Daher-TLI UCSC Wash Process - Lessons Learned from Handling a Legacy Cylinder - 16506

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Daher-TLI

ABSTRACT

The Daher-TLI UF6 Cylinder Service Center (UCSC) began operation in 2013 and functions as a dedicated wash, recertification, storage and disposal facility for 122 cm uranium hexafluoride (UF6) cylinders. The primary purpose of the facility is to provide cylinder cleaning and recertification services to the UF6 industry for cylinders that previously contained natural or depleted UF6. The facility also has the ability to recover most of the uranium in the form of uranyl peroxide (UO4) or triuranium octoxide (U3O8). Small residues of UF6 (commonly referred to as a heel) from natural cylinders are removed and treated in a patented three-step purification process that recovers U3O8 that meets the ASTM specification. The wastewater ordinarily contains a mixture of sodium salts (77% sodium sulfate, 23% sodium nitrate) along with minute traces of uranium (1 – 2 mg/L) and fluoride (10 – 20 mg/L).

Over a period of 6 months, lab analyses were performed on the filtrate from a legacy cylinder in an attempt to separate uranium and fluoride from this stream. These pilot results established near quantitative recovery of uranium (< 1 mg/L) and near complete separation of fluorides (5 – 15 mg/L). This paper follows the efforts of the Daher-TLI UCSC to process the abnormal heeled UF6 cylinder. This paper also documents the lessons learned from this experience and how those lessons were used to improve the UCSC wash process. These modifications served to recover 99.87% of the input uranium as UO4 while simultaneously creating a waste stream with only trace amounts of impurities.

INTRODUCTION

Worldwide, commercial quantities of UF6 are stored and shipped in special steel cylinders of primarily 76 cm and 122 cm diameter. In order to maintain the integrity of credentials required for continued use as a transportation container, each of these cylinders must be washed and recertified prior to refilling 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 are performed. According to the American National Standards Institute (ANSI N14.1-2012), heel quantities in 122 cm cylinders shall not exceed 22.7 kg. In industry, heel weights are typically less than 6.8 kg. 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 UF6 fabricators, enrichment plants or conversion plants. Often, those performing the work look upon the process as a necessary nuisance. However, the

UCSC has revolutionized this process by adding extra steps to remove internal scale from the inner cylinder walls and by incorporating a process to recapture and de-convert the residual heel to UO4 or U308 (1). This is achieved in a newly developed three-step purification process that recovers between 85-95% of the original uranium in a form that meets the ASTM specification, so the uranium returned to the customer requires no further processing before being re-introduced to their process.

THEORY AND PROJECT BACKGROUND

Normally, a cylinder wash consists of a dilution process the converts the solid UF6 heel to a solution mixture of hydrofluoric acid and uranyl fluoride. However, the UCSC has added key features that substantially improve the effectiveness of the washing. These features serve to not only recover the heel uranium, but substantially improve the purity of the recovered uranium as well. The first part of the modification enhances the cleaning of the cylinder by intentionally adding a dilute solution of hydrofluoric (HF) acid rather than water as the first wash medium (patent pending) followed by one or more water rinses. The calculated 7% HF assures an adequate supply of cleansing agent to remove any scale or rust [primarily Iron(III)Oxide (Fe2O3)] that adheres to the cylinder walls. This was recorded in a Patent (2) that the UCSC was designed upon. This is displayed below in equations one and two.

$$UF_6 + H_2O = UO_2F_2 + 4HF \qquad (1)$$

$$Fe_2O_3 + 6HF = 2FeF_3 + 3H_2O \qquad (2)$$

The uranium leaves the cylinder and undergoes successive chemical transformations, each transformation serving to remove different impurities, and finally is precipitated as UO4, which can be converted to ASTM grade U3O8. Similar processes (3,4,5) were studied thoroughly prior to testing and evaluation in a laboratory environment and many of the design elements utilized there (6) were carried over to the design of the UCSC process.

In the course of discussing the benefits of the facility with current and prospective clients, one customer proposed the possibility of having the Daher-TLI UCSC service a legacy cylinder that the customer was unable to process further.

