CONF-860317 - - 5
DRAFT

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

R. J. Vedder
E. D. Collins
P. A. Haas

CONF-860317--5

DE86 005029

Oak Ridge National Laboratory*
P. O. Box X
Oak Ridge, Tennessee 37831

For presentation at Waste Management '86
Tucson, Arizona, March 2-6, 1986

---

*Operated by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

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

R. J. Vedder
E. D. Collins
P. A. Haas

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 liquid nitrate feed solution is shown in Table 1. 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 concentration of ^{232}U and its alpha and beta emitting decay daughters--- particularly ^{208}Tl, which also emits a very energetic gamma ray--- requires all equipment to be located inside shielded, alpha-contained enclosures, and to be operated remotely. Thus the solidification process was designed to be operated in such a facility (called the CEUSP Facility) which is located within the Radiochemical Processing Plant at Oak Ridge National Laboratory.[1]

Table 1. 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 to react 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 can (which eventually becomes the primary storage container) and, 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, can be encountered. These were seen in early tests of the full-scale equipment and required a significant process development study and equipment improvement program to circumvent difficulty. Equipment modifications that were made to minimize plugging problems at the feed entrance and in the off-gas line included redesign of (1) the nozzle which 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 of a cylindrical heating furnace, as illustrated in Fig. 1. The entire batch is fed at 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 a 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 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.

