CONF-860317 --6

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

R. Hall
B. D. Patton
P. A. Haas

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

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

MASTER

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

R. Hall
B. D. Patton
P. A. Haas

Oak Ridge National Laboratory[*]
Oak Ridge, TN 37831

ABSTRACT

A safe, controlled method for reacting formaldehyde with excess nitric acid, while simultaneously concentrating a fissile uranium nitrate solution, was developed and is being used successfully at Oak Ridge National Laboratory in a remotely operated thermosiphon evaporator. The operation was adapted from laboratory studies to semicontinuously process multikilogram batches. Thus far, experience with this system includes the successful processing of more than 260 batches (2.7 kg per batch) of solution.

INTRODUCTION

The reaction of formaldehyde and nitric acid in a remotely operated

thermosiphon evaporator is a key step in an overall process designed to

solidify ~1000 kg of highly fissile and radioactive uranium, ~300 kg of

cadmium, and ~40 kg of gadolinium — all contained in ~8000 L of a

nitrate solution which has been stored at Oak Ridge National Laboratory

(ORNL) for 16 years. (The cadmium and gadolinium were added to the

stored solution to absorb neutrons from the fissile uranium and maintain

subcriticality.) This project, the Consolidated Edison Uranium

Solidification Program (CEUSP), is being carried out to prepare a stable

uranium form for long-term storage. Multiple batches of the solution —

each containing ~2.7 kg of uranium — are being processed to solidify the

nitrate salts and decompose them to oxides. Following the evaporation/ formaldehyde—nitric acid reaction step, the concentrated salts are processed by means of a thermal denitration step, which is carried in-situ in the storage can.[1] All of the process equipment is contained in the CEUSP Facility — a heavily shielded, remotely operated facility located within the Radiochemical Processing Plant at ORNL.[2]

The evaporation step was included in the process design to reduce the overall time requirement for the solidification process. In the evaporation, the feed solution is concentrated by a factor of ~2.5. This procedure can be done in a 2- to 3-h time period and is much faster than the thermal denitration, which requires ~24 h. Thus the facility includes three denitration systems, which are operated in a parallel mode, but only one evaporation system. During the evaporation, the concentrations could be increased to a level in which the solubility of the metal nitrate salts is exceeded and crystallization occurs. To prevent this, part of the nitric acid is removed by reaction with formaldehyde.

The simultaneous evaporation/formaldehyde—nitric acid reaction is extremely complex and difficult to control. Process studies were made to determine satisfactory operating conditions and to develop correlations of operating parameters. The induction period preceding the reaction, the hydraulic behavior (foaming, liquid entrainment, etc.), and the process safety were of particular concern in these studies.

PROCESS DESCRIPTION

A thermosiphon evaporator was chosen to allow large-scale processing of fissile uranium within a geometry that is favorable for

nuclear subcriticality (taking no credit for the soluble neutron poisons). The process equipment is illustrated schematically in Fig. 1. The evaporator was designed for an operating volume of ~10 L, using (as a basis) Kern's method for process design given by Ludwig.[3] The minimum volume that will allow the thermosiphoning operation was experimentally determined to be ~3 L.

The batch size is ~21 L of CEU feed solution, and the concentrations of major components in the feed solution include 0.56 $\underline{M}$ $UO_2(NO_3)_2$, 0.36 $\underline{M}$ $Cd(NO_3)_2$, 0.036 $\underline{M}$ $Gd(NO_3)_3$, and 1.6 $\underline{M}$ HNO_3. Thus the total metal nitrate salt concentration is 1.95 $\underline{M}$, and the total nitrate concentration is 3.55 $\underline{M}$.

Initially, 6 L of feed solution is charged to the evaporator, filling it to just below the thermosiphon return leg. The solution is heated to boiling, and additional feed is added as required to maintain the level in the evaporator. The sequence of key steps in a typical operation is shown in Fig. 2.

