SELECTIVE RECOVERY OF ENRICHED URANIUM FROM INORGANIC WASTES

Richard T. Kimura
Framatome Advanced Nuclear Products, Inc.
2101 Horn Rapids Road, Richland, WA, 99352, USA

ABSTRACT

Uranium as U(IV) and U(VI) can be selectively recovered from liquids and sludge containing metal precipitates, inorganic salts, sand and silt fines, debris, other contaminants, and slimes, which are very difficult to de-water. Chemical processes such as fuel manufacturing and uranium mining generate enriched and natural uranium-bearing wastes. This patented Framatome ANP (FANP) uranium recovery process reduces uranium losses, significantly offsets waste disposal costs, produces a solid waste that meets mixed-waste disposal requirements, and does not generate metal-contaminated liquids.

At the head end of the process is a floating dredge that retrieves liquids, sludge, and slimes in the form of a slurry directly from the floor of a lined surface impoundment (lagoon). The slurry is transferred to and mixed in a feed tank with a turbine mixer and re-circulated to further break down the particles and enhance dissolution of uranium. This process uses direct steam injection and sodium hypochlorite addition to oxidize and dissolves any U(IV). Cellulose is added as a non-reactive filter aid to help filter slimes by giving body to the slurry. The slurry is pumped into a large recessed-chamber filter press then de-watered by a pressure cycle-controlled double-diaphragm pump. U(VI) captured in the filtrate from this process is then precipitated by conversion to U(IV) in another Framatome ANP-patented process which uses a strong reducing agent to crystallize and settle the U(IV) product. The product is then dewatered in a small filter press.

To-date, over 3,000 Kgs of U at 3% U-235 enrichment were recovered from a 8100 m^2 hypalon-lined surface impoundment which contained about 10,220 m^3 of liquids and about 757 m^3 of sludge. A total of 2,175 drums (0.208 m^3 or 55 gallon each) of solid mixed-wastes have been packaged, shipped, and disposed. In addition, 9463 m^3 of low-U liquids at <0.001 KgU/m^3 were also further processed and disposed.

INTRODUCTION

Uranium as U(IV) and U(VI) can be selectively recovered from liquids and sludge containing heavy metal precipitates, inorganic salts, sand and silt fines, debris, other slimy contaminants which are very difficult to de-water. Chemical processes such as nuclear fuel manufacturing and uranium mining generate enriched and natural uranium-bearing wastes.

FANP manufactures nuclear fuel in a chemical conversion process which turns uranium hexafluoride (UF_6) gas into uranium oxide (UO_2) using both the ammonium diuranate (ADU) and the Dry Conversion UF_6 to UO_2 chemical processes. Trace amounts of U(IV) and U(VI) were discharged into the lagoons from inefficiencies in the chemical conversion and other processes. A portion of the plant wastes that contained ammonium hydroxide, ammonium nitrate, and ammonium fluoride have historically been neutralized with sulfuric acid and discharged into lagoons and solar-evaporated into a concentrate. In addition, other process wastes containing zirconium, aluminum, metals, and other compounds were discharged into the lagoons. Because of process improvements and regulatory requirements, a plan was developed to process these legacy wastes, and then the lagoons would be emptied and closed.

The lagoons also accumulated other kinds of waste over the years such as windblown sand and dust, paper and plastic trash, and vegetation such as tumbleweeds and plant seeds. Fluorides also reacted with the silica from the sand and dust to form other compounds over time.

This FANP-patented uranium recovery process (Reference 1) reduces uranium losses, significantly offsets waste disposal costs, produces a solid waste that meets mixed-waste disposal requirements, and does not generate heavy metal-contaminated liquids.

To-date, one large Framatome ANP surface impoundment (lagoon), about 8100 m^2 in area and containing 10,220 m^3 of concentrated inorganic liquid and solid wastes, was emptied using this process. Work is now beginning on a second lagoon.

SLUDGE RETRIEVAL

At the head end of the process is a floating dredge, equipped with a 74,600W sludge pump which retrieves liquids and sludge from floor of the lagoon impoundment in the form of a slurry at 0.038 m^3/s (Figure 1). The sludge consists of metal precipitates of aluminum, silica, zirconium, iron, uranium; and inorganic salts such as ammonium nitrate, ammonium fluoride, ammonium sulfate; sodium and other salts that have been concentrated via solar evaporation.

