BRIEFING NOTE

URANIUM HEXAFLUORIDE (UF$_6$) TAILINGS

CHARACTERISTICS, TRANSPORT AND STORAGE

AT THE

SIBERIAN CHEMICAL COMBINE (SIBKHIMKOMBINAT) TOMSK

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URANIUM HEXAFLUORIDE UF$_6$

Uranium hexafluoride, or UF$_6$, is a compound used almost exclusively as feedstock in the uranium enrichment process towards the fabrication of low-enriched fuel for commercial nuclear reactors, for highly enriched fuel for research reactors and naval (mostly submarines) propulsion reactors, and for the fissile (HEU) components of nuclear weapons.

The process of producing uranium hexafluoride feedstock includes dissolving uranium ore concentrate or yellowcake (U$_3$O$_8$) in nitric acid to yield a UO$_2$(NO$_3$)$_2$ uranyl nitrate which is treated with ammonia producing ammonium diuranate AD. Reduction in hydrogen gives UO$_2$, which is converted with hydrofluoric acid (HF) to UF$_4$. Oxidation with fluorine finally yields UF$_6$. In its final form uranium hexafluoride is in the solid crystalline phase of solid whitish-grey crystals (like rock salt) at standard temperature and pressure (STP), it is highly toxic, reacts violently with water (including humidity in air) and is corrosive to most metals.

Essentially, enrichment of uranium increases the content of the fissile Uranium-235 component from about the naturally occurring 0.7% to 2 to 4% for commercial reactor fuels, to in excess of 20, 40, 60% and greater for research reactor fuels, and at 93%+ U-235 for USN/RN naval reactors and the fissile components of nuclear weapons. Since fluorine has only a single stable isotope, the isotopes of UF$_6$ differ in their molecular weight based solely on the uranium isotope present, so by high speed centrifuge the uranium 235 and 238 isotopes may be separated.

The enrichment process incrementally diffuses or centrifuges a uranium hexafluoride uranium-bearing gas into an enriched stream, with the feedstock stream being depleted below the 0.7% natural abundance which is referred to as DUF6. For the low levels of uranium enrichment required for civil nuclear reactor fuels, about 90% of the original feedstock mass remains in the DUF6 tails (ie ideally 1 tonne of uranium enriched to 3.5% U-235 results in 7 tonnes of depleted uranium at 0.3% U-235).

To extract the enriched uranium from the enriched stream to triuranium octaoxide U$_3$O$_8$, a dry conversion process vaporises the UF$_6$ by reaction with steam and hydrogen in a fluidised bed conversion unit. Subsequent conversion processes reduce the triuranim to a dioxide which is sintered into nuclear fuel pellets and plates.

DUF6 TAILINGS

It is the tailings DUF6 stream that is considered further here.

Uranium enrichment for civil and military purposes by a number of nuclear power and weapons capable states has resulted in some very large stockpiles of DUF6 tailings. The United States, for example, is estimated to have a DUF6 tailings stockpile of 705,000 tonnes and there is, most probably, a similarly large stockpile in the Russian Federation and some of the former Soviet Republics. The United Kingdom considers DUF6 not to be radioactive waste so there is no entry for the volumes held in the UK's radioactive waste inventory. Similarly, it is difficult to track down the French holdings of DUF6, although there is a specified tailings stockpile of triuranium octaoxide (U$_3$O$_8$) reckoned to be at about 220,000

tonnes (uranium) in France, although this may be a derived projection from holdings of DUF6 in France.

When UF_6 is stable and unreactive with oxygen, nitrogen and carbon dioxide but it reacts violently with water, including water vapour in the air, forming corrosive hydrogen fluoride (HF) and a uranium-fluoride compound called uranyl fluoride (UO_2F_2). Because of this instability, DUF6 is stored and transported in leakproof containers requiring compliance with IAEA TS-R-1 for conveyance between states.

