NRC FORM 680 (11-2002) NRCMD 10.159	U.S. NUCLEAR REGULATORY COMMISSION	FOR PROCESSING USE ONLY
DIFFERING PROFESSIONAL OPINION		1. DPO CASE NUMBER DPO-2005-002

INSTRUCTIONS: *Prepare this form legibly and submit three copies to the address provided in Block 14 below.*	2. DATE RECEIVED 1/19/2005

3. NAME OF SUBMITTER	4. POSITION TITLE	5. GRADE
Alexander P. Murray	Senior Chemical Process Engineer	15

6. OFFICE/DIVISION/BRANCH/SECTION	7. BUILDING	8. MAIL STOP	9. SUPERVISOR
NMSS/FCSS/SPB/MOFLS	TWFN	T8F42	Stewart Magruder

10. DESCRIBE THE PRESENT SITUATION, CONDITION, METHOD, ETC., WHICH YOU BELIEVE SHOULD BE CHANGED OR IMPROVED.
(Continue on Page 2 or 3 as necessary.)

The applicant has proposed strategies for controlling potential red oil events in open and closed systems. The applicant has not followed the accepted DOE practice nor provided a clear rationale or calculational basis for their control strategies. The strategy for open systems does incorporate some aspects from the accepted practice at DOE facilities that limit reaction temperatures and organic compounds, and provide for vent sizes that have adequate margin within the recommended safe range identified by DOE and the Defense Nuclear Facilities Safety Board (DNFSB). For closed systems, the applicant's approach focuses primarily on the control of a single parameter - temperature. The temperature design basis is higher than the effective temperature in open systems. By comparison to the accepted practice at DOE facilities, the temperature design basis and vent sizing for closed systems are well into the unsafe range.

11. DESCRIBE YOUR DIFFERING OPINION IN ACCORDANCE WITH THE GUIDANCE PRESENTED IN NRC MANAGEMENT DIRECTIVE 10.159.
(Continue on Page 2 or 3 as necessary.)

As the Lead Chemical Safety Reviewer for MOX, I accept the applicant's approach only for open systems. Acceptance of the applicant's approach for open systems highlights significant safety concerns with the closed system approach of using a higher effective design basis temperature limit and extremely limited venting capability. The applicant's proposed approach for closed systems is well into the range considered unsafe by the DOE/DNFSB and the applicant has not provided assurances that the proposed safety strategy will function adequately.

I conclude that the prevailing management/staff position accepting the applicant's closed system approach for NRC regulatory purposes is too simple a position arrived at too expediently that, if allowed, would endorse the use of a safety control strategy, controls, and design bases (limits) that do not provide for adequate assurances of safety, as required by the regulations.

12. Check (a) or (b) as appropriate:

☑ a. Thorough discussions of the issue(s) raised in item 11 have taken place within my management chain; or

☐ b. The reasons why I cannot approach my immediate chain of command are:

SIGNATURE OF SUBMITTER *Alexander P. Murray*	DATE January 14th 2005	SIGNATURE OF CO-SUBMITTER *(if any)*	DATE

13. PROPOSED PANEL MEMBERS *ARE (in priority order):*	14. Submit this form to:
1. Mr. Walt Schwink	Differing Professional Opinions Program Manager
2. NTEU Recommendation #1	Office of: _____
3. NTEU Recommendation #2	Mail Stop: _____

15. ACKNOWLEDGMENT

THANK YOU FOR YOUR DIFFERING PROFESSIONAL OPINION. It will be carefully considered by a panel of experts in accordance with the provisions of NRCMD 10.159, and you will be advised of any action taken. Your interest in improving NRC operations is appreciated.	SIGNATURE OF DIFFERING PROFESSIONAL OPINIONS PROGRAM MANAGER (DPOPM) *Renee M. Pedersen*
	PRECONDITIONS MET ☑ YES ☐ NO	DATE OF ACKNOWLEDGMENT 1/25/2005

NRC FORM 680
(11-2002)
NRCMD 10.159

U.S. NUCLEAR REGULATORY COMMISSION

DIFFERING PROFESSIONAL OPINION
(Continued)

CONTINUE ITEM 10, ITEM 11, AND/OR ITEM 12 FROM PAGE 1. *(Indicate the block number to which this information applies.)*

Item 10:

The prevailing management/staff position accepts the applicant position for both open and closed systems. No calculations or clear logical arguments are provided. A consensus process was not followed. Instead, a voting process involving unqualified reviewers was used and subsequently endorsed by NRC management.

Item 11:

My concerns fall into the following main areas:

1. Contradictions with DOE/DNFSB RAGAGEP are not explained. In particular, the RAGAGEP shows the applicant's proposal for closed systems being entirely in the unsafe regime (Figure 2).

2. There is inadequate margin in the design basis temperature.

3. The venting is insufficient to avoid choked flow and pressurization, which has the ability to rapidly raise the temperature even with the applicant's proposed strategy functioning.

4. Controls on organic compounds are inadequate - the applicant has indicated organic carryover is an anticipated event.

5. There are no controls on acid or solvent concentrations.

6. The evaporators at the proposed facility have a high aspect ratio which is more favorable for red oil reactions to occur and potentially cause pressure excursions.

7. The NRC management decision accepting the applicant's proposal is based upon a voting process that included unqualified reviewers. It is not a consensus process.

8. Efficiency arguments were used by management as part of the rationale for accepting the applicant's proposal. However, efficiency is not mentioned in the regulations or as part of the SRP acceptance criteria.

9. A significant portion of the management decision relies upon future commitments, efforts, and experiments to define/refine current PSSCs and design bases that are not RAGAGEP.

10. Overall, safety concerns from the NRC staff's Revised Draft Safety Evaluation Report (RDSER) are not addressed, including inconsistencies with other limits and a clear logical or calculational basis from the applicant indicating their integrated control strategy has the ability to meet the regulations. The applicant has made an assertion - supporting information from the applicant and the prevailing staff opinion is non-existent or inadequate to support a conclusion of adequate assurances of safety.

I request that (1) the NRC management/staff decision to accept the applicant's strategy for closed systems be reversed; (2) Issue CS-01 on red oil reactions for the MOX application be reopened; (3) for the construction application, the applicant is requested to submit on the docket adequate justification for its safety approach for red oil in closed systems and provide adequate justification for differences with the safety strategy used in DOE facilities and accepted by DNFSB/DOE; or, alternatively, apply a construction permit condition that imposes the DOE/DNFSB safety strategy until the applicant justifies its approach..

MEMORANDUM
JANUARY 14th, 2004

TO: Renee Pedersen, Acting Differing Professional Opinions
                Program Manager
                Office of Enforcement

FROM: Alexander P. Murray, Senior Chemical Process Engineer
                Mixed Oxide Facility Licensing Section
                Special Projects Branch
                Division of Fuel Cycle Safety
                 and Safeguards (FCSS)
                Office of Nuclear Material Safety
                 and Safeguards (NMSS)

SUBJECT: DIFFERING PROFESSIONAL OPINION (DPO) ON RED OIL EVENTS
                AT THE PROPOSED MIXED OXIDE (MOX) FUEL FABRICATION
                FACILITY
                DOCKET NUMBER: 070-03098

I am requesting a DPO review of the safety issue involving potential red oil events damaging
systems and structures at the proposed MOX facility, resulting in a loss of confinement and the
dispersal of plutonium materials into the environment.

I have attached a short writeup of the DPO in addition to the completed NRC Form 680. I am
neither in favor of nor against the proposed facility - I am impartial. I am concerned about
adequate assurances of safety. In summary, the DPO discusses potential red oil events and
their safety controls at the proposed MOX facility and other facilities regulated by the NRC
under 10 CFR Part 70. Red oil is a group name for nitrated organic materials that form in
solvent extraction systems using Tributylphosphate (TBP) and nitric acid. Under certain
conditions, sufficient quantities of red oil can accumulate and undergo rapid reactions that can
damage equipment, breach confinement structures, and release radioactive and radiochemical
species to the environment. Several red oil accidents and incidents have occurred at nuclear
facilities in the past, including a 1993 explosion at Tomsk in the Former Soviet Union that
resulted in significant personnel exposures, significant damage to the building, loss of
confinement of radiochemical materials, and contamination of the environment. Direct
personnel injuries were only avoided by alert (and lucky) operators evacuating the building. All
of the events involved relatively small quantities of materials (tens to low hundreds of gallons),
comparable to those anticipated for the proposed facility.

The proposed MOX Fuel Fabrication Facility (MFFF) involves the use of significant quantities of
plutonium. Any potential red oil event could result in the explosive release and dispersal of
multi-kilogram quantities of weapons grade plutonium into the environment.

The accepted practice at Department of Energy (DOE) facilities uses multiple safety controls on multiple parameters - temperature, pressure relief/vent size, total organic content, nitric acid concentration, and building confinement.

The applicant has proposed strategies for open and closed systems, which are described further in Attachment 1 to this memorandum. The applicant has not followed the accepted DOE practice nor provided a clear rationale or calculational basis for their control strategies. The strategy for open systems does incorporate some aspects from the accepted practice at DOE facilities that limit reaction temperatures and organic compounds, and provide for vent sizes that have adequate margin within the recommended safe range identified by DOE and the Defense Nuclear Facilities Safety Board (DNFSB). For closed systems, the applicant's approach focuses primarily on the control of a single parameter - temperature. The temperature design basis is higher than the effective temperature in open systems. By comparison to the accepted practice at DOE facilities, the temperature design basis and vent sizing for closed systems are in the unsafe range.

The prevailing management/staff position accepts the applicant position for both open and closed systems, and is described in Attachment 2 to this memorandum. No calculations or clear logical arguments are provided. Attachment 2 incorrectly states this is a consensus position - in fact, a consensus process was not followed. Instead, a voting process involving unqualified reviewers was used and subsequently endorsed by NRC management.

As the Lead Chemical Safety Reviewer for MOX, I accept the applicant's approach only for open systems. Acceptance of the applicant's approach for open systems highlights significant safety concerns with the closed system approach of using a higher effective design basis temperature limit and extremely limited venting capability. As shown in Figure A, the applicant's proposed approach for closed systems is well into the range considered unsafe by the DOE/DNFSB and the applicant has not provided assurances that the proposed safety strategy will function adequately.

I conclude that the prevailing management/staff position accepting the applicant's closed system approach for NRC regulatory purposes is too simple a position arrived at too expediently that, if allowed, would endorse the use of a safety control strategy, controls, and design bases (limits) that do not provide for adequate assurances of safety, as required by the regulations. As discussed in more detail in the attachment, my concerns fall into the following main areas:

1. Contradictions with DOE/DNFSB RAGAGEP (Reasonable And Generally Accepted Good Engineering Practice) are not explained. In particular, the RAGAGEP shows the applicant's proposal for closed systems being entirely in the unsafe regime (Figure 2).

2. There is inadequate margin in the design basis temperature.

3. The venting is insufficient to avoid choked flow and pressurization, which has the ability to rapidly raise the temperature even with the applicant's proposed strategy functioning.

4.   Controls on organic compounds are inadequate - the applicant has indicated organic carryover is an anticipated event.

5.   There are no controls on acid or solvent concentrations.

6.   The evaporators at the proposed facility have a high aspect ratio which is more favorable for red oil reactions to occur and potentially cause pressure excursions.

7.   The NRC management decision accepting the applicant's proposal is based upon a voting process that included unqualified reviewers. It is not a consensus process.

8.   Efficiency arguments were used by management as part of the rationale for accepting the applicant's proposal. However, efficiency is not mentioned in the regulations or as part of the SRP acceptance criteria.

9.   A significant portion of the management decision relies upon future commitments, efforts, and experiments to define/refine current PSSCs and design bases that are not RAGAGEP.

10.   Overall, safety concerns from the NRC staff's Revised Draft Safety Evaluation Report (RDSER) are not addressed, including inconsistencies with other limits and a clear logical or calculational basis from the applicant indicating their integrated control strategy has the ability to meet the regulations. The applicant has made an assertion - supporting information from the applicant and the prevailing staff opinion is non-existent or inadequate to support a conclusion of adequate assurances of safety.

I request that (1) the NRC management/staff decision to accept the applicant's strategy for closed systems be reversed; (2) Issue CS-01 on red oil reactions for the MOX application be reopened; (3) for the construction application, the applicant is requested to submit on the docket adequate justification for its safety approach for red oil in closed systems and provide adequate justification for differences with the safety strategy used in DOE facilities and accepted by DNFSB/DOE; or, alternatively, the NRC should apply a construction permit condition that imposes the DOE/DNFSB safety strategy until the applicant justifies its approach.

I request that the DPO panel allows me the opportunity to clarify my views and provide additional information on this complex and important subject, as discussed in NRC Management Directive (MD) 10.159. Also, per MD 10.159, I propose Mr. Walt Schwink as a qualified individual who can serve on a review panel for this DPO. He has indicated his willingness to serve on the panel. I have contacted other senior NRC staff about being potential candidates for a DPO Panel, and they have declined to be considered because of concerns that their participation would negatively impact their careers. Thus, if Mr. Schwink is unable to participate, I will discuss the matter further with the National Treasury Employees Union (NTEU) for potential candidates. Finally, I will continue to monitor the emphasis on the schedule and the issue closure process.

