



UNITED STATES
NUCLEAR REGULATORY COMMISSION

WASHINGTON, D.C. 20555-0001

February 21, 2007

MEMORANDUM TO: Jack R. Strosnider, Director
Office of Nuclear Material Safety
and Safeguards

FROM: William H. Ruland, Deputy Director *William H. Ruland*
Licensing and Inspection Directorate
Division of Spent Fuel Storage and Transportation
Office of Nuclear Material Safety
and Safeguards

SUBJECT: REPORT FROM AD HOC PANEL ON POTENTIAL RED OIL EVENTS
AT THE PROPOSED MIXED OXIDE FUEL FABRICATION FACILITY,
DPO-2005-002

On March 2, 2005, you established an Ad Hoc Panel to review the above Differing Professional Opinion. The Panel has completed its review. The enclosed Report documents the Panel's review, conclusions, and recommendations. The panel did not find sufficient basis in the DPO to recommend reversing the staff's decision to issue the construction authorization for the MOX facility. The Panel also highlighted several areas that warrant additional staff attention during the license application review stage.

The Panel is available to discuss our report with you, as you deem appropriate. Also, the Panel used a contractor, the Center for Nuclear Waste and Regulatory Analysis (CNWRA, the "Center") for technical assistance. The Center supplied a written report, which is included as an attachment to our report. The Center could also be made available for a briefing.

Also, the Panel recommends some changes to the DPO process, based on its experience. We have provided those recommendations to the DPO program manager.

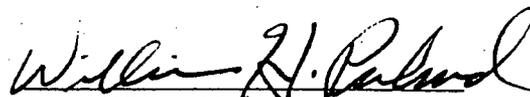
Enclosure:

DPO-2005-002 Panel report, with attachments

cc: Submitter
DPO Program manager
J. Davis
W. Schwink

Enclosure

REPORT OF THE AD HOC PANEL
CONVENED BY THE NMSS DIRECTOR TO REVIEW THE DIFFERING PROFESSIONAL
OPINION PERTAINING TO RED OIL EVENTS AT THE PROPOSED MIXED OXIDE (MOX)
FUEL FABRICATION FACILITY (NMSS-DPO-2005-002)


William H. Ruland, Chairman


James Davis, Member


Walter Schwink, Member

Date: February 21, 2007

MEMORANDUM TO: Jack R. Strosnider, Director
Office of Nuclear Material Safety
and Safeguards

FROM: William H. Ruland, Deputy Director
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DPO Program manager
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DISTRIBUTION:

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NAME:	JDavis <i>JAD</i>		WSchwink <i>WS</i>		<i>WRuland</i>	
DATE:	02/06/07		2/21/07		2/21/07	

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Introduction

In accordance with Nuclear Regulatory Commission (NRC) Management Directive (MD) 10.159, *The Differing Professional Opinions Program* dated May 16, 2004; by memorandum¹ dated March 2, 2005 (Attachment 1 to this report), the Director of the Office of Nuclear Material Safety and Safeguards (NMSS) appointed a Panel to review a *Differing Professional Opinion (DPO) on Red Oil Events at the Proposed Mixed Oxide (MOX) Fuel Fabrication Facility*. Red oil is a hydrolysis product that has caused explosions resulting in damage at plutonium purification facilities operated by the Department of Energy (DOE) and by others in the world. The DPO concerns the adequacy of information in the NRC docketed MOX Construction Authorization Request (CAR) submitted for NRC approval in accordance with 10 Code of Federal Regulations (CFR) Part 70.23(b). The NMSS Director asked the Panel to: (1) review the DPO to determine if the submitted DPO included sufficient information for the Panel to begin its review, (2) meet with the DPO submitter to ensure the Panel's understanding of the DPO, (3) document the Panel's understanding of the DPO, (4) request DPO subject matter technical expert assistance (if necessary), (5) review the DPO, and (6) make recommendations to the NMSS Director for resolution of the DPO.

The Panel met with the DPO submitter on April 18, May 2, and May 5, 2005, to discuss and ensure its understanding of the DPO. In a June 15, 2005 memo (see Attachment 2), the submitter provided the Panel with additional information explaining his DPO and remedies for DPO resolution. The Panel documented its understanding of the DPO in an August 5, 2005 memo (see also Attachment 2 to this report) provided to the submitter. The Panel did not receive contradictions to its understanding of the DPO. The Panel also met with NRC MOX Project Managers and a management representative from Fuel Cycle Safety and Safeguards (FCSS) which is the NRC division responsible for CAR review. (Attachment 3 to this report lists management and staff that met with the Panel.) The Panel considered MOX related documentation from the submitter, MOX Applicant, Division of Fuel Cycle Safety and Safeguards (FCSS), Advisory Committee on Reactor Safeguards (ACRS), The Center for Nuclear Waste Regulatory Analysis (CNWRA) (hereinafter referred to as the Center) and the Commission. (Attachment 4 to this report lists major documents considered by the Panel.) The aforementioned meetings and documentation provided information for the Panel to begin its review of the DPO. During its review of the DPO, the Panel utilized subject matter expert technical assistance from NRC's contractor, the Center. Attachment 5 to this report presents the Center's assessment of red oil runaway reactions potentially causing explosions in the MOX plant aqueous polishing process units.

The Panel did not find sufficient basis in the DPO to recommend reversing the staff's decision to issue the construction authorization. NRC construction authorization, based on review of the applicant's submittal, was intended to preclude the need for substantial plant backfitting to obtain a future NRC license. The MOX plant applicant relied on a different approach than

¹ The NMSS Director's memo has two attachments, the DPO and NRC MD 10.159. The DPO has four attachments: "ATTACHMENT 1, MOX APPLICANT'S PROPOSED SAFETY STRATEGY, CONTROLS, AND DESIGN BASES" (for controlling MOX plant "red oil" risks); "ATTACHMENT 2, NRC MANAGEMENT DECISION TO ACCEPT THE APPLICANT'S PROPOSED SAFETY STRATEGY" (includes two attachments); "ATTACHMENT 3, DNFSB REPORT ON RED OIL; and ATTACHMENT 4, NRC Form 680."

DOE—with additional research—to preclude red oil events. The DPO submitter objected to this approach. The applicant, by relying on future research, accepted the risk that the staff could find their approach unacceptable. Further, the contractor for the panel did not identify significant costs associated with any potential backfit.

The parties involved in reviewing the red oil issue at the proposed MOX facility generally agree that there is insufficient safety and technical information supplied in the CAR for the license application review. Although the specific technical questions differed, the submitter, FCSS, ACRS, the Center, and the Panel concluded that significant technical questions remain unanswered. The technical questions have been highlighted in the Center's report (Attachment 5).

The Panel recommends that:

1. The construction authorization for the MOX plant should not be revisited.²
2. The staff should review the Panel's report, particularly the attached Center's report, and for technical issues during the license application review of the MOX plant.
3. The staff should ensure that technical insights gained from the Center's report are factored into the inspection program, as appropriate.
4. The staff should review the Center's hazard analysis for possible application during the license application review.

The Panel found merit in the DPO submitter's safety concerns; i.e., a MOX plant red oil explosion could have "high consequences." As stated above, the Panel also understands that the NRC staff and ACRS, and the Panel, all recognize that these concerns need to be addressed by the applicant through the results of their research, the Integrated Safety Assessment results, or modifications/backfitting as appropriate. Hereinafter, each of the DPO submitter's concerns is listed along with the Panel's response and recommendation.

Discussion

Background

The MOX plant is being designed and constructed to process plutonium from nuclear weapons into fuel for commercial nuclear power reactors to generate electricity and therefore is subject to the requirements of 10 CFR Part 70. Part 70 involves a two step process, i.e., an NRC authorization to construct the plant and then prior to possessing nuclear material, an NRC license. For plant construction authorization, NRC requires an acceptable *design bases* for the principal structures, systems, and components (PSSCs) relied on to control natural phenomena and accident caused risks in accordance with Part 70.61 performance requirements. In accordance with 10 CFR 70.23(b), construction of the PSSCs of a plutonium processing and fuel fabrication facility will be approved when the Commission determines that the design of the PSSCs and the quality assurance program provide reasonable assurance of protection against natural phenomena and the consequences of potential accidents. The PSSCs are based on a preliminary design bases, rather than on an integrated safety analysis (ISA) of the final design, which must be completed and included as part of the docketed license application. The

²The license application for the MOX plant has been docketed by the NRC.

underlying purpose of the NRC construction authorization is to assure that adequate preliminary consideration has been given to natural phenomena hazards and postulated accidents at the proposed plant so that subsequent substantial back-fits will not be necessary to satisfy NRC's Part 70 licensing requirements for possession and use of nuclear material, e.g., special nuclear material (SNM).

On February 28, 2001, Duke Cogema Stone & Webster (DCS), the applicant, submitted to the NRC, a CAR, for NRC authorization to design and construct a MOX Plant on a portion of the DOE Savannah River Site (SRS). The CAR, which is required by Part 70.23(b), continued to be amended and supplemented with information by the MOX applicant until NRC authorized (CAMOX-001) MOX Plant construction on March 30, 2005. The NRC authorization was based on the FCSS CAR evaluation documented in NUREG-1821, "Final Safety Evaluation Report on the Construction Authorization Request for the Mixed Oxide Fuel Fabrication Facility at the Savannah River Site, South Carolina." The FCSS safety evaluation of the CAR concluded that Part 70.23(b) requirements were satisfied, i.e. the design basis 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.

In a letter to the NRC Chairman dated February 24, 2005, the ACRS described its review of the FCSS Safety Evaluation Report (SER) and concluded: 1) information from DCS provides sufficient assurance to proceed with MOX Plant construction and 2) the "wide-ranging, technically competent" report should be issued. Regarding prevention/mitigation of red oil caused explosions in closed systems, the ACRS offered that the applicant's technical bases are not clear for its claims that sufficiently large vents and provision for quenching can be used to control temperatures below 125°C to prevent runaway reactions resulting in closed systems explosions.

The DPO dated January 14, 2004 disagreed with the FCSS safety evaluation conclusions concerning prevention of red oil explosion consequences in MOX Plant closed systems. The submitter's differing view is that the NRC docketed MOX CAR does not provide sufficient red oil caused explosion prevention/mitigation design bases information to satisfy the requirements of Part 70.23(b). In the DPO and in a memo dated June 15, 2005, the submitter further explained his concerns with supporting rationale and requested certain remedies.

MOX Plant Design Bases to Prevent/Mitigate Red Oil Explosion Consequences (CAR)

The proposed MOX fuel fabrication facility plant utilizes a solvent extraction process with two immiscible liquid phases, an aqueous phase (nitric acid) and an organic phase (tri-*n*-butyl phosphate or TBP) to separate out plutonium. Above certain temperatures, when the two phases are in contact, red oil can be formed. The organic phase can degrade over time. However, at elevated temperatures, it can degrade rapidly, producing compounds that change the color of the organic phase from amber to dark red—hence the name "red oil." When heated, the red oil formation is exothermic, and can become autocatalytic, and if the vessel is not sufficiently vented or the temperature is not sufficiently controlled, an explosion can occur. An explosion could permit uranium and plutonium to escape the process and building containing the process. The red oil caused explosion could have high consequences for worker and public safety, as well as the environment.

In the CAR, the MOX applicant proposes a red oil consequence prevention/mitigation strategy that differs from practices recommended by the Department of Energy (DOE)/Defense Nuclear Facilities Safety Board (DNFSB). Rather than providing vents of sufficient size in certain parts of the process to preclude a red oil explosion, the applicant proposes the following for closed systems: (1) evaporative cooling rate safety margins, (2) temperature limits, (3) residence time limits for organic compounds in the presence of oxidizers and radiation fields, (4) aqueous phase addition in the event of temperature excursions, and (5) use of organic diluents which are resistant to red oil phenomena. As noted in the staff Final Safety Evaluation Report (FSER), DCS commits in the CAR to perform research to confirm the effectiveness of the proposed strategy's prevention and mitigation of red oil consequences. The research also will evaluate the effect of impurities on the red oil phenomena initiation temperature. The MOX Plant CAR describes the mix of features to avoid over-pressurization and thereby reduce the risk of red oil explosion caused consequences in closed systems. An off-gas system is intended to vent vessels/equipment that may potentially contain TBP and associated byproducts in nitric acid. A design basis steam temperature and a maximum heating rate are intended to limit the heat generation rate. Further risk reduction is achieved by means of a maximum design basis bulk fluid temperature, a diluent used as a chemical safety control, and a non-safety diluent washing system to preclude the transfer of organics to heated equipment. In addition, an aqueous injection system is intended to mitigate potential red oil reactions if the temperature should exceed a design basis temperature.

DPO

The FCSS safety evaluation of the CAR concluded that Part 70.23(b) requirements were satisfied, i.e. the design basis 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. The DPO disagrees with the FCSS conclusion as it pertains to prevention/mitigation of red oil caused explosions in MOX plant closed systems. Specifically, the DPO submitter is of the view that the CAR does not contain sufficient information about the design basis for the principal structures, systems, and components to provide reasonable assurance of protection against the consequences of potential accidents involving red oil caused explosions in closed systems. In the DPO, the submitter provides the rationale for the differing professional opinion and requests the following remedies to resolve the DPO: (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; or, alternatively, apply a construction permit condition that imposes the DOE/DNFSB safety strategy until the applicant justifies its approach. By memo dated June 15, 2005, the submitter provided additional proposed remedies, i.e., (1) communicate the safety concerns to the applicant as soon as possible, (2) impose the Routinely Accepted or Generally Accepted Good Engineering Practices (RAGAGEP) on the applicant, (3) inspect the applicant's test program and results on a routine basis, and (4) inspect red oil strategy evolution during detailed design and construction. Hereinafter, the DPO submitter's specific concerns are provided together with the Panel's responses and recommendations.

Concern 1

Some 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, see Paddleford and Fauske). In other words, DCS did not provide any calculations or technical basis for not meeting the RAGAGEP, specifically because they did not design all affected systems to avoid the "unsafe region" in Paddleford and Fauske, Figure 2.

Panel Response

The MOX CAR proposed red oil related prevention/mitigation strategy differs from DOE safety practices (e.g. RAGAGEP). The Panel found that FCSS, ACRS and CNWRA (Attachment 5, p. 11,) agree that the proposed strategy does not implement all DOE safety practices (e.g., RAGAGEP) for closed systems. The attached DNFSB report (Attachment 1) describes the safe practices as follows:

- Maintain process temperature of less than 130°C;
- Provide sufficient venting for the process;
- Remove organics from the process; and
- Maintain nitric acid less than 10M (mole/liter)

(b)(2)High



FCSS (with ACRS endorsement) issued its FSER which accepted the DCS strategy for red oil related preventing/mitigation involving a partially vented closed system involving:

- Independent multiple temperature controls;
- Use of an aqueous phase evaporative (off-gas treatment) system;
- Exclusion of cyclic chain hydrocarbons; and
- A commitment to conduct additional research and development on the runaway initiation temperature and the effect of impurities on the initiation temperature for the red oil reaction.

