APPENDIX P

RELATED CHEMICAL SAFETY INITIATIVES AT DOE

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I. The Surplus Facility Inventory and Assessment Project

The Department of Energy's (DOE) change in mission, aging infrastructure, and declining program budgets have resulted in a dramatic increase in the number of surplus facilities (i.e., facilities no longer needed to support operational, programmatic, or departmental missions). The Department responded to this dynamic growth in the inventory of surplus contaminated facilities in 1992 by establishing the Office of Facility Transition and Management (EM-60) within the Office of Environmental Management (EM) and by tasking the new office to manage the acceptance and deactivation of surplus facilities. A number of major facilities were subsequently designated as surplus and transferred to EM-60. These included most facilities at the Rocky Flats Plant, the Plutonium and Uranium Extraction Facility and the Fast Flux Test Facility at the Hanford Site, and the Idaho Chemical Processing Plant at the Idaho National Engineering Laboratory. Currently, two entire sites (the Mound and Pinellas Plants) and a number of select facilities at other sites (Savannah River reactors and Oak Ridge National Laboratory isotope facilities) are being prepared for transfer to EM-60 under memorandums of agreement (MOAs). Although these MOAs provide a vehicle to transfer assets from other program offices to EM, they serve only as "stop-gap" measures until a formal and comprehensive transfer policy and acceptance process are developed.

Paralleling these events was the appointment of a new Secretary of Energy and Assistant Secretary for Environmental Management. Driven by recognition of an aging complex, growing frustrations with cleanup efforts, and an increasing inability to respond to questions from the Office of Management and Budget and the General Accounting Office about the legacy of surplus facilities, Secretary Hazel O'Leary and Assistant Secretary Thomas Grumbly requested an accurate accounting of the number of surplus facilities within the DOE complex. Unfortunately, such an accounting could not be provided. Several factors precluded obtaining a timely and accurate determination of these assets. These factors ranged from the recurring Cold War mentality of placing an asset in "standby" for quick restart to the inability of departmental data systems to provide information needed for planning, budgeting, and managing contaminated surplus assets. A further examination of this growing problem revealed (1) that the determination of what to declare as surplus generally coincides with the DOE budget cycle, creating a situation in which neither the "donor" program nor the "receiving" program has the opportunity to plan and budget adequately for the facility, and (2) that the determination of what to declare as surplus is a dynamic process subject to many internal and external factors, some of which (e.g., Congressional budgets) are not within the program's control. Thus, the ability to provide long-range forecasts of facility surpluses is, at best, limited. The need to address these issues directly, coupled with the inability to respond fully to outside questions, provided the impetus for an initiative aimed at identifying the number of surplus facilities and defining the resources needed to manage them. In response to these needs, the Surplus Facility Inventory and Assessment (SFIA) Project was developed in June 1993.

Overview

The Secretary of Energy formally initiated the SFIA on October 4, 1993, and tasked EM with responsibility for managing the project. (EM-60 was assigned the day-to-day management of the project.) The purpose of the ongoing SFIA effort is to determine the following:

(1) The number of contaminated facilities that are, or will be, designated as surplus before fiscal year (FY) 99;

(2) The condition of surplus facilities (e.g., physical structure and level of chemical and radiological combination) and the associated risks, liabilities, and costs required for adequate surveillance, maintenance, and characterization; and

(3) The priority for transferring these facilities to EM for deactivation, decommissioning, and final disposition.

The SFIA project consists of three phases, each with stated goals that provide the foundation for the next phase. This three-phased approach reflects the input received from the field during the development of the project.

Phase 1, which was completed in January 1994, involved the development of an accurate inventory of all DOE facilities, with special emphasis on process-contaminated facilities and their associated ancillary units. With the exception of the Power Marketing Administrations, Naval Reactors, and selected structures considered to have a low probability of being contaminated, all DOE facilities were included in Phase 1 of the effort.