<u>Attachments:</u>
Attachment 1: Applicant's proposed approach
Attachment 2: Prevailing management/staff position and decision
Attachment 3: DNFSB report on safety controls for red oil
Attachment 4: Completed NRC Form 680
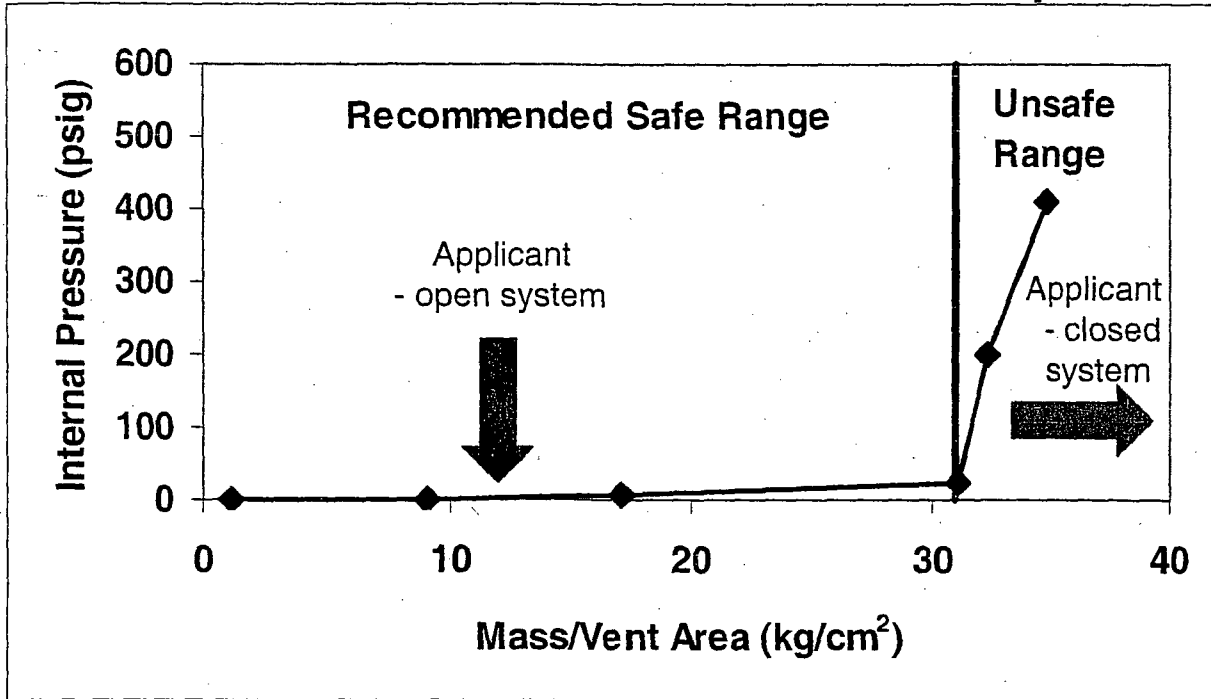

cc:
Russ Irish
Rossanna Raspa
Dale Yeilding

Figure A: Comparison of the Applicant's Red Oil Safety Strategies with DOE/DNFSB (formerly Open Item CS-01) Recommendations

CS-01: Red Oil
Pressure Vent Relationship

DIFFERING PROFESSIONAL OPINION ON
RED OIL EVENTS AT THE
PROPOSED MIXED OXIDE (MOX) FUEL FABRICATION FACILITY
DOCKET NUMBER: 070-03098

1.   Summary:

Prevailing NMSS Staff/Management Position: This is presented in the transcripts of the 507th ACRS Meeting, November 6th 2003 Session, on page 157 et seq., and in a management decision memorandum. These indicate the acceptance of the applicant's approach for controlling red il events in closed systems. The applicant's proposed approach is included in Attachment 1 and Attachment 2 contains the NRC management acceptance memorandum. Attachment 2 incorrectly states this is a consensus position - in fact, a consensus process was not followed. Instead, a voting process involving unqualified reviewers was used and subsequently endorsed by NRC management.

My Assessment As the Lead Chemical Safety Reviewer for MOX: I accept the applicant's approach only for open systems. However, acceptance of the applicant's approach for open systems highlights significant safety concerns with the closed system approach of using a higher effective design basis temperature limit and extremely limited venting capability. The applicant's approach for closed systems is significantly different from the safety approach accepted by DOE/DNFSB - no adequate explanation for these differences has been provided by the applicant or the prevailing NRC management/staff opinion; the DOE/DNFSB approach is RAGAGEP (Reasonable And Generally Accepted Good Engineering Practice) and is included in Attachment 3. I conclude that the prevailing management/staff position accepting the applicant's closed system approach for NRC regulatory purposes is too simple a position arrived at too expediently that, if allowed, would endorse the use of a safety control strategy, controls, and design bases (limits) that do not provide for adequate assurances of safety, as required by the regulations.

My concerns fall into the following main areas:

1.   Contradictions with DOE/DNFSB RAGAGEP are not explained. In particular, the RAGAGEP shows the applicant's proposal for closed systems being entirely in the unsafe regime (Figure 2).

2.   There is inadequate margin in the design basis temperature.

3.   The venting is insufficient to avoid choked flow and pressurization, which has the ability to rapidly raise the temperature even with the applicant's proposed strategy functioning.

4.   Controls on organic compounds are inadequate - the applicant has indicated organic carryover is an anticipated event.

5.   There are no controls on acid or solvent concentrations.

6.   The evaporators at the proposed facility have a high aspect ratio which is more favorable for red oil reactions to occur and potentially cause pressure excursions.

7.   The NRC management decision accepting the applicant's proposal is based upon a voting process that included unqualified reviewers. It is not a consensus process.

8.   Efficiency arguments were used by management as part of the rationale for accepting the applicant's proposal. However, efficiency is not mentioned in the regulations or as part of the SRP acceptance criteria.

9.   A significant portion of the management decision relies upon future commitments, efforts, and experiments to define/refine current PSSCs and design bases that are not RAGAGEP.

10.   Overall, safety concerns from the NRC staff's Revised Draft Safety Evaluation Report (RDSER) are not addressed, including inconsistencies with other limits and a clear logical or calculational basis from the applicant indicating their integrated control strategy has the ability to meet the regulations. The applicant has made an assertion - supporting information from the applicant and the prevailing staff opinion is non-existent or inadequate to support a conclusion of adequate assurances of safety.

DPO Position: I request that (1) the NRC management/staff decision to accept the applicant's strategy for closed systems be reversed; (2) Issue CS-01 on red oil reactions for the MOX application be reopened; (3) for the construction application, the applicant is requested to submit on the docket adequate justification for its safety approach for red oil in closed systems and provide adequate justification for differences with the safety strategy used in DOE facilities and accepted by DNFSB/DOE; or, alternatively, apply a construction permit condition that imposes the DOE/DNFSB safety strategy until the applicant justifies its approach.

Significance: If the prevailing position is not reversed, potential red oil events may not be adequately controlled and prevented. A red oil event would likely be explosive in nature, and result in significant damage, loss of confinement, and release of radioactive materials, including plutonium. Significant injuries and/or fatalities could result to workers and the public from such potential events. There would also be significant financial liabilities from actual injuries and deaths, insurance payments, likely litigation, repairs, and lost operations. There could also be international repercussions due to the agreements involved in plutonium disposition. This would negatively impact the NRC strategic goals of safety, security, effectiveness, and openness (stakeholder and public confidence). The potential news impact of such an event would be extremely critical of the NRC and could result in increased Congressional oversight.

2. The NRC, Chemical Safety, and the Regulations:
2.1 The Regulations

The NRC is the lead regulatory agency at its licensee facilities. The NRC regulates three main categories of chemical safety at its licensees: hazardous chemical effects from radioactive materials (e.g., for MOX, the chemical toxicity of depleted uranium), hazardous chemical effects from chemicals produced from radioactive materials (e.g., for MOX, nitric acid fumes from nitrate solutions or nitrogen tetraoxide releases via the oxidation column), and chemical hazards that affect the safe handling of radioactive materials (this is sometimes referred to as facility conditions affecting the safe handling of licensed radiative materials). In general, the NRC does not strictly regulate only chemical hazards.

For the proposed MOX facility, the principal governing regulation is 10 CFR Part 70 which also reiterates the chemical hazards regulated by the NRC: 70.61(b)(4), 70.61(c)(4), 70.62(c), and 70.64(a)(5) outline the three categories of chemical hazards the NRC currently regulates, simply put as:

Category 1:   chemical hazards that are caused by the radioactive material,

Category 2:   chemical hazards from chemicals released by radioactive materials, and

Category 3:   chemical hazards that affect the safe handling of radioactive materials (essentially facility conditions in 70.64(a)(5)).

Chapter 8 of the MOX Standard Review Plan (SRP - NUREG-1718) also reiterates these three categories of chemical safety regulated by the NRC.

Parts 70.61(b)(4), 70.61(c)(4), and 70.65(b)(7) mention the requirement for appropriative quantitative standards (i.e., chemical consequence levels) for acute chemical exposures to licensed materials or hazardous materials. Appropriate chemical consequence levels are needed for high and intermediate consequence events, and for the two receptors of the worker and the individual located outside the controlled area. The latter individual is usually identified as having limits appropriate for a member of the public. This approach is usually interpreted by staff and licensees/applicants with three chemical consequence levels - low, intermediate, and high. No chemical standards are identified for 70.64(a)(5), which includes the third category of chemical safety. However, in practice, the same limits are usually used.

Part 70.62(c) (iii) further elaborates that the ISA (Integrated Safety Analysis) should identify facility hazards that could affect the safety of licensed materials and thus present an increased radiological risk. Finally, the chemical protection baseline design criterion in 70.64(a)(5) specifies that the design "must provide for adequate protection against *chemical risks produced from licensed material, facility conditions which might affect the safety of licensed material,* and *hazardous chemicals produced from licensed material.*" Note that a specific dose level is not specified for either the chemical or radiological effect in facility hazards and facility conditions.

Part 70 also contains a general safety statement:

70.23(b): "The Commission will approve construction of the principal structures, systems, and components of a plutonium processing and fuel fabrication plant ... when the Commission has determined that the design bases of the principal structures, systems, and components, and the quality assurance program, provide reasonable assurance of protection against natural phenomena and the consequences of potential accidents."

Note that this general statement has no restriction on potential chemical accidents; if such chemical accidents are possible, have high consequences, and present undue risk, then the applicant is required to provide reasonable assurance of protection against the consequences of such potential accidents.

In addition, the Atomic Energy Act (AEA) also contains general clauses "... to protect the health and safety of the public" (Section 2, paragraphs (d) and (e)). Section 161(b) states in part, "... to protect health or to minimize danger to life or property." Section 182(a) contains a similar statement.

Thus, the NRC regulates the three categories of chemical safety. Potential red oil events fit into Categories 2 and 3 of chemical safety and involve both chemical and radiation exposures, and, thus, are regulated by the NRC.

2.2   The MOX Standard Review Plan (SRP - NUREG-1718):

Chapter 8 of the SRP discusses chemical safety.

Section 8.4.3.2 mentions the list of hazardous chemicals is acceptable if it includes, among other items, associated exposure limits such as OSHA Permissible Exposure Limits (PELs), Emergency Response Planning Guidelines (ERPGs), etc. It also mentions it is acceptable if it includes potential interactions, such as the potential deleterious effects of the degradation products of solvent/organic compounds (e.g., red oil) on licensed material.

Section 8.4.3.3 discusses acceptance criteria for chemical accident sequences. Paragraph A mentions the chemical accident sequences are acceptable if they are supported by applicable data and references. Paragraph C mentions a conservative estimate of potential consequences.

Section 8.4.3.4 discusses the acceptance criteria for chemical accident consequences. Paragraph A mentions the applicant should provide information supporting the conclusion that, among other items, the assumed data input leads to a conservative estimate of potential consequences. Paragraph C states the consideration of uncertainty and errors in comparing accident consequences to the performance requirements.

Section 8.4.3.5 discusses the acceptance criteria for process safety information. Paragraph A mentions that the controls used to prevent or mitigate potential accidents should be supported by the appropriate safety analyses, and the applicant provides reasonable assurance that these

controls will be available and reliable upon demand. Paragraph C states a description of the features and controls should be included.

Section 8.5.1 mentions the safety assessment of the design basis (i.e., for a CAR - Construction Authorization Request) should consider the above, among other items, consistent with the level of the design.

The applicant's proposed approach in Attachment 1 for controlling potential red oil events does not meet the acceptance criteria in SRP Sections 8.4.3.3, 8.4.3.4, and 8.4.3.5. The management decision accepting the applicant's proposed approach does not adequately address the missing information.

3. Overview of Chemical Consequence Documents and Events:

3.1 MOX Construction Application Request (CAR - DCS-NRC-000038):

The applicant submitted the CAR on February 21, 2001. The CAR approach has hazardous chemicals in three main areas and activities: the MOX fuel fabrication area of substantial construction (includes the main contaminated processing areas, with gloveboxes and cells), an immediately adjacent reagents building of simple construction, and chemical deliveries by vehicles. In addition, there is a separate gas storage area that could present an asphyxiation concern. No safety controls for chemical effects are identified apart from the air supply to the Emergency Control Room. The CAR indicates chemical effects to the public, site worker, and facility worker would be low. In addition, the applicant stated on page 8-14 that principal structures, systems, and components (PSSCs) defined for radiological events may be applicable to process units where chemicals mix with radiological material. In Chapter 8, a single control approach for potential red oil events was identified using temperature as the controlled variable.

3.2 NRC Staff Analyses in the Draft Safety Evaluation Report (DSER) - April 2002:

The staff review indicated concerns with the safety strategy and design bases proposed by the applicant. Based upon the available experience and literature on the red oil phenomena, the staff concluded that the applicant's proposed approach of a single, safety control of a temperature design basis of 135 C is insufficient and did not provide adequate assurances of safety. As a particular example, the event at Tomsk did not measure a temperature exceeding the 45-50 C range. In addition, the applicant's design basis included an indirect control strategy that did not appear to be consistent with the available experience and literature on red oil. The DSER noted the applicant is continuing design activities and has identified over 50 action items from a HAZOP on one of the evaporators; over ten of these apply to the red oil phenomena. HAZOP analyses for the other two evaporator systems had not been performed at the time. Also, considerable control system efforts remained to be completed. Consequently, the staff identified this as an Open Item [CS-01] requiring resolution. The DSER noted the applicant should identify additional design bases and PSSCs or justify why the proposed design basis and PSSC are acceptable.

