMENT PROCESS

	Proportion of the total activity (%)	Activity concentration (Bq/g)	
		Th-232 series	U-238 series
Ilmenite	100	0.04–2	0.03–0.4
Neutralized acid effluent solids	70–75	1.5–2.1	<1
SREP product	Th-232, U-238: 8–20 Ra-228, Ra-226: ~50	Th-232 0.16–0.37 Ra-228: 0.5–1.3 but normally <1	U-238: 0.04–0.15 Ra-226: <0.2
Non-magnetic fines	8–20	4	1.3
Iron oxide solids	3–5	<1	<1
Sintered reduced ilmenite lumps	<1	<1	<1

Note: SREP — synthetic rutile enhancement process.

Residues from the production of titanium slag and upgraded slag (essentially dust from the smelting operation and solid metal oxides from the upgraded slag process) are generally found to have radionuclide activity concentrations well below 1 Bq/g. For processes using ilmenite sand, the activity

concentrations in the furnace dust may occasionally exceed 1 Bq/g, depending on the characteristics of the feedstock. In some situations that are not considered representative of normal production, the furnace dust has been reported to contain ^{210}Pb and ^{210}Po at concentrations of 2.1–4.0 Bq/g in the coarsest of the dust fractions sampled and 8.5–13.5 Bq/g in the finer fractions [26].

4.3. OCCUPATIONAL EXPOSURE

4.3.1. Exposure pathways

As with any type of operation involving minerals with elevated activity concentrations, workers engaged in the handling, storage or upgrading of titaniferous feedstocks or in the management of residues from the upgrading process are exposed to gamma radiation when working close to large quantities of material. However, workers normally spend only limited periods at such locations. Smaller quantities of material with higher activity concentrations, such as radium rich scale, may also give rise to exposure to gamma radiation.

Internal exposure to natural radionuclides may result from the inhalation of airborne mineral dust. This may occur while working in the operational areas of the plant, during the handling of residues and the handling, cleaning or refurbishing of contaminated equipment (including equipment containing radium rich scales). Some fines may be generated during the upgrading of ilmenite to synthetic rutile and when crushing titanium slag. This may have implications for occupational exposure. The upgrading processes for synthetic rutile and chloride slag generally include a screening step to remove such fines, as they are difficult to retain within chloride process reactors due to the use of fluidized bed reactors. In sulphate slag, however, some residual fines can be tolerated because, as a first step in the sulphate process, this feedstock is ground to increase its solubility in acid. The presence of these fines may therefore require that greater attention be paid to dust exposure pathways.

In high temperature operations, such as the smelting of ilmenite, workers may inhale the volatile radionuclides ^{210}Pb and ^{210}Po entrained in the off-gas system, including during maintenance operations to remove the dust from the filters. Internal exposure to radon released from process material may sometimes need to be considered in poorly ventilated areas.

4.3.2. Exposure levels

4.3.2.1. Gamma radiation

Gamma dose coefficients, expressed as dose rates per unit activity concentration, are reported in Ref. [7] for exposure to bulk quantities of different types of NORM at a distance of 1 m. The values for ilmenite feedstocks (0.58 and 0.39 $\mu\text{Sv/h}$ per Bq/g for the ^{232}Th and ^{238}U decay series, respectively) are at the higher ends of the ranges reported for the various materials. Assuming that these dose coefficients also apply to other types of titaniferous feedstock, the incremental gamma dose rates associated with the handling, storage or upgrading of feedstocks can be calculated from the activity concentration data given in Tables 7 and 8. The results, expressed as incremental dose rates above background¹³, are presented in Table 11, along with direct measurements made in feedstock upgrading facilities and values published in material safety data sheets. The two sets of data are in good agreement, with the calculated data extending over wider ranges, as would be expected from the wide ranges of activity concentration data reported in Tables 7 and 8.

TABLE 11. INCREMENTAL GAMMA DOSE RATES IN WORKPLACES INVOLVING TITANIFEROUS FEEDSTOCKS

	Dose rate ($\mu\text{Sv/h}$) at 1 m from source	
	From calculations using dose coefficients for ilmenite	From facility specific measurements and material safety data sheets
Ilmenite stockpiles	0.03–1.32	0.01–0.76
Rutile stockpiles	0.07–0.51	0.33–0.34
Leucoxene stockpiles	0.25–2.1	0.43–0.70
Material in synthetic rutile and SREP plants	—	0.1–0.4
Synthetic rutile stockpiles	0.09–1.4	0.25–0.47

Note: SREP — synthetic rutile enhancement process.

¹³ When determining gamma exposure levels, it is common practice to establish the background gamma dose rates in the vicinity of the industrial facility. These are then subtracted from the values measured in the workplace to give incremental dose rates above background.

4.3.2.2. *Inhalation of radionuclides in mineral dust*

Airborne dust exposure levels measured in synthetic rutile and SREP plants are reported to be in the range of 0.13–0.34 mBq/m³. The gravimetric dust concentrations corresponding to these values depend on which radionuclides were included in the activity measurements (in particular, whether only long lived alpha emitters were included or whether other radionuclides were included as well¹⁴) and on the type of material involved. Based on the activity concentration ranges for ilmenite, synthetic rutile and SREP given in Tables 7 and 8, the reported range of airborne activity concentrations corresponds to gravimetric dust concentrations in the range 0.005–1.3 mg/m³. This is typical of the range one would expect to find in workplaces of this type, with a conservative value of 1 mg/m³ having been assumed in Ref. [7].

4.3.2.3. *Inhalation of radionuclides in furnace dust*

Activity concentrations of ²¹⁰Pb and ²¹⁰Po measured in furnace dust collected in an ilmenite smelting facility are reported in Section 4.2.4, but no facility specific data are available on exposure levels. In Ref. [7], a gravimetric dust concentration of 1 mg/m³ is conservatively assumed for the airborne furnace dust inhaled in a typical high temperature process involving NORM. On the basis of this assumption, and assuming in addition that the activity concentrations in the dust particles are of the order of 1 Bq/g (see Section 4.2.4), the corresponding exposure level is of the order of 1 mBq/m³.

4.3.3. **Effective dose**

4.3.3.1. *Gamma radiation*

No facility specific data are available on the periods of exposure of workers to sources of gamma radiation. When considering typical exposure scenarios for NORM industries, it was assumed in Ref. [7] that a worker spends 400 h/a at a distance of 1 m from a large, unshielded volume of material. Applying this assumption to the full range of dose rate measurements reported in Table 11 (0.01–0.76 µSv/h) gives an incremental effective dose from gamma radiation in the range 0.004–0.3 mSv/a.

¹⁴ Gross alpha counting is widely used for routine analysis of activity in airborne dust particles [4]. Owing to the possibility of escape of radon from the dust particles, only the long lived radionuclides can be guaranteed to remain at their original activity concentrations.

4.3.3.2. Inhalation of radionuclides in mineral dust

The ranges of activity concentration given in Tables 7, 8 and 10 for various process materials, together with the dose coefficients listed in Table 5, provide the starting point for estimating the committed effective dose received by a worker from inhalation of dust. However, in the absence of additional facility specific data, the values of some additional exposure parameters have to be assumed. The assumptions made in Ref. [7] for typical exposure scenarios in NORM industries, together with comments on how these might apply to facilities handling or upgrading titaniferous feedstocks, are given in the following:

- (a) The dust AMAD is assumed to be 5 μm . As explained in Section 3.3.1, this value may be conservative for facilities handling and processing feedstocks and, depending on the exact nature of the process, particle size measurements conducted in the workplace concerned may indicate that a higher value such as 10 μm is more appropriate.
- (b) A worker is assumed to inhale dust at a rate of 1 mg/h. This rate of intake corresponds to an airborne dust concentration of approximately 1 mg/m^3 without the use of respiratory protection. As reported in Section 4.3.2, the range of gravimetric dust concentrations derived from dust activity concentration measurements in feedstock upgrading plants is 0.005–1.3 mg/m^3 . The assumed rate of intake of 1 mg/h thus lies towards the upper end of the estimated range.
- (c) A worker is assumed to inhale dust for the full annual working period (2000 h). In practice, the exposure period could be shorter, depending on the nature of the work.

The inhalation doses estimated on the basis of these assumptions can therefore be considered as reasonable but conservative. The results of the calculations are presented in Table 12.

4.3.3.3. Inhalation of radionuclides in furnace dust

The activity concentrations measured in furnace dust samples from an ilmenite smelting plant (see Section 4.2.4) in conjunction with the dose coefficients listed in Tables 5 and 6 can be used to estimate the committed effective dose received by a worker. However, in the absence of further facility specific data, values of certain additional exposure parameters have to be assumed. The following assumptions are based on a consideration of typical exposure scenarios for NORM industries in Ref. [7]:

- (a) The fine and coarse fractions of the dust samples are assumed to have AMADs of 1 and 5 μm , respectively.
- (b) All of the dust samples are assumed to contain ^{210}Pb and ^{210}Po with activity concentrations of the order of 1 Bq/g.
- (c) A worker is assumed to inhale dust at a rate of 1 mg/h. This rate of intake corresponds to an airborne dust concentration of approximately 1 mg/m^3 without the use of respiratory protection.
- (d) A worker is assumed to inhale the finer dust particles for a period of 600 h/a while working in an area near the furnace where the air is contaminated with fume. During maintenance of the dust filtration system, a worker is assumed to inhale the coarser dust particles for a period of 100 h/a.

The results of the dose assessment are given in Table 13. The annual committed effective dose is in the range of 0.0002–0.006 mSv.

4.3.3.4. *Total effective dose*

In a worst case situation, in which all of the above mentioned exposure pathways apply simultaneously to a worker, the total effective dose received by that worker in a year would be in the range of <0.01–0.81 mSv.

TABLE 12. CONSERVATIVE ESTIMATES OF DOSES RECEIVED BY WORKERS FROM INHALATION OF RADIONUCLIDES IN MINERAL DUST

Inhaled material	Committed effective dose (mSv) in a year
Ilmenite sand	<0.01–0.23
Rutile	0.01–0.09
Synthetic rutile	0.02–0.24
SREP	0.05–0.10
UGI: titanium slag	<0.01–0.10
UGI: upgraded slag	<0.01
Non-magnetic fines (SREP production)	0.5

Note: SREP — synthetic rutile enhancement process; UGI — upgraded ilmenite.

TABLE 13. DOSES RECEIVED BY WORKERS FROM INHALATION OF RADIONUCLIDES IN FURNACE DUST

Lung class	Dose per unit intake ($\mu\text{Sv/Bq}$)		Annual dose per unit dust activity concentration ($\mu\text{Sv per Bq/g}$)	Assumed dust activity concentration (Bq/g)	Annual committed effective dose (mSv)
	Pb-210	Po-210			
<i>Workers in furnace area (600 h/a)</i>					
S	5.2	3.9	9.1	1	0.006
M	1.0	3.0	4.0	1	0.002
F	0.89	0.60	1.49	1	0.000 9
<i>Workers maintaining the dust filtration system (100 h/a)</i>					
S	4.3	2.7	7.0	1	0.000 7
M	0.74	2.2	2.94	1	0.000 3
F	1.1	0.71	1.81	1	0.000 2

4.4. PUBLIC EXPOSURE

As reported in Section 4.2.4, the activity concentrations in most process materials are low, but there are some instances in which members of the public could become exposed to materials containing moderately elevated levels of radioactivity. Members of the public in the vicinity of industrial operations in which titaniferous feedstocks are handled, stored or upgraded could be exposed to external gamma radiation from bulk quantities of material and to inhalation of dust. There are also potential pathways arising from the management of solid residues and the discharge of effluents from the feedstock upgrading process. These pathways may include external gamma exposure, inhalation of dust and ingestion of contaminated food and water. However, measures consistent with good environmental practice should be sufficient to ensure that exposures do not become significant. Data furnished to regulators in the course of normal operations indicate that doses are unlikely to exceed a small fraction of the public dose limit.

4.5. REGULATORY CONSIDERATIONS

Reference to Section 4.2.4 demonstrates that the radionuclide activity concentrations in most of the process materials are likely to be below 1 Bq/g, implying that many of the process steps would not need to be formally regulated. Even where the activity concentration exceeds 1 Bq/g, as may be the case for non-magnetic fines arising from SREP production, furnace dust from ilmenite smelting and radium scales from wet chemical processes, the effective doses received by workers are likely to be below 1 mSv/a. This is especially the case if normal OHS measures (possibly supplemented by restrictions on occupancy periods in certain areas) and environmental protection measures are in place to control non-radiological hazards. Activities involving these materials are therefore candidates for exemption or, at most, notification without the need for formal authorization. NORM residues designated for disposal as waste, for instance, in landfill disposal facilities, are unlikely to require any special controls beyond those normally in place for dealing with industrial waste. Similarly, it is likely that normal requirements for industrial effluent treatment will be sufficient to take care of any radiological considerations.

The activity concentration information given in Section 4.2.4 indicates that all titaniferous feedstocks and most of the other process materials will fall outside of the scope of the Transport Regulations [3] and will therefore be exempt from any requirements during transport. The activity concentrations of some process residues produced in small quantities, such as furnace dust and radium rich scale, may be high enough to bring such materials within the scope of the Transport Regulations.

5. PRODUCTION OF TITANIUM DIOXIDE BY THE SULPHATE PROCESS

5.1. PROCESS DESCRIPTION

5.1.1. Main process

The sulphate process involves the use of concentrated sulphuric acid to dissolve ilmenite or sulphate slag. A schematic view of the process typically used is shown in Fig. 9, although variations of this process exist. Where ilmenite is used as the feedstock, the content of titanium dioxide equivalent has to be relatively low in order to provide the preferred minimum iron content. Where slag is used, a titanium dioxide content of 87% is probably the maximum that can be tolerated without unacceptable losses in conversion efficiency.

Ilmenite and titanium slag feedstocks are normally brought in by bulk carrier through a nearby port in shipments of up to 25 000 t. Offloading takes place onto the dockside or directly into trucks for immediate transfer to the production site. Storage of the material, whether at the dockside or the production site, involves stacking in open piles or transfer to warehouses or silos. Where necessary for aiding the acid digestion process, the feedstock is milled to an average particle size of 15–30 µm in a ball mill and dried.

The ilmenite or titanium slag (or a carefully controlled blend) is digested with highly concentrated sulphuric acid (80–95%) to form titanyl sulphate and ferrous sulphate. A highly exothermic reaction is initiated at a temperature of about 140°C by the addition of measured quantities of steam, water and diluted acid. The basic digestion reaction is:



Digestion of the feedstock is carried out as a batch process or, less commonly, as a continuous process. During the batch process, the exothermic reaction raises the temperature of the reactor to 180–210°C and water is evaporated. The off-gases, which contain sulphur oxides and dust, are cleaned by scrubbing systems. The resulting solid cake is dissolved in a mixture of dilute acid ('weak acid' recovered from subsequent washing steps) and water.

