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**21G-03-0059**
**GOV-01-55-04**
**ACF-03-0076**

Please docket 70-143 Thank you!

Director
Office of Nuclear Material Safety and S
U.S. Nuclear Regulatory Commission
Attention: Document Control Desk
Washington, DC 20555

References:
1) Docket No. 70-143; SNM License 124
2) Letter from B.M. Moore to NRC, License Amendment Request to Support the Uranyl Nitrate Building at the BLEU Complex, dated February 28, 2002 (21G-02-0051)
3) Letter from B.M. Moore to NRC, Nuclear Criticality Safety Evaluation for the BLEU Complex Uranyl Nitrate Building, Revision 1, dated February 27, 2003 (21G-03-0058).

**Subject:** **Nuclear Criticality Safety Evaluation for the BLEU Complex Uranyl Nitrate Building, Revision 1 (Non-Proprietary)**

Dear Sir:

Nuclear Fuel Services, Inc. (NFS) hereby submits the subject Nuclear Criticality Safety Evaluation that contains non-proprietary information and should not be withheld from public disclosure. Submittal of this safety basis document supports the referenced licensing action for the Blended Low-Enriched Uranium (BLEU) Project.

If you or your staff have any questions, require additional information, or wish to discuss this, please contact me, or Mr. Rik Droke, Licensing and Compliance Director at (423) 743-1741. Please reference our unique document identification number (21G-03-0059) in any correspondence concerning this letter.

NMSS01

Sincerely,

**NUCLEAR FUEL SERVICES, INC.**

B. Marie Moore
Vice President
Safety and Regulatory

JSK/smd
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B.M Moore to Dir., NMSS
March 3, 2003

21G-03-0059
GOV-01-55-04
ACF-03-0076

**Attachment**

# Nuclear Criticality Safety Evaluation for the BLEU Complex Uranyl Nitrate Building

## Revision 1

*Non-Proprietary Version*

54T-02-0014
NCS-07-02
Revision 1

# Nuclear Criticality Safety Evaluation for the BLEU Complex Uranyl Nitrate Building

Framatome ANP/Nuclear Fuel Services, Inc.

August 2002

Revision 1

**NON-PROPRIETARY VERSION**

# Nuclear Criticality Safety Evaluation for the BLEU Complex Uranyl Nitrate Building

## Revision 1

J. M. Deist — 10/17/02
Criticality Safety Analyst — Date

R. D. Montgomery — 10-17-02
Technical Reviewer — Date

C. J. Yeager — 10/17/02
Process Engineer — Date

C. J. Yeager — 10/17/02
ISA Coordinator — Date

Framatome ANP, Inc. and Nuclear Fuel Services, Inc.

# Table of Contents

## Index of Tables and Figures

**Table 1 List of Acronyms**

| Acronym | Definition |
|---|---|
| BLEU | Blended Low Enriched Uranium |
| CA | Compressed Air |
| CCE | Configuration Controlled Equipment |
| CCS | Central Control System |
| CMF | Common Mode Failure |
| DIW | Deionized Water |
| DP | Differential Pressure |
| FL | Failure Limit |
| FHA | Fire Hazards Analysis |
| FRA-ANP | Framatome ANP, Inc. |
| FRP | Fiberglass Reinforced Plastic |
| HAZOP | Hazard and Operability |
| ID | Inside Diameter |
| IM | Interspersed Moderator |
| IROFS | Item Relied On For Safety |
| ISA | Integrated Safety Analysis |
| LCO | Limiting Condition of Operation |
| NCS | Nuclear Criticality Safety |
| NCSE | Nuclear Criticality Safety Evaluation |
| NFS | Nuclear Fuel Services, Inc. |
| NUN | Natural Uranyl Nitrate |
| OCB | Oxide Conversion Building |
| OD | Outside Diameter |
| PHA | Process Hazards Analysis |
| ROL | Routine Operating Limit |
| SCALE | Standardized Computer Analyses for Licensing Evaluation |
| SL | Safety Limit |
| SNM | Special Nuclear Material |
| SOP | Standard Operating Procedure |
| SRE | Safety Related Equipment |
| SRS | Savannah River Site |
| UN | Uranyl Nitrate |
| UNB | Uranyl Nitrate Building |

## 1.0 Introduction

The purpose of this Nuclear Criticality Safety Evaluation (NCSE) is to provide adequate criticality safety controls that will ensure the safe operation of the Uranyl Nitrate Building (UNB) for receiving and storing uranyl nitrate (UN) enriched to

The UNB is located at the NFS site in Erwin, TN.

