Production of titanium dioxide

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Abstract. Titanium dioxide pigments provide whiteness and opacity to a vast range of everyday products from coatings and plastics, to inks and even cosmetics and food. Manufacture takes place using two different processes, the so called 'sulphate' and 'chloride' routes, to produce more than 4.5 million t per year worldwide. Both routes start from impure titanium dioxide based feedstocks which may contain naturally occurring radioactive materials (NORM). Experts from the TiO_2 production industry and feedstock suppliers are working with the International Atomic Energy Authority to develop a Safety Report covering the use of NORM containing materials within the TiO_2 industry. The data assessment shows that for both process routes, the main activity reports to the solid process wastes and there are no areas of concern related to products, co-products or liquid or gaseous effluents for production units operating to current environmental standards. Risk assessment for the landfill of solid process waste similarly did not indicate any areas of concern where current waste management practices were followed. In-process deposits, typically scale material, can build up with an increased activity level related to concentration of radium. Specific management practices such as controlled vessel entry to restrict worker exposure to these materials may be necessary. No worker exposure giving rise to an annual dose exceeding 1mSv is predicted.

1. Introduction

Titanium dioxide is a simple inorganic compound produced as a pure white powder. It is commonly available in two main crystal forms, anatase and rutile and typically supplied to the market in a range of package sizes or in bulk. Sales as water based slurry are also common in the USA.

It is the properties and uses of titanium dioxide that make it an interesting and valuable chemical and overshadow its rather mundane appearance.

It has a very high refractive index of ca. 2.7 which compares with values of only 2.0 and 1.6 for zinc oxide and china clay respectively. This high refractive index gives the potential for producing much greater opacity or hiding power, making TiO_2 a much better pigment than the other chemicals mentioned.

So titanium dioxide is the best white pigment available but this does not just restrict its use to anything that is white, the opacity is also used in combination with coloured pigments to give them the required hiding power they need.

The crystal size of the TiO_2 also needs to be optimised to maximise its effectiveness as a pigment, the optimum for light scattering being around 0.2 μm.

These properties give a highly versatile product with worldwide sales of around 4.5 million t. The main uses are in coatings such as paints, followed by plastics, then high grade papers and printing inks (see Fig. 1). There is also a wide range of minor uses in total volume terms many of which are still important and include uses such as pharmaceuticals, foodstuffs, and cosmetics.
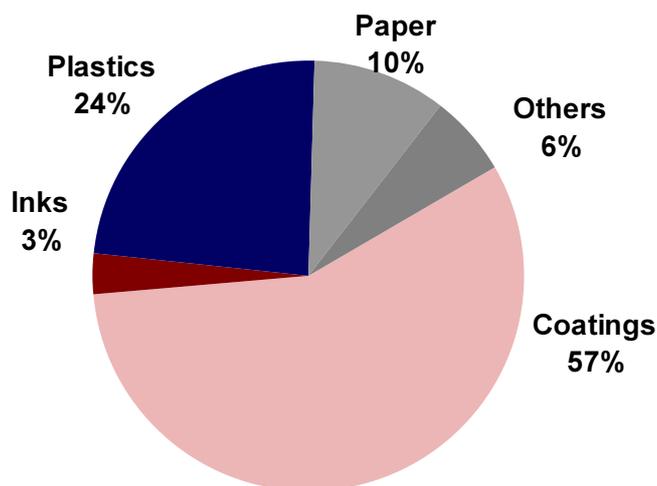
FIG. 1. Market segments for titanium dioxide

2. IAEA Safety Report

The TiO_2 industry uses feedstocks based on minerals that contain low levels of naturally occurring radioactive material i.e. it is a NORM user and there is various information in the public domain relating to the impact of this usage. Much of the data is inaccurate or now out of date so when the International Atomic Energy Authority (IAEA) proposed the development of a Safety Report on titanium dioxide production, this was strongly supported by the industry.

The scope of the report covers titanium dioxide feedstock production, titanium tetrachloride production and titanium dioxide production by the two commercial routes – sulphate and chloride. The report is now close to completion.

There has been direct involvement with the report from Huntsman Pigments/Tioxide Europe Ltd, Lyondell/Millenium, Rio Tinto, Tronox, Dupont, Iluka and ANSTO and indirect involvement of other titanium dioxide manufacturers, Kemira, Sachtleben, Cinkarna and Precheza, through the European Chemical manufacturers trade association CEFIC.

3. Titanium dioxide manufacture

The overall process of manufacture is to take an impure TiO_2 feedstock and to convert this into the pure white TiO_2 pigment. In essence the process sounds very simple but to achieve this it is necessary to chemically convert the impure TiO_2 into another chemical, separate out the impurities then to convert back to pure TiO_2 — in effect a chemical purification.

There are two commercial processes used to achieve this, the so called 'chloride' and 'sulphate' process routes.

3.1. The chloride process route

The overall chemistry of this process can be represented as:-

$$TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO + CO_2$$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$
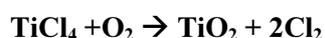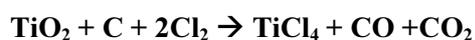
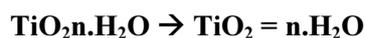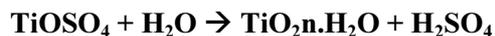The chlorine released when the titanium dioxide is reformed is recycled back to the beginning of the process such that the only chlorine consumed is that which reacts with impurities. The unit operations involved in the process are depicted in Fig. 2.

Chlorination is carried out at a temperature of around 1000^0C in a fluidised bed reactor in the presence of coke. The resulting gas stream contains titanium tetrachloride, oxides of carbon and all the impurity metals from the feedstock in the form of metal chlorides. The gas stream is contacted with recycled liquid $TiCl_4$ which cools it to a level in at which the other metal chlorides separate out as solids. The $TiCl_4$ goes forward with further cooling to be condensed as a liquid and then fed to a high temperature oxidation reactor where it is reacted with oxygen in a plasma reactor or toluene burner to reform titanium dioxide and release the chlorine which is recycled back to the beginning of the reaction. This pure titanium dioxide is subject to a range of chemical surface treatments, milling and drying operations to give a range of products with particular properties in terms of dispersion and durability, suitable for particular end use applications. The metal chloride impurities that are removed by the processing are typically neutralised with lime or limestone and sent for disposal via landfill.

