DEVELOPMENT OF THE IN-STORAGE-CAN THERMAL DENITRATION STEP IN THE CEUSP PROCESS

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ABSTRACT

As part of the Consolidated Edison Uranium Solidification Program, a semicontinuous process has been developed for thermal denitration of concentrated liquid nitrate waste solutions containing radioactive uranium nuclides. Solids handling problems are minimized by feeding batches of the concentrated waste solution directly into a can that serves as the primary storage container. The solution is evaporated to dryness by careful, zone-controlled heating of the can inside a furnace, decomposing the nitrates and leaving a solid oxide residue. The can is then sealed before final storage. Processing problems of foaming, splattering, and line plugging have been eliminated through a significant process development study and equipment modifications.

INTRODUCTION

The goal of the Consolidated Edison Uranium Solidification Program (CEUSP) is to convert ~1000 kg of highly fissile and radioactive uranium (~75% ^{235}U, ~10% ^{233}U, ~140 ppm ^{232}U) from a liquid nitrate solution form to a solid oxide form. The solid form is more stable and, thus, is safer for long-term storage. The composition of the ~8000 L of CEU solution is shown in Table I. Significant amounts of cadmium and gadolinium have been added to the uranium nitrate solution to act as neutron absorbers and, thus, to provide criticality safety. The high concentrations of ^{232}U and its alpha- and beta-emitting decay daughters — particularly ^{208}Tl, which also emits a very energetic gamma ray — require that all equipment be located inside shielded, alpha-contained enclosures and operated remotely. The solidification process selected for this program was designed for operation in such a facility. This CEUSP Facility is located within the Radiochemical Processing Plant at Oak Ridge National Laboratory.[1]

TABLE I

COMPOSITION OF THE CEU SOLUTION

Component	Concentration
Total U	132 g/L
Cd	40.4 g/L
Gd	5.7 g/L
H^+	1.6 N

Prior to the thermal denitration process step, the CEU solution is concentrated approximately two- to three-fold by means of evaporation, and the free acid concentration is reduced to ~0.5 M by adding formaldehyde. This reacts with HNO_3, producing carbon dioxide, water, and nitrogen oxide gases.[2]

The thermal denitration step is a semicontinuous process in which a batch of the concentrated CEU solution is fed into a heated can (which eventually becomes the primary storage container); as it is fed in, the solution is evaporated to dryness and the nitrate is decomposed, leaving a solid oxide cake in the can. This process minimizes solids handling problems. However, several serious processing problems, such as foaming, splattering, and line pluggage, were encountered in early tests of the full-scale equipment. A significant process development study and an equipment improvement program were required to circumvent these difficulties. Equipment modifications that were made to minimize plugging problems at the feed entrance and in the off-gas line included redesigning (1) the nozzle that connects the feed and off-gas lines to the can, (2) the off-gas line, and (3) the condensate collection system. The process study described below included (1) a determination of the effects of the feed components on the behavior of the process, (2) a theoretical and experimental examination of conditions inside the can as it is filled, and (3) interpretation of the effects of process variables such as feed method, feed rate, and time/temperature profiles in the furnace.

PROCESS DESCRIPTION

In the denitration process, each batch of CEU concentrate feed solution (containing ~3 kg of uranium) is fed continuously into a storage can which is located inside a cylindrical heating furnace, as illustrated in Fig. 1. The entire batch is fed at a rate of 9 mL/min during a 16-h period in which the temperatures in the bottom, middle, and top zones of the furnace are independently increased by means of a programmable controller. Following feed addition, a bakeout period of 3 h at ~800°C completes the solidification. Off-gases from the denitration, primarily water vapor and nitrogen oxides, exit the can through a jacketed line to a liquid collection tank. During the feed addition period, the off-gas line is washed with nitric acid to dissolve any entrained solids. The collection tank is vented through a chilled-water-cooled condenser, and condensables are drained back into the tank.

A progressive cavity pump called "Ramoy" by its manufacturer, the Robbins and Myers Co., is used to feed the CEU concentrate into each can. Although the pump is not a low-flow-rate metering pump, it was found to be reliable for rates as low as 5 mL/min. The pump has a stainless steel rotor and a Viton stator. Chemical attack of the Viton by either nitric acid or nitrites (which are produced in the

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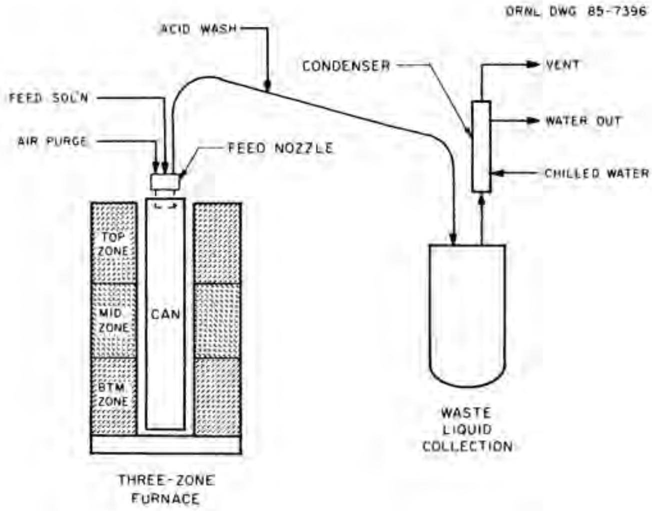

Fig. 1. CEUSP Denitration System.

evaporation/acid-destruction step) and radiation exposure can cause the Viton to swell, loosening the fit between the rotor and stator. In spite of this problem, the Ramoy was judged to be the most acceptable pump of those tested. Even so, failure of the pumps during the project was anticipated, and preparations for their replacement were made.

