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Manual on the Safe Production, Transport, Handling and Storage of Uranium Hexafluoride

MANUAL ON THE SAFE PRODUCTION,
TRANSPORT, HANDLING AND STORAGE
OF URANIUM HEXAFLUORIDE

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MANUAL ON THE SAFE PRODUCTION, TRANSPORT, HANDLING AND STORAGE OF URANIUM HEXAFLUORIDE

INTERNATIONAL ATOMIC ENERGY AGENCY
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Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
tel.: +43 1 2600 22529 or 22530
email: sales.publications@iaea.org
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For further information on this publication, please contact:

Nuclear Fuel Cycle and Materials Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
Email: Official.Mail@iaea.org

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FOREWORD

This publication offers a comprehensive overview of the properties of uranium hexafluoride (UF₆) and potential challenges associated with its production, transport, handling and storage. Technical personnel involved in any of these activities will benefit from the detailed information provided. This publication is also of value for facility operators seeking to enhance various aspects of their existing programmes, such as management systems, safety, and emergency preparedness and response. The content covers a range of topics, including the properties of UF₆ and its associated products, by-products and waste materials; safety considerations throughout the production processes; and detailed descriptions of management systems, safety analysis programmes, and emergency preparedness and response programmes.

This publication is a revision of IAEA-TECDOC-771, Manual on Safe Production, Transport, Handling and Storage of Uranium Hexafluoride, which was published in 1995. This revision reflects the latest developments in processes, practices, technical knowledge, and safety and environmental regulations related to UF₆ production, transport, handling, and storage, providing current and accurate information.

Uranium hexafluoride is critical to the nuclear fuel cycle, serving as the industry standard form of uranium used in current enrichment processes to produce the enriched uranium required for nuclear reactor fuels. The IAEA has taken steps to enhance the safety and security of the transport of UF₆ within the broader context of radioactive material transport. However, the numerous on site operations involving UF₆, such as production at conversion facilities, processing at enrichment plants, management at fuel fabrication sites and storage of substantial amounts of depleted material, entail their own various technical and safety considerations. This publication aims to provide practical information to technical personnel and facility operators regarding all these aspects of UF₆ production and use. It details the well understood radiological and toxicological properties of the materials used in UF₆ production, highlighting the associated hazards and risks to workers, the public and the environment. The publication consolidates comprehensive information on UF₆ into a single resource.

The IAEA acknowledges the contributions of the experts who participated in the drafting and review of this publication. The IAEA officers responsible for this publication were Y. Kultayev, C. Good and B. Moldovan of the Division of Nuclear Fuel Cycle and Waste Technology.

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1. INTRODUCTION

1.1. BACKGROUND

Production, transport, handling, and storage of uranium hexafluoride (UF₆) is an important aspect within the nuclear fuel cycle. Uranium hexafluoride is the industry standard form of uranium used in the enrichment process to produce the enriched uranium required for nuclear reactor fuel. Uranium hexafluoride is the preferred form of uranium for enrichment as fluorine exists naturally in only one isotopic form (¹⁹F) and the physical processes used for enrichment of ²³⁵U (currently centrifugation, diffusion in the past decades) increase only the concentrations of the fissionable ²³⁵U isotope.

From a safety perspective, UF₆ is radioactive because of its uranium content and is chemically reactive because of its high fluorine content. From a risk management perspective, the chemical hazards are more significant than the radiological hazards at low enrichments. Several important steps in the nuclear fuel cycle, namely, uranium refining, conversion, enrichment, and reconversion involve the production, transport, handling, storage, and waste management of UF₆ and related products. In addition, at room temperature, it exists as a solid, but it can readily undergo state changes and exist as a gas or a liquid at slightly elevated temperatures. This requires special considerations for the storage of UF₆. Due to the hazardous properties of UF₆, these operations have to be carried out in a safe manner to protect workers, the public and the environment.

Advances in the technology of UF₆ processing have been significant in the last fifty years and development of safety techniques and protective measures have improved accordingly.

1.2. OBJECTIVE

The purpose of this publication is to provide information to technical personnel and facility operators on the hazards associated with UF₆ operations to ensure that the workers, the public, and the environment are adequately protected. This publication is a revision of IAEA-TECDOC-771, Manual on Safe Production, Transport, Handling and Storage of Uranium Hexafluoride [1] which was published in 1995.

This revision considers the latest changes in processes, practices, technical knowledge, and safety and environmental regulations relating to UF₆ production, handling, transport, and storage, and consequently to provide current and accurate information.

1.3. SCOPE

This publication compiles experiences from current industrial and commercial facilities, processes and activities for the production, transport, handling, and storage of UF₆ (currently UF₆ enriched in ²³⁵U up to 5%, and potentially up to 10 % in the future). The publication addresses only the gas centrifuge enrichment process, which is currently the only process used for uranium enrichment on an industrial scale. Gaseous diffusion process, which was previously used for enrichment of uranium, is no longer being used and is thus no longer within the scope of this publication.

This publication focuses on the aspects of safe production, transport, handling, and storage of UF₆. Other aspects, such as security, material accountability, safeguards, nuclear liability, and customs regulations, are out of the scope of this publication.

1.4. STRUCTURE

The publication consists of nine sections and five appendices.

Section 1 describes the background, objective, scope, and structure of the publication.

Section 2 provides information about the properties and hazards of UF₆.

Section 3 describes the elements that might be included in an integrated management system.

Section 4 provides information about the methods and chemical processes for the production and handling of UF₆, extending from the production of uranium ore and concentrates to nuclear fuel, including conversion, enrichment, and reconversion.

Section 5 provides information about the regulations applicable to the safe transport of UF₆ on the public domain, the packages that are used and other transport considerations.

Section 6 provides information about the storage of UF₆, both short and long term storage, including indoor and outdoor storage facilities, with consideration of site selection and associated criteria, equipment and capability needs, and corrosion aspects.

Section 7 provides information on the management of radioactive and non-radioactive waste at the different stages of the processes, i.e. the facilities for conversion, enrichment, and reconversion.

Section 8 describes how a safety analysis might be conducted.

Section 9 provides information about emergency preparedness and is focused on recommendations for the cases related to production, transport, handling, and storage of UF₆.

Appendix I gives examples of processing off-gases in the hydrofluorination processes in conversion facilities.

Appendix II makes available information about the separative work unit (SWU), the measure for enrichment work.

Appendix III makes available information about ²³⁴U-to-²³⁵U ratio dependence on enrichment and available models to estimate this ratio in literature.

Appendix IV introduces the methods for the management of liquid waste from conversion and enrichment.

Appendix V provides examples of postulated initiating events (PIEs) that might be relevant to production, handling, or storage of UF₆, and to on-site and off-site transport of UF₆.

Annex provides information about definitions of levels for commonly used exposure guidelines for planning of emergency releases of airborne chemicals.

2. PROPERTIES AND HAZARDS OF UF₆ AND ASSOCIATED COMPOUNDS

This section discusses the physical properties of UF₆ (Section 2.1), chemical properties of UF₆ (Section 2.2) and some of the main hazards of UF₆ and associated compounds (Section 2.3).

The main hazards in UF₆ facilities are provided in IAEA Safety Standards Series publications No. SSG-5 (Rev. 1), Safety of Conversion Facilities and Uranium Enrichment Facilities [2] and No. SSG-6 (Rev. 1), Safety of Uranium Fuel Fabrication Facilities [3]. These include: potential release of UF₆ and chemicals, hydrogen fluoride¹ (HF), fluorine, potential nuclear criticality events (see Section 2.5), thorium and its decay products and external exposure from cylinders, particularly those that recently emptied and contained reprocessed uranium (see Section 2.4).

Section 2.3 further discusses uranium chemicals used in UF₆ facilities and associated hazards with a focus on hazards associated with release of UF₆ (see Section 2.3.1), hydrolysis by-products formed during the contact with moisture such as uranyl fluoride (UO₂F₂) (see Section 2.3.2) and HF (see Section 2.3.3). The precautions associated with release of UF₆ are discussed in Section 2.3.4.

2.1. PHYSICAL PROPERTIES

In the nuclear fuel cycle, all three phases (solid, liquid, and gas) of UF₆ are handled during industrial processing. Because UF₆ is contained within processing equipment or transport containers, it is not directly observable. Thus, it is important to understand the chemical and physical properties of UF₆ to interpret the indirect observations and readings (for instance, changes in pressures or weights) from instrumentation used during the processing of UF₆.

2.1.1. Phases of UF₆

At ambient temperature (20°C), UF₆ is a nearly white, almost colourless, dense, high molar mass solid (352.02 g/mol) with a significant, but less than atmospheric, vapour pressure (14.2 kPa/106.5 mmHg) [5].

From its solid form, UF₆ can be readily transformed into:

- Either a colourless gas at atmospheric pressure (101.3 kPa/760 mmHg) at temperatures above 56.4°C (sublimation point at atmospheric pressure)
- Or a colourless liquid phase by raising the temperature above 64.02°C and increasing the pressure above 151.7 kPa (1137.5 mmHg) (triple point).

¹ The chemical formula for hydrogen fluoride is HF. It can exist in both the liquid and gaseous states and is readily miscible with water, including atmospheric moisture. Hydrofluoric acid refers to a solution of hydrogen fluoride in water.

In this publication, the term ‘HF’ is generally used to refer to hydrogen fluoride when there is no need to specify or distinguish its form, when the form is unknown, or when both forms coexist. This term applies to hydrogen fluoride in any state, whether as pure compound (anhydrous HF, not diluted in water) or as a solution in water (hydrofluoric acid)). When it is necessary to distinguish the forms, pure HF is designated as anhydrous HF, and a solution of hydrogen fluoride in water is designated as hydrofluoric acid.

In other documents or facility labels, pure HF (anhydrous HF) may be abbreviated as AHF. However, this abbreviation is not used in this publication. Similarly, hydrofluoric acid, a solution of hydrogen fluoride in water, may be referred as aqueous HF and abbreviated as AqHF in other documents or facility labels. This designation and abbreviation are not used in this publication.

The United Nations, Recommendations on the Transport of Dangerous Goods, Model Regulations (the UN Model Regulations) [4], explicitly distinguish between anhydrous hydrogen fluoride and hydrofluoric acid. Anhydrous hydrogen fluoride is classified as UN 1052 with the proper shipping name “HYDROGEN FLUORIDE, ANHYDROUS”, whereas hydrofluoric acid is classified as UN 1790 with the proper shipping name “HYDROFLUORIC ACID”.

All three phases coexist in equilibrium at one unique point on the diagram, called the triple point (64.02°C, 151.7 kPa). Only the gaseous phase exists above the critical temperature of 230.2°C and the critical pressure of 4.6 MPa [6, 7]. Finally, the vapour pressure above the solid reaches 101.3 kPa (760 mmHg, atmospheric pressure) at 56.4°C, the sublimation temperature.

A complete UF_6 phase diagram illustrating the vapour pressure and temperature relations is provided in Figure 1. The vapour phase exists in the region to the right and below the continuous blue line. The liquid phase exists above the continuous blue curve and to the right of the triple point temperature (vertical solid grey line). For the liquid phase, the temperature range is relatively wide, and the critical pressure is relatively high. The area to the left of the vertical solid grey line and above the continuous blue curves represents conditions under which the solid UF_6 exists.

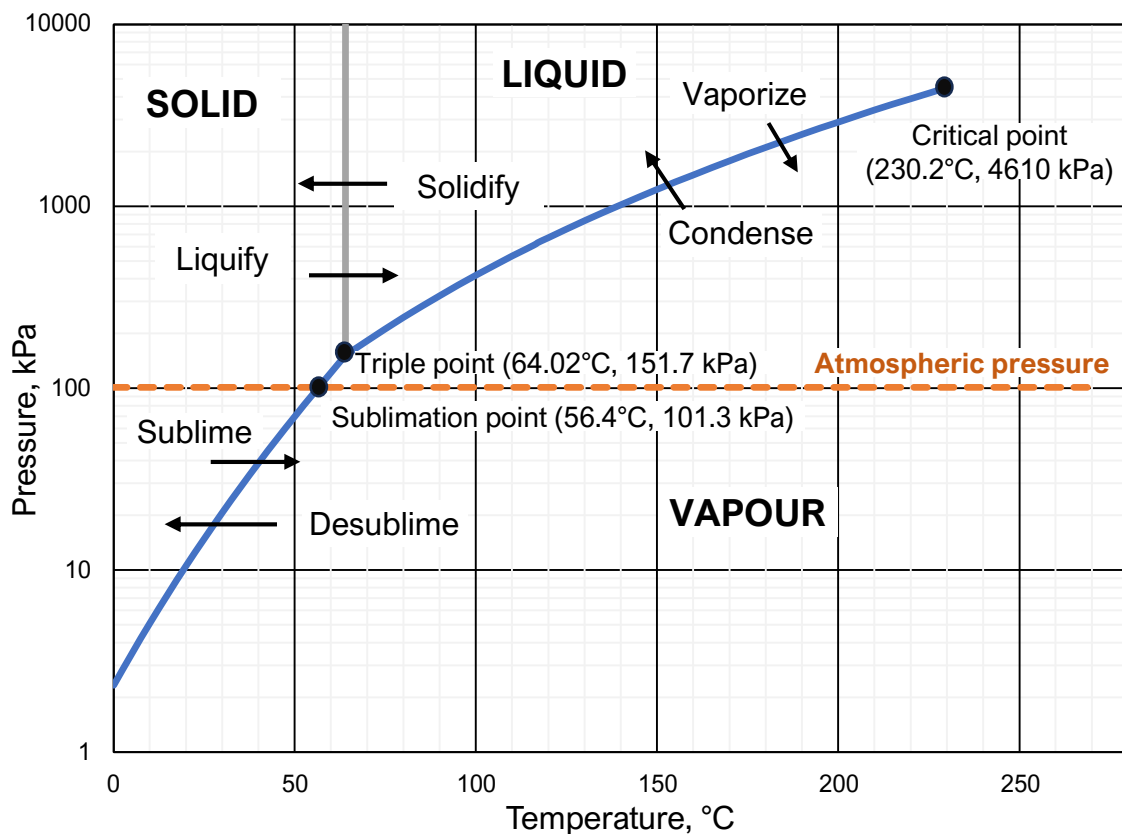


FIG. 1. Phase diagram of UF_6 .

Figure 1 illustrates that the sublimation temperature is below the triple point. This has implications for the safe processing and handling of UF_6 . For UF_6 to be handled as a liquid the pressure has to be maintained above 151.7 kPa (1137.5 mmHg) and the temperature above 64.02°C. Therefore, systems involved with processing and handling liquid UF_6 , which requires elevated pressure above atmospheric pressure, have to be adequately engineered to contain this pressurized liquid. Transfers below 1.497 atmosphere (151.7 kPa/1137.5 mmHg) or below 64.02°C involve moving vapor that is produced by sublimation and removed by desublimation (crystallization) in a cold trap.

It is worth mentioning that when solid UF_6 is formed by freezing (solidifying) the liquid phase, the resulting solid UF_6 exhibits a dense crystalline structure with an irregularly shaped coarse grains morphology. In contrast, when solid UF_6 is formed through the desublimation of the vapor phase, the resulting solid UF_6 takes the form of a shapeless amorphous mass [8].

The relatively small² value for the heat of vaporization (81.6 kJ/kg at 64°C) [9] implies that sublimation and condensation occur readily. Consequently, unexpected material transfer and clogging of lines can occur, which could result in complications during production and handling operations.

2.1.2. Density of solid and liquid UF₆

Uranium hexafluoride is a relatively expanded solid and liquid; that is, the number of molecules present per unit volume of liquid and solid is relatively small when compared to the majority of other materials. However, the density of UF₆ is quite high, as illustrated in Figure 2, which depicts the density of solid and liquid UF₆ as function of temperature. Equations for the density of the solid and the liquid as a function of temperature are taken from Barber [10].

During the transition from solid to liquid state, UF₆ density undergoes a large decrease, with solid UF₆ being approximately 35–40% denser than liquid UF₆. The expansion of UF₆ in the liquid phase is exponential as temperature increases, resulting in a considerable increase in volume.

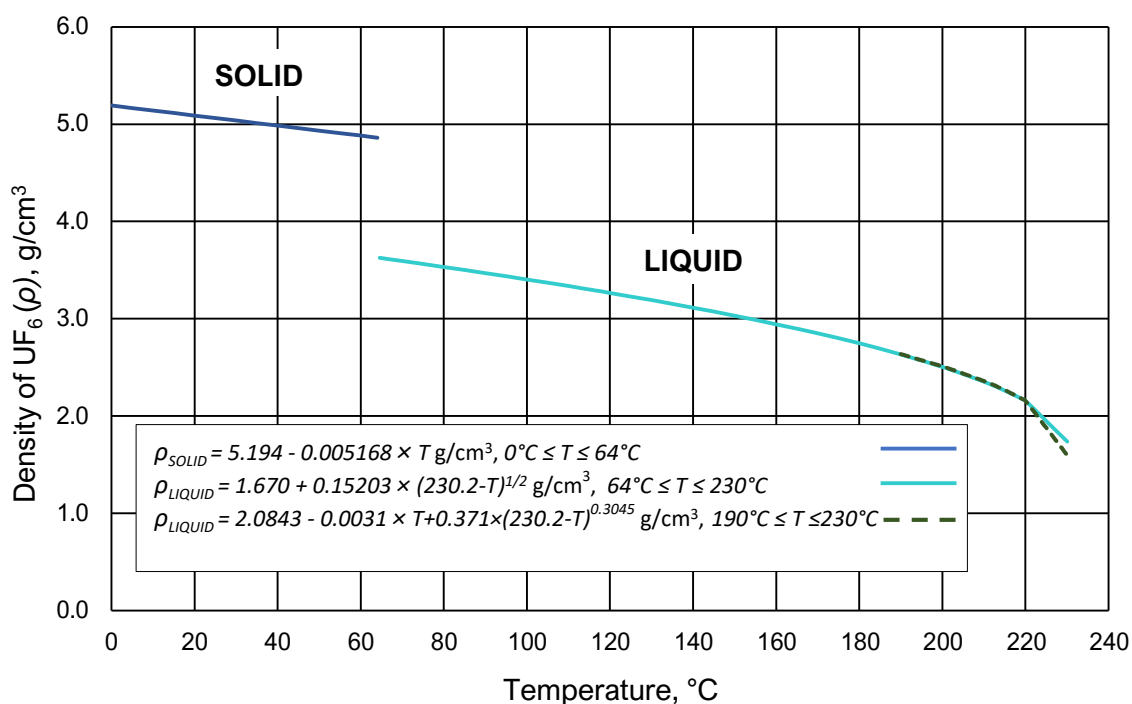


FIG. 2. Density of solid and liquid UF₆.

Maintaining control over the physical state of UF₆ is crucial to ensure safety. When UF₆ is filled in vessels with restricted volumes such as cold traps and containers, it is essential to consider volume changes that occur across the working temperature range. The volumes of three different masses of UF₆ at varying temperatures in a 48Y cylinder are detailed in Table 1. Inadequate ullage could lead to high pressure and the risk of hydraulic rupture [11].

² For example, the heat of vaporization for water is 22.6×10^5 J/kg.

TABLE 1. VARIATION OF VOLUME OCCUPIED BY UF₆ IN A 48Y CYLINDER^a WITH TEMPERATURE

T (°C)	UF ₆ density (g/cm ³)	Volume occupied by UF ₆					
		Filled 12.5 tonnes		Filled 13 tonnes		Filled 13.5 tonnes	
		(m ³)	(%)	(m ³)	(%)	(m ³)	(%)
20	5.090 (solid)	2.456	60.7	2.554	63.2	2.652	65.6
65	3.624 (liquid)	3.449	85.3	3.587	88.8	3.725	92.2
80	3.532 (liquid)	3.539	87.6	3.680	91.1	3.822	94.6
95	3.437 (solid)	3.636	90.0	3.782	93.76	3.927	^b
112	3.316 (liquid)	3.769	93.3	3.920	^b	4.071	^b
120	3.263 (liquid)	3.830	94.8	3.984	^b	4.137	^b
125	3.225 (liquid)	3.875	95.9	4.031	^b	4.186	^b

^a 48Y cylinder volume 4.040 m³

^b Overfilled

2.1.3. Summary of the properties

Several of the more important physical properties of UF₆ are presented in Table 2 below.

TABLE 2. SUMMARY OF PHYSICAL PROPERTIES OF UF₆

Property	Value
Sublimation Point at 101.3 kPa	56.6°C
Triple point	152 kPa (64.1°C)
Density	(g/cm ³)
Solid (20°C)	5.090
Liquid (64.1°C)	3.629
Liquid (95°C)	3.437
Liquid (112°C)	3.316
Liquid (120°C)	3.263
Heat of Sublimation (64.1°C)	135.4 J/kg
Heat of Fusion (64.1°C)	54.7 J/kg
Heat of Vaporization (64.1°C)	81.6 J/kg
Specific Heat	
Solid (27°C)	477 J/kg/K
Liquid (72°C)	54 J/kg/K
Critical Pressure	4610 kPa
Critical Temperature	230.2°C

2.2. CHEMICAL PROPERTIES

Uranium hexafluoride is a very reactive compound and a very strong fluorinating agent (oxidizing agent) at higher temperatures [12]. UF₆ chemistry relies heavily on the exceptional stability of the uranyl ion (UO₂²⁺), enabling it to react with water, oxides, hydroxides, and salts containing oxygen-bearing anions without the need to release molecular oxygen O₂, a process

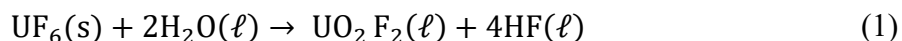
with a high potential barrier. Conversely, UF₆ shows no reactivity towards oxygen, carbon dioxide, nitrogen, or dry air.

2.2.1. Reactivity with water

An important reaction involving UF₆ is its vigorous reaction with water, including the water vapour in the air, resulting in the formation of the soluble reaction products UO₂F₂ and HF.

The hydrolysis reaction of UF₆ is strongly exothermic, which occurs in both solid state in presence of liquid water and in the gas phase with water vapour.

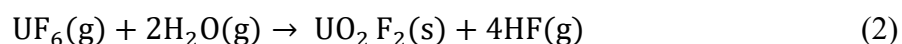
(a) In the solid state:



where ΔH^3 equals to -211.4 kJ/mole UF₆.

When UF₆ is in the solid state, its reaction with water may be impeded by the creation of a hydrated UO₂F₂ layer on the surface of solid UF₆. This layer forms a diffusion barrier, thus slowing down the reaction with surrounding water.

(b) In the gas phase:



where ΔH equals to -101.7 kJ/mole UF₆.

When gaseous UF₆ is released into the atmosphere, it quickly reacts with water vapour to produce HF and UO₂F₂. The reaction is rapid, near instantaneous, and the kinetics is dependent on the amount of water present. To hydrolyse 1000 kg of UF₆ requires around 100 kg of water. At 25°C and 70% relative humidity, this quantity of water is found in 6000 m³ of air. Following a large scale release of UF₆ outside, the atmospheric dispersion is governed by meteorological conditions. Depending on the quantity released, the HF plume may contain UO₂F₂ and unreacted UF₆, even after travelling several hundred meters. During hydrolysis, 1 kg of UF₆, which contains 0.68 kg of uranium, produces 0.23 kg of HF. Following hydrolysis, UO₂F₂, typically in a hydrate form, can settle as a fine solid while HF remains in the gas plume. Indoors, the reaction products create a dense, white fog that severely limits visibility, obstructing evacuation and emergency response efforts. Fog formation can also occur in open areas with high humidity.

The reaction between UF₆ and water is hastened in a fire, due to the abundant formation of H₂O during combustion.

2.2.2. Reactivity with metals

Uranium hexafluoride is known to fluorinate some metals, such as nickel, copper, and iron. A protective passivation film is formed by reaction of UF₆ with the metal, minimizing the corrosion on the surface of these metals. The general chemical formula of the protective film is MF₂ (M = Ni, Cu or Fe). For instance, nickel and nickel alloys⁴ (MONEL, INCONEL,

³ Energy values for Eqs (1, 2) derived from Ref. [13] and Ref. [9], respectively.

⁴ Steel is a common material used for low temperature (less than 100°C) applications and nickel-based materials are typically used for higher temperature applications.

HASTELLOY) are usually suitable materials for processing equipment in contact with UF₆ due to the formation of a passivating and protective nickel fluoride layer (NiF₂) according to the reaction shown below:



Sodium and mercury are attacked in cold conditions, and lead, zinc, tin, steel or iron are attacked on heating or in the presence of water. Platinum and gold react with UF₆ only above 400°C. It is to be noted that the handling and storage temperature range for UF₆ steel cylinders (less than 100°C) ensures that these materials can be exposed to UF₆ without excessive corrosion.

2.2.3. Reactivity with organic compounds

In the gas phase, with organic compounds like alcohol, ether, benzene or toluene, immediate fluorination takes place with formation of HF and carbon or carbonaceous material. These organic compounds are highly reactive with UF₆ because of being electron rich (double bonds) or oxygen bearing [12].

The reactivity of UF₆ with fully fluorinated hydrocarbons is minimal. Nevertheless, UF₆ has the potential to dissolve in these fluids, therefore, caution needs to be exercised.

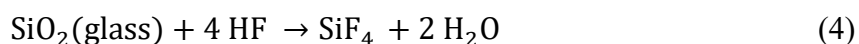
In contrast, reaction of liquid UF₆ with hydrocarbon compounds is unpredictable and extremely exothermic with formation of UF₄ and low molar mass fluorinated compounds (CF₄, C₂F₆, etc.), and explosions in cylinders [9] have been attributed to these reactions. According to the standard specification for UF₆ [14], the total carbon based compounds is not to exceed 0.01 mol% of the UF₆ in order to prevent an exothermic reaction upon heating.

2.2.4. Compatibility

As explained in Section 2.2.2, nickel, copper and some aluminium alloys are generally the key materials for processing equipment in contact with UF₆ through the formation of protective fluoride films on the surface of these metals or alloys. This phenomenon is called ‘passivation’ (see Section 4.7.2.1) for a similar process in the presence of fluorine gas instead of UF₆.

Adverse physical or chemical factors (such as mechanical turbulence, erosion, or chemical complex formation) that disrupt this protection mechanism can lead to unanticipated degradation in the performance of these materials. Hence, it is crucial for design specifications for vessels and processing equipment to consider the purity of the UF₆, as well as the velocity and turbulence conditions that are likely to be encountered during normal operations.

In contrast, storage and handling of UF₆ are usually not performed in glass vessels or other silicon containing components because SiO₂ is likely to be attacked by HF (formed in the presence of moisture) according to the reaction shown below:



Furthermore, there have been cases where small quantities of hydrocarbon oil have reacted violently, leading to explosive reactions. It is essential to exercise extreme caution to ensure that all equipment is clean and free from organic contamination. This is especially critical in operational scenarios involving UF₆, such as during the transfer or pressure reduction of UF₆ using oil based vacuum pumps. When utilizing these pumps, a reservoir or oil trap capable of

holding the entire oil contents of the pump needs to be installed between the pump and any UF₆ to prevent oil backflow into the UF₆ system. The use of UF₆ compatible oils is advised.

2.3. HAZARDS OF UF₆ AND ITS RELATED COMPOUNDS

Exposure to uranium may cause both chemical and radiological effects. Radiological effects from uranium compounds are influenced by the isotopic composition of the uranium. The radiation exposure pathway from uranium is mainly internal, but external exposure can also be a concern, especially for chronic exposure, as uranium decays through complex chains involving beta, gamma, and X ray emissions. The severity of harm resulting from contact with uranium compounds is determined by the solubility of the compound and the pathway of exposure. In most dose assessments, only inhalation or ingestion is taken into account, as skin absorption of certain soluble compounds is feasible but typically not considered significant in relation to industrial emissions. There is a significant occupational health risk from the inhalation of uranium compounds. The risk from soluble compounds differs from the risk presented by relatively insoluble compounds. Health effects of uranium are described in detail in Annex D of the UN Scientific Committee on the Effects of Atomic Radiation, Report to the General Assembly with Scientific Annexes published in 2016 [15] and in chapter 6 of the recent IAEA Technical Report Series No. 488, The Environmental Behaviour of Uranium [16]. Several papers were published on radiological and chemical toxicity of uranium including renal, bone and other organs effects (see Refs. [17-21]). Several publications of the International Commission on Radiological Protection (ICRP)⁵ provide information related to assessment of hazards involving exposure to uranium compounds including on occupational radiation protection, dose assessment and risk from exposure. The uranium compounds produced or used in UF₆ facilities can vary widely in chemical composition, oxidation state, and physical form but can be divided into two general categories depending on their solubility:

- Soluble compounds, including UO₃, UO₄, (NH₄)₂U₂O₇ (ammonium diuranate), UO₂(NO₃)₂, UO₂(CO₃), UF₆, and UO₂F₂;
- Relatively insoluble compounds, including UF₄, U₃O₈, and UO₂.

For soluble compounds, such as UO₂F₂, it is more likely for the compound to be dissolved by lung fluids and moved to the bloodstream where the kidneys filter the heavy metal. The uranium will travel to the urinary tract and be excreted. If a significant amount of uranium is inhaled and reaches the kidneys, there is an increased risk of physiological damage to the kidneys. In this case, chemical toxicity is of main importance.

The chemical toxicity of uranium to the kidney is significantly influenced by the solubility of its compound, as demonstrated by the studies involving different uranium compounds tested on animals [22]. Findings also suggest that acute renal toxicity from uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O), a highly soluble form, occurred at levels below that for radiotoxicity.

For relatively insoluble compounds, such as UO₂, the inhaled uranium compound will remain in contact with the lung tissue for an extended period. Although the radiation emitted by the compound is small, the close proximity with the lung tissue and the extended period that the compound is resident in the lungs will cause a significant radiological risk to the nearby lung tissue.

The hazards of UF₆ and compounds such as HF and UO₂F₂ formed during the release of UF₆ are considered further in Sections 2.3.1, 2.3.3 and 2.3.4 below. Detailed information about the

⁵ <https://www.icrp.org/page.asp?id=5>.

hazards and toxicity of other uranium compounds can be found in the International Commission on Radiological Protection (ICRP) Publication 137, Occupational intakes of radionuclides [23] and ICRP Publication 150, Cancer Risk for Exposure to Plutonium and Uranium [24]. In addition, detailed information about radiological hazards of other uranium compounds in the context of occupational radiation protection in the uranium mining and processing industry can be found in IAEA Safety Reports Series No.100, Occupational Radiation Protection in the Uranium Mining and Processing Industry [25].

2.3.1. Hazards of UF₆

Solubility and small particle size are the most important properties of an inhaled compound of uranium when considering standards for worker's protection, as reflected in current regulatory guides, as it is easily absorbed into the bloodstream.

The uranyl ion UO₂²⁺ is the most stable uranium species in solution and the most likely form of uranium to be present in body fluids because of bodily intake of uranium bearing particles. Evidence indicates that inhalation represents the primary mode of occupational exposure to uranium, while alternative modes of absorption include dermal contact, entry through wounds, and ingestion are also a potential means of exposure [22]. The primary health and safety hazard from release of UF₆ (gas) is mainly inhalation and ingestion of its two hydrolysis products: HF and UO₂F₂.

Acceptable chemical exposures to UF₆ are defined by the Emergency Response Planning Guidelines (ERPG) established by the American Industrial Hygiene Association [26]. ERPG levels estimate the concentrations at which most people will begin to have health effects if exposed to hazardous airborne chemicals for 1 hour.

Acute Exposure Guideline Levels (AEGL), established by the National Advisory Committee for Acute Guideline Levels for Hazardous Substances [27, 28], are guidelines designed to help with emergencies involving chemical spills or other catastrophic events where the general public is exposed to such airborne chemicals [28] and describe the human health effects from rare, or once-in-a-lifetime, exposure to airborne chemicals. Definitions of ERPG and AEGL levels are summarized in Annex.

ERPG and AEGLs values for UF₆ are given in Table 3 below. These values may be used as guidance in emergency planning as well as for making safety decisions (e.g. if accident analysis indicates that the exposure of the most exposed person can exceed the value given, more stringent safety conditions would be required).

TABLE 3. ERPG AND AEGL VALUES FOR URANIUM HEXAFLUORIDE

ERPG (mg UF ₆ /m ³)		AEGL (mg UF ₆ /m ³)					
	1 hr		10 min	30 min	1 hr	4 hr	8 hr
ERPG-1	5	AEGL-1	3.6	3.6	3.6	NR*	NR
ERPG-2	15	AEGL-2	28	19	9.6	2.4	1.2
ERPG-3	30	AEGL-3	216	72	36	9	4.5

* NR: Not recommended due to insufficient data

2.3.2. Hazards of UO_2F_2

Uranyl fluoride (UO_2F_2) is a hygroscopic solid that ranges in colour from yellow to white and is highly soluble in water. Its hazards are attributed to its toxicological and radiological properties.

The important factors to be considered in the assessment of UO_2F_2 hazards are the enrichment level of uranium and the accident conditions. However, in the case of gaseous UF_6 release, the development of UO_2F_2 as a critical system is highly unlikely due to the dispersion of uranium into a large volume of air. The installation of ventilation systems with gas scrubbers⁶ in the facilities could effectively minimize the formation of UO_2F_2 during leaks of gaseous UF_6 .

2.3.2.1. *Radiological hazards*

Accidental releases of UF_6 can result in UO_2F_2 settling as a solid particulate material over a wide area. The radiological effects of UO_2F_2 can occur through direct inhalation of UO_2F_2 aerosols or through secondary intake resulting from environmental contamination due to the deposition of UO_2F_2 as a solid around the incident.

Uranium at low enrichments is considered to be less of a radiological hazard and more of a toxicological hazard. As a result, the toxic chemical effects on an individual exposed to UO_2F_2 would be more severe than the radiological effects for uranium at a low enrichment level.

2.3.2.2. *Internal contamination*

Uranium hexafluoride exists in vapour form, but it is converted to uranyl fluoride aerosol upon contact with moisture in the atmosphere or respiratory tract. Consequently, exposure generally includes both chemical forms, along with hydrogen fluoride fumes, and is therefore classified as an aerosol rather than a vapour [23]. Following deposition in the lungs, uranium compounds are cleared from the different biological compartments in the lungs by solubility. The lung model outlined in ICRP Publication 66, Human Respiratory Tract Model for Radiological Protection (the ICRP Publication 66) [29] acknowledges the existence of three clearance classification types; F (Fast), M (Medium) and S (Slow). The ICRP Publication 137 [23] considers UO_2F_2 as aerosol formed from UF_6 in the presence of water in the atmosphere and the respiratory tract classified as absorption Type F. Type F compounds show 100% absorption with a half-time of 10 minutes. The model is applicable for particle sizes from 0.6 nm to 100 μm and the default value recommended is 5 μm activity median aerodynamic diameter [30].

It was established that UO_2F_2 (soluble compound) accumulates primarily in the kidneys and is typically flushed out in the urine stream in a matter of hours. Under high exposure conditions, uranium can cause renal degeneration, other kidney damage and disfunction [31], and in severe instances renal failure⁷.

The toxicological effects of soluble uranium compounds have been discussed by Just [32] and McGuire [33]. These studies rely on toxicity experiments on animals and limited human data from a panel of toxicologist [34], employing the following four health effect classifications:

⁶ UO_2F_2 produced from the hydrolysis of UF_6 is an exceptionally fine particulate typically less than 3 microns in size. Removal of particulate by liquid contact requires a fine liquid droplet of equivalent size for adequate contact to take place. If the ventilation gas is suitable, the use of high efficiency particulate air filters is also an effective method for particulate removal.

⁷ <https://www.iaea.org/topics/spent-fuel-management/depleted-uranium>.

- Lethal: exposure resulting in 50% mortality;
- Renal injury: significant physiological damage to the kidneys;
- Possible mild health effects: observable biological effects, but without short or long term impairment in the body's ability to function;
- No effect.

Based on updated ICRP models [29, 35], a more recent study [36] recalculated '50% lethality' and 'threshold for permanent damage' levels, using a 27.6% fraction. Table 4 presents these recalculated values, as well as uranium intake values for the other two categories, also calculated using the 27.6% fraction.

TABLE 4. HEALTH EFFECTS FROM INTAKE OF SOLUBLE URANIUM

Health effect	Uranium per kg body weight (mgU/kg)	Uranium (mg) in 70 kg person	Uranium intake ^a (mg) by 70 kg person		
			McGuire ^b	Just ^c	Derived ^d
50% lethality	1.63	114	230	265	410
Threshold for permanent renal damage	0.3	21	40	49	75
Threshold for transient renal injury or effect	0.058	4.06	8.3	9.44	14.71
No effect	0.03	2.1	4.3	4.9	7.6

^a intake is defined as total amount of material inhaled into the body

^b ICRP 30 model is with the assumption that 49% of intake will be excreted through the kidneys [33].

