UNITED STATES
NUCLEAR REGULATORY COMMISSION
OFFICE OF NUCLEAR MATERIAL SAFETY AND SAFEGUARDS
WASHINGTON, D.C. 20555

January 29, 1999

NRC INFORMATION NOTICE 99-03: EXOTHERMIC REACTIONS INVOLVING DRIED URANIUM OXIDE POWDER (YELLOWCAKE)

Addressees:

All operating uranium recovery facilities that produce uranium oxide powder (U_3O_8)(yellowcake).

Purpose:

The U.S. Nuclear Regulatory Commission (NRC) is issuing this information notice (IN) to alert licensees to recent incidents involving strong exothermic reactions that occurred during the packaging of low-temperature or vacuum-dried U_3O_8 hydrogen peroxide precipitated (yellowcake) powder. It is expected that recipients will review this information for applicability to their licensed activities and consider actions, as appropriate, to avoid similar problems. However, suggestions contained in this IN are not NRC requirements; therefore no specific action nor written response is required.

Description of Circumstances:

On four separate occasions involving different licensees, dry U_3O_8 hydrogen peroxide precipitated (yellowcake) powder, packaged in 208.2 liter (55 gallon) drums, was observed to have undergone strong exothermic reactions after the drying and packaging process. These scenarios can be placed into two categories: 1) generation of oxygen as a byproduct of the production process; and 2) hydrocarbon contaminants reacting with U_3O_8 hydrogen peroxide precipitated (yellowcake) product. The incidents date as far back as 1984 and as recently as July 1998.

Category 1: On two separate occasions, licensees experienced expansion of the sealed drums from generation of oxygen from the decay of hydrogen peroxide. In the production process, hydrogen peroxide is used to precipitate uranium in the form of uranium oxide (U_xO_x). This precipitate is then pressed through a filter, dried in an oven and packaged in drums for shipment. Even though the dryer temperatures reached 537.7° C (1000°F), converting the precipitate to uranate peroxide ($UO_4 \cdot 2H_2O$), sufficient hydrogen peroxide either remained in the product or was generated to develop oxygen pressure by the following reactions:

$$UO_4 + 4H_2O \rightarrow UO_3 + H_2O_2 \uparrow + 3H_2O \uparrow$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$$

The production of gases was sufficient to bulge the lids and sides of the drums, as well as cause a pressure excursion, when a lid was removed, sufficient to eject about one-fourth of the drummed U_3O_8 (yellowcake) 90.7 kilograms (~200 pounds) onto workers and through isolation doors.

Category 2: On two separate occasions, licensees experienced a violent exothermic reaction when hydrocarbon contaminants were mixed with U_3O_8 hydrogen peroxide precipitated (yellowcake) product. At one facility, a leaky flange in a bag filter allowed lubricating oil to leak into the production process, and a deformed tank paddle allowed oil seepage into the mixing tank. At another facility, oils from various process stages were introduced into the sump system and eventually reintroduced into the production line. Both cases yielded an energetic exothermic reaction. With one barrel, the lid had been melted onto the rim in one spot, and another reached a temperature of 648.9°C (1200°F) within the drum. Subsequent examination of the contents revealed several discolored layers, indicating extreme oxidation of product powder in various stages.

Discussion

Category 1: Analyses of the incidents estimated 103.4 kilopascal (15-pounds-per-square-inch) pressure on the lids. Drum pressure began to rise most rapidly in the first hour, but peaked at 3-4 hours. Pressure began to subside at 5 hours. Other drums showed bulges and deformities, but excess gases had bled off. Analysis of the trapped gases yielded 62 percent oxygen, further indicating an oxygen generation from the decay of hydrogen peroxide. Although no workers were injured, several received uptakes of uranium even though respiratory protection was used.

