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Large UF6 Cylinder Cleaning and Maintenance

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ABSTRACT

Worldwide, commercial quantities of UF_6 are stored and shipped in special steel cylinders of primarily 30 inch and 48 inch diameter. In order to maintain the integrity credentials required for continued use as a transportation container, each of these cylinders must be washed and re-certified every five years. A small residue of UF6, called a "heel" is first washed from the cylinder then a series of physical tests designed to demonstrate the integrity of the cylinder is performed. Successful completion of the physical testing "re-certifies" the cylinder for five additional years of service.

The washing and re-certification tasks are usually performed as an ancillary effort at uranium UF_6 fabricators, enrichment plants or conversion plants. Often the process is looked upon as a necessary nuisance by those performing the work. DAHER-TLI, however, is currently developing what is believed to be the first of its kind stand-alone cylinder washing and re-certification facility. At first it will process only 48 series cylinders containing less than 1% ^{235}U UF_6. The process is unique in that extra steps are taken to remove internal scale from the inner cylinder walls. A newly developed three-step uranium recovery process for the wash solutions produced during the cylinder washing is also featured. A high-purity uranium by-product results from this work. Recertification of each cylinder follows the washing and uranium recovery. Options to dispose of retired cylinders are mentioned.

INTRODUCTION

Cylinder Populations

Commercial UF_6 containers were developed from steel pressure cylinders originally designed to hold liquefied chlorine gas. Two basic sizes have evolved over the years, a 30 inch diameter cylinder that holds about 2.25 metric tons of solidified UF_6, and a 48 inch diameter cylinder that holds either 10 metric tons (48X) or 14 metric tons (48Y) depending on its length. The current predominant designs are the 30B and 48Y.

UF6 cylinders in service worldwide consist of a "working" population of about 8,000 30B cylinders that are used to store and transport primarily low enriched (< 5 wt% ^{235}U) UF_6 from enrichment plants to conversion plants where the UF_6 is converted into UO_2 to make power reactor fuel. Another working population of about 12,000 of 48X and 48Y cylinders is used to store and transport natural UF_6 from UF_6 generating plants to enrichment plants or conversion plants. A third very large population of about 90,000 48X, 48Y and 48G (a thinner-walled version of the 48Y) cylinders is used for long-term storage of depleted UF_6 tailings from enrichment plants. Many of these cylinders have long exceeded their transport certification limit and cannot be moved out of their storage sites without special dispensation by government authorities.

The two working populations of cylinders require recertification of their physical integrity every five years in order to continue as shipment transport containers. Empty cylinders containing a small residue of UF_6 called a "heel" first must be internally washed to remove the heel material and then subjected to a series of physical tests to assure they are suitable for another five-year service period.

Cylinder Washing Developments

Internal washing of cylinders before recertification testing has been a fertile field of experimentation and variants. Many different techniques, operating procedures, additives, and approaches to do this work have been and still are evident at different facilities throughout the world. Nearly all of the efforts are sideline ventures ancillary to the primary business of the facilities and often looked upon as a necessary nuisance by those facilities. There are also indications that some of the techniques used actually fail to thoroughly clean the cylinders or leave additive residues in them after the washing is completed.

Daher-TLI is developing an approach for setting up a stand-alone facility for the express purpose of cylinder servicing including washing and recertification, external cleaning and re-painting, and decontamination and dismantling of scrap cylinders for metal recovery. Processes to purify and recover uranium from the washing solutions are also included in the facility. The plan is first to establish a natural UF_6 cylinder processing capability in order to avoid the cost and extra start-up time needed for licensing an LEU facility, and then translate the techniques evolved to a safe-geometry analog process for 30B cylinders at a later date.

