UNCLASSIFIED

DPSPU 76-11-1

SEP-E-UF
SFP-F9

EXPLOSION AND FIRE IN THE URANIUM TRIOXIDE PRODUCTION FACILITIES AT THE SAVANNAH RIVER PLANT ON FEBRUARY 12, 1975

A Works Technical Report

Compiled by
J. M. McKibben

E. I. du Pont de Nemours & Company
Savannah River Plant

DATE DISTRIBUTED

October 1976

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT AT(07-2)-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

CONTENTS

Abstract	1
Introduction and Summary	1
Process Description	2
General	
Facilities	
Solvent Decantation	
Evaporation	
Purification with Silica Gel (Optional)	
Evaporation to Hydrate	
Denitration	
Uranium Oxide Handling	
Incident Description	4
Events Leading to Incident	
The Explosion and Fire	
Causes of Incident	6
Analytical Data	
Laboratory Tests	
Basis for Resumed Operation	9
General	
Control of Organic Accumulations	
Analyses of Evaporator Feeds	
Dense Organic Layers	
Denitrator Operation	
Temperature Control	
Off-gas Control	
Operating Experience Since Startup	14
TBP Behavior	
Minor Problems	
Additional Improvements	
Appendix	
Figures	A-1
Tables	A-13

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

CONTRIBUTORS

This report was compiled from several internal technical and investigative reports. Principal contributors to those internal reports include the following.

J. N. Beatty
W. S. Durant
L. W. Gray
H. D. Harmon
M. L. Hyder
W. C. Perkins
P. A. Soltys
J. B. Starks
B. Tiffany

**EXPLOSION AND FIRE IN THE UO_3 PRODUCTION FACILITIES
AT THE SAVANNAH RIVER PLANT
ON FEBRUARY 12, 1975**

Compiled by
J. M. McKibben
Separations Technology Department

Abstract

On February 12, 1975, an explosion and fire occurred in the denitrator room of the separations A-Line facility, resulting in minor injury to two employees and about \$230,000 damage to the building and equipment. The facility, which converts uranyl nitrate solution to UO_3 had operated for 20 years without major accident.

Accidental transfer of tributyl phosphate - uranyl nitrate adduct into a denitrator was followed by rapid decomposition of the organic material. Combustible gases were released into the denitrator room and ignited. No contamination was spread outside the facility.

A-Line returned to operation August 11, 1975, after equipment and procedures were modified to lower the probability of similar incidents to a very low level.

Introduction and Summary

The A-Line facility in F Area began operation in December 1954. The process receives depleted uranium nitrate (UN) at 90 g U/l from the Purex solvent extraction process. This solution is concentrated in two evaporators to molten uranyl nitrate hexahydrate (1200 g U/l), then fed to denitrator pots where it is thermally decomposed to produce uranium trioxide (UO_3).

At 10:28 a.m., February 12, 1975, the contents of one of the denitrator pots underwent reaction, caused by the thermal decomposition of tributyl phosphate - uranyl nitrate (TBP-UN) that had been accidentally added to the pot. The reaction caused dense fumes and forcibly ejected much of the pot contents into the room. The room was filled with red-brown NO_2 fumes and with combustible gases from the decomposition of the TBP. The gases ignited, causing the explosion and fire.

Two operators in the denitrator room observed the fumes and were exiting by separate doors when the pressure of the explosion forcibly pushed them through the open doors. They received only minor injuries and returned to work the same day after being examined by plant medical personnel.

Uranium and other radioactive contamination was confined within the fenced, Regulated Area of the A-Line facility. Urinalyses indicated that none of the seven employees in the A-Line facilities at the time of the incident received any significant uptake of uranium.

The incident caused considerable damage to the "Transite" walls and internal equipment. Structural members were undamaged. Direct costs for restoration were about \$230,000.

As the facility was being restored, numerous equipment modifications, additional monitoring instruments, and operating procedure changes were instituted to lower the probability of similar incidents to a very low level.

Operation resumed August 11, 1975, and has continued safely since that time.

Process Description

GENERAL

The primary A-Line function is to convert UN solution to UO_3 powder. Dilute uranium solution from the solvent extraction process is decanted to remove entrained 30% TBP and concentrated about fourfold by evaporation. Previously, the concentrate was routinely passed through a bed of silica gel to reduce the residual concentration of fission products. This step is currently bypassed because the additional decontamination is not needed. The solution is then evaporated a second time to yield molten uranyl nitrate hexahydrate (UNH). The UNH is heated in a denitrator to yield the UO_3 powder. The powder is put in drums for onsite storage or packaged for shipment offsite.

A dissolver is provided in A-Line for preparation of UN solution (from UO_3 and nitric acid) when needed as a process stream in the solvent extraction process. This dissolver is also used for recycle of off-standard A-Line product.

The off-gas from the denitrators, mainly nitrogen dioxide and oxygen, is reacted with water in an absorber tower to produce 40 to 50% nitric acid solution; this absorber also recovers nitric acid from the off-gas generated in the Building 221-F canyon dissolvers.

Flow diagram for the A-Line process is shown in figure 1.

FACILITIES

The A-Line is located in F Area, one of two separations areas at SRP, outside the southeast corner of the 221 canyon building in which fuel dissolving, solvent extraction, and plutonium finishing (B-Line) operations are performed. Figure 2 presents a plan of the entire A-Line facility. Figures 3 through 6 show more detailed plans and elevations.

SOLVENT DECANTATION

Entrained process solvent (30% TBP - 70% n-paraffin diluent) is removed from the UN solution by decantation prior to evaporation. This solvent would be a potential hazard in subsequent process steps because TBP decomposes rapidly when heated with nitrate at temperatures in the 140° to 160°C range. This could occur in the 1EU evaporator if the temperature controller failed. Large quantities of TBP must be kept from reaching the hydrate evaporators and the denitrators, where the higher temperatures of these steps, in conjunction with TBP decomposition reactions, poses an explosion hazard. Entrained solvent is therefore removed in the Building 221-F canyon by a decanter located under the 1E bank. For added efficiency, the 1EU solution also passes through a second box decanter installed outside the canyon. Decanted 1EU solution is received in A-Line and stored in a tall, cylindrical tank. Because the residence time of the 1EU solution in this tank is relatively large compared to that in a box decanter and because some of the entrained solvent coalesces rather slowly, solvent can accumulate in this tank. Consequently, the solvent is removed periodically by skimming.

EVAPORATION

The 1EU evaporator (figure 3) concentrates uranium to about 26 wt % (400 g U/l), as indicated by a boiling point of 106°C and a specific gravity of 1.5 at the product exit temperature (65 to

80°C). Concentrate is discharged continuously from the evaporator to a tank that can also act as a feed tank for the silica gel beds. Concentrated 1EU solution has a crystallization point of about -20°C. Further concentration in the 1EU evaporator is undesirable since the crystallization point rises rapidly with increasing concentration; more-concentrated solutions could precipitate UN if allowed to stand in unheated A-Line tanks in cold weather. Condensate from the evaporator is collected in the 1EU condensate tank for subsequent disposal to the seepage basins.