FCSS
ex 2

The Center reported that:

- "The proposed safety margin for the design basis fluid bulk temperature of 125°C is not supported by an adequate technical basis to ensure that chemical process safety controls can prevent or mitigate potential (red oil) accidents." This conclusion was based on several factors, for example: (a) the size and insulation of the reactor vessel may lower the temperature when the pressure spike from the red oil reaction would occur; (b) there is considerable uncertainty of the initiation temperature of a runaway reaction as revealed by reactive chemicals testing; and (3) steam temperature supplied to the steam chest for the evaporator may be higher than anticipated due to superheating.
- "The proposed safety controls to suppress red oil runaway reaction by isolating steam and activating aqueous injection may not be available and reliable upon demand during the time period when the highly energetic runaway reactions may limit or restrict aqueous injection in the evaporator." This conclusion was based on questions about whether or not the specific design includes certain valving features to ensure reliable operation.
- "The 20-percent safety margin in the off-gas control system may not be adequate to remove heat via evaporative cooling during a red oil event." This was based on a concern that, if the temperature control system failed, the vent size may be inadequate to properly vent the thermosiphon evaporator.
- DCS has proposed using saturated noncyclic diluents to minimize the degradation of diluents in radioactive environments, which the Center found adequate. Also, DCS has proposed to implement diluent washing to preclude the transfer of bulk organic quantities to heated equipment. However, diluent washing systems were not credited as PSSCs. The Center stated that "...it is not evident whether DCS plans to conduct periodic monitoring for degradation products and assaying prior to introduction into the evaporators."
- The "Selection of maximum operating temperature and vent size for thermosiphon evaporators for acid recovery and oxalic acid destruction are not based on accepted practices currently adopted at the H-Canyon facility at the SRS and recommended by the DNFSB. The Center acknowledged the lack of regulatory standards for handling reactive chemicals and the existence of Occupational Health and Safety Administration (OSHA) and that Environmental Protection Agency (EPA) regulations generally apply to this area. They suggest that these regulations and other standards provide a RAGAGEP *framework* (emphasis added) and that RAGAGEP "...warrant the same level of attention as NRC guidance."

- "Details are needed to evaluate whether DCS research plans would provide sufficient insights on red oil runaway reactions."

The MOX applicant proposed in the CAR a red oil related prevention/mitigation strategy that differs from the DOE/DNFSB safety practice (RAGAGEP). NRC promulgates regulatory requirements (e.g., regulations) normally with accompanying guidance describing an NRC acceptable approach (strategy) for satisfying the requirements. Sometimes, NRC approves alternate approaches provided the requirement is still satisfied. In proposing an alternate approach, the MOX applicant assumes the risk of future plant back-fitting to satisfy regulatory requirements since NRC review could find the alternate approach unacceptable. Albeit not yet reviewed/accepted by the NRC, the DOE safety practices (e.g., RAGAGEP) for prevention/mitigation of red oil related consequences, could be an acceptable approach.

The intent of the 70.23(b) CAR review and approval as noted in SECY-188, is to preclude substantial back-fitting at the license application review stage. During the construction application review, the applicant proposed additional research to answer the staff questions concerning their red oil explosion mitigation strategy. Thus, the applicant accepted the uncertainty associated with the research. Namely, that the results of the research could show that their mitigation strategy could not be justified or that the staff concludes that additional analysis was needed or modifications/backfitting were required. In this context, FCSS determined that 70.23(b) requirements had been satisfied. The ACRS, in its letter dated February 24, 2005, that recommend issuance of the Final Safety Analysis Report (FSAR), concluded that the technical bases for the applicant's control strategy was not clear and noted that, during the license review stage, the staff needs to develop adequate confidence that the red oil control strategy for closed systems can indeed prevent runaway reactions. On page 14 of its report, the Center concluded that regarding potential red oil related back-fits for effective solutions for the issues they raised, the backfit costs "...would not be a substantial component of total facility costs." Thus, the acceptance criteria for issuing the construction authorization was met. During the license application review stage, the burden is on the applicant to demonstrate, to the staff, adequate protection of public health and safety and the environment with respect to preventing or mitigating red oil runaway reactions. The applicant, by providing in the CAR less detail about the research, had accepted the risk that the staff may not find the research, by itself, sufficient to address staff concerns during the license application review stage.

The panel concluded that the staff issuance of the construction application for the MOX facility was appropriate. As pointed out by the submitter, the staff, and the ACRS, significant technical questions remained unanswered. Further, if modifications are required to alter the red oil mitigation strategy, the costs likely involved would not be substantial.

Panel Recommendation

- The staff should review the Center's report (Attachment 5) as part of its license application review and document the disposition of the issues.

- The staff should review the MOX inspection processes to insure that the red oil issue is appropriately reviewed.

The above recommendations also apply to the rest of the technical concerns below, and will not be repeated.

Concern 2

There is inadequate design in the design basis temperature. DOE uses 120°C as the design basis temperature for closed systems vice DCS's choice of 125°C. The submitter claims that at 125°C, the increase in bulk enthalpy in the process liquid is 80% due to the heat generated by the reactants instead of by heating steam. Thus, the 120°C setting already compromises safety.

Panel Response

The Panel's response for Concern 1 (above) also responds to Concern 2.

Concern 3

The venting (of closed systems) 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. The submitter believes there was insufficient information provided on the docket to determine if the vents would preclude choked flow.

Panel Response

As noted in CNWRA's Report, the applicant did not, in all cases, implement the organic (TBP) mass-to-vent area (310 g/mm^2), above which red oil runaway reactions can be initiated (Paddleford and Fauske, 1994). Instead, the NRC staff accepted the DCS approach of shutting down the steam and injection of aqueous phase material and for DCS to conduct future research but without providing detailed plans for that research. As discussed in the Panel's response to Concern 1 (above), and as reported by the Center, it is unclear how the design basis provided in the CAR will provide adequate protection from the consequences of potential red oil related accidents. In its report (Section 3.3), the Center posed several questions about the performance and effectiveness of the DCS approach for venting in closed systems. The Panel's response for Concern 1 (above) also applies to Concern 3.

Concern 4

DCS provided no controls on organic compounds. Given their other controls, this is an insufficient basis to insure that red oil reactions will not occur.

Panel Response

The CAR did not indicate whether or not DCS plans to conduct periodic monitoring for degradation products and assaying prior to introduction into the evaporators. In its

report, the Center elaborates on the importance of controlling organic compounds. The Panel's response for Concern 1 (above) also applies to Concern 4.

Concern 5

DCS provided higher nitric acid or TBP concentrations in the process than warranted. This leads to increases in the hydrolysis reaction, which may contribute to the likelihood of a red oil reaction.

Panel Response

As noted in the DNFSB and the Center reports, the concentrations of nitric acid and TBP affect the reaction rate of potential red oil reactions. The Panel's response for Concern 1 (above) also applies to Concern 5.

Concern 6

DCS provided evaporators with an aspect ratio (height/diameter) of about 5 to 10, which is higher than the typical 1 to 2³. This information on aspect ratio was not in the docketed submittal, so that, given the way DCS is controlling the other key parameters, no conclusion could be reached about whether or not this part of the design was satisfactory.

Panel Response

In its Report, the Center noted the size and insulation of the reactor vessel could affect the initiation of a red oil runaway reaction. The Panel's response for Concern 1 (above) also applies to Concern 6.

Concern 7

The NRC management decision process used to accept the DCS proposal to control red oil reactions was improper. Management held a vote to determine the acceptability of the DCS proposal but only two qualified reviewers participated in the vote. The implication here is that only technical reviewers are qualified to make this type of decision.

Panel Response

The Panel has little basis to determine whether or not the management decision process was improper or not. However, the Panel can judge whether or not the technical issues that were the subject of the management process described above were appropriately considered.

³ The DCS design uses an aspect ratio that ranges from a ratio of 5 to a ratio of 10, while the DOE recommendation is an aspect ratio of between 1 and 2. The aspect is the ratio between the height and diameter.

As defined in Management Directive 10.159, a DPO is, "A conscientious expression of a professional judgement that differs from the prevailing staff view, disagrees with a management decision or policy position, or takes issue with a proposed or an established agency practice involving technical, legal, or policy issues." This concern deals with the agency practice, as allegedly applied in this case, of using a vote to decide the acceptability of the resolution of the technical issue.

NRC management, up to and including the Commission, are required to make decisions on technical and policy matters and use a variety of means to arrive at those decisions. Technical organizations routinely resolve issues through healthy discussions between management and staff. The Panel believes that the key issue at stake in this concern is whether or not all appropriate parties have had an input into the decision process, and whether, after the decision has been made—by whatever process—an appeal process exists to address contrary views. The submitter's concerns were submitted to his management and addressed accordingly in writing. In addition, the submitter was afforded the opportunity to discuss his concerns before the ACRS. Finally, the submitter documented his concerns via this DPO. Therefore, the Panel concludes that this concern is resolved.

Concern 8

NRC management used process efficiency arguments as part of the rationale to accept the DCS proposal on limiting red oil events. Namely, by selecting the values of parameters for control at the values proposed, DCS will generate less waste but this is not an acceptance criterion in the Standard Review Plan (SRP).

Panel Response

NRC, prior to issuance of an operating license, must conclude, in accordance with 10 CFR 70.23(a)(2) and (3), that the applicant's proposed equipment, facilities, and procedures are adequate to protect health and minimize the danger to life or property. The MOX applicant has proposed certain plant design bases to ensure safety in a manner that optimizes process efficiency.

The panel believes that process efficiency is an appropriate goal for the applicant. The NRC license approval is predicated on the staff finding that adequate protection is provided to the public and the environment. Since both criteria must be met, the panel concludes that this issue is resolved.

Concern 9

The NRC management decision to accept the DCS red oil control strategy incorrectly relied on future commitments for research or actions to refine or define the current PSSC and design basis. In your words, "technically, we have approved the plant." That is, the submitter believes that the NRC has inappropriately created the bounds for the plant, and he questions whether or not the NRC has a clear basis for accepting the design.

Panel Response

The Panel disagrees with the submitter's assertion that, "...technically, we (NRC) approved the plant." If that was the case, staff review of the license application would be an unnecessary pro-forma review. As demonstrated recently by the MOX applicant's substantial modifications to its license application to satisfy NRC's acceptance review of the application, and the extensive standard review plan, the staff has not approved the plant. The panel considers this concern resolved.

Concern 10

The final issue is that the NRC staff did not correctly disposition the safety issues in the Revised Draft Safety Evaluation Report (RDSE). (b)(2)High (b)(2)High the projected dose due to a red oil explosion could be as high as 80 Rem TEDE with > 25 Rem at the site boundary. This information, in the submitter's opinion, argues for a detailed review at the construction authorization stage, unlike the inadequate or non-existing analysis from the applicant.

FOIA
ex 2

Panel Response

The submitter's concern about sufficient information to resolve the technical issue is shared by FCSS, ACRS, the Center, and the Panel. However, there is disagreement regarding the need for and how much design information with supporting justification for the proposed red oil consequence related prevention/mitigation strategy should be in the CAR. All agreed that docketed design information with supporting technical justification is required in a docketed application for NRC licensing of the MOX plant. The Panel concluded that essentially the issue--the difference between the staff and the submitter--is about the balance between the scope and detail of docketed information for NRC approval of the CAR and information required in a docketed application for NRC licensing of the plant. SECY - 188 explains that the intent of 70.23(b) CAR approval is to preclude substantial plant back-fitting to license possession of plutonium. As discussed in the Panel's Response to Concern 1, the CAR proposed red oil related prevention/mitigation strategy differs from industry safety practices (RAGAGEP). Further, the CAR does not describe research for confirming the practicability of the proposed strategy. The intent of 70.23(b) is to preclude substantial back-fitting of the 3 billion dollar MOX plant at the licensing stage, the applicant accepts back-fitting risks comporting with the design information with supporting justification (including details of the confirmatory research) not provided in the CAR. In this context, FCSS determined that 70.23(b) requirements have been satisfied. This was supported by the ACRS. The Panel's response for Concern 1 (above) also applies to Concern 10.

Conclusion

The Panel concluded that the technical issues associated with the DPO need to be resolved at the license application review stage. The submitter's and the Center's questions need to be dispositioned during that stage of the review.

ATTACHMENT 1 to Panel Report

Memorandum⁴ dated March 2, 2005- Director of the Office of Nuclear Material Safety and Safeguards (NMSS) appointed a Panel to review a *Differing Professional Opinion (DPO) on Red Oil Events at the Proposed Mixed Oxide (MOX) Fuel Fabrication Facility*.

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

March 2, 2005

MEMORANDUM TO: William H. Ruland
Division of Licensing Project Management
Office of Nuclear Reactor Regulation

A. James Davis, Ph.D.
Division of Engineering Technology
Office of Nuclear Regulatory Research

Walter S. Schwink
Division of Fuel Cycle Safety
And Safeguards
Office of Nuclear Material Safety
and Safeguards

FROM:

Jack R. Strosnider, Director
Office of Nuclear Material Safety
and Safeguards

A handwritten signature in black ink, appearing to read "Jack R. Strosnider", written over the typed name and title.

SUBJECT:

AD HOC REVIEW PANEL - DIFFERING PROFESSIONAL OPINION
ON RED OIL EVENTS AT THE PROPOSED MIXED OXIDE (MOX)
FUEL FABRICATION FACILITY (DPO-2005-002)

In accordance with Management Directive (MD) 10.159, "The NRC Differing Professional Opinions Program," I am appointing you as members of a Differing Professional Opinion (DPO) Ad Hoc Review Panel to review a DPO regarding potential red oil events at the proposed Mixed Oxide (MOX) Fuel Fabrication Facility. Copies of the DPO and MD 10.159 are attached.

I have designated Mr. William H. Ruland chairman of this panel. He has selected Mr. Walter S. Schwink, who was proposed by the DPO submitter, as the third member of the panel, pursuant to MD 10.159. I task the panel to do the following:

- Review the DPO to determine if there is enough information for a detailed review of the issue.
- Schedule and conduct a meeting with the submitter, generally within 8 calendar days of the date of this memorandum, to discuss the scope of the issue. The scope of the panel's review should remain fully focused on the issues as defined in the original written DPO, and will not exceed those issues.

CONTACT: Robert L. O'Connell, IMNS/NMSS
(301) 415-7877

- Document the panel's understanding of the submitter's issues following the meeting, and send the submitter a copy of that documented understanding, with a copy to me.
- Establish a schedule of milestones for the disposition of the DPO.
- Request technical assistance through me, if necessary.
- Do a detailed review of the issues and conduct any record reviews, interviews, and discussions you deem necessary for a complete, objective, independent, and impartial review. The review should include periodic discussions between the full panel and the submitter to provide the submitter the opportunity to further clarify his views and to facilitate the exchange of information. However, there should be no separate communication between individual panel members and the submitter or key staff members on these issues during the review, except with the knowledge and agreement of all panel members.
- Make recommendations to me regarding the disposition of the issues presented in the DPO.
- Once the panel determines that it has received sufficient information to begin the review, the panel should normally complete the DPO review and submit its report and recommendations to me within 30 days.

All correspondence associated with your review should include the DPO number (DPO-2005-002) in the subject block. The correspondence should *not* be placed in the Agency Documents Access and Management System (ADAMS) until the case is closed. DPO-related time should be charged to Activity Code ZG0007.

Although the submitter has not filed this DPO confidentially, the matter should be treated as though he had. The submitter's name should not be used in discussions (the person may be referred to as the "DPO submitter"), documents should be distributed on an "only as needed" basis, and managers and staff should be counseled against "hallway talk" on the matter.

I appreciate your willingness to serve and your dedication to completing an objective review of this DPO. Successful resolution of the issues is important for NRC and its stakeholders. Since the DPO process has been undergoing revision, as you conduct your review, please note any changes you would recommend to the new management directive. If you have any questions, please contact me. You may also direct questions to the NMSS DPO Coordinator, Robert O'Connell, or the Acting NRC DPO Program Manager, Renee Pedersen, in the Office of Enforcement.

I look forward to receiving your independent review results and recommendations.