The staff believed adequate assurances of safety may be achievable if the applicant identifies appropriate safety design bases and values that incorporate the cited experience on the red oil phenomena. Such an evaporator design basis would likely involve a significantly lower temperature than that proposed by the applicant, and might include other design bases such as multiple (spatial) temperature sensors, organic phase existence (absence), concentration controls, time/aging limits, and mixing and venting requirements. In addition, some of these design bases may also need to be applied to other locations, vessels, and tanks in the proposed facility, particularly vessels that receive hot streams from the evaporators.

A photograph of the damage from the red oil event at Tomsk was removed from the DSER during editing. It is included as Figure 1, on the next page. Note that the event initiated in a shielded cell underneath the building, with relatively small quantities of materials reacting. Comparable quantities of organic materials could be present at the proposed MOX facility. A separate appendix on red oil events was also omitted from the DSER.

**Figure 1:** Example of Facility Damage from a Red Oil Event - Tomsk, 1993.
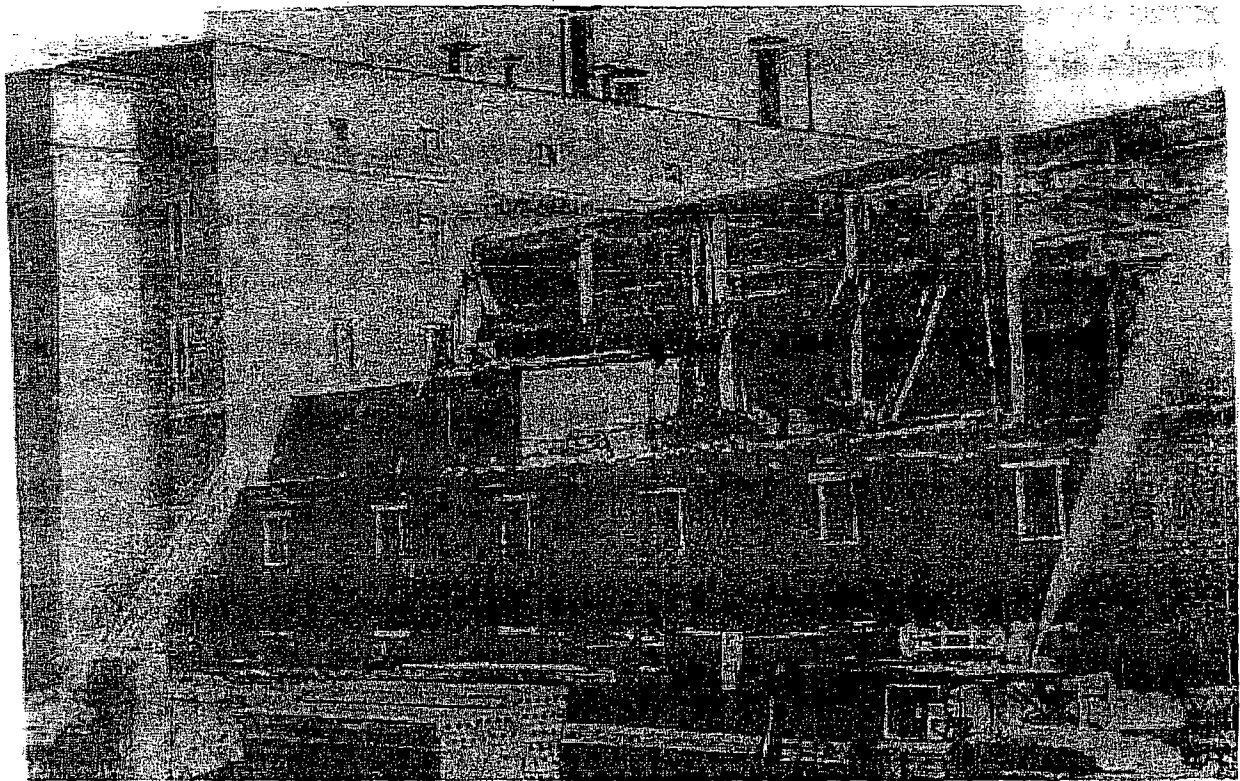
3.3   Revised Construction Application Request (RCAR) - October 2002:

Sections 5.5. and 8 of the RCAR summarize the chemical accident consequences. Red oil is listed in the explosion event group.

The applicant had adopted a preventive safety strategy to protect the worker, site worker, public, and the environment (revised CAR, Section 5.5.2.4.6.7 and References 8.3.64 and 66). The PSSCs were as follows:

(b)(2)High
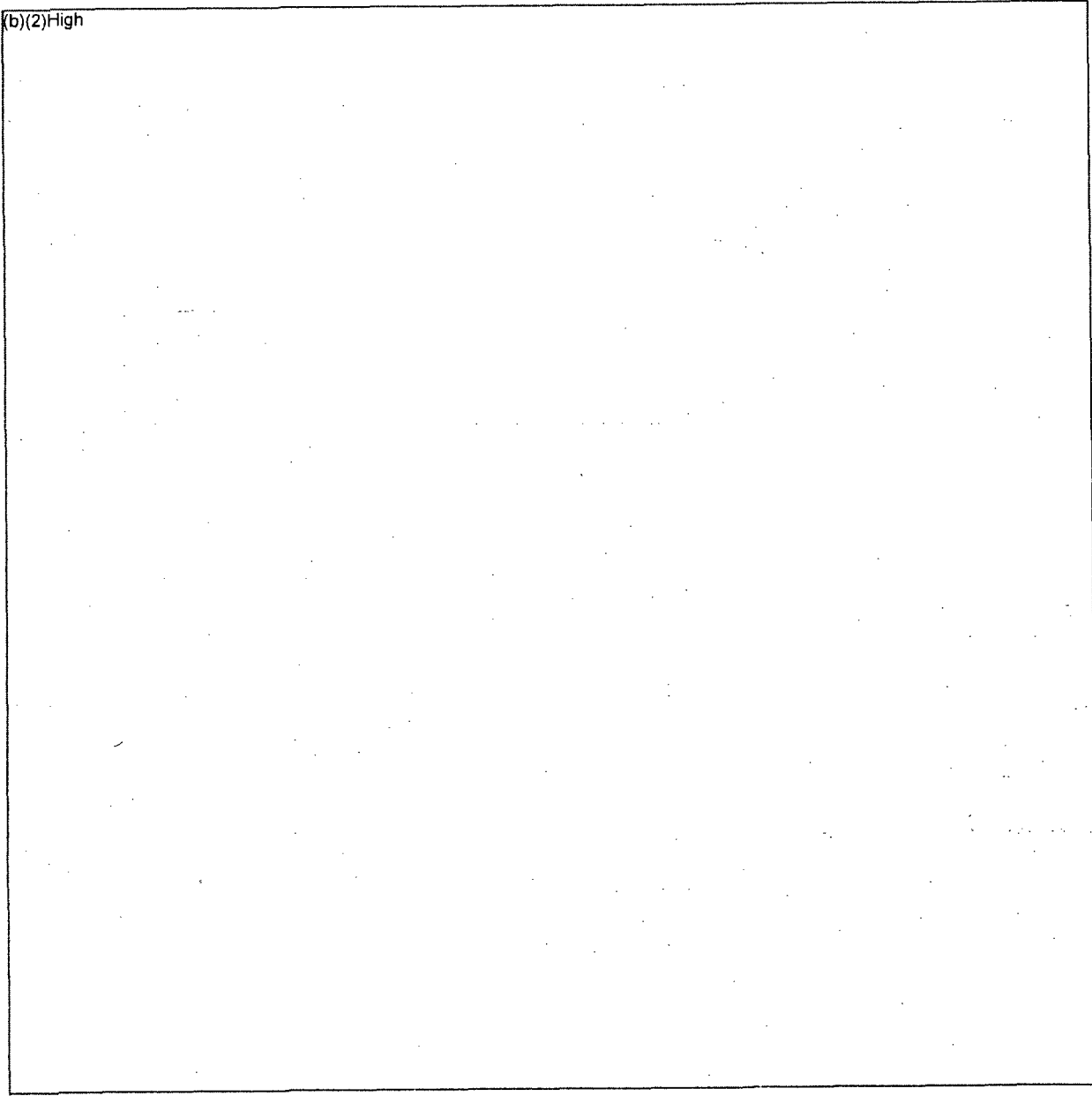
FOIA
ex 2

The staff noted that subsequent information from the applicant makes a greater distinction about open and closed systems than shown in the revised CAR. The applicant initially identified open systems as at atmospheric pressure while closed systems could be pressurized. In the subsequent information, the applicant based the definitions on the system's ability to accommodate solvent; an open system can be 100% solvent and use a non-pressurization correlation for the design basis of the safety function, whereas a closed system cannot be 100% solvent and must use an evaporative cooling correlation.

3.4   NRC Staff Analyses in the Revised DSER - April 2003:

The staff review found that the TBP-nitrate runaway reactions (e.g., red-oil) are similar to many other chemical runaway reactions that occur in the chemical process industry. The red-oil reactions liberate large amounts of thermal energy and non-condensable gases that, if not properly controlled, can rupture process equipment and injure plant personnel. The applicant proposed an approach based on:

1.   Use of a non-cyclic hydrocarbon diluent that will not contribute significantly to the formation of degradation products through radiolysis or chemical breakdown.

2.   Diluent properties related to foaming will be considered to limit possible effects on the vent system used to assure adequate evaporative cooling.

3.   Control of the amount of TBP degradation products created through radiolysis or hydrolysis by limiting the residence time of organics in process vessels containing oxidizing agents and potentially exposed to high temperatures and in radiation fields.

4.   Solutions containing organics will be restricted to temperatures within safety limits to control the energy generation rate.

5.   An adequately sized exhaust path will be provided for aqueous phase evaporative cooling. For closed systems, the vent size will accommodate sufficient mass transfer to prevent initiation of a runaway reaction. A safety margin of 120% of the combined heat input plus heat generation was proposed.

6.   Evaporator steam temperature limits of 133°C.

The applicant also committed to conducting confirmatory experiments to verify or determine the key safety characteristics of several process variables, including: (1) reaction kinetics to determine heat generation rates, (2) diluent foaming - vent size, (3) metal ion effects on the runaway reaction initiation temperature, and (4) allowable residence time to identify the degraded product concentration limits for heat generation.

The staff noted that the applicant's approach envelopes many, but not all of the published DOE practices. Specifically, DOE facilities control evaporator steam temperatures to 120°C while the applicant is proposing 133°C, which is close to the 135°C initiation temperature. The applicant is relying on adequate evaporative cooling to limit the temperature of the evaporator liquids.

The NRC staff review concluded that the phenomena is associated with contact between nitric acid and TBP solutions. Radiolysis can contribute to the reactions involved in the phenomena but it is not required. As with all chemical reactions, increases in temperature(s) and concentrations increase the kinetics. Lower concentrations provide more water that functions both as a diluent, a heat transfer enhancer, and a heat removal agent (by evaporation - obviously, the cooling benefits of too much evaporation can be offset by concentrating the nitrates and TBP, and other organic compounds). The degradation phenomena for TBP with nitric acid appears to involve the lysis of TBP into smaller organic compounds, such as DBP, MBP, and n-butanol, with some nitration of the species (e.g., butyl nitrate). This can occur in the liquid phases and in the metal/nitrate/TBP compounds - adducts - due to the intramolecular presence of nitrate and TBP. The adduct of plutonium contains more nitrate and is likely to be more reactive. The organic compounds may be dissolved in the aqueous phase or entrained - suspended - due to poor separation or density changes (similarities). A discrete organic phase may form in lower temperature equipment (e.g., tanks) or in low flow areas (i.e., lack of mixing) that allow the entrained organic species to agglomerate. The presence of a discrete organic phase can further concentrate these degradation species (i.e., due to their higher affinity - equilibrium constant Kd - for the organic phase) and thermally isolate the reaction from its surroundings, allowing the reactions to accelerate. Vaporization and gas evolution can occur as these reactions continue, leading to additional species such as 1-butene and carbon monoxide. This may produce two phase mixtures and foams that can diminish the effectiveness of venting and pressure relief devices, and, in a closed system, this can allow the pressure to increase. If this occurs, the pressure rise further increases the gas phase concentrations, and, because no material leaves the system, no cooling occurs. Ultimately, the pressure may become sufficient to rupture the vessel and the vapor/aerosol cloud may find an ignition source, which could produce a second explosion. However, if venting is adequate (i.e., an open system), the gaseous and vapor species can leave the system, thus removing reactants and providing cooling that may mitigate or even prevent an actual explosion.

The staff review indicated that no one single variable appears uniquely capable of excluding the formation of red oil under all conditions. Only low temperatures (near ambient) appear capable of reducing reaction rates to the point where intermediate formation is small and natural heat removal is effective, and, thus, the red oil reactions no longer become a concern. In addition, the reported events appear to have involved relatively small quantities of materials and the initiating conditions that form red oil could credibly exist in the proposed MFFF .

Thus, the staff found that the information summarized above requires DCS to address the following functions for addressing red oil concerns:

- Monitoring and cooling below a maximum temperature.
- Maintaining heat fluxes below a specified range or contact (skin) temperature.
- Excluding the introduction of a separate liquid phase into heated equipment.
- Monitoring and controlling concentrations of certain species, such as nitric acid, TBP, and total organic.
- Monitoring and excluding the presence of degradation products, such as DBP, MBP, and butyl compounds.

- Limiting the time between liquid phase purification and processing operations.
- Adequate venting of the system, perhaps based upon a minimum vent area for a bounding TBP or total organic content or concentration.
- Designing monitoring systems to account for localized variations and effects.

Based upon the available experience and literature on the red oil phenomena, the staff concluded that the applicant's proposed approach of a temperature design basis of 135°C is insufficient and does not provide adequate assurances of safety. As a particular comparison, the event at Tomsk did not measure a temperature exceeding the 45-50°C range and the accident reconstruction did not postulate an initial, localized temperature above circa 90°C, both of which are significantly below the applicant's proposed design basis of 135 C. In addition, the applicant's design basis includes an indirect control strategy on steam heating that does not appear to be consistent with the available experience and literature on red oil nor does it address the functions needed to control the phenomena.