When ilmenite is used as the primary feedstock, a reduction step is needed at this stage, in which the digester liquor is contacted with scrap iron to convert ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}). This prevents the iron from remaining with the titanium dioxide during the subsequent processing steps. The reduction process generates a small amount of hydrogen that is normally released to the

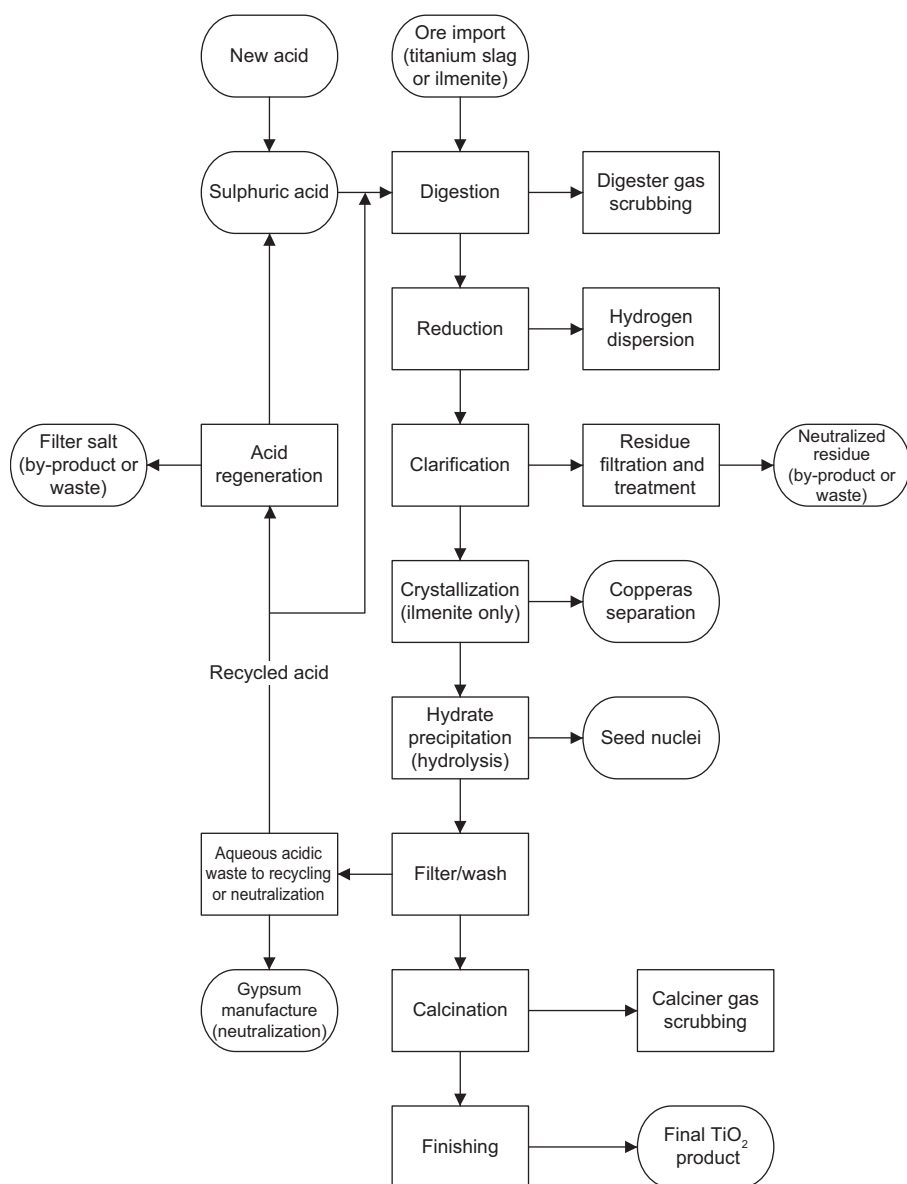


FIG. 9. The sulphate process.

atmosphere. The reduction step is not necessary when the primary feedstock is slag or a blend of slag and ilmenite.

Undissolved feedstock and other solids suspended in the acid solution are removed by flocculation in a clarification vessel, filtered and washed with weak

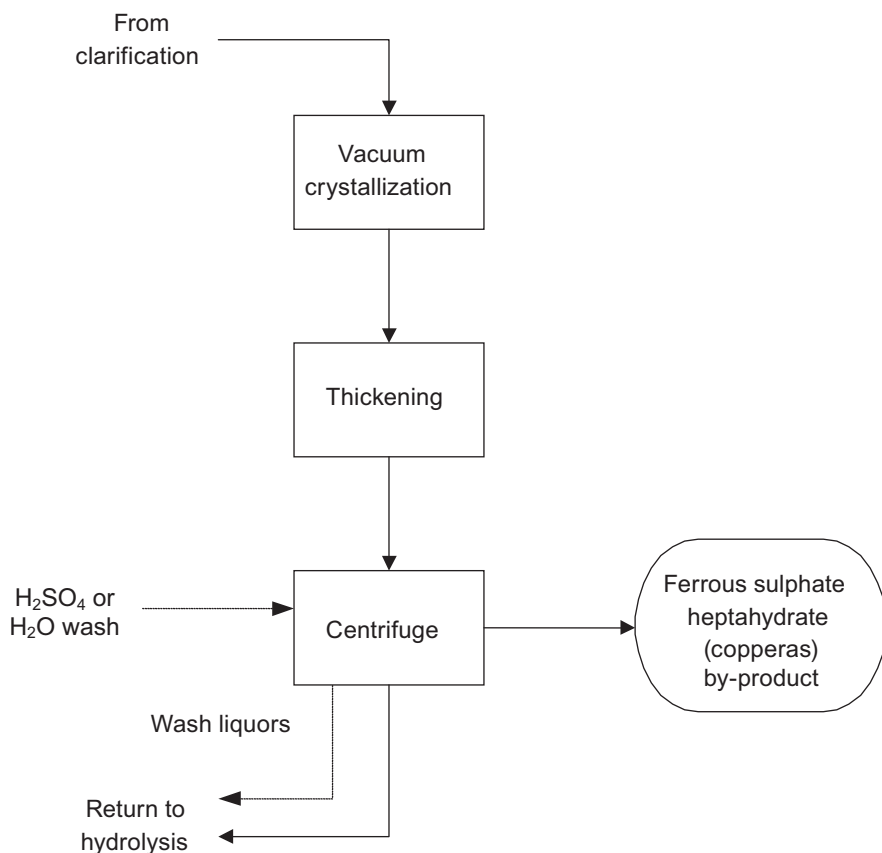
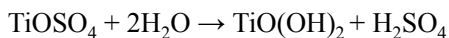


FIG. 10. Separation of copperas from the titanyl sulphate solution.

acid to recover the titanyl sulphate. The acidic filtrate liquors from this washing process are recycled back to the process and the solid ‘digester residue’ is used as a by-product or disposed of as waste.

When ilmenite is the primary feedstock, the clarified solution is usually pumped to batch cooler crystallizers where the bulk of the iron sulphate is separated as crystalline ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), known as copperas. The separation process, shown schematically in Fig. 10, involves vacuum crystallization followed by thickening and removal by centrifuge.

The titanyl sulphate solution is then hydrolysed with steam in mild steel vessels lined with rubber or brick to produce hydrated titanium dioxide:



After boiling for several hours, the liquor is cooled to 60°C to precipitate the hydrated titanium dioxide. Control of the final crystal size and form (anatase or rutile) of the titanium dioxide is achieved through the addition of titanium-containing seed nuclei.

The precipitated hydrated titanium dioxide is separated from the 'mother liquor' (which, with a strength of about 20–25% H_2SO_4 , is commonly referred to as 'strong acid') using vacuum filters known as Moore filters. If the strong acid filtrate is to be recovered, it is reconcentrated by multistage evaporation to about 80% and used in the digestion step or sold as a by-product. The increases in temperature and acidity associated with this reconcentration process lead to the precipitation or crystallization of ferrous sulphate monohydrate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), which is removed by filtration. Alternatively, the strong acid filtrate may be neutralized with lime or limestone to generate gypsum.

After separation from the mother liquor, the hydrated titanium dioxide filter cake is washed with water or weak acid. The resulting solid is mixed with dilute sulphuric acid to form a slurry. Aluminium or a solution of trivalent titanium is usually added as a reducing agent to maintain the residual iron in the ferrous state. The slurry is subjected to leaching (sometimes called bleaching) at 50°C to remove the final traces of iron and then undergoes final washing and drying to a pulp. This pulp still contains adsorbed sulphuric acid that cannot be removed by washing. Conditioning agents and rutile seed nuclei can be added to the pulp at this stage to enhance crystallite growth and determine the final crystal form. The pulp is then fed to rotary kilns, where it is calcined to expel water and oxides of sulphur while moving under gravity, counter-currently to the combustion gases. Titanium dioxide dust particles are removed from the gas by scrubbing and recycled to the process.

In the so-called 'finishing' step, the resulting solid is cooled, milled, coated, washed, dried, finely ground ('micronized') and packed. The milling is a two stage process, with the particle size being reduced first to 75–100 μm and then to 0.2–0.4 μm , the optimum size for use as a pigment. The coating step improves pigment durability, lessens the yellowing that occurs in certain types of paints and improves pigment dispersibility. Coating involves the addition of coating agents such as soluble sulphates or chlorides and adjustment of the pH to cause deposition of small amounts of silica, titania, zirconia or alumina onto the pigment surfaces. After washing and drying, the pigment is entrained in high velocity steam in a fluid energy mill ('micronizer') to break down pigment agglomerates into very small particles. Many titanium dioxide pigments are also given a light organic surface treatment to improve their dispersibility in a variety of media. This is usually carried out during the final milling stage. Various organic compounds are used, the most common being polyols, amines and

silicone derivatives. The final product is packed in sacks or ‘semi-bulk’ containers, or is dispatched in bulk using road tankers.

5.1.2. Generation of by-products

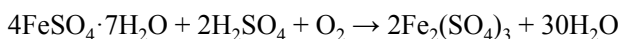
5.1.2.1. Iron sulphate

When ilmenite is used as the feedstock, copperas (ferrous sulphate heptahydrate) is separated from the main process stream after the clarification step (see Fig. 10). The desired free acid content of this by-product is obtained by washing with water or acid. It contains a small amount of free moisture and is sometimes referred to as ‘damp crystal’. To improve the handling properties, this free moisture may be removed by drying. For some applications, the material is further dried to produce ferrous sulphate monohydrate. Ferrous sulphate monohydrate is also generated during the recycling of strong acid from the hydrolysis step. This material is usually referred to as filter salt and may be used as a by-product or neutralized and disposed of as waste.

Significant quantities of copperas are converted to ferric sulphate by oxidation, either using a mixture of sulphuric and nitric acids:



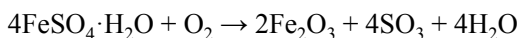
or using oxygen and sulphuric acid at a temperature of at least 150°C and a pressure of about 1.5 MPa:



Copperas generated after the clarification step and ferrous sulphate monohydrate generated from the strong acid recycling process may both be converted into iron oxide (Fe_2O_3) by roasting, according to the reactions:



and



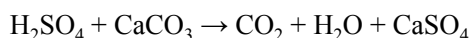
Sulphur oxides released from the process are usually absorbed into water to generate sulphuric acid. This can be used in the digestion process or sold as a by-product. The iron oxide from copperas roasting is used as a pigment in a wide range of decorative finishes where yellow, red and black pigmentations are

required. The iron oxide from acid recycling is used as a lower purity pigment, typically in the construction industry.

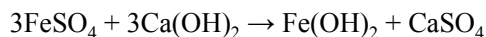
The principal uses of the various iron sulphate by-products are summarized in Table 14.

5.1.2.2. *Gypsum*

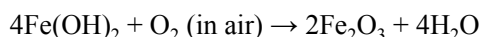
The alternative to recovery of the strong acid by reconcentration is neutralization with lime or limestone to produce gypsum as a by-product. Even when it is decided to recover the strong acid, gypsum may still be produced by neutralization of the weak acid stream. Typically, the acid is first neutralized with calcium carbonate to produce a pure form of gypsum ('white gypsum'):



Then, by increasing the pH to above 7 using calcium hydroxide, the remaining ferrous sulphate is precipitated as a less pure form of gypsum ('red gypsum') along with iron compounds:



and



White gypsum is used in the construction industry as a component of plasterboard and cement and in the paper industry as a filler or coating. Red gypsum is used as an agricultural soil conditioner and for landscaping. An investigation has shown that red gypsum is also suitable for use as a setting retardant in cement [29] — currently, natural (white) gypsum is used for this purpose by adding it to the clinker at a concentration of 3–5%.

5.1.2.3. *Digester residue*

Material that is not dissolved in the digestion step, comprising unreacted feedstock and silicates, is separated at the clarification stage. It is usually dewatered by filtration and neutralized with lime or limestone. The neutralized material is used as a by-product in the construction industry or disposed of as waste at a landfill site. The choice depends on available markets, the feedstock

TABLE 14. USES OF IRON SULPHATE BY-PRODUCTS

Area of application	Use	By-product		
		Copperas	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (dried) and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ from copperas treatment	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$ from strong acid recovery (filter salt) $\text{Fe}_2(\text{SO}_4)_3$
Water treatment	Coagulant	X		X
Agriculture, horticulture	Prevention of iron chlorosis in plants grown on iron deficient soils	X		X
	Moss control	X	X	
	Raw material for production of fertilizer for iron deficient soil			X
Pigments	Conditioning of alkaline soil	X		X
	Raw material for iron oxide pigments	X		X
Cement	Reduction of Cr (VI) to Cr (III) to prevent chromium dermatitis	X	X	X
	Iron supplement		X	
Chemical products	Various	X		X
Sulphuric acid	Source of sulphur	X		X

type (including its radionuclide content) and local environmental regulations. Another possibility is for the residue to be combined with the waste acid stream destined for neutralization to produce gypsum.

5.1.2.4. Sulphuric acid

Sulphuric acid recovered from the main process (see Section 5.1.1) or from the roasting of ferrous sulphate monohydrate (see Section 5.1.2.1) is recycled directly to the process or sold as a by-product.

5.1.2.5. Carbon dioxide

Where it is decided that sulphuric acid from the process is to be neutralized with calcium carbonate to produce gypsum (see Section 5.1.2.2), the use of a closed reaction vessel allows the carbon dioxide released from the process to be collected and, after purification and liquefaction, sold as a by-product.

5.1.3. Management of waste

5.1.3.1. Atmospheric emissions

The sulphate process involves some emissions to the atmosphere, primarily dust (from the size reduction of raw material and final product) and sulphur dioxide (from the digestion and calcining processes). Lesser emissions include hydrogen sulphide from the digestion process (particularly for slag feedstocks) and acid mist, dust and nitrogen dioxide from the calcining process. Dust emissions are minimized by the high density of the ore and the use of cyclones and bag filters. Gaseous emissions from the digestion process are minimized by the use of water and caustic scrubbing systems. Sulphur dioxide emissions from the calcining process are minimized in most plants by the use of catalytic systems that convert sulphur dioxide to sulphur trioxide, which is subsequently absorbed into water for the production of sulphuric acid for use as a by-product or for recycling into the process.

5.1.3.2. Liquid effluents

In facilities where gypsum is produced, the main effluent comprises the residual water following removal of the gypsum solids by filtration or settling. Much of the weak acid resulting from the various washing steps is recycled. If discharged as an effluent, the levels of sulphate and metals (particularly iron) are the main environmental concerns. These contaminants are closely monitored and

are usually controlled by local discharge limits. During the deposition of surface coatings on the titanium dioxide pigment as part of the finishing step, the use of caustic reagents to adjust the pH generates sodium sulphate. This is discharged into the water system along with suspended solids also generated in the finishing step. Wastewater streams are generated from the scrubbing of gases in the digestion step and also from the calcining and finishing steps.

5.1.3.3. Solid wastes

Neutralized digester residue, iron sulphates and gypsum are normally sold as by-products. Where suitable markets cannot be found — for instance, owing to an unfavourable production location, oversupply or fluctuating demand — these materials are disposed of in a landfill facility. Such a situation is rare for copperas or white gypsum, but can be more common for ferrous sulphate monohydrate (filter salt) and iron oxide from acid recycling and for red gypsum from acid neutralization. The use of neutralized digester residue in construction applications may require consideration of its radioactivity content.

The accumulation of scales and sludges is known to occur in the sulphate process. The most likely areas for their formation are those where cooling, filtration and precipitation take place. These scales and sludges are removed during maintenance or decommissioning. In addition, some of the equipment used in the sulphate process is rubber lined and is at some stage refurbished (involving replacement of the lining) or discarded. The landfill disposal of scales and rubber linings, as well as the reuse, decontamination or disposal of the equipment to which they are attached, may require special consideration because the concentrations of certain radionuclides, particularly radium isotopes, in these materials are sometimes significantly elevated. For instance, it may be necessary to use decontamination or disposal facilities specially authorized for the acceptance of radioactive material.

