#### U.S. NUCLEAR REGULATORY COMMISSION

#### REGION III

Report %o. 40-3392/90004

Dock at No. 40-3392

License No. SUB-526

Licansee: Allied-Signal, Inc.

P.O. Box 430

Metropolis, IL 62960

Facility Name: Metropolis Works

Inspection At: Metropolis, Illinois

Inspection Conducted:

Inspectors: G. M. France, III

C. H. Robinson

D. J. Sreniawski, Project Director Fuels Facilities and Contaminated Reviewed By:

Sites

Approved By:

Bruce S. Mallett, Ph.D., Chief

Nuclear Materials Safety Branch

07/13/90

Inspection Summary

Inspection on June 18-20, 1990 (Report No. 40-3392/90004(DRSS)

Areas Inspected: Special safety inspection including: the radiological protection (IP83822) and operations review (IP88020) of the circumstances that led to an unplanned release and the safety significance of the incident. Results: cight concerns for immediate corrective action and one concern for a commitment to implement as a long range corrective action were identified. One violation (failure to instruct a worker prior to entering a restricted area) was identified.

#### DETAILS

### 1. Persons Contacted

W. M. Davis, Technical Supervisor (Analytical)

\*P. G. Gasperini, Manager, Plant Production

\*J. E. Honey, Manager, Regulatory Affairs

M. D. Kosmider, Plant Manager

A. W. Long, Shift Foreman

\*H. C. Roberts, Supervisor, Health Physics

The principle distillation operators; one contractor employee and other Allied-Signal staff members involved with this event were also interviewed.

#### NMSS Representatives

C. H. Robinson, NMSS Project Engineer

#### Normal Operations

Natural uranium ores are received from uranium mining and milling facilities as uranium concentrates. At Metropolis Works Facility, the uranium concentrates are converted to uranium hexafluoride (UF $_6$ ) and stored in 2.5 ton, 10-ton and 14-ton cylinders. After the UF $_6$  conversion is completed, the material is exported or shipped to DOE contractors for enrichment for reactor fuel fabrication.

### a. Uranium Ore Conversion to Uranium Hexafluoride

Uranium ore concentrates are converted first to uranium dioxide  $(\text{UF}_2)$  then to uranium tetrafluoride  $(\text{UF}_4)$  and eventually to  $\text{UF}_6$ .  $\text{UF}_6$  is formed from the reaction of  $\text{UF}_4$  and elemental fluorine  $(\text{F}_2)$  in the fluorination process. In normal operations, cold traps are used to collect (freeze out) UF $_6$  formed during fluorination. Cold traps are later heated to transfer (via liquid dump) the UF $_6$  to still feed tanks (SFTs) for subsequent feed to a distillation system which purifies the UF $_6$ . The heating and cooling in the cold traps is provided by circulating an ethylene glycol and water solution through tubes inside the cold trap in a heat exchanger type operation. From distillation the UF $_6$  is collected in product cylinders.

# b. Product Sampling

Each cylinder of UF $_6$  is sampled to assure that the purity of UF $_6$  is within the specified range. A sample from the cylinder is taken after the cylinder is heated 5-6 hours in a steam chest (212°F) to achieve a homogenous state of liquid UF $_6$ .

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There are four product cylinder fill-stations. Each station is equipped with a steam chest and two identical sample lines (No. 1 and No. 2). A product cylinder filled at anyone of the four fill-stations can be sampled for purity by connecting a transfer line (pigtail) from the cylinder to either of the sample lines. Both sample lines are independently traversed from the fill-stations to the sampling unit. Similar to the product fill-line each sample line is heat traced with ethylene glycol. A vacuum gauge located at the sampling unit is used to determine if the sample line is under a vacuum through to the cylinder. The licensee noted that the chemical/physical properties of UF6 are such that either moist air and/or a cold spot (temperature less than 147°F) could cause hydrolysis of the UF6 to form UO2F2-HF and solidify within the line. Either condition (UO2F2 or solid UF6) could cause a blockage in the line and give an indication on the vacuum gauge that the line is evacuated from the sampling unit to the cylinder. Under normal conditions the system is purged with nitrogen to test for leaks. Afterwards the system is evacuated prior to transferring UF6 from the cylinder to the sampling unit.

