

CONTROL OF RED OIL EXPLOSIONS
IN DEFENSE NUCLEAR FACILITIES
2003

Defense Nuclear Facilities Safety Board

Technical Report



November 2003

**CONTROL OF RED OIL EXPLOSIONS
IN DEFENSE NUCLEAR FACILITIES
2003**

This report was prepared for the Defense Nuclear Facilities Safety Board by the following staff members:

Randall N. Robinson
David M. Gutowski
William Yeniscavich

with assistance from:

John S. Contardi
Ray S. Daniels
Timothy L. Hunt

EXECUTIVE SUMMARY

This report is an assessment of the potential for a red oil explosion in the Department of Energy's (DOE) defense nuclear facilities complex (complex) for the year 2003. Red oil is defined as a substance of varying composition formed when an organic solution, typically tri-*n*-butyl phosphate (TBP) and its diluent, comes in contact with concentrated nitric acid at a temperature above 120°C. Red oil is relatively stable below 130°C, but it can decompose explosively when its temperature is raised above 130°C. Three red oil events have occurred in the United States: at the Hanford Site in 1953, and at the Savannah River Site (SRS) in 1953 and 1975. A red oil explosion also occurred in 1993 at the Tomsk-7 site at Seversk, Russia.

Generic types of equipment capable of producing red oil in the complex are categorized as evaporators, acid concentrators, and denitrators. The chemicals necessary to produce red oil are, at a minimum, TBP and nitric acid; other, contributory chemicals can include diluent (kerosene-like liquid used to dilute TBP) and/or aqueous phase metal nitrates.

Controls for prevention or mitigation of a red oil explosion are generally categorized as controls for temperature, pressure, mass, and concentration. Maintaining a temperature of less than 130°C is generally accepted as a means to prevent red oil explosions. Sufficient venting serves to keep pressure from destroying the process vessel, while also providing the means for evaporative cooling to keep red oil from reaching the runaway temperature. Mass controls utilize decanters or hydrocyclones to remove organics from feedstreams entering process equipment capable of producing red oil. Limiting the total available TBP is another mass control that mitigates the consequence of a red oil explosion by limiting its maximum available explosive energy. Finally, concentration control can be utilized to keep the nitric acid below 10 *M* (moles/liter). A conclusion of this study is that none of the controls should be used alone; rather, they should be used together to provide effective defense in depth for prevention of a red oil explosion.

Three facilities in the complex are identified as capable of producing a red oil explosion: H-Canyon at SRS, and to a lesser extent, F-Canyon at SRS and Building 9212 at the Y-12 National Security Complex. These facilities contain the necessary process equipment and chemicals to form red oil and bring it to the runaway temperature. These facilities have adequate controls in place to prevent a red oil explosion.

One facility, the Chemical Processing Plant Facility at the Idaho National Engineering and Environmental Laboratory, is identified as capable of, but not likely to produce red oil. This facility contains small amounts of TBP, and the required process equipment is either decommissioned or not available for operation. This facility possesses adequate controls to prevent a red oil runaway reaction.

The Mixed Oxide Fuel Fabrication Facility at SRS, presently in the design stage, will have the capability to produce red oil. This fuel fabrication facility is regulated by the Nuclear Regulatory Commission. Except for research and development activities, all other facilities investigated in the complex either have no operating process equipment or little or no available TBP to make them capable of producing red oil.

TABLE OF CONTENTS

Section	Page
1. INTRODUCTION	1-1
2. BACKGROUND: SOLVENT EXTRACTION AND RED OIL	2-1
2.1 Solvent Extraction and tri- <i>n</i> -butyl phosphate	2-1
2.2 Diluent	2-1
2.3 TBP Degradation	2-1
3. RED OIL: DEFINITION AND FORMATION	3-1
3.1 Equipment Capable of Producing Red Oil	3-1
3.2 Indication of Red Oil Formation.	3-2
3.3 Red Oil Explosion Scenario	3-2
3.4 Necessary Conditions for Red Oil Formation	3-3
4. CONTROLS FOR THE RED OIL PHENOMENON	4-1
4.1 Temperature Control	4-1
4.2 Pressure Control	4-3
4.3 Mass Control	4-3
4.4 Concentration Control	4-4
5. RED OIL SCENARIOS IN THE COMPLEX	5-1
5.1 Previous Red Oil Incidents in the United States	5-1
5.2 Potential Red Oil Facilities	5-1
5.3 Unlikely Red Oil Facility	5-5
5.4 Future Red Oil Producing Facility	5-6
5.5 Other Facilities Within the Complex	5-6
6. CONCLUSIONS	6-1
REFERENCES	R-1
GLOSSARY OF ACRONYMS AND TERMS	G-1

1. INTRODUCTION

Three red oil events have occurred in the Department of Energy's (DOE) defense nuclear facilities complex (complex): at the Hanford Site in 1953, and at the Savannah River Site (SRS) in 1953 and 1975 (Vandercook, 1991; Watkin, 1993). A red oil explosion also occurred in 1993 at the Tomsk-7 facility in Seversk, Russia. The lessons learned from these occurrences must not be forgotten. Red oil explosions are a reality; therefore, the engineered controls preventing reoccurrences must be well designed and periodically reviewed to ensure that no flaws exist in the control scheme.

As background, this report describes the connection between the process of solvent extraction and red oil production. The mechanism of red oil production and the controls necessary to prevent a red oil explosion are also described. The types of process equipment and the necessary materials capable of producing red oil are identified.

The purpose of this report is to define what red oil is and what conditions cause it to decompose in a runaway reaction, to identify facilities in the complex possessing equipment and materials capable of producing red oil, and to identify the types of safety controls required to prevent or mitigate the consequences of a red oil explosion. Facilities are also identified that are capable of but not likely to produce red oil. The Mixed Oxide Fuel Fabrication Facility (MFFF) at SRS, now in the design stage, is identified as a future facility having the capability of producing red oil explosions.

2. BACKGROUND: SOLVENT EXTRACTION AND RED OIL

2.1 SOLVENT EXTRACTION AND TRI-*N*-BUTYL PHOSPHATE

An effective process to recover, purify, or separate metals important in the complex is liquid-liquid extraction, or more briefly, solvent extraction. In general, solvent extraction refers to a process that transfers one or more components between two immiscible (or nearly immiscible) liquid phases. Many solvents can effectively extract uranium, plutonium, or thorium from acid solutions. However, when discussing the red oil phenomenon in the complex, the solvent involved is the organophosphate tri-*n*-butyl phosphate (TBP).