To control discharges to the atmosphere, dust particles are removed from various off-gas streams. The dust originates mainly from the milling of feedstocks (where this is found to be necessary), the calcining of titanium dioxide pulp, the milling and micronizing of titanium dioxide product and the hot air drying of gypsum. The dust is returned to the process or disposed of as waste in landfill facilities.

5.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

5.2.1. Migration of radioactive species

5.2.1.1. Uranium and thorium

Since uranium and thorium oxides are soluble in hot sulphuric acid, most of the uranium and thorium remains in solution during the clarification and hydrolysis stages and eventually leaves the main process stream via the strong acid filtrate from the Moore filters. Thereafter, two possibilities exist:

- (i) If the strong acid filtrate is neutralized to form gypsum, the increase in pH value causes uranium and thorium oxides to come out of solution. With full neutralization, the mass dilution is about four- to fivefold compared with the original feedstock, so the activity concentrations of uranium and thorium isotopes in the gypsum by-product are low. Should neutralization be incomplete, some uranium and/or thorium could end up in the liquid effluent stream, but this is considered unlikely.
- (ii) If the strong acid filtrate is recycled by reconcentration, a significant fraction of the uranium and/or thorium is removed with the ferrous sulphate monohydrate.

5.2.1.2. Radium

Radium sulphates are highly insoluble, so most of the radium (evidence suggests 75–90%) leaves the main process stream via the digester residue, giving rise to enhanced radium concentrations in this residue. The remainder of the radium remains with the process flow, and some of it subsequently precipitates in areas of temperature change and solid–liquid separation, particularly where there are abrupt decreases in pressure such as occurs during copperas crystallization. Thus, scale deposited in areas such as the copperas crystallizers, Moore filters and precipitation tanks exhibits high radium concentrations. The radium in scale is often associated with barium sulphate.

5.2.1.3. Lead

Lead sulphate is only slightly soluble in acid, so some lead leaves the main process stream with the digester residue, although in lesser amounts than radium, and some deposition occurs as scale. Any lead remaining in solution is readily precipitated with gypsum during neutralization of the strong acid filtrate.

5.2.1.4. *Bismuth*

Bismuth oxides are soluble in sulphuric acid. Thus, a significant amount of bismuth remains in solution (evidence suggests 40–75%) and, like uranium and thorium, eventually leaves the main process stream with the strong acid filtrate from the Moore filters. Bismuth sulphate tends to decompose in water and, although removed by neutralization, some deposition associated with wash streams is possible. Since the liquid effluent stream, if not fully neutralized, comprises primarily wash streams, it is therefore likely that the amount of bismuth in the effluent will be even smaller than the amounts of uranium and thorium. Since the half-life of ^{210}Bi is only 5 d, equilibrium with its parent ^{210}Pb is largely re-established within a month.

5.2.2. **Activity concentrations in process materials**

Industry data for sulphate process materials derived from a variety of feedstocks show no evidence of radionuclide activity concentrations exceeding 1 Bq/g in the following eight types of process material:

- (1) Titanium dioxide product;
- (2) Copperas by-product;
- (3) Iron oxide by-product;
- (4) Ferrous sulphate monohydrate by-product from acid recycling;
- (5) White and red gypsum by-products;
- (6) Sulphuric acid by-product;
- (7) Dried clarifier tank sediment and sediment in sewage;
- (8) Dust from off-gas filters.

The radionuclide activity concentrations in four of these eight process materials — titanium dioxide product, copperas by-product, iron oxide by-product and dust from off-gas filters — are below 0.1 Bq/g. In some of these materials, the detailed analytical data indicate disturbance of equilibrium conditions in the ^{232}Th and/or ^{238}U decay chains; however, considering the low activity concentrations, this does not have significant implications for radiation

protection.¹⁵ Recently published activity concentration data for TiO₂ production using ilmenite [30] or a mixture of 85% ilmenite and 15% titanium slag [29] are consistent with the above mentioned general industry data (see Table 15).

Radionuclide activity concentrations measured in samples of digester residue, scale and discarded filter cloths are found to be highly variable and, in the case of scale and filter cloths, can sometimes reach values of the order of 1000 Bq/g. The radionuclide concentrations are generally higher for the ²³²Th decay series than for the ²³⁸U series. The results are presented in Tables 16–18 and can be summarized as follows:

- (a) Radionuclide activity concentrations in digester residue derived from ilmenite feedstocks are in the range of <0.04–2.6 Bq/g. The concentrations in material derived from feedstocks containing 90% or more slag are less than 1 Bq/g. Regardless of the type of feedstock used, there is evidence of enhanced concentrations of ²²⁸Ra (or ²²⁸Ac) and ²²⁶Ra.
- (b) Radionuclide activity concentrations in scale deposited in various steps of the process vary over a very wide range (<0.1 to 1644 Bq/g), with the highest values being found in scale from the pre-hydrolysis heat exchanger.
- (c) Radionuclide activity concentrations in discarded filter cloths from Moore filters vary over a very wide range (0.04–968 Bq/g). The concentrations in a cloth from a gypsum filter were found to be less than 1 Bq/g.

Contaminant levels in liquid effluent streams are generally controlled in accordance with environmental regulations, and analyses confirm that the radionuclide content is low, ranging from non-detectable levels up to maximum values of 0.3 and 1.0 Bq/L for ²³⁸U and ²³²Th decay series radionuclides, respectively. In most of the samples analysed, the concentrations do not exceed 0.02 Bq/L. Before treatment, radionuclide concentrations can of course be considerably higher — values of 1.5–12.4 Bq/L were found in one untreated

¹⁵ Some evidence of ²²⁸Ra and/or ²²⁶Ra disequilibrium is found in the pigment product and gypsum by-product derived from ilmenite and slag feedstocks and in copperas derived from ilmenite. For a feedstock blend of 90% slag and 10% ilmenite, samples of recycled sulphuric acid and the associated ferrous sulphate and oxide have been found to contain enhanced thorium and/or uranium concentrations. Ferrous sulphate derived from ilmenite shows, in one instance, a depletion of ²²⁸Ra and ²²⁶Ra and, in another two instances, enhanced concentrations in the lower part of the ²³²Th decay chain (²¹²Pb and ²¹²Bi) compared with the concentration higher in the chain (²²⁸Ac). In some instances, enhanced concentrations of ²¹²Pb and ²¹²Bi are found in both white and red gypsum derived from ilmenite. Other data show depleted concentrations of ²²⁶Ra and ²²⁸Ra in white gypsum but little or no depletion in red gypsum.

TABLE 15. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN SULPHATE PROCESS MATERIALS

	Radionuclide activity concentration (Bq/g)					Ref.
	Th-232 decay series			U-238 decay series		
	Th-232	Ra-228	Th-228	U-238	Ra-226	
Digestion liquor	0.018	0.003	0.130	0.020	0.12	[30]
Copperas	0.008	nd ^a	0.009 1	0.0009	nd	[30]
	0.013	0.004	— ^b	0.001 5	nd	[29]
Ferrous sulphate monohydrate	0.365	0.044	0.411	0.053	0.011	[30]
	0.365	0.043	—	0.053	0.009 1	[29]
Red gypsum	0.115	0.088	0.122	0.019 4	0.014	[30]
	0.127	0.091	—	0.020	0.014	[29]
TiO ₂ pulp	0.005	0.025	0.008	0.003	0.006	[30]

^a nd: not detectable.

^b —: not reported.

TABLE 16. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN DIGESTER RESIDUE

Residue	Radionuclide activity concentration (Bq/g) ^a (maximum in parentheses)															
	Th-232 decay series								U-238 decay series							
	Th-232	Ra-228	Ac-228	Th-228	Th-228	Pb-212	Bi-212	Tl-208	Not specified	U-238	Th-234	Th-230	Ra-226	Pb-214 Bi-214	Pb-210	Not specified
From ilmenite digestion	— ^b	—	—	—	—	—	—	—	(<1)	—	—	—	—	—	—	(<LLD) ^c
From ilmenite digestion	—	0.557	—	0.053	—	—	—	—	—	—	<0.09	<0.04	1.292	—	—	—
From ilmenite digestion [30]	0.373	2.616	—	0.704	—	—	—	—	—	0.312	—	—	0.877	—	—	—
From ilmenite digestion, neutralized, dry (for landfill)	—	—	1.9	—	—	—	0.5	—	(2.5)	—	—	—	—	—	—	0.6 (0.8)
From ilmenite digestion, unneutralized, damp	—	—	1.25	—	—	0.6	0.8	0.2	(1.4)	—	0.15	—	0.75	0.44	0.28	(1.0)
From slag digestion, neutralized	—	—	—	—	—	—	—	—	(<0.1)	—	—	—	—	—	—	(<0.1)
From 90% slag, 10% ilmenite digestion	—	<1	—	—	—	—	—	—	—	—	—	—	<0.1	—	—	—

^a Industry data except where a more specific reference source is given.
^b —; not reported.
^c LLD: lower limit of detection.

TABLE 17. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN PROCESS SCALE

Origin of scale ^a	Radionuclide activity concentration (Bq/g) ^b (maximum in parentheses)							Comment
	Th-232 decay series				U-238 decay series			
	Ra-228	Ac-228	Th-228	Bi-212	Not specified	Ra-226	Not specified	
Not specified	— ^c	18	—	26	(35.2)	—	31 (41.1)	Two samples
Pre-hydrolysis heat exchanger	1644	—	1499	—	—	415	—	One sample, Ref. [24]
Crystallizer tank	325	—	124	—	—	77	—	One sample, Ref. [24]
Crystallizer tank	~100	—	—	—	—	~100	—	Ref. [30]
Hydrolysis liquid collection tank	—	—	—	—	(<0.1)	—	(<0.1)	
Moore filter tank	83.2	—	3.9	—	—	13.5	—	One sample
Settler for clarification after reduction step	—	—	—	—	<1	—	<1	
Hydrolysis pulp cooler	—	—	—	—	<0.1	—	<0.1	
Hydrolysis liquid collection tank	—	—	—	—	(<0.1)	—	(<0.1)	
Not specified	(40)	—	—	—	1	(10)	1	Feedstock 90% slag, 10% ilmenite

^a Samples were obtained from facilities using ilmenite as a feedstock, except where stated otherwise.^b Values reported are industry data, except where a more specific reference source is given.^c —; not reported.

TABLE 18. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN DISCARDED FILTER CLOTHS

Origin of filter cloth ^a	Radionuclide activity concentration (Bq/g) ^b									Comment	
	Th-232 decay series					U-238 decay series					
	Ra-228	Ac-228	Th-228	Pb-212	Bi-212	Not specified	Th-234	Ra-226	Bi-214		Po-210
Moore filter	1.96	— ^c	—	0.04	—	—	—	0.044	0.04	—	—
Moore filter	—	0.35	—	—	0.1–0.5	—	<0.36	—	0.1	0.1	—
Moore filter	396 (14.7–968)	—	288 (3.4–728)	—	—	—	—	129 (2.5–333)	—	—	—
Gypsum filter	—	—	—	—	—	<1	—	—	—	—	<1
Average of four samples after ashing, range in parentheses, Ref. [24]											

^a All samples were obtained from facilities using ilmenite as a feedstock.

^b Industry data, except where a more specific reference source is given.

^c —; not reported.

effluent (including sediment) [24], while ^{232}Th values of about 100 Bq/L have been measured in untreated Moore filter wash water.

5.3. OCCUPATIONAL EXPOSURE

5.3.1. Exposure levels

5.3.1.1. *Gamma radiation*

Exposure data are presented here as incremental gamma dose rates, determined by subtracting the local background value from the workplace measurements. Local background measurements in the range of 0.08–0.14 $\mu\text{Sv/h}$ are reported. Where the background dose rate is not given, a value of 0.1 $\mu\text{Sv/h}$ has been assumed.

The gamma exposure levels associated with production operations in sulphate process plants using ilmenite as a feedstock are presented in Tables 19 and 20. The incremental dose rates are moderate in most production areas (below 1 $\mu\text{Sv/h}$) but can be several times higher in a few specific locations — up to 12 $\mu\text{Sv/h}$ in the copperas crystallization area and up to 50 $\mu\text{Sv/h}$ in the hydrolysis area. In plants using titanium slag (or a mixture of 90% slag and 10% ilmenite) as a feedstock, the dose rates are considerably lower than in ilmenite plants — less than 0.1 $\mu\text{Sv/h}$ at all locations except for the digester residue storage area (1.3 $\mu\text{Sv/h}$) and the hydrolysis area (<0.1–0.7 $\mu\text{Sv/h}$). Dose rates above neutralized digester residue deposited in a landfill facility are reported to be 0.06 $\mu\text{Sv/h}$ when covered by 1 m of chalk and 0 when additionally covered by 1 m of topsoil.

Incremental gamma dose rates associated with maintenance activities are presented in Table 21. Maintenance work, by its very nature, tends to involve proximity to residues in which radioactivity has become concentrated. In many cases, such as during tasks requiring entry into vessels, shielding is no longer provided by metal enclosures. This results in the general levels of gamma exposure being higher than that observed during normal production work.

Gamma dose rates tend to be measured either in contact with (or very close to) the source of gamma radiation or, more usually, at a distance of 1 m. Where the measurement distance has not been specified, the reported dose rates can, in most cases, be assumed to have been measured at a distance of about 1 m. Dose rates measured in contact with process material can of course be much higher — the highest value reported is 50 $\mu\text{Sv/h}$ for scale inside hydrolysis heat exchanger pipes.

TABLE 19. INCREMENTAL GAMMA DOSE RATES ASSOCIATED WITH THE MAIN TiO₂ PIGMENT PRODUCTION PROCESS

	Dose rate (μSv/h) ^a
<i>Feedstock preparation</i>	
Bulk feedstock storage	0.01–0.2
Bulk feedstock storage, seven measurements (derived from Ref. [30])	0.13–0.31
Feedstock conveyors and silos	0–0.1
Belt weighing machines	0.05–0.2
Feedstock milling	0
Feedstock milling (derived from Ref. [30])	0.03–0.17
<i>Acid digestion</i>	
Digester area	0.06
Digester area (derived from Ref. [30])	0.02–0.15
Post-reduction filters or clarification	1–6
Polishing filter	0.1
Ilmenite residue thickener	0.1–0.2
Digester residue storage	0.06–0.5
Digester residue storage, six measurements (derived from Ref. [30])	0.47–0.55
Digester residue filters	0.06–0.2
Digester residue separation area (derived from Ref. [30])	0.01–0.15
Liquor settlers (inlet)	0.46–0.6
Liquor pre-heating and pumping tank	1.4–2.4
<i>Copperas production and storage</i>	
Copperas crystallizer	1.4–1.9
Crystallization area [30]	0.06–12.52
Outside copperas crystallization feed tank	0–0.1
Copperas centrifuge discharge	0.02–0.06
Copperas storage, three measurements [30]	0
Ferrous sulphate areas	<0.1–0.2

TABLE 19. INCREMENTAL GAMMA DOSE RATES ASSOCIATED WITH THE MAIN TiO₂ PIGMENT PRODUCTION PROCESS (cont.)

	Dose rate (μSv/h) ^a
<i>Hydrolysis</i>	
Hydrolysis area, five measurements	1–12
Hydrolysis area (derived from Ref. [30])	0.01–0.58
Hydrolysis area, pipes near walkway	50
Moore feed tank (full)	3
<i>Washing and finishing</i>	
Washing area (derived from Ref. [30])	0.06–0.20
TiO ₂ pigment finishing area (derived from Ref. [30])	0.01–0.04

^a The values reported are industry data, except where a more specific reference source is given. Measurements were generally made 1 m from the source. All feedstocks were ilmenite.

TABLE 20. INCREMENTAL GAMMA DOSE RATES ASSOCIATED WITH THE PRODUCTION OF BY-PRODUCTS

	Dose rsate (μSv/h) ^a
<i>Gypsum production</i>	
Acid storage, gypsum production	0–0.02
Neutralization plant, gypsum production	0
Neutralization area, red gypsum production [30]	0.01–0.07
Gypsum and ilmenite residue handling	0.05
Red gypsum storage [30]	0.03–0.04
<i>Acid recovery and filter salt (ferrous sulphate monohydrate) production</i>	
Acid concentration	0–0.02 (maximum 3.5)
Ferrous sulphate maturation area [30]	0.01–0.47
Storage of ferrous sulphate from acid recycle	0–0.06
Storage of ferrous sulphate from acid recycle [30]	0.05–0.06

^a The values reported are industry data, except where a more specific reference source is given. Measurements were generally made 1 m from the source. All feedstocks were ilmenite.

