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DP-MS-83-142

CONF-840392--1

"RED OIL" EXPLOSIONS AT THE SAVANNAH RIVER PLANT

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DP-MS--83-142

DE84 008185

A paper proposed for publication in the
Training Course on Prevention of
Significant Nuclear Events

Presented by U. S. Department of Energy,
Office of Nuclear Safety and
Argonne National Laboratory,
Division of Educational Programs

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ABSTRACT

Two "red-oil" explosions occurred at the Savannah River Plant. The first of these was in an evaporator at the semiworks prior to plant operation. The second occurred 22 years later in an A-Line facility calciner (called a denitrator).

INTRODUCTION

The Savannah River Plant has experienced two explosions because of the rapid thermal decomposition of the adduct $UO_2(NO_3)_2(TBP)_2$. In both cases, tributylphosphate and an organic diluent were not known to be present in solutions of uranyl nitrate. The solutions were heated and damaging explosions resulted. The first of these occurred in an experimental evaporator at the semiworks with unirradiated materials. The description that follows is based on the state-of-the-art technology at the time of the occurrence.[1] The second explosion was initiated in a calciner, called a denitrator, used to convert decontaminated uranyl nitrate solution to uranium trioxide powder by controlled thermal decomposition.[2-4] A more comprehensive investigation of the second explosion resulted in extensive modifications to equipment and operating procedures.

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* The information contained in this article was developed during the course of work under Contract DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCUSSION

The TNX Explosion and Its Causes

On January 12, 1953, while concentrating a uranyl nitrate-nitric acid solution, a semiworks evaporator was destroyed by an explosion. Two minor injuries to personnel also resulted. At the time of the incident, a special series of evaporations was in progress to remove about 50% of the nitric acid from 1800 gallons of uranyl nitrate (UN) solution. Equipment size necessitated that the deacidification be carried out in several batches of approximately 500 gallons each and three batches had been successfully processed. The fourth and final charge consisted of the 70 gallon heel of the original solution plus 160 gallons of previously evaporated material which had been diluted with water. The additional 160 gallons were required to make a minimum evaporator charge.

Because the liquid temperature recorder was broken and since the required degree of concentration was beyond the range of the specific gravity recorder, the evaporation was being carried out for a specified length of time based on past experience. Five minutes prior to the scheduled completion of this fourth evaporation, a violent reaction took place with sufficient pressure to destroy the evaporator pot and cause extensive damage to the building.

The operator present at the time stated later that he heard a rumbling noise, and then observed orange-colored fumes evolving from the top of the column with a high-pitched roar. This observation is considered evidence that a reaction vigorous enough to produce copious quantities of gas or vapor was taking place. On the basis of previous experience, it was suspected that the reaction was accompanied by considerable frothing. This suspicion was confirmed when a later examination of the column bubble-trays revealed that the lower trays were at least partially plugged with solid material. This partial plugging of the column could well have facilitated a pressure buildup in the evaporator, prior to its rupture.

Due to its use in semiworks studies, all of the aqueous uranyl nitrate fed to the evaporator had at one time been in contact with solvent (30/70 TBP/kerosene). Although none of this organic solvent was thought to have been present in the feed, it was discovered, subsequent to the explosion, that kerosene diluent was present in the distillate catch tank. From the quantity of kerosene collected, and from phosphorus analysis of the evaporator residue, it was estimated that about 80 lbs. of tributyl phosphate (TBP) had been present in the evaporator charge. It was theorized that a reaction between uranyl nitrate and organic material could have occurred in the evaporator. This theory was supported by reports in the literature of such runaway reactions. The odor of butyric acid, present after the explosion, was additional evidence of an oxidation reaction involving TBP.

An experimental program was initiated to determine whether a violent reaction could be produced under conditions similar to those postulated to have existed at the time of the evaporator incident.