This NCSE is applicable to UN solutions processed and stored in the UNB. With its very large UN storage capacity, the UNB approximates an infinite system. **Table 2** lists infinite system maximum $k_{eff}$ (including $2\sigma$) values for various concentrations of UN enriched to .

Criticality safety is demonstrated using a combination of passive engineered design features, active engineered design features, and administrative limits and controls to provide double contingency protection. Very conservative modeling assumptions are used throughout the NCSE. In many cases, more than two controls are present, providing defense in depth.

**Table 2 Summary of Infinite UN System**

| $k_{eff} + 2\sigma$ | ~Concentration (g U/l) |
|---|---|
| | |
| | |
| | |
| | |

**Section 2.0** describes the operation of the UNB. **Section 3.0** presents the hazard identification methodology and results.

**Section 4.0** documents the accident analysis/evaluation performed. In **section 4.0**, potential process upsets that were identified are discussed. Methods and results of neutronics calculations are also documented in this section.

**Section 5.0** presents the analysis assumptions. **Section 6.0** describes the passive and active engineered controls, as well as the administrative limits and controls. **Sections 7.0, 8.0,** and **9.0** summarize the conclusions, area of applicability, and references, respectively.

**Appendix A** provides sample input files for the KENO-V.a and XSDRN calculations performed in support of this report. **Appendix B** contains copies of some references used for this analysis. **Appendix C** contains all supporting calculations and data. **Appendix D** contains the technical review checklist and comments.

## 2.0 Equipment, Process, and Material Descriptions

### *2.1 Equipment Description*

The general arrangement, including elevation views, of the UNB is shown on drawing **ADU-01-701** (see **Appendix B**).

2.1.1 UN Receipt

2.1.2 UN Storage

2.1.3 NUN Storage

The current revision of this NCSE does not allow operation of the NUN equipment. Therefore, all NUN lines are disconnected and capped. Tags on disconnected or capped lines are posted with "Do not remove or reconnect without prior written approval from NCS", or other similar words. This prevents an inadvertent connection or a reconnection during construction of the OCB.

## *2.2 Process Description*

2.2.1 UN Receipt

2.2.2 UN Storage

2.2.3 NUN Storage

As previously discussed, the current revision of this NCSE does not allow operation of the NUN equipment. Therefore, all NUN lines are disconnected and capped. Tags on disconnected or capped lines are posted with "Do not remove or reconnect without prior written approval from NCS", or other similar words. This prevents an inadvertent connection or a reconnection during construction of the OCB.

### *2.3 Material Description*

UN transferred to and stored in the UNB has concentrations between , temperatures between , acid contents between , and is essentially clear and free of suspended solids. UN with these characteristics is compatible with the materials of construction used for handling UN in the UNB ( ). See **section 2.1** for material descriptions of the various tanks in the UNB.

The floor of the UNB is constructed of concrete. The walls and roof of the UNB are metal construction.

## 3.0 Nuclear Criticality Hazard Identification

### *3.1 Hazard Identification Method*

A hazard identification and analysis was performed for the UNB operation. This operation relies heavily on engineered controls to ensure that fissile solutions transferred to the UNB meet safety requirements. The engineered controls are further supported by administrative controls.

Identification of hazards and accident conditions that lead to undesirable consequences was accomplished by conducting a Process Hazards Analysis (PHA). A PHA was conducted for the UNB process system **(Reference 3)** with joint consideration of radiological, criticality, fire, and chemical hazards using the Hazard and Operability (HAZOP) technique as prescribed in **Reference 4**. A qualified team was utilized in the conduct of the PHA. Specifically included in the PHA team meetings were (1) a team leader trained in the methodology being used, (2) a person familiar with the design and operation of the process, and (3) one or more persons familiar with radiological, environmental, fire, and criticality safety.