TABLE 21. INCREMENTAL GAMMA DOSE RATES ASSOCIATED WITH MAINTENANCE OPERATIONS

	Feedstock	Dose rate ($\mu\text{Sv/h}$) ^a at 1 m from source
<i>Acid digestion</i>		
Digester residue or sludge filter cloth	Slag	1.8
Digester residue filter rubber boot with white scale	Slag	0.48
<i>Copperas separation</i>		
Inside copperas crystallization feed tank	Ilmenite	0.01–0.15
Inside copperas vacuum crystallizer vessel	Ilmenite	5–10
<i>Hydrolysis</i>		
Removal of hydrolysis tank and brickwork	Ilmenite	1.2
Removal of brickwork and pipework from vats ^b	Ilmenite	1.1
Inside Moore feed tank	Not reported	3–5
Inside Moore feed tank	Ilmenite	1
Maintenance of Moore feed tank	90% slag	1–5
Moore filters	90% slag	0–0.9
Moore filters	Ilmenite	0.3–1.9
Inside weak acid stock tank	Not reported	10
<i>Unspecified process steps</i>		
Equipment and scale inside waste disposal store	Not reported	10
Filter plates, cloths, tubes	Ilmenite	0.07

^a The values reported are industry data.

^b Alternatively, could be associated with the acid digestion step.

5.3.1.2. Inhalation of radionuclides in airborne dust

The areas likely to involve the most significant exposures to airborne dust are the feedstock handling area (including storage) and the feedstock milling and drying area, although the high density of the feedstock helps to minimize the

suspension of dust. Dust is also likely to be generated during the landfill disposal of digester residue.

In feedstock storage areas, dust levels are likely to be low except when the material is disturbed, such as during loading and unloading. Milling and drying of feedstocks encourage the formation of dust, but are carried out using enclosed equipment. Industry data indicate that the maximum airborne dust concentrations that can be expected are 1 mg/m³ in feedstock handling areas and 1.7 mg/m³ in feedstock milling and drying areas. In a plant using ilmenite sand as a feedstock, the average airborne dust concentration was found to be 0.14 mg/m³, about an order of magnitude below these maximum values [30]. Using the average radionuclide activity concentrations measured in the feedstock at that plant (which were close to the mid-points of the ranges given in Table 7), this dust concentration corresponded to average airborne activity concentrations of 0.05 and 0.01 mBq/m³ for ²³²Th and ²³⁸U, respectively. For titanium slag feedstocks, the corresponding airborne activity concentrations would typically be an order of magnitude lower because of the lower activity concentrations in the feedstock material.

For subsequent processing steps, such as digestion and hydrolysis, no airborne dust concentration data are available, but such operations are inherently non-dusty because they are carried out with wet or damp materials.

No dust concentration data are available for maintenance operations. However, the conditions inside vessels, such as weak acid stock tanks, are likely to be non-dusty and the use of high pressure water jets to remove scale from equipment helps to minimize any dust generation.

5.3.2. Effective dose

The values of annual effective dose calculated from the exposure data in Section 5.3.1 and presented in Sections 5.3.2.1–5.3.2.7 can be considered as conservative estimates or upper bounds, for the following reasons:

- (a) The instantaneous dose rates used in the dose assessment calculations are those measured at a distance of 1 m. In practice, workers will not be this close to the source or will not remain this close throughout the specified occupancy period.
- (b) The specified occupancy periods are maximum values and are based on the assumption that the task involved is not rotated between different workers. Since all production operations are conducted on a 24 h basis, some tasks will be subject to rotation as a result of shift work.

- (c) Doses from the inhalation of dust are calculated assuming that protective respiratory equipment is not used. In practice, such equipment is used during dusty operations.

5.3.2.1. *Feedstock preparation*

Maximum gamma exposure periods are reported to be 500 h/a in feedstock storage and conveying areas, 200 h/a in belt weighing areas and 1700 h/a in feedstock milling areas. It can be deduced from the dose rates reported in Section 5.3.1.1 that the maximum external dose likely to be received by a worker in a year is about 0.16 mSv in the storage and handling areas and about 0.29 mSv in the milling area, with average doses being perhaps half these values.

For a worker in a plant using ilmenite feedstock, reference to the airborne dust activity concentrations reported in Section 5.3.1.2 and the inhalation dose coefficients reported in Table 5 (assuming an AMAD of 5 μm and a breathing rate of 1.2 m^3/h) suggests that the inhalation dose received over a 2000 h annual exposure period is about 0.007 mSv. In a worst case situation, the radionuclide activity concentrations in the ilmenite could be about five times higher than those reported in Ref. [30], and the dust mass concentrations in air could be about ten times higher. This would give a maximum dose from dust inhalation of about 0.35 mSv in a year. For a worker in a plant using titanium slag feedstock, the corresponding doses would be an order of magnitude lower because of the lower radioactivity content of the feedstock.

The total effective dose received by a feedstock preparation worker is the sum of the external and internal doses. In a plant using ilmenite feedstock, the average total effective dose received in a year would therefore be about 0.1 mSv, with a maximum of about 0.5 mSv. In plants using titanium slag as a feedstock, the doses would be an order of magnitude lower.

5.3.2.2. *Acid digestion*

At one location in an ilmenite plant, dose rates in the range of 1–6 $\mu\text{Sv}/\text{h}$ are reported (see Table 19). Although the occupancy period is not stated, the annual effective dose at this location is reported to be less than 1 mSv, implying that the occupancy period is a few hundred hours per year or less. Elsewhere, the dose rates are much lower (see Section 5.3.1.1) and maximum annual gamma exposure periods are reported to be 2000 h for the general digester area, 600 h for the digester residue filters, 200–250 h for digester residue storage and 250 h for the polishing filter, ilmenite residue thickener and inlet to the liquor settlers. It can be deduced from these data that the maximum external dose received by a worker in a year is in the range 0.02–0.3 mSv.

5.3.2.3. *Copperas separation*

The annual exposure period at all gamma dose rate measurement locations is reported to be, at most, 250 h. In one plant, the annual exposure period in the area with the highest gamma dose rates (the crystallization area) is reported to be less than 50 h [30]. It can be deduced from the dose rates reported in Table 19 that the maximum external dose received by a worker in a year is in the range of 0.02–0.6 mSv.

5.3.2.4. *Hydrolysis*

Reference to Table 19 shows that, in ilmenite plants, this area is associated with particularly high gamma dose rates and, by implication, the potential for high annual effective doses. In an area with a maximum occupancy period of 500 h/a, the reported gamma dose rates of 1–12 $\mu\text{Sv/h}$ imply a maximum external dose of 0.5–6 mSv received in a year by a worker. At the Moore feed tank, where the maximum annual exposure period is 2000 h, the reported dose rate of 3 $\mu\text{Sv/h}$ implies a maximum external dose of 6 mSv in a year. For pipes near a walkway, where the dose rate is reported to be 50 $\mu\text{Sv/h}$, the occupancy period is not specified but is evidently very short because the annual dose is reported to be less than 1 mSv. For a plant using a feedstock containing 90% titanium slag, the dose rates are lower (see Section 5.3.1.1) and measurements in an area with a maximum annual exposure period of 1700 h correspond to a maximum external dose of 1.2 mSv.

5.3.2.5. *Gypsum production and acid recovery*

The maximum annual exposure periods are reported to be 1000 h for ferrous sulphate storage areas and 2000 h elsewhere. For the dose rates reported in Table 19, these correspond to annual effective doses of less than 0.1 mSv.

5.3.2.6. *Calcination and finishing*

Dose rates are very low in these areas, and even with annual exposure periods of up to 2000 h, the annual effective dose received by a worker is less than 0.2 mSv.

5.3.2.7. *Landfill disposal of digester residue*

Landfill workers are assumed to be exposed to gamma radiation and airborne digester residue particles for periods of up to 2000 h in a year. The

incremental gamma dose rate from unshielded bulk digester residue is reported to be in the range of 0.06–0.5 $\mu\text{Sv/h}$ (see Table 19). This corresponds to an annual effective dose of 0.1–1 mSv. However, once the digester residue is covered by 1 m of chalk, the dose rate is only 0.06 $\mu\text{Sv/h}$ (see Section 5.3.1.1), giving an annual effective dose of 0.1 mSv. For inhalation of airborne digester residue particles, the annual effective inhalation dose derived from the results of personal exposure measurements is reported to be less than 0.11 mSv. Over the course of a year, therefore, the maximum effective dose from gamma radiation and airborne dust particles is estimated to be in the range of 0.2–1.1 mSv, with values at the lower end of this range being more likely.

5.3.2.8. Maintenance work

For maintenance work involving entry into vessels, the exposure periods are limited by the nature and frequency of the work. In those instances where dose rates exceeding 1 $\mu\text{Sv/h}$ are found, the maximum annual exposure periods are reported to be 10–50 h. A similar situation is reported for exposure to equipment and scale inside a waste disposal store. It can be deduced from the dose rates reported in Table 21 that the maximum external dose received by a maintenance worker in a year is in the range of 0.05–0.5 mSv.

Maintenance of filtration systems in the acid digestion and hydrolysis areas involves gamma exposure to the filters for maximum annual periods of 250 h (digester residue filters) or 1200 h (Moore filters) at instantaneous dose rates ranging from 0 to 1.9 $\mu\text{Sv/h}$ (see Table 21). Annual effective doses are reported to be less than 1 mSv, although there is clearly the potential for higher doses should the exposure periods be longer.

5.3.3. Measures to reduce doses

5.3.3.1. Routine operation

It is evident from Section 5.3.2 that, during routine plant operation (notably in plants using ilmenite as a feedstock), the hydrolysis area is the one location where, because of elevated gamma dose rates, there is significant potential for a worker to receive an annual effective dose exceeding 1 mSv. It is reported from one plant that this area is designated as a supervised area to which access is restricted and where occupancy periods are recorded. Measures such as this are generally sufficient to ensure that occupancy periods are minimized to the extent that annual effective doses exceeding 1 mSv are largely avoided.

Since annual effective doses from dust inhalation in feedstock preparation areas are well below 1 mSv (see Section 5.3.2.1), there is generally no need to

depend on measures designed specifically to reduce doses. However, dust may be controlled in various plant areas as part of normal OHS requirements and good industrial practice. For instance, relatively simple measures may be effective in avoiding unnecessary drying out of material such as digester residue and consequent generation of dust. The use of respiratory protective equipment may become mandatory if airborne dust levels are high (more than 10 mg/m^3 , for instance). It is reported from one plant using ilmenite as a feedstock that respiratory protective equipment is worn routinely in feedstock handling areas, even though the dust levels are less than 1 mg/m^3 .

5.3.3.2. *Maintenance work*

Entry into vessels such as copperas vacuum crystallizers, Moore feed tanks and weak acid stock tanks for maintenance purposes is generally controlled, particularly from the point of view of external gamma exposure. The internal area may be formally designated as a controlled area, with a gamma dose rate being established as a criterion for permitting entry — one such criterion is reported to be a dose rate of $20 \text{ } \mu\text{Sv/h}$ at 0.5 m from the internal surface of the vessel. Doses received by maintenance workers undertaking such operations are assessed and recorded. Dose assessment may be based on personal dosimetry or on a consideration of instantaneous dose rate measurements and occupancy periods. An investigation may be required if the dose accumulated over a year exceeds 1 mSv . Although the conditions are generally wet, respiratory protective equipment may be required if there is potential for airborne dust generation, and clothing and tools may need to be checked for contamination at the end of the maintenance operation to prevent the spread of contamination. Waste generated by the maintenance operation, such as scale and sludge, is collected and disposed of under controlled conditions as described in Section 5.1.3.3.

Areas for the decontamination of equipment removed from the plant may also need to be formally designated as controlled areas. Doses received by decontamination workers are assessed, for instance, using personal dosimetry, and, as in the case of vessel entry, an investigation may be required if the dose accumulated over a year exceeds 1 mSv . Individual contaminated items may be assessed against a criterion, the numerical value of which is related to the measurement technique and instrument used, for example, a given number of counts per second. This can be used as a quick method for determining whether special decontamination techniques such as water jet cleaning need to be carried out under controlled conditions to avoid the spread of contamination. If, after such decontamination, the criterion is still exceeded, the item concerned remains under control, for example, by holding it in a locked container. Scale removed by water jet cleaning is collected in filters, mixed with sand to facilitate handling and

packed into drums to prevent the spread of contamination. The method of disposal of such containers and drums, as well as other material such as scrap rubber linings, depends on the level of activity, and specialized disposal may be required, as described in Section 5.1.3.3.

5.4. PUBLIC EXPOSURE

Members of the public could be exposed to airborne dust from feedstock piles. However, since such feedstocks represent a valuable raw material, precautions such as the use of closed silos or windbreaks are taken to prevent loss of material. Discharges to air from production plants are strictly controlled within limits on the quantity of solids permissible in the gas stream. It is also standard practice to design stacks to achieve good dispersion. In such situations, there will be no significant exposure of members of the public via such discharges.

Non-radiological controls on industrial effluents, and in particular, controls to limit the sulphate content, may effectively set an upper limit on the radionuclide content, since a reduction of sulphate discharge levels can be achieved only by neutralization and filtration or by concentration and recycling of the acid content — both treatments remove radionuclides from the liquid effluent stream. Members of the public are unlikely to be directly exposed to such effluent discharges but, in the event of such an exposure, the low radionuclide content would ensure that no significant dose could be received.

Other waste streams that may be specifically regulated for non-radiological purposes include:

- (a) Solid waste, including digester residue;
- (b) Strong acid waste (the filtrate from the hydrolysis step);
- (c) Acid treatment waste (material generated by the neutralization or concentration of strong acid waste, including filter salts).

No information is available on the public exposure implications of using digester residue as a component of construction material. Such use would need to be examined on a case by case basis. The disposal of digester residue as waste would normally occur within the confines of the production facility or by means of external specialist landfill operations. In either case, public access would be restricted; however, in some cases, it may be necessary to consider the long term use of the site and ensure that engineering controls such as landfill capping are adequate. Given the relatively low activity of this material and the normal requirements for landfill construction, public exposure to digester residue at landfill sites is not likely to be of significant concern.

Relatively highly active waste material generated during maintenance and decontamination of equipment, notably scale, rubber linings and filter cloths, could give rise to significant exposure of members of the public if not disposed of in an appropriate manner.

An environmental assessment has been carried out for a production facility using ilmenite feedstock with full neutralization of acid effluent to produce red gypsum. The assessment compared activity concentrations measured during plant operation with those measured prior to the construction of the plant. The assessment shows that:

- (a) Gamma dose rates and radon and thoron progeny concentrations within a 5 km radius of the facility are the same as those prior to operation.
- (b) Concentrations of ^{226}Ra and ^{228}Ra in airborne dust measured at an off-site station were each less than 0.1 mBq/m^3 , the same as those prior to operation.
- (c) Concentrations of ^{226}Ra and ^{228}Ra at two groundwater sampling sites downstream of the facility were less than 1 Bq/L , the same as those at two sampling sites upstream of the facility.
- (d) Concentrations of ^{226}Ra and ^{228}Ra in the surrounding environment were $0.035\text{--}0.085 \text{ Bq/g}$ in soil and less than 1 Bq/L in seawater, the same as those prior to operation.

It was concluded that members of the public were not receiving any additional dose associated with operation of the facility nor was there any detrimental effect on the environment.

