



UNITED STATES
NUCLEAR REGULATORY COMMISSION

WASHINGTON, D.C. 20555-0001

December 29, 1999

MEMORANDUM TO: Melanie A. Galloway, Acting Chief
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Division of Fuel Cycle Safety
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SUBJECT: DECEMBER 1, 1999 MEETING WITH UNITED STATES ENRICHMENT
CORPORATION (USEC) ON LOSS OF MODERATION CONTROL EVENT

SUMMARY:

On December 1, 1999, the Nuclear Regulatory Commission (NRC) management and staff (Ms. Elizabeth Ten Eyck, Ms. Melanie Galloway, Mr. Yawar Faraz, Mr. Charles Cox, Mr. Jack Davis, Mr. Lawrence Berg, and Dr. Christopher Tripp) from the Division of Fuel Cycle Safety and Safeguards (FCSS) held a public meeting with several representatives of the United States Enrichment Corporation (USEC) to discuss safety concerns raised by a recent event at the Portsmouth Gaseous Diffusion Plant (PORTS). This event, which occurred on September 24, 1999, involved the loss of moderation control in the PORTS side purge cascade piping caused by discovery of an unprecedented compound of uranium following a fire in December 1998. USEC gave a presentation which described the events surrounding the fire and the discovery of the uranium deposit, the controls that existed to prevent criticality, and newly performed analysis that demonstrated the subcriticality of the as-found condition under the worst case conditions. USEC provided most of the information that was requested by NRC in a Request for Additional Information (RAI) dated November 4, 1999. Topics discussed at the meeting involved the safety significance of the initial event and its impact on bounding criticality safety assumptions as well as broader concerns regarding the content and accuracy of criticality safety events reported under NRC Bulletin 91-01. [USEC's written response to NRC's questions was transmitted on December 3, 1999.]

DISCUSSION:

Background

On September 24, 1999, the Portsmouth Gas Diffusion Plant (GDP) discovered an unknown uranium oxychloride hydrate in deposits in the side purge cascade piping of Building X-326. The compound was identified through laboratory analysis as $\text{UO}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, which has a

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stoichiometric H/U = 5. The Safety Analysis Report (SAR) and plant safety analyses (nuclear criticality safety approvals/evaluations; NCSA/Es) assume a maximum H/U of 4 for criticality safety purposes. The existence of compounds which exceed the bounding value challenges a key assumption supporting moderation control in the cascade. This event was reported as a 4-hour Bulletin 91-01 event. This was a 4-hour event because it represented an unanalyzed condition.

USEC claimed in the event report that this compound was formed as a result of the X-326 lube oil fire; NRC staff was not convinced of this because the compound was not predicted. Moreover, USEC claimed that mass control was maintained such that there always remained at least one criticality control to ensure subcriticality. The as-found mass was less than a minimum critical mass for the enrichment (approximately 6wt% ^{235}U), but it is not apparent that more mass could not accumulate or that any positive control over mass had been established. Moreover, most of the equipment associated with the cascade handles a large mass inventory and thus is singly contingent on moderation control.

The safety significance of the as-found condition appeared to be low in that: (1) typical deposits in process equipment are smeared over the inside surfaces of the equipment, rather than in a compact configuration; (2) the deposit mass was approximately 159 g ^{235}U ; and (3) the reported moderation level is significantly less than the most reactive value of H/U. However, NRC still had significant concerns in several areas, including:

- NRC did not have assurance that the worst-case conditions that could have resulted from the accident were adequately subcritical.
- NRC did not have assurance that mass was actually controlled, as reported in the original event report. It was not clear that there remained at least one barrier to an accidental criticality.
- NRC did not have assurance that similar deposits did not exist or could not have formed elsewhere in the cascade, or that similar events in the future were unlikely.
- The event raised questions concerning the content and accuracy of nuclear criticality safety event reporting in general.

Each of these areas is discussed in the meeting summary below.