The reaction of formaldehyde with nitric acid must be conducted at a temperature >95°C to obtain an instantaneous, controllable reaction. Thus the CEUSP Facility contains a safety interlock on the formaldehyde addition pump to prevent addition at a vapor-space temperature of <95°C. When the solution initially charged to the evaporator has been heated to 95°C, the formaldehyde solution (an aqueous-methanol solution containing 37% formaldehyde) addition is started. A period of 25 to 30 min is required for the formaldehyde solution to fill the addition line and begin to enter the evaporator. The acidity of the solution in the evaporator is estimated to be ~3 $\underline{M}$ HNO_3 at the start of the reaction. Because the reaction is exothermic, the heat input to the evaporator via
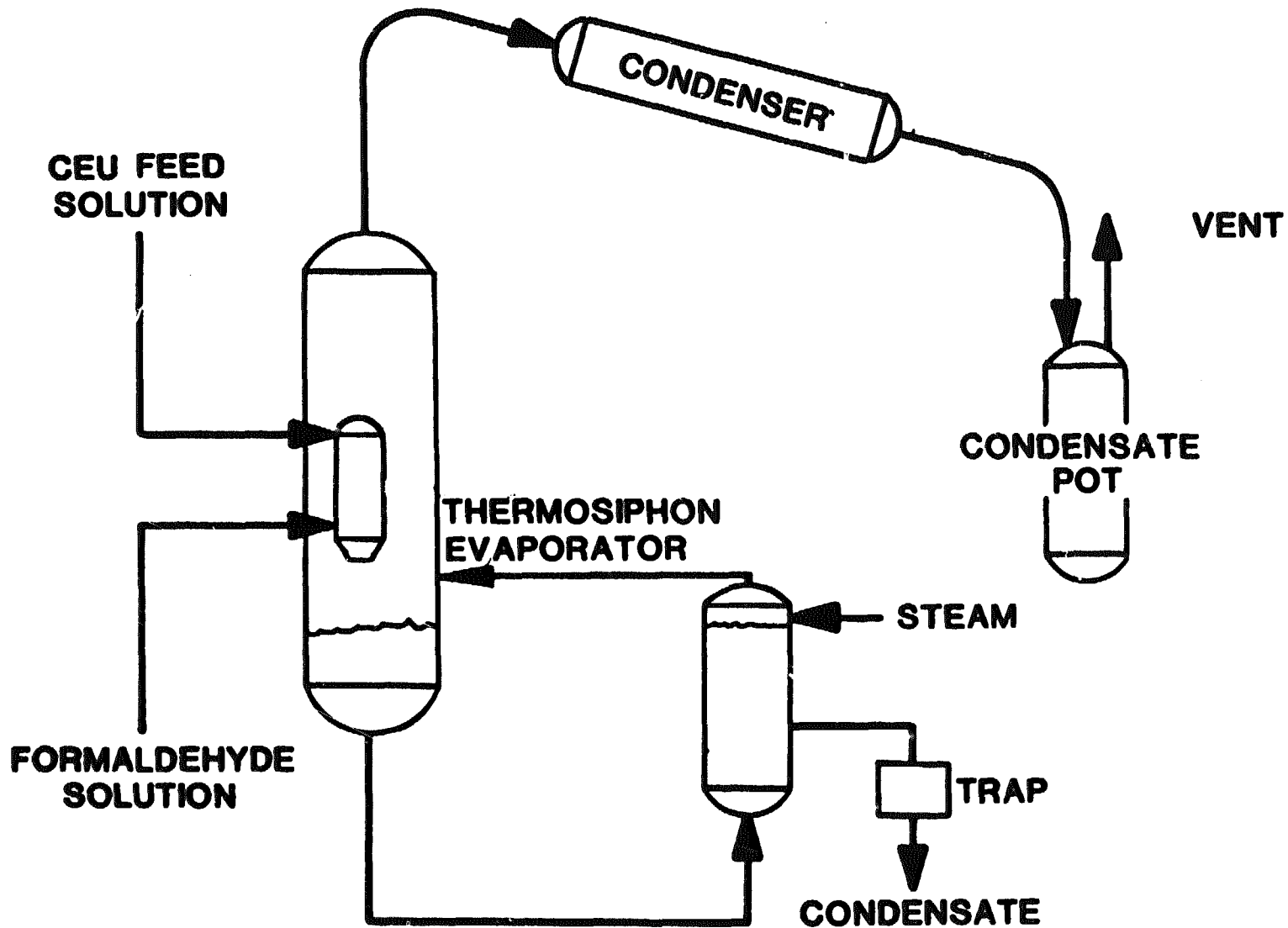
Figure 1. Process equipment for concentrating fissile uranium solutions
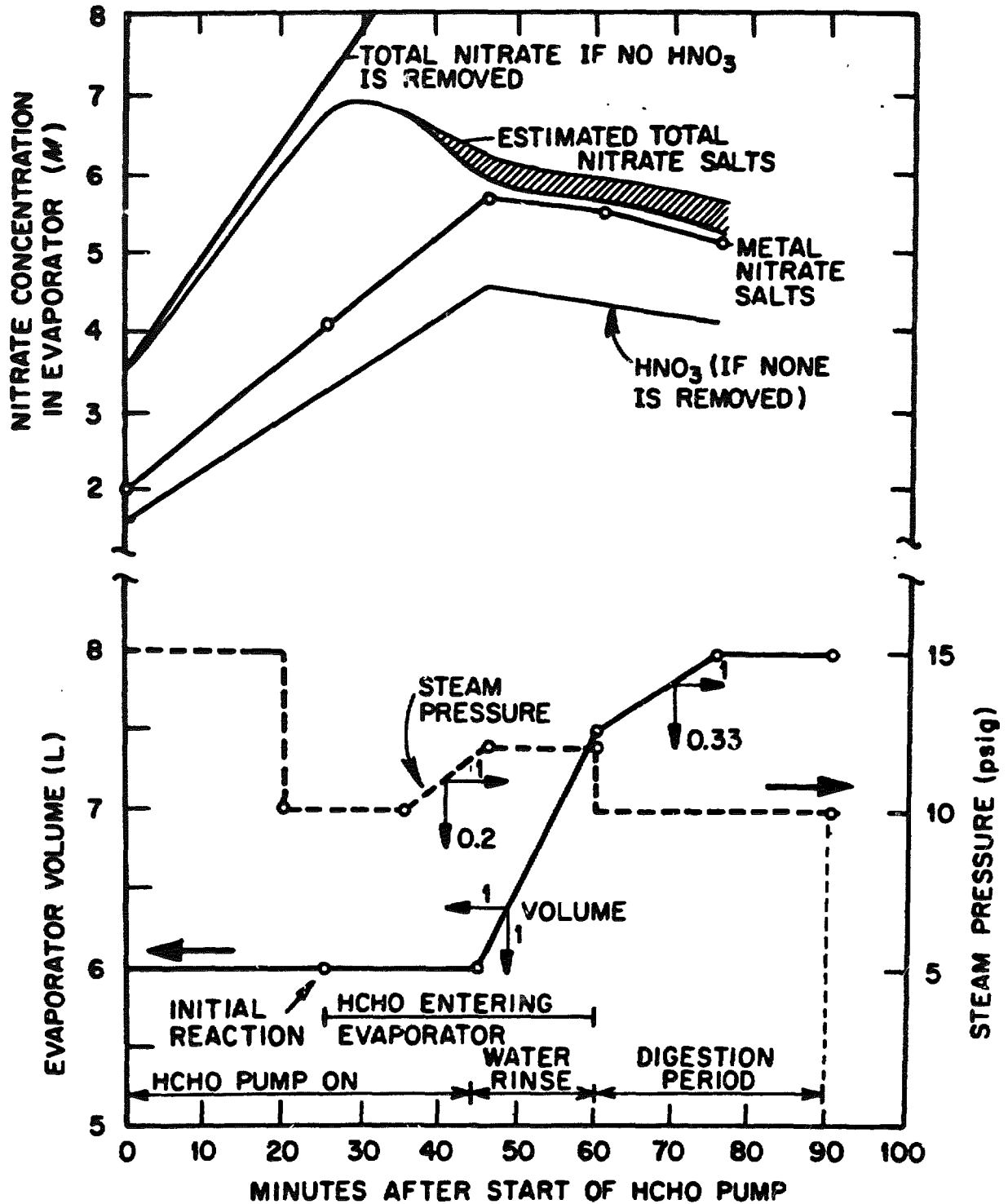in a thermosiphon evaporator.

