

Proceedings of the Nuclear Energy Agency International Workshop on Chemical Hazards in Fuel Cycle Facilities Nuclear Processing

Appendix C

The non-radiological risks involving dangerous chemicals in nuclear fuel cycle facilities

- French framework regulation -

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Accidents involving hazardous chemicals pose a significant threat to the population and the environment. Among nuclear facilities, this threat applies in particular to the fuel cycle facilities. As a consequence, the activities related to hazardous chemicals are covered by a legal framework that, depending on the nature of the activity and the associated risks, aims to guarantee that, they will not be likely to be detrimental to safety, public health and environment [1].

The aim of this article is to present a summary of the main regulations involving dangerous chemicals in nuclear fuel cycle facilities that have to be taken into account in the safety demonstration. The latter must prove that the risks of an accident - radiological or not - and the scale of its consequences, given the current state of knowledge, practices and the vulnerability of the installation environment, are as low as possible under acceptable economic conditions.

Key words : nuclear fuel cycle facilities, safety demonstration, principle of defence in depth, deterministic approach, probabilistic approach, dangerous chemicals, non-radiological risks, Seveso Directive, domino effects.

1. THE DANGEROUS SUBSTANCES IN NUCLEAR FUEL CYCLE FACILITIES

1.1. List of main fuel cycle facilities

In France, **the nuclear fuel cycle** includes uranium conversion, uranium enrichment, fuel manufacturing and fuel reprocessing facilities [2]. These facilities are different from each other, each concerning a different stage of the nuclear fuel cycle. The list of these facilities (both manufacturing and reprocessing facilities) and their locations are shown in Figure 1.

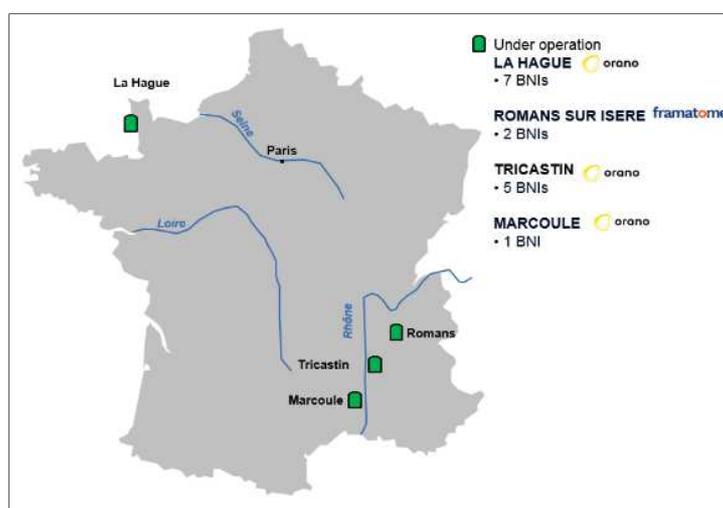


Figure 1 : location of main fuel cycle facilities

In general, these are subject to the order of the 7 february 2012 setting the general rules relative to basic nuclear installations (BNI) [3]. It provides the general rules that can be applied to the design, construction,

operation, final shutdown, dismantling, maintenance and monitoring of BNI, to protect the interests mentioned in article L. 593-1 of the Environmental Code (public security, health and safety, protection of nature and of the environment).

The licensee has to provide a **safety demonstration** which must prove that the risks of an accident - radiological or not - and the scale of its consequences, given the current state of knowledge, practices and the vulnerability of the installation environment, are as low as possible under acceptable economic conditions.

According to the article 3.1 of the order of the 7 february 2012 [3], the safety demonstration is based on **the principle of defence in depth** (Figure 2) “*which consists in deploying successive and sufficiently independent levels of defence aiming, with regard to the licensee, at :*

- *preventing incidents ;*
- *detecting incidents and applying measures that will firstly prevent them from leading to an accident, and secondly restore a normal situation or, in case of failure, place and maintain the installation in a safe condition ;*
- *controlling accidents that cannot be avoided or, in case of failure, limit their severity by regaining control of the installation in order to return it to and maintain it in a safe condition ;*
- *managing accident situations that could not be controlled so as to mitigate the consequences, especially for humans and the environment”.*

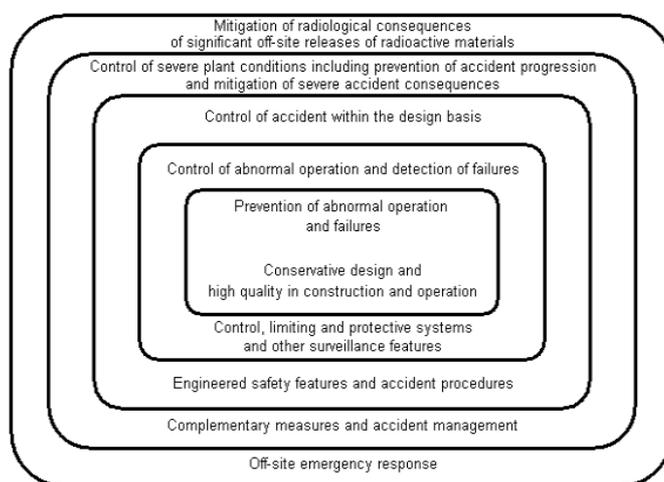


Figure 2 : the defence in depth concept (International Nuclear Safety Advisory Group)

Other internal hazards mentioned in article 3.5 of the order of the 7 february 2012 [3] to be considered in the safety demonstration include : fires, explosions, hazardous substance emissions. The BNI where **dangerous chemicals** may be present in quantities exceeding a certain threshold can lead to an accident such as a toxic emission, a fire, or an explosion resulting from uncontrolled developments during an operation of any BNI, and consequently may give rise to the need for specific safety requirements in addition to nuclear safety requirements.

The implementation of the safety demonstration concerning non-radiological risks involving dangerous substances has to be in line with the **Seveso Directive**¹ whose purpose is to prevent and control such accidents. The Directive was transposed into the French regulation.

Depending on the quantities of dangerous substances listed in the first appendix (**Part 1** - Dangerous substances or **Part 2** - Named substances) to Seveso Directive, the BNI or the establishments including several BNI in the whole location under the control of the same licensee, are categorized in :

¹ The Seveso Directive (Directive 82/501/EEC) was amended in view of the lessons learned from later accidents such as Bhopal, Toulouse or Enschede resulting into Seveso-II (Directive 96/82/EC). In 2012 Seveso-III (Directive 2012/18/EU) was adopted taking into account, amongst others, the changes in the Union legislation on the classification of chemicals and increased rights for citizens to access information and justice.

- no Seveso ;
- lower tier Seveso ;
- upper tier Seveso.

1.2. Part 1 of the first appendix to Seveso Directive : categories of dangerous substances

Dangerous substances covered by the hazard categories are listed in Column 1 of Part 1 of the appendix to Seveso Directive. These are subject to the qualifying quantities set out in Columns 2 (Low tier) and 3 (Upper tier) of Part 1. An excerpt is shown on Figure 3.

Column 1	Column 2	Column 3
Hazard categories in accordance with Regulation (EC) No 1272/2008	Qualifying quantity (tonnes) of dangerous substances as referred to in Article 3(10) for the application of	
	Lower-tier requirements	Upper-tier requirements
HEALTH HAZARDS		
ACUTE TOXIC Category 1, all exposure routes	5	20
ACUTE TOXIC — Category 2, all exposure routes — Category 3, inhalation exposure route (see note 7)	50	200
STOT SPECIFIC TARGET ORGAN TOXICITY – SINGLE EXPOSURE STOT SE Category 1	50	200
PHYSICAL HAZARDS		

Figure 3 : excerpt of the Annex I (Part 1)

The dangerous substances referred to in the first appendix (Part 1) of the Seveso Directive are from the European regulation EC n° 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures, called the “CLP Regulation”. The latter aligns the previous EU legislation with the GHS (Globally Harmonised System of classification and labelling of chemicals), a United Nations system used to identify hazardous chemicals and inform users about these hazards. It also has links to the European regulation EC n° 1907/2006 on Registration, Evaluation, Authorization and Restriction of Chemicals, called “REACH legislation”.

The hazards of chemicals are communicated through a standard hazard statement. Hazard statement means a statement assigned to a hazard class and category that describes the nature of the hazards of a hazardous substance or mixture, including, where appropriate, the degree of hazard.

A code, starting with the letter H and followed by 3 digits is designated for each hazard statement :

- H2xx : physical hazards ;
- H3xx : health hazards ;
- H4xx : environmental hazards.

The hazard statement linked to Part 1 of Annex 1 is on Figure 4.

Hazard	H statement	
Physical	200, 201, 202, 203, 204, 205 (Explosives) 220, 221, 222, 223, 224, 225, 226 (Flammable) 240, 241, 242, 250, 260, 270, 271, 272 (Self reactive/pyrophoric/in contact with water, emit flammable gases/Oxidizing) 014, 029 (Reacts violently with water., contact with water liberates toxic gas)	 GHS01  GHS03  GHS02
Health	300, 301, 310, 330, 331, 370	 GHS06
Environment	400, 410, 411	 GHS09

Figure 4 : hazard statement linked to Seveso Directive

Many substances stored, used or produced in the fuel cycle facilities are subject to the Seveso Directive. For example, hydrofluoric acid present in the BNI is shown in Figure 5.

Hydrofluoric acid (UF6)		
H300	Acute Tox. 2	 GHS06
H310	Acute Tox 1	
H314	Skin Corr 1A	 GHS05
H330	Acute Tox 2	

Figure 5 : hazard statement linked to Seveso Directive

The qualifying quantity of these substance as referred to in the Seveso Directive is for the application of :

- lower-tier requirements : 5 tonnes ;
- upper tier requirements : 20 tonnes.

1.3. Part 2 of the appendix to Seveso Directive : named dangerous substances

48 dangerous substances are included in Part 2 of the appendix to Seveso Directive. Where a dangerous substance is covered by Part 1 of this appendix and is also listed in Part 2, the qualifying quantities set out in Columns 2 and 3 of Part 2 have to be applied. Among these 48 substances, some substances of those are used in the BNI are directly subject to Part 2. For example : hydrazine and petroleum products and alternative fuels.

The qualifying quantity of these substances as referred to in the Seveso Directive is :

- Hydrazine (lower-tier : 0,5 tonnes / upper tier : 2 tonnes)
- Petroleum products (lower-tier : 2 500 tonnes / upper tier : 25 000 tonnes)

1.4. Categorisation of establishments as regards the Seveso Directive

4 establishments (3 upper tier and 1 low tier) including several BNI are considered to present major hazards due to the potential accident risk associated with the presence of dangerous substances as defined by the Seveso Directive (Figure 6).

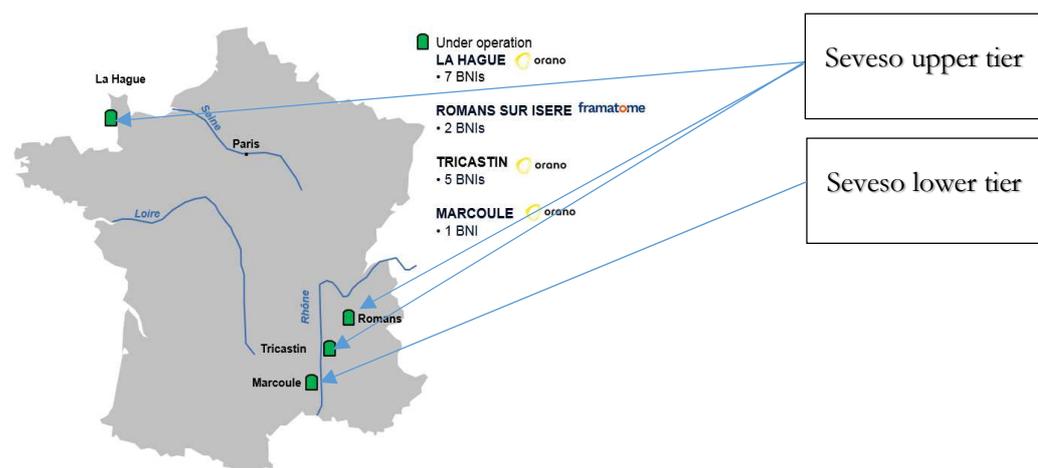


Figure 6 : categorisation of establishments

In the safety demonstration, the requirements are the same for these 3 categories (no Seveso, lower tier Seveso, upper tier Seveso). Information has to be given with regard to the quantity and nature of dangerous substances produced, used and stored , the circumstances under which an accident might occur and the measures to prevent such accidents and to mitigate their consequences.

The main difference is the update of the elements needed for the safety demonstration linked to non-radiological risks :

- **for the upper tier category** : at least once every five years ;
- **for the no Seveso and lower tier categories** : at least once every ten years.

2. THE ELEMENTS TO PROVIDE FOR THE SAFETY DEMONSTRATION LINKED TO NON-RADIOLOGICAL RISKS

2.1. General principle of the safety demonstration involving dangerous chemicals

For the contemplated incidents and accidents involving dangerous chemicals, the safety demonstration includes an assessment of the non-radiological potential consequences as shown on Figure 7. For each scenario, this assessment includes at least the information referred to in the second appendix of the Seveso Directive and in the order of the 7 February 2012 [3] to provide the safety demonstration.

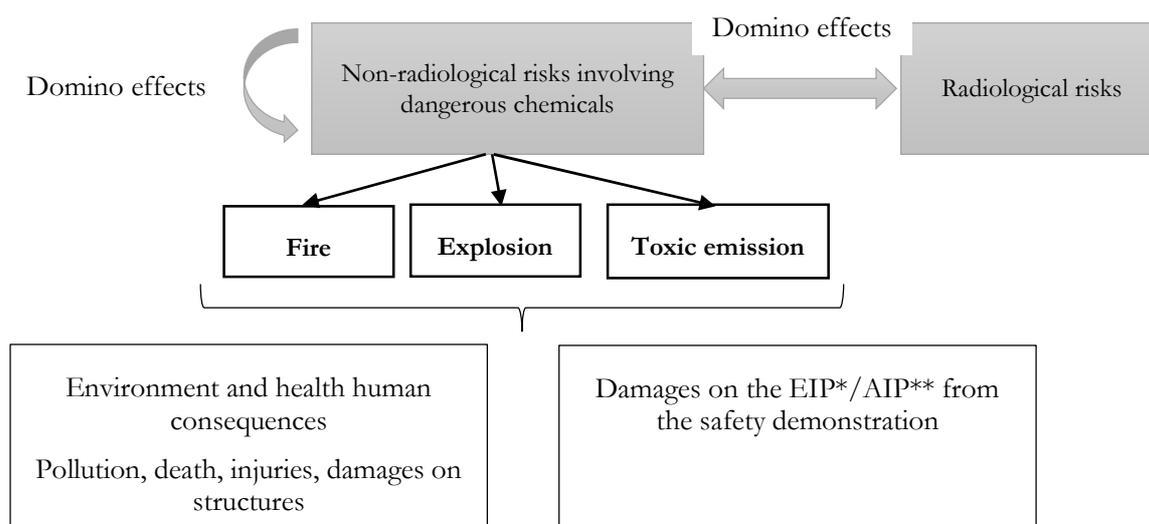


Figure 7 : consequences linked to non-radiological risks involving dangerous chemicals

EIP* : Important Element for the Protection of public security, health and safety, nature and environment. That is to say a structure, an equipment, a system (programmed or not), hardware, a component or software present in a basic nuclear installation or placed under the responsibility of the licensee, fulfilling a function necessary for the demonstration mentioned.

AIP**: Important Activity for the Protection of public security, health and safety, nature and environment. That is to say activities participating in the technical or organizational provisions.

2.2. Minimum data and information to be considered in the safety demonstration

According to article 3.2 of the order of the 7 february 2012 [3], the safety demonstration is demonstrated by a prudent **deterministic approach**. This procedure integrates the technical, organisational and human dimensions, and takes into account all the possible statuses of the installation, whether permanent or transient. In addition to the postulated single initiating events, the demonstration of safety addresses plausible situations of combined initiating events.

According to article 3.3 of the order of the 7 february 2012 [3], the safety demonstration shall also include **probabilistic analyses** of accidents and their consequences.

According to Article 3.7 of the order of the 7 february 2012 [3], for each scenario, this assessment includes :

- a presentation of the assumptions used in the release calculations and exposure scenarios ; the release calculation assumptions must be **reasonably pessimistic** and **the exposure scenarios must be based on realistic parameters**, but without considering any population protection actions that could be implemented by the public authorities ;

- an estimation of the effective doses and the intensity of the non-radiological phenomena to which persons and the environment could be exposed in the short, medium and long term, distinguishing the different age classes where necessary, and considering the different hazardous substance transfer pathways ; the estimation includes equivalent doses to the thyroid in the event of radioactive substance releases that justify this ;
- an estimation of the extent of the areas likely to be affected ;
- for incidents or accidents having consequences outside the site, the kinetics of the development of the hazardous phenomena and the propagation of their effects.

The intensity of the non-radiological hazardous phenomena is defined with respect to reference values expressed as toxic effects, overpressure effects, thermal effects, and effects associated with the impact of a projectile on humans and structures. The reference values to use are those figuring in appendix II of the order of 29 September 2005 [4] (Figure 8).

The effect thresholds	On human	On structures
Thermal radiation	8 kW/m ² or heat load of 1800 (kW/m ²) ^{4/3} .s : first significant deaths 5 kW/m ² or heat load of 1000 (kW/m ²) ^{4/3} .s : first deaths 3 kW/m ² or heat load of 600 (kW/m ²) ^{4/3} .s : first irreversible effects	200 kW/m ² : significant glass broken 20 kW/m ² : concrete's performance in fire during several hours and most severe on concrete structures 16 kW/m ² : most severe on structures, excluding the concrete structure 8 kW/m ² : domino effect threshold and most severe on structures 5 kW/m ² : significant glass broken
Overpressure	200 mbar : first significant deaths (5%) 140 mbar : first deaths (1%) 50 mbar : first irreversible effects 20 mbar : injuries caused by broken glass	300 mbar : most severe on structures 200 mbar : domino effect threshold 140 mbar : severe on structures 50 mbar : moderate damage 20 mbar : significant glass broken
Toxic dose	Based on Lethal Concentration 5% and exposure time (passage of the cloud) - first significant deaths (5%) Based on Lethal Concentration 1% and exposure time (passage of the cloud) - first deaths (1%) Based on irreversible effects (first injuries) and exposure - first irreversible effects	

Figure 8 : the reference values

Some substances can have a double effect : radiological and non-radiological like uranium hexafluoride (UF₆) to and from enrichment plants. Uranium is in the form of UF₆, which has low levels of radioactivity, but significant chemical toxicity, especially because it will be hydrolyzed in hydrofluoric acid (HF) in contact with the humidity of the air. So, the safety demonstration has to provide for the both effects.

Finally, the assessment of the extent and severity of the consequences of identified major accidents have to include maps as shown on Figure 9.

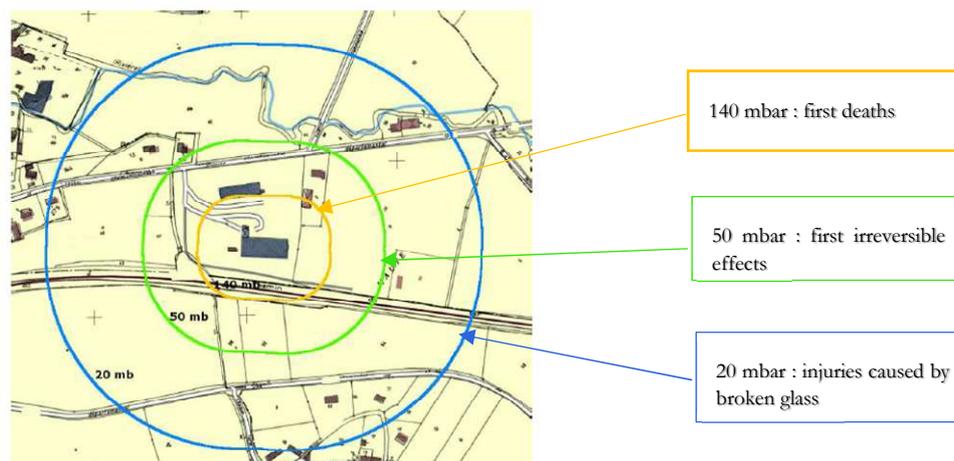


Figure 9 : distance of overpressure effects

3. **REFERENCES**

- [1] <http://ec.europa.eu/environment/seveso>
- [2] Chapter 13 – Annual report ASN - 2016
- [3] Order of 7 February 2012 setting the general rules relative to basic nuclear installations
- [4] Order of 29 September 2005 relative to the evaluation and integration of the probability of occurrence, the kinetics, the intensity of the effects and the severity of the consequences of potential accidents in the hazard studies of classified installations subject to authorization

Chemical Effects and their Evaluation Methods for Accidental Release of Uranium Hexafluoride

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This paper is mainly a summary of English translation of chapters 2 to 4 of the Japanese report, JNES-RE-2013-2021¹⁾, concerning chemical effects of UF₆ for uranium processing facilities. In addition, the author of this paper described the utilization of the result of this report in the part of chapter 1 and chapter 5 of this paper.

Abstract

After the accident at the Fukushima Daiichi Nuclear Power Station occurred in March 2011, the new regulatory requirements for nuclear fuel fabrication facilities were enforced in December 2013, which require licensees of UF₆ enrichment and reconversion activity to evaluate chemical effects on the work environment after a UF₆ leakage in an accident that could lead to severe accidents.

Preparatory to enforcement of this new regulatory requirements, the Incorporated Administrative Agency, Japan Nuclear Energy Safety Organization (JNES), has, as one of the efforts to consider the evaluation methods of UF₆ chemical effects and criteria for UF₆ leakage required for the regulation, investigated and studied UF₆ chemical effects and the regulatory statuses in the U.S., France and U.K..

As the result, it was clarified that it is important to evaluate the consequences of UF₆ leakage accidents focused on the acute chemical exposure effects. Concerning the evaluation methods of chemical effects, views, methods and items to be considered about acute chemical exposure effects were investigated. The results were issued as the JNES report JNES-RE-2013-2021¹⁾.

In order to share the information on the safety assessment of UF₆ chemical effects to the members of OECD/NEA/WGFCS (the Organisation for Economic Co-operation and Development/the Nuclear Energy Agency/the Working Group on Fuel Cycle Safety) as a good practice of the safety assessment of UF₆ chemical effects in Japan, outlines of the original JNES report and some of the latest information were shown in this paper.

1. Introduction

IAEA (International Atomic Energy Agency) Safety Standards Series No. NS-R-5, "Safety of Nuclear Fuel Cycle Facilities²⁾" and GS-R-2, "Preparedness and Response for a Nuclear or Radiological Emergency³⁾" require specific responses against the chemical toxicity of UF₆.

In Japan, the handling method has been regulated to prevent health hazards due to UF₆. Moreover, HF produced by the hydrolysis reaction of UF₆ and the moisture in the air has been regulated for the control of venting and work environments.

After the accident at the Fukushima Daiichi Nuclear Power Station occurred in March 2011, the new regulatory requirements for nuclear fuel fabrication facilities were enforced in December 2013, which require licensees of UF₆ enrichment and reconversion activity to evaluate chemical effects on the work environment (inside and outside UF₆ processing buildings) after a UF₆ leakage in an accident that could

lead to severe accidents. Moreover, in the same month, the NRA requested licensees to evaluate chemical effects of UF₆ on the public and to report the results to the NRA by the time when the verification examination for conformity to the new regulatory requirements is completed⁴.