Phase 2, which was completed in April 1994, involved identified surplus assets and included determining and assessing the condition of physical structures and systems contamination (radiological and chemical) status; waste and chemical inventory; the chemical and radiological contents of storage tanks; safeguards and security requirements; immediate and serious problems or conditions with respect to workers, the public, the environment, and the structure itself; the order and priority for transfer based on a threat-based ranking system; and first-order cost estimates for managing high-ranking facilities designed for transfer to EM in FY 96.

Phase 3, which is scheduled for completion by December 1994, involves developing cost estimates to support owner program and/or landlord budgets, including costs for managing, maintaining, and characterizing surplus contaminated facilities that will not be transferred to EM during FY 96.

II. The U.S. Department of Energy Lessons Learned Program for Preventing Accidents Similar to the Tomsk-7 April 6, 1993, Incident

Background

On April 6, 1993, a sequence of events occurred at the Tomsk-7 nuclear fuel reprocessing plant in Siberia, Russia, that caused substantial physical damage to the facility. A runaway

exothermic chemical reaction occurred in a large process vessel containing a concentrated solution of uranyl nitrate, nitric acid, plutonium nitrate, residual fission products (totaling about 560 curies), and amounts of organic constituents derived from the solvent extraction process. The reaction produced large amounts of flammable organic and inorganic gases and steam, which pressurized and breached the vessel and dislodged the concrete cell cover. Based on the available evidence, ignition then occurred in the area immediately above the cell. The resulting explosion caused substantial damage to the crane bay area, nonreinforced masonry wall, and the roof and its internal components. The accident contaminated an area of about 123 square kilometers with about 40 curies of radioactive material, including 30 grams of plutonium.

This accident has been attributed to a chemical reaction between degraded organic material and concentrated nitric acid, which had been added to adjust the pH of the solution for subsequent purification by solvent extraction. The degraded organic material was the result of an accumulation of process residual chemicals that had been allowed to age over a period of at least 6 months. The accident was attributed to several operator errors, the most serious of which was the failure to operate the mixing (gas-sparging) system as required by procedure.

Exothermic tri-n-butyl phosphate (TBP)-nitrate reactions are frequently referred to as "red oil" reactions. Red oil generally refers to a mixture that is reddish or orange in color and contains TBP, its complexes with uranyl nitrate and nitric acid, and its degradation products (e.g., dibutyl phosphate and various nitrated cyclic hydrocarbons). Red oil can be formed as a result of the prolonged contact at elevated temperatures of uranyl nitrate and nitric acid with a solution of TBP in an organic hydrocarbon diluent, such as that used in solvent extraction operations. It should be noted that the presence of the colored compound is not necessary for exothermic reactions to occur in TBP-nitrate mixtures.

Three events similar to the incident at Tomsk-7 had previously occurred at DOE facilities (i.e., at Savannah River Site on January 12, 1953; Hanford Site in July 1953; and Savannah River Site on February 12, 1975). However, all three DOE facility events occurred when a heavy metal nitrate solution containing, or in contact with, TBP was heated in excess of 130 °C. The event at Tomsk-7 differed from the U.S. events in that no external heat was added to the Tomsk-7 tank. The primary control present to prevent red oil reactions in DOE facilities has been to limit the temperature of the solution to less than 130 °C. There were no external heat sources at Tomsk-7, but there were multiple sources of "self-heating." The hazards associated with mixing organic compounds and oxidizing agents has been an issue in processing nuclear fuels. The Tomsk-7 accident has emphasized the need to investigate the potential for self-heating in such mixtures and the potential consequences from such reactions. To this end, the Department initiated a proactive effort to ensure that similar conditions do not exist for DOE processing vessels.

Overview

The DOE Tomsk-7 Lessons Learned Program was initially tasked with accomplishing the following tasks:

(1) Survey and develop an inventory of potentially hazardous tanks and equipment.

(2) Develop a consensus of understanding concerning the Tomsk-7 incident.

(3) Perform analytical mechanism and modeling studies.

(4) Conduct site-specific reviews and prepare site reports for each of the following:

- Savannah River Site,
- Idaho Chemical Processing Plant,
- Westinghouse Hanford Company,
- Fernald Environmental Management Project, and
- Oak Ridge.

(5) Prepare final summary reports.