Evaluation of Event

USEC presented a description of the circumstances surrounding the formation and discovery of the uranium compound. A fire occurred in Cell 25-7-2 of the cascade side purge in Building X-326 on December 9, 1998. The ultimate cause of the fire was presumed to be an exothermic hot metal reaction between the aluminum shell of a compressor and the process gas, as a result of mechanical friction. USEC stated that the interior surfaces of process equipment are typically coated with aluminum fluoride (AlF_3) film to prevent such a reaction, but this protective film can be eroded at excessive temperatures. This exothermic reaction is highly favored at temperatures of several hundred degrees Celsius. The fire led to extensive equipment damage within the cell, causing the cell coolant system to be breached and to dump several thousands of pounds of coolant into the cell. The chemical reaction between the refrigerant and the process gas led to the

formation of uranyl fluoride (UO_2F_2) deposits within the cascade and the formation of several incomplete reaction products in the cooler regions of piping outside the cell, including uranium chloride hydroxide ($\text{UO}_2\text{Cl}(\text{OH})$).

Several factors were identified which were cited by USEC as making a similar occurrence in an on-stream cell unlikely. First, the small inventory of UF_6 in the side purge was responsible for the relatively small accumulation of mass in the deposit, but at the same time permitted the high temperatures that damaged the cooler. Larger on-stream cells typically contain several tons of UF_6 , but this gas inventory functions as a heat reservoir, quenching the reaction heat before it can lead to equipment breaching. USEC stated that this was the first time that they had experienced a coolant breach as the result of a fire. Secondly, the oxychloride compounds are incomplete reaction products that were only formed in the side purge piping outside the cell itself, over a relatively short span of piping where the temperature range was favorable for their formation. The entire inventory of cell coolant was exhausted in the reaction, which was driven to completion to UO_2F_2 in Cell 25-7-2 itself. The equipment where the deposit was discovered consists of 2200 feet of supply and return piping that is a much more favorable geometry for criticality safety. Thirdly, the reaction occurred in a reaction that involved only Freon ($\text{C}_2\text{F}_4\text{Cl}_2$) and UF_6 and therefore did not occur in the presence of water moderator. At the time of formation the deposit would have been un-hydrated.

USEC's evaluation demonstrated that the conditions leading to the formation of the dihydrate compound $\text{UO}_2\text{Cl}(\text{OH}) \cdot 2\text{H}_2\text{O}$ occurred in three stages: (1) a hot metal reaction phase; (2) a cooling off phase during which the reaction products were formed; and (3) a remediation phase during which the equipment was open and hydration was possible.

Safety of As-Found Condition

At the time of the meeting, USEC had characterized all 2200 feet of side purge cascade piping by sectioning the piping into 22-foot units and using non-destructive assay (NDA) methods to determine the total quantity of uranium in the piping. The highest gamma scan reading taken over a 2-foot section was applied to the entire 22-foot unit to give a conservative estimate of the mass. These NDA measurements showed that there was approximately 6000 g ^{235}U deposited in the piping (~60 kgU in the piping and 60 kgU in the cell, at a nominal enrichment of 7wt% ^{235}U). The $\text{UO}_2\text{Cl}(\text{OH}) \cdot 2\text{H}_2\text{O}$ compound was discovered during sampling to determine the chemical form. The deposits consisted primarily of UO_2F_2 but there was a significant amount of several unusual intermediate compounds. $\text{UO}_2\text{Cl}(\text{OH}) \cdot 2\text{H}_2\text{O}$ was the only one of these compounds which exceeded an H/U of 4. This consisted of a black tacky substance which contained an estimated total of 159 g ^{235}U . The compound was confined to units 25-3 and 25-5 near the middle of the side purge piping.

At the time of the meeting, USEC stated they had not fully analyzed the criticality safety effects of this new compound or revised its nuclear criticality safety approvals and evaluations (NCSA/Es) for this operation. USEC stated, however, analysis indicated that this material has a maximum density of ~4 g/cc, while UO_2F_2 has a density of ~5.5 g/cc. USEC stated that preliminary results indicated that the lower density resulted in the new compound being less neutronically reactive than UO_2F_2 , even with a higher H/U ratio. This result, if borne out, would mean that the new reaction products are bounded by the existing analysis. In addition, experiments indicate that this compound is stable against further hydration, and thus H/U = 5 is the maximum that can reasonably be expected to form for this compound without the intrusion of liquid water.

