URANIUM HEXAFLUORIDE IN TRANSPORT ACCIDENTS

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Abstract

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After a brief description of the physical and chemical properties of UF and of the products of its hydrolysis, UO_2F_2 and HF, the problem of the radiological and chemical risks in transport accidents is analysed. 'Acceptable levels of exposure' for making rough safety decisions based on chemical hazards are suggested. The present practice in the transport of UF_6 is described and some apparent inconsistencies and the different levels of safety used to protect against chemical or radiological hazards in transport are noted. Finally, a mass limit for UF_6, based on chemical hazards, is derived and the main questions to be answered in relation to safety requirements in the transport of UF_6 are presented.

1. INTRODUCTION

In the nuclear power industry, large quantities of uranium are converted from one chemical form to another and, when the nuclear fuel cycle is based on enriched uranium, one of the most widely handled and transported chemical forms is uranium hexafluoride (UF_6). As a gaseous compound of uranium at relatively low temperature, the UF_6 is used in the enrichment process at diffusion or centrifugation plants. Therefore, massive amounts of natural, depleted or enriched uranium are transported as UF_6 to and from enrichment facilities.

At room temperature and atmospheric pressure, uranium hexafluoride is a white solid of relatively high density (about 5 $g \cdot cm^{-3}$) that sublimes slowly in dry air. Under higher pressures and temperatures (e.g. 0.4 MPa and 70°C), the solid UF_6 melts to form a colourless liquid of high density (about 3.6 $g \cdot cm^{-3}$) that, when the temperature increases, converts into vapour. At high temperatures and at atmospheric pressure or below, the solid can be converted directly into vapour (the atmospheric sublimation point is about 56.4°C) [1]. While the gaseous form is used in the enrichment process, the liquid form is usually employed in the operations of filling or emptying storage and transport containers and the product is transported as a solid at pressures slightly below atmospheric pressure [2].

Uranium hexafluoride is highly reactive with hydrogenous compounds, such as water and oils. When UF_6 reacts with water, a substance always expected to be present in a transport environment, the reaction products are uranyl fluoride

(UO_2F_2) and hydrogen fluoride (HF). Therefore, when UF_6 is released into the atmosphere, it rapidly reacts with ambient moisture to form an aerosol of UO_2F_2 and HF. Anhydrous UO_2F_2 is hygroscopic, as is HF, and both substances tend to become hydrated. The particulate UO_2F_2 is easily visible as a white cloud or 'smoke'. The combination of possible releases of UF_6 under different conditions relating to the presence of water, the further reaction or combination of the UF_6 or of its initial hydrolysis products with the moisture in the air and the possible interactions among them do not allow for a reasonable prediction of the actual products to be found and of their aerosol characteristics at different distances from the release point [3, 4].

2. RADIOLOGICAL AND CHEMICAL RISKS

Both UF_6 and UO_2F_2 present chemical and radiological risks, while HF is a highly corrosive substance and only involves chemical risks. Although the radiological hazard of UF_6 increases with enrichment, due to the increase of ^{234}U, the consequences of an accidental release of UF_6 during transport are largely associated with the chemical hazards caused by UF_6, UO_2F_2 and HF.

The criticality risk, only possible with significantly enriched UF_6, does not appear to be a problem because the criticality control of UF_6 systems is not difficult under normal conditions by controlling the presence of HF in the UF_6 system, and because the accidental incorporation of a common moderator, such as water, produces immediately the exothermic reaction indicated above. Therefore, a critical configuration during or after the chemical reaction of UF_6 with water [5, 6] is quite improbable and, in some cases, physically impossible in a transport accident.

2.1. Radiological risk

The radiological risk of uranium increases with enrichment because the enrichment process produces a relative increment of the ^{234}U content. The final relative content of ^{234}U, for a defined $^{235}U/^{238}U$ ratio, is a function of the way in which the enrichment plant is operated and of the previous history of the uranium processed [7, 8]. Conservative estimates of the maximum expected concentration of ^{234}U as a function of the degree of enrichment can be made [8, 9].

Even for very high enrichments (e.g. 90%), the mass of ^{234}U is negligible if compared with the sum of the masses of ^{235}U and ^{238}U, but its semidisintegration period is significantly shorter than those of the others and, therefore, its contribution to the total alpha activity ranges between 50% in natural uranium and practically 100% in very highly enriched uranium. Consequently, the specific activity of enriched uranium increases significantly with the degree of enrichment, while the mass intake – equivalent to the Annual Limit of Intake (ALI) – is smaller for highly enriched uranium than for low enriched or natural uranium.

