MODULE 3.0: URANIUM CONVERSION

Introduction

Welcome to Module 3.0 of the Fuel Cycle Processes Directed Self-Study Course! This is the third of nine modules available in this directed self-study course. The purpose of this module is to be able to discuss the NRC regulations of and describe conversion facilities; identify the basic steps of the dry fluoride volatility conversion process and contrast with the wet acid digestion conversion process; identify sampling and measurement activities for the dry conversion process and the radiological and non-radiological hazards associated with the dry conversion process. This self-study module is designed to assist you in accomplishing the learning objectives listed at the beginning of the module. There are five learning objectives in this module. The module has self-check questions and activities to help you assess your understanding of the concepts presented in the module.

Before you Begin

It is recommended that you have access to the following materials:
- ◙ Trainee Guide

- ◙ Sequoyah Fuels Accident Slides (on CD accompanying course manual)

- ◙ "Release of UF_6 from a Ruptured Model 48Y Cylinder at Sequoyah Fuels Corporation Facility: Lessons-Learned Report," U.S. Nuclear Regulatory Commission, NUREG-1198, June 1986.

- ◙ "Assessment of the Public Health Impact from the Accidental Release of UF_6 at the Sequoyah Fuels Corporation Facility at Gore, Oklahoma," U.S. Nuclear Regulatory Commission, NUREG-1189, Vol. 1, March 1986.

Complete the following prerequisites:
- ◙ Module 1.0: Overview of the Nuclear Fuel Cycle

How to Complete this Module

1. Review the learning objectives.

2. Read each section within the module in sequential order.

3. Complete the self-check questions and activities within this module.

4. Check off the tracking form as you complete the self-check questions and/or activity within the module.

5. Contact your administrator as prompted for a progress review meeting.

6. Contact your administrator as prompted for any additional materials and/or specific assignments.

7. Complete all assignments related to this module. If no other materials or assignments are given to you by your administrator, you have completed this module.

8. Ensure that you and your administrator have dated and initialed your progress on the tracking form.

9. Go to the next assigned module.

MODULE 3.0:   URANIUM CONVERSION

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LEARNING OBJECTIVES

3.1   Upon completion of this module, you will be able to discuss the NRC regulations of and describe conversion facilities; identify the basic steps of the dry fluoride volatility conversion process and contrast with the wet acid digestion conversion process; identify sampling and measurement activities for the dry conversion process and the radiological and non-radiological hazards associated with the dry conversion process.

3.1.1   Identify NRC regulation of conversion facilities.

3.1.2   Identify the geographic location of NRC regulated conversion facility.

3.1.3   Identify the basic steps of the dry fluoride volatility conversion process, including:

◉   sampling and measurement activities.

◉   radiological and non-radiological hazards.

3.1.4   Identify British and French conversion processes.

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Learning Objective

When you finish this section, you will be able to:

3.1.1 Identify NRC regulation of conversion facilities.

3.1.2 Identify the geographic location of NRC regulated conversion facility.

NRC REGULATION OF CONVERSION FACILITIES

After the ore concentrate (in any of the following forms: ammonium diuranate, ADU - $(NH_4)_2U_2O_7$; triuranium octoxide - U_3O_8; and/or yellowcake) is produced at the mill, the next step is conversion into pure uranium hexafluoride (UF_6) suitable for use in enrichment operations. Two basic routes can be followed. The first route uses a dry, fluoride volatility route to first convert the uranium to UF_6, and then to purify it via distillation. The second route uses aqueous processes (that include acid digestion and solvent extraction) to first purify the uranium, followed by conversion to UF_6. Figure 3-1 shows the two basic routes. The fluoride volatility route has fewer steps but has a higher inventory of volatile chemicals and potentially more environmental safety and health (ES&H) concerns. In practice, acceptable ES&H parameters can be achieved by either route.