## Description of the Event

At approximately 11:45 a.m. on Monday, June 18, 1990, the licensee notified Region III that UF6 had been accidentally released from the Feeds Material Building (FMB) while distillation operators were attempting to dislodge a restriction in the sample line caused by solidified UF6/U0 $_2$ F2 in the No. 1 sample line. The U0 $_2$ F $_2$ /HF plume (formed from the reaction of UF6 and moisture in the air) was visible outside the FMB, but did not appear to go offsite. The licensee indicated that no assistance was required from offsite agencies to protect members of the public. That concern, coupled with the observation that the plume did not travel of site, allowed the licensee to classify the release as an "alert." According to the licensee's Radiological Contingency Plan, Appendix A, page 3-4, a release that travels offsite (requiring assistance to protect members of the public) is classified as a "site area emergency." The second release that occurred around 1:00 p.m. was apparently confined to the FMB.

The following is the sequence of events as determined by the inspector. On June 18, 1990, during the 07:00 a.m.-3:00 p.m. shift a distillation operator and a shift breaker attempted to transfer liquid UF6. Normally, an aliquot of liquid UF6 product is collected in a small sample container and analyzed for purity. However, in this instance, the vacuum transfer of UF6 could not occur, because the sample line was blocked. Although the line was heat traced with ethylene glycol, it was apparently restricted with solid UF6/U02F2. The operators made several attempts to dislodge the restriction. An operator closed the block valve on the No. 1 sample line and maintained a vacuum between the valve and the sampling unit (see Attachment, Figure 1). The sampling pigtail (connection between the cylinder and the sample line) was disconnected leaving a transfer line of 7 feet between the block valve and the sampling pigtail. A rubber vacuum

line (wand) that transfers UF6 to a dust collector was placed at the opening to contain any UF6 emissions. The operators observed small bursts of UF6/UO2F2 exiting the line indicating that the blockage was in the 7 foot section of the sample line between the block valve and the pigtail connection. Finally the UF, blockage broke free (due to the action of heat and vacuum) and emissions of UF6 exceeded the trapping capacity of the wand. Hence, a release of  $UF_6/UO_2F_2$ -HF was evident. This forced the operators to close-off the line (reconnect the pigtail), evacuate the area, and notify the control room to sound the evacuation siren. The incident (an unplanned release of  $UF_6$ ) occurred over a period of about 10 minutes between 10:40 and 10:50 a.m. The release occurred while the building exhaust fan was running and the cylinder bay access door was open. The shift foreman indicated that the emissions were such that the UF6/UO2F2-HF plume was withdrawn from the building through the exhaust fan (mounted on a vertical side wall) and not the open bay door. Workers located outside of the building thought that the plume exited the bay door. Apparently, the plume was drawn through the exhaust fan and directed to the bay door outside the building by an 8 m.p.h. (NNE) wind. The Health Physics Supervisor was in his office at the time the alarm sounded. His path to the FMB should have brought him in midst of the plume. However, the plume had dissipated by the time he approached the FMB. Indications are that the plume swirled around the building and within minutes dissipated prior to reaching the boundary fence.

During the course of the release the operators were wearing half-face masks. In accordance with the Radiological Contingency flan a response team (organized for re-entry) was fitted with SCBA respiratory gear and rubber suits (anti-corrosive to HF vapors) and re-entered the plant. They proceeded to use the engineering supply of  $\rm CO_2$  to cool and solidify any UF $_3/\rm UO_2F_2$  remaining in the line. The UO $_2\rm F_2/\rm UF_6$  trapped in the pigtail and the sample line was now solidified. The pigtail was immersed in water where residual UO $_2\rm F_2$  was dissolved. With the blockage mostly removed during the release, the sample line was capped and evacuated.

