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The Red-Oil Problem and Its Impact on Purex Safety

D. O. Campbell
J. C. Mailen

CONSOLIDATED FUEL REPROCESSING PROGRAM

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THE RED-OIL PROBLEM AND ITS IMPACT ON PUREX SAFETY

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Chemical Technology Division

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J. C. Mailen

ABSTRACT

There have been a few incidents in which a chemically unstable composition was formed during a reprocessing operation and the material then decomposed rapidly, with the result that the pressure inside the equipment increased and caused some significant effect. The consequences have varied from a rupture of the process vessel to ejection of decomposition gases, the vessel contents, or both. These incidents were restricted to uranyl nitrate evaporators or calciners operating at elevated temperatures. In each case, the processing operation was nonroutine, large amounts of the organic phase containing tri-*n*-butyl phosphate (TBP) and extracted uranium nitrate were present, and conditions were outside the normal range.

The problem was attributed to (1) the presence of metal nitrate–TBP complexes; (2) the formation of degraded organic compounds, at least partly derived from the diluent; or (3) a combination of both. The term "red oil" is commonly used to describe these materials. The red oil entered into an exothermic chemical decomposition that increased in rate as the temperature rose, leading to excess pressure, rupture of the equipment, and dispersal of the contents.

Laboratory studies led to an understanding of the reaction and of ways to avoid the problem. The most important restrictions are (1) to limit the amount of organic phase that enters these high-temperature operations and (2) to maintain the temperature low enough that the decomposition reaction does not release heat faster than it can be removed by the system, even if reactive organic material is present. The first requirement limits the amount of energy available for release. The second requirement limits the rate of energy release and avoids the autocatalytic cycle between increasing temperature and increasing reaction rate.

There is evidence that the maximum "safe" temperature depends on the chemical system, particularly the nature of the TBP diluent. It appears to be lower with diluents high in naphthene (cyclic) hydrocarbons, as were diluents used many years ago when the first two incidents occurred. Under

the worst conditions, this safe temperature is ~135°C; and maximum permissible temperatures in the range of 125 to 130°C are generally specified. More recent studies indicate that, when pure normal hydrocarbon diluents are used, unstable diluent degradation products are not formed; and the problem is then caused by compounds such as $UO_2(NO_3)_2 \cdot 2TBP$. In this case, safe temperatures are above 150°C. However, an increase in the maximum permissible temperature has not been recommended.

The plutonium nitrate–TBP complex shows a reactivity similar to that of the uranium complex, so the same considerations must be applied. The nitric acid–TBP complex is considerably less reactive, requiring higher initiation temperatures even with very high nitric acid concentrations. Therefore, in the absence of an extractable metal (as in a waste evaporator), normal operating temperatures are well below the region of concern.

1. INTRODUCTION

The term "red oil" has been used since two incidents occurred in 1953, one at Hanford and one at Savannah River, involving rapid chemical decomposition reactions that overpressurized semiworks or pilot-plant evaporators for the concentration of uranyl nitrate. Examination of the residue remaining after the incidents identified a red-colored organic phase containing uranium, TBP, nitrate, and probably additional organic material derived from the diluent; this is presumably the source of the name. Laboratory studies were undertaken at both sites, and it was reported that red oil was readily produced by refluxing TBP, nitric acid, uranium or plutonium, and the diluent which, at that time, contained a large fraction of naphthenes.

At elevated temperatures, the red oil or other constituents of the system could react or decompose exothermically at a rate sufficiently rapid that heat was generated faster than it could be removed by available heat transfer mechanisms. This caused a further temperature increase that led to an even more rapid reaction. The reaction, which was generally accompanied by foaming and by the evolution of brown-colored gases (N_2O_4), apparently occurred to a smaller and limited extent on numerous occasions. However, in these two cases, gaseous reaction products and steam eventually caused overpressurization, leading to ejection of the contents and, in the one case, rupture of the equipment.

Conditions were defined which prevented the rapid decomposition reaction from starting. One constraint was to limit the amount of organic material present, but a more fundamental one was to ensure that the temperature could not exceed a specified value in the range of 125 to 135°C. Accordingly, this problem is not of significance in those parts of the Purex process that do not operate at high temperatures. However, it must be considered in regard to any evaporators that may reach such temperatures and also to calciners, which necessarily operate at high temperatures.

The major mechanisms for heat removal are heat transfer to the outside of the equipment, which is slow and limited, and evaporation of water or some other constituent, which is fast. As long as the system is boiling and a substantial amount of water is present, the latter mechanism will generate steam and limit the temperature rise even if an exothermic reaction is initiated, thereby limiting the rate of that reaction. As evaporation proceeds beyond the composition of uranyl nitrate hexahydrate, progressively less water is left to evaporate and the boiling point rises rapidly. Accordingly, a temperature increase leading to an unstable situation can occur.

Over the years since the first two incidents, the diluents used in the Purex process have been changed, in most reprocessing plants, to normal paraffin hydrocarbon mixtures having very low naphthene contents. More recent laboratory studies with such diluents have been unable to duplicate the earlier reports of red-oil formation or of material that would enter into an uncontrolled decomposition reaction at such low temperatures. However, other materials that may be present in evaporators do react in a similar way, although only at temperatures considerably higher than 135°C. These include adducts such as $UO_2(NO_3)_2 \cdot 2TBP$,

$Pu(NO_3)_4 \cdot 2TBP$, $HNO_3 \cdot TBP$, etc. Compounds of this type are explosives in the usual sense of the word.

A third incident, which occurred in 1975 at the Savannah River Plant (SRP) in a calciner used to convert $UO_2(NO_3)_2 \cdot 6H_2O$ [UNH] to UO_3, was attributed to the reaction of the $UO_2(NO_3)_2 \cdot 2TBP$ adduct. This reaction started at a temperature believed to be in excess of 170°C. Extensive laboratory data are available to verify that compounds such as these will enter into rapid exothermic decomposition reactions if the temperature becomes high enough, as it must in a calciner. However, these adducts are not identical to red oil (as it was originally defined), although they may be present in red oil; and they may have been a major component contributing to the incidents in 1953.

1.1 INFORMATION SOURCES

The compilation of reports[1-21] supplied by the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC) was a major source of information for this study. Some additional literature sources were obtained from references listed in some of the papers in the compilation, and a few newer reports were identified. In general, all these reports are of two types: (1) they resulted directly from the three incidents in the United States, giving descriptions of the events as they occurred and reporting on research studies to gain an understanding of them; or (2) they were the result of reevaluations of these same reports, which were conducted at a later time in support of proposed reprocessing operations, and of research work relating the earlier information to those operations.