In this report, solvent extraction refers to a process using an organic phase solution consisting of 3–30 percent TBP in purified kerosene or kerosene-like diluent in contact with an aqueous phase solution consisting of water, nitric acid, and metal nitrates. The metal nitrates can consist of one or all of $\text{UO}_2(\text{NO}_3)_2$ or uranyl nitrate (UN), plutonium nitrate, thorium nitrate, fission product nitrates, or salting agents. The metal nitrates are preferentially extracted into the organic phase, enhanced by the salting agents. Although other solvents may extract these metal nitrates more efficiently, TBP was originally chosen for its overall superiority in operation, safety, physical properties, radiation resistance, and economics. One of the most desirable attributes of TBP is its high flash point, 146°C, compared with other solvents. The boiling point of TBP is reported in the range $284 \pm 5^\circ\text{C}$, where purity of the TBP is the major contributor to uncertainty (Schultz and Navratil, 1984). The reported density of TBP at 25°C is $0.9727 \pm 0.0004 \text{ g/cm}^3$.

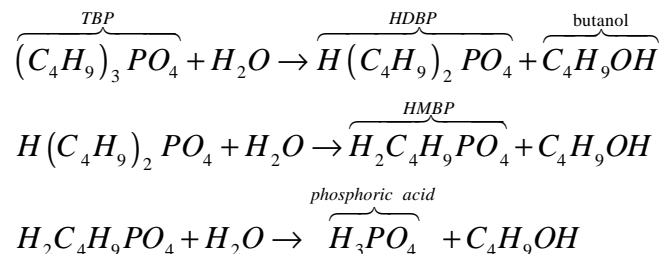
2.2 DILUENT

The TBP is always diluted in an organic matrix, or diluent, to improve the physical characteristics of the organic phase. The diluent reduces the viscosity and density of the organic phase to improve phase separation characteristics and reduces criticality concerns by limiting the maximum actinide concentration in the organic phase. The diluent is chosen on the basis of radiation stability and inertness to the species in the solvent extraction process. From a purely technical perspective, the alkane hydrocarbon dodecane, $\text{C}_{12}\text{H}_{26}$, is the best diluent to use because it is inert and highly radiation resistant. Dodecane can be purified to be free of aromatics that can react with some of the components in the solvent extraction environment. However, dodecane is very expensive. For this reason, purified kerosene or kerosene-like diluents, such as AMSCO-125-90W, that have properties nearly equivalent to those of dodecane are used instead. However, AMSCO-125-90W and other kerosene-like diluents contain small amounts of tramp organic compounds (i.e., impurities such as aromatics or alkenes) that can contribute to the red oil phenomenon. AMSCO-125-90W has a flashpoint of 56°C (Stoller and Richards, 1961), a boiling range of 186–199°C, and a density of 0.757 g/cm^3 at 25°C.

2.3 TBP DEGRADATION

Although TBP is a highly robust chemical in the solvent extraction environment, it decomposes very slowly in the presence of water and nitric acid by hydrolysis to lower organo-phosphate acids at normal operating temperatures. However, even small amounts of degradation products in the organic

phase can reduce the effectiveness of the extraction of the actinides. The presence of these TBP degradation products also contributes to the red oil phenomenon. The hydrolysis of TBP proceeds with the stepwise reactions to form dibutyl phosphoric acid (HDBP), butyl phosphoric acid (HMBP), phosphoric acid, and butanol as follows:



The above TBP degradation reactions proceed very slowly at normal operating solvent extraction temperatures. Over a period of time (i.e., months), however, there is a slow buildup of decomposition products. Also at very slow rates, the tramp organics in the diluent react with components in the aqueous phase to form nitro-aromatic compounds. The diluent degrades sufficiently so that after a few months of operation, it changes color from water-white to light amber. The butanol from the TBP degradation also can react with nitric acid to form butyl nitrate, an explosive material. Degradation rates for both the TBP and its diluent increase with increasing temperature. At 100°C, the fractions of TBP, HDBP, and HMBP decomposing per hour in contact with 2 *M* nitric acid are 0.113, 0.043, and 0.03 (Stoller and Richards, 1961), respectively. To form red oil, however, the TBP organic phase must be in contact with boiling nitric acid at a concentration of greater than 10 *M* (greater than 48 wt%). At temperatures above 120°C, degradation rates are high enough to produce concentrations of nitrated organics that change the color of the organic phase from amber to dark red—hence the name “red oil.”

3. RED OIL: DEFINITION AND FORMATION

Generically, red oil is a substance that can form when an organic comes in contact with nitric acid. There are several organics that can exhibit this phenomenon. Specifically for this report, red oil is the name of a substance of nonspecific composition formed when an organic phase consisting of TBP and diluent in contact with concentrated nitric acid is heated above 120°C under reflux. Reflux is a stream consisting of condensed overheads that is returned to the boiling liquid for purposes of increasing or decreasing the concentration of one or more components in the boiling liquid. The red color imparted to the organic phase is believed to be nitrated organic species. Red oil can be produced in contact with less than 10 *M* nitric acid, but only at temperatures above 137°C (Enos, 2002). Red oil can also be produced with pure TBP in contact with boiling 14.9 *M* nitric acid under total reflux. At temperatures above 130°C, the degradation of TBP, diluent, and nitric acid proceeds at rates fast enough to generate heat and voluminous amounts of detonable vapor. The generated heat further increases the temperature of the liquid, which in turn increases the rate of reaction (i.e., a runaway or autocatalytic reaction).

3.1 EQUIPMENT CAPABLE OF PRODUCING RED OIL

The simplest process condition for the production of red oil is nitric acid heated while in contact with TBP. To be capable of red oil production, equipment must have the capability of heating its contents. Also, the same equipment must have the possibility of containing both nitric acid and TBP. There are three generic types of process equipment in the complex that meet the conditions for red oil formation: evaporators, acid concentrators, and denitrators (DNTs). Steam jets were considered but were found not to be capable of forming red oil.