DAHER-TLI CYLINDER WASH PROCESS

The Daher-TLI washing technique is based on using a small volume of water and/or weak HF acid solution (nominal 15 gallons for 48 series cylinders, 19 liters for 30B cylinders) as the wash liquid. A cylinder is placed on a modified tilt/roll table, and the wash liquid is input through the cylinder valve using a quick-disconnect supply hose. Once the wash liquid transfer is complete, the valve is closed and the hose disconnected. The cylinder in the horizontal position is rolled about its axis for about 10 minutes, tilted 45 degrees up and rolled for 10 more minutes, and tilted 45 degrees down and rolled for 10 minutes. This series of actions provides for contact of the wash liquid with all the internal surfaces of the cylinder. At the finish of the roll program the cylinder is stopped in a tilted down position with the valve located at the bottom. Another quick-disconnect supply hose is connected to the valve, the valve opened, and the wash liquid is pumped out of the cylinder to the first of a series of processing tanks. A duplicate series of steps is then performed using 15 gallons of plain water to rinse out the cylinder. When the rinse sequence is complete, the rinse water is pumped to a holding tank where it is sampled for ppm uranium. A lab result of 3,000 ppmU or less indicates a successful washing after which the rinse solution is transferred to the wash liquid supply tank where the HF acid content is adjusted by the factor derived from the next cylinder's heel weight. The adjusted wash liquid is then held at ready until the next cylinder is set up to wash.

Tilt/Roll Table

The tilt/roll table is a key component of the wash system. It features a closed system washing operation, complete and assured contact of the wash liquid with the inner surfaces of the cylinder, a short cleaning cycle, and almost no operator exposure to washing fluids. It also makes it practical to safely strengthen the washing liquid for a more effective washing result. The table design is of rugged construction and has a history of 30+ years of very low maintenance operation. To enhance the wash capability, Daher-TLI developed a unique cylinder end support mechanism that accommodates all three 48-inch series cylinders on the same table. 30B cylinders will be processed on a smaller version of the same tilt/roll table design.

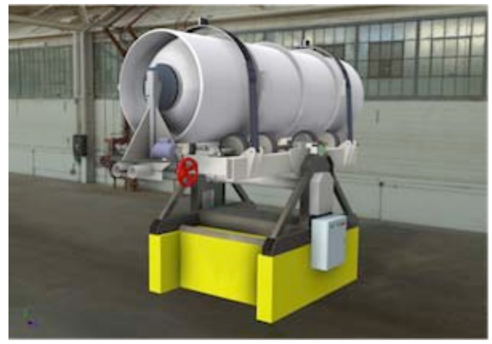

Figure 1: Rendering of tilt/roll table with end support device

Wash Chemistry

The chemistry of the wash operation is based on proven experience that an optimum HF solution is the best cleansing agent for the washing. The basic reaction of the water in the wash liquid with the UF_6 heel always creates some HF acid. (See equation 1 below).

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF \qquad [1]$$

However, because heel weights in the cylinders vary considerably, the strength of the acid produced by this reaction can also be quite variable. Very small heel weights produce so little HF that its cleaning ability is substantially diminished.

To counteract this weak HF solution, Daher-TLI has refined the wash process by adjusting the wash liquid with commercial HF based on a heel weight factor so that the HF strength of the wash liquid in each cylinder is constant at about 7wt%. This better assures a uniform cleaning solution and an active removal of scale buildup and any UF_6 entrapped in the scale on the inside cylinder surfaces. Scale buildup is a tightly adhering, complex mixture of rust, iron fluorides, miscellaneous residues from previous additives, and uranium salts. Characterized as rust, the attack by the wash liquid can be described by the formula:

Figure 2: Cylinder wash solution (UO2F2)

$$Fe_2O_3 + 6HF \rightarrow 2FeF_3 + 3H_2O \quad [2]$$

The FeF_3 forms a slightly soluble light green sediment that freely flows out of the cylinder with the spent wash liquid when it is pumped out at the end of the wash cycle.

The cylinder wash process ends with a clean empty cylinder that is ready for recertification or disposal, and uranium-laden wash solution that is sent to the uranium recovery and purification process.