TBP can enter the 1EU concentrate from two sources. Traces of entrained process solvent can be fed to the 1EU evaporator in spite of the precautions explained above; this 30% TBP is concentrated to about 90% TBP during 1EU evaporation. Also, TBP has a measurable solubility in UN solutions (figure 7). As the concentration of UN is increased by evaporation, the solubility of TBP decreases, forcing TBP from solution as a fine suspension. The suspended TBP from these two sources can coalesce slowly if unagitated, so that a separate organic phase accumulates in time.

Prior to the explosion on February 12, all tanks downstream of the 1EU evaporator were unagitated and were periodically skimmed to remove floating solvent. Since that time all of these tanks (except for batch tank C-1-2) are being agitated to preclude accumulation of a potentially hazardous quantity.

Most of the TBP in 1EU concentrate is in the form of $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$, the adduct of UN and TBP. This adduct is soluble in TBP - n-paraffin solutions, insoluble in aqueous solutions, and has a composition and specific gravity dependent on the TBP and UN concentrations (figure 8). Since the adduct has a higher specific gravity than that of some aqueous UN, the organic phase in unagitated tanks or columns can float on the UN, disperse in the UN, or form a layer under the UN, depending on the concentration of the UN solution. Normally, the 1EU concentrate is denser than adduct and the organic phase floats if not agitated.

PURIFICATION WITH SILICA GEL (OPTIONAL)

Operation of silica gel columns depends on the need to reduce the ^{95}Zr - ^{95}Nb content of the solutions. The maximum activity level of these isotopes permitted in the hydrate evaporator is 2.3×10^4 d/m/ml. Adequate decontamination is usually attained in the Purex process and the silica gel columns are not used. When additional decontamination of uranium from Zr-Nb fission products is necessary, concentrate from the evaporation step may be pumped down through either of two silica gel beds. This process removes about 90% of the residual zirconium and niobium activity and filters out any suspended matter. Each bed was designed for a superficial linear flow of 33 liters/(hr m²) and a bed residence of about 20 minutes.

EVAPORATION TO HYDRATE

The 1EU concentrate, from either the silica gel columns or the 1EU evaporator, is concentrated to 45 wt % uranium in one of the three hydrate evaporators to permit utilization of maximum denitrator pot capacity and to simplify denitration. This concentration step leaves a mixture of UN and water corresponding to UNH at about 1200 g U/l.

The hydrate evaporators are operated batchwise. Feed is charged to an empty evaporator, boiled down to the desired concentration as indicated by a boiling point of 129°C, and discharged by gravity directly to one of six denitrators. The desired uranium content is at least 45 wt % to allow sufficient freeboard in the denitrators and below 60 wt % to avoid crystallization. Steam pressure at the evaporator heating coils is kept below 80 psig (160°C) to prevent denitration.

Traces of TBP can be present in the UNH produced in this step. As discussed under Evaporation, TBP has a measurable solubility in concentrated UN. TBP is stable, or decomposes very slowly, under

conditions in both the 1EU evaporator and the hydrate evaporator, and is therefore not destroyed prior to the denitration step (figure 9). Also, formation of a TBP-UN adduct inhibits distillation of TBP during evaporation.

DENITRATION

The denitration step converts UNH to UO_3 by thermal decomposition. The denitrator is shown in figure 10. The overall reactions are:

The batch of UNH is transferred by gravity to an empty denitrator pot. During boiloff of water and nitric acid, foaming may result from the effects of any TBP-UN adduct present. Foaming can be reduced by lowering the heating rate through the critical temperature range (120 to 200°C) and by addition of an antifoaming agent. Under current operating conditions only about 10% of the denitrations produce enough foaming to require action.

When the temperature reaches about 200°C, foaming ceases and denitration begins. At this point, the solution is red and becomes more viscous. Vigorous denitration begins at about 220°C. As NO_2 is evolved, the mixture becomes first soupy and then doughy. At the dough stage, agitator power consumption reaches its maximum. Continuous agitation must be maintained during this period, else the dough will harden into a rock-like mass. After reaching the powder stage, the oxide is heated further to ensure that nitrate content is less than 0.5%.

URANIUM OXIDE HANDLING

Uranium trioxide is removed from the denitrators by suction hoses, called "gaspers," and carried pneumatically to a bag-type dust collector. Oxide is withdrawn continuously from the collector to a storage bin from which it may be fed to a hammer mill. Oxide from the mill drops into another storage bin from which it is loaded by screw conveyor into containers.

Incident Description

EVENTS LEADING TO INCIDENT

The canyon was shut down on January 16 and the A-Line on January 17 for scheduled maintenance. During this outage one of the silica gel columns was regenerated. It was also flushed with 14,000 liters of dilute nitric acid to lower radiation for a scheduled inspection. This flush solution was transferred to concentrate hold tanks S-1-8, and S-1-9, which contained normal concentrate. The resultant mixture had a nominal uranium concentration of 250 g/l and density of 1.3 g/cc, compared with normal concentrate which is 400 g U/l and 1.53 g/cc. This was the material being processed at the time of the explosion.

A-Line started operation on February 11 and encountered abnormally high foaming and some discoloration of pot contents during denitrations in all pots. One batch foamed out onto the floor

from pot C-3-2. Supervision was aware of this and issued instructions that batch size be reduced and that heatup rate be reduced by lowering the temperature of the outside skin of the pot from 500°C to 200-300°C. These occurrences were not highly unusual, and those instructions had been successful in the past in controlling troublesome material.

Even though the material processed on February 11 was discolored and foamed during the early stages of the denitration, the final UO_3 was acceptable.

THE EXPLOSION AND FIRE

Pot C-3-4 was charged about 7:15 a.m. on February 12. One of the operators who came in at the 8 a.m. shift change was told that pot C-3-4 had foamed up a little when charged into the warm (less than 200°C) pot. The day shift Foreman told the two operators stationed in the denitrator room that both should remain in the room when heatup was started on this pot and should turn the furnace off if there was any difficulty.

One of the operators inspected the contents and observed some streaks of foam on clear liquid. Following standard procedure he added a commercial silicone antifoam and started the pot agitator. At 9 a.m. he ignited the pot burner and set the temperature controller for the pot skin at 250°C.