3.2. The sulphate process route

The overall chemistry of the process can be represented as:-

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O$$

$$TiOSO_4 + H_2O \rightarrow TiO_2 n.H_2O + H_2SO_4$$

$$TiO_2 n.H_2O \rightarrow TiO_2 = n.H_2O$$

The sulphate process is more complicated in terms of the number of unit operations involved. These are detailed in Figure 3

The feedstock is first digested in strong sulphuric acid which converts the titanium components into titanyl sulphate and the iron into sulphates. Where the feedstock used is ilmenite based, a reduction step is required in which iron is added to convert any ferric iron to the ferrous form to aid separation later in the process. This is followed by a clarification step to remove any undigested material from the liquor. For an ilmenite process crystallisation typically follows which separates out co-product ferrous sulphate heptahydrate (copperas), though it is also possible to extract copperas later in the process. Copperas is sold for a range of applications including water treatment, agriculture and use in cement. The liquor passes forward to a hydrolysis stage in which the oxysulphate is reacted with water to produce a hydrated titanium dioxide product and releases sulphuric acid. The hydrated TiO_2 passes forward to a rotary kiln where it is calcined to produce the anhydrous titanium dioxide product. Further processing (finishing), is then analogous to the chloride process involving chemical surface treatments (coating), milling and drying operations. The acid that is released at hydrolysis is not strong enough to be used directly at digestion so it is subject to one of two processes, either acid concentration; or neutralisation to produce gypsum. In the former the acid is typically subjected to a number of heating, concentration and filtration cycles to increase the strength of the acid to a level allowing reuse in the process or sale. The process also concentrates residual iron that is separated as a ferrous sulphate monohydrate co-product. The alternative process, of gypsum production, treats the acid with a calcium salt to give gypsum which is used in plasterboard manufacture, agriculture and cement.
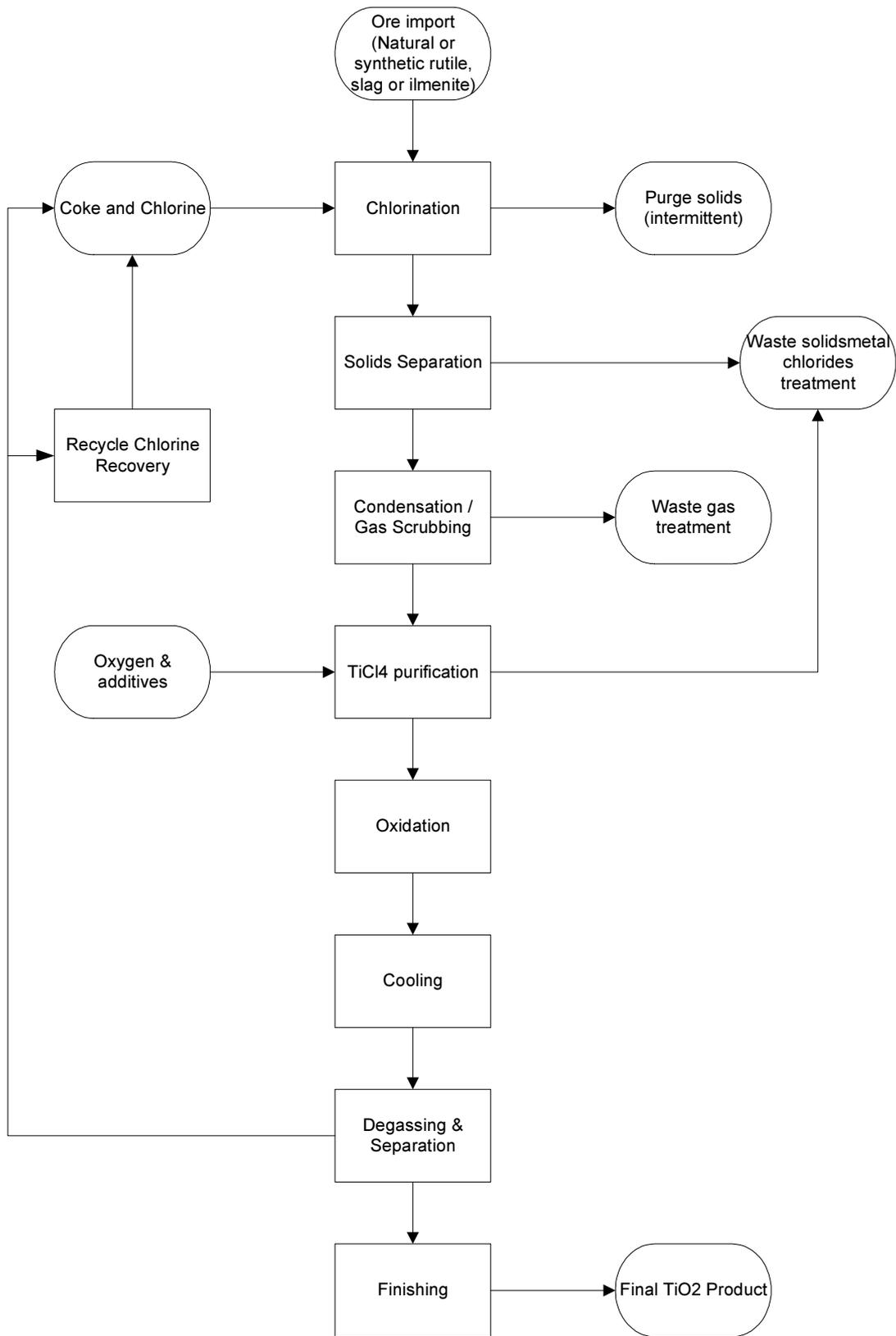
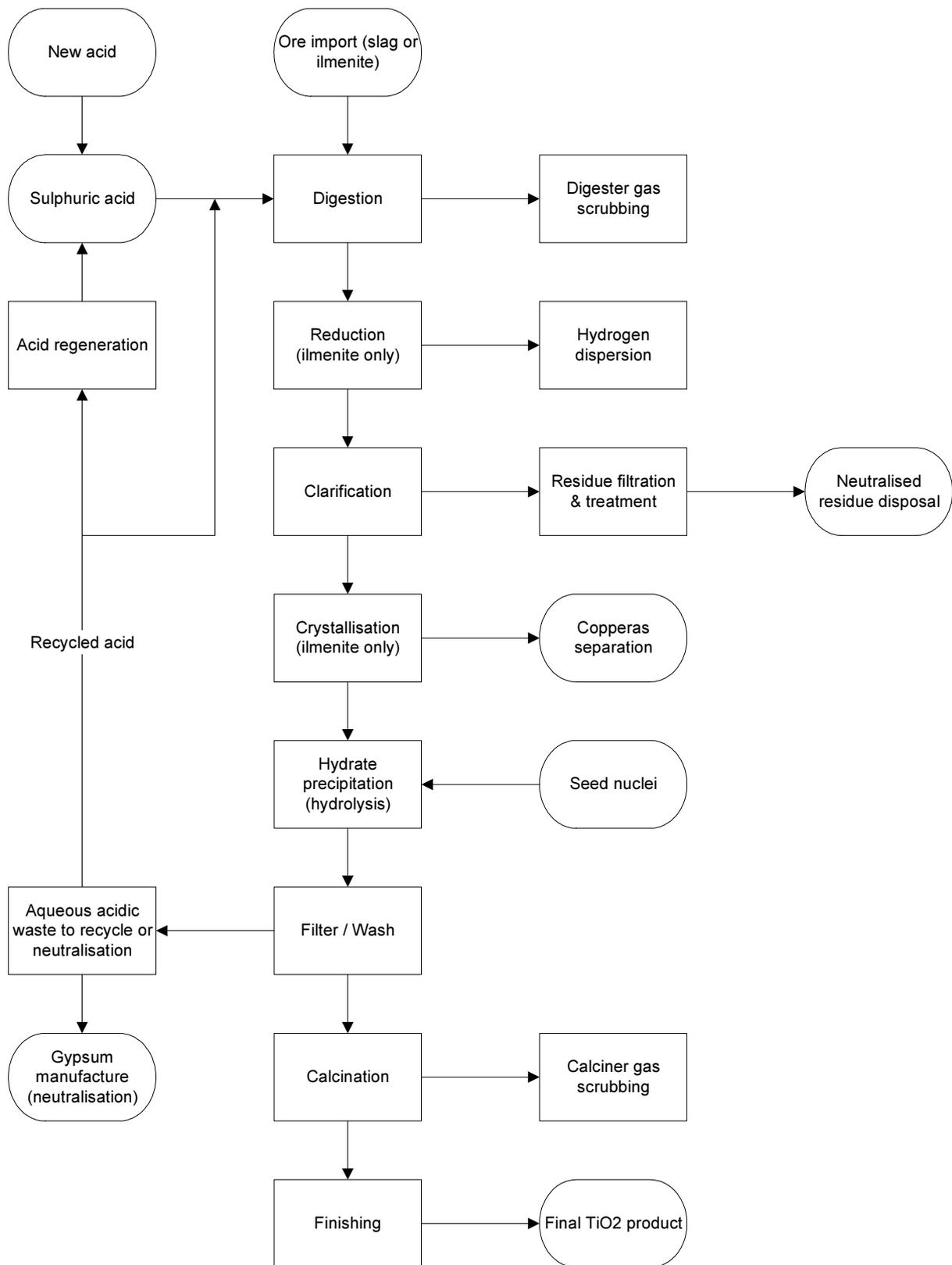*FIG. 2: The chloride process TiO₂ production route*