A hydraulic-powered auger (cutter head) drives sludge to the center of the dredge head as the dredge is propelled forward with a winch on a steel cable. The centrifugal pump transfers the slurry through a 0.1524 m diameter floating line to the facility.

The slurry is screened, passed through a grinder/shredder, and pumped into a 53 m^3 volume feed tank. Debris from the screens are collected and disposed. The Hypalon™ lagoon liner is protected from the cutter head by wheels which prevent auger contact and liner damage.

Criticality safety is maintained using uranium (U) concentration, U-235% enrichment, and gadolinium (Gd) poison controls. The concentration of U is kept under 22 KgU/m^3 in the sludge phase and 1 g/l in the liquid phase. The enrichment is kept under 4% U-235. And Gd concentrations are maintained over 0.2 KgGd/100KgU for this moderated system.

Figure 1. Surface Impoundment and Dredge During Startup

FEED PRETREATMENT

The slurry is mixed in the feed tank with a turbine mixer and re-circulated to further break down the agglomerated particles through attrition and enhance dissolution of uranium.

This process uses direct steam injection into the re-circulation loop that heats the waste slurry to over 71 C (Figure 2). A sodium hypochlorite (12.5% solution) strike then follows which converts uranium (U) from U(IV) to U(VI). The U(IV) is insoluble and the U(VI) becomes soluble at these conditions.

The sodium hypochlorite dissolves U(IV) but the trace heavy metals contaminants such as lead, cadmium and chromium are not dissolved as would normally occur with more aggressive oxidants such as nitric acid. The extra capital investment and operating costs to treat waste containing heavy metals would have reduced the uranium recovery savings by about $450K.

Cellulose is added to the slurry feed as a non-reactive filter aid to help filter metal slimes by giving body to the slurry. It is also used to pre-coat the filter press cloths, and is discussed further in the next section.

Figure 2. Feed Pretreatment

FILTRATION

A 2.27 m^3 volume recessed-chamber filter press is used to de-water the slurry (Figure 3). Disposal of the solids requires that there be no freestanding liquids in the waste. This filter aid adds structure for improved filtration of slimes. The cellulose was chosen because does not extract uranium, which occurs with the use of filter aids such as diatomaceous earth or other inorganic filter aids.

The filter plates, 1.2 m x 1.2 m square, are also pre-coated with cellulose by circulating a cellulose-water slurry through the filters at 0.025 m3/s to apply a 0.0032 m layer to the cloth. The pre-coat step protects the cloth from metal slimes, which can blind (plug) the cloth, and allows for a quick release of the de-watered solid cake.

The slurry is pumped to the filter press using a pressure controlled double-diaphragm pump. The pump pressure is ramped up slowly to prevent blinding the cake and to maximize the amount of solids in each filter press cycle. Cycle lengths vary from 2 – 4 hrs, yielding up to 2.27 m^3 of solids in a batch. Low pressure filtration and use of a filter aid makes it possible for water to be expressed from the slimy metal sludge.

The clear filtrate is pumped through bag filters to a 53 m^3 filtrate collection tank. The filtration time is dependent upon the solids levels and slime content, which varies widely from one region of the lagoon to another. The pressure control is self-regulating in that the controller would ramp up the pressure as needed for a wide variety of feeds. The diaphragm pump frequency is monitored and the pressure is increased in small increments as pump frequency decreases.

Figure 3. Filter Press

Once the cycle is complete, air is used to pressure blow any residual freestanding liquid from the filter cake. The filter plates are then opened and the filter cake dumped into a trough equipped with an auger to drive the cake into drums staged below. The solid waste is then sampled, manifested and disposed. The filter press is housed in a ventilated enclosure to minimize the airborne contamination exposure to the worker.

Filtration Criticality Safety

Criticality safety for processing sludge in the filter press is maintained by using U concentration, U-235% enrichment, and Gd poison control.