Preparatory to enforcement of this new regulatory requirements, JNES¹ has, as one of the efforts to consider the evaluation methods of UF₆ chemical effects and criteria for UF₆ leakage required for the regulation, investigated and studied actual UF₆ chemical effects and the current regulatory statuses in the U.S., France and U.K.. The investigation and study results have been referred to during the above-mentioned activities for "verification of chemical effects on the public" directed to the UF₆ processing plants by the NRA. Moreover, the investigation and study results were issued as the JNES report JNES-RE-2013-2021.

2. Summary of the UF₆ leakage accident

- (1) The cause of death during UF₆ handling at UF₆ leakage accidents is inhalation of HF produced by the reaction of UF₆ with the moisture in the air⁵.
- (2) Acute or chronic exposure to UF₆ causes chemical and radiological effects. Since uranium enrichment and reconversion facilities in Japan process the uranium within confined equipment, the chronic exposure of workers taking a small amount of uranium continuously during normal operation is hard to consider. Therefore, this report outlines the acute exposure due to UF₆ leakage accidents only. Serious acute chemical exposure consequences caused by UF₆ leakage accidents are hazardous to people due to the heavy metal toxicity (deterioration of kidney function) of accumulated uranium in the kidney and HF produced by the hydrolysis addressed in item (1). The classification of health effects due to exposure to substances, including uranium, is investigated and shown in Table 2.1. Late chemical effects in Table 2.1 are shown in parentheses because clear evidence of late effects, including carcinogenicity, due to uranium exposure was not found and a zero rate of the person's carcinogenicity was not confirmed yet.
- (3) The HF generated by a UF₆ leakage is very corrosive and stimulative. Chemical effects of HF inhalation include stimulation and damage to the nasal cavity mucosa, bronchus and alveolar. The increase of the exposure concentration worsens the symptoms, leading to bronchitis, pulmonary-edema or injury, bleeding and other symptomatic states of the pancreas, which may cause pneumonia. Further increase of exposure concentration may cause dyspnea and result in death.

Table 2.1 Classification of health effects due to chemical exposure

Acute effects	Chemical effects	Various injuries, death (late effects)
	Radiation effects	Cataracts, Epilation, death (+ stochastic effects)
Chronic effects	Chemical effects	Malignant symptoms of workers (late effects)
	Radiation effects	Increase of the carcinogenic rate

3. Characteristics of UF₆ (property and behavior)

3.1. Radiation and chemical effects due to UF₆ intake

The specific activity of UF₆ enriched to 5% or less used for Japanese light water reactors is 121

¹ JNES was unified into the NRA in March 2014.

Bq/mg-U, and the amount of uranium corresponding to the committed effective dose of 1 mSv for 50 years is 13 mg and 370 mg for inhalation and ingestion, respectively². The effect of inhalation is more significant than that of ingestion.

Figure 3.1 shows the inhalation quantity of soluble uranium and its acute effect (classified into three endpoints depending upon the inhalation quantity) and the chronic exposure limit (obtained from Subpart Z of U.S. OSHA (Occupational Safety and Health Administration) 29 of CFR 1910.1000⁶). This figure shows that, for example, the chemical effect of inhalation of 13 mg-U, which is equivalent to the committed effective dose of 1 mSv for 50 years, is level 2, and 40 mg-U which is about 3 times 13 mg-U is level 3, leading to a potentially fatal adverse effect to health, which may cause a critical incurable renal impairment. On the other hand, the committed effective dose for 50 years of 40 mg-U is approx. 3 mSv, which is a value that not only acute radiation effect can not be caused but also significant carcinogenic effects are not seen.

From the above result, the evaluation of the acute effect of inhalation focused on the chemical effect of a UF₆ leakage accident is considered necessary³.

4. Evaluation method of UF₆ diffusion and migration in the air at the UF₆ leakage accident and the criteria of chemical effects

4.1 Evaluation method of UF₆ diffusion and migration in the air

Concerning the evaluation method of chemical accident consequences, the situation of each country was investigated, and the U.S. evaluation method was referred to.

4.1.1. Evaluation method of UF₆ diffusion and migration in the air in U.S.

NUREG-1520 Rev. 1¹⁰) shows requirements concerning the evaluation method of chemical accident consequences. The requirements are to prove that the model to be used provides conservative evaluation results and that the diffusion model for the calculation of the UF₆ concentration and its reaction products conform to the guidance for the model applicability specified in NUREG/CR-6481¹¹). Moreover, it is required that the analysis of the degree of effect must follow the guide, NUREG/CR-6410¹²), concerning the atmospheric dispersion and consequence modeling.

² Fell T.P. et al; Assessment of internal doses of workers potentially exposed to enriched uranyl fluoride and uranium tetrafluoride, NRPB-W56, 2004. Obtained from the value of U.K. HSE publication. In the case of natural uranium, the radiation effect becomes smaller.

³ Since the UO₂F₂ is soluble like UF₆, the acute effect by the UO₂F₂ and UF₆ inhalation is, if the uranium inhalation quantity is the same, considered to be the same. As mentioned later, U.S. regulation specifies similarly.

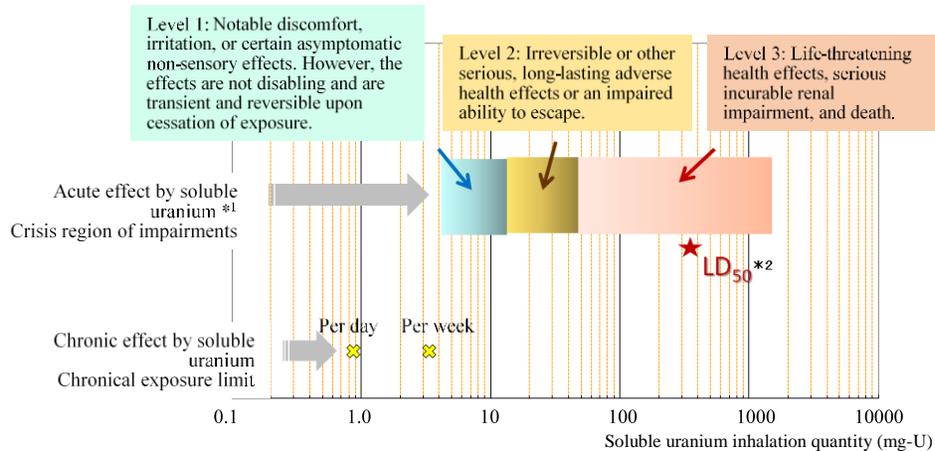


Figure 3.1 Relationship between the inhalation quantity and the chemical effect of soluble uranium (Acute thresholds and limits of normal operation)

- *1 The lower limits of the acute effect level 1 to 3 due to UF₆ were calculated based on the adult's respiration rate (1.2 m³/h) and other factors referring to the UF₆ threshold concentration of the AEGL level 1 to 3, which is the acute exposure guideline of U.S. EPA⁷⁾ to be mentioned later.
- *2 Concerning LD₅₀ of uranium for persons, various values have been reported. Although NUREG-1391⁸⁾ defines the value to be 230 mg for persons of 70 Kg, another report⁹⁾ defines it to be 1.0 g. For this report, the value of NUREG-1391 is used.

As a specific application, the 5-factor-method data of NUREG/CR-6410 or the former DOE (U.S. Department of Energy) DTL (Dangerous Toxic Load) handbook¹³⁾ are used for the source term evaluation. Moreover, the evaluation method according to the atmospheric dispersion models for safety analysis of nuclear power reactor facilities of the U.S., R.G. 1.145¹⁴⁾ (hereinafter referred to as "R.G. 1.145 model"), and the evaluation method using a calculation code, "HGSYSTEM" and "RASCAL3.0.5 and ARCON96" are approved by NRC (U. S. Nuclear Regulatory Commission).

Where, the evaluation method according to the atmospheric dispersion models means the method to calculate the substance concentration in the air by multiplying the release rate of radioactive materials to the relative concentration obtained assuming that the spacial substance concentration is a horizontally and vertically normal distribution based on the specified meteorological conditions, such as the atmospheric stability and wind speed, during the accident period. However, the building effect is adjusted, if any.

The HGSYSTEM/UF₆ code evaluates the diffusion after the UF₆ is released to the atmosphere. The chemical and thermodynamic model of UF₆ is incorporated into the code based on the HGSYSTEM Version 3.0 code developed by Shell Research Ltd. The code can treat high-density gas, drying and wetting deposition, involvement effect of the building, plume floating, and effects of complex topography^{15) ~ 17)}. NUREG/CR-6481 "Review of Models Used for Determining Consequences of UF₆ Release"¹¹⁾ specifies criteria of the source term evaluation and criteria of atmospheric dispersion evaluation, and shows a pairwise applicability comparison of two or more calculation codes, suggesting that the HGSYSTEM/UF₆ code is excellent as of 1997.

The RASCAL code was developed by the US NRC, and the NRC emergency activity center uses the code to evaluate the exposure dose by radiological materials released to the atmosphere in an accident at present.

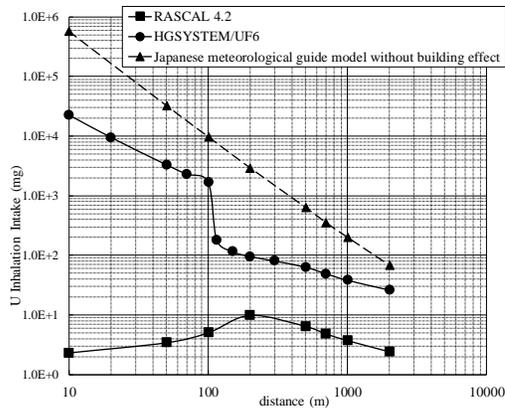
4.1.2. Results of JNES study on the evaluation of UF₆ diffusion and migration in the air

JNES started, using simple calculation methods⁴ according to the R.G. 1.145 model and the atmospheric dispersion model which is used in Japan^{5, 18)} (hereinafter referred to as "Japanese meteorological guide model") and the method of RASCAL4.2 and HGSYSTEM/UF6 codes, evaluation and analysis of diffusion and migration of UF₆ in the air for the following two typical cases;

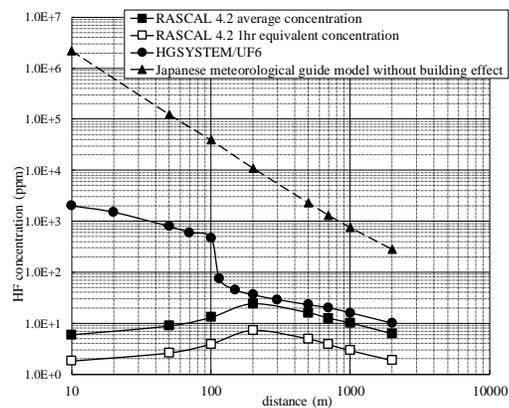
- (1) Liquid UF₆ leakage accident due to 30B cylinder damage;
- (2) UO₂F₂ + HF leakage accident.

Examples of the results are shown in Figure 4 .1 and Figure 4 .2.
Consequently, the following results were obtained;

- The simple calculation method according to the Japanese meteorological guide model (in the case of no involvement effect by buildings) gives the most significant inhalation value.

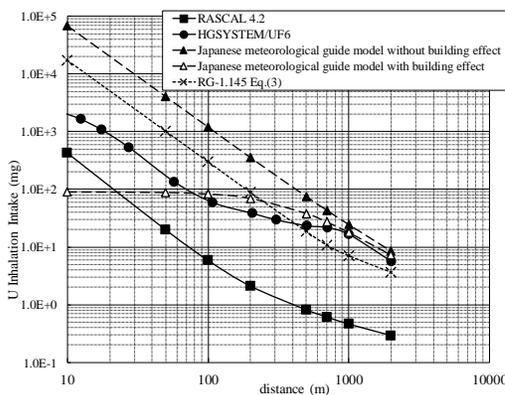


Uranium inhalation from the release point

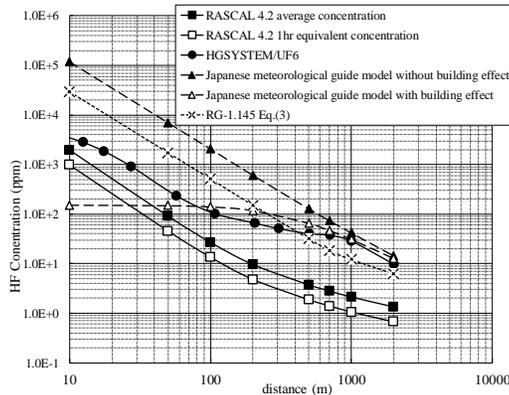


HF concentration from the release point

Figure 4.1 Liquid UF₆ leakage accident due to 30B cylinder damage



Uranium inhalation from the release point



HF concentration from the release point

Figure 4.2 UO₂F₂ + HF leakage accident

⁴ The simple calculation method means the method to obtain the relative concentration supposing the severe simple meteorological condition (atmospheric stability: F type, wind speed: 1 m/s, etc.), avoiding statistical processing of meteorological observation data.

⁵ Although R.G. 1.145 model and Japanese meteorological guide model use the same evaluation formula when the involvement effect of buildings is not considered, those models use different evaluation methods when the involvement effect of buildings is considered.

- In the case of including the involvement effect of buildings in the short distance where the involvement effect is significant, the simple calculation method according to the R.G. 1.145 model gives a relatively larger inhalation value than the Japanese atmospheric dispersion model.
- Concerning the liquid UF₆ release accident, since the HGSYSTEM/UF6 code incorporates the volatile phenomena from a failed part, it provides detailed analysis and is considered more suitable than the RASCAL4.2 code.

4.2. Criteria of chemical effect

4.2.1. Criteria of U.S.

As shown in Table 4.2, NUREG-1520 classifies significance (degree of incidence) into three levels and considers the levels of ERPG (Emergency Response Planning Guidelines) of the AIHA (American Industrial Hygienist Association) and AEGL (Acute Exposure Guideline Level) of the EPA (U.S. Environmental Protection Agency) so that definitions of the amount of chemical dose (CD) of each effect rate of Codes of Federal Regulation and each level of ERPG⁶ and AEGL⁷ are consistent.

AEGL has the minimum number of authorized compounds. It is due to strict scientific examination by experts, which is considered more reliable. TEEL (Temporary Emergency Exposure Limits) data contain chemical substances handled by DOE facilities (more than one thousand and several hundred), which have no threshold in AEGL and ERPG data and are temporarily specified to evaluate the toxicity, and substances and the values are reviewed each year, and the substances open to AEGL or ERPG are deleted.

In the U.S., there are three threshold data types of chemical substance exposure, as compared in Table 4.3. The DOE specifies on the webpage that the priority for adopting the thresholds is AEGL > ERPG > TEEL⁷.

Table 4.2 Classification of significance by the Codes of Federal Regulation 10 CFR 70.61 and NUREG-1520

	Workers	Offsite Public	Environment
High significance	* RD > 1 Sv	RD > 250 mSv	
	** CD = endanger life. (Exceeding ERPG-3 or AEGL-3)	30 mg soluble uranium intake, CD = irreversible or other serious and long-lasting health effects (Exceeding ERPG-2 or AEGL-2)	
Medium significance	250 mSv < RD ≤ 1 Sv	50 mSv < RD ≤ 250 mSv	Radioactive release > 5000 x threshold limits specified in Table 2 of the supplementary provision B of 10 CFR Part 20
	CD = irreversible or other serious and long-lasting health effects (Exceeding ERPG-2 or AEGL-2)	CD = mild transient health effects (Exceeding ERPG-1 or AEGL-1)	
Low significance	Accidents with lower radiological and chemical exposures than those above in this column	Accidents with lower radiological and chemical exposures than those above in this column	Radioactive releases producing lower effects than those referenced above in this column

* RD: Radiological Dose (effective dose)

* *CD: Chemical Dose, (XX) show the data of NUREG-1520.

⁶ <http://response.restoration.noaa.gov/oil-and-chemical-spills/chemical-spills/resources/emergency-response-planning-guidelines-erpgs.html>

⁷ <https://orise.orau.gov/emi/scapa/chem-pacs-teels/default.htm>

Furthermore, the standard review plan, NUREG-1718¹⁹⁾, of MOX fuel fabrication facilities states that ERPG or AEGL may be adopted. It also describes that, when other data are to be used, materials that prove the validity must be shown. Table 4.4 shows the AEGL and ERPG thresholds of UF₆ and HF.

Moreover, NIOSH (National Institute for Occupational Safety and Health) has released the IDLH (Immediately Dangerous to Life or Health) values of the case of exposure time of 30 minutes of workers⁸.

4.2.2. Criteria of France

The threshold criteria of France are shown in Appendix 2 of the arrêté (Ministry Order) of September 29, 2005. The classification of thresholds of acute toxicity effects, which is described in Appendix 2, is shown in Table 4.5.

The threshold of each chemical substance is specified for the land use plan based on Table 4.5 by the expert group of toxicology⁹. Table 4.6 shows a part of the France thresholds of UF₆ shown in the report²⁰⁾ and of HF shown in the report²¹⁾, which are research reports published by Institut national de l'environnement industriel et des risques (INERIS) (National Institute for Industrial Environment and Risks) as the France thresholds of acute toxicity effects. Moreover, Reference 22, which incorporates some of the results of European project ACUTEX²³⁾, describes that persons of high susceptibility are not included in the population exposed to chemical substances.

Table 4.3 Comparison of toxic threshold data on chemical substances in U.S.

	AEGL	ERPG	TEEL
Responsible organization	EPA	AIHA	DOE
Purpose of the data	Evaluation of the acute exposure health effects, planning of emergency response measures	Planning of emergency response measures, evaluation of the acute exposure health effects	Implementation of the impact evaluation of chemical substances not contained in the AEGL or ERPG data
Assumed exposed persons	All persons, including individuals of high susceptibility (Note)	Excluding individuals of high susceptibility (Note)	All persons, including individuals of high susceptibility (Note)
Level of health effect	1, 2, 3	1, 2, 3	0, 1, 2, 3
Exposure time	10 minutes, 30 minutes, 1 hour, 4 hours, 8 hours	1 hour	15 minutes including the time of the maximum concentration; in the future, 1 Schedule unified into a time To be unified in 1 hour in the future
Number of open compounds	130 (as of the middle of 2013)	145 (as of the middle of 2013)	> 3000

Note: Individuals of high susceptibility mean infants, children, and persons whose resistance capability of the lung functions, such as pneumoconiosis, pulmonary emphysema, and liver function, cardiac function and immune function is weak, who are expected to show health effects often.

⁸ <http://www.cdc.gov/niosh/idlh/intridl4.html>. IDLH values are specified assuming that the workers can maintain the capability to evacuate within 30 minutes not resulting in death or irreversible health effects.

⁹ Organized by Ministère de l'Écologie, du Développement durable et de l'Énergie Institut national de l'environnement industriel et des risques (INERIS) Institut national de la recherche scientifique (INRS), Institut de radioprotection et de sûreté nucléaire (IRSN), university hospital centre, industry representative, and toxicologist.

INERIS showed the guideline for licensees to decide the not-described (ND) values in the research report²⁴⁾ in 2009. For the "land use plan," the first priority is to refer to the references used to specify U.S. AEGL, ERPG and other criteria, and to decide the values according to the France method described in the INERIS research report, the second priority is to use values of ERPG, IDLH (SEI values only) and others, and the third priority is to use the values of AEGL¹⁰. The priority of the values for the "emergency response" is ERPG, AEGL, IDLH (SEI values only), and TEEL. Since SER of Table 4.6 for UF₆ specifies the not-described (ND) values, the specified values are adopted based on the base data of U.S. AEGL-1 or ERPG-1 according to the way of thinking mentioned above.

Table 4.4 AEGL and ERPG thresholds of UF₆ and HF

UF ₆ (mg-UF ₆ /m ³) Level \ Exposure time	AEGL					ERPG	
	10 min.	30 min.	1 hr.	4 hr.	8 hr.	Level \ Exposure time	1 hr.
AEGL-1	3.6	3.6	3.6	NR	NR	ERPG-1	5
AEGL-2	28	19	9.6	2.4	1.2	ERPG-2	15
AEGL-3	216	72	36	9.0	4.5	ERPG-3	30

HF (ppm) Level \ Exposure time	AEGL					ERPG	
	10 min.	30 min.	1 hr.	4 hr.	8 hr.	Level \ Exposure time	1 hr.
AEGL-1	1.0	1.0	1.0	1.0	1.0	ERPG-1	2
AEGL-2	95	34	24	12	12	ERPG-2	20
AEGL-3	170	62	44	22	22	ERPG-3	50

<http://www.epa.gov/oppt/aegl/pubs/final.htm>

Table 4.5 Classification of thresholds of acute toxicity effect in France²⁴⁾

Threshold	Description
SER (Seuil des Effets Réversibles)	Reversible Effects threshold Concentration of substances in the air that may cause reversible effects when exceeding the specified exposure time
SEI (Seuil des Effets Irréversibles)	Irreversible Effects threshold Concentration of substances in the air that may cause irreversible effects when exceeding the specified exposure time
SPEL (SEL) *1 (Seuil des Premiers Effets Létaux (Seuils des Effets Létaux))	First Lethal Effects threshold or Lethal Effects Threshold Concentration of substances in the air that may cause 1% death when exceeding the specified exposure time
SELS (Seuil des Effets Létaux Significatifs)	Significant Lethal Effects threshold Concentration of substances in the air that may cause 5% death when exceeding the specified exposure time

*1: Appendix 2 describes SPEL as SEL.

¹⁰ Reference 25 describes that although AEGL is scientifically reliable, the guideline is too conservative as the criteria used for the purpose of land use plan since individuals of high susceptibility are also taken into consideration.

Table 4.6 France thresholds of UF₆ and HF acute toxic effects

UF ₆ (mg-UF ₆ /m ³)	Source: INERIS-DRC-10-1009947-04672A							ND: Not Described
	1-min	10-min	20-min	30-min	1-hr	2-hr	4-hr	8-hr
SER	ND	ND	ND	ND	ND	ND	ND	ND
SEI	ND	123	ND	41	21	ND	ND	ND
SPEL	7,790	3,614	1,800	1,210	605	302	144	72
SELS	12,614	5,861	2,923	1,958	979	490	245	115

HF (ppm) Source: INERIS-DRC-08-94398-12729A ND: Not Described

	1-min	10-min	20-min	30-min	1-hr
SER	60	12	7	5	1
SEI	ND	600	ND	200	100
SPEL	11,100	1,123	563	377	189
SELS	17,147	1,705	851	567	283

4.2.3. Criteria of U.K.

The criteria of U.K. include SLOT (Specified Level of Toxicity) and SLOD (Significant Likelihood of Death) for HF specified by the British Health and Safety Executive (HSE). SLOT is specified for the land use plan as the following level: all persons in the area suffer from intense pain, considerable persons require a doctor's medical examination, some seriously injured persons require treatment over a long period, and highly susceptible persons die, and, on the other hand, SLOD is specified as a level of 50% lethality²⁶). Both criteria are indicated as the amount of toxic loading (= concentration (ppm) x exposure time (min)), In the case of HF, it is 12,000 for SLOT and 21,000 for SLOD.

4.2.4. Criteria of Japan

The criteria of Japan concerning UF₆ and HF are as follows: there is no quantitative limit for public safety since the criteria of UF₆ is for registration and notification. The standard of HF is for venting and work-environment control, not for an accident. Therefore, the criteria of Japan cannot be used as criteria for accidents that could lead to severe accidents

(1) For UF₆ (soluble uranium, including UO₂F₂)

- The duty of registration and notification concerning sale, manufacturing, handling and other activities according to the Poisons and Deleterious Substances Control Law.