3.1.1 Evaporators

Solvent extraction leaves the aqueous product streams in a diluted state. Concentrating the aqueous streams allows for efficient subsequent processing and/or recycling of nitric acid. Evaporators are commonly used to concentrate the metal nitrates in the aqueous streams by boiling away the more volatile water and nitric acid components. Evaporation, in contrast to distillation, is defined as the vaporization of one or more species from one or more nonvolatile species using heat and/or pressure regulation.

3.1.2 Acid Concentrators

Distillation, the process used for acid concentration, is the separation of solutions, where all the species are volatile, using heat and/or pressure regulation. In acid concentrators, metal nitrates may be present in small concentrations (i.e., parts per million). However, the basic process conditions for red oil production are possible if inadvertent amounts of TBP are present with the nitric acid.

3.1.3 Denitrators

Denitrators, also known as calciners, are heating devices that heat concentrated solutions of metal nitrate to the point of decomposition. For example, when denitrating UN, the process is

conducted at very high temperatures until uranium oxide (UO_3) is produced. If traces of TBP are in the UN, the temperatures for denitration are more than adequate (greater than 250°C) for red oil to form and reach autocatalytic temperatures.

3.1.4 Steam Jets

Steam jets are commonly used in the complex to transport liquids from one vessel to another. The steam jet is a device that lowers the pressure by increasing the steam velocity according to the Bernoulli principle. Liquid is drawn into the jet and is co-transported with the steam. The steam will heat the liquid but cannot bring it to a boil or else transport will be lost. Hence, steam jets are not considered capable of forming red oil.

3.2 INDICATION OF RED OIL FORMATION

The first sign of red oil formation and progression of red oil decomposition is the development of brown fumes caused by nitrogen dioxide in gases evolved. The generation of these fumes is nonviolent and occurs at temperatures below 130°C . Above 130°C , the rate of the decomposition of red oil becomes rapid enough to generate voluminous explosive gases. The decomposition reaction is exothermic. Before every red oil occurrence, large amounts of red-brown fumes have been detected in the offgas streams. Depending upon the mass, geometry, and heat removal capacity of the process equipment involved, the heat generated during red oil decomposition above 130°C can overcome the heat removal capacity of the equipment, and the reaction can become autocatalytic, with catastrophic results.

3.3 RED OIL EXPLOSION SCENARIO

The following scenario illustrates how a red oil explosion can occur in an evaporator that is insufficiently vented. A solution of dilute nitric acid and UN is continuously introduced into an evaporator and brought to a boil. Inadvertently, a small amount of TBP and diluent is allowed to enter the evaporator in the feed stream. The less-dense, immiscible organic phase floats on the aqueous phase, and because the boiling point of the organic phase is significantly higher than that of the aqueous phase, it does not boil.

As the UN and nitric acid begin to concentrate, the boiling point increases and the temperature rises. Vapor bubbles from the boiling aqueous phase below continually agitate the floating organic phase, aiding in the removal of any heat generated in the organic phase. The higher boiling temperature causes more of the diluent to evaporate, concentrating the TBP in the organic phase. If enough UN is present in the aqueous phase, the TBP will quickly become saturated with UN (2 moles of TBP per mole of UN) because of solvation.

When the boiling point increases to 120°C and the nitric acid in the aqueous phase concentrates to greater than 10 M , red oil begins to form nonviolently in the organic phase. The presence of red-brown fumes in the vapor is the first indication of red oil formation. The organic phase continues to float on the aqueous phase, and agitation by bubbles provides enough convection to produce sufficient removal of the heat produced by red oil decomposition. As the UN and nitric acid continue to concentrate and diluent

continues to evaporate, the TBP concentrates in the organic phase. Eventually, the density of the organic phase, containing TBP saturated with uranium, increases to the point where “phase inversion” occurs.

Phase inversion takes place when the organic and aqueous phases reverse positions. With the organic phase now at the bottom, convective heat transfer is reduced significantly in the nonboiling organic phase. As the aqueous phase continues to concentrate and the temperature increases through the exothermic red oil reaction, the temperature of the organic phase further increases because of the poor heat transfer to the aqueous phase. The higher organic phase temperature causes faster decomposition and ultimately a runaway reaction. When the generated gases overcome the vent path, the reaction further accelerates because of the higher pressure, and the vessel pressurizes and eventually fails. The escaped explosive gases come in contact with air and an ignition source and explode violently.

3.4 NECESSARY CONDITIONS FOR RED OIL FORMATION

The necessary conditions for a runaway red oil reaction to occur are:

- ! The presence of TBP in organic phase
- ! Organic phase in contact with nitric acid greater than 10 M
- ! Solution temperature greater than 130°C
- ! Insufficient venting area

All of the above conditions are necessary for a pressure explosion to occur. Even if there is sufficient vent area and the reaction does not run away, the gases generated if the TBP and nitric acid are heated above 130°C can detonate. Higher solution temperatures can be tolerated with less than 10 M nitric acid. If no diluent is present in the organic phase, it is more likely that the nitric acid in the aqueous stream must be closer to 14.5 M for a runaway reaction to occur (Enos, 2002). Two additional conditions can exacerbate the red oil runaway reaction:

- ! The presence of a diluent
- ! The presence of metal ions in the aqueous phase that can solvate with TBP in the organic phase and cause phase inversion

4. CONTROLS FOR THE RED OIL PHENOMENON

The following controls can be used to prevent a red oil event:

- ! Temperature: maintain at less than 130°C.
- ! Pressure: provide a sufficient vent for the process.
- ! Mass: remove organics from the process.
- ! Concentration: maintain nitric acid less than 10 *M*.

There are two concerns with a red oil runaway reaction: pressurization and detonation. In the case of the Tomsk-7 incident, the vessel temperature and composition were optimum for red oil formation, and the vessel pressurized and eventually ruptured. A secondary explosion occurred when the escaping gases detonated. For the other red oil incidents that have occurred, either overpressurization or detonation took place after phase inversion.

4.1 TEMPERATURE CONTROL

No red oil runaway reaction has occurred at a temperature of less than 130°C. The use of temperature sensors with appropriate temperature controls (e.g., steam pressure interlocks) is adequate to prevent a red oil runaway reaction in sufficiently vented vessels. However, there can be situations in which temperature control alone may fail. The set point control for maximum temperature is crucial. Since the red oil reaction is exothermic, unless there is sufficient heat transfer available, controls to limit excessive temperature may not be adequate if no method to cool the reaction is applied. It has been shown that venting provides a passive method to cool the solution by evaporative heat transfer (Fauske and Associates, Inc., 1994). Sufficient venting prevents the red oil reaction from becoming autocatalytic.