At 9:50 a.m. the day shift Foreman inspected all pots and found no abnormalities. He commented to the operators that it appeared the foam problems had subsided. One of the operators told the Foreman that he intended to increase the temperature in pot C-3-4 if the denitration continued normally. At 10:20 a.m. the operator observed that it was continuing normally, then increased the temperature controller to 400°C. About two minutes later both operators observed a puff of red-brown smoke from pot C-3-4. They immediately turned off the heat to C-3-4 and turned on an emergency off-gas system to provide extra exhaust capacity for that pot. Fuming was controlled for a few seconds then intensified. One operator went to a telephone on the east wall to notify supervision, but the fumes became so dense he did not complete the call. He then began moving toward the south exit. At this time visual contact between the operators was lost, and the other operator was moving toward the northeast exit at the end of the room. Both operators reported hearing a "muffled boom" or "bang" and being "pushed" by the pressure of the explosion through the doors — one through the northeast exit, one through the south exit. Neither reported seeing any flash or flame.

The operator exiting south took shelter behind a supply shed until debris stopped falling. Then, seeing a fire in the southwest corner of the building, he ran to a fire alarm station and pulled the switch.

The other operator was pushed through the northeast exit and struck the west wall of the motor control center. After regaining his footing he left the building by the loading platform door.

There were five other employees in the building at the time of the incident. An E & I mechanic was in the motor control center. Two Separations Department supervisors and one operator were in offices on the second floor. One operator was in the control room on the second level.

The mechanic in the motor control center heard a loud, muffled sound and went to the northeast denitrator room door. The room was filled with smoke containing black particles and a strong, unfamiliar odor. He left the building through the loading platform door.

Personnel on the second floor reported they heard a sharp bang and the breaking of wall panels in the corridor. Immediately following this, a dense black smoke filled the corridor, severely reducing visibility. They left the building by the north stairwell.

Other employees outside the building heard a thud comparable to the sound of a jet breaking the sound barrier. Flames were seen outside the building but these rapidly subsided (described as a flash of fire); the flames were followed by dense smoke.

Plant fire-fighting forces responded immediately to the alarm. All building personnel were accounted for and electrical power and other services were turned off. Water was used to quench small isolated fires in the denitrator room.

The operators who were in the denitrator room had minor injuries. One had a small laceration of the upper lip and a bump on the head. The other had a mild irritation of the lungs from the inhalation of fumes. There were no cases of skin or nasal contamination or uranium assimilation by any employee. Radioactive contamination was confined within the fenced, Regulated Area.

Although there was considerable damage to the "Transite" walls in the building, no damage was done to the building's structural support. Damage amounted to \$230,000, based on actual direct restoration costs. Walls, room exhaust system, insulation, lighting, and painting were major items of repair. Fire damage was confined to the processing room. Cleanup of the floor, overhead piping, denitrator pots, etc., was required.

The photograph (figure 11) looking north in the denitrator room shows the deposits of ejected material on floor, walls, piping, and equipment. These can also be seen in figure 12, which shows where the "Transite" panels were blown out of the south wall. Figure 13 shows some of the scorched paint on the walls and other blown-out "Transite" panels in the southeast corner of the denitrator room. Figures 14 and 15 show the east and west outside walls of the facility.

Causes of Incident

Inspections, analyses, and laboratory tests were made to establish the causes and detailed circumstances of the incident. The fire and explosion were caused by the ignition of flammable organic gases given off during the rapid decomposition of approximately 120 liters of TBP-UN adduct that was accidentally added to the denitrator.

The TBP may have been present initially in an organic layer atop the silica gel column that was regenerated or on the surface of tanks S-1-8, S-1-9, or C-1-1; or all of these sources could have contributed. When the dilute acid flush solution from the silica gel column was added to S-1-8 and S-1-9, an aqueous phase was produced with density lower than the density of the TBP-UN (figure 8) so that the TBP-UN went to the bottom of the tank and was transferred to the C-1-1 tank. The same process was repeated in the C-1-1 tank, transferring the TBP-UN to the hydrate evaporator and on to the denitrators.

During many years of operating experience, organic layers often floated in the process tanks and were periodically removed by skimming. The presence of these layers was not considered a hazard since the drawoff piping was near the bottom of the tanks and they were kept full enough to prevent transferring the organic layer. A-Line day supervision had planned to skim these tanks during an extended shutdown of A-Line that was to have begun about the first of March.

The possibility of a phase inversion occurring was not recognized prior to the incident; therefore, none of the A-Line procedures or Technical Standard limits contained any provision for avoiding it. The density data in figure 8 were developed after the incident.

ANALYTICAL DATA

After the incident, organic layers found in the silica gel feed tank (S-1-1), silica gel product tanks (S-1-8 and S-1-9), and concentrate transfer tank (C-1-1) were measured and sampled. The silica gel feed tank and product tank S-1-9 had a 0.15-cm continuous layer of floating organic. The concentrate transfer tank had a 2.5-cm layer. Organic was observed in the other silica gel product tank (S-1-8), but not in sufficient quantity to form a continuous floating layer.

Denitrator pot C-3-1 had been charged but not denitrated at the time of the incident. Upon cooling, this material solidified. Pockets of organic material were found in this solidified mass and were sampled.

These organic layers were characterized by the use of infrared spectroscopy, gas chromatograph, neutron activation analysis, and wet chemical analyses. Results are summarized in tables 1 and 2. In each case, the organic was identified as a $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ - TBP - n-paraffin mixture. The TBP adduct, as fraction of total organic, varied from 30% prior to evaporation in A-Line to 99% after the hydrate evaporators (table 1). The $\text{UO}_2(\text{NO}_3)_2$ was removed from the samples of organic phase of tank S-1-9 by washing with 0.5M Na_2CO_3 ; the TBP content of the remaining organic layer was 96.9 ± 1.9 wt % by wet chemical methods. Elemental analyses (table 2) of the organic from each of the tanks gave values that agree with theoretical values, assuming that greater than 95% of the TBP is in the form of the adduct, $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$.

Samples of the aqueous layers from tanks B-3-1, E-1-3, E-1-4, S-1-1, SG-1, S-1-8, S-1-9, and C-1-1 were analyzed for aqueous carbon, total and inorganic PO_4^{3-} , U, acid, and density. Results are summarized in table 3. Most significant here was the confirmation of the density stratification in tank S-1-8.

The aqueous C/ PO_4 ratios in samples from B-3-1, E-1-3, E-1-4, and C-1-1 are far higher than can be accounted for by dissolved TBP alone. It is assumed that the high C/ PO_4 ratios before the first evaporator can be accounted for by the presence of n-paraffin diluent from entrained 30% TBP solvent. Directly after the evaporator, in which the diluent would volatilize, the C/ PO_4 ratios are approximately as expected for dissolved TBP.

The material ejected from the pot and deposited on walls, floor, piping, etc., was either yellow $[\text{UNH}, \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ or black (figure 16). Some of the black material was gummy and some was very hard and porous, like pumice (figure 17).

Samples of the pumice-like black material were removed from concrete structural members and from back of the motor and the motor baseplate of denitrator C-3-4.