These results, while preliminary, strongly implied that the existing analysis on UO_2F_2 deposits is likely to bound any of the compounds discovered during the side purge cascade remediation. NRC also noted that deposits typically form on the inner surfaces of cascade equipment, and thus are in a much less reactive configuration than the spherical configuration which is used to determine the minimum critical mass. The NRC participants therefore stated that there did not appear to be an immediate safety concern resulting from the discovery of the new compounds, based on this preliminary work presented at the meeting.

NCS Safety Basis

NRC had raised concerns regarding the safety significance of the event as a result of the loss of double contingency, which goes beyond the immediate safety of the as-found deposits. The September 24, 1999, event report stated that this resulted in a loss of moderation control in the cascade, but that mass control was maintained so that only one control relied on for double contingency remained in place. From the way the event report was written, it was not apparent that mass control had been established or maintained during this event. The UF_6 cascade contains several tons of process gas at one time, and criticality safety is based on moderation control alone (singly contingent). The event appeared to invalidate one of the main criticality safety assumptions relied on in establishing moderation control, that of the maximum moderation level that could be achieved in a uranium deposit.

During the December fire, several holes were made in the side purge cascade piping; since the side purge cascade was operating at a compressor high-side pressure of a few psia, reaction products, and possibly some moisture, were pulled into the X-326 unit bypass (side purge cascade supply and return) piping. Immediately after the fire was detected, the side purge cascade was isolated. This stopped the addition of any more moisture needed to fully hydrate the new compounds at that time.

The USEC presentation demonstrated that, because of the event chemistry, the deposits would not have become fully hydrated until the third phase (remediation). During this phase, the equipment was opened to the atmosphere and sections of piping were removed for decontamination. The hydrated compound was only discovered after several large expansion joints were removed from the side purge piping. This activity produced several large openings through which wet air could be introduced into the piping. During these maintenance activities that were part of this third (remediation) phase, the side purge piping was covered by the NCSA PLANT_062. Unlike the cascade operations NCSA, PLANT_062 established controls on both mass and moderation by limiting the affected equipment to less than a safe mass ($\leq 43\%$ of minimum critical mass) and restricting the sources of liquid water. The staff noted that restricting the equipment to less than a safe mass is very conservative, as the minimum critical mass is derived assuming spherical geometry, optimal moderation, and full reflection. USEC stated that in October of 1999 a new NCSA, NCSA_0326_042, was written that established a new safe mass limit for this area. Staff therefore acknowledged that controls were established on mass and thus not all controls relied on for double contingency were lost during this event.

Several NRC concerns remained following the discussion. USEC determined that occurrence of this event did not constitute an Unreviewed Safety Question (USQ) because accidents involving coolant intrusions and exceeding the cascade limiting moderation of $\text{H/U} = 4$ were analyzed in the SAR. Several of the accident scenarios described in the SAR involve exceeding an H/U of 4, such as from the addition of moderator from sprinkler activation. NRC responded that these particular

compounds and this particular mechanism had not been discussed in the SAR or in applicable NCSAs. The SAR typically contains accident analysis information at a very high level and not at the detailed level of the NCSA/Es. NRC management expressed doubts that the fact that the consequences of a particular scenario is bounded by a high-level discussion of some similar accident in the SAR means there is not a USQ. NRC noted that the fact that a new NCSA was issued as a result of this event (NCSA_0326_042) called into question whether the event was bounded by existing accident analysis.

NRC staff also inquired about the worst-case conditions resulting from a similar occurrence in the future, and what other locations in the cascade would be likely areas where a cooler could breach. USEC did not clarify whether it was possible for this to occur in an on-stream cell, or the size of the largest credible deposit in an on-stream cell. However, USEC presented results of criticality calculations that showed that the material is bounded by UO_2F_2 at an H/U of 4, so there was no immediate safety concern.

