Potential for Phosgene in UF_6 Cylinders

John A. Hoffmeister
Lewis T. Gordon
Washington Safety Management Solutions
105 Mitchell Road
Oak Ridge, TN 37830
865-425-7041/865-425-7007
john.hoffmeister@wsms.com

Abstract

The Department of Energy (DOE) Office of the Inspector General (IG) identified a concern that the oldest uranium hexafluoride (UF_6) cylinders in the DOE's inventory may contain some phosgene ($COCl_2$) or fluorophosgene (COF_2) that could pose a significant hazard to the public and the workers. Phosgene converts to hydrochloric acid (HCl) and carbon dioxide (CO) in the presence of water, so an additional concern was raised that the cylinders may be corroding internally due to the presence of HCl. Many of the early Model 30A cylinders were obtained from the Chemical Warfare Service (CWS), where they may have been used in the production cycle for phosgene, but the principle basis for believing that phosgene might exist is qualitative laboratory data from 1946. Cooperative efforts between the Bechtel Jacobs Company LLC (BJC), the United States Enrichment Corporation (USEC), and Uranium Disposition Services (UDS) resulted in development of a protocol for screening the cylinders based on documented history of the cylinders. On application of the protocol to the Model 30A cylinder population at the East Tennessee Technology Park, all cylinders but one were eliminated from consideration and the final system required confirmation by testing.

History

At the end of World II, a number of cylinders (Fig. 1) were obtained from the CWS for storage and handling of uranium hexafluoride (UF_6) used as a process gas in the Gaseous Diffusion Plant (GDP) built in Oak Ridge, Tennessee as a part of the Manhattan Project. This facility later became known as the ORGDP. Chlorine cylinders obtained directly from the manufacturer and those manufactured specifically for UF_6 service do not have any potential to have been exposed to phosgene, so they are excluded from this study. The CWS cylinders were suitable for handling and storage of chlorine and phosgene and proved to be suitable for UF_6 service except that the valves on the cylinders were not large enough or in the proper location for use with the UF_6 handling requirements. Most, but not all, of the cylinders were modified by removing two center valves plugging and welding the openings, and welding a fitting for a 1 in. valve near the outer perimeter of one end. At least one functional plug remained at the other end of each cylinder. Given that phosgene has a vapor pressure of 1.6 atmosphere at 68 ºF, it is highly likely that any cylinder with residual phosgene would have been discharged through the openings in the cylinder with the application of heat and would have presented a significant hazard to the workers performing this task.

*Bechtel Jacobs Company LLC managing the Environmental Management activities under Contract DE-AC05-98OR22700 for the U. S. Department of Energy.