Until 1994, it was believed that the red oil phenomenon occurred when the combination of water, nitric acid, TBP and its diluent, and heavy metal nitrates (i.e., uranyl nitrate, plutonium nitrate, thorium nitrate) were heated to temperatures high enough to cause the diluent, TBP, and nitric acid to decompose rapidly, forming a variety of volatile organic species. These volatile species include flammable and explosive components. In response to the Tomsk-7 event in 1993, DOE commissioned experiments (Smith and Calvin 1994) that demonstrated that red oil can be formed by heating only TBP with nitric acid in closed (i.e., unvented) systems with the same results.

To verify earlier reports (Colvin, 1956) that established 130°C as the “always-safe” temperature to prevent red oil explosions, the Savannah River Technology Center (SRTC) conducted additional experiments (Rudisill and Crooks, 2000). These experiments included the effects of additional dissolved solids (i.e., inextractable salts) in the aqueous phase. Inextractable salts were purposely used in the experiments to avoid phase inversion. The authors concluded that the “runaway red oil reaction involving aqueous solutions containing no dissolved solids were [sic] in good agreement with data from the 1950s.” The authors also verified the earlier conclusions that 130°C is the “always-safe” temperature (Cowan, 1994; Paddleford and Fauske, 1994; Westinghouse Savannah River Company, 1995; Gordon, 1985).

A combined plot of the data reported by Colvin (1956) and Rudisill (2000) is shown in Figure 1. The minimum initiation temperature for red oil runaway using 14–15 *M* nitric acid without dissolved solids was 137°C (Rudisill, 2000). These results are consistent with the earlier measurements of 132–137°C with 15.7 *M* nitric acid (Colvin, 1956). The presence of dissolved solids lowered the initiation temperature; however, except for experiments using 20 percent inextractable solids, the initiation temperature remained above 130°C. At very high solids content (20 percent) and 9.6 *M* nitric acid, Colvin (1956) reported an initiation temperature close to 129°C. Therefore, at high acid concentrations or with high solids content, there is little margin for a runaway reaction if temperature controls are set near 130°C.

Figure 1 shows some scatter for the initiation temperatures measured for samples at the same acid concentration. For pure 15.9 *M* nitric acid contacting TBP, a runaway reaction temperature as low as 132°C was indicated for one sample. The trend indicates initiation temperature decreases with increasing nitric acid concentration. Keeping the nitric acid below 10 *M* and the temperature below 130°C for solutions without nitrate salts provides a greater margin against a runaway reaction. Colvin’s two data points for solutions with high dissolved solids are of concern because the initiation temperatures for these data points are 129 and 132°C. Therefore, with solutions containing high dissolved solids, the “always safe” temperature of less than 130°C is not as conservative as solutions without dissolved solids. As a result of these observations and allowing for experimental error, the staff of the Defense Nuclear Facilities Safety Board (Board) believes that a limit below 130°C should be established to provide an adequate safety margin for the prevention of a red oil explosion.

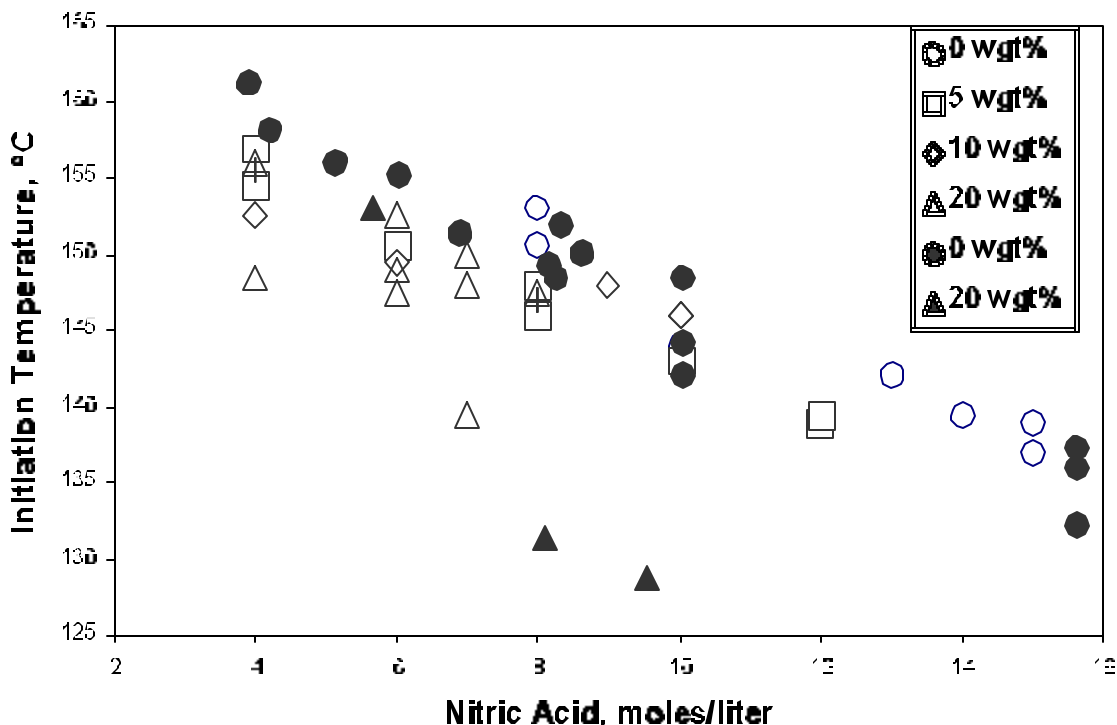


Figure 1. Effect of Nitric Acid Concentration (moles/liter) and Solids Content (wt%) on Red Oil Initiation Temperature. Sources: Solid symbols, Colvin (1956); open symbols, Rudisill (2000).

In the experiments for Figure 1, inextractable salts were used as the solids in the aqueous phase to keep the phases from inverting. If an extractable nitrate such as UN were used, the phases could invert. Once the organic phase is at the bottom, heat transfer becomes poorer, and the possibility of a runaway reaction increases. In this case, a runaway reaction can be avoided only if the organic phase is kept below 130°C. Normally, temperature control is provided by controlling the steam pressure to heating coils in a vessel. If solution temperature sensors are used it is important that they be located such that the organic phase temperature can be measured with or without phase inversion.