Event Reporting

NRC management expressed concerns regarding the accuracy and thoroughness of event reports that have been received from the Portsmouth and Paducah plants recently. One of the observed deficiencies in this initial event report was that the safety basis of the affected portion of operations was not clearly defined. NRC could not determine what controls had been established prior to and remained in effect after the event for the side purge cascade piping. This is a serious impediment to the NRC's ability to accurately assess the criticality safety significance of reportable events. Staff also expressed the concern that event reports typically did not have enough information to permit a finding of safety significance, required detailed follow-up, and tended to contain inaccurate information. Staff identified this information as consisting of statements to the effect that specific controls were maintained during the event, even though these were not part of the formally documented safety basis and appeared to be identified after the fact. Staff also identified as a weakness the policy that loss of a criticality control is not significant unless a controlled parameter actually happens to exceed its safety limit.

NRC stated that many of the initial concerns that resulted from the initial event report could have been eliminated with a more thorough and accurate report. USEC acknowledged that the report as delivered could have led to confusion and a misunderstanding of the circumstances surrounding the event.

CONCLUSIONS:

At the conclusion of the meeting, NRC was satisfied that there was not an immediate safety hazard as a result of this event and that the circumstances surrounding the event had been thoroughly analyzed. Information presented at the meeting demonstrated that the as-found deposits were highly subcritical, and the discovered materials appeared to have been bounded by existing analysis. USEC discussed the sequence of events leading to this occurrence, and enumerated several necessary conditions that would have had to occur before formation of this compound was possible: (1) existence of a strong localized heat source such as a hot-metal reaction; (2) a massive coolant breach; (3) the attainment of several hundreds of degrees needed to sustain the chemical reactions without driving it to completion; (4) the lack of an efficient heat removal mechanism; and (5) moisture intrusion sufficient to hydrate the compound. Based on the understanding of the initial event report and the meeting discussions, NRC concluded that these

optimal process conditions appeared at least unlikely, and resulting conditions appeared to have been demonstrated to be adequately subcritical. This was the basis for the preliminary conclusion that there did not appear to be an immediate safety hazard.

NRC stated, however, that there were deficiencies with the content of recent event reports that fall into two broad categories: (1) a lack of sufficient information to permit NRC to make an assessment of the safety significance of the events; and (2) claims that controls remain in place which are not part of the pre-declared and pre-analyzed safety basis and conflict with the underlying NCSA. NRC underscored its conclusion that additional USEC management attention should be given to the thoroughness and accuracy of criticality safety event reports.

Docket: 70-7002

Attachment: USEC Slides



USEC/NRC Meeting Regarding the September 24, 1999 NCS Event Notification

December 1, 1999

Introduction

- On December 9, 1998, an exothermic chemical reaction and fire occurred in Cell 25-7-2
- During remediation, problems have been experienced with reaction/fire compounds
- A loss of moderation event notification was made on September 24, 1999

Presentation Outline

- Background
- Chemistry of Reaction Products
- Basis for Nuclear Criticality Safety
- Interim Actions and Current Status
- Does the Condition Involve a USQ?
- Assurance Facility Condition Is Safe
- Long Term Measures to Resolve Issue

Background

- Exothermic reaction/fire occurred in Cell 25-7-2 on December 9, 1998
- NDA monitoring performed immediately after fire
- Material sampled from January to March to determine recovery options
- Limited equipment removal and additional sampling April to present

Reaction Products Chemistry

- Complex chemistry
- First time exothermic/coolant reaction at PORTS
- Relatively small amounts of UF_6 involved
- Chemistry changed with exposure to atmospheric moisture
- Reaction areas isolated from rest of cascade

Initial Reaction Products

- In cell and unit
 - Formed UF_4 , UO_2 and AlF_3 prior to coolant release
 - Formed uranium chloride and aluminum chloride compounds after coolant release
- In side purge supply and return piping
 - Nothing prior to freon coolant ($\text{C}_2\text{F}_4\text{Cl}_2$) breach
 - Formed uranium chloride, uranium fluoride, aluminum oxide and aluminum chloride