The oxygen generation incidents were isolated incidents that originated with the use of newer drums or other modifications of equipment which allowed excessive pressures. For one licensee, the incident was a result of using newer drums with airtight seals. Older drums had less efficient seals that allowed pressure to escape as it was generated. Both licensees instituted corrective actions consisting mainly of leaving the lids off the drums for a minimum of 3 hours after filling. Corrective actions appear to have been sufficient to prevent future incidents.

Category 2: Since uranium is a pyrophoric metal, especially in fines or powder form, any contaminant in contact with yellowcake powder can be hazardous. Hydrocarbons such as lubricating oils and grease are very likely to cause an unstable condition in the packed yellowcake powder.

In one incident, a leaky flange on a bag filter allowed lubricating oil to leak into and mix with the yellowcake powder in a dryer tank. Once the exothermic reaction began, temperatures rose sufficiently to turn residual water to steam, covering the room with yellowcake powder. The leak was found and repaired, but the room had to be decontaminated. As the next batch of yellowcake was processed, a severely bent paddle inside the mixing tank allowed further oil to again mix into the yellowcake. After the product was packaged, temperatures again rose inside the drum to produce sufficient steam pressure to blow the lid off. The licensee then found and corrected the bent paddle. Corrective actions included installation of oil pressure relief valves and a hot oil boiler cutoff with a temperature controller.

In a recent incident, a licensee had routinely washed equipment contaminants into a dryer room sump. This contained not only uranium contamination, but exposed oils and grease from equipment maintenance and dryer heating oils from spills and leaks. The sump contents were transferred to a holding tank, where the yellowcake and contaminants settled to the bottom.

When the system was cleaned, the heel from this tank was put into a thickening tank to recover any trapped product. The process, however, did not remove the contaminants. Yellowcake tended to agglutinate onto the hydrocarbons, preventing them from being surface-skimmed, and final dryer temperatures were not sufficient to drive off the hydrocarbons. When the contaminated yellowcake was packaged into drums, the residual heat from dryer operations initiated an exothermic oxidation reaction. Since yellowcake is relatively dense, it acted as an insulator, retaining reaction energy that further increased the rate of reaction. Seven drums of product reacted with increased temperatures and oxidation of material. Corrective actions included installation of oil drip pans for collecting all possible oil/grease leaks, and sending the oil-yellowcake contaminants as waste rather than attempting to recover product through the system.

This IN requires no specific action nor written response. If you have any questions about the information in this notice, please contact the technical contacts listed below, or the appropriate NRC office.

Joseph J. Holonich for

John T. Greeves, Director
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99-01	Deterioration of High-Efficiency Particulate Air Filters in a Pressurized Water Reactor Containment Fan Cooler Unit	1/20/99	All holders of licences for nuclear power, research and test reactors; and fuel cycle facilities.
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98-30	Effect of the Year 2000 Computer Problem on NRC Licensees and Certificate Holders	8/12/98	All material and fuel cycle licensees and certificate holders
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98-17	Federal Bureau of Investigations (FBI) Awareness of National Security Issues and Responses (ANSIR) Program	5/7/98	All U.S. Nuclear Regulatory Commission fuel cycle and power and non-power reactor licensees

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98-45	Cavitation Erosion of Letdown Line Orifices Resulstin in Fatigue Cracking of Pipe Welds	12/15/98	All holders of operating licenses for nuclear power reactors, except those that have permanently ceased operations and have certified that fuel has been permanently removed from the reactor.
98-44	Ten-year Inservice Inspection (ISI) Program Update for Licensees that Intend to Implement Risk-Informed ISI of Piping	12/10/98	All holder of operating licenses for nuclear power reactors, except those that have permanently ceased operations and have certified that fuel has been permanently removed from the reactor
98-43	Leaks in the Emergency Diesel Generator Lubricating Oil and Jacket Cooling Water Piping	12/04/98	All holder of operating licenses for nuclear power reactors, except those licensees that have permanently ceased operations and have certified that fuel has been permanently removed from the reactor vessel

OL = Operating License
CP = Construction Permit

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