Attachments:

1. DPO-2005-002
2. NRC MD 10.159 (05/16/04 Revision)

cc: Submitter
DPOPM

ATTACHMENT 4
COMPLETED NRC FORM 680 FOR A DPO

DIFFERING PROFESSIONAL OPINION

1. DFO CASE NUMBER
DFO-2005-0072

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: Alexander P. Murray
4. POSITION TITLE: Senior Chemical Process Engineer
5. GRADE: 15

6. OFFICE/DIVISION/BRANCH/SECTION: NMSS/FCSS/SPB/MOFLS
7. BUILDING: TWFN
8. MAIL STOP: T8F42
9. SUPERVISOR: 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):
1. Mr. Walt Schwink
2. NTEU Recommendation #1
3. NTEU Recommendation #2

14. Submit this form to:
Differing Professional Opinions Program Manager
Office of: _____
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
PRE-CONDITIONS MET:
 YES NO
DATE OF ACKNOWLEDGMENT: 1/25/2005

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 (RDSE) 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)

Alise

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 (RDSEER) 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.

Attachments:

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

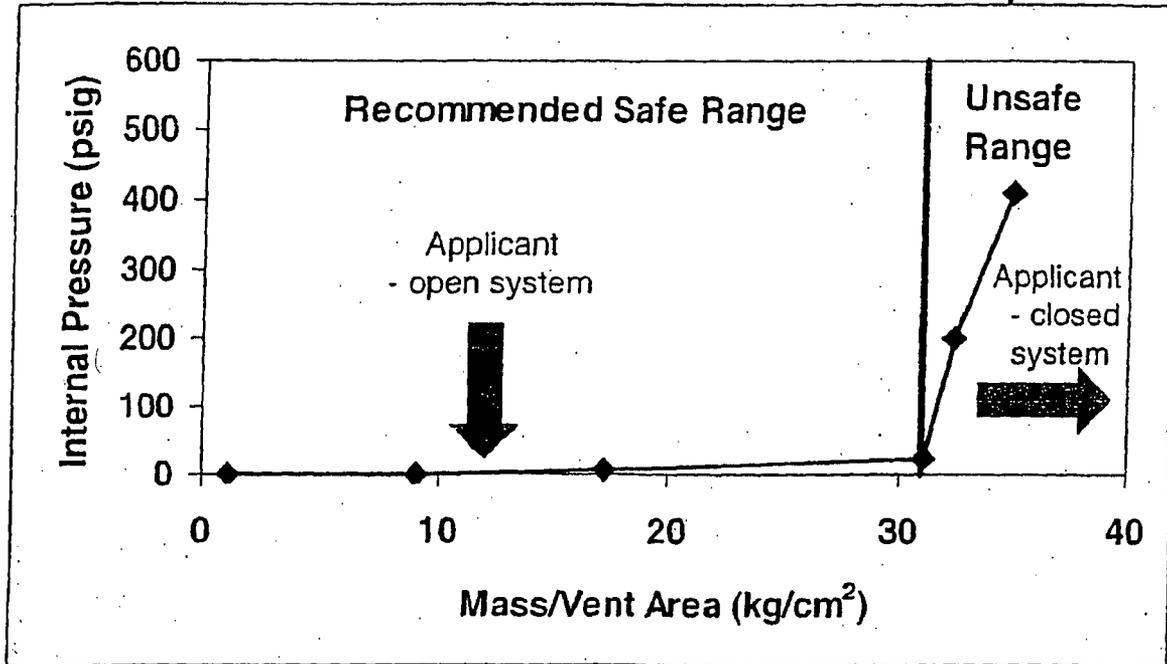
Rossanna Raspa

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 oil 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 appropriate 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 Tormsk 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.



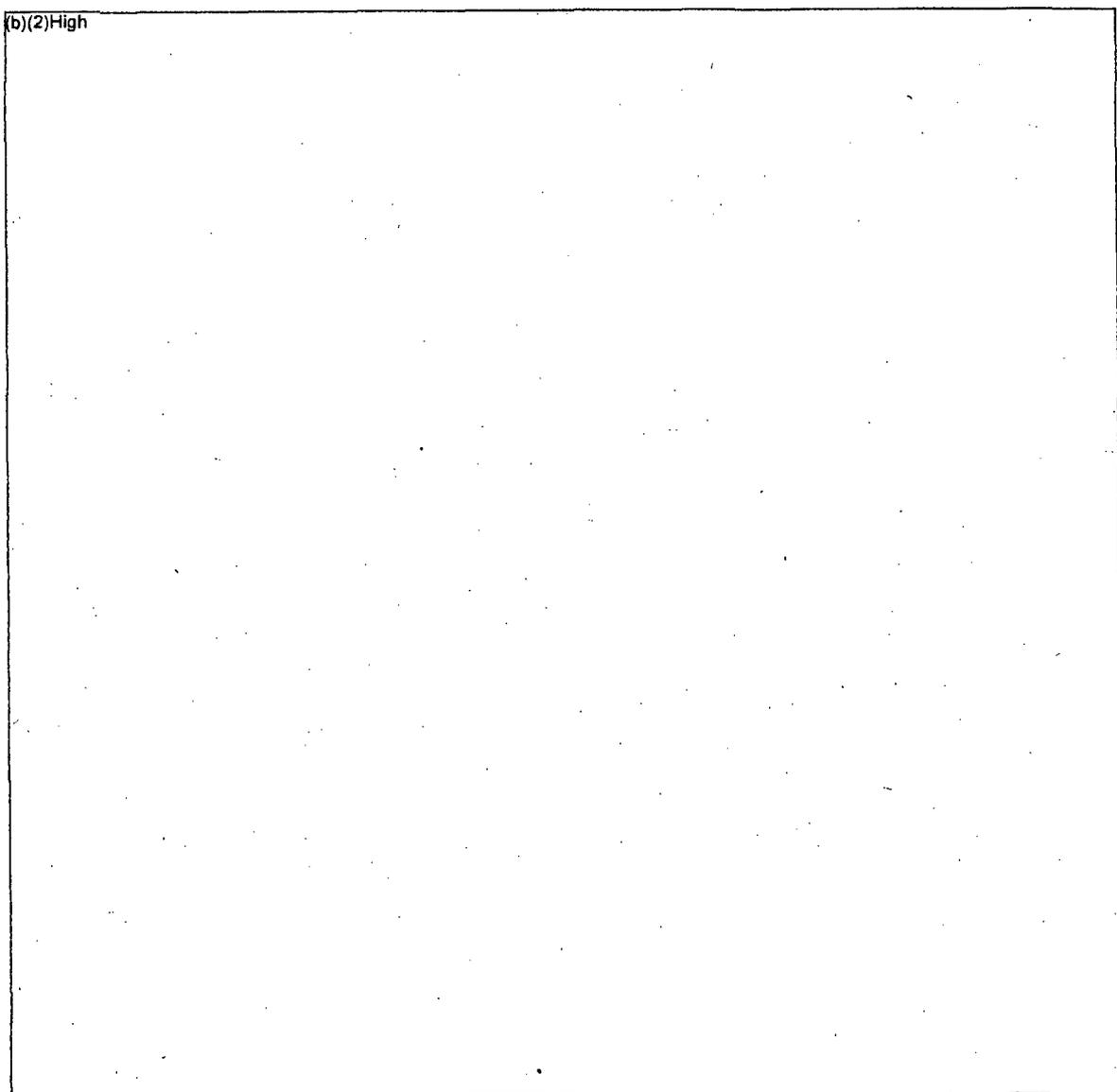
NOTE: CAR info was previously released per to
SUNST. The guidance is not to release
this information.

2

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:



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 K_d - 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 [REDACTED]. 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.

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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 [REDACTED] 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.

FOIA
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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; $> 0.063 \text{ mm}^2/\text{g}$ of TBP ($< 15.9 \text{ g TBP}/\text{mm}^2$ or $< 1.59 \text{ kg TBP}/\text{cm}^2$). It also mentions 312 g of red oil/ mm^2 ($31.2 \text{ kg}/\text{cm}^2$). With some safety margin, it recommends no more than 208 g of red oil/ mm^2 ($20.8 \text{ kg}/\text{cm}^2$) (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 $< 32.7 \text{ kg TBP}/\text{cm}^2$ of vent. Note that the applicant (DCS) is using $0.008 \text{ mm}^2/\text{g}$ of organic compound ($12.5 \text{ kg}/\text{cm}^2$).

Mass Control:

This applies to the organic phase, by keeping it from entering heated equipment (prevention) or by omitting 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 as 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 safety

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 HNO₃. 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 RDSE) 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:

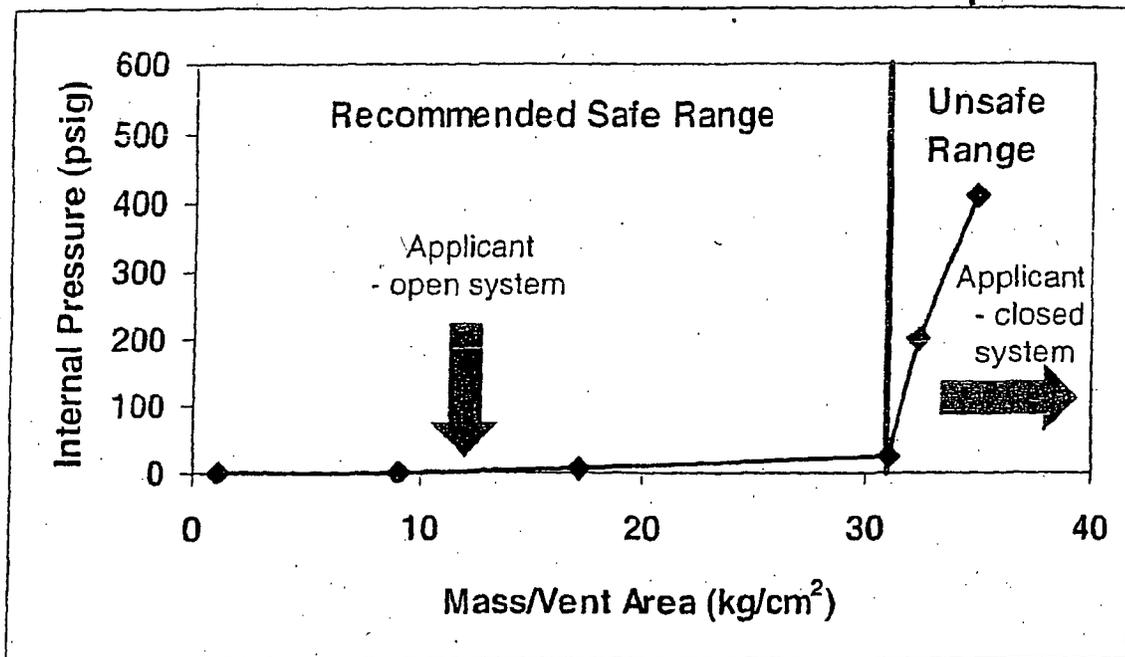
1. Contradictions with DOE/DNFSB RAGAGEP are not explained. In particular, the RAGAGEP shows the applicant's proposal for closed systems being entirely in the unsafe regime (Figure 2).
2. There is inadequate margin in the design basis temperature.
3. The venting is insufficient to avoid choked flow and pressurization, which has the ability to rapidly raise the temperature even with the applicant's proposed strategy functioning.

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 (RDSEER) 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

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CAR CHAPTER 5

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CAR CHAPTER 8

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Page: 8-19

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MFFF Construction Authorization Request
Docket No. 070-03098

Revision: 07/28/03
Page: 8-25

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

3

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

FROM: Joseph Gitter, Chief *Joseph G. Gitter*
Special Projects Branch NMSS/FCSS

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

Robert Pierson, Director *Robert Pierson*
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

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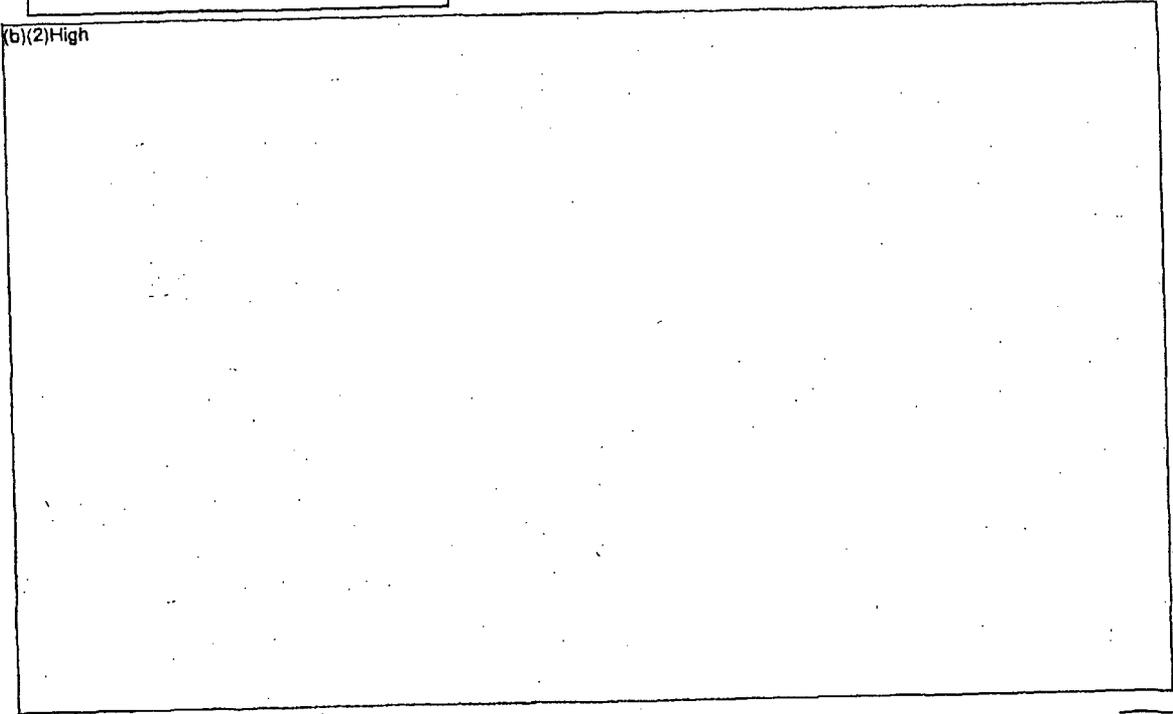
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(b)(2)High Staff have differing views on only that portion of
the applicant's safety assessment that pertains to the acid recovery evaporators. There are two types of systems utilized in the applicant's proposed design, "open" systems and "closed" 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

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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.

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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 as 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 autocatalytic 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-

April 12, 2004

H. Peterson

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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. Glitter 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. Glitter, 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

Distribution:

FCSS r/f

ML041040656 (package)

~~P:\Closure of Item CS-1, Red Oil\VE~~

*See previous concurrence

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

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H. Peterson

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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

Attachment 1

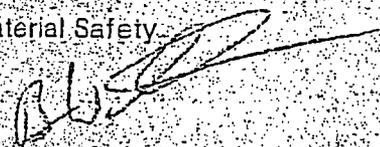


UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

December 30, 2003

~~Pre-Decisional - Do Not Cite or Quote~~

MEMORANDUM TO: Joseph G. Glitter, 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)

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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.

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

Operational Parameters

The mixture of nitric acid and water forms a maximum boiling point azeotrope 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-azeotropic 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.

Venting

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.