A Fire Hazards Analysis (FHA) was performed and is documented in **Reference 10**. The use of water for fire fighting (including discharge of the fire sprinklers) will not interfere with the ability to prevent a criticality accident. Even in the unlikely event of a fire that causes a UN spill, addition of water will dilute the UN, moving the system into a safer condition with respect to NCS.

The PHA **(Reference 3)** did not identify any natural phenomena events, e.g. high wind, seismic event, flooding, that would result in a NCS hazard. Neither were any vehicle interaction accidents identified that would result in a NCS hazard. These events may result in radiological and/or environmental concerns. It is left to the Integrated Safety Analysis (ISA) to address these concerns.

### *3.2 Hazard Identification Results*

The events identified in the HAZOP analysis that could yield an accidental criticality as a consequence are summarized by number in **Table 3** and further analyzed in **section 4.1**.

**Table 3 HAZOP Hazard Identification Matrix for UNB**

| Case # & PHA Initiating Event # | Deviation | Cause | Consequence | Comments |
|---|---|---|---|---|
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**Table 3 HAZOP Hazard Identification Matrix for UNB**

| Case # & PHA Initiating Event # | Deviation | Cause | Consequence | Comments |
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**Table 3 HAZOP Hazard Identification Matrix for UNB**

| Case # & PHA Initiating Event # | Deviation | Cause | Consequence | Comments |
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## 4.0 Nuclear Criticality Hazard Evaluation

### *4.1 Contingency Analysis for NCS Hazards*

As discussed above, the HAZOP technique was used to identify process upsets that could potentially lead to a nuclear criticality scenario. These events are further examined here to determine that the double contingency principle is satisfied for credible process upsets. The double contingency principle may be stated as: "*The design of process equipment and systems to incorporate sufficient factors of safety to require at least two unlikely, independent, and concurrent changes in process conditions before a criticality accident is possible.*"

### *4.2 Calculations*

Calculations are provided to demonstrate that the equipment in the UNB can be maintained in a subcritical state during normal operations and should anticipated upsets occur provided that the limits and controls **(section 6.0)** are observed.

#### 4.2.1 Calculational Method

The calculations were performed using the KENO-V.a and XSDRN modules in the Standardized Computer Analyses for Licensing Evaluation (SCALE), Version 4.4a-PC **(Reference 1)**, to calculate the neutron multiplication factors, $k_{eff}$ and $k_{inf}$, respectively. ENDF/B-V 238-group cross sections were used in the evaluation. SCALE 4.4a-PC and associated modules using ENDF/B-V 238-group cross sections were validated on FRA-ANP computer PIN #21487.54 and #21487.62 in **Reference 2.** The calculations in this NCSE are bounded by the **Reference 2** validation report. Based on the results of the validation report, a system is considered subcritical if $k_{eff}+2\sigma$ is less than 0.97. Example input decks are contained in **Appendix A** of this NCSE.

#### 4.2.2 Description of Model

The following three sets of models were prepared and analyzed in this report:

- Infinite UN system
- Infinite UN slab
- UNB interaction model

All models used uranium enriched to 5.0 wt% $^{235}U$ in all tanks, including the NUN tank. While the infinite UN system and infinite UN slab models are self-explanatory, the UNB interaction model requires some discussion.

| Tank # | Diameter (in) | | Height (in) | |
|---|---|---|---|---|
| | Actual | Model | Actual | Model |
| | | | | |
| | | | | |
| | | | | |

A 3-D picture of the interaction model is provided in **Figure 1.**

**Figure 1 UNB Interaction Model**

4.2.3 Results

Infinite UN System

Several calculations were performed with KENO-V.a to create a plot of $k_{eff}+2\sigma$ (approximating $k_{inf}$) vs concentration (g U/l) of UN at . The first set of calculations produced this data for UN with various amounts of acid. **Table 6** through **Table 10** present the results for UN with . This data is shown graphically in **Figure 2**.

Additional calculations were performed to study enrichment effects. These calculations explored the effects of enrichments varying from $^{235}U$ and concentrations of for an infinite UN system. **Table 11** and **Table 12** present the results numerically. This data is shown graphically in **Figure 3**.

In order to determine whether the UNB tanks individually approach an infinite system, the concentration study calculations previously discussed were performed with finite dimensions similar to tanks TK-10 and TK-10U. All of these calculations used UN with . **Table 6, Table 13,** and **Table 14** present the results for UN in an infinite system, TK-10, and TK-10U, respectively. This data is shown graphically in **Figure 4**.