X-ray analyses showed the crystalline portion of the material to be UO_2 . The widths of the x-ray lines compared to a pure sample of UO_2 (brown uranium oxide) indicate that a large portion of this material was either amorphous or weakly crystalline. This would be expected from very rapid formation and cooling. Attempts to prepare this black material in the laboratory under conditions that would give only organic reduction of the uranium trioxide, using heating rates $\leq 100^\circ\text{C}$ per minute, produced only amorphous materials.

Elemental analyses of some of these ejected materials are given in table 4. Using an average of all results, the quantity of TBP in the denitrator was calculated to be 120 ± 40 liters. For comparison, the average phosphorous content of UO_3 produced August through December 1975 gives a calculated TBP content of 0.25 liter per denitrator batch.

This black UO_2 had a much lower density than normal brown UO_2 , and unlike normal UO_2 , would not dissolve in hot oxidizing mineral acids. Fusion with $\text{K}_2\text{S}_2\text{O}_7$ was necessary to bring the samples into solution. These facts suggest the binder preventing dissolution is possibly a type of phosphate glass. The material appeared to be expanded as if it were blown glass. The material did not soften upon heating to 1200°C . As its temperature of formation was equal to or greater than its softening point, the formation temperature was estimated to have been at least as high as 1500°C .

Two types of material were removed from blown-out "Transite" panels: one panel contained only a black material; other panels contained a black material that looked as if it had been blown into a yellow material. The black material was identified by x-ray as UO_2 , was much denser than that removed from the concrete structural members, and contained NO_3^- . This material decomposed on the thermal balance starting at about 900°C , evolving H_2O , N_2 , NO , N_2O , and NO_2 (identified by mass spectrograph). The yellow material was identified by x-ray as $\text{UO}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. This material therefore had not been exposed to temperatures above about 200°C .

Samples of a yellow-and-black mixture of residual products were removed from the bottom of denitrator pot C-3-4. For spark source mass spectrometric (SSMS) and x-ray analyses, the yellow and black particles were physically separated under a microscope. X-ray diffraction showed both the yellow and black materials to be $\text{UO}_3 \cdot 0.8 \text{H}_2\text{O}$. Upon grinding the black material, its true yellow became evident, i.e., the black appeared to be a coating of soot. SSMS show the two materials to be the same except for a small amount of carbon in the black material.

X-ray analyses also showed small amounts of $\text{UO}_3 \cdot 1.0 \text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.5 \text{H}_2\text{O}$ and traces of UO_2 on the surface samples of the pot C-3-4 floor residues. The presence of these products places certain restrictions on the temperatures inside pot C-3-4 at the time of the incident, as follows.

1. In certain areas of the denitrator the temperature did not exceed 200°C , since $\text{UO}_2(\text{NO}_3)_2$ decomposes to UO_3 between 200° and 350°C .
2. The highest possible temperature was about 600°C , since UO_3 decomposes rapidly to U_3O_8 at temperatures above 600°C .
3. The hydrates are formed by the reaction of steam with UO_3 through the following reactions.

Hence the average temperature of the material that remained at the bottom of pot C-3-4 may have been less than 200°C , even though surface temperature may have been greater than 280°C but less than 350°C . Material that stuck to the top of pot C-3-4, however, is UO_2 and has been exposed to temperatures of 1200°C or more. Spalling of UO_2 from the top portion probably sprinkled the lower layer of $\text{UO}_3 \cdot 0.8 \text{H}_2\text{O}$ with the UO_2 found there.

LABORATORY TESTS

Many test denitrations were performed on synthetic and process solution mixtures of UN and TBP-UN adduct to determine the effect of process variables on TBP-UN decomposition and to obtain a better understanding of the decomposition reactions. Additional decomposition experiments were performed on TBP-UN alone.

Differential thermal analysis (DTA) was also performed on similar materials. The DTA tests showed that mixtures of UN and adduct, and adduct alone, initially undergo endothermic decomposition, which may be followed by exothermic oxidation of the decomposition products. In one such experiment with a $2^\circ\text{C}/\text{min}$ heatup rate, the decomposition of the "pure" adduct proceeded as follows: water volatilized between 90° and 160°C ; TBP decomposition began about 170°C with gas evolving at 20 mg of gas per gram of original adduct per minute. Applying these data to the incident in pot C-3-4 gives a calculated total gas release of about 500 m^3 (STP) at a maximum rate of $18 \text{ m}^3/\text{sec}$. Decompositions of UN-adduct solutions, up to 1.0 vol % adduct in 400 g U/l, gave only nonflammable mixtures of gases. Illustrative data is shown in tables 5 and 6. However, when adduct was separated from the UN and heated, the mixture of off-gases was flammable (table 7).

From the estimated quantity of TBP in denitrator C-3-4 at the time of the incident, calculations indicated the total energy release for the incident was about 7×10^5 kcal. Calculated maximum temperature and pressure behind the shock wave were 4650°K and 30 to 40 atmospheres. This was more than adequate to produce the pumice-like UO_2 and to blow out the "Transite" walls.

The specific source of ignition was not determined. However, there were a number of possible sources, including free radical reactions in the gaseous phase and sparks from denitrator motors or other electrical components such as switches or rheostats.

Basis for Resumed Operation

GENERAL

Safety of resumed A-Line operation is enhanced by a combination of improvements in administrative control, procedures, process instrumentation, and process control. These improvements significantly reduce the potential for an excessive quantity of organic material to reach the denitrators, and increase the quantity of organic material that can be processed safely in the denitrators.

The major improvements are listed in tables 8 and 9. Included is a fivefold reduction in the allowable quantity of organic material (TBP) in a process batch. This new limit is implemented by increased sampling frequency, so that all feed to the denitrator is analyzed. New analytical procedures have been established and evaluated. The potential for accumulation of hazardous amounts of organic material in A-Line vessels is reduced by improved written procedures that require increased frequency of tank inspection and organic removal, as well as by agitation of some tanks to prevent accumulation between inspections. The specific gravity of solutions of concentrate is controlled above a minimum value to ensure that the aqueous phase is denser than the organic phase so that organic cannot accumulate at the bottom of the tank.

New process instrumentation has been installed to determine that new limitations on denitration conditions are being met. These limitations include a more gradual increase of operating temperature and an air purge of the vessel to dilute gaseous reaction products to safe concentrations within the off-gas system.

This new instrumentation also provides for more rapid response to violation of critical controls, either manually following an alarm, or automatically. Should a denitrator again be charged, in spite of these new controls, with the same quantity of organic material that caused the explosion, corrective action can be taken sooner to reduce the consequences.