The experimental data showed that a vigorous reaction occurs between TBP and UN and/or HNO_3 at temperatures greater than 130°C. The severity of the reaction and the pressure developed were found to be directly affected by the amount of TBP present and the rate at which the mixture was brought to its initiation temperature.

It was tentatively concluded that UN-HNO_3-TBP is potentially a pressure producing system and reaction can be initiated if the system is heated above 130°C at atmospheric pressure. The pressure produced was found to be a function of the pressure in the system at the time of reaction and the amount of TBP present. Thus, at a TBP/UN ratio of 0.06 (estimated to have been the incident charge), a reaction occurring against a 50 psig backpressure (plugged column plates) would produce ~ 200 psi in about 0.2 seconds. The impact strength of the evaporator shell was estimated to be 120 to 150 psi.

The incident appeared to be the result of the following series of events:

- Presence of TBP (~ 80 lbs.) in the aqueous uranyl nitrate solution.
- Concentration of the solution to greater than 78% UN/total aqueous at temperatures greater than 130°C.
- Buildup of a 50 to 100 psi backpressure due to partially plugged plates.

This incident and the investigation subsequently led to establishing operating limits on organic concentrations and on temperature for evaporators at the Savannah River Plant.

The A-Line Explosion and Its Causes

On the morning of February 12, 1975, about 10:25 a.m., a denitrator emitted a dense cloud of gases into the denitrator room. Organic vapors contained in the emitted gases ignited and exploded, causing damage to the building and starting small fires. Personnel, warned by the gaseous cloud, had reached the exits to the room before the explosion, so injuries were minor. However, damage to the building required about 6 months to repair. Operation of the process resumed on August 11, 1975, following repairs, installation of safety equipment and control instrumentation, tests of the new equipment, and implementation of revised procedures designed to prevent recurrence of the incident.

Investigation revealed that the most probable cause of the explosion was the inadvertent introduction into Denitrator 4 of approximately 30 gallons of TBP in the form of $UO_2(NO_3)_2(TBP)_2$, its adduct with uranyl nitrate. TBP decomposes when heated with nitrates to temperatures >130°C and produces flammable gases. This reaction had been thoroughly studied as the result of an earlier evaporator explosion at the Savannah River Plant. In the A-Line incident, the decomposition became so rapid that the gases could not be removed through the off-gas line from the denitrator. These gases, along with part of the liquid contents of the denitrator, erupted through the vessel port into the adjacent area where they ignited and exploded. The denitrator was essentially undamaged. Hydrated uranium compounds were found inside the vessel, which indicated that the overall temperature in the denitrator had not exceeded 200°C. However, uranium dioxide was found on the walls of the denitrator room; therefore, local temperatures in the area of the explosion must have exceeded 1000°C, the temperature at which UO_3 decomposes to UO_2.

Investigation of the incident further revealed that the TBP introduced into Denitrator 4 was only part of the TBP that had accumulated in the process tanks over a period of time. About 28 gallons of 30% TBP and 45 gallons of 90% TBP in NPH* were recovered from various hold tanks and process vessels following the incident. The quantity involved in the explosion (~ 30 gallons of 100% TBP) was determined from phosphate analyses of the residues. Appreciable TBP, perhaps 15 to 20 additional gallons of 100% TBP, may have been in the eight batches processed prior to the explosion.

Such a quantity of TBP was not expected to accumulate within the system, nor was it expected that TBP could be pumped from one process tank to the next. Organic material such as TBP was assumed to float and be retained in the tanks. This organic material was removed periodically by skimming off the top layer of solution from each hold tank.

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* NPH: n-paraffin hydrocarbon, a kerosene containing predominantly 13- and 14-carbon n-paraffins and having an average molecular weight of 191.

The movement of the TBP through the A-Line process was attributed to the following sequence of events:

- About a year had elapsed since the last thorough cleanout of A-Line tanks. A cleanout had been planned, but had not been made at the startup of this processing campaign.