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┌──────────────┐              ┌──────────────────┐
│   New acid   │              │ Ore import (slag │
└──────┬───────┘              │    or ilmenite)  │
       │                      └─────────┬────────┘
       │                                │
       ▼                                ▼
┌──────────────┐              ┌──────────────┐        ┌──────────────────┐
│Sulphuric acid├─────────────▶│   Digestion  ├───────▶│  Digester gas    │
└──────────────┘              └──────┬───────┘        │   scrubbing      │
       ▲      ▲                      │                └──────────────────┘
       │      │                      ▼
┌──────┴──────┐               ┌──────────────┐        ┌──────────────────┐
│    Acid     │               │  Reduction   ├───────▶│    Hydrogen      │
│ regeneration│               │(ilmenite only)│       │   dispersion     │
└──────┬──────┘               └──────┬───────┘        └──────────────────┘
       ▲                             │
       │                             ▼
       │              ┌──────────────┐   ┌──────────────────┐   ┌──────────────────┐
       │              │ Clarification├──▶│Residue filtration├──▶│   Neutralised    │
       │              └──────┬───────┘   │  & treatment     │   │ residue disposal │
       │                     │           └──────────────────┘   └──────────────────┘
Recycled acid                ▼
       │              ┌──────────────┐        ┌──────────────────┐
       │              │Crystallisation├──────▶│    Copperas      │
       │              │(ilmenite only)│       │   separation     │
       │              └──────┬───────┘        └──────────────────┘
       │                     │
       │                     ▼
       │              ┌──────────────┐        ┌──────────────────┐
       │              │   Hydrate    │◀───────┤   Seed nuclei    │
       │              │ precipitation│        └──────────────────┘
       │              │ (hydrolysis) │
       │              └──────┬───────┘
       │                     │
┌──────┴───────┐             ▼
│Aqueous acidic│      ┌──────────────┐
│waste to      │◀─────┤  Filter / Wash│
│recycle or    │      └──────┬───────┘
│neutralisation│             │
└──────┬───────┘             ▼
       │              ┌──────────────┐        ┌──────────────────┐
       ▼              │  Calcination ├───────▶│  Calciner gas    │
┌──────────────┐      └──────┬───────┘        │   scrubbing      │
│   Gypsum     │             │                └──────────────────┘
│ manufacture  │             ▼
│(neutralisation)│    ┌──────────────┐        ┌──────────────────┐
└──────────────┘      │  Finishing   ├───────▶│ Final TiO2 product│
                      └──────────────┘        └──────────────────┘
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FIG. 3: The sulphate process TiO$_2$ production route

3.3. Feedstocks used

The main feedstocks used within the industry are detailed in Table 1. Those most commonly used for the chloride process are depicted in blue and in red for the sulphate route process, though one major manufacturer does use ilmenite in the chloride process. In general higher grade (% TiO_2) feedstocks are used for the chloride process than for the sulphate process.

TABLE 1: MAIN FEEDSTOCKS USED

Feedstocks	TiO_2	U series		Th series	
	(%)	ppm	Bq/g ^{238}U	ppm	Bq/g ^{232}Th
Rutile	93 – 96.5	10 - 60	0.1 - 0.74	20 - 90	0.08 - 0.36
Synthetic Rutile	88 - 95.5	3 - 60	0.04 - 0.80	35 - 480	0.14 - 1.9
Chloride Slag	85 – 86	0.2 - 6	0.002 – 0.08	0.2 - 30	0.001- 0.12
Sulphate Slag	79 – 86	0.2 - 6	0.002 – 0.08	0.2 - 30	0.001- 0.12
Ilmenite	45 - 65	6 - 80	0.1 - 1.0	20 - 500	0.08 – 2.0

The upper activity levels detailed for each of the feedstocks represent the highest activity we believe is used within the industry but invariably producers operate with a blend of feedstocks so the upper limit represents the highest activity material that might be used within a blend rather than what might be processed at the 100% level.