Design Concepts

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 PSSGs 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 (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 FX2

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:

$$\text{evaporative cooling} = 1.2 [\text{steam energy input at } 133^{\circ}\text{C} + \text{energy generated chemically}]$$

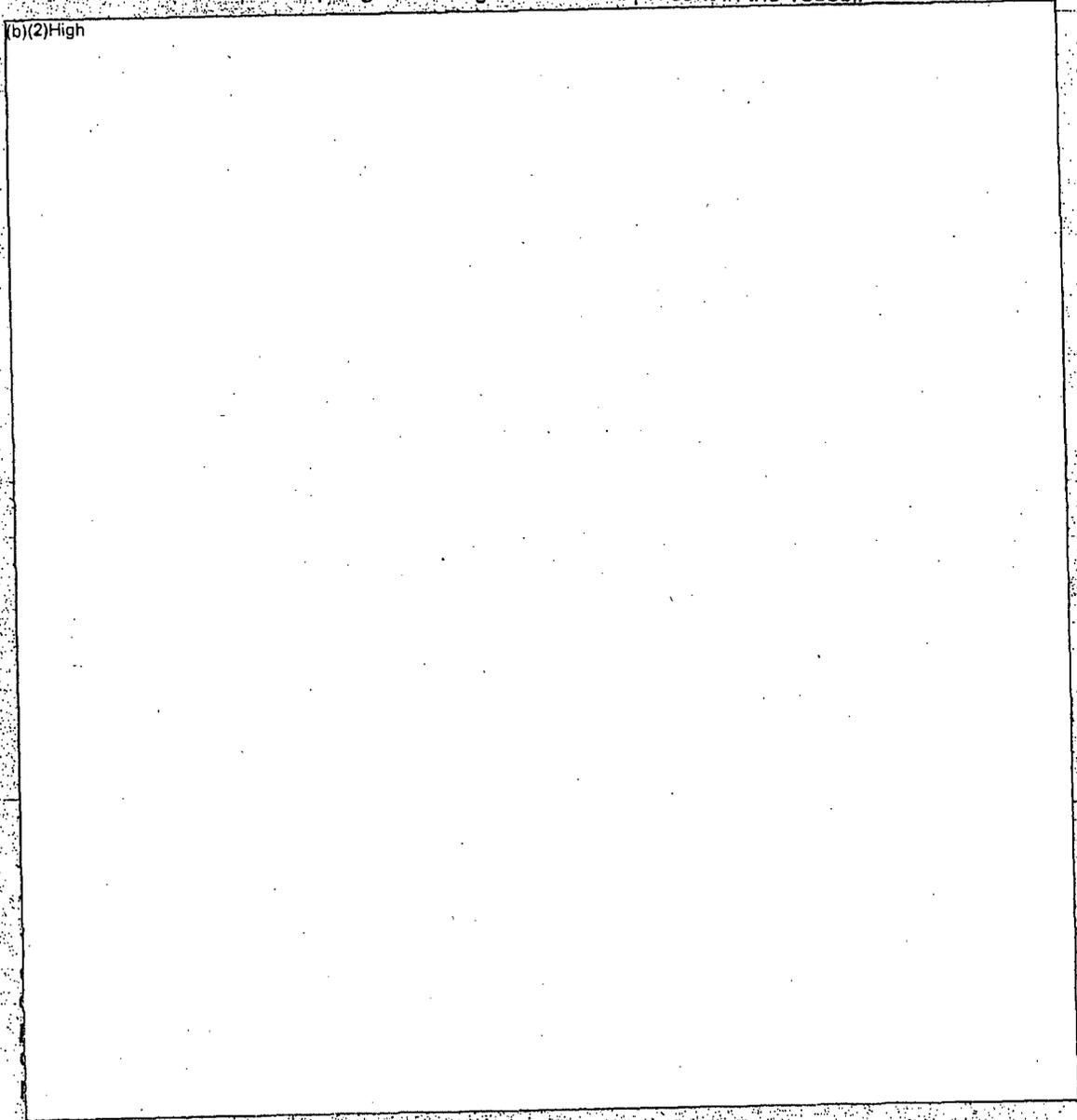
¹ Per 10 CFR 70.61(c)(3), environmental consequences are a ratio of the 24-hour average concentration at the restricted area boundary to a value 5000 times that appearing in 10 CFR 20, Appendix B, Table 2, Column 2.

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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.



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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, WSRG, 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."

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- 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 $(137^{\circ}\text{C} - 125^{\circ}\text{C}) = 12^{\circ}\text{C}$ 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 off-gas 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 ΔT 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.

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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 (W.S.P.C. 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

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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 HNO₃ 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 losses (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-HNO₃" 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-HNO₃" 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

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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-layered 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;

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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.

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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.

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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 assurances 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

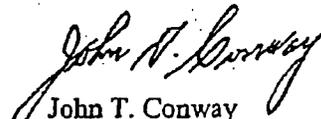
The Honorable Spencer Abraham
Secretary of Energy
1000 Independence Avenue, SW
Washington, DC 20585-1000

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 Toms-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

DNFSB/TECH-33

CONTROL OF RED OIL EXPLOSIONS
IN DEFENSE NUCLEAR FACILITIES
2003

Defense Nuclear Facilities Safety Board

Technical Report



November 2003

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

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

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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.

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1. INTRODUCTION

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

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

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

2. BACKGROUND: SOLVENT EXTRACTION AND RED OIL

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

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

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

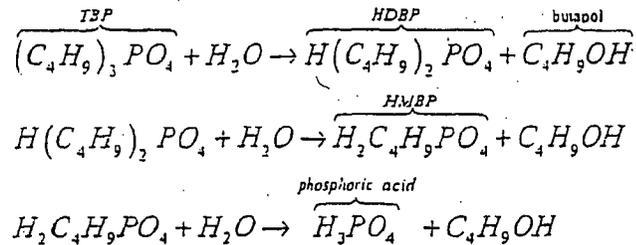
2.2 DILUENT

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

2.3 TBP DEGRADATION

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

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



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

3. RED OIL: DEFINITION AND FORMATION

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

3.1 EQUIPMENT CAPABLE OF PRODUCING RED OIL

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

3.1.1 Evaporators

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

3.1.2 Acid Concentrators

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

3.1.3 Denitrators

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

conducted at very high temperatures until uranium oxide (UO_2) is produced. If traces of TBP are in the UN, the temperatures for denitration are more than adequate (greater than 250°C) for red oil to form and reach autocatalytic temperatures.

3.1.4 Steam Jets

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

3.2 INDICATION OF RED OIL FORMATION

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

3.3 RED OIL EXPLOSION SCENARIO

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

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

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

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

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

3.4 NECESSARY CONDITIONS FOR RED OIL FORMATION

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

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

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

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

4. CONTROLS FOR THE RED OIL PHENOMENON

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

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

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

4.1 TEMPERATURE CONTROL

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

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

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

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

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

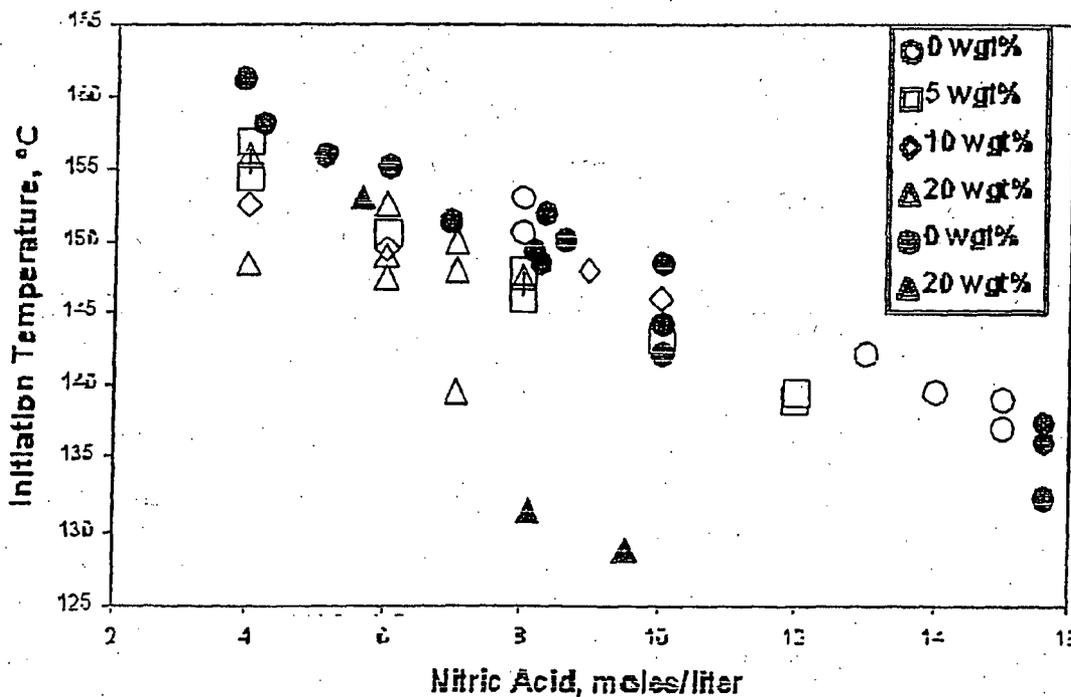


Figure 1. Effect of Nitric Acid Concentration (moles/liter) and Solids Content (wt%) on Red Oil Initiation Temperature. Sources: Solid symbols, Colvin (1956); open symbols, Rudisill (2000).

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

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

4.2 PRESSURE CONTROL

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

4.3 MASS CONTROL

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

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

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

4.4 CONCENTRATION CONTROL

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

5. RED OIL SCENARIOS IN THE COMPLEX

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

5.1 PREVIOUS RED OIL INCIDENTS IN THE UNITED STATES

5.1.1 Hanford, 1953

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

5.1.2 Savannah River Site, 1953

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

5.1.3 Savannah River Site, 1975

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

5.2 POTENTIAL RED OIL FACILITIES

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

5.2.1 Savannah River Site H-Canyon

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

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

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

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

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

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

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

5.2.2 Savannah River Site F-Canyon

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

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

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

5.2.3 Y-12 National Security Complex

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

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

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

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

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

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

5.3 UNLIKELY RED OIL FACILITY

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

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

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

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

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

5.4 FUTURE RED OIL PRODUCING FACILITY

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

5.5 OTHER FACILITIES WITHIN THE COMPLEX

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

6. CONCLUSIONS

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

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

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

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

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

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

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

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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
<i>M</i>	moles/liter
MFFF	Mixed Fuel Fabrication Facility
OF-H	H-Canyon and Outside Facilities of H-Canyon
PEW	process equipment waste
PIE	primary intermediate evaporator
ppm	parts per million
psig	pounds per square inch gauge
SAR	Safety Analysis Report
SIE	secondary intermediate evaporator
SRS	Savannah River Site
SRTC	Savannah River Technical Center
TBP	tri- <i>n</i> -butyl phosphate
UN	uranyl nitrate or $UO_2(NO_3)_2$
UO ₃	uranium oxide
WFE	wiped film evaporator

ATTACHMENT 2

August 5, 2005 memo⁴ documenting the DPO Panel's understanding of the DPO.

⁴The August 5, 2005 memo documenting the DPO Panel's understanding of the DPO has one attachment, i.e., "ATTACHMENT 1, JUNE 15, 2005 MEMO RE: FURTHER THOUGHTS ON THE RED OIL DIFFERING PROFESSIONAL OPINION (DPO) AND REMEDIES."



UNITED STATES
NUCLEAR REGULATORY COMMISSION

WASHINGTON, D.C. 20555-0001

August 5, 2005

MEMORANDUM TO: Alex P. Murray, Sr. Chemical Engineer
Division of Fuel Cycle Safety and Safeguards
Office of Nuclear Material Safety and Safeguards

FROM: Ad Hoc Review Panel¹ - DPO 2005-002

Handwritten signature of William H. Ruland, Chairman of the Ad Hoc Review Panel.

SUBJECT: PANEL'S UNDERSTANDING OF YOUR DPO ISSUES REGARDING
RED OIL EVENTS AT THE PROPOSED MIXED OXIDE (MOX) FUEL
FABRICATION FACILITY

This memorandum provides you our current understanding of your issues, based on: (1) our reading of the Differing Professional Opinion (DPO) you submitted on January 19, 2005; (2) our meetings with you on April 18 and May 2, 2005; and (3) our review of other documents related to the Red Oil issue. We are sending you this memorandum in accordance with the March 2, 2005, memorandum from Jack Strosnider to the Panel, where he established the panel and tasked us to document the panel's understanding of your issues with a copy to him.

Your DPO was made during the Construction Authorization review stage, not at the license application review stage. Thus, the panel infers that you concluded that Duke Cogema Stone & Webster (DCS) has not met the criteria that, as stated in 10 CFR 70.24(b), "...the *design bases*² 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." (emphasis added)

Using your ten concerns listed in your DPO and repeated here for clarity, we understand your concerns as follows:

1. *Your statement* - 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 (Figure2).

Panel understanding - The applicant, DCS, did not provide any calculations or other technical basis why DCS was not designing their system to meet the Department of Energy (DOE)/Defense Nuclear Facility Safety Board (DNFSB) criteria for system design. You described that criteria as RAGAGEP, or Routinely Accepted or Generally Accepted Good Engineering Practices. While DCS meets some of the criteria, they do not meet all DOE design practices and, in particular, they have not designed all their affected systems to avoid the "unsafe region" described in Paddleford and Fauske, "Safe Venting of 'Red Oil' Runaway Reactions."

¹William H. Ruland, Chairman; Walter S. Schwink and A. James Davis, Ph.D, members

²Design Bases as defined in 10 CFR 50.2.

2. *Your statement* - There is inadequate margin in the design basis temperature.

(b) (2) High

FOIA
EX 2

3. *Your statement* - 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.

Panel understanding - DCS has provided insufficient information on the docket for you to determine if the vents provided in the system would preclude choked flow upon increased temperature, and thus you had insufficient information to determine whether or not the vents were sized properly to prevent a red oil reaction.

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

Panel understanding - DCS provided no controls on organic compounds. Given their other controls, this is insufficient to ensure that red oil reactions will not occur.

5. *Your statement* - There are no controls on acid or solvent concentrations.

Panel understanding - DCS provided higher nitric acid or Tributylphosphate concentrations in the process than warranted. This leads to increases in the hydrolysis reaction, which may contribute to the likelihood of a red oil reaction.

6. *Your statement* - 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.

(b) (2) High

FOIA
EX 2

7. *Your statement* - 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.

Panel understanding - The NRC management decision process used to accept the DCS proposal to control red oil reactions was improper. Management held a vote to

determine the acceptability of the DCS proposal but only two qualified reviewers participated in the vote. The implication here is that only technical reviewers are qualified to make this type of decision.

8. *Your statement* - 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.

Panel understanding - NRC management used process efficiency arguments as part of the rationale to accept the DCS proposal on limiting red oil events. Namely, by selecting the values of parameters for control at the values proposed, DCS will generate less waste but this is not an acceptance criterion in the Standard Review Plan.

9. *Your statement* - 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.

Panel understanding - The NRC management decision to accept the DCS red oil control strategy incorrectly relied on *future* commitments for research or actions to refine or define the *current* Primary Structures, Systems, and Components (PSSC) and design basis. In your words, "technically, we have approved the plant." That is, you believe that the NRC has inappropriately created the bounds for the plant, and you question whether or not the NRC has a clear basis for accepting the design.

10. *Your statement* - Overall, safety concerns from the NRC staff's Revised Draft Safety Evaluation Report (RDSE) 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 no-existent or inadequate to support a conclusion of adequate assurances of safety.