^c it is assumed that 43% (0.43) of the inhaled uranium would be absorbed by the body [32].

^d values and fraction of 27.6% given in Ref. [36] are used to obtain threshold level values.

Reference [37] proposes alternative toxicity threshold levels for the acute uranium intake in soluble compounds for adult humans, as summarized in Table 5.

Kathren et al. [36] state that based on more recent ICRP models [29, 38] the value of 40 mg of soluble uranium (permanent renal damage) in Table 4 corresponds to a peak kidney burden of 8.4 $\mu\text{gU/g}$ kidney. In many countries, occupational exposure limits for soluble uranium compounds are based on a maximum kidney concentration of 3 $\mu\text{g U/g}$ tissue, with any resulting effects considered minor and reversible⁸. For example, an airborne concentration limit of 0.2 mg/m^3 was adopted by the American Conference of Governmental Industrial Hygienists and US Nuclear Regulatory Commission for occupational exposures, based on the 3 $\mu\text{U/g}$ of tissue value [39].

⁸ <https://www.iaea.org/topics/spent-fuel-management/depleted-uranium>.

TABLE 5. TOXICITY THRESHOLD LEVELS FOR THE ACUTE INTAKE OF URANIUM (SOLUBLE) FOR HUMAN ADULTS

Risk	Acute ingestion(mg)	Acute inhalation(mg)
Estimated median lethal dose (LD₅₀)	5000	1000
Life endangerment	2500	500
Irreversible or long lasting adverse effects	1400	100
Mild transient adverse effects	410	30

Different studies have assessed the chemical toxicity of UF₆ compared to the chronic and acute effects of radiation, depending on levels of ²³⁵U enrichment. Research by Ringot et al. [40] and McGuire [33] highlight these differences. Ringot et al. [40] concluded that for normal conditions, radiological risk becomes greater at enrichment levels exceeding 3%. Conversely, McGuire [33] found that in cases of acute exposure, the intake of uranium in soluble compounds is primarily limited by chemical toxicity rather than radiation exposure. This conclusion is based on the uranium mass required to produce a 250 mSv (25 rem) dose, which exceeds 100 mg at higher enrichments. McGuire's selected dose level corresponds with the once in a lifetime accidental or emergency dose for radiation workers, as noted in 10 CFR 100.11 [41] and Advance Notice of Proposed Rulemaking in the regulation of uranium enrichment plants (53 FR 13276) [42]. This dose is 12.5 times higher than the annual limits on intake (ALI) (20 mSv).

Table 6 illustrates that the likelihood of receiving doses of more than 1 ALI depends on uranium enrichment, with natural uranium presenting an intake of 1293 mg, while uranium enriched to 90% ²³⁵U shows a considerably lower intake of 14 mg. The change of specific activity for uranium upon enrichment is mainly attributable to the increase in ²³⁴U content (see Section 4.3).

TABLE 6. DOSE COEFFICIENTS AND ANNUAL LIMIT OF INTAKE (ALI) FOR DIFFERENT ENRICHMENT LEVELS (TYPE F)

Enrichment % ²³⁵ U	Specific activity (Bq/g U)	Dose coefficient (μSv/Bq)	ALI (kBq)	(mg U)
Natural	25361	0.61	32.8	1293
1	32753	0.62	32.4	991
5	135008	0.63	31.6	234
10	262782	0.64	31.4	119
20	518427	0.64	31.4	61
50	1285486	0.64	31.3	24
90	2308284	0.64	31.3	14

^a Specific activity values are calculated based on ²³⁴U estimation model provided by Shephard et al. [43] (see Appendix III) and 0.25% tail assay.

^b Dose coefficients calculated based on assumptions detailed for lung absorption Type F and activity median aerodynamic diameter of 5 μm.

For chronic exposures, the US Occupational Safety and Health Administration sets an air concentration limit for chemical toxicity at 0.05 mg/m³ for type 'F' material (permissible exposure limit for soluble compounds). According to Table 6, the comparable radiological air

concentration limit⁹ (mass equivalent to ALI/2400 m³) surpasses¹⁰ the chemical toxicological threshold only at enrichment levels above 10% ²³⁵U in routine daily operations. However, there is broad consensus that the chemical nephrotoxic effects of soluble uranium, whether ingested or inhaled, outweigh its radiotoxic effects, particularly at ²³⁵U enrichment levels below 20% [32, 37, 44-48].

For acute exposures, the short term exposure limit (fifteen minutes) provided by US Occupational Safety and Health Administration for type ‘F’ material is 0.6 mg/m³ (see Table 7), which corresponds to an intake of 0.16 mg for reference man, who breathes 1.2 m³ air in 1 hour or 0.4 m³ air in 15 minutes (0.6 mg/m³ × 0.4 m³). This value is lower than the uranium mass equivalent in Table 6 for all enrichment levels, indicating that chemical toxicity is the primary limiting factor for acute exposures across all enrichment levels.

A summary of exposure limits for soluble uranium compounds, as set by different health and safety authorities, is provided in Table 7 [49].

Additional details on radiation protection can be found in Section 4.7.1.

TABLE 7. SUMMARY OF EXPOSURE LIMITS FOR SOLUBLE URANIUM COMPOUNDS

Source	Effect	Concentration in air (mg U/m ³)	Exposure time
US National Institute for Occupational Safety and Health	Recommended Exposure Limit - Time weighted average (REL-TWA)	0.05	10 h
US Occupational Safety and Health Administration	Permissible exposure limit - Time weighted average (PEL-TWA)	0.05	8 h
American Conference of Governmental Industrial Hygienists	Threshold limit value - Short Term Exposure Limit (TLV-STEL)	0.6	15 min
	Threshold limit value - Time weighted average (TLV-TWA)	0.2	8 h

2.3.3. Hazards of HF

Hydrogen fluoride is one of products formed during the possible release of UF₆. Moreover, HF is one of most important reagents consumed and dealt with in the production of UF₄ and UF₆ in conversion process (see Section 4.2). In addition, it is generated as a by-product during dry route of reconversion processes (see Sections 4.4 and 4.5).

Anhydrous HF is a colourless fuming corrosive liquid which boils at 19.5°C to become gas. In UF₆ releases, HF is typically seen as part of a white gaseous cloud with a pungent odour which is detectable at concentrations above 0.02–0.13 ppm [50].

⁹ The volume of air a worker breathes in a work year (2400 m³) required for calculating the air concentration limit assumes that a worker breathes for 2000 hours in a year with a respiration rate of 1.2 m³/hour.

¹⁰ It is important to note that the data provided in Table 6 is intended solely for educational purposes, and any use in facilities should be adapted to the specific materials being handled.

Hydrogen fluoride is considered to be one of the most destructive inorganic agents to human tissue, causing severe injuries to the skin, eyes and mucous membranes (chemical burns). Exposure by inhalation or ingestion can lead to severe toxic systemic effects and potentially death.

The skin may experience burns from even minimal exposure, and symptoms may be noticeable right away. In severe instances, the skin may exhibit a blue-green discolouration [51]. Hydrogen fluoride can cause hypocalcaemia, which is a condition that happens when the levels of calcium in the body are too low.

When inhaled, HF can lead to symptoms in the upper respiratory tract, including coughing, sore throat, and shortness of breath. Low doses mainly affect the upper respiratory tract due to HF being absorbed by mucous membranes. However, exposure to high concentrations can also impact the lower respiratory tract, potentially causing pulmonary oedema, which may take up to 36 hours to develop [51].

Hydrofluoric acid ingestion may result in mouth and throat burning, nausea, vomiting, and abdominal pain. In more serious instances, it can lead to oesophageal or gastric perforation.

When there is ocular exposure, it can result in conjunctival oedema, conjunctivitis, corneal epithelial coagulation, and necrosis. The severity of eye burns from HF is attributed to the pH and toxicity of the F^- ion. The initial damage from the acidity of hydrogen fluoride allows the fluoride ion to penetrate deeper tissue layers, resulting in severe eye lesions.

The workplace exposure limits are generally set by national regulations or safety authorities to protect the health of workers. Table 8 provides information on the exposure limits that may be used as a reference. The values of air concentration of HF are applicable to workers exposed in routine conditions, such as workers at F_2 production facilities or UF_6 production or enrichment facilities in normal conditions of operation.

In case of acute exposure to HF, the health hazards are the induction of pneumonitis and pulmonary oedema. Acute exposure through any means can result in systemic consequences, including disruptions in electrolyte levels that may result in seizures, decreased function of the central nervous system, and irregularities in the conduction of the heart.

Limited data is available regarding the impact of prolonged exposure to HF. One of the effects after long term exposures is fluorosis, a syndrome distinguished by loss of weight, bone brittleness, anaemia, and general poor health.

Similar to ERPG and AEGL values provided for UF_6 (see Section 2.3.1), ERPGs and AEGLs values for HF intended for emergency planning and response operations are summarized in Table 9 [52].

TABLE 8. SUMMARY OF ESTIMATES OF HF TOXICITY IN CASE OF CHRONIC AND ACUTE EXPOSURE

Source	Effect	Concentration in air, mg HF/m ³ (ppm)	Exposure time
US National Institute for Occupational Safety and Health	Recommended Exposure Limit - Ceiling (REL-C)	5 (6)	15 min
	Recommended Exposure Limit - Time weighted average (REL-TWA)	2.0 (3)	10 h
	Immediately Dangerous to Life or Health (IDLH) level	24 (30)	30 min
US Occupational Safety and Health Administration	Permissible exposure limit - Time weighted average (PEL-TWA)	2.0 (3)	8 h
American Conference of Governmental Industrial Hygienists	Threshold limit value - Ceiling (TLV-C)	2.6 (2)	
	Threshold limit value - Time weighted average (TLV-TWA)	0.4 (0.5)	8 h

TABLE 9. ERPG AND AEGL VALUES FOR HYDROFLUORIC ACID

ERPG (mg HF/m ³)		AEGL (mg HF/m ³)					
	1 hr		10 min	30 min	1 hr	4 hr	8 hr
ERPG-1	1.6	AEGL-1	0.8	0.8	0.8	0.8	0.8
ERPG-2	16.4	AEGL-2	78	28	20	9.8	9.8
ERPG-3	41	AEGL-3	139	51	36	18	18

The hazard from hydrofluoric acid is sometimes less obvious. It is less likely to vaporize and can have the appearance of water. On contact with skin at low concentrations, burns are often not detected immediately, but can later be very painful, resulting in skin and tissue damage. Hydrofluoric acid solutions between 20–50% may take as long as 8 hours to take effect, whereas solutions with less than 20% may require up to 24 hours to show any effect. Suitable personal protective equipment and respirator protection are required for maintenance operations involving plant and equipment that could contain anhydrous HF or hydrofluoric acid as flush outs are not 100% effective.

More detailed information about HF can be found in Hydrogen Fluoride Study [53] and Emergency Preparedness and Response Guidelines for Anhydrous Hydrogen Fluoride (AHF) and Hydrofluoric acid (HF) [52].

2.3.4. Precautions associated with release of UF₆

Effective control of UF₆ releases necessitates advance planning for emergency procedures and necessary equipment. This includes having respiratory protective equipment, leak mitigation tools like wooden plugs and patches, a detection and alarm system, and a cooling mechanism readily accessible in areas where UF₆ is being processed (see Section 9.3 for more information).

Entering dense clouds resulting from UF₆ leaks, primarily composed of HF gas, poses a significant risk and necessitates the utilization of protective gear and respiratory equipment that can effectively block HF and particulate inhalation. It is crucial to wear protective clothing to avoid skin burns.

Evacuation of individuals who lack proper training and protection is necessary in areas affected by the release.

2.4. ACTIVITY OF UF₆

The activity of a mass of UF₆ is dependent upon several factors:

- Origin of uranium, natural or reprocessed;
- Degree of enrichment in ²³⁵U;
- Time elapsed since processing;
- Radioactive impurities.

2.4.1. Activity of natural and enriched UF₆

Natural UF₆ is primarily used as feed for enrichment processes.

The activity of UF₆ with the natural content of its isotopes supplied for enrichment is around 1.7×10^4 Bq/g [54]. This specific activity value refers to a freshly prepared substance in which all the progenies due to the decay of the uranium series are absent. Hence, it is slightly lower than that of natural uranium. Natural uranium has a specific activity of 2.5×10^4 Bq/g U [25]. The isotopes ²³⁴U and ²³⁸U each contribute about half of the activity of UF₆ with the natural content of its isotopes.

The activity in unirradiated UF₆ is determined by the enrichment of ²³⁵U. However, with the enrichment of the ²³⁵U isotope, the contribution from ²³⁴U, which enriches more quickly than ²³⁵U, becomes the primary factor (see Section 4.3). For instance, at the enrichment level of 5% for ²³⁵U, 80% of the total activity is attributed to the ²³⁴U content.

While specific activity of enriched uranium depends on proportion of the isotopes, Guide of Good Practices for Occupational Radiological protection in Uranium Facilities [39] provides approximation¹¹ which adjusted for SI units can be written as:

$$S = 14800 + 14100 \times E + 126 \times E^2 \quad (5)$$

where S is the specific activity (Bq/g), and E is the wt% ²³⁵U.

¹¹ The approximation is applicable to enriched UF₆ obtained with gaseous diffusion process.

Discussion on change of ^{234}U concentration (as a result of enrichment process), one of the main drivers of specific activity, are provided in Section 4.3.3.

The extended self-irradiation of UF_6 can lead to the buildup of fluorine gas, especially cylinders containing high assay uranium. This is because, in the presence of intense alpha radiation, UF_6 slowly breaks down into solid UF_5 and gaseous fluorine, despite its inherent stability as a compound.

The alpha radiation from uranium does not pose a risk since UF_6 is constantly enclosed within sealed vessels due to its chemical properties. It is important to note that the effects from chemotoxicity are more significant than the radiological toxicity for all typical enrichments.

However, the decay products of uranium include nuclides which emit more penetrating beta and gamma radiation. The main source of radiation comes from beta particle emitters ^{234}Th and ^{234}Pa (half-life of 24.1 day and 1.1 minute respectively), formed after decay of ^{238}U according to the following decay scheme:



After UF_6 is vaporized from a vessel or transport cylinder, the non-volatile decay products are left behind and can build up on internal surfaces of the transport cylinder. In the absence of the shielding and absorption provided by the bulk of UF_6 , the gamma radiation levels can rise considerably, potentially reaching as high as 2 mGy/h. The most intense radiation levels are usually detected immediately following the emptying process.

Appropriate detectors and multichannel analysers can be utilized to measure the ^{235}U assay of materials within vessels and cylinders by measuring the gamma activity generated by ^{235}U (186 keV).

2.4.2. Activity of depleted UF_6

Depleted UF_6 is a by-product of uranium enrichment (see Section 4.3). Typical enrichment of Depleted UF_6 is 0.2–0.3% ^{235}U , one-third of its original value. The activity of depleted UF_6 is about 60% the activity of natural uranium. The comparison of detailed contributions of each isotope to total activity for depleted uranium against natural uranium is shown in Table 10 [55, 56].

Depleted UF_6 may contain traces of ^{236}U from cross-contamination occurring when the same equipment has been used for handling both non-irradiated and irradiated uranium.

TABLE 10. COMPARISON BETWEEN THE ACTIVITY OF NATURAL URANIUM AND DEPLETED URANIUM (0.2% ^{235}U)

Isotope	Activity in 1mg of natural uranium (Bq/mg)	Activity in 1mg of Depleted uranium (Bq/mg)	Activity in 1mg of Depleted uranium with traces of ^{236}U (Bq/mg)
^{234}U	12.4	2.26	2.30
^{235}U	0.57	0.16	0.16
^{236}U	—	—	0.0074
^{238}U	12.40	12.40	12.41
Total	25.28	14.80	14.88

2.4.3. Activity of UF_6 from irradiated uranium

In addition to ^{234}U , ^{235}U , and ^{238}U , UF_6 produced from irradiated and reprocessed uranium may also include:

- Other uranium isotopes, e.g. ^{232}U , ^{233}U , ^{236}U , ^{237}U ;
- Transuranic nuclides, e.g. ^{237}Np , ^{239}Pu ;
- Fission product impurities, e.g. ^{106}Ru , ^{99}Tc ;
- Decay products of these species, e.g. ^{228}Th , ^{208}Tl .

During the conversion to UF_6 , the ratios existing at reprocessing remain unchanged since the chemical processes do not affect the isotopic composition of uranium. An exception is ^{237}U which has a notably short half-life (6.75 days) and is a decay product of ^{241}Pu .

Differences in stabilities of PuF_6 and NpF_6 compared to UF_6 leads to the removal of Pu and Np, particularly during the fluorination stage.

Uranium-234, found in unirradiated uranium, holds great importance in the specific activity of reprocessed uranium. Enrichment of ^{235}U leads to a larger increase in ^{234}U concentration than in ^{235}U (see Section 4.3 below). In the reactor, ^{234}U is consumed at half the rate of ^{235}U by neutron interaction, resulting ^{234}U contributing more to the specific activity of reprocessed uranium than fresh fuel. Following re-enrichment, ^{234}U plays a key role in determining the A_2 value for transport purposes.

Uranium-236 does not present any notable safety concerns, but its presence can be used as an indicator of contamination by irradiated materials. The specification for natural UF_6 generally limits the presence of this isotope to less than 20 parts per million. Furthermore, ^{236}U has a parasitic neutron absorption property, making it undesirable in nuclear fuel.

The importance of ^{232}U lies in its decay chain to ^{208}Tl (gamma emitter) through ^{228}Th . Although this chain can be disrupted through chemical processes (solvent extraction or volatilization), equilibrium is restored with a 30% regrowth within a year. Consequently, post-reprocessing procedures need to be carried out quickly to minimize gamma radiation dose.

To illustrate the impact of various nuclides on the dose rate and how it evolves over the time after processing, Figure 3 provides the estimated dose rate (air kerma at 1 meter) of one gram of various types of Uranium: natural, natural enriched at 4%, reprocessed, and reprocessed enriched at 4.5%. Natural uranium contains a typical 0.72% of ^{235}U . Enriched Uranium contains 4% of ^{235}U , with the quantity of ^{234}U adjusted to maintain the same ratio as for natural uranium. The data for reprocessed and reprocessed enriched uranium is based on quantities of ^{238}U , ^{234}U , ^{235}U , ^{236}U , and ^{232}U from the IAEA-TECDOC-1630, Use of Reprocessed Uranium [57](mean values of different vectors provided in pages 67, 73, 92 and 117). It is important to note that this graph is intended solely for educational purposes, and any use in facilities needs to be adapted to the specific materials being handled. The key insights that could be derived from the graph are:

- The dose rates of enriched uranium, regardless of whether it has been reprocessed or not, are notably higher than those of natural uranium;
- For natural uranium, a first equilibrium is established within few months, following which the dose rate remains relatively steady for an extended period. It is worth noting that approximately 95% of the dose rate is reached within period of 3 months);
- The dose rate of reprocessed uranium will experience a noticeable increase within the first 10 years; without enrichment, the increase from 3 months to 10 years is approximately 25%; after reprocessed uranium enrichment, this increase can reach 50%.

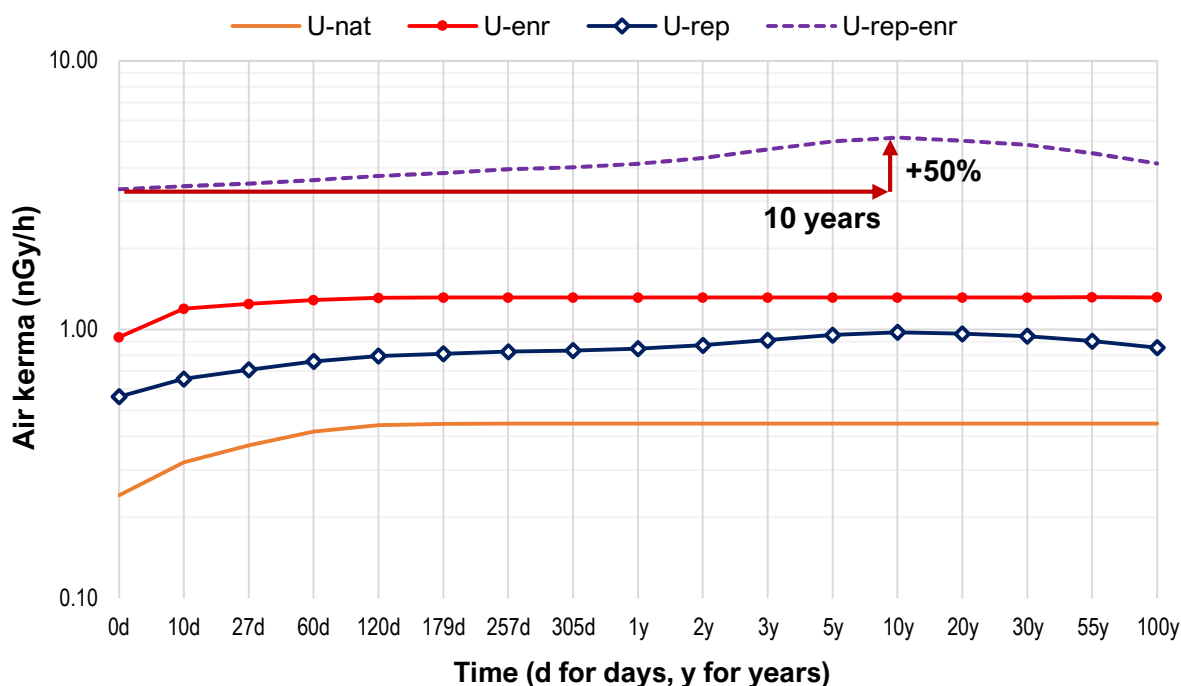


FIG. 3. Relationship between air kerma and time for natural, enriched, reprocessed, reprocessed enriched UF_6 (1 g) at 1 meter.

Reprocessed uranium's composition is influenced by various factors such as reactor type, burnup, cooling history, impurity removal efficiency, time elapsed since reprocessing and conversion operations. The conversion of uranium oxide to UF_6 leads to impurities being concentrated in the waste stream. Processes involving UF_6 transfer in the gas phase tend to concentrate non-volatile species in residues. Volatile species like ^{106}Ru and ^{99}Tc can impact activity in process vessels and cylinders, as well as contaminate effluent streams from wet

scrubbing processes. Pu and Np can be volatilized in a flame reactor, with Np partially volatilizing in fluidized beds while Pu is retained in CaF₂. Therefore, it is essential to include such species in site regulation and monitoring procedures.

2.5. CRITICALITY

The distinguishing characteristic of a fissile nuclide such as ²³⁵U is that it is capable of initiating a self-sustaining neutron chain reaction. A fission chain is propagated by neutrons. Since a chain reaction is dependent upon the behaviour of neutrons, fissile materials are handled, packaged, and shipped under requirements designed to control neutron behaviour in a manner to ensure subcriticality and, thus, provide criticality safety.

There are three possible fates for a neutron in fissile material:

- It may encounter a fissile nuclide and induce fission, producing neutrons to continue the chain;
- It may be absorbed by other materials or by a fissile nuclide without fission;
- It may leak out of the system.

Criticality is achieved when there is a balance between neutron production by fission and loss by neutron absorption in and leakage from the fissile material. The three possible outcomes for a neutron are controlled to provide criticality control. The fraction of neutrons leaking is affected by the geometric configuration, both individual package and of the spacing between packages. Neutrons leaking from a vessel may enter other similar containers and produce a fission. Neutron interaction can be influenced by package dimensions, which determine the spacing of the fissile material. Neutrons may also be removed from the system using neutron absorbers. Good design embodies a balance of many parameters and assures subcriticality. This objective is achieved by applying specific restrictions on ²³⁵U enrichment, as well as on geometry, volume, mass, spacing, and moderation. In certain cases, the neutron absorption properties of the vessel and cylinder are also used.

The amount of UF₆ which may be contained in an individual vessel or cylinder and the total number of vessels or cylinders accumulated as a group are determined by the nuclear properties of the UF₆.

The use of model 30B, 48X, and 48Y cylinders at ²³⁵U enrichments of 5.0% and 4.5% respectively is dependent upon limiting the availability of hydrogen – a neutron moderator. A hydrogen-to-uranium atomic ratio of less than 0.088, which is equivalent to a specification of greater than 99.5% UF₆ (assuming the impurity is hydrogen), is required by American Society for Testing and Materials (ASTM) specifications C787-20, Standard Specification for Uranium Hexafluoride for Enrichment [14] and C996-20, Standard Specification for Uranium Hexafluoride Enriched to Less than 5% ²³⁵U [58].

The shipment of UF₆ of enrichment greater than 1% but less than 5% requires the use of an approved overpack. For enrichments above 5%, geometric and mass limits are employed as well as overpack protection.

Changes in the quantity, form, arrangement, physical or chemical state, or changes in the packaging could affect the neutron multiplication factor and invalidate the criticality safety

index (CSI¹²) of the package [59]. The requirements set forth in the certificate of approval for a package are necessary to assure safety during transport. The criticality safety assessment performed includes a range of parameters. These parameter ranges need to be described in the application for transportation approval.

A series of different types of chemical traps are utilized (depending on the design) after the cold traps in UF₆ facilities as a part of the ventilation system, which captures UF₆, HF, and uranic contaminants before discharging off-gas to the atmosphere. This system is crucial for satisfying effluent control and monitoring requirements for personnel and public safety. The design of chemical traps needs to avoid criticality. Extra care is to be given to chemical traps utilizing charcoal (activated carbon) which has a strong absorbing ability and is a good neutron moderator.

3. INTEGRATED MANAGEMENT SYSTEM

3.1. GENERAL

An integrated management system will include all those planned and systematic actions necessary to provide confidence that adequate measures are specified and applied for relevant UF₆ facilities and activities to ensure safe and reliable production, transport, handling, and storage of UF₆.

Safety, environment, health, human-and-organizational-factor, quality, societal and economic elements need to be integrated into management systems. IAEA Safety Standards Series No. GSR Part 2, Leadership and Management for Safety [60] provides high level requirements on that subject. In accordance with GSR Part 2 [60], “The management system supports the achievement of the fundamental safety objective of protecting people and the environment from harmful effects of ionizing radiation”. People include both workers and the public.

For instance, an integrated management system for a UF₆ storage facility need to address material handling, cylinder safety, and storage monitoring. When establishing the integrated management system, the following topics are considered: safety, security, material accountability, safeguards, health, environmental, quality, societal and economic impacts of system failures such as cylinder leakage due to corrosion, handling damage, or damage from earthquake, storm, or other external forces. In addition, the following are also considered: cylinder inspections; storage monitoring; maintenance of auxiliary facilities for weighing, filling, sampling and emptying; cylinder handling; waste management; emergency management; human-and-organizational-factor; personnel training; description of the nuclear material flows to and out of the storage with control measurement points including for safeguarding purposes; and preparation and maintenance of operating procedures.

Principle 1 of Fundamental Safety Principles, IAEA Safety Standards Series No. SF-1, Fundamental Safety Principles [61], states that “**The prime responsibility for safety must rest with the person or organization responsible for facilities and activities that give rise to radiation risks.**” According to GSR Part 2 [60], “Leadership and management for safety are therefore of fundamental importance for organizations that are responsible for facilities and

¹² “Criticality safety index (CSI) assigned to a package, overpack or freight container containing fissile material shall mean a number that is used to provide control over the accumulation of packages, overpacks or freight containers containing fissile material.” (para. 218 of SSR-6 (Rev. 1) [59]).

activities that give rise to radiation risks and that therefore have the prime responsibility for the safety of such facilities and activities.”

Establishing, sustaining and continuously improving leadership and management for safety is essential to fostering and sustaining a strong safety culture within an organization. This, in turn, is critical aspect in preventing and mitigating accidents.

Several international standards that provide guidance on the management system have been developed, such as the following:

- IAEA Safety Standards Series No. GSR Part 2, Leadership and Management for Safety [60];
- IAEA Safety Standards Series No. GSR Part 3, Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards [62];
- IAEA Safety Standards Series No. GS-G-3.1, Application of the Management System for Facilities and Activities [63];
- IAEA Safety Standards Series No. GS-G-3.5, The Management System for Nuclear Installations [64];
- IAEA Safety Standards Series No. SSR-4, Safety of Nuclear Fuel Cycle Facilities [65];
- IAEA Safety Standards Series No. SSR-6, Regulations for the Safe Transport of Radioactive Material [59];
- IAEA Safety Standard Series No. SSG-26 (Rev. 1), Advisory Material for the IAEA Regulations for the Safe Transport of Radioactive Material [54];
- IAEA Safety Standards Series No. SSG-78, Compliance Assurance for the Safe Transport of Radioactive Material [66];
- IAEA Safety Standards Series No. TS-G-1.4, The Management System for the Safe Transport of Radioactive Material [67];
- International Organization for Standardization (ISO) standard ISO 9001, Quality management systems – Requirements [68].

The important aspects of the management system, including policy, safety culture, organization, risk minimization, and procedures are further detailed below.

3.2. POLICY

A corporate, or organization’s policy for safety, health, environment, and quality might include a commitment to the following principles:

- Complying with and moving beyond legal requirements;
- Optimizing protection and safety of workers and members of the public, i.e. according to para 1.15 of GSR Part 3 [62], “...ensuring that the likelihood and magnitude of exposures and the number of individual exposed are as low as reasonably achievable with economic, societal and environmental factors taken into account” (colloquially known under the abbreviation ALARA);
- Preventing pollution;
- Ensuring quality of processes, products and services;
- Continually improving overall performance.

3.3. SAFETY CULTURE

Accountability, continual improvement, and a commitment to maintaining safe and efficient operations by every individual in the organization, contributes to operational excellence.

Enhancing the safety culture might ensure that all employees exhibit a questioning attitude that contributes significantly to risk mitigation. The safety culture is also strengthened by processes and a positive environment for all employees to raise concerns. Leadership behaviours play a key role in reinforcing this environment and ensuring that concerns lead to constructive action. For this purpose, significant resources need to be committed to enhancing safety culture. It is essential to implement targeted actions to establish a sufficient degree of confidence in protection and safety measures, as well as to ensure these measures are regularly evaluated and reassessed. In addition, IAEA Safety Standard Series No. GSG-7, Occupational Radiation Protection [69] states that: “A safety culture should be promoted and maintained at all levels within the organization.” The management system needs to also account for human factors, promoting optimal performance and practices that help prevent human and organizational errors. This includes designing equipment that minimizes or prevents such errors, developing effective operating procedures, defining limits and conditions, providing adequate training, and utilizing safety systems to mitigate the effects of human errors. Lessons learned from operational experience and benchmarking with other facilities where UF₆ is produced, transported, handled and stored might also contribute to continually improving overall performance [70]. Additional information is available in the following publications:

- IAEA Safety Standards Series No. GS-G-3.1, Application of the Management System for Facilities and Activities¹³ [63];
- IAEA Safety Standards Series No. GSG-16, Leadership, Management and Culture for Safety in Radioactive Waste Management [72];
- IAEA Nuclear Energy Series No. NG-G-2.1 (Rev. 1), Managing Human Resources in the Field of Nuclear Energy [73];
- IAEA Nuclear Energy Series No. NG-T-2.7, Managing Human Performance to Improve Nuclear Facility Operation [74];
- Institute Of Nuclear Power Operations, Human Performance Reference Manual, rep. 06-003 [75];
- Institute Of Nuclear Power Operations, Human Performance Tools for Workers, rep. 06-002 [76];
- Institute Of Nuclear Power Operations, Human Performance Tools for Engineers and Other Knowledge Workers, rep. 05-002 [77].

3.4. ORGANIZATION

Each facility and activity for UF₆ need to be organized to ensure that all responsibilities are appropriately assigned and clearly understood. Each individual organization within a facility for UF₆ needs to include, or interface with, the following activities:

- Administration.
- Procurement.
- Operations.
- Maintenance.
- Occupational health and safety, including industrial hygiene, industrial safety and fire safety.
- Radiation protection and nuclear safety.
- Storage of UF₆.
- Transport:

¹³ IAEA publication DS513, Leadership, Management and Culture for Safety [71] is currently being prepared to substitute GS-G-3.1 [63].

- On-site;
- Off-site.
- Quality control:
 - Inspection;
 - Testing (for instance, for storage of UF₆, shell thickness, magnetic examination, penetrant examination, etc.).

3.5. MINIMIZING THE RISKS

Multiple layers of measures are commonly implemented to minimize the risks (safety, security, health, environmental and quality) and ensure reliable production, transport, handling, and storage transport of UF₆. This might include both engineering features and operator actions to minimize risks at all stages of the production, transport, handling, and storage processes.

These measures typically cover the following topics:

- Governance;
- Internal regulations;
- Risk management;
- Project management;
- Design control;
- Supply chain management;
- Work control;
- Conduct of operation;
- Configuration management.

The following are examples of elements that might be considered when assessing such topics:

- Safe design of process – Ensuring safe designs of any process is one of the first critical layers of measures to minimize risks and assure reliability. This applies to both the original design of the UF₆ facility and its modifications. A rigorous design change procedure is necessary and needs to assess all changes with respect to safety, security, health, environment, and quality impacts. This also needs to include careful selection of vessel capacities and system operating pressure, to minimize the scale of a release cloud should containment be lost. The scope of safe design needs to consider the entire lifecycle of facilities, including maintenance, post-operational clean out and decommissioning. SSR-4 [65] establishes the requirements for the safe design of all types of nuclear fuel cycle facilities, including uranium conversion and enrichment facilities. SSG-5 Rev. 1 [2] provides recommendations on design considerations in these facilities.
- Construction – Construction activities need to be subjected to a variety of controls. For instance, civil work may require the development of inspection and tests plans, identifying the tasks and inspections for each task. As another example, electrical systems might be governed by several electrical standards, to ensure that the implementation of new electrical systems or the repair of old systems meets the requirements.
- Process controls – Process controls are essential throughout every phase of production. UF₆ facilities need to be operated within the safe process design parameters, providing a layer of defence between the hazard and the engineered safety interlock systems. Excursions beyond the safe process design parameters are subject to appropriate investigation, offering continuous improvement opportunities.

- Alarms and operator intervention – The UF₆ facilities may incorporate both engineered and operator-activated systems to ensure rapid identification and mitigation of risks. This can include regulatory compliance; training for all employees and contractors; constant operator monitoring of the UF₆ production, transport, handling, and storage; documentation and auditing of housekeeping standards; fire detection and alarm activation devices; fluoride detection alarms; and emergency response instructions. The system design needs to consider human factors and be engineered to ensure strong ergonomics, aiding operators' responses to alarms without unnecessary complexity.
- Safety interlock systems – Safety interlock systems automatically activate to enhance safety when needed. These systems may include:
 - Detect and divert systems, which deactivate heating and ventilation systems while activating emergency ventilation to contain and neutralize potential releases in UF₆ facilities;
 - Remote shutdown capabilities and automated shutdown sequences for relevant processes;
 - Process smoke detectors, providing coverage along with HF detectors in the UF₆ areas of the UF₆ facilities. Air locks may be employed to isolate UF₆ areas from the general process area.
- Protective devices – Protective devices contribute to risk minimization. These include:
 - Failsafe design, incorporating spring-loaded valves and pressure relief systems;
 - Sprinkler systems in the UF₆ building, including internal sprinkler protection for all dust collectors and select scrubbers, based on combustible loading.
- Administrative control – Maintaining a minimum nitrogen inventory can ensure that hydrogen, fluorine and other hazardous chemicals are purged from production circuits when needed.
- Containment systems – Potential releases in the UF₆ facility are managed through detection and containment systems designed to direct the release to dust collection and/or scrubbing systems. Examples of such systems include:
 - An emergency ventilation system in the first enclosure of the cylinder filling area, which can be activated by local operators or, preferably, automatically via a reliable emergency system, if loss of containment is detected. The local control room is isolated from the general heating and ventilation system for the process area and has its own separate ventilation system maintaining positive pressure relative to the process area;
 - A secondary enclosure around the UF₆ cylinder filling station. A solid CO₂ injection system can be piped into this enclosure: in the unlikely event of a significant UF₆ release, the CO₂ cooled enclosure would allow for UF₆ freeze-out and reduce the amount of UF₆ vapour to UO₂F₂ and HF.
- Emergency planning, response, and recovery – A comprehensive defence in depth approach includes appropriate emergency arrangements in place, both on-site and off-site, as necessary (see Section 9).