At 1:00 p.m., the production and/or maintenance crew checked the sampling line to include the condition of the pipe threads used for connections prior to sampling a cylinder at the No. 4 fill-station. No. 1 sample line was opened and a surge of UF6 was again released into the room. Apparently, the sample line had UF6/U02F2 trapped between the block valve and the end of the line where the pigtail is connected. The line was recapped and the workers evacuated the area. During an interview with the shift-breaker it was indicated that this second evacuation was probably not necessary. The shift-breaker indicated that the sudden surge of UF6 discharging from the line appeared pressurized to the point of dislodging the connecting cap from his hand. Considering both releases, the licensee estimated that less than 100 grams of UF6 was released.

# 4. Conclusion

The inspector determined the adequacy of the licensee's operation, management and equipment response after review of the sequence of events, interviews of plant personnel and observation of system components.

#### a. Cause of Event

The release of UF $_6$  to the surrounding environment occurred while the operators were trying to dislodge solidified UF $_6/\text{UO}_2\text{F}_2$  from the No. 1 sample line. The blockage in the line probably occurred from the reaction of air and moisture with UF $_6$  and or perhaps a cold spot in the sample line. The inspector was unable to discern a precise cause of the blockage. However, the following conditions discovered when the licensee was cleaning out the sampling system probably contributed to the release:

- The No. 1 sample line at the No. 1 product fill-station had not been used in 6 weeks. Residual UF<sub>6</sub> probably coated the line between the sample line block valve and the pigtail connection (7 foot line). This is plausible since the block valve was found to be leaking. A redundant seal in the valve (by design) prevented the leakage of UF<sub>6</sub> to the atmosphere. When liquid UF<sub>6</sub> is admitted to the sample line from a cylinder located in either one of the four product filling stations, it is possible that liquid UF<sub>6</sub> makes contact with the four block valves located in the No. 1 sample line. Under these conditions UF<sub>6</sub> seepage could occur between a leaking valve and the capped end of the line (7 foot length of line where the pigtail is connected). If cold spots were present some f eeze out of UF<sub>6</sub> in the line would also occur.
- A pin hole leak was discovered with steam pressurization in the No. 1 sample line at the No. 2 fill station, although no cylinders at the No. 2 station were sampled. This hole could allow the transfer of moist air into the sample line.
- The block valve in the No. 1 sample line at the No. 3 fill station was leaking (bleeding through).
- The block valve in the No. 1 sample line at the No. 4 fill station was discovered to be slightly open. This might have accounted for a build up of  $UF_6/UO_2F_2$  between the blocked valve and the capped end of the line (hence, contributing to the second release).
- Moisture could have been present in the sample pigtails. UF<sub>6</sub> readily reacts with moisture to form  $\mathrm{UO}_2\mathrm{F}_2$ . Solid  $\mathrm{UO}_2\mathrm{F}_2$  has a consistency similar to that of cement.
- The pressure in the heat trace line (heated ethylene glycol) was about 20 to 25 pounds. This may have been an indication that the temperature was less than the optimum operating temperature of 200°F. After the heat trace line was flushed (similar to flushing an automobile radiator) to remove solid debris, the on-line pressure of the ethylene glycol returned to 40 pounds (best operating range 40-45 lbs).
- The sampling line was subjected to air, moisture, and possibly a lower temperature (cold spot in the line) all of which can cause a blockage of UF<sub>6</sub> or UO<sub>2</sub>F<sub>2</sub> in the line.

### b. Damage to the Plant

The licensee has not discovered any damage to process equipment as a result of the incident. The leaking block values are designed to seal metal to metal and can be reground for a leak tight seal. All block valves in the sample line were inspected and replaced with repaired or new seals if necessary, and tested before return to service. The licensee determined that valve fatigue occurred over a period of months and was not due to the recent release of UF<sub>6</sub>.