Some more recent discussions appear in books concerned with reprocessing.[2] In addition, an investigation is currently under way at Kernforschungszentrum Karlsruhe (KFK) in Germany, which has resulted in one publication[22] involving the uranium system; it is our understanding that a similar publication relating to the plutonium system will be released shortly. A very recent reexamination of unexpected incidents in reprocessing operations has been completed at Savannah River.[23]

However, we were unable to identify any new experimental work on this problem in the United States during the last few years.

1.2 DEFINITION OF TERMS

There is some confusion about names for this and certain other phenomena. The term "red oil" was probably applied because some red-colored organic "oil" was found in the residue after the two incidents in 1953, and a red organic liquid was formed in laboratory studies conducted at the time. The red color probably resulted from the nitration of relatively unstable constituents in the diluent, and these diluent degradation products are likely to be responsible for the lower initiation temperature of red oil, as compared with that of the adducts noted above. Once decomposition started and the temperature increased, however, the major reactants were probably these adducts.

This term, red oil, subsequently came to be used in the United States to describe any organic material that appeared during concentration operations in the HNO_3–heavy-metal nitrate–TBP–diluent system and then decomposed exothermically. It should be realized, however, that the red-oil incidents in 1953 almost certainly included a distinct factor, namely the high naphthene content of the diluent, that is not present in the Purex process today [except in the United Kingdom (UK)]. It would be less confusing if the term could be applied only to unknown mixtures involving the diluent and degradation products, and not to the adducts that can be identified and studied quantitatively.

In the broad sense, red oil is any organic-based material that forms or accumulates during an operation at high temperature (e.g., evaporation) and is unstable, as the temperature increases, to a decomposition reaction yielding gaseous products and heat. The material may be a degraded organic reaction product (such as nitrated or oxidized diluent or butyl groups from the TBP) or an organic-nitrate complex such as the $UO_2(NO_3)_2 \cdot 2TBP$ adduct, or possibly something else. However, the association of organic material and nitrate within the same molecular species is probably necessary in order for the material to decompose exothermically.

Unfortunately, the term "third phase" was sometimes applied to this same phenomenon, especially in the United Kingdom. There are two different situations in solvent extraction systems which also have been referred to as third-phase formation, and which may become confused with the red-oil problem, as follows:

1. A normal aqueous phase, a normal organic phase, and a reasonably stable emulsion (sometimes called a third phase) consisting of a mixture of the two normal phases, are present. In this case the emulsion is not a separate phase, but a mixture of the other two. This can cause operational problems but does not present a special safety risk, in itself. It is not considered further in this discussion.

2. A normal aqueous phase and two organic phases, (a) a light phase consisting primarily of diluent with much less TBP and extracted species than the normal organic phase, and (b) a dense phase containing very little diluent but much more TBP and extracted metal nitrate or nitric acid than the normal organic phase, are present. All three phases are, or can be, in chemical equilibrium with each other at normal temperatures and with high metal loadings in the organic. This phenomenon occurs more commonly, or over a wider range of conditions, when tetravalent metals (thorium, plutonium) are present, but it can also exist with uranium and even nitric acid alone.

   This situation is generally considered intolerable for process operation and is avoided. In limited cases, however, it might occur as a transient condition in only part of a contactor bank without destroying the operability of the system. This phenomenon, properly called third-phase formation, is described in numerous publications, including one of the references provided for review,[1] and in a recent UK publication defining the boundaries for third-phase formation in Purex systems with different diluents.[24]

   The organic phase of high TBP concentration also has high contents of extracted heavy metal and nitrate. It can be similar, or perhaps even identical in the limiting case, to the adducts such as $UO_2(NO_3)_2 \cdot 2TBP$ or $HUO_2(NO_3)_3 \cdot 2TBP$, which are commonly included in the concept of red oil, as noted above, and were the cause of the incident in 1975 at Savannah River. However, it probably cannot encounter an environment conducive to thermal decomposition, since third-phase formation is reversed by increasing temperatures. There is no indication that third-phase formation directly presents a special safety problem with regard to chemical instability; on the other hand, it could present a criticality problem and it might cause a phase inversion leading to organic following the aqueous stream.

Even if red oil is chemically similar to the heavy organic phase, it is formed by a different mechanism (evaporation of aqueous-organic mixtures and possibly chemical degradation of the diluent). Thus, third-phase formation should not lead directly to red oil, and, therefore, is not considered further in this discussion.

In contrast to the two materials defined above, red oil is a new chemical species or mixture of species that is (1) formed at high temperatures, (2) is different from the normal phases, and (3) is not necessarily in equilibrium with any other phases present. It has caused "explosions" in a few instances because it can chemically react at a sufficiently rapid rate that the pressure within the process equipment increases to a value above that which the equipment can contain. Laboratory studies conducted following these incidents have allowed us to develop a reasonably good understanding of its properties. However, different compositions of red oil can probably be formed, depending on the specific conditions and materials present, so it represents more than a single constituent. The remainder of this discussion will be concerned with red oil.

2. SUMMARY OF DESTRUCTIVE INCIDENTS

Two incidents involving unanticipated rapid chemical reactions in process equipment occurred in the United States in 1953; a third occurred in 1975. The first was the TNX semiworks evaporator incident at the SRP on January 12, 1953.[9,10] This was followed by the uranium concentrator incident in Building 321 at Hanford on July 1, 1953.[14,25] Approximately 22 years later, an incident occurred on February 12, 1975, in the A-line calciner at the SRP.[9,11,12]

2.1 EVAPORATOR INCIDENTS IN 1953

Two incidents, one at Savannah River and one at Hanford, occurred in 1953. Both involved reasonably large evaporators that were used to concentrate uranium nitrate–nitric acid product solutions. During normal evaporation of water and nitric acid, the uranyl nitrate solution increases in concentration to a composition approximating $UO_2(NO_3)_2 \cdot 6H_2O$, with a boiling point of 129°C. Further heating will increase the boiling point as the water of hydration is removed; and finally, at about 200°C, the nitrate begins to decompose to UO_3; this denitration becomes vigorous at about 220°C. At the same time, the solution becomes more viscous and eventually a solid product is formed.

If some of the TBP-diluent organic phase is introduced into the process sequence, it will evaporate to some extent or nearly completely, depending on the conditions, due to steam-distillation. The diluent will evaporate more rapidly than the TBP, leaving a higher-boiling, TBP-rich composition that will complex uranyl nitrate and can approach the composition of the adducts noted earlier. If organic remains in the evaporator long enough and its constituents are not chemically stable, decomposition and reaction can occur, leading to oxidized and nitrated species that may be subject to exothermic decomposition at elevated temperatures. Such a problem arises only when several conditions exist in combination.