Emphasis has been placed on preventing an excessive quantity of organic in a denitrator. Procedures are designed to control the quantity of TBP reaching the denitrator to below a fiftieth of the quantity that caused the explosion. At reduced heatup rate this smaller quantity of organic will decompose in the denitrator at a slow rate, so that the air purge maintains the concentration of the gaseous reaction products below the flammable limit, assuming complete conversion of TBP to its most flammable butyl degradation product.

Risk analyses, using the fault-tree technique, have been made for A-Line under the old and new modes of operation. These analyses conclude that the expected frequency of an explosion in the A-Line denitrator room has been reduced from once in 20 years to once in about 4000 years as a result of modifications to equipment and procedures. The consequence of an explosion is assumed unchanged, thus the decrease in risk is directly proportional to the decrease in probability. The probability of accumulation and transport of gross quantities of organic material (which initiated the recent explosion) has been reduced by 2×10^5 ; however, other potential mechanisms, such as material handling errors, limit the reduction of risk. The occurrence of foam-outs (release of liquid as foam from a denitrator), which are a sensitive indicator of increases in the quantity of organic in denitrator feed, is expected to decrease by a factor of about 10, or to about once per year.

Administrative control has been strengthened by increasing supervisory and technical support to the routine operation of the facility and by improving internal auditing.

CONTROL OF ORGANIC ACCUMULATIONS

Accumulation of substantial amounts of TBP solutions in the A-Line process is avoided by the following precautions.

1. Purex solvent (30% TBP - 70% n-paraffin) in feed to the 1EU evaporator is minimized by repeated decantation.
2. Gradual accumulation of dilute or concentrated TBP in process tanks is minimized by frequent inspection and removal (skimming) and by agitation of stored concentrate solutions.
3. The organic content of all evaporator feed is measured; an evaporation does not begin until the limits on organic content are met — by additional skimming if necessary.
4. The density of evaporator feed is maintained so that any organic present will float and will be detected by inspections conducted at least weekly.

The quantity of Purex solvent associated with canyon 1EU product is minimized during processing by decantation. Four decantations are made: the 1E bank decanter in Building 221-F, the box decanter, tank B-3-1, and tank E-1-3.

Plant experience indicates that the quantity of entrained organic escaping the 1E bank decanter and removed in the box decanter is routinely small or undetectable. The box decanter acts as a backup to the 1E bank decanter. Tank B-3-1 (8 × 11 ft) is a transfer tank. Solution flows in by gravity from the box decanter and is pumped from the bottom of this tank to tank E-1-3. Decantation in the 12 × 40-ft silo-type tank (E-1-3) allows entrained organic a longer time (1 to 2 days) to settle out as a floating layer than is allowed in the decanters upstream. The shape of this tank reduces the surface-to-volume ratio of solutions and thereby increases the efficiency of inspections to detect floating organic layers and of skimming to remove these layers. Tank B-3-1 is less efficient as a decanter because the residence time of solutions in this tank is shorter than in tank E-1-3.

Decantation efficiency in this part of the A-Line process is enhanced by procedures and by physical controls. No agitators are installed on these tanks. Procedures place minimums on the liquid levels in each tank (40% in B-3-1, 52% in E-1-3), so that they are never pumped empty and floating organic layers (which are never very thick) cannot be pumped forward. A low-level alarm sounds and the pump cuts off automatically if tank E-1-3 is pumped below the minimum level. Tanks B-3-1 and E-1-3 have inlet baffles that ensure smooth blending of incoming solutions with stored solutions and avoid splashing or re-entrainment of organic layers.

Additional methods of organic material control prevent slow accumulation. 1EU fed to the 1EU evaporator contains both dissolved TBP and traces of entrained 30% TBP. Evaporation concentrates the entrained 30% TBP and also reduces the solubility of dissolved TBP from 100 mg TBP per liter of 1EU to 32 mg TBP per liter of concentrate (figure 7). The net result of these two effects is that a layer of 90% TBP can form slowly on the 1EU concentrate. The TBP coalesces very slowly, however, and since all tanks containing concentrate are kept agitated, nearly all of the TBP present in the feed to the 1EU evaporator remains entrained and is transferred to the denitrator. This method of operation maintains an acceptably low quantity of TBP in each denitrator batch and, at the same time helps prevent accumulation of potentially hazardous quantities.

All tanks are visually inspected at weekly intervals, after turning off agitators and waiting at least two hours. The tank is skimmed if the quantity of floating organic material approximates a continuous layer.

ANALYSES OF EVAPORATOR FEEDS

Feed to the 1EU evaporator is measured in samples taken at the tank E-1-3 outlet through a sample tap on the pump. Since tank E-1-3 has no agitator, these samples of settled solution are representative of solution fed to the 1EU evaporator. Samples are taken during each eight-hour shift during process operation.

The allowable quantity of entrained 30% TBP in the 1EU evaporator feed is 0.13 vol %, in addition to the soluble TBP (0.01 vol % or 100 ppm). This concentration must be maintained in order to meet the subsequent limits for the hydrate evaporator (0.2 vol % or 4.5 l TBP/batch). Since there may be no subsequent organic removal, because the concentrate hold tanks are agitated to homogenize the aqueous and organic phases, it is important to limit the quantity of entrained organic in 1EU evaporator feed. Procedures require that, should the average of triplicate samples exceed 0.10 vol % organic-to-aqueous (O/A), the feed from tank B-3-1 is stopped to allow tank E-1-3 contents to settle; tank E-1-3 is then skimmed and resampled. Feed for the 1EU evaporator is not drawn from tank E-1-3 until acceptable sample results are received.

Feed to the hydrate evaporators is sampled from tanks S-1-8 and S-1-9. The solution from one of these tanks is fed to tank C-1-1 while the other tank is being filled. Samples are taken with the agitator running so they will be representative of the entire tank contents; homogeneity has been demonstrated in plant tests with mixtures of known proportion. A batch of hydrate evaporator feed is then pumped from tank C-1-1 to tank C-1-2, which empties into the evaporator. The maximum allowable quantity of TBP in a batch of hydrate evaporator feed is the smaller of 0.2 vol % or 4.5 l. This concentration can be reliably measured and is the maximum safe quantity in a denitrator batch, as discussed later.

This quantity of TBP is also safe in the hydrate evaporator. Previously, this evaporator has been operated with a Technical Standard limit of 0.5 wt % organic in the feed and a maximum temperature of 125°C. At this temperature there is no hazard from TBP, because the rate of decomposition is too low. The 120 liters of TBP in the February incident were heated safely in the hydrate evaporator because the temperature reached only 121°C.

In practice the operating limit on the O/A volume ratio is set at 0.1% for hydrate evaporator feed. Further, a set of three samples are taken that must give an average result less than 0.1% O/A. This procedure is designed on the basis of plant sampling tests and a statistical analysis of the results, indicating 95% confidence that a value reported as 0.1% will have a true value less than 0.15% O/A.