Reaction Products Change

- Initial sampling indicated low H/U ratios
- Equipment removed (elbows & X-joints) to allow sampling exposed deposits to moisture in air and caused reactions
- In September, found compound that had hydrogenous appearance
 - Identified as uranyl chloride hydroxide dihydrate (H/U of 5)
 - Other aluminum chloride compounds identified
- Plant condition within the SAR bounding analyses

Nuclear Criticality Safety

- Small amount of uranium involved
 - NDA showed less than “safe mass” in cell
 - NDA showed no deposits greater than “safe mass” in side purge supply and return piping
 - No credible mechanism for collecting reaction products in one location
 - Equipment isolated from rest of cascade
- Coolant reaction widely dispersed reaction products including uranium

Deposit Moderation

- During and immediately after exothermic reaction (12/98)
 - Deposits essentially unmoderated
 - Water entered cell due to sprinklers and fire-fighting
 - Initial sampling indicated minimal moderation
- Equipment removal and sampling (3/99 to present)
 - Water vapor reacted with reaction products and formed HF, HCl and moderated deposits
 - Formed new compounds, e.g. uranyl chloride hydroxide

NCS Controls

- Cell 25-7-2 storage - NCSA-0326_029
- Maintenance - NCSA-PLANT062
- Side purge supply and return piping - NCSA-0326_042
- Controls based on <safe mass present in equipment; limiting moderation from liquid water

Hydrogenous Compounds Impact

- Hydrogenous compounds identified
 - Uranyl chloride hydroxide dihydrate
 - Aluminum chloride compounds
 - Aluminum oxide compounds
- Compounds above could result in moderation above H/U of 4 by atmospheric moisture

Uranyl Chloride Hydroxide Dihydrate

- Neutronics evaluated for compound $[\text{UO}_2\text{Cl}(\text{OH})\cdot 2\text{H}_2\text{O}]$
 - used density found in literature
 - used only 25% of available chlorine in model
 - evaluated various enrichments to bound situation at hand
- Compound is less neutronically active than uranyl fluoride from 2-40% enrichment
 - non-volatile so no significant release potential

Mechanism for Formation of Compound

- Presence of HCl
- Presence of a UO_2F_2 deposit
- Elevated temperature to convert layered uranyl fluoride structure to salt crystal structure of uranyl chloride
- Absence of significant quantities of aluminum
- Exposure of uranyl chloride to water molecules

Does the Condition Involve a USQ?

- The condition does not involve a USQ
 - SAR described potential release and reaction of coolant during exothermic reaction
 - SAR conclusion was that there would be no significant release of hazardous material
 - SAR conclusion was that it was very unlikely that a critical mass would be formed
- As-found condition is within SAR bounding analyses

December 29, 1999

M. A. Galloway, FSPB

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optimal process conditions appeared at least unlikely, and resulting conditions appeared to have been demonstrated to be adequately subcritical. This was the basis for the preliminary conclusion that there did not appear to be an immediate safety hazard.

NRC stated, however, that there were deficiencies with the content of recent event reports that fall into two broad categories: (1) a lack of sufficient information to permit NRC to make an assessment of the safety significance of the events; and (2) claims that controls remain in place which are not part of the pre-declared and pre-analyzed safety basis and conflict with the underlying NCSA. NRC underscored its conclusion that additional USEC management attention should be given to the thoroughness and accuracy of criticality safety event reports.

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(4) the lack of an efficient heat removal mechanism; and (5) moisture intrusion sufficient to hydrate the compound. Based on the understanding of the initial event report and the meeting discussions, these optimal process conditions appear at least unlikely, and resulting conditions appear to have been demonstrated to be adequately subcritical. This is the basis for the finding that there is no immediate safety hazard.

NRC concludes, however, that there are deficiencies with the content of recent event reports that fall into two broad categories: (1) a lack of sufficient information to permit NRC to make an assessment of the safety significance of the events; and (2) claims that controls remain in place which are not part of the pre-declared and pre-analyzed safety basis and conflict with the underlying NCSA. NRC believes that additional USEC management attention should be given to the thoroughness and accuracy of criticality safety event reports.

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