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REACTION OF FORMALDEHYDE AND NITRIC ACID IN A REMOTELY OPERATED THERMOSIPHON EVAPORATOR

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INTRODUCTION

Special equipment was recently installed in a heavily shielded hot cell to convert multikilogram amounts of fissile uranium contained in a 1.6 N nitric acid solution to the oxide (U_3O_8) form. This project, the Consolidated Edison Uranium Solidification Program (CEUSP), is being conducted to prepare a safe form of the uranium solution for long-term storage. The solution, which contains uranium (~75% ^{235}U and ~10% ^{233}U) at a concentration of ~130 g/L, also contains significant amounts of cadmium (0.31 g per gram of uranium) and gadolinium (0.05 g per gram of uranium) that were previously added as neutron absorbers to maintain nuclear subcriticality.

The solidification process consists of two steps — evaporation and thermal denitration. The primary objective of the evaporation step is to prepare feed material for efficient thermal denitration. In the evaporation, the uranium-cadmium-gadolinium nitrate salts and the nitric acid are concentrated. During this operation, the concentrations could be increased to a level above which the solubility of the metal nitrate salts is exceeded and crystallization would occur. To prevent this, an acid-destruction technique based on the use of formaldehyde was adopted and conditions were developed for large-scale application.

PROCESS AND EQUIPMENT

The process equipment is illustrated schematically in Fig. 1. A thermosiphon evaporator was chosen to allow large-scale processing of

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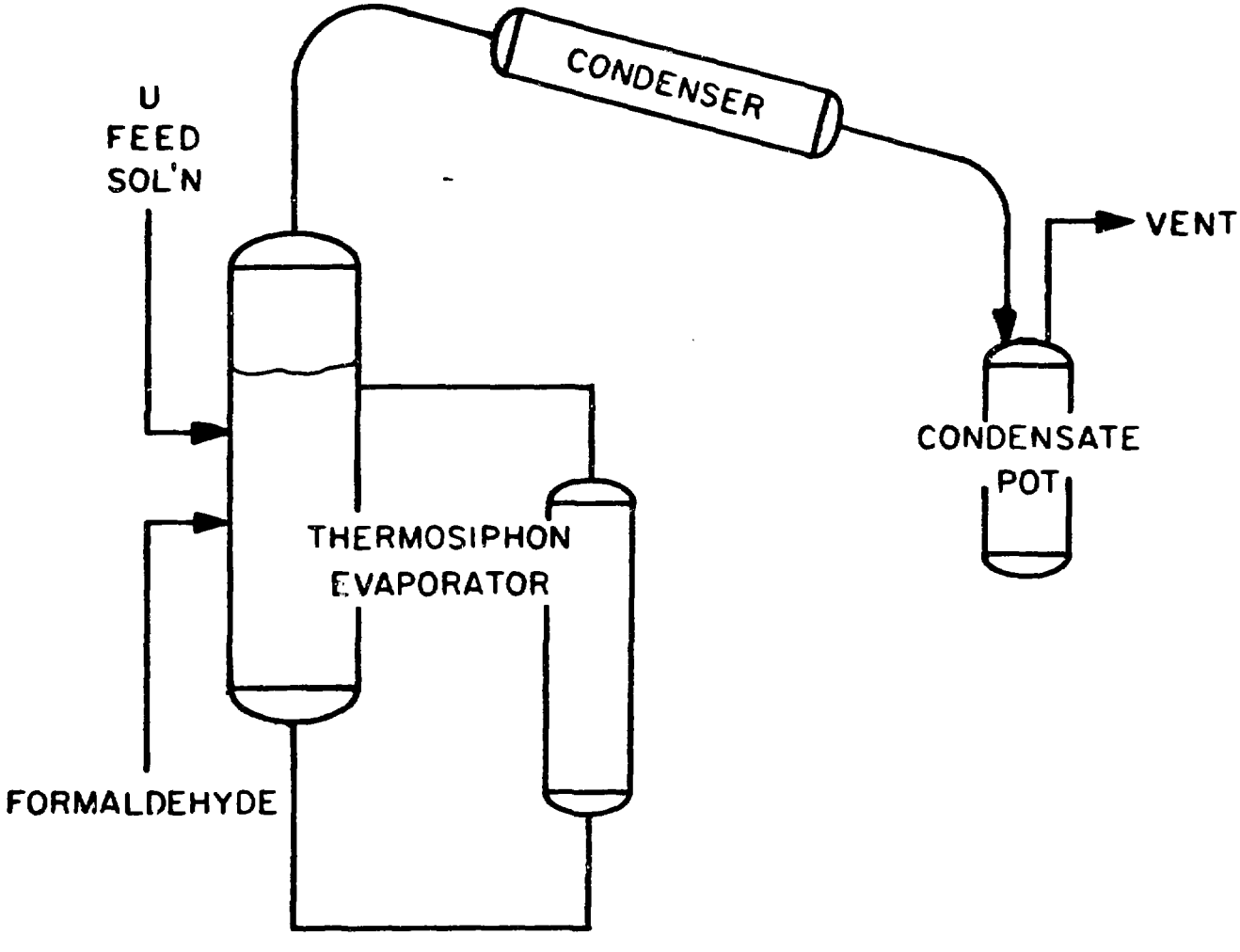