ORNL-DWG 86-17

Fig. 2. Operating Conditions during the Reaction of Formaldehyde with Nitric Acid while Concentrating a Fissile Uranium Solution in a Thermosiphon Evaporator.

the steam heat exchanger must be reduced appropriately in order to prevent an excessive evaporation rate and liquid entrainment or expulsion. After the formaldehyde addition has been completed, the addition line is rinsed with water and the volume in the evaporator is allowed to increase from 6 to 8 L. Finally, after all of the feed solution has been added, the boil-off rate is reduced during a 30-min digestion period at ~104°C. (Water is added if it is needed to maintain an adequate volume in the evaporator.) The solution is then cooled; water is added to return the volume to 8 L.

PROCESS STUDIES

Early testing in the full-scale equipment indicated that the evaporation/formaldehyde—nitric acid reaction would be difficult to control because of several factors that include (1) the turbulence of the recirculating solution in the thermosiphon leg, (2) the continuous and simultaneous addition of feed solution and formaldehyde solution, (3) the changing nitrate concentration in the evaporator (see Fig. 2), with the corresponding change in the boiling temperature, (4) the exothermic reaction of formaldehyde and nitric acid, and (5) the continuous evolution of steam, CO_2, and nitrogen oxide gases. In addition, the extent of the formaldehyde—nitric acid reaction could be insufficient, causing a supersaturated concentrate to be produced; or, if excess formaldehyde is added, uranyl formate will precipitate. Thus experimental tests were conducted in the following laboratory equipment: (1) a one-quarter-scale glass evaporator which allowed observation of the hydraulic characteristics of the process; and (2) the full-scale

evaporator. Correlations of operating parameters were developed, and
satisfactory operating conditions were determined.

Hydraulic Characteristics

The feed solution and formaldehyde enter the evaporator through a
common nozzle and are swept downward through the evaporator by the
recirculating liquid from the thermosiphon leg. When the formaldehyde
first enters the evaporator there is a surge of effervescence and tur-
bulence; therefore, the heat input via the steam heat exchanger in the
thermosiphon leg must be reduced (see Fig. 2) to compensate for the heat
input from the exothermic reaction. This step will prevent excessive
entrainment of liquid into the condenser. The most stable liquid level
position was found to be just below the return line from the thermo-
siphon loop. At this level, the volume in the evaporator is ~6 L.

Formaldehyde Addition

Mechanisms and rate constants for the reaction of formaldehyde with
nitric acid have been studied previously and have been reported in the
literature.[4,5] In those studies, reaction mechanisms were shown which
indicated that from 1.3 to 4 mol of HNO_3 could be destroyed for each
mol of formaldehyde reacted. The effects of the presence of metal
nitrate salts were not described and were apparently not evaluated. The
occurrence of an induction period — dependent on acidity, nitrite con-
tent, and temperature — was noted.

In our laboratory studies, reaction mechanisms and kinetics were
not specifically examined. However, observations were made that the
initial reaction between nitric acid and formaldehyde in glassware

equipment occurred only after induction periods of 3 min up to greater than 20 min unless the nitrite ion was added or produced by catalysis with iron. In stainless steel equipment, no addition of iron was required. Thus the reaction of formaldehyde is more likely to occur with nitrous acid ($HNO_2 \rightleftharpoons H^+ + NO_2^-$) rather than directly with nitric acid, but nitric acid is probably the donor for the continued production of nitrous acid.