#### c. Release to the Environment

The inspector determined that UF<sub>6</sub> product escaped to the outside environment, but, based on observer's statements, the plume appeared to dissipate prior to reaching the boundary fence. To verify these observations and to determine the extent of any contamination in the environment, the licensee performed the following:

- (1) Air samples were collected at the fence boundary sample stations (No. 10 and 12) which most likely would have been in the pathway of the plume. The highest result (in microcuries per milliliter) 8E-15 uCi/ml represented about 0.17% of the NRC limit of 5E-12uCi/ml for natural uranium. It was also noted that air sampling station No. 11 which was not in the pathway of the plume indicated a result of 3.3E-14 uCi/ml or 0.7% of the NRC limit.
- (2) The licensee calculated that the 7 foot line from the block valve to the end of the line could hold 5 pounds of liquid UF<sub>6</sub>, while the sampling pigtail could hold about 60 grams of liquid UF<sub>6</sub>. The licensee estimated that no more than 60 grams of UF<sub>6</sub> released from the FMB.
- (3) An examination of smears (paper swipes) collected from the outside surface of a tractor-trailer and a chemical tank car located near the bay door indicated less than 20 dpm/100 cm<sup>2</sup>. These results are significantly below the licensee's action level of 200 dpm/100 cm<sup>2</sup>.

# d. Adequacy of Licensee's Response

The inspector concluded that the licensee using the experienced personnel assessed the radiological and operational aspects of the problem, implemented necessary elements of the Radiological Contingency Plan, and after an extensive maintenance review and cleanup returned the sampling system to a normal operating mode.

# Radiological Impact

The inspector observed that the licensee's investigation during the inspector's onsite time was incomplete and that the bioassay sampling of workers was still ongoing. The initial bioassay data indicated that

five employees exposed to the release inside the FMB excreted uranium levels in excess of the action level (35 ug U/1). The highest excretion level for any one worker was 395 ug U/1 (5 MPC hours). During the course of the release, the workers were wearing half-face masks. The most significant uranium excretion level outside of the FMB was 10 ug U/1 or about one-third of the licensee's action level.

The inspector determined that three contractor workers observed the plume. One contractor worker (on-site to replenish the liquid nitrogenesupply) was engulfed by the plume. However, the worker's excretion data (bioassay urinalysis) indicated a level of 4 ug U/1, which is considerably lower than the licensee's action level of 30 ug U/1. One of the other contractor workers submitted a urinalysis on June 20, 1990, or two days after the event. His bioassay result was less than 2 ug U/1. On June 26, 1990, the licensee informed the inspector that results of the urinalysis on the third worker was also less than 2 ug U/1.

The licensee noted that an excretion level of 395 ug U/l calculates to an uptake of 1.4 mg of uranium. Based on these findings, it appears that the derived NRC 40-hour intake limit of nine and six-tenths milligrams (9.6mg) soluble uranium in a work-week was not exceeded by any of the workers. Nonetheless, the plant physician plans to counsel the worker with the higher uranium excretion level (395 ug U/l or 5 MPC-hours) and the contractor worker (4 ug U/l or less than 1 MPC-hour) who was engulfed in the  $\mathrm{UO}_2\mathrm{F}_2\text{-HF}$  plume.

During the unplanned release a worker contracted to replenish the licensee's supply of liquid nitrogen was engulfed in the UO2F2/HF plume. According to 10 CFR 19.12, the licensee is required to provide instructions about health protection associated with exposure to radioactive materials to any worker in the restricted area. In addition, workers shall be instructed in the appropriate response to warnings made in the event of any unusual occurrence or malfunction that may involve exposure to radioactive material. Although, the licensee has a mechanism in place to prepare workers for performing in the restricted area, the licensee failed to do so. The licensee's guards are equipped with visitor information cards that describe the alarms and responses and instructs the visitor to evacuate the restricted area to a specific location in case of an emergency. The worker did not receive or review verbally a statement concerning evacuation procedures, nor was he officially escorted. Furthermore, as a vendor contracted to supply liquid nitrogen to the plant, the worker entered the plant on three occasions during the month of June. There was no indication that instructions were provided prior to any of his entries to the restricted area. Hence, the licensee failed to comply with 10 CFR 19.12.