Finally, the inextractable salt in the aqueous phase, which represents the total nitrate salt concentration in actual processes, clearly has an effect on the initiation temperature, according to Figure 1. In an evaporator without reflux, the salt and acid concentrations are controlled by vapor-liquid equilibrium; therefore, two variables, such as temperature and density, are needed to determine both the salt and acid concentration. For example, a solution of UN and nitric acid boiling at 120°C with a density of 1.38 g/cm³ has a single composition of 16 wt% UN and 10 M nitric acid. If this solution were left to continue boiling with adjustments to the feed stream to keep the boiling temperature at 120°C until the density increased to 1.53 g/cm³, the composition would be 27 wt% UN and 8 M nitric acid. Both of these conditions are considered safe from a red oil perspective since the temperature is less than 130°C, and the nitric acid is less than or equal to 10 M. However, 27 wt% UN is greater than the maximum 20 wt% dissolved solids used in the experimental conditions of Colvin (1956) and Rusidill (2000). Therefore, there is uncertainty about the initiation temperature and temperature margin at this condition. To be assured that red oil conditions are not present in an evaporator, controls for temperature, pressure, and concentration should all be utilized. As noted earlier, none of these controls alone can ensure prevention of a red oil runaway reaction.

4.2 PRESSURE CONTROL

Sufficient venting of heated vessels can prevent the pressure explosion that could occur in unvented or inadequately vented tanks if a red oil reaction occurs. Sufficient venting of a heated vessel also has the added benefit of allowing the solution to self-cool by evaporative heat transfer. Fauske and Associates Inc. (1994) reported that a vent area of 0.063 mm²/gram of TBP was sufficient to reduce the pressure from a runaway red oil reaction to less than 2 pounds per square inch gauge (psig). Experimental results for venting sufficiency indicate the vent sizes needed to control the pressure of red oil reactions (Paddleford and Fauske, 1994). These results indicate that the vessel cannot pressurize if the ratio of red oil mass to ventilation cross-sectional area is maintained at no more than 312 grams of red oil/mm² of vent cross-sectional area, and the organic phase remains lighter than the aqueous phase. With some safety margin, it is recommended that no more than 208 grams of red oil/mm² be used to guarantee a maximum vessel pressure of 2 psig as a result of a red oil runaway. Although the pressure control prevents a pressure explosion, it does not prevent the detonation of released gases. Therefore, other controls should also be employed to prevent the red oil reaction.

4.3 MASS CONTROL

Mass control devices are used to ensure that the organic phase is removed from the solution fed to an evaporator, acid concentrator, or denitrator. Without TBP, a red oil event cannot occur. However,

TBP has a slight solubility in water and nitric acid. Therefore, in large systems, this effect can allow the TBP to separate and accumulate in heated vessels. Liquid-liquid centrifuges, hydrocyclones, and decanters are some devices that can be used to remove small amounts of organics from aqueous feedstreams. However, phase inversion in these devices can cause them to work improperly and allow organic phase to pass into the heated vessel. Additionally, degradation products of TBP that have greater solubility in the aqueous phase can also lead to red oil reactions.

Another form of mass control is to limit the total amount of TBP in vessels or in a facility. This control can be used in robust, remotely operated facilities (e.g., canyons) capable of containing the maximum possible explosion produced by the total mass of TBP. This type of control does not prevent a red oil explosion, but mitigates the consequences.

4.4 CONCENTRATION CONTROL

Except at very high metal nitrate concentrations, maintaining the temperature below 130°C and the nitric acid at or below 10 *M* will prevent a red oil runaway reaction. In systems consisting of nitric acid with other salts, it was shown earlier that more variables must be measured to control the nitric acid concentration. In a system of nitric acid and UN, both the boiling temperature and density must be measured to determine their concentrations. Therefore, concentration control usually requires both density and temperature measurement of the solutions.

5. RED OIL SCENARIOS IN THE COMPLEX

In the past, when reprocessing was common in the complex, many facilities used TBP-based solvent extraction for reprocessing, purification, and separation of uranium and plutonium. As noted earlier, there have been three known red oil incidents in the complex: one event at the Hanford Site in 1953, and two explosions at SRS in 1953 and 1975. In 2003, three remaining facilities continue to have the potential for red oil incidents, one other has an unlikely potential for red oil incidents because considerable effort would have to be made to restart equipment and only small amounts of TBP exist at the site, and one facility in the design stage will have the potential for a red oil incident.

5.1 PREVIOUS RED OIL INCIDENTS IN THE UNITED STATES

5.1.1 Hanford, 1953

A red oil incident occurred at the Hanford Site on July 1, 1953, in Building 321. A feed pump failed during the initial operation of a new evaporator using unirradiated uranium. TBP was inadvertently present in the feed. Despite the pump failure, the evaporation process continued above normal concentrations and temperature. The temperature increased until the UN was nearly molten and “incipient calcination” had begun. A great deal of red fumes escaped the evaporator vent before it was shut down. No personnel injuries or destruction of equipment occurred. Red oil was found, but the vent size was large enough to remove the decomposition gases before they could pressurize the tank.

5.1.2 Savannah River Site, 1953

On January 12, 1953, a UN solution was being batch concentrated in the TNX Facility to remove excess nitric acid from solution. The UN was in contact with 30 percent TBP solvent in kerosene. Approximately 80 lbs of TBP was inadvertently present in the feed. The temperature measurement was inoperable and the density indications were off-scale. The vessel was damaged in the resulting overpressure, but no personnel were injured. No secondary detonation occurred. The condition of the solution was not known since neither temperature nor density was recorded.

5.1.3 Savannah River Site, 1975

On February 12, 1975, a red oil incident occurred in a DNT in the H-Canyon Outside Facilities at SRS. UN was being calcined to UO_3 along with an unknown amount of organic. Prior to the explosion, dense red fumes were emitted into the DNT room. The gas detonation caused damage to the equipment and building. No major personnel injuries were recorded.

5.2 POTENTIAL RED OIL FACILITIES

The following are descriptions and scenarios for three facilities with the potential for red oil incidents in 2003.