**Figure 2 Infinite UN System with Various Acid Contents (region of interest is expanded)**

**Figure 3 Infinite UN System, , , Various Enrichments**

**Figure 4 Infinite UN System vs UN in TK-10 and TK-10U (region of interest is expanded)**

The results in this subsection show that the system reactivity decreases by approximately with a increase in the UN acid molarity over the range tested ( ). The results also show that the UNB tanks indeed approach an infinite system. Therefore, the infinite system results should be used in determining concentration limits. The concentrations at various infinite system reactivities are provided in **Table 2.**

The enrichment effects sensitivity study shows that an infinite system of UN at achieves criticality at approximately ( yields $k_{eff}$<0.97) and an infinite system of UN at achieves criticality at approximately ( yields $k_{eff}$<0.97).

Infinite UN Slab

Calculations were performed with XSDRN to determine the minimum critical UN slab thickness at various concentrations and reactivities. All of these calculations used UN with and an infinite slab reflected on the left and right with . **Table 15** through **Table 18** present the results for $k_{inf}$ values of 0.89, 0.94, 0.96, and 0.99, respectively. This data is shown graphically in **Figure 5**.

**Figure 5 Infinite UN Slab Thickness**

UNB Interaction Model

Three sets of KENO-V.a calculations were performed with the UNB interaction model in order to investigate the following conditions:

•

All of these calculations have reflector on all sides except the , where is used. A 3-D picture of the interaction model is provided in **Figure 1**.

Normal Conditions:

The results are provided in **Table 19** and presented graphically in **Figure 6**. As expected, this curve is very flat, showing that the system is very well moderated and, again, that the UNB system approaches an infinite UN system. Therefore, no further sensitivity studies involving variations in IM amounts are necessary.

**Figure 6**

Basin Study:

**Figure 7**

**Figure 7**

Stratification Study:

**Figure 8**

4.2.4 Dimensional Limits

The following dimensional limits are required by this NCSE:

### *4.3 Nuclear Criticality Parameter Discussion*

This section provides a discussion of the parameters that can affect criticality safety during normal operations and under upset conditions.

**Mass:**

**Enrichment:**

**Volume:**

**Geometry:**

**Concentration:**

**Density:**

**Moderation:**

**Interaction:**

**Reflection:**

**Neutron Absorption:**

**Homogeneity:**

**Table 5 Summary of Concentration Control Limits**

| Description | Concentration Value | Associated Concentration Value $k_{eff}$ | Applied Measurement Uncertainty[1] | Applied Code Bias $k_{eff}$ | Applied Code Bias Uncertainty $k_{eff}$ | Applied $k_{eff}$ Margin | Corrected or Applied Concentration Value |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
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## 5.0 Analysis Assumptions

The following assumptions are made in this NCSE:

## 6.0 Passive and Active Engineered Controls and Administrative Limits and Controls

Criticality safety of the UNB is provided by a combination of passive engineered controls, active engineered controls, and administrative limits on activities. Each control relied upon in the double contingency analysis is discussed in this section.

### *6.1 Safety Related Equipment (SRE)*

If equipment or a design feature (1) is an active engineered control or (2) can change (degrade) with time, then that equipment or design feature is specified as SRE. As such, it is placed in the SRE program, with specific surveillance, preventative maintenance, and functional testing requirements. The NCSE may

specify SRE requirements for a particular piece of equipment or design feature, or may leave that determination to process engineering.

### *6.2 Configuration Controlled Equipment (CCE)*

Equipment and/or a design feature is defined as CCE if it meets one of the following criteria: (1) it can be demonstrated that the equipment will not change with time, (2) a criticality is not possible even if the equipment does change with time, or (3) the equipment is supplemented by other controls to form one leg of double contingency.

6.2.8 NUN Equipment and Feed Lines

Requirement: All NUN lines SHALL be disconnected and capped. Disconnected or capped lines SHALL be posted with tags reading "Do not remove or reconnect without prior written approval from NCS", or other similar words.