Should a set of samples give results greater than 0.1% average O/A, procedures require that the tank be settled (i.e., no agitation) for at least 4 hours, skimmed to remove organic, agitated 30 minutes, and resampled. During this period of reanalysis, no solution may be processed from the tank, and the process is shut down if no other feed is available.

DENSE ORGANIC LAYERS

One of the specific causes of the February incident was the inversion of aqueous and organic layers when the density of the aqueous was reduced by dilution. The organic of highest density likely to be present is 100% TBP saturated with UN, with a density of about 1.44 g/ml (figure 8). To protect against the possibility of accumulating such dense organic layers at the bottom of tanks, the density of the aqueous material is controlled above 1.50, using both in-line and laboratory analyses. This also ensures that the weekly visual inspections will detect organic floating on the top, if present.

DENITRATOR OPERATION

As described in the previous section, organic material (principally TBP) will normally be fed to the denitrators at acceptably low concentrations; existing equipment cannot completely remove organic from denitrator feed. The lower limit of TBP concentration is set by the small but significant solubility of TBP in feed to the hydrate evaporator, 32 mg/l, or the equivalent of 83 ml TBP per metric ton of uranium. More TBP will normally be present since the quantity of entrained TBP in 1EU concentrate is increased by the decrease in TBP solubility that occurs in the 1EU evaporator. This entrained TBP coalesces slowly and would not be easily decanted. Since complete removal of TBP from denitrator feed is impractical in existing equipment, safe operating conditions have been defined for the limited amount of TBP permitted in the denitrator.

Safe denitrator operation depends on three principles.

1. The quantity of organic in the denitrator, as measured by the O/A volume ratio in feed to the hydrate evaporator, is maintained as low as practicable and below a reliably detectable value.
2. The rate of temperature rise of the denitrator contents is limited so that the allowable quantity of TBP decomposes at a controlled rate.
3. The flow of air through the denitrator during TBP decomposition is adequate to dilute gaseous decomposition products below their flammability limit, assuming the most unfavorable conditions.

These principles are interdependent. For instance, at a given temperature, doubling the quantity of TBP requires that the airflow be doubled to produce the same off-gas concentration. As the rate of temperature rise increases, a given quantity of TBP decomposes more rapidly and the airflow must be increased accordingly. Laboratory studies of the thermal decomposition of TBP in UN solution have established the interdependent relationship of these three parameters under safe operating conditions, which can be summarized by a correlating equation.

$$1.67 \geq V_o \cdot \Delta T \cdot 1/F$$

where:

- V_o = volume of organic material, liters
- ΔT = rate of temperature rise of denitrator contents between 150° and 200°C, °C/min
- F = off-gas flow, m³/min

The correlating value is conservatively chosen from calculated values varying from 1.67 to 1.87, for temperature rates between 0.5°C-2.0°C/min, off-gas flows up to 5.66 m³/min, and TBP volumes up to 4.5 liters (0.2 vol % in a U charge of 0.9 metric tons). The correlating value is also conservative in maintaining gaseous decomposition products below their flammability limits because of the following assumptions.

1. Three moles of combustible gas are produced per mole of TBP decomposed.
2. The flammability limit (1.5% by volume in air) is based on the most combustible gas that can be produced, butyl nitrate. (Actually a complex mixture of C₄ hydrocarbons, CO₂, and nitrogen compounds is produced, with percentages dependent on temperature and mixing conditions.)
3. No credit is taken for dilution by noncombustible gases (e.g., CO₂) produced, nor for gases with higher flammability limits.

Using this equation it can be calculated that it would be safe to denitrate a batch containing 4.5 liters TBP (over twice as much as allowed by operating procedures) at a heatup rate of $1^{\circ}\text{C}/\text{min}$ (limited by procedure to $0.7^{\circ}\text{C}/\text{min}$) if the dilution airflow is $2.72\text{ m}^3/\text{min}$. Since the decomposition of TBP is essentially complete at 200°C (figure 9) the temperature and airflow limitations are not imposed after denitrator contents reach 200°C .

TEMPERATURE CONTROL

New instrumentation has been installed in the denitrators to measure temperature of pot contents in addition to the outside denitrator bottom (known as the skin temperature). Plant tests were performed with TBP-free UN solutions to correlate skin temperature with contents temperature during a heat cycle on each of the denitrators. Using those correlations, at the start of a denitration, the skin temperature is set to give an average heatup of $0.6^{\circ}\text{C}/\text{min}$ and a maximum at any portion of the cycle of $0.7^{\circ}\text{C}/\text{min}$, during the critical range of 150° to 200°C . The potential heat of reaction from partial oxidation in situ of products from the decomposition of TBP can increase the temperature of denitrator contents. However, no exothermic effect from partial combustion of organics has been observed since startup in August 1975; the organic content has always been well below the 0.2 vol % limit. Surveillance of the rise in temperature of pot contents is provided in conjunction with control by pot skin temperature.

After pot contents reach 200°C in normal operation, the skin temperature controller is manually increased 50°C above its previous setting. At this point decomposition of organic material is practically complete, and increasing heat input reduces the time necessary for complete denitration. The skin temperature is limited to the 50°C increase to avoid damage to the denitrator kettle.

OFF-GAS CONTROL

The minimum gas flow from the denitrator to the off-gas system is ensured by determining that air is flowing into the denitrator at the required rate. A calibrated orifice on each denitrator provides the required air purge at the minimum denitrator vacuum of 1.3 cm H_2O . Air leakage at other points or a higher vacuum provide additional airflow through the denitrator. Plant tests indicate that a vacuum of at least 2.5 cm H_2O can be maintained in each of six operating denitrators if three are in the air purge cycle. If the 1.3 cm H_2O vacuum cannot be maintained during a denitration run, the denitrator must be shut down. Audiovisual alarms alert both the control room and denitrator room personnel if header vacuum drops to 1.5 cm H_2O . In this situation, off-gas capacity is available in addition to the Nash exhausters. A steam-operated stack jet can be activated manually in response to the alarm; the jet is automatically activated whenever the header vacuum drops to 1.3 cm H_2O (previously set to activate at 0.64 cm H_2O). When the jet is operating, the off-gas route is automatically changed to bypass the acid absorber column. The route can also be changed manually in response to the alarm. This route change results in increased flow of off-gas with a loss of HNO_3 that could have been recovered from the stacked fumes.

Pluggage of the off-gas system could cause low airflow and inadequate vacuum. An acid boilout is usually made weekly in each denitrator to dissolve any solids that have accumulated in the off-gas piping. This boilout consists of boiling to dryness about 750 l of nitric acid (analyzed and found to contain less than 0.1 vol % organic). Plant experience indicates that off-gas piping is effectively cleaned by this procedure.