- One week prior to the explosion, one of the silica gel columns for removing residual fission products was flushed and regenerated. In the flushing procedure, uranium is flushed from the column with dilute nitric acid. The column is then regenerated by an upflow of oxalic acid solution. The oxalic acid solution is removed separately and discarded; the aqueous uranium flush solution is mixed with normal process solution (1EU concentrate) in tanks downstream from this column.

- The above flush-regenerate sequence was run five times in succession to maximize removal of fission products and reduce personnel exposure so as to allow visual inspection and replacement of the silica gel. In each sequence, the dilute nitric acid flush was made even though practically all of the uranium was presumably removed in the first flush. As a result, an unusually large flush solution was mixed with 1EU concentrate and sent through the process. Normally, fewer than five flushes are made if the silica gel is not to be inspected.

- Appreciable quantities of TBP-UN adduct probably had accumulated in the process tanks over a long time. The slight solubility of TBP in the UN solution is considerably decreased in the first evaporation; and thus, even if all undissolved TBP is removed prior to evaporation, there is a ready mechanism for slow accumulation of a separate phase in the tanks downstream.

- It is also possible that the silica gel columns acted as de-entrainment columns, and that the flushes contained some TBP-UN washed from the column.

- When the aqueous phase in each tank became sufficiently dilute from the addition of the flushes, the organic layer unexpectedly settled at the bottom of the tanks and was pumped forward through the process. The specific gravities of UN solutions in the first two tanks were reduced to 1.19 and 1.35, respectively; the specific gravity of organic material in these tanks was about 1.39.

- Hydrate evaporation of the flush-concentrate mixture was conducted without incident because temperatures in the hydrate evaporators are not high enough to cause rapid decomposition or reaction of TBP. Rapid reaction occurred on heating to higher temperatures in the denitrator, with the consequences previously described.

Investigation determined that this incident stemmed from both procedural and technical deficiencies in the operation of the process.

Procedural deficiencies include ambiguities in some procedures enabling Production personnel to follow the requirements without achieving the intents of the procedures. In addition, sampling and removing organic layers were not being done as frequently as specified in the procedures, because a high degree of confidence had arisen in the effectiveness of the equipment for separating and retaining organic material.

It had long been established, however, that these organic layers would not float on a more dilute aqueous solution, but could sink and might therefore be pumped forward from the bottom of the tank. The specific gravity of the organic phase depends on the concentration of TBP in the organic phases and on the concentration of uranium in the aqueous phase. This possibility was not mentioned in the process documentation available to operating personnel; hence, they were not aware that conditions could exist in which the process tanks were ineffective for separating and retaining organic material.

Lessons Learned

A number of lessons were learned from both incidents, including:

- Literature reports of the instability of mixtures of tributylphosphate and uranyl nitrate were not adequately investigated or heeded prior to operating the equipment at the semiworks.

- Lessons learned in early years are soon forgotten if not routinely reviewed. Since 1974, the Savannah River Laboratory has maintained a comprehensive data bank of incidents of process upsets, human errors, equipment failure, and procedural problems to aid in overcoming this. About 115,000 events are currently catalogued. The data bank serves as the primary basis for mandatory five-year reanalyses of all designated facilities in the reprocessing areas. These updated reports include trend analyses of the significant events.

- The unexpected usually occurs during times of nonstandard operation. In the case of the denitrator incident, nonstandard flush solutions were being processed in which the offending material sank below the aqueous layer rather than floating as it would have under standard operating conditions.
- People tend to become complacent in observing for rare conditions, especially if operating experience has been favorable. Lack of adequate analysis for the organic materials is such a case.
- Technical data are not always transmitted to those who need to know; specifically, that a phase inversion could occur under certain conditions.
- It was not recognized that a quantity of organic material might be safe in an evaporator (where the temperature is less than 130°C), but could be unsafe in a denitrator (where the temperature routinely reaches 225°C). Rather, the converse was believed true; hydrate evaporators were placed in remote areas behind shielding, while denitrators are in an open room where they are directly maintained during operation.

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