A review of the environmental effects of the Laporte sulphate plant in Australia is described in Ref. [24]. Thorium was reported to have remained soluble and mobile in the environment until the sulphate and free acidity had been reduced by neutralization in the environment. The thorium was removed from solution as iron precipitates. There was no significant uptake of radioactivity by local shellfish, although further studies were proposed. It is apparent from this work that the disposal of plant scales containing accumulated radioactivity and of contaminated equipment would need to be managed to avoid public exposure. There was no evidence of other significant exposure pathways from the radioactivity contained in the major effluents. This review was conducted thirty years ago, and is not considered representative of current practice. In modern plants, effluent streams are usually neutralized prior to discharge.

5.5. REGULATORY CONSIDERATIONS

5.5.1. Normal plant operation

During normal plant operation, the hydrolysis step is the only part of the process where the annual effective dose received by a worker may significantly exceed 1 mSv and, even then, only when ilmenite is used as the feedstock. This is a result of high external gamma doses rates in areas of considerable accumulation of radionuclides. Relatively simple measures, notably restrictions on access and the recording and control of occupancy periods, have proved to be effective in providing the necessary level of worker protection. While, in terms of the graded approach to regulation (see Section 3.1.2.2), notification would be an appropriate minimum requirement, authorization (most likely in the form of registration) may be needed in some situations as a mechanism for enforcing the above mentioned control measures, so as to provide the regulator with the necessary assurance that workers are being adequately protected.

5.5.2. Maintenance and decontamination of equipment

Elevated gamma dose rates are encountered during maintenance and decontamination operations; as in the case of workers in the hydrolysis area, restrictions on access and recording and control of occupancy periods have proved to be effective for ensuring protection. In addition, however, control measures to address other exposure pathways are usually considered. For the control of occupational exposure, these measures include the possible need for respiratory protective equipment where dust may be generated, controls to prevent the spread of contamination and the use of specific decontamination techniques to prevent the generation and spread of airborne contamination. For control of public exposure, control measures are likely to include appropriate methods for the disposal of high activity waste such as scale, rubber linings and filter cloths. Again, in some situations, authorization (most likely in the form of registration) may be needed in addition to notification in order to provide the necessary assurance that adequate protection, in this case of both workers and members of the public, is being maintained.

5.5.3. Process material falling outside the scope of regulatory control of practices

The radionuclide activity concentrations in much of the solid material involved in the sulphate process are below 1 Bq/g, and such material therefore falls outside of the scope of regulatory control for practices. This includes all

titanium slag feedstocks, some ilmenite feedstocks, the final titanium dioxide pigment product and all by-products except some of the digester residue produced in plants using ilmenite feedstock. Some waste from the sulphate process also has radionuclide activity concentrations below 1 Bq/g — this includes some sediments, dust from off-gas filtration systems and gypsum filter cloths.

Liquid effluents are also likely to contain low radionuclide concentrations, in this case, as a result of them already being subject to discharge controls to limit the levels of pollutants such as sulphates and metals. The regulatory body would therefore be expected to take this into account when considering any need for further controls aimed specifically at limiting the radionuclide content.

5.5.4. Digester residue

The use of digester residue as a component of construction material or its disposal as waste would need to be considered on a case by case basis to determine whether there is any need for control. Generally, landfill disposal is already regulated to the extent that the need for additional controls for radiological purposes is unlikely and, again, this is something that the regulatory body would be expected to take into account.

5.5.5. Applicability of the Transport Regulations

Reference to Section 5.2.2 in conjunction with Section 3.1.3 shows that most of the material involved in the sulphate process does not fall within the scope of the Transport Regulations [3] because of its relatively low radionuclide activity concentration. While such material may therefore be transported without restrictions of a radiological nature, the observance of good environmental practice usually ensures that certain measures are taken to reduce any impact on the public or the environment. Such measures may be aimed at preventing dust generation when transporting feedstocks in bulk, such as:

- (a) The suspension of loading and transfer operations during very windy conditions (which may, in any case, be required to meet safety requirements for crane or grab operation).
- (b) The use of covers or other forms of closure during road or rail transport. This may apply even to the transport of nominally wet material, such as digester residue, because of the possibility of it drying out before it is transported.

Reference to Tables 17 and 18 in conjunction with Section 3.1.3 shows that some scale and filter cloths fall within the scope of the Transport Regulations and have to be treated accordingly.

6. PRODUCTION OF TITANIUM DIOXIDE PIGMENT AND TITANIUM METAL BY THE CHLORIDE PROCESS

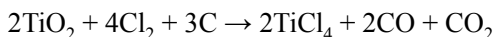
6.1. PROCESS DESCRIPTION

6.1.1. Production of titanium dioxide pigment

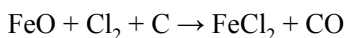
6.1.1.1. Main process

The chloride process is suitable for use with a wide range of titaniferous feedstocks — ilmenite sand, rutile, synthetic rutile, SREP and UGI (chloride slag and upgraded slag). The choice of feedstock is dictated by many factors, but especially the nature of the impurities. Some heavy metal impurities are not acceptable, since trace levels in the final product can influence its whiteness and brightness. Another consideration is the level of radioactivity in some feedstocks. Both considerations can lead to the blending of feedstocks. Some plants require the feedstock to be dried before use. This is usually done in dryers directly heated by flue gas at about 120°C.

The chloride process is shown schematically in Fig. 11. The titaniferous feedstock, along with high purity coke as a reducing agent, is reacted exothermically with chlorine gas at 900–1000°C in a fluidized bed reactor, known as a chlorinator, to produce gaseous titanium tetrachloride (TiCl₄), along with other metal chlorides such as vanadium oxychloride and iron chloride (ferrous chloride (FeCl₂) and/or ferric chloride (FeCl₃)). The primary reactions are:



and



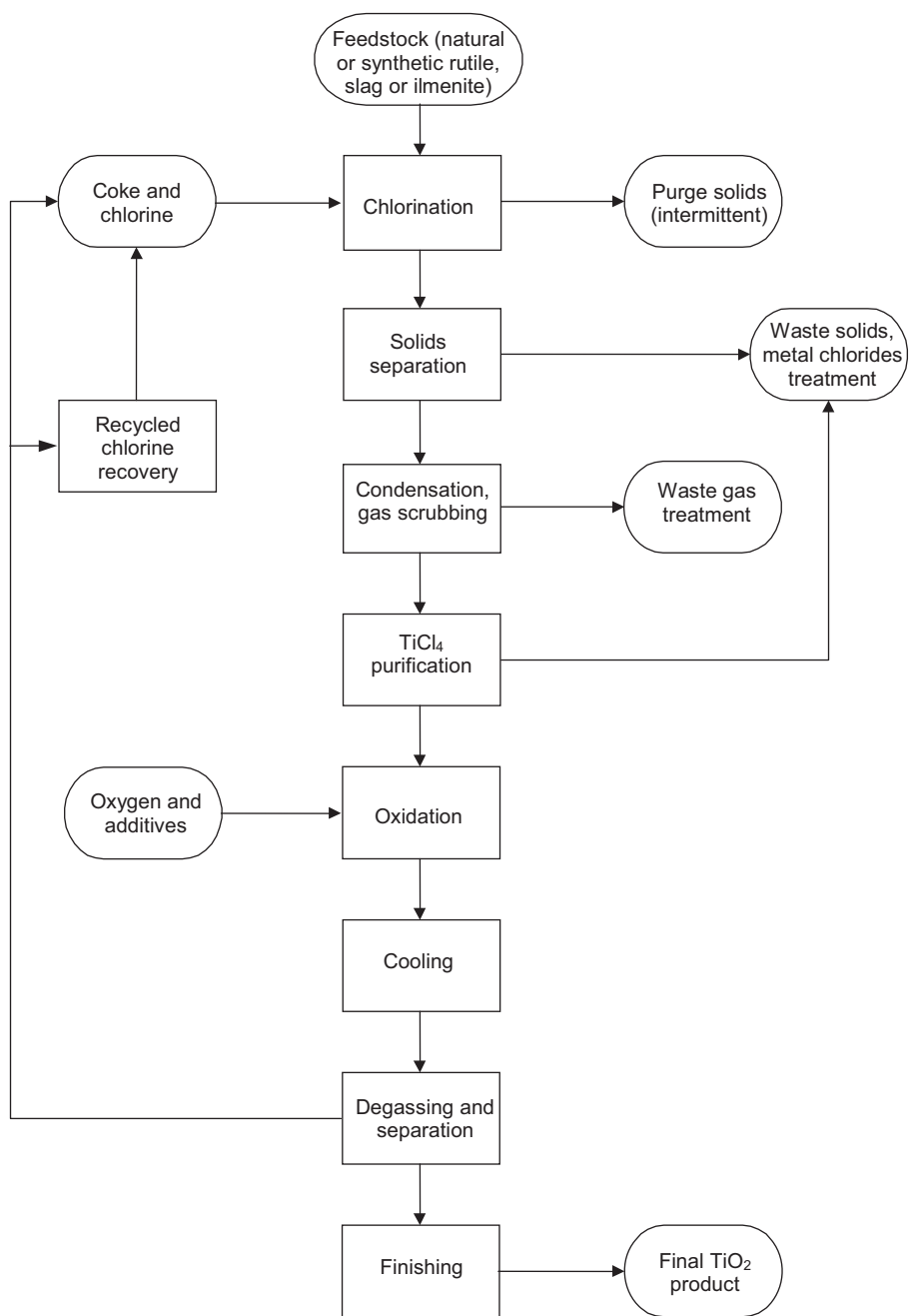
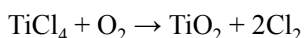


FIG. 11. The chloride process.

The TiCl_4 and other volatile metal chlorides leave the chlorinator as overhead vapour. The vapour is cooled with cold, recycled TiCl_4 , which allows removal of some impurities using physical separation equipment such as cyclones. The majority of the TiCl_4 is then condensed from the gas stream and pumped to a dedicated storage facility. More impurities and TiCl_4 are removed from the gas stream by further cooling stages, and these are also pumped to storage. The gas stream is then subjected to waste gas treatment. Impurities in the feedstock, such as silica and zirconium, may not chlorinate and may consequently accumulate in the reactor, although the off-gases serve as a vehicle for natural removal of the feed carry-over of fines, and this may be sufficient to prevent buildup. The non-volatile chlorides, the unreacted coke and any unreacted titaniferous feedstock solids are removed from the gas stream and, periodically, from the bottom of the chlorinator. The reactors may require total bed replacement from time to time, typically once per year.

Further purification of the TiCl_4 is carried out by distillation, in readiness for oxidation to TiO_2 or, in some cases, for sale as an intermediate product. Vanadyl chloride has a boiling point similar to that of TiCl_4 and is not separated upstream of the distillation process and furthermore would not be separated by conventional fractional distillation. The separation is achieved by the addition of an appropriate quantity of mineral or organic oil to the liquid being distilled. Vanadyl chloride forms a complex with this oil, which is then separated as a sludge and recycled back to the solids separation step for removal from the process stream.

The fully purified TiCl_4 is oxidized to TiO_2 at a temperature of 900–2000°C, either in a plasma arc furnace or in a toluene fired furnace, using oxygen injection. The reaction involved is:



The oxidation phase is used to control the final TiO_2 crystal size to enable the product to be used as a pigment. Light metal chlorides (usually of aluminium and alkali metals) are used to aid this process. The reaction products are cooled and the TiO_2 is collected in bag filters, while the chlorine is recycled to the chlorinator. Sand, salt or granular TiO_2 may be used to scour TiO_2 from the oxidation cooler. It is separated through lock hoppers or sand screens and then either reused or disposed of in a landfill facility.

The pure TiO_2 is slurried with water and transferred to the finishing process. The finishing of TiO_2 pigments from the chloride process is the same as that for pigments from the sulphate process and includes milling, the addition of inorganic and organic surface treatments and/or spray drying of the product TiO_2 . Further details are given in Section 5.1.1.

6.1.1.2. *Management of residues*

Small amounts of titaniferous feedstock and coke remain unreacted within the chlorinator. A portion of this unreacted material becomes part of the solid residue that forms in the bed of the reaction vessel and, after removal of this residue, may be separated and reused as raw material feed. Alternatively, the entire residue may be disposed of as solid waste. The remainder of the unreacted material is carried over with the gases from the reactor.

An acid solution, usually called iron chloride waste acid, is generated when the combined stream of unreacted feedstocks (coke and titanium-bearing material), metal chloride solids and vanadium compounds is slurried using water or residual hydrochloric acid from the reaction scrubber. Unreacted coke is sometimes recovered at this stage and stockpiled for reuse within the process or for sale as a by-product. The acid solution may be disposed of using deep well injection into geologically stable formations — the selection of alkaline formations such as carbonate based rock serves to neutralize the acidity. Alternatively, the acid solution may be neutralized with a slurry of chalk or lime, or with sodium hydroxide or other alkaline solution to render the residual metals insoluble. The metals are precipitated and stabilized. The aqueous filtrate from the neutralization filter is discharged, with treatment if necessary, to an appropriate surface water body.

The solid metal chloride residue has applications as a by-product. It can be combined with cement to form a neutralized solid for use in applications that require an aggregate material. Alternatively, provided that the unreacted coke has been removed earlier in the process, the metal chloride residue stream can be used in unneutralized form as a coagulant in water treatment applications after further processing. In situations where the material does not have application as a by-product, it is disposed of as solid waste at an on-site or off-site landfill facility. In rare cases, solid metal chlorides are disposed of in alkaline rock caverns.

Scales tend to form on the internal surfaces of pipes and other metal components, rubber linings and filter cloth. These scales may contain high concentrations of radium co-precipitated as a sulphate. The refurbishment or recycling of affected components (by decontamination or melting, for instance) or their disposal as waste may have to be assigned to specially authorized facilities rather than normal industrial facilities. This would depend on the results of contamination monitoring and, in the case of decontamination, on the extent to which radioactivity may become concentrated during the decontamination process. Decontamination is generally carried out using water jets or chemical treatment. In at least one plant in the USA, a permit has been obtained to feed contaminated filter cloths back into the chlorinator. There are also anecdotal reports of other residues such as rubber linings and scaled piping being

reintroduced into the chlorinator in this way, during periods of shutdown where appropriate.

Waste sands from the finishing (milling) of the TiO_2 , the scouring of oxidation process units and the sandblasting of reactor internal surfaces before refractory replacement are also generated. Wastewater treatment solids are generated from the neutralization and settling of the combined process and non-process wastewater.

Process and non-process wastewaters are generated from the reaction and oxidation scrubbers, the treatment of spent chemicals, product finishing, the hydrochloric acid storage vent scrubber, the oxidation unit tank and equipment vents, the supernatant from residual coke and feedstock solids separation, and disposal impoundments associated with wastewater treatment. A significant proportion of the liquid effluents can originate from the finishing section of the plant. This liquid consists of slightly alkaline solutions of alkali metal sulphates and chlorides together with suspended solids (TiO_2) resulting from the coating process. The final effluent can be acidic or alkaline. In all cases, the authorized limits on effluent composition are influenced by the nature of the receiving environment.

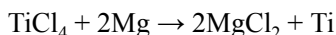
The off-gases from the chlorination step include carbon dioxide, carbon monoxide, hydrogen chloride, carbonyl sulphide, residual TiCl_4 and, in some instances, unreacted chlorine. In some plants, a thermal oxidizer is included in the process line to convert carbon monoxide and carbonyl sulphide to carbon dioxide and sulphur dioxide. Carbon dioxide can potentially be recovered and sold as a by-product, although this is not currently practised. Hydrogen chloride is removed using aqueous scrubbers. If demineralized water is used for scrubbing, it becomes practicable to produce, as a by-product, commercial grade hydrochloric acid that is free of metal chlorides. Caustic (sodium hydroxide) scrubbing may be used to remove sulphur dioxide and, where appropriate, any unreacted chlorine. This is achieved either by using a dedicated caustic scrubber with backup caustic injection available or by direct injection of sodium hydroxide into an aqueous scrubber in the event that chlorine is detected. Caustic scrubbing of chlorine produces sodium hypochlorite, which may be sold as a by-product.