In late 2014, the UCSC began work on the legacy cylinder, which reportedly contained a 106.6 kg heel. An enrichment facility had previously vacuum educted the cylinder several times in an attempt to remove the UF6, however the heel size remained unchanged. A special washing protocol involving initial larger than normal wash volumes and multiple rinses and internal inspections was utilized to completely remove the heel. Once the heel material had been removed from the cylinder as a wash liquid and processing had been initiated, several anomalies became apparent. Evidence was found of unknown components in the wash liquid.

A special protocol was devised to process this abnormal wash liquid. Impurities were removed in successive steps until a final precipitate comprised of UO4 was achieved. The filtrate from the final UO4 precipitation had retained uranium and sodium fluoride and therefore was re-precipitated as SDU and analyzed under the premise of separating uranium and fluoride impurities from the waste stream. These pilot results established near quantitative recovery of uranium (< 1 mg/L) and near complete separation of fluorides (5 – 15 mg/L) in the waste stream.

DESCRIPTION

A protocol was devised to process the abnormally large heeled cylinder. The protocol included special considerations and enough extra measurement and flexibility to allow in-process adjustments as the washing unfolded. This is illustrated below.

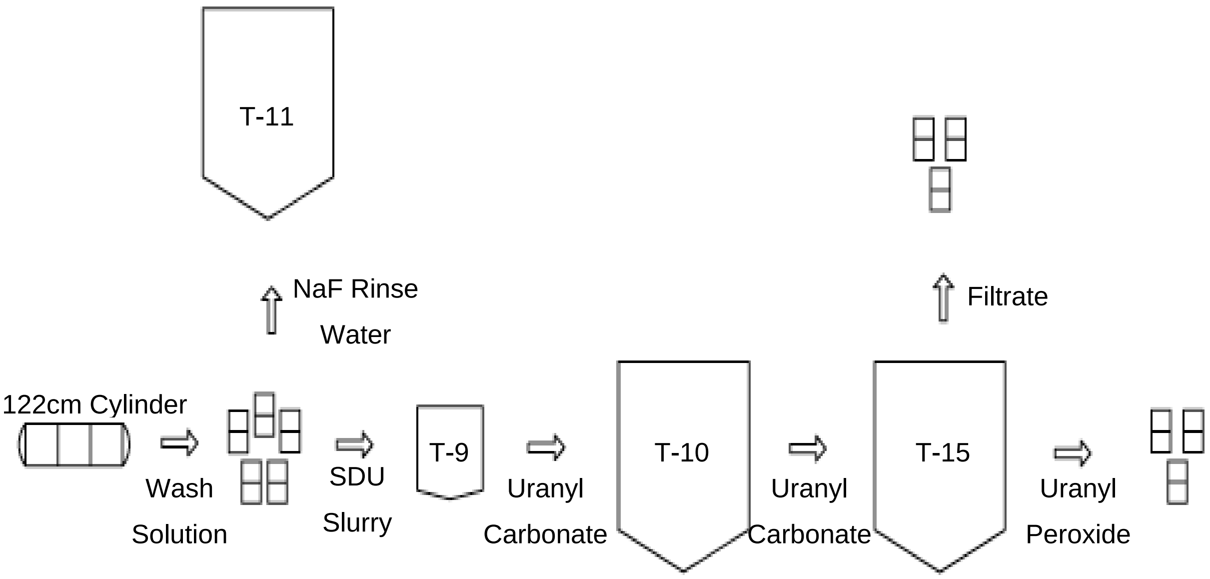

Fig. 1. Process Schematic: Starting from Cylinder Wash

A high volume initial wash was employed with 227 L of water plus two additional washes with 56.8 L aliquots of 7% HF in water plus five intermediate rinses with water.

The 625 L of wash and rinse liquid was collected in five 208 L drums where it was precipitated as sodium diuranate (SDU). The supernate from this precipitation was separated and the SDU slurry was promptly transferred to a carbonate extraction tank and re-dissolved as a uranyl carbonate complex (NaUCO3) (7). The insoluble iron was removed from this solution and the liquid NaUCO3 was precipitated as UO4. The filtrate was analyzed and the results showed high levels of uranium still in solution, indicating an incomplete precipitation. However, during this analysis, it was found that the solution also contained a high fluoride concentration. Thus it was decided to precipitate the solution as an SDU, rinse out the fluorides and re-process the uranium.