Rutile is a natural high grade titanium dioxide mineral.

Synthetic Rutile is produced by reducing the iron oxide in ilmenite to metallic iron using carbon monoxide, followed by reoxidation and separation from the TiO_2 rich fraction (Becher process) or leaching with hydrochloric acid (Benelite process).

Slag feedstocks are produced by the smelting of ilmenites with coal at high temperature. The process is adjusted to produce the different particle size requirements for sulphate or chloride use.

Ilmenite is a naturally occurring titanium/iron oxide found either in rock form or as a heavy mineral sand.

3.3.1. Choice of feedstock — chloride process

Ilmenites are only used by one chloride route producer, in relative terms, ilmenites are low cost and have a low TiO_2 content which leads to high chlorine losses and high volumes of waste products.

Slags have low activity level, but a low TiO_2 content and give a high volume of waste products. Synthetic Rutiles have higher activities, higher TiO_2 content and give an intermediate level of waste products. Natural rutiles are of intermediate activity, the highest TiO_2 content, give the lowest waste volumes but have the highest purchase price.

3.3.2. Choice of feedstock — sulphate process

In relative terms ilmenites for the sulphate process have higher activity, low cost, low TiO_2 content and when used generate a high volume of co-products or wastes. Slag based feedstocks have low activity, a higher TiO_2 content and produce lower co-product or waste volumes but have a higher purchase price. Rutile feedstocks cannot be digested in sulphuric acid, so they can only be used for the chloride process.

The feedstock choice the manufacture makes will depend on how the plant has been configured at the design stage, Environmental, Health & Safety (EHS) requirements and the overall processing costs.

The overall costs will relate to the feedstock purchase price, its TiO_2 content, the cost of dealing with wastes arising and any EHS requirements which will include consideration of radiation implications and effluent discharge requirements. Particularly for sulphate route production plants, co-product production will be an integral part of the process so the choice of operating when using either ilmenite or slag will have been defined at the design stage.

4. Radiological aspects of the sulphate process

4.1. Activity within the process, and in wastes and products

Clearly activity levels will relate to the feedstocks used and in general, activity levels when using slag based feedstocks will be low throughout the process. Whereas when ilmenites are used, some concentration will take place within the process.

There are 3 types of process change that influence the distribution and impact of radionuclides within the process.
- Selectivity of different radioelements within the natural decay chains due to the chemistry involved.
- Concentration or dilution due to volume change within the process.
- Deposition / precipitation of radioelements due to changes in physical conditions within the process.

4.2. Digestion

A key step as far as the process is concerned and in terms of its impact on the distribution of activity is the digestion step. All the feedstock is digested with sulphuric acid which results in some disequilibrium.
- U – believe majority will pass forward in liquor
- Th – as for U
- Ra – low solubility, evidence suggests 75 – 95% not digested
- Pb – low solubility expect majority to remain
- Bi – chemistry predicts the majority will pass forward, evidence implies a value of 40 -75% passing forward.

After digestion the solid volume is reduced by a factor of 5 – 6 and the overall impact is increased activity of the remaining digester residue that is separated after the reduction stage.

The activity concentration for digester residue from an ilmenite feedstock is typically:
- ^{238}U series = 0.6-1.0 Bq/g (maximum – some disequilibrium) (cf feedstock = 0.1 - 0.2)
- ^{232}Th series = 1.2 – 2.5 Bq/g (cf feedstock = 0.4 - 0.5)

4.3. Post-digestion

Following on from the digestion operation the majority of the radionuclides would be expected to remain in solution when the titanyl sulphate ($TiOSO_4$) is hydrolysed and separated out as a solid from the liquor. The main product TiO_2 which is produced via hydrolysis of the titanyl sulphate stream therefore does not contain any activity. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$ – copperas), which is extracted from the liquor either prior to or after hydrolysis of the titanyl sulphate, also does not contain appreciable activity.

The radionuclides remain in the acidic liquor until this is treated typically either via an acid re-concentration process, or by neutralisation to produce gypsum.

4.4. Gypsum production and neutralisation

The acidic liquor comprises mainly sulphuric acid and iron sulphate and this is typically neutralised by lime or limestone to produce gypsum and iron hydroxides.

- $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4.2H_2O$
- $FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$

The effective volume dilution factor if all of the acid is neutralised to make gypsum is approximately a value of 4 when compared to the feedstock but this will depend on the level of neutralisation, the efficiency of copperas/ferrous sulphate extraction (if employed) and the feedstock used. The end result is that the activity level of gypsum is low and of no concern, whether used as a product or disposed of as a waste.

4.5. Acid concentration

The other option for treatment of the acid liquor is acid concentration. The acid released when titanyl sulphate is hydrolysed can not be reused directly in the process as it is not strong enough. If the acid concentration option is chosen then the acid can be reused in the process, or sold. This process also concentrates residual iron salts to produce an iron sulphate monohydrate co-product.

The process is one of sequential heating, concentration and precipitation stages and the radionuclides that pass forward can end up either in the concentrated acid or the iron salt.
Overall maximum activity levels here are likely to be similar to the starting feedstock

An overview of activity levels within the process based on the processes described is presented in Fig. 4. The representation is based on three activity levels, < 1.0Bq/g, > 1.0 and < 10Bq/g and >10Bq/g. The lower level was chosen based on the exclusion threshold specified in RS-G-1.7[1].

4.6. Concentration of radionuclides within the process

The activity of the main process materials does not give the full story in terms of the distribution of radionuclides. Where physical and chemical changes take place, radionuclides may be deposited, particularly those of marginal solubility such as Radium. This leads to deposits of increased activity that may build up with time as material referred to as process scale.

These deposits are of low volume but considerably more active than the main input or output flows to or from the system. In practice the radium scale is often associated with barium sulphate and particular areas where it is found are at the copperas crystallisers, in the hydrolysis area and in the Moores filtration area. The former is where the acid stream is concentrated and cooled to precipitate out iron salts, hydrolysis is where titanyl sulphate product is converted to hydrated titanium dioxide and the latter where this precipitated material is separated from the acidic liquor.

Areas within the process where this concentration of radionuclides takes place are illustrated in Fig. 5.