With the large volume of DUF6 in storage the number of containers is correspondingly large with, for example, the United States having, in 1992, 46,422 containers in use for DUF6 storage dispersed over the open stockyards of three sites (Portsmouth, Paducah, and K-25 Oak Ridge). Generally, because the container filling procedure requires quite complex heating and cooling support plant, the same container is used for storage and transportation of UF_6 (including DUF6).

DUF6 containers (specified by a limit of 1% U-235 content) are long cylinders of about 3:1 aspect on an outer diameter of 1,200mm constructed in rolled steel alloy plate of 16mm thickness, and carry approximately 12,700kg of DUF6. When filled the solid, crystallised DUF6 occupies about 60% of the container, with the remaining ullage space comprising UF_6 vapour with impurities (hydrogen, fluoride, air, etc). The higher vapour pressure of the impurities can result in higher internal cylinder pressure during cylinder heating when the containers are filled, although at the time of filling the container's ullage vapour can be removed by 'cold burping'. Since the initial fill pressure is below atmospheric, prolonged storage of DUF6 can result in ingress of air, an increased impurity content and, with this, a higher ullage volume and corrosion of the internal ullage space container surface.

DUF6 Storage at Portsmouth, Ohio

ENVIRONMENTAL IMPACT OF MASS STORAGE

Usually sitting out in the open, the steel containers are subject to external corrosion. Pin holes and fissures arising from corrosion are initially plugged by the reaction of the UF_6 with moist air and iron leached from the container steel alloy, forming hydrates of the more stable uranium tetrafluoride (UF_4) which partially seals up the breach.

Even with external surface painting to reduce corrosion, the number of breaches increases with container age, to the extent that the US DUF6 containers are reckoned to

Corroded M48 Containers at Portsmouth

reach a failure rate by about 2039 at which the uranium concentrations in the groundwater of the three US sites would exceed the 20µg/l guideline and, earlier in 2020, the air concentrations of hexafluoride uranyl fluoride (UO_2F_2) vapour will exceed the permissible levels around the storage sites, with the accompanying high radiation exposure to individuals working in and nearby the storage areas.

Another form of dispersal is where one or more DUF6 containers are breached by external fire. Upon heating the crystalline DUF6 undergoes phase change from its normally solid state and sublimate to vapour at temperatures above 56.5^{o}C the result of which is the UF_6 ullage vapour expands from about 60% of the container volume to 93% of the volume, with the container wall being stressed loaded from the pressure within rising to a rupture pressure of 23^{+}MPa. In the event of a sudden breach of the container any liquid phase UF_6 would flash off or immediately partition to a vapour which, in turn, reacts exothermically with any water vapour in the surrounding air thereby heating and lofting the release plume. Analysis of the time to failure under the IAEA TS-R-1 thermal test conditions (800°C for 30 minutes) of the most common type of DUF6 container (48G) predicts rupture to occur 12 minutes 20 seconds from the onset of fire. At the point of rupture, the UF_6 liquid and vapour temperatures have reached 127°C and 356°C respectively, giving an airborne release of about 1,750kg of the 12,700 kg total DUF6 contents.

DISPOSAL TO THE ENVIRONMENT

DUF6 in the form of depleted uranium hexafluoride is not suited to direct disposal because of the phase state instability and its chemical reactivity with water. Reducing DUF6 to uranium tetrafluoride renders the material, so it is claimed, more suited to direct disposal to the environment.

Uranium tetrafluoride is granular (green salts), non-volatile, non-hygroscopic and only slightly soluble in water. However, it reacts very slowly with moisture at ambient temperatures to form UO_2 and hydrogen fluoride which, itself, would enhance the corrosion rate of disposal containers (barrels). Disposal barrels have to be rigid and very resistance to moisture ingress.