The filtrate was captured in three 208 L drums and small aliquots of 25% sodium hydroxide (NaOH) were added to increase the alkalinity to 7.5 pH at which point precipitation began to form as SDU. After a period of rinsing and settling, the supernate was separated from the precipitate and analyzed. The precipitation was, overall, deemed successful and the solutions were grouped based on the degree of success. Those solutions that had a uranium concentration less than 200 mg/L were transferred to storage tank T-11 with the rest of the sodium fluoride (NaF) rinse solution from the original wash precipitation. Those solutions that still had high concentrations of uranium were transferred to storage tank T-10. This is illustrated below

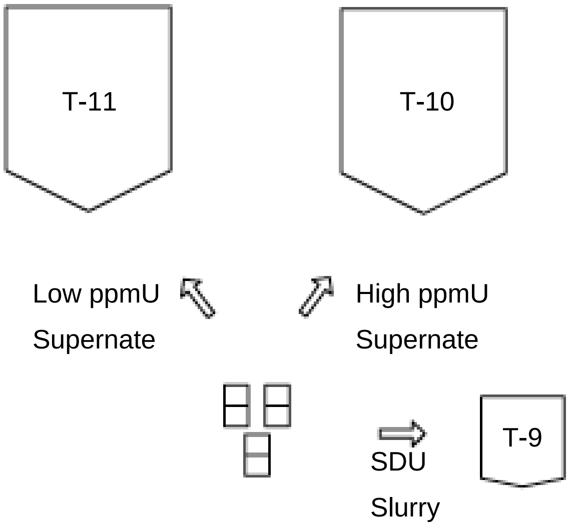

Fig. 2. Process Schematic: Starting from Filtrate

The SDU precipitate was considered un-processed original content and thus was transferred to the carbonate extraction tank (T-9) and re-dissolved as a NaUCO3.

At this stage, there were approximately 1,893 L of solution characterized by high uranium (4251 mg/L), high fluoride (7369 mg/L) NaUCO3 in T-10, 946 L of high uranium (8603 mg/L), high fluoride (4960 mg/L) in T-9 and 3,785 L of semi-low uranium (152 mg/L), high fluoride (5416 mg/L) in T-11. It was determined that fluoride played a role in the retention of uranium in the supernate from precipitation of UO4 and thus, without a method of removing fluorides, none of these solutions could be processed further to re-capture UO4 (8).

A strategy was conceived to remove fluorides while in the NaUCO3 phase via calcium carbonate (which is also commonly referred to as crushed limestone). This is shown in the equation 3 below.

$$2NaF + CaCO_3 = CaF_2 + Na_2CO_3 \qquad (3)$$

An 18.9 L sample was attained from T-9 NaUCO3 solution. This sample made 3 passes through a bed of calcium carbonate, each pass requiring re-acidification with

20% nitric acid until pH of 6.5 was attained. Standards were previously analyzed and a curve was generated that predicted the amount of acid to add to each pass based on effluent column pH value. This is shown in equation 4 below.

$$y = 0.7393e^{0.6931x} \qquad (4)$$

After the fluoride concentration had decreased to 17 mg/L, the 18.9 L sample was divided into two, 9.46 L solution volumes. One of the volumes was charged to a reaction vessel and the other was held in reserve. The reaction vessel consisted of a 18.9 L reaction vessel with an overhanging agitator. Aliquots of 20% nitric acid, 3% hydrogen peroxide and the other half of the starter batch solution were added at metered flows that balanced the pH at 4. The reaction is shown below in equations 5 and 6.

$$Na_4UO_2(CO_3)_3 + 6HNO_3 = UO_2(NO_3)_2 + 3CO_2 + 3H_2O + 4NaNO_3 \quad (5)$$

$$UO_2(NO_3)_2 + H_2O_2 + 2H_2O = UO_4 \cdot 4H_2O + 4NaNO_3 \qquad (6)$$

After all reagents had been added, the vessel was agitated for 48 hours (this served to promote crystal growth). The filtrate was decanted and the uranium concentration was analyzed at 46 mg/L. This was acidified with 0.6 L of 20% nitric acid and 0.6 L of 3% hydrogen peroxide and allowed to digest for 64 hours. After digestion, there was a small layer of sediment and the supernate uranium concentration was analyzed at 9 mg/L. An extended settling period of 3 weeks was allowed and the resulting uranium concentration held in solution was below 1 mg/L. Although the fluoride concentration after calcite treatment was 17 mg/L, some had been co-precipitated as a double salt with UO4 because the fluoride concentration was now at 3.7 mg/L.