Led by the Office of Defense Programs, a core Tomsk-7 team and multidisciplinary site-specific teams, including technical experts from DOE and contractor organizations, were formed to review DOE sites for hazards associated with organic-oxidizer mixtures. The review was conducted to determine the potential for red oil reactions in DOE operations and to evaluate the controls in place to minimize the chance of potential accidents. The review scope included assessing the adequacy of safety analysis reports (SARs), technical safety requirements, procedures, employee training, process design, safety systems designs, instrumentation, and management systems. When safety deficiencies were noted, the scope of the review was expanded horizontally to include other safety-related concerns.

The initial focus of the Tomsk-7 Lessons Learned Program (referred to as Tomsk I) was on those process areas deemed to exhibit the highest vulnerability for such exothermic chemical reactions. The current understanding of the Tomsk-7 event stresses the probable nitration and energetic decomposition of a substantial quantity of organic liquids, particularly tri-n-butyl phosphate (TBP) and its diluent, through contact with concentrated nitric acid and metal nitrates. This scenario resulted in self-heating, which was exacerbated by the restricted means of heat dissipation due to the lack of mixing with the large amount of liquid in the same vessel. Based on these circumstances, the DOE Lessons Learned Program concentrated on process and interim storage operations involving inventories of organic diluents, TBP, nitric acid, and nitrates with a minimum threshold of 25 liters of material (i.e., those expected for pilot and full-scale operations as opposed to laboratory bench-scale activities). The 25-liter threshold was consistent with the philosophy that the Occupational Safety and Health Administration and Environmental Protection Agency had adopted to designate threshold quantities for toxic and flammable substances.

Conclusions and Followup Activities

A team of DOE technical experts visited the Tomsk-7 facility for a firsthand review of post-accident conditions. This information was documented and has been used to support the DOE Lessons Learned Program.

Five DOE facilities were visited, and all were found to be in a safe condition with no red oil event imminent. However, vulnerabilities were identified that lessen the apparent safety margin. Two examples of these generic vulnerabilities are as follows:

(1) Self-heating reactions (as occurred at Tomsk) of nitrate-organic mixtures are not recognized in SARs, operator training, or emergency procedures. As a result, operating procedures generally are not based on such reactions.

(2) The significance of TBP degradation during long-term storage has not been taken into account during safety evaluations.

The results of these site-specific reviews have been completed and documented and should be referenced for more specific information.

Senator John Glenn (D-Ohio), Chairman of the Governmental Affairs Committee, followed the DOE's Tomsk-7 review process closely. Senator Glenn commended the Department for its review effort but recommended that the scope of the review be extended to include waste storage tanks and their associated vapor spaces. Consequently, the scope of the DOE Lessons Learned Program was expanded to include (but was not limited to) other processes and operations having the potential for combustion, self-heating, and/or other exothermic reactions due to nitrate-organic mixtures.

Based on lessons learned from the Tomsk I review of DOE facilities, a self-assessment questionnaire was transmitted through the operations offices to the sites for contractor response. This questionnaire forms the basis of the Tomsk II review. Because of the number of facilities involved (33 DOE facilities and more than 300 different reporting locations), followup visits were scheduled only when responses to the questionnaire indicated a need for more indepth information. Evaluation of these responses and preparation of the report are being performed concurrenty with the Chemical Safety Vulnerability Review, and conclusions of the Tomsk II review are not yet available. Preliminary data suggest the following conclusions:

(1) No significant generic vulnerabilities for nitrate-organic chemical reactions have been identified.

(2) No systematic design defects or significant processing equipment deficiencies were noted.

(3) Well-characterized plans are in place to monitor or remediate the flammability and other reaction hazards for waste storage tanks.

(4) Ion-exchange resins exposed to nitrate media are being handled properly and, where possible, are being removed from nonoperating process systems and scheduled for disposal.

(5) Stored materials are segregated according to chemical compatibility and are separated with physical barriers.

The Tomsk II report is expected to include chemical holdings tabulated by facility for organics and nitrates. Additional information will be provided on how these chemicals are segregated and on the potential for adverse reactions.