Basis: Use of the NUN equipment is not allowed by this NCSE. This requirement prevents an inadvertent connection during

### *6.3 Administrative Limits and Controls*

This section lists the limits and controls required to provide double contingency protection against an accidental criticality.

## 7.0 Conclusion

A criticality analysis of operations in the UNB of the NFS / FRA-ANP BLEU Complex has been completed. Criticality safety is demonstrated using a combination of passive engineered design features, active engineered design features, and administrative limits and controls to provide double contingency protection. Very conservative modeling assumptions are used throughout the NCSE. In many cases, more than two controls are present, providing defense in depth.

## 8.0 Area of Applicability

The configuration control requirements, as well as limits and operational controls in this NCSE are applicable to all UNB operations. This specifically includes operation of the UNB receipt and download area, the UN receipt tank , the UN storage tanks , UN transfer to the OCB, transfer of NUN from the OCB, the NUN storage tank , and the NUN download area.

## 9.0 References

1) *SCALE (CCC-545): A Modular Code System for Performing Standardized Computer Analyses for Licensing Evaluation*, NUREG/CR-0200, Rev. 6 (ORNL/NUREG/CSD-2/R6), Volumes I, II, and III, March 2000.

2) *Validation of SCALE 4.4a-PC for Homogeneous Uranium Systems with Enrichments between 0.72 and 5.0 wt% $^{235}U$ Using the 238-Group ENDF/B-V Cross Section Library*, .54T-01-0015, Revision 0, Framatome ANP, Inc. and Nuclear Fuel Services, Inc., February 2002.

3) *Hazards Analysis – BLEU Uranyl Nitrate Building (UNB)*, 54T-02-006, NCS-07-02, Framatome ANP, Inc.

4) Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples, Center for Chemical Process Safety of the American Institute of Chemical Engineers, 1992.

5) Certificate of Compliance No. 9291, "Liqui-Rad (LR) Transport Unit Package for the Transportation of Type B Fissile Uranyl Nitrate Solutions, US NRC.

6) R. C. Kispert, J. H. Cavendish, N. R. Leist, and G. P. Miller, "Crystallization Characteristics of Acidic Uranyl Nitrate Solutions," National Lead Company of Ohio, Revised July 9, 1968. A copy of this reference is included in **Appendix B**.

7) K. D. Barlow, "UNH Evaporation Calculations," KDB:01:001, Framatome ANP, Inc., December 3, 2001. A copy of this reference is included in **Appendix B**.

8) C. F. Holman, "Uranyl Nitrate Building (UNB) Solution Freezing Calculation," CFH:02:002, Framatome ANP, Inc., March 5, 2002. A copy of this reference is included in **Appendix B**.

9) ARH-600, Criticality Handbook, Atlantic Richfield Hanford Company.

10) *Fire Hazards Analysis – BLEU Uranyl Nitrate Building (UNB)*, Materials Design Evaluation, August 2002.

11) C. F. Holman, "Uranyl Nitrate Storage Tank Fire Evaporation Calculation," CFH:02:003, Framatome ANP, Inc., August 9, 2002. A copy of this reference is included in **Appendix B**.

# APPENDIX A

## Calculation Input Decks

## APPENDIX B

### Supplied Reference Copies

# CRYSTALLIZATION CHARACTERISTICS OF ACIDIC URANYL NITRATE SOLUTIONS

R. C. KISPERT, J. H. CAVENDISH, N. R. LEIST, and G. P. MILLER
*National Lead Company of Ohio, Cincinnati, Ohio 45239*

KEYWORDS: *uranyl nitrate, solutions, acidity, crystallization, temperature, stability, transport, storage, safety, enrichment, uranium-235, criticality*

Received January 24, 1968
Revised July 9, 1968

*Crystallization temperatures of impure acidic uranyl nitrate solutions have been correlated with the total and free nitrate concentrations. This correlation may be used to predict the solution stability under the varying ambient conditions encountered during transportation and storage and should promote nuclear safety in the handling of uranyl nitrate solutions enriched in $^{235}U$.*

## INTRODUCTION

An important consideration in the safe transportation or storage of solutions of enriched uranium is crystallization, which may cause the uranium concentration to exceed the safe limits. Holding the uranium concentration below a specified level is sometimes the primary means of control in preventing a criticality accident. This safety control can be negated if localized concentration of the uranium occurs in some way, such as by crystallization of a uranium compound from solution. When transporting uranyl solutions, the concentrations of the uranium salt and nitric acid can be adjusted to ensure that, should crystallization occur, the uranium concentration of the solution will never exceed the safe limit. The solution stability required to maintain processing operations and assure safety can be provided by adequate temperature control.