DISCUSSION

During precipitation of SDU from uranyl fluoride wash solution, it was found that with a very slow addition of NaOH, the precipitation yielded very compact, high-density SDU particles. This fact, paired with the limitations of a closed-head 208 L drum reactor resulted in an inefficient rinsing of solids, which left significant sodium fluoride. It was later found that some of the sodium fluoride was also loosely bonded to the SDU. However, this technique for sodium hydroxide addition proved useful when it was applied to the uranyl nitrate solution in the filtrate from the original UO4 precipitation (see Fig. 2.). Normally precipitation from a nitrate solution yields smaller particles that require long periods of digestion and settling to separate from a solution

As previously discussed, the supernate from SDU precipitation of UO2F2 wash solution was separated in drums and the SDU slurry was promptly transferred to a 946 L carbonate extraction tank (T-9) which contained 435 L of 6% NaHCO3. The SDU slurry was heated to 38 degrees C and re-dissolved as NaUCO3 over a period of 24 hours. At this point, the solution was not analyzed for fluorides. With such a large starting heel, more fluoride was to be expected, however this was accounted for by rinsing the insoluble precipitate 7 times in drums. This final rinse liquid was analyzed for fluorides and the results showed insignificant amounts of sodium fluoride. (In a later experiment, it was discovered that a large portion of the loosely bonded sodium fluoride had been chemically tied to the SDU solids. Consequently, they weren't released into solution until the dissolution of the SDU as NaUCO3.)

Once the NaUCO3 had been formed, the insoluble iron was removed via filtration from this solution and the liquid UCO3 was precipitated as UO4. The filtrate from this protocol measured at a pH of 4.2, which was very close to the desired target of 4.0. The filtrate also, however, measured high in uranium (8,775 mg/L) and very high in fluoride (10,189 mg/L) indicating that something was hindering precipitation and that the rinsing technique used on the SDU source of the NaUCO3 was not adequate.

The filtrate was captured in three 208 L drums and small aliquots of 25% NaOH were added to increase the alkalinity to 7.5 at which point precipitation began to form as SDU (see Fig. 2.). After a period of rinsing and settling, the supernate was separated from the precipitate and analyzed. Liquid scintillation counting for uranium isotopes showed that precipitation was fairly successful, the three batches having final uranium counts at 685, 330 and 22 mg/L, respectively. Those solutions that had a concentration of uranium that was less than 200 mg/L were added to a 3,785 L tank (T-11) with the rest of the NaF rinse solution from the original wash precipitation. Those solutions that still had high concentrations of uranium were transferred to a 3,785 L tank (T-10). The SDU precipitate was considered un-processed original content and thus was transferred back to the carbonate extraction tank (T-9) and re-dissolved as NaUCO3. This time, a standard fluoride ion selective electrode (ISE) was employed and gave reported 5,000 mg/L. The results suggested that the loosely bonded sodium fluoride tied to the SDU solids had been released into solution upon dissolution of the uranium compounds. This phenomenon was re-captured on a small-scale lab experiment. Data is reported below.