(2) For HF

- Emission standard (minimum) of Enforcement Regulations of Air Pollution Control Act: 1 mg/Nm³ (1.5 ppm)
- Ministry Order of Effluent Standard for the Water Pollution Control Act (Fluorine and its Compounds): 8 mg/liter (except offshore areas), and 15 mg/liter (offshore areas)
- Control standard of the workspace concentration according to the Prevention of Hazards due to Specified Chemical Substances of Industrial Safety and Health Act: 0.5 ppm

4.3. Discussion

4.3.1. The UF₆ chemical effect evaluation method for accidents that could lead to severe accidents

The way of thinking, methods, and items to be considered to identify to perform the UF₆ chemical effect evaluation for accidents that could lead to severe accidents are as follows:

- (1) Identification of accidents that could lead to severe accidents
- (2) Evaluation of the source term of each identified accident that could lead to severe accidents
 - To evaluate the chemical effects for each of the worker of the processing room, on-site staff, and the public in the vicinity of the site, the source term of severe accidents must be obtained for both the building inside (processing room) and building outside.
 - Identify the UF₆ leaked and the pathway of the reaction products.
- (3) Exposure concentration evaluation of hazardous chemical substances
 - The exposure concentration should be evaluated for each of UF₆, UO₂F₂ and HF.
 - For the evaluation considering the diffusion outside the building, the following method i results in conservative effects. However, if the effect is too conservative, the following method ii may be applied to the evaluation considering the chemical and thermodynamic effects of UF₆.
 - i. Evaluation method according to the Japanese meteorological guide model
 - ii. Evaluation method using the proved and verified calculation codes (HGSYSTEM/UF₆ code, RASCAL4.2 code etc.)
- (4) Evaluation of exposure time
 - The exposure time assumed for each of the worker, the staff and the public should be specified appropriately based on the condition of the facilities considered, and the basis should be shown.
- (5) UF₆ chemical effect evaluation for accidents that could lead to severe accidents
 - The UF₆ chemical effect is evaluated based on the exposure concentration and time.
 - AEGL is desirable to use as the criteria of chemical effect evaluation because of the following reasons. When other criteria are used, the appropriateness of the criteria should be explained.
 - (a) AEGL is considered most reliable since many references are available, strict examination by experts has been performed, and it is utilized for evaluation of most UF₆ related facilities in the U.S.
 - (b) Individuals of high susceptibility are also included in the study, and the thresholds are conservative compared with other data.

4.3.2. Validation of measures against UF₆ leakage in accidents that could lead to severe accidents

The following items should be considered for the validation:

- (1) Acceptability of chemical effect evaluation results of the above item (5) is judged for the public in the vicinity and workers, with due consideration of the following two endpoints.
 - (a) For the defenseless public in the vicinity, the effect does not cause any “mild transient health effects”.
 - (b) For the workers and staff to whom defenses and exercises are available, the effect does not cause any “irreversible or other serious and long health-lasting effects”.
- (2) Based on these items to be considered, AEGL is used to determine the acceptability of the effect. The measures are appropriate when acceptable, but further measures should be taken when not acceptable.

5. Confirmation of current status of licensees with enrichment and reversion activities

Learning from the lessons of the accident of the Fukushima Daiichi Nuclear Power Station, the "Act for the Regulation of Nuclear Source Material, Nuclear Fuel Material and Reactors (Nuclear Regulation Act)" was revised in June 2012. Moreover, new regulatory requirements for nuclear fuel and other facilities were enforced in December 2013. For the enforcement, it was decided that the new regulatory requirements should not interfere with the fuel processing for five years after the enforcement. But, the NRA requested, by its direction⁴⁾, licensees who manage the equipment of UF₆ treating processes under positive pressure: the licensees of enrichment activity (JNFL: Japan Nuclear Fuel Limited who owns the homogenizing and blending equipment for the enriching process) and the licensees of reversion activity (MNF: Mitsubishi Nuclear Fuel Co. LTD, who owns the UF₆ evaporation and hydrolysis equipment for the reversion process) to confirm that there is no possibility of the risk or remarkable chemical effects due to excessive radiation exposure on the public and to report the results to the NRA. The contents addressed in this paper were reflected in the evaluation by licensees for such confirmation, and it was recommended to use the AEGL values as the criteria and appropriate evaluation methods like the Japanese meteorological guide model or HGSYSTEM/UF6 code, etc. for the analysis.

The secretariat of NRA evaluated the reports^{27), 28)} submitted by JNFL and MNF and the evaluation results were accepted in the NRA meetings in April 2017 and September 2017, respectively.

6. Conclusion

The new regulatory requirements of the nuclear fuel cycle facilities in Japan incorporated measures against the UF₆ chemical effect in accidents that could lead to severe accidents. The current statuses of the U.S., France and U.K. were investigated in the study of the method to evaluate UF₆ chemical effects necessary to enforce the related regulations, and the results were summarized in the report, JNES-RE-2013-2021¹⁾. Moreover, the results, such as using AEGL values as the criteria and using the Japanese meteorological guide model or HGSYSTEM/UF6 code for UF₆ exposure concentration evaluation, were applied to the confirmation conducted by licensees of enrichment and reversion activity to verify that UF₆ leakages did not result in a remarkable radiation and/or remarkable chemical effects to the public based on the direction of the NRA⁴⁾.

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Chemical Safety Requirements in the United States for Commercial Fuel Cycle Facilities

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ABSTRACT

Chemical safety regulatory requirements and practices vary somewhat between countries. This paper presents the regulatory requirements and regulatory practices for commercial fuel cycle facilities in the United States (U.S.). Regulations regarding chemical safety for commercial U.S. fuel cycle facilities are found in Title 10 of the Code of Federal Regulations (CFR) Part 70, Domestic Licensing of Special Nuclear Material. The U.S. Nuclear Regulatory Commission (NRC) regulations for fuel cycle facilities that process fissile material have performance assessment requirements for acute chemical exposures and a requirement that licensees or applicants conduct a safety analysis to assess compliance with the performance requirements. This paper presents an overview of these chemical safety performance requirements and discusses the NRC's approach to its review of an applicant or licensee or safety assessment. Specifically, this paper addresses the analysis of toxic and reactive chemicals used at U.S. commercial fuel cycle facilities, quantitative standards used to assess consequences and acute chemical exposures to workers via different pathways.

I. OVERVIEW OF NRC REGULATIONS AND REGULATORY GUIDANCE

Part 70 of Title 10 of the U.S Code of Federal Regulations provides the regulatory framework for licensing of special nuclear material (SNM). SNM is defined as plutonium, uranium 233, and uranium enriched in ^{233}U or ^{235}U . NRC regulations, 10 CFR 70 Subpart H, provides specific requirements addressing chemical safety requirements and requires applicants and licensees to perform an integrated safety analysis (ISA). The ISA is a systematic analysis that identifies: (a) facility and external hazards; (b) the potential of these hazards to initiate accident sequences; (c) what these potential accident sequences are, including their likelihood and consequences; and (d) items relied on for safety (IROFS).

The U.S. also has a Memorandum of Understanding (MOU) between the U.S. Occupational Safety and Health Administration (OSHA) and the NRC, assigning the responsibility for the management of chemical hazards related to processing radioactive material to the NRC. As specified in 10 CFR Part 70, a fuel cycle facility applicant or licensee must develop and maintain an ISA. They must identify the chemical hazards associated with NRC-licensed material as well as the hazardous chemicals produced from licensed material. The term hazardous chemicals produced from licensed materials includes substances having licensed material as precursor compound or substances that physically or chemically interact with licensed materials; and that are toxic, explosive, flammable, corrosive, or reactive to the extent that they can endanger life or health if not adequately controlled. These include substances commingled with radioactive material, and include substances such as hydrogen fluoride that is produced by the reaction of uranium hexafluoride and water, but do not include substances prior to process addition to licensed material or after process separation from licensed material.

Additionally, a fuel cycle facility applicants or licensees must identify in its ISA, facility hazards that could affect the safety of licensed materials and thus present an increased radiological risk. For chemical hazards, applicants and licensees must limit the risk of accidents involving such chemicals at their facilities. The performance requirements for acute chemical exposures state that accident sequences with high consequences must be highly unlikely. High consequence events are those that could endanger the life of a worker or lead to irreversible or other serious, long lasting health effect to an individual located outside of the controlled area (e.g. site's property boundary). The performance requirements also state that accident sequences that could lead to irreversible or other serious, long lasting health effect to a worker or cause mild transient health effects to any individual located outside of the controlled area are considered events with intermediate consequences and must be unlikely. Highly unlikely and unlikely are terms defined by the applicant or licensee which identifies the frequency of occurrence of an event.

The regulations require an applicant or licensee to conduct an ISA that identifies credible chemical hazards, accident sequences that could lead to the chemical hazards, and estimate the likelihood and consequences of the accident sequences. The results are then compared to the performance requirements for acute chemical exposures. The analysis is also used to determine if controls are required to ensure compliance with the performance requirements. The regulations define such controls as, "items relied on for safety" or IROFS.

NRC Regulations requires an applicant or licensee to describe in its ISA Summary proposed quantitative standards, "used to assess the consequences to an individual from acute chemical exposure to licensed material or chemicals produced from licensed materials." The purpose of these standards is to help classify the consequences into high or intermediate in the ISA.

NRC documents available to provide guidance on how to analyze chemical hazards and consequences include: NUREG1513, "Integrated Safety Analysis Guidance Document;" NUREG/CR-6410, "Nuclear Fuel Cycle Facility Accident Analysis Handbook;" Information Notice 2007-022, "Recent Hydrogen Fluoride Exposures at Fuel Cycle Facilities;" and NUREG-1520, "Standard Review Plan for Fuel Cycle Facilities License Application." These documents provides guidance on how to consider chemical hazards in an ISA and address relevant exposure pathways (e.g., dermal and ocular pathways).

The following sections will provide details regarding the NRC's evaluation of proposed quantitative standards.

II. NRC REVIEW OF CHEMICAL SAFETY ANALYSIS

The NRC examines the methodology and information used by the applicant or licensee to identify hazards and accident sequences that could result in an acute chemical exposure to workers and individuals outside the controlled area. The methodology should be systematic and use information about the applicant or licensee's material quantities, process, process equipment, and operations. The NRC encourages the use of historical experience at similar facilities and operations.

When evaluating chemical hazards, the NRC considers typical material properties such as toxicity, flammability, and reactivity. The NRC evaluates the applicant or licensee's identification of credible chemical hazards that could potentially produce "high" or "intermediate" acute chemical exposure events. Table 1 provides information on the toxic or hazardous characteristics of some common chemicals used at fuel cycle facilities. Table 1 references sources of publically-available information on toxic or hazardous characteristics of chemicals commonly present at U.S. fuel cycle facilities. However, this is not an exhaustive list of chemicals that may be used at such facilities.

The NRC recognizes that accidents often occur: (1) during non-routine operations including maintenance where the hazards and controls are different from those of normal operation, (2) as a result of unanalyzed plant modifications where new hazards might be introduced, and (3) as a result of operations being conducted outside of conditions examined in previous safety analyses. Any locations where hazardous licensed material, including fissile material, could inadvertently be located should also be considered. A review of previous accidents related to similar operations is useful when evaluating the hazards present at a fuel cycle facility.

Review of Chemical Accident Consequences

NRC generally uses a multistep process to examine how the applicant or licensee has evaluated these potential chemical exposures consequences. When reviewing chemical exposure consequences, it is important to understand whether the receptor is a worker inside the controlled area, or is an individual outside the controlled area. This is important because the high-consequence and intermediate-consequence events described in the performance requirements are different.

The first step involves assessing the material's form and its concentration as it moves from the release point to the receptor location, and the major physical processes involved in the initial release and subsequent transport. Estimating and classifying chemical exposure consequences further involve an assessment of multiple parameters such as vessel size and pressure, hole size, building ventilation characteristics, building dimensions, and local meteorology. Methods for conducting these types of analyses are discussed in NUREG/CR-6410, "Nuclear Fuel Cycle Facility Accident Analysis Handbook," and the Center for Chemical Process Safety's, "Guidelines for Chemical Process Quantitative Risk Analysis," published in 1999. The NRC determines if the methods for estimating release rate and release conditions are reasonable (i.e., the results are not clearly biased in a way that underestimates consequences) for the physical properties of the material being released.

The second step involves determining the nature (e.g., exposure pathways) and the approximate duration of the chemical exposure. This estimate requires an understanding of the properties of the transported material (developed by the first step), an estimate of the effectiveness of any protective equipment, and an awareness of any actions of the exposed individual that would influence exposure (e.g., exposure time). The NRC then determines if the methods the applicant or licensee uses for estimating exposures are reasonable given factors such as the layout of the plant and the qualifications and training of the workers. In general, for chemical exposures via the inhalation pathway, it is reasonable to expect that both workers and individuals outside the

controlled area may be subject to such exposures. For non-inhalation chemical exposures, it is reasonable to expect that only workers would be subject to such exposures.

The third step involves the assessment of the consequences from the exposure event. This evaluation requires an understanding of the estimated exposure (developed during the second step) and information on the toxic characteristics of the released material or its anticipated reaction products. The same information on chemical toxicity characteristics that is used to estimate consequences is generally used to identify proposed standards.

Estimation of dermal and ocular exposure consequences for workers is generally more challenging than estimating inhalation exposure consequences. Dermal and ocular exposure often involve liquids or aerosols (gas-liquid mixtures), and the estimation of exposure parameters, such as exposure location on the receptor (e.g., hand vs. chest), the percent of impacted body surface area, and the duration of exposure may be difficult. Effects of dermal and ocular exposure often correlate to the concentration of the material involved in the exposure (e.g., severe skin burns are associated with short exposure to nitric acid in concentrations greater than 20 percent). So, in many cases, it may be more practical to estimate whether an exposure is likely and, if it is, correlate exposure effects to the concentration of the material involved in the exposure.

The NRC examines the method(s) the applicant or licensee used to estimate exposure of the worker or the individual outside the controlled area. The NRC evaluates the reasonableness of any model used for the analysis and the specific parameters used in the analysis.

Review of Chemical Accident Likelihood

The NRC reviews the methods the applicant or licensee used to estimate the likelihood of an acute chemical exposure event. The regulation in 10 CFR 70.61 also specifies the permissible likelihood of occurrence of accident sequences of different consequences. High-consequence accident sequences must be “highly unlikely” and intermediate-consequence accident sequences must be “unlikely.” Implicitly, accidents in the low-consequence category can have a likelihood of occurrence less than “unlikely” or simply “not unlikely.”

The NRC review consists of examining the overall estimate of the scenario frequency to make sure there is reasonable assurance that the overall likelihood is not unreasonably low. Historical information for similar facilities and processes is examined when it is available to support the NRC’s review. Additional information on NRC’s review of likelihood can be found in NUREG 1520, “Standard Review Plan for License Applications for Fuel Cycle Facilities.”

Review of Quantitative Standards

An applicant or licensee must describe in their ISA Summary proposed quantitative standards to assess the consequences to an individual from an acute chemical exposure to licensed material or chemicals produced from licensed materials. The proposed quantitative standards serve to identify the event consequence categories for the ISA’s chemical safety discussions. The NRC

verifies that the proposed quantitative standards used to assess consequences to an individual from acute chemical exposures are appropriate.

When evaluating the proposed quantitative standards, the NRC considers specific accident sequences described in the ISA Summary. If the accident sequence is determined to be highly unlikely, no proposed quantitative standards are required. Similarly, if the accident sequence is determined to result in consequences that are less than the intermediate events, no proposed quantitative standards are required.

The proposed quantitative standards should be based on generally available information from independent sources (e.g., government agencies or organizations, well-recognized professional organizations) describing the chemical's toxicity and hazardous properties. The applicant or licensee should provide a basis for the use and applicability of any proposed quantitative standard. It is not expected that they will need to conduct their own experimental testing or toxicity tests to generate data supporting their proposed standards.

Standards may have many forms. For inhalation exposures, the standard may be based on air concentration for a given exposure time. For non-inhalation exposures, the standard may be based on body surface area (BSA) exposure for a given time. The NRC reviewer ensures that the proposed standard is consistent with available toxicological information, and that the use of the proposed quantitative standard provides a reasonable estimate of event consequence (i.e. does not result in an underestimate of the event's severity).

The following paragraphs provide specific examples of information sources that are acceptable to the NRC when evaluating an applicant or licensee's proposed quantitative standards for classifying acute chemical exposure events as of high or intermediate consequence.

When reviewing exposure scenarios, the NRC has identified several useful information sources to evaluate a applicant or licensee's proposed quantitative standards. Acceptable exposure standards include, but are not limited to, those based on the Emergency Response Planning Guidelines (ERPGs), the Acute Exposure Guideline Levels (AEGLs), Temporary Emergency Exposure Levels (TEELs), the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), and the exposure limits established by OSHA or other Federal agencies and scientific organizations.

The two most common data sources for the NRC to use when reviewing proposed quantitative standards are the AEGLs and ERPGs. The AEGLs¹ are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, typically accidental exposure to airborne chemicals. The American Industrial Hygiene Association (AIHA) establishes the ERPGs². While these standards were developed for other purposes, such as emergency guidelines for once in a lifetime exposures, the NRC accepts the ERPG values to define "high" and "intermediate" consequences in ISAs. These are inhalation exposure limits that the NRC has previously accepted as meeting the quantitative standards requirement.

¹ The history and nature of AEGLs is discussed on an Environmental Protection Agency Web site: <http://www.epa.gov/oppt/aeql/index.htm>

² ERPGs are discussed on an American Industrial Hygiene Association Web site: <https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Documents/ERPGIntroText.pdf>

Another common data source that the NRC uses when reviewing proposed quantitative standards are the TEELs, which were developed by the U.S. Department of Energy (DOE). TEELs are temporary and alternative guidelines used for chemicals that do not have established ERPGs and AEGLs values³.

The NRC may also use the information available in the GHS database when evaluating a proposed standard. The GHS is an internationally standardized system for characterizing and labeling chemical hazards to help protect consumers, transportation workers, and emergency responders. The GHS defines different types of hazards (physical, health, and environmental) and establishes methods for assigning standardized GHS hazard statements used to communicate information about the severity of the hazard for specific exposure routes⁴. OSHA's Hazard Communication Standard has been aligned with the GHS to improve the quality and consistency of hazard information in the workplace.⁵ Table 1 provides GHS hazard statements for common chemicals in the fuel cycle process.

Table 2 presents the descriptions from the various information sources (i.e. AEGLs, ERPGs, and GHS) and compares it to the descriptions of "high" and "intermediate" consequence chemical exposure events specified in NRC regulations. The hazard statements in the GHS database are considered useful when reviewing proposed standards, particularly when AEGLs, ERPGs, or TEELs are not available.

The NRC uses the National Institute for Occupational Safety and Health (NIOSH) Skin Notations as another useful data source when reviewing proposed quantitative standards. The NIOSH Skin Notations involve the assignment of multiple skin notations for distinguishing systemic (SYS), direct (DIR), and sensitizing (SEN) effects caused by exposure of skin (SK) to chemicals. These notations are useful for understanding the health effects and consequence of a specific chemical. For example, in the past, NRC has used the skin notation profile for hydrofluoric acid to assess a licensee's quantitative standard for HF.

In summary, the NRC verifies that an applicant or licensee's proposed quantitative standards are consistent with available and technically sound information or well-established data sources. If the applicant or licensee proposes other sources of information as the basis for a proposed standard, the NRC assesses the adequacy of the information the applicant or licensee is referencing.

³ TEELs are discussed in a DOE Handbook DOE-HDBK-1046: http://orise.orau.gov/emi/scapa/files/doi-hdbk-1046-2008_ac.pdf

⁴ Globally Harmonized System of Classification and Labelling of Chemicals (GHS), fifth revised edition, 2013, Part 3 Health Hazards

⁵ Occupational Safety and Health Administration, Final Rule on Hazard Communication, *Federal Register*, Vol. 77, No. 58, March 26, 2012, pp. 17574-17896.

Table 1 – Acute Exposure Hazard Information for Common Fuel Cycle Process Chemicals⁶

Chemical	GHS Hazard Statement in GHS database ⁷ (Inhalation, dermal, ocular, ingestion exposure)	NIOSH skin notation ⁸	Noted by OSHA list for skin adsorption ⁹	AEGL; ERPG ¹⁰ ; TEEL (Inhalation exposure)
ammonium hydroxide (NH ₄ OH)	H314 1B (causes severe skin burns and eye damage) H335 (may cause respiratory irritation): C ≥ 5 %	No	No	Yes
ammonium fluoride (NH ₄ F)	H301 (toxic if swallowed) H311 (toxic in contact with skin) H331 (toxic if inhaled)	No	No	No
hydrochloric acid (HCl)	H314 1B (causes severe skin burns and eye damage): C ≥ 25% for 1 hour exposure H335 (may cause respiratory irritation): C ≥ 10 %	No	No	Yes
hydrofluoric acid (HF)	H300 (fatal if swallowed) H310 (fatal in contact with skin) H314 (causes severe skin burns and eye damage): C ≥ 7% for 3 minute exposure; 1% ≤ C < 7% for 1 hour exposure H330 (fatal if inhaled)	SK: SYS (FATAL)-DIR (COR): may be potentially lethal or life-threatening following exposure of the skin ; corrosive following exposure of the skin	Yes	Yes
hydrogen peroxide (H ₂ O ₂)	H302 (harmful if swallowed) H314 (causes severe skin burns and eye damage): C ≥ 70% for 3 minute exposure; 50% ≤ C < 70% for 1 hour exposure H322 (harmful if inhaled) H335 (may cause respiratory irritation) C ≥ 35%	No	No	Yes
nitric acid (HNO ₃)	H314 (causes severe skin burns and eye damage): C ≥ 20% for 3 minute exposure; 5% ≤ C < 20% for 1 hour exposure	No	No	Yes
perchloroethylene (C ₂ Cl ₄)	H315 (causes skin irritation)	No	No	Yes
sodium hydroxide (NaOH)	H314 (causes severe skin burns and eye damage): C ≥ 5% for 3 minute exposure; 2% ≤ C < 5% for 1 hour exp.	SK: <u>DIR (COR)</u> . corrosive following exposure of the skin	No	Yes
sulfuric acid (H ₂ SO ₄)	H314 (causes severe skin burns and eye damage): C ≥ 15% for 3 minute exposure	No	No	Yes
Tributyl phosphate ((CH ₃ CH ₂ CH ₂ CH ₂ O) ₃ PO)	H302 (harmful if swallowed) H315 (causes skin irritation)	No	No	Yes
uranyl nitrate (UO ₂ (NO ₃) ₂)	H300 (fatal if swallowed) H330 (fatal if inhaled)	No	No	Yes

Note: Exposure to chemicals with hazard or skin notation statements in bold would generally be considered a high consequence event in the context of an ISA. Exposure to chemicals with a hazard or skin notation statement that is underlined would generally be considered an intermediate consequence even in the context of an ISA. Skin Corr 1A is for exposure less than 3 minutes. Skin Corr 1B is for exposure less than 1 hour.

⁶ The user should verify that current information is used because the sources identified in Table 1 are occasionally revised.

⁷ GHS information source: <http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-Stoffdatenbank/index-2.jsp>

⁸ NIOSH skin notation profiles: http://www.cdc.gov/niosh/topics/skin/skin-notation_profiles.html

⁹ Table A-1 of OSHA Technical Manual Section II, Chapter 2: https://www.osha.gov/dts/osta/otm/otm_ii/otm_ii_2.html

¹⁰ The AEGL and ERPG levels were established considering the more vulnerable receptors in the exposed public (elderly, children).