(b)(2) High

FOIA
2/2

Also, you requested three remedies in your original DPO submitted in January 2005. As part of our interview with you on May 2, 2005, we asked if your proposed remedies had changed, since the Construction Authorization had now been issued. By memo dated June 15, 2005, (attached) you restated some of your original concerns; supplied us with additional comments, including your views on the March 23, 2005, Strosnider to Reyes memorandum "Notification of NMSS Licensing Actions"; restated your original proposed remedies; and suggested that, "Perhaps a compliance plan and schedule could be established to address the safety issue."

Also in your June 15th, 2005, memo to the DPO Panel, you have offered some additional potential remedies as part of your proposed compliance plan:

- (1) Communicate these risk significant safety concerns about functionality and operability of the red oil controls to the applicant as soon as possible;
- (2) Impose the DOE/DNFSB RAGAGEP as a permit condition or amendment until the applicant demonstrates that their proposed safety control strategy can actually perform its intended safety functions;
- (3) Inspect test program and results on a routine basis; and
- (4) Inspect red oil control strategy evolution (i.e., from system to component basis) during detailed design and construction.

As you have stated in your memo, your basic proposed remedies have not changed. Rather, you are seeking additional remedies in the form of communication with the applicant about the issue (No. 1 above), the imposition of a permit condition (No. 2 above); and the addition of inspections as part of a "compliance plan" (Nos. 3 and 4 above).

Panel Conclusions on Proposed Additional Remedies

Remedy No. 1 - Communication about safety concerns will be a natural outgrowth of any panel decision, based on the merits of the issues brought before the panel. Therefore, no additional action is warranted on this proposed additional remedy.

Remedy No. 2 - This issue is already captured by concerns Nos. 1 and 9 in the original DPO. Therefore, no additional action is warranted.

Remedy Nos. 3 and 4 - Inspection is one possible way to address issues that come before a DPO panel. As contained in the memorandum that chartered the panel, we were asked to "Make recommendations to me (Mr. Strosnider) regarding the disposition of the issues presented in the DPO." The panel has discretion on whether or not to recommend inspections as part of the resolution to the DPO. We conclude that it would be premature to make a recommendation now. However, based on our ability to do so later, we conclude that no additional action is warranted on these proposed additional remedies at this stage in our review.

Thank you for providing us your concerns. We will contact you during our review with any additional questions that we may have. Please feel free to provide any additional clarification that you feel may be necessary on our understanding of your issues.

Attachment: As stated

cc: Jack Strosnider, NMSS
Renee Pedersen, OE
DPO Panel members

June 15th, 2005

To: Bill Ruland
Walt Schwink
Jim Smith

Subject: Further Thoughts on the Red Oil Differing Professional Opinion (DPO) and Remedies

First, thank-you for taking the time to discuss the red oil issue and the DPO with me.

Second, let me add a follow-on comment regarding the Part 70 regulations and the MOX SRP (NUREG-1718). Part 70 regulates special nuclear materials, and includes facilities like enrichment and fuel fabrication plants. As we discussed, Part 70 specifically requires NRC approval of the principal structures, systems, and components (PSSCs) of a plutonium processing and fuel fabrication plant. This approval requires a determination that the design bases of the PSSCs and the QA program provide reasonable assurance of protection against natural phenomena and the consequences of potential accidents (70.23(b)). The intent of the rule is multipurpose - educate staff and licensee, and address safety issues early, thus minimizing the potential for delays, expensive backfits, or facility abandonment. I am concerned that the letter and the spirit of the regulation have not been met for closed systems susceptible to the red oil phenomena - I cannot find a supporting basis for the determination of reasonable assurances of adequate safety, the available information contradicts the acceptability of the applicant's design bases, there is no support for adequate margin and conservatism, and I am concerned the NRC could be placed in the position of requiring costly backfits or exempting an as-built facility.

Third, some general statements on the issue: The applicant has identified the red oil event as a high consequence event with high safety significance (high consequence event is defined in the context of Part 70.61 - the performance requirements). There is unanimity between staff and management that the NRC agrees with the applicant that this is a high consequence event. The applicant has proposed controls (PSSCs and design bases) to prevent the event from occurring. No information has been supplied by the applicant to support the functionality and reliability of the proposed safety strategy (PSSCs and design bases) for closed red oil systems. The NRC FSER does not provide information to support the regulatory requirement for a determination regarding the proposed PSSCs and design bases for closed systems. There are multiple statements about future tests but these also neither address the regulatory requirement nor do they provide for adequate margin and conservatism - i.e., if the regulator is not sure about the applicant's proposal, why is it being accepted?

Fourth, documents transmitting the MOX FSER package do not fully communicate the context of the safety reviews and include half-truths and errors. For example, the March 23, 2005 memorandum - "Notification of NMSS Licensing Action" - mentions the following:

- "The planned issuance of the CA [Construction Authorization] will occur before a related differing professional opinion (DPO) is resolved." This neglects to mention that there are three other DPVs/DPOs that the "system" is preventing from entering the DPO process.
- "An NMSS staff member filed DPO-2005-002 ..." - this is out of context: the "NMSS staff member" is actually the Lead Chemical Safety Reviewed assigned to MOX safety reviews by the Agency.
- "After specifically considering the red-oil hazard, the ACRS concluded that the FSER should be issued." This is only partially true. The ACRS issued a dichotomous letter some five pages long that recommended issuance of the FSER but also identified safety concerns, including hazardous chemical release, fire hazards, red oil, hydroxylamine nitrate, and waste handling. For the red-oil hazard, the ACRS specifically stated "The applicant's technical basis for these conclusions [prevent runaway red oil reactions] are not clear to us." Significantly, none of the ACRS safety concerns are mentioned in the "Notification" memorandum.
- "The NMSS staff consensus is that the MOX CA should be issued ..." No consensus process was used and the staff has actually had meetings to try and define "consensus."
- "The staff's consensus view is that DCS' proposed red-oil safety strategy is adequate." This is incorrect - there is no staff consensus among qualified chemical safety reviewers that the safety strategy is adequate - the memoranda are initiated and concurred upon by managers and program managers.
- "DCS has several design options [for the red-oil hazard] that require neither a significant redesign nor a retrofit of the facility." Such specific design option discussions did not occur with the applicant. As regards the organic phase decanter, the applicant specifically stated that it could not perform safety functions due to its poor reliability (i.e., an organic material carryover incident every one or two years).
- The memorandum does not mention the lack of discussion with the Lead Chemical Safety Reviewer regarding the safety issues. Obviously, how can an informed decision be made without listening to both sides of the safety issues?
- I also have concerns regarding the memorandum's statements on DPO appeals. The responses to the DPO appeals completely contradict the findings of the DPV panels, repeat the management position, and provide no regulatory clarity.

Fifth, I want to reiterate - it is erroneous to state the red oil safety conclusions (i.e., acceptance) presented in the FSER and its accompanying memoranda are the results of a consensus process. I, as the Lead Chemical Safety Reviewer, expressed concerns and would not accept the red oil strategies, PSSCS, and controls proposed by the applicant. Management brought in another chemical safety reviewer to support the management position of acceptance. The applicant changed their strategy several times; this addressed the concerns for the open system but I still had concerns with the closed system. The other chemical reviewer supported

the management desire for acceptance and did not have concerns with the closed system. Thus, there is one reviewer against acceptance and one reviewer for acceptance. This is not consensus, no consensus process was used, and it is incorrect and misleading for the management letters to state consensus was used.

Sixth, the ACRS has reviewed the proposed MOX facility and CAR. The MOX management team requested ACRS to provide a simple (less than one page) letter. The ACRS provided a five page letter (i.e., long by ACRS standards) dated February 24, 2005. This endorsed the issuance of the FSER, construction, and proceeding with an integrated safety analysis. However, the ACRS letter raised several safety issues. For closed systems susceptible to the red oil phenomena, the letter states (page 4, second paragraph):

"The applicant claims that sufficiently large vents and provision for quenching can be used to control temperatures below _____ which will prevent runaway reactions. The applicant's technical bases for these conclusions are not clear to us." (My emphasis added.) FOIA EX 2

The meeting transcripts also contain numerous questions and concerns the ACRS raised during staff presentations on MOX. Thus, it appears that the ACRS agrees with the DPO that an adequate basis (rationale) has not been provided for the applicant's proposed safety strategy. This raises the obvious question - why has the NRC accepted the applicant's safety strategy given these concerns which imply the regulatory requirement has not been met?

Finally, let me discuss potential remedies. The DPO requested the following in January 2005:

- (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 (i.e., the RAGAGEP - reasonable and generally accepted good engineering practice); or, alternatively, the NRC should apply a construction permit condition that imposes the DOE/DNFSB safety strategy as the design basis until the applicant justifies its approach.

The ACRS letter was issued in February, while the FSER and construction authorization permit were issued in late March. NRC activities on MOX are at a low level due to delays in the DOE side of the program - significant activities may not resume until December 2005 or even sometime in 2006 - this delay was known when NRC issued the FSER and construction authorization. In light of this information and by comparison to construction permits for reactors, all three remedies proposed in the DPO still seem reasonable and valid. Perhaps a compliance plan and schedule could be established to address the safety issue.

I note that it is likely the prevailing opinion held by some members of management and staff is in alignment with my technical safety concerns and this should be acknowledged by the DPO report. Thus, as part of a compliance plan, it also seems prudent and reasonable during this program delay to:

- communicate these risk significant safety concerns about functionality and operability of the red oil controls to the applicant as soon as possible.
- impose the DOE/DNFSB RAGAGEP as a permit condition or amendment until the applicant demonstrates that their proposed safety control strategy can actually perform its intended safety functions.
- inspect test program and results on a routine basis.
- inspect red oil control strategy evolution (i.e., from system to component basis) during detailed design and construction.

Therefore, as part of a remedy, I would like to see a recommendation for a compliance plan and schedule, perhaps with the above items identified as possible milestones, in order to address the red oil issue in a timely manner.

Please contact me if you have any questions.

ATTACHMENT 3 to Panel Report

LIST OF PERSONS CONTACTED BY THE DPO PANEL

Alexander Murray,	Sr. Chemical Reviewer, NRC/FCSS
Andrew Persinko,	Former MOX Project Manager, NRC/FCSS
Bill Troskoski,	NRC/FCSS
Don Stout,	NRC/FCSS
Dave Brown,	Former MOX Project Manager, NRC/FCSS
Wes Patrick, Ph. D	Vice-President, CNWRA
Vijay Jain, Ph. D	Manager, Corrosion Science & Process Engineering, CNWRA
R. Page Shurtum, PE	RPS Engineering
James Smith	NRC/FCSS
David Turner, Ph. D	Asst. Director, Non-Regulatory Programs, CNWRA
Asadul Chaudry, Ph. D	Manager, Mining, Geotechnical, and Facility Engineering, CNWRA

ATTACHMENT 4 to Panel Report

Documents

- 03/17/71 *Proposed Amendments to Part 70: Pre-Construction Review of Plutonium Processing and Fuel Fabrication Plants*, AEC SECY-R 188 [Non-Public Record - Official Use Only. See **Federal Register**, Volume 36, Number 104, Pages 9786 - 9787 (Proposed Rule) and Volume 36, Number 171, Pages 17573 - 17575 (Final Rule)]
- 10/21/88 *Memorandum of Understanding Between the U.S. Nuclear Regulatory Commission and the Occupational Safety and Health Administration*, [Public Record. See **Federal Register**, Volume 53, Number 210, Page 43950 (10/31/88), and NRC Information Notice 88-100 (12/23/88)]
- 09/04/92 *Memorandum of Understanding Between the Environmental Protection Agency and Nuclear Regulatory Commission Concerning Clear Air Act Standards for Radionuclide Releases from Facilities other than Nuclear Power Reactors Licensed by NRC or its Agreement States, Subpart I, 40 CFR Part 61*, [Public Record. See **Federal Register**, Volume 57, Page 60778 (12/22/92)]
- 12/15/99 *Nuclear Regulatory Commission Management Directive 10.159, The NRC Differing Professional Opinions Program* [Public Record - See subsequent revision of this directive dated 05/16/04]
- 04/23/02 DCS letter to NRC, *Clarification of Responses to NRC Request for Additional Information*, [Public Record - ML021160037 - Docket Number 070-03098]
- 07/09/02 DCS letter to NRC, *Evaluation of the Draft Safety Evaluation Report (DSER) on Construction of a Mixed Oxide Fuel Fabrication Facility* [Public Record - ML021910605 - Docket Number 070-03098]
- 02/18/03 DCS Letter to NRC, *Mixed Oxide (MOX) Fuel Fabrication Facility Construction Authorization Request Change Pages*, [Public Record - ML030520595 - Docket Number 070-03098]
- 02/18/03 DCS Letter to NRC, *Responses to Financial Qualification, Fire, Safety, Chemical Safety, Aqueous Processing, Material Processing and Ventilation Open Items/Additional NRC Questions on Construction Authorization Request (CAR) Revision*, [Public Record - ML030520464 - Docket Number 070-03098]
- 03/10/03 Memorandum from Robert Pierson through Martin Virgilio to Carl Paperiello, *Regulatory Authority Over Chemical Hazards at Fuel Cycle Facilities* [Public Record - ML030700317]
- 02/24/05 ACRS Chairman letter to the NRC Chairman entitled "REVIEW OF THE FINAL SAFETY EVALUATION REPORT FOR THE MIXED OXIDE FUEL FABRICATION FACILITY CONSTRUCTION AUTHORIZATION"

Paddleford, D.F. and H.K. Fauske. "Safe Venting of 'Red Oil' Runaway Reactions." WSRC-MS-94-0649. Aiken, South Carolina: Savannah River Site. 1994.

09/04/06 NRC's Public Web Site Page on "Mixed Oxide Fuel Fabrication Facility Licensing" (<http://www.nrc.gov/materials/fuel-cycle-fac/mox/licensing.html>).

ATTACHMENT 5 to Panel Report

**Center for Nuclear Waste Regulatory Analysis (CNWRA) Report
Assessment of red oil runaway reactions potentially causing explosions in the MOX aqueous
polishing process units.**

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ASSESSMENT OF RED OIL RUNAWAY REACTIONS IN THE AQUEOUS POLISHING PROCESS UNITS OF THE MIXED OXIDE (MOX) FUEL FABRICATION FACILITY

Prepared for

**U.S. Nuclear Regulatory Commission
Contract NRC-02-03-002**

Prepared by

**V. Jain
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**Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas**

October 2006

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ABSTRACT

On February 28, 2001, Duke Cogema Stone & Webster (DCS) submitted a request to the U.S. Nuclear Regulatory Commission (NRC) to construct a Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF) on the U.S. Department of Energy (DOE) Savannah River Site (SRS) near Aiken, South Carolina (DCS, 2001). In March 2005, NRC documented its review in the final safety evaluation report, and approved the DCS request for the construction of a MFFF (NRC, 2005). However, an NRC staff disagreed with the proposed DCS approach and the NRC staff evaluation pertaining to the potential for red oil events and filed a Differing Professional Opinion (DPO) (Strosnider, 2005). This report addresses concerns identified in the NRC DPO-2005-002 (Strosnider, 2005) pertaining to red oil runaway reaction in the Aqueous Polishing process units of the proposed MFFF. The Center for Nuclear Waste Regulatory Analyses assessment, based on review of the principal structures, systems and components (PSSC) and the preventive and mitigative solutions, indicates that red oil runaway reactions could be classified as not-unlikely high-consequence events for thermosiphon evaporators. The PSSC adopted by the DCS for preventing red oil runaway reactions for the closed thermosiphon evaporators may not be adequate. However, a review of some potential backfit options indicates that effective solutions can be obtained without an extensive retrofit and without significant construction cost implications.