The feed and purge air enter the can through a process connection nozzle, illustrated in Fig. 2. Gases evolved during the denitration exit the can through the same nozzle. This design features (1) concentric entry of the purge air around the feed and off-gas line, (2) a feed line entry that permits flushing of the off-gas entrance to the nozzle, (3) the largest diameter off-gas line that is possible with the fixed-size opening in the can, (4) a steam-jacketed off-gas line which is sloped downward to the condensate collection vessel, and (5) a means to add an acid flush to the off-gas line to dissolve any entrained solids which might otherwise accumulate and plug the line. Several other nozzle designs were tried during the pilot studies but none were satisfactory, primarily because frequent nozzle or line pluggage occurred. The purge air supply line contains a high-pressure alarm to notify the operator if a plug or restriction occurs in the off-gas system. However, this has not occurred since employment of the nozzle shown in Fig. 2 and the off-gas system shown in Fig. 1, even during test runs where process conditions were chosen to cause entrainment of solids.

A Lindberg 5018-V-5 crucible furnace supplies the heat required for the feed denitration. The electrically heated cylindrical furnace is composed of three independent heating zones; each zone has a maximum power input of 1 kW and a maximum operating temperature of 1200°C. Five thermocouples are located in each zone to monitor the furnace temperature. Air can be pulled down through the furnace, to rapidly cool the can.

DENITRATION PROCESS STUDIES

Denitration tests were made using a simulated CEU solution containing depleted uranium as a substitute for the fissile material. The study included (1) a determination of the effects of the feed components on the behavior of the process, (2) a theoretical and experimental examination of conditions inside the can as it is filled, and (3) an interpretation of the effects of process variables such as feed method, feed rate, and time/temperature profiles in the furnace.

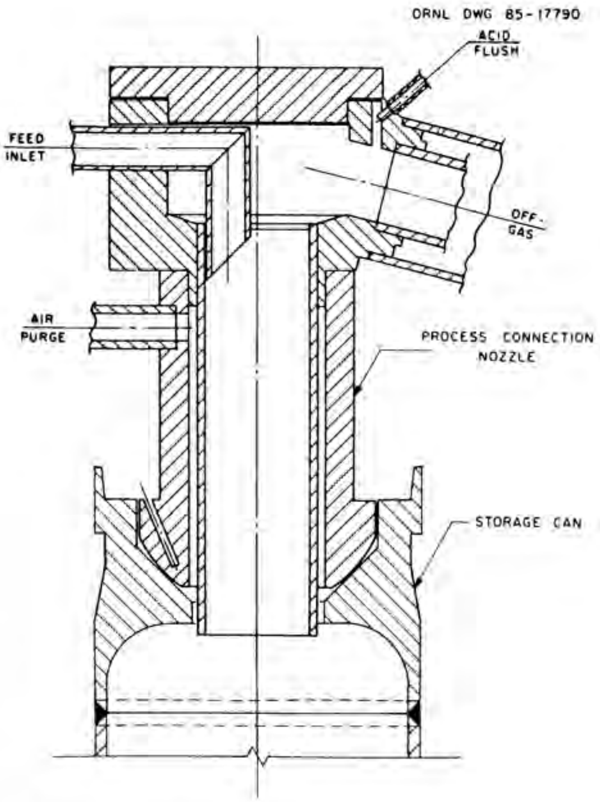

Fig. 2. Process Connection Nozzle Positioned in a Can.

The process was found to be extremely susceptible to entrainment of solids in the process connection nozzle or the off-gas line. This was caused by either splattering of solids in the can, foaming inside the can, or eruption of embedded, incompletely decomposed nitrates.

Feed Composition

The CEU concentrate, which is the feed for the thermal denitration step, typically contains ~320 g/L of uranium, ~97 g/L of cadmium, ~14 g/L of gadolinium, and is <0.5 $\underline{M}$ HNO_3. The ratio of metal ions was not expected to vary during actual operation, but tests were made with varying ratios and concentrations to determine the effects of each component. Tests were made in glass equipment in order to observe the behavior of the reacting mixture during evaporation and thermal denitration. In general, uranium nitrate tended to decompose with a splattering action, while cadmium nitrate decomposed with a foaming action. At optimum conditions, the foam produced from the cadmium nitrate tended to act as a knockout medium for the splattered droplets produced from the uranium nitrate decomposition. Thus, splattering was a problem only when the cadmium concentration was <50 g/L.