The staff has also found concerns with the venting strategy. The applicant has indicated they expect changes in vent sizes to be minimal as compared to designing for a non-red oil system. However, this appears to be predicated on a safety strategy that prevents excessive quantities of solvent and TBP from entering the vessel or system. However, staff review of the literature indicates a relatively high probability (unlikely to anticipated range) for significant solvent and TBP carryover into equipment downstream from solvent extraction columns. In addition, the applicant has indicated solvent carryover would be an anticipated event. In other words, the vent could not perform its safety function. Thus, the staff concludes this is a potential common mode failure that has not been adequately considered and addressed by the safety strategy.

The staff also noted red oil involves phenomena that are inherently uncertain. The proposed strategies, PSSCs, and design bases do not appear to adequately address these uncertainties.

The remaining staff concerns focused on four principle areas:

1. The evaporator steam temperature design basis of 133°C is close to the runaway reaction initiation temperature of 135°C, presenting a limited margin. Additionally, system impurities can lower the reaction initiation temperature by an undefined amount.

2. An adequate safety margin has not been demonstrated for the complete, integrated approach, including temperature and heat removal capacity, and adequate consideration of uncertainties.

3. The applicant has stated that the design bases to preclude a runaway reaction must be viewed in the aggregate (Section 8.5.1.5.5 of the revised CAR). However, the significance of the relative contributions of each safety control towards meeting the preventative safety strategy for the "highly unlikely" performance requirements of 10 CFR 70.61, particularly as they apply to open and closed systems, have not been identified.

4.   Since the applicant has indicated that solvent carryover is an anticipated event, the potential for common mode failure mechanisms that could challenge the venting and heat transfer controls (i.e., impact from organics through foaming, two-phase flow, pressurization, etc.) has to be considered when determining the "highly unlikely" performance requirements of 10 CFR 70.61.

In addition to the above, the staff noted that the applicant is continuing design activities in this area and has identified several action items which apply to the red oil phenomena. Consequently, the staff identified the red oil phenomena as an open item requiring resolution. The applicant should provide additional PSSCs and design bases for addressing the red oil concerns in the evaporators and associated vessels, equipment and piping, and provide adequate margin, or provide adequate justification why the proposed safety strategy, PSSCs, and design bases are acceptable. The red oil phenomena continued to be identified as Open Item CS-01.

3.5   Public Meetings with the Applicant - December 2002 to July 2003 - and Revised Revised Construction Application Request (Revised RCAR) - June 2004:

The NRC held public meetings with the applicant in this timeframe. The applicant refined the safety strategy for red oil several times. As previously noted, the applicant's current safety is stated in the Revised RCAR and relevant portions are included in Attachment 1.

3.6   DOE/DNFSB Safety Controls:

The SRS currently operates evaporators in H Canyon. These evaporators are subjected to DOE Safety Class (i.e., for the public) and Safety Significant (i.e., for the workers) controls to prevent a potential red oil runaway reaction and explosion (i.e., frequency under 1E-6/yr). The controls are generally divided into two categories - those that prevent excessive amounts of TBP entering the evaporators and those to prevent overheating. Significantly, the latter include a 120°C temperature safety limit (used in an analogous manner as design basis), a high steam coil pressure interlock, and an alarm for the operator to manually check that the steam flow has been terminated. The staff notes that the 120°C temperature limit corresponds to the normal boiling point of the water-nitric acid azeotrope.

The Defense Nuclear Facilities Safety Board (DNFSB) recently issued a technical report on the control of red oil explosions - this is Attachment 3. This report emphasizes controls on temperature, pressure, mass, and concentration (acid), and that the controls should be used together to provide effective defense-in-depth for prevention of a red oil explosion. The report discusses the controls as follows:

Temperature control:
The report identifies an initiation temperature of 130° C for the runaway red oil reactions. The report further indicates lower temperatures are needed for operationally protected temperatures and setpoints. For H Canyon, it notes the operational protected temperature (Technical Safety Requirement - design basis like) of 120°C and an overtemperature safety setpoint of 117°C

(i.e., 3°C is allowed for instrument errors and biases). The report mentions steam interlocks at H - Canyon for the steam heat - these are set at not to exceed 25 psig, which corresponds to 269°F or about 132°C.

Pressure control:
The report mentions passive vents per the Fauske correlation; > 0.063 mm^2/g of TBP (< 15.9 g TBP/mm^2 or < 1.59 kg TBP/cm^2). It also mentions 312 g of red oil/mm^2 (31.2 kg/cm^2). With some safety margin, it recommends no more than 208 g of red oil/mm^2 (20.8 kg/cm^2) (page 4-3). Page 5-2 of the DNFSB report mentions 6.44 in^2 as the minimum vent for 3000 lbs of TBP. This corresponds to < 32.7 kg TBP/cm^2 of vent. Note that the applicant (DCS) is using 0.008 mm^2/g of organic compound (12.5 kg/cm^2).

Mass Control:
This applies to the organic phase, by keeping it from entering heated equipment (prevention) or by omiting TBP (or equivalent) mass/concentration (mitigation). For H-Canyon, the TBP concentration in the organic phase is limited to 7.5%.

DCS is using a concentration of 30% TBP in branched dodecane (THP). DCS has no limits on organic mass going into open systems. DCS has stated that any limits on total organic mass entering closed systems will be developed at the ISA stage and will be a substantial fraction of the volume (e.g., 40-60%). DCS has indicated organic materials entering open and closed systems are anticipated events.

Concentration control:

This applies primarily to nitric acid (less than 10 M) and, to a lesser extent, nitrate salts/UN (less than 20%). DCS is concentrating to over 13.6 N HNO3. DCS has no limits on acid concentration.

In summary, the DNFSB report identifies the MFFF as a facility in the design stage with the capability to produce red oil and would likely recommend more controls with more conservative design bases (i.e., lower temperatures, larger venting capability, less organic phase carryover,, and lower concentrations) than those currently accepted by the NRC.

3.7   NRC Management Decision - April 2004:

The management decision is included in Attachment 2. In summary, it accepts the applicant's position. Its conclusion is as follows:

"The applicant has proposed that the design operating temperature be the temperature, 120.4° C, of the nitric acid-water azeotrope. This operating temperature is about 10° C lower than the initiating temperature considered plausible for an autocatalytic red oil reaction. The Department of Energy has opted to use 130° C as the minimum initiation temperature for a red oil reaction. However, there is some disagreement as to what this initiating temperature is with other

investigators agreeing that an initiating temperature for an autocatalytic red oil event is about 135° C. Operating at the azeotrope, which provides a stable operating region, as well establishing a bulk fluid design basis of 125° C and maintaining the bulk fluid design heatup rate to a maximum value of 2° C/minute after startup, coupled with the applicant's other proposed PSSC's for this system, provides sufficient margin to ensure that the autocatalytic red oil reaction is not initiated. As long as the red oil autocatalytic reaction is not initiated a closed system provides adequate ventilation. An open system would be important to preclude a system overpressurization event if the safety controls are judged insufficient to prevent a red oil auto catalytic reaction."

"Staff is preparing the final safety evaluation for the MFFF construction authorization. The applicant has committed to further evaluate the red oil phenomena, including continuing analyses and experiments which could result in an increase or decrease of the temperature at which action is required to remain below the design basis value. The applicant is also evaluating the effect of impurities in the initiation temperature in closed systems. If the outcome of this evaluation determines that the final design does not provide sufficient assurance that the red oil initiation temperature will not be exceeded then additional safety margin could be credited to assure safety. For example, the operating temperature could be lowered (a lower operating temperature is otherwise not desired since the system is less efficient and generates more waste), an open system could be designed (this might be difficult to achieve if the design was complete) or additional features could be identified as PSSCs such as crediting a system which would ensure the aqueous phase is available in the evaporator if either the temperature limit or the ramp rate is exceeded."

"The applicant's safety basis should be assessed with respect to the design submitted. For the Construction Authorization the applicant has provided sufficient detail and committed to sufficient design basis to ensure that the resulting design will provide adequate safety. In addition, we can not conclude that because DOE has different control strategies for its applications that the applicant's approach is incorrect or less conservative. For the Construction Authorization approval the applicant has proposed a suitable suite of controls. These controls can be refined or enhanced as necessary during the final application review."

The management team directed the staff to close CS-1 in the final safety evaluation report for the MFFF construction authorization.

3.8   NRC Draft Final Safety Evaluation Report (FSER):

This reiterates the management decision from Attachment 2. No analysis or new information is provided.

4.   Discussion:

The applicant's proposed strategy in the Revised CAR (see Attachment 1) does not include or cite supporting analyses, logical statements, calculational bases, or operating experience. It is an assertion. The DNFSB red oil report (in Attachment 3) represents the DOE/DNFSB RAGAGEP - Reasonably Accepted And Good Engineering Practice - approach for safely

controlling the red oil phenomena. The applicant's proposal contradicts the DOE/DNFSB RAGAGEP in the following key areas:

- **Temperature:** DOE/DNFSB use a lower temperature limit of 120 C as compared to the applicant's 125 C. Note that setpoint analysis would be applied to both limits - DOE applies a setpoint of about 117 C.. Note that Russian researchers have observed the red oil pressurization effect in several tests below 130 C, and one was around 125 C. The reaction rates increase exponentially with temperature and, as noted in the DSER and RDSER, the reacting organic/nitrate mixture transitions in the 120-130 C range to a self-heating mixture (i.e., the majority - > 90% - of the enthalpy accrues from the red oil reactions).

- **Pressure/Venting:** DOE/DNFSB use a pressure/vent relationship (Figure 2) that is well within the safe range identified from experimental testing. The applicant's approach for open systems is also well within the safe range. In contrast, the applicant's approach for closed systems (i.e., evaporative cooling) far exceeds the safe limit and is well into the unsafe range. Common mode failure is likely - reaction products from the red oil reactions cannot escape and provide evaporative cooling, resulting in choked flow, which increases temperature, resulting in suppressed evaporation, which increases temperature, resulting in increased red oil reaction rates etc. - ultimately, this leads to a runaway reaction and explosion. The loss of evaporative cooling effectiveness above 120 C is noted in articles cited in the staff's DSER and RDSER.

- **Mass Control (Organic):** DOE/DNFSB utilize to organic mass controls - controls to prevent carryover (decanters, hold tanks, and hold times) and limits on the TBP content of the organic phase. The applicant does not have these controls and indicates organic carryover is an anticipated event. The applicant has controls on limiting impurities, cyclic hydrocarbons, and organic residence time, but these represent controls on initiation temperature for the red oil reactions.

- **Concentration Control (Aqueous):** DOE/DNFSB applies limits, primarily to nitric acid (less than 10 M) and, to a lesser extent, nitrate salts/UN (less than 20%). DCS is concentrating to over 13.6 N HNO_3. DCS has no limits on acid concentration.

The applicant can propose alternatives to accepted practice, such as the DOE/DNFSB control strategy. However, given the significant differences with RAGAGEP and the lack of supporting information, a conclusion of adequate assurances of safety cannot be made for the applicant's control strategy. At the December 2002 public meeting, a member of the public also noted this disparity and stated it seemed reasonable for the applicant to provide such an explanation.

As regards the NRC management decision, I note the following:

- It mentions a consensus position. A consensus process was not used. Instead, a voting process that included non-qualified staff members was used to circumvent the concerns of the assigned lead chemical safety reviewer. Additional information was not sought from the applicant.
- The management decision discusses temperature efficiency concerns. Efficiency concerns are not listed in either the regulations or the SRP, and are irrelevant for a safety conclusion.
- It is an assertion - there is no supporting data, calculations, supporting analysis, or clear logical argument to support acceptance of the applicant's strategy.
- It cites DOE/SRS experiments that show limited heating of the organic phase in the presence of aqueous solutions. However, this is selective use of DOE/SRS experiments (the SRS evaporators use the DOE/DNFSB RAGAGEP as the safety strategy); the DOE/SRS experiments are based upon the specific geometries of the SRS evaporators (low aspect ratios - relatively "fat") and the use of steam jets. The latter induce mixing, and impart kinetic energy and mass flow that increase evaporation rates. In contrast, the evaporators proposed by the applicant have high aspect ratios and do not use steam jets; no analysis, calculations, or explanation are provided to justify the relevance of the DOE/SRS experimental analogue.
- A significant portion of the management decision relies upon future commitments, efforts, and experiments to define/refine current PSSCs and design bases that are not RAGAGEP. This is a reversal of the normal licensing approach.

At the July 2003 public meeting, the applicant drew a diagram of a typical evaporator for the proposed facility and indicated it would be perhaps 15 cm in diameter and 8-10 meters high. This is considered a high aspect ratio design. High aspect ratio designs are not recommended by DOE (see the staff's DSER and RDSER) and contributed to the accident at Tomsk. If a slug of organic material enters and forms a layer on top of aqueous phases in such high aspect ratio evaporators, the static head alone will pressurize the aqueous phase and result in higher temperatures at the interface (i.e., the boiling point is elevated).

My concerns are summarized as follows:

1. Contradictions with DOE/DNFSB RAGAGEP are not explained. In particular, the RAGAGEP shows the applicant's proposal for closed systems being entirely in the unsafe regime (Figure 2).

2. There is inadequate margin in the design basis temperature.

3. The venting is insufficient to avoid choked flow and pressurization, which has the ability to rapidly raise the temperature even with the applicant's proposed strategy functioning.

Page 16 of 22

4. Controls on organic compounds are inadequate - the applicant has indicated organic carryover is an anticipated event.

5. There are no controls on acid or solvent concentrations.

6. The evaporators at the proposed facility have a high aspect ratio which is more favorable for red oil reactions to occur and potentially cause pressure excursions.

7. The NRC management decision accepting the applicant's proposal is based upon a voting process that included unqualified reviewers. It is not a consensus process.

8. Efficiency arguments were used by management as part of the rationale for accepting the applicant's proposal. However, efficiency is not mentioned in the regulations or as part of the SRP acceptance criteria.