Table 2 – Chemical Exposure descriptions and statements related to the performance requirements in 70.61

	Description in 70.61	Description in AEGL ¹¹	Description in ERPG ¹²	Description in GHS Hazard Statements
High Consequences	Could endanger the life of a worker	AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.	ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.	H330 Fatal if inhaled H310 Fatal in contact with skin
	Could lead to irreversible or other serious, long-lasting health effects to any individual located outside the controlled area	AEGL-2 is the airborne concentration 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.	ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.	H331 Toxic if inhaled
Intermediate Consequences	Could lead to irreversible or other serious, long-lasting health effects to a worker	AEGL-2 is the airborne concentration 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.	ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.	H331 Toxic if inhaled H311 Toxic in contact with skin H314 Causes severe skin burns and eye damage H318 Causes serious eye damage
	Could cause mild transient health effects to any individual located outside the controlled area	AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.	ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor.	H332 Harmful if inhaled

¹¹ The Acute Exposure Level Guidelines have been developed primarily to provide guidance in situations where there can be a rare, typically accidental exposure to a particular chemical that can involve the general public. They are based primarily on acute toxicology data and not subchronic or chronic data. They are designed to protect the general population including the elderly and children, groups that are generally not considered in the development of workplace exposure levels.

¹² The Emergency Response Planning Guideline (ERPG) values are intended to provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects as described. The ERPG values should not be expected to protect everyone but should be applicable to most individuals in the general public. Since these values have been derived as planning and emergency response guidelines, not exposure guidelines, they do not contain the safety factors normally incorporated into exposure guidelines. They are estimates, by the committee, of the thresholds above which there would be unacceptable likelihood of observing the defined effects. The estimates are based on the available data that are summarized in the documentation. In some cases where the data are limited, the uncertainty of these estimates is large. Users of the ERPG values are encouraged strongly to review carefully the documentation before applying these values.

III. CONCLUSION

The NRC regulations for SNM use risk informed performance standards. Assessment of compliance with the performance standards requires a thorough identification of credible hazards, including chemical hazards, potential accident scenarios, and an evaluation of these scenarios in terms of likelihood and consequences. New hazards may be introduced as the result of the introduction of new tech and /or new processes. Therefore, it is important that regulators and operators maintain the safety mindset and conduct thorough analysis and review of the new hazards. Additionally, it is important that guidance and reports be routinely updated as new information comes out (e.g. toxicity information, new safety datasheets and safety practices).

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Prevention of chemical risks in Chemical Facilities in France

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The French legislation regarding the prevention of risks in the Chemical industry has been elaborated since the beginning of the 19th century. It was based on the knowledge of hazards posed by a tremendously evolving science at that time: Chemistry.

This legislation has fed the European directive on major-accident involving dangerous substances, like the need for operators to provide a safety report to the national competent authorities. The mechanisms linked to the elaboration of safety reports were also used by the nuclear industry, and especially by the nuclear fuel cycle facilities management, although the sector reclaimed specific researches in fluorine chemistry. Other principles, like the defence-in-depth principle, were more, at least at the beginning, used in the Nuclear industry. Nevertheless, there have been always interactions between the sectors of Chemistry and Nuclear, as the matter of a comprehensive field called “prevention of hazards”.

1°) Some examples of industrial accidents through the world :

Since the beginning of its operation, the chemical sector has experienced accidents that led to, in some occasions, dramatic consequences. A few of them still remains in the memories of the specialists of industrial hazards,

- The Flixborough accident in the United Kingdom in 1974

A huge explosion and fire resulted in 28 facilities, personal injury both on and off-site, and the complete destruction of the industrial site. It also had a domino effect on other industrial activity in the area, causing the loss coolant at a nearby steel works which could have led to a further serious accident.

- The Bhopal Accident – India, 1984

At a pesticide manufacturing plant set up in 1969, a release of about 40 tonnes of methyl isocyanate (MIC) and other toxic gases continued for 2 hours during the night of 2nd to 3rd December 1984, subsequent to a runaway reaction caused by the addition of water into a MIC tank. The consequences of this release were uncontrolled due to many safety systems being defective or shunted for purposes of lowering operating costs.

These toxic emanations led to a tremendous number of victims among the local population: between 3,000 and 25,000 deaths, and 170,000 to 800,000 intoxications according to sources. The injured streamed into hospitals which were under-equipped and not prepared for such a surge of victims and so were quickly saturated, requiring makeshift installations to be assembled. Due to the company's lack of communication and a denial regarding the potential presence of hydrogen cyanide in the discharge, physicians faced with extreme symptoms (acute oedema in the lungs, respiratory distress, persistent coughing, ocular lesions, etc.) were hard pressed to identify a suitable treatment.

- The Seveso Accident – Italy, 1976

At about 12:37 p.m. local time on July 10, 1976, a runaway industrial chemical reaction ruptured a pressure disk in a reaction vessel at the small ICMESA chemical manufacturing plant in the Lombardy region of Italy--just north of Seveso, Italy, and about 16 miles (25 kilometers) north of Milan, Italy. It released from one to fifteen pounds (0.45 to 6.8 kilograms) of the extremely toxic compound 2,3,7,8-tetrachlorodibenzopara-dioxin (TCDD), or dioxin, into the air. A light breeze blew the dioxin cloud southward over the surrounding neighborhoods, while contaminating the area, killing many birds and small animals, and injuring many people in its path. No people died from the accident, however, it resulted in what was considered, at the time, the highest known exposure to TCDD in a residential area.

- The AZF Accident in Toulouse – France - 2001

Between 20 and 120 tonnes of a stock containing more than 300 tonnes of ammonium nitrate refuse detonated in the AZF fertiliser plant in Toulouse. The causes and circumstances surrounding the accident would give rise to several investigations and expert appraisals during the following months. Over a 250-m² floor area, the depot formed a band 25 m long, 8 to 10 m wide and 2 to 4 m high. The explosion, corresponding to a 3.4 magnitude earthquake on the Richter scale, could be noticed up to 75 km away. Its intensity was evaluated as equivalent to 20-40 tonnes of TNT.

At the time of the explosion, 266 plant employees and 100 subcontractors were working onsite. 31 deaths are recorded:

- 21 deaths occurred at the AZF facility. Five of the casualties were working for subcontractors and 5 others were performing a range of onsite activities (delivery, elevator repair, etc.) or just passing by
- 1 was assigned to the SNPE neighbouring site
- 9 were located outside the facility, all of whom were killed either immediately by the explosion or over the following days.

Moreover, hundreds of serious injuries were reported, of which 300 victims remained in hospital for over 6 days. On the whole, thousands of people in the vicinity would require hospitalisation. On October 17th, 2001, the Haute-Garonne Prefecture tallied a total of 2,442 individuals affected by the accident. Property damage to the plant was considerable: an oval crater 65 m long, 45 m wide and 7 m deep occupied the spot where the depot once stood; 80 ha of the plant were largely devastated. This facility and 5 nearby chemical sites also affected by the accident were required to suspend activities and ensure safety at their respective locations, by disposing over the course of a few months their inventories of hazardous products; 1,300 other firms, combining industries, retail businesses and the building trades, affected to varying degrees (accounting for a total workforce of 21,000) were gradually inventoried over the subsequent weeks. Within a 3-km radius, 26,000 dwelling units were damaged, including 11,200 seriously, and more than 1,200 families had to be relocated. Insurance companies assessed overall property damage at between €1.5 and €2.3 billion.

2°) A legal framework on the prevention of chemical accident in Europe

After almost three years of negotiations in Council and European Parliament, the Seveso I directive was adopted in 1982. In the decade since the Directive's adoption, its strict reporting requirements resulted in the identification of some 130 major accidents European wide.

This directive contained a list of particular installations described by a number of activities. It had a two-tier approach, which means that, for each substance of generic category of substances, two

different qualifying quantities (threshold levels) were mentioned. The directive imposes more obligations on upper tier than on lower tier establishments.

On 9 December 1996, directive 96/82/EC on the control of major-accident hazards (so-called 'Seveso II Directive') was adopted by the council of the European Union. It entered into force on 3 February 1997.

The aim of the 'Seveso II Directive was twofold:

- Firstly, the Directive aims at the prevention of major accident hazards involving dangerous substances,
- Secondly, as accidents do continue to occur, the Directive aims at the limitation of the consequences of such accidents not only for man (safety and health aspects) but also for the environment (environmental aspects).

The Seveso-III-Directive (2012/18/EU) was adopted 4th of July 2012.

The legal framework established by the Directive creates a continuous improvement cycle of prevention, preparedness and response to major accidents. The cycle is closed by provisions on lesson learning.

The main obligations for the operators are:

- Need to take all necessary measures to prevent major accidents and to limit their consequences for human health and the environment. The requirements include:
- Notification of all concerned establishments to the national authority¹;
- Deploying a major accident prevention policy;
- Producing a safety report for upper-tier establishments;
- Producing internal emergency plans for upper tier establishments;
- Providing information in case of accidents;

There are also obligations for Member State authorities

Member States need to ensure that a number of requirements are fulfilled, those include:

- Producing external emergency plans for upper tier establishments;
- Deploying land-use planning for the siting of establishments;
- Making relevant information publically available;
- Ensuring that any necessary action is taken after an accident including emergency measures, actions to ensure that the operator takes any necessary remedial measures and informing the persons likely to be affected;
- Reporting accidents to the Commission;
- Prohibiting the unlawful use or operation of establishments;
- Conducting inspections.

¹ A "severity" scale was made official in February 1994 by the Committee of Competent Authorities (CCA) of EU Member States as a means of applying the SEVESO Directive.

It is based on a series of 18 technical parameters intended to objectively characterise the effects or consequences of accidents. Each of these parameters contains 6 levels, with the highest level determining the accident's index rating.

Member States may maintain or adopt stricter measures than those contained in the Seveso Directive. This is the case in France where the main obligations of the directive, like the safety report are required also for lower tier establishments. Another legal obligation that applies in France as a consequence of the AZF accident in 2001 is the possibility to regulate the construction and the inhabitation in the vicinity of upper-class Seveso establishments, through the Technological Risk Prevention Plans (PPRT). The aim of the PPRT is to ensure the compatibility of the industrial activities with the presence of population, the local development projects and the interests of local residents.

Finally, Citizens' rights are guaranteed.

- The public concerned needs to be consulted and involved in the decision making for specific individual projects;
- Subject to the conditions outlined, Member State authorities need to make available any information held pursuant to the Seveso Directive;
- Access to justice needs to be granted.

All the principles that have been established for the prevention of major accidents in chemical plants can be relied to principles used in legal prescriptions for nuclear facilities. Since the beginning of the industrial developments of nuclear installations, cross safety assessments have been realized in both fields.

The exhaustive assessments of actions generated by initiator events (earthquake, floodings, aircraft crash...) in the safety report or the common use of alternative probabilistic approach and deterministic approach, that are complementary to enhance the safety of chemical or nuclear facilities shows that, in many countries, there is no tight border between the two fields. Nevertheless, the legal obligations still remain in different regulations, more due to the fact that the choice to rely on nuclear to provide energy is a political choice that remains in the hand of political leaders of European countries.

3°) International cooperation frameworks

The effects of major accidents do not stop at national borders. EU citizens can be seriously affected by accidents in neighbouring countries. Therefore it is necessary to co-operate internationally and to aim at a high level of protection also in non-EU countries. The strengthening of civil societies and providing a level playing field for industry are welcome side-effects of this cooperation.

In addition to bilateral activities and cooperation in the context of EU enlargement, the EU is also active in all relevant international fora, some of which are listed below. Furthermore, actions on major accident hazards also contribute to the international efforts to achieve Sustainable Development Goals and to the Sendai Framework for Disaster Risk Reduction

UNECE: Convention on the Transboundary Effects of Industrial Accidents

The Convention on the Transboundary Effects of Industrial Accidents of the United Nations Economic Commission for Europe is also known as 'Industrial Accident Convention', Helsinki Convention or under the abbreviation 'TEIA'. It was signed in Helsinki (Finland) on 18 March 1992 and entered into force on 19 April 2000. It aims at protecting human beings and the environment against industrial accidents capable of causing transboundary effects and at promoting active international cooperation between the contracting parties before, during and after such accidents.

The Seveso-III-Directive (2012/18/EU) is the main legislative instrument implementing the TEIA-convention in EU law.

UNEP: Flexible Framework on Accident Prevention and Preparedness guidance

The United Nations Environmental Programme (UNEP) is leading the international 'Flexible Framework Initiative for Addressing Chemical Accident Prevention and Preparedness' which promotes chemical accident prevention and preparedness (CAPP) primarily in fast growing economies and developing countries.

OECD: Programme on chemical accidents

The Organisation for Economic Cooperation and Development (OECD) programme on chemical accidents addresses three major areas:

- Development of common principles, procedures and policy guidance
- Analysis of issues of concerns and recommendations for best practices
- Sharing and communication of information and experience.

R&D TO IMPROVE ASSESSMENT OF EXPLOSION RISKS ASSOCIATED WITH RED OIL PHENOMENA IN ORANO LA HAGUE REPROCESSING PLANTS

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The PUREX process is the main industrial process applied to recover uranium and plutonium from spent nuclear fuel. Linked to such processes, the “red oil” phenomena come from the possible reaction between an organic phase (the extractant TBP and its degradation products) and an acidic phase (concentrated nitric acid potentially containing extractable heavy metal nitrates). These complex reactions can lead to a thermal runaway in the plant’s equipment followed by an explosion. They caused several significant accidents in the nuclear industry, especially in the USA and Russia.

In design phase of La Hague plants (1980-1985), the explosion risks due to red oil compounds formation were considered: the risk control measures adopted then were based on lessons learned from previous accidents and scientific knowledge of the time. However, Tomsk accident (1993) feedback and the substantial research works carried out to better understand the phenomena have confirmed the need to reassess the criteria and safety parameters chosen initially to control these explosion risks.

In 2013, an important experimental research programme started as part of an ORANO, CEA and IRSN collaboration. It aims to a better understanding of the phenomena and the main influential parameters, as well as acquiring thermokinetic and physicochemical data to support the modelling studies that are being developed simultaneously by ORANO and IRSN. The results already obtained have allowed IRSN to formulate recommendations regarding the enhancement of red oil risks control, as part of the safety review of the plants, and ORANO to suggest concrete actions to limit risks of overpressure and to improve explosion risks prevention in future equipment.

I. INTRODUCTION

In France, the reprocessing of spent nuclear fuel using the PUREX (“Plutonium Uranium Refining by Extraction”) chemical process is carried out within two plants, UP3-A and UP2-800, located on the ORANO (ex AREVA) La Hague site. In these plants, after the spent fuel assemblies are dissolved in nitric acid, TBP (tributyl phosphate) diluted in HTP (hydrogenated tetrapropylene – TPH in French) is used to extract uranium and plutonium from fission products and minor actinides.

Under the process operating conditions in La Hague plants, reactions between TBP and its degradation products on the one hand, and nitric acid, its derivatives and extractable heavy metal nitrates (uranyl nitrate or plutonium nitrate) on the other hand, can lead to the formation of unstable,

nitrous organic compounds known as “red oil”. These can violently decompose and generate potentially explosive gases.

The formation of these compounds has already led to several accidents, notably in the United States in 1953 and 1975 and, more recently, in Russia in 1993, generally resulting in the destruction of the equipment and rooms involved and in significant radioactive releases to the environment [1]. The feedback and lessons learned from these accidents were the subject of an earlier report in which IRSN presented its state of knowledge at the time [2].

II. REX before 1990

In 1953, the first known red oil incident took place during the evaporation of a solution of uranyl nitrate hexahydrate in nitric acid at the Savannah River plant. The presence of TBP in the evaporator coupled with the absence of sufficient control methods led to an over-evaporation of the solution reaching its thermal decomposition point and causing a violent thermal runaway reaction between TBP and nitrates, followed by an explosion. The equipment was totally destroyed and the building was severely damaged.

The same year a similar event happened at Hanford site, caused by an undetected failure in the pump feeding the uranyl nitrate to the evaporator, by the presence of TBP in the equipment and by the absence of safety control. The consequences were less important thanks to the presence of a rupture disk in the evaporator.

An incident involving plutonium took place at Oak Ridge laboratory in 1959 at a stripping tower used for preparation of plutonium nitrate concentrate. The presence of TBP in the equipment led to an explosion, the destruction of the evaporator and the building and the radioactive contamination of the surroundings.

In 1975, a new explosion occurred at the Savannah River plant. Over 100 L of TBP were unexpectedly carried over with the concentrated uranyl nitrate solution even though it had already passed two evaporators. While the solution was undergoing denitration, in a boiler-type batch evaporator used for conversion into uranium trioxide, and although the established procedures were undertaken, temperature rose from 200°C to 450°C, flammable gases were massively produced and finally, despite the start of the safety ventilation, an explosion occurred. The accident's cause was the phase inversion of concentrated TBP due to reduced uranium concentration during rinsing operation that led ultimately to the inadvertent transfer of bulk solvent to a uranium denitrator and to the accident [[3]]. Prior to this explosion, the possibility of a phase inversion was not properly recognized and all tanks were only periodically skimmed to remove floating organic solution (TBP-HTP). No agitation was planned. Over 200 L of TBP were recovered from various hold tanks and process vessels following the accident investigation. Such a quantity was not expected to accumulate within the system, nor was it expected that TBP could be pumped from one process tank to another. Indeed, TBP organic phase was assumed to float over the aqueous phase and should have remained in the first tank, since the solution is pumped from the bottom of the tank but not entirely in order to avoid carrying over the floating organic phase. Following the accident, agitation was implemented to ensure that organic compounds do not build-up in process vessels [1] [3] [4] [5].

These incidents showed that the amount of TBP, the solution temperature, the nitrates' concentration in the solution and the adequate equipment venting play a significant role in the red oil runaway reaction.

III. ORANO La Hague UP2-800 & UP3-A plants' design

During the design of the UP2-800 and the UP3-A plants, in the 1980s, the risks of explosion associated with red oil compounds were taken into account in the safety analysis of the evaporators used to concentrate acidic aqueous streams, coming from different extraction or purification cycles as well as from effluent management units, containing nitrates (either nitric acid or uranyl and plutonium nitrate) and residual amounts of organic solvent. The units identified as concerned by this risk were the uranyl nitrate concentration units, the intercycle concentration units, the high-level effluents concentration units, the fission products concentration units, the acid recovery units and the oxalic liquor treatment units. Several measures were implemented based on the state of knowledge and available operating experience feedback available at that time. These included maintaining the evaporator temperature below 135°C (to avoid any thermal runaway reaction below this temperature threshold), and very low concentrations of solvent (TBP) in the solutions fed to the evaporators [3]. These two functional requirements were adopted in the safety demonstrations and incorporated in the general operating rules of the facilities concerned.

The organic effluents treatment units are also concerned by red oil risks. In these units, the feeding stream is mainly composed of organic solvent and therefore the risk prevention measures consist in minimizing the amount of nitrates that it contains.

To guarantee a temperature below 135°C in the evaporators under normal operating conditions, the heating loop is equipped with temperature and pressure controllers as well as a high temperature and high pressure alarms which, once breached, will shut off the heat fluid supply. Moreover, the circuit also has two relief valves that limit its pressure rise, and therefore, the heating fluid's temperature.

The organic effluents treatment units are equipped with liquid falling film evaporators, with pressure and temperature controllers located on the heating system as well as high pressure and temperature warnings. At the upstream of the evaporator, the solvent temperature is also controlled.

Regarding the TBP amount limitation in the evaporators feeding solutions, a permanent diluent wash is implemented for the aqueous feeds arriving from the extraction cycles: this wash is carried out in a battery of mixer-settlers or in a pulsed column. A solvent flushing operation also takes place, periodically, in the tanks located upstream the evaporators, allowing to separate TBP from the feeding stream by decantation. These measures allow the aqueous stream to limit its TBP content to a few dozen milligrams per litre.

As not all streams feeding the evaporators can be washed, a systematic control of the TBP concentration is realized before transfer to an evaporator. Moreover, the evaporator's feeding tank is not completely emptied to avoid the transfer of any eventually floating TBP.

For the specific case of the organic effluents treatment units, before arriving to the units, the feeding stream undergoes a carbonate and soda treatments as well as water wash to reduce the nitrate concentration.

IV. Tomsk accident - REX

In 1993 at Tomsk plant, an accident happened in a full-scale tank equipped with a cooling/heating jacket and a bubbler-mixer at the bottom. Upon discharge from an evaporator in TOMSK-7 PUREX first extraction cycle, an aqueous solution carried over a "substantial volume" of TBP and its degradation products into a 35 m³ pressurized process tank containing 25 m³ of uranyl nitrate and plutonium at around 40°C. The volume carried over is reported to have sat for at least several months. In addition, the uranyl nitrate solution contained various other nitrates and residual fission products. After this long period, 1.5 m³ of concentrated nitric acid (14 N) was added to the tank, which had no mixing and was only cooled from the bottom. This addition led to the formation of three phases: a heavy phase of aqueous uranyl nitrate, a second one of used solvent and a third floating one of

concentrated nitric acid. The uranyl nitrate phase heated to around 80°C leading to the progressive heating of the second phase until its self-heating reaction with nitric acid caused the mixture to boil for over two hours, producing a gaseous mixture at an accelerated rate (possibly butene, butane, butanol, carbon monoxide, and other explosive vapours, along with steam). All the produced gases generated a pressure increase, causing two explosions in the evaporator buffer tank and releasing around 20 TBq of alpha and beta emitters to the environment.

The feedback acquired from Tomsk accident showed an incapacity to manage the heat duty and the produced gases at temperatures higher than 70/80°C during the initiation TBP degradation step. It has led to an increase of pressure and temperature reaching the threshold temperature of red oil runaway, where red oils reaction occurred. Such phenomena could be observed in unheated equipment, such as buffer tanks, relay or storage tanks and transfer pots. The explosion was the result of the combination of several factors: sufficient amount of organics, lack of agitation, reduction of the blowdown section, increase of nitric acid concentration, insufficient temperature and pressure monitoring and presence of easily oxidizing degradation products in the organic phase. Separately, these factors would not have been able to lead to an explosion.

Since that accident, considerable international R&D work has been carried out to better identify reaction mechanisms and key parameters that may lead to red oil runaway reactions and to learn more about the factors or conditions that could help control this risk.

The R&D and feedback led to review the control measures to prevent red oil explosions in nuclear facilities. In 2003, an assessment of the potential for red oil explosion in the Department of Energy's (DOE) defence nuclear facilities stated that four controls could be used to prevent a red oil event: a temperature below 130°C, a sufficient vent for the process, an optimal organic removal from the process and a nitric acid concentration below 10 M [5]. Nevertheless, more research was needed since Tomsk accident started below 130°C.

V. R&D

After an extensive literature review carried out by ORANO and IRSN in 2012, an experimental programme, led jointly by ORANO, IRSN and CEA, was launched in 2013 in order to acquire new scientific knowledge on red oil thermal runaway phenomena and the parameters that influence and govern them (nitric acid concentration, presence of uranium and of organic impurities, phase ratio, pressure, etc.) with the objective of improving safety measures implemented to control such risks. This R&D experimental programme is still underway at the CEA Marcoule laboratory.

More precisely, the aim of the programme was to improve thermochemical knowledge of biphasic systems (TBP/HTP – HNO₃) at temperatures higher than the boiling point under the operating conditions prevailing in the evaporation-concentration units of the UP3-A and UP2-800 plants at La Hague. In particular, this involves reviewing the conditions under which thermal runaway is initiated (T_{onset} values), the maximum permissible variation ranges of control parameters (temperature, acidity, pressure, etc.), the possible impact on equipment and facilities, and prevention and mitigation measures aimed at controlling these risks when the units are in operation.

This experimental programme was performed using closed cells which provide penalising results, and was divided in two different tasks. Firstly, an extensive campaign was performed in order to identify the most influential parameters for the TBP-HNO₃ thermal runaway reaction. The investigated species were: nitric acid (present in every solution), nitrous acid, butanol, butyl nitrate, DBP (di-butyl phosphate), uranium, HTP, nitrates and fission products (as metallic ions). This campaign took place in a non-adiabatic calorimeter TSU (thermal screening unit – Figure 1) [6], equipment designed for fast hazard screenings and therefore perfectly suitable for heterogeneous liquid systems like the two-phase TBP and nitric acid one.