Until November of 1992, there were two conversion plants operating in the United States. Since 1992, Sequoyah Fuels in Gore, Oklahoma, has been in the process of decommissioning its UF_6 operations. The Oklahoma facility used a wet acid digestion process. The only operating conversion plant in the United States is the Honeywell facility located in Metropolis, Illinois, which uses a dry fluoride volatility conversion process. The Honeywell facility is about 5 miles from the Paducah Gaseous Diffusion Plant (Figure 3-2). This facility is a multiproduct chemical manufacturing facility that produces sulfur hexafluoride, iodine, and antimony pentafluorides, liquid fluorine, synthetic calcium fluoride, and uranium hexafluoride. Figure 3-3 shows an ariel view. Figure 3-4 is a schematic of the conversion plant.

The production of uranium hexafluoride requires licensing by the NRC pursuant to the provisions of 10 CFR Part 40, Domestic Licensing of Source Material. The licensed facility is designed to produce about 14,000 short tons per year of uranium as UF_6 from uranium concentrates. The plant feed usually assays about 75% uranium, and the final UF_6 product contains less than 300 parts per million impurities.

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In general terms, "source material" means either the element thorium or the element uranium, provided that the uranium has not been enriched in the isotope uranium-235. Source material also includes any combination of thorium and uranium, in any physical or chemical form, or ores that contain by weight one-twentieth of one percent (0.05 percent) or more of uranium, thorium, or any combination thereof. Depleted uranium (left over from uranium enrichment) is considered source material.

Source material can result from the milling and concentration of uranium contained in ore mined for its uranium content. It can also be generated in the process of refining ores mined for other precious metals. In addition, source material can arise from the reprocessing of spent nuclear fuel (no commercial reprocessing is currently licensed in the U.S.) and, also, as depleted uranium (contains lower levels of U-235 than natural uranium) from the process of enriching uranium in the isotope uranium-235.

A conversion facility processing source material is required to submit an accident analysis and an emergency plan. Accident analyses are deterministic - accident sequences are analyzed and, if the consequences are found to be too high, specific safety controls are implemented.

For additional information on conversion, see also the Westinghouse Columbia Fuel Fabrication Facility in Module 5.0. The facility utilizes an ADU process for converting UF_6, or uranyl nitrate (UN) to uranium oxides U_3O_8 and UO_2. This is a wet conversion application which involves continuous processing of solutions and slurries of nuclear material.

Recent Standard Review Plans (SRPs) that are applicable to uranium conversion are:

◉ "Standard Review Plan for the Review of a License Application for a Fuel Cycle Facility," NUREG-1520, June 2003

◉ "Standard Review Plan for the Review of a License Application for a Mixed Oxide (MOX) Fuel Fabrication Facility," NUREG-1718, October 2002