<u>The Hanford incident</u> took place during the very first operation of a new concentrator with uranium present, when a feed pump to the evaporator failed. As a result of this failure, the evaporation process continued to a higher concentration than normal and the temperature increased to "incipient calcination." The decomposition reaction was characterized by emission of brown fumes from the concentrator vent, but no destruction of the equipment occurred.

The concentrator contained vertical–tube heaters to boil the solution, within a 3-ft-diam steam chest. The stripping section, located above the boiler, was 6 ft in diameter with an 18-ft-long section packed with 2-in. Raschig rings for removal by steam-stripping of organic phase that might accompany the aqueous feed. Above the stripping section, there was an additional 3-ft-long packed section for de-entrainment. The vapor exiting the tower was condensed by a jet condenser that was vented to the atmosphere. The concentrator was fed directly from the aqueous effluent de-entrainment section of the uranium strip column, using a pump and a control valve to regulate the column interface.

Using manual control, the steam flow (100-psi steam supply) was being adjusted to maintain a specified liquid density in the concentrator as dilute feed was pumped in from the strip column. Feed flow was interrupted several times because of interactions between the feed pump, the flow control valve, and the column interface controller. During one such interruption, the liquid level fell below the upper dip tube of a differential-pressure density device, thereby giving an indicated density reading lower than the true value. As a result, the steam flow was not decreased; and both the concentration and the temperature increased to excessive values. The reaction that followed caused emission of brown fumes from the condenser vent, a hissing noise, and the odor of butyric acid.

The rapid evolution of gases was relieved by the large cross-sectional area of the stripping section, and the equipment was not significantly damaged. However, the Raschig rings showed evidence of damage, and the feed distributor showed signs of having been battered by the ceramic rings. The uranium content of the residue was estimated to vary from about 8 to 72%, with the mass having a "putty-like" consistency. The red-oil content of the residue was estimated at between 3 and 10 gal; thus, a large amount of organic (probably many tens of liters) had been carried into the evaporator during the short time (about 90 min) that the system had been operated. "Incipient calcination" implies a temperature much higher than 135°C, and probably near or above 160°C, when the reaction was initiated.

The Savannah River incident was somewhat similar, although the reaction was more destructive, ripping the evaporator pot into six major pieces and distorting the bubble-cap trays. A uranyl nitrate solution was being concentrated to remove excess nitric acid in an unusual (or nonroutine) operation and was inadvertently overconcentrated to the point of "incipient calcination." In this case, the temperature measurement was inoperative and the density measurement was off-scale; so, as in the previous case, the condition of the system (both temperature and composition) was not known.

The reaction caused a "rumbling noise," followed by the emission of orange fumes along with a "high-pitched roar," immediately before rupture of the pot. The TNX evaporator contained steam coils in a 3-ft-diam pot, which was topped, successively, by a 6-ft-diam shell and a 2.5-ft-diam tower containing eight bubble-cap trays. After the incident, the lower bubble-cap trays were partially plugged with solids, probably as a result of the foaming of the liquid during the decomposition reaction. The increased pressure, because of the plugging, would cause the reaction to be more violent.

Examination of the residue after the incident showed the presence of hydrated uranium compounds; thus, the overall temperature was <200°C. However, UO_2 was found in the room outside the evaporator, so localized temperatures exceeded 1000°C. The residue also contained phosphorus from the TBP. It was estimated that 80 lb of TBP had been present in the evaporator, probably complexed with uranyl nitrate as $UO_2(NO_3)_2 \cdot 2TBP$. As for the Hanford incident, this corresponds to many tens of liters (probably more than a hundred) of organic.

2.2 DENITRATOR INCIDENT IN 1975

The second incident at Savannah River occurred on February 2, 1975, in the A-line batch calciner (or denitrator). The uranium product from the Purex process is first concentrated to about 400 g/L (boiling point, 106°C, specific gravity, 1.5) in one of a set of evaporators and then further concentrated in a second set of "hydrate" evaporators to the approximate composition of UNH $[UO_2(NO_3)_2 \cdot 6H_2O]$ at about 1200 g/L (to a boiling point of 129°C). The uranium content is at least 45 wt % but not more than 60 wt %. Different reports state that the hydrate evaporator was heated with <80-psig steam to maintain a temperature

<160°C to prevent denitration[11] or with 25-psig steam with a maximum temperature of 129°C.[12]

This molten UNH is then transferred to a pot calciner and heated to much higher temperatures to dehydrate and denitrate it, yielding UO_3. The incident occurred during this operation. Foaming was sometimes observed during the boil-off of HNO_3 and water. One provision for controlling this situation is to heat slowly through the temperature range 120 to 200°C. At about 200°C, foaming normally ceases and the denitration reaction begins, becoming vigorous at about 220°C. Heating is continued to yield UO_3.

The incident occurred during denitration of a series of nonroutine batches that had presented a foaming problem. It should be noted that the melt could be observed, and foaming during the heating below 200°C was not unusual. In this case, such foaming had occurred but had nearly stopped; the skin temperature of the pot was then increased to 250°C. Foaming ceased during the following 80 min, after which time the temperature was increased. About 2 min later, the incident began with the release of red-brown fumes.

The operators took certain preventive actions over a period of a few seconds before starting to exit as brown fumes filled the room. Within several seconds, the contents of the calciner were forcibly ejected into the room, and then an explosion occurred, which caused only minor injuries. This was followed by some small, isolated fires that were readily contained. The explosion occurred outside the calciner and was caused by the ignition of organic vapors which resulted from the decomposition of the uranium nitrate–TBP complex and were mixed with air in the room. There was extensive damage to the room, but none to the denitrator.

Analytical data showed that the temperature of some portion of the calciner contents was <200°C. It was estimated that the surface temperature of the pot may have been about 280°C,[11] and that the temperature of the bulk of the denitrator contents was between 150 and 160°C.[12] Based on analyses of many samples, it was further estimated that the reaction involved decomposition of ~190 kg of the $UO_2(NO_3)_2 \cdot 2TBP$ adduct (containing ~110 kg of TBP), which began at about 170°C. Such a reaction would release ~500 m^3 (STP) of gas at a maximum rate of about 18 m^3/s. The maximum energy release when this gas mixed with air and exploded was estimated to be $\sim 7 \times 10^5$ kcal.

It is clear that any TBP that accompanies the UNH and enters the calciner will undergo a chemical decomposition, because the calciner necessarily operates at a temperature high enough to initiate the reaction. The decomposition reaction occurs in the temperature range from somewhat >130°C to <200°C and is complete before uranyl nitrate denitration becomes significant (at ~200°C). It should also be recognized that a small amount of TBP will normally be present (unless unusual means are taken to remove it) because of entrainment, the finite solubility of TBP in aqueous solutions, the decrease in volume during evaporation, and the decrease in TBP solubility as the uranyl nitrate concentration increases.