Crystallization temperatures of pure solutions of uranyl nitrate in nitric acid are published,[1-3] but similar data for impure solutions are unavailable. Therefore, the purpose of this work was to develop criteria for predicting the crystallization temperatures of impure uranyl nitrate solutions and techniques for the safe transportation and processing of enriched uranyl nitrate solutions.

## PURE SOLUTIONS

The crystallization behavior[3] of pure solutions is presented in Fig. 1 as a function of the free acid concentration and uranium concentrations. If the same data are plotted as a function of the total and free nitrate concentrations, as in Fig. 2, then at total nitrate concentrations less than the eutectic concentrations the crystallization temperatures decrease with increasing total nitrate concentrations and fall on a common line for all free acid concentrations. In this concentration region, ice is the crystallized species. The eutectic temperature is a function of the free acid concentration and decreases with increasing free

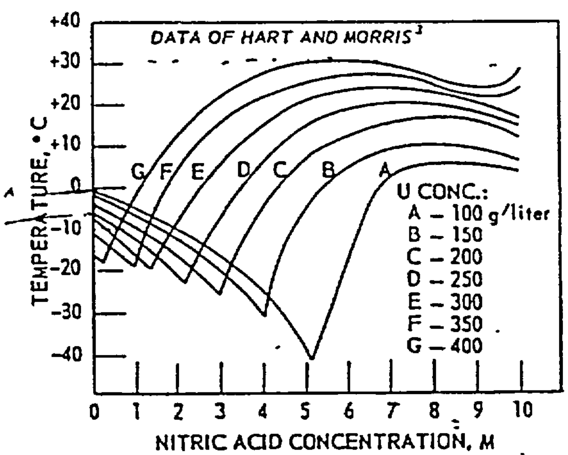


Fig. 1. Crystallization temperatures of pure $UO_2(NO_3)_2$-$HNO_3$ solutions.



Reference 6 Page 1/4

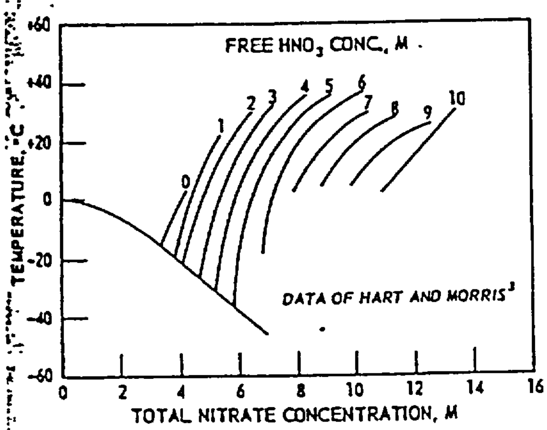


Fig. 2. Crystallization temperatures as a function of solution nitrate concentrations.

acid concentration while the corresponding eutectic concentrations shift toward higher total nitrate concentrations. If the eutectic concentration is exceeded, the crystallization temperature increases rapidly with increased total nitrate concentrations, and a solvated uranyl nitrate crystallizes from the solution. Solution stability in the total nitrate concentration regions to the right of the eutectic concentration in Fig. 2 is controlled by uranyl nitrate solubility.

## IMPURE SOLUTIONS

To test this correlation for impure solutions, 43 acidic uranyl nitrate solutions were prepared, ranging in concentration from 3.7 to 12.4 *M* $NO_3^-$. Each contained one of the following nitrate impurities: iron, aluminum, calcium, copper, chromium, or ammonium. The concentration of the cation impurity ranged from 0.1 to 3.0 *M*.

The crystallization temperature was determined for each solution by observing the arrest in the cooling rate curve of the solution. Samples of each solution were agitated in a liquid-nitrogen-cooled Dewar flask containing a thermocouple. Millivolt readings were recorded on a continuous plotter that graphically presented the cooling curve. Nitrate concentrations were determined by spectrophotometric methods.