9. A significant portion of the management decision relies upon future commitments, efforts, and experiments to define/refine current PSSCs and design bases that are not RAGAGEP.

10. Overall, safety concerns from the NRC staff's Revised Draft Safety Evaluation Report (RDSER) are not addressed, including inconsistencies with other limits and a clear logical or calculational basis from the applicant indicating their integrated control strategy has the ability to meet the regulations. The applicant has made an assertion - supporting information from the applicant and the prevailing staff opinion is non-existent or inadequate to support a conclusion of adequate assurances of safety.

Figure 2: Comparison of the Applicant's Red Oil Safety Strategies with DOE/DNFSB (formerly Open Item CS-01) Recommendations

CS-01: Red Oil
Pressure Vent Relationship
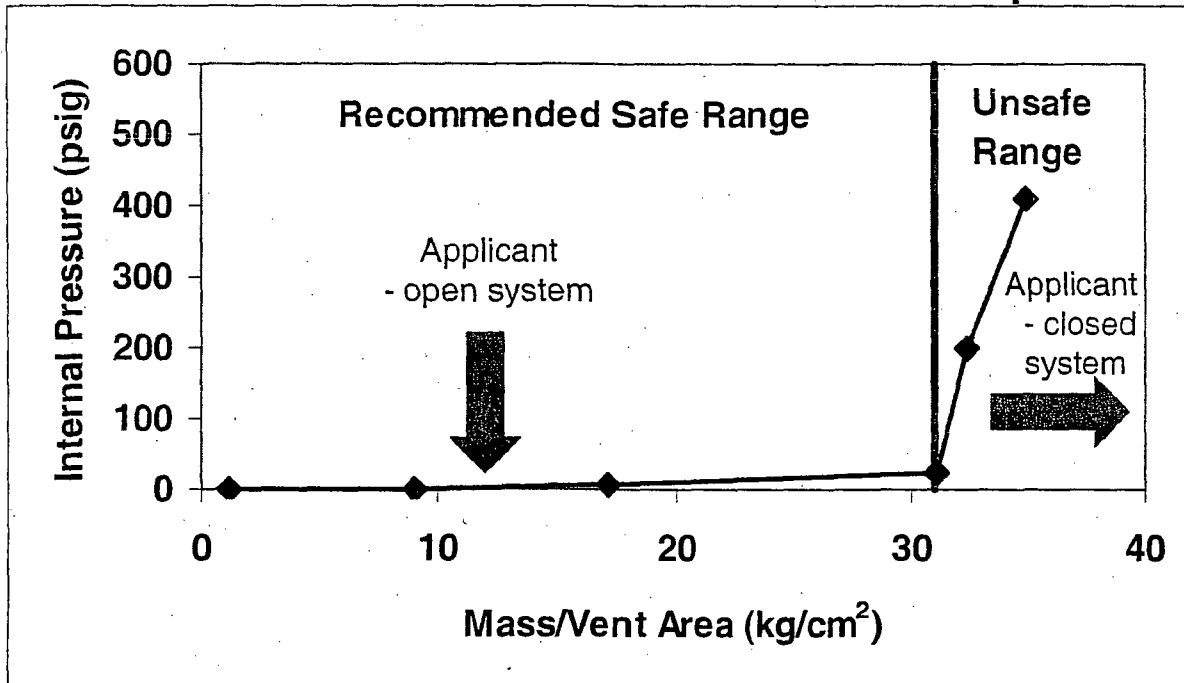
ATTACHMENT 1

APPLICANT'S PROPOSED SAFETY STRATEGY, CONTROLS, AND DESIGN BASES

ATTACHMENT
FOIA
EX. 2

Withhold entire
Attachment

Note:

Although CAR was previously made
public, it was done prior to SUNSI,
The guidance has been that even though
we are not pulling the info from ADAMS,
we will not re-release it

ATTACHMENT 2

NRC MANAGEMENT DECISION TO ACCEPT THE
APPLICANT'S PROPOSED SAFETY STRATEGY FOR RED OIL

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

April 12, 2004

MEMORANDUM TO: Hironori Peterson, Acting Section Chief
Mixed Oxide Facility Licensing Section
Special Projects Branch, NMSS/FCSS

FROM: Joseph Giitter, Chief
Special Projects Branch, NMSS/FCSS

Joseph Holonich, Deputy Director
Division of Fuel Cycle Safety and Safeguards, NMSS

Robert Pierson, Director
Division of Fuel Cycle Safety and Safeguards, NMSS

SUBJECT: DETERMINATION ON POSITION FOR CLOSURE OF CHEMICAL
SAFETY ITEM CS-1 PERTAINING TO RED OIL EXPLOSIONS

In a memorandum dated December 30, 2003 (Attachment 1) Brian Smith provided the views of
the staff in your section who conducted the review of the Mixed Oxide Fuel Fabrication Facility
(MFFF), on chemical safety open item CS-1 pertaining to red oil explosions. The memo
contained background on the issue, a discussion of the consensus staff position which accepts
the applicants proposed safety measures and as such recommends closure of the open item
(position 1) and a dissenting view from the lead chemical safety reviewer (LCSR) in your
section (position 2) who has identified concerns with the applicant's approach to closure of the
red oil issue, CS-1. The purpose of this memorandum is to provide you with a management
decision on the positions presented in Attachment 1.

As described in the enclosure to your memorandum, a red-oil reaction is a runaway exothermic
chemical reaction involving hydrolysis of tri-butyl phosphate (TBP) and related degradation
products by strong nitric acid. The reaction is a safety concern because the reaction is highly
exothermic and can create a rapid overpressurization through the generation of a large amount
of non-condensable gas. (b)(2)High

(b)(2)High

(b)(2)High   Staff have differing views on only that portion of
the applicant's safety assessment that pertains to the acid recovery evaporators. There are two
types of systems utilized in the applicant's proposed design, "open" systems and "closed"
systems. Open and closed systems and their attributes are described in Attachment 1. The
staff is satisfied with the applicant's proposal for open systems. This memorandum will address
the staff views with respect to closed systems for the acid recovery evaporators.

The following are the applicant's proposed design basis for these closed systems: 1) limit steam
to 133° C; 2) utilize a diluent that does not contain cyclic chain hydrocarbons; 3) size the offgas
treatment system to relieve 1.2 x combination of energy generation and energy input to the
system; 4) limit the residence time of organics in the presence of oxidizers; 5) limit bulk

temperature to 125° C ; 6) limit heat-up rate to 2° C per minute; and 7) stop heating and add aqueous phase to maintain these limits. The process safety control system has three functions: 1) to ensure adequate aqueous phase to provide evaporative cooling; 2) to ensure that the bulk temperature of the solutions that may contain degraded organic is restricted within safety limits to control the energy generation rate; and 3) to limit residence time of organics in the presence of oxidizers. (b)(2)High (b)(2)High (b)(2)High
(b)(2)High

(b)(2)High

The LCSR has expressed a number of concerns with the applicants approach which are summarized in Staff Position 2 of Attachment 1. Included in these concerns is the LCSR's contention that the steam temperature of 133° C is too close to the "red oil" runaway reaction initiation temperature. However, utilizing a maximum steam temperature of 133° C should not be interpreted as allowing a solution temperature of 133° C. Steam at 133° C is required to efficiently heat the nitric acid-water azeotrope to its boiling point of 120.4° C. Under normal conditions this boiling point should not be exceeded and operating at atmospheric pressure provides a stable range, the azeotrope, at which the system operates. In Staff Position 2 the LCSR also is concerned that an adequate safety margin has not been demonstrated for the complete, integrated approach, including temperature and heat removal capacity, and adequate consideration of uncertainties. The LCSR is also concerned that the applicant's approach envelopes many but not all of the DOE practices.

In an e-mail dated February 5, 2004, "Further Thoughts on Red Oil," (Attachment 2) the LCSR provided additional comments on the review process for MOX and red oil in particular. Of particular concern to the LCSR was the limited information provided in the Construction Authorization Report and the fact that the applicant had originally proposed an "open system" for the acid recovery evaporators of the aqueous polishing system, but in subsequent design

revisions was now proposing a "closed system." According to the February 5, 2004, e-mail, staff had concluded that the approach for controlling red oil events in open systems had the ability to be implemented to meet 10 CFR Part 70 requirements and thus was acceptable for the construction authorization phase; however, the applicant's design change to use a closed system for the acid recovery evaporators could no longer demonstrate 10 CFR Part 70 requirements. The LCSR also states in his e-mail that adequate assurances of safety can be achieved by a lower design basis temperature (he suggests 110-115° C) and more venting capability (all other controls remaining the same), or by the applicant following a DOE control strategy.

The applicant has proposed that the design operating temperature be the temperature, 120.4° C, of the nitric acid-water azeotrope. This operating temperature is about 10° C lower than the initiating temperature considered plausible for an autocatalytic red oil reaction. The Department of Energy has opted to use 130° C as the minimum initiation temperature for a red oil reaction. However, there is some disagreement as to what this initiating temperature is with other investigators agreeing that an initiating temperature for an autocatalytic red oil event is about 135° C. Operating at the azeotrope, which provides a stable operating region, as well establishing a bulk fluid design basis of 125° C and maintaining the bulk fluid design heatup rate to a maximum value of 2° C/minute after startup, coupled with the applicant's other proposed PSSC's for this system, provides sufficient margin to ensure that the autocatalytic red oil reaction is not initiated. As long as the red oil autocatalytic reaction is not initiated a closed system provides adequate ventilation. An open system would be important to preclude a system overpressurization event if the safety controls are judged insufficient to prevent a red oil auto catalytic reaction.

Staff is preparing the final safety evaluation for the MFFF construction authorization. The applicant has committed to further evaluate the red oil phenomena, including continuing analyses and experiments which could result in an increase or decrease of the temperature at which action is required to remain below the design basis value. The applicant is also evaluating the effect of impurities in the initiation temperature in closed systems. If the outcome of this evaluation determines that the final design does not provide sufficient assurance that the red oil initiation temperature will not be exceeded then additional safety margin could be credited to assure safety. For example, the operating temperature could be lowered (a lower operating temperature is otherwise not desired since the system is less efficient and generates more waste), an open system could be designed (this might be difficult to achieve if the design was complete) or additional features could be identified as PSSCs such as crediting a system which would ensure the aqueous phase is available in the evaporator if either the temperature limit or the ramp rate is exceeded.

The applicant's safety basis should be assessed with respect to the design submitted. For the Construction Authorization the applicant has provided sufficient detail and committed to sufficient design basis to ensure that the resulting design will provide adequate safety. In addition, we can not conclude that because DOE has different control strategies for its applications that the applicant's approach is incorrect or less conservative. For the Construction Authorization approval the applicant has proposed a suitable suite of controls. These controls can be refined or enhanced as necessary during the final application review.

In summary, based on the information provided in the above referenced December 30, 2003, memorandum, the supplemental information provided by the LCSR in his February 5, 2004, e-

mail, and the licensee's proposed PSSC's in its submittals of July 28 and October 6, 2003, the management team unanimously agreed that the consensus staff position, Staff Position 1 in Attachment 1, supports the closure of chemical safety item CS-1 in the final safety evaluation report for the MFFF construction authorization. Therefore, you are directed to close CS-1 in the final safety evaluation report for the MFFF construction authorization.

Attachments:
1. Memorandum from B. Smith to J. Giitter dated December 30, 2003, re "Safety Evaluation and Staff Positions on the Closure of Remaining Chemical Safety Open Item CS-1 Pertaining to Red Oil Explosions"
2. E-mail from A. Murray to J. Giitter, J. Holonich, and R. Pierson dated February 5, 2004, re "Further Thoughts on Red Oil"

cc: M. Virgilio
        M. Federline
        B. Smith
        A. Murray
        J. Hull
        A. Persinko

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cc: M. Virgilio
       M. Federline
       B. Smith
       A. Murray
       J. Hull
       A. Persinko

OFFICE	NMSS/FCSS	NMSS/FCSS/SPB	NMSS/FCSS	
NAME	J.Holonich*:lcg	J.Giitter*	R.Pierson*	
DATE	04/12/2004	04/07/2004	04/07/2004	

OFFICIAL RECORD COPY

Attachment 1

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

December 30, 2003

MEMORANDUM TO: Joseph G. Giitter, Chief
Special Projects and Inspection Branch
Division of Fuel Cycle Safety
and Safeguards
Office of Nuclear Material Safety
and Safeguards

FROM: Brian Smith, Chief
Special Projects Section
Special Projects and Inspection Branch
Division of Fuel Cycle Safety
and Safeguards, NMSS

SUBJECT: SAFETY EVALUATION AND STAFF POSITIONS ON THE CLOSURE
OF REMAINING CHEMICAL SAFETY OPEN ITEM CS-1 PERTAINING
TO RED OIL EXPLOSIONS

The purpose of this memorandum is to communicate the views of the staff on the chemical
safety open item CS-1, regarding prevention of red oil explosions. This open item was
documented in the April 30, 2003, Draft Safety Evaluation Report (DSER) for the Mixed Oxide
Fuel Fabrication Facility (MFFF).

Since April 2003, staff have conducted several in-office reviews at DCS facilities and held many
open meetings with DCS to discuss and resolve the open items. Additional information that the
staff have considered in its review include DCS presentations and written commitments at open
meetings, letters, phone call summaries, and page changes to the revised CAR.

The Attachment to this memorandum provides the staff's safety evaluation of the applicant's
proposal to prevent red oil explosions. A consensus staff position is presented as "Staff
Position 1 - Acceptable", which supports closure of the item. A dissenting view from the Lead
Chemical Safety Reviewer, "Staff Position 2 - Unacceptable", is also presented.

I recommend including the consensus staff position as the staff's position in the Final Safety
Evaluation Report.