Generally, the quantity of TBP that accompanies the aqueous uranyl nitrate is small enough that it causes no problem. The resulting heat of reaction does not appreciably increase the temperature of the system, and the gaseous products released are readily handled by the off-gas system. However, in the present case, large quantities of TBP had accumulated in hold tanks and process vessels. After the incident, 28 gal of 30% TBP and 45 gal of 90% TBP in NPH were recovered from such tanks, in addition to the ~30 gal of 100% TBP in the calciner at the time of the accident. It is clear that there have been occasions when quite large amounts of TBP were inadvertently supplied to the evaporators and, in this case, the calciners. Under such circumstances, there is no doubt that an exothermic reaction will occur; the question is how rapid and extensive the reaction will be.

All of these incidents had several factors in common. First, they involved a nonroutine operation with feed material substantially different from the normal; as a result, large quantities of organic material were unknowingly introduced into the system. Second, they involved operation at high temperature (certainly above 135°C and probably above 160°C) because of the absence of temperature measurement. Third, they involved concentration of uranium nitrate beyond the UNH composition, again because of the absence of instrumentation (density measurement) in the two evaporator cases. Because of the low residual water content in the overconcentrated uranyl nitrate the evaporation of water was no longer an adequate mechanism for heat removal, as it is during evaporation at lower uranium concentrations. Accordingly, the conditions necessary for a runaway reaction were present.

3. LABORATORY STUDIES

Laboratory studies of energetic reactions involving nitric acid, diluent, TBP, and uranyl nitrate have been carried out at Hanford,[3,5,7] the Savannah River Laboratory,[4,10,26] GA Technologies,[13] and in Germany.[22] All of these investigations showed that energetic reactions between uranyl nitrate and red oil occur only under conditions of incipient calcination when operating at atmospheric pressure. The reaction is usually accompanied (or preceded) by extensive foaming and a rapid evolution of nitrogen oxides. Confinement of the reaction mixture can result in more rapid reactions and very high pressures in equipment.[10] Plutonyl nitrate[7] and thorium nitrate[13] can participate in the reactions similarly to uranyl nitrate.

3.1 EFFECT OF DILUENT

The early experiments (about 1953) in forming red oil used Shell Spray Base, a diluent which is much more prone to chemical attack by nitric acid than modern diluents such as the paraffinic hydrocarbons. Later studies which attempted to duplicate these earlier results have used solvents that are not identical to those used earlier. The solvent used in the Hanford Plant at the time of the accident and during laboratory studies which succeeded in producing red oil was Shell Spray Base.[3,5] This solvent contained <1 vol % of aromatics but 20 to 30 vol % of naphthas (saturated ring or cyclic compounds).[13] Chemical stability data are not available for this material,[27] but are available for Shell Purex Diluent, which may be similar.

Amsco (unknown grade, but possibly 125-82 for which information is available[27]) was used at the SRP in 1953. Amsco 125-82, which is a specially prepared aviation naphtha, consists of a mixture of (1) five- and six-carbon naphthas that have various short-, normal-, and branched-chain substituents; (2) branched-chain hydrocarbons; (3) a small amount (a few percent) of normal hydrocarbons; and (4) a still smaller amount (~1%) of olefinic species. At the time of the second incident in the calciner at Savannah River the diluent was NPH, a mixture of C_{10} to C_{14} n-paraffin hydrocarbons with very low contents of other constituents.

The order of resistance to chemical degradation by nitric acid is: n-paraffin (most stable) > branched-chain aliphatic >> cyclic (naphthenes). The least stable position is the point of branching on naphthene rings. This can be seen in the reported order of resistance to degradation by nitric acid[27] as NPH > Amsco 125-82 >> Ultrasene > Shell Purex Diluent, all of which have been used as diluents. The latter may be identical, or is at least similar in chemical resistance, to Shell Spray Base. Thus, the likelihood that nitration of the diluent was a factor is significant for the Hanford incident and probably also for the first Savannah River incident, but quite small for the later Savannah River incident. While the presence of nitrated diluents may allow the initiation of heat-generating reactions at somewhat lower temperatures, in all cases it is likely that most of the energy was released by decomposition of the uranyl nitrate and nitric acid complexes with TBP.

3.2 CONCLUSIONS FROM LABORATORY STUDIES

The following conclusions may be drawn from the laboratory studies:

1. The only conditions that have produced red oil involve total reflux with a substantial quantity of organic phase in contact with nitric acid containing uranium or thorium. Red oil was formed only when the organic phase contained TBP and when the diluent contained substantial quantities of naphthenic compounds.[3,5,7] Red oil was not formed from the diluent containing naphthenic compounds in the

absence of TBP.[3] Significantly, the formation of red oil was not possible when using the newer, saturated straight-chain hydrocarbon diluents.[13,23]

2. When laboratory concentrators were operated with removal of a portion of the distillate, as in the German studies,[23] practically all of the diluent and most of the TBP were steam-stripped from the aqueous phase in the pot.

3. The uranium–TBP adduct can be decomposed in rapid chemical reactions if present when the temperature reaches at least ~150°C (only the early work at Savannah River[10] indicates that the reaction may start at 135°C). The plutonium–TBP adduct decomposes at approximately the same temperature as does the uranium adduct.[7]

3.3 SUMMARY OF EXPERIMENTAL STUDIES

3.3.1 Tests with Shell Spray Base

Red oil for use in these studies was readily prepared by the following method.[3] A 100-mL volume of 30% TBP–70% Shell Spray Base was added to 800 mL of 50% IAW–50% ICU (resulting aqueous concentration = 0.1 $\underline{M}$ UNH and 1.1 $\underline{M}$ HNO_3) and refluxed for 72 h before a third heavy phase with a specific gravity of 1.14 was observed in the reflux mixture. The mixture was then evaporated to approximately one-third volume, and the specific gravity of the yellow-orange heavy phase reached 1.36. This phase (75 mL) was the red oil used in the various experiments.