References

DCS. "Mixed Oxide Fuel Fabrication Facility Construction Authorization Request." Docket 070-03098. Charlotte, North Carolina: DCS. 2001.

NRC. NUREG-1821, "Final Safety Evaluation Report on the Construction Authorization Request for Mixed Oxide Fuel Fabrication Facility at the Savannah River Site South Carolina." Washington, DC: NRC. 2005.

Strosnider, J.R. "Ad Hoc Review Panel—Differing Professional Opinion on Red Oil Events at the Proposed Mixed Oxide Fuel Fabrication Facility." Letter (March 2) to W. H. Ruland, NRC. DP-2005-002. Washington, DC: NRC. 2005.

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ACKNOWLEDGMENTS

This report was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC-02-03-002. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of Fuel Cycle Safety and Safeguards. The report is an independent product of CNWRA and does not necessarily reflect the views or regulatory position of NRC.

During the course of these analyses, CNWRA staff participated in both face-to-face meetings at NRC headquarters and teleconferences with the Differing Professional Opinion (DPO) Panel. The authors thank the DPO Panel for insights gained from the discussions at these meetings.

The authors thank Drs. W. Patrick and B. Sagar for participating in technical discussions and providing insights, L. Yang for his thorough technical review, B. Sagar for his programmatic review, and E. Percy for his editorial comments and recommendations. The administrative support provided by L. Selvey is also greatly appreciated.

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: Relative hazard index determined in Appendix B was calculated using information provided in the Mixed Oxide Fuel Fabrication Facility Construction Authorization Request (Duke Cogema Stone & Webster, 2001 with change pages). The Microsoft® Excel Version 2002 SP3 program was used for calculations.

ANALYSES AND CODES: None.

Reference:

Duke Cogema Stone & Webster. "Mixed Oxide Fuel Fabrication Facility Construction Authorization Request." Docket 070-03098. Charlotte, North Carolina: Duke Cogema Stone & Webster. 2001.

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EXECUTIVE SUMMARY

On February 28, 2001, Duke Cogema Stone & Webster (DCS) submitted a request to the U.S. Nuclear Regulatory Commission (NRC) to construct a Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF) on the U.S. Department of Energy (DOE) Savannah River Site (SRS) near Aiken, South Carolina (DCS, 2001). In March 2005, NRC documented its review in the final safety evaluation report, and approved the DCS request for the construction of a MFFF (NRC, 2005). However, a member of the NRC staff disagreed with the proposed DCS approach and with the NRC staff evaluation pertaining to the potential for red oil events and filed a Differing Professional Opinion (DPO) (Strosnider, 2005). This DPO was assigned DPO-2005-002.

The licensing of the (MFFF) under 10 CFR Part 70 is a two step process. Authorization for construction is followed by authorization to receive and possess. 10 CFR 70.23(b) provides requirements for construction authorization, which specifically requires the Commission to conclude, prior to approving a construction authorization that the design bases of the principal structures, systems, and components (PSSC), and the quality assurance program provide reasonable assurance of protection against natural phenomena and the consequences of potential accidents. Furthermore, statements of consideration provided in the Office of Secretary (SECY) R-188 (NRC, 1971) indicate that the underlying purpose of construction authorization (first step of the two-step licensing process) is to ensure that adequate preliminary consideration has been given to natural phenomena hazards and postulated accidents at the proposed facility so that subsequent extensive retrofits will not be necessary to meet NRC requirements for possessing and using licensed materials (second step of the two-step licensing process).

This report addresses concerns identified in the NRC DPO-2005-002 pertaining to solvent-extraction related red oil runaway reactions in the Aqueous Polishing process units of the proposed MFFF. Red oil is defined as an organic mixture of C₁₀-C₁₃ branched aliphatic hydrocarbons containing a complexation agent, tributyl phosphate (TBP), and its complexes with plutonium, nitric acid, and degradation products of TBP (normally monobutyl and dibutyl phosphates, alcohols, and organic nitrates). Between 1953 and 1993, there were six documented red oil explosions (Usachev and Markov, 2003).

The Center for Nuclear Waste Regulatory Analyses assessment, based on the review of the proposed PSSC and the preventive and mitigative solutions indicates that red oil runaway reactions could be classified as not-unlikely high-consequence events. The PSSC adopted by the DCS for preventing red oil runaway reactions for the closed thermosiphon evaporators may not be adequate. However, review of the potential backfit options indicates that effective solutions can be obtained without an extensive retrofit and without significant construction cost implications.

References

DCS. "Mixed Oxide Fuel Fabrication Facility Construction Authorization Request." Docket 070-03098. Charlotte, North Carolina: DCS. 2001.

NRC. NUREG-1821, "Final Safety Evaluation Report on the Construction Authorization Request for Mixed Oxide Fuel Fabrication Facility at the Savannah River Site South Carolina." Washington, DC: NRC. 2005.

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———. SECY-R 188, "Proposed Amendments to Part 70 to Provide Pre-Construction Review of Plutonium Processing and Fuel Fabrication Plants." Washington, DC: NRC. 1971.

Strosnider, J.R. "Ad Hoc Review Panel—Differing Professional Opinion on Red Oil Events at the Proposed Mixed Oxide Fuel Fabrication Facility." Letter (March 2) to W. H. Ruland, NRC. DP-2005-002. Washington, DC: NRC. 2005.

Usachev, V.N. and G.S. Markov. "Incidents Caused by Red Oil Phenomena at Semi-Scale and Industrial Scale Radiological Units." *Radiochemistry*. Vol. 45, No.1. pp. 1-8. 2003.

1 INTRODUCTION AND OBJECTIVES

1.1 Introduction

The licensing of the MOX Fuel Fabrication Facility (MFFF) under 10 CFR Part 70 is a two-step process. Authorization for construction is followed by the authorization to receive and possess special nuclear material. 10 CFR 70.23(b) provides requirements for construction authorization, which specifically requires the U.S. Nuclear Regulatory Commission (NRC) to conclude, prior to approving a construction authorization that the design bases of the principal structures, systems, and components (PSSC), and the quality assurance program provide reasonable assurance of protection against natural phenomena and the consequences of potential accidents. Furthermore, statements of consideration provided in the Office of Secretary (SECY) R-188 (NRC, 1971) indicate that the underlying purpose of construction authorization (first step of a two-step licensing process) is to ensure that adequate preliminary consideration has been given to natural phenomena hazards and postulated accidents at the proposed facility so that subsequent extensive retrofits will not be necessary to meet NRC requirements for possessing and using licensed materials (second step of the two-step licensing process).

On February 28, 2001, Duke Cogema Stone & Webster (DCS) submitted a request to NRC to construct a MFFF on the U.S. Department of Energy (DOE) Savannah River Site (SRS) near Aiken, South Carolina (DCS, 2001). In March 2005, NRC documented its review in the final safety evaluation report, and approved the DCS request for the construction of a MFFF (NRC, 2005). However, the Senior Chemical Process Engineer, who is also the lead Chemical Safety Reviewer for NRC, disagreed with the proposed DCS approach as well as the NRC staff evaluation pertaining to the potential for red oil events and filed a Differing Professional Opinion (DPO) (Strosnider, 2005). This DPO was assigned DPO-2005-002.

1.2 Objectives

In order to address concerns raised in DPO-2005-002, the key objectives of this report are to (i) assess the proposed classification of principal structures, systems and components (PSSC), (ii) assess the DCS design philosophy to mitigate or prevent red oil events in Aqueous Polishing process units, and (iii) evaluate backfit options that may be necessary to address concerns raised in DPO-2005-002.

2 BACKGROUND INFORMATION

2.1 Red Oil Runaway Reaction

Tributyl phosphate (TBP) is a widely used organic solvent in radioactive material reprocessing plants in the initial cycles of the Plutonium Extraction (PUREX) process to co-extract plutonium and uranium, leaving behind fission products such as cesium and technetium. TBP is mixed with diluents, which are C₁₀-C₁₃ branched aliphatic hydrocarbons such as hydrogenated propylene tetramer (HPT) that are used as density control solvents (approximately 70 percent by weight). Red oil is defined as a mixture of C₁₀-C₁₃ branched aliphatic hydrocarbons containing a complexation agent, TBP, and its complexes with plutonium or uranium, nitric acid, and degradation products of TBP (normally monobutyl and dibutyl phosphates, alcohols, and organic nitrates). Between 1953 and 1993, there were six documented red oil explosions

(Usachev and Markov, 2003). In the United States, two explosions occurred at the Savannah River Site, South Carolina; and one each at Hanford, Washington; and Oak Ridge, Tennessee. There also was one accident in Canada and one in Russia. Five out of six accidents took place in uranium reprocessing lines and one took place in a plutonium line. All accidents, except at Hanford, caused significant damage to structures and components. The evaporator at the Hanford reprocessing line was fitted with a rupture disk that provided rapid pressure equalization and minimized the effects of the explosion.

The rate of reaction between nitric acid and TBP is controlled by the TBP hydrolysis rate that produces dibutyl phosphate and n-butanol. The n-butanol can either volatilize at 117.5 °C [243.5 °F] or can be oxidized in the presence of nitric acid or nitrates. If oxidation occurs before volatilization, the heat of oxidation may exceed evaporative cooling causing an energetic runaway reaction and possibly an explosion in a confined space (Hyder, 1994a). In an open system, however, evaporative cooling assisted by removal of water vapor and gaseous reaction products limits the generation of heat and the buildup of pressure in the evaporators. Hyder (1994b) indicated that below 80 °C [176 °F] the self-heating is so slow that the natural processes provide adequate cooling. However, he cautioned that care is needed to ensure that adequate cooling is available at higher temperatures.

Paddleford and Fauske (1994) experimentally examined the role of venting in reducing the likelihood of a red oil accident. Samples were heated at a rate of 1–2 °C/min [1.8–3.6 °F/min] until self-heating was observed. In the vented system, boiling was observed around 115–125 °C [239–257 °F] with no self-heating until 130 °C [266 °F]. In the closed system, self-heating was observed at 116 °C [241 °F]. Using pure TBP saturated with 15 N nitric acid, Paddleford and Fauske (1994) showed that overpressurization initiates if the organic (TBP) mass-to-vent area ratio is greater than 310 g/mm² [7,055 oz/in²].

Rudisill and Crooks (2001) examined the red oil runaway reaction temperature in a mixture containing one volume of TBP with five volumes of aqueous solution, and showed that the runaway reaction temperature decreases with increasing amounts of nitric acid. The lowest runaway reaction temperature in a 15 N nitric acid solution was 134 °C [273 °F] with an average initiating temperature of 137 °C [277 °F]. The decrease in the runaway reaction temperature was attributed to the increased extraction of nitric acid in the organic phase. Colvin (1956), which was referenced in Rudisill and Crooks (2001), indicated that red oil runaway reaction initiation could occur at a temperature as low as 129 °C [264 °F] in 9.6 M nitric acid solution. Rudisill and Crooks (2001), however, noted that the Colvin (1956) datapoint was an outlier.

In 2003, the Defense Nuclear Facilities Safety Board (DNFSB), partly based on the data by Rudisill and Crooks (2001), recommended that in addition to designing an adequate vent size, limits should be imposed on operating temperature and pressure, maximum organic mass, and maximum nitric acid concentration. A single control should not be used to prevent a runaway red oil reaction and explosion (Conway, 2003).

2.2 Summary of the DCS Approach

DCS has adopted a mix of preventive and mitigative safety strategies to avoid overpressurization in thermosiphon evaporators during a red oil runaway reaction event.

• Acid Recovery Unit (KPC)

FOIA
ex. 4

FOIA
EX 4

DCS has established principal structures, systems, and components (PSSC) to implement a preventive safety strategy for thermosiphon evaporators, including

- Offgas treatment system
- Process safety control subsystem
- Chemical safety control

The safety function of the proposed offgas treatment system is to provide venting from vessels/equipment that may potentially contain TBP and associated byproducts in nitric acid solution. The design basis for the proposed vent size is consistent with the recommendation of Paddleford and Fauske (1994)

FOIA
EX 4

DCS has still credited the proposed offgas treatment system as PSSC for providing an exhaust path for aqueous phase evaporative cooling. The vent size is sufficient to remove the heat input and heat generated by the exothermic self-sustained red oil reactions.

DCS has proposed a design basis steam temperature of 133 °C [271 °F] and a maximum heating rate of 2 °C/min [3.6 °F/min] after startup to limit the heat generation rate. Furthermore, DCS has proposed 125 °C [257 °F] as the maximum design basis bulk fluid temperature. This ensures that diluents will not undergo degradation, and is below the lowest runaway reaction temperature. DCS stated that this finding is based on the experimentally determined minimum initiation temperature for a closed system; however, no reference was provided in the DCS Construction Authorization Request (CAR).

DCS has also identified the selection of a diluent, such as HPT, as a chemical safety control PSSC. In addition, DCS has proposed to implement the diluent washing by using either pulsed columns or mixer-settlers to preclude the transfer of bulk organic quantities to heated equipment. However, diluent washing systems were not credited as PSSC. In addition, DCS plans to include an Aqueous Injection system to mitigate potential red oil runaway reactions if the temperature exceeds design basis temperature.

2.3 Summary of the NRC Review

The NRC staff summarized their assessment on the red oil runaway reactions separately for open and closed thermosiphon evaporator systems in Section 8.1.2.5.5 of NRC (2005).

2.3.1 Open Thermosiphon Evaporator System

The NRC staff concluded that for the open (i.e., vented) thermosiphon evaporator system, the proposed organic (TBP) mass-to-vent area is well below the organic (TBP) mass-to-vent area of 310 g/mm² [7,055 oz/in²] above which red oil runaway reactions can

FOIA
EX 4

be initiated (Paddleford and Fauske, 1994). Therefore, the NRC staff concluded that the vent size is large enough to maintain pressure at atmospheric levels.

2.3.2 Closed (Partially Vented) Thermosiphon Evaporator System

The NRC staff evaluated the design basis temperature for red oil runaway reactions and concluded that the average initiation temperature of 137 °C [279 °F] (range from 134–140 °C [273–284 °F]) for TBP in a 13.6 N nitric acid solution is appropriate. The NRC staff accepted that shutting down the steam and injection of aqueous phase material into the closed system evaporator is an adequate methodology to maintain bulk fluid temperature below 125 °C [257 °F].

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For the closed thermosiphon evaporator system, the NRC staff concluded that DCS has provided sufficient defense-in-depth by proposing an approach that includes independent multiple temperature controls, an aqueous phase evaporative cooling (offgas treatment) system, and the exclusion of cyclic chain hydrocarbons. In addition, DCS committed in the amended license application to conducting additional research and development on the runaway initiation temperature and the effect of impurities on the initiation temperature, however, detailed plans were not provided for review.

2.4 DPO-2005-002 Summary

Based on the proposed approach by DCS in the MFFF CAR (DCS, 2001 with change pages) and the NRC review documented in Section 8.1.2.5.5 of NRC (2005), the following concerns related to the potential for red oil formation in thermosiphon evaporators were cited in DPO-2005-002 (Strosnider, 2005):

- The design basis maximum bulk fluid temperature of 125 °C [257 °F] has an inadequate safety margin.
- The DCS proposal for a closed system should be considered as entirely in the unsafe zone based on Reasonable and Generally Accepted Good Engineering Practice (RAGAGEP).
- In the closed system, venting is insufficient to avoid choked flow and pressurization.
- Controls on organic compounds are inadequate—the applicant has indicated organic carryover is an anticipated event.
- There are no controls on acid or solvent concentrations.