One violation was identified.

# 6. Exit Meeting

The scope and findings of the inspection were discussed with licensee representatives (Section 1) at the close of the onsite inspection on June 20, 1990.

The licensee acknowledged that the training program for contractors, truck drivers, and visitors entering the restricted area would be revised. The licensee agreed to submit a written report to Region III based on its findings as to the cause of the unplanned event.

During the course of the inspection and the exit meeting, the licensee did not identify any documents or inspector statements and references to specific processes as proprietary.

Attachment: Attachment 1, Figure 1, UF<sub>6</sub>, Cylinder Sampling System

UFE Samphing System to sampling Sychem YOCHIMM GAMPS Block Severa footline
Pright to Block No.2 Sample Line Cappal Line Right Connection to Mort line Sand Line No. 2 Somple Patril Liquid UF AHACHMENT !

SHOWING NO. 4 NO. 2 SANDLE LINES Figure 1., UF, CYLINDER SAMPLING SYSTEM;

#### Region III and NMSS Concerns

While investigating the circumstances surrounding the unplanned release that occurred on June 18, 1990, at Metropolis Works, the NRC developed the following concerns, which the licensee should address. Items a-i can most likely be resolved in the short term. Item j will probably require longer terms to resolve.

a. The radiological impact of the release of UF<sub>6</sub> to the individual workers was less than 40-MPC-hours (9.6 mg). However, the excretion level of 395 ug U/l which calculates to an uptake of 1.4 mg or 5 MPC-hours is several orders of magnitude above the action level of 30 ug U/l.

Review the techniques of proper fitting of respiratory equipment with each of the workers involved in the release. Consider the use of full face protection during the connection/disconnection of sample pigtails and product fill pigtails.

- b. Remove the sample pigtails from the steam chest until needed; consider heating the pigtail prior to reconnection (to eliminate moisture).
- c. Consider the application of  ${\rm CO_2}$  to solidify any residual UF $_6$  that may be trapped in the line prior to connecting and/or disconnecting the pigtail.
- d. The operators use a special technique to ensure that the vacuum of the sample line is open from the sampling unit to the product cylinder. The capped line is opened and the block valve is opened so that the suction of air is audible as an indication that the vacuum is working. The written procedure allows that the block valve should be closed until all connections are made. Which is the preferred method of assuring that the sample line is open between the vacuum gauge and the cyclinder? Redefine this procedure and firm up an appropriate recipe to assure uniformity and safe practices.
- e. Review the possibility of shortening the distance between the block valve and the capped end of the sample line; install a vacuum gauge for this portion of the system.
- f. Review the maintenance/preventive maintenance program on the sampling line and sampling unit to assure gauges, valves, connections and heat trace requirements are operable.
- g. Improve the vacuum (high exhaust) in the local sampling lines by installing an auxiliary cold trap arrangement that would eliminate the use of the dust collector for this purpose. Hence, evacuation of small emissions of UF<sub>6</sub> using a vacuum wand (elephant trunk, etc.)

would traverse to a high exhaust cold trap. If this is not a feasible arrangement, what are the safety and/or operational concerns that favor the use of the dust collector?

- h. A weakness exists in the methods used to provide instruction's to contractors and/or truck drivers prior to their entering the restricted area. The licensee's approach to this program should be restructured to comply with 10 CFR 19.12.
- i. What assurance does Allied have that the radiological training provided by contractor crew chiefs for their subordinates is adequate for meeting 10 CFR 19.12? It appears that all of the training required for contractors relative to Allied's radiological health and safety program should be performed by Allied Signal Metropolis Works. Please explain why this should be different.
- j. Implementation of the in-line sampling device may require three individual units to manage the sampling requirements of four product cylinder stations. Provide the earliest date that the existing sampling device can be used for product sampling. Provide the earliest date that the two planned sampling devices can be used for product sampling.