Figure 3-1. Process Routes
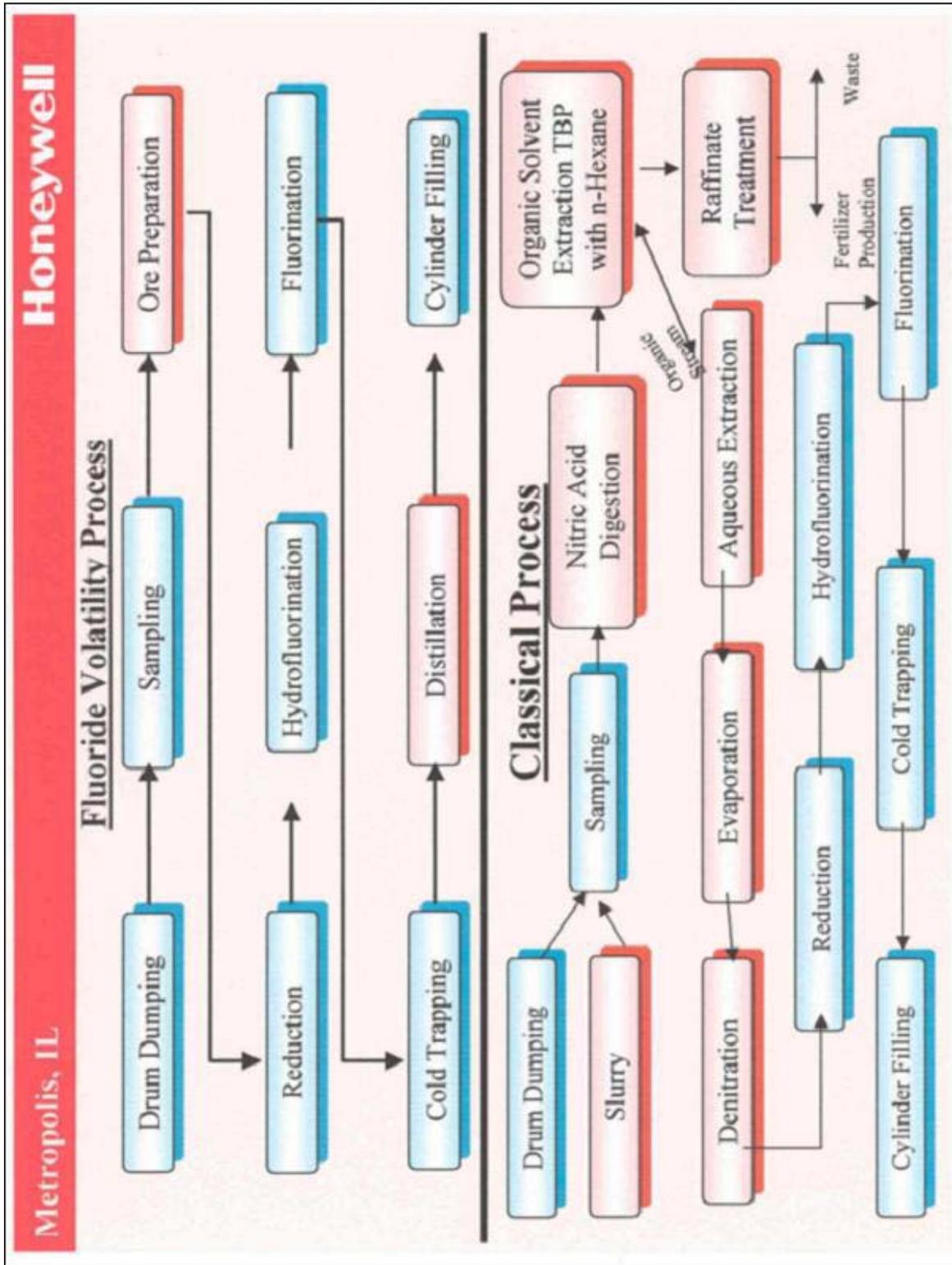
Figure 3-2. Location of Honeywell Plant
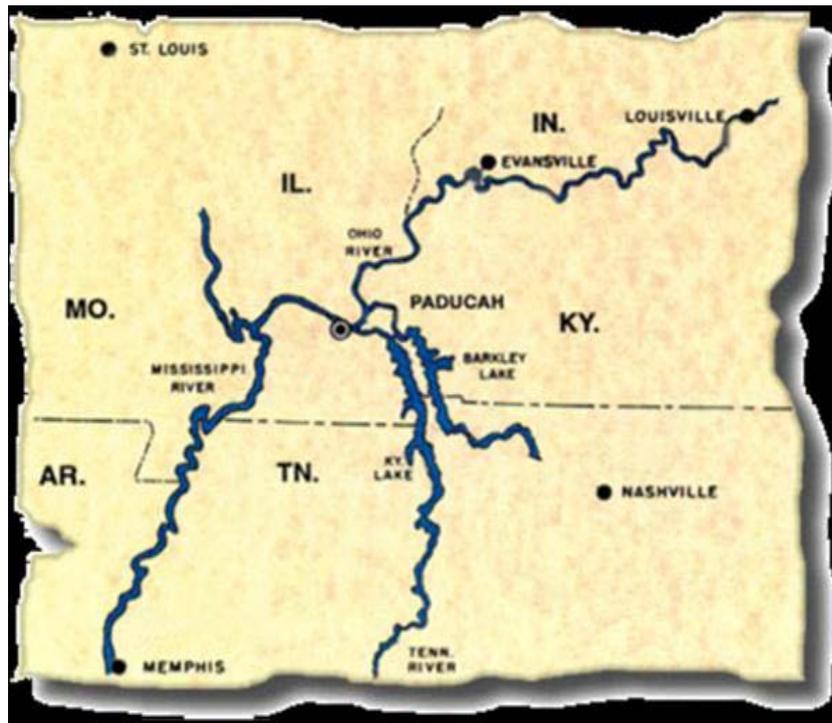
Figure 3-3. Ariel View of Honeywell Plant