U concentrations can increase from the compaction of sludges in the filter press, but are also lowered by filter aid addition. Feed tank slurry samples are pre-concentrated in a bench-top centrifuge then analyzed via GEA and ICP/MS to predict the maximum U concentration in the filter cake after compacting in the filter press. The maximum critically safe uranium concentration is 280 KgU/m^3 at 5 wt% U-235 enrichment, but a conservative operating limit of 140 KgU/m^3 and 4% enrichment are imposed to give both concentration and enrichment safety margins. The maximum allowable U concentration in the lagoon sludge feed is 24 KgU/m^3.

The maximum observed uranium concentration in the centrifuged sludge feed to-date is 28 KgU/m^3, one-fifth of the conservative operating limit. The maximum observed liquid-phase concentration was 0.38 KgU/m^3, 38% of the 1 KgU/m^3 operating limit. In every case the Gd neutron poison levels were well above the >0.2 KgGd/100KgU limit for the moderated slurry, and were typically 1 – 10 KgGd/100KgU. Each batch of retrieved slurry is analyzed for U, Gd, and U-235 enrichment in both the sludge and liquid phases.

URANIUM PRECIPITATION

U(VI) captured in the filtrate from each process batch (up to 41.6 m^3) is transferred into two 22.7 m^3 batch precipitators. The U(VI) is converted back to U(IV) by chemical reduction in another FANP-patented process (Reference 2) using sodium hydroxide to adjust the pH and sodium hydrosulfite as a strong reducing agent. The U(IV) in the salt solution forms crystalline $NaNH_4UF_6$, a green flat hexagonal platelet.

U crystal growth proceeds with timer-controlled stirring and settling steps. The U product is separated from solution by gravity settling into the cone-bottom of the tank. U settling is sometimes aided by addition of a small amount of polymer. The clear decant liquid is pumped to a low-U lagoon and the green U product slurry is pumped into a small 0.017 m^3 filter press and de-watered. The U concentration in the filter press increases to 200 - 300 KgU/m^3 in the filter cake after de-watering. About 99% of the U is recovered in each batch, and the green U is then dissolved in nitric acid and purified via solvent extraction. In total, over 3,000 KgsU have been recovered and used to fabricate nuclear fuel.

Precipitation Criticality Safety

Criticality safety is maintained with U filtrate feed concentration control (<1 KgU/m^3), mass control (<15 KgU), and geometry control (20.8 m^3 volume filtrate batch size and 0.015 m^3 product containers). Process interlocks and controls required that the tanks be emptied each batch before refilling. Actual filtrate feed concentrations remained under 0.38 KgU/m^3, and U remained under 8 Kg U per precipitator batch at an average U-235 enrichment of 3%.

DISPOSAL OF DECANTED LOW-URANIUM LIQUIDS

The decanted liquid waste to-date, about 9,840 m^3 containing less than 2 ppm U, was then processed in an Ammonia Recovery Facility (ARF) for the removal of over 99% of the ammonia.

The ARF converts ammonium salts to ammonium hydroxide. In the ARF process steam is used to strip the ammonia from solution, and the ammonium hydroxide is then condensed, collected, and stored. The distilled ammonia product is sold and the resulting low-ammonia wastes are then polished in an ion exchange column to bring the U to less-than-detectable levels.

The liquids, which now meet state and federal licenses and permit requirements, are sent to the sewer.

RESULTS AND SUMMARY

To-date, a 8,100 m^2 hypalon-lined surface impoundment containing about 10,220 m^3 of liquids and about 757 m^3 of sludge has been emptied (Figure 4). Sludges were de-watered and over 3,000 Kgs of U(IV) at 3% U-235 enrichment were recovered via filtration and precipitation and re-used after purification via solvent extraction.

A total of 2,175 drums (0.208 m^3 or 55 gallon each) of solid mixed-waste were packaged, shipped, and disposed and 9,463 m^3 of low-uranium liquids at <0.001 KgU/m^3 were processed and disposed. Heavy metals extraction was not required, reducing processing costs.

Figure 4. Surface Impoundment Nearing Completion

REFERENCES

1. United States Patent No. 6,101,671, Process for Selective Recovery of Uranium from Sludge, Richard T. Kimura

2. United States Patent No. 4,668,482, Recovery of Uranium from Solutions, R. A. Hermens, J. B. Kendall, J. A. Partridge