Figure 1. Process Equipment for Concentrating Fissile Uranium Solutions in a Thermosiphon Evaporator.

fissile uranium within a geometry that is favorable for nuclear subcriticality (taking no credit for the soluble neutron poisons). In the semicontinuous process, a ~21-L batch of the feed solution (containing ~3 kg of uranium) is concentrated threefold. First, ~6 L of the solution is fed into the evaporator and heated to boiling temperature (~104°C). Then, the remaining feed (~15 L) is added over a ~1-h period. During the first two-thirds of this period, formaldehyde solution is added at a constant rate and reacts with nitric acid in the evaporator; H_2O, CO_2, and nitrogen oxide gases are evolved.

A combination of exothermic reactions occur during the destruction of nitric acid by formaldehyde.[1] At nitric acid concentrations greater than 2 N, the overall reaction equation is:

$$4HNO_3 + 3CH_2O = 4NO + 3CO_2 + 5H_2O \quad . \qquad (1)$$

For nitric acid concentrations less than 2 N, the equation is:

$$2HNO_3 + CH_2O = HCOOH + 2NO_2 + H_2O \quad . \qquad (2)$$

At nitric acid concentrations less than 0.5 N, formic acid reaction predominates, yielding the following equation:

$$3HCOOH + 2HNO_3 = 3CO_2 + 2NO + 4H_2O \quad . \qquad (3)$$

Equation (3) proceeds very slowly after all the formaldehyde has reacted with nitric acid.

The reaction of formaldehyde with nitric acid can be very violent; therefore, it must be carefully controlled. In previous studies,[1] uncontrolled reactions have occurred when the reactants were mixed and then heated. Thus, temperature control interlocks were installed in the

CEUSP Facility equipment to prevent the addition of formaldehyde at evaporator temperatures of <95°C.

The process can be further complicated by hydraulic behavior (foaming, liquid entrainment, etc.) and by the formation of insoluble nitrate salts or uranium formate precipitates. Unfavorable results are also obtained if the proper formaldehyde volume is not used or the control of the formaldehyde/nitric acid reaction is not maintained.

EXPERIMENTAL WORK

Because of the potential process complications, a small-scale glass evaporator was built and used to develop satisfactory operating conditions. More than 100 tests were performed using depleted uranium as a stand-in for the fissile material. Optimum conditions were determined for the volume of formaldehyde (37 wt %) used, the formaldehyde and feed solution addition rates, the reaction temperature, and the liquid level in the evaporator. Additionally, a linear relationship was determined between the amount of formaldehyde added and the amount of nitric acid destroyed.

PLANT OPERATIONS

Operating conditions developed in the small-scale evaporator were utilized in preoperational tests of the full-scale equipment in the CEUSP Facility. Only slight adjustments were required.

The process was then used to concentrate the fissile uranium solutions. No significant difficulties have been encountered in operations to date. Losses of uranium to the condensate solutions have routinely

been <0.6%. The concentrate solutions have been generated with predictable nitric acid concentrations, and no solids formation has occurred.

SUMMARY

Conditions have been developed for the safe and successful use of a method for reacting formaldehyde with excess nitric acid, while simultaneously concentrating a fissile uranium nitrate solution. This process, which is being conducted in a remotely operated thermosiphon evaporator, has been adapted to plant scale and is being used to process multikilogram batches.

REFERENCES

1. Healy, T. V., Davis, (Mrs.) B. L., "The Destruction of Nitric Acid by Formaldehyde, Part II," A.E.R.E. C/R 1739, Feb. 22, 1956.