Table I. Bench Scale Fluoride Tracking

Sequential Process Steps	Fluoride Concentration (ppmF)
Uranyl Nitrate Solution	1017
Supernate from SDU Precipitation	617
SDU Water Rinse #1	196
SDU Water Rinse #2	39
SDU Dissolution (Carbonate Extraction)	468

A strategy was conceived to remove fluorides while in the NaUCO3 phase via reaction with crushed limestone (calcium carbonate). An 18.9 L sample was attained from the T-9 NaUCO3 solution containing the dissolved sodium fluoride. The fluoride concentration was 5,138 mg/L. Uranium analysis showed 9,280 mg/L prior to charging solution to column. This sample made 3 passes through a 7.62 cm diameter x 122 cm tall bed of calcium carbonate; throughput in the 7.62 cm diameter calcite column was 12 L/hr (face velocity of 0.5 cm/s). Each pass required re-acidification with 20% nitric acid until pH of 6.5 was attained. After the third pass, the column effluent solution had a fluoride concentration of 17 mg/L (99.5% column efficiency) and a uranium concentration of 8603 mg/L. This indicated that some uranium was held up in the bed of calcium carbonate. This was likely due to the presence of excess sodium and nitric acid as an acid buffer. Another acid such as sulfuric acid should be explored here. (A small-scale lab version of this experiment was performed. Data from a 1.91 cm x 10.2 cm calcite column is reported below.)

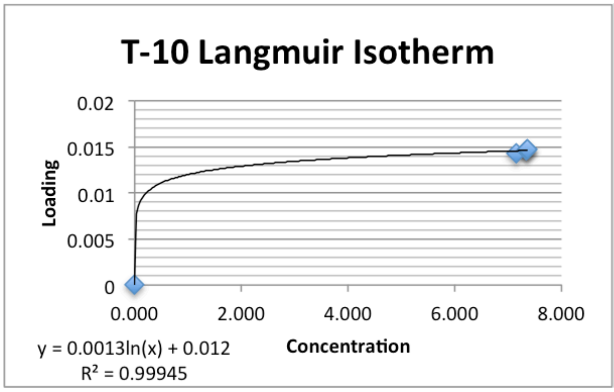

Fig. 3. T-10 Langmuir Isotherm

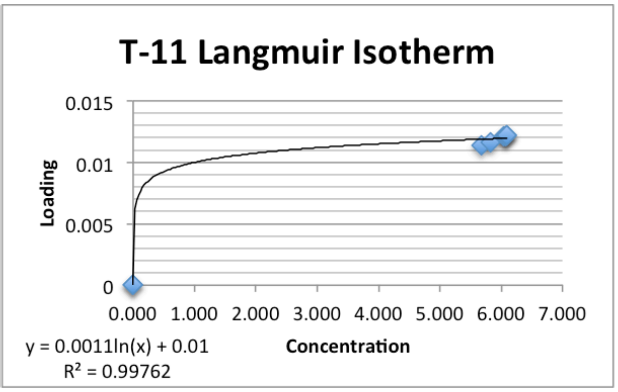

Fig. 4. T-11 Langmuir Isotherm

The 18.9 L column effluent sample was divided into two, 9.46 L solution volumes. One of the volumes was charged to a reaction vessel and the other was held in reserve. The reaction vessel consisted of a 18.9 L reaction vessel with an overhanging agitator. Aliquots of 20% nitric acid, 3% hydrogen peroxide and the other half of the starter batch solution were added at metered flows that balanced the pH at 4 and kept peroxide in excess. After 64 hours of digestion, the pH remained at 4 indicating very little if any continued reaction. This was verified by the fact that the uranium concentration was only 9 mg/L in the supernate. An extended settling period of 3 weeks was allowed and the resulting solution was below 1 mg/L.

CONCLUSIONS

The UCSC was presented with a legacy, off-spec cylinder and a protocol was devised to process the abnormally large heeled cylinder. The protocol included special considerations and enough extra measurement and flexibility to allow in-process adjustments as the washing unfolded. After processing was complete, large amounts of impurities were discovered in the effluent filtrate. In re-processing this liquid, it was determined that the flowrates of the reagents are a variable to particle size when precipitating from an acidic uranyl solution. Lower flowrates give the larger particles time to grow and assimilate the smaller particles. This yields denser, more compact SDU particles that settle quicker. It was also discovered that NaF becomes chemically tied up to the SDU particles. It was proven that by dissolving the SDU in a weak sodium bicarbonate solution, the uranium and fluoride could be released into solution and then treated in a bed of Calcite to remove fluorides with minimal uranium loss. Finally, it was discovered that an increase in the amount of hydrogen peroxide reagent in the peroxide precipitation reaction, would facilitate a near quantitative recovery of uranium in the form of a solid uranate.

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