The reaction rates become exponentially more rapid with increasing temperature. Therefore, safety concerns dictated that the formaldehyde be added only when the maximum temperature had been reached in the evaporator. If the addition was made at a lower temperature, a buildup of the formaldehyde concentration in the evaporator could occur and an uncontrolled rapid reaction could result as the temperature increased. Thus an electrical interlock was installed on the formaldehyde feed pump to prevent operation until the evaporator temperature reached >95°C.

In essentially all operations and tests, the formaldehyde addition has been started at the beginning of the evaporation. Consideration was given to adding all of the CEU feed solution to the evaporator and removing part of the nitric acid by distillation before starting the formaldehyde addition. This method was rejected out of concern that the concentrated solution would solidify if the steam supply to the evaporator failed.

A linear relationship was noted between the volume of formaldehyde added and the final acidity in the concentrated product solution, as illustrated in Fig. 3. This relationship is apparently empirical but indicates the consistency with which the run conditions can be repeated.
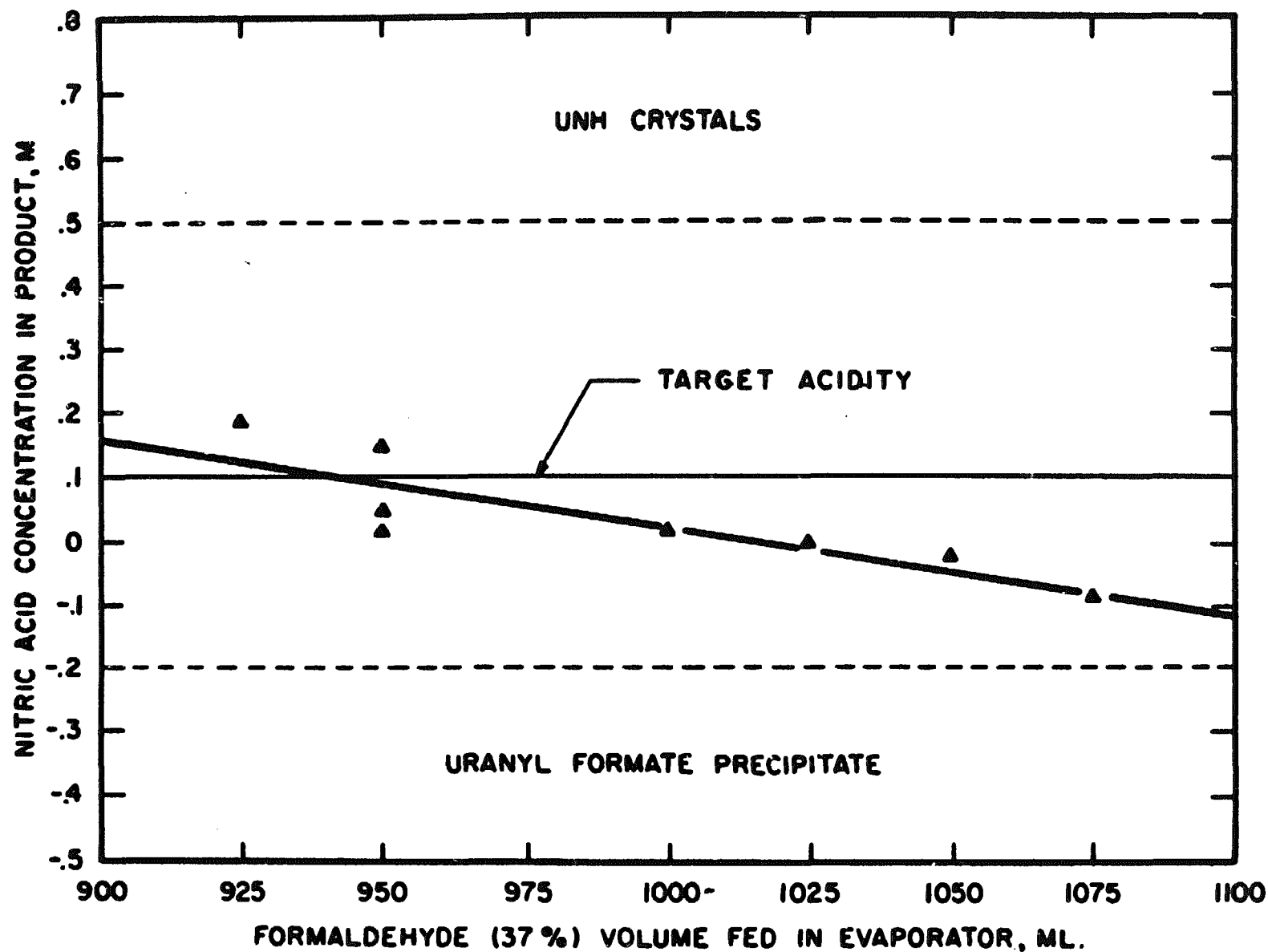
Figure 3. Effect of formaldehyde on residual nitric acid.