3.6. PROCEDURES

Standard operating procedures are expected to be prepared for all routine operations in UF₆ production, transport, handling, and storage (including cylinder cleaning and inspection, handling, storage, monitoring, and removal from storage). For instance, when a cylinder is removed from storage status (i.e. handled), procedures need to be followed to ensure that the cylinder meets the criteria for the intended application or destination and that all safety, criticality, and environmental conditions are satisfied.

All procedures and associated risk assessments need to be categorized based on safety and environmental significance. They need also to be subjected to regular periodic review, with the frequency guided by the categorization. Outcomes from change management processes and lessons learned need to be incorporated into the relevant procedures, and appropriate operator training updates carried out.

4. PRODUCTION AND HANDLING

4.1. INTRODUCTION TO CONVERSION, ENRICHMENT AND RECONVERSION

The sequence of operations involving the production and handling of UF₆ extends from the processing of uranium ore concentrate (UOC) to nuclear fuel and includes conversion, enrichment, and reconversion (see Sections 4.2, 4.3, 4.4 and 4.5). Different methods and chemical processes are currently used. Each of them has its advantages and disadvantages. Conversion and enrichment operations require supporting operations such as reagent preparation, fluorine production, waste processing, and gas purification (see Section 4.6).

Production and handling of UF₆ impose stringent safety measures (see Section 2 and Sections 4.6, 4.7, and 4.9). The supporting operations have their own safety considerations (see Sections 4.6, 4.7, and 4.9). Conversion and reconversion utilize other materials in addition to UF₆. The particular safety considerations with regard to those materials (fluorine, HF, ammonia, hydrogen, nitric acid, etc.) have to be dealt with (see Section 4.7). Specificities with the production and handling of reprocessed uranium need to be considered (see Section 4.8).

The design of a UF₆ facility requires special considerations. Good practices for the general layout of a UF₆ facility and for building containment are to be taken into account (see Section 4.9).

This section will highlight the significant issues at the three types of UF₆ facilities that handle UF₆ conversion, enrichment and reconversion. All these facilities provide a sequential manufacturing process to produce fuel for power reactors that will meet the needs of the end user. When coupled with facilities that supply the UOCs there are four distinct processes. Product specifications have been developed to define acceptable product at the output of each of these four processes and address the requirements of the facilities to make acceptable reactor fuel.

ASTM Standards [14, 58] have been established to define the impurity and uranium isotope limits for commercial grade UF₆ and limit hydrogen content for nuclear criticality safety.

In the sequence of operations involving UF₆ from UOCs to nuclear fuel, uranium products may appear in many different forms. The typical appearance of the different uranium products is presented hereafter in Table 11.

TABLE 11. TYPICAL APPEARANCE OF THE DIFFERENT URANIUM PRODUCTS

Following the mining and milling of uranium ore, UOCs are produced and used as feed to the conversion process. The typical chemical form produced by the commercial mines is currently either triuranium octoxide (U_3O_8 ¹⁴) or uranyl peroxide (UO_4).

Historically, ammonium polyuranate was a commonly utilized chemical form, characterised by its distinctive yellow colour, which led to its colloquial designation as 'yellow cake'. UOCs are still occasionally referred to as 'yellow cake' due to this historical context, despite not being ammonium polyuranate and lacking yellow colouration.



Uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) – This compound is obtained by dissolving uranium salts, uranium metal, or uranium oxide in nitric acid. This is the typical uranium compound used in the solvent extraction process.



Uranium trioxide (UO_3) – This compound is typically obtained by thermal denitration of $\text{UO}_2(\text{NO}_3)_2$ after the impurities have been removed.



¹⁴ U_3O_8 – This is the most stable and common form of uranium, often used for storage purposes. The U_3O_8 can have various isotopic levels when used for storage but is typically less than the natural isotopic concentration.

TABLE 11. TYPICAL APPEARANCE OF THE DIFFERENT URANIUM PRODUCTS (CONT.)

Uranium dioxide (UO_2) – UO_2 is used in different areas of the fuel cycle.

In conversion, UO_2 is an intermediate product from the reduction of UO_3 and used as the feed material to the hydrofluorination process.

Following reconversion, UO_2 – UO_2 powder, which is generally enriched at 3 to 5 % in the ^{235}U fissile isotope, is compressed into pellets and used in light water reactors.

Non-enriched UO_2 is used as fuel in heavy water reactors.

In the conversion of reprocessed uranium, UO_2 from spent fuel elements is the feed stock for direct fluorination to UF_6 .



Uranium tetrafluoride (UF_4) – This is a chemically stable form of uranium, which is required in the process towards UF_6 .



Uranium hexafluoride (UF_6) – The only uranium compound that becomes gaseous at low temperature. The gaseous form is necessary for current isotopic enrichment processes. UF_6 is used in its crystalline (solid) form for treatment and storage, in gaseous form for enrichment, and in liquid or gaseous form for sampling and isotopic adjustment.



Note: image of U_3O_8 (courtesy of Cameco), images of $\text{UO}_2(\text{NO}_3)_2$, UO_3 , UO_2 , UF_4 , UF_6 (courtesy of Orano).

4.2. URANIUM REFINING AND CONVERSION TO UF_6

4.2.1. General

There are multiple facilities¹⁵ in the world that convert UOC to UF_6 . The UOC is usually in the form of U_3O_8 or UO_4 .

The feed material (natural uranium or reprocessed uranium) used for conversion needs to meet specific requirements for uranium content, chemical and isotopic composition (in the case of reprocessed uranium), and physical properties. As such, the quality of UOCs and the downstream intermediate products, such as UO_3 and UF_4 , is expected to ensure the desired

¹⁵ IAEA Nuclear Fuel Cycle Database <https://infcis.iaea.org/NFCFDB>.

quality of UF_6 , taking into account the capabilities of the conversion technology used. In turn, UF_6 produced is required to meet specific chemical and physical requirements.

For that purpose, in international trading and cooperation, ASTM C967-20, Standard Specification for Uranium Ore Concentrate [78] and ASTM C787-20 [14] standard specifications are generally used for the production of UOC and production of UF_6 , respectively.

4.2.2. Process description

The various unit operations in the conversion facilities are illustrated in Figure 4.

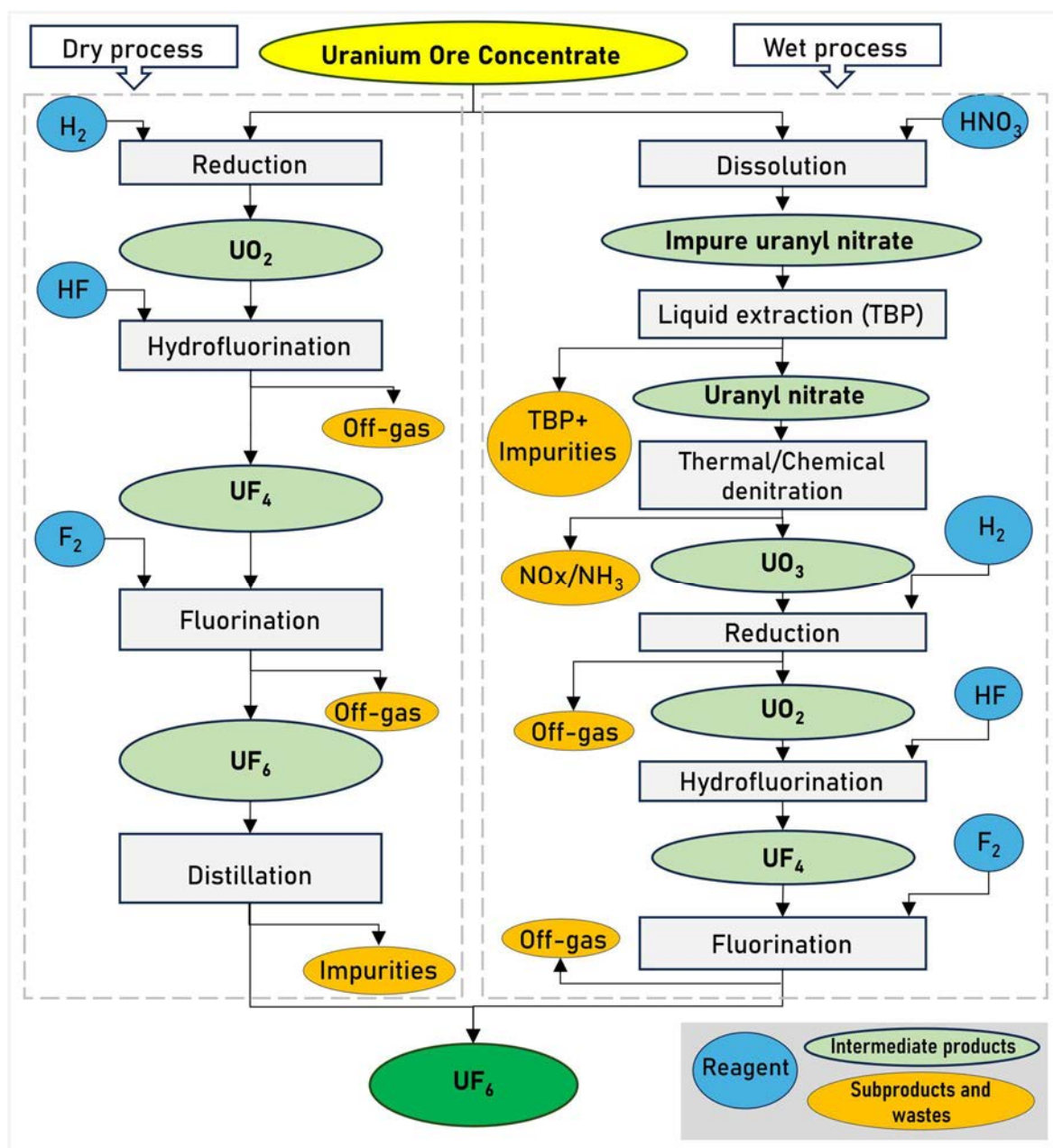


FIG. 4. Dry and wet conversion processes.

The general approach includes refining of UOCs (dissolving them in nitric acid) and subsequently converting it into UF_6 , a process which requires the usage of a liquid solution, and

is therefore called wet process. An alternative way to obtain UF_6 from UOCs includes UOCs conversion to impure UF_6 , which is then refined by distillation. This alternative is called dry process.

Figure 4 shows that there are common processing steps, regardless of the process: conversion of UOCs to UO_2 , hydrofluorination of UO_2 to UF_4 , and fluorination of UF_4 to UF_6 with elemental fluorine.

In the wet process, the impurities are removed from the UOC using solvent extraction. The concentrate is dissolved in nitric acid to form $\text{UO}_2(\text{NO}_3)_2$ solution and this crude solution is purified using a solvent extraction process. The solvent is typically 20–30% tri-n-butyl phosphate (TBP) in organic diluent chemical such as hexane or kerosene. The solvent extraction process can be carried out using pulsed columns, mechanically mixed phase columns, centrifugal columns, or mixer/settlers. Uranyl nitrate is contacted in a counter-current flow of solvent with TBP in these columns, where the uranium is predominantly taken up in the organic phase, leaving impurities in the aqueous phase (also called raffinates). The purified uranium from the organic phase is extracted (re-extracted) with dilute nitric acid to form a dilute $\text{UO}_2(\text{NO}_3)_2$ solution. Depending on the facility, the resulting dilute $\text{UO}_2(\text{NO}_3)_2$ product stream is then heated and concentrated to produce uranyl nitrate hydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot n \text{H}_2\text{O}$). After that, it is chemically or thermally denitrated to U_3O_8 or UO_3 . During the thermal denitration process, water and nitrogen oxide are removed (as a gas) by heating $\text{UO}_2(\text{NO}_3)_2$, which decomposes to UO_3 . Finally, the UO_3 is ultimately reduced to UO_2 using either cracked ammonia or pure hydrogen. Nitrogen oxides and water removed during the thermal denitration process are reacted and converted to concentrated nitric acid in multiple processing steps, which can be recycled back into the upstream of dissolution.

The organic phase, after the uranium has been extracted from it, is regenerated, and recycled to the front end of the extraction process. The aqueous or raffinate waste from the extraction step contains the impurities and is either treated to recover the nitric acid for recycle to the initial dissolution step or directly neutralized for disposal.

In the dry process, the concentrate is first calcined at 850°C to produce U_3O_8 and/or reduced to UO_2 in its impure state. The reduction step can be carried out with hydrogen using fluid bed or rotary kiln reactors. The excess hydrogen gas is filtered or scrubbed prior to being discharged to the atmosphere.

In both processes, the resulting UO_2 is converted to UF_4 with HF either via dry or wet processes. Common equipment used in the dry process are fluid beds or kilns. In the wet process, UO_2 is reacted with anhydrous HF and hydrofluoric acid mixture to produce UF_4 and then the resultant UF_4 slurry is dried. The off-gas streams from both wet and dry processes are scrubbed before discharge to the atmosphere (an example of monitoring and recycling of gaseous HF is provided in Appendix I, Section 1.1).

Uranium tetrafluoride is fed in a dry powder state into tower fluorination reactors and reacts with preheated fluorine gas to produce the gaseous UF_6 product. In most of the conversion facilities, fluorine is produced on site by the electrolysis of an electrolyte melt ($\text{KF} \cdot 2\text{HF}$). This electrolyte is prepared by the addition of liquid anhydrous HF to potassium bifluoride ($\text{K}[\text{HF}_2]$) and kept at a temperature above 90°C during electrolysis. Both fluorine and hydrogen are generated during electrolysis (see Section 4.7.2.1 for further information on fluorine). The UF_6 produced by reacting UF_4 with fluorine is extracted from the gas stream using cold traps. The remaining off-gas contains residual uranium, fluorine and HF which requires treatment before

it is released to atmosphere (an example of treatment of this off-gas is provided in Appendix I, Section 1.2).

When producing UF_6 from reprocessed feed materials (in the form of oxide or concentrated $\text{UO}_2(\text{NO}_3)_2$), the additional activity of fission products, decay products, and complex waste streams need to be safely managed. One option is to simplify the wet conversion process by excluding the reduction operation to UO_2 and the conversion operation of UO_2 to UF_4 . In this case, U_3O_8 is supplied to tower-type devices, and directly fluorinated with elemental fluorine. The elimination of the UO_2 and UF_4 steps, significantly reduces the technological scheme and reduces the process time, which in turn minimizes radiation dose rates to the workforce. The production of elemental fluorine is energy intensive, and therefore when assessing the relative merits of direct fluorination, the additional fluorine demand needs to be accounted for. Another option for managing radiation dose when producing UF_6 from reprocessed feed material, is to implement automation, shielding and distancing at strategic points in the process. In this case, a $\text{U}_3\text{O}_8/\text{UO}_3$ to UO_2 to UF_4 to UF_6 processing approach can be utilized. The benefit of this process selection is that the required radiation dose mitigations are based on worst case material feed and fault conditions. However, the process is more complicated, and it is likely that the initial investment will be higher. In both processes, the phase change associated with the fluorination step to UF_6 will result in a separation of radioactive decay products from the parent uranium. It is very important at this stage to employ prompt processing to ensure the product is delivered to the downstream enrichment process as quickly as possible. This is because the immediate decay product of ^{232}U , ^{228}Th will grow back producing increasing higher quantities of ^{208}Tl ; which is a high energy gamma emitter.

The product UF_6 in the gaseous state is typically filtered to remove the particulates and condensed as a solid in cold traps. After that, UF_6 is transferred into shipping cylinders (see 4.6.3). As required, UF_6 is heated to achieve a liquid state and is allowed to drain directly into shipping cylinders where it solidifies. In the dry process, where the concentrate is directly reduced, hydrofluorinated and fluorinated to UF_6 , the resulting impure UF_6 is vaporized and fed into distillation columns where fractional distillation removes the remaining impurities. Following purification, UF_6 is collected in a cold trap and then fed directly to shipping cylinders as noted above. After sampling (see Section 4.6.4), the cylinder is stored, ready for shipment to the enrichment facilities.

The waste resulting from refining and conversion of UOC to UF_6 are generally common to all facilities. Waste arises from two sources, waste products originating from the concentrates and waste products originating from the process reagents. In general, wastes are handled by treatment and recycle or treatment and disposal. Waste management is described in Section 7.

4.2.3. Process comparison

A detailed process comparison is provided in Ref. [79]. Some of the higher level differences between wet and dry processes are outlined in this section below.

In the dry process, sodium and potassium in the feed UOC form non-volatile salts such as Na_2UF_8 , which reduce uranium recovery and lower the sintering temperature in the fluidized bed, leading to undesirable lump formation. Although pretreatment can remove these alkali metals, the wet process inherently rejects them without additional steps or waste generation—particularly advantageous when uranium oxide concentrates consistently contain high levels of alkali metals.

Additionally, in the dry process, impurities increase HF and F₂ consumption during the fluorination step, making the wet process more favourable in cases of high impurity content. When, in addition to UF₆ production, there is a need to produce CANDU reactor fuel or uranium metal, the wet process is particularly advantageous, as it also yields nuclear-grade intermediates like UO₃ and UF₄, which are especially useful for these applications.

Conversely, dry processing has its own benefits. Distillation at the end of the dry process effectively removes impurities, including those from equipment corrosion. If enriched uranium needs to be converted, a dry process may be safer due to the reduced risk of criticality in the absence of water. The dry process also handles organic impurities more effectively, as these compounds can cause problematic emulsification in wet process but are typically less troublesome in dry process.

4.3. ENRICHMENT

4.3.1. General

A key step in the nuclear fuel cycle is changing the concentration or assay of the ²³⁵U isotope. An assay level of ²³⁵U higher than the 0.72% found in natural uranium (generally in the range of 3% to 4.95%) is generally required to produce nuclear fuel for nuclear power plants. This is accomplished through enrichment. The selection of specific assay of ²³⁵U is driven by the specific nuclear reactor design requirements such as reaching certain burnup levels. Since the 1960s, there were two principal processes in commercial use. Gaseous diffusion is the oldest but is now obsolete so there will be no further discussion of the process. The second commercial method is the gas centrifuge process which is more energy efficient and can be built in modular fashion. Currently, this technology is commercially used in China, France, Germany, the Netherlands, Russia, UK, and USA. For more information, see World Nuclear Association market report [80].

In both processes, enrichment is accomplished by taking advantage of the (slight) difference in the atomic masses of the ²³⁵U and ²³⁸U isotopes. Both methods require a gaseous form for uranium – hence the interest in UF₆¹⁶.

Separative work unit is the world recognized measure for enrichment work. The amount of it characterizes the measure of effort needed for the production of enriched uranium with specific product assay from natural uranium under certain tails assay. For more details, see Appendix II.

In considering the enrichment of reprocessed uranium feed material, the increased presence of fission products and decay products adds an extra level of complexity and hazard. To safely manage the radiation hazard, it is important to utilize prompt processing during all production, quality, and logistical steps. For example, on vaporization of UF₆ from a feed cylinder, the radioactive decay products of ²³²U are left behind in ‘the heel’. This creates a short window whilst the ²³²U decay products grow back towards secular equilibrium and at this stage radiation dose rates are manageable. A typical target processing time is approximately six months from

¹⁶ The enrichment process via gas centrifugation cannot be done in the solid state nor in the liquid state. Some halogenates of uranium can be gaseous under specific conditions of pressure and temperature (~54 °C and 1 atm). The one example is uranium chloride, usage of it in enrichment process hinders the enrichment considering chlorine has two natural isotopes (~76% of chlorine-35 and 24% of chlorine-37). For this reason, UF₆ is the preferred form for the enrichment of the ²³⁵U isotope because fluorine has only one isotope: ¹⁹F and during the process fluorine does not contribute to the difference in mass.

the enrichment phase change to the vaporization phase change at reconversion (fuel fabrication).

The material used for enrichment needs to meet specific chemical and physical requirements. The quality of UF_6 is essential for achieving the desired quality of enriched UF_6 , taking into account the capabilities of the enrichment technology used. In turn, enriched UF_6 produced is required to meet specific chemical, physical, and isotopic requirements. For that purpose, in international trading and cooperation, ASTM C787-20 [14] and ASTM C996-20 [58] standard specifications are generally used for feed to and product from enrichment respectively.

4.3.2. Gas centrifugation

The centrifugation process separates isotopes of uranium by making use of the principle of centrifugal force. When gaseous UF_6 is fed into the spinning rotor of a centrifuge machine, the lighter molecules containing ^{235}U gather along the central axis of the rotor (near the light fraction scoop in counterflow centrifuge) and the heavier molecules containing ^{238}U move to the outside (to the heavy fraction scoop in counter-current centrifuge) due to the density gradient created by centripetal force and induced, axial, counter-current flow of gaseous UF_6 [81]. Figure 5 illustrates a basic schematic of a gas centrifuge. The UF_6 gas in which ^{235}U is slightly concentrated is drawn and is fed to the next stage of the cascade. The UF_6 stream containing a higher concentration of ^{238}U is removed and is fed to the next downstage centrifuge.

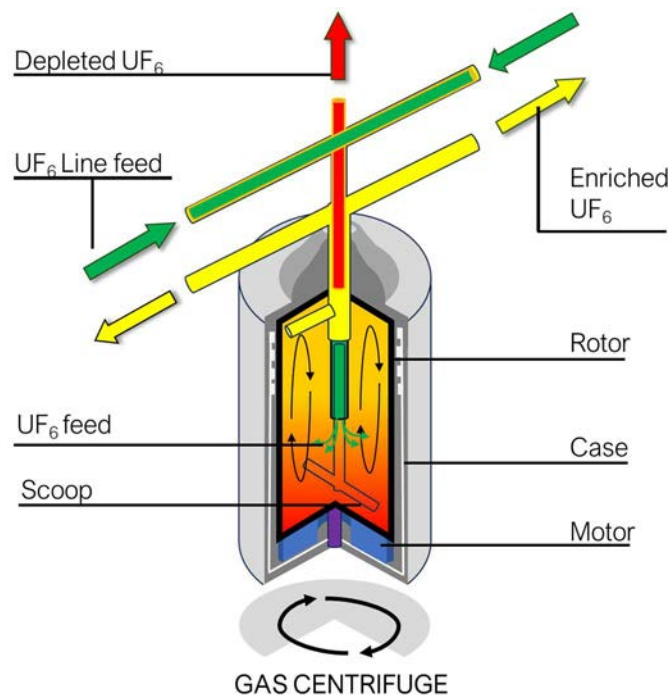


FIG. 5. Basic schematic of gas centrifuge.

Because the amount of actual isotope separation accomplished by a single centrifuge machine is small, a large number of centrifuges operate in parallel in a single stage, which in turn can be arranged in a cascade configuration similar to the gaseous diffusion process (Figure 6). The centrifuge enrichment process operates at subatmospheric pressures. In addition, a uranium enrichment facility also has: UF_6 feed system, UF_6 withdrawal system, UF_6 cylinder handling,

UF₆ cylinder weighing, UF₆ transfer and sampling systems. These supporting operations are described in Section 4.6.



FIG. 6. Cascade hall with centrifuges (courtesy of TVEL).

4.3.3. Enriched and depleted UF₆ from enrichment process

Upon completion of the enrichment process, the enriched UF₆ gas flows, into the containers where it desublimates from a gas to a solid. This is discussed in greater detail in Section 4.6. The enriched UF₆ is then transported (see Section 5) to fuel fabrication facilities where it is reconverted into UO₂ powder to make fuel pellets for fuel assemblies (see Section 4.4). Transport of UF₆ in liquid phase is not allowed.

It is to be noted that enriched UF₆ contains higher than natural proportions of ²³⁴U (0.0055%), whereas the depleted UF₆ contains less of this isotope. For example, concentration level of ²³⁴U depending on the enrichment level applicable to enriched uranium obtained from gaseous diffusion process is provided in Ref. [82] and can be approximated as:

$$\text{wt}\% \text{ } ^{234}\text{U} = 0.0015 + 0.0058 \times E + 0.000054 \times E^2 \quad (7)$$

where E is the wt% ²³⁵U in enriched UF₆.

After the enrichment process, the concentration of ²³⁴U in the enriched UF₆ product and the depleted UF₆ product depends on:

- The process used for the isotopic separation (enriched UF₆ obtained by gaseous centrifuge process has higher ²³⁴U/²³⁵U ratio);

- The %²³⁵U of depleted UF₆ (the higher the number of SWU that are used, the higher the ²³⁴U/²³⁵U ratio in the enriched product).

The detailed discussion on this topic is provided in Ref. [43]. Different models to estimate the ²³⁴U/²³⁵U ratio found on open literature are provided in Appendix III.

The depleted UF₆ (tails) flows into containers where it desublimates from a gas to a solid. These containers (typically 48X or 48Y cylinders) are placed in storage areas, typically located on site (see Section 6). Concerns regarding the reactivity of UF₆, in the event of a container breach, when the containers are stored over extended periods (more than 50 years) has caused most countries to undertake a process known as ‘reconversion’ to convert the depleted UF₆ to more stable forms such as U₃O₈ (see Section 4.5).

Although some processes in the downstream of enrichment process are similar to conversion facilities, nuclear criticality has to be considered and is taken into account by designing suitable vessels for the process and specific storage layout.

4.4. RECONVERSION FOR FUEL FABRICATION

4.4.1. General

Enriched UF₆ is reconverted to UO₂ powder for fuel fabrication purposes. Brief descriptions of the overall operations of the processes for fuel fabrication are given below.

The Depleted UF₆ from the enrichment process may also be reconverted to a more stable chemical form for long term storage. A description of these processes is provided in Section 4.5

Generally, all fuel fabrication facilities have a reconversion stage onsite. UO₂ pellets are used in the manufacturing of fuel rods that are assembled with grids in fuel assemblies. Generally, UF₆ is transported from the enrichment facility to a fuel manufacturing facility in cylinders with volume less than 1000 litres – usually in 30B cylinders (see Section 5).

Enriched UO₂ for fuel fabrication is produced from enriched UF₆ either using aqueous processing routes through precipitation of ammonium diuranate (ADU) or ammonium uranyl carbonate, or alternatively using dry processing routes through gas phase reactions of UF₆ with steam and hydrogen.

The material used for reconversion needs to meet specific chemical, physical, and isotopic requirements. The quality of UF₆ is essential for achieving the desired quality of UO₂. In turn, UO₂ produced is required to meet specific chemical, physical, and isotopic requirements. For that purpose, in international trading and cooperation, ASTM C996-20 [58] and ASTM C753-16a, Standard Specification for Nuclear-Grade, Sinterable Uranium Dioxide Powder [83] standard specifications are generally used for enrichment and fuel fabrication, respectively.

Similar to enrichment, when dealing with enriched UF₆, nuclear criticality is taken into account by designing suitable vessels for the process and specific storage layout.

4.4.2. Process description

Enriched UO₂ for fuel fabrication is produced from enriched UF₆ either through gas phase reactions of UF₆ with steam and hydrogen (using so called dry process in this Section 4.4) or,

alternatively, through precipitation of ADU (using so called aqueous processing route or wet process in the following Section 4.4).

The most common routes (respectively, Integrated Dry Route and ADU route) for the dry and wet processes are illustrated in the diagram below (Figure 7).

In the dry process, gaseous UF_6 is injected into a reaction chamber and is contacted with steam to produce UO_2F_2 particulate and HF . UO_2F_2 is fed into and calcined in a kiln to produce UO_3 . In this process, H_2 is introduced at the powder discharge end of the kiln to complete the reduction to UO_2 (Figure 8).

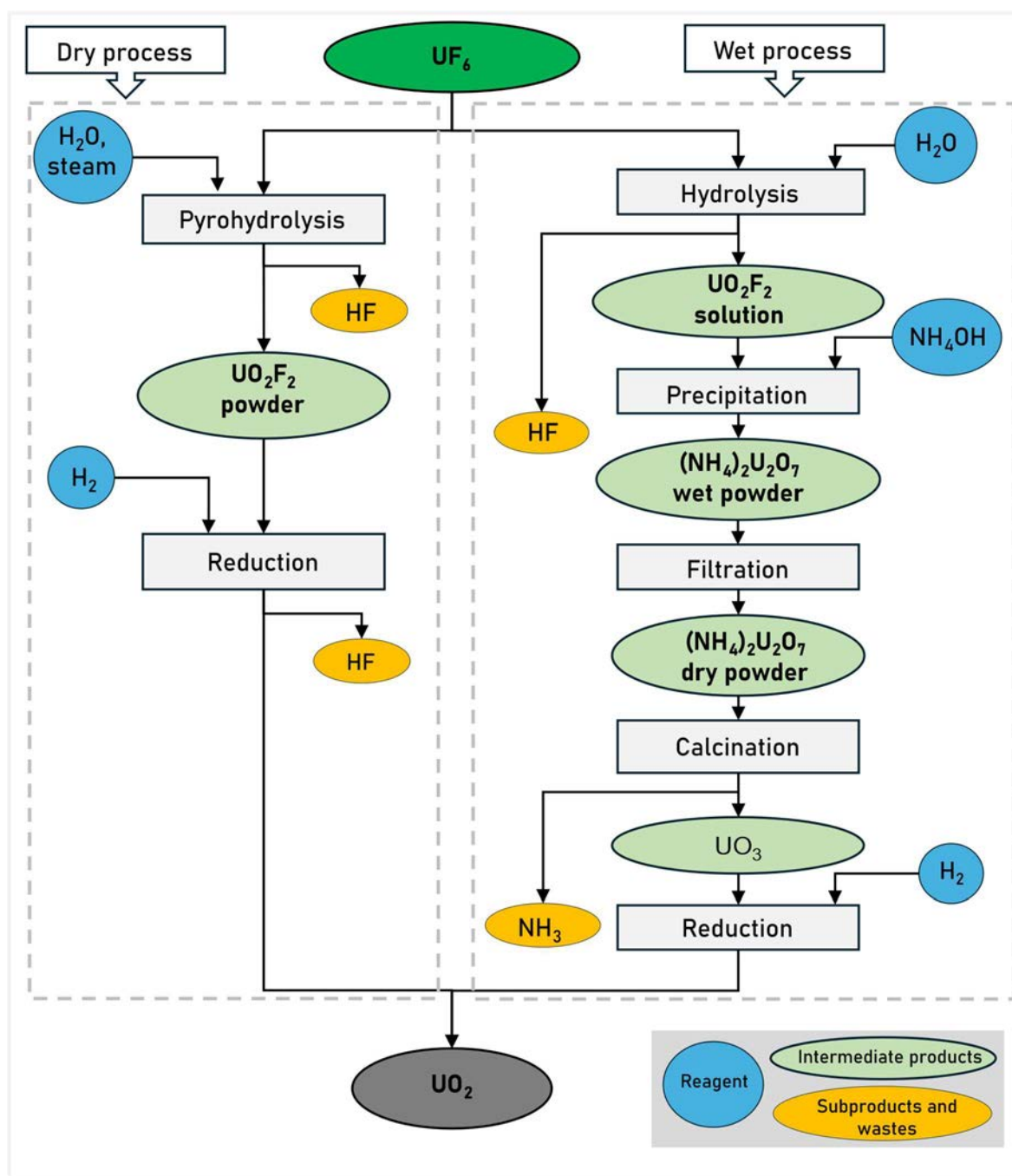


FIG. 7. Dry and wet processes (Integrated Dry Route and ADU processes).

In this process, HF is generated in the reaction chamber, then passes through metal filters to remove any solids and is directed to HF recovery. Alternatively, other different reactor configurations and processes have been developed, one of which is a dry process using multiple fluidized-bed reactors connected in series without using a rotary kiln.

In the wet process, UF_6 is first hydrolysed to produce a liquid solution of UO_2F_2 and hydrofluoric acid. Ammonium hydroxide is then added to precipitate uranium as ADU. The precipitated ADU is then separated from the liquid and dried before it is calcined to U_3O_8 and then reduced to UO_2 using hydrogen. The calcination and reduction are typically carried out as a single step in a kiln.

Other dry processes (e.g. the fluidized bed process and the GECO process (registered trademark of the General Electric Company) and wet processes (e.g. ammonium uranyl carbonate) are available. These processes are not discussed further in this publication.



FIG. 8. Rotary kiln for reduction to UO_2 (courtesy of Westinghouse UK/Springfield Fuels Limited).

4.4.3. Process comparison

The dry process is more common as a commercial enterprise. The powder produced has a more irregular powder morphology which requires controlled blending of powder such as U_3O_8 to meet the required pellet specification. The process equipment is compact, but all process effluents are gaseous, so filters, scrubbers and condensers are required. The most significant effluent is hydrofluoric acid. Waste disposal costs can be reduced significantly if an industrial recycling route can be developed.

The wet process has more discreet process steps which results in more process equipment. The first three processing steps are carried out in solution so there is no significant off-gas to treat. The precipitation step allows better control of powder morphology and therefore produces a more easily sintered pellet. The amount of HF per kg processed is similar to the dry process but

the mixing of other process effluents in solution with the HF makes waste disposal the most likely route for any fluoride produced. In the event of fluoride removal as CaF_2 , the number of moles of F_2 in the CaF_2 produced is equal to the number of moles of F_2 in the UF_6 reconverted. Comparison of the reversion processes are given in the Table 12 below.

TABLE 12. COMPARISON OF THE RECONVERSION PROCESSES

Process	Advantage	Disadvantage
Dry	<ul style="list-style-type: none"> • Easy recycling of HF • Low environmental impact 	<ul style="list-style-type: none"> • Irregular particle size of UO_2 powder • Gaseous effluents
Wet	<ul style="list-style-type: none"> • Sinterability due to morphology of UO_2 powder • Liquid effluent 	<ul style="list-style-type: none"> • Liquid waste

4.5. RECONVERSION FOR LONG TERM STORAGE

Due to the significant amount of depleted UF_6 resulting from the enrichment process, there is increased risk of chemical and radiological hazard for people and the environment. This volume of depleted UF_6 also generates significant storage and maintenance costs. Generally, reversion of depleted UF_6 into a safer physical form for long term storage of depleted tails is part of a national strategy for dealing with depleted uranium in the countries where enrichment facilities are located.

The depleted UF_6 is converted either to UF_4 or U_3O_8 , in which form, long term storage is easier and requires less surveillance than for UF_6 (Figure 9). Although the U_3O_8 form is preferred, in some cases storage as UF_4 offers a flexibility in terms of conversion to uranium metal or conversion back to UF_6 for nuclear reactor fuel.

The dry route processes used to convert UF_6 to UO_2 (see Figure 7) can also be used with changed operational parameters to produce U_3O_8 from UF_6 . This U_3O_8 , after mechanical densification, can be stored in stainless¹⁷ steel containers (Figure 10) for long periods of time (at least 80–100 years). It is important to protect the package during storage from sunlight, rain, and wide daily temperature variation in order that gaskets maintain their seal.

¹⁷ Stainless steel may not be required if the percentage of residual fluorides inside U_3O_8 is low enough. In this case the containers should be painted and stored in suitable conditions (e.g. sheltered from rain).



FIG. 9. Reconversion equipment (courtesy of TVEL).



FIG. 10. Containers for long term storage of depleted oxides (courtesy of TVEL).

4.6. SUPPORTING OPERATIONS AND SAFETY CONSIDERATIONS

4.6.1. General

The following sections describe the operations that are performed in support of the main process operations. There are many safety considerations that need to be recognized and properly addressed to provide a high level of both personnel safety and protection of the environment.

Each section also addresses some of the most significant safety considerations and recommended safety practices in UF₆ processing operations.

For all UF₆ processing, standard operating procedures need to be developed to ensure nuclear, radiation and industrial safety. Operations need to be performed by qualified personnel in accordance with these standard operating procedures. SSR-4 [65] establishes requirements for training, retraining and qualification of personnel and development of operating procedures in a nuclear fuel cycle facility. SSG-5 Rev. 1 [2] provides further guidance for implementation of these requirements in uranium conversion and enrichment facilities.

Design, handling and treatment of UF₆ cylinders are extensively covered in USEC-651 (Revision 10), The UF₆ Manual: Good Handling Practices for Uranium Hexafluoride (USEC-651) [9], International Standard ISO 7195:2020, Nuclear energy-Packagings for the transport of uranium hexafluoride (ISO 7195) [84], American National Standards Institute (ANSI) N14.1-2023, Uranium Hexafluoride Packagings Transport (ANSI N14.1) [85], and others. Such references can be used to obtain the information to develop procedures to be followed for safe UF₆ handling operations.