Crystallization temperatures were then related to the total and free nitrate concentrations defined below:

$$\text{Total } NO_3^- = [NO_3^-]_{UO_2(NO_3)_2} + [NO_3^-]_{HNO_3} + [NO_3^-]_{impurity} \quad (1)$$

$$\text{Free } NO_3^- = [NO_3^-]_{HNO_3} + [NO_3^-]_{impurity} \quad . \quad (2)$$

Concentration units are expressed in molarity. The terms on the right-hand side of the equations are the nitrate contribution to the solution from the source subscripted. The nitrate contribution from uranyl nitrate is considered to be associated with the uranyl ion and, therefore, is not dissociated (free) nitrate in aqueous solution. Consequently, it is necessary to subtract the $NO_3^-$ complexed with uranyl ion from the total nitrate concentration in order to relate the crystallization temperature to the free nitrate concentration in a manner similar to pure solutions. Experimental data for impure solutions are superimposed on the curves for pure solutions (Fig. 3). Equations (1) and (2) reduce to the parameters for pure solutions since the impurity nitrate would have a zero value in pure solutions and, thus, become compatible with Fig. 2. No effect was observed from the nature of the cation species, since crystallization temperatures correlate with the total and free nitrate concentrations defined above, regardless of which salt was used to prepare the impure solution. Consequently, the crystallization temperature of impure solutions may be predicted from a knowledge of the nitrate concentrations.

## EQUILIBRIUM CONSTANT CORRELATION

An explanation of the correlation can be offered by assuming that the solubility of uranyl nitrate obeys an equilibrium for which a constant may be written and related to the crystallization temperature,

$$K = [UO_2^{++}]\,[NO_3^-] \quad . \quad (3)$$

A van't Hoff correlation between *K* and temperature was attempted and is shown in Fig. 4.

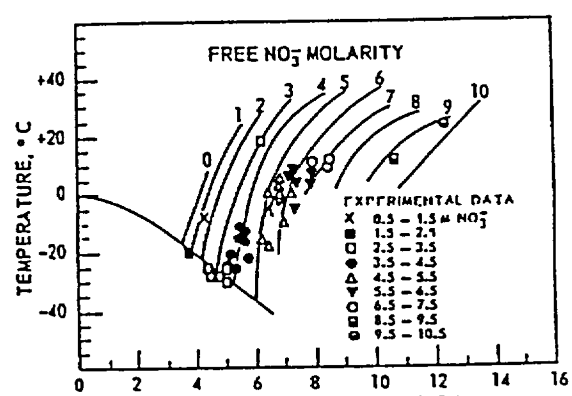


Fig. 3. Crystallization temperatures of impure $UO_2(NO_3)_2$-$HNO_3$ solutions.





Reference 6 Page 2/4

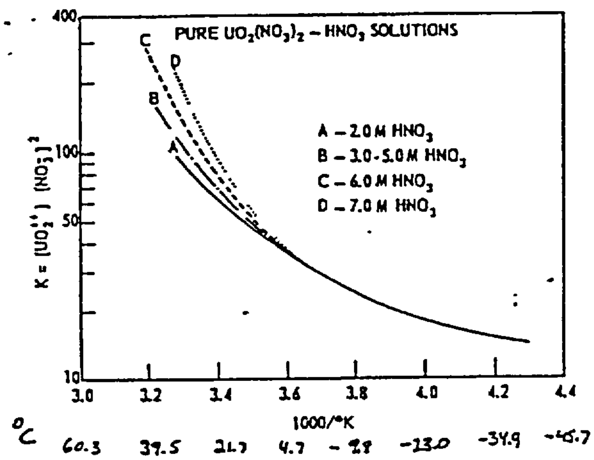


Fig. 4. Variation of equilibrium constant with crystallization temperature.

Although a linear relationship did not result, values of the equilibrium constant were found to be independent of the free acid or total nitrate concentrations in the lower concentration range. Some departure was observed at higher nitrate concentrations and probably resulted from the increasing nonideality of the solution. Perhaps, the association of uranyl nitrate becomes greater at higher overall concentrations. Using activities instead of concentration units may yield a more rigorous relation.