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Application of the Concepts of Exclusion, Exemption and Clearance, Safety Standards Series No. RS-G-1.7, IAEA, Vienna (2004).
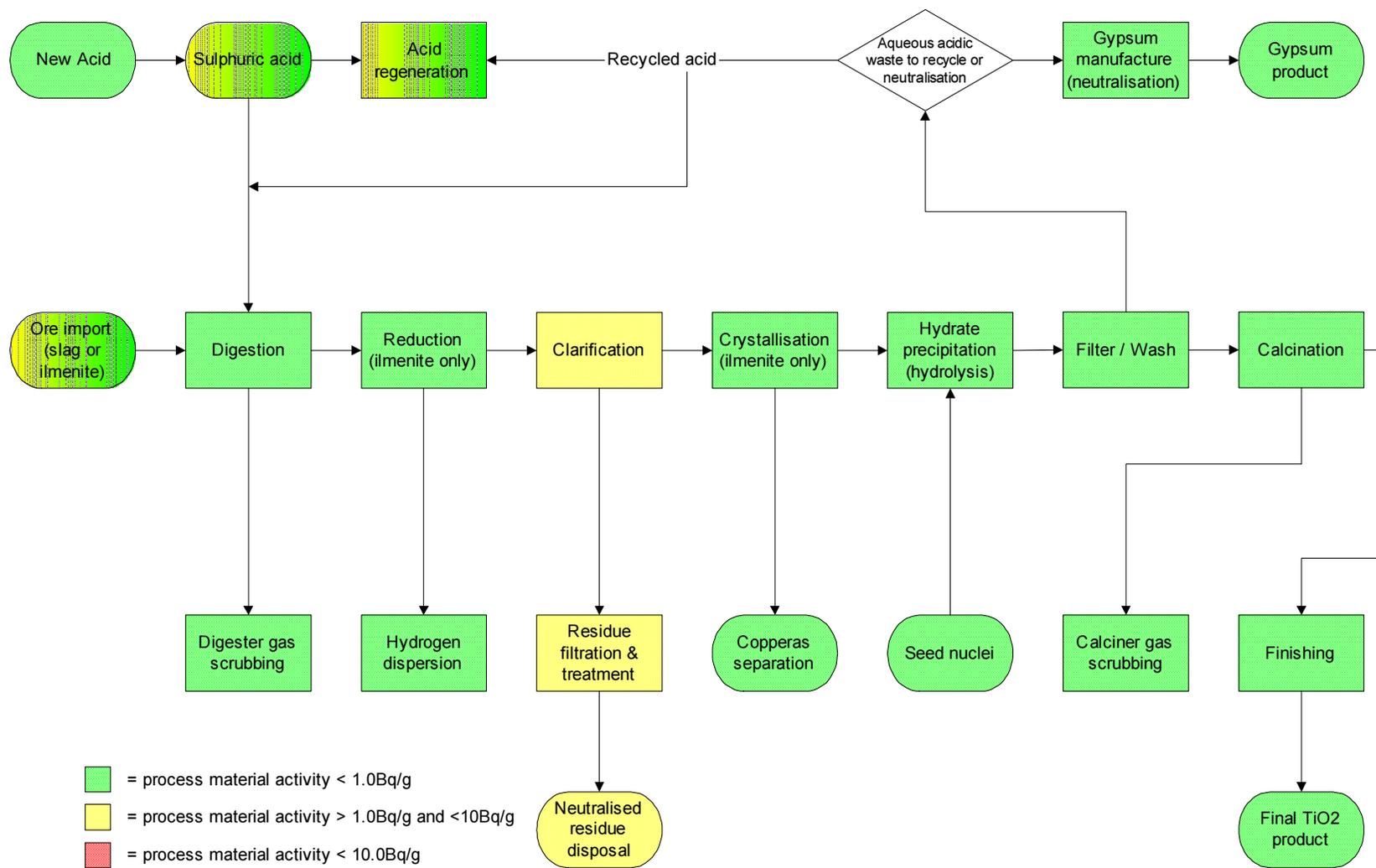
New Acid → Sulphuric acid → Acid regeneration ← Recycled acid ← Aqueous acidic waste to recycle or neutralisation → Gypsum manufacture (neutralisation) → Gypsum product

Ore import (slag or ilmenite) → Digestion → Reduction (ilmenite only) → Clarification → Crystallisation (ilmenite only) → Hydrate precipitation (hydrolysis) → Filter / Wash → Calcination

Digestion → Digester gas scrubbing

Reduction (ilmenite only) → Hydrogen dispersion

Clarification → Residue filtration & treatment

Crystallisation (ilmenite only) → Copperas separation

Seed nuclei → Hydrate precipitation (hydrolysis)

Filter / Wash → Calciner gas scrubbing

Calcination → Finishing

Residue filtration & treatment → Neutralised residue disposal

Finishing → Final TiO2 product

■ = process material activity < 1.0Bq/g
■ = process material activity > 1.0Bq/g and <10Bq/g
■ = process material activity < 10.0Bq/g