The storage and preparation of feedstocks are intermittent sources of dust emissions. Any dust from the dried feedstock is separated from the flue gas by cyclones and filters and fed to the chlorinators. Emission levels are of the order of 5 g per tonne of TiO_2 . Under normal operating conditions, other emissions to air contain no solids, apart from minimal amounts of TiO_2 from the finishing stage.

6.1.2. Production of titanium metal

Almost all commercial production is carried out using the so-called Kroll process, a reduction process using metallic magnesium for conversion of TiCl_4 into titanium metal (see Fig. 12). The initial part of the process involves the production of high purity TiCl_4 . The process is essentially the same as that used in the production of TiO_2 pigment via the chloride route (see Section 6.1.1.1) except that, in order to obtain sufficiently high levels of purity, the feedstocks used are restricted to those with a higher TiO_2 content, namely, rutile, synthetic rutile and upgraded slag. The TiCl_4 is purified using multiple distillation stages, resulting in purity levels that can be as high as 99.997% for some applications. Most titanium metal producers operate their own TiCl_4 production plants, but some purchase TiCl_4 from TiO_2 pigment producers; in such cases, the titanium metal producer may need to further purify the purchased TiCl_4 by distillation before it can be used for metal production.

In the reduction step, the TiCl_4 is reacted with metallic magnesium in an argon atmosphere at about 1000°C to produce titanium metal sponge and magnesium chloride. The reaction is as follows:



The titanium sponge is then refined by vacuum distillation in a furnace to remove traces of magnesium and magnesium chloride, which are then separated by electrolysis into chlorine gas, which is recycled to the chlorinator, and magnesium, which is used again in the reduction step. Titanium sponge production is a batch process. A typical batch cycle for an 8–11 t reactor takes approximately fifteen days: approximately four days for reduction including charging, about four days for vacuum distillation, approximately four days for cooling, and about two days for disassembling, crushing and packing for shipment. Different grades of sponge exist (e.g. normal, high and extra high purity), depending on the quality of the TiCl_4 and the exact process used. The products are crushed to different sizes, depending on client specifications. Some sponge is converted into ingots (with or without alloying elements such as aluminium and vanadium) for use in the production of titanium mill products. In order to produce ingots, the sponge is compacted by a press to produce sponge blocks, which are then welded together inside a vacuum leak control system followed by vacuum arc melting or electron beam melting and plasma, depending on whether pure or alloy ingots are desired.

A reduction process using metallic sodium rather than magnesium, known as the Armstrong process, is used for the production of titanium in powder form. A reduction process, known as the Hunter process, also uses metallic sodium but

The residues from TiCl_4 production for conversion to titanium metal are the same as those associated with the production of TiCl_4 for conversion to TiO_2 pigments (see Section 6.1.1.2). Because of the high purity of the TiCl_4 produced, the residues from its conversion into metal (including any radioactivity content) are insignificant.

6.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

6.2.1. Migration of radioactive species

6.2.1.1. Uranium and thorium

Uranium and thorium oxides are converted to solid chlorides in the chlorination step. These solids become separated from the TiCl_4 during the solids separation step (see Fig. 11) and follow the iron chlorides to the iron chloride waste acid solution. On neutralization, they are precipitated with the iron chlorides and are disposed of as part of the neutralized solid waste. If neutralization is incomplete, some loss of uranium and thorium to the liquid effluent stream may be expected.

6.2.1.2. Radium

Radium resembles an alkali metal with high solubility. The radionuclides ^{224}Ra , ^{226}Ra and ^{228}Ra migrate in a different manner from other radionuclides. Precipitation of radium as a sulphate or carbonate complex leads to the generation of radium rich scales during the solid metal chlorides treatment step. The co-precipitation of radium with barium is influenced by factors such as the pH, the temperature and the presence of other trace elements. Evidence suggests that where the pH is relatively high in the neutralization stage, 90–95% of the radium migrates — up to 20% to the scales and more than 80% to the solid waste — with only a minimal amount remaining in the liquid phase.

6.2.1.3. Lead and bismuth

Lead and bismuth chlorides are formed during the chlorination step. With boiling points of 950°C and 440°C , respectively, it is expected that both chlorides will follow the iron chlorides to the neutralized solid waste. Owing to the short half-life of ^{210}Bi , equilibrium with its parent ^{210}Pb will be restored within about one month.

6.2.1.4. Radon

Radon and thoron escape to the atmosphere as stack emissions along with other gases from the process. Some thoron may decay before it has a chance to escape because of its short half-life of 55 s.

6.2.2. Activity concentrations in process materials

Analyses of samples from chloride process facilities using a variety of feedstocks show no evidence of significantly elevated radionuclide activity concentrations in the following process materials:

- (a) Titanium dioxide product (all samples <0.1 Bq/g);
- (b) Titanium tetrachloride (all samples <0.1 Bq/g);
- (c) Hydrochloric acid by-product (all samples <0.1 Bq/g);
- (d) Metal chlorides by-product (all samples <0.1 Bq/g);
- (e) Miscellaneous solids by-product (all samples <1 Bq/g);
- (f) Liquid non-neutralized waste (all samples <1 Bq/g (^{232}Th series) and <0.1 Bq/g (^{238}U series));
- (g) Dust from air filters (all samples <0.1 Bq/g);
- (h) Air emissions (all samples <0.1 Bq/g).

Significantly elevated radionuclide activity concentrations may be found in other process materials, as shown in Table 22.

Measurements conducted on liquid effluent show a maximum activity concentration of 0.35 Bq/L for ^{232}Th series radionuclides and 0.24 Bq/L for ^{238}U series radionuclides. The activity is associated predominantly with the suspended solids. Radionuclide activity concentrations in leachate from the landfill disposal of neutralized solid waste are less than 0.1 Bq/g.

When considering the Kroll process described in Section 6.1.2 for the conversion of TiCl_4 to titanium metal, it can be concluded that the materials involved are essentially free of radioactivity — only very pure TiCl_4 is used and the only other addition is magnesium metal.

6.3. OCCUPATIONAL EXPOSURE

The exposure data reported in this section relate only to the production of TiCl_4 and its subsequent conversion to TiO_2 pigment. As mentioned in Section 6.2, the conversion of TiCl_4 to titanium metal involves materials that are

TABLE 22. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN CHLORIDE PROCESS MATERIALS

Process material	Feedstock	Radionuclide activity concentration (Bq/g) ^{a, b}	
		Th-232 series	U-238 series
Unreacted bed material and refractory materials removed periodically from chlorinator	All feedstocks	13–24	<0.1–2.7
Solid wastes from chlorinator	Rutile, synthetic rutile, titanium slag blend	<1–6	<0.1–2.5
Neutralized solid waste	Titanium slag	<1 ^c	<1
	Blend (Th and U <0.01%)	<1	<1
	Ilmenite, rutile, synthetic rutile, titanium slag blend	1.1–2.5	<1
	Rutile, titanium slag blend	1.1–10.4	<1–1.4
	Synthetic rutile	1.1–14.8	<1–1.9
Coarse filter cloth, average	Not reported	40	23
Coarse filter cloth, maximum	Not reported	46	26
Fine filter cloth, average	Not reported	588	297
Fine filter cloth, maximum	Not reported	780	430

TABLE 22. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN CHLORIDE PROCESS MATERIALS (cont.)

Process material	Feedstock	Radionuclide activity concentration (Bq/g) ^{a, b}	
		Th-232 series	U-238 series
Neutralization plant scale	Synthetic rutile	1–103	<1–3.2
	Rutile, synthetic rutile, titanium slag blend	<1–8.5	<1–3
	Ilmenite, rutile, synthetic rutile	1.75–1530	<0.1–902

^a The values given are those for the decay series radionuclide with the highest activity concentration.

^b The data cited are examples and may not be representative of current operations.

^c The maximum activity concentration may be about 2 Bq/g when using certain feedstocks that are new on the market.

essentially free of radioactivity and therefore does not give rise to occupational exposure.

6.3.1. Exposure levels

6.3.1.1. Gamma radiation

Dose rate measurements have been made during plant operation, waste disposal and maintenance work. The incremental dose rates, after subtraction of the local background level, are shown in Table 23. Maintenance work, by its very nature, results in greater access to accumulations of high activity process residues. It is to be expected, therefore, that workers receiving the highest doses are generally those involved in such work.

TABLE 23. INCREMENTAL GAMMA DOSE RATES

	Dose rate ($\mu\text{Sv/h}$) ^a
<i>Plant operation</i>	
Open transfer of feedstock handling	≤ 0.10
General feedstock handling area	0.10–0.15
Neutralization area, ≤ 0.1 m from equipment	0.10–2.7
By-product processing, open handling area	0.30–0.35
<i>Landfill disposal of solid metal chloride waste</i>	
On-site worker	0.10–0.5
Truck driver	0.10–0.5
<i>Plant maintenance</i>	
Inside chlorinator, refurbishment work	1.0–2.5
Servicing of neutralization filter	0.10–10
Inside neutralization tank, general work	5–35
Inside neutralization tank, descaling work	10–90
Storage of scale prior to disposal as waste	0.10–10
Storage of contaminated rubber lined pipes	0.10–15

^a Measured at a distance of about 1 m, except where stated otherwise.

6.3.1.2. Inhalation of radionuclides in airborne dust

Airborne dust concentrations determined from measurements of mass concentration or activity concentration during plant operation, waste disposal and maintenance work are given in Table 24. The airborne mass concentrations are within the range typically found in open systems in similar industrial processes.

6.3.2. Effective dose

Annual committed effective doses received by workers in the production of titanium dioxide pigment have been determined from the gamma dose rates and airborne dust concentrations given in Tables 23 and 24 and estimated annual exposure periods. The results are shown in Table 25. The evidence suggests that

TABLE 24. AIRBORNE DUST CONCENTRATIONS

	Mass concentration in air (mg/m ³)	Activity concentration in air (mBq/m ³) ^a
<i>Plant operation</i>		
Open transfer of feedstock	5–20	3
Neutralization area	Very low dust levels	
By-product processing, open handling area	2.7	(2)
<i>Landfill disposal of solid metal chloride waste</i>		
On-site worker	Very low dust levels	
Truck driver	Very low dust levels	
<i>Plant maintenance</i>		
Inside chlorinator, refurbishment work	Potentially high dust levels ^b	
Purging of chlorinator bed	20	(<100)
Chlorinator area	<1	(<4)
Servicing of neutralization filter	Very low dust levels	
Inside neutralization tank, general work	Very low dust levels	
Inside neutralization tank, descaling work	Potentially high dust levels ^b	

^a Figures in parentheses are derived values.

^b Although the dust levels are not quantified, it is reported that the workers are required to wear respiratory protection in the form of face masks.

TABLE 25. DOSES RECEIVED BY WORKERS

	Annual exposure period (h)	Annual committed effective dose (mSv)		
		Gamma radiation	Dust inhalation	Total (rounded)
<i>Plant operation</i>				
Open transfer of feedstock	1000–2000	0.1–0.2	0.5	0.6–0.7
General feedstock handling area	≤2000	<1	— ^a	0.6–0.7
Neutralization area	200	0.54	Insignificant	0.5
By-product processing, open handling area	1000	0.3–0.35	0.15	0.5
<i>Landfill disposal of solid metal chloride waste</i>				
On-site worker	400	0.2	Insignificant	0.2
Truck driver	400	0.2	Insignificant	0.2
<i>Plant maintenance</i>				
Inside chlorinator, refurbishment work	<400	<1	Insignificant ^b	<1
Purging of chlorinator bed	<100	<0.1	<1	<0.1
Chlorinator area	350	<0.2	<0.1	<0.1
Servicing of neutralization filter	60	0.6	Insignificant	0.6

TABLE 25. DOSES RECEIVED BY WORKERS (cont.)

	Annual exposure period (h)	Annual committed effective dose (mSv)		
		Gamma radiation	Dust inhalation	Total (rounded)
Inside neutralization tank, general work	<3	<0.1	Insignificant	<0.1
Inside neutralization tank, descaling work	<15	0.75–1.35	Insignificant ^b	1
Storage of scale prior to disposal as waste	<100	<1	Insignificant	<1
Storage of contaminated rubber lined pipes	<70	<1	Insignificant	<1

^a —: not reported.

^b Assuming respiratory protection is worn.

doses received by workers do not exceed about 1 mSv in a year during normal plant operation, although for workers involved in maintenance and decontamination of equipment (e.g. refurbishment of the chlorinator and descaling of the neutralization tank), this is likely to be the case only if respiratory protection is worn.

6.3.3. Measures to reduce doses

Although gamma exposure levels are generally moderate during routine plant operation, simple administrative measures help to ensure that workers do not spend unnecessary time close to equipment in which radioactivity tends to accumulate (particularly equipment in the neutralization area). Dust control and protective measures in place for general OHS purposes, including the wearing of respiratory protection where appropriate, are effective in minimizing inhalation exposure in areas where process material is handled in open systems.

The potential for significant occupational exposure is greatest during maintenance operations. Access controls and restrictions on occupancy time are generally in force during maintenance involving close contact with material in which radioactivity becomes concentrated, for example, the purging of chlorinator beds and work involving entry into chlorinators and neutralization tanks. For scale-prone acidic streams, the use of ceramic or plastic materials has been found to mitigate the formation of scale. The use of protective clothing such as overalls, gloves and footwear during chlorinator and neutralization tank maintenance, in conjunction with washing down of contaminated items such as boots and equipment, helps to minimize the spread of radioactive contamination. Decontamination of scaled components is undertaken by trained individuals using appropriate engineering controls and personal protective equipment. The use of high pressure water jets reduces the potential for airborne dust. Where high dust levels are unavoidable, such as might be the case during descaling operations inside neutralization tanks and other confined spaces, protective respiratory equipment is worn. Separate areas with strict access control are set aside for the storage of contaminated components (such as rubber lined pipes) after removal from the circuit and for the storage of scale prior to disposal in controlled facilities.

6.4. PUBLIC EXPOSURE

Members of the public could be exposed to airborne dust from feedstock piles or transport/transfer activities. However, since such feedstocks represent a valuable raw material, precautions such as the use of closed silos, windbreaks or

procedures to minimize handling losses are taken where appropriate, such as in windy conditions, to prevent loss of material.

Discharges to air from production plants are strictly controlled within limits on the quantity of solids permissible in the gas stream. It is also standard practice to design stacks to achieve good dispersion. In such situations, there will be no significant exposure of members of the public via this kind of discharge.

For liquid discharges, non-radiological controls on solids contained in industrial effluents are likely to set an upper limit on the radionuclide content. Typically, the chloride solid waste stream will be neutralized by mixing with water and neutralizing agent, converting the chlorides into hydroxides, which are separated by filtration. Since the oxides and hydroxides of the radionuclides involved are of low solubility, they will also be removed from the liquid that forms the industrial effluent. Members of the public are unlikely to be directly exposed to such effluent discharges but, in the event of such exposure, the low radionuclide content would ensure that no significant dose could be received.

Most of the radionuclides entering the process typically leave as part of the solid waste, which will go for landfill disposal or underground disposal of some form. The activity concentrations in such materials will still be relatively low due to the presence of other impurities from the starting feedstock. There will be no significant exposure of the public once the material is buried, provided that there is no intrusion into the disposal facility.

Any scale removed from or remaining within equipment is potentially of much higher activity concentration than the routine process waste streams. Such residues are likely to require specialist handling, disposal and possibly authorization. Specific control measures may be needed to limit public exposure to acceptable levels.

6.5. REGULATORY CONSIDERATIONS

Reference to Sections 4 and 6.2.2 indicates that the TiO_2 product and TiCl_4 intermediate product, as well as the by-products, most feedstocks and some solid residues, have radionuclide activity concentrations below 1 Bq/g. Such material would therefore fall outside the scope of regulatory control. However, some of the process residues formed during pigment production may have radionuclide activity concentrations exceeding 1 Bq/g. The radium rich scales that are formed inside pipes and vessels can exhibit activity concentrations significantly higher than the feedstock materials. In terms of the standards, therefore, the production of TiO_2 pigment using the chloride process needs to be considered for regulatory control as a practice.