Significantly, the Shell Spray Base was said to be only slightly attacked by refluxing with concentrated nitric acid, indicating that the mixture containing TBP and uranyl nitrate was more reactive, perhaps by forming (or retaining, as the TBP complex with HNO_2) more NO_x. It is known that NO_2 is the reactive ingredient in the attack of nitric acid on hydrocarbons.[28] In recent years, this procedure for making red oil has been repeated[13,22] using $\underline{n}$-paraffin diluents, but no red oil product was formed. In contrast, tests using a highly naphthenic diluent were successful in producing red oil.[13]

The conclusions of the early Hanford studies[3] were as follows:

1. A rapid reaction of explosive violence is obtainable from mixtures of red oil and uranium solutions only under conditions of incipient calcination (temperature, ~150 to 160°C).
2. Eight experiments under reflux conditions (for 6 to 8 h) to simulate the Purex uranium concentrators and three additional reflux experiments simulating the Purex waste concentrators (UNH concentration = 0.1 M) resulted in a slow evolution of NO_2 but no uncontrolled reaction of explosive violence.
3. The residual solutions from the reflux studies, when combined and evaporated, showed rapid decomposition only as calcining conditions were approached. The violence of the decomposition appears to be a function of the absolute amount of red oil present and the ratio of UNH to red oil.

In other studies,[7] the evaporation of TBP–plutonium nitrate mixtures with a TBP/plutonium ratio of 0.15 or higher led to violent reactions when evaporations were carried out to pot temperatures >150°C. No reactivity was noted at lower weight ratios or lower temperatures. This result is comparable to that found in studies made at Savannah River,[10] where a critical ratio of 0.12 was found for TBP/uranium nitrate (see next section).

3.3.2 Studies Using Amsco

A study at Savannah River[10] following the incident in the TNX evaporator used small-scale atmospheric distillations of various mixtures of uranyl nitrate, HNO_3, Amsco, TBP, and water to indicate the following:

1. TBP must be present to promote a noticeable exothermic reaction.
2. Mixtures of TBP, UNH, HNO_3, and water will react exothermically with varying degrees of vigor, depending on the heating rate and composition, but no reaction will take place at atmospheric pressure until enough water and HNO_3 have been distilled away to permit the temperature of the charge to rise above 135°C [78% uranyl nitrate (UN)].
3. The vigorousness of the reaction (observed by the extent of the sudden temperature rise) increases as the TBP/UN ratio is increased, but in no case was any reaction observed at a ratio below 0.12 under the conditions investigated.

4. Less TBP is required to promote a self-sustained reaction at a high heating rate (1°C/min) than at a low heating rate (0.1°C/min).

5. The TBP/UNH/water mixtures will yield a self-sustained reaction, but the reaction is more vigorous when HNO_3 is present.

6. The TBP/HNO_3/water system will react with considerable violence if heated rapidly to temperatures above 150°C.

7. Tests in closed bombs indicated that at elevated pressures lower concentrations of reactants can give self-sustained reactions, but only at the higher temperatures that are attainable.

8. Based on the information revealed by the two series of laboratory experiments and the probable presence of TBP in the TNX evaporator, it was concluded that an exothermic reaction between TBP and UNH or between TBP and HNO_3, or both, was responsible, either directly or indirectly, for the rupture of the evaporator.

3.3.3 Savannah River Studies with NPH Diluent

After the second incident at Savannah River, laboratory studies were initated to examine the following areas relating to the properties of TBP-HNO_3-UN systems, as well as chemical reactions that take place in the systems.[26] In this incident, chemical decomposition released an organic vapor that mixed with air in the operating room and then exploded, so there was interest in the gaseous products of the decomposition reaction. The data available are summarized below.[26]

1. **Distribution of TBP into Uranyl Nitrate Solutions**. TBP concentrations were determined by both total phosphate and infrared analyses. These measurements were then compared with values obtained from a tracer method using ^{32}P. The counting method gave intermediate values. The results include plots of distribution as a function of uranyl nitrate concentration. The distribution data at elevated temperature are not usable since hydrolysis was significant during the long equilibration times used (up to 80 h).

2. **Specific Gravity of TBP (in equilibrium with UNH solutions) and Uranyl Nitrate Solutions**. Specific gravities were measured using standard methods with volumetric flasks. The effect of temperature was determined.

3. **Thermal Decomposition of Pure Adduct**. Thermogravimetric analysis (TGA) studies revealed two successive reactions at temperatures ≥170°C, but only one reaction at lower temperatures. The rate equation for the first reaction was determined (see Table 1) for

Table 1. Least-squares fit of Arrhenius equation to adduct decomposition rate constants

Source	Slope	Intercept	E_a (kcal/mol)
Helium atmosphere	-6603	14.85	30.3
80% He–20% O_2 atmosphere	-5158	11.59	23.6
Combined data	-5704	12.81	26.1
Nichols[a]	-6067	13.96	27.8[b]

[a] G. S. Nichols, DP-526 (1960).

[b] Nichols reported E_a value of 26.8 kcal/mol in DP-526 (1960).

decomposition in helium and in 80% helium–20% oxygen; data from a previous study are also given.[4] The data followed first-order kinetics for the disappearance of adduct:

$$\log C_t = (-k_1/2.303)t + C_o \ ,$$

where C_t is the concentration of adduct at time t, k_1 is the first-order rate constant, t is the time in hours, and C_o is the initial concentration of adduct.

The composition of the off-gas from thermal decomposition was determined. It should be noted that the gas samples were collected by water displacement. This makes the concentrations of H_2O (not reported), NO, CO_2, NO_2 (not found), and any alcohols or organic acids (not found) too low. A thermogravimetric–mass spectral analysis indicated the presence of all these materials. The volume of gases collected was also not given; this would have allowed a material balance to be made on gases formed in the destruction of the adduct and would have allowed an accurate calculation of the heat of reaction.

4. <u>Effect of Heatup Rate on Initiation Temperature of Foaming</u>. A slight increase in the temperature at which foaming starts was observed when the heatup rate was increased.

5. <u>Effect of Adduct Concentration</u>. No foaming or fuming was observed at temperatures <130°C (evaporator conditions). Foaming started at $\geq$134°C, while fuming started at $\geq$150°C. The report gives a table showing the effect of adduct concentration. Brown fumes, indicating oxidation/reduction reactions, were not observed below 150°C and an adduct concentration of 0.1 vol %.

6. **Effect of Antifoam**. The addition of antifoam agents was studied. Such an agent does not appear to be necessary.

7. **Analysis of Gaseous Decomposition Products of a 1 vol % Adduct**. The report gives the effect of the decomposition temperature on the off-gas composition; again, very little combustible gas was formed.

8. **Calculation of Maximum Flammable Gas Evolution During Denitration**. A calculation based on the measured rate of decomposition and the assumed evolution of 3 mol of butyl compound per TBP was made. It appears that the experimental data of the report would predict that much less butyl compound than this is formed. In their tests, most of the butyl portion of TBP was apparently oxidized to CO_2 and H_2O.