At cadmium concentrations >80 g/L, excessive accumulation of metal nitrates in the can was found to be a problem. (The amount of accumulation was determined by difference, using the measured volume and acidity of the condensate.) When the can inventory exceeded ~8.5 mol of metal nitrates, the foam boiled out of the can. The foam was ~30% by volume liquid, with a uranium concentration of ~1000 g/L liquid. At room temperature the foam solidifies, and, in early tests, this material completely plugged the off-gas, feed, and air lines, causing the can to rapidly pressurize.

Conditions in the Can

The can size and geometry were not considered to be process variables, since the designs of the storage wells and can handling equipment are related to the can dimensions. However, the amount of feed loaded into each can (batch size) and the manner and rate of feed addition are processing conditions which can be varied. In order to choose the optimum conditions, a computer modeling study and experimental tests were made.

The solid layer that builds as the metal nitrates are fed into the can and converted to oxides decreases the heat transfer area and insulates the center of the can from the furnace. This limits the amount of oxide that can be loaded in a can, because the rate of heat transfer becomes so low that excessive nitrates accumulate in the can.

The computer code HEATING5 was used to determine the allowable can loading.[3] The heat transfer calculation determined the decomposition rate as a function of solids loading in the can. Calculations were made for heat transfer from the outside of the can, through the stainless steel and oxide, and into the reacting mixture. The time required to decompose a given volume of feed was determined. This result implied an average feed rate at which continuous denitration is possible. By varying the oxide profile, the effect of can loading on the denitration rate was examined.

The HEATING5 code was run for can loadings as low as 2.8 kg of uranium. Even at this loading, the calculations indicated that, at a reasonable feed rate (~5 mL/min), the heat transfer rate was insufficient to provide continuous denitration. However, experimental tests, made to investigate loadings from 2.8 to 4.0 kg, showed that continuous denitration was not required. It is only necessary to have continuous evaporation and partial denitration to keep the inventory of metal nitrates to <8.5 mols. A loading of 3.0 kg was determined to be satisfactory. When this loading is completed, the solids occupy ~66% of the volume of the can which is inside the furnace. However, in integrated operations of the CEUSP Facility equipment, conditions in the initial evaporation/acid-destruction step have limited the batch size to ~2.7 kg.

Method of Feed Addition

Two tests were made in which the simulated concentrate was added intermittently at a high rate (20 mL/min), allowing time for complete denitration between additions. This feeding technique was found to cause more severe fouling of the process connection nozzle than did the continuous feed addition.

Feed Addition Rate

Initially, the denitration test runs were made at continuous feed rates which decreased from 20 to 5 mL/min throughout the run. The objective was to decrease the feed rate at a rate proportional to the decrease in effective heat transfer in the can. Later tests showed that the same effect could be obtained by holding the feed rate constant while increasing the furnace zone temperatures throughout the run. Feed addition at 9 mL/min was found to produce an acceptable denitration rate and run time; thus, this rate was chosen for actual operations.

Furnace Temperature Profiles

Several temperature/time gradients for each of the three furnace zones were tested. In general, the temperature in the bottom zone was increased first, then that in the middle zone, and finally that in the top zone. This method was found to minimize foaming and splattering and to decrease the likelihood of forming a solid dome over undecomposed nitrates.

The furnace temperature/time profiles that were determined to enable optimum nitrate decomposition rates started with the bottom and middle zones at 400°C. As the run progressed, these zones were ramped to ~800°C. The top zone temperature was increased from ~250°C to 550°C over the last half of the run.

INTEGRATED OPERATION

Twenty verification runs were made at the established conditions during preoperational testing of the CEUSP Facility equipment. No problems were encountered.

Processing of the actual CEU solution began on April 11, 1985. During the initial runs, no significant difference was observed in operation of the thermal denitration process and equipment with actual CEU solution rather than with the simulated solution. Production operations were then started. Approximately 70% of the CEU solution has been processed, and no problems have been encountered in the thermal denitration step.

SUMMARY

A process for thermal denitration of radioactive liquid waste solutions within a vessel which ultimately becomes the storage container has been developed for use in the CEUSP Facility. This process is being used to convert ~1000 kg of highly fissile and radioactive uranium to a solid form for safe long-term storage. The material being solidified also contains ~300 kg of cadmium and ~40 kg of gadolinium which had been combined with the uranium to provide criticality safety. The unique thermal denitration process was found to be extremely susceptible to entrainment of solids by splattering, foaming, or expulsion actions. The process connection nozzle, through which the feed solution and purging air are supplied and the emerging off-gases are discharged, and the off-gas handling system were modified extensively to permit operation without plugging of the nozzle or process lines by an accumulation of solid deposits. A process study was made to determine the effects of various feed components and process variables on the tendency of the reacting mixture to splatter, foam, or be expelled. Because of these equipment modifications and the selection of appropriate processing conditions, the feed material is being denitrated without significant problems.

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