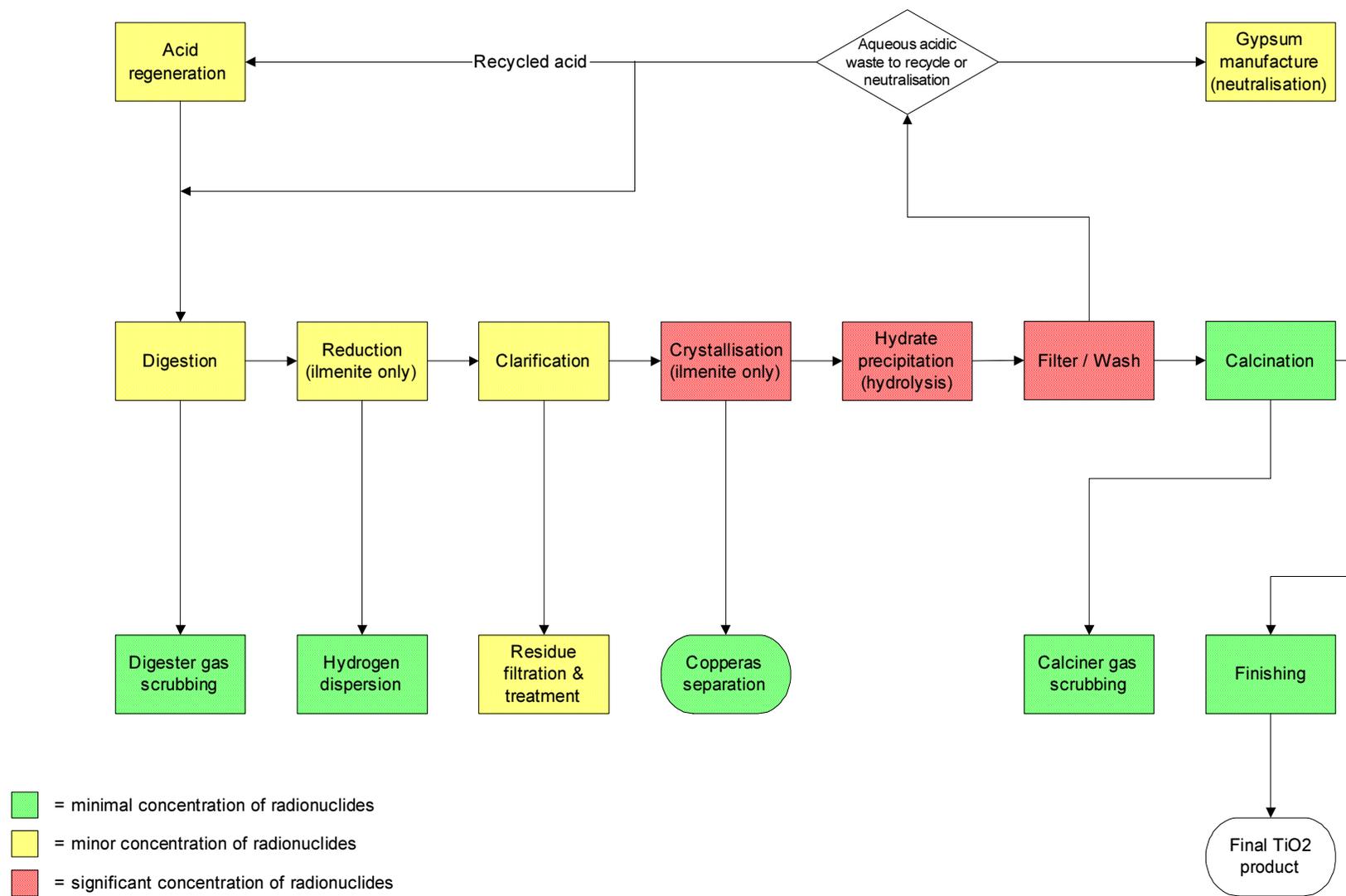FIG. 4. Activity concentrations of process materials within the sulphate process

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FIG. 5. Concentration and deposition of radionuclides within the sulphate process

4.7. Occupational exposures and doses

Measured instantaneous dose rates and calculated occupational exposures for sulphate process workers are summarised in Table 2. These reflect the low activities of the process materials and low occupancy for many process activities. In general the effective dose received by workers is much less than 1mSv/a and could not approach the international 20mSv/a limit for workers.

The areas where some form of control may be required in particular relate to vessel entry in areas with potential for the build up of process scale e.g. copperas crystalliser vessels, hydrolysis tanks, Moores tanks, acid stock tanks and the decontamination of equipment removed from these areas of the process. In practice these activities would be managed to restrict doses to 1mSv/yr or less as required.

TABLE 2: EXPOSURE AND DOSES RECEIVED BY WORKERS – SULPHATE PROCESS

Process Area	Instantaneous Dose Rate (uSv/h)	Effective Dose (mSv/y)	Comment	Measures to Minimise
Feedstock Handling	0.05 - 0.3	<1	High specific gravity	Miimise dust, supervised areas ,RPE
Digester Residue Operations	0.2 - 1.5	<1	Material normally damp	
Digester Residue Landfill	0.16 - 0.5	0.4 - 1.1	Overestimate due to capping of material	Minimise drying out and dust formation
Copperas Crystallisers	0.2 - 10.0	<1	High dose rate relates to vessel entry	Low occupancy
Hydrolysis Area	0.2 - 50.0	<1 - 6	Highest mesurement close to piece of equipment. Highest area mesurement of 12uSv/h	Consider need for restricted access, supervised area, logging of hours
Moores Filtration Area	1.0 - 21.0	<1 - 6	Highest dose rates for vessel entry	As above
Weak Acid Stock Tanks	10	<1	Vessel entry, low occupancy	Restricted access
Decontamination of Equipment	Equipment dependent	<1	Removal of scale, check activity, defined actions	Controlled area or personal dosimetry. Operate process to minimise build up. Chemical treatment e.g. neutralisation required

5. Radiological aspects of the chloride process

5.1. Activity within the process, and in wastes and products

As for the sulphate process, the activity within the process will depend on the feedstock used, selectivity of radioelements due to the chemistry, concentration due to volume change and deposition/precipitation of radioelements due to changes in physical conditions within the process. The chloride process is simpler in terms of the number of unit operations involved. There are consequently less changes in physical conditions for the chloride process.

5.2. Chlorination

The principal reaction in this process is chlorination at approximately 1000^0C under reducing conditions. The following chemistry is anticipated:
- U – will chlorinate and pass forward in gas stream
- Th – vast majority will pass forward (b.pt 940^0C)
- Ra – $RaCl_2$ only melts at 1000^0C so there is the possibility of some retention within the chlorinator
- Pb – vast majority will pass forward (b.pt 950^0C)
- Bi - will chlorinate and pass forward in gas stream

- Rn – will remain in gas phase

There is the possibility of some absorption of volatile chlorides into chlorinator refractory lining.

5.3. Quench/solids separation

The gas stream produced in the chlorinator comprising $TiCl_4$, CO, CO_2, and metal chlorides, passes forward and is quenched with recycled liquid $TiCl_4$, lowering the temperature and condensing out metal chloride solids. These solids contain the vast majority of the radionuclides. Some polonium may stay with the $TiCl_4$ that goes forward in the process but will be returned as part of a recycle stream when the $TiCl_4$ is distilled.

The separated metal chloride solids are slurried in water and neutralised typically with lime. Neutralisation will precipitate essentially all the radionuclides. The level of neutralisation will determine losses to liquid effluent. For full neutralisation everything will go to solid waste.

5.4. Solid wastes

Apart from some loss of Rn which will be highly dispersed, all radionuclides will remain within the chlorination solids handling areas. If you compare a damp neutralised waste solid with the starting feedstock the volume is likely to have reduced with a concentration factor in the range of about 1.0 to 2.5 depending on the type of feedstock used. Some build up of activity within the chlorinator bed over a period of time is also likely but the activity concentration when removed will be a function of operating regime. Higher temperatures and higher flow rates will lead to lower activity build up within the chlorinator.