If pluggage occurs during a denitration run so that vacuum on an individual pot is decreased but the header vacuum is unaffected, an alarm on a vacuum recorder on each pot alerts denitrator room personnel that manual response is required. The header vacuum can be increased by the stack jet or by bypassing the absorber column. If these methods are ineffective because of severe pluggage, the denitrator room is evacuated and the furnace is shut down by pressing an emergency button outside the denitrator room.

Operating Experience Since Startup

By August 1975, restoration of A-Line was complete (figure 18), revised procedures had been prepared, and new instrumentation for increased surveillance (described in the last section) had been installed.

Initial operation used a "cold" feed prepared by dissolving UO_3 in nitric acid. The feed contained no TBP. During this initial operation, the operators were trained in the new procedures, new equipment was tested, and heatup rates for the contents of each denitrator were calibrated as a function of outside (skin) temperature.

Normal feed was started on August 11. Operation during the following six months was satisfactory and produced no significant incidents.

TBP BEHAVIOR

TBP arrives in A-Line either as entrained 30% TBP - n-paraffin solvent or as soluble TBP. Nearly all of the entrained solvent separates in tank E-1-3, from which it is skimmed. Plant experience with entrainment has been good. The amount of solvent skimmed from this tank weekly has consistently been less than one liter. In fact, the total organic material skimmed from all six tanks in A-Line each week has averaged only about 1 liter.

The soluble TBP stays in solution until it is evaporated to 400 g U/l in the 1EU evaporator. Nearly all of the TBP in the concentrate stays dispersed (entrained) in the agitated tanks and is transferred to the hydrate evaporators and denitrators. This TBP decomposes in the denitrator, leaving the phosphorous as an impurity (presumably as orthophosphate, PO_4^{-3}) in the final UO_3 product.

Analyses for phosphate were made on composited UO_3 samples representing all production from August through December 1975. These indicated that the amount of TBP being fed to the denitrators was only 0.25 liter per batch; the O/A analyses of hydrate evaporator feed gave a higher average value - 0.76 liter per batch. A calculation of the amount of TBP per batch based simply on the solubility of TBP in A-Line feed gives 1.7 liters. All of the reasons for these differences have not yet been determined, but these values are all below the value that has been conservatively determined to be the maximum safe quantity - 4.5 liters.

MINOR PROBLEMS

There have been no foam-outs since startup and only four instances when the foaming was sufficient to require a decrease in heatup rate. Samples of the material (either solution or oxide, or both) from the foaming batches were taken. Analyses have indicated that none of these instances of foaming were caused by excessive TBP.

There have been three instances of fume release in which a puff of red-brown smoke was ejected from a denitrator while pot contents were in the powder stage. All instances were caused by a loss of denitrator vacuum when a butterfly valve in the 15-cm off-gas line became plugged with uranium solids. Being in the powder stage, these incidents occurred several hours after all TBP had decomposed.

The responses of instruments (low vacuum alarm) and operators to these events were in accordance with the new procedures. The room was evacuated, and heat to the furnace turned off until vacuum could be re-established by the emergency stack-jet.

In all of these cases of fume release, UO_3 final product was being removed (by gulper) from another denitrator at the same time. This gulping operation increased the vacuum in the off-gas header that is shared by all the denitrators, thereby producing a higher off-gas rate. It is believed that this higher off-gas flow hastens pluggage by carrying a larger amount of entrained uranium solids into the off-gas piping.

ADDITIONAL IMPROVEMENTS

Equipment modifications in progress are expected to eliminate the pluggage and fume releases.

1. The off-gas header is being instrumented to maintain a constant vacuum.
2. New regulator-controlled valves are being installed, replacing the manually operated butterfly valve in each denitrator off-gas line to control each denitrator vacuum within narrow limits.
3. New automatic valves are being installed for dilution air bleed control.

FIGURE 1. A-LINE CONCENTRATION AND DENITRATION FLOW DIAGRAM

FIGURE 2. PLOT PLAN OF A-LINE FACILITY

FIGURE 3. 1EU EVAPORATION EQUIPMENT ARRANGEMENT

FIGURE 4. A-LINE SECTIONAL ELEVATION

FIGURE 5. A-LINE FIRST FLOOR PLAN

FIGURE 6. A-LINE SECOND FLOOR PLAN

FIGURE 7. SOLUBILITY OF TBP
IN AQUEOUS URANYL NITRATE
SOLUTIONS AT 25°C

FIGURE 8. SPECIFIC GRAVITY OF
A-LINE SOLUTIONS AT 25°C

FIGURE 9. THERMAL STABILITY OF
 $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ ADDUCT

FIGURE 10. A-LINE DENITRATOR ASSEMBLY

FIGURE 11. DENITRATOR ROOM - LOOKING NORTH.
DPSPF 18758-18.

FIGURE 12. DENITRATOR ROOM - LOOKING SOUTH.
DPSPF 18758-14.

FIGURE 13. DENITRATOR ROOM – SOUTHEAST CORNER,
DPSPF 18758-7.

FIGURE 14. A-LINE BUILDING – OUTSIDE EAST WALL,
DPSPF 18758-48.

FIGURE 15. A-LINE BUILDING - OUTSIDE WEST WALL.
DPSPF 18758-41.

FIGURE 16. DEPOSITS ON WALL OF DENITRATOR ROOM.
DPSPF 18763-19.

FIGURE 17. CLOSEUP OF DEPOSITS ON WALL.
DPSPF 18766-3.

FIGURE 18. DENITRATOR ROOM AFTER RESTORATION.
DPSPF 19950-2.

TABLE 1
GAS CHROMATOGRAPHIC (GC) ANALYSIS OF ORGANICS

Tank ^a	GC Peak Height		% TBP ^b	
	n-paraffin	TBP	Volume	Weight
B-3-1 (EU Basin Receipt Tank)	208	90	30.20	33.1
E-2-2	(Continuous evaporator)			
S-1-1 (Conc Receipt Tank)	4	60	93.75	94.5
SG-1 or -2	(Silica gel column)			
S-1-9 (Conc Hold Tank)	50	400	88.89	90.2
C-1-1 (Conc Transfer Tank)	90	850	90.43	9.15
C-2-1, -2, or -3	(Hydrate evaporator)			
C-3-1 (Denitrator)	2	140	98.59	98.8

^a Tanks are listed in the proper processing sequence.

^b Assumes only TBP and n-paraffin are present in significant quantities [does not include the $\text{UO}_2(\text{NO}_3)_2$].

TABLE 2
ELEMENTAL ANALYSES OF ORGANICS

Tank ^a	Weight %				
	C	H	N	P	U
B-3-1	55.6	11.0	2.18	ND ^b	ND
E-2-2	(Continuous evaporator)				
S-1-1	31.6	9.9	2.71	ND	ND
SG-1 or -2	(Silica gel column)				
S-1-9	32.8	8.49	3.24	6.64	25.18
C-1-1	31.5	6.83	3.24	ND	ND
C-2-1, -2, or -3	(Hydrate evaporators)				
C-3-1	31.0	6.02	3.06	ND	ND
Average ^c	31.7	7.81	3.06	6.65	25.18
Calculated for $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$	31.11	5.87	3.02	6.69	25.68

^a Tanks are listed in the proper processing sequence.