Attachment: Staff Evaluation of Red Oil Explosion Open Item (CS-1)

Staff Evaluation of Red Oil Explosion Open Item (CS-1)

Background

Safety Concern

For the purposes of this discussion, a "red-oil" reaction is a runaway exothermic chemical reaction involving the hydrolysis of tri-butyl phosphate (TBP) and related degradation products by strong nitric acid. This reaction is a safety concern because it is highly exothermic and can generate a large amount of non-condensable gas. Unless properly vented, the non-condensable gas can overpressurize and rupture process vessels and equipment, which could result in a release to the environment and radiation doses to nearby site worker and the public.

Reaction Kinetics

The actual chemical reaction is a complex set of reactions that involve a number of volatile chemical intermediates. The hydrolysis rate for the standard TBP-nitrate reactions is a strong function of temperature and becomes very fast at temperatures in the range of 130-150°C. As the temperature increases, the heat generation rate reaches the point where the reaction becomes self-heating. Laboratory experiments have demonstrated that with sufficient venting, the removal of those volatile chemical intermediates can limit the total system energy by up to 90 percent. This phenomena is important for controlling red oil reactions because it significantly limits the rate of energy input into the system as well as the pressure increase. By limiting the pressure increase, the reaction rate of the gaseous components, which have the potential of contributing up to 90 percent of the total system energy, is also controlled. Thus, proper venting limits the overall reaction rate by limiting solution temperature and gaseous pressure. Limits on the gaseous pressure is also important to assure that the solution boiling point is maintained at a sufficient margin below the red-oil initiation temperature.

Initiation Temperature

In one literature report (Rudisill and Crooks, 2000), the initiation temperature for a "runaway" reaction has been measured as a function of nitric acid and dissolved solids concentrations using thermal analysis techniques involving the use of a nearly adiabatic calorimeter equipped with temperature and pressure sensors. The solution was heated at 1°C/minute and the initiation temperature was defined by the time period when a rapid increase of pressure was initially seen. The initiation temperature range for the most conservative case was observed to be in the 134-140°C range, averaging 137°C. Other reports from DOE identify a range of temperatures, with initiation as low as 132°C. DOE has opted to use 130°C as the minimum initiation temperature for the autocatalytic reactions in its safety analyses. DOE has set the solution temperature limit (TSR - Technical Safety Requirement) as not exceeding 120 C.

Attachment

Normal operations are below this limit. Experimental work recently reported in Russia has identified initiation temperatures of 123-127° C in concentrated nitric acid.

<u>Operational Parameters</u>

The mixture of nitric acid and water forms a maximum boiling point <u>azeotrope</u> which has a boiling point at 1 atmosphere pressure of 120.4°C.

> Note: *An azeotrope is a solution that has a higher or lower vapor pressure, at a given temperature, than any of the pure components of which it is composed. In the case of nitric acid and water, the vapor pressure is lower, and the solution is called a "maximum boiling point azeotrope." As a result, the mixture boils at a temperature higher than either pure component. Also, the vapor in equilibrium with an azeotrope has the same concentration as the liquid. Azeotropes, therefore, like pure substances, distill without change. Therefore, a non-azeotrophic solution of nitric acid and water is "distilled" in the acid recovery process to the azeotropic concentration of 67% nitric acid, but it cannot be distilled further to a higher nitric acid concentration.*

Since nitric acid and water forms a maximum boiling point azeotrope, the overall system temperature would be limited to the maximum boiling point of 120.4°C as long as (1) an adequate aqueous inventory is maintained to boil off and cool the system, and (2) the pressure is not allowed to increase above 1 atmosphere. Should the pressure increase, the boiling point will correspondingly increase. A significant pressure increase can result in the boiling point exceeding the initiation temperature for a red-oil runaway reaction.

<u>Venting</u>

The applicant has defined the use of the terms "open" and "closed" system. As used in the application, an "open" system can adequately vent a full runaway red-oil reaction. A "closed" system vent is sized to provide sufficient mass transfer to ensure adequate evaporative cooling. However, a "closed" system cannot vent a full runaway red-oil reaction. This usage is somewhat different from that often found in the literature.

<u>Design Concepts</u>

The applicant is developing the MOX process based on the French design. However, there are differences between the French regulatory approach and the 10 CFR Part 70.61 performance criteria that DCS must meet. While the French process has a number of features that would tend to limit the amount or probability of TBP being added to the evaporator, the applicant has chosen not to take credit for them. Hence, those features are not identified by DCS as PSSCs and are not considered in the safety evaluation.

Event Sequence

A red oil event can occur when an organic phase solution of TBP in an organic diluent is degraded by hydrolysis reactions. This condition exists in the purification unit of the AP process, where solvent extraction is used to purify plutonium. At the MFFF, the hydrolysis of TBP results from intimate contact of organic phases containing TBP with nitric acid solutions. Since radioactive material would also be present in both phases, then radiolysis would also contribute to the degradation of TBP. TBP degradation products include, for example, dibutyl phosphates, butyl alcohol, monobutyl phosphate, butanol and butyl nitrate.

The aforementioned reactions occur normally and continuously in solvent extraction systems with TBP. However, the rate of this reaction is temperature dependent. A quantity of TBP and nitrate which is heated to the point that it begins to rapidly react will begin to release more heat energy from the chemical reactions than the process vessel loses from radiative and convective heat losses. As a result, a reaction can become self-sustaining, and the temperature of the organic phase can continue to rise. Above an "initiation temperature," the reaction runs away, rapidly consuming TBP until the quantity of oxidizer that is soluble in the organic phase (nitric acid) is consumed.

The runaway reaction could release between 67 and 368 kcal / mole, as TBP converts to carbon dioxide, phosphoric acid, and water. The total energy release would be limited by the solubility of nitric acid in the organic phase and the fact that the nitric acid would be consumed before the reaction is complete. Given that the molecular weight of TBP is 266 g / mole, then this reaction energy yields between 250 and 5800 J / g. The energy release of TNT is 4564 J / g.

Therefore, the generation of large amounts of gaseous by-products and heat in a red oil event would rupture the process vessel in which the reaction occurs, unless adequate venting is provided to accommodate the reaction.

Consequences

The largest inventory of radioactive material in which the red oil event could occur is in the purification cycle of the aqueous polishing workshop. This unit contains tanks with up to 40 kg of plutonium in solution. However, staff have differing views on only that portion of the applicant's safety assessment that pertains to the acid recovery evaporators. The maximum inventory is in an evaporator (EV2000) that would contain approximately 1.4 kg of americium-241.

Assumptions:
- All of the material is involved in the event (damage ratio, DR = 1);
- The atmospheric release fraction and respirable fraction for explosions is 0.01 x 1.0.
- No leak path factor is applied for the final two stages of HEPA filtration (LPF = 1.0).
- The source term is 1.4 kg x 1.0 x 0.01 x 1.0 x 1.0 = 1.4 kilograms Am

Acute, Total Effective Dose Equivalent (<24 hour exposure, 50 year TEDE)

Facility Worker (qualitative)	Site Worker (rem)	Environment[1] (sum of fractions)	Public (rem)
HIGH	80	12,000	80

The red oil explosion is a high consequence to the facility, site workers, and public, and an intermediate consequence to the environment.

Applicant's Proposal

In Chapter 5 of the October 2002 CAR, the applicant identified two sets of principal structures, systems and components (PSSCs) to prevent the overpressurization event.

An *open* system is defined by the applicant as one in which the vent area associated with the offgas treatment system is sufficient to prevent overpressurization, if the runaway reaction occurs. A *closed* system is one in which the vent area is not sufficient to prevent overpressurization, if the runaway reaction occurs.

(b)(2)High

Offgas Treatment System

For *closed* systems, the safety function of the offgas treatment system is to provide an exhaust path for aqueous phase evaporative cooling in process vessels. The design basis is:

evaporative cooling = 1.2 [steam energy input at 133°C + energy generated chemically]

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[1] Per 10 CFR 70.61(c)(3), environmental consequences are a ratio of the 24-hour average concentration at the restricted area boundary to a value 5000 times that appearing in 10 CFR 20, Appendix B, Table 2, Column 2.

where 1.2 is a safety factor.

An additional function of the offgas treatment system in *open* systems is to provide venting of vessels and equipment that potentially contain TBP and its associated by-products to prevent over-pressurization, should the runaway reaction occur. The design basis value for the vent size is 0.008 mm² per gram of organic material present in the vessel.

(b)(2)High
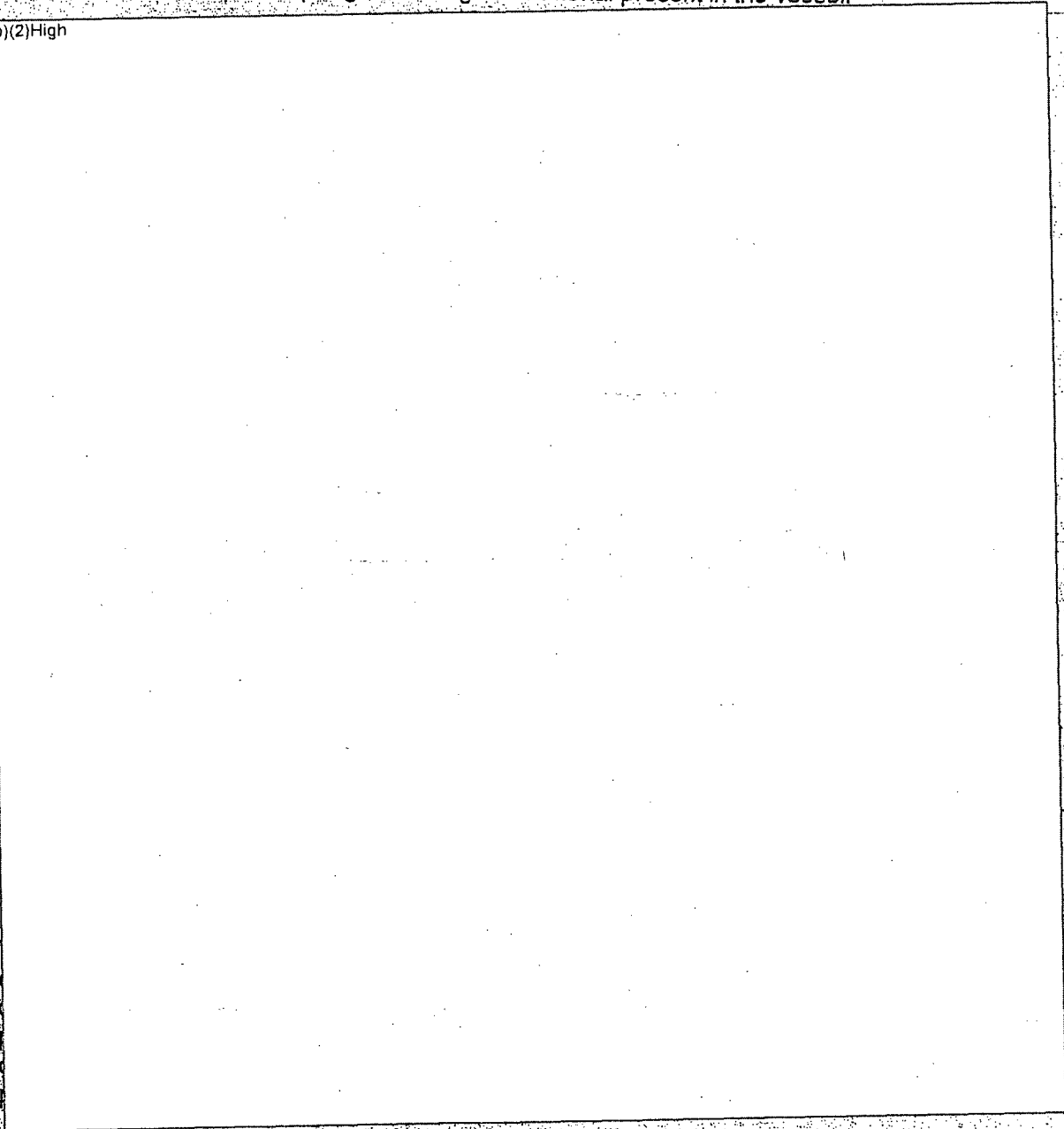
Further Research

DCS has committed to further evaluate the red oil phenomena, including continuing analyses and experiments which could result in an increase or decrease of the temperature at which action is required to remain below the design basis value. DCS is also evaluating the effect of impurities on the initiation temperature in closed systems (DCS, Dec. 10-12, 2002 meeting with NRC).

Staff Positions

The staff evaluation has been completed for all facets of the red-oil runaway reaction except the Acid Recovery evaporator. Consensus has been reached on the acceptability of all of the applicant's proposed design bases except for the acceptability of the 125°C not-to-exceed bulk fluid limit for the closed system. The two staff positions relative to this temperature safety limit are discussed below.

Staff Position 1 - Acceptable

Staff Evaluation of Temperature Limit
Staff evaluated whether the average solution temperature limit of 125 °C is adequate. Staff evaluated literature from the Savannah River Site which supports a safety limit of no greater than 130 °C for evaporators containing nitric acid and TBP. The literature reviewed by the staff include:

• H-Canyon Safety Analysis Report, WSRC-SA-2001-00008, Rev. 4, sections 8.3.2.2.1, "EXPLOSION - TBP-NITRIC ACID ("RED OIL") RUNAWAY REACTIONS."
    NOTE: This SAR recommends an "always safe" limit of less than 130 °C, but cites a 135 °C temperature at which initiation of a runaway reaction between TBP and concentrated (70 wt%) nitric acid was observed to occur. The text also states "Literature data indicates that a runaway red oil reaction is not initiated in an open (vented to atmosphere) vessel below 135 °C."

• Initiation Temperature for Runaway Tri-n-Butyl Phosphate/Nitric Acid Reaction, Rudisill, Tracy S. and William J. Crooks III, WSRC, WSRC-MS-2001-00214
    NOTE: This report, using contemporary methods but similar experiment conditions, concludes that some of the Colven data from 1956, which support initiation temperatures as low as 129 °C, are outliers. The minimum initiation temperature found by these authors is 137 °C for 15 M nitric acid.