4.6.2. UF₆ transfer from a cylinder

UF₆ can be withdrawn from cylinders by using several methods. The two most common variants for UF₆ withdrawal are determined by pressure and temperature: evaporation via the liquid state (this includes heating the cylinder by induction heater or with heat carrier (usually with hot air)) or sublimation from the solid state (evacuation to a low pressure with a pump). A comparison of these variants is given in the Table 13 below. A combination of the methods mentioned above can also be considered.

TABEL 13. COMPARISON OF EVAPORATION AND SUBLIMATION

Process	Advantage	Disadvantage
Vaporization	<ul style="list-style-type: none"> • High flow rate (smaller number of feed stations) 	<ul style="list-style-type: none"> • Secondary containment needed • Potential hazard of release of UF₆
Sublimation	<ul style="list-style-type: none"> • No liquid phase • No secondary containment (e.g. autoclave) required 	<ul style="list-style-type: none"> • Low flow rate (greater number of feed stations)

4.6.2.1. Vaporization via the liquid state

Heating cylinders in feed station with steam or hot air to a temperature greater than the triple point of UF₆ causes solid UF₆ to liquefy and creates sufficient UF₆ gas pressure to feed the downstream processes. Figure 11 shows feed station autoclaves.

Before cylinders are put into feed station and heated, they need to be inspected for defects, and both the weight of UF₆ and the internal cylinder pressure need to be verified. Both measured values are required to be within safe limits. Note that heating cylinders which are overfilled may result in rupture of the cylinder or equipment, and the release of UF₆ as a superheated liquid.



Motorized tool to close the valve inside the feeding station if needed.

FIG. 11. Feeding station (courtesy of Orano).

After the cylinder is positioned within the autoclave, the low molecular weight contaminant gases, such as HF and air present within the cylinder are evacuated. If these gases are not evacuated, they can be compressed by volume expansion of liquid UF_6 during heating, which will result in high internal cylinder pressure.

Heating of cylinders is performed only by controlled heat sources. It is essential that temperatures never exceed the cylinder design temperature (generally 121°C). Localized heating of cylinders is to be avoided without safety evaluation because of associated rupture hazard. During heating, the cylinder valve needs to be open and cylinder pressure monitored. As a good safety practice, the facility system needs the ability to automatically abort the process if the pressure exceeds the limits, for example the motorized tool as shown in Figure 11. Facilities where UF_6 cylinders are heated need the capability to contain UF_6 releases within a secondary containment; autoclaves can be used to provide for secondary containment around the UF_6 cylinder. If this capability does not exist, UF_6 release accident scenarios need to be assessed to identify potential impact to personnel and environment and mitigative strategies need to be developed.

Any scenario for evaporation of the content of a damaged cylinder needs to be carefully evaluated.

Under certain circumstances the cylinder valve stem can become seized in the open (or non-closed) position. During this process, it is crucial to have the ability to close the valve if needed to prevent liquid or gaseous UF_6 leaks. Any cylinder having a damaged valve (body or stem) needs to be emptied using the sublimation process to avoid pressurizing the cylinder.

Evaporation via the liquid state method allows higher gas flow from the cylinder to the enrichment cascades or to the reconversion facility systems. Thereby, the facility requires a smaller number of feed stations, which results in a more compact layout. Nevertheless, from the safety standpoint this method is more hazardous and currently some producers prefer to implement alternative sublimation method from solid state, as described in Section 4.6.2.2.

4.6.2.2. Sublimation from the solid state

Heating cylinders in feed station with steam or hot air to a temperature below 56°C and UF_6 causes solid UF_6 to sublime and creates enough UF_6 gas pressure to feed the downstream processes. Figure 12 shows a feed station operating on the principle of sublimation from the solid state.



FIG. 12. Feeding stations (courtesy of TVEL).

Before cylinders are put into feed stations and heated, they need to be inspected for defects, and both the weight of UF_6 and the internal cylinder pressure need to be verified. Both measured values are required to be within safe limits. Heating cylinders which are overfilled may result in rupture of the cylinder or equipment, and release of UF_6 as a superheated liquid.

Heating of cylinders are performed only by controlled heat sources. To guarantee sublimation of solid UF_6 to gas and to avoid a pressure greater than atmospheric in a cylinder, the temperature needs to be limited to the sublimation point (56°C) with some margin. Localized heating of cylinders is to be avoided without careful safety evaluation because of the associated rupture hazard.

During heating, the cylinder valve needs to be open and cylinder pressure monitored.

4.6.3. UF_6 transfer into a cylinder

The function of the UF_6 transfer system is to collect the gaseous UF_6 streams from conversion or enrichment processes, to remove impurities, and to discharge UF_6 into the appropriate cylinders for shipment.

In a wet conversion facility, the UF_6 gas produced in the fluorination process is typically desublimed in a cold trap as a batch operation. When the cold trap is full, it is then heated to liquify the UF_6 which is dropped by gravity from the cold trap into a shipping cylinder. However, before UF_6 enters the cylinder, the liquid UF_6 is passed through a set of filters to remove metal fluorides and UO_2F_2 , which are produced by moisture in the air that has leaked into the system.

In a dry conversion facility, the pure UF₆ from the distillation process is collected as a liquid in cold traps as a batch operation. When the cold trap is full, the liquid UF₆ is dropped by gravity into a shipping cylinder.

The centrifuge enrichment facility typically avoids the cold trap liquification step by drawing UF₆ through the cascade under vacuum. The enriched stream flows from the vacuum compressor into a cooling box containing a UF₆ cylinder. The temperature and pressure in the shipping cylinder are controlled to desublime the UF₆ directly as a solid. A separate stream containing the tails (depleted UF₆) flows through a vacuum compressor into a cooling box where the tails are desublimed directly into a cylinder.

UF₆ can be withdrawn from the process installation after conversion or enrichment by using two types of equipment:

- (1) Cold traps which desublime the gas into a solid and then liquify the UF₆ to fill a cylinder by gravity transfer;
- (2) Cold boxes which chill a transport cylinder or intermediate cylinder and allow the gaseous UF₆ to be desublimed directly into a container at a pressure below atmospheric. These containers can be shipped to a customer or used on site for further processing (sampling, storage, blending, etc). In an enrichment facility, the equipment for product and tail withdrawal can be different.

A comparison of these two methods is given in the Table 14 below.

Liquid transfer allows the cylinder to fill faster, but from a safety standpoint this method is more hazardous and currently some manufacturers prefer to implement alternative methods for desublimation as a solid in the cylinder. Liquid transfer from a homogenized cylinder to a sampling cylinder is still required when determining impurities within the source cylinder.

For cylinder filling operations, the correct UF₆ cylinder needs to be selected based on the ²³⁵U assay and further use of the cylinder, i.e. storage or transport. Cylinders in filling stations need to have means to prevent movements while connected to the process discharge piping (manifold). Such interlocks can be electrical and/or mechanical.

TABLE 14. COMPARISON OF THE GAS AND LIQUID TRANSFER PROCESSES TO FILL CYLINDERS

Process	Advantage	Disadvantage
Liquid transfer	<ul style="list-style-type: none"> • High speed per unit (short time to fill the cylinder) • Reduced number of filling stations for required capacity 	<ul style="list-style-type: none"> • Secondary containment needed • Potential hazard of release of liquid UF₆ as the liquid cylinder (cold trap) is typically above atmospheric pressure
Gas transfer	<ul style="list-style-type: none"> • Easy maintenance • No liquid phase • No secondary containment (e.g. autoclave) required 	<ul style="list-style-type: none"> • Low speed per unit (long time to fill the cylinder)

Cylinder weights are to be carefully monitored or calculated during filling operations to avoid overfilling. Cylinders that are accidentally overfilled are never to be transported outside the facility and need to be clearly identified, for example by weather resistant and durable markings or tags, to ensure compliance. An overfilled cylinder needs to have the excess UF_6 removed as soon as possible following approved procedures (see also Section 4.6.3.5). This operation is to be conducted without heating to avoid the possibility of rupture. If possible, overfilled cylinders are not to be removed from a facility until the overfilled condition has been corrected.

4.6.3.1. Liquid filling of cylinders

Before cylinders are filled with UF_6 , they need to be inspected, and the cylinder pressure verified to confirm cleanliness, leak tightness, etc. A leak test of all connections to the filling manifold is also to be completed. UF_6 withdrawal from the conversion process into the shipping cylinders is generally carried out by draining the liquid UF_6 from heated cold traps by gravity. The manifold needs to be heated to avoid condensation of UF_6 inside it.

4.6.3.2. Filling cylinders by direct desublimation

Before cylinders are filled with UF_6 , they need to be inspected, and the cylinder pressure verified to confirm cleanliness, leak tightness, etc. A leak test of all connections to the filling manifold is also to be completed. UF_6 withdrawal from the enrichment process is generally carried out by flowing the gas into a container in a cold box where the gas desublimates.

4.6.3.3. Filling cylinders by solid transfer

UF_6 can be withdrawn from the conversion process as solid snow. In this case the cold trap is vertically oriented and the UF_6 is collected on the chilled internal surfaces. When the cold trap is ready to be emptied the process coolant is warmed and the solid starts to melt which allows the mass to drop from the internal surfaces of the cold trap. The solids are collected in a vertical container¹⁸ similar to the one shown in Figure 13. The filled cylinder can be shipped to other facilities or used for further processing on site.



FIG. 13. Vertical UF_6 cylinder (courtesy of TVEL).

¹⁸ Vertical cylinder shown in Figure 14 is not currently part of ISO 7195 [84] or ANSI N14.1 [85] standards.

4.6.3.4. *Transferring UF₆ between cylinders*

Uranium enrichment operations often require the transfer of UF₆ from one cylinder directly to another one. This operation may be necessary for some of the following examples:

- Transfer from one intermediate cylinder to one shipping cylinder (for example from producer cylinder to customer cylinder);
- Transfer from one cylinder/container to several smaller cylinders (for example from one 48Y to several 30B cylinders);
- Transfer from one cylinder (damaged, non-valid (more than 5 years since its last certification), overfilled) to another one;
- Transfer from two intermediate cylinders to one shipping cylinder (for blending ²³⁵U assays).

There are two possible variants: transfer in liquid state or transfer in gas state.

Transferring from a fully liquefied cylinder to a cylinder at ambient temperature and similar elevation is rarely done in the current industry facilities. Liquefaction of a cylinder creates an elevated hazard for UF₆ release to the environment as the internal pressure of the liquid cylinder is significantly above atmospheric pressure.

The transfer rate to the receiving cylinder via the gas phase is controlled by the heat loss and resulting solidification of the UF₆ which creates a pressure difference between the source cylinder and the receiving cylinder. Given the typical volume to be transferred, more than 2 tonnes for a 30B and more than 12 tonnes for a 48Y, the liquid transfer process would take 2–4 days for the receiving cylinder to fully cool and have a pressure below atmospheric pressure and remove the risk of UF₆ release from the cylinder.

Regarding the gas transfer there are two options:

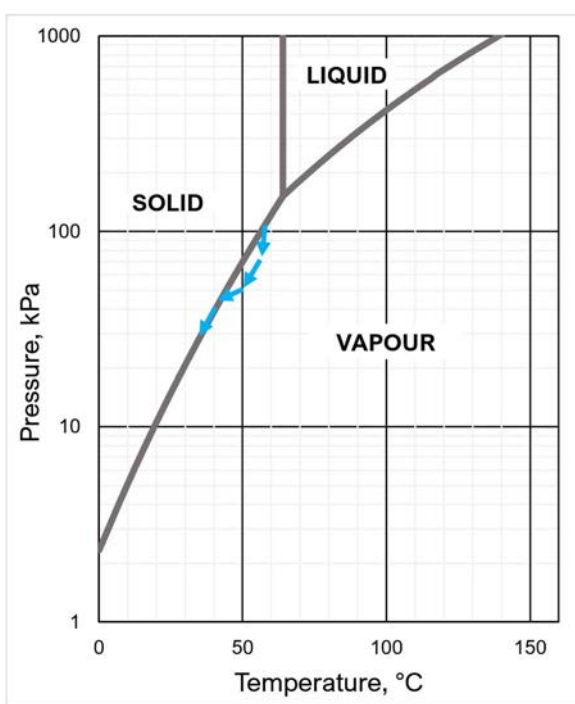
- A. Gas transfer under atmospheric pressure;
- B. Gas transfer with a pump and a condenser to increase the flow.

In option A, the UF₆ may be heated up to a temperature slightly lower than 64°C (triple point) that can be indicatively 56°C to keep a sufficient margin to transition to liquid phase, the bulk of UF₆ remains in the solid state and the vapour pressure of UF₆ is maximized. The receiving cylinder is cooled (in a cooled chest) to generate the flow from the source to the receiving cylinder. The greater the temperature gap between source and receiving cylinder, the greater the flow rate, no pump is needed.

In option B, the source cylinder is heated in the same conditions and, to increase the flow, a pump and a condenser (gas to liquid) is used to transfer the UF₆ in the receiving cylinder. The receiving cylinder may be cooled to accelerate the solidification of the liquid UF₆.

The phase changes of UF₆ during these processes are represented on the following Figure 14.

Option A. Transfer from a heated source cylinder to a cooled receiving cylinder; in between the pipes need to be heated to ensure there will be no desublimation



Option B. Transfer from a heated source cylinder to a cooled receiving cylinder. First, the UF_6 gas is pumped out of the source cylinder (red arrow); then the compressed UF_6 is condensed in a condenser to a liquid state (green arrow) and the liquid UF_6 comes into the receiving cooled cylinder and changes state to solid (blue dotted [to show the arrow follows the equilibrium lines] arrow). At any given moment, the quantity of liquid UF_6 is small, the main part of UF_6 is solid (with UF_6 gas in equilibrium). In between the pipes need to be heated to ensure no change of state can happen.

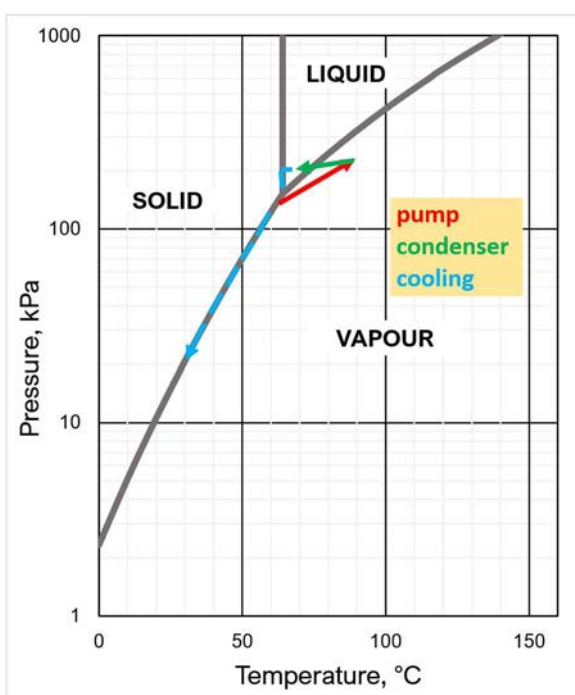


FIG. 14. Representation of UF_6 change of state during these two gas transfer processes.

A comparison of these variants is given in Table 15 below.

TABLE 15. COMPARISON BETWEEN THE TWO MAIN PRINCIPLES OF TRANSFER OF UF₆ BETWEEN TWO CYLINDERS

Case	Advantage	Disadvantage
A	<ul style="list-style-type: none"> No pump (flow is generate by heated source cylinder/cooled receiving cylinder) No liquid phase 	<ul style="list-style-type: none"> Low flow rate (more than one week to empty a 30B cylinder)
B	<ul style="list-style-type: none"> High flow (a few days to empty a 30B cylinder) 	<ul style="list-style-type: none"> Part of the transfer is liquid and necessitate appropriate safety measures

In both cases, connecting pipes need to be heated to ensure that the temperature is high enough to avoid undesired change of state of UF₆ inside the pipes.

Heating the source cylinder can be realized with steam or hot air until the UF₆ reach the desired temperature/pressure.

4.6.4. Sampling of UF₆

UF₆ samples are taken from the homogenized liquid phase in cylinders to determine uranium and isotopic concentration of the process material and their compliance with specifications, including impurity contents. For these purposes, 1S (see Figure 15), 1SW, 2S and 2SW cylinders, Croft UF₆ Sample Bottle 2926 (see Figure 16), and P-10 tubes are generally used as sample volumes. Sampling of UF₆ from a cylinder can be done by removal of the sample from the liquid or gas phases.



FIG. 15. 1S Cylinder (courtesy of Urenco).



FIG. 16. Croft Associates Ltd. UF_6 Sample Bottle 2926.

Procedures for liquid UF_6 sampling require the cylinder to be heated in order that its contents are totally homogenized. It to ensure the sample removed from the cylinder is representative of the full cylinder contents (to get all impurities in the sample), the cylinder is heated until the contents are fully liquid and there has been sufficient convective mixing. Heating is performed by either steam or hot air in a similar manner as described in Section 4.6.2.1. After homogenization, the cylinder position is changed to shift the cylinder valve below the liquid level in order that a small amount of UF_6 can be poured into a sample container and solidified. The requirement for a fully liquid, homogenized cylinder typically makes the sampling of UF_6 cylinders the largest single volume of liquid UF_6 above atmospheric pressure. The elevated risk for a significant loss of product requires careful analysis of procedures and the use of additional containment such as an autoclave for heating the cylinder.

Figure 17 shows autoclaves for homogenizing 30-inch cylinders (see Table 16). Methods of changing the position of the cylinder containing liquid UF_6 may vary depending on equipment available and procedures. Cylinders may be tipped slightly by elevating the plug end of the cylinder causing the liquid level to move above the cylinder valve or by rotating the cylinder to change the valve position from the 12 o'clock point to a point below the liquid level. This is normally between the 3 o'clock and 9 o'clock positions, according to USEC-651 [9].

During sampling and liquid transfer operations all transfer piping and vessels need to be heated by temperature-controlled devices. Overheating of UF_6 transfer lines, using torches or uncontrolled heat sources, can lead to pipe ruptures if a significant mass of UF_6 has solidified.

The standard sampling practices of natural and enriched UF_6 are extensively covered in documents such as ASTM C1689-21, Standard Practice for Subsampling of Uranium Hexafluoride [86], ASTM C1052-20, Standard Practice for Bulk Sampling of Liquid Uranium Hexafluoride [87], and ASTM C1883-19, Standard Practice for Sampling of Gaseous Enriched

Uranium Hexafluoride [88], ASTM C1703-18, Standard Practice for Sampling of Gaseous Uranium Hexafluoride for Enrichment [89], respectively. These standards are generally used in UF₆ facilities to obtain and analyse UF₆ samples.

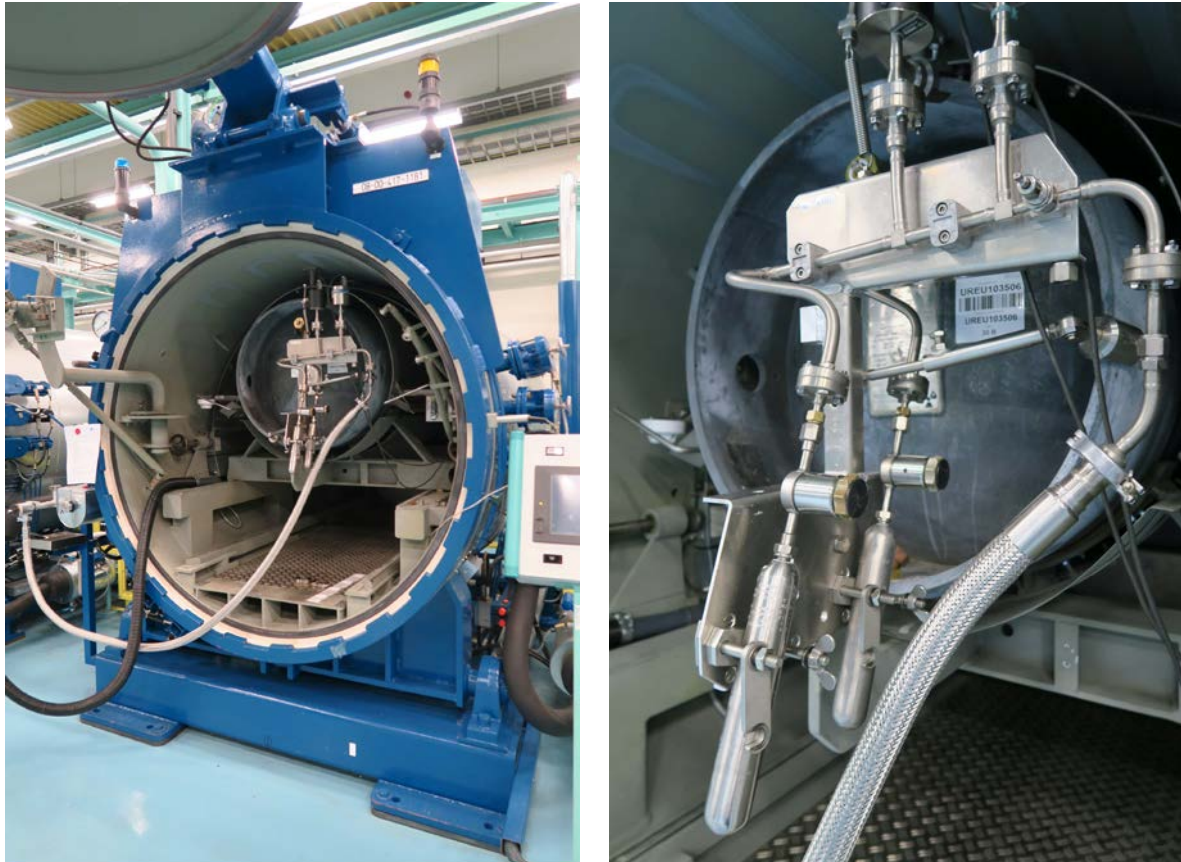


FIG. 17. UF₆ sampling (courtesy of Urenco).

Gas phase samples can be taken from a cylinder at ambient temperature by connecting the valve to a small sample container, previously pumped at a pressure which will be lower than the internal cylinder pressure. The gas sample can be solidified by using either ice water or liquid nitrogen.

4.6.5. UF₆ cylinders valves closure requirements

For cylinders containing enriched UF₆, IAEA Safety Standards Series No. SSR-6 (Rev. 1), Regulations for the Safe Transport of Radioactive Material (the Transport Regulations) [59] requires tests to demonstrate closure of each cylinder before each shipment. This ensures the validity of the criticality safety assessments (no water ingress). Associated specific criteria may exist in the certificates of approval issued by competent authorities, e.g. torque measurements or leak tightness tests.

Moreover, leak tightness tests are required during fabrication and maintenance operations. Those leak tightness tests and the torques for assembling and installing the valves are specified in ISO 7195 [84] and ANSI N14.1 [85] standards.

For all cylinders containing UF₆, a leak tightness test can ensure that the internal pressure will not be above atmospheric pressure when presented for transport, as required in the Transport Regulations [59].

4.6.6. Weighing UF₆ cylinders

Accurate weighing of UF₆ cylinders before and after filling is important when handling and processing UF₆ to obtain the mass of uranium and ²³⁵U in the cylinder. During filling operations, the cylinder weight needs to be frequently monitored or accurately calculated to avoid overfilling. Overfilling can result in hydraulic rupture of the cylinder if exposed to high temperatures. After filling, the final cylinder weight is determined using a calibrated and certified scale or weighing bridge (Figure 18). A similar weight verification is to be carried out on all UF₆ cylinders before they are heated.

The scale is checked periodically for accuracy using the test weights. If the scale produces any variations from the acceptable range, it is removed from the service and cylinders measured by this scale since the last check are considered for reweighing. During the weighing, outside factors that can affect measurement accuracy is to be minimized such as wind drafts, equipment contamination with grease and weight of air contained in empty cylinders. Personnel performing weighing operations need to be qualified.



FIG. 18. UF₆ cylinder weighing operations.

Detailed examples of weighing programmes are given in USEC-651 [9].

4.6.7. UF₆ cylinder handling

Movement of UF₆ cylinders within a facility (see Figures 19 and 20) is a necessary operation supporting several phases of the main process operations. Under normal operating conditions, both empty and filled cylinders will have to be handled. Basic rules for handling heavy loads are expected to be applied to avoid damage to cylinders and equipment. Cranes and mobile equipment used in handling cylinders, together with the lifting fixtures and other hardware need

to be properly inspected and maintained (see Figures 20 and 21). UF₆ cylinder handling needs to be performed by qualified personnel.



FIG. 19. Rail wagon for on-site 30B cylinders transport (courtesy of Orano).



FIG. 20. Road trailer for on-site 48Y cylinder transport (courtesy of Orano).



FIG. 21. UF₆ cylinders (48Y and 30B) handling (courtesy of Orano).

Cylinder handling is to be carried out when UF₆ is in solid form. The movement of cylinders containing liquid UF₆ is a significantly more hazardous operation and is to be avoided (see Section 4.7.6). Cylinders with liquid UF₆ are not to be moved until 3–4 days under ambient conditions to ensure the contents are no longer liquid. If such an operation is necessary, its safety needs to be assessed before implementation.

4.6.8. UF₆ cylinder maintenance and repair

UF₆ cylinders together with their valves, plugs and valve protectors are to be maintained and, if necessary, repaired following the appropriate national and international standards and guides, e.g. ISO 7195 [84], ANSI N14.1 [85], and USEC-651 [9]. General information on the most commonly used types of UF₆ cylinders is provided in Section 5.4.2. A quality assurance programme is to be developed to ensure compliance with the manufacture's guidelines and provide for documentation of inspections, maintenance and repairs.

Cleanliness of UF₆ cylinders is of significant concern to the nuclear industry, because the reaction of UF₆ with hydrocarbon oils and some other impurities, even in small quantities, is quite vigorous and can result in explosions. Also, the purity of the UF₆ can be appreciably affected, which may create product quality problems. Periodic cylinder cleaning therefore has to be carried out with great care. Evacuation of air from the cylinders is not to be attempted with oil vacuum pumps which have no provisions to prevent backflow of oil into the cylinder.

Prior to each operational use, cylinders need to be carefully inspected to ensure that all requirements for safe use as specified in ISO 7195 [84], ANSI N14.1 [85], and USEC-651 [9] have been met. Rejected cylinders are to be clearly identified to prevent using for UF₆ filling, for example by a uniform method of weather resistant and durable markings or tags indicating the reason for rejection. Replacement of defective valves on cylinders containing UF₆ needs to be carried out following approved procedures based on guidelines in ISO 7195 [84], ANSI N14.1 [85], and USEC-651 [9]. Valve rebuilding and valve testing procedures are to comply with ISO 7195 [84], ANSI N14.1 [85], and USEC-651 [9].

All information on UF₆ cylinders relating to safe limits for filling, storage, shipping and heating is to be kept readily available for engineering and operating personnel. Relevant data needs to be incorporated into specific operating procedures and not be left open for interpretation. Any time new ISO 7195 [84], ANSI N14.1 [85], or USEC-651 [9] revisions are issued, procedures are updated.

Each facility needs to always keep records of the UF₆ cylinder inventory.

4.7. OTHER SAFETY CONSIDERATIONS

4.7.1. General

Safety considerations which need to be addressed are combinations of radiological, industrial, environmental safety and safety for effects of chemotoxicity. This section covers safety concerns in general, and adds to Section 2, where UF₆ properties and subsequent safety considerations are described, and Section 4.6, where some general safety considerations for processing and handling of UF₆ are covered. This is not intended to be all inclusive, but to give the reader some ideas as to the variety of considerations required. The information in this section for radiological and chemical protection to personnel involved with handling UF₆ also applies to UF₆ storage.

For personnel protection, standard safety equipment listed in this Section is necessary for process facilities and in UF₆ storage. Personnel handling UF₆ cylinders need to have access to respiratory protective equipment that provides chemical protection from UF₆ and HF and from particulates in the event of a UF₆ release. Protective clothing, hand protection, self-contained breathing equipment, acid proof goggles, face shields, and safety shoes and helmets are to be worn when needed. All protective clothing needs to be clean and free of hydrocarbons because HF and F₂ will react with hydrocarbons and thus could penetrate the protective equipment. All protective clothing and equipment need to be resistant to UF₆ and HF.

Because hazards exist from both the chemicals and radioactivity, adequate training of all employees is needed. The training is to be comprehensive, including indoctrination and recognition of chemical and radiological hazards. Other specialized training is to be provided as necessary.

To ensure proper radiation protection, a radiation protection programme is expected to be established and maintained including personnel and workplace monitoring programme to assure that personnel do not receive excessive radiation exposure. SSR-4 [65] and GSR Part 3 [62] establish requirements for radiation protection programme in a nuclear fuel cycle facility. SSG-5 Rev. 1 [2] and GSG-7 [69] provide further guidance for implementation of these requirements in uranium conversion and enrichment facilities. For external exposure, passive dosimeters (e.g., thermoluminescence dosimeter or optically stimulated luminescence dosimeter) are to be worn by each occupationally exposed worker while in a relevant process area. In addition, internal monitoring arrangements need to be made. Appropriate personal protective equipment, including protective clothing, is to be provided and worn, and good housekeeping is essential in maintaining low radiation and airborne contamination levels and general safety. On receipt, UF₆ cylinders are to be monitored for radiation dose rate and contamination levels. UF₆ cylinders which exceed established radiation and other guidelines need to be identified and isolated from other cylinders. Corrective actions are to be initiated¹⁹.

The health surveillance programme is required in the uranium processing facility (GSR Part 3 [62] and GSG-7 [69]). Usually, the programme includes a pre-employment examination to detect pulmonary, renal, or haematological disease. Also, periodic scheduled physical examination is carried out to monitor the health of the employees. Routine urinalysis for uranium is performed to determine the exposure level of the employee with a baseline monitoring.

More information on the radiation protection programme and health surveillance are provided in GSR Part 3 [62] and GSG-7 [69].

4.7.2. Process chemicals

Conversion and reconversion take place within a chemical processing facility with associated chemical hazards along with the radiological concerns. Extensive literature is available for the various chemicals used in the processes. Some of the main chemicals used in the production of UF₆ are addressed in this section to illustrate the requirements for safety.

The principal chemicals used in the purification, conversion, and their waste treatment operations are nitric acid, sulphuric acid, TBP, fluorine, hydrogen, HF, and KOH. Material

¹⁹ The recently emptied cylinders present the most significant dose rates. The longer UF₆ is stored inside a cylinder before emptying, the greater the dose rate is (see Section 2.4).

safety data sheets are available from vendors for most of these chemicals. The properties of HF and UF₆ have been previously covered in Section 2.

4.7.2.1. *Fluorine*

Fluorine is one of the most hazardous chemicals used in the production of UF₆, being both toxic and corrosive. Fluorine is an extremely strong oxidizing agent. Many materials combine with and burn spontaneously in the presence of fluorine as it is the most electronegative element and the most reactive element known. Fluorine is a pale, green-yellow gas with a penetrating odour. Its odour is so intense it can be detected by the sense of smell at concentrations below the threshold limit value of 0.1 ppm (0.16 mg/m³). Fluorine attacks skin and respiratory tract causing a thermal burn and by reaction with water (even in the form of moisture) creates HF.

Care is to be taken that the equipment used to transport and store this gas is properly prepared. The corrosion resistance of a metal towards fluorine is based on the formation of a surface fluoride layer which protects against further attack by fluorine. This procedure is referred to as 'passivation'. If the equipment in which fluorine is to be used is not properly cleaned and passivated before use, reactions of the fluorine with metals can take place and can lead to the burning of the valves, manometers, reactors, and the lines. The following measures are essential. All parts need to be very carefully cleaned of impurities and degreased with a suitable solvent. The solvent is then completely removed by drying, and the equipment flushed with nitrogen. After the system has been completely checked for leakages, it is passivated. For this operation slow nitrogen flow is passed through the apparatus, to which an increasing proportion of fluorine is added, until finally pure fluorine flows into the apparatus. All valves are to be closed, and time allowed for passivation. When sufficient passivation has been attained the apparatus is ready for operation. An alternative method is to evacuate the system and allow the fluorine to flow into the system slowly, until atmospheric pressure is reached. The fluorine is left in the equipment for some hours for passivation. Improved stability results if the system can be heated to a controlled temperature.

Qualified and well-trained staff are to be employed for direct work with fluorine. Personal protective equipment is to be worn at all times. If work is carried out with equipment containing fluorine, hand protection, respiratory protection, protective headwear with face-shield of plastic and protective clothing are to be worn. Furthermore, all the standard safety measures for the handling of highly toxic gases are to be applied. In emergency situations, self-contained breathing apparatus may be necessary (see also Section 9 about Emergency Preparedness and Response). All protective clothing and equipment need to be clean and free of hydrocarbons.

Serious events with fluorine leaks can pose serious consequences to personnel health and environment. It is to be noted that typical fluorine production from electrolytic cells (see Figure 22) also contains about 5–7 vol.% gaseous HF as a result of the partial pressure from HF in the electrolyte.

4.7.2.2. *Electrolyte*

The electrolyte used to generate fluorine is usually based upon KF·2HF. This electrolyte is prepared by addition of liquid anhydrous HF to potassium bifluoride (K[HF₂]). Anhydrous HF (boiling point 19.5°C), when in contact with skin, can result in serious skin burns and tissue damage. The longer the exposure and the thinner the skin, the more rapidly the lesions appear. The subsequent pain and white necrosis can be severe.

4.7.2.3. Cell maintenance

(a) Cell removal

The principal hazards associated with a fluorine cell are of electrical nature and chemotoxicity. Before starting to work on a cell, maintenance personnel ensures that the cell has been electrically isolated, and that the rectifier has been locked and tagged off. When taking a cell ‘off-line’, the cell needs to be purged using N₂ gas before isolation from the fluorine/hydrogen headers. Protective chemical suits, respiratory protection, face shields and gloves are to be worn when cleaning out headers. The carryover is electrolyte, and it contains HF.



FIG. 22. Cells for fluorine generation (courtesy of TVEL).

(b) Electrolyte transfer

Electrolyte transfer requires the presence of a safety standby operator and the use of a protective chemical suits, respiratory protection, face shields and gloves because of HF contained in electrolyte. Fumes will be generated during this operation which could cause burns if skin is exposed, or fumes are inhaled.

4.7.3. UO₃ to UO₂

The principal safety concerns in UO₃ to UO₂ reduction area are handling of ammonia and / or hydrogen, and the hazards associated with high operating temperatures. The safe handling of hydrogen is primarily concerned with preventing the formation of an explosive mixture with air. The following are examples of recommended safety measures:

- Integrity of seals at the inlet and outlets of the reactor system is ensured;

- Inert gas is used for purging and seal pots need to be used to avoid air entering the reduction reactors;
- Hydrogen analysers are located near equipment containing hydrogen;
- All major equipment have a sufficient design pressure, in addition, sufficient pressure to withstand an explosion is considered;
- Sprinklers are installed in the UO_3/UO_2 baghouses in cases of fire;
- Spark detectors are installed in the inlet and outlet ducts from the baghouses.

4.7.4. UO_2 to UF_4

The principal safety concerns in UO_2 to UF_4 hydrofluorination area are handling of HF, and the hazards associated with high operating temperatures. The safe handling of HF is primarily concerned with containment of the liquids and gases. The following are examples of recommended safety measures:

- Integrity of seals at the inlet and outlets of the reactor system is ensured or the process vessels is under negative pressure from a fume removal system;
- HF and uranium detection is employed to give an early warning in the event of process upsets;
- Stringent safety systems are employed for process equipment handling pressurized HF;
- Sprinklers are installed in the UF_4 baghouses in cases of fire;
- Spark detectors are installed in the inlet and outlet ducts from the baghouses.

4.7.5. UF_4 to UF_6

In the process of fluorination of UF_4 to UF_6 , hazards are created by handling F_2 , HF, UF_6 and UF_4 . Gaseous F_2 , HF and UF_6 are found in the UF_6 reactors and UF_6 filter areas as well as in the process piping.

When maintenance work is to be performed on any process equipment, lines or process vents, care is to be taken to ensure that they have been previously isolated and purged. A good practice is to demand a verification of the purge and the isolation by the person in charge of the maintenance operation prior to the first line break operation.

UF_4 dust is a chemical hazard as well as a radiological hazard. Exposure can result in damage to the viscera: therefore, respiratory protection is to be used at all times if there is a potential for UF_4 to become airborne.

UF_6 may also contain fluorides which, in contact with the skin will produce HF (possible burn); therefore, proper personal protection is to be worn.

There are also some radiological concerns in the process areas. Internal and external exposures in the form of alpha, beta and gamma radiation can be obtained from the filters, headers, valves, reactor discharge lines, and ash collectors.