CYLINDER RECERTIFICATION

After the washing is complete, the cylinder is unloaded from the tilt/roll table and moved to the recertification area. The recertification process is a straightforward series of tests and inspections to qualify it for another five years of service. The process follows the guidelines spelled out in ANSI N14-1, which is the standard for such work. Below is a summary of the different operations that are carried out.

1. Perform internal visual inspection to verify cleanliness.
2. Fill cylinder completely with water and perform 400-psig leak test.
3. Dry cylinder to -35° C dew point using air, dry nitrogen, or vacuum.
4. Install new valve and new end plug.
5. Pressurize cylinder to 100 psig with dry N_2 and perform leak check.
6. Perform 40-point cylinder wall thickness test.
7. Establish new tare weight.
8. Refill cylinder with dry nitrogen to 5-psig.
9. Release cylinder for shipment.

Typically it takes 2.5 to 3 working hours per cylinder to complete the above tasks, not including an overnight to complete the drying step.

URANIUM RECOVERY AND PURIFICATION

As mentioned above, the cylinder wash liquid is comprised of a solution of UO_2F_2, left over HF, and iron-based sediments. Non-uranium contamination levels are high enough to render the mixture unfit for use in fuel applications without significant purification steps. Daher-TLI has developed a three-step purification process for the wash liquid using a combination of extraction and separation techniques that have a long history in established uranium chemical operations, but have not been applied to a cylinder washing solution purification regimen in the specific manner described below.

<u>Step I – Fluoride removal</u>

The first separation removes the fluoride present by adding enough NaOH solution to the wash liquid to convert all of the UO_2F_2 solution to sodium diuranate (i.e., $Na_2U_2O_7$ or SDU) precipitate, and to neutralize the remaining HF to NaF. This raises the pH of the mixture to about 11.

$$2UO_2F_2 + 6NaOH \rightarrow Na_2U_2O_7 + 4\mathrm{NaF} + 3H_2O \quad [3]$$

The NaOH also converts the FeF_3 sediment to $Fe(OH)_3$ sediment and precipitates the soluble iron to $Fe(OH)_3$. With all the fluoride now converted to an NaF solution, the combined SDU and $Fe(OH)_3$ precipitate from the NaF solution. This can be seen in Figure 3. After settling, the NaF solution is transferred to storage to await further processing to remove the fluorides. The SDU precipitant containing iron is treated next.

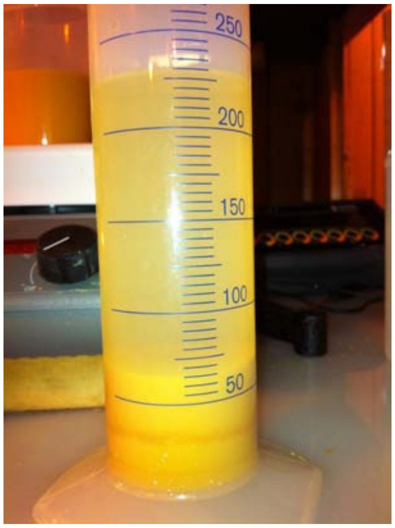

Figure 3: SDU settling with iron sediment layer

Step II – Removal of Iron Contamination

The next separation involves the removal of iron contamination to produce a soluble carbonate complex solution with the uranium. This is accomplished by mixing the precipitate mixture from Step I with a sodium carbonate (Na_2CO_3) solution as indicated below:

$$Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O \rightarrow 2Na_4UO_2(CO_3)_3 + 6\text{NaOH} \qquad [4]$$

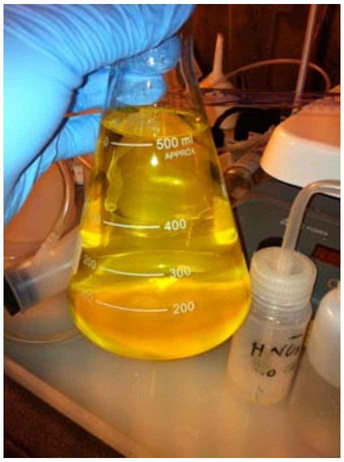

Figure 4: Uranium carbonate solution

In this environment the $Fe(OH)_3$ remains in precipitated solid form. The uranium-bearing carbonate solution is decanted off, leaving the iron residue. Figure 4 shows the uranium bearing carbonate solution.