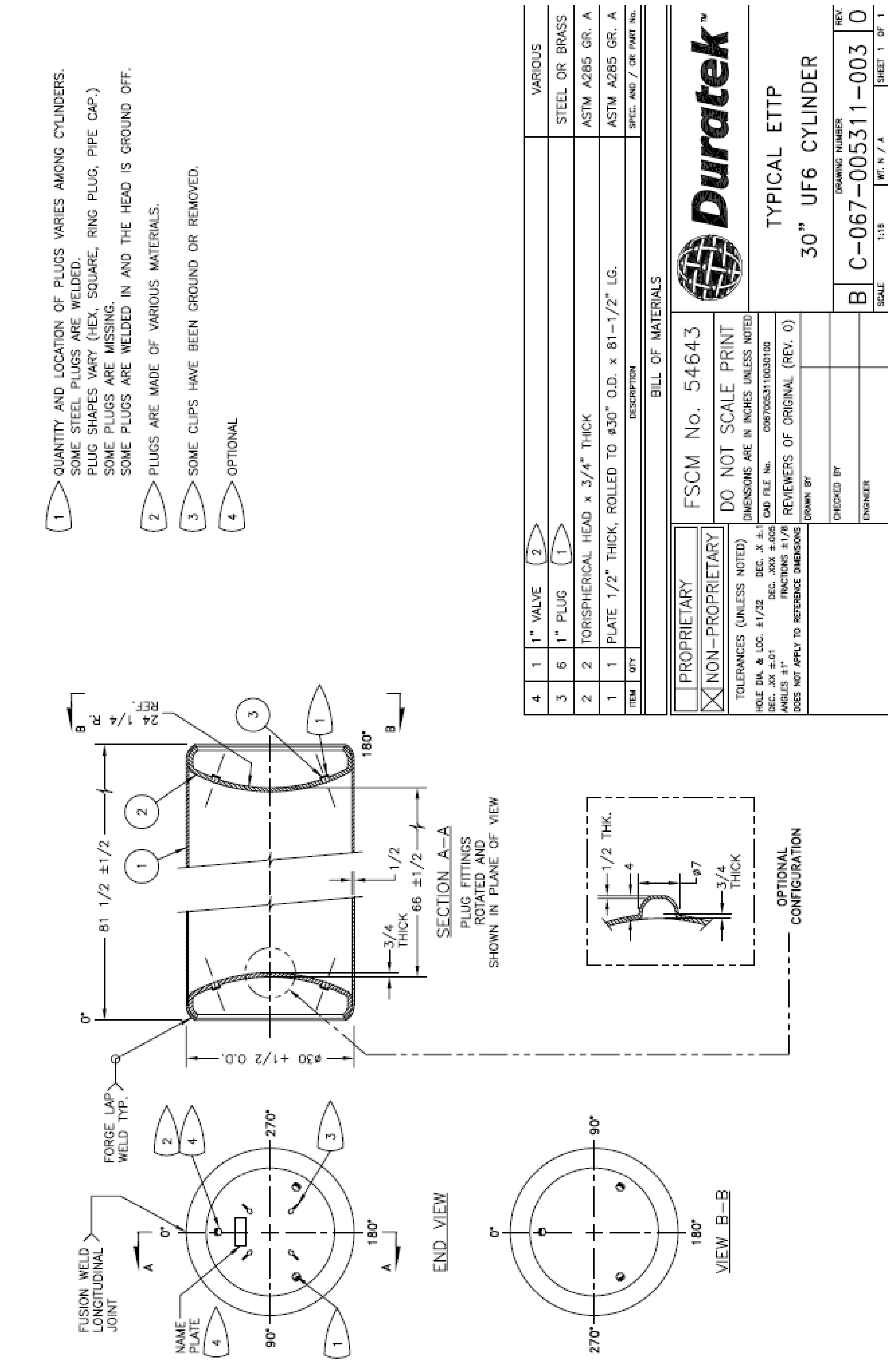

Figure 1. Typical Model 30A Cylinder

Upon transition from solid to liquid at 147.3 ºF, the volume of UF_6 undergoes a 33% increase, i.e. 1.00 ft^3 of solid becomes 1.33 ft^3 of liquid, increasing to about 1.49 ft^3 at 250 ºF. Fill limits were established for the cylinders that leave a 5% void space or ullage at 250 ºF to allow a margin to prevent hydraulic rupture. All of the cylinders were filled with liquid UF_6 at a maximum nominal temperature of 200 ºF with a volume of about 22.4 ft^3 as compared to the minimum cylinder volume of 25.64 ft^3. Thus, the UF_6 would have occupied approximately 87 % of the volume in a filled cylinder.

The principle reason for believing that phosgene could have been present in the Model 30A cylinders at ORGDP is a laboratory report from 1946 citing 22 detections of phosgene in 458 cylinders sampled. There is no report of the phosgene concentrations detected, nor is there a description of equipment used, lower limits of detection, statistical errors, or sampling technique. Depending on the sampling technique, the detections could have represented phosgene, fluorophosgene, mistaken identification, interference, chlorine, or chlorine reaction products.

Evaluation

Pressure vessel codes in place at the time that these cylinders were modified would have required hydrostatic pressure testing of the cylinders prior to placing in service. Current procedures first documented in the Handling Guide issued in 1966 require that the cylinders be completely filled with water and tested to 500 psig. Due to the recognized hazard of phosgene, it is not likely that the cylinders would have been reconfigured without first rinsing them to remove traces of both chlorine and phosgene. In addition, the highly reactive nature of UF_6, makes it highly likely that any cylinders would have been cleaned and dried prior to filling prior to use, but there is no documentation that rinsing and drying took place. Phosgene reacts slowly with water to form HCl and CO, so these processes would have resulted in elimination of virtually all of the phosgene in pressure-tested or rinsed cylinders. Fortunately, the hydrostatic testing was documented by physically stamping (embossing) symbols on the end skirt or the data plate of the cylinder and this is considered evidence that the cylinder was virtually free of phosgene prior to filling with UF_6.

The reaction between water and UF_6 proceeds rapidly, so that the water associated with any hydrochloric acid that may have remained in the cylinder after washing would have been scavenged by the UF_6, leaving only HCl vapor. This could have remained as a noncondensible vapor in the head space or could have been involved in the complex set of reactions that can occur in the halogenated compounds in the cylinders.