The ALI value recommended by the International Commission on Radiological Protection for uranium is 5×10^4 Bq [10], equivalent to an annual intake of a mass of about 2×10^3 mg of natural uranium, 135 mg of 20% enriched uranium, or 23 mg of 90% enriched uranium. A quantity, named Radiological Daily Derived Mass of Intake (RDDMI), can be obtained for each degree of enrichment by dividing the mass value, equivalent to the ALI, by the number of working days in a year (usually 250). Moreover, since uranium is toxic, there is a Toxic Daily Limit of Intake (TDLI), based on potential kidney injuries in routine exposures (the TDLI value for very soluble uranium compounds, such as UO_2F_2, is about 2 mg per day). From enrichments higher than about 10%, the RDDMI is lower than the TDLI; in these cases and *in routine exposures,* efforts to control the intake for radiological reasons are more stringent than the ones required for toxicological reasons. It is said that 'the radiological risk dominates the toxicological risk'. Obviously, this statement is not applicable to accidental situations because the RDDMI can be exceeded by a factor 10^3 without any significant radiological consequences, while, if the TDLI is exceeded by an order of magnitude or more, the person exposed could suffer severe health effects or die. Therefore, the radiological risk is not further considered in the context of this paper.

2.2. Chemical risks

In a transport accident, it is better to consider the toxicity of UF_6 as the sum of the toxicities of UO_2F_2 and HF, in view of the readiness with which UF_6 reacts with atmospheric water. Uranyl fluoride is one of the most soluble compounds of uranium and, as such, it presents a high toxicity hazard when inhaled. The health effect of UO_2F_2 is kidney damage, which could imply the death of the exposed person if the intake is high (e.g. 200 mg), disregarding likely remedial actions. Hydrogen fluoride is a highly corrosive substance and, under acute exposure conditions, the health hazard is the induction of pneumonitis and pulmonary oedema [11, 12].

For making safety decisions in UF_6 transport accidents, one of the main problems is defining an 'Acceptable Level of Exposure' (ALE). The ALE is a condition of exposure such that, if not exceeded, no person will be significantly affected in accidental cases. From the information available on recommended values for acute exposures to UF_6, UO_2F_2 and HF [11, 12], as well as the comparison among them and among the values recommended for routine occupational exposures [13], it is the authors' opinion that – for short exposure times (e.g. 30 minutes) – the ALE value for UO_2F_2 could be 150 $\text{mg-U} \cdot \text{m}^{-3} \cdot \text{min}$ and the ALE value for HF could be 300 $\text{mg-HF} \cdot \text{m}^{-3} \cdot \text{min}$, assuming a breathing rate of about 1.2 $\text{m}^3 \cdot \text{h}^{-1}$ for both cases.

Although it is recognized that the health effects will vary with the age and individual susceptibility of the exposed persons, these values seem to be adequate for making rough safety decisions, such as those related to the safety level required for the packages, and it is in this sense that they are used in this paper.

3. THE PRESENT PRACTICE IN THE TRANSPORT OF UF_6

The present practice in the transport of UF_6 seems to be established on a historical and pragmatic basis. As stated in Section 2, the chemical risk dominates in most transport accidents and, therefore, a level of safety equivalent to that used for the transport of substances of similar chemical risks, such as HF and HCl, was initially used as a reference. The ANSI N14.1 standard [8] is widely used with some adaptations to domestic conditions. In this standard, the level of safety of the primary vessel is mainly based on the conjunction of an artificially high internal design pressure (associated more with the load/unload process of the cylinders than with the transport itself) and of detailed material specifications. Although attempts were made by the nuclear industry to evaluate the performance of these vessels in cases of impact or fire (for instance Ref. [14]), it should be recognized that performance requirements directly related to potential transport accidents are not yet available. Therefore, the development of an international standard by the ISO will not occur until those requirements are developed [15].

As the radiological risk is not relevant, the IAEA Transport Regulations [9] establish low package requirements for the transport of depleted, natural or low enriched uranium. A Type B package is required for high enriched uranium when the A_2 value is exceeded. In addition, the IAEA Regulations require criticality controls when the enrichment is higher than 1%, but this requirement does not necessarily imply the use of packages with a high level of safety, such as Type B, because criticality controls can be obtained by other means, such as limiting the total mass per shipment. On the other hand, some recommendations in the ANSI standard seem to be far from the IAEA requirements and not related to the chemical risk problem. For instance, if on the basis of the reasons stated above, the following assumptions are made: (a) chemical risk dominates radiological risk, (b) criticality control of low enriched UF_6 is not difficult and in accidental cases can be based on requirements which do not imply the retention of the content of the package, and (c) chemical risk is proportional to the UF_6 mass content in a package or shipment; it cannot be technically explained why, as in the present practice, a Type B package should be used for the transport of about 2 kg of UF_6 (1.1% enrichment), with zero criticality risk, and packages of a lower level of safety can be used for the transport of some tons of UF_6 if enrichment is lower than 1%.

As a final observation, it is noted that the level of safety used to control the chemical risk of UF_6, although similar to that used for other dangerous chemical substances [16], is lower than the level of safety used to control the radiological risk of radioactive substances which, in the event of a transport accident, could produce similar or lower consequences in terms of health effects or number of deaths.