US PREVENTATIVE MEASURES – FUTURE DECONVERSION PLANT

In view of the impact of so many age-related transport-storage container failures be predicted, the United States authorities now have in place the construction[1] of DUF6 conversion plant which will reduce the UF_6 to the more stable uranium tetrafluoride UF_4 form for permanent disposal in drums, but with the option for a further reduction stage reducing to a uranium oxide if the demand for the metal justifies. Deconverting to uranium tetrafluoride yields about a 10% reduction of mass of the waste product, although this is offset by the proposal to cement encapsulate the waste for permanent disposal.

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[1] Conversion of Depleted Uranium Hexafluoride as required by Public Law 105-204 [DOE 1999b]

Two DUF6 deconversion plants are to be built (announced July 2004) at a cost of $588M, one in Piketon (Portsmouth) Ohio, and at Paducah Kentucky, with the Oak Ridge tailings being transported to these sites. The overall rate of deconversion of each of two plants is believed to be 13,500 tonnes per year which will take about 18 years to clear the Portsmouth stockpile.

Although the enriched uranium hexafluoride stream is converted to triuranium octaoxide U_3O_8, and thence to uranium dioxide for nuclear fuel fabrication, these facilities do not have the capacity to switch to working off the much larger (generally x9 for 3% enrichment) DUF6 tailings stockpile.

DUF6 IN EUROPE

The United Kingdom plans for a deconversion (from DUF6 to U_3O_8) campaign at Capenhurst from 2020 through to 2042 at a rate of 3,000 tonnes U per year, although this would not cover the entire UK DUF6 stockpile. At Gronau in Germany about 38,000 tonnes of DUF6 is presently in storage and this may be deconverted at the French plant at Perrelatte which commenced operations on the French DUF6 (220,000 tonne U) stockpile in or about 1998.

RUSSIAN DUF6 SITUATION

The most available source of information on the Russian Federation DUF6 situation, particularly relating to imports of DUF6 is given by Peter Diehl, although and understandably this is sketchy in parts.

According to Diehl, since 1996 depleted uranium tails from Urenco and Eurodif have and continue to be sent to the Siberian Chemical Combine (Sibkhimkombinat – near Tomsk) Russia for re-enrichment. In Russia, the imported DUF6 are fed into surplus enrichment cascades as feedstock and the enriched product is mostly natural-equivalent uranium plus some reactor-grade low-enriched uranium. These products are sent back to Urenco and Eurodif. Diehl gives an annual import of 14,000 tonnes U combined from Urenco and Eurodif which, following the claimed 're-enrichment', leaves a net of 11,672 tonnes U annually remaining in Russia for storage or disposal, although no details of this are available.

On Diehl's unsubstantiated figures, the Russia recovery ratio of 3 to 4% enrichment for the return stream, seems to be far too high for DUF6 imports that are likely to be depleted to around 0.3 to 0.4%.

If annual imports have been consistent since 1996, the DUF6 imported stockpile should now be about 90,000 tonnes U (about 7,000 containers) in addition to what is believed to have been a smaller import trade that commences about 1990 or earlier.[2] Some depleted

uranium (probably in oxide form) from chemical separation (reprocessing) of irradiated fuel is also believed to have been imported into Russia.

The general consensus of observers outside the uranium processing industry is that DUF6 imports into Russia are little more than a wheeze to save on DUF6 post processing costs in Europe.

TRANSPORT OF DUF6 UNDER IAEA TS-R-1

DUF6 (and feedstock and enriched streams of UF_6) is transported in sealed containers. Prior to transport containers are filled and cooled with the DUF6 assuming it crystalline state, and the container is evacuated to a slight negative pressure and then sealed with a non-venting valve. The maximum mass contents of certain containers held for long term storage of high purity DUF6 is set by defining a 5% ullage at a working temperature of 113^oC (based on a UF_6 mass of $3.33 g/cm^3$).

These International Atomic Energy Agency (IAEA) recommendations are generally accepted by all signatory states, being introduced in 1996. Since January 2002 specific requirements in TS-R-1 determine the transport of non-fissile and fissile excepted uranium hexafluoride which includes the transportation, although not on-site storage of DUF6.