ORNL DWG 85-7396

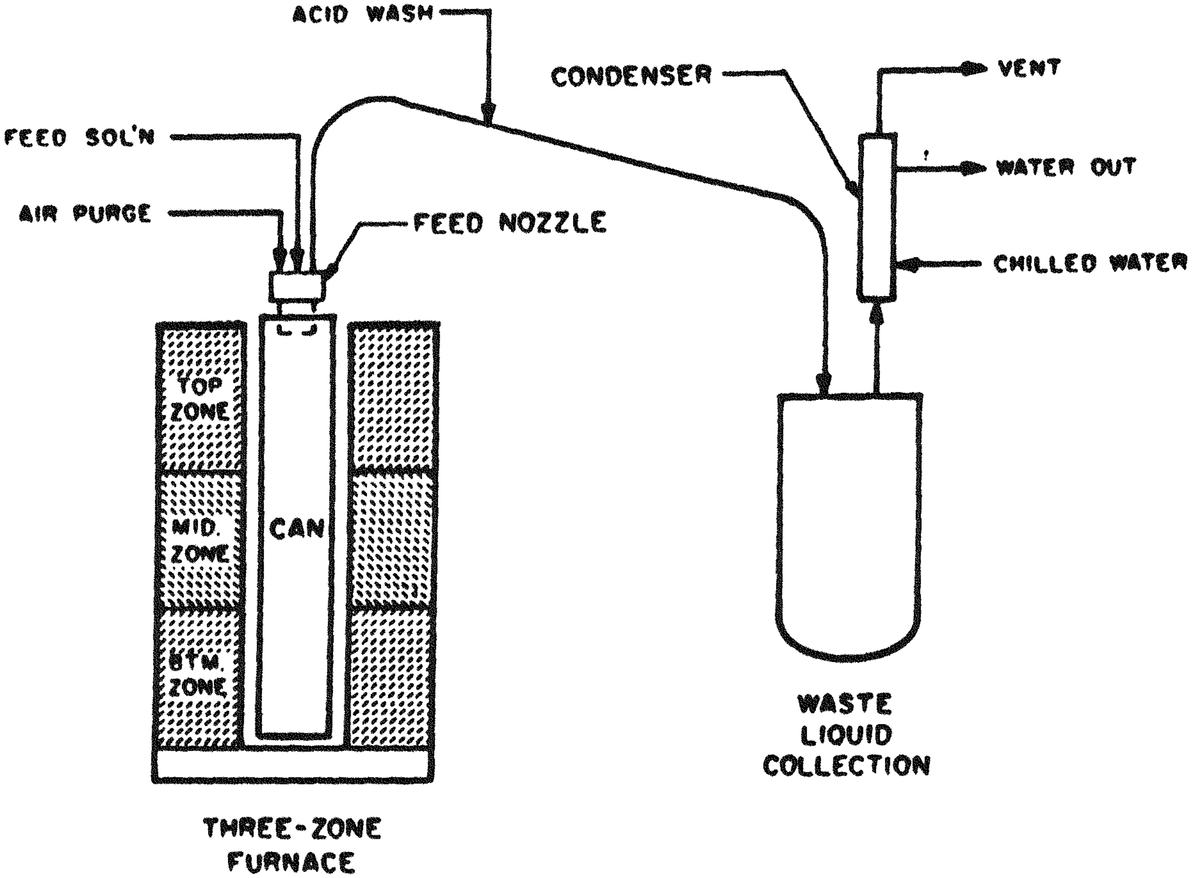

Fig. 1. CEUSP Denitration System.

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 which can 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.