During normal plant operation, the chlorination step and the solids separation step are the only parts of the process where there is the potential for a worker to receive an annual effective dose exceeding 1 mSv, mainly as a result of gamma radiation from accumulations of process residues with elevated activity concentrations. Simple measures, such as restrictions on access and the recording and control of occupancy periods, have proven effective in providing the necessary level of worker protection. There is also the potential for workers to receive annual effective doses exceeding 1 mSv during maintenance operations, but the adoption of good OHS work practices ensures that access to reaction vessels is restricted, airborne dust is controlled, personal protective equipment (possibly including respiratory protective equipment) is used where appropriate, and measures are taken to prevent the spread of contamination. In addition, the discharge of effluents and the disposal of waste have to meet environmental protection requirements, with particular attention having to be given to the disposal of higher activity wastes such as scale, rubber linings and filter cloths. As a result, the exposure of workers and members of the public appears to be adequately controlled, and annual effective doses do not exceed 1 mSv. Without the assurance of such good work practices being followed, there is always the potential for doses to be significantly higher, particularly in the case of workers undertaking maintenance work. The most appropriate regulatory option is likely to be a minimum requirement for notification of the practice. Where the adoption of good OHS and environmental protection practices cannot be assured, the regulatory body may decide that a formal authorization in the form of a registration is needed.

Radium rich scales removed from or remaining within pipes and vessels, as well as unreacted bed material and refractory materials removed periodically from the chlorinator, appear to be the only materials likely to fall within the scope of application of the Transport Regulations [3]. Other materials may be transported without any radiological restrictions, although the observance of good environmental practice provides further assurance that the impact on the public and the environment is minimized (see Section 5.5.5).

The conversion of TiCl_4 to titanium metal or other titanium-containing products does not involve the use of radioactive materials and therefore does not require regulatory consideration as a practice.

Appendix

THORIUM AND URANIUM DECAY SERIES

The ^{232}Th and ^{238}U series are the main decay series of interest. The ^{235}U decay series is less important for radiation protection purposes, except for the radionuclide ^{227}Ac , which can contribute significantly to inhalation exposure. If necessary, the presence of ^{235}U (and, by implication, its decay progeny) can be taken into account on the basis of the abundances of ^{235}U and ^{238}U in natural uranium (0.711 and 99.284 wt%, respectively) — the corresponding ^{235}U : ^{238}U activity ratio is 0.046. Details of the ^{232}Th and ^{238}U decay series, as reported in Ref. [31], are given in Tables 26 and 27.

TABLE 26. THORIUM-232 DECAY SERIES

	Half-life	Mode of decay ^a	Gamma energy (keV) ^b
Th-232	1.405×10^{10} a	Alpha	
Ra-228	5.75 a	Beta	
Ac-228	6.15 h	Beta	911.204 (25.8%), 968.971 (15.8%)
Th-228	1.912 a	Alpha	
Ra-224	3.66 d	Alpha	240.986 (4.10%)
Rn-220	55.6 s	Alpha	
Po-216	0.145 s	Alpha	
Pb-212	10.64 h	Beta	238.632 (43.6%)
Bi-212	60.55 min	Beta 64.06% Alpha 35.94%	727.330 (6.67%)
Po-212	0.299 μs	Alpha	
Tl-208	3.053 min	Beta	583.191 (84.5%), 2614.533 (99.16%)
Pb-208	Stable	—	

^a Only major modes of decay are shown.

^b Only major gamma emissions of interest are shown.

TABLE 27. URANIUM-238 DECAY SERIES

	Half-life	Mode of decay ^a	Gamma energy (keV) ^b
U-238	4.468 × 10 ⁹ a	Alpha	
Th-234	24.10 d	Beta	63.29 (4.8%), 92.38–92.8 (5.6%)
Pa-234m	1.17 min	Beta	1001.03 (0.837%)
U-234	245 700 a	Alpha	
Th-230	75 380 a	Alpha	
Ra-226	1 600 a	Alpha	186.211 (3.59%)
Rn-222	3.823 5 d	Alpha	
Po-218	3.10 min	Alpha	
Pb-214	26.8 min	Beta	351.932 (37.6%)
Bi-214	19.9 min	Beta	609.312 (46.1%), 1764.491 (15.30%)
Po-214	164.3 μs	Alpha	
Pb-210	22.20 a	Beta	46.539 (4.25%)
Bi-210	5.012 d	Beta	
Po-210	138.376 d	Alpha	
Pb-206	Stable	—	

^a Only major modes of decay are shown.

^b Only major gamma emissions of interest are shown.

REFERENCES

- [1] EUROPEAN ATOMIC ENERGY COMMUNITY, FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS, INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR ORGANIZATION, INTERNATIONAL MARITIME ORGANIZATION, OECD NUCLEAR ENERGY AGENCY, PAN AMERICAN HEALTH ORGANIZATION, UNITED NATIONS ENVIRONMENT PROGRAMME, WORLD HEALTH ORGANIZATION, Fundamental Safety Principles, IAEA Safety Standards Series No. SF-1, IAEA, Vienna (2006).
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards – Interim Edition, IAEA Safety Standards Series No. GSR Part 3 (Interim), IAEA, Vienna (2011).
- [3] INTERNATIONAL ATOMIC ENERGY AGENCY, Regulations for the Safe Transport of Radioactive Material: 2009 Edition, IAEA Safety Standards Series No. TS-R-1, IAEA, Vienna (2009).
- [4] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Occupational Radiation Protection in the Mining and Processing of Raw Materials, IAEA Safety Standards Series No. RS-G-1.6, IAEA, Vienna (2004).
- [5] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Radioactive Waste from the Mining and Milling of Ores, IAEA Safety Standards Series No. WS-G-1.2, IAEA, Vienna (2002).
- [6] INTERNATIONAL ATOMIC ENERGY AGENCY, Application of the Concepts of Exclusion, Exemption and Clearance, IAEA Safety Standards Series No. RS-G-1.7, IAEA, Vienna (2004).
- [7] INTERNATIONAL ATOMIC ENERGY AGENCY, Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials, Safety Reports Series No. 49, IAEA, Vienna (2006).
- [8] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Protection and NORM Residue Management in the Production of Rare Earths from Thorium Containing Minerals, Safety Reports Series No. 68, IAEA, Vienna (2011).
- [9] UNITED STATES GEOLOGICAL SURVEY, Mineral Commodity Summaries, January 2011, USGS, Reston, VA (2011).
- [10] BROWN, T.J., et al., World Mineral Production 2004–08, British Geological Survey, Keyworth, UK (2010).
- [11] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Occupational Radiation Protection, IAEA Safety Standards Series No. RS-G-1.1, IAEA, Vienna (1999).
- [12] INTERNATIONAL ATOMIC ENERGY AGENCY, INTERNATIONAL LABOUR OFFICE, Assessment of Occupational Exposure Due to Intakes of Radionuclides, Safety Standards Series No. RS-G-1.2, IAEA, Vienna (1999).
- [13] VAN DER STEEN, J., et al., Strategies and Methods for Optimisation of Protection against Internal Exposures of Workers from Industrial Natural Sources (SMOPIE), Rep. 20790/04.60901, Nuclear Research Group, Petten, Netherlands (2004).

- [14] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, Human Respiratory Tract Model for Radiological Protection, ICRP Publication 66, Pergamon Press, Oxford (1994).
- [15] TERRY, K.W., Alpha self-absorption in monazite dusts, *Health Phys.* **69** (1995) 1–4.
- [16] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, ICRP Database of Dose Coefficients: Workers and Members of the Public, Version 2.0.1, Elsevier, Amsterdam (2003) CD-ROM.
- [17] SILK, T.J., KENDALL, G.M., PHIPPS, A.W., Revised estimates of dose from ores and mineral sands, *J. Radiol. Prot.* **15** 3 (1995) 217–222.
- [18] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION, Age-dependent Doses to Members of the Public from Intake of Radionuclides: Part 5, Compilation of Ingestion and Inhalation Dose Coefficients, ICRP Publication 72, Pergamon Press, Oxford (1996).
- [19] MORAVANSKA, H., LACIOK, A., “Presence of technologically-enhanced naturally-occurring radioactive materials in the Czech Republic”, Naturally Occurring Radioactive Materials, (NORM IV): Proceedings of an international conference held in Szczyrk, Poland, 17–21 May 2004, IAEA-TECDOC-1472, IAEA, Vienna (2005) 202–212.
- [20] SCHOLTEN, L.C., ROELOFS, J., VAN DER STEEN, J., A Survey of Potential Problems for Non-Nuclear Industries Posed by Implementation of New EC Standards for Natural Radioactivity, Rep. 40059-NUC 93-5203, KEMA, Arnhem, Netherlands (1993).
- [21] INTERNATIONAL ATOMIC ENERGY AGENCY, Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation, Technical Reports Series No. 419, IAEA, Vienna (2003).
- [22] COOPER, M.B., Naturally Occurring Radioactive Materials (NORM) in Australian Industries — Review of Current Inventories and Future Generation, Rep. ERS-006 prepared for the Radiation Health and Safety Advisory Council, EnviroRad Services, Beaumaris, VIC (2003).
- [23] JOHNSTONE, G., An evaluation of radiation and dust hazards at a mineral sand processing plant, *Health Phys.* **60** 6 (1991) 781–787.
- [24] COOPER, M.B., STATHAM, J.R., WILLIAMS, G.A., Natural Radioactivity in the Production of Titanium Dioxide Pigment: A Study of the Laporte Plant and Environmental Behaviour of Radionuclides at Bunbury, Western Australia, Rep. ARL/TR 037, Australian Radiation Laboratory, Yallambie, Victoria (1981).
- [25] PUCELJ, B., MARTINČIČ, R., “Concentration of natural radioactivity in a TiO₂ production process”, 6th International Congress of the International Radiation Protection Association (IRPA 6) (Proc. Conf. Berlin, 1984), IRPA, Fontenay-aux-Roses, France (1984).
- [26] GRASHCHENKO, S., GRITCHENKO, Z.G., SHISHKUNOVA, L.V., ALOY, A.S., “Distribution of natural radionuclides in some Russian non-nuclear industrial technologies”, Radiological Problems with Natural Radioactivity in the Non-Nuclear Industry (Proc. Conf. Amsterdam, 1997), KEMA, Arnhem, Netherlands (1997).

- [27] INTERNATIONAL ATOMIC ENERGY AGENCY, Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation, Technical Reports Series No. 419, IAEA, Vienna (2003).
- [28] HARIDASAN, P.P., PILLAI, P.M.B., TRIPATHI, R.M., PURANIK, V.D., Thorium in ilmenite and its radiological implications in the production of titanium dioxide, *Radiat. Prot. Dosim.* **129** (2008) 381–385.
- [29] GÁZQUEZ, M.J., BOLÍVAR, J.P., MANTERO, J., GARCÍA-TENORIO, R., VACA, F., “Physico-chemical and radioactive characterization of co-products from the titanium dioxide NORM industry for their use in cement manufacturing”, Naturally Occurring Radioactive Material (NORM VI) (Proc. Conf. Marrakech, Morocco, 2010), IAEA, Vienna (2011) 433–442.
- [30] BOLÍVAR, J.P., GARCÍA-TENORIO, R., MANTERO, J., GÁZQUEZ, M.J., LOZANO, R., “Occupational exposure assessment at a titanium dioxide plant located in the south-west of Spain”, Naturally Occurring Radioactive Material (NORM VI) (Proc. Conf. Marrakech, Morocco, 2010), IAEA, Vienna (2011) 109–117.
- [31] NATIONAL NUCLEAR DATA CENTER, BROOKHAVEN NATIONAL LABORATORY, NuDat2 Decay Radiation Database, version of 28 November 2005, Brookhaven Natl Lab., Upton, NY (2005).

Annex I

MINING AND BENEFICIATION OF HEAVY MINERAL SAND

The radiological aspects of the mining and beneficiation of heavy mineral sand are described in detail in another publication in the IAEA Safety Reports Series [I-1]. This annex is a summary of the information contained in that report.

Heavy mineral sand deposits may occur underwater or may form part of sea beaches or coastal dunes created by wind action over long periods of time. They may also occur inland in coastal strips up to a few tens of kilometres wide. The titanium-bearing mineral ilmenite is usually the main product of heavy mineral sand operations, typically accounting for 45–75% of total heavy mineral production. The other heavy minerals produced commercially are mostly zircon and the titanium-bearing mineral rutile, each of which typically accounts for 2–20% of total heavy mineral production.

I-1. PROCESS DESCRIPTION

Heavy mineral sand deposits are mined by dry mining methods using conventional earth-moving equipment such as front end loaders, bulldozers and scrapers or by wet dredging from ponds. The various heavy minerals of commercial value, accounting for 5–50% of the raw sand, are separated from the remaining, low value materials ('gangue' minerals) using screens, hydrocyclones and wet separation techniques that rely on differences in density. This process, referred to as the primary separation process, is usually carried out at the mine site and produces a concentrate with a heavy mineral content of at least 80–85%. The residues from the mining and primary separation processes include sand tailings, oversize solids, topsoil, peat, clay, shells and vegetation. They are returned to the mining void or used for topping of refilled areas.

In the next stage of the processing operation, referred to as the secondary separation process, the heavy mineral concentrate is dried and its constituent minerals are extracted in a series of dry separation steps using magnetic and electrostatic separators, as well as gravity and screening techniques. The residues from the secondary separation process include sand tailings, oversize solids, dust particles and clay fines. Monazite sand, a heavy mineral containing thorium and rare earths, is also treated as a residue if there is no intention of recovering the mineral content. The residues are sent to disposal areas at the mine site, usually the mining void. Monazite, because of its relatively high radioactivity content, is blended with tailings prior to disposal. After completion of the disposal

operation, the residues are covered with suitable topping material and the area is revegetated.

I-2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

Typical radionuclide activity concentrations are given in Table I-1. The ranges of activity concentrations in the following process materials extend (or may extend) beyond 1 Bq/g:

- (a) Heavy mineral concentrate, ilmenite, zircon, monazite, xenotime and leucoxene;
- (b) All residues from the secondary separation process (tailings, oversize solids, clay fines and airborne dust).

The activity concentrations in all other process materials, including all residues from the primary separation process, are typically less than 1 Bq/g.

I-3. OCCUPATIONAL EXPOSURE

Exposures arising from the mining and primary separation processes are of no significant concern because of the low activity concentrations in the process materials. During the primary separation process, the moisture content of the heavy mineral concentrate prevents any significant dust generation.

During the secondary separation process, external exposure can be an important pathway where monazite is handled in significant concentrations (typically where the monazite represents more than 0.5% of the total mineral content). Following the removal of ilmenite (often the first stage of the process), the remaining non-magnetic mineral fractions become progressively enriched with monazite. Annual effective doses received by workers from external exposure in dry separation plants have, in the past, regularly exceeded 10 mSv, particularly in plants where monazite was produced commercially. In recent years, as a result of improvements in working procedures and plant layout and design, as well as dwindling monazite production, doses have been much lower, typically 1–4 mSv.

Inhalation of airborne dust is a major exposure pathway in dry separation plants because the heavy mineral concentration is increased and significant concentrations of airborne dust can be generated as a result of the requirement for free running material. Each of the physical separation steps may produce copious amounts of airborne dust. Exposure to airborne dust is always a concern,

TABLE I-1. TYPICAL RADIONUCLIDE ACTIVITY CONCENTRATIONS IN PROCESS MATERIALS

	Activity concentration (Bq/g)	
	Th-232	U-238
<i>Minerals</i>		
Raw mineral sand	0.2–1	0.03–0.2
Heavy mineral concentrate	0.3–8	0.1–2
Ilmenite	0.04–2	0.03–0.4
Rutile	0.06–0.4	<0.1–0.7
Zircon	0.5–1	1–4
Monazite	140–250	6–40
Xenotime	60	50
Leucoxene	0.3–3	0.2–0.8
<i>Primary separation residues</i>		
Tailings	0.05–0.1	0.01–0.02
Oversize solids	<0.20	<0.12
Clay fines	<0.12	<0.12
<i>Secondary separation residues</i>		
Tailings	1–20	0.1–10
Oversize solids	0.3–2.6	0.6–1.9
Clay fines	2	0.4
Airborne dust within plant	1–20	0.1–10
Stack particulates	2–20	0.1–6

particularly in circuits where monazite-rich streams of material are being treated. Annual effective doses received by workers from dust inhalation in dry separation plants have, in the past, regularly reached some tens of millisieverts. Again, with lower monazite production and through improvements in engineering and administrative controls, doses have been reduced dramatically and are now as low as about 1 mSv in well managed plants.