5.2.1 Savannah River Site H-Canyon

In the H-Canyon Safety Analysis Report (SAR), 10 pages are devoted to a description of the scenarios for a red oil explosion. H-Canyon and Outside Facilities of H-Canyon (OF-H) contain all three types of process equipment with the potential for a red oil incident: evaporators, acid concentrators, and denitrators. A red oil explosion is classified as unlikely, and the “consequences are classified as high, resulting in a Scenario Class I event” (Westinghouse Savannah River Company, 2002, p. 8-34). The passive engineered safeguards considered to mitigate a red oil explosion are the canyon building itself and “ever-open” sufficient vents. The H-Canyon SAR describes a red oil event in which TBP and nitric acid (or UN) are mixed and heated in the same vessel to temperatures exceeding 130°C.

The H-Canyon SAR states that if a red oil explosion were to occur inside the canyon, the canyon building and canyon ventilation system would mitigate radiological effects of the event. If the reaction occurred outside the canyon, there would be very little if any protection available to mitigate the consequences of the event. In outside facilities, facility workers could be exposed to the blast effects of the event, and there could be potential long-term radiological effects in the accident clean-up process.

The controls to prevent a red oil incident in H-Canyon are temperature, pressure, and mass. According to the H-Canyon SAR, since the red oil event initiation temperature is 130°C, several controls are in place to protect against a vessel reaching this temperature. These controls include temperature sensors and alarms, pressure indicators, and passive (or “ever-open”) vents. The vents are credited for temperature control because they provide a mechanism for the solution to cool by convective cooling. Because of the uncertainty of experimental measurements of the red oil initiation temperatures, for actual operations, a safety margin of 10°C is applied to the temperature control with an additional 3°C for instrument error. The H-Canyon Technical Safety Requirement states that “the high temperature steam flow interlock shall close the steam isolation valves before the pot temperature exceeds 120°C” (Westinghouse Savannah River Company, 1998, p. B2/4 1.4-3). As a result, the operational protected temperature is 120°C with over-temperature instrument setpoint controls set to 117°C. For pressure control, the passive vents are again credited. Mass control is provided by using an organic mixture containing 7.5 percent TBP, which limits the total mass available as fuel for the red oil explosion. Analysis of the potential red oil event indicates that if less than 3000 lbs of TBP were involved, the canyon structure could withstand the detonation. With 7.5 percent TBP, it is not possible to have more than 3000 lbs of TBP in a canyon vessel. Furthermore, analysis of vessels in the canyon that may contain the constituents for a red oil event and can be heated indicates that a vent area of 6.44 in² is sufficient to relieve the pressure from any red oil reaction involving 3000 lbs of TBP. Vents larger than 6.44 in² are provided for all heated vessels. Mass control is also provided by decanters that prevent organic phase from being transported to heated vessels.

The instrumentation for maintaining controls against a red oil event is designed to be at least safety-significant. For example, the temperature sensors, alarms, and interlocks on the H-Canyon evaporators are safety-class controls. Safety-class interlocks on steam pressure (and thus steam temperature) are set at 25 psig. Level detectors and alarms on decanters feeding evaporators are also designated as safety class.

For the OF-H areas, heat sources connected to the solvent storage tanks have been removed to create an air gap between the steam lines and steam coils in the tanks. With the steam lines removed, there is no method to heat TBP in the outside storage tanks to above 130°C.

The acid recovery unit (ARU) in the OF-H area is a distillation column for nitric acid recovery from high-activity waste (HAW) and low-activity waste (LAW). Any TBP in the feed stream to evaporators in the canyon can be distilled into the overheads that are sent to the ARU. The ARU is located outdoors in an area accessible to facility personnel. The consequences of an explosion in the ARU are high for facility workers; thus controls are required to protect the workers from a red oil explosion. Since there are no metal salts present in the ARU feed, there is no mechanism for phase inversion.

The control for the ARU is simple and achieved by maintaining the ARU preheater and reboiler at or below 120°C. Additionally, the ARU feed tanks are inspected periodically, and any accumulated organic is skimmed off as necessary. However, the ARU feed can still contain dissolved TBP and its degradation products in trace quantities. As the acid concentrates in the reboiler of the ARU, the solubility of TBP in the acid can decrease to a point where a separate organic phase forms, setting up conditions for red oil production. However, the amount of TBP dissolved in the aqueous phase carried into the reboiler is so small that if a red oil event occurred, there would not be enough mass to pressurize the ARU or enough fuel to cause a large detonation.

5.2.2 Savannah River Site F-Canyon

Per the suspension plan for F-Canyon (Westinghouse Savannah River Company, 2002), the facility is being shut down in four phases. Phase 1 consisted of product stabilization. Phase 2 involved deinventory of plutonium to discardable levels. At the end of phase 2, the facility is in warm standby (i.e., the facility is capable of restart if necessary). Phase 3 stabilizes the facility and places the equipment into isolation or shutdown mode. At the end of phase 3, the facility will be in cold standby (i.e., restart anticipated to take several years). Finally, phase 4 will place the facility in a surveillance and maintenance mode. To activate the facility from this mode would require extensive investment, staffing, and time. Presently, F-Canyon is in the process of completing phase 3. Phase 3 requires, among other things, removal of solvent from the facility and shutdown and isolation of PUREX equipment. At the end of phase 3, a red oil event will not be possible. Until phase 3 is completed, all the scenarios indicated in the SRS H-Canyon SAR are applicable but are less likely to occur because the solvent in F-Canyon is being stripped and washed during phase 3.

During phase 3, all of the solvent remaining in vessels in F-Canyon is being stripped by contacting it with 2 wt% nitric acid (0.32 *M*) to remove traces of heavy metal nitrates. The solvent is further washed with aqueous 4 wt% sodium carbonate (~0.4 *M*). The carbonate solution removes the degradation products of TBP, particularly HDBP, by “washing” them into the aqueous phase. If a small amount of TBP were inadvertently added to an evaporator containing carbonate, as the TBP decomposed by hydrolysis, its decomposition products would be washed into the carbonate preventing the formation of red oil in the

organic phase. Also, the nitric acid concentration below 2 *M* has never been shown to sustain a red oil runaway reaction. With stripping and washing operations combined with the red oil controls similar to H-Canyon already in place, a red oil incident in F-Canyon is less likely. At the end of phase 3 operations, a red oil event will be extremely unlikely.