4.7.6. Liquid UF_6 handling

Liquid UF_6 has the greatest release potential because the vapor pressure is above atmospheric pressure and UF_6 is at an elevated temperature (more than 64°C). When a system containing liquid UF_6 is breached and the pressure falls below 1.5 atmospheres, the liquid UF_6 immediately converts to the solid and vapor states. Because of the high transformation energy available, the

solid and vaporized UF₆ will be extensively spread unless there is secondary containment to control it.

In all areas where liquid UF₆ operations are carried out, all safety considerations that are relevant to building areas where process equipment contains UF₆ at above atmospheric pressure are applicable (see 4.9.2 for more information).

It is recognized that the number of operations and quantity of liquid UF₆ to be handled is, in most cases, determined by design of a facility and individual site operating procedures. The movement of liquid UF₆ is to be eliminated when designing new facilities, when possible. Due to the high risk and the consequences of a system failure, liquid UF₆ handling operations are to be avoided, or actions taken to minimize risk.

Further, special care is needed when moving cylinders containing liquid UF₆ (especially partially filled), because surging of the liquid may result in cylinder tipping. Both lift heights and transportation distances are to be minimized.

Systems containing liquid UF₆ are to be designed to permit quick isolation of minimum volumes to reduce the quantity of liquid UF₆ released. Quick automatic operating type isolation valves are desirable in most applications.

All personnel performing liquid UF₆ handling operations are to receive systematic and frequent adequate periodic training and be fully qualified. Training completion is to be documented.

4.7.7. Temperature and pressure monitoring

For emptying or feeding UF₆ cylinders, UF₆ needs to be heated. The supervisor of the operation needs to keep in mind that:

- When heating a cylinder of UF₆, the monitored pressure of the cylinder will rise at a consistent and predictable rate if the cylinder contents meet the applicable ASTM standards;
- If the monitored pressure of the cylinder rises at a much slower rate than is normal, the heat needs to be removed and the accuracy of the pressure reading confirmed as there may be a plug or restriction causing the pressure reading to be lower than the actual pressure within the heated cylinder;
- If the monitored pressure of the cylinder rises at a much faster rate than normal, the cylinder may contain elevated levels of volatile gasses like HF. These volatile gasses need to be removed before the cylinder can be fully heated.

It is to be noted that the purity of the cylinder contents will also guarantee that the pressure within the cylinder will be below atmospheric pressure when the temperature returns to the ambient temperature (without volatile gasses like HF or O₂).

4.7.8. Reconversion operations of UF₆ to UO₂, UF₆ to U₃O₈ and UF₆ to UF₄

Safety considerations for reconversion of UF₆ to either UO₂, to U₃O₈ or to UF₄ are mostly covered by those discussed in Section 2.3 and this Section 4. This section covers similar safety concerns for UF₆ cylinder heating, and gas phase reactions using H₂ for both wet and dry processes, HF is recovered within the dry process. The details of these items are described in Section 4.4. Recovered HF in the dry conversion process is at concentrations between 40 to 70

wt% and poses a corrosion and toxicity hazard. In handling this material, great care is needed in the selection of materials and in the measures to protect personnel.

4.7.9. Liquid effluent

In the liquid effluent treatment area, the hazards are mostly associated with chemical handling. Personal protective equipment such as eye protection and rubber gloves are recommended. Radiological hazards are minimal in this area except when UF₆ filters are cleaned. Normally, these filters are stored until they decay to a safe handling level. However, radiation checks are to be part of a routine procedure before they are handled. Workers are to wear personal dosimeters whenever the filters are cleaned.

4.8. SPECIFIC CONSIDERATIONS FOR REPROCESSED URANIUM PRODUCTION AND HANDLING

The radiological dose exposure rate for reprocessed uranium is greater than the radiological dose rate from uranium which has not been reprocessed.

This increase in the radiological dose rate is essentially due to:

- The percentage of ²³²U in uranium (reprocessed uranium);
- The time spent between the filling of the cylinder and the emptying of the cylinder.

During this period, the uranium isotopes decrease, and decay products increase (see Figure 3). These decay products generate high dose rates, and their chemical forms are not volatile. Therefore, when UF₆ is removed from a cylinder, these isotopes remain inside the cylinder. Consequently, the longer the reprocessed UF₆ remains in the cylinder, the higher the quantities of decay products and the higher the dose rates are.

The dose rate from an emptied UF₆ cylinder that have contained reprocessed U will decrease by 50% after around two years as compared to a natural UF₆ cylinder where the dose rate will decrease by 50% after around one month from the end of emptying. Consequently, a cylinder that contains reprocessed UF₆ needs to be thoroughly cleaned before re-filling. This will ensure that there will be no accumulation of isotopes which can generate very high dose rates.

The personnel work time when dealing with equipment, cylinders, and waste of materials, containing reprocessed uranium (including, but not limited to, operations in Section 4.6) is to be limited.

4.9. DESIGN CONSIDERATION OF UF₆ FACILITIES

4.9.1. Design and equipment

SSR-4 [65] establishes safety requirements for design of a nuclear fuel cycle facility. SSG-5 Rev. 1 [2] provides further guidance for implementation of these requirements in uranium conversion and enrichment facilities.

It is very important that the construction materials for processing equipment are compatible with the process. Temperature and pressure conditions need to be considered. An example is the use of 300 series stainless steel for nitric acid or Monel for HF.

Design of the equipment is another important safety factor. Adequate fume or dust removal systems with provisions for maintenance are to be included when the process is being designed.

All connections for acid fume removal systems need to be welded or watertight to avoid any leakage. Whenever practical, the design is to consider ‘in-leakage’ vs. ‘out-leakage’, i.e. the design need to ‘pull’ rather than ‘push’ any fumes or dust through a duct.

An appropriate alarm system to detect any abnormalities in the process system is desirable. There are two types, one being process alarms and the other being the detection in the working atmosphere. Examples of the types of alarms are gaseous detectors for hydrogen, fluorine and HF and conductivity alarms for liquids. Also, redundant containment is widely used for environmental and personnel protection and is recommended. Continuous monitoring systems within facilities and on all emission streams are recommended as part of the facility design.

4.9.2. Categorization of building areas and specific safety considerations

The pressure and physical state of the UF₆ is of importance for the determination of the safety measures and procedures required. Leaks in process systems containing UF₆ at or above atmospheric pressures will result in an immediate release of UF₆, while leaks in a UF₆ process system at or below atmospheric pressure will result in a leakage of ambient air into the process system, followed by a delayed slow release of UF₆ reaction products. Systems with pressure below 1.5 atmospheres can contain only solid and gaseous UF₆. Systems with pressure above 1.5 atmospheres pressure can contain any of the three physical states of UF₆. The pressure and physical states of UF₆ determine the potential hazard. Therefore, facility production areas can be categorized based on the following principles:

- Building areas where process equipment contains UF₆ at above atmospheric pressure;
- Building areas where process equipment contains UF₆ at below atmospheric pressure.

Each area category is to be given specific safety consideration.

4.9.2.1. Safety consideration for areas where UF₆ is contained above atmospheric pressure

System failures (leaks) in building areas where process equipment contains UF₆ at above atmospheric pressure areas immediately result in release of UF₆ and consequently cause airborne and surface contamination. UF₆ release detector systems are to be provided in these areas. Such detector systems are to actuate alarms locally and in the control room. Where required, automatic systems are to be activated to isolate parts of the facility affected to permit adequate clean-up of contaminated ventilation outlet air. By cleaning the ventilation air while maintaining a negative air pressure inside the building section, spread of contamination to the environment can be reduced or avoided. Local exhaust provisions, e.g. fume extraction hoods, are to be available during operations when UF₆ facility systems have to be opened – for example after disconnection of UF₆ cylinders.

Facilities to check for possible contamination of wastewater before disposal, need to be available.

4.9.2.2. Safety consideration for areas where UF₆ is contained below atmospheric pressure

Safety measures, like monitoring UF₆ release, are less relevant in building areas where process equipment contains UF₆ at below atmospheric pressure. Due to operation under vacuum, the primary result of a UF₆ system failure in these areas will be an in-leakage of air. As a result, no immediate releases of UF₆ are to be expected. Nevertheless, it is necessary to apply

contamination control measures when disconnecting components. It is necessary that the process system is adequately evacuated and purged before opening. Exhaust provisions are used to protect workers against fumes and contamination when process systems are opened. The exhausted air is to be cleaned (filtered and scrubbed) before release to the environment.

4.9.3. Components and connecting lines

Fixed and flexible connecting lines (such as ‘pig tails’) are to be designed, fabricated, and inspected to accepted standards. Connecting lines are to be inspected by qualified personnel before each use (Figure 23). Upon installation of components and connecting lines, leak testing and functional testing are to be carried out. Depending on the temperature and pressure of UF_6 contained in process lines, it may be necessary to apply heat tracing to avoid unwanted liquefaction and/or solidification of UF_6 . Whenever possible, trace heaters need to be designed to be self-limiting rather than depending upon a control device. Uncontrolled localized heat sources, such as torches, are never to be applied to connecting lines or other components containing liquid or solid UF_6 .

Care is to be exercised in the selection of pumping systems for evacuation of UF_6 in process lines and cylinders. Vacuum pumps containing hydrocarbon oil need to be equipped with an oil backflow reservoir of sufficient volume or a chemical trap (e.g. activated carbon) to prevent oil from entering the UF_6 system in the event of pump stoppage.



FIG. 23. UF_6 cylinder connected to heated pigtail.

5. TRANSPORT

This section addresses with issues related to the transport of UF_6 in the public domain, with a focus on safety requirements. Legal requirements in terms of nuclear liability, safeguards, security, material accountability, custom regulations and other applicable requirements are not

considered in this section but need also to be taken into account. Transports within a nuclear site are performed by specialized personnel, using specialized equipment, under national licensing arrangements and governed by the requirements applicable to the site operations. They are also not considered in this section.

5.1. INTERNATIONAL, REGIONAL AND NATIONAL TRANSPORT REGULATIONS OF DANGEROUS GOODS

The requirements for the safe transport of radioactive material, including UF₆, are included in the more general requirements that apply to the safe transport of dangerous goods.

International, regional, and national regulations, agreements, conventions, recommendations and guides on the safe transport of dangerous goods take into account that transport of such dangerous goods is often international. For that purpose, they share a common basis, which is provided in the Recommendation on the Transport of Dangerous Goods, Model Regulations (commonly known as the ‘United Nations Model Regulations’ or ‘The Orange Book’) [4].

These provisions of the UN Model Regulations [4] are transcribed into the regulatory instruments for the different modes of transport (modal regulations), which are legally binding instruments. For international transport, these transport regulations need to be complied with if they are applicable to the mode of transport.

The most important international regulations for the transport of dangerous goods (including UF₆) are the following:

- International Maritime Dangerous Goods (IMDG) Code, of the International Maritime Organization [90] (Transport by sea – Worldwide);
- Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAO-TI), of the International Civil Aviation Organization [91] (Transport by air – Worldwide);
- For practical reasons, the industry applies the Dangerous Goods Regulations, of the International Air Transport Association [92] (Transport by air – International Air Transport Association member airlines), which is based on the Technical Instructions for the Safe Transport of Dangerous Goods by Air [91] and includes special provisions depending on states and transport companies.

The application of the ICAO-TI [91] for air transport and the IMDG Code [90] for sea transport is mandatory for states that are party to those conventions.

Additionally, there are regional agreements, conventions and regulations concerning the safe transport of dangerous goods, including radioactive material, which may be mandatory for states that are party to these agreements, conventions and regulations. Examples of other important agreements, conventions and regulations for the transport of dangerous goods, which have a regional rather than international scope, include the following:

- Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) [93] (Transport by road – All European and some Asian and African countries);
- Regulations concerning the International Carriage of Dangerous Goods by Rail (RID) [94] (Transport by rail – All European and some Asian and African countries);
- MERCOSUR/MERCOSUL Agreement of Partial Reach to Facilitate the Transport of Dangerous Goods (Argentina, Brazil, Paraguay and Uruguay [95];
- Agreement on International Goods Traffic by Rail [96] and its annex 2.

International and regional regulatory instruments are then often legally implemented into national law through national ordinances or acts.

Paragraph 3.5 of SSG-78 [66] states: “...owing to specific national circumstances, a State may need to deviate from, or add to, the provisions of the Transport Regulations or of other international regulations and guidelines.” These specific provisions are included in relevant national regulations and guides. For example, for the United States:

- Title 49, Code of Federal Regulations, Parts 100–199, United States of America [97];
- Title 10, Code of Federal Regulations, Part 71, United States of America [98].

International and regional regulations do not exempt stakeholders from complying with the national regulations.

The UN Model Regulations [4] establish nine classes of dangerous goods. The following classes are the most relevant for UF₆:

- Class 7 – Radioactive material;
- Class 6.1 – Toxic substances;
- Class 8 – Corrosive substances.

5.2. REGULATIONS FOR THE SAFE TRANSPORT OF RADIOACTIVE MATERIAL, INCLUDING UF₆

The provisions concerning the transport of radioactive material in the UN Model Regulations [4] (Class 7) are directly derived from those in the Transport Regulations [59].

The Transport Regulations [59] are complemented by a number of Safety Guides:

- IAEA Safety Standards Series No. SSG-26 (Rev. 1), Advisory Material for the IAEA Regulations for the Safe Transport of Radioactive Material [54];
- IAEA Safety Standards Series No. SSG-65, Preparedness and Response for a Nuclear or Radiological Emergency Involving the Transport of Radioactive Material [99];
- IAEA Safety Standards Series No. SSG-78, Compliance Assurance for the Safe Transport of Radioactive Material [66];
- IAEA Safety Standards Series No. TS-G-1.4, The Management System for the Safe Transport of Radioactive Material [67];
- IAEA Safety Standards Series No. SSG-86, Radiation Protection Programmes for the Transport of Radioactive Material [100];
- IAEA Safety Standards Series No. SSG-33 (Rev. 1), Schedules of Provisions of the IAEA Regulations for the Safe Transport of Radioactive Material (2018 Edition) [101];
- IAEA Safety Standards Series No. SSG-66, Format and Content of the Package Design Safety Report for the Transport of Radioactive Material [102].

As stated in para.104 of the Transport Regulations [59],

“The objective of these Regulations is to establish requirements that must be satisfied to ensure safety and to protect people, property, and the environment from harmful effects of ionizing radiation during the transport of *radioactive material*. This protection is achieved by requiring:

- Containment of the radioactive contents;

- Control of external dose rate;
- Prevention of criticality;
- Prevention of damage caused by heat²⁰.”

Paragraph 110 of the Transport Regulations [59] stipulates that “For *radioactive material* having subsidiary hazards...” (in addition to the radioactive and fissile properties) “...the relevant transport regulations for dangerous goods shall apply in addition to these Regulations.” The relevant transport regulations are discussed in Section 5.1.

The chemical toxicity of UF₆ obtained from natural, depleted, low enriched or highly enriched uranium generally overrides its radiological hazards. However, despite this situation, because UF₆ is carried solely for use in the nuclear energy industry, it was considered appropriate that the IAEA be the focal point for setting formal requirements. Specific requirements for the transport of UF₆ are included in the Transport Regulations [59] and all other regulations for the transport of dangerous goods.

5.3. UF₆ CHARACTERIZATION IN THE DANGEROUS GOODS TRANSPORT REGULATIONS

In accordance with para. 419 of the Transport Regulations [59], packages containing UF₆ (in any form) can only be assigned to one of the following UN numbers²¹ and proper shipping names for their transport:

- UN 2977 RADIOACTIVE MATERIAL, URANIUM HEXAFLUORIDE, FISSILE;
- UN 2978 RADIOACTIVE MATERIAL, URANIUM HEXAFLUORIDE;
- UN 3507 URANIUM HEXAFLUORIDE, RADIOACTIVE MATERIAL, EXCEPTED PACKAGE.

For UN 2977 and UN 2978, in accordance with paras 546 (c) and (d) of the Transport Regulations [59], the transport documents are required to include “The UN dangerous class number “7”” and “The subsidiary hazard or division number(s) corresponding to the subsidiary hazard label(s)”. These are Division 6.1 and Class 8 for UN 2977 and UN 2978.

For UN 3507 (Excepted package), paras 546 (c) and (d) do not apply, and the rules from the UN Model Regulations [4] are relevant. In this case, the radioactive hazard of UF₆ no longer takes precedence over its other dangers for classification purposes. The material is designated by a UN number and proper shipping name from the class of the predominant danger (Division 6.1 - Toxic substances), and the subsidiary hazards are classes 7 and 8 for UN 3507.

The above classification requirements apply regardless of the quantity of UF₆. Therefore, as long as it has not been cleaned and washed with residual quantities of radioactive material under the limits for exclusion of the Transport Regulations [59], an empty cylinder that has contained UF₆ necessitates being transported by using one of these three possibilities, depending on the remaining amount of UF₆ (solid and gaseous UF₆) and fissile nuclides (especially ²³⁵U) contained.

²⁰ The heat load generated by UF₆ is negligible. Consequently, the prevention of damage caused by heat is not an issue for the transport of UF₆.

²¹ The UN number is used internationally to assist hazard identification during transport and in emergency response situations.

The determination of the UN numbers and proper shipping names to be used are not impacted by the origin of the UF₆ (from natural uranium or from irradiated uranium). The UN number assigned depends primarily on the quantity of UF₆, the activity level of the radionuclides contained in the package, and the fissile or non-fissile properties of the material to be shipped. It is necessary to refer comprehensively to the Transport Regulations [59] to determine the appropriate UN number and proper shipping name. However, guidance for this determination is provided in Fig.1, “Flow diagram for the classification of radioactive material with the appropriate UN number”, in SSG-33 [101], as well as in Table 16 below. As a preliminary approach, the following may serve as a useful starting point, subject to confirmation by reviewing all applicable regulatory requirements:

- UN 3507 might be used for less than 0.1 kg of UF₆ with uranium enriched up to 5% in ²³⁵U;
- UN 2978 might be used for natural, depleted and low enriched UF₆ (enrichment up to 1% in ²³⁵U) or a quantity of ²³⁵U less than 45 g;
- UN 2977 might be used for enriched UF₆ that cannot be classified as UN 3507 or UN 2978 (e.g. enrichment higher than 1% and more than 45 g of ²³⁵U).

It is to be noted that, with regard to “Marine pollutant”, UF₆ does not need to be considered as ‘marine pollutant’, as defined in the UN Model Regulations [4] and all other regulations based on them (see above Section 5.1). This is because the classification for ‘environmentally hazardous substances (aquatic environment)’ does not apply to Class 7 material (UN 2977 and UN 2978) and since the provisions applicable to ‘environmentally hazardous substances’ or ‘marine pollutant’ does not apply to packages containing less than 5 kg of material per package (UN 3507).

In addition to the above, regarding the “High consequence dangerous goods”, UF₆, due to its toxic properties (Class 6.1 – Packing Group I, see the UN Model Regulations [4]), is considered in the UN Model Regulations [4] and all other regulations based on (see above Section 5.1) as high consequence dangerous goods for which transport security plans are required to be adopted, implemented and complied with by carriers, consignors and other participants to minimize theft or misuse of this material by malevolent people. When UF₆ is transported as a nuclear material in compliance with the Convention on Physical Protection of Nuclear Material [103] and the IAEA Nuclear Security Series No. 27–G, Physical Protection of Nuclear Material and Nuclear Facilities (Implementation of INFCIRC/225/Revision 5) [104], the requirement for security plans is deemed to be complied with.

5.4. URANIUM HEXAFLUORIDE TRANSPORT PACKAGES

5.4.1. General

In accordance with para. 104 of the Transport Regulations [59], the requirements for containment of the radioactive contents, control of external dose rate, prevention of criticality, and prevention of damage caused by heat:

“... are satisfied firstly by applying a graded approach to contents limits for *packages* and *conveyances* and to performance standards applied to *package designs*, depending upon the hazard of the *radioactive contents*. Secondly, they are satisfied by imposing conditions on the *design* and operation of *packages* and on the maintenance of *packagings*, including consideration of the nature of the *radioactive contents*. Thirdly, they are satisfied by requiring administrative controls, including, where appropriate, *approval* by *competent authorities*. Finally, further protection is provided by making

arrangements for planning and preparing emergency response to protect people, property and the environment.”

Further guidance is given in para. 104.1 of SSG-26 [54]: “...To the extent feasible, safety features are required to be built into the design of the package. By placing primary reliance on the package design and preparation, the need for any special actions during carriage (i.e. by the carrier) is reduced...”

UF₆ is transported in packages (see Figures 24 and 25) that comply with the Transport Regulations [59]. These packages meet the objective of providing protection for people, property, and the environment from their hazards during transport.



FIG. 24. DN30 outer protection containing a 30B cylinder (courtesy of Orano).

It is worth noting that, according to para. 231 of the Transport Regulations [59], “*Package* shall mean the complete product of the packing operation, consisting of the *packaging* and its contents prepared for transport...” In the case of UF₆, packaging means the assembly of the cylinder, and additional protective mechanical and/or thermal equipment if applicable.

The Transport Regulations [59] defines eight types of packages, that are subject to activity limits and material restrictions, and to corresponding requirements commensurate with those activity limits and material restrictions, in accordance with a graded approach. These eight types of packages are:

- Excepted package;
- Industrial package Type 1 (Type IP-1);
- Industrial package Type 2 (Type IP-2);
- Industrial package Type 3 (Type IP-3);
- Type A package;
- Type B(U) package;
- Type B(M) package;
- Type C package.

Additional requirements apply to packages containing UF₆ (see paras 631–634 of the Transport Regulations [59]) or fissile material (see paras 673–686 of the Transport Regulations [59]).

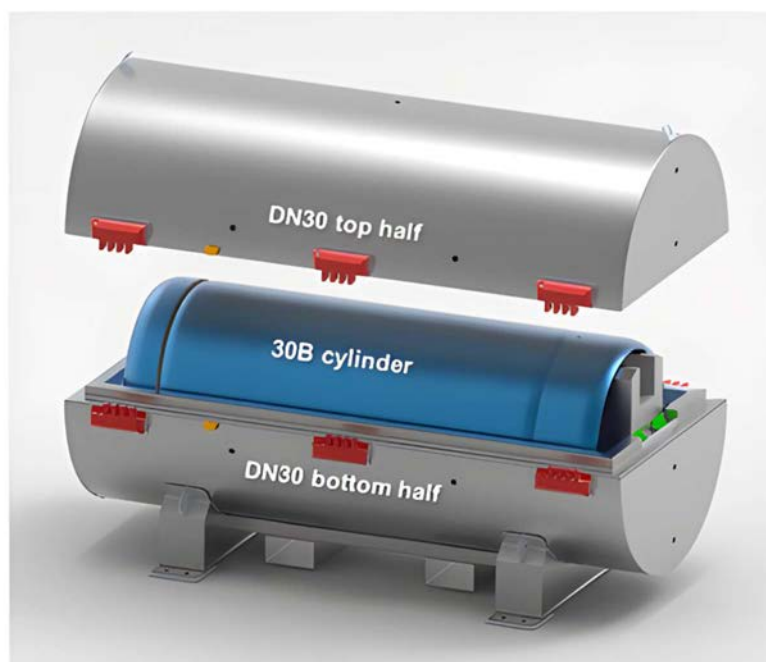


FIG. 25. Schematic image of outer protection and cylinder (courtesy of Orano).

5.4.2. Compliance with ISO 7195 and ANSI N14.1 standards

Paragraph 631 of the Transport Regulations [59] stipulates:

“...Except as allowed in para. 634, uranium hexafluoride in quantities of 0.1 kg or more shall also be packaged and transported in accordance with the provisions of the International Organization for Standardization document: Nuclear Energy — Packaging of Uranium Hexafluoride (UF₆) for Transport (ISO 7195)...”.

For cylinders that do not comply with ISO 7195 [84], para. 634 of the Transport Regulations [59] stipulates:

“Subject to *multilateral approval*, packages designed to contain 0.1 kg or more of uranium hexafluoride may be transported if the *packages* are designed:

- (a) To international or national standards other than ISO 7195, provided an equivalent level of safety is maintained...”.

Additional guidance is provided in para. 631.2 of SSG-26 (Rev. 1) [54]: “Uranium hexafluoride cylinders manufactured, tested and maintained to ANSI N14.1 can be considered to be in accordance with ISO 7195 for the purpose of compliance with the Transport Regulations.”

In summary, cylinders designed to contain 0.1 kg or more of UF₆ are required to comply with ISO 7195 [84] or ANSI N14.1 [85] standards; if they do not meet these standards, they are subject to multilateral approval.

5.4.3. Compliance with the applicable requirements

In accordance with para. 802 of the Transport Regulations [59],

“*Competent authority approval* shall be required for the following:

(a) *Designs* for:

- ...
- (iv) *Packages* containing 0.1 kg or more of uranium hexafluoride (see para. 807);
- (v) *Packages* containing *fissile material*, unless excepted by para. 417, 674 or 675 (see paras 814–816 and 820);
- (vi) *Type B(U) packages* and *Type B(M) packages* (see paras 808–813 and 820);
- ...”

For packages containing 0.1 kg or more of UF₆, the requirements are detailed in para. 807 of the Transport Regulations [59]:

“The *approval of designs* for packages containing 0.1 kg or more of uranium hexafluoride requires that:

- (a) Each *design* that meets the requirements of para. 634 shall require *multilateral approval*.
- (b) Each *design* that meets the requirements of paras 631–633 shall require *unilateral approval* by the *competent authority* of the country of origin of the *design*, unless *multilateral approval* is otherwise required by these Regulations.
- (c) The application for *approval* shall include all information necessary to satisfy the *competent authority* that the *design* meets the requirements of para. 631 and a specification of the applicable *management system*, as required in para. 306.
- (d) The *competent authority* shall establish a certificate of *approval* stating that the approved *design* meets the requirements of para. 631 and shall attribute to that *design* an identification mark.”

For packages containing fissile material, the requirements for approval are detailed in paras 814–816 of the Transport Regulations [59]:

“814. Each *package design* for *fissile material* that is not excepted by any of the paras 417(a)–(f), 674 and 675 shall require *multilateral approval*.

815. An application for *approval* shall include all information necessary to satisfy the *competent authority* that the *design* meets the requirements of para. 673 and a specification of the applicable *management system*, as required in para. 306.

816. The *competent authority* shall establish a certificate of *approval* stating that the approved *design* meets the requirements of para. 673 and shall attribute to that *design* an identification mark.”

In accordance with para. 801 of the Transport Regulations [59],

“For *package designs* where it is not required that a *competent authority* issue a certificate of *approval*, the *consignor* shall, on request, make available for inspection by the relevant *competent authority*, documentary evidence of the compliance of the *package design* with all the applicable requirements.”

For all types of package design, whether requiring approval by the competent authority or not, useful guidance is provided in SSG-66 [102].

5.4.4. Type of package for the transport of UF₆

Depending on the radioactive properties of the material to be transported, packages designed to transport 0.1 kg or more of UF₆ may be of Type IP-1, Type IP-2, Type A, Type B(U) or Type B(M). For UF₆ from non-irradiated uranium, it is expected that a Type IP-1 package or a Type IP-2 package will be appropriate (this needs to be confirmed on a case-by-case basis). Special attention is drawn to UF₆ from reprocessed material. This material might exceed the limits for low specific activity (LSA) material and might need to be transported in Type A or Type B(U) or B(M) packages. In addition, the dose rate from irradiated uranium can be significantly higher than from non-irradiated uranium.

It is necessary to refer comprehensively to the requirements in the Transport Regulations [59] and in the UN Model Regulations [4] to identify all the requirements for packages containing UF₆. However, guidance for this identification is available in SSG-33 [101]. Additional advisory information is available in SSG-26 (Rev. 1) [54]. For a preliminary approach, Table 16 might serve as a useful starting point, to be confirmed by considering all the regulatory requirements.

TABLE 16. REQUIREMENTS IMPOSED ON UF₆ TRANSPORT PACKAGES BY IAEA TRANSPORT REGULATIONS²²

Quantity of UF ₆ package	Additional requirements on the content/package	Uranium enrichment (% of ²³⁵ U)	Quantity of ²³⁵ U	Material classification	Maximum dose rate	Fissile material classification	Fissile packaging requirements	UN number	Packaging requirements	Approval requirement	Labelling
< 0.1 kg	Activity ≤ 10 ⁻³ A ₂ (422)	Natural or depleted or enriched	-	Limited quantity in excepted package	5 µSv/h on the external surface of the package (516)	Non fissile excepted (417.c) or (417.e))	None	3507	Combination packaging for solid Packing Group I material + Excepted package (e)	None	Class 6.1 & Class 8 labels
≥ 0.1 kg	Filling ≤ 95% (g)	Natural or depleted (≤ 0.72%)	-	LSA-I (a)	10 mSv/h at 3 m from unshielded contents (517) (h), and 2 mSv/h on the surface of the package (527), or 10 mSv/h on the surface of the package (528) under the conditions of (527)	Non-fissile (222)		2978	Type IP-1 + requirements for packages containing UF ₆	H(U) or H(M)	Category I-WHITE, II-YELLOW or III-YELLOW label + Class 6.1 & Class 8 labels
		>0.72% and ≤1.0%		LSA-I or LSA-II (a)		Fissile excepted (417.a))			Type IP-1 or IP-2 (a) + requirements for packages containing UF ₆		
				LSA-I or LSA-II (a) or non-LSA (d)		Fissile excepted (417.c) or (417.e))			Type IP-1 or IP-2 (a) or Type A, or Type B(U) or Type B(M) (d) + requirements for packages containing UF ₆		
≥ 0.1 kg		>1.0%	-	LSA-II (b) or non-LSA (d)		Fissile	Requirements for packages containing fissile material (674) (c)	2977	Type IP-2 (a) or Type A, or Type B(U) or Type B(M) (d) + requirements for packages containing UF ₆	IF, AF, B(U)F or B(M)F	Category I-WHITE, II-YELLOW or III-YELLOW label + FISSILE (CSI) labels + Class 6.1 & Class 8 labels
							Requirements for packages containing fissile material (676-686)				

²² Numbers in parentheses indicate relevant paragraph numbers from the Transport Regulations [59].

TABLE 16. REQUIREMENTS IMPOSED ON UF₆ TRANSPORT PACKAGES BY IAEA TRANSPORT REGULATIONS (CONT.)

^a	In the case of irradiated uranium, when criteria for LSA-I are exceeded, the material have to be classified as LSA-II (subject to confirmation that the specific activity is lower than 10^{-4} A ₂ /g) and have to be packaged in a Type IP-2.
^b	Except when the material is fissile-excepted, LSA-I cannot include fissile material. Only LSA-II can be classified as 'FISSILE'.
^c	Packages for fissile material meeting para. 674 of the Transport Regulations [59] are not subject to approval for 'package designs to contain fissile material' (para. 814 in Transport Regulations [59]).
^d	When classification as LSA is not possible (particularly in the case of irradiated uranium), the material has to be transported in a Type A (if activity $\leq 1A_2$) or a Type B(U) or Type B(M) package.
^e	Packing instruction P603 of UN Model Regulations [4] applies in addition to the requirements for excepted packages in the Transport Regulations [59].
^f	The limit of 45 g is for all fissile nuclides on a conveyance and requires 'exclusive use'. Other possibilities are offered through paras 417 and 570 of the Transport Regulations [59] but are not listed here in order to simplify reading of the table.
^g	The degree of filling (less or equal 95%) is given at the maximum temperature of the package, as specified for in the plant systems where the package might be used. Other additional requirements are given in the corresponding para. 420 of the Transport Regulations [59].
^h	Only for LSA material.

5.4.5. Cylinders

Compliance with ISO 7195 [84] and ANSI N14.1 [85] standards is further addressed in Section 5.4.2. Cylinders used for transport also serve as process cylinders during filling and emptying operations. The types of cylinders most frequently used are 48Y cylinders (see Figure 26) for the transport of natural and depleted UF₆ and 30B cylinders (see Figure 27) for UF₆ enriched up to 5% in ²³⁵U. The design and manufacturing specifications of UF₆ cylinders are covered in ISO 7195 [84] and ANSI N14.1 [85]. These standards also include the recertification, maintenance and repair requirements for UF₆ cylinders as well as any design requirements for valves, valve protectors and plugs for UF₆ cylinders.



FIG.26. 48Y cylinders without outer protection.



FIG.27. 30B cylinders without outer protection.

The list of all types of cylinders, as can be found in ISO 7195 [84] at the time of publication of this document, is given in Table 17 hereunder. It is not fully consistent with the one that is available in ANSI N14.1 [85].

TABLE 17. INDICATIVE LIST OF CYLINDER MODELS AS AVAILABLE IN THE ISO 7195 [84] STANDARD

Model number	Nominal diameter mm (in)	Material	Minimum volume m ³ (ft ³)	Approximate tare (without valve protection) kg (lb)	Maximum enrichment g of ²³⁵ U/ 100 g of U	Maximum fill limit ^a kg (lb) of UF ₆
1S	38,1 (1.5)	Ni or Ni-Cu alloy	1.50×10^{-4} (5.3×10^{-3})	0.794 (1.75)	100	0,45 (1.0)
2S	88,9 (3.5)	Ni or Ni-Cu alloy	7.19×10^{-4} (2.54×10^{-2})	1.9 (4.2)	100	2.2 (4.9)
5B	127 (5)	Nickel	8.04×10^{-3} (0.284)	25 (55)	100	24.9 (54.9)
8A	203,2 (8)	Ni-Cu alloy	37.35×10^{-3} (1.319)	54.4 (120)	12.5	115 (255)
12B	304.8 (12)	Ni-Cu alloy	0.067 4 (2.38)	83.9 (185)	5	208 (460)
30B and 30C	762 (30)	Steel	0.736 (26.0)	635.0 (1 400)	5 ^{b,d}	2 277 (5 020)
48X	1 219.2 (48)	Steel	3.084 (108.9)	2 041 (4 500)	4.5 ^{b,c}	9 539 (21 030)
48Y	1 219.2 (48)	Steel	4.040 (142.7)	2 359 (5 200)	4.5 ^{b,c}	12 501 (27 560)

^a The maximum fill limit may be adjusted in accordance with the actual volume, maintaining the ullage limits specified hereafter. Fill limits are based on liquid UF₆ density at a maximum temperature of 121°C (250°F), 3257 kg/m³ (203.3 lb/ft³), certified minimum internal volumes for all cylinders, and a minimum cylinder ullage of 5% as specified in the Transport Regulations [59]. ISO 7195 [84] with regard to operating limits states that “These operating limits apply to UF₆ with a minimum purity of 99.5%. More restrictive measures are required if additional impurities are present. This maximum temperature (121°C (250°F)) shall not be exceeded during filling”.

^b With regards to maximum enrichment levels ISO 7195 [84] states that “These maximum enrichments require moderation control equivalent to a UF₆ purity of 99.5%. Without moderation control, the maximum permissible enrichment is 1.0%.”

^c “Enrichment up to 5% is allowed subject to additional criticality safety assessment and approval by the competent authority” ISO 7195 [84].

^d “Enrichment up to 6% is allowed subject to additional criticality safety assessment and approval by the competent authority” ISO 7195 [84].

Cylinders have to be periodically certified (i.e. inspected, tested, weighed and stamped) throughout their service life at intervals not to exceed five years (clause 5.3.4.2.1 in ISO 7195 [84]). Cylinders containing UF₆ at the five-year expiration date, including heeled cylinders, are exempted from this requirement provided that, prior to next shipment, they are inspected in accordance with a monitoring programme. For more detailed information, see ISO

7195 [84] and ANSI N14.1 [85] standards. A cylinder with an expired pressure test date needs to be recertified before refilling with UF₆, except as otherwise excepted by site licenses.

Attention is to be paid to the acceptable construction codes for cylinders that may differ from one country to another (as an example, only cylinders complying with the American Society of Mechanical Engineers Code are acceptable for import into and transport within the USA).

Proper maintenance, preparation and use before transport of cylinders ensure the performance of safe transport. The minimum inspection, maintenance and preparation requirements are referenced either in package design safety reports or listed in the certificates of approval issued by the competent authorities (if applicable). Particular attention is for example paid to checking the correct engagement of the screw threads of the valves inside the cylinders, for example with gauges or other appropriate visual means.

There are several cylinder washing facilities in operation worldwide. These facilities use different methods and washing solutions to clean the cylinders.

These cleaning methods have a significant impact on the quantity of residual material in the emptied cylinders, in particular the quantity of fissile material. It is important to take care to have documentation and/or tests to justify that the process guarantees the material classification of the ‘heels’ which will be proposed at the end of the washing operations.