Due to the fact the cylinders modified for UF_6 service have only one valve, it was necessary to evacuate the cylinders to approximately 5 psia prior to filling them. At this pressure, the ideal gas law is appropriate for estimating the quantity of phosgene that may have remained in a cylinder if it had not been rinsed. The 30A cylinder has an internal volume of 25.64 ft^3, so at 68 ºF and 1 atmosphere, 6.5 lb. of phosgene gas could be in the cylinder prior to evacuation and that amount would be reduced to 2.24 lb at 5psia. For cylinders that were filled with the maximum 4800 lb of UF_6, it can conservatively be assumed that only phosgene remained in the void at 5 psia meaning that about 0.29 lb (130 g) was left. A release of 130 g over 5 minutes has been modeled with EPICode and the maximum concentration determined at 200 m is 3.1 mg/m^3.

ERPG-1 for phosgene is 0.1 mg/m^3, so the maximum release that would keep the air concentration below that value would be 4.2 g.

If phosgene is not soluble in UF_6, then it would have built up a backpressure in the cylinder during filling and the filling process would have been interrupted to evacuate the cylinder back to 5 psia. This process would have removed the phosgene in the ullage and, once the cylinder was filled and cooled, the phosgene in the ullage would be in the proportion to the volume. On heating the cylinder to feed the contents, the vapor space phosgene would mix with the UF_6 and would most likely flow out of the cylinder first. If phosgene is soluble in UF_6, it would be assumed that the phosgene was removed form the cylinder in overall proportion to the UF_6. Conservatively, the maximum remaining phosgene would be proportional to the UF_6, so reducing the source term by the ratio of ERPG-1 value to the maximum evaluated concentration (0.1/3.1) would suggest a limit of 155 lb UF_6 to assure that there would be no increase in consequence to the public.

At ETTP, the IG indicated that 309 cylinders had the potential to contain phosgene, but that number was reduced to 297 once the origin of the cylinders was determined. Of the 297 cylinders, 274 were eliminated from further consideration based on location of a legible hydrotest stamp on the cylinder. This stamp verified that the cylinder had been hydrotested since being modified for UF_6 service, which is one of the criteria identified above. Records have been kept for each cylinder documenting each time that the cylinder is filled and emptied. On the basis of such records, 22 cylinders were eliminated from consideration due to having multiple fill cycles leaving one cylinder that required testing.

The cylinder that required testing was located in a radiological facility previously used to withdraw the "tails" or depleted UF_6 from the gaseous diffusion cascade. Available records showed that the cylinder was full with an assay of 0.24 weight percent of ^{235}U. Based on this assay, there was no concern with a nuclear criticality event. Because the building temperature was 40 ºF, it was determined that the cylinder needed to be heated to about 60 ºF to assure that the phosgene would not be condensed and a sample from the vapor space would contain phosgene if it were present. The method for heating the cylinder involved placing electric heating blankets over the cylinder and heating for about 24 hours. Four blankets were required to get even heating, but this introduced the potential to overheat the cylinder possibly resulting in hydraulic rupture which would result in the bounding event accident previously evaluated for the UF_6 Cylinder Program. This required an evaluation of safety and approval by the BJC Safety Basis Review Board with oversight by the local DOE office. Thermostats for the heating blanket to limit the temperature of the heating blankets to a point well below the melting point were required. Because these units perform a safety-related function, but documentation was not readily available, the surface temperature of the cylinder was monitored over the heating period.

Industrial Hygiene maintained monitoring equipment around the cylinder and sampled the cylinder gas with a Draeger sampling tube selective for phosgene. All sampling was performed by workers in protective suits using supplied air. Gas samples were taken and sent to the Oak Ridge National Laboratory for analysis. The analysis from ORNL did not indicate the presence of phosgene above the detection limit for any of the samples taken. One sample, which also was the only one with detectable UF_6, detected fluorophosgene at 120 ppm. This compound has been observed in samples taken from other types of cylinders and is thought to result from leakage of refrigerant-114 into the cascade with the reaction possibly assisted by heat resulting from compressor failures.

Conclusions

After exhaustive research, interviews with employees involved in early operations, and limited sampling data, it has been concluded that there is no evidence that phosgene is present in the Model 30A cylinders at the ETTP site. It is almost certain that current operating practices, including the safety basis process, would prevent introduction of such material onsite today. As these practices rapidly evolved from experience in the early days of operation, it is also highly unlikely that the cylinders would have been used for UF_6 service without cleaning and conditioning to prevent accidents and loss of valuable product.

References

[1]Alfred K. Walter, “Management Alert on Uranium Hexafluoride (UF6) Storage,” Department of Energy Office of the Inspector General, September 30, 2005.

[2] N. H. Ketchan and R. H. Rainey, “Summary Report of the Nature of the Chemical Contaminants found in the Atmosphere in the K-25, K-27, and Fercleve Areas,” Clinton Engineering Works, Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, 11, October 1946.

[3]*Uranium Hexafluoride Handling Procedures and Container Criteria*, ORO-651, Rev. 0, Union Carbide, 1966.