^b ND - Not Determined. Infrared analysis, however, showed all organics to contain the $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ adduct.

^c Average for S-1-1, S-1-9, C-1-1, and C-3-1.

TABLE 3
ANALYSIS OF AQUEOUS SAMPLES FROM A-LINE TANKS

Tank	Sampling Location	C μg/ml	PO ₄ --- (Total), μg/ml	PO ₄ --- (Inorganic), μg/ml	U g/l ^a	U g/l ^b	H ⁺ ^c	Density
B-3-1	Top	4700	59.6	13.8	96.1	87.3	0.07	1.120
E-1-3 ^d	Top	2800	41.9	31.3	88.5	91.2	.07	1.123
E-1-4 ^e	Top	7500	39.8	10.7	149	141.5	.08	1.194
S-1-1	Top	<250	58.7	21.5	576	553	.25	1.731
S-8-1 ^f	Top	<250	34.1	18.5	566	538	.29	1.730
S-1-8 ^g	Top	<250	34.2	22.1	(270.5) ^h	271	.20	1.376
	Middle					279	.18	1.379
	Bottom					454	.24	1.615
S-1-9	Top	<250	35.1	25.9	486	449	.24	1.615
						457	.24	1.620
						457	.26	1.620
C-1-1	Top	8500	88.5	17.9	400	384	.26	1.526
	Middle					386	.22	1.524
	Bottom					386	.22	1.526
C-2-2						408	.27	1.555
C-2-3						409	.25	1.557
						408	0.24	1.553

^a By neutron activation analysis

^b Density-acid nomograph (used for normal process quality control)

^c Normality

^d EU storage tank

^e Miscellaneous storage tank

^f Silica gel column sample tap

^g Product tank

^h Colorimetric analysis (used as standard for NAA)

TABLE 4
ELEMENTAL ANALYSES OF MATERIAL ON
CONCRETE STRUCTURAL MEMBERS AND EQUIPMENT

Location	Weight %			P/U ^a
	C	P	U	
East wall ^{b,c} between C-3-4 and C-3-3	1.63	1.66	73.8	0.173
East wall opposite C-3-4	1.50	1.45	72.3	.154
From panel opposite C-3-4	5.8	1.04	62.4	.128
Back of motor C-3-4	0.88	1.03	49.2	.161
Motor base- plate C-3-4	1.07	0.72	44.0	.125
Inside pot C-3-4	0.17	1.26	56.4	0.172

^a Mole ratio.

^b Analyses by
SSMS: C ≤ 8%, N ≤ 10, O = 56, P = 9,
S ≤ 0.07, U = 17.

^c Analyses by CHN analyzer. C = 1.34%,
N < 0.2%.

TABLE 5
ANALYSIS OF DENITRATION OFF-GAS
COLLECTED OVER WATER^a

Compound	Concentration in Off-Gas, vol %	
	Sample 1	Sample 2
O ₂	0.7	0.7
N ₂	52.8	57.0
NO	25.3	20.8
N ₂ O	10.6	10.7
CO	2.5	3.9
CO ₂	8.1	7.1
Ethane	4 ppm	4 ppm
Propane	5 ppm	-

^a Denitration reaction mixture
contained initially 1 vol %
adduct.

TABLE 6
ANALYSIS OF ORGANIC COMPOUNDS IN
DENITRATION OFF-GAS AT VARIOUS TEMPERATURES

Compounds	Concentration of Gas, ppm ^a		
	105°C	160°C	170°C
n-butyl nitrate ^b	-	400	60
Butyric acid ^c	900	800	1000
Total organic	2400	6000	2900

^a Gas samples were withdrawn
from the same denitration
reaction containing initially
1 vol % adduct when the re-
action reached the indicated
temperature.

^b Identified by gas chromatograph
(GC) retention data and quad-
rupole mass spectrometry.

^c Identified by GC retention
data only.

TABLE 7
GAS CHROMATOGRAPHIC - QUADRUPOLE MASS SPECTRAL
ANALYSIS OF GASES EVOLVED BY THERMAL
DECOMPOSITION OF PURE TBP-UN ADDUCT

Gas	Concentration, vol %
O ₂	0.06
N ₂	21.6
NO	29.7
CO	16.7
N ₂ O	11.4
CO ₂	31.3
Ethene	0.06
Propene	0.10
1-butene	12.2

Total → 123.1^a

^a Deviation of this
value from 100% is
indicative of ana-
lytical uncertainty.

TABLE 8
MAJOR CHANGES IN A-LINE OPERATING PROCEDURES

	Old	New
O/A operating limits, vol %		
Feed to LEU evaporator	0.5	0.1
Feed to hydrate evaporator	0.5	0.1
O/A sampling frequency		
E-1-3	1/day ^a	1/shift
S-1-8 and S-1-9	1/day ^b	1/tankful
Inspection and skimming frequency		
B-3-1	None	1/week
E-1-3	1/week ^c	1/week
S-1-1	None	1/week
S-1-8 and S-1-9	2/month ^c	1/week
C-1-1	1/week ^c	1/week
Operating mode		
S-1-8 and S-1-9	Decanter	Agitated
C-1-1	Decanter	Agitated
Minimum specific gravity of LEU concentrate	None	1.50 ^d
Minimum denitrator vacuum ^e	None	1.27 cm H ₂ O
Initial denitrator skin temperature	500°C	g
Normal heatup rate	1°C/min ^f	<0.7°C/min

^a In recent practice, about once a month.

^b In recent practice, about twice a week.

^c In recent practice, about once a year.

^d Corresponds to 370 g U/l. See figure 8.

^e As explained in the text, this requirement provides an air purge through the denitrator.

^f Not measured, determined after the explosion.

^g Varies among denitrators - between 450° and 500°C.

TABLE 9
NEW A-LINE CONTROLS AND INSTRUMENTATION

- Automatic pump cutoff at low liquid level in tank E-1-3.
- Temperature monitoring of denitrator contents.
- Air purge to denitrator (inlet orifice).
- Denitrator pot vacuum recorder (low vacuum alarm).
- Emergency furnace shutdown and stack jet start (button and alarm, exterior to room).
- Interlock to shut down denitrator furnace if skin temperature limit is violated.
- Explosive gas monitor (and alarm) on room exhaust.
- Automatic cutoff for high steam pressure to hydrate evaporators.
- Alarm for high skin temperature.
- Alarm for agitator failure.
- Automatic control of pot vacuum.
- New backlighted alarm panels.
- Automatic control of vacuum in exhaust manifold.