5.2.3 Y-12 National Security Complex

Building 9212 at Y-12 has material and equipment capable of producing a red oil event. The explosion scenarios have lower consequences than those for H-Canyon at SRS because of the smaller scale and the absence of transuranic metal nitrates and fission products. The process equipment in Building 9212 having the capability for red oil production was identified as the high-capacity evaporator (HCE), the primary intermediate evaporator (PIE), the secondary intermediate evaporator (SIE), the wiped film evaporator (WFE), and the DNT. Although the HCE, PIE, SIE, and WFE all have sufficient vent paths sized to the recommended 208 grams of red oil/mm² of vent cross-sectional area, each contains valves capable of isolating the vent path. Credit was taken for the vents, but at an increased frequency of occurrence that the vent could be isolated. The primary control for red oil production in these vessels is mass control utilizing decanters. The Y-12 Basis for Interim Operation (BWXT-Y-12, 2002, p 5-108) describes other controls for red oil production: “The environment required to initiate or support a red oil reaction is not established during operation of these systems. Examples include the nitric acid concentrations and operating temperatures.”

The normal operation of the intermediate evaporators is to concentrate aqueous feed containing 8 wt% (1.3 *M*) nitric acid with varying small amounts of UN (approximately 10 parts per million [ppm]). Depending on the final UN or acid concentration desired, a red oil reaction is possible if nitric acid is allowed to increase above normal operating concentrations and TBP is inadvertently introduced into the evaporators.

The WFE is used to concentrate UN essentially nitric acid-free. A red oil reaction would be possible if both nitric acid and TBP were inadvertently introduced, and the process were operated above the normal operating range.

The DNT is used to convert UN into solid uranium oxide. A red oil event could occur if both nitric acid and TBP were introduced into the DNT. However, process conditions and the use of mass control for the DNT virtually eliminate nitric acid and organic, both components necessary for red oil production.

The consequences of a red oil explosion in Building 9212 are rated as high because of the potential for a worker fatality as a result of the contact maintenance feature of Building 9212 facilities. The consequences of a red oil event to the public and collocated workers are deemed low because the amount of fuel and release fractions associated with red oil explosions are small.

The primary control to mitigate a red oil explosion in Building 9212 is mass. Mass control is accomplished by the use of decanters in the feed stream of these potential red oil event processes. Properly sized venting of all vessels with potential red oil events is also credited. The decanters are contact maintained, and sections are made of glass so operators can directly observe any accumulation of organic phase. The WFE and DNT are also credited with sufficient vent area for pressure control.

5.3 UNLIKELY RED OIL FACILITY

One facility in the complex has an unlikely potential for a red oil event because it is currently being deactivated. However, this facility still has a small amount of TBP on site and equipment capable of applying heat to a TBP/nitric acid system.

5.3.1 Chemical Processing Plant Facility at Idaho National Engineering and Environmental Laboratory

The Chemical Processing Plant Facility (CPP) at Idaho National Engineering and Environmental Laboratory (INEEL) is considered capable but extremely unlikely to produce a red oil event. The facility does have operational waste evaporators, but only very small amounts of TBP remain in the acidic high-sodium wastes. Current safety documentation (Idaho Nuclear Technology Engineering Center, 2001) for INEEL does analyze the potential for red oil incidents. However, since TBP is no longer used and has been largely removed, there are insufficient quantities or concentrations for a red oil incident to be plausible. The two evaporator operations having red oil analyses are the process equipment waste (PEW) evaporators (Lockheed Martin, 1997) and the high-level liquid waste evaporator (HLLWE).

The PEW evaporators concentrate all aqueous waste except for the waste coming from solvent extraction. For a red oil incident to occur in the PEW evaporators, organics containing TBP would have to be routed to this evaporator accidentally when it was running with high-concentration nitric acid. Steam that heats the evaporator is shut off if the evaporator temperature reaches 110°C, and the entire evaporator is shut down if the temperature continues to rise after the steam is shut off.

The HLLWE reduces high-level acidic waste volumes by evaporation. None of the high-level waste at INEEL has significant concentrations of TBP. Waste tanks have remnants of TBP with concentrations in the range of several parts per billion. Thus, there is not enough mass of TBP to cause a red oil explosion with sufficient energy to warrant concern with the evaporator. The HLLWE has temperature controls similar to those of the PEW evaporators. It operates at 95–108°C. Temperature controls shut off steam at 117°C, and even if shutoff did not occur, with slightly less than ideal heat transfer conditions, the 35 psig steam used would not heat the evaporator contents above the “always safe” temperature of 130°C. Since there is only a small residual amount of TBP remaining at INEEL from halted processes, there is very little possibility of a red oil accident occurring there. The two evaporators have temperature, pressure, and mass controls to prevent a red oil event.

5.4 FUTURE RED OIL PRODUCING FACILITY

There is one facility presently in the design stage that will be capable of producing red oil and its accompanying runaway reaction. This facility—the MFFF to be built at SRS—is not under the Board’s purview. The design, construction, and operation of this facility are regulated by the Nuclear Regulatory Commission.

5.5 OTHER FACILITIES WITHIN THE COMPLEX

Other facilities within the complex located at the Hanford Site, Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Fernald Closure Project, Rocky Flats Environmental Technology Site, Miamisburg Closure Project, and West Valley were reviewed for the potential for red oil incidents. Except for developmental or research and development activities that may exist, none of these sites currently has enough TBP or the process equipment necessary to produce red oil.

6. CONCLUSIONS

Three types of process operations within the complex have been identified as capable of producing red oil when TBP and nitric acid are in contact with each other: evaporators, acid concentrators, and DNTs.

Several controls have been identified to mitigate or prevent a red oil explosion. They are controls for temperature, pressure, mass, and concentration.

- ! **Temperature.** Maintaining a temperature of less than 130°C is generally accepted as a means to prevent any red oil explosions.
- ! **Pressure.** Sufficient venting serves to prevent an over-pressure from destroying the process vessel while also providing the means for evaporative cooling to keep red oil from reaching the runaway temperature.
- ! **Mass.** Mass control utilizes decanters or other liquid-liquid separation equipment to remove TBP from feedstreams entering heated process equipment, eliminating one of the necessary components to form red oil. In robust containment (i.e., canyons), mass control can be used to mitigate the consequences of a red oil explosion by limiting vessel size and organic concentration to a maximum available explosive energy the containment can withstand.
- ! **Concentration.** Concentration control can be utilized to keep the nitric acid below 10 M.