Step III – Uranyl Peroxide

The final purification step involves separating the sodium from the uranium by first acidifying the uranium carbonate complex solution and then precipitating the uranium as uranyl peroxide using hydrogen peroxide as the reagent. The acid lowers the pH to a level that promotes uranyl peroxide formation and in the process destroys the carbonate ions via carbon dioxide evolution.

$$Na_4UO_2(CO_3)_3 + 6HNO_3 \rightarrow UO_2(NO_3)_2 + 3CO_2 + 3H_2O + 4\text{Na}NO_3 \qquad [5]$$

$$UO_2(NO_3)_2 + H_2O_2 \rightarrow +UO_4H_2O + 2HNO_3 \qquad [6]$$

The uranyl peroxide crystals are then recovered by a third physical separation, and dried or heated to convert them to U_3O_8, and packaged for storage or shipment to complete the uranium purification process. This material is very close to ASTM spec uranium.

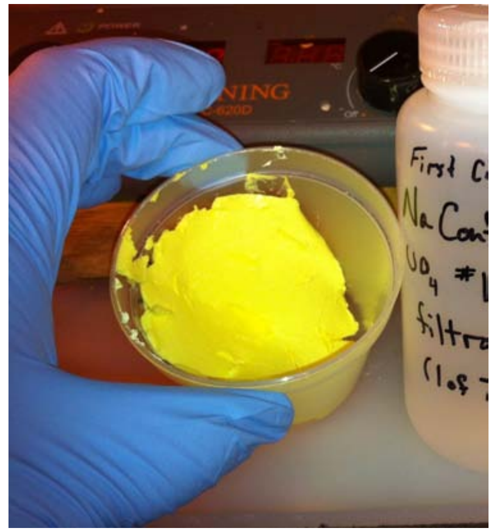

Figure 5: Uranyl peroxide cake

By-Product Disposal

The fluoride by-product from Step 1 above is treated to convert the NaF solution into a fluorspar-like product, which can be sold or disposed of as a chemical waste. The technique used is to adjust the NaF solution pH to just below neutral pH (about pH 6.0), warm it up to about 70° C, and trickle it through a bed of calcite particles.

$$2\mathrm{NaF} + \mathrm{Ca}CO_3 \rightarrow +\mathrm{Ca}F_2 + Na_2CO_3 \qquad [7]$$

FUTURE CYLINDER SERVICE FACILITY OFFERINGS

The Daher-TLI Cylinder Service Facility will at first provide storage, wash, and recertification services for its clients. Future plans may include other options such as external refurbishment (cleaning and re-painting), and scrap and disposal or decontamination and metal recovery for cylinders that are not to be recertified.

CONCLUSION

Daher-TLI Cylinder is developing the first dedicated large cylinder service facility that will provide comprehensive cylinder storage, refurbishment, and disposal services to cylinder owners. The initial phase of the facility is under construction. It will offer a wash capability that features three significant improvements to existing cylinder washing processes that have been developed, including improved wash capability, an improved tilt/roll table, and a three step purification process that converts wash liquor into ASTM grade uranium by-product.

REFERENCES

1. US Patent application 13757177 – “Cylinder Wash Process Modification”.
2. US Patent application 13776785 – “Uranium Recovery from UF_6 Cylinders”.
3. US Patent application 61821845 – “Tilt/roll Table Modification”.