Alternatively, the data can be presented as "mol of formaldehyde added" and "mol of nitric acid removed." The ratio of these data (mol of nitric acid removed per mol of formaldehyde added) is an indication of the efficiency of the formaldehyde for the removal of nitric acid. This molar efficiency decreased from a value of 2.61 (when 925 mL of formaldehyde was added) to a value of 2.24 (when the volume of formaldehyde added was increased to 1075 mL).

The plot shown in Fig. 3 and the nomograph shown in Fig. 4 (which was developed from laboratory data) were useful in (1) determining the regions where the amount of formaldehyde added is insufficient, resulting in the potential formation of metal nitrate crystals; and (2) determining the regions where formaldehyde addition is excessive, resulting in the precipitation of uranyl formate.

INTEGRATED OPERATION

Twenty preoperational runs were made in the integrated CEUSP Facility equipment at the process conditions established in experimental runs. Actual operation was begun in April 1985 and during the first nine months of operation, ~70% of the feed material was processed as planned.

No significant difficulties have occurred. The operation of the evaporation/formaldehyde—nitric acid reaction has been tedious, as expected, requiring close operator attention. The most delicate period in each run is when the formaldehyde first enters the evaporator. In several runs, liquid has been expelled from the evaporator, requiring recycle of the condensate (and a unique set of operating conditions for
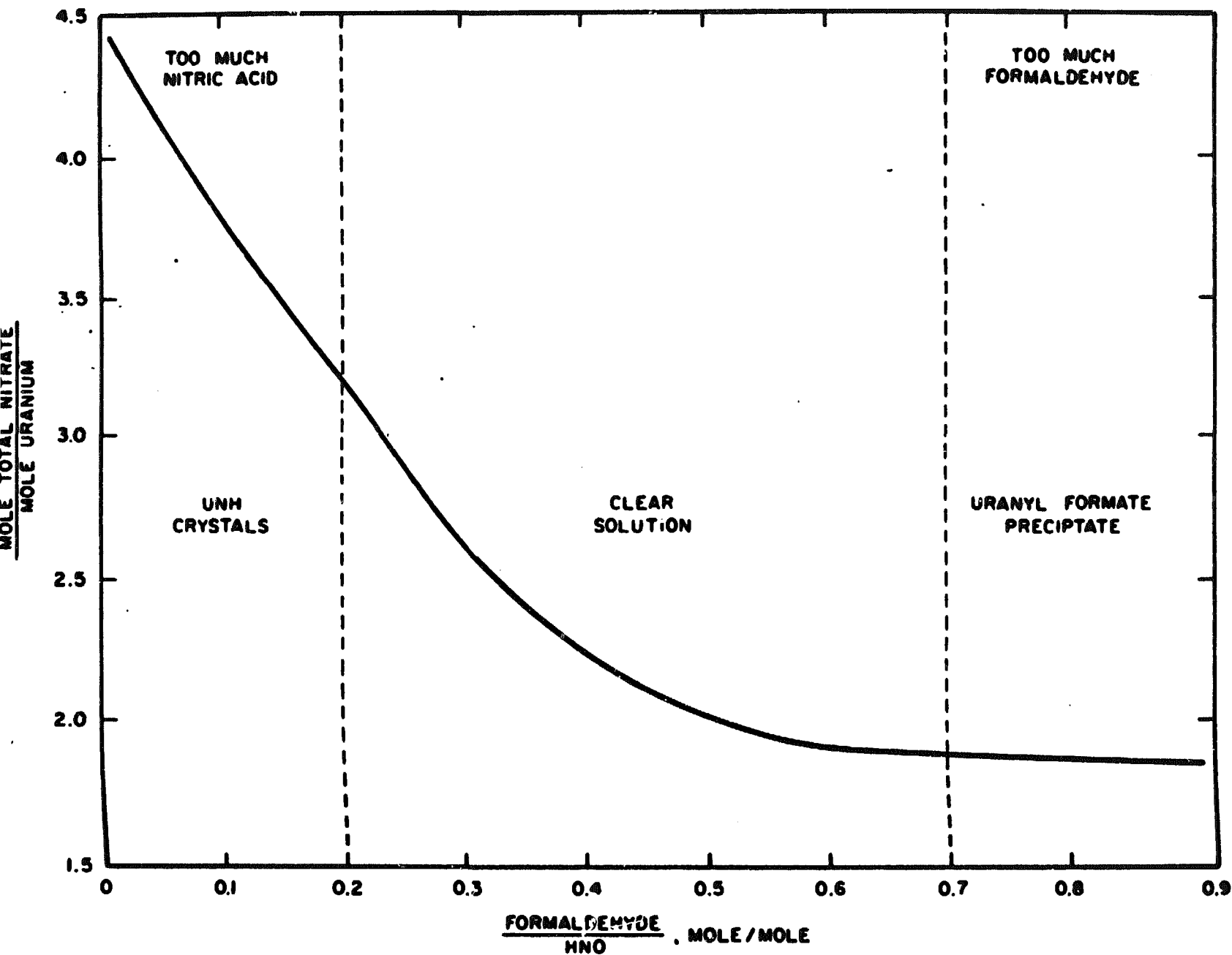
Figure 4. Nomograph developed in laboratory studies to determine operating conditions.