• Safe Handling of TBP and Nitrates in the Nuclear Process Industry (U), Hyder, M.L., WSRC-TR-94-0372
    NOTE: This author recommends that "Evaporators in which TBP may be present should be controlled to prevent local high temperatures. No portion or surface of the evaporator should exceed 130 °C, and operating temperatures substantially lower than this are desirable."

• Safe Venting of "Red Oil" Runaway Reactions, Paddleford, D.F. and H. K. Fauske, WSRC-MS-94-0649
  NOTE: These authors conclude that a runaway reaction is possible in open system, i.e., at atmospheric pressure, where self heating was observed at temperatures in vicinity of 130 °C.

• Safe Conditions for Contacting Nitric Acid or Nitrates with Tri-N-Butyl Phosphate (TBP), Hyder, M.L., WSRC-TR-94-059
  NOTE: This author recommends a maximum temperature for acidic nitrate evaporation of aqueous solutions potentially containing TBP of 130 °C, and further states that this temperature is valid when the conditions of mixing and heat transfer ensure that reaction heat will evaporate water.

The applicant has committed to design the Acid Recovery evaporator system such that the bulk fluid temperature will not exceed 125 °C. This will be accomplished by shutting off the steam and injecting aqueous phase material into the system. As long as the pressure is maintained at about 1 atmosphere pressure, the bulk fluid cannot exceed the nitric acid/water azeotrope boiling point, which is 120.4 °C. Providing a vent path that can provide sufficient mass flow to remove 1.2 times the heat input from the steam and the heat generated from hydrolysis and an adequate aqueous phase inventory, provides the physical conditions necessary to limit the bulk temperature to about 120.4 °C. Therefore, the applicant has proposed a shutdown temperature margin of (137 °C - 125°C) = 12°C for the evaporators, plus an additional 20% margin for heat removal capacity by the off-gas treatment system.

The 125°C bulk fluid limit provides operational flexibility. The only way to increase the system temperature to 130°C or above is to (1) boil off all of the aqueous phase, and/or (2) pressurize the evaporator by blocking the vent path. With respect to system pressurization, staff evaluated the change in system pressure which would raise the 120.4°C azeotrope boiling point to 125°C. The pressure increase required to raise the temperature 4.6°C is about 10% of ambient offgas treatment system pressure - a relatively small amount. However, the availability and reliability of the vent path is not at question here, as it will be addressed during the ISA phase. With the steam temperature limited to 133°C and the bulk fluid temperature at 125°C, the total heat input from the steam will only be about 3 percent of the heat generated by the chemical reaction due to the small delta-T driving force. However, cool aqueous phase will be injected into the system.

Past DOE experiments (WSRC-TR-98-00171) have analyzed steam heating of TBP/N-paraffin/nitric acid mixtures to determine whether a mixture of steam and air from an empty tank could heat the organic layer until an exothermic, runaway reaction could take place. A jet of superheated steam (90%) and air (10%) at 139°C was used. The jet was cooled to the organic layer temperature, which reached a maximum temperature of 128°C. The organic layer was effectively limited to this temperature through evaporative cooling. This work demonstrates that red-oil reactions are not susceptible to source point initiation caused by minor temperature variations that may be encountered during operations.

Since DCS has not committed to PSSCs for this event that prevent the introduction of organic mass into the evaporators, staff requested information concerning the potential for foaming, two-phase flow and, ultimately, pressurization of the evaporator by blockage of the off-gas treatment system vent (NRC Dec. 10-12, 2002 meeting with DCS). DCS committed to developing a fundamental understanding of the system by evaluating the mechanism and behavior of such events through modeling and experimentation, as needed. This fundamental understanding is intended to allow a determination of the appropriateness of the relationship of the vent area-to-mass organic ratio, including the potential for two-phase flow.

Staff evaluated controls used by DOE at the Savannah River Site H-Canyon evaporators. DOE acknowledges the 137°C red oil initiation temperature for 14-15 M nitric acid in closed systems, and has identified an always safe solution temperature limit of 130°C for its systems (WSRC-SA-2001-00008, Rev. 4, H-Canyon Safety Analysis Report). An always safe value of 130°C ensures the red oil initiation temperature lies above this value for all foreseeable acid concentrations in either open or closed systems. To protect this always safe value, DOE has implemented operational limits (Safety Class set points, as specified in Technical Safety Requirements) on solutions in H-Canyon evaporators at 120°C. However, DOE routinely processes nitric acid solutions with concentrations less than 50 wt%. This is lower than the 67 wt% azeotrope concentration that DCS proposes as part of its nitric acid recovery system. As a result, the DOE 120°C limit is sufficiently above the actual boiling point of non-azeotropic H-Canyon solutions, and allows evaporators to both operate efficiently and maintain an adequate safety margin. Since DCS proposes to recover the azeotrope, an always safe ("not to exceed") value of 125°C, which is lower than the DOE 130°C value, allows the recovery of the azeotrope (B.P. = 120.4°C) while maintaining a 12°C margin from the 137°C initiation temperature for 14-15 M nitric acid in closed systems. DCS will establish safety set points, with margin, less than the 125°C design basis value as part of aqueous polishing final design.

An Issue Arising from the Shape of the Evaporator
Staff evaluated the shape of the proposed acid recovery evaporators. Specifically, staff evaluated the hypothesis that a tall and thin (a.k.a. "high aspect ratio") thermosiphon evaporator would have a high likelihood of inducing the separation of organic and aqueous phases. This potential would be highest during startup and shutdown modes of operation. However, the condition of two separate phases is already assumed in the safety assessment - i.e., the red oil phenomena would occur in a separate organic phase after its contact with nitric acid. This organic phase could be lighter than the aqueous phase and float on the surface. Or, the organic phase may be heavier than the aqueous phase (due to complexation of the TBP with heavy metals such as uranium or plutonium) and be located on the bottom, which is a condition referred to as "phase inversion." In either case, the safety functions of the proposed red oil controls do not rely on the miscibility of the organic phase with aqueous solutions. The applicant assumed that a distinct and separate organic phase *may be present* which requires temperature controls, venting, active cooling, and anti-foaming controls. In its November 2003 report, the DNFSB noted that "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." Staff agree in principle with this recommendation as important to the final design of temperature measurement IROFS. However, information on the placement of temperature measurement devices is not required at the construction approval request stage of licensing.

Russian Research

Staff also evaluated a recent draft Russian publication that cites a run-away reaction initiation temperature as low as 123 °C. This temperature is cited for two-phase experiments, which includes both organic and aqueous phases present in a 1:2 volume ratio. The nitric acid concentration in the aqueous phase was 14.0 M. However, this experiment was performed in a closed reaction vessel, with neither aqueous evaporative cooling nor removal of volatile intermediate degradation products of TBP. The rate of temperature rise for the experiment is not known. In the Russian paper several paragraphs after the table with the 123 C entry, the authors state:

"Heating at aqueous phase boiling temperatures of two-phase mixtures of TBP and HNO_3 at concentration up to 12 moles / L in open-air autoclave was not followed with self-heating and growth of gas-evolution rate."

In a later section titled "Consideration of Results," the authors further conclude that:

"The possibility of progressive self-heating of mixtures due to oxidizing processes running depends upon the relation between heat release within reacting mixtures and heat removal from reaction area. Heat release depends upon reaction's thermal effect, its rate, concentration of oxidants and temperature. Heat removal is caused by heat loses (sic) to heating of the walls of reaction vessel and mixtures' components, and also to evaporation and boiling of liquids.

The experiments have indicated that heat leakage at the heating of «TBP-HNO_3» mixtures in open vessel are so large that exothermal effects are either small (for single-phase mixtures), or absent (for two-phase mixtures). This is also supported with removal of nitrogen oxides from reaction area together with gaseous reaction products.

That is why in open vessels the development of oxidizing processes in «TBP-HNO_3» mixtures, accompanied by progressive growth of mixtures temperature and gas-evolution rates, as respects, should be considered as highly improbable."

It is important to note here that the Russian authors' usage of the word "closed" or "open" is not the same as that used by the MOX facility applicant. The Russian use of "closed" is based on the use of an experimental apparatus that is not vented to allow either evaporative cooling or removal of the volatile intermediate TBP degradation products. At the U.S. MOX facility, no process vessels would be closed in this sense. Rather, the applicant has defined "closed" as meaning those vessels for which the always-present vent is not of sufficient size

to relieve the runaway reaction. Since the applicant proposes to provide for adequate evaporative cooling and heat removal (with a safety factor of 1.2) using vents on those vessels where the vent does not meet the Fauske minimum size design basis for relief of the red-oil excursion, the Russian observation regarding open vessels actually describes the condition for all vessels at the MOX facility.

November 2003 DNFSB Technical Report

On November 13, 2003, the DNFSB issued a technical report titled "Control of Red Oil Explosions in Defense Nuclear Facilities, 2003." In the report, DNFSB recommends that two or more of the following controls should be used to prevent a runaway red oil reaction and explosion of the detonable gases produced by the reaction:

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.

In describing the temperature control of the evaporators (Section 4.1 of the report), the DNFSB staff provided the following specific recommendation:

"... To be assured that red oil conditions are not present in an evaporator, controls for temperature, pressure, and concentration should all be utilized." (p. 4-3).

Of the four controls listed above, the applicant has identified only temperature controls for the closed acid recovery evaporators at the MOX facility. By definition of a closed system, the pressure controls in these vessels are not adequate to prevent an over-pressure from destroying the process vessel. Also, mass controls, though present in the design, are not credited in the safety assessment as PSSCs, and there are no limits on nitric acid concentration.

However, the staff conclude that the applicant has provided sufficient defense-in-depth by committing to a multi-tiered approach that includes: (1) a combination of multiple, independent temperature controls; (2) adequate aqueous phase evaporative cooling provided by the offgas treatment system; (3) the exclusion of cyclic chain hydrocarbons;

and (4) the commitment to additional research on the runaway initiation temperature and the effect of impurities on the initiation temperature.

For the Construction Authorization stage, the applicant has provided sufficient controls and margin such that the bulk temperature will not exceed 125°C. This temperature is 5°C below the 130°C initiation temperature established by DOE, and 9-15°C below the 134-140°C range of experimentally measured runaway initiation temperature data (which averaged 137°C). The applicant's proposed aqueous injection system goes beyond the safety requirements at DOE facilities and the operating French MOX facility. Other possible operational concerns related to the evaporator startup, shutdown and possible abnormal conditions are best addressed during the ISA phase when specific design information will be available.

Staff Position 2 - Lead Chemical Safety Reviewer - Not acceptable

In the revised DSER, staff identified concerns about red oil (page 8.0-35 et seq). The following concerns have not been addressed by applicant submittals since the revised CAR and are still valid:

1. The applicant's approach envelopes many but not all of the DOE practices.

2. The evaporator steam temperature design basis of 133°C is close to the runaway reaction initiation temperature of 135°C, presenting a limited margin [NB - per more recent information from DOE and DCS, this initiation temperature is 130 °C). Additionally, system impurities can lower the reaction initiation temperature by an undefined amount.

3. An adequate safety margin has not been demonstrated for the complete, integrated approach, including temperature and heat removal capacity, and adequate consideration of uncertainties.

4. The applicant has stated that the design bases to preclude a runaway reaction must be viewed in the aggregate (Section 8.5.1.5.5 of the revised CAR). However, the significance of the relative contributions of each safety control towards meeting the preventative safety strategy for the "highly unlikely" performance requirements of 10 CFR 70.61, particularly as they apply to open and closed systems, have not been identified.

5. Since the applicant has indicated that solvent carryover is an anticipated event, the potential for common mode failure mechanisms that could challenge the venting and heat transfer controls (i.e., impact from organics through foaming, two-phase flow, pressurization, etc.) has to be considered when determining the "highly unlikely" performance requirements of 10 CFR 70.61.

6. The applicant should provide additional PSSCs and design bases for addressing the red oil concerns in the evaporators and associated vessels, equipment and piping, and provide adequate margin, or provide adequate justification why the proposed safety strategy, PSSCs, and design bases are acceptable.

The applicant has made assertions that their proposed strategy has the ability to meet the highly unlikely criterion for a preventative strategy. However, the assertions are not supported by calculations or clear logic, and references and non-applicant calculations exist that raise significant questions about the ability of the applicant's strategy to meet the highly unlikely criterion. In addition, there is a transition in the phenomena at 120 °C and above, where evaporative cooling becomes less effective and the solution becomes considerably self heating.

Of particular concern, the DCS approach directly contradicts five control concepts and recommendations from DOE, without explanation. First, DCS indicates the evaporator solution temperature will not exceed 125 °C - in contrast, the DOE not to exceed temperature limit is 120 °C. (TSR) and DOE actually operates at temperatures below this. Second, DCS intends to concentrate to circa 13-14 M (approximately 70%) nitric acid while DOE does not concentrate beyond about 5-6 M (approximately 50%) - lower concentrations are safer. Third, DCS has indicated there are no general controls on the organic phase carryover, while DOE identifies several controls. Fourth, the venting size of the DCS system is far to the right of the DOE/Fauske recommended minimum and is in the danger zone. Fifth, DCS has a high aspect ratio (tall and thin) design that is significantly more sensitive to phase separation and thermal isolation as compared to the large vessel/low aspect ratio designs used by DOE.

The applicant has not provided any assurance that the quench system and 125 °C limit will prevent red oil events. In addition, the quench system proposed by the applicant may have unintended consequences. As depicted at the July Public Meeting, the evaporators are about 5 or more meters high and narrow (perhaps 15 cm or so diameter). Cessation of steam heating in the 120 -125 °C solution temperature range removes relatively little heat input from the system (the great majority of the heat accrues from the red oil reactions). Shutdown of the steam supply will also stop agitation in the system and allow the phases to separate. This will thermally isolate the organic layer and stop the evaporation of the aqueous phase by the imposition of pressure from the organic fluid head. Any addition of cooler aqueous material would appear to be irrelevant in the absence of mixing and would also stop any evaporative cooling (no vacuum is applied to the evaporator). Furthermore, separation of layers has been observed to result in a temperature gradient (increase) in the organic phase. This situation will likely lead to a runaway red oil reaction as the reactions continue in the organic layer. Thus, it is not likely that the performance requirements of 70.61 can be met by the applicant's approach.