ORNL DWG 85-17790

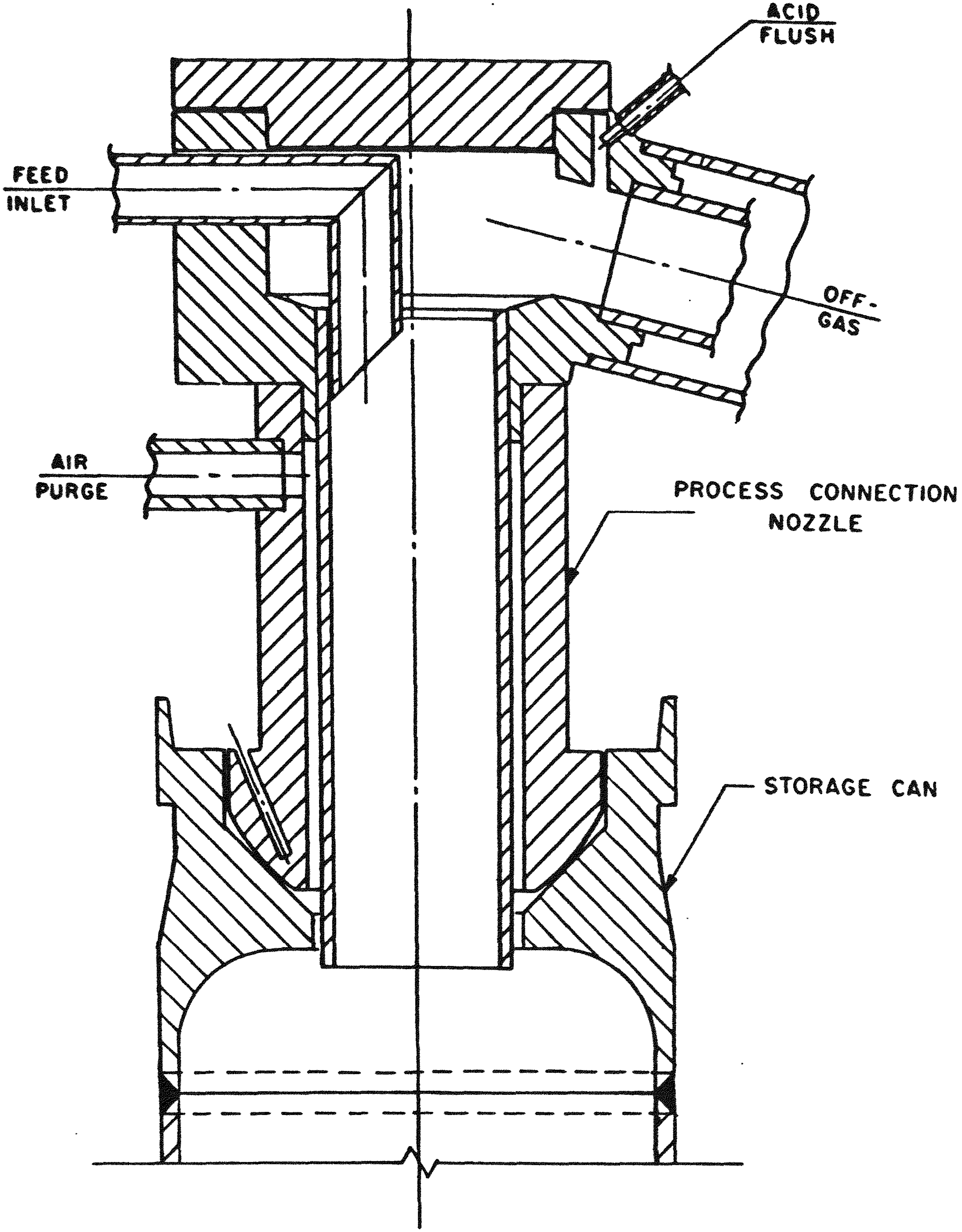

Fig. 2. Process Connection Nozzle Positioned in a Can.

DENITRATION PROCESS STUDIES

Denitration tests were made using a simulated CEU solution which contained depleted uranium as a stand-in 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 effect of process variables, such as feed method, feed rate, and time/temperature profiles in the furnace. The process was found to be extremely susceptible to entrainment of solids into the process connection nozzle or the off-gas line. This was due to either splattering of solids in the can, foaming inside the can, or eruption of embedded, incompletely decomposed nitrates.

1. 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 evaporation--- thermal denitration reacting mixture. 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 media for the splattered droplets produced from the uranium nitrate.

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 mols 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, and was a solid at room temperature. In early tests, this material completely plugged the off-gas, feed, and air lines and caused the can to rapidly pressurize.

2. Conditions in the Can

The can size and geometry were not considered to be a process variable since the design of the can handling equipment, storage wells, etc. 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 these conditions, a computer modeling study and experimental tests were made.

The oxide layer which 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 too low and excessive nitrates accumulate in the can.

The computer code HEATING5[3] was used to determine the allowable can loading. 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, until the mixture temperature reached 250°C, the phase change temperature. The time required to decompose a given volume of feed was determined. This result implied an average feed rate at which continuous denitration (or, by lowering the phase change temperature, continuous evaporation) is possible. By varying the oxide profile the effect of can loading on the denitration rate was examined.

The 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, and that it is only necessary to have continuous evaporation and to keep the inventory of metal nitrates to less than 8.5 mols. A loading of 3.0 kg was determined to be satisfactory. When this loading is completed, the solids occupy approximately 2/3 of the volume of the can which is inside the furnace. However, in integrated operation of the CEUSP Facility equipment, conditions in the initial evaporation/acid destruction step have limited the batch size to ~2.7 kg.

3. 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 when continuous feed addition was used.

4. Feed Addition Rate

Initially, the denitration test runs were made at feed rates which were continuous but were lowered 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.

5. 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 which were determined to enable decomposition rates that were neither too rapid or too slow, 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 between operation of the thermal denitration process and equipment with CEU solution rather than the simulated solution. Production operations were then started. Approximately two-thirds of the CEU solution has been processed and no problems have been encountered in the thermal denitration step.

SUMMARY

A thermal denitration in-the-storage-can process 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 development of nozzle or line pluggage due to accumulation of solid deposits. A process study was made to determine the effects of feed components and process variables on the tendency of the reacting mixture to splatter, foam, or be expelled. Because of the equipment modifications and the selection of appropriate processing conditions, the feed material is being denitrated without significant problems.

REFERENCES

1. C. P. McGinnis, E. D. Collins, and B. D. Patton, "A Remotely Operated Facility for In-Situ Solidification of Fissile Uranium," to be published in the Proceedings of Waste Management '86, Tucson, Arizona, March 1986.

2. R. Hall, B. D. Patton, and P. A. Haas, "Reaction of Formaldehyde and Nitric Acid in a Remotely Operated Thermosiphon Evaporator," to be published in the Proceedings of Waste Management '86, Tucson, Arizona, March 1986.

3. W. D. Turner, D. C. Elrod, and I. I. Siman-Tov, "HEATING5 - An IBM 360 Heat Conduction Program," Oak Ridge National Laboratory, Oak Ridge, Tennessee, March, 1977 (ORNL/CSD/TM-15).