An overview of activity levels within the chloride process based on the processes described is presented in Fig. 6.

5.5. Concentration of radionuclides within the process

The chloride process is a continuous process rather than batch like the sulphate process and with much fewer unit operations. As a consequence there is less opportunity for the build up of radionuclides within the process other than related to the process materials. Consequently Fig. 7 which shows these areas is similar to Fig. 6.

5.6. Occupational exposures and doses

Measured instantaneous dose rates and calculated occupational exposures for chloride process workers are summarised in Table 3. These reflect the low activities of the process materials and low occupancy for many process activities. In general the effective dose received by workers is much less than 1mSv/a.

The areas where some form of control is required in particular relate to vessel entry into areas with potential for the build up of process scale e.g. neutralisation area and areas or activities where dust levels may be high. In practice these activities would be managed to restrict doses to 1mSv/a or less.
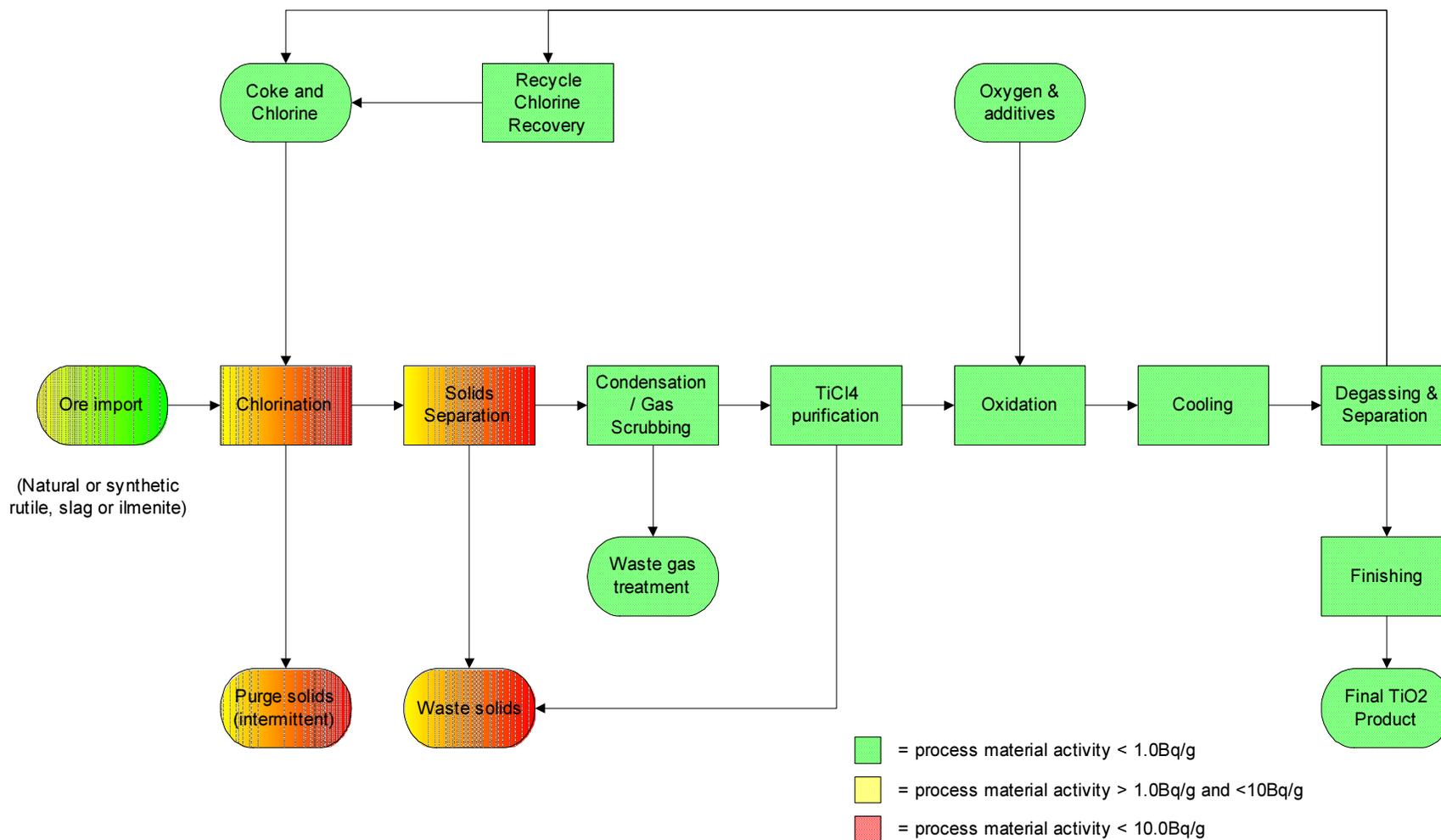
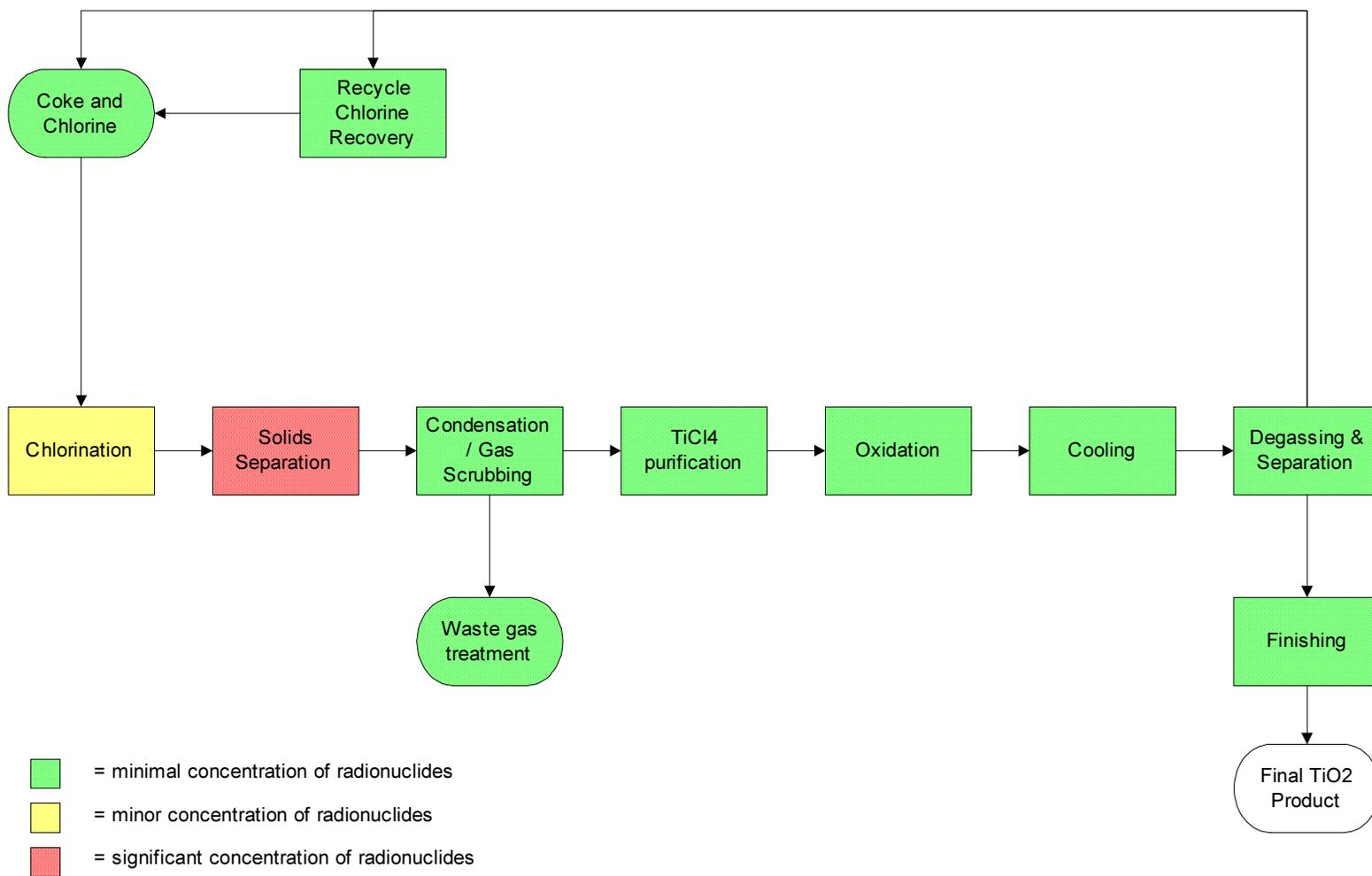FIG. 6. Activity of process materials within the chloride process