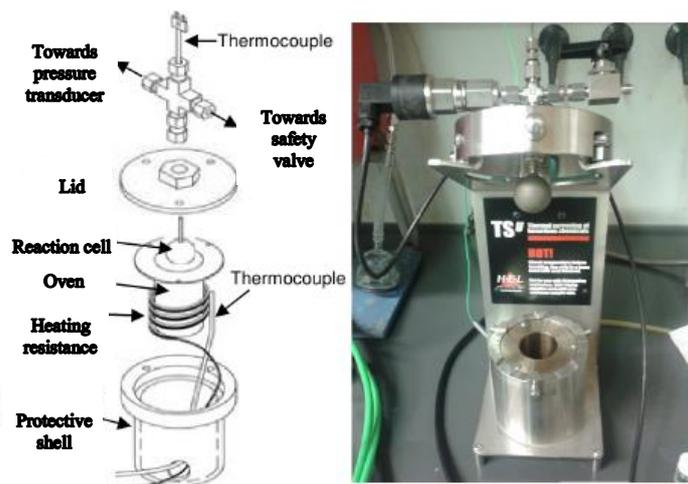


Figure 1: Thermal screening unit (TSU) calorimeter

In addition, the steel cell selected can withstand the very high pressure variation associated with the highly exothermic reactions. Nevertheless, its volume was small (8 cm^3) leading to a phi factor¹ larger than 1, typically around 2. Given this fact, these first experimental results shall be considered as qualitative data from the thermochemical point of view.

Experiments were conducted with an aqueous-organic phase (A/O) volume ratio of 4 using a 2.5 mL solution where the organic phase was always saturated with nitric acid beforehand. The heating ramp was settled at $1^\circ\text{C}\cdot\text{min}^{-1}$.

From these experiments, the following conclusions can be drawn. The nitric acid concentration is the main factor affecting the thermal runaway: as the acidity rises up to 13.8 M, the onset temperature (the threshold of the self-sustained thermal runaway) decreases and the rate at which temperature and pressure rise increases. At low nitric acid concentration (1 M), the presence of uranyl nitrate leads the solution towards a runaway behaviour, certainly due to the increase of nitrate concentration in the organic phase. However, its effect at higher acidity seems to be negligible. Like the organic solvent, the diluent HTP similarly reacts with nitric acid leading to thermal runaway but this substance may be less stable due to a decrease of the onset temperature compared to a system with undiluted TBP.

Secondly, the identified parameters were tested with a targeted set of experiments in order to accurately investigate temperature and pressure behaviour and to determine thermo-kinetic data like heat release and pseudo rate constant. For this task, a pseudo-adiabatic calorimeter Phi-Tec II model, as shown in Figure 2, was used [7].



Figure 2: Phi-Tec II calorimeter and its external reactor (left), reaction cell (right)

¹ Phi-factor, or adiabatic factor: ratio of the thermal mass of sample and container over the thermal mass of sample; the closer it is to 1, the more adiabatic the experiment.

This calorimeter is often considered as a reliable instrument to generate quantitative kinetic and thermodynamic data allowing the scale-up to the industrial level. The data are extracted from recorded thermograms by applying the methodology described by McIntosh & Waldram [8]. In addition, the large volume of the cell, about 100 cm³, allows for more representative studies. To avoid some repeatability issues regarding the reactivity of the diphasic solution, the linear ramp rate mode was chosen instead of the heat-wait-search one.

1. Development of the experimental protocol

Several input parameters have been optimised in order to define the most reliable protocol to investigate the phenomena related to the red oil risks. The Phi-Tec II calorimeter is operated with a closed cell, therefore the quantity of solution (or filling ratio) as well as the phase ratio affect the development of the thermal reaction. These parameters are inter-dependent, the variation of one of them modifying the optimal value of the other one. Therefore, the filling ratio value was constant (30% and 55%, representative ratio in the evaporators of the PUREX process). The aqueous to organic (A/O) phase volume ratio modifies the heat release, which is also a function of nitric acid concentration. Thus, for each acidity, the A/O ratio selected reflected the maximum of heat release. An example of such evolution of the heat release (ΔH), expressed by mole of organic solvent, is shown in Figure 3. This phenomenon, already mentioned by different authors [9] [10], indicates that the chemical runaway may not only be driven by the degradation of TBP or that a bias may come from the evaluation of the heat capacity of the solution. The intensity of the exothermic process in two-phase systems remains an open issue. In these experiments, the nitric acid concentration varied from 2.5 M to 13.8 M and the corresponding optimal A/O ratios always evolved between 20 and 30. To obtain accurate thermochemical data, the value of phi-factor was carefully checked for each run. That implies the mandatory use of Hastelloy cells, instead of glass ones. For the experiments performed at a 30% filling ratio (the most unfavourable value), the adiabatic factor was close to 1.1.

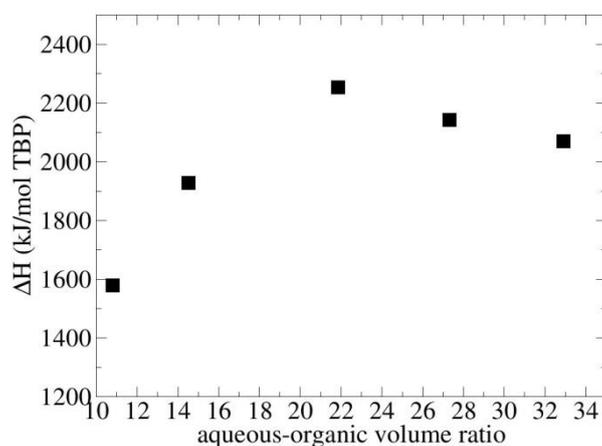


Figure 3: Example of classical effect of the aqueous-organic phase volume ratio on the heat of reaction - conditions: organic phase TBP-aqueous phase HNO₃ 8.5 M, filling ratio 30 %

2. Overview of main results

The main accomplishments of this study are its completeness and its realistic conditions, excepted the use of penalising closed cells, as the evaporator's working conditions in terms of acidity as well as filling ratio were taken into account.

The trend about the onset temperature previously highlighted during the first task has been confirmed and evaluated. The nitric acid concentration has an important effect, indeed onset temperature

gradually decreases when the acidity rise occurs to tend towards 105°C for the highest investigated value (13.8 M). It is to be noted that experimental onset temperatures cannot be directly extrapolated to industrial equipment (open system, heat transfer...). The runaway rate as well as the maximal temperature increase when the amount of organic solvent increases or when the aqueous volume decreases. Nevertheless, for these criteria, the acidity has a fairly low effect especially in [5-13.8 M] range. A similar trend was noticed regarding the pressure data. The uranyl nitrate modifies the thermal runaway only at low acidity (1 M of nitric acid). For this set of experiments, the increases of maximal temperature and of pressure and temperature rise rates were dependent on the uranyl nitrate concentration. That is certainly due to a highest extracted amount of nitrate compounds in the organic solvent. The experiments showed no influence of uranyl nitrate on onset temperature which is in agreement with the ascertainment of Chandran *et al.* [11], whereas former study made by Glossop [9] predicted the opposite behaviour.

Regarding the thermochemical results, all experiments presented a runaway behaviour which follows a pseudo first order kinetic rate law. It agrees with most of the published data (see reviews [12][13] and references therein) and corroborates the fact that the degradation process is driven by the hydrolysis of TBP as the principal reaction. The obtained activation energies always decrease if the acidity increases, confirming the catalytic effect of the nitric acid on the chemical processes. For the 8.5 M acidity, the following Arrhenius parameters are obtained at optimal A/O ratio: the activation energy (E_a) and the pre-factor logarithm ($\ln(A)$, A in s^{-1}) equal 108 $\text{kJ}\cdot\text{mol}^{-1}$ and 23.4, respectively. These parameters of the overall decomposition rate are in good agreement with previous ones obtained with single organic phase saturated with nitric acid [11] [14]. Indeed, Chandran *et al.* [11] reported (for both acidity 8 M and 15.6 M) the following datasets: E_a between 108.8-103.5 $\text{kJ}\cdot\text{mol}^{-1}$ and $\ln(A)$ varying from 24.8 to 22.5, while Nichols' kinetic parameters were 112 $\text{kJ}\cdot\text{mol}^{-1}$ and 24.5. These data seem to show similar rates in one-phase organic and in two-phase TBP-nitric acid systems; nevertheless, as the ascertainment is not substantiated, further investigations in one-phase system using the same aqueous acidity range as studied (from 2.5 M to 13.8 M) will be carried out. However, it confirms that the exothermic processes could occur at the interface or inside the organic phase.

An increase in nitric acid aqueous concentration (from 2.5 M to 13.8 M) does not have a significant effect on heat release: from 2000 $\text{kJ}\cdot\text{mol}^{-1}$ to 2300 $\text{kJ}\cdot\text{mol}^{-1}$. The comparison of these experimental data with theoretical calculations, based on heats of formation coupled to postulated degradation paths, is difficult due to the lack of accurate chemical speciation of liquid end-products (to estimate the oxidation extend of TBP by-products) as well as the existence of parallel processes which participate to the overall heat release. In addition, corresponding estimation does not take into account the enthalpies of solvation of each species and the temperature effect, inducing a bias on the enthalpy of reaction.

3. Ongoing R&D

In order to assess the quantity of solvent that is likely to accumulate in the evaporators and to simulate their dynamic behaviour during normal operation and accident condition, a simulation tool is being developed at IRSN and will be validated by the experimental data obtained as part of the ongoing research programme. This tool is built from some ASTEC [15] modules dealing with the thermal and the chemical phenomena.

Once the tool has been validated, computation and resolution of the kinetic equations system for the known reaction scheme of TBP (see reference [12] for the detailed scheme therein) will take place. Thermal and chemical phenomena are taken into consideration by two different modules: a thermal and a kinetic one; the values of heat and gas generation determined by the chemistry module are used to feed the thermal one.

To feed the tool, a theoretical study based on quantum chemistry has been carried out in order to improve the knowledge of some physical properties for the key species [16]. For example, the thermodynamic properties are mandatory to calculate the heat generated by chemical reactions. Similar approach is ongoing regarding the uranyl nitrate-TBP complexes. Additional data will be obtained experimentally in order to establish a more precise reaction mechanism of red oil reactions (kinetics, speciation, etc.).

In the near future, the current simulation efforts will contribute to the expertise analysis regarding the enhancement of red oil risks control.

VI. ORANO's new control parameters

Even though the programme was not completely finished, the results allowed ORANO to strengthen safety demonstrations for the UP3-A plant as part of its safety review. As a matter of fact, ORANO has modified its red oil risk analysis in line with the safety principles adopted at the design stage [3]. The new phenomenological approach taken by ORANO indicates that the simultaneous conditions are required for a red oil runaway reaction to occur:

- an organic phase containing TBP and/or its degradation products;
- a concentrated nitrate ion phase (nitric acid, nitrates coming from salts);
- a temperature higher than the runaway initiation temperature;
- a ventilation system that lacks the capacity to remove the gases generated.

This new approach confirms that control of the red oil risk must be demonstrated not on the basis of temperature alone, but simultaneous control of the quantity of solvent in the equipment, the temperature and acidity of the medium, and adequate removal of process gases. Thus, assuming that the evaporators contain a significant quantity of solvent (whether due to gradual accumulation or sudden inlet), the risk of thermal runaway in units concerned by the red oil risks cannot be ruled out simply by limiting the evaporator temperature.

ORANO identified the heated units and equipment concerned by these risks in the UP3-A plant. In addition, unheated equipment such as storage, receiving, and feeder tanks or buffer tanks were studied as, based on feedback from Tomsk accident, they could also be concerned by red oil risks. The analysis of the associated risks in tanks is currently being performed by ORANO.

For future fission products concentration units, ORANO has suggested concrete actions to improve explosion risks prevention and to limit overpressure in the identified equipment in case of a thermal runaway, particularly regarding generated gases extraction.

VII. CONCLUSION

As part of the La Hague plants periodic safety review, studies were carried out in order to better understand TBP organic phase behaviour when in contact with acidic aqueous solutions at different temperatures. Datasets of interest were determined by means of a TSU calorimeter to confirm the major influential parameters. Among these datasets, the thermokinetic parameters were measured using a pseudo-adiabatic calorimeter (in closed system) under chemical conditions similar to those of the equipment identified as "at risk" in terms of red oil reactions at La Hague plants.

Consequently, qualitative and quantitative research made by an experimental programme has allowed IRSN and ORANO to determine specific values of thermokinetic data for the TBP-HNO₃ reaction as well as the influence of other species, like diluent or uranyl nitrate. IRSN will use the results of this research in a computational tool to simulate specific scenarios based on industrial conditions, in order to support its ongoing assessment of the periodic safety review file for the UP2-800 spent fuel reprocessing plant at ORANO La Hague site.

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R&D PROGRAMME ON VOLATILIZATION AND TRANSPORT BEHAVIOUR OF RUTHENIUM UNDER A LOSS OF COOLING ACCIDENT ON HIGH LEVEL LIQUID WASTE (HLLW) STORAGE TANKS IN REPROCESSING PLANTS AND MITIGATION STRATEGIES

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The reprocessing of spent nuclear fuel produces high level liquid waste (HLLW). Due to the decay heat, the concentrated solutions containing fission products (FP) are stored in cooled tanks to prevent the solution from boiling, evaporating and drying out, which could lead to large releases of radioactive materials to the environment, especially ruthenium volatile species. The loss-of-cooling accident on HLLW storage tanks, considered as a beyond-design-basis accident (BDBA) in the design stage of the La Hague reprocessing plants, is one of the accident scenarios taken into account in defining the on-site emergency plan. Within the scope of the current La Hague reprocessing plants safety reviews and post-Fukushima complementary safety assessments (CSAs), a review of the initial studies carried out on this accident scenario in the design stage confirmed the lack of reliable data on the behaviour of ruthenium. It also highlighted the limits of the models used at the time to evaluate the source term of the accident.

On the basis of a comprehensive literature review, an IRSN research programme has been defined firstly to re-examine the phenomenology of the accident scenario, to acquire missing or updated data concerning the volatilization and transport behaviour of volatile ruthenium and to reassess the associated source term. The second objective of this programme is to investigate the possible implementation of additional ultimate mitigation measures to limit radioactive releases, in case of a failure of the prevention and mitigation measures adopted by the licensee.

I. INTRODUCTION

In the La Hague reprocessing plants, after a period of radioactive decay in pools, the spent nuclear fuel assemblies undergo shearing and leaching in hot nitric acid. The radionuclides present in the leaching solution are separated by solvent extraction (PUREX¹ process) in three fluxes: uranium, plutonium and fission products with minor actinides (designated as FP solutions). FP solutions are concentrated then transferred in dedicated storage tanks for an additional radioactive decay time, before being incorporated in vitrified waste. The concentrated FP solutions exhibit a very high radioactivity associated with a considerable heat release (about 10 watts per litre for a PWR fuel irradiated to 33 000 MWday per ton and cooled for three years before reprocessing), thus the storage tanks need to be cooled permanently. Indeed, due to self-heating, a prolonged shutdown of the tank cooling system

¹ PUREX: Plutonium Uranium Refining by Extraction

could cause the progressive evaporation of the FP solutions to dryness, and culminate in the formation of volatile species of ruthenium and their release in the tank venting circuit up to the environment.

The cooling systems are designed and maintained to perform their function with a very high level of reliability, so that a tank cooling system failure is extremely improbable. The study of the consequences of such an occurrence was nevertheless conducted in the design stage (1980s) as part of the safety demonstration of the La Hague plants, especially in order to determine the time interval after which a substantial release of radioactive materials could take place and to evaluate the effectiveness of the measures planned in the on-site emergency plan to get such a situation under control [1]. Nevertheless, this study presents several limitations. Firstly, it is based on old or incomplete data that need updating, as a result of the few studies that had been carried out on the behaviour of the different forms of volatilized ruthenium, the reaction mechanisms in air/H₂O/HNO₃/NO_x medium, the transport behaviour of these materials and the ruthenium chemistry on the basis of local conditions and compositions of gaseous phases. Secondly, there are uncertainties on modelling calculations as a result of the assumptions adopted for transfer coefficients calculations (air flow, relative humidity, emission rate, size and concentration of aerosols, flow mode, diffusion, sedimentation, etc.). This confirms the need of reassessing the source term and transport behaviour of volatile ruthenium under a total loss of cooling of FP storage tanks accident.

These initial studies have been reassessed within the frame of the post-Fukushima complementary safety assessments and the first periodic safety reviews of the La Hague plants, in light of the recent knowledge acquired since then thanks to many experimental works that have been recently undertaken on this subject, especially in Japan [2].

II. ACCIDENT SCENARIO: ON-SITE EMERGENCY PLAN AND POST-FUKUSHIMA COMPLEMENTARY SAFETY ASSESSMENTS

The principle of a concentrated FP solutions storage unit in La Hague plants is presented in Figure 1.

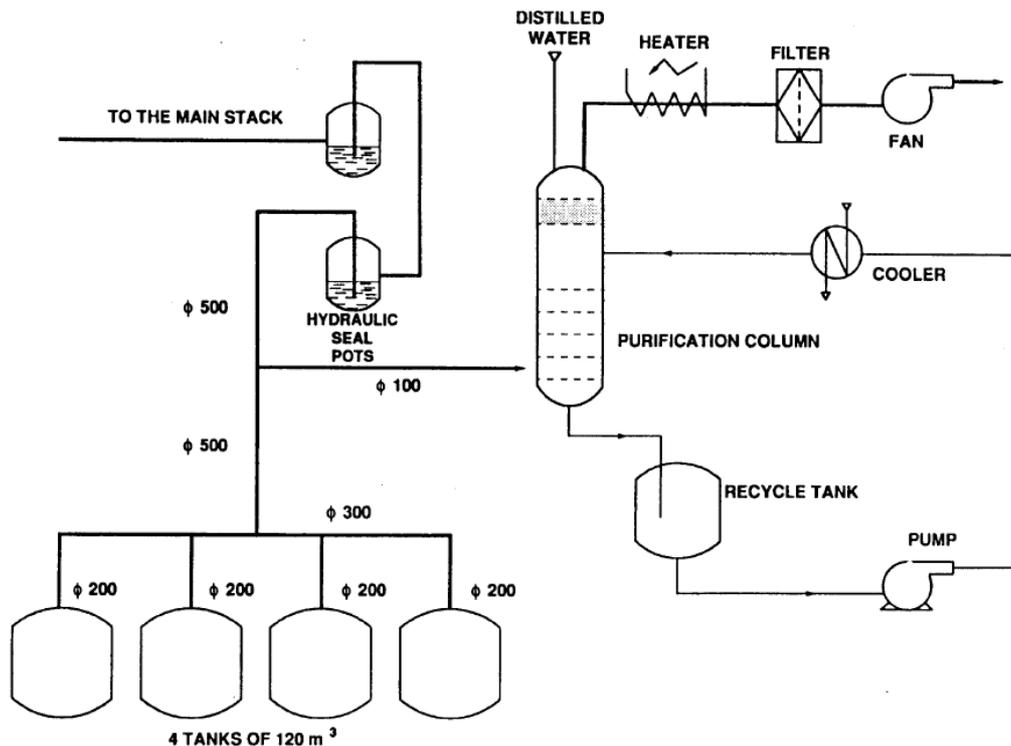


Figure 1: HLLW storage - Vents in normal operating conditions and in accident conditions

In normal operation, the gases and vapours emanating from the storage tanks are extracted to the purification system schematised on the right side of the figure: the inner diameter of the evacuation duct is 100 mm. In case of boiling, this pipe is not sufficient to ensure the evacuation of the vapours produced; the pressure inside the tanks increases until the tanks are connected with the bypass pipe of a larger diameter (500 mm) linking the vents of the tanks to the main chimney stack (100 m high) of the plant. This bypass system, intended to limit the abnormal increases in pressure in the tanks, is protected in normal operating conditions by two hydraulic seal pots (water) installed in series.

The beyond-design-basis accident scenario considered in the on-site emergency plan is the following:

- the initiating event is a total loss of the cooling function of the concentrated FP solutions storage tanks;
- due to self-heating of the highly radioactive FP solutions, their temperature increases progressively in the storage tanks;
- in case of non-intervention of the operators, the temperature of the FP solutions rises up to the boiling point: the time to reach the boiling point depends on the initial temperature of the solutions and their thermal power;
- during boiling, a vapour flow rate appears in the solution in the form of bubbles bursting at the surface of the liquid: droplets are formed and carried along by the vapour out of the tanks, which constitute a radioactivity transfer vector of elements in aerosol form;
- due to transport phenomena, part of the radioactive materials released from the storage tanks deposit in the ventilation ducts and filters, which become irradiating, while the other part is transferred up to the chimney stack, causing radioactive releases to the environment;
- in addition, the evaporation of the solution causes an increase in nitric acid concentration and of the boiling temperature, which leads to the formation of volatile species of ruthenium by oxidation that contribute to a large amount of the effective dose to the population.

The measures presented in the on-site emergency plan, that could be implemented in order to manage the accident situation until the initial failure is fixed, are the following:

- implement means to extend the delay before reaching the boiling point, such as transferring the solutions in order to divide them among all the available storage tanks, dilute them with demineralised water to decrease their temperature, acidity and thermal power, sprinkle externally the storage tanks to decrease their temperature, etc.;
- use the fire extinction network in an open loop in order to supply the cooling system (internal or external circuits) of the storage tanks.

Additionally, after the Fukushima-Daiichi accident, the French nuclear licensees were required to perform Complementary Safety Assessments (CSAs) of their facilities, in order to check the robustness of the nuclear facilities and of the existing organizations to face extreme situations that were not taken into account at the design stage (extreme natural hazards - earthquake, flooding, natural events - higher than required in the initial design standards and total loss of power supply and cooling functions). The CSAs carried out for La Hague plants identified several severe accidents or “dreaded situations”, i.e. a degraded state of the facilities that could lead to a cliff-edge effect and has therefore to be prevented or its consequences to be limited. Remediation means, mitigation means and crisis management means were defined in order to enable the operator to be in total autonomy during the first 48 hours after a dreaded situation, whatever the site conditions, without any complementary human or material means brought from outside the site.

The loss of the cooling function of the concentrated FP solutions storage tanks leading to their boiling was identified by the licensee as a dreaded situation. As such, in order to prevent the solutions from reaching their boiling point, the remediation strategy is to supply cooling water, coming from the on-

site storm-water tank and nearby dam, to the internal cooling coils of the tanks, in an open loop configuration or with a recycling system. The water is supplied using flexible hoses that are connected directly on the cooling coils of the tanks. In case of a failure of this remediation means, additional mitigation means were proposed, in order to inject water directly into the tanks using existing decontamination or instrumentation piping.

These new means complete the measures implemented within the frame of the on-site emergency plan and could be also deployed to manage the accident situation described previously.

While this remediation strategy and the organizational and material means deployed were deemed satisfactory on principle by the Nuclear Safety Authority in order to prevent the solutions from reaching the boiling point, no mitigation means were formally identified by the licensee in order to limit the radiological consequences if the boiling point is nevertheless reached and FP releases to the environment occur.

Consequently, in accordance with the defence-in-depth concept, the possible implementation of additional mitigation measures to limit the releases of FP to the environment, and more particularly ruthenium, if the measures proposed by the licensee fail for any reason, is under investigation. To this purpose, the phenomenology associated with the total loss of cooling of FP storage tanks accident scenario needs to be re-examined, in order to reassess the source term and transport behaviour of volatile ruthenium species in the light of new available knowledge and simulation tools available, and to identify possible additional mitigation measures to reduce radioactive releases. The R&D programme described below attempts to answer these objectives.