High concentrations of thoron and radon progeny are unlikely to be found in dry separation plants owing to the low emanation of thoron and radon from the process material, the short half-lives of the radionuclides involved and the good ventilation conditions in the processing plants. The inhalation of thoron and radon is therefore not usually an exposure pathway of concern.

Effective doses arising from the combined effects of external exposure and dust inhalation are nowadays typically in the range of 1–7 mSv per year. Because of the potential for doses to approach or even exceed the dose limit for workers, comprehensive monitoring programmes and a combination of engineering and administrative controls continue to be required in dry separation plants.

I-4. PUBLIC EXPOSURE

Exposure of members of the public has been shown to be minimal. There are no significant exposure pathways from separation plants, and doses received in the vicinity of mining operations, after the refilling of the mined-out area, are likely to be lower than previous natural background levels.

REFERENCE TO ANNEX I

- [I-1] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Protection and NORM Residue Management in the Production of Rare Earths from Thorium-Containing Minerals, Safety Reports Series No. 68, IAEA, Vienna (2011).

Annex II

MANAGEMENT OF RESIDUES FROM SYNTHETIC RUTILE PRODUCTION

The information presented in Table II–1 is cited as an example of best practice in Australia for the management of residues from the production of synthetic rutile via the Becher process [II–1].

TABLE II–1. AUSTRALIAN BEST PRACTICE FOR RESIDUE MANAGEMENT

Residue	Management
Kiln scrubber solids	From wet scrubbers: pumped as slurry to lined dams. Subsequently, either rehabilitated in situ or, still wet, dug out and trucked to final disposal site. From dry scrubbers: directly trucked to final disposal site. Wetted prior to trucking to prevent dusting during transport. In either case, solids must be allowed to settle and dry before capping and rehabilitation of the disposal site.
Kiln discharge oversize	Collected into a bunded paddock from where trucked to lined dry waste disposal site. Alternatively, can be crushed and recycled, or used as a road base.
Non-magnetic fines	Collected into plant storage bins, loaded into trucks, wetted and transported to final disposal site. Alternatively, transported as slurry through pipeline to lined dams at the disposal site. Must be allowed to settle and dry before site capping and rehabilitation to pasture, for example.
Inert solids	Collected from plant dust extraction system via wet or dry scrubbers, followed either by an intermediate storage in dams or direct trucking to final lined disposal sites. Dry scrubber solids are wetted prior to trucking to prevent dusting during transport.

TABLE II-1. AUSTRALIAN BEST PRACTICE FOR RESIDUE MANAGEMENT (cont.)

Residue	Management
Iron oxide solids	Stored in lined dams to allow settling and drying. Dry material can either be rehabilitated in situ or trucked for final disposal to repository site. Alternatively, trucking of the dry material may be replaced by transporting it as slurry through pipeline directly to the lined dams of the final disposal site. This way dust generation from handling the dry material is eliminated. The solids must be allowed to settle and dry before site capping and rehabilitation to pasture, for example. A promising commercial scale technology of processing iron oxide solids to produce iron has been under development in Western Australia. If successful, it could result in practical elimination of this large solid waste stream from synthetic rutile production.
Neutralized acid effluent solids	Pumped to solar drying ponds from where, still wet, they are dug out and trucked to final disposal site. Alternatively, transported as slurry through pipeline to lined dams of the disposal site. Must be allowed to settle and dry before site capping and rehabilitation to pasture, for example. An alternative, recently developed option is to utilize the solids as an agricultural slow-release sulphur fertilizer.

REFERENCE TO ANNEX II

[II-1] RADIATION PROTECTION SUB-COMMITTEE OF THE TITANIUM MINERALS COMMITTEE OF THE CHAMBER OF MINERALS AND ENERGY OF WESTERN AUSTRALIA, Best Practice Radioactive Waste Management Guidelines in the Western Australian Mineral Sands Industry, Chamber of Minerals and Energy of Western Australia, Perth, Western Australia (1999).

CONTRIBUTORS TO DRAFTING AND REVIEW

Collier, D.	Australian Nuclear Science and Technology Organisation, Australia
Filion, D.	Rio Tinto Iron and Titanium (Consultant), Canada
Finley, N.	Millennium Chemicals, United Kingdom
Fountain, C.	Iluka Resources, Australia
García-Tenorio, R.	University of Seville, Spain
Haridasan, P.P.	International Atomic Energy Agency
Kletter, M.J.	DuPont Titanium Technologies, United States of America
McNulty, G.S.	Huntsman Pigments, United Kingdom
Schlittler, C.E.	Tronox (Consultant), United States of America
Simmons, C.T.	Thompson and Simmons, United States of America
Wymer, D.G.	International Atomic Energy Agency

Consultants Meetings

Vienna, Austria: 1–5 March 2004, 1–5 November 2004,
18–22 April 2005, 5–7 December 2011



IAEA

International Atomic Energy Agency

No. 22

Where to order IAEA publications

In the following countries IAEA publications may be purchased from the sources listed below, or from major local booksellers. Payment may be made in local currency or with UNESCO coupons.

AUSTRALIA

DA Information Services, 648 Whitehorse Road, MITCHAM 3132
Telephone: +61 3 9210 7777 • Fax: +61 3 9210 7788
Email: service@dadirect.com.au • Web site: <http://www.dadirect.com.au>

BELGIUM

Jean de Lannoy, avenue du Roi 202, B-1190 Brussels
Telephone: +32 2 538 43 08 • Fax: +32 2 538 08 41
Email: jean.de.lannoy@infoboard.be • Web site: <http://www.jean-de-lannoy.be>

CANADA

Bernan Associates, 4501 Forbes Blvd, Suite 200, Lanham, MD 20706-4346, USA
Telephone: 1-800-865-3457 • Fax: 1-800-865-3450
Email: customer@bernans.com • Web site: <http://www.bernans.com>

Renouf Publishing Company Ltd., 1-5369 Canotek Rd., Ottawa, Ontario, K1J 9J3
Telephone: +613 745 2665 • Fax: +613 745 7660
Email: order.dept@renoufbooks.com • Web site: <http://www.renoufbooks.com>

CHINA

IAEA Publications in Chinese: China Nuclear Energy Industry Corporation, Translation Section, P.O. Box 2103, Beijing

CZECH REPUBLIC

Suweco CZ, S.R.O., Klecakova 347, 180 21 Praha 9
Telephone: +420 26603 5364 • Fax: +420 28482 1646
Email: nakup@suweco.cz • Web site: <http://www.suweco.cz>

FINLAND

Akateeminen Kirjakauppa, PO BOX 128 (Keskuskatu 1), FIN-00101 Helsinki
Telephone: +358 9 121 41 • Fax: +358 9 121 4450
Email: akatilaus@akateeminen.com • Web site: <http://www.akateeminen.com>

FRANCE

Form-Edit, 5, rue Janssen, P.O. Box 25, F-75921 Paris Cedex 19
Telephone: +33 1 42 01 49 49 • Fax: +33 1 42 01 90 90
Email: formedit@formedit.fr • Web site: <http://www.formedit.fr>

Lavoisier SAS, 145 rue de Provigny, 94236 Cachan Cedex
Telephone: + 33 1 47 40 67 02 • Fax +33 1 47 40 67 02
Email: romuald.verrier@lavoisier.fr • Web site: <http://www.lavoisier.fr>

GERMANY

UNO-Verlag, Vertriebs- und Verlags GmbH, Am Hofgarten 10, D-53113 Bonn
Telephone: + 49 228 94 90 20 • Fax: +49 228 94 90 20 or +49 228 94 90 222
Email: bestellung@uno-verlag.de • Web site: <http://www.uno-verlag.de>

HUNGARY

Librotrade Ltd., Book Import, P.O. Box 126, H-1656 Budapest
Telephone: +36 1 257 7777 • Fax: +36 1 257 7472 • Email: books@librotrade.hu

INDIA

Allied Publishers Group, 1st Floor, Dubash House, 15, J. N. Heredia Marg, Ballard Estate, Mumbai 400 001,
Telephone: +91 22 22617926/27 • Fax: +91 22 22617928
Email: alliedpl@vsnl.com • Web site: <http://www.alliedpublishers.com>

Bookwell, 2/72, Nirankari Colony, Delhi 110009
Telephone: +91 11 23268786, +91 11 23257264 • Fax: +91 11 23281315
Email: bookwell@vsnl.net

ITALY

Libreria Scientifica Dott. Lucio di Biasio "AEIOU", Via Coronelli 6, I-20146 Milan
Telephone: +39 02 48 95 45 52 or 48 95 45 62 • Fax: +39 02 48 95 45 48
Email: info@libreriaaeiou.eu • Website: www.libreriaaeiou.eu

JAPAN

Maruzen Company, Ltd., 13-6 Nihonbashi, 3 chome, Chuo-ku, Tokyo 103-0027
Telephone: +81 3 3275 8582 • Fax: +81 3 3275 9072
Email: journal@maruzen.co.jp • Web site: <http://www.maruzen.co.jp>

REPUBLIC OF KOREA

KINS Inc., Information Business Dept. Samho Bldg. 2nd Floor, 275-1 Yang Jae-dong SeoCho-G, Seoul 137-130
Telephone: +02 589 1740 • Fax: +02 589 1746 • Web site: <http://www.kins.re.kr>

NETHERLANDS

De Lindeboom Internationale Publicaties B.V., M.A. de Ruyterstraat 20A, NL-7482 BZ Haaksbergen
Telephone: +31 (0) 53 5740004 • Fax: +31 (0) 53 5729296
Email: books@delindeboom.com • Web site: <http://www.delindeboom.com>

Martinus Nijhoff International, Koraalrood 50, P.O. Box 1853, 2700 CZ Zoetermeer
Telephone: +31 793 684 400 • Fax: +31 793 615 698
Email: info@nijhoff.nl • Web site: <http://www.nijhoff.nl>

Swets and Zeitlinger b.v., P.O. Box 830, 2160 SZ Lisse
Telephone: +31 252 435 111 • Fax: +31 252 415 888
Email: infoho@swets.nl • Web site: <http://www.swets.nl>

NEW ZEALAND

DA Information Services, 648 Whitehorse Road, MITCHAM 3132, Australia
Telephone: +61 3 9210 7777 • Fax: +61 3 9210 7788
Email: service@dadirect.com.au • Web site: <http://www.dadirect.com.au>

SLOVENIA

Cankarjeva Založba d.d., Kopitarjeva 2, SI-1512 Ljubljana
Telephone: +386 1 432 31 44 • Fax: +386 1 230 14 35
Email: import.books@cankarjeva-z.si • Web site: <http://www.cankarjeva-z.si/uvoz>

SPAIN

Diaz de Santos, S.A., c/ Juan Bravo, 3A, E-28006 Madrid
Telephone: +34 91 781 94 80 • Fax: +34 91 575 55 63
Email: compras@diazdesantos.es, carmela@diazdesantos.es, barcelona@diazdesantos.es, julio@diazdesantos.es
Web site: <http://www.diazdesantos.es>

UNITED KINGDOM

The Stationery Office Ltd, International Sales Agency, PO Box 29, Norwich, NR3 1 GN
Telephone (orders): +44 870 600 5552 • (enquiries): +44 207 873 8372 • Fax: +44 207 873 8203
Email (orders): book.orders@tso.co.uk • (enquiries): book.enquiries@tso.co.uk • Web site: <http://www.tso.co.uk>

On-line orders

DELTA Int. Book Wholesalers Ltd., 39 Alexandra Road, Addlestone, Surrey, KT15 2PQ
Email: info@profbooks.com • Web site: <http://www.profbooks.com>

Books on the Environment

Earthprint Ltd., P.O. Box 119, Stevenage SG1 4TP
Telephone: +44 1438748111 • Fax: +44 1438748844
Email: orders@earthprint.com • Web site: <http://www.earthprint.com>

UNITED NATIONS

Dept. I004, Room DC2-0853, First Avenue at 46th Street, New York, N.Y. 10017, USA
(UN) Telephone: +800 253-9646 or +212 963-8302 • Fax: +212 963-3489
Email: publications@un.org • Web site: <http://www.un.org>

UNITED STATES OF AMERICA

Bernan Associates, 4501 Forbes Blvd., Suite 200, Lanham, MD 20706-4346
Telephone: 1-800-865-3457 • Fax: 1-800-865-3450
Email: customercare@bernan.com • Web site: <http://www.bernan.com>

Renouf Publishing Company Ltd., 812 Proctor Ave., Ogdensburg, NY, 13669
Telephone: +888 551 7470 (toll-free) • Fax: +888 568 8546 (toll-free)
Email: order.dept@renoufbooks.com • Web site: <http://www.renoufbooks.com>

Orders and requests for information may also be addressed directly to:

Marketing and Sales Unit, International Atomic Energy Agency

Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Telephone: +43 1 2600 22529 (or 22530) • Fax: +43 1 2600 29302
Email: sales.publications@iaea.org • Web site: <http://www.iaea.org/books>

**RADIATION PROTECTION AND NORM RESIDUE MANAGEMENT
IN THE ZIRCON AND ZIRCONIA INDUSTRIES****Safety Reports Series No. 51**

STI/PUB/1289 (149 pp.; 2007)

ISBN 92-0-100607-1

Price: €36.00

**RADIATION PROTECTION AND THE MANAGEMENT
OF RADIOACTIVE WASTE IN THE OIL AND GAS INDUSTRY****Safety Reports Series No. 34**

STI/PUB/1171 (130 pp.; 2004)

ISBN 92-0-114003-7

Price: €21.00

**RADIATION PROTECTION AND NORM RESIDUE MANAGEMENT
IN THE PRODUCTION OF RARE EARTHS FROM THORIUM
CONTAINING MINERALS****Safety Reports Series No. 68**

STI/PUB/1512 (259 pp.; 2011)

ISBN 978-92-0-115710-2

Price: €45.00

**RADIATION PROTECTION AND SAFETY OF RADIATION SOURCES:
INTERNATIONAL BASIC SAFETY STANDARDS — INTERIM EDITION****IAEA Safety Standards Series No. GSR Part 3 (Interim)**

STI/PUB/1531 (138 pp.; 2011)

ISBN 978-92-0-120910-8

Price: €65.00

OCCUPATIONAL RADIATION PROTECTION**IAEA Safety Standards Series No. RS-G-1.1**

STI/PUB/1081 (73 pp.; 1999)

ISBN 92-0-102299-9

Price: €14.50

**OCCUPATIONAL RADIATION PROTECTION IN THE MINING
AND PROCESSING OF RAW MATERIALS****IAEA Safety Standards Series No. RS-G-1.6**

STI/PUB/1183 (95 pp.; 2004)

ISBN 92-0-115003-2

Price: €21.00

This Safety Report provides detailed information on the processes and materials involved in the titanium dioxide and related industries. It explains the radiological considerations that need to be taken into account by the regulatory body in determining the nature and extent of the radiation protection measures to be taken. It has been developed under the IAEA's programme on the application of its safety standards. The information provided will assist in the implementation of a graded approach to regulation. In terms of the graded approach, application of the requirements of the safety standards has to be commensurate with the characteristics of the practice or source and with the magnitude and likelihood of the associated exposures. This report is concerned primarily with the titanium dioxide industry but is also relevant to industries involved in the mining and beneficiation of mineral sands for the extraction of heavy minerals such as zircon, monazite and ilmenite.

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA
ISBN 978-92-0-132110-7
ISSN 1020-6450