## APPLICATION TO CRITICALITY CONTROL

From this investigation, conditions were determined which would assure safe operation in the transportation and processing of enriched uranyl nitrate solutions. Safe operation requires control of uranium and acid concentrations in transportation and control of temperature in processing operations. Uranium and acid concentrations may be adjusted to keep all solutions in the region of the phase diagram where ice, rather than uranyl nitrate, crystallizes. The eutectic point of the solution must, therefore, remain below the critical uranium concentration. In this region, when the temperature is reduced, ice crystallizes from solution, and the uranium and acid concentrations increase until the eutectic point is reached. At this point the remaining solution will freeze as a mixture of intimately mixed phases with no further change in the effective uranium concentration. Therefore, if all solutions are kept in this phase region, they can freeze solid with no danger of the critical uranium concentration being reached.

From data on the crystallization temperature of pure solutions of uranyl nitrate in nitric acid,[3] a series of curves was drawn showing the crystallization temperature as a function of uranium concentration at different free acid levels. These curves are presented in Fig. 5. Nuclear safety regulations[4] require that the initial concentration of $^{235}U$ in the solutions not exceed the safe concentration of 5 g/liter when safe mass quantities are exceeded. However, an increase to a maximum concentration of 10 g/liter by ice crystallization could be allowed since the minimum critical concentration is 12.1 g $^{235}U$/liter. The safe eutectic point or maximum allowable uranium concentration is considered to be one whose total uranium concentration is less than double the safe uranium concentration for that enrichment. This means that the $^{235}U$ concentration at the eutectic point will be $<10$ g/liter, and the critical concentration of 12.1 g/liter cannot be reached regardless of the temperature.

The method can be illustrated by using an example in conjunction with Fig. 5. Suppose that a solution containing 4.0% $^{235}U$ is to be shipped at a concentration of 125 g U/liter. The maximum allowable uranium concentration at this isotopic level is 250 g U/liter. To prevent the solution concentration from exceeding 250 g U/liter, should crystallization occur, the free acid concentration must be maintained between 3.0 and 4.0 *M* $HNO_3$. This assures that the maximum attainable uranium concentration never exceeds the higher eutectic concentration of 200 g U/liter (point D, Fig. 5). This eutectic is less than the maximum safe concentration of 250 g U/liter. The method can be applied similarly for other isotopic assays.

The establishment of the lower acid limit guarantees that the solution conditions lie in the ice crystallization region of the phase diagram.

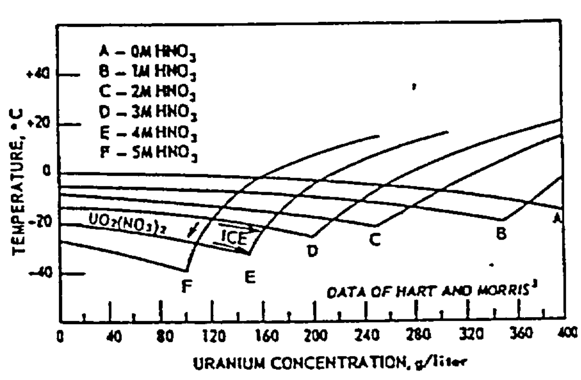


Fig. 5. Crystallization temperature data for criticality control.

However, it is necessary to establish an upper acid limit to avoid the possibility of following an equilibrium curve that would result in the crystallization of uranyl nitrate. In the above example, the use of 5.0 *M* $HNO_3$ would have established the initial conditions on the right-hand side of the eutectic and, therefore, would have resulted in uranyl nitrate crystallization upon cooling.

The utilization of phase diagrams in preventing a criticality accident in the handling of enriched uranium solutions has great application. However, it must be emphasized that a correct interpretation requires a fundamental understanding of the equilibrium behavior. Therefore, persons using this approach must be thoroughly proficient in their knowledge and application of phase equilibria.

## REFERENCES

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2. M. K. HARMON, "Freezing Point Data for UNH-$H_2O$-$HNO_3$ Systems," HW-8309, Hanford Atomic Products Operation (December 17, 1947)

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# APPENDIX C

## Supporting Calculations and Data

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# APPENDIX D

## Technical Review Checklist and Comments

**Technical Review Checklist**

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## Technical Review Comments Regarding Revision 0

**Technical Review Comments Regarding Revision 1**