III. LITERATURE REVIEW AND R&D PROGRAMME

The behaviour of ruthenium in nitric acid solution has been studied for several decades, following the issues mentioned above. Research works mentioned in the literature can be classified in several categories as listed below:

- general information on ruthenium chemistry in a nitric medium, mechanisms for the formation of ruthenium tetroxide RuO_4 ;
- behaviour of volatile forms of ruthenium in presence of steam, nitric acid and nitrogen oxides (recombination, decomposition, etc.);
- transfer phenomena of the different gaseous species containing ruthenium, solid or liquid species formed, taking into account the conditions of the accidental scenario considered.

Subsequently, the efficiency and performance of various systems that can be used to trap and filter ruthenium (gas/liquid absorbers, steel filters, etc.), or even prevent its volatilization (recombination, addition of reducing agents *in situ*, etc.) has been investigated by research teams, taking into account the different physical and chemical forms expected of this element.

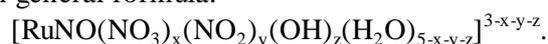
Thus, on these findings, the literature review performed by IRSN allows to identify several areas of work to try to improve knowledge on this topic, described thereafter:

- ruthenium in nitric acid solution;
- means of prevention to avoid ruthenium release;
- ruthenium chemistry in gaseous phase;
- transfer of ruthenium volatile compounds.

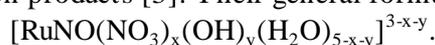
Ruthenium in nitric acid solution:

First, the chemical equilibrium of nitric acid is rather difficult to study, including many redox reactions involving appearance or disappearance of several chemical species. Besides, if a nitric acid solution is subjected to γ radiation, new radical species may appear in solution under the effect of water and nitric acid radiolysis (H^\bullet , HO^\bullet , NO_3^\bullet). These compounds are likely to form secondary harmful species, mainly H_2 and H_2O_2 [3].

Ruthenium in concentrated nitric acid solution ($10^{-2}M \leq [HNO_3] \leq \approx 10M$ during reprocessing process, $\approx 2M$ in HLLW) presents a particular chemistry, with a potential coexistence of very many chemical species, especially complex ions. It is mostly characterized by the formation of nitrosyl ruthenium ion ($RuNO^{3+}$), relatively stable. It consists of a Ru^{2+} complex bound with a nitrosonium ion (NO^+). Moreover, $RuNO^{3+}$ can form octahedral complexes nitrated (linker NO^3^-), nitrous (linker NO^2^-), and mixed nitrated-nitrous with general formula:



Among these chemical species, nitrated nitrosyl ruthenium complexes have been particularly studied and analysed, as they are supposed to be responsible for the difficulties in decontaminating the flow of uranium and plutonium in fission products [3]. Their general formula is as follows:



The important diversity of potentially existing nitrated nitrosyl ruthenium isomers (21 species) is illustrated in Figure 2. Among these complexes, the predominance of one or more species depends mainly on the concentration of nitric acid and nitrate ions.

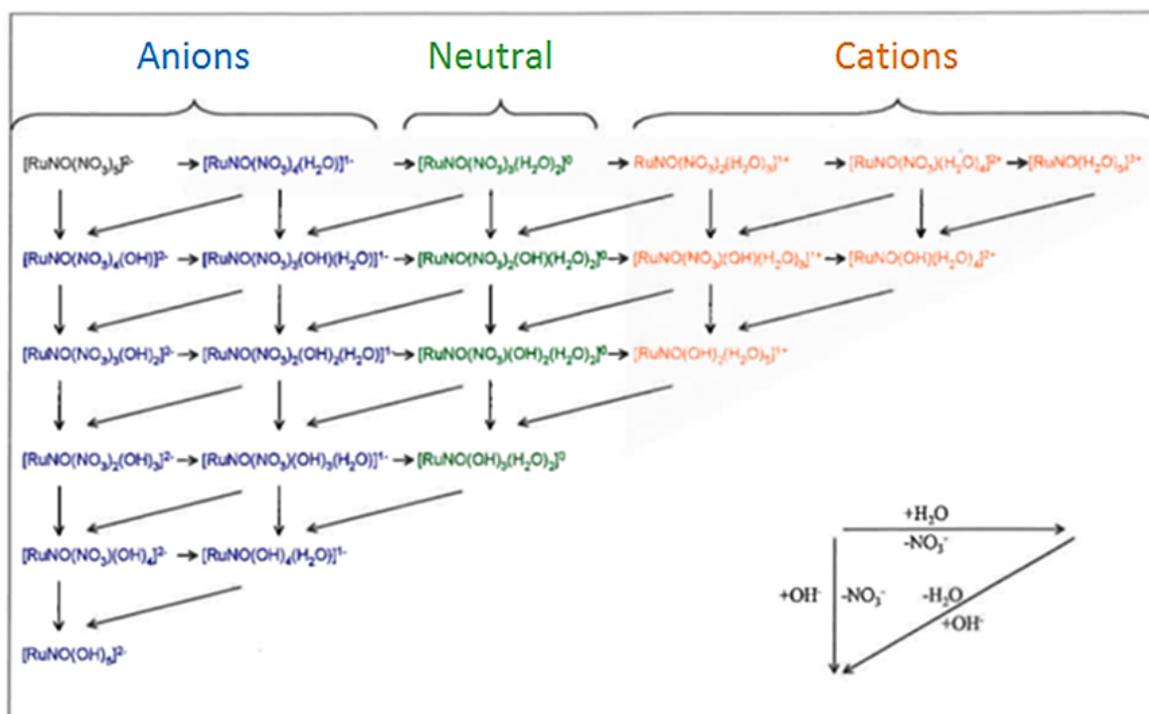


Figure 2: Potentially existing isomers of nitrated nitrosyl ruthenium complexes [3]

In addition to these varied complex ions, ruthenium can also take other minor forms in nitric acid:

- soluble species:

- soluble oxides, mainly Ru(VIII) in H_2RuO_5 i.e. hydrated form of RuO_4 ;
- Ru(IV) in ion $Ru_4O_6^{4+} \cdot xH_2O$, from the reduction of Ru(VIII);

- insoluble species:
 - Ru(0) in metallic ruthenium;
 - Ru(IV) in ruthenium dioxide RuO₂.

R&D outlooks for characterization of ruthenium species:

In the R&D programme planned by IRSN, ruthenium in nitric acid solution will be studied, in order to determine if particular chemical species mentioned above lead preferentially to the formation of volatile compounds containing Ru. To perform this, the feasibility of identification of ruthenium species by ion-exchange chromatography will be investigated in a simplified analytical nitric solution, for several pH and temperature conditions. Indeed, literature mentions works using high performance liquid chromatography to separate ruthenium species in nitric solution [4]. Information collected by these analyses will be crossed with other analytical methods available in the laboratory (ultraviolet-visible spectrometry, ICP-AES²), in order to refine the species identification.

Means of prevention to avoid ruthenium release:

Various methods are listed in the literature for ruthenium trapping in a nitric solution. They mainly depend on the phase of the ruthenium species during trapping mechanism. In general, two types of trapping are identified:

- gas phase trapping of ruthenium (*a priori* in the RuO₄ form) already volatilized;
- *in situ* trapping in nitric solution, by addition of a specific reducing chemical compound, inhibiting the volatilization of ruthenium species.

Gas phase trapping of ruthenium:

Igarashi et al. [5] have performed experimental tests of ruthenium absorption in water, in order to evaluate the influence of the presence of nitrogen oxides (NO and NO₂) on the quantities absorbed. When NO or NO₂ concentration increases in the gas flow, quantities of gaseous Ru decrease sensibly (see Figure 3).

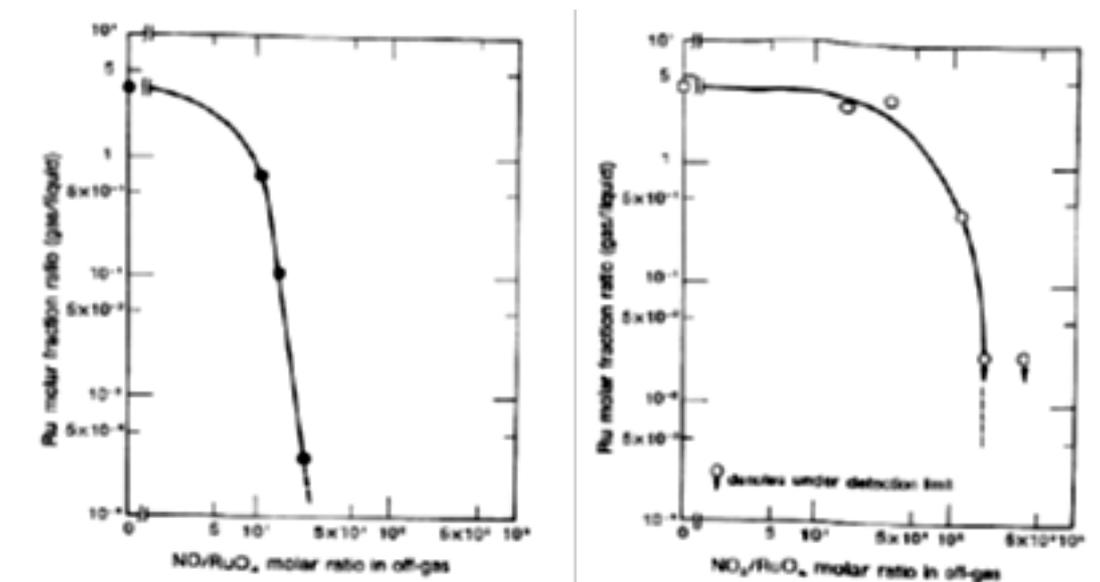


Figure 3: Effects of NO (left) and NO₂ (right) injection on RuO₄ absorption into water [5]

² ICP-AES: Induction Coupled Plasma - Atomic Emission Spectrometry

Analyses performed to determine the nature of ruthenium species trapped in the experimental device suggest that this phenomenon may be due to RuO_4 transformation into nitrated nitrosyl ruthenium complex, less volatile and more absorbable into water. Thus, RuO_4 trapping is better with NO_x injection in presence of water.

In the frame of the RSNR-MiRE³ project, IRSN has developed a test bench for characterization of RuO_4 retention by different devices. The first step has been to characterize the PWR containment depressurization line devices, namely the sand filter and the metallic prefilter. Figure 4 shows an outline of this test bench, divided into three modules, corresponding to generation, filtration and trapping for analysis of gaseous RuO_4 .

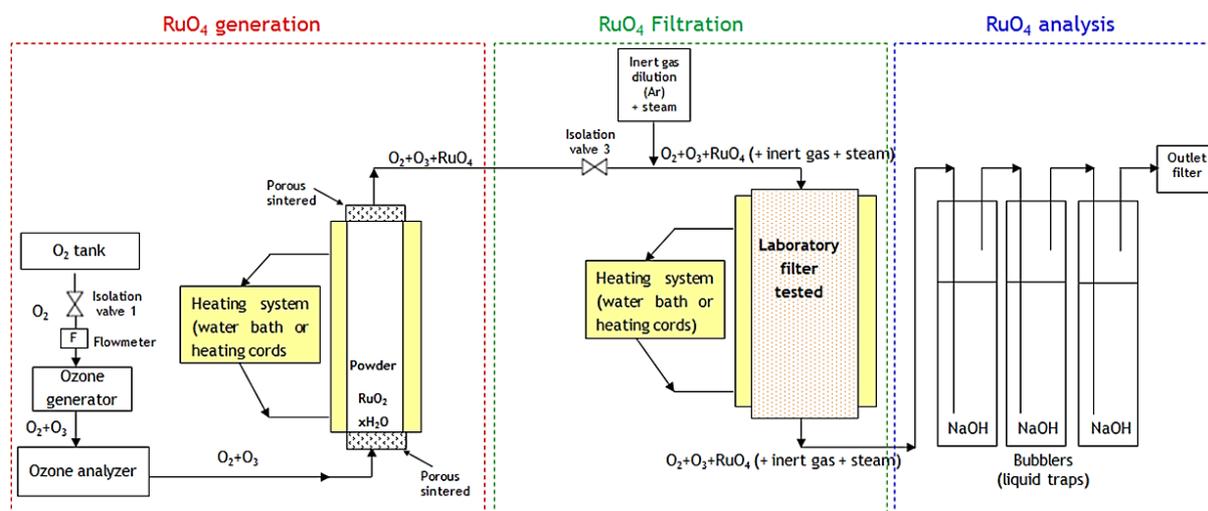


Figure 4: Schematic outline of RuO_4 generation and filtration test bench [6]

Figure 5 shows results obtained, respectively with sand filter and metallic prefilter.

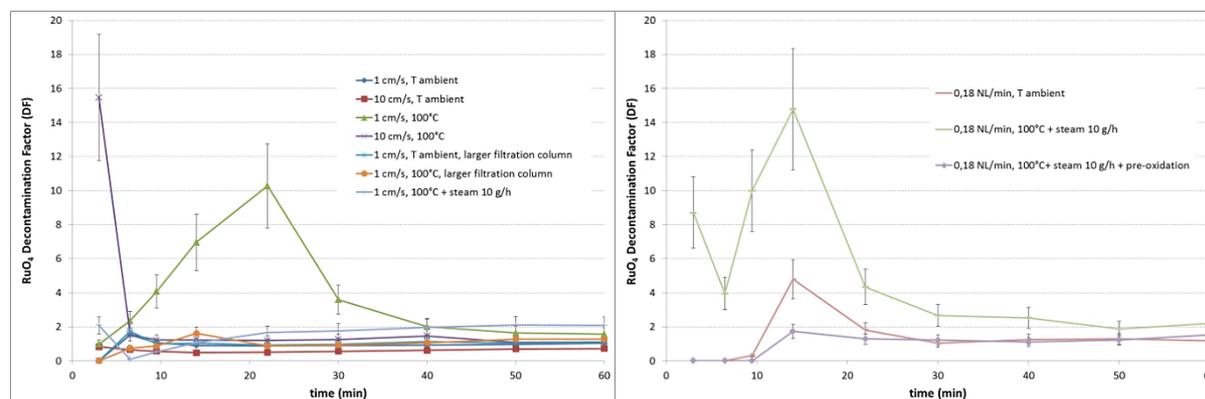


Figure 5: Decontamination Factor obtained for RuO_4 with 10 cm thick sand bed (left) and metallic prefilter (right) [6]

Tests with a 10 cm thick sand bed in the filtration column show no significant retention of gaseous RuO_4 , for different operating conditions ($1 \leq \text{DF}^4 \leq 2$ after 1 h of test for all configurations tested, $\text{DF}_{\text{max}} < 16$, see Figure 5 left [6]). More generally, the experimental results obtained with sand bed show that sand does not trap RuO_4 . Similarly, retention of RuO_4 is low on metallic prefilter

³ Research on Nuclear Safety and Radiation protection - Mitigation of Releases to the Environment, <https://gforge.irsn.fr/gf/project/mire/>

⁴ Decontamination Factor

($1 \leq DF \leq 3$ after 1 h of test for the three configurations tested, $DF_{max} < 15$, see Figure 5 right [6]). Thus, devices with design similar to the metallic prefilter of the containment depressurization line are not suitable for trapping volatile ruthenium such as RuO_4 .

R&D outlooks in gaseous phase:

The operational test bench presented on Figure 4 is currently used to characterize other materials likely to trap gaseous RuO_4 as a function of temperature and gas composition. It is planned to test the following compounds:

- zeolites;
- MOFs (Metal Organic Framework);
- active charcoals.

The objective is to evaluate the DF of each material tested for different configurations (temperature, gas flow rate, relative humidity). These tests started late 2017 and are planned throughout 2018.

In situ trapping in nitric solution

Sato and Motoki [4] focus on the trapping of ruthenium species in nitric solution by means of a decontamination column. The solution used is a real aqueous waste. According to the test considered, the decontamination column consists of different mixtures of zinc, graphite and active charcoals. Tests carried out with decontamination columns, containing, on the one hand a zinc-active charcoal mixture, on the other hand a zinc-graphite mixture followed by a second purification performed 6 months later with only activated carbon, show a good retention of ruthenium. Indeed, the DFs obtained are respectively greater than 6500 and 3650~7300 (global DF). Conversely, columns with a zinc-graphite mixture alone and active charcoal alone show less efficient purification of Ru ($5 \leq DF \leq 10$). Finally, zinc alone seems to retain very few Ru ($1 \leq DF \leq 2$). These results show that flowing the solution in the zinc-graphite mixture transforms the initial ruthenium species into more adsorbable compounds on the activated carbon alone.

In the same way, Ishio et al. [7] and Sawada et al. [8] evaluated the effect of sucrose addition in solutions containing fission products, especially Ru. Ishio et al. [7] used a genuine HLLW sample, called high active concentrate (HAC) derived from a liquid waste of the PUREX process. Results show no decrease in the release of ruthenium if the molar ratio $C_{12}H_{22}O_{11}/HNO_3 = 1/48$ (4% Ru released), but an important decrease with a sufficient addition of sucrose: 0.16% Ru released if the molar ratio $C_{12}H_{22}O_{11}/HNO_3 = 1/24$, and 0.03% Ru released if the molar ratio $C_{12}H_{22}O_{11}/HNO_3 = 1/12$. This decrease in Ru release is probably due to the decomposition of HNO_3 by sucrose (denitration). The oxidation by HNO_3 of Ru present in solution to form volatile compounds such as RuO_4 is then inhibited. Sawada et al. [8] also mention the addition of sucrose to limit the release of Ru, in a study dealing with the influence of sodium nitrate $NaNO_3$ in a nitric solution of fission products. The solution used is a simulated HLLW with only inactive compounds. Tests with sucrose addition have been carried out at 180°C. As mentioned before in Ishio et al. [7], this addition appreciably decreases the amounts of Ru released, from 1.33% to 0.11% without $NaNO_3$ and from 1.71% to 0.18% with $NaNO_3$. The same explanation as proposed by Ishio et al. is advanced, namely a significant decomposition of HNO_3 by sucrose.

Another way for trapping Ru is the separation by electro-volatilization, studied by Mousset [9]. The industrial implementation of this method would reduce the purification operations by eliminating Ru from the dissolution liquors before separating operations of the PUREX process, and thus avoid the addition of chemical species in the nitric solution.

The experimental results of this study show that electro-volatilization yields obtained depend on many parameters, such as the nature of the nitric solution (real fuel dissolution solution or RuNO_3^{3+} commercial solution) and the equipment used for electro-volatilization. For example, the elimination efficiency of Ru from a solution with $[\text{RuNO}_3^{3+}] = 5 \cdot 10^{-3} \text{ mol.L}^{-1}$ and $[\text{HNO}_3] = 3\text{M}$ is about 50% after 18 min.

R&D outlooks for in situ trapping in nitric solution:

The objective of IRSN is to study the ruthenium release, coming from the heating of a nitric solution containing dissolved ruthenium, with or without additional compound leading to inhibition of volatilization. To quantify a potential $\text{RuO}_4(\text{g})$ release from a simplified analytical solution containing ruthenium, representative in terms of acidity and temperature of real HLLW, the experimental setup shown in Figure 6 is considered.

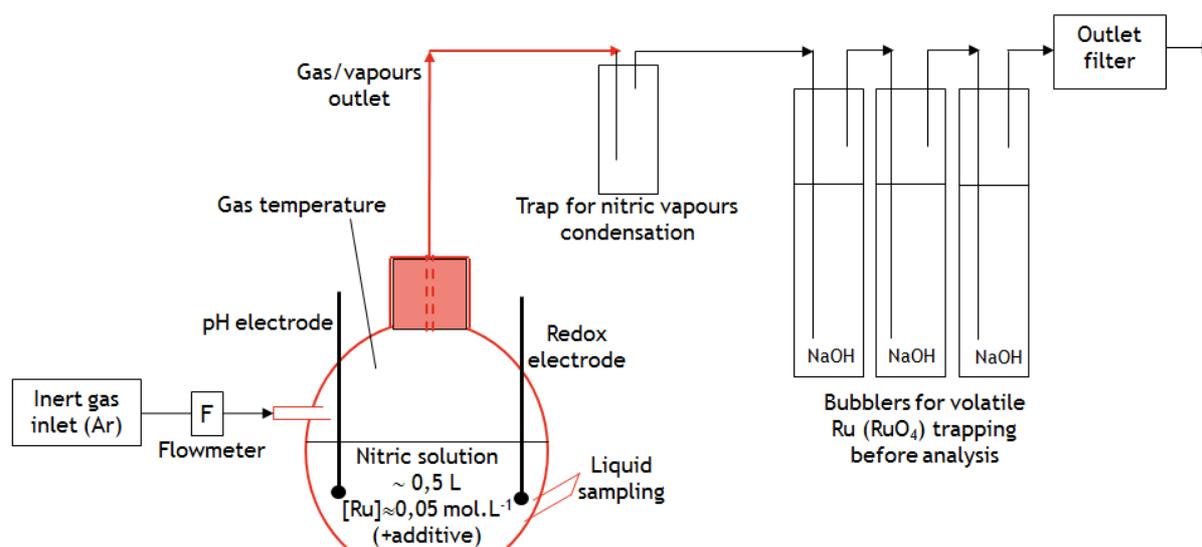


Figure 6: Schematic outline of the experimental test bench designed for characterization of Ru in HNO_3 solution

The reactor and the outlet line present a controlled heating device (liquid bath or heating cords according to the configuration test), in order to set a fixed temperature or impose a heating ramp. The acidity of the nitric solution will be fixed for each test in the range $1\text{M} \leq [\text{HNO}_3] \leq 5\text{M}$, its evolution will be monitored by a pH electrode, as well as redox potential with a specific electrode. The upper-vapour phase of the reactor is continuously swept by a controlled argon flow, in order to optimize the gas outlet and the bubbling downstream the reactor, up to a potential drying out of the solution. Bubblers with NaOH are used for the same function as on the test bench used for RuO_4 filtration (see Figure 4), i.e. trapping RuO_4 for analysis. The difference between quantities of RuO_4 trapped with or without addition of a specific compound (solid or liquid) in the reactor will provide information about the absorption/inhibition efficiency of this compound. The potential trapping compounds to be tested are reductive chemical species, porous materials, MOFs... Pre-tests are currently being carried out by IRSN before elaborating a definitive test matrix for 2018-2019.

Ruthenium chemistry in gaseous phase

The form of ruthenium, in which it is supposed to distil from the nitric acid solutions, is $\text{RuO}_4(\text{g})$. This assumption is made according to the fact that ruthenium is known to mainly vaporize under this form at low temperatures (below 200°C). Indeed, Nikol'skii [10] determined its vapour pressure between 0°C and boiling point to 140°C whereas the gas speciation was not known. In steam conditions, it was

recently shown by Miradji et al. [11] from equilibrium calculations that the $\text{RuO}_2(\text{OH})$ hydroxide would be favoured at low temperature but with pressures well below $\text{RuO}_4(\text{g})$ pressure. However the composition of the vapour phase above a prototypic waste solution in evaporating/boiling conditions remains largely unknown for different reasons. The release of ruthenium from nitric acid solutions, deeply studied, has been mainly investigated up to now by analysing the condensed distillate and such an approach is not really appropriate to identify the speciation of the gas phase. Other reasons are linked with gaseous ruthenium tetroxide itself. It is strongly instable regarding the $\text{RuO}_2 + \text{O}_2(\text{g})$ decomposition and can react with surfaces [12,13, 14, 15, 16]. It is consequently difficult to separate the respective effects of the spontaneous decomposition of $\text{RuO}_4(\text{g})$ and/or interaction with surfaces from interaction with the other gases released from the solution.