Attachment 2

From: Alex Murray
To: Joseph Giitter; Joseph Holonich; Robert Pierson
Date: 2/5/04 6:49PM
Subject: Further Thoughts on Red Oil

All,

In our meeting about Red Oil on January 16th, I was asked to comment on the review process for MOX (and red oil in particular) and what I would consider acceptable for red oil. My comments and recommendations follow,

Alex.

MOX Review Process:

A partial list of summary observations from the past three years.

Applicant :
1. Limited information provided in original CAR.
2. Approaches often different from accepted analogs (e.g., DOE, codes), fewer controls, more risk based than risk-informed, performance based, frequently no supporting calculations
3. Multiple changes in approach, design bases - from CAR, to RCAR, to meetings. For red oil, the DCS approach was not really finalized until Spring 2003 for open systems and August 2003 for closed systems
4. Discrepancies and differences rarely addressed first time or adequately - "fundamental approach" for red oil has not materialized.
5. Submittals/approaches often are assertions without supporting information/references, calculations
6. Information, references/citations, calculations often not provided with submittal or in a timely manner
7. Sometimes reluctant to provide information (e.g., DOE, French experience), particularly when it disagrees with the DCS approach. The July meeting is a good example for red oil.
8. Sometimes, the focus is on language/semantics in submittals ("design basis like Fauske")
9. Not prepared for meetings, writeups/submittals inadequate/inconsistent/change
10. There are multiple, competing groups within DCS - e.g., licensing sometimes seems decoupled from design group

NRC :
1. Allowed meetings without receipt of information prior to meeting, applicant unprepared
2. Scheduled meetings when Lead Chemical Safety Reviewer unavailable
3. Acceptance criteria from SRP often diluted, alternatives not supplied
4. Burden not placed on Applicant (e.g., per PM manual)
5. Management perception of two part licensing - first part faster, OK because of "second bite at the apple."
6. Consensus process - conclusion often provided by management, then staff asked.
7. Tracking system and backup documentation not adequate.

Both:
1. Chemical safety underappreciated

Red Oil:

The applicant's proposal for open systems was finalized in the Spring of 2003. Limited information was supplied by DCS to support the assertion of a preventative strategy capable of attaining a "highly unlikely" likelihood. The staff review included checking with analogs (DOE and France), literature citations, and

DOE/DNFSB colleagues. The staff also conducted a top-level fault tree analysis. Staff concluded that the approach for controlling red oil events in open systems had the ability to be implemented to meet Part 70 requirements (70.61 on Performance Requirements and Baseline Design Criteria 3 and 5 [fire/explosion and chemical]) and, thus, was acceptable for the construction authorization phase.

The applicant finalized their approach for closed systems in August 2003 after several changes from the RCAR submittal (October 2002). The proposal is different from the July 2003 public meeting where discussions indicated what would be acceptable to the staff. The applicant's submittal does not include any information, references, or calculations to support the assertion of meeting Part 70 requirements. DNFSB also released a document on appropriate controls for preventing red oil events in late 2003. The staff review included checking with analogs (DOE and France), literature citations, and DOE/DNFSB colleagues. The staff also conducted a top-level fault tree analysis which expressed concerns about accuracy of the temperatures and approach. I concluded that the approach for controlling red oil events in closed systems did not have the ability to be implemented to meet Part 70 requirements (70.61 on Performance Requirements, and 70.64(a) on Baseline Design Criteria 3 and 5 [fire/explosion and chemical]) and, thus, was not acceptable for the construction authorization phase. I concluded additional discussions with and information from the applicant are needed to adequately address this issue - fundamentally, how is adequate safety assured when a system that has significantly less venting capability is allowed to have a temperature design basis some 5 C higher than an open system, and where 90%+ of the heating accrues from the red oil reactions?

Several members of the staff also had similar concerns. However, in a meeting, management asked for a vote on the acceptability of the red oil response for closed systems. Management voted first, in favor of acceptance. I was the only one willing to vote non-acceptance in front of management. No one else was willing to express their concerns in front of management. My position and rationale were well received at the ACRS meeting of November 6, 2003.

I conclude adequate assurances of safety can be achieved by a lower design basis temperature (say, 110-115 C) and more venting capability (all other controls remaining the same), or by DCS following the DOE control strategy. I conclude DCS would be unable to provide adequate assurances of safety for their current safety strategy for closed systems in a timely manner, based upon their interactions with the NRC to date. Fundamentally, the NRC needs to function as a regulatory agency and take charge of the situation. I would like to see a letter from FCSS management go to DCS that communicates this and get the proverbial ball rolling - say, something like the following:

"The NRC has been reviewing the issue of potential solvent-nitrate (red oil) interactions at the proposed facility for almost three years, and the staff has had numerous interactions and meetings with DCS on the subject. The DCS strategy and design bases have changed several times. In the Spring of 2003, DCS proposed a definition and safety strategy for open systems using active engineered and administrative controls. Staff reviewed the situation and concluded the safety strategy, PSSCs, and safety functions provided reasonable assurances of safety, and the only remaining item concerned the design basis. After additional clarifications, DCS provided a design basis. After review, the staff concluded this provided adequate assurances of safety for prevention of the red oil phenomena in open systems and would be acceptable for construction authorization under Part 70."

"In August 2003, DCS provided another change to its safety strategy for preventing the red oil phenomena in closed systems. The submittal did not include any information, references, or calculations to support the assertion of meeting Part 70 requirements. The staff review included checking with analogs (DOE and France), literature citations (including a recently released DNFSB document on controls for red oil), and DOE/DNFSB colleagues. The staff also conducted a top-level fault tree analysis which expressed concerns about accuracy of the temperatures and approach. The staff has concluded that the information for the approach proposed by DCS for controlling red oil events in closed systems does not have the ability to be implemented to meet Part 70 requirements (70.61 on Performance Requirements, and 70.64(a) on Baseline Design Criteria 3 and 5 [fire/explosion and chemical]) and, thus, this is not acceptable for the construction authorization phase. Fundamentally, how is adequate safety assured

when a system that has significantly less venting capability is allowed to have a temperature design basis some 5 C higher than an open system, and where 90%+ of the heating accrues from the red oil reactions?"

"Additional information is needed from DCS to address this red oil issue for closed systems. The staff has concluded adequate assurances of safety can be achieved by a lower design basis temperature (say, 110-115 C) and more venting capability (all other controls remaining the same), or by DCS following the DOE control strategy, as outlined in the recent DNFSB report. Alternatively, DCS can provide additional asurances on their current approach. However, I have concerns that DCS would be unable to provide adequate assurances of safety for their current safety strategy for closed systems in a timely manner, based upon their interactions with the NRC over the past three years."

"This information needs to be submitted to the NRC in a timely manner to allow for adequate review by the staff, preferably within the next 30 days."

A letter like this should be followed up with a phone call on the subject.

ATTACHMENT 3

DNFSB REPORT ON RED OIL

John T. Conway, Chairman

A.J. Eggenberger, Vice Chairman

John E. Mansfield

R. Bruce Matthews

DEFENSE NUCLEAR FACILITIES
SAFETY BOARD

625 Indiana Avenue, NW, Suite 700, Washington, D.C. 20004-2901
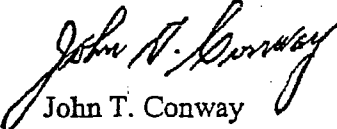(202) 694-7000

November 13, 2003

The Honorable Spencer Abraham
Secretary of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

Dear Secretary Abraham:

The Defense Nuclear Facilities Safety Board (Board) has been acutely aware of the safety concerns of the red oil phenomenon in nuclear chemical processing facilities ever since the red oil explosion at Tomsk-7 in 1993. The Board urges the Department of Energy to continue to periodically assess the controls that are in place to prevent a red oil explosion. As long as there are organics, nitric acid, and process equipment capable of heating these components, red oil explosions will continue to be a threat to safety in the defense nuclear complex.

Enclosed for your information and for use by those responsible for nuclear process safety is a technical report, DNFSB/TECH-33, *Control of Red Oil Explosions in Defense Nuclear Facilities*. The report identifies 3 types of typical process equipment in defense nuclear facilities that are capable of red oil formation. Four generic controls are identified to prevent red oil explosions.

Sincerely,

John T. Conway
Chairman

c: The Honorable Linton Brooks
    The Honorable Jessie Hill Roberson
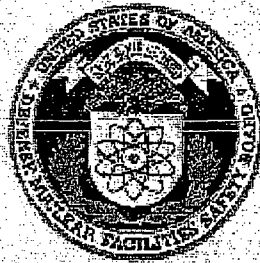   Mr. Mark B. Whitaker, Jr.

Enclosure

CONTROL OF RED OIL EXPLOSIONS IN DEFENSE NUCLEAR FACILITIES 2003

Defense Nuclear Facilities Safety Board

Technical Report

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:

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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

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 $UO_2(NO_3)_2$ 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 ± 5°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 ± 0.0004 g/cm³.
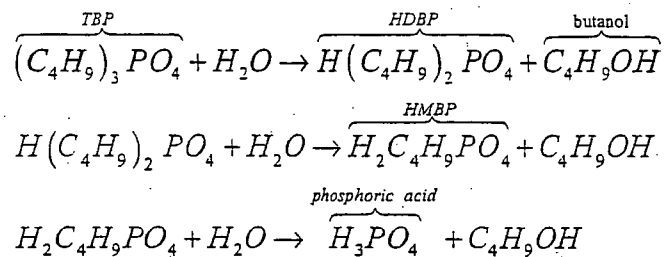
2.2 DILUENT

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, $C_{12}H_{26}$, 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/cm³ 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:

$$\overbrace{\left(C_4H_9\right)_3 PO_4}^{TBP} + H_2O \rightarrow \overbrace{H\left(C_4H_9\right)_2 PO_4}^{HDBP} + \overbrace{C_4H_9OH}^{butanol}$$

$$H\left(C_4H_9\right)_2 PO_4 + H_2O \rightarrow \overbrace{H_2C_4H_9PO_4}^{HMBP} + C_4H_9OH$$

$$H_2C_4H_9PO_4 + H_2O \rightarrow \overbrace{H_3PO_4}^{phosphoric\ acid} + C_4H_9OH$$

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 $\underline{M}$ 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 $\underline{M}$ (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 $\underline{M}$ 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 $\underline{M}$ 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 $\underline{M}$.

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.
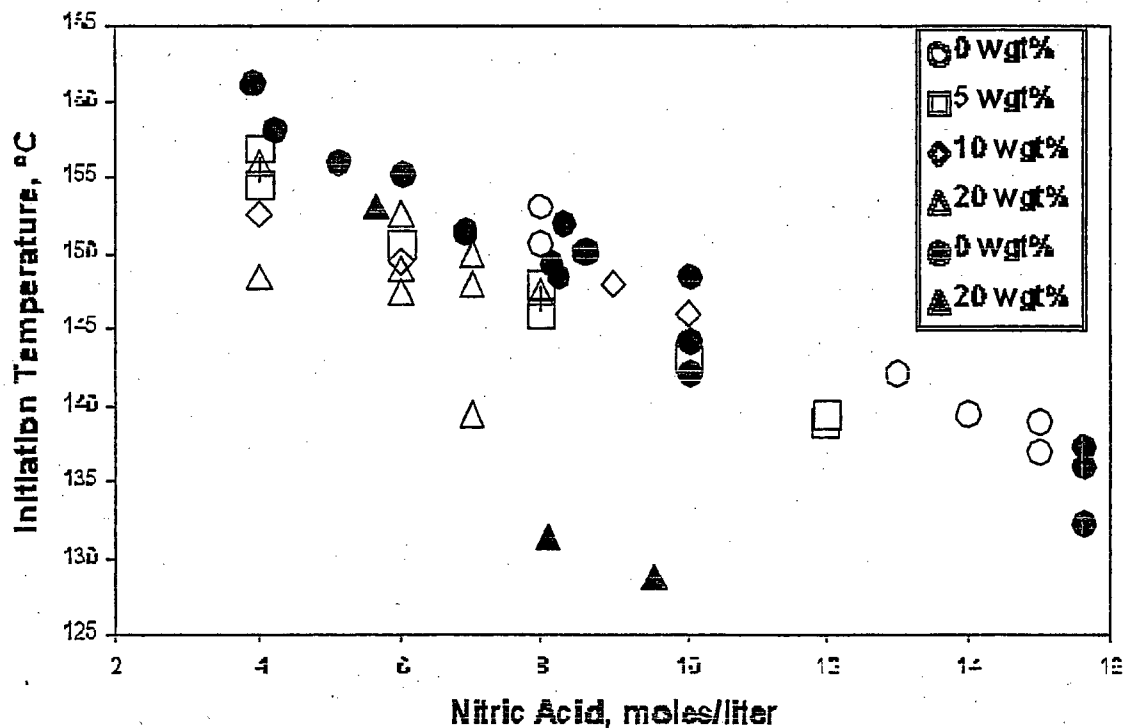

Figure 1. Effect of Nitric Acid Concentration (moles/liter) and Solids Content (wt%) on Red Oil Initiation Temperature. Sources: Solid symbols, Colvin (1956); open symbols, Rudisill (2000).

In the experiments for Figure 1, inextracable 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/cm^3 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/cm^3, 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 mm^2/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/mm^2 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/mm^2 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 in^2 is sufficient to relieve the pressure from any red oil reaction involving 3000 lbs of TBP. Vents larger than 6.44 in^2 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/mm^2 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 $\underline{M}$.

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.

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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
M	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-n-butyl phosphate
UN	uranyl nitrate or $UO_2(NO_3)_2$
UO_3	uranium oxide
WFE	wiped film evaporator

ATTACHMENT 4

COMPLETED NRC FORM 680 FOR A DPO