5.4.6. Outer packaging

Protection of cylinders might be required to fulfil the requirements of the Transport Regulations [59]. For packages designed to contain more than 0.1 kg of UF₆, thermal protection, as shown in Figure 28, might be necessary to withstand the thermal test required by the Transport Regulations [59] (see para. 632 (c) of the Transport Regulations [59]). For packages designed to transport fissile UF₆, outer protection might be necessary to withstand accident conditions of transport, i.e. to guarantee sub-criticality following accident conditions of transport (a breach of a cylinder containing enriched UF₆ could result in an ingress of water and potentially lead to criticality). Approved designs of outer protective packaging (e.g. COG-OP-30B, DN30, MST-30, UX-30 (see Figure 29)) ensure that the containment provided by the cylinder will remain intact, by providing mechanical protection and thermal insulation, and subsequently will prevent any ingress of water.

Proper maintenance of the outer protective packaging is essential to ensure the integrity of the package as a fire and shock resistant protection. The outer protective packaging have to be kept structurally sound, provide a tight seal between the cover and base, and be protected from damage to the insulation by moisture. The same recommendations also apply to the preparation of the outer protective packaging before departure. The minimum inspection and maintenance requirements are referenced either in respective licensed package design safety reports or listed in the certificates of approval issued by the competent authorities.

The designs of packages for fissile UF₆ (i.e. packages which meet the specification of the last line of Table 16) are incompatible with the requirements applicable to package designs for fissile material to be transported by air. It is then impossible to carry them by air. For instance, compliance with the requirements applicable to shipment by air of enriched uranium in 30B cylinders is impossible to demonstrate, whatever the outer packaging design choice.



FIG. 28. 48Y with thermal protection²³ (courtesy of Cameco).

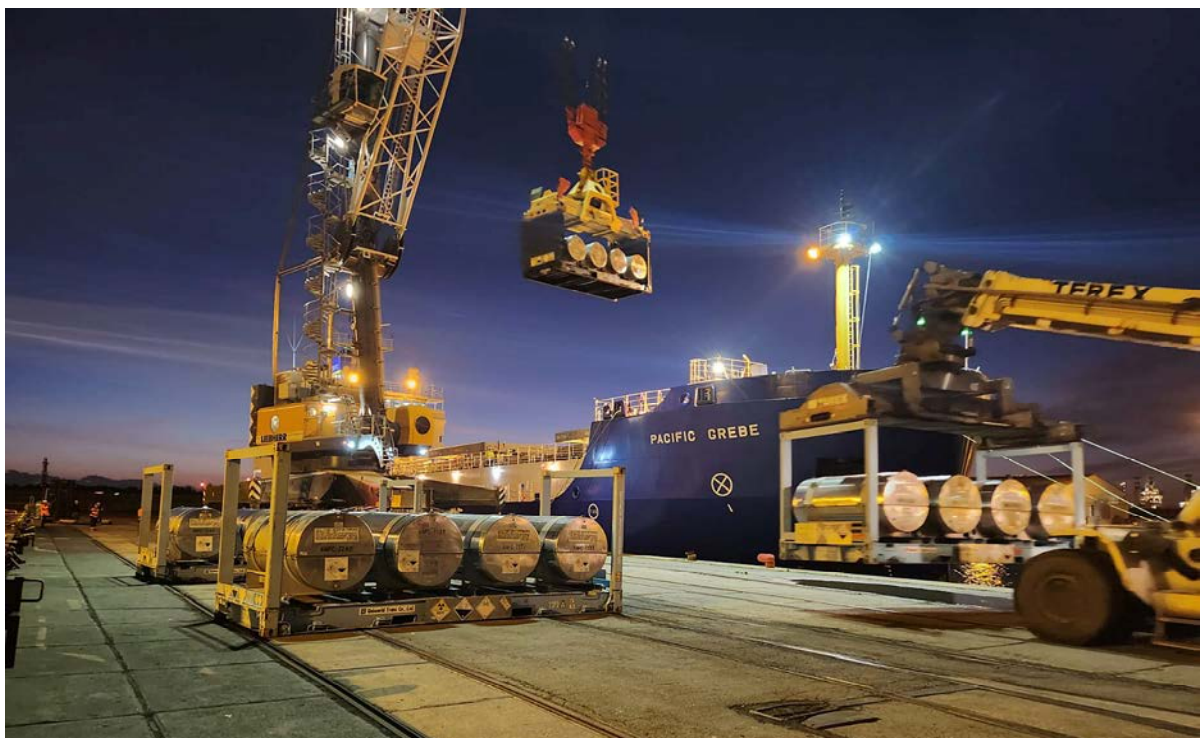


FIG. 29. 30B cylinders with protective overpacks being transferred to a ship (courtesy of Orano).

5.4.7. Sample packaging

Typically, UF_6 is produced and managed in large-scale quantities, which can vary from 1 to 14 tons. Characterization of this material necessitates the collection of representative samples,

²³ Class 6.1 labels are not shown.

which are utilized to ascertain compliance with relevant commercial specifications, specifically ASTM C996-20 [58] and ASTM C787-20 [14], through appropriate testing techniques (for instance, the techniques described in ASTM C1689-21 [105] and ASTM C761-18, Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride [106]).

As explained in Sections 5.3 and 5.4.1, for small quantities of UF₆, the toxic and corrosive dangers take precedence over the radioactive danger and therefore the sample packages need to comply with the requirements for solid Packing Group I substances and, in addition, with the general requirements for packages containing radioactive material. These require that the primary receptacles containing UF₆ are packed into leakproof secondary packages, and these are packaged into a rigid outer package. The detailed requirements can be found in the Packaging Instructions 603 of the UN Model Regulations [4].

Packages to be transported by air are subject to additional requirements concerning temperatures and pressures (see paras 619–621 of Transport Regulations [59]). For fissile UF₆, the last statement in Section 5.4.6 regarding the transport by air of large quantities of fissile UF₆ also applies.

5.5. OTHER TRANSPORT CONSIDERATIONS

5.5.1. General

In order to meet the basic requirements and the declared purpose of the Transport Regulations [59], and to avoid inadvertent non-compliance with safety features, effective management systems and compliance assurance programmes are required. Detailed information is available in TS-G-1.4 [67] and SSG-78 [66]. See also Section 3 in this publication.

These ensure, for example, that:

- The personnel involved in the transport activities (preparation and execution of the transports) have received appropriate training commensurate with their responsibilities, including the necessary knowledge of the applicable hazards presented by the radioactive material;
- Radiation protection programmes, whose nature and extent of the measures to be employed are related to the magnitude of and likelihood of incurring exposure, have been established and implemented by all entities involved in transport, handling and transshipment operations (Detailed information regarding radiation protection programme is available in SSG-86 [100]);
- Appropriate and sound packages (i.e. packaging manufactured and maintained in accordance with the specifications) are used;
- The activity of radioactive material, the quantity of fissile nuclides and the quantity of material in each package does not exceed the general limits specified in the regulations for that material and package type, and the specific (e.g. maximum, and in some cases minimum) limits for the package design to be used;
- Physical and chemical state of the material, filling rate and inner pressure comply with the regulatory requirements (para. 420 of the Transport Regulations [59]);
- The external dose rate arising from, and the contamination levels on surfaces of, the packages do not exceed the appropriate limits – on this subject, it is important to ensure compliance with the specific provisions associated with the use of deferred

measurements (for instance, transposition of a result from a measurement on a cylinder side to a measurement on a bottom) and with taking into account the different types of radiation that may be encountered (the share of neutron radiation needs be estimated for full cylinders, and justified when not taken into consideration; gamma radiation of recently emptied cylinders with heels needs special consideration);

- Packages are properly marked and labelled, and transport documents are completed, and meet the requirement of the applicable national, regional and international regulations;
- The number of packages containing radioactive material in a conveyance is within the regulatory limits;
- Packages are securely stowed in conveyances and are stored at a safe distance from persons and photo-sensitive materials;
- Transport and lifting devices are in good mechanical condition and are compliant with applicable standards.

These management systems programmes might also consider additional control for other reasons, e.g. safeguards, physical protection, material accountability, nuclear liability and custom regulations. It is recognized that an integrated management system covering all aspects will be beneficial in order that one of them does not compromise safety (and vice-versa), and that any deficiencies identified in one aspect is also assessed with a safety perspective.

The Transport Regulations [59] also require appropriate emergency response arrangements to deal with the consequences of potential transport incidents to be established. Detailed information is available in IAEA Safety Standards Series No. SSG-65, Preparedness and Response for a Nuclear or Radiological Emergency Involving the Transport of Radioactive Material [99]. See also Section 9 in this publication.

The consignor of the radioactive material has the primary responsibility for safe transport and, in accordance with para. 547 of the Transport Regulations [59], has to declare in the transport documents that the UF₆ to be transported is “fully and accurately described ... by the proper shipping name” and is “classified, packaged, marked, and labelled/ placarded, and are in all respects in proper conditions for transport according to the applicable international and national governmental regulations.”

The accumulated experience of all the parties involved is of great value for transport of UF₆. For example, a set of regulations, however comprehensive, cannot provide the criteria necessary to choose the 'right' carrier. Nor can it illustrate the most effective means of load securing which is suitable both for the packaging and the vehicle. A part of this accumulated experience can be found worldwide through guidance or fact sheets provided by international organizations, such as World Nuclear Transport Institute, that publishes documents on various topics such as overall fact sheets on UF₆ [107], standard for cylinder identification [108], guides on valves and plugs installation [109], on transport in small quantities [110] and on the transport index and criticality safety index limits for sea shipments [111].

5.5.2. Organization of transport

The transport organization has to comply with safety regulations, and with all the other applicable regulations, including nuclear liability, safeguards, security, material accountability, and customs regulations. The procedures in each country are different and depend on national regulations.

Radiation protection necessitates adequate consideration when considering the choice of a transport solution, to minimize exposure to workers, including non-nuclear workers, and the

public, during transport and transshipment operations (ALARA principle). The carrier has to take appropriate precautions to protect people during transit.

Differences in the applicable regulations, as well as in the applicable certificates of approval, exist from country to country and need to be considered when preparing an international transport of UF₆. Compliance with all applicable international, regional and national regulations for transport of dangerous goods and certificates of approval which have to be applied is to be considered prior to starting an international shipment. Examples of those differences between national regulations and the Transport Regulations [59] at the time of drafting this document are:

- Fissile exceptions in the USA – The specifications for fissile-excepted materials differ from those in the Transport Regulations [59] and exceptions from package approval for fissile material based on para. 674 of the Transport Regulations [59] do not exist in the US regulations;
- Type of package for fissile material in the USA – An industrial package cannot be used to transport fissile material in accordance with the US regulations. Only a Type A, a Type B(U) or a Type B(M) is permitted;
- Dose rate limits in Japan – Dose rate limits around vehicles in Japan are lower than in the Transport Regulations [59].

5.5.3. Choice of the carrier (or freight forwarder)

The carrier (or freight forwarder) is an important actor in the transport of UF₆, particularly when several modes of transport (such as road, rail and sea, and even air for samples) are used. The carrier's importance increases with the distance and the number of different means of transport used. Consequently, the carrier's ability (or freight forwarder's ability), organization and experience need to indicate that he can carry out the task. Economic factors is to never be the primary criteria to select a carrier (or freight forwarder). Their installations and their experience, equipment and the qualification of their personnel are key for safe transport of the material. Almost all countries require carriers engaged in transport of radioactive material to be licensed by a competent authority. The consignor and carrier (or freight forwarder) have responsibilities for the material and is expected therefore to choose the type of transport to be used.

National competent authorities require that civil authorities who would be involved in case of an accident are informed about an intended transport before departure.

5.5.4. Package stowage and retention during transport

Equipment for transport might be chosen from a large variety of options. The most often used are:

- Flat racks (see Figure 30);
- Wooden or metal cradles;
- Pallets;
- Various jigs (custom-made tool used to control the location and/or motion of the cylinder);
- Frames, spreaders, fasteners, most often made of wood;
- Chains, straps, ropes, tensioners, bolts, pins, serving to fix the container and its bearer to the transport vehicle.



FIG. 30. DN30 outer protection on a flat rack (courtesy of Urenco).

In order to transport safely radioactive material in packages, para. 564 of the Transport Regulations [59] requires that “*Consignments* shall be securely stowed”.

Requirements for tie down of UF_6 packages may be prescribed package design safety report and instructions for use of the packagings and, in addition, in the applicable package design approvals for those package designs subject to approval.

Designers of the package (as presented for transport), and competent authorities issuing its package design certificates of approval when required, need to consider the recommendations contained in Appendix IV of the SSG-26 (Rev. 1) [54] for the design of the attachment points of the package that could be used for securing the package on its conveyance (a vehicle, a container, a seagoing vessel, or an aircraft).

The requirements for tie-down are those prescribed for the different transport modes by the international organizations in charge of those transport modes and/or the competent authorities of the different countries through or into which the transport is going to be performed.

Examples of standards that can be used and that might be mandatory for tie-down in certain countries are:

- IMO/ILO/UNECE Code of Practice for Packing of Cargo Transport Units (CTU Code) [18] (This code might be mandatory in certain countries for tie down of cargo inside vehicle or container to be carried by road, rail and sea);
- UIC Loading Guidelines [112] (These guidelines are generally made mandatory by European railways companies for tie down of cargo on railcars for carriage by rail);
- EN 12195-1 Standard, Load restraining on road vehicles – Safety - Part 1: Calculation of securing forces [113] (Tie-down following this standard is considered as satisfactory for carriage of dangerous goods by road in countries where Ref. [93] is applicable);

- National Safety Code Standard 10, Cargo Securement (Canada)²⁴;
- 49 CFR 393.102 (Subpart I) – Federal Motor Carrier Safety Administration – Protection Against Shifting and Falling Cargo (USA)²⁵.

There are two categories of devices that can be used for securing a cylinder on its means of transport:

- Rigid devices;
- Sliding devices.

Both categories can be used for the transport of all UF₆ packages. The rigid devices, however, are commonly used for lightweight packages (5-, 8-, 12-, 30-inch cylinders, see Table 17) equipped with outer protective packaging. These devices are intended to solidly secure the container to the floor or wall of the transport vehicle or container and to prevent any movement of the load during transport. They have to resist to the force of an emergency stop of a road vehicle or the buffering of a rail car. The sliding devices are used for the transport of 48-inch cylinders by rail. These devices retard and stop the longitudinal movement of the load after a sudden shock within a given distance.

Attention is to be given to the way of securing 48-inch cylinders (typically 48X and 48Y, see Table 17) by use of the lifting lugs the cylinder is equipped with. Forces acting on each lug during lifting and during transport are to act as tangentially as possible to the cylinder and be in the plan of the lug. Lifting a full cylinder cannot be done by use of only two lugs (the four lugs have to be used together when used for lifting the full cylinder).

6. STORAGE OF URANIUM HEXAFLUORIDE

6.1. INTRODUCTION AND GENERAL CONSIDERATIONS

Storage of UF₆, both short and long term, occurs at many locations globally, including both indoor and outdoor storage facilities. While short term storage safety considerations involve radiation protection, criticality safety and safe handling, long term storage safety considerations also include aspects of confirmation of container integrity and validity of the certification of the cylinders. In addition, issues other than safety, such as security and nuclear material accountability are also to be considered but are out of the scope of this publication. Feed stock of enriched UF₆ may experience extended pauses in its flow through the nuclear fuel cycle, including long term storage in a fuel bank. Depleted UF₆ deserves special attention concerning storage because large amounts of this material are generated at enrichment plants, and it is then stored for very long periods. Figure 31 shows a typical outdoor UF₆ staging area. It is assumed that UF₆ is stored as a solid in cylinders such as those described in ISO 7195 [84] and ANSI N14.1 [85] standards (for examples, see Table 17 of Section 5).

Many factors are common to both short and long term storage, including safety, stacking, and spacing considerations (criticality, radiological, and mechanical), chemical activity, quality control, management system and emergency planning. For extended storage, the selection and qualification of a storage site, cylinder maintenance, monitoring, control and inspection, are important. The factors which affect short term storage will be described separately when they differ significantly from long term storage practices or requirements. Worldwide experience

²⁴ The reference takes its sources from the North American Cargo Securement Standard [114] (Transport by road in North America (Canada and USA)).

²⁵ The reference takes its sources from the North American Cargo Securement Standard [114] (Transport by road in North America (Canada and USA)).

with UF₆ storage in cylinders demonstrated that the shell of cylinders designed to ISO 7195 [84] and ANSI N14.1 [85] standards is robust and unaffected by internal corrosion over several decades. Nor is the shell affected by external corrosion, as long as its coating is corrosion resistant, and the storage conditions do not generate undue risks for accumulation of water (e.g. storage of cylinders directly on the ground where water could accumulate is an issue, and ensuring there is no water buildup in the skirt). Finally, the body of a cylinder can be monitored for defects by non-destructive examination methods, if needed.



FIG. 31. Typical UF₆ cylinder staging area (before movement to long term storage pad) (courtesy of Honeywell).

6.1.1. General criteria for UF₆ storage

All cylinders used for storage of UF₆ are equipped with a nameplate in accordance with ISO 7195 [84] and ANSI N14.1 [85] standards. All cylinder storage is supported by an accountability records system to identify cylinder contents as well as to maintain a history of each cylinder. This system includes the following:

- Complete fabrication data (drawings, materials of construction, applicable codes, standards deviations, date of fabrication, and serial number);
- Test data;
- Certificate of approval for the package design in accordance with the Transport Regulations [59], when applicable;
- Transport experience;
- Inspection results;
- Maintenance and repair records.

All cylinders scheduled for storage of UF₆ are to:

- Be equipped with valves and plugs that are properly installed (valves and plugs might need to be approved, subject to the provisions of the site licence);
- Be secured from unauthorized access;

- Have all defects, deviations, discrepancies, dents, and damage identified (defective or damaged cylinders need to be set aside for repair or other action as appropriate);
- Have identified internal contaminants (i.e., non-UF₆) that are above UF₆ specifications for further use (e.g. enrichment, deconversion specifications).

Cylinders placed in the storage facility in accordance with a standard operating procedure. For UF₆ cylinders containing enriched material, this is to avoid the creation of nuclear critically conditions. That procedure ensures that all UF₆ cylinders are grouped for storage in arrays with the following criteria:

- Cylinder model;
- ²³⁵U enrichment;
- Scheduled storage period;
- Final destination of material;
- Contents (i.e. full, empty, clean, etc.);
- Accessibility requirements;
- Site license requirements.

Fire prevention is of particular importance for UF₆ storage areas as fire represents an opportunity for significant material release. As a precaution, it is essential not to store flammable materials in the proximity of UF₆ cylinders. Access to cylinder storage areas needs to be restricted to personnel who are qualified and who need to have access. This restriction applies to storage of all cylinders, empty as well as filled. Figure 32 shows model 48Y cylinders for storing UF₆.

Within the indoor UF₆ storage facilities, special requirements for heating and ventilation systems need to be considered. The use of water pipelines and use of any liquids for technical use, especially for fire extinction within these premises needs to be considered as the interaction between UF₆ and water might lead to release of HF, and to a reduction in margin for criticality in case of storage of enriched material.



FIG. 32. 48Y cylinders for storing UF₆ (courtesy of Cameco).

6.2. SITE SELECTION AND CRITERIA

6.2.1. Selection

IAEA Safety Standards Series No. SSR-1, Site Evaluation for Nuclear Installations [115] establishes requirements for site evaluation of all nuclear installations including UF₆ storage facilities. IAEA Safety Standards Series No. SSG-35, Site Survey and Site Selection for Nuclear Installations [116] provides recommendations and guidance on establishing a systematic process for site survey and site selection for a number of preferred candidate sites, from which one could be selected for the construction and operation of a nuclear installation.

The choice of a site for the safe storage of UF₆ cylinders is often predetermined by the location of processing facilities and the economics and safety of additional transport movements. The physical location can be characterized by factors such as local topography, hydrology, demography, geology, seismology, and climate. Associated with the site will be buildings and structures housing equipment used in receipt and storage, and the appropriate infrastructure. The site will usually be capable of transferring UF₆ in both the liquid and the gas phases. A storage site will require provision of services for personnel exposure protection and safety, management system, surveillance, inspection, and maintenance.

A comprehensive risk assessment of the potential impact of the location of the site in regard to environmental conditions needs to be completed. This includes consideration of natural phenomena and situations that could lead to an accidental release of UF₆, including low-probability events. The presence of adjacent sources of atmospheric pollution can significantly affect storage acceptability. Exhausts from chimneys, chemical stacks, and water cooling towers can influence the pH of rainfall or provide particulate deposition which may accelerate cylinder corrosion rates. The degradation of cylinders will also be affected by coastal salt-bearing winds and the general humidity. Temperature variation, both diurnal and seasonal, are to be considered in relation to UF₆ physical properties and cylinder design criteria.

6.2.2. Site criteria

- Site selection is to consider fire, earthquake, and damage from other natural phenomena;
- The site is to be well drained and not be subject to flooding. Capability for temporary holding and monitoring of runoff is to be provided. Figure 33 shows a typical UF₆ cylinder storage yard;
- The site is to provide a stable surface for cylinder storage;
- The site is to be served by transportation facilities suitable for its needs;
- Containment of accidental releases of UF₆ needs to be possible;
- The site is to have facilities for the transfer of UF₆ from one cylinder to another.



FIG. 33. Typical UF₆ cylinder storage yard (courtesy of Honeywell).

6.3. EQUIPMENT AND CAPABILITY NEEDS FOR A STORAGE FACILITY

Maintaining a UF₆ storage facility requires the concurrent maintenance of a range of auxiliary support facilities. Capabilities required for UF₆ cylinder storage include cylinder handling equipment, a system for material accountability and control of UF₆ which includes the description of the nuclear material flows in and out of the storage with control measurement points, management system (including a mechanism to correct deficiencies), and emergency response. GSR Part 2 [60] establishes requirements for establishing, sustaining and continuously improving leadership and management for safety, and an effective management system.

Cylinders need to be positioned on saddles, storage racks or other devices to prevent movement. Cylinder handling capabilities such as lifting fixtures and hardware, straddle carriers, forklifts, cranes, and specialized cylinder handling machinery are needed.

Cylinder damage due to handling activities and cylinder shell thinning due to corrosion processes may render a container unsuitable for transport. Therefore, capability to transfer UF₆ from one cylinder to another is needed. An alternative would be to have the capability of transporting rejected cylinders to another site.

The occasional need to change valves makes it necessary to have the equipment and trained personnel to make such changes.

Storage facilities for UF₆ also require leak detection equipment or a process to detect cylinder leaks and sometimes for the purposes of safeguards implementation equipment for collecting sample in the field.

6.4. CRITERIA APPLICABLE TO THE STORAGE OF CYLINDERS OF UF₆ WHERE CRITICALITY SAFETY IS OF CONCERN

General information about criticality safety can be found in the IAEA Safety Standards Series No. SSG-27 (Rev. 1), Criticality Safety in the Handling of Fissile Material [117].

6.4.1. Administrative safety criteria

- Operations and storage arrangements follow established practices to prevent accidental nuclear criticality incidents;
- Methods and practices are described in written procedures;
- Personnel involved in cylinder movement and storage are fully aware of the written procedures;
- Compliance with the procedures is periodically verified by inspections;
- Measures to be implemented in case of accidents is prepared in advance.

6.4.2. Nuclear criticality safety practices

- Experimental data and/or validated computational results provide the basis for approved storage arrays;
- Individual cylinders of UF₆ are subcritical under conditions of total submersion in water;
- The design, fabrication, and maintenance of facilities and structures for storage are in accordance with good engineering practices. Analysis shows accidental criticality does not occur even if fire, flood, earthquake, and other natural phenomena do occur;
- The use of physical barriers including fixed storage positions, bird cages, etc., which are sturdy and non-combustible are preferred to administrative controls to preclude criticality incidents during storage;
- A criticality detection and alarm system is installed to alert personnel of a nuclear criticality accident.

6.5. RADIOLOGICAL, PHYSICAL AND CHEMICAL CONSIDERATIONS

UF₆ cylinders are often emptied by evaporation (see Section 4). Some radioactive impurities may remain and collect at the low points in the cylinder when the UF₆ is evaporated. Thus ‘empty cylinders’ may have a higher external dose rate (i.e., beta and gamma radiation) than full cylinders where the impurities are dispersed through the UF₆ and are shielded to some extent.

Uranium is also an alpha emitter. Personnel are protected from alpha radiation and from the chemical properties of UF₆ by the cylinder containment. The guidelines outlined previously (Sections 2, 4.7, 5, and 9) for radiological and chemical protection of personnel involved with handling UF₆ (both monitoring and emergency) also apply to UF₆ storage.

6.6. HANDLING, SHIPPING, AND RECEIVING CYLINDERS

It is essential to prepare procedures for all routine operations in UF₆ storage including cylinder cleaning and inspection, handling, storage, monitoring, and removal from storage. When a cylinder is removed from the storage area (i.e. handled), procedures need to be followed to maintain accountability and to ensure that the cylinder meets the criteria for the intended application or destination and that all safety, criticality, and environmental conditions are satisfied. The cylinder selected for shipping is inspected and tested to ensure that the pressure within the cylinder is not above atmospheric pressure. It is then inspected to ensure compliance

with other handling and shipping criteria. When the cylinder is found to be suitable for shipping, it can then be weighed and moved to a staging area for transfer to a qualified carrier. Cylinders that do not meet internal pressure, external damage, or shell-thickness requirements are rejected and identified. They are then submitted for corrective action or marked and set aside for later repair of defects, if appropriate.

6.6.1. Storage status

The following steps are followed before removing cylinders from storage:

- The cylinder internal pressure is checked to ensure below atmospheric internal pressure;
- The cylinder is inspected for cracks, bulges, dents, valve damage, and other defects;
- A weight determination is made for reconciliation with the entry weight;
- Valve protection is provided, as appropriate.

6.6.2. Storage and transport interface

A staging area may be provided for UF₆ cylinders between storage areas and transport and for their receipt upon arrival. Approved operating procedures need to be established for moving cylinders within the site. These procedures need to include UF₆ cylinder preparation and inspection and UF₆ cylinder receiving and inspection prior to storage. For off-site transport, requirements can be found in Section 5 and the documents referenced there.

6.7. ORIENTATION AND STACKING OF CYLINDERS

Inventory of UF₆ is generally managed by cylinder serial number. Storage arrays will normally be limited to double rows so that any cylinder is accessible to lifting equipment. The 30-inch and 48-inch cylinders are to be stored horizontally with the valve in the 12 o'clock (top centre) position. The cylinder contents tend to redistribute themselves over time. If this redistribution is not considered, some types of lifting equipment (notably the H-frame with cables) might be operated outside of their safe load range with an eccentrically loaded cylinder. The lifting equipment needs to account for the redistribution of cylinder contents. Long term storage requires attention to such factors as cylinder support (chocks), visibility of the cylinder serial number, and physical condition of the cylinder (corrosion effects, valve condition, dents, or other physical damage). It is essential that arrays have sufficient clearance between rows to permit inspection of both ends of each cylinder for monitoring the progress of atmospheric corrosion, shell thinning, and other damage. Cylinders need to be stored in orientations and arrays suited for the effective use of handling equipment.

Storage arrays is expected to permit close visual access to the cylinder nameplate, valve, and support points as well as general access to surfaces exposed to corrosion processes. The storage arrays need to allow for ease of removal of specific cylinders with a minimum of movement of other cylinders in the array.

Enriched material is to be stored in cylinders of suitable geometry and/or with suitable moderation control in order to meet criticality considerations.

6.8. CORROSION ASPECTS

Unprotected steel cylinders in outside storage facilities are susceptible to general corrosion if no corrosion resistant coating is applied. Corrosion rates depend on weather conditions. It increases when humidity and airborne particles (SiO₂, charcoal, etc.) in the air increase. It also

increases with atmospheric acidity and chlorine concentration, and particulate deposition. The wide variation in weather with location is illustrated in Table 18. It is apparent that location will directly influence anticipated storage life. Shell thinning in specific sections of the cylinder may also be expected. Welds, dissimilar material junctions, contact points between cylinders, supports, shaded areas and other regions where drying might be restricted deserves special attention. Most corrosion occurs when the steel surfaces are covered with a thin film of moisture. If conditions preclude drying, accelerated corrosion is likely. Humidity control, ventilation and corrosion resistant coatings can dramatically reduce cylinder corrosion, particularly when the cylinder surface is not rusty.

Cylinder corrosion studies have concluded that UF₆ cylinders can have extremely long lives – 70 years or more, the main criterion regarding the lifetime of the cylinder is the minimum shell thickness of the cylinder. Any such observed attack mechanism is evaluated in the context of long term cylinder storage (see Figure 34). The strength of the cylinders is reduced with a decrease in shell thickness. Table 19 provides the minimal shell thickness for various models of UF₆ cylinders for operations and transport. For some transport packages the minimum shell thickness varies from these values in Table 19 to guarantee criticality control during transport. Cylinders with shell thicknesses below these values which contain UF₆ will require special handling when UF₆ is removed. These cylinders are not to be transported and can only be heated at approved lower temperatures.

Protective coatings, where practical, can be very effective in limiting corrosion. These work best when they incorporate galvanic protection. Adequate surface preparation prior to painting is very important in assuring integrity and promoting durability of the protective coatings.

TABLE 18. ATMOSPHERIC STEEL CORROSION BY LOCATION

Location	Weight loss after two years (g)
Norman Wells, NWT, Canada	0.73
Phoenix, Arizona, USA	2.23
Fort Amidor Pier, Panama	7.10
Melbourne, Australia	12.7
Pittsburgh, Pennsylvania, USA	14.9
Miraflores, Panama	20.9
London (Battersea). UK	23.0
Manila, Philippine Islands	26.2
Brazos River, Texas, USA	45.4
London (Stratford), UK	54.3
Kure Beach, North Carolina, USA	71.0

Source: Table 18 adapted from ASTM, Corrosiveness of Various Atmospheric Test Sites as Measured by Specimens of Steel and Zinc [118]. Based on weight loss of 10 cm by 15 cm cold-rolled carbon steel coupons after two-year exposures.



FIG. 34. Measuring corrosion attacks (courtesy of Urenco).

TABLE 19. MINIMUM CYLINDER SHELL THICKNESS ([84] and [85])

Cylinder model	Minimum shell thickness	
	(mm)	(in)
1S and 2S	1.59	1/16
5B and 8A	3.18	1/8
12B	4.76	3/16
30B and 30C	7.94	5/16
48X and 48Y	12.7	1/2

Aluminium-bronze and Monel valves are susceptible to stress corrosion cracking in the presence of HF. Hydrolysis of small amounts of UF₆ leaking through the valve or left in the valve body after valve closure may produce HF if the valve cap is not tightly secured or if the valve packing allows moist air to leak in. Interior UF₆ corrosion of steel cylinder shells is generally of less concern than exterior corrosion. Interior steel corrosion proceeds at rates of at least an order of magnitude less than external corrosion. However, the presence of impurities in either solid UF₆ or in the vapor phase can impact corrosion rates. For example, both pitting and stress corrosion cracking of valve components have been traced to the presence of arsenic in the UF₆ feed material.

Cracked packing nuts have been observed in some UF₆ cylinders; while this does not represent a serious problem, periodic inspections of stored cylinders allows to note such conditions because they may indicate seat and packing leakage. In addition to HF, atmospheric carbon dioxide (CO₂) may also be responsible for some of the observed cracking. Long term deterioration of the pressure vessel and corrosion damage to the valves and plugs from both internal and external influences are recognized as sources of potential problems. As such, the progress of such deterioration is monitored by establishing a formal programme of observation and record keeping. The data thus generated will serve as a basis for scheduling corrective actions in the most effective manner to assure continuing safety in long term storage of UF₆.

In practice, considerations are to be given to the following:

- Periodic inspection to record the status of atmospheric corrosion for cylinders in long term storage;

- Visual inspection of cylinder valves and plugs for evidence of leakage, cracking, or unusual surface deterioration. Leakage is to be verified by use of radioactive detection instruments, chemical analysis, etc;
- Ultrasonic measurement of shell-thickness to monitor any pitting, corrosion, and general rusting. Cylinder contents need to be transferred if the shell thickness approaches the minimum acceptable value provided in Table 19.

6.9. MONITORING AND INSPECTION ACTIVITIES

New cylinders may be procured in advance of operational need. Changing schedules may result in some cylinders remaining in stock, unused for more than five years following the manufacturer's hydrostatic test. Because the purpose of the testing is to demonstrate serviceability, unused five-year-old cylinders are retested before being placed in UF₆ service. Used cylinders intended for storage are similarly inspected and retested before filling, if necessary. By this procedure, all cylinders used for long term storage conform to the test requirements when filled with UF₆.

It is essential to establish a monitoring programme at long term storage facilities to determine the condition of the cylinders, including shell-thickness degradation, pitting, valve integrity, dents or other physical damage, and the physical condition of supporting structures. The monitoring programme verifies cylinder records, specifically cylinder identification, location, manufacturing and use history, and certification records. Data from periodic inspections needs to be evaluated to track the condition of cylinders, to discover changing environmental effects, and to plan actions in a safe, economical, and timely fashion. The monitoring programme need also to determine the heel mass in the cylinder (see Table 20). There have been a small number of cylinders with valves that have leaked. There is no predictive test of valves for filled cylinders, which can only be monitored for leak-tightness responsively.

TABLE 20. ALLOWABLE CYLINDER HEEL MASSES ([84] and [85])

Cylinder model	Heel mass	
	(kg)	(lb)
5B	0.045	0.1
8A	0.227	0.5
12B	0.454	1.0
30B and 30C	11.3	25.0
48X and 48Y	22.7	50.0

6.9.1. Cylinders scheduled for storage

Cylinders scheduled for storage need to be:

- Subject to the same internal cleanliness and damage criteria as those scheduled for active service;
- Inspected for external damage before filling;
- Hydrostatically tested and inspected before filling.

6.9.2. Cylinders in storage status

Cylinders in storage status are to be:

- Periodically inventoried for accountability;
- Periodically inspected for surface valve and plug condition, and physical damage;
- Periodically sampled for non-destructive shell thickness determination;
- Periodically inspected for leakage.

6.9.3. Cylinder storage areas

Cylinders storage areas are to be checked for:

- Stability or deterioration of supporting surfaces or structures;
- Absence of flammable materials;
- Conditions which might enhance corrosion such as accumulated moisture.

6.9.4. Cylinders alternative five-year periodic inspection and tests

For 30B, 48X, and 48Y cylinders that were built to the ISO 7195 [84] Clause 5.2.2 alternative design without backing bars, completed a 100% radiography of seams, and had an additional magnetic examination or penetrant examination testing performed, may be recertified to the alternative five-year periodic inspection and tests. This inspection allows for the cylinder to be recertified (minus the leak test and tare weight requirement) and be eligible for transport within its five-year periodic inspection.

6.10. CLEANING AND MAINTENANCE

Cylinders intended for the storage of UF₆ are expected to meet all applicable standards such as those given in ISO 7195 [84] and ANSI N14.1 [85]. These standards address external and internal surfaces of new and in-service cylinders and include cleanliness requirements for new and in-service cylinders. Cylinders for storage of UF₆ are acceptable for use if they are within the 5-year of their most recent hydrostatic tests when filled. However, cylinders already filled prior to the 5-year expiration date do not need a full test programme while remaining in storage. A UF₆ cylinder is removed from service (for repair or replacement) when it is found to have leaks, excessive corrosion, cracks, bulges, dents, gouges, defective valves, damaged stiffening rings or skirts, or other conditions that, in the judgment of the qualified inspector, render it unsafe or unserviceable in its existing condition. Cylinders are no longer be used in UF₆ service when their shell and/or head thicknesses have decreased below minimum acceptable values (see Table 19 for shell thickness of cylinders).

6.11. CYLINDERS' LIFETIME

Given the over-design of cylinders and a rigorous programme of inspection and care, there is no need to specify an age limit for filled cylinders in storage (see Section 6.10). Subject to the provisions described above, the life-limiting component for a cylinder is likely to be its valve.

7. RADIOACTIVE (AND NON-RADIOACTIVE) WASTE MANAGEMENT

7.1. INTRODUCTION

The management of radioactive waste in UF₆ facilities includes the handling, storage, pretreatment, treatment, conditioning, transportation, and disposal of radioactive waste materials generated from the production of UF₆. IAEA Safety Standards Series No. GSR Part 5, Predisposal Management of Radioactive Waste [119] establishes the requirements for the predisposal management of radioactive waste and IAEA Safety Standards Series No. SSR-5,

Disposal of Radioactive Waste [120] establishes the requirements for disposal of radioactive waste. IAEA Safety Standards Series No. GSG-1, Classification of Radioactive Waste [121] provides comprehensive guidance on the classification of radioactive waste.