Two derivative references[11,12] state that the Savannah River studies indicate an endothermic reaction, perhaps followed by an exothermic reaction. The original report[26] does not include any information indicating endothermicity; all that is given is the activation energy of the first decomposition reaction. The basis of this statement may lie in work done by other investigators.

3.3.4 Studies at GA Technologies

A new series of studies was initiated to examine safety in concentrators, as a part of the HTGR program.[13] This report attempted to duplicate the earlier Hanford work in the preparation of red oil using Chevron Deodorized Spray Base Solvent 450, a diluent which has ~63% naphthenic compounds. The results of this study led to the following conclusions:

1. The hydrocarbon diluent employed has an important role in solvent nitration.

2. The normal paraffin hydrocarbon (NPH) diluent currently being used in most fuel reprocessing studies is more resistant to nitration than diluents used in early plant applications of the Purex process. Red oil (an organic–phase mixture of heavy-metal nitrate and organic decomposition products) was not formed in tests using TBP/NPH as the solvent system during concentration of thorium and uranyl nitrate solutions under literature conditions[3] reported to produce red oil with Shell Spray Base. Red oil was produced when Chevron Deodorized Spray Base Solvent 450, which contains ~63% naphthenic compounds, was tested.

3. No vigorous, uncontrolled reactions were observed for the TBP/NPH/

temperatures up to 150°C under experimental conditions described in this paper.

4. The paper concludes that, with suitable concentrator design (to control foaming and to vent flammable gases), an inadvertent temperature excursion to 150°C does not constitute an undue safety hazard if a nitration-resistant diluent is used.

3.3.5 German Studies

The most recent study of vigorous reactions in concentrators was performed in Germany.[22] A series of tests was designed to determine the chemical identity of the compounds formed in evaporators, their formation conditions, and their thermochemical behavior. A laboratory circulation evaporator with feed solutions containing 70 g U/L in 0.1 $\underline{M}$ HNO_3 and varying amounts of TBP was used in the studies. The solutions were concentrated sufficiently to give uranium contents up to 480 g/L.

The results of the various tests performed are summarized in the subsections that follow.

3.3.5.1 First Group of Tests

Test 1 was made up with 0.1 $\underline{M}$ HNO_3 that had been equilibrated with TBP to contain 180 to 200 mg TBP/L. Concentrate from test 1 was diluted with water that had been equilibrated with TBP to prepare the feeds for subsequent tests. Seven concentrator runs were performed; nearly all the TBP was recovered in the condensate (it had been steam-stripped) and 2% in the bottoms. The TBP material balance was 98 to 100%. Between 15 and 30 mg HDBP/L were then added, and the concentrator was operated as before; this yielded a "heavy organic" with a TBP/DBP ratio of ~1.

3.3.5.2 Second Group of Tests

The method used in these tests was to add 0.2 vol % of entrained (30 vol % TBP-Alkan) solvent to the UNH and evaporate the mixture. In one series of evaporations, the concentration step was repeated three times and yielded 6 mL of heavy organic phase. In another series, evaporation was repeated four times to yield 3 mL of heavy organic. The heavy organic was a mixture of TBP and DBP complexes of uranium.

3.3.5.3 Third Group of Tests

The behavior of $UO_2(NO_3)_2 \cdot 2TBP$ in TBP-saturated UNH solutions was examined. (Note that the studies in the first two groups of tests used UNH, not the complex.) A 20-mL volume of solution was introduced into the evaporator feed (5 L). One set of evaporations was performed without added HDBP, another with 20 mg/L HDBP, and a third with 300 mg/L HDBP. The quantity of organic phase that did not disappear through steam-stripping of TBP increased with increasing DBP content; and the residual organic composition tended toward a TBP/DBP ratio of 1, perhaps indicating the formula $UO_2(NO_3) \cdot DBP \cdot TBP$. Such a formula would agree with results of other studies, indicating that a stable complex of uranium with one TBP and one DBP molecule is formed. At ORNL, we have observed that low-acid stripping of uranium from a solvent containing DBP (30% TBP) removes uranium efficiently only down to a U/DBP ratio of 1, suggesting the formation of a stable uranyl nitrate complex with one TBP and one DBP molecule.

3.3.5.4 TGA on $UO_2(NO_3)_2 \cdot 2TBP$

Thermogravimetric analyses indicated two decomposition reactions that occurred at 225°C (enthalpy of -331 KJ/mol) and 289°C (enthalpy of +216 KJ/mol), respectively. These reactions were identified as (1) oxidation of two butyl groups by the nitrate anions and (2) dealkylation of four butyl groups to yield butene. The latter reaction is the source of the butene that has been implicated in the fire at the SRP. The self-ignition temperature of the gas phase was estimated to be 176°C.

3.3.5.5 TGA on DBP and MBP Complexes

All of the reactions were found to be endothermic. The reactions were identified as dealkylation to release butene between 180 and 192°C (MBP complexes only) and dehydration at 285 to 305°C.

Studies of the thermal decomposition of evaporator residues showed that the reactions were similar to those with the TBP complex, but with a lower energy yield for the exothermic reaction since some nitrate had been substituted by DBP.

Red oil was not observed in any of the German studies. The authors conclude that, even with reasonable entrainment, no operational problems such as exothermal excursions should be expected.

4. PREVENTION OF THE RED-OIL PROBLEM

4.1 IMPACT OF RED OIL ON THE FLOWSHEET

All of the red-oil incidents have been associated with gross operational errors with uranium product evaporators or calciners in which very large quantities of organic were unknowingly added to a system that was taken to a high temperature. The reactions involving uranium have been thoroughly studied over a long time span. Precautions necessary to effectively eliminate the likelihood of such a reaction have been defined. However, various modifications of the flowsheet have been proposed to further reduce the probability of energetic chemical reactions.

Laboratory data indicate that the TBP must be present at some fraction of the uranyl (or other extractable metal) nitrate content, with that fraction depending on several factors such as the size of the charge, composition, overpressure, etc. At atmospheric pressure, the TBP/U mol ratio probably must be in the vicinity of 0.1 or higher for the decomposition reaction to become autocatalytic. Thus, it is not necessary to reduce the organic to a very low value, but it is necessary to avoid introducing gross amounts. This can be accomplished by reasonably efficient decantation. An additional safety factor could be provided by including a system to detect a large amount of organic material if it should be inadvertently added.

No incidents have occurred in plutonium product evaporators or waste evaporators. Plutonium evaporation is normally carried to only a modest concentration (~400 g/L), and the oxide is produced by precipitation rather than calcination. As a result, temperatures remain below the critical value for an autocatalytic reaction. A plutonium reaction would be expected to be more severe than uranium in its consequences because of the higher nitrate/organic ratio of the adduct, as well as the properties of plutonium; however, the initiation temperature is apparently about the same as that for uranium. It appears advisable to avoid the evaporation of plutonium to higher concentrations (temperatures) and to limit the use of direct calcination techniques except in continuous equipment in which an accumulation of organic cannot occur. Since the equipment is generally small in any case (because of criticality), this is not very restrictive.