FIG.7. Concentration and deposition of radionuclides within the chloride process

Boxes:
- Coke and Chlorine
- Recycle Chlorine Recovery
- Chlorination
- Solids Separation
- Condensation / Gas Scrubbing
- TiCl4 purification
- Oxidation
- Cooling
- Degassing & Separation
- Waste gas treatment
- Finishing
- Final TiO2 Product

Legend:
= minimal concentration of radionuclides
= minor concentration of radionuclides
= significant concentration of radionuclides

TABLE 3: EXPOSURE AND DOSES RECEIVED BY WORKERS — CHLORIDE PROCESS

Process Area	Instantaneous Dose Rate (uSv/h)	Effective Dose (mSv/y)	Comment	Measures to Minimise
Feedstock Handling	0.1 - 0,15	<1	Minimise losses and dust generation	Respiratory protection for dust is adequate to protect from radiation hazard
Inside chlorinator	2.5	<1	Access during refurbishment	Respiratory protection, systems of work that minimise internal access requirements
Bed purging		<1	Limited occupancy - high temperature hazard. Infrequent operation.	
Neutralisation area	10	<1	Filter maintenance	Manage exposure time
	35	<1	Tank entry	Consider need to classify as contolled area, restrict access, respiratory protection, disposable clothes and equipment wash down
	50 - 90	<1	Internal tank descaling	As above
	2.7	<1	Working in area	Limited time close to equipment
Landfill operation	0.5	<1	Limited occupancy	Shielding by cover materials
In process scale and rubber linings	15		Removed from process equipment	Segregation of equipment, restricted access
Co-product processing	0.3 - 0.35	<1	Dependent on co-product & feedstock, numbers represent maxima	

5.7. Environmental impacts and public exposure

Supported by Directive 92/112/EEC on 'procedures for the reduction and eventual elimination of pollution caused by waste from the titanium dioxide industry' in Europe and by environmental requirements in other parts of the world, discharges of waste to the aquatic environment from titanium dioxide production have been significantly reduced or stopped entirely.

Essentially all radioactivity is returned to the solid phase either as a waste or co-product. There are no problems associated with the activity levels of co-products and good waste management practices related to disposal ensure risks are well controlled and low.

This is supported by work carried out to assess the environmental impacts of a production site and a waste landfill.

Radiological assessment of a sulphate route, ilmenite based production site was carried out involving sampling within and beyond the site boundary. The following data was obtained when comparing operational with pre-operational measurements:
  ▪ A comparison of external radiation dose at five external stations showed no detectable difference in dose rate comparing operational with pre-operational measurements
  ▪ No detected difference in radon/thoron progeny
  ▪ No difference in radium concentrations of airborne particulate
  ▪ No difference in radium concentrations in ground water
  ▪ No difference in radium concentrations detected in soil or in seawater when comparing the operational with pre-operational phase
It was concluded that there was no additional dose to members of the public from operation of the process.

The landfill operation for one producer involving disposal of ilmenite based sulphate process digester residue was subject to a radiological risk assessment. The assessment concluded that the techniques employed reduced external dose rates to background levels and that risks were reduced to trivial levels. This assessment was carried out on a landfill prior to the introduction of enhanced waste disposal requirements under the EU landfill directive so it would be expected that risk levels would have now reduced further.

The other possible route of public exposure relates to transport of feedstock. Typically this may involve movement of bulk cargo in ships with transfer to truck, rail, or conveyor at the destination port. This material is of a high value leading to a desire to minimise losses and shipping and dockside transfer would normally be operations that would not be accessible to members of the public. Practices used to minimise risk could include, as necessary; stopping transfer activities in windy conditions, covering of loads on trucks and use of respiratory protective equipment by workers should there be a risk of significant exposure to dust.

6. Conclusions

Titanium dioxide is manufactured via two process routes from feedstocks containing low levels of naturally occurring radioactive material (NORM). None of the input activity transfers to the titanium dioxide products. For the co-products generated there is either minimal transfer, or the level in the co-product can be disregarded on the basis of exclusion principles. The majority of the input activity transfers to process wastes which are disposed of to land. However in both processes there is the potential of generating process scale deposits which contain increased radionuclide levels. Where appropriate, management practices are implemented to limit worker exposures to these materials.