The TS-R-1 requirements stipulate a unilateral approval H(U) requirement by 31 December 2003 being, essentially, satisfactory performance when subject to a structural internal pressure test of 2.76 MPa, 0.6m high drop test, survival of the 30 minute 800^oC thermal (fire) engulfment. Low levels of enrichment (hence non-fissile) DUF6 containers when in transport have to bear the label '*UN 2978*' with the proper shipping name '*RADIOACTIVE MATERIAL, URANIUM HEXAFLUORIDE*'. Other than the distinction between non-fissile and fissile consignments of UF_6, all uranium hexafluoride (DUF6 or otherwise) has to be transported in IAEA TS-R-1 compliant containers (other than a transit mass of less than 0.1kg)

Containers with H(U) approval can be recognised by the valve protector shroud located at one end although newer designs (post 2002 48Y model) may have overcome the design weakness (where upon impact the shroud rim deforming inwards and damaged the valve stem).

Valve Protecting Shroud

Compliance and protection against prolonged fire engulfment is less obvious and seems to be under continuing review by the IAEA HEXT Working Group. The claim is that the existing container designs have survival times of 25 to 35 minutes for an unprotected container so that, to meet the TS-R-1 30 minute compliance 'only a small adjustment' to the container's fire resistance is required, although this is contrary to the previously cited US analysis.

The IAEA Co-ordinated Research Programme (CRP) has evaluated the performance of UF_6 containers subject to fire conditions and, although actual testing with a UF_6 filled container is not mandatory being considered not to be 'a realistic option' (and has never been undertaken), the CRP

Prototype Thermal Pack

cannot agree (2003-4) on a general computer/calculation model to predict container performance under fire engulfment. Present 'solutions' to the doubts over thermal performance include thermal over-packs, and fire shields for the transport vehicles.

Once that the container has finished with its transportation role there is not, apparently, any internationally binding requirements relating to the adequacy of inspection and upkeep for the storage role. Only when the container is reused for transportation of UF_6 will compliance with IAEA TS-R-1 be required.

CONCLUDING COMMENTS

The situation seems that, in the West, the uranium fuel enrichers (namely the United States, France and the UK) are beginning to address the problem of managing the very large and accumulating stockpiles of depleted uranium hexafluoride or DUF6. The route to this seems to be the construction of plants that will 'deconvert' the DUF6 to a more stable product, at least to uranium tetrafluoride, for permanent disposal in sealed drums.

In the interim the DUF6 is held in thousands of containers in the stockyards of the enrichment plants. In the United States concern has been raised about the physical condition of the containers and the future time at which the rate of corrosion prompted failures will result in the environmental and health levels being exceeded – at Oak Ridge, Portsmouth Ohio and Paducah Kentucky, unacceptable and environmentally intolerable DUF6 container failure rates could occur from about 2020.

Running alongside this concern, there seems to have developed a steady trade in exporting DUF6 to the Russian plant at Tomsk with as much as 90,000 tonnes entering Russia from Western Europe over the last 10 or so years. It is not clear if the transportation of this DUF6 during this period, particularly since 31 December 2003, has been in containers that have been H(U) approved to the IAEA TS-R-1 standard, particularly in that there is continuing ambiguity about the capability of the present design of containers to comply with the thermal test requirements. Once at Tomsk, there is no information publicly available on for how long the containers will act as storage for DUF6 and, if this period is prolonged (which it is likely to be), if the inspection and maintenance regimes will be sufficient to prevent leakage of DUF6 to the environment.

If the export of DUF6 to Russia is nothing more than a wheeze to lessen the growing stockpiles of DUF6 in Western Europe then the weakness of this trade might be in non-compliance of the containers used for the transport. Here the rationale is that the older stocks of DUF6 would be exported to Russia, these being already stored in older, pre-2003 compliant containers (because it is too costly to transfer the DUF6 to new, compliant containers) – this might be confirmed or otherwise by actual inspection containers under transport or those containers newly arrived at the Tomsk DUF6 stockyard.

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