the run in which the recycled material is reworked). The tendency for this situation to occur has appeared to worsen as the number of batches processed has increased. The cause was believed to be due to the accumulation of solid deposits in the evaporator or off-gas line. Special cleanouts of the equipment, using water flushing or boiling nitric acid, have been made periodically and have appeared beneficial.

SUMMARY

A safe, controlled method for reacting formaldehyde with excess nitric acid (while simultaneously concentrating a fissile uranium nitrate solution) was developed and is being successfully conducted in a remotely operated thermosiphon evaporator. The operation was adapted from laboratory studies to semicontinuously process multikilogram batches. A significant process development program was required to elucidate the behavior and characteristics of the process and equipment and to develop operating parameters and successful operating conditions.

REFERENCES

1. R. J. VEDDER, E. D. COLLINS, and P. A. HAAS, "Development of the Thermal Denitration In-Storage-Can Step in the CEUSP Process," in Proceedings of Waste Management '86, Tucson, Arizona (March 1986).

2. C. P. McGINNIS, E. D. COLLINS, and B. D. PATTON, "A Remotely Operated Facility for In Situ Solidification of Fissile Uranium," in Proceedings of Waste Management '86, Tucson, Arizona (March 1986).

3. E. E. LUDWIG, Applied Process Design for Chemical and Petrochemical Plants, vol. 3, 2nd ed., p. 132, Gulf Publishing Co., Houston, Texas, (1983).

4. T. V. HEALY and B. L. DAVIS, The Destruction of Nitric Acid by Formaldehyde, Part II, AERE-C/R-1739 (Feb. 22, 1956).

5. T. V. HEALY, "The Reaction of Nitric Acid with Formaldehyde and with Formic Acid and its Application to the Removal of Nitric Acid from Mixtures," J. Appl. Chem. (Sept. 8, 1958).