Figure 3-4. Schematic of the Honeywell Conversion Plant

Self-Check Questions 3-1

INSTRUCTIONS: Circle the correct response. Answers are located in the
answer key section of the Trainee Guide.

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1. Which one of the following conversion facilities is operating in the United States?

    A. Honeywell, Inc. in Metropolis, Illinois
    B. Sequoyah Fuels in Gore, Oklahoma

2. Which one of the following conversion facilities is undergoing decommissioning?

    A. Honeywell in Metropolis, Illinois
    B. Sequoyah Fuels in Gore, Oklahoma

3. The production of uranium hexafluoride requires licensing by the Commission pursuant to
    the provisions of _____.

    A. 10 CFR Part 19
    B. 10 CFR Part 20
    C. 10 CFR Part 40
    D. 10 CFR Part 50

4. What type of facility in the nuclear fuel cycle sends their product to a conversion facility for
    processing?

    A. Mining
    B. Recovery
    C. Enrichment
    D. Fuel Fabrication

5. What is the final product of the conversion process?

    A. Ammonium diuranate
    B. Triuranium octoxide
    C. Yellowcake
    D. Uranium hexafluoride

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

Learning Objective

When you finish this section, you will be able to:

3.1.3   Identify the basic steps of the dry fluoride volatility conversion process, including:
- sampling and measurement activities.

- radiological and non-radiological hazards.

DRY FLUORIDE VOLATILITY CONVERSION PROCESS

In the Honeywell dry fluoride volatility conversion process, the ore concentrates received from the mill are carried through the successive steps of feed preparation, reduction, hydrofluorination, fluorination, and distillation. Chemical reactions are carried out in fluid bed reactors. A simplified flow chart of the manufacturing process is presented in Figure 3-5. After initial sampling through the auger sampling system, the ore concentrate goes through seven basic steps:

- Step 1 - Pretreatment

- Step 2 - Prepared Feed and Calcination

- Step 3 - Reduction

- Step 4 - Hydrofluorination

- Step 5 - Fluorination

- Step 6 - Distillation

- Step 7 - Product Loading and Shipping

Each of these basic steps will be discussed in this directed self-study module in a sequential order. Figure 3-6 provides an overview of intermediate and final products produced in each step of the conversion process.