The most extensive study of ruthenium chemistry in the gas phase was performed by Brittain et al. [17] who used a Knudsen cell coupled to a mass spectrometer in order to assess the impact of H_2O , HNO_3 , N_2O , NO and NO_2 on the RuO_4 vapour pressure between 25°C and 130°C . The main conclusion is that it was never possible to detect other ruthenium gaseous species than RuO_4 in the presence of the species mentioned above. More precisely, these experiments showed that in the presence of NO or NO_2 , the pressure of RuO_4 tends to decrease whereas, for its part, the presence of N_2O has no effect. The addition of steam alone leads to a decrease in the RuO_4 vapour pressure (but to a lesser extent than in NO or NO_2) but Brittain indicated that the effect is not reproducible. The addition of HNO_3 was also evaluated, in a $\text{NO}_2 + \text{H}_2\text{O}$ atmosphere (equal proportions) with addition of 10% of HNO_3 . The experiment shows that the reduction of the RuO_4 signal is of the same amplitude as that observed in the presence of NO_2 alone. The influence of the temperature is significant on the pressure of RuO_4 since between 293 and 403 K, the signal decreases by 20% to disappear at 463 K. Recent studies carried out in a Knudsen effusion cell coupled with a mass spectrometer have been performed by Kato et al. [18]. They consisted in a sublimation of a sample prepared from a nitric acid solution, containing $\text{Ru}(\text{NO})(\text{NO}_3)_3$ dried to 353 K. The sample was then continuously heated up to 753 K. The spectrum shows the presence of $\text{RuO}_4(\text{g})$ between 390 K and 500 K with a maximum at 440 K. The intensity ratios of ion current for Ru , RuO , RuO_2 and RuO_3 to RuO_4 (Table 2 in [18]) are significantly higher than those reported by Dillar (Table 1 in [19]) obtained from sublimation of a $\text{RuO}_4(\text{c})$ sample for a similar ionization potential, likely indicating a possible interaction between NO_x (or other) molecules. In their interpretation, Kato assumed the existence of monatomic oxygen in the gas phase able to promote the formation of $\text{RuO}_4(\text{g})$ from oxidation of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ on the basis of the observation of the O^+ ion pic in the experimental spectrum.

R&D outlooks on ruthenium chemistry in gaseous phase:

The ASTEC code developed by IRSN is the European reference code for severe accident simulations in Pressurised Water Reactors. Among large number of functionalities, the ASTEC lumped-parameter code can compute thermal-hydraulic conditions and fission product transport and chemistry in reactor coolant systems (RCS) and in the containment. The SOPHAEROS module of ASTEC is based on modelling using control volumes. In each control volume, it can compute vapour speciation assuming a thermodynamic equilibrium. In this case, the speciation is based on Gibbs energy of species involved in vapour speciation and element inventory in the control volume. For each species, thermodynamic data are the key factor to accurately compute the speciation at equilibrium. So the first step towards an adaptation of this module to the present issue for reprocessing plants would be an improvement of the thermodynamic properties of the gaseous species. The different following items could be investigated:

- consolidation of the thermodynamic properties of condensed RuO_4 by ab-initio calculations;
- investigation of the interaction with steam (with different concentrations of H_2 and O_2) to eventually put in evidence the formation of volatile acids (as H_2RuO_5);

- detailed study of the gaseous phase speciation ($\text{RuO}_4(\text{g})$, nitrates, hydrated compounds...) above dried samples prepared from nitric acid solutions by Knudsen effusion cell spectrometry;
- tests in open-flow reactor to study chemical reactivity between RuO_4 and mixture of various gaseous species, including NO_x (start mid-2019).

Transfer of ruthenium volatile compounds:

Literature review did not provide much information about ruthenium transport, deposition (in RuO_2 form for example) and its possible resuspension during accidental situation in nuclear facilities, especially in ventilation ducts. Nevertheless, this point is very important for nuclear safety, notably in terms of radiological protection (accumulation of radioactive Ru in specific areas) and to reassess the source term released at the main stack of the plant. Thus, the R&D programme planned by IRSN will deal with transport of ruthenium including experimental works on a thermal gradient tube with a controlled injection of $\text{RuO}_4(\text{g})$, see Figure 7. The ruthenium deposits profile will be analysed in a first step using a glass tube. MEB or XPS surface analyses will be performed to characterise ruthenium deposits. The thermal gradient and gas composition, including NO_x and/or HNO_3 , will be investigated to study the thermal stability of ruthenium tetroxide. Later on, possible investigations of ruthenium deposits remobilisation could be carried out.

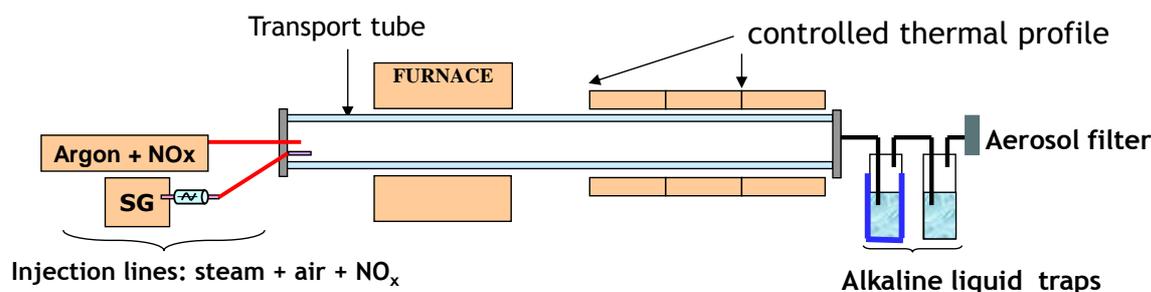


Figure 7: START (Study of the TrAnsport of RuThenium) experimental set-up

IV. CONCLUSION

In nitric solution, literature review clearly shows that chemical properties of ruthenium nitrosyl ion lead to the potential formation of a very large variety of nitrated, nitrous or mixed complexes, which speciation mainly depends on the acidity and the temperature of the solution. That explains why the accurate inventory of ruthenium species in HLLW storage tanks is difficult to establish. Two kinds of methods are identified in the literature for trapping volatile ruthenium from a nitric solution: gas phase trapping for Ru already volatilized on the one hand, and *in situ* trapping in nitric solution by addition of a chemical compound inhibiting volatilization of ruthenium species on the other hand. Most of these methods have interesting efficiencies (*in situ* methods in particular). Following this literature review, the objective of IRSN in 2018 is to initiate a R&D programme to improve knowledge on these topics. It first concerns a better identification of ruthenium species in simplified analytical nitric solution, to continue with a qualitative and quantitative characterization of trapping devices, both in the gas phase and in a nitric solution. Transport and deposition of Ru in accidental scenario will be studied in a second time, from 2019.

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Canadian Nuclear Fuel Cycle Facilities: The Regulation of Chemical Hazards in Canada

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Radiation hazards at nuclear facilities are typically the focus of attention of nuclear regulators and the public alike, but at nuclear fuel cycle facilities (FCFs), chemical hazards may pose a greater risk to the workers and the public if not managed properly. In Canada, the *Nuclear Safety and Control Act* (NSCA), authorizes the Canadian Nuclear Safety Commission (CNSC) to regulate all of the activities in the nuclear fuel cycle, from mining and milling to spent fuel management. Operating commercial FCFs in Canada include: uranium mines and mills, front-end uranium processing facilities, interim spent fuel storage facilities and several isotope processing and research and development facilities. With a wide range of front-end fuel cycle facilities comes a wide range of chemical hazards. FCF operators are required to take all reasonable precautions to ensure control of hazards from radioactive and hazardous substances that are associated with licensed activities.

The CNSC uses a regulatory framework with 14 safety and control areas that ensure requirements and guidance on various aspects of safety associated with the operation of FCFs. The CNSC regulates several aspects of use of chemicals in FCFs which include facility management, personnel training, process design, assessment and control of hazards, occupational exposure, personal protective equipment, environmental releases, environmental monitoring, transportation, emergency management and dissemination of information including operational experiences from events and incidents associated with chemical hazards and safety.

This paper provides an overview of two events involving chemical hazards (hydrofluoric acid and beryllium) at Canadian FCFs with the goal of sharing operational experiences with the global FCF community. Sharing operation experiences are important in the nuclear industry to share lessons learned and helping reduce the possibility of similar events occurring elsewhere. This paper will also provide an overview of the CNSC's approach to conducting compliance.

I. INTRODUCTION

The Canadian Nuclear Safety Commission (CNSC) is the regulatory body created under the *Nuclear Safety and Control Act* (NSCA) by the Parliament of Canada, to regulate the use of nuclear energy and materials to protect the health, safety and security of persons and the environment; to implement Canada's international commitments on the peaceful use of nuclear energy; and to disseminate objective scientific, technical and regulatory information to the public.

The NSCA established the CNSC as the regulatory body for nuclear activities in Canada and among other things, gave the CNSC the power to make regulations and the authority to grant licences. There are 13 regulations made under the NSCA, several that apply to all activities regulated by the CNSC such as the *Radiation Protection Regulations* and some specific sector-focused regulations such as the *Uranium Mines and Mills Regulations*. The Canadian nuclear regulatory framework consists of the NSCA, associated Regulations, licences, licence conditions handbooks and regulatory documents (Figure 1).



Figure 1: The CNSC's regulatory framework is made up of the *Nuclear Safety and Control Act*, the Regulations made under the Act, licences accorded by the Commission and regulatory documents.

Under the NSCA, one of the CNSC's key responsibilities is protection of the environment. To meet this responsibility, the CNSC requires the potential environmental effects of all nuclear facilities or activities to be considered and evaluated when licensing decisions are made. The CNSC conducts environmental assessments (EAs) under the Canadian Environmental Assessment Act (CEAA) or under the NSCA. An EA under CEAA is a planning and decision-making tool, its objectives are to minimize or avoid adverse environmental effects before they occur, and incorporate environmental factors into decision making for designated projects. An EA under CEAA is carried early in the licensing process (before any licence is granted) and considers the entire proposed lifecycle of a project. It includes information prepared by the applicant and CNSC staff, as well as comments received from Aboriginal groups and the public. An EA under the NSCA is conducted for projects not listed in the *Regulations Designating Physical Activities* or for projects previously assessed under CEAA. The nuclear industry is also subject to the provisions of the Canada Labour Code and the associated Regulations which in part deal with regulating occupational exposure to hazardous substances and management of workplace safety.

The decision making body with respect to major nuclear facilities in Canada is the independent quasi-judicial administrative tribunal of the CNSC (the Commission), made up of up to seven permanent members. Licensing decisions related to major facilities are made by the Commission transparently in public hearings. The Commission provides public and other interested parties opportunities to participate when major decisions are under contemplation. Roughly 800 scientific, technical and professional staff support the Commission. Staff review applications and make recommendations to the Commission and are also responsible for regulatory compliance verification and enforcement.

II. CANADIAN NUCLEAR FUEL CYCLE FACILITIES

At the present time, Canada has four operating nuclear power plants (NPPs) and one plant in safe shutdown. All of Canada's power reactors are CANDU (Canadian Deuterium-Uranium) reactors. These pressurized heavy water reactors use natural uranium as fuel and heavy water as a coolant and moderator. Operating commercial FCFs in Canada include: Uranium mines and mills, front-end uranium processing facilities, interim spent fuel storage facilities and one FCF research & development facilities (Chalk River Laboratories). Spent fuel is also stored at the respective reactor sites. There are no enrichment facilities or re-processing facilities in Canada.

Radiation hazards are often the focus of nuclear regulators and the public at nuclear FCFs, while chemical hazards if not controlled effectively, may have a higher risk to the workers and the public. With a wide range of facilities comes a wide range of chemical hazards and FCF operators are required to take all reasonable precautions to ensure control of hazards from radioactive and hazardous substances that are associated with licensed activity.

This paper provides an overview of two events involving chemical hazards (hydrofluoric acid and beryllium) at Canadian FCF's with the goal of sharing operational experiences with the global FCF community. Sharing operation experiences are important in the nuclear industry to share lessons learned, helping reduce the possibility of similar events occurring elsewhere. This paper will also provide an overview of the CNSC's approach to conducting compliance. A brief description of Canadian uranium processing facilities is provided below and in Figure 2.

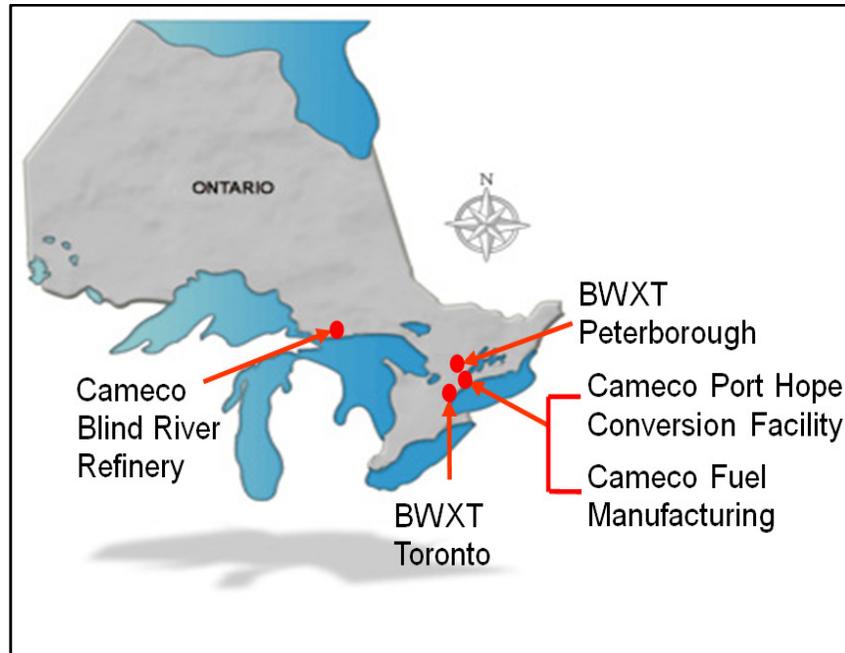


Figure 2: Location of uranium processing facilities in Ontario, Canada

The Blind River Refinery (BRR) facility is located near Blind River, Ontario. The facility refines uranium concentrates (yellowcake) received from uranium mines worldwide to produce uranium trioxide, an intermediate product of the nuclear fuel cycle.

The Port Hope Conversion Facility (PHCF) is located in Port Hope, Ontario. The facility primarily converts uranium trioxide (UO_3) powder to uranium dioxide (UO_2) and uranium hexafluoride (UF_6). UO_2 is used in the manufacture of CANDU reactor fuel, whereas UF_6 is exported for further processing into fuel for light water reactors.

Cameco Fuel Manufacturing Facility (CFM) is also situated in Port Hope, Ontario. It receives natural and depleted uranium dioxide powder (UO_2) from the PHCF and fabricates ceramic fuel pellets and thereafter manufactures finished fuel bundles for CANDU reactors for use in Canadian nuclear power reactors and research reactors.

BWXT Nuclear Energy Canada (BWXT), whose operations are similar to CFM, operates two uranium-processing facilities in Ontario. The Toronto facility processes natural UO_2 powder from the PHCF into ceramic pellets. The majority of these pellets are shipped to BWXT's Peterborough facility where they are assembled into CANDU reactor fuel bundles.

III. CNSC COMPLIANCE PROGRAM

The CNSC compliance monitoring program consists of verification, enforcement and reporting. These processes are in place to ensure that CNSC licensees operate their facilities safely and exhibit a high level of compliance with the regulatory framework. These activities enable the CNSC to provide assurance to Canadians of the continuing compliance and safety performance of licensees.

Compliance verification activities consist of on-site inspections of the various safety and control areas and assessments of periodic reports submitted by licensees of their own monitoring of licensed activities. Through inspections of nuclear facilities, activities and processes, as well as through the review of licensee reports, CNSC staff continuously monitor the nuclear industry to ensure that licensees are operating safely, securely, and in compliance with the requirements set out in the NSCA, its associated Regulations, and licences. In cases of non-compliance, CNSC staff will use various enforcement actions, in a graded approach, to ensure that licensees take effective and timely corrective actions. Enforcement actions can range from issuing a written notice for corrective actions for minor infractions to issuing orders, issuance of Administrative Monetary Penalties (AMP), recommending licensing actions (including suspension and revocation) withdrawal of certification or prosecution for more serious violations. In certain situations, licensees may be called to appear before the Commission.

The CNSC has implemented its Independent Environmental Monitoring Program (IEMP) to verify that the public and the environment around licensed nuclear facilities are safe. It is separate from but complementary to, the CNSC's ongoing compliance verification program. The IEMP involves taking samples from public areas around the facilities, measuring and analyzing the amount of radiological (nuclear) and hazardous substances in those samples using the CNSC's laboratory. The IEMP process consists of developing site-specific sampling plans for each nuclear facility, and then processing and analyzing the samples collected. The sampling plans focus on measuring concentrations of contaminants in the environment at publicly accessible locations such as parks, residential communities and beaches, and in areas of interest identified in environmental risk assessments (ERAs). Samples may be taken for air, water, soil, sediment, vegetation (e.g., grass and weeds) and some food (e.g., meat and produce).

Samples are analyzed at the CNSC's state-of-the art laboratory by highly qualified scientists using best industry practices. Samples are measured for both radiological and non-radiological contaminants related to the activities of the nuclear facility and as identified in the site-specific ERA. Contaminant levels are compared to those in applicable guidelines and/or natural background levels to confirm there is no impact on health or the environment. Conclusions and data are published on the CNSC website, illustrated in a user-friendly map [Ref 1].

CNSC staff regularly communicates the status of the nuclear industry to Canadians through reports published on our website and through social media [Ref 1]. In addition, the CNSC requires licensees to develop and implement public information and disclosure programs for all phases of the FCF's lifecycle. The licensee is required to proactively post information on general site operations, events, environmental sampling results and other pertinent information on its website [Ref 2].

IV. SAFETY AND CONTROL FRAMEWORK

To ensure that licensees in Canada meet all of their regulatory requirements and expectations, CNSC staff assesses, evaluates, reviews, and verifies how well licensees are complying with these requirements. CNSC staff base their evaluation on safety and control areas (SCAs). Each SCA includes technical areas and topics, which are selected based on the risks of the specific licensed activity. Consistently using the same terms when referring to the same SCA, facilitates communication internally as well as externally, with licensees, the public and the Commission. In total, there are 14 SCAs that can be broadly sorted into three functional areas: management, facility and equipment, and core controls and processes.

Management-specific SCAs address the organizational and human elements of safety in the Canadian nuclear facilities. Specifically, they cover management systems, human performance management, and operating performance. CNSC staff ensure that licensee staff are adequately trained, knowledgeable, and equipped to handle all safety duties. Performance, safety culture, organizational contingency plans, and many other specific measures are all covered under this functional area.

Facility and equipment SCAs include safety analysis, physical design, and fitness for service. These areas assess the potential hazards and risks of operating (as well as the preventative measures taken to minimize risk), the integrity of facility infrastructure design, and the overall long-term performance of equipment and systems. When CNSC staff analyze safety on the basis of facility and equipment, they are looking to verify a wide breadth of measures, ranging from the facility's safety as a structure down to the maintenance of components.

Core controls and processes form the largest functional area. These SCAs include radiation protection, conventional health and safety, environmental protection, emergency management and fire protection, waste management, security, safeguards and non-proliferation, and packaging and transport. What these SCAs have in common is that they all cover how a facility operates, they measure actions and plans that are in place, all against the unique and specific nature of each facility. The different core controls and processes, as well as the associated regulatory requirements are all outlined in facility licensing agreements.

SCAs are a template for confirming regulatory compliance and facility safety. All 14 SCAs are evaluated at the Canadian FCFs using a long term compliance program. The licence and licence conditions handbooks for all Canadian FCFs identify requirements for all SCAs. CNSC staff use these requirements as compliance verification criteria during inspections and reviews.

V. 2017 HF EVENT AT CAMECO'S PORT HOPE CONVERSION FACILITY

Cameco's PHCF is a uranium conversion facility operating in Ontario where nuclear materials have been processed at the site since the 1930's. In February 2017, Cameco was issued a 10 year operating licence by the CNSC following a public hearing in Port Hope, Ontario in November 2016.

On May 5, 2017 Cameco reported a small release of hydrogen fluoride (HF) at its UF₆ plant. HF is a highly corrosive acid which can cause significant health impacts if inhaled, absorbed into the eyes or makes contact with the skin. HF differs from other highly corrosive acids in that the fluoride ion readily penetrates the skin causing destruction of deep tissue layers and if left untreated this can continue for days [Ref 3]. During the night shift a junior instrumentation technician was independently performing maintenance work on the HF transfer tank system. The employee was in the process of calibrating a differential pressure transmitter mounted to the wall next to the tank. When the junior technician opened the connection to the impulse line, HF gas was released creating a mist of gas above the transmitter. At the time of the event, the HF transfer tank was depressurized with an internal pressure slightly above atmospheric pressure. An isolation valve was not activated and was left in the open position. The emergency ventilation system was activated by a local HF detector. Upon arriving to the affected area, Cameco's emergency response team secured the connection to the impulse line. The junior technician was directed to Cameco's medical department where he received precautionary medical attention due to exposure to HF. The worker was not injured and there were no environmental impacts as a result of this event.

According to Cameco's management system, the maintenance plan for this task requires that prior to commencing work the necessary permits and clearances shall be obtained from the production supervisor. These clearances and permits are important to protect all workers and verify that all hazardous energy sources have been isolated, the necessary permits obtained and controls are in place. Work clearances are required to ensure that all hazardous energies, including in this case HF, are isolated removing any risk to the workers and the public. The maintenance plan also stipulates that the valve for the impulse line shall be closed.

As per the CNSC regulatory requirement, the licensee was required to do a detailed investigation of this reported event and submit a final report for review by CNSC staff. Cameco conducted an investigation into the event and determined that the impulse line of the pressure transmitter was not properly closed from the HF transfer tank system. The required work clearance and permits were not obtained prior to the start of the maintenance work at the HF transfer tank. Cameco determined that the necessary work clearances and permits were completed after the leak occurred and not before the job, as required by Cameco's procedures. The junior instrument technician did not request a job clearance from the UF₆ production supervisor and failed to inform the senior instrument technician of the planned work activity as required by Cameco's procedures.

Cameco determined that the junior and senior instrument technicians were performing maintenance activities without the necessary work clearances and permits for an unspecified period of time. This was not an isolated incident and this practice was known to the UF₆ production supervisor. As a result of the event, Cameco's management team issued a bulletin notice to all staff stressing the importance of completing work clearances. Cameco terminated the junior instrument technician and the UF₆ production supervisor and the senior instrument technician was suspended from work. Cameco concluded from their investigation that they had interviewed other UF₆ supervisors and reviewed job safety clearances of other teams and no other issues were identified. As a result, Cameco treated this incident as an isolated event. Cameco posted this event on its website in compliance with the CNSC requirements.

Cameco initiated three corrective actions:

- a) Improve maintenance work management process for assigning work tasks to shift maintenance employees. The improved work process should include more visibility and accountability for the work assigned to shift maintenance employees to the production supervisors allowing improved communication with the tradesperson.
- b) Evaluate and assess current work clearances and permits to ensure they provide clear and unambiguous direction and eliminate any needless requirements.
- c) Perform an assessment of the site audit program to determine what is required to enhance the audit program to better monitor programs, especially during shift work.

Following the event CNSC inspectors conducted an unplanned, reactive inspection [Ref 4]. CNSC staff determined that Cameco had not been conducting verification activities related to this maintenance activity. Cameco's licence conditions handbook provides clarity, compliance verification criteria and guidance on meeting the CNSC requirements and expectations. Under the management system SCA the requirement states "licensees shall implement and maintain a management system". CNSC staff assessed the May 5, 2017 event and the compliance history of procedural non-adherence and determined that Cameco failed to verify whether work is being performed correctly and according to approved procedures, as required by its management system.