DPO-2005-002 (Strosnider, 2005) concerns are based on DCS not following the DNFSB (Conway, 2003) recommendations to implement multiple safety controls on multiple parameters such as temperature, pressure relief/vent size, total organic carbon, nitric acid concentration, and building confinement. In addition, DPO-2005-002 (Strosnider, 2005) states that DCS has not adopted DOE practices at the H-Canyon Facility located at the SRS for its control strategy (e.g., a limit of less than 10 N on nitric acid concentration, adequate vent size, and limiting the

operating temperature) (NRC, 2005). For open systems, DPO-2005-002 (Strosnider, 2005) states that DCS has adopted some practices that provide a sufficient safety margin (e.g., vent size). However, for the closed (partially vented) system DCS has proposed a vent size that is in an unsafe regime compared to the DOE H-Canyon Facility.

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3 ASSESSMENT OF RED OIL RUNAWAY REACTION IN AQUEOUS POLISHING PROCESS UNITS

In this chapter, the DPO-2005-002 issues are addressed by examining (i) the proposed classification of PSSC, (ii) the DCS design philosophy to mitigate or prevent red oil runaway reactions in Aqueous Polishing process units, and (iii) the backfit options that may be necessary to prevent red oil runaway reaction.

3.1 Classification of PSSC

Evaluation of PSSC in accordance with the Sections 5.4.3.1(E) and (F) of NUREG-1718 (NRC, 2000) requires consideration of the likelihood of occurrence of events and the associated consequences (i.e., radiation dose if events do occur). The mathematical product of the likelihood and consequence estimate provides an expected dose or dose risk.

Likelihood estimate. There have been six documented red oil accidents since 1953, indicating approximately one accident per decade (Usachev and Markov, 2003). If one assumes that there are 10 similar facilities worldwide, an approximate (because the number of data points is limited) likelihood of an accident can be estimated as 0.01 per facility per year [6 accidents / (10 facilities x 60 years)]. Based on this very gross estimate, it appears that the likelihood of such an accident during the lifetime of the proposed facility is not negligible. Consistent with this estimate, the DCS also categorized postulated explosive events as "not unlikely" (i.e., DCS did not exclude explosive events based on their low probability of occurrence). Although more than 10 facilities may have been operating during this period, which could lower the likelihood of postulated accidents, it is highly unlikely that the resulting probability estimate would reduce the categorization to Likelihood Category 2 (unlikely).

Consequence estimate. The CAR (Table 5.5-26) estimates a maximum mitigated dose to an individual outside the controlled (IOC) area located at 160 m [524.9 ft], as a result of a bounding explosion event, to be less than 0.003 Sv [300 mrem]. This estimate uses conservative assumptions with one potentially important exception: airborne particles are assumed to be filtered prior to release from the MFFF building. Taking credit for filtration tacitly (and perhaps unrealistically) assumes that the building would not be significantly damaged by a postulated explosion. The consequence calculations in the CAR for explosive events did not consider the potential failure of the roof of a building similar to what occurred as a result of the Tomsk-7 red oil event, where the explosion damaged the roof, thus providing a direct release path (Gilbert, et al., 1993).

DCS used a factor of 10,000 reduction in airborne particles based on a leak path factor (LPF) of 1×10^{-4} to mitigate explosion consequences. Assuming a linear relation between release and dose, the unmitigated dose (e.g., if the building is damaged such that filtration is completely ineffective) from an explosion event could be as great as 3,000 rem to an IOC located at 160 m

[524.9 ft] from the MFFF stack. This may classify explosions, based on consequences, as a high consequence event. Whether such a scenario is credible at the MFFF will require a more detailed examination of explosive power, structural design, and potential release pathways. Such information was not provided in the CAR.

Expected dose. The DCS calculation of expected dose (risk) is the same as described in the consequence calculation above, because the event is assumed to occur (i.e., the probability is 1.0). Using information currently available, the CNWRA estimates for the postulated case of a breach of the containment building, the expected value of the unmitigated dose is $(30 \text{ Sv}) \times 0.01 = 0.3 \text{ Sv}$ [(3,000 rem) \times (0.01) = 30 rem] to the IOC. Based on this estimate, the postulated red oil runaway reaction would be classified as a high-consequence event. The above estimate, however, includes structural failure of containment. If the containment structure remained substantially intact following such an event, the risk would be further reduced.

Review of the MFFF CAR for structural systems indicates that DCS has committed to designing the Aqueous Polishing Cell structures to meet applicable codes and standards including designing for internal explosions. However, DCS has not committed to specific design parameters for applying the cited codes or standards.

3.2 Unit Operations

[Table A-1 of Appendix A shows the hazard index for various unit operations, relative likelihood of red oil runaway reactions in various components of each unit operation, and summarizes DCS proposed safety features that either mitigate or prevent red oil runaway reactions. The methodology for calculating relative hazard index is provided in Appendix B.

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the kinetics of a red oil runaway reaction are expected to be extremely slow because nitric acid concentration (less than 4.5 N) and temperature (below 60 °C [140 °F]) are both well below the reported threshold values for potential red oil runaway reaction conditions. Hyder (1994b) also indicated that below 80 °C [176 °F] the self-heating is so slow that the natural processes provide adequate cooling through adiabatic losses to prevent a thermal runaway. If a system was of a large enough scale, however, such that the surface area to volume of the equipment did not meet the assumptions of Hyder (1994b), a runaway reaction could occur. For example, large process tanks with little or no throughput flow, and the possibility of accumulating TBP degradation products might not be cooled sufficiently, allowing temperatures to rise over time.

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Another possible scenario for a red oil runaway reaction includes a phase (density) inversion between the aqueous and organic phases. A phase inversion is postulated to occur at a point where the uranium complexed by the TBP in the organic phase results in an organic phase density that is greater than the surrounding acid (aqueous) phase density. In this scenario, the resultant trapped TBP phase would react and release heat by bubbling (boiling) through the overlying aqueous phase, reducing effective heat transfer and generating substantial surface area (mixing) between the acid and TBP phases in the interfacial region. [

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At this degree of boil-up, a very turbulent and high velocity (high Reynold's number) flow condition would exist in the liquid path. The kinetics of chemical reactions, such as the hydrolysis of TBP, where there is limited solubility between reactants in immiscible phases (e.g., acid water and TBP), are often maximized when the interfacial reaction becomes dominant. This effect requires some level of shear rate intensity to generate the required surface area for mass transfer. To quantify the TBP kinetics for these potential scenarios, a calorimeter would need to be operated at the same shear rate as the thermosiphon reboiler, for example, using both phases present simultaneously.

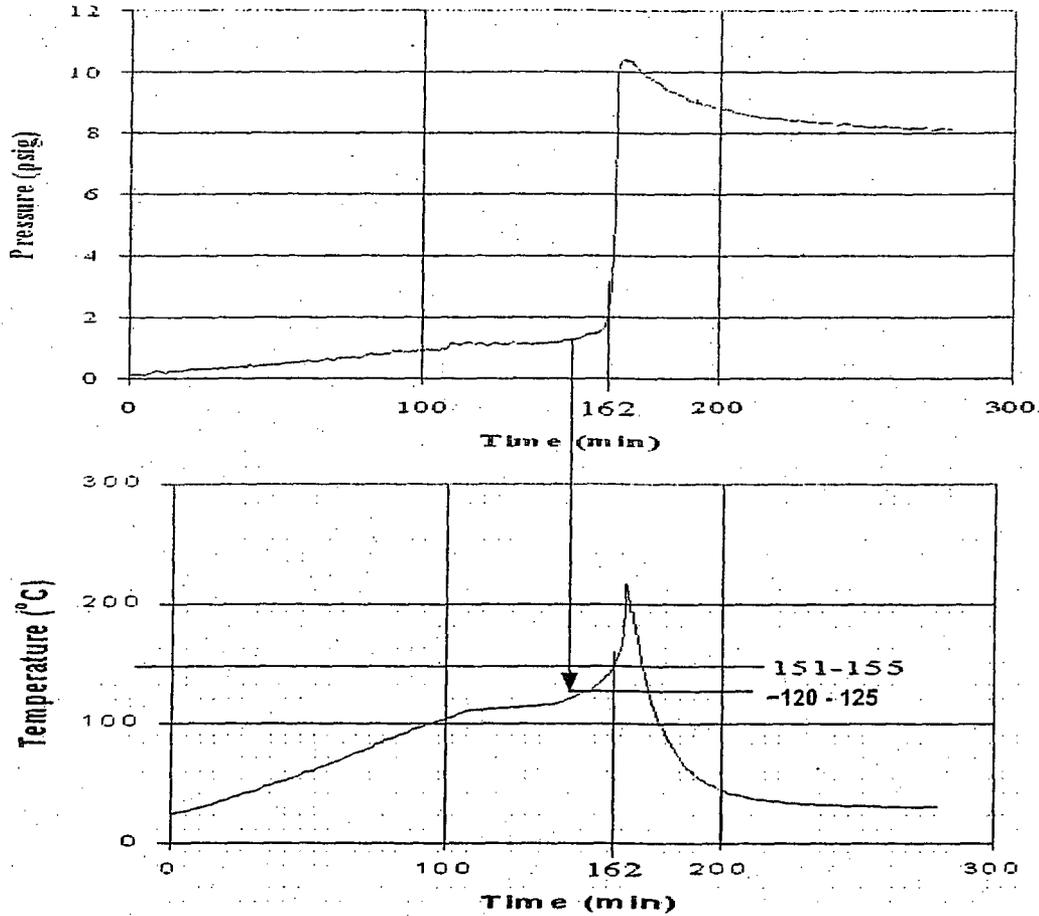
3.3 DCS Design Philosophy

The CNWRA staff examined the proposed DCS design philosophy to prevent or mitigate red oil runaway reactions in thermosiphon evaporators. While DCS has indicated that the MMMF is based on the similar facility in France, detailed information on the French facility is not available for review at this time. The assessment, based on Section 8.3(A)-(E) of NUREG-1718 (NRC, 2000), resulted in the following observations.

3.3.1 Design Basis Temperature

DCS has proposed using multiple independent temperature controls and monitoring equipment for temperature control in thermosiphon evaporators (NRC, 2005, p. 8-51). The proposed use of multiple independent temperature controls is adequate because it provides a good measure of temperature variability within evaporators.

Rudisill and Crooks (2001) examined the red oil runaway reaction temperature. The temperature of runaway reaction was based on the time at which the pressure spike occurred, as shown in Figure 3-1. A detailed examination of the Figure 3-1 indicates that the inflection in temperature (temperature versus time curve) could occur at a much lower temperature (approximately 30 °C [54 °F]) than the pressure spike temperature of 151 °C [304 °F].



Arrow indicates inflection point

Figure 3-1. Calorimetry Data Showing Temperature and Pressure Profile for a Typical Mixture of Tributyl Phosphate and Nitric Acid. The Arrow Shows the Inflection Point in Temperature Prior to the Pressure Spike at 162 Minutes (Rudisill and Crooks, 2001).

Additional tests may be needed to determine the minimum temperature for self-heating. The inflection point indicates a change in the heat generation rate due to self-heating. The temperature at which a pressure spike is observed is indicative of the progression of the red oil runaway reaction. The difference between the temperature at the inflection point and the temperature at which the pressure spike occurs depends on the physical properties of the reactor vessel (e.g., size and insulation). The difference may represent a delay in pressure buildup. If enough time is allowed, the pressure spike may occur at the inflection point. Therefore, the inflection point in the temperature profile where the temperature starts a sharp ascent may be considered as the upper limit beyond which controls would be ineffective, and throttling back to safe condition would be extremely difficult. Paddleford and Fauske (1994) observed the initiation of self-heating in a closed system at 116 °C [241 °F], which supports the

observation by Rudisill and Crooks (2001) that the inflection point is the runaway reaction initiation temperature.

Furthermore, the temperature control setpoint of the evaporators under examination is very close to the observed self-heating temperature of the process fluids, assuming full excursions of chemical concentrations. Based on differential scanning calorimetry, the industrial and Materials Technologies Programme of the European Commission Project BET2-0572 (HarsNet, 2005) recommends the safety margin ($T_{\text{onset}} - T_{\text{Process, maximum}}$) as 100 °C [180 °F] for reactions with enthalpies above 80 kJ/mole [19.1 kcal/mole]. However, a general safe operating temperature margin for cases such as red oil runaway reaction usually starts with a design basis temperature which is 50 °C [90 °F] based on accelerating rate calorimetry data (HarsNet, 2005). The U.S. Chemical Safety and Hazard Investigation Board report on the October 13, 2002, First Chemical Corporation of Pascagoula, Mississippi, incident, concluded that a safety margin of between 20 and 42.2 °C [36 and 76.0 °F] for the design basis temperature of 210 °C [410 °F] proved to be inadequate in this case of organic nitrates. Also cited by the U.S. Chemical Safety and Hazard Investigation Board was an August 7, 1972, case at the Union Carbide Company facility in South Charleston, West Virginia, where another organic nitrate runaway reaction occurred. Previous experience with reactive chemicals testing at Union Carbide Company had indicated that the design margin of 42.2 °C [76.0 °F] for the design basis temperature of 232 °C [450 °F] was adequate. Neither of these cases prove that the red oil reaction would run away, but are used to illustrate that there is substantial uncertainty in determining a safety margin of temperature based on reactive chemicals testing (accelerated rate calorimetry).

Additionally, information presented by Conway (2003, p. 5-2) and NRC (2005, p. 8-43) implies that the steam temperature supplied to the steam chest of the evaporator is that of saturated steam at the regulated pressure. No details of the steam station design have been provided, though this assumption would generally be analyzed carefully in low safety temperature margin designs. If the temperature of the steam supply is not monitored and no desuperheater is employed, the steam can be hotter than the pressure dictates due to superheating. In such applications, steam temperature generally would be considered in a closed (partially vented) system thermosiphon evaporator design with a low temperature safety margin.

Moffat and Thompson (1961) examined the role of zirconium in TBP and nitric acid reactions and concluded that zirconium extracted into the organic phase from the aqueous phase greatly accelerates TBP decomposition. Hou, et al. (1996) did not observe red oil runaway reactions in the presence of zirconium; however, they attribute this to test conditions that were not appropriate for the study of red oil runaway reactions. DCS has not provided an assessment of the potential catalytic reactions that can initiate runaway red oil reactions at a lower temperature (DCS, 2001, with change pages). The NRC assessment in the safety evaluation report (NRC, 2005) indicates that DCS has, however, committed in the application as amended to conduct research and development to determine the effect of impurities.

The NRC staff review documented in Section 8.1.2.5.5 of NRC (2005) indicates a safety margin range of [] However, the difference between the design basis temperature (125 °C [257 °F]) and minimum temperature (134 °C [273 °F]), based on the temperature at which a pressure spike occurs, is only 9 °C [16 °F]. Based on the foregoing discussion, the proposed safety margin is questionable. In addition, the NRC assessment indicates that the pressure increase required

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to raise the temperature by 4.6 °C [8.3 °F] is about 10 percent of the ambient offgas treatment system pressure (NRC, 2005). This analysis assumes there is no self-heating due to the initiation of red oil reactions and neglects generation of reaction products. Given only 9 °C [16 °F] safety margin in the design basis bulk fluid temperature, the occurrence of red oil reactions during normal operations and the frequent use of the aqueous injection system to suppress red oil runaway reactions cannot be ruled out.

Given that red oil runaway reaction could be classified as not-unlikely high-consequence event, the proposed safety margin for the design basis of the fluid bulk temperature of 125 °C [257 °F] is not supported by an adequate technical basis to ensure that chemical process safety controls can prevent or mitigate potential accidents.