There have been no incidents in waste or any of the various recycle evaporators, because the temperature is generally well below the lower limit for such reactions. Waste solidification does require some consideration, however, since drying or calcining of nitrate wastes could conceivably lead to a problem. The presence of an extracted metal nitrate complex, which appears necessary, is highly unlikely in any of these operations. Again, the use of a continuous calciner to avoid accumulation of organic material appears advantageous.

Flowsheet modifications have been suggested to remove organics from aqueous streams to a greater extent. These include steam-stripping or diluent washing of aqueous streams before evaporation. Each process is designed to remove dissolved and entrained organic from aqueous streams. In fact, all incidents have involved far more organic than would have been carried into the system by normal entrainment or solubility. It is doubtful that either approach would have prevented the incidents because the system would have been overloaded by the large amounts of organic introduced. The Hanford evaporator included steam-stripping.

Because it introduces additional equipment, a new operation, and a chemical stream with a different composition that must be dealt with, diluent washing appears to be disadvantageous. Steam-stripping can be accomplished as part of the evaporation process, which will be present in any case, so it introduces no new operation; it will involve a stripping section larger than would be present otherwise. Accordingly, if any such means is to be used to reduce the likelihood of organics entering the evaporator, steam-stripping appears to be a reasonable choice. Of greatest value, however, is the assurance that organics are not fed to an evaporator or calciner because of poor phase separation, phase inversion, or other unanticipated reasons.

4.2 EVAPORATOR OPERATIONAL RESTRICTIONS

As noted elsewhere, the essential limitations to prevent a red-oil excursion are (1) to limit the amount of organic that enters the evaporator and (2) to maintain the temperature at the desired level. The first goal is adequately accomplished by ensuring reasonably good phase separation; and extreme means to remove organics from the aqueous are not necessary. The second requirement can be met with simple instrumentation; it is especially noteworthy that both of the previously discussed incidents occurred when such instrumentation was absent or inoperable and large amounts of organic were unknowingly added.

It is essential that the evaporator have temperature and density measurement devices, and that both the temperature and the density be positively limited to some specified value. Presently, temperatures of 125 to 130°C are specified. These limits are really based on studies carried out >30 years ago using less stable diluents, which are suspected to have caused the initiation temperature for the excursion to be lower. Although a higher temperature is almost certainly acceptable, it is likely that additional study for the particular system to be used would be required before a higher temperature would be permitted. The density limitation is a backup for the temperature limit (via the boiling point) and also confirms that sufficient water is still present to provide a reasonable heat removal mechanism.

One way to ensure that the temperature limit is met is to limit the steam supply pressure for the evaporator. The disadvantage is that higher boilup rates cannot then be used when evaporating dilute solutions. However, this method is recommended because of its inherent safety.

Additional safeguards, such as detectors for organic constituents or CO_2 in the evaporator overheads, could be used to shut down the system or additionally limit the temperature if excess organics were present. However, it is doubtful that these would be worthwhile for an evaporator because of their complexity as compared with the simplicity and effectiveness of the other methods.

4.3 CALCINER OPERATIONAL RESTRICTIONS

The calciner incident was perhaps more surprising than the evaporator incidents because one would expect organic constituents to have been steam-distilled away or decomposed in the evaporator before reaching the calciner. Instead, organic compounds can accumulate in the evaporator product receiver, especially if the evaporator temperature is much below the organic decomposition temperature. Clearly, in the Savannah River system, a major accumulation of organic material in the calciner feed occurred over a long time period. Such an accumulation must be avoided. It is also obvious that normal calcining conditions (unlike evaporation) will cause formation and decomposition of organic adducts if TBP is introduced.

The essential preventive method is careful decantation to prevent substantial amounts of organics from being introduced with the calciner feed. Since phase inversion (the organic phase being more dense than the aqueous) may occur under certain off-standard conditions, special precautions must be taken at such times. This was a contributing cause of the Savannah River calciner incident. Other approaches include:

1. Increasing the temperature of a batch calciner more slowly, especially through the critical range from about 135°C to near 200°C, to decompose any organics below the temperature required for the autocatalytic reaction.

2. Analyzing the calciner off-gas for combustion products or organic vapors to detect the inadvertent introduction of organic material. Although not recommended for the evaporator because other and simpler methods are adequate, this approach may be advantageous for the denitrator.

3. Using a continuous calcination process, such as that which occurs in a fluidized bed or screw conveyor. This ensures the slow and continuous introduction of feed, which is immediately reacted at the high operating temperature, so that the accumulation of organic

material necessary for an autocatalytic reaction cannot occur. A continuous fluid-bed calciner has been developed and tested at the Idaho Chemical Processing Plant.[29] A possible variation on standard denitration which could be explored is the addition of ammonium nitrate to the uranyl nitrate; this facilitates the denitration process by eliminating the mastic stage.[30] Continuous denitration is an attractive option that could improve operability and eliminate potential safety hazards; therefore, it should be evaluated for this application.

5. RECOMMENDATIONS

Prior experience and literature data provide a reasonable understanding of the red-oil problem and an adequate definition of conditions that will ensure that the problem is avoided. The most important recommendations can be summarized as follows:

1. Provide reasonably effective decantation of organic from aqueous streams immediately before they are evaporated, calcined, denitrated, or otherwise heated to high temperatures. Modest amounts of organic can be tolerated, and only exceptionally large additions have caused red-oil incidents. In particular, normal entrainment and solvent solubility do not cause problems either operationally or because of product purity.

2. Extreme measures to eliminate organics, such as steam-stripping or diluent washing, are not necessary. If such a method will be used anyway, steam-stripping appears preferable because it can be incorporated into the vapor recovery system and does not introduce a new process stream. However, the primary objective is to prevent introduction of large quantities of organics, not to remove small traces.

3. Maintain temperatures in evaporators at <135°C. It is very likely that a higher temperature (probably 150°C or more) is satisfactory if a normal paraffin hydrocarbon diluent is used, but further verification would be required. If desired, evaporation could be carried out under reduced pressure; but that does not appear to be necessary.

4. To ensure that temperatures remain within the specified range, the maximum pressure of steam used to heat evaporators should be appropriately controlled.

5. Evaporators and denitrators should never be operated unless the necessary instrumentation is functioning properly. Such instrumentation includes temperature and density measurement for

evaporators, as well as temperature and probably off-gas monitoring for denitrators.