IAEA Safety Standards Series No. SSG-41, Predisposal Management of Radioactive Waste from Nuclear Fuel Cycle Facilities [122] states:

“Radioactive waste (radioactive material for which no further use is foreseen, and with characteristics that make it unsuitable for authorized discharge, authorized use or clearance from regulatory control) arises from a number of activities involving the use of radioactive material.”

This chapter is intended to provide an insight into the typical wastes generated and in general, these wastes can be divided into two broad categories, for classification of individual wastes, guidance is available in GSG-1 [121]:

- (a) Wastes that can be treated within the facility to recycle uranium back into the UF₆ product;
- (b) Wastes containing no or very small quantities of uranium, to be disposed of in a suitable licensed facility.

Noting that the treatment of waste from category (a) typically results in waste that fall into category (b).

It is assumed that uranium recovered from category (a) wastes can be recycled back into the UF₆ product within the scope of the relevant specification. At some UF₆ facilities this may not be the case. Table 22 provides a summary of radioactive waste management practices at some UF₆ conversion plants.

The boundaries of the radioactive wastes discussed in this section are from receipt of uranium (typically UOCs) at conversion through enrichment to reconversion at fuel manufacturing facilities. Therefore, sources and types of radioactive waste at conversion, enrichment and reconversion plants are considered in Sections 7.3–7.5. The wastes are generically described, the criteria for radioactive waste minimization and management are provided by IAEA-TECDOC-1115, Minimization of Waste from Uranium Purification, Enrichment and Fuel Fabrication [123] and IAEA-TECDOC-241, Management of Wastes from the Refining and Conversion of Uranium Ore Concentrate to Uranium Hexafluoride [124].

Section 7.6 provides an introduction to the most significant non-radioactive wastes. Non-radioactive wastes are also handled, treated, stored, transported, and disposed of in a safe and environmentally responsible manner. The waste presenting the greatest hazard and volumes are discussed further in this section. It is to be noted that specific waste will be generated depending on the technology employed at each individual production and handling facility.

7.2. SAFETY PRINCIPLES AND REQUIREMENTS

Safe management of radioactive waste (and its by-products) involves the application of technology and resources in an integrated and regulated manner, so that occupational and public exposure to ionizing radiation is controlled and the environment is protected in accordance with national regulations and international consensus documents.

To meet this overall objective, the following IAEA publications are recommended references:

- IAEA Safety Standards Series No. SF-1, Fundamental Safety Principles, [61] — there are ten associated principles;
- IAEA Safety Standards Series No. GSR Part 5, Predisposal Management of Radioactive Waste [119];
- IAEA Safety Standards Series No. SSR-5, Disposal of Radioactive Waste [120];
- IAEA Safety Standards Series No. GSG-1, Classification of Radioactive Waste [121].
- IAEA Safety Standards Series No. SSG-41, Predisposal Management of Radioactive Waste from Nuclear Fuel Cycle Facilities [122];

The internationally agreed upon safety principles described in SF-1 [61], are fundamental to the responsible management of both radioactive and non-radioactive wastes generated whilst processing UF₆.

SSG-41 [122] sets out a series of steps for the management of radioactive wastes up to the disposal, as follows:

- “
- Pretreatment, which may include waste assay and characterization, waste collection, waste segregation, chemical adjustment and decontamination;
 - Treatment, which may include volume reduction, removal of radionuclides and changing the composition of the waste;
 - Conditioning, which involves those operations that transform radioactive waste into a form suitable for subsequent activities such as handling, transport, storage and disposal; conditioning may include immobilization of the waste, placing of the waste into containers and provision of additional packaging;
 - Storage, which refers to the temporary placement of radioactive waste in a facility where appropriate isolation and monitoring are provided; storage is an interim activity performed with the intent to retrieve the waste at a later date for clearance from regulatory control, for authorized use (e.g. subsequent to a decay period), for processing and/or for disposal, or in the case of effluent, for authorized discharge.”

All the above are considered in the remainder of this chapter, including the management of non-radioactive wastes.

7.3. SOURCES AND TYPES OF RADIOACTIVE WASTE AT CONVERSION PLANTS

Radioactive waste is predominantly generated from two generic sources at conversion plants:

- Waste products originating with the UOCs;
- Waste products originating from the chemical reaction process steps of taking uranyl nitrate to uranium oxide to uranium fluoride compounds. These wastes are sometimes contaminated with concentrated radionuclides and toxic reagents.

The majority of the radioactive waste containing a significant amount of uranium is treated to recover the uranium. This is because of the inherent value of the uranium and to decrease the activity and volume of waste prior to disposal.

Table 21 characterizes a list of the typical radioactive wastes that arise at conversion facilities.

The management of these wastes differs significantly between facilities (see Table 22).

TABLE 21. LIST OF TYPICAL RADIOACTIVE WASTES THAT ARE PRODUCED AT CONVERSION FACILITIES

Waste Description	Characterization
Raffinate	The major waste stream generated in the refining of UOC to UO_3 . It may contain metallic impurities, nitric or sulfuric acids, natural thorium and decay products of uranium relative to abundance in the UOC.
Solvent extraction treatment waste	This waste stream may be slightly radioactive and may contain degradation products of kerosene and TBP. Fine silicate solids (if present in the feed) are typically retained in the aqueous raffinate phase due to their hydrophilic nature, under normal solvent conditions, are not expected to enter the organic phase waste stream.
Ammonium nitrate	This can be found in solvent extraction raffinates. It is normally contaminated with traces of uranium.
Calcium fluoride	<p>Calcium hydroxide ($Ca(OH)_2$) and potassium hydroxide (KOH) scrubber solutions are reacted to convert potassium fluoride to KOH and to precipitate the fluoride as insoluble calcium fluoride, containing very small quantities of uranium, i.e. less than 0.5%.</p> <p>Some scrubber systems use water to scrub HF, and dilute hydrofluoric acid is reacted with lime to form calcium fluoride.</p> <p>Calcium fluoride can also arise from fluidized bed fluorination reactors as a dry solid containing uranium and other non-volatile fluoride species, including relatively short lived radioactive decay products.</p>
Fluorination ash	This is material arises from reactor filters. It normally contains short lived decay products of uranium.
Distillation waste	Impurities resulting from the distillation of crude UF_6 at facilities where purification by solvent extraction is not employed. The impurities contain short lived decay products of uranium.
Process Filters	A range of filter materials are utilized within the direct chemical processes to process off-gas systems to ventilation systems. The materials include paper, cloths, porous carbon, plastics, and metals. The filter materials are normally contaminated with uranium to varying levels. Decontamination prior to disposal can significantly reduce the contamination levels.
Soft and solid materials including scrap metal	These materials include packaging, worn and redundant equipment, process paper documents, electronic equipment, etc. These materials may be contaminated with small quantities of uranium. The operators have a responsibility to minimize these materials by either reducing materials taken into the containment areas or by local decontamination and recovery of uranium.

TABLE 22. SUMMARY OF RADIOACTIVE WASTE MANAGEMENT PRACTICES

Conversion facilities	Raffinate	Solvent Extraction Treatment Waste	Calcium Fluoride	Ammonium Nitrate	Reactor Ash/Fluorspar (CaF ₂)	UF ₆ Distillation	Sodium Removal
Cameco	Concentrated and denitrated with the resulting product shipped to a mill for uranium recovery.	Drummed and shipped to a mill for uranium recovery.	The KF Process dries a continuous stream of scrubber solution to produce a KF salt that is recycled to a mill for uranium recovery.	None	None	None	None
Orano Chimie Enrichissement	To raffinate pond.	To radioactive waste treatment process for uranium recovery followed by disposal of remaining radioactive wastes	Drummed and disposed of at a permitted disposal site.	None	Recycled	None	None
Honeywell Metropolis Works	None.	None.	Disposed of at a permitted disposal site.	None.	Material is sent to a permitted facility where uranium is recovered.	Disposed of at a permitted disposal site.	Disposed of at a permitted disposal site. Effluent flows to settling ponds.

TABLE 22. SUMMARY OF RADIOACTIVE WASTE MANAGEMENT PRACTICES (CONT.)

Rosatom Chemical Plant)	(Siberian Chemical Plant)	Currently chemically treated and transferred to a national operator for disposal. In the future, after capacity for concentration and denitration is established, the resulting product will be shipped to a mill for uranium recovery.	Processing together with raffinates	None	After sorption purification it is used in the production of ammonia compounds	Recycled	None	None
Springfields Limited*	Fuel	None	None	None	None	None	None	None
<i>Practices for a potential restart are shown in italics</i>	<i>Heavy metal removal circuit, neutralization and monitored discharge to local estuary.</i>	<i>To local licensed radioactive waste disposal site.</i>	<i>To local licensed radioactive waste disposal site.</i>	<i>None</i>	<i>None</i>	<i>CaF₂ treated and uranium recycled. Residues to local licensed radioactive waste disposal site.</i>	<i>None</i>	<i>None</i>

* The UF₆ conversion facilities at Springfields have been shut down since 2014 and managed via a care and maintenance strategy. Westinghouse is developing plans to re-establish natural uranium conversion capability at Springfields from 2030 onwards.

7.4. SOURCES AND TYPES OF RADIOACTIVE WASTE AT UF₆ ENRICHMENT PLANTS

The main source of radioactive waste material at enrichment plants arises from UF₆ cylinder cleaning (see Figure 35) and plant component decontamination processes. These wastes are predominantly liquid solutions. They are treated, filtered and in some cases the uranium is recovered. Other radioactive wastes include solid chemical trap materials and scrubber solutions which are treated before discharge. It is considered necessary to recover as much enriched uranium as possible to avoid wasting valuable separative work.



FIG. 35. Cylinder cleaning (courtesy of TVEL).

Cylinder cleaning, often referred to as ‘cylinder washing’ is performed before cylinder recertification (see Section 4.6.8) can be safely carried out. There are two main internationally recognized types of UF₆ transport cylinders, as described in ISO 7195 [84] and ANSI N14.1 [85]:

- (i) Type 48Y – predominantly used for the transport of UF₆ with a ²³⁵U content of less than 0.95%;
- (ii) Type 30B – predominantly used for the transport of UF₆ with a ²³⁵U content of less than 5.00%²⁶.

Wastes from cylinder washing are considered in this section, although it is to be noted that this process is also carried out at some conversion and reconversion facilities.

²⁶ Note that ²³⁵U enrichments up to 6% can be transported with additional criticality assessment and controls. This includes the development of new cylinder and packaging variants for LEU+ and even HALEU (up to 20% ²³⁵U).

Chemical and water washes are employed to remove residual UF_6 and other impurities. The cylinders are thoroughly inspected both internally and externally, they are then pressure (strength) tested and finally leak tested after installation of new valves and plugs. At this point, the cylinder can be recertified for a further 5 years of operation.

Criticality safety is a major consideration for facilities handling and processing liquid and solid wastes, due to the levels of ^{235}U enrichment. Typical enrichments can range between 0.95% and 5% ^{235}U , but enrichments up to 20% ^{235}U are expected to become more prevalent, for example, products for LEU+ and HALEU fuel, i.e. Small Modular Reactors and advanced reactors. Criticality safety measures, including safe mass and geometry, along with moderator controls are required when handling wastes containing enriched uranium.

In addition, the facilities need to consider the prevention of long term deposition of uranium containing materials in process pipelines or valves. Effective liquid sampling and monitoring, and effective material balance accounting are to be completed to prevent the risk of nuclear criticality.

If the facility processes either natural or enriched uranium the external irradiation flux is not significant. However, special attention needs to be focused on recently emptied cylinders as radioactive decay products are residual in the small quantity of material left behind, known as the 'heel'. Initially, the decay products are concentrated and more problematic as the shielding effect of the parent uranium has been removed. Typically, this problem can be managed by a period of controlled decay, where operator working times are kept to a minimum. Depending on the quantity of radioactive decay products, the cylinders can usually be safely handled after 3–6 months of decay. It is to be noted that the problem is more significant for reprocessed uranium cylinders, where decay periods of up to 10 or 20 years could be envisaged.

Notwithstanding the special requirements for external radiation dose rates for cylinders, the main radioactive source term from a human health perspective when handling wastes at enrichment facilities is from loss of containment and contamination. Therefore, engineered controls are required to prevent elevated internal radiation dose rates for operators involved with handling such wastes. For further reading on methods for the management of liquid waste from conversion and enrichment facilities, see Appendix IV.

7.5. SOURCES AND TYPES OF RADIOACTIVE WASTE AT RECONVERSION PLANTS

The main sources of radioactive waste at UF_6 reconversion plants are filtrate from ammonium uranyl carbonate and ADU associated with wet processing for uranium recovery of scrap UO_2 products. Another source of ADU is liquid solutions from UF_6 cylinder cleaning as described in Section 7.3.

During dry reconversion processes, HF is recovered from off-gas recovery systems. The HF is in the form of hydrofluoric acid as water is typically introduced by either the process (as steam) or in scrubber systems. The hydrofluoric acid can be recycled into upstream processes in conversion, sold for non-nuclear use or neutralized. The hydrofluoric acid can be designated as non-radioactive as there is very little breakthrough of uranium is experienced. For further information on HF recovery and treatment from off-gas systems in conversion facilities, see Appendix I.

Filtrate, normally comprised of ammonium fluoride, is neutralized by means of lime to give ammonia hydroxide and calcium fluoride. Recovered ammonia is recycled to the process

precipitation stage for wet processes. Calcium fluoride with a small amount of uranium is directly stored or used for industrial purposes. If the hydrofluoric acid contains significant quantities of uranium, it can be removed, hydrofluoric acid is neutralized by lime to produce calcium fluoride. Calcium fluoride is either stored or reused.

More details on the properties and hazards of the above material can be found in Section 2 of this publication.

7.6. SOURCES AND TYPES OF NON-RADIOACTIVE HAZARDOUS WASTE

There are a variety of non-radioactive hazardous waste materials generated at facilities involved in the processing of UF₆. They can include packaging, redundant equipment, by-product chemicals and decontaminated materials. This section is not intended to encompass all these waste materials, it is included to introduce some of the hazardous wastes that operators have a duty of care to dispose of responsibly. Table 23 characterizes some of the most important hazardous non-radioactive waste²⁷.

TABLE 23. EXAMPLES OF IMPORTANT NON-RADIOACTIVE WASTES

Waste description (or by-product – see footnote 27)	Characterization
Hydrogen fluoride	Hydrogen fluoride is an inorganic compound with the chemical formula HF. It is a very toxic, colourless gas or liquid that dissolves in water to form a highly corrosive and toxic aqueous solution (hydrofluoric acid) and is a by-product of UF ₄ production and UF ₆ deconversion. It can be recycled, chemically neutralized, or sold for use in other industries.
Broken anodes from fluorine production	Anodes are generally made from carbon and need to be replaced. Broken anodes become a solid waste that is pretreated before disposal, as there is typically residual HF present.
Spent electrolyte from fluorine production	Electrolyte is typically based on liquid anhydrous HF added to potassium bifluoride(K[HF ₂]). At the end of its useful life, it is neutralized and separated, if possible, from uranic effluent steams, prior to disposal.
Hydrogen from fluorine production	Hydrogen is a by-product of fluorine production using electrolytic cells. It can be cleaned prior to discharge via flame traps or flaring. Alternatively, it is possible to recycle for use in upstream parts of the conversion process.
Nitrogen Oxides (NO _x) and nitric acid	NO _x is typically produced during the purification of UOC at conversion facilities, specifically during dissolution and denitration. It is possible to collect these materials via off-gas recovery systems and then to recycle a large proportion into the production process.

²⁷ It should be noted that in some cases the materials can be categorized as a by-product, i.e. they can be directly recycled into the production process or sold for use in other industries.

8. SAFETY ANALYSIS

8.1. PROCESS OF SAFETY ANALYSIS

Safety analysis is the

“Evaluation of the potential *hazards* associated with the operation of a *facility* or the conduct of an *activity*. The formal *safety analysis* is ... part of the systematic process that is carried out throughout the design process (and throughout the *lifetime* of the *facility* or the *activity*) to ensure that all the relevant *safety requirements* are met by the proposed (or actual) design” [125].

The process of safety analysis includes, in general, the following steps:

- (1) Identification of facility characteristics;
- (2) Identification of hazards and selection of PIEs;
- (3) Evaluation of event sequences;
- (4) Analysis of facility states;
- (5) Summary and conclusions.

More detailed information about these five steps is, respectively, provided in the following Sections 8.3 to 8.7.

Typically, the safety analysis process is conducted in an iterative manner with the design process such that the acceptable levels of safety and the classification of structures, systems or components in accordance with their importance to safety are completed, with iterations between the design and the analysis of safety performance. The level of detail and the scope of the safety analysis is expected to increase along with progression of the design such that the safety analysis addresses all new or changed aspects of the design. Conducting safety analysis alongside the design provides essential guidance for designing a new UF₆ facility or modifying the facility that already exists [126].

Before the safety analysis begins, certain preliminary activities need to be completed and documented. This is typically included in the introductory section of the safety analysis chapter of the safety analysis report (referred to as ‘the Introduction’ in the text below). These activities are briefly described below:

1. A statement of the objective of the safety analysis is established and presented in the Introduction;
2. Rules, methods and approaches used in the analysis are selected. UF₆ facilities follow a set of rules, methods and approaches which are established for fuel cycle facilities in general. Detailed description of those can be found in the IAEA Safety Reports Series No. 102, Safety Analysis and Licensing Documentation for Nuclear Fuel Cycle Facilities [126];
3. Safety analysis acceptance criteria are established. For example, acceptance criteria used for postulated off-site releases at UF₆ conversion facilities are to include uranium concentration, hydrogen fluoride concentration, and fluorine concentration for a specific duration of the exposure;
4. Methods used for identification and evaluation of hazards, and methods used for identification and selection of PIEs are established. Guidance on suitable methods can be found in Refs [127, 128]. The IAEA-TECDOC-1267, Procedures for Conducting Probabilistic Safety Assessment for Non-Reactor Nuclear

Facilities [129] provides information on conducting probabilistic safety assessment for nuclear fuel fabrication facilities. Table I.1 of Ref. [129] highlights the main differences between UF₆ facilities and nuclear reactors.

8.2. CONTENT OF THE ANALYSIS REPORT

SSR-4 [65] establishes specific requirements for the implementation of the general requirements for safety analysis that are established in IAEA Safety Standard Series No. GSR Part 4 (Rev. 1), Safety Assessment for Facilities and Activities [130]. In addition, further guidance is provided in the IAEA Safety Reports Series No. 102, Safety Analysis and Licensing Documentation for Nuclear Fuel Cycle Facilities [126]. SRS-102 [126] elaborates on the following requirements of SSR-4 [65], which are deemed to be the most relevant and important ones:

“Requirement 1: Licensing documentation

The operating organization shall demonstrate the safety of its facility through a set of documents known as the licensing documentation (or safety case). The licensing documentation shall provide a basis for the safety of the facility at all stages of its lifetime and shall be updated periodically, to take account of modifications made to the facility and other changes. The licensing documentation shall be considered by the regulatory body in determining whether the authorizations necessary under national legislative and regulatory requirements are to be granted.

.....

Requirement 14: Design basis for items important to safety

The design basis for items important to safety for a nuclear fuel cycle facility shall specify the necessary capability, reliability and functionality for the relevant operational states, for accident conditions and for conditions arising from internal and external hazards, to meet the specific acceptance criteria over the lifetime of the facility.

.....

Requirement 15: Internal hazards

All foreseeable internal hazards shall be identified and all facility conditions that could directly or indirectly affect safety shall be examined.

.....

Requirement 16: External hazards

All foreseeable external events, both individually and in credible combinations, shall be evaluated.

.....

Requirement 19: Postulated initiating events

Postulated initiating events, including human induced events, that could affect safety shall be identified and their effects, both individually and in credible combinations, shall be evaluated.

.....

Requirement 20: Design basis analysis

A comprehensive safety analysis shall be carried out in the design process for a nuclear fuel cycle facility. Systematic and recognized methods of deterministic analysis shall be used, complemented by probabilistic assessments where appropriate, in accordance with a graded approach. The purpose of the analysis shall be to ensure that the design provides an adequate level of safety and meets the required design acceptance criteria.

.....

Requirement 21: Design extension conditions

A set of design extension conditions shall be derived on the basis of deterministic analysis and engineering judgement with complementary probabilistic assessments (as appropriate), in accordance with a graded approach, to further improve the safety of the nuclear fuel cycle facility by enhancing its capabilities to withstand, without unacceptable consequences, accidents that are either more severe than design basis accidents or that involve additional failures. The design extension conditions shall be used to identify the additional accident scenarios to be addressed in the design and to plan practicable provisions for the prevention of such accidents or mitigation of their consequences.

.....

Requirement 22: Analysis of fire and explosion

The potential for external and internal fires and explosions shall be analysed and related potential initiating events shall be identified for use in the safety analysis. Specific controls required for fires and explosions shall be identified clearly.”

As discussed in IAEA Safety Report 102 [126], the suggested content of the safety analysis report for nuclear fuel cycle facilities (including UF₆ facilities) is outlined below:

1. Introduction and general description of the facility;
2. Site characteristics;
3. Safety objectives and general design requirements;
4. Processes and items important to safety;
5. Radiation protection;
6. Nuclear criticality safety;
7. Safety analysis;
8. Operational limits and conditions;
9. Conduct of operations;
10. Waste management and management of radioactive discharges;

11. Non-radiological hazards (Industrial safety);
12. Environmental impact assessment;
13. Commissioning programme;
14. Management system;
15. Emergency preparedness and response;
16. Preparation for decommissioning.

8.3. FACILITY CHARACTERISTICS

A summary of the facility parameters and characteristics such as pressure, temperature, flow rates, electrical power, as well as the range of operating conditions used in the analysis need to be presented in the safety analysis report. It is essential to include a comprehensive overview of the range of acceptable facility parameters, along with their tolerances and related uncertainties. Additionally, it is to include a description of the safety systems of the facility that are relevant to the safety analysis, particularly concerning event sequences and the range of allowable facility parameters [126].

8.4. IDENTIFICATION OF HAZARDS AND SELECTION OF PIEs

Adequate information about the known hazards in the facility needs to be identified and documented. Typically, UF₆ facilities deal with radiological, chemical, fire and industrial hazards. Examples of radiological or chemical hazards associated with UF₆ facilities include:

- UF₆ in gaseous, liquid or solid state in various production or storage stages;
- UF₆ in gaseous or liquid state in cylinders;
- HF and F₂ (fluorine) in gaseous or liquid state in production or storage areas;
- Hydrofluoric acid in tanks;
- Residual fluorine and fluorine fumes;
- UF₄ ash in drums.

Examples of other relevant chemical and physical hazards include:

- Glycol and freon in support systems;
- Hydrogen and nitrogen under high pressure;
- Carbonate wash for cylinder cleaning;
- Hydraulic oil and transmission fluid in heavy equipment;
- Fire and explosion hazards.

Additional information is available in SSG-6 (Rev. 1) [3] and SSG-5 (Rev. 1) [2].

Based on the identified hazards, a full list of the PIEs is expected to be developed and a justification for exclusion of any PIE from the assessment needs to be documented. The term ‘postulated initiating event’ (or simply ‘initiating event’) refers to an unintended event, including an operating error (within and external to the facility), equipment failure or an external influence, which directly or indirectly challenges basic safety functions. PIEs that are caused by naturally occurring events (e.g. seismic events, tsunami) are included based on criteria established by national or international standards. The PIEs that are excluded from further analysis are to be documented along with a justification of why they were not included in the list of PIEs. The following PIEs are examples of exemptions from further analysis:

- Low consequences events that are bounded by other PIEs;
- Non-credible events.

The information might additionally outline the description of how PIEs are grouped and the rationale behind this grouping. Additionally, it could also detail the process for identifying and selecting bounding (or limiting) events [126].

A generic list of PIEs for nuclear fuel cycle facilities can be found in the Appendix to SSR-4 [65]. A list of examples of PIEs for UF₆ facilities is provided in Appendix V of this publication.

8.5. EVALUATION OF EVENT SEQUENCES

An evaluation of event sequences is to be performed and documented. Detailed information on the consequences of selected PIEs typically includes identification of causes, sequence of events and facility safety system operations, including a detailed description of sequences, step-by-step from the initiation of the event till the final stabilization. Operators' actions in the course of event sequences are also to be included in the description.

8.6. ANALYSIS OF FACILITY STATES

A detailed analysis of facility states is to be presented, including the methods used to perform the safety analysis. The analysis covers the assessment of any physical parameters and phenomena relevant to the event sequence that may influence the facility's safety performance, as well as the physical barriers. It is essential to provide comprehensive estimates of the radiological source term and methods for assessing the toxicological or radiological impacts on the facility personnel, the surrounding community, and the environment for each facility state and each analysed accident. Furthermore, a detailed discussion of the exposure pathways and the models utilized to analyse the dispersion of released radioactive materials, as well as the subsequent exposure risks to both personnel and the public caused by the event, is to be included [126].

8.6.1. Anticipated operational occurrences

In accordance with defence in depth principle, the main objective of safety analysis of anticipated operational occurrences (AOOs) is "to verify that the facility's operational systems can prevent occurrences from evolving into accident conditions and that the facility can return to normal operation following an AOO" [126]. Thus, safety analysis of AOOs is to prove that "safety functions are performed adequately and the limits specified in the design basis for AOOs are not exceed" [126].

For UF₆ facilities, the following events could lead to AOOs (which depends on frequency of occurrence and the consequences):

- Loss of off-site power;
- Loss of compressed air;
- Loss of leak tightness of equipment;
- Handling errors such as a drop of a container with radioactive material;
- Loss of confinement or leakage;
- Loss of ventilation system;
- Equipment failure or malfunction which could lead to non-operability of a non-redundant system.

8.6.2. Design basis accidents

The main objective of safety analysis of design basis accidents (DBAs) is to confirm that “the risk of design basis accidents is acceptably low and that the likelihood of an accident has been minimized to the extent practicable” (para. 6.66 of SSR-4 [65]). As such, the purpose of safety analysis of DBAs is “to demonstrate that safety functions are performed adequately and limits specified in the design basis for DBAs are not exceeded” [126].

For UF₆ facilities, the following DBAs are typical [126]:

- Leakage/break of a UF₆ pipe;
- Explosion of reaction vessel;
- Explosion of a rotary kiln;
- Fire in a protected fire zone (fire compartment);
- Spillage of uranium powder;
- Collision of a motorized vehicle with a barrel of powder outside a factory building
- Collision involving a UF₆ cylinder;
- Drop of a storage container for radioactive waste from the maximum eligible height;
- Release of uranium after a natural disaster (e.g. earthquake, hurricane, tornado).

8.6.3. Design extensions conditions

The main objective of safety analysis of design extensions conditions is to demonstrate that the design of the facility is such that it is able to prevent accident conditions not considered as DBAs, or to mitigate their consequences as far as reasonably achievable (para. 6.73 of SSR-4 [65]).

For nuclear fuel cycle facilities (including UF₆ facilities), the following events are typically included in DEC:

- Credible events and event sequences that are outside of scope for DBA;
- Naturally induced events that are more severe than those included in DBA.

Further examples of DEC for nuclear fuel cycle facilities are provided in Annex IV of SSR-4 [65].

8.7. EVALUATION OF CONSEQUENCES AND COMPARISON AGAINST THE ACCEPTANCE CRITERIA

In this step of the safety analysis, consequences of analysed accidents are evaluated and documented. Typically, this part of the documentation includes:

- Descriptions of the bounding (or limiting) accident sequences and their consequences;
- Summaries of comparisons of the consequences against safety acceptance criteria;
- Key findings derived from the safety analysis;
- Assessment of the safety acceptance of the design of the facility, along with the sufficiency of the defined operational parameters and conditions.

This documentation could also provide information on possible improvements to the facility's structures, systems or components, and any administrative measures that could be established to improve safety.

Detailed information about evaluation of consequences and comparison against the acceptance criteria can be found in sections 3.5 and 3.6 of the IAEA Safety Reports Series No. 102 [126].

8.8. TOPICS FOR SAFETY ANALYSES FOR TRANSPORT

The principles, and the associated requirements to ensure safety and to protect people, property and the environment from harmful effects of ionizing radiation during the transport of UF₆, are set forth in national, regional and international regulations for the transport of dangerous goods, which are generally based on the Transport Regulations [59] published by the IAEA, and complemented by SSG-26 (Rev. 1) [54].

The basic principle is that protection against the dangers of radioactive material in transport is provided by the packaging in which it is carried. In the case of UF₆, packaging means the assembly of the cylinder, and additional protective mechanical and/or thermal equipment if applicable.

Information about the regulations applicable to the safe transport of UF₆ in the public domain and the packages that are used are provided in Section 5.

9. EMERGENCY PREPAREDNESS AND RESPONSE

9.1. GENERAL

The IAEA Safety Standards Series No. GSR Part 7, Preparedness and Response for a Nuclear or Radiological Emergency [131], establishes requirements for preparedness and response for a nuclear or radiological emergency. GSR Part 7 [131] states:

“The response to a nuclear or radiological emergency may involve many national organizations (e.g. the operating organization and response organizations at the local, regional and national levels) as well as international organizations. The functions of many of these organizations may be the same for the response to a nuclear or radiological emergency as for the response to a conventional emergency. However, the response to a nuclear or radiological emergency might also involve specialized agencies and technical experts. Therefore, in order to be effective, the response to a nuclear or radiological emergency has to be well coordinated, and emergency arrangements have to be appropriately integrated with arrangements for the response to a conventional emergency and with the response measures for a nuclear security event.”

Emergency arrangements need to be in place irrespective of the initiator of the emergency, which could be a natural event, a human error, a mechanical or other failure, or a nuclear security event. Organizations responsible for the management of emergencies (including conventional emergencies) recognize that good preparedness in advance of any emergency can substantially improve the emergency response. One of the most important elements of emergency preparedness is the coordination of arrangements among the different bodies involved to ensure clear lines of responsibility and authority.

9.2. BASIS

The IAEA Safety Standards Series No. GSG-2, Criteria for Use in Preparedness and Response for a Nuclear or Radiological Emergency [132] and IAEA Safety Standards Series No. GS-G-2.1, Arrangements for Preparedness for a Nuclear or Radiological Emergency [133] elaborate on the requirements established in GSR Part 7 [131] and provide recommendations and

guidance on their implementation. Guidance is provided by the IAEA Safety Standards Series No. GSG-11, Arrangements for the Termination of a Nuclear or Radiological Emergency [134] on the necessary arrangements to be implemented for the termination of a nuclear or radiological emergency. It describes the detailed conditions that need to be fulfilled before the authorities can formally announce the termination of an emergency and provides guidance on adaption and lifting protective measures.

In addition, IAEA Safety Standards Series No. SSG-65, Preparedness and Response for a Nuclear or Radiological Emergency Involving the Transport of Radioactive Material [99] provides guidance on planning and preparing for emergency response to transport accidents involving radioactive material.

9.3. SPECIFIC CONSIDERATIONS FOR UF₆ FACILITIES

9.3.1. Production, transport, handling and storage of UF₆

Hazards and precautions associated with UF₆, UO₂F₂ and HF are described in Sections 2.3 and 2.4. Data about HF toxicity is available in Section 2.3.3 ‘Hazards of hydrogen fluoride’. This includes emergency exposure limits (concentration in air, exposure time) which could be used as guidance in emergency planning as well as for making safety decisions (e.g. if risk analysis indicates that the exposure to the most exposed person can exceed the value provided, more stringent safety conditions would be required).

Serious events associated with fluorine leaks can pose serious consequences to health of personnel and environment. For conversion facilities where the fluorine is generated onsite, de-energizing the fluorine cell room is usually the initial mitigation for significant fluorine releases. In the event of fluorine release, the release area is evacuated, and emergency ventilation system is activated until the area is safer to entry. Entry into the area has to be avoided until fluorine concentration is low enough because high concentrations of fluorine may react with protective clothing. It is to be noted that typical fluorine production from electrolytic cells also contains about 5–7 vol.% gaseous HF as a result of the partial pressure from HF in the electrolyte.

When necessary, operating personnel is expected to wear respiratory equipment in addition to the personal protective equipment required for working around HF and UF₆. In addition, appropriate protective clothing has to be worn for routine operations to minimize the spread of radiological contamination.

It is essential that procedures are developed for emergency situations, which may cover for example handling accidents, equipment failures, fires or other natural disasters (e.g. earthquakes, floods, and storms), or man-made situations (accidental damage or intentional breaches of security, such as aircraft impact, vehicle damage, sabotage, theft). These procedures enables operators and emergency response personnel to respond to accidental material releases, from small leaks to major spills. Procedures to handle a nuclear criticality accident when dealing with enriched UF₆ are to be detailed.

System failures (leaks) in building areas where the process plant contains UF₆ at levels above atmospheric pressures immediately result in the release of UF₆ to the atmosphere and consequently result in airborne and surface contamination. UF₆ release detector systems are to be provided in these areas to warn operations personnel working in the area. Such detector systems are to actuate alarms locally (flashing light or audible, or both) and in the control room including on the operator interface control system.

Evacuation of individuals who lack proper training and protection is necessary in areas affected by the release. Personnel working in building areas where process plant contains UF₆ at above atmospheric pressures need to have defined escape routes and training for emergency situations. An example is a handrail installed to serve as a guide to direct personnel out of the immediate release area. In the case of cab operated cranes in those areas, respiratory masks and a means to egress is to be provided. In the event of a cylinder rupture or a UF₆ release, it is essential that the personnel without personal protective equipment promptly evacuate the area to avoid any contact with UF₆ or HF. Assembly points need to be established upwind of potential UF₆ release areas.

Where required, automatic systems are expected to be activated following a detected release of UF₆ to isolate parts of the facility affected in order to permit later cleanup of contaminated areas within the facility. In addition, cleaning the ventilation air while maintaining a negative air pressure inside the building section, will help to limit the spread of contamination to the environment. Local exhaust provision, e.g. fume extraction hoods need to be available during operations when UF₆ plant systems are opened; for example, after disconnection of UF₆ cylinders.

Respiratory protective equipment to be worn in emergency situations and needs to be available in areas where UF₆ or HF is processed. Entry into dense clouds of UF₆ during accident conditions requires the use of protective clothing and self-contained breathing apparatus capable of preventing inhalation of HF and particulates.

Availability of showers is necessary for skin decontamination (see Section 9.3.2). Similarly, the availability of eye wash stations is also necessary in case of eye contamination.

9.3.2. Skin protection and medical care

Skin protection via adequate personal protective equipment is necessary to prevent chemical burns. Appropriate methods, such as laundering, are to be used to decontaminate contaminated personnel clothing. To mitigate skin burns, the workers are to be provided with first aid and also with training that is specific to the job.

Medical advice is required immediately in case of serious contamination. Medical assistance is necessary in case of intrusive methods of decontamination, including removal of tissue.

Paragraph 9.52 of GSG-7 [69] states:

“Medical treatment of injuries takes precedence over radiological considerations. Emergency medical care should be administered immediately for wounds involving radionuclides. However, decontamination efforts should also be started immediately to prevent uptake of soluble radionuclides into the blood.”

With regard of conditions, there are several ways to remove uranium compounds on the skin. For example, when hands and other exposed skin are polluted, they can be repeatedly brushed with EDTA–Na₂ soap, soft brushes and lukewarm water until the contamination falls below the control level. Finally, skin can be covered by oil. If the skin is heavily contaminated, it can be washed with soap and clean water without delay to quickly remove large amounts of contaminant, but care is to be taken not to break the skin. Then the skin is further cleaned with proper methods according to practical conditions. Another direction for immediate medical care consists of continuously applying a 2.5% calcium gluconate until the doctor arrives. In the case of an open wound, the skin can be rinsed with a bicarbonate serum [135].

Any suspected skin contact with hydrofluoric acid needs to immediately be washed with continuously running clean water, followed by the application of calcium gluconate gel and prompt medical attention. In case of delayed detection of a suspected HF burn, it is recommended that all operators who work with HF or hydrofluoric acid, are provided with calcium gluconate gel for home use. The electrolyte used to generate fluorine is usually based upon $\text{KF} \cdot 2\text{HF}$. This is prepared by addition of liquid anhydrous HF to potassium bifluoride ($\text{K}[\text{HF}_2]$).