4. ESTIMATED UF_6 MASS LIMIT

Under the framework defined in Sections 1–3 of this paper, one of the problems to be addressed seems to be a determination of the maximum UF_6 mass which could be packaged without special transport package requirements. This is a concept equal to the one used for defining the transition from a Type A package to a Type B package on the basis of the radiological risk, but now the approach is based on the chemical risk. Two outdoor scenarios were considered: (a) rupture of the cylinder by mechanical forces with the presence of water as a liquid on the ground and as humidity in the air, and (b) rupture of the cylinder during a fire. The latter situation appears as non-conservative, owing to the high dispersion associated with a fire. The former situation was developed under the following assumptions: (i) the ALE levels defined in Section 2.2 will not be exceeded, (ii) there will be a total rupture of the cylinder, (iii) there will be enough water on the ground to react with the total content but without a significant reduction of the atmospheric release by dilution of the hydrolysis products of UF_6 (it is assumed that 10% of the total mass content will be released into the atmosphere), (iv) a person will be exposed at a relatively short distance from the release point (15–30 m) and (v) the exposure time will be about 30 minutes.

As stated above, for short distances from the release point, it is impossible to model the atmospheric dispersion or to estimate the composition of the release products with accuracy. Furthermore, for short dispersion distances and low level releases, it seems impossible to develop a general dispersion model, particularly considering the effects of buildings, trees or the ground shape on the phenomenon. Assuming no dispersion along the vertical axis (heavy cloud), no deposition on the ground (short distances) and a relatively low wind velocity (about $1\ m \cdot s^{-1}$), a comparison of the results obtained from different dispersion models [17, 18] suggests that, for short distances from the release point (15–20 m) and at a low altitude from the ground level (2–3 m), a dilution factor of about $10^{-2}\ s \cdot m^{-3}$ could be adopted. This value corresponds to a steady-state condition and a further assumption of constant concentration during the exposure time is implicitly made.

The reaction of one unit of mass of uranium as UF_6 with the formation of the anhydrous components UO_2F_2 and HF implies the reaction of about 1.48 units of mass of UF_6 with 0.15 unit of mass of H_2O and the formation of 1.29 and 0.34 units of mass of UO_2F_2 and HF, respectively; with the ALE value for uranium ($150\ mg\text{-}U \cdot m^{-3} \cdot min$) and a dilution factor of $10^{-2}\ s \cdot m^{-3}$ ($1.7 \times 10^{-4}\ mg\text{-}U \cdot m^{-3} \cdot min$), the mass of uranium which can be released into the atmosphere without exceeding the ALE value is 0.88 kg (I). With the ALE value for HF ($300\ mg\text{-}HF \cdot m^{-3} \cdot min$) and the same dilution factor, the mass of HF which can be released without exceeding the respective ALE value is 1.8 kg and this corresponds to a uranium mass of 5.3 kg (II). From a comparison between (I) and (II), it is clear that the uranium toxicity dominates under the assumptions made in this paper, disregarding potential remedial actions on the exposed person (it should be noted that at long distances, where deposition of UO_2F_2 could be significant, the situation could be reversed). Taking the lower mass of uranium (0.88 kg) and assuming that only 10% of the total mass content of the package will be released into the atmosphere, the mass limit for uranium as UF_6 in a package which is not designed to withstand accidents is 8.8 kg of U or 13 kg of UF_6. Therefore, in the light of present information, a rounded value of 10 kg of UF_6 is suggested as the maximum allowed mass in an UF_6 package not designed to withstand accidental conditions.

5. GENERAL COMMENTS

It is recognized that the main factors used to derive the value of the mass limit, namely the ALE values, the assumed fraction of mass released and the dilution factor could perhaps be modified after a detailed revision or additional studies. However, it is the authors' opinion that a combination of these modifications leading to a significant change in the suggested mass limit is quite improbable.

6. CONCLUSIONS

The present practice in the transport of UF_6 [8] ensures a level of safety equal or higher than the level of safety recommended for the transport of similar dangerous goods [16], but some basic questions arise requiring the attention of the nuclear industry and competent authorities: (a) Is it reasonable to establish a lower level of safety for chemical risk than for radiological risk, particularly in the case of UF_6, a material closely related with the nuclear fuel cycle? (b) Is it reasonable to design transport packages on the basis of pressure vessel requirements and of material specifications, or should transport performance requirements be developed? Both questions will require an answer in the near future and, if a decision is made to apply a level of safety equivalent to the one provided by Type B packages, this level should only be applied when the content exceeds a given mass limit. Besides, if transport performance tests are developed, such as those concerning impact and fire, the acceptable leakage after tests should be expressed as a function of the ALE values for chemical risks.

This paper has attempted to describe the UF_6 transport problems and to present preliminary estimates, based on the chemical hazards of UF_6 and its hydrolysis products. These problems refer both to the mass limit and to ALE values for chemical risks, as a first step in improving the requirements for the safe transport of UF_6. Finally, it is noted that the best way to improve safety seems to be the use of an outer packaging aimed at providing an additional capacity for the primary vessel to withstand impact and fire performance tests [19].

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