6. The exact nature of the denitrator off-gas monitoring requires further study. Organic vapors that might form explosive mixtures are the primary concern, and the presence of such gases or of CO_2 would indicate the decomposition of organic material, which could signify the potential initiation of a red-oil excursion. Such indications would require that the temperature not be further increased until the organic material has been reacted.

7. The preferred approach for denitration, with respect to safety, is to use a continuous process or one utilizing repetitive, small additions of feed so that an accumulation of organic material cannot occur. It is recommended that continuous high-temperature processes, such as those associated with the fluidized bed or screw conveyor, be evaluated.

8. Perhaps most important, any high-temperature operation, such as evaporation or calcination, should be carefully reevaluated if any aspect of it is nonroutine or different from the normal. Every incident discussed in this report occurred during the processing of nonstandard material (from startup operations, equipment cleanout or decontamination, or rework); and both evaporator incidents occurred when essential instrumentation was not functional.

Recommendations (3), (6), and (7) suggest the need for additional research and development studies that might lead to process improvements and safer operation. In addition, recommendation (1) would benefit from the development of better ways to detect organic material in aqueous feed streams.

6. REFERENCES

1. N. Boukis and B. Kanellakopulos, Extraktive Phasenverteilung des Uranylnitrats mit Tri(n-butyl)phosphat II: Die Bildung einer dritten Phase im System $UO_2(NO_3)_2$-TBP-HNO_3, KfK-3352 (1983).

2. W. W. Schulz and J. D. Navratil, Science and Technology of Tributyl Phosphate, Vol. I, CRC Press, Inc., Boca Raton, Florida, pp. 152-53 (1984).

3. R. M. Wagner, Investigation of Explosive Characteristics of Purex Solvent Decomposition Products (Red Oil), HW-27492 (1953).

4. G. S. Nichols, Decomposition of the Tributyl Phosphate-Nitrate Complexes, DP-526 (1960).

4. G. S. Nichols, Decomposition of the Tributyl Phosphate-Nitrate Complexes, DP-526 (1960).

5. R. M. Wagner, Nitration Reactions of Shell Spray Base under Purex Waste Recovery Process Conditions, HW-26517 (1952).

6. R. Becker, L. Stieglitz, H. Bautz, and R. Will, Bildung und thermochemische Eigenschaften von schweren organischen Phasen des PUREX Prozesses, KfK-3983 (1985).

7. R. A. Pugh, Notes Pertaining to RECUPLEX Product Evaporation, HW-32100 (1954).

8. L. Finsterwalder and W. Hame, TBP und seine Zersetzungsprodukte in den verdampfern der Wiederaufarbeitungsanlage Karlsruhe, WAK-323 (1982).

9. W. S. Durant, "Red-oil" Explosions at the Savannah River Plant," DP-MS-83-142 (1983).

10. T. J. Colven, Jr., G. M. Nichols, and T. H. Siddall, TNX Evaporator Incident, January 12, 1953," DP-25 (1953).

11. J. M. McKibben, Explosion and Fire in the Uranium Trioxide Production Facilities at the Savannah River Plant on February 12, 1975, DPSPU-76-11-1 (1976).

12. L. W. Gray, "An Explosion and Fire During Conversion of Liquid Uranyl Nitrate to Solid Uranium Oxide," *Nucl. Safety* 19, 91-99 (1978).

13. R. G. Wilbourn, Safety Aspects of Solvent Nitration in HTGR Fuel Reprocessing, GA-A14372 (1977).

14. J. J. Shefcik, Safety Aspects of Purex Plant Concentrator Operation, HW-40556 (1955).

15. L. T. Lakey, "A Safety Analysis for the Nuclear Fuel Recovery and Recycling Center," *Nucl. Safety* 43, 213-21 (1979).

16. J. P. Nichols, The Effects of a Detonation Within a Process Cell, ORNL/CF-59-11-115 (1959).

17. "Safety Evaluation by the Division of Materials Licensing, United States Atomic Energy Commission, in the Matter of General Electric Company Midwest Fuel Recovery Plant, Grundy County, Illinois," Docket No. 50-268, p. 30.

18. "Safety Evaluation by the Irradiated Fuels Branch, Division of Materials Licensing, in the Matter of Nuclear Fuel Services, Inc., and New York State Atomic and Space Development Authority, Docket No. 50-201, p. 39.

19. "Extraction from BNFL Safety Analysis," Docket No. 50332-44.

20. P. Leroy, Surete des Laboratoires et Usines, La Surete et Le Retraitement, Rapport DSN No. 389 (in French), p. 45.

21. Extraction from "Design and Analysis," Midwest Fuel Recovery Plant (MFRP).

22. L. Stieglitz, R. Becker, H. Bautz, and R. Will, "Properties of Heavy Organic Phases and Their Formation in the Purex Process," pp. I-239-44 in Proceedings of International Solvent Extraction Conference, ISEC'86, 11-16 Sept 1986, München, FRG.

23. W. S. Durant, L. W. Gray, R. M. Wallace, and W. W. F. Yau, Explosions and Other Uncontrolled Chemical Reactions at Non-Reactor Nuclear Facilities of the Savannah River Plant, DP-MS-88-15 (1988).

24. P. D. Wilson and J. K. Smith, "Boundaries of Third-Phase Formation by Uranium(IV) and Plutonium(IV) in TBP/Diluent Systems," pp. I-201-8 in Proceedings of International Solvent Extraction Conference, ISEC'86, 11-16 Sept 1986, München, FRG.

25. G. Sege, Overconcentration in Initial Operation of Uranium Evaporator - 321 Building, HW-28690 (July 1953).

26. H. D. Harmon, M. L. Hyder, B. Tiffany, L. W. Gray, and P. A. Soltys, Behavior of Tributyl Phosphate in A-Line Processes, DP-1418 (August 1976).

27. W. W. Schulz and J. D. Navratil, Science and Technology of Tributyl Phosphate, Vol. I, CRC Press, Inc., Boca Raton, Florida, 1984, pp. 78-81, 119-22.

28. A. I. Titov, "The Free Radical Mechanism of Nitration," Tetrahedron 19, 557-80 (1963).

29. D. V. Croson, J. A. Rindfleisch, and A. V. Petig, Pilot Plant Operation of a Geometrically Safe Denitrator at the Idaho Chemical Processing Plant, WINCO-1037 (June 1987).

30. P. A. Haas, R. D. Arthur, and W. B. Stines, Development of Thermal Denitration to Prepare Uranium Oxide and Mixed Oxides for Nuclear Fuel Fabrication, ORNL-5735 (September 1981).

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