An AMP was issued to Cameco on September 6, 2017 in accordance with section 6(1)(b) of the CNSC's *Administrative Monetary Penalties Regulations*, for the violation of failure to comply with a condition of a licence, in accordance with paragraph 48(c) of the NSCA [REF 5]. The purpose of the AMP was to promote compliance with licence conditions and deter future violations. The value of the AMP was \$17,830. Cameco was given a period of 35 days to review the AMP and pay the penalty or request a review of the AMP by the Commission. On October 11, 2017 Cameco requested a review of the AMP which is scheduled for March 2018 [REF 6].

The CNSC will submit this event to the International Atomic Energy Association (IAEA) and Nuclear Energy Agency (NEA) Fuel Incident Notification and Analysis System (FINAS) to share operational experience with other FCF operators and regulators.

VI. BERYLLIUM EXPOSURE LEVEL EXCEEDANCE AT BWXT'S PETERBOROUGH FACILITY

BWXT manufactures nuclear fuel bundles using the fuel pellets from the Toronto facility together with zircaloy tubes manufactured in-house. The zircaloy tubes, spacers and bearing pads that form the CANDU[®] nuclear fuel bundle are assembled through a process called brazing. Brazing is a metal joining process used to join two metallic components using a filler metal as a brazing agent. BWXT uses beryllium as the brazing agent and the spacers and bearing pads are coated with beryllium before brazing. The beryllium coating process of the spacers and bearing pads create airborne particulates of beryllium that can be an occupational hazard for workers at the facility.

Beryllium particulates in air are a chemical hazard and due to this, occupational exposure of beryllium to workers in Canada is regulated by establishing Occupational Exposure Limits (OEL). OELs are applicable to workers within a facility and not to be confused with release limits for emissions and effluents from a facility which have an impact on the public and the environment. The *Canada Occupational Health and Safety Regulations* [REF 7] specifies that employers shall use the American Conference of Governmental Industrial Hygienists[®] published Threshold Limit Value[®] of $0.05\mu\text{g}/\text{m}^3$ as the OEL for beryllium particulates in air - the time weighted average exposure of 8 hours that a worker can be exposed to, above which there may be adverse health effects. With prolonged exposure, beryllium is known to produce adverse health effects including scarring of lung tissue, beryllium sensitization and a condition called chronic beryllium disease. BWXT's licence stipulates a value of $0.05\mu\text{g}/\text{m}^3$ as the OEL for workers to control hazards associated with beryllium particulates present in the air. Occupational Exposure to beryllium for workers is controlled by engineered controls (room ventilation), safe work procedures, protective clothing and the use of full face respirators as personal protective equipment (PPE). The workplace is monitored through area monitors and personal air monitors to ensure safety.

For non-routine work or high risk tasks such as cleaning, maintenance and spillage handling (when airborne beryllium levels are expected to be above the OEL), the approach to safety is to perform the work under a work permit system that includes identification of hazards present, confirm appropriate training and the use of PPE like Powered Air Purifying Respirators (PAPRs) with cartridges/filters specific for the type of hazard present.

The use of PAPRs with appropriate cartridges/filters specific to the type of hazard present provides a protection factor of 1000 to the hazard to which the worker is exposed. This allows workers to perform these operations in a safe manner. Workers performing these tasks rely on the PAPRs to ensure beryllium exposure is below the OEL. Workers performing these tasks, accessing beryllium process areas prone for significant airborne beryllium particulates are specifically trained in beryllium hazards and are monitored regularly through blood tests to detect any beryllium sensitization.

On August 22, 2017 BWXT discovered that incorrect respirator cartridges/filters were being used with PAPRs as PPE while performing non-routine work. As per the CNSC regulatory requirement, the licensee was required to do a detailed investigation of this reported event and submit a final report for review by CNSC staff. BWXT's investigation report was provided to CNSC staff. CNSC staff issued a request under subsection 12(2) of the *General Nuclear Safety Control Regulations* as the report did not provide sufficient information about the measures BWXT has taken to minimize beryllium air concentrations in the affected area in the future. BWXT provided a more detailed response as requested. BWXT determined that incorrect filters for PAPRs were procured in March 2013. Based on available general area air sampling results from the affected areas between December 4, 2015 and August 23, 2017 BWXT determined the average and maximum air concentration values were $0.12\mu\text{g}/\text{m}^3$ and $0.29\mu\text{g}/\text{m}^3$ respectively. General room air samples cannot be correlated to OELs and as a result, BWXT transitioned from conducting routine general room air samples to routine personal air samples in late 2015. As a result, most of the air sampling data for the period is from personal air sampling.

Based on available personal air sampling results from the affected areas between December 4, 2015 and August 23, 2017 the average air concentration (8-hour time weighted average) was $0.39 \mu\text{g}/\text{m}^3$ and the maximum was $4.63 \mu\text{g}/\text{m}^3$. Based on available air sampling data for that time period, a total of 15 instances were identified where exposure to airborne beryllium by the two workers was likely to have occurred above the OEL. Fourteen of the identified instances impacted one worker and the other single instance impacted a second worker. Both workers were referred to the plant occupational health nurse and physician for follow up which includes screen tests for beryllium sensitivity. Both workers have subsequently returned to normal duties. No health effects have been noted since the discovery of the error. Both workers are under increased monitoring for any potential long term effects of exposure to beryllium.

BWXT's investigation determined a number of causal factors leading to the use of incorrect filters including inadequate verification of the newly procured filters when received from supplier and the purchase orders issued did not contain an adequate description of the item. The critical to safety list used for enhanced purchasing controls included PAPRs but did not identify filters as critical to safety individually by part numbers. Finally, BWXT personnel and workers did not recognize that incorrect cartridge/filters were issued by the facility stores for use with PAPRs.

BWXT initiated several corrective actions to prevent a future occurrence of a similar event. The critical to safety list was updated to include respirator filters individually by part number. BWXT implemented a documented process for new or changed critical to safety items, including an approval process to ensure workers with permissions are trained accordingly and items received are properly verified. In addition, BWXT implemented training to include correct filter/cartridge type identification for work performed that require respirator wearer training and provided refresher training to personnel conducting pre-job briefs in relation to non-routine work conducted under the environmental health and safety work permit systems, to ensure identified PPE is adequately explained.

CNSC inspectors conducted an unplanned, reactive inspection in response to the event [REF 8]. The inspection confirmed that BWXT has responded to the event as per requirements and the root causes and associated corrective actions were appropriate. CNSC staff also presented the event to the Commission as an Early Incident Report, where the Commission was able to ask both BWXT and Cameco questions on the event and the corrective actions taken. BWXT posted this event on its website in compliance with the CNSC requirements.

The CNSC will submit this event to FINAS to share operational experience with other FCF operators and regulators.

VII. CONCLUSIONS

The CNSC's regulatory framework provides many mechanisms for ensuring that nuclear activities in Canada are conducted safely, ensuring the health and safety of workers, the public and the environment. The NSCA is especially powerful, as it provides the CNSC with the regulatory oversight of hazardous substances at nuclear facilities.

The CNSC compliance program is multifaceted with many tools available to CNSC staff and inspectors in ensuring compliance with regulatory requirements. This paper outlined two specific examples of events that occurred at Canadian FCFs and highlighted the different approaches used by CNSC staff in ensuring the health and safety of workers.

Sharing operational experiences provides the opportunity for both regulators and operators to learn from events at other FCFs. From the regulators perspective there were a number of lessons learned from these events that have been applied to the compliance program for all FCFs in a graded approach. This includes supply chain validation, confirming the licensee's audit program covers all aspects of the work activity and a closer examination of licensee self-assessments. The CNSC strongly encourages licensees to share lessons learned amongst the industry. In addition the CNSC utilizes FINAS to share operational experiences with Canadian FCF operators.

VIII. REFERENCES

REF 1 – www.nuclearsafety.gc.ca

REF 2 – RD/GD 99.3 Public Information and Disclosure March 2012

REF 3 – Cameco Site Information Handbook April 2017

REF 4 – CNSC Staff Inspection Report PHCF May 11 and 12, 2017

REF 5 – Administrative Monetary Penalty Notice of Violation Cameco PHCF

REF 6 – Request for Review of Administrative Monetary Penalty: Cameco Corporation–2017-AMP-06

REF 7 – *Canada Occupational Health and Safety Regulations* 2017

REF 8 – CNSC Staff Inspection Report BWXT October 5, 2017

Comparison of Operating Experience from Nuclear Fuel Cycle Facilities and Industrial Chemical Plants

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Abstract: While nuclear fuel cycle facilities and commercial industrial plants have different regulatory schemes and process requirements, both use hazardous chemicals to manufacture their products. This paper discusses operating experience feedback from nuclear fuel cycle facilities and from commercial industrial plants in order to identify lessons in the safe management of chemical hazards.

Introduction

This paper compares lessons learned from industrial chemical incidents with those from nuclear fuel cycle facilities. While nuclear fuel cycle facilities are often more regulated and held to stricter safety standards and inspections by regulatory authorities, lessons can be learned from operating experience gained from industrial incidents.

Incidents that occurred during maintenance or non-routine activities at nuclear fuel cycle and industrial chemical facilities were selected for comparison. In most cases, the causes of the incidents involve: (1) inadequate procedures or procedural adherence, (2) inadequate process hazards analyses or improper assumptions, (3) inadequate management of change control process, and (4) improper configuration management and equipment lineup.

Lessons learned and actions taken to address causes apply to many situations. While each incident is different, a robust safety culture that includes a wide variety of operating experience is helpful in preventing the occurrence or lessening the severity of future incidents.

Background

The U.S. Chemical Safety Board is an independent U.S. Federal agency that investigates industrial chemical incidents, determines the root causes for the incidents, identifies lessons learned, and develops recommendations to address the identified weaknesses. Their reports are publicly available on the internet¹. Information about nuclear fuel cycle incidents, causes, and lessons learned are maintained in the joint Nuclear Energy Agency/International Atomic Energy Agency Fuel Incident Notification and Analysis System² (FINAS) database of operating experience. Information about the incidents analyzed in this paper was gathered from these sources.

Periods of non-routine operations, such as maintenance, have greater risk significance because they are not frequently performed; equipment may be out of service; equipment configuration may be different; and procedural knowledge and accuracy may not be adequate. Four incidents, two industrial chemical and two nuclear fuel cycle, were selected for comparison. The incidents, causes, and lessons learned are described in the Discussion section.

¹ U.S. Chemical Safety Board investigation reports are available at www.csb.gov.

² FINAS database is available at www.iaea.org.

Discussion

La Hague Plutonium Oxide (PuO₂) Spill³

Process Description

Spent nuclear fuel assemblies are processed in various workshops at La Hague. One of these workshops is used to purify, convert, and package plutonium oxide recovered from spent fuel. The PuO₂ powder is poured into a homogenizer. The powder is then directed by a pipe, which is monitored by neutron counters, to a sieve. The latter is watched by a camera and supplies a filling head. The downstream part of the filling head is located in a glove box. A can is bound to the downstream part of the filling head to be filled with PuO₂ powder. The full can is weighed, sealed and transferred into another glove box to be put into a case by means of a bracket before being stored in another workshop.

Safety controls are in place for filling the cans with PuO₂ powder and for packaging the filled cans into cases. In the filling process, a can is bound to the filling head, and its mass is monitored by means of spring scales. The spring scales automatically stop the filling process when a set point for the PuO₂ mass in the can is reached. In addition, a sensor, located in the filling head, stops the filling process when the can is full.

When the can is full, a valve closes the filling head to prevent the loss of PuO₂ powder into the glove box. In the workshop, the operating employees monitor the process with several process software controllers (PSC). At this point, an operator undocks the full can from the filling head, transfers it to another glove box, and it is then packaged into a case.

Description of Incident

On September 18, 2008, the workshop was not in operation, and the operator decided to modify one of the PSCs in order to reduce the packaging time of the cans (by reducing the height of the transfer by the bracket from 2 m to 0.5 m). The change was governed by a modification authorization document. Only post-modification testing of the semi-automatic mode of operation was performed, because the automatic control mode can only be tested when the workshop is in operation.

On September 23, 2008, a new campaign to fill the cans with PuO₂ powder and to package these into cases was started. This enabled post-modification testing of the automatic control mode. During that testing phase, a malfunction in the automatic control mode concerning the bracket occurred. Subsequently, the bracket was then used in the semi-automatic control mode.

On September 24, 2008, in the morning a maintenance team began the repair of the deficient controller. During the maintenance, no movement of the cans was permitted in the associated glove box. So, the supply of PuO₂ powder to the filling head was stopped. At that time an empty can was bound to the filling head and a full can remained in the glove box to be transferred.

In the beginning of the afternoon, an operator, who was not aware of the ongoing maintenance activities, restarted filling of cans and continued for an hour and a half. The operator then put

³ FINAS incident #142

the glove box back to the same condition as reported 2 hours earlier, except now a full can was connected to the filling head.

Shortly thereafter, the maintenance employees came back to perform their work. They tested that operation in the semi-automatic mode was correct.

The facility was then put back in operation to validate the modification to the automatic mode, and the operator restarted the filling process. He monitored the task from the control room. Within 20 minutes, he observed that the increase of the mass of the can was unusual so he stopped the filling operation.

Since the sensor in the filling head had not been triggered, the manufacturing manager thought that the spring scales were deficient and decided to undock the can from the filling head to confirm his hypothesis (not realizing that the can and the filling pipe were full of PuO₂ powder). During the undocking, PuO₂ powder spilled into the glove box and the full can was re-docked to the filling head.

Around 15 kilograms (kg) of PuO₂ powder had accumulated in the pipe of the filling head and approximately 600 grams of PuO₂ powder spilled into the glove box. This did not present a criticality risk and, due to the design of the glove box, the incident had no consequence to the staff or environment.

Causes of Incident

1. The modification procedure did not consider that the validation tests after completion of the modifications resulting from maintenance were being performed while the facility was in operation. The procedure was not revised to account for the PuO₂ powder in the can docked to the filling head.
2. The sensor in the filling head failed. Therefore, it did not perform its safety function to stop the filling of the docked can.
3. The process hazards analysis regarding the sensor was incomplete. The geometry of the glovebox ensured criticality safety. So, the sensor in the filling head was mistakenly not considered in the process hazards analysis. Because of this, it was not surveilled or maintained.

Lessons Learned

1. Adequate procedures for controlling modifications are critical. They should require process hazards analyses to consider the risk caused by new features of a modification.
2. Thoroughness of process hazards analyses is important such that equipment like the sensor will be identified as a safety control and will undergo periodic surveillance.

Nuclear Fuel Services (NFS) Generation of Nitrogen Oxides (NOx)⁴

Process Description

The Uranium (U)-Aluminum bowl cleaning station system is designed to remove uranium from centrifuge bowls by circulating nitric acid through the bowls. The system has historically produced NOx during the nitric acid dissolution process. Safety controls include a NOx detection system with sensors located at the nitric acid knockout column's siphon break (potential NOx release point if process ventilation fails) and at the employee working level.

Description of Incident

On October 13, 2009, NFS began using the bowl cleaning station system to dissolve U-Aluminum fines rather than adding them to the normal dissolver column. Laboratory testing indicated that dissolving the fines with caustic in the normal dissolver column was not recommended due to potential for a vigorous reaction. The fines were loaded into strainers and placed directly into the bowls to be dissolved with nitric acid. After the dissolution process began, the operator noticed that the temperature of the system was increasing and that NOx (in the form of a brown cloud) was beginning to form inside the bowl cleaning station containment vessels. The system was shutdown. The NOx detector alarmed and the facility was evacuated.

The safety assessment determined that NFS experienced an unexpected exothermic reaction. The elevated temperatures from the reaction created nitrogen compound gases within the associated process off-gas piping. An instrument located near the ceiling of the facility detected these gases and generated an alarm which resulted in the evacuation of employees from the affected area. Additionally, the elevated temperature of these gases caused portions of the off-gas piping to deform and sag in the nearby area. NFS personnel took action to shut down the system. As a result, no personnel were injured and offsite environmental releases during the period associated with the event were within regulatory limits.

Laboratory analysis of similar U-Aluminum fines material was conducted and a NOx generation rate specific for the fines material was estimated. Based on engineering calculations, it was determined that the NOx generation for the fines was significantly higher than the previously analyzed NOx generation for the U-Aluminum ingots.

Causes of Incident

The incident was caused by the failure to recognize the possibility of increased NOx generation due to the greater surface area and aluminum content of the material to be dissolved. Although the safety basis assumed that NOx would be generated during processing and controls were in place to alert workers to evacuate, the consequence calculations did not include a NOx generation rate that specifically addressed the differences between the U-Aluminum fines material and the material previously processed in the bowl cleaning station. No equipment failed; however, the steam evolved during the chemical reaction forced solution and slurry into ventilation piping which resulted in deformation of the polyvinylchloride off-gas piping.

⁴FINAS incident #148

Specifically, the causes included:

1. Inadequate management oversight of facility process changes; and
2. Inadequate process safety hazard evaluation with inaccurate assumptions.

Lessons Learned

1. Robust process hazards analyses with technically justifiable assumptions are necessary to ensure that appropriate safety controls are identified and implemented to provide adequate protection and to ensure that management controls for those controls are sufficient, such that they are available and reliable to perform their intended safety function when needed.
2. Management expectations for strong safety culture set the example for all the employees. Management presence and engagement on the process floor enables open and timely communication of potential safety concerns.
3. Effective change management process should include a requirement that changes to procedures associated with processes, process parameters, and process inputs be clearly defined prior to implementation.

ExxonMobil Refinery Explosion⁵

Process Description

On February 18, 2015, an explosion occurred in the ExxonMobil refinery's electrostatic precipitator (ESP) in Torrance, California. The incident occurred when the operator was attempting to isolate the equipment for maintenance while the unit was in an idled mode of operations. Preparations for maintenance caused a pressure deviation that allowed hydrocarbons to backflow through the process and ignite the ESP. Debris from the explosion was thrown into other units of the refinery directly surrounding the ESP. One of these pieces of debris hit scaffolding in the refinery's alkylation unit, narrowly missing a tank containing tens of thousands of pounds of hydrofluoric acid (HF). Had the debris struck the tank, a rupture could have been possible, resulting in a potentially catastrophic release of toxic HF into the neighboring community.

Description of Incident

The sequence of events that eventually led to the explosion at the refinery began on February 12, 2015, when problems with a piece of equipment called an expander caused the refinery's fluid catalytic cracking (FCC) unit to be put into an idled condition.

With the FCC unit shut down, steam was forced into a reactor to prevent hydrocarbons from flowing back from the main distillation column. On the morning of the incident, this steam was escaping through an open flange on the expander, preventing operators from continuing their maintenance work. It had traveled through a leaking slide valve connected to the reactor.

⁵ U.S. Chemical Safety Board ExxonMobil Torrance Refinery Electrostatic Precipitator Explosion Torrance California Investigation Report, Published May 2017, No. 2015-02-I-CA

An outside supervisor then reduced the amount of steam being forced into the reactor so that work could continue. However, at the time, workers were unaware that hydrocarbons were leaking into the main distillation column from interconnected equipment. As the pressure of the steam dropped, the hydrocarbons flowed back into the reactor, out through the leaking slide valve, and eventually into the ESP. There, the hydrocarbons found an ignition source and exploded.

Causes of Incident

Multiple process safety management deficiencies helped contribute to the incident.

1. In order to perform work to bring the FCC unit back online, the operators determined they needed to deviate from several existing operating procedures. So, they used a written temporary deviation from normal operating procedures. This deviation was created in 2012 to address problems with the expander. However, ExxonMobil did not conduct a management of change review before implementing this outdated deviation, even though conditions within the FCC unit had changed over the previous three years.
2. ExxonMobil performed inadequate process hazards analyses, which could have identified more effective safeguards against the flow of hydrocarbons, such as installation of instrumentation to detect flammable hydrocarbons flowing through the equipment into the ESP, or establishment of safe operating limits for the FCC unit.

Lessons Learned

1. It is essential to identify and define safe operating limits for all modes of operation and measure process conditions and parameters that can verify the operation of the process relative to those safe operating limits. When a facility relies on operating parameters that only indirectly provide information on critical process parameters it can lead to the inability to identify when a process is in an unsafe mode.
2. When implementing a deviation from an existing procedure, it is critical that the company conduct a management of change review to verify and authorize the technical basis and the implementation time period and to identify any new or affected hazards and associated mitigation strategies.
3. It is essential to schedule and perform maintenance of safety critical equipment, such that the equipment is available to perform its safety critical function.
4. It is important to consider all modes of operation including non-routine operations when performing process hazards analyses. Incident scenarios could be possible during non-routine modes of operation that may not have been considered when analyzing process hazards for normal continuous operation.
5. Companies should develop procedures for all modes of operations that detail safe operating limits, consequences of deviating from those limits, and specific actions to implement in the event that the process deviates outside of its safe operating limit.
6. Robust management of change practices are needed when making changes to procedures. Similar to process hazards analyses, conducting management of change as a multidisciplinary

group composed of individuals with different areas of expertise can assist in identifying hazards introduced by the procedure change.

Williams Geismar Olefins Plant – Reboiler Rupture and Fire⁶

Description of Incident

On June 13, 2013, a catastrophic equipment rupture, explosion, and fire occurred at the Williams Geismar Olefins Plant in Geismar, Louisiana, in which two employees were killed. The incident occurred during non-routine operational activities that introduced heat to a reboiler which was offline, creating an overpressure event while the vessel was isolated from its pressure relief device. The introduced heat increased the temperature of the liquid propane mixture confined within the reboiler shell resulting in a dramatic pressure rise within the vessel. The reboiler shell catastrophically ruptured causing a boiling liquid expanding vapor explosion and fire.

Causes of Incident

Process safety management program weaknesses at the facility during the 12 years leading up to the incident caused the reboiler to be unprotected from overpressure. These weaknesses include deficiencies in:

1. Implementation of management of change reviews or conduction of pre-start up safety reviews. As a result, the company did not evaluate and control all hazards introduced to the process by those changes.
2. Performance of adequate process hazards analyses such that effective over-pressure protection by either a pressure relief valve or administrative controls would be applied.
3. Development of procedures for the non-routine operation performed the day of the incident.

Lessons Learned

1. Robust management of change practices are needed to ensure the review analyzes hazards affected by the change in the entire process. Similar to process hazards analyses, conducting management of change reviews as a multidisciplinary group can assist in identifying hazards introduced by a process change.
2. Pre-startup safety reviews are key opportunities to verify effective implementation of design intent, accuracy of process safety information, and proper installation and configuration of field equipment.
3. Ensure that the selected safety control adequately addresses the original safety concern identified by the process hazards analysis team.
4. Operating procedures need sufficient detail to ensure effective performance of critical steps including performing steps in the correct order. Affected employees should receive training on

⁶ U.S. Chemical Safety Board Williams Geismar Olefins Plant Reboiler Rupture and Fire Geismar, Louisiana Case Study, published October 2016, No. 2013-03-I-LA

the procedures. Management should establish expectations to maintain and follow accurate procedures.

5. Process hazards analyses and management of controls teams should effectively use the hierarchy of controls to the greatest extent feasible when evaluating safeguards.

Conclusions

While the incidents described in this paper have different causes and consequences, the lessons learned from the operating experience are applicable to industrial chemical and nuclear fuel cycle facilities. These lessons can be summarized as the importance of conducting robust process hazards analyses and diligent management of the change process. Process hazards analyses should be conducted by a multidisciplinary team and ensure that assumptions are technically justifiable. The safety controls and operating limits identified by the analyses should include the implementation of management controls to ensure that the established controls will be available and reliable when called upon to perform their intended safety function. The management of change process should ensure that procedures are adequate and expectations that they must be followed are established. Additionally, the management of change process should ensure that a process hazards analyses is conducted for the maintenance evolution and the modified operation.

Through the sharing of operating experience from a variety of sources and the consideration of lessons learned, improvements will continue to be realized in chemical process safety.