Anhydrous HF (boiling point 19.5°C), when in contact with skin, can result in serious skin burns and tissue damage. The longer the exposure and the thinner the skin, the more rapidly the lesions appear. The subsequent pain and white necrosis can be severe. Treatment for HF burns has been based upon injection of sterile 10% calcium gluconate or topical application of iced alcoholic/aqueous solutions of quaternary ammonium compounds. In general, ingestion of fluorides needs to be controlled because of toxicity.

9.3.3. Termination of UF_6 release

Wooden plugs (including tapered plugs), patches, crimpers, valve cappers, detection and alarm systems, and some type of cooling mechanism are expected to be available in areas where UF_6 or HF is processed. A UF_6 release may be terminated by using dedicated means available on the scene of the accident, such as towels, sponges, patches, and plugs depending on the pressure within the system.

If the hole or tear in a cylinder is small, the application of wet towels or sponges can plug the hole with hydrolysis products. This works for both solid and liquid UF_6 . Hydrolysis products will develop immediately and provide an effective plug sooner than by freezing the UF_6 . Also, the hydrolysis products will not melt.

For larger holes, the wooden plugs are designed to be inserted into holes that might occur as a result of broken or defective valves, line breakage, etc. Patches may be shaped to fit the contours of the UF_6 cylinders to seal a leak. In some circumstances, the release will be terminated by freezing the UF_6 at the leak in the system with appropriate cooling. This cooling is usually provided by a water stream. Water is never to be streamed directly into a cylinder opening. Dry ice or pressurized CO_2 from a large capacity source may be used safely to freeze off leaks. If the cylinder content is liquid, extended freeze off periods will be required. It is not practical to attempt to seal a large opening in a liquid UF_6 system.

When dealing with enriched UF_6 , nuclear criticality and safety evaluations are made beforehand to ensure the absence of unsafe accumulations of uranium.

Having the possibility to isolate drain and sewer systems from other general sewer systems is needed. Facilities need to be available to check or test for possible contamination of wastewater before disposal.

9.3.4. Water mitigation

With regards to the potential hazards associated with HF, and in the framework of applying the concept of defence in depth, one effective mitigation strategy used by industry is water mitigation (colloquially known as ‘water curtain’) in case of a large release of HF. Water mitigation reduces the consequences associated with a major accidental release of HF by using a copious amount of water in an effective spray pattern to remove airborne HF. To be effective, it is necessary to use sensors or other methods to identify an HF leak, and then quickly apply

water in sufficient quantities. A comprehensive and precise design of water systems is crucial and is to be undertaken by qualified professionals to address specific parameters of each site and unit, ensuring sufficient water-to-HF ratios for effective mitigation coverage [136].

In case the water curtain is used, there is a need to drain, contain and neutralize large volumes of contaminated water before sending it to treatment facilities. The facility needs to be designed accordingly.

APPENDIX I.

EXAMPLE OF PROCESSING OFF-GASES IN THE HYDROFLUORINATION PROCESSES IN CONVERSION FACILITIES

Like many chemical processes, the hydrofluorination of UO_2 to UF_4 can be forced to completion by an excess of the reagent HF. The higher the excess HF, the more scrubber solution will be consumed to meet the discharge limits for fluorides to the environment. This example looks at a method to measure the excess HF in the discharge gas in real time as means to control the excess with greater accuracy. The example also discusses alternatives of neutralizing versus recycling the excess HF in the off-gas. This example is based on operating experience around the Lit Courant reactors at Orano's Malvési Site.

I.1. OFF-GASES OF HYDROFLUORINATION PROCESS

The kinetics of the reaction in the hydrofluorination process require that the HF atmosphere be in excess to ensure that the reaction is complete. In most processes, off-gases of hydrofluorination contain a certain amount of HF. In earlier processes, the percentage of surplus HF could reach more than 100%, with the percentage of HF in off-gases even higher. Therefore, off-gas treatment of hydrofluorination process is extremely important. A good off-gases process (including recycling process) can have both economic and environmental benefits.

I.1.1. Real-time measurement of HF in off-gases

A key step in off-gas treatment is to accurately measure the content of HF in off-gas. In the past, the percentage of HF was measured by collecting samples of off-gases and then by measuring conductivity of the samples. This method was hardly instant, and it has been replaced by on-line analysis system of continuous measurement with new conductance method.

The core principle of for successful and rapid conductivity measurement is to condense the off-gases and measure the conductivity of the condensed fluid in order to determine the percentage of HF. The key in practice is to obtain an effective cold trap, which can rapidly and fully condense the off-gases above 200°C and which can resist the corrosion of HF.

The principles of the present continuous on-line measurement system are as follows:

- Off-gases are drawn by a vacuum system and continuously transferred into the condenser through the connecting valve;
- HF in the off-gases and water steam are condensed together into hydrofluoric acid;
- Incoagulable gases are separated by the gas-liquid separation system;
- The liquid phase enters the conductance cell to measure its conductivity and is collected into a collecting tank.

A well-designed continuous measuring system can measure hydrofluoric acid content in condensate with mass fraction of 6% to 28%, with a relative less than 10% error.

I.1.2. Treatment of off-gases and recycling of HF

In principle, there are two types of processing methods of off-gases from the hydrofluorination process. One is to directly neutralize HF with alkali solution, with most alkali solutions being KOH and NaOH solutions or, according to the process techniques, ammonia solution and carbolic solution. The other is to recycle HF.

1.1.2.1. Neutralization scheme

This routine is suitable for a system with low concentration of HF in off-gases. The direct neutralization of off-gases simplifies the production process of UF₄ and is relatively economical.

If the process for producing UF₄ from the raw material is not adequately controlled, it will be necessary to increase the quantity of fluorine in the process to make UF₆. This will cause more HF in the off-gases to be treated, more alkali solution (KOH or NaOH solution) to neutralize HF, and more final solid waste. Then, it is important to master the production process, in order to save fluorine for the production of UF₆, on the one hand and to reduce the quantity of off-gases to be treated as well as to reduce the amount of waste, on the other hand. Control of these factors will improve the economic and environmental benefits of the facility.

Neutralization is usually done in the shower tower, where the alkaline detergent enters from the top of the tower through a circulating pump and neutralizes with the off-gas coming in from the bottom of the tower. When the concentration of Fluoride ions in the detergent increases to a certain level, the fluoride is removed as CaF₂. The CaF₂ will contain measurable levels of uranium based on the steps used to treat the off-gas from hydrofluorination. The activity of the produced CaF₂ is extremely low and it can be disposed directly near surface or just buried.

1.1.2.2. Recycling scheme

The process objective of condensing HF from off-gases of the hydrofluorination reaction is to produce a constant boiling point mixture (azeotrope) of HF–H₂O with mass concentration of 38%. The anhydrous component of the recycled HF is returned into the hydrofluorination process by evaporating the constant boiling point mixture.

The difficulty in carrying out this plan is that the materials of the equipment (pipes, valves, etc.) of the recycling system needs to have good performance against corrosion by HF. Anhydrous HF can be treated in carbon steel equipment, but dilute hydrofluoric acid is very corrosive, especially around its boiling point (116°C).

Materials commonly used include Monel alloy (for high temperature but non-boiling equipment), resin impregnated graphite (impervious graphite) for gas-liquid conversion under boiling conditions (steam bubble towers, evaporators, etc), plastic and rubber for the lining of storage tanks, valves, and pipelines.

I.2. OFF-GASES OF DIRECT FLUORINATION PROCESS

When uranium oxides are directly fluorinated, off-gases often contain a large amount of oxygen and fluorine. In some UF₆ facilities, the off-gases go through a carbon reactor for absorption and then are treated with a shower of 5–10% sodium carbonate solution. The reaction between fluorine and carbon is intense because of the heat released and the presence of oxygen.

An alternative treatment is to absorb with CaHNaO₂ (soda lime). The structure of the adsorbing equipment is a cylindrical tower made of carbon steel. Soda lime is mounted on the porous plate at the bottom of the tower to form a fixed bed and covered by a copper mesh to prevent fine particles of sodium lime from spattering. A cooling water jacket is welded outside the adsorption tower to dissipate the resulting reaction heat. After adsorption, the gases can enter the exhaust air purification centre with the exhaust air of the workshop.

APPENDIX II.

SEPARATIVE WORK UNIT

Separative work unit (SWU) is the world recognized measure unit for enrichment work. Its amount characterizes the effort needed for production of enriched uranium with specific product assay from feed material under certain tails assay. Separative work unit has dimension of mass.

The amount of work $W(SWU)$ required to divide a feed mass F with an assay k_f into a product mass P with an assay k_p , and tails mass T with an assay k_t is defined by the expression:

$$W(SWU) = P \times V(k_p) + T \times V(k_t) - F \times V(k_f) \quad (8)$$

where $V(X)$ is the value function defined as $V(X) = (1 - 2 \times X) \times \ln [(1 - X) / X]$

Different feed quantity and SWU combination can be used to obtain the same amount of enriched uranium. Two examples can be found in Table 24 below considering a pressurized water reactor (PWR) of 1300 MWe using 25 t of uranium enriched to 3.75 % per year.

TABLE 24. COMPARISON OF FEED UF_6 AND SEPARATION WORK COMBINATION REQUIRED FOR THE PRODUCTION OF 25 TONS OF ENRICHED URANIUM (3.75% ^{235}U)

Example A	Example B
<ul style="list-style-type: none"> 210 t of natural uranium (percentage of ^{235}U of 0.711%) and 120 kSWU^a with percentage of ^{235}U in tails of 0.3% 	<ul style="list-style-type: none"> 174 t of natural uranium (percentage of ^{235}U of 0.711%) and 150 kSWU^b with percentage of ^{235}U in tails of 0.2%

^a 1 MSWU enrichment plant is able to enrich enough uranium for 8 PWR of 1300 MWe

^b 1 MSWU enrichment plant is able to enrich enough uranium for 6.6 PWR of 1300 MWe

One of the valuable features of the production of enriched uranium is the possibility of selecting the quantity of feed UF_6 with the required separation work (by selecting the tails assay). If the price of SWU compared to the price of feed UF_6 is cheaper, enrichers can use more separative work (by lowering the tails assay) and use less feed UF_6 to produce the same quantity of enriched UF_6 . If the price of feed UF_6 compared to the price of SWU is cheaper, enrichers can use more feed UF_6 and less separative work (by increasing the tails assay) to produce the same quantity of enriched UF_6 . Same replacements can also be used in case of a gap in separative capacity or shortage of feed UF_6 . Table 23 gives examples of needs of feed UF_6 and separation work to produce 1 kg of U of enriched UF_6 (3.75% ^{235}U).

TABLE 25. FEED UF_6 AND SEPARATION WORK REQUIREMENT FOR THE PRODUCTION OF 1 KG OF ENRICHED URANIUM (3.75% ^{235}U)*

Feed UF_6 (kgU)*	Separative work (SWU)	UF_6 tails assay (%)
7.0	5.91	0.2045
7.5	5.396	0.2434
8.0	5.029	0.2769
8.5	4.753	0.3058

* Unrecoverable losses during the production not taken into account.

APPENDIX III.

DEPENDENCE OF U-234 CONTENT ON ENRICHMENT AND INTRODUCTION TO METHODS FOR APPROXIMATION OF U-234 CONTENT

The following Figure 36 provides dependence of $^{234}\text{U}/^{235}\text{U}$ ratio in enriched UF_6 against its level of enrichment obtained using different product and tail enrichments (SWU quantity). For the same product assay, the higher the SWU (or lower tail assay) is used, the higher $^{234}\text{U}/^{235}\text{U}$ ratio in product UF_6 . Model provided by Shephard [43] summarized in Table 26 was used to obtain the Figure 36.

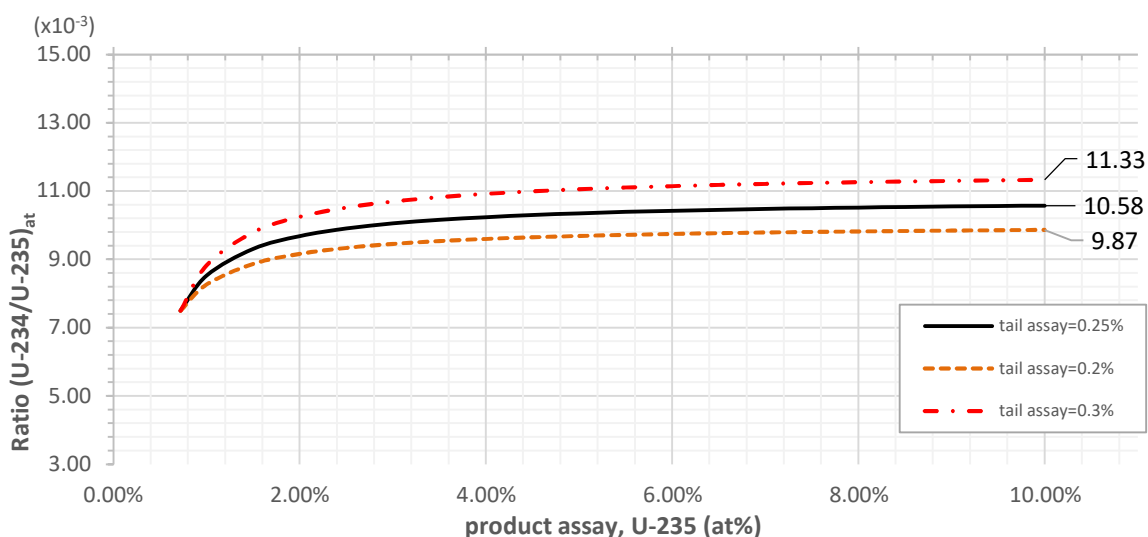


FIG. 36. U-234/U-235 ratio in enriched UF_6 obtained with different tail assay ($\text{U-234}_{\text{feed}}=0.0054\%$ and $\text{U-235}_{\text{feed}}=0.72\%$ atomic proportions).

The following Figure 37 provides dependence of $^{234}\text{U}/^{235}\text{U}$ ratio in depleted UF_6 against its enrichment level obtained using different product and tail enrichments (SWU quantity). For the same assay in depleted UF_6 , the higher the SWU (or higher product assay) is used, the lower U-234/U-235 ratio in depleted UF_6 . Model provided by Shephard [43] summarized in Table 26 was used. Table 26 summarizes list of different models found in literature.

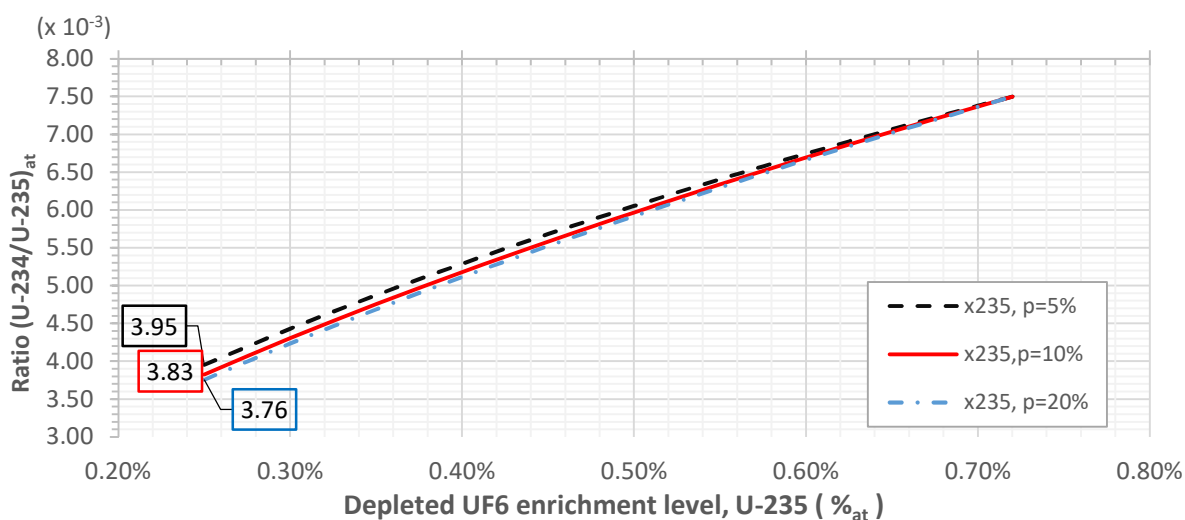


FIG. 37. U-234/U-235 ratio in depleted UF_6 resulted after enrichment of products with different assay ($\text{U-234}_{\text{feed}}=0.0054\%$ and $\text{U-235}_{\text{feed}}=0.72\%$ atomic proportions).

TABLE 26. U-234 FRACTION AND U-235/U234 RATIO MODELS

Model	
K/PO/SUB-79/31057/1^{a,b,f} [137]	$\frac{w_{235}}{w_{234}} = 102.2 + 21.7235/(w_{235} \cdot 100\%)$ (9)
K/HS/593^{a,d,f} [138]	$(w_{234} \cdot 100\%) = 0.0015 + 0.0058 \times (w_{235} \cdot 100\%) + 0.000054 \times (w_{235} \cdot 100\%)^2$ (10)
Solov'ev et al.^{a,b,f} [139]	$x_{234,P} = x_{234,F} \left(\frac{x_{235,P} - x_{235,W}}{x_{235,F} - x_{235,W}} \right) / \left\{ 1 + \left[\left(\frac{1 - x_{235,F}}{x_{235,F}} \right)^{5/3} - \left(\frac{1 - x_{235,W}}{x_{235,W}} \right)^{5/3} \right] / \left[\left(\frac{1 - x_{235,F}}{x_{235,F}} \right)^{5/3} - \left(\frac{1 - x_{235,P}}{x_{235,P}} \right)^{5/3} \right] \right\}$ (11)
BJC/OR-2862^{a,c,e} [140]	$\frac{w_{235}}{w_{234}} = \frac{157.72237 - 155.6896 \times (w_{235})^{0.5}}{1 - 0.95152907 \times (w_{235})^{0.5}}$ (12)
DOE-STD-1136-2017^{a,d,f} [39]	$w_{234} = 1.2 \times \frac{w_{234,F}}{w_{235,F}} \times w_{235}$ (13)
Shephard et al.^a [43]	$x_{234,P} = x_{234,F} \frac{x_{235,P}}{x_{235,F}} \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,P}}{1 - x_{235,P}} \right] / \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,W}}{1 - x_{235,W}} \right] \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,P}}{1 - x_{235,P}} \right]^{5/3} - 1$ (14a)
	$x_{234,W} = x_{234,F} \frac{x_{235,W}}{x_{235,F}} \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,W}}{1 - x_{235,W}} \right] / \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,P}}{1 - x_{235,P}} \right] \left[1 + \frac{x_{235,F}}{1 - x_{235,F}} \frac{x_{235,W}}{1 - x_{235,W}} \right]^{5/3} - 1$ (14b)

^a w_i and x_i are weight and atom fraction, respectively.^b applicable to w_{235} greater than 0.711 wt% ^{235}U or x_{235} greater than 0.720 at% ^{235}U .^c applicable to w_{235} greater than 20 wt% ^{235}U .^d applicable range not specified or known.^e uncertainty specified at $\pm 10\%$ (relative at 95% confidence).^f no uncertainty specified.

APPENDIX IV.

INTRODUCTION TO METHODS FOR THE MANAGEMENT OF LIQUID WASTE FROM CONVERSION AND ENRICHMENT

UF₆ conversion and enrichment operations generally produce liquid waste containing fluorine and uranium. Gaseous effluents are treated by wet scrubber systems, which also contributes to these liquid wastes. The beta and gamma activity of the liquid waste produced is generally low and manageable. However, non-volatile fluorides of uranium decay products evolving from the fluorination step (UF₄ to UF₆) and UF₆ cylinder vaporization steps, are notable radioactive exceptions. These materials are typically decayed for a short period to reduce activity before processing to enable uranium recovery or onward disposal.

Due to the uranium and fluorine content, ammonia, nitric acid, and other substances are widely used to recover and treat the waste. The resultant liquid effluent needs to be properly handled and disposed of. The uranium elements are recovered as much as possible within an overall sustainability assessment. The fluorine is expected to be chemically complexed to avoid adverse effects on the environment.

In general, most of the uranium-containing waste produced by chemical processing of UF₆ are aqueous solutions. Some processes utilize a solvent extraction step that will produce an amount of organic phase containing some uranium. To protect the environment and reduce operating costs, the uranium is generally recovered by distillation or precipitation, and most of the organic solvents (TBP, sulfonated kerosene) are recovered and reused.

A small amount of liquid phase enriched with most radioactive decay products and impurity ions can be sent to a calcining process to reduce the volume of waste. The incineration off-gas can be filtered to reduce the volume of material containing radionuclides and yield a manageable solid fraction of radionuclides. Currently, chemical precipitation methods and evaporation-ion exchange methods are widely used to achieve this purpose.

The chemical precipitation method is a robust and industry accepted method for the treatment of fluoride bearing liquid effluents from UF₆ processes. The principle is to utilize the insolubility of calcium fluoride to precipitate the fluoride ion (F⁻) to form calcium fluoride by adding flocculant (such as calcium hydroxide, etc.) to the effluent containing uranium and fluorine. This approach generally requires pretreatment, including adjusting the ionic composition in the effluent, for example, removal of ammonia. Following pretreatment, a flocculant is added to complete the precipitation through gentle stirring, and then the solid components are separated from the liquid phase through press filtration. Once the removal of F⁻ and uranium ions is achieved to within specific discharge limits, the effluent can be evaporated and concentrated to further reduce emissions.

Chemical precipitation is a mature technology with the advantage that is relatively simple and robust in that it can treat effluent containing a wide range of uranium and fluorine concentrations. The lifecycle cost of the technology is manageable, assuming that the materials of construction are carefully employed to meet the specific chemistry of the effluents being processed. Additionally, it is necessary to assure that the correct process is chosen, suspended solids, biochemical oxygen demand and other species limits can be met within the requirements of local regulations.

Shortcomings of deploying chemical precipitation include low to medium decontamination efficiency and the generation of radioactive precipitation filter cakes. The solid cakes require

appropriate treatment, conditioning and disposal. In addition, the technology is not readily conducive to the recovery of uranium with more than 0.95% ^{235}U , where criticality controls will limit throughput. This limits its use in facilities handling higher enriched uranium.

It is feasible to utilize precipitation-based methods for the abatement of liquid effluent from facilities handling enriched uranium. However, safe mass, geometry or moderator controls are required to guard against criticality. Another option for effluent treatment in facilities handling enrichment levels above natural uranium is pressure-driven membrane separation treatment. For example, cylinder washing effluent undergoes microfiltration and ultrafiltration to recover materials and remove pollutants with a step-by-step method. For facilities with higher enrichment, more advanced membrane treatment methods such as nanofiltration and reverse osmosis can be considered to better recover the valuable uranic compounds.

In summary, the chemical, physical, radioactive, and biological properties of the effluent need to be considered when designing any of the above effluent treatment processes. The relative advantages and disadvantages liquid waste treatment methods is captured in Table 27.

TABLE 27. ADVANTAGES AND DISADVANTAGES OF TREATMENT METHODS FOR LOW AND MEDIUM LEVEL RADIOACTIVE LIQUID WASTES IN UF_6 CONVERSION AND ENRICHMENT FACILITIES

Treatment Method	Description including relative advantages
Chemical precipitation	<p>Compounds of radionuclides including hydroxides, phosphates, carbonates, etc. in liquid waste are mostly insoluble. Therefore, chemicals are added to precipitate the radionuclides as solids in suspension for traditional filtration separation from the liquid phase, or as pretreatment for the other methods in this table or volume reduction.</p> <p>This method can be used for treating large volumes of low level waste. The advantages of this method are that it has a wide range of applications, is suitable for most facilities, is a mature and inexpensive method. The disadvantages are that the decontamination efficiency is not high and the resulting radioactive precipitate sludge requires further treatment and conditioning to make suitable for disposal.</p> <p>When working with reprocessed uranium during conversion, enrichment and reconversion, several challenging radioactive isotopes, such as ^{208}Tl (daughter of ^{232}U and ^{228}Th) and ^{237}Np are typically present.</p>
Evaporation	<p>A treatment method involving heating and boiling liquid waste containing radionuclides that are difficult to precipitate and non-volatile, to reduce the volume of liquid. In principle, an evaporator vessel is used to heat the liquid phase, which evaporates and then condenses to collect and discharge, and the soluble radionuclide salts remain in the distillation residue. The resulting evaporator concentrate (also known as evaporator bottoms) needs further treatment, conditioning to make suitable for disposal.</p> <p>The advantage is that the radionuclide removal efficiency is very high, especially in the case of complex types. It is also relatively simple to operate, flexible and can be used alone or in combination with other methods. It is also a mature technology.</p> <p>The disadvantage is that the energy consumption is very high, at more than 20 times that of chemical precipitation. It is not suitable for liquid waste containing volatile components, wastewater containing more organic matter, and wastewater containing scaling, corrosive, and explosive substances, and these components need to be removed in advance.</p>

TABLE 27. ADVANTAGES AND DISADVANTAGES OF TREATMENT METHODS FOR LOW AND MEDIUM LEVEL RADIOACTIVE LIQUID WASTES IN UF₆ CONVERSION AND ENRICHMENT FACILITIES (CONT.)

Treatment Method	Description including relative advantages
Ion exchange	<p data-bbox="475 309 1398 517">Ion exchange method is one of the most widely used chemical separation methods in chemical industry. It is becoming more prevalent in the nuclear industry, due to the development of new, radiation-stable ion exchange resins. A unique benefit of ion exchange processing is the ease of recovery of nuclides, making it particularly suitable for concentrators that require recovery of valuable enriched uranium.</p> <p data-bbox="475 533 1398 703">The ion exchange method typically requires a pre-treatment to remove suspended solids to prevent interference on the surface of resin, which would otherwise render the process inefficient. In addition, the total salt content and non-electrolyte content in the liquid waste should not be too high, otherwise the ion exchange efficiency will be greatly reduced.</p> <p data-bbox="475 719 1398 792">The spent ion exchange resins require further treatment and conditioning prior to disposal.</p>
Membrane	<p data-bbox="475 808 1398 882">This method employs polymer semipermeable membranes for liquid-phase nuclide separation.</p> <p data-bbox="475 898 1398 1137">Advantages include low energy consumption, small particle sizes can be targeted, suitability for azeotropic systems and maintenance is relatively easy. Additionally high decontamination rates can be achieved, and volume reduction effect is good. In most cases, membrane separation if properly combined with other conventional separation technologies, good treatment outcomes can be achieved. The resulting separated radionuclides need conditioning to put in a form suitable for disposal.</p> <p data-bbox="475 1153 1398 1249">At present, the membrane treatment devices used in nuclear industry facilities mainly use pressure difference driven membranes, such as reverse osmosis, nanofiltration, ultrafiltration, microfiltration, etc.</p> <p data-bbox="475 1265 1398 1469">When using the membrane treatment process, it is necessary to pay attention to the operational performance of the membrane to prevent sedimentary contamination and the membrane from being compacted. Continuously monitoring of operational performance using computer-aided analysis of the daily data can be employed to focus maintenance activities and system efficiency.</p>

In nuclear fuel cycle facilities, the amount of radioactive organic waste produced is relatively small. These wastes are managed by accounting for not only radioactivity, but also chemical toxicity, and flammable and explosive properties. Nuclear fuel cycle facilities are rarely equipped with equipment for the treatment of a large volume of organic waste liquids. Such materials are generally temporarily stored and treated in special tertiary waste treatment facilities after accumulating to a certain amount. Radioactive waste disposal facilities limit organic material due to its potential to degrade, generate flammable gases, compromise waste stability, and mobilize radionuclides, posing safety and containment risks.

The main sources of radioactive organic waste liquid are generally oil, TBP and its diluent from mechanical components such as pumps, and other lubricated equipment.

The principle of temporary storage is that waste liquids with different chemical compositions are stored separately and waste liquids containing short lived nuclides are not mixed with waste liquids containing long lived nuclides.

APPENDIX V.

EXAMPLES OF POSTULATED INITIATING CONDITIONS

A generic list of selected PIEs for nuclear fuel cycle facilities can be found in the Appendix to SSR-4 [65].

The following PIEs may be relevant to production, handling or storage of UF₆:

- Spills or releases:
 - UF₆ gas release;
 - HF release;
 - HF liquid spill;
 - Uranium emissions;
 - Fire / Explosion;
 - Hydrogen leaks or explosions;
 - Fluorine gas release;
 - Freon release to water or air;
 - Spills of caustic contaminated liquid;
 - Contaminated liquid spills.
- Accidents involving failure of process systems, scrubbers, or on-site support and miscellaneous systems including utilities, power supply, waste recovery operations, liquid hydrogen or liquid nitrogen supply systems.

The following PIEs may be relevant to the on-site transport of UF₆:

- Chemical spills to roads, site areas, the environment, of substances such as:
 - UF₆;
 - Anhydrous HF;
 - Hydrogen;
 - HCl;
 - Potassium fluoride by-product containing traces of radionuclides.
- Rupture or leak of transmission, hydraulic or other fluids from heavy equipment.
- Fires or explosions associated with:
 - Diesel fuel;
 - Gasoline.

Further information related to selection of PIEs can be found in IAEA Safety Reports Series No. 102 [126].

Postulated initiating events that have to be considered during off-site transport are described in the Transport Regulations [59].

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ANNEX

DEFINITIONS OF ERPG AND AEGL LEVELS

TABLE 28. AMERICAN INDUSTRIAL HYGIENE ASSOCIATION ERPG LEVELS [A-1]

ERPG-1	the maximum airborne concentration below which nearly most people could be exposed for up to one hour without experiencing more than mild, transient adverse effects, or without perceiving a clearly defined odour.
ERPG-2	the maximum airborne concentration below which nearly most people could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
ERPG-3	the maximum airborne concentration below which nearly most people could be exposed for up to one hour without experiencing or developing life-threatening health effects.

TABLE 29. NATIONAL ADVISORY COMMITTEE FOR ACUTE GUIDELINE LEVELS FOR HAZARDOUS SUBSTANCES AEGL LEVELS [A-1]

AEGL-1 (Non-disabling)	the airborne concentration (expressed as parts per million or milligrams per cubic meter [ppm or mg/m ³]) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
AEGL-2 (Disabling)	the airborne concentration (expressed as ppm or mg/m ³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long lasting adverse health effects or an impaired ability to escape.
AEGL-3 (Lethality)	the airborne concentration (expressed as ppm or mg/m ³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

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GLOSSARY

The following definitions based on the IAEA Nuclear Safety and Security Glossary. Terminology Used in Nuclear Safety, Nuclear Security, Radiation Protection and Emergency Preparedness and Response. 2022 (Interim) Edition.

acceptance criteria. Specified bounds on the value of a functional indicator or condition indicator used to assess the ability of a structure, system or component to perform its design function.

activity. The quantity A for an amount of radionuclide in a given energy state at a given time, defined as:

$$A(t) = \frac{dN}{dt}$$

where dN is the expectation value of the number of spontaneous nuclear transformation from the given energy state in the time interval dt . See also “radioactivity”.

anticipated operational occurrence. A deviation of an operational process from normal operation that is expected to occur at least once during the operating lifetime of a facility but which, in view of appropriate design provisions, does not cause any significant damage to items important to safety or lead to accident conditions.

Note - Examples of anticipated operational occurrences are loss of normal electrical power and faults such as a turbine trip, malfunction of individual items of a normally running plant, failure to function of individual items of control equipment, and loss of power to the main coolant pump.

baghouse. A filtration system used in nuclear fuel cycle facilities to capture and remove particulate matter from air or gas stream.

design basis accident. A postulated accident leading to accident conditions for which a facility is designed in accordance with established design criteria and conservative methodology, and for which releases of radioactive material are kept within acceptable limits.

design extension conditions. Postulated accident conditions that are not considered for design basis accidents, but that are considered in the design process of the facility in accordance with best estimate methodology, and for which releases of radioactive material are kept within acceptable limits.

Note – Design extension conditions comprise conditions in events without significant fuel degradation and conditions in events with melting of the reactor core.

event. Any occurrence unintended by the operator, including operating error, equipment failure or other mishap, and deliberate action on the part of others, the consequences or potential consequences of which are not negligible from the point of view of protection and safety.

postulated initiating event. A postulated event identified in design as capable of leading to anticipated operational occurrences or accident conditions.

Note - The primary causes of postulated initiating events may be credible equipment failures and operator errors (both within and external to the facility), human induced events or natural events.

radioactivity. The phenomenon whereby atoms undergo spontaneous random disintegration, usually accompanied by the emission of radiation.

In this publication, radioactivity refers to the phenomenon, and activity refers to the physical quantity or to an amount of a radioactive substance.

safety analysis. Evaluation of the potential hazards associated with the operation of a facility or the conduct of an activity.

Note - The formal safety analysis is part of the overall safety assessment; that is part of the systematic process carried out throughout the design process (and throughout the lifetime of the facility or the activity) to ensure that all the relevant safety requirements are met by the proposed (or actual) design.

ullage. The volume for gas above the liquid in a container.

LIST OF ABBREVIATIONS

ADU	ammonium diuranate
AEGL	Acute Exposure Guideline Levels
AHF	anhydrous hydrogen fluoride
ALI	annual limits on intake
AMAD	activity median aerodynamic diameter
ANSI	American National Standards Institute
AOO	anticipated operational occurrence
ASTM	American Society for Testing and Materials
CSI	criticality safety index
DBA	design basis accident
DEC	design extensions condition
ERPG	Emergency Response Planning Guidelines
HALEU	high-assay low enriched uranium
ICRP	International Commission on Radiological Protection
ISO	International Organization for Standardization
TBP	tri-n-butyl phosphate
LEU	low enriched uranium
LEU+	low enriched uranium (from 5 to 10%)
LSA	low specific activity
PIE	postulated initiating event
SWU	separative work unit
UN	United Nations
UOC	uranium ore concentrate

CONTRIBUTORS TO DRAFTING AND REVIEW

Amamoto, I.	Power Reactor and Nuclear Fuel Development Corporation, Japan
Biaggio, A.	Comisión Nacional de Energía Atómica, Argentina
Dekker, B. G.	Urenco Nederland Operations, Kingdom of the Netherlands
Didyk, J. P.	Atomic Energy Control Board, Canada
Finucane, J. S.	International Atomic Energy Agency
Hayes, T. J.	British Nuclear Fuels, United Kingdom
Henson, H.	Oak Ridge National Laboratory, United States of America
Hirasawa, T.	Japan Nuclear Fuel Industries, Japan
Jakobsen, G.	ABB-ATOM, Sweden
Kos, H.	COGEMA-Pierrelatte, France
Onishi, A.	Japan Nuclear Fuel Industries, Japan
Pchelkin, V. A.	Ministry of Atomic Power & Industry, Union of Soviet Socialist Republics
Rojas, J. L.	International Atomic Energy Agency
Sykes, W. E.	Paducah Gaseous Diffusion Plant, United States of America
Tanaka, R. T.	Eldorado Resources Limited, Canada
Tokarenko, A. I.	All-Union Scientific and Planning Institute of Complex Power, Union of Soviet Socialist Republics
Tsuruno, H.	Japan Nuclear Fuel Industries, Japan
Yoneta, R.	Japan Nuclear Fuel Industries, Japan
Yoshikawa, K.	Mitsubishi Heavy Industries, Japan

Contributors to drafting and review for Revision 1

Belyakov, O.	International Atomic Energy Agency
Charette, M.-A.	Cameco, Canada
Chesher, D.	Cameco, Canada
Darras, F.	Orano, France
Derbyshire, D.	Westinghouse, United Kingdom
Desnoyers, B.	Orano, France
Dong, B.	China Atomic Energy Authority, China
Dronishinets, A.	TENEX, Russian Federation
Efremov, G.	International Uranium Enrichment Center, Russian Federation
Fernando, A.	Cameco, Canada
Good, C.	International Atomic Energy Agency
Gusev, A.	TVEL, Russian Federation

Hansen, S.	TAM International, United States of America
Indyk, S.	TVEL, Russian Federation
Khotylev, V.	Canadian Nuclear Safety Commission, Canada
Kruehler, J.	Urenco, Germany
Kudoyarova, O.	TENEX, Russian Federation
Kultayev, Y.	International Atomic Energy Agency
Malesys, P.	Consultant, France
Milanole, G.	Orano, France
Moldovan, B.	International Atomic Energy Agency
Novokshonov, K.	TVEL, Russian Federation
Okyar, B.	International Atomic Energy Agency
Plessy, O.	Orano, France
Reber, E.	International Atomic Energy Agency
Robins, R.	International Atomic Energy Agency
Schelkanov, V.	TENEX, Russian Federation
Tovstenko, A.	TENEX, Russian Federation
Valiveti, L.	International Atomic Energy Agency
Whitaker, M.	Oak Ridge National Laboratory, United States of America

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