It is the conclusion of this study that none of the controls should be used alone, but rather should be used in combination to prevent a runaway red oil reaction and explosion of the detonable gases produced by the reaction.

Three facilities in the complex have been identified as having the potential for producing red oil in 2003—H-Canyon at SRS and, less likely, F-Canyon at SRS and Building 9212 at Y-12. A red oil explosion in H-Canyon at SRS is prevented by proper temperature, pressure, and mass controls. The mass controls include engineered controls such as decanters and, as a mitigator, additional control is provided by limiting the total quantity of TBP to 3000 lb per vessel. This additional mass control allows the building structure to mitigate the effects of a potential red oil explosion. A red oil explosion in F-Canyon is prevented by the same controls used in H-Canyon combined with the additional solvent stripping and washing operations currently being performed that make the event even less likely. A red oil explosion in Building 9212 at the Y-12 facility is prevented by mass controls using decanters with sufficient vents on evaporators providing defense in depth.

The CPP facility at INEEL is identified as having the means to produce red oil in 2003, but the amount of TBP available is too small and there are no plans to introduce the TBP into heated vessels.

Finally, the MFFF at SRS is in the design stage and will be capable of producing a red oil event. The design, construction, and operation of this facility is being regulated by the Nuclear Regulatory Commission.

REFERENCES

BWXT-Y-12 (2002), *The Basis for Interim Operation for Building 9212 Enriched Uranium Operations Complex*, Y/MA-7254, Rev. 15, July.

Christensen, L. W. and R. E. Vail (1995), *Fault Tree Analysis of Red Oil Reactions in the H-Canyon Evaporators*, Westinghouse Savannah River Company, S-CLC-H-00227, February 24.

Colvin, Jr., T. J. (1956), *Nitric Acid Recovery Units Permissible Steam Pressure in Reboilers*, E. I. du Pont de Nemours and Company, DPST-56-243, E. I. Savannah River Plant, April 27.

Cowan, M. L. (1994), *Uncontrolled TBP-Nitric Acid BIO Risk Analysis*, Westinghouse Savannah River Company, EPD-SSS-94010, June 20.

Enos, C. C. (2002), *Design Analyses and Calculations: Organic-Nitric Acid Reaction Evaluation*, Y-12 National Security Complex, DAC-GPEQ-003, June 6.

Fauske and Associates, Inc. (1994), *Tributyl Phosphate-Nitric Acid Reaction and Vent Requirements*, FAI/94-68, July.

Gordon, R. J. (1985), *Environmental Testing-Explosion Hazards of TBP/Nitrate Stability*, E. I. du Pont de Nemours and Company, May 15.

Idaho Nuclear Technology and Engineering Center (2001), *Facility Specific Safety Analysis SAR-103 New Waste Calcining Facility*, SAR-103, December 3.

Lockheed Martin (1997), *Temperature Limit of PEW Evaporators*, TS-4.2A2, July 21.

Paddleford, D. F. and H. K. Fauske (1994), *Safe Venting of Red Oil Runaway Reactions*, Westinghouse Savannah River Company, WSRC-MS-94-0649, December 21.

Rudisill, T. S. and W. J. Crooks (2000), *Initiation Temperature of Runaway TBP/Nitric Acid Reactions*, Westinghouse Savannah River Company, WSRC-TR-2000-00427, Rev. 0, October.

Schulz, W. W. and J. D. Navaratil (1984), *Science and Technology of Tributyl Phosphate*, Vol. I, CRC Press.

Smith, J. R. and W. S. Cavin (1994), *Isothermal Heat Measurements of TBP-Nitric Acid Solutions*, Westinghouse Savannah River Company, WSTRC-TR-94-0540.

Stoller, S. M. and R. B. Richards (1961), *Reactor Handbook*, 2nd Edition, Vol. II: *Fuel Reprocessing*, Interscience Publishers.

Treybal, R. E. (1968), *Mass-Transfer Operations*, 2nd Edition, McGraw-Hill Book Co.

Vandercook, R. E. (1991), *Summary of Red Oil Issues at Hanford*, WHC-WM-TI-466, January 28.

Watkin, J. G., P. L. Gordon, and S. F. Agnew (1993), “*Red Oil*” *Safety Evaluation Project*, briefing presented to the Defense Nuclear Facilities Safety Board, September 2.

Westinghouse Savannah River Company (2002), *Safety Analysis Report, Savannah River Site H-Canyon and Outside Facilities, H- Area*, Rev. 1., WSRC-SA-2001-00008, July.

Westinghouse Savannah River Company (2002), *F-Canyon/FB-Line Facilities PUREX Suspension Plan*, NMM-PRG-0793, Rev. 0, February 19.

Westinghouse Savannah River Company (1995), *Evaluation of H-Canyon Red Oil Analysis Produced by SAIC*, S-CLC-H-00228, Rev. 0, March 31.

Westinghouse Savannah River Company (1998), *H-Canyon & Outside Facilities TSR*, WSRC-TS-96-19, Rev 2A., July.

GLOSSARY OF ACRONYMS AND TERMS

Abbreviation	Definition
ARU	acid recovery unit
Board	Defense Nuclear Facilities Safety Board
CPP	Chemical Processing Plant
complex	Department of Energy defense nuclear facilities complex
DNT	denitrator
DOE	Department of Energy
HAW	high-activity waste
HCE	high-capacity evaporator
HDBP	dibutyl phosphoric acid
HLLWE	high-level liquid waste evaporator
HMBP	butyl phosphoric acid
INEEL	Idaho National Engineering and Environmental Laboratory
LAW	low-activity waste
<u>M</u>	moles/liter
MFFF	Mixed Fuel Fabrication Facility
OF-H	H-Canyon and Outside Facilities of H-Canyon
PEW	process equipment waste
PIE	primary intermediate evaporator
ppm	parts per million
psig	pounds per square inch gauge
SAR	Safety Analysis Report
SIE	secondary intermediate evaporator
SRS	Savannah River Site
SRTC	Savannah River Technical Center
TBP	tri- <i>n</i> -butyl phosphate
UN	uranyl nitrate or $\text{UO}_2(\text{NO}_3)_2$
UO_3	uranium oxide
WFE	wiped film evaporator