3.3.2 Aqueous Injection System

The proposed aqueous injection system, which is a mitigative feature, is activated if the maximum fluid temperature exceeds the design basis temperature (NRC 2005, p. 8-51). The proposed aqueous injection system, which is a subsystem of the process safety control system, may not be adequate to provide relief on demand during a potential red oil event.

The Rudisill and Crooks (2001) data indicate that the pressure spike occurs perhaps within a minute. The response time of the process control system on demand to isolate steam and initiate aqueous injection may not be quick enough to counter a pressure buildup. Any automatically controlled valving for the purpose of blocking and isolating additional steam entry into the steam chest during a thermal excursion or other emergency triggering event generally would be actuated from an independent process variable monitoring device and accomplished with an independent block valve (not the main control valve), or more commonly a double block and bleed arrangement. Standard practice would classify this equipment as "critical to safety" and establish periodic testing and documentation to verify desired performance.

The Westinghouse Hanford Company (1994, p. 2-4) and Kudriavtsev (1994, p. 70) indicate problems with the use of valves in series with pressure relief equipment. This is reported to have possibly been a contributing factor in the Russian Tomsk-7 incident and warrants examination for the proposed design. Placing any manual or actuated valve in series with a safety relief device is unacceptable in the chemical processing industry. Furthermore, the aqueous ebulliently cooled design seems to rely on a pressure relief device to initiate the safe mode failure response. Safety relief valves are designed to relieve at a given pressure for a one-time response and a successful re-seating after relief. It is not standard industry practice or RAGAGEP to design an extended and dynamically controlled, ebulliently cooled excursion system to use a standard relief device. The intermittent operation caused by the inherent capacity-pressure drop response (C_v curve) of this type of device could cause premature failure of the valve, piping, or process equipment. It may not be reliable for a second excursion without removal and retesting.

In cases where design is based on a closed (partially vented) system condition and the relieving equipment is expected to provide an exhaust path for ebullient cooling, the process generally requires a secondary and parallel relief equipment for an unanticipated process excursion with the vent-to-mass area ratio similar to primary relief devices. It is not evident whether the offgas exhaust attached to the thermosiphon evaporator has a secondary and parallel relief system for unanticipated process excursions.

A study of approximately 13,000 relief valves from chemical and petrochemical industries indicate that 13 percent opened at more than 110 percent of their set pressure and 3 percent never engaged (Smith, 1995). In addition, relief valves can be fouled with solids and crystallization products that restrict or plug the injection of water in the evaporator. The effectiveness of valves for the proposed aqueous injection system is uncertain.

The proposed safety controls to suppress red oil runaway reaction by isolating steam and activating aqueous injection may not be available and reliable upon demand during the time period when the highly energetic runaway reactions may limit or restrict aqueous injection in the evaporator.

3.3.3 Offgas System

The 20-percent safety margin in the off-gas control system may not be adequate to remove heat via evaporative cooling during a red oil event. During a failure of the process (temperature) control system, the vent size of the thermosiphon evaporator could allow both temperature and pressure to increase steeply in a short time due to exothermic reactions accompanied by a large increase in the volume of reaction products, and therefore increase overall risk.

3.3.4 Use of Diluents

DCS has proposed using saturated noncyclic diluents to minimize the degradation of diluents in radioactive environments. The proposed use of a saturated noncyclic diluent, such as HPT, by DCS is adequate; cyclic diluents usually degrade in radioactive environments and may initiate red oil runaway reactions at a lower temperature. In addition, DCS has proposed to implement diluent washing by the use of either pulsed columns or mixer-settlers to preclude the transfer of bulk organic quantities to heated equipment. However, diluent washing systems were not credited as PSSC. From the information provided by DCS (2001, including change pages), it is not evident whether DCS plans to conduct periodic monitoring for degradation products and assaying prior to introduction into the evaporators.

3.4 Use of RAGAGEP

There are no regulatory standards for handling reactive chemicals. This lack of definitive guidelines is likely to remain for years to come. In October 2005 a large group of academic scholars, government regulators, and industrial leaders (about 200 experts) met at the Mary Kay O'Conner Process Safety Symposium in College Station, Texas, to discuss the potential sharing of reactive chemical data via a National Science Foundation funded database. No consensus could be reached and the proposal was tabled after several hours of heated discussion. The key roadblocks were liability issues and lack of standards in reactive chemicals testing procedures. Another prevailing issue is the accuracy of available data relative to the rapidly progressing instruments and data analysis tools that are being used in recent months and years. Most data are constantly being regenerated with more advanced calorimetry to obtain improved models and guidelines for safe designs and operational practices. It was also noted that many mixtures of interest can accelerate or decelerate to a self-heating rate by several orders of magnitude due to impurity levels in the low parts per million. This phenomenon has been observed on "pure" compounds as well as mixtures, further increasing concern regarding data sharing among companies, agencies, and universities. Both

Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA), however, have adopted RAGAGEP.

RAGAGEP appears in OSHA regulation titled Process Safety Management of Highly Hazardous Chemicals—29 CFR 1910.119. Specifically, it states

1910.119(d)(3)(ii)—The employer shall document that equipment complies with recognized and generally accepted good engineering practices.

RAGAGEP also appears in EPA regulation titled Chemical Accident Prevention Provisions—40 CFR Part 68. Specifically, it states

68.56(d)—The owner or operator shall perform or cause to be performed inspections and tests on process equipment. Inspection and testing procedures shall follow recognized and generally accepted good engineering practices. The frequency of inspections and tests of process equipment shall be consistent with applicable manufacturers recommendations, industry standards or codes, good engineering practices, and prior operating experience.

RAGAGEP has been adopted in voluntary consensus standards such as Responsible Care Process Safety Code by the American Chemistry Council. These regulations and standards provide a RAGAGEP framework. The details are found in consensus standards, recommended practices and guidelines. For example, HARSNET provides guidance for establishing process controls for highly reactive chemical systems.

Since the memorandum of understanding between OSHA and NRC gives authority to NRC to conduct chemical safety evaluations for conditions leading to potential nuclear accidents, the implementation of RAGAGEP for highly reactive chemical systems warrant the same level of attention as NRC guidance. Feedback may be provided by NRC to OSHA, as appropriate.

The OSHA regulation was developed to avoid catastrophic accidents after the Bhopal accident at the Union Carbide facility in India. According to the U.S. Chemical Safety and Hazard Investigation Board (2002), reactive chemical accidents are a major safety problem. However, the report was not able to quantify the extent of the problem because only a limited number of accidents specific to certain chemicals were OSHA-reportable. The report identified 167 reactive chemical accidents in the past 20 years that claimed 108 lives (an average of 5 lives per year).

Selection of maximum operating temperature and vent size for thermosiphon evaporators for acid recovery and oxalic acid destruction are not based on accepted practices currently adopted at the H-Canyon facility at the SRS and recommended by the DNFSB.

3.5 Additional Research

DCS has proposed to conduct additional research on the following.

- (1) Runaway initiation temperature
- (2) Effect of impurities on initiation temperature.

Additional research on runaway initiation temperature is a very broad topic. Details are needed to evaluate whether DCS research plans would provide sufficient insights on red oil runaway reactions. A possible scenario for a red oil runaway reaction includes the contribution of the interfacial reaction between organic and aqueous phases at equal mixing (kinetic energy dissipation) levels encountered in a thermosiphon evaporator. Prevention of organic phases contacting an acid aqueous phase could provide an insufficient safeguard. Furthermore, more testing may be needed to derive the minimum temperature at which self-heating starts. However, DCS has included the presence of organics in the unit operations and therefore the components of the unit operation requires supplementation with mitigation solutions, such as an open system relief path design.

Assuming a perfect research plan, execution, and a resulting perfect data set of red oil thermo kinetics, it is not evident how the new knowledge would be incorporated in to the process design so that it improves the operational safety margin for an evaporator with a closed system relief design that is operating at a design basis temperature of 125 °C [257 °F].

3.6 Backfit Options

The CNWRA preliminary assessment of the PSSC classification shows that a red oil event could be classified as a not-unlikely high-consequence event. Therefore, the PSSC adopted by the DCS for preventing a red oil runaway event for the closed thermosiphon evaporators may not be adequate. In this context, the CNWRA staff examined backfit options following construction authorization. Results are summarized in Table 3-1.

Options 1 to 3 provide effective solutions to avoid extensive retrofit without significant potential construction cost implications.

Review of similar facilities (\$3 billion or more) in the commercial non-nuclear industry indicates no generally accepted rules-of-thumb for defining a costly backfit as a fraction of total plant investment. Industrial investments are made on a risk-reward basis relative to product profits anticipated. Furthermore, it is difficult to find private facilities of this investment scale that are not relatively risk free, from a technology and design basis, through long-term operations and scale-up from smaller facilities over decades of commercial experience. To date, there are no similar examples for NRC licensed facilities under 10 CFR Part 70.

3.7 Summary

There is very limited information in the open literature on the preventive or mitigative solutions that are adopted by other facilities that can be used to review the proposed DCS methodology for preventing red oil runaway reactions. According to a DNFSB report (Conway, 2003), the H-Canyon facility at SRS is designed

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- To control the TBP mass by using a mixture of 7.5 percent TBP organic mixture (DCS plans for 30-percent TBP, which is less conservative compared to the Canyon facility)

Table 3-1. Backfit Options and Potential Cost Implication to Prevent Red Oil Runaway Reactions in Closed Thermosiphon Evaporators. Only Capital Costs Are Considered.

Number	Backfit Option	Potential Construction Cost*/Efficiency Implication
1	Reduce operating and maximum bulk fluid temperature to provide a sufficient safety margin (i.e., below the onset of exothermic reactions plus safety margin).	No substantial cost implication. Significant reduction in process efficiency.
2	Increase the vent size of thermosiphon evaporators to meet open-system requirements.	Cost associated with engineering design change. Marginal reduction in process efficiency.
3	Install secondary and parallel independent pressure relief system to thermosiphon evaporators for unanticipated process excursions exceeding the design temperature. The vent area/organic mass for this relief system should meet open thermosiphon evaporator requirements.	Cost associated with engineering design change, installation of additional equipment (pressure relief and associated control systems). Process efficiency could be maintained.
4	Rigorous control on the amount of organic mass that could enter thermosiphon evaporators.	Cost associated with engineering design changes, installation of monitoring and chemical analyses systems. A mechanism to handle out-of-specification feed stock. Process efficiency could be compromised.
5	Conduct additional research to show that the red oil runaway reaction temperature of 134 °C [273 °F] is conservative. This approach would need to consider that the presence of impurities could further reduce the red oil runaway reaction temperature.	Results unknown. Could provide new insights in understanding red oil runaway reaction.

*Costs were not considered in detail due to the preliminary nature of the information available in the Duke Cogema Stone & Webster Construction Authorization Request. The Center for Nuclear Waste Regulatory Analyses engineering judgement indicates that these costs would not be a substantial component of the total facility costs.

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- For the evaporator to have an over-temperature set point at
- With passive vent size
- For regular inspection of storage tanks for organic layers and skimming of accumulated organic layers—no such inspections are discussed by DCS
- To concentrate dilute solutions to 50 percent nitric acid (DCS plans to concentrate nitric acid to 13.6 N, which is less conservative compared to the Canyon facility)

The proposed DCS design philosophy excludes

- Use of a rupture disk that could provide an additional layer of protection to limit the consequences of runaway reaction leading to an explosion (mitigative)
- Use of pressure control system that may provide an additional indication for runaway reaction (mitigative)
- Use of a larger vent size to limit the over pressurization in the thermosiphon evaporators (preventive)
- Control on organics in the process flowsheet. Inadvertent transfer of organics to concentrated nitric acid solutions at high temperature is considered an expected event (preventive)

The use of a larger vent size for thermosiphon evaporator is not addressed in the design basis/construction. Whereas this is not an expensive backfit, it could reduce the consequences from not unlikely to highly unlikely. The CNWRA review does not indicate any cost prohibitive backfits. However, reliable temperature and pressure controls would help to ensure that the temperature does not exceed decomposition of TBP to butene at 150 °C [302 °F] that could cause detonation.

4 CONCLUSIONS

The CNWRA assessment, based on the review of the PSSC and the proposed preventive and mitigative solutions indicates that red oil runaway reactions could be classified as not-unlikely high-consequence events. The PSSC adopted by the DCS for preventing a runaway red oil event for the closed thermosiphon evaporators may not be adequate. However, review of the potential backfit options indicates that effective solutions can be obtained without extensive retrofit and without significant potential construction cost implications

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APPENDIX A

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APPENDIX B

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HAZARD ANALYSIS SUMMARY BY PROCESS SECTION

This quantitative analysis of each process section is based on the kinetic theory of chemical reactions. The rate of a chemical reaction, such as the hydrolysis of tributyl phosphate, is the first derivative of concentration with respect to time. Therefore, the relative quantity of chemical that is transformed due to reaction is proportional to the product of the rate and residence time. The energy release is proportional to the amount of chemical transformed times the heat of reaction. The rate is calculated from the product of the chemical concentrations, catalyst concentrations, and a kinetically weighted temperature as shown in Table B-1. The kinetically weighted temperature is determined as a product frequency factor and the exponential of the activation energy divided by the universal gas constant, R and the absolute temperature. This product of rate and residence time is proportional to the probability of occurrence or hazard index associated with a given unit operation or section of the process. The higher the hazard index, the higher the probability of a red oil event.

A ranked pictorial representation of the relative likelihood of an auto-thermal event due to the red oil chemistry occurring in a given section of the aqueous polishing process is illustrated in Figure B-1. Figure B-1 is based on the data in Table B-1. It can be seen that this method of analysis is strongly influenced by the temperatures inside a given section of the process. This analysis cannot predict the possibility of a trapped organic phase in a high residence intermediate storage vessel containing high acid concentration. For cases other than this extremely hazardous scenario chemical kinetic theory is reliable indicator of the hazardous potential of a given section of the process relative to other parts of the process. A more detailed application of chemical kinetic theory at the process unit operation level could provide a method to evaluate specific hazards inside each process section. To apply such an analysis, process details at the material balance flowsheet stage of design would be required.

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ATTACHMENT 6 to Panel Report

LIST OF ACRONYMS

ACRS	Advisory Committee on Reactor Safeguards
ALARA	As Low As Reasonable Achievable (used only in strike out area)
CAR	Construction Authorization Request
CFR	Code of Federal Regulations
CNWSRA	The Center for Nuclear Waste Regulatory Analysis
DCS	Duke Cogema Stone & Webster
DNFSB	Defense Nuclear Facility Safety Board
DOE	Department of Energy
DPO	Differing Professional Opinion
EPA	Environmental Protection Agency
FCSS	Fuel Cycle Safety and Safeguards
FSAR	Final Safety Analysis Report
FSER	Final Safety Evaluation Report
HPT	Hydrogenated Propylene Tetramer
ISA	Integrated Safety Analysis
MD	Management Directive
MOX	Mixed Oxide
NMSS	Office of Nuclear Material Safety and Safeguards
NRC	Nuclear Regulatory Commission
OSHA	Occupational Health and Safety Administration
PSSC	Principal Structures, Systems, and Components
RAGAGEP	Routinely Accepted or Generally Accepted Good Engineering Practices
RDSEER	Revised Draft Safety Evaluation Report
SECY	Secretary of the Commission, Office of the (NRC)
SER	Safety Evaluation Report
SNM	Special Nuclear Material
SRP	Standard Review Plan
SRS	Savannah River Site
TBP	Tributylphosphate
TEDE	Total Effective Dose Equivalent