Figure 3-5. Flow Schematic of the U$_3$O$_8$ to UF$_6$ Conversion Process
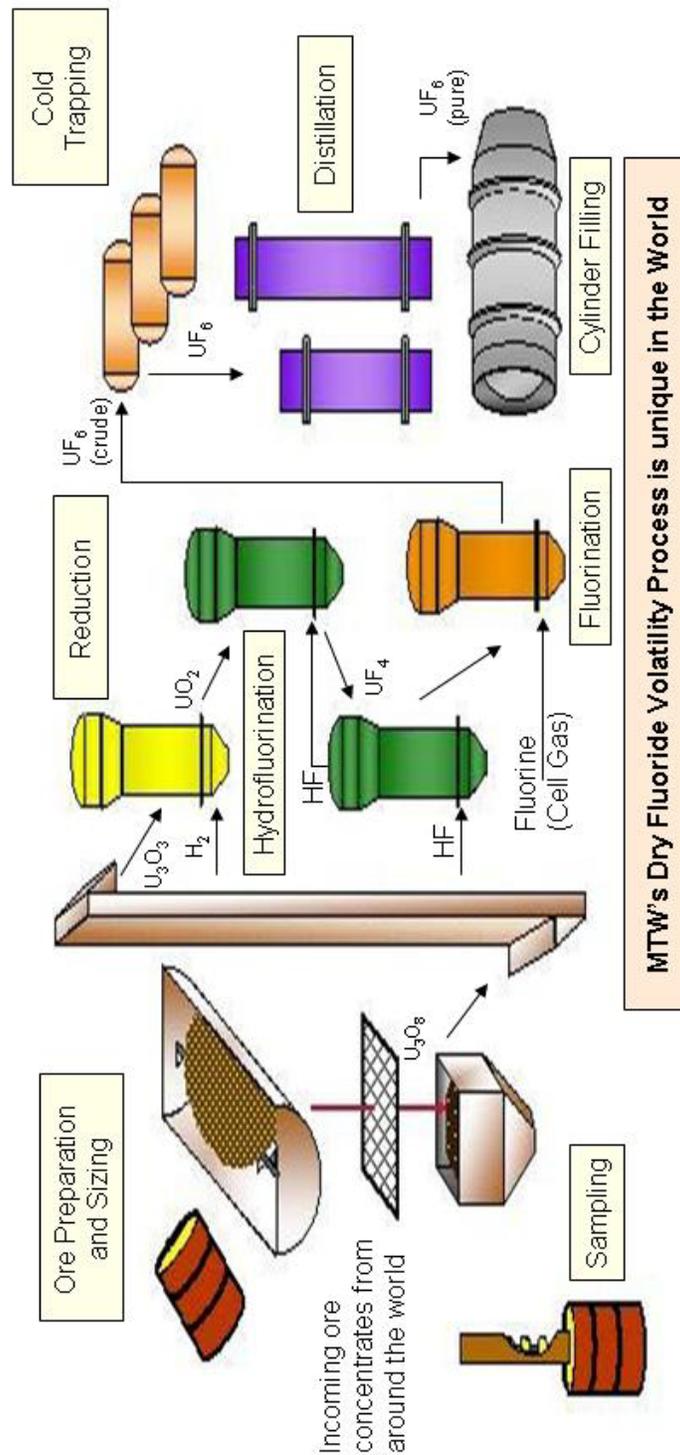
Figure 3-6. Intermediate and Final Products of the Dry Fluoride Volatility Conversion Process

Step 1: Pretreatment

Product in: Could be a mixture of:
- Ore concentrate
- Triuranium octoxide (U_3O_8)
- Yellowcake

Product out: The same as product in with less impurities

Step 7: Product Loading and Shipping

Product in: Purified UF_6

Product out: Purified UF_6

Step 2: Prepared Feed and Calcination

Product in: Same as product out from Step 1

Product out: Black oxide (a form of U_3O_8)

Step 6: Distillation

Product in: Crude UF_6

Product out: Purified UF_6

Step 3: Reduction (with hydrogen)

Product in: Black oxide

Product out: Brown oxide (Uranium dioxide) (UO_2 powder)

Step 5: Fluorination

Product in: Green salt

Product out: Crude UF_6 (Uranium hexafluoride)

Step 4: Hydrofluorination

Product in: Brown oxide

Product out: Green salt (Uranium tetrafluoride) (UF_4)

Note 1: Steps 1 through 5 indicate intermediate products. The final product in the dry fluoride volatility conversion process is purified UF_6.

Note 2: Prepared feed and calcination are the same as ore preparation from Figure 3-2.

Auger Sampling System

Prior to conversion, an agreement concerning the amount of uranium being supplied must be reached between the supplier and the conversion plant. If the yellowcake ore concentrate (U_3O_8) contains less than 60% percent uranium by weight, it is not accepted by the conversion plant. An auger sampling system is used to ascertain the purity and quantity of uranium. See Figure 3-7, Auger Sampling System.

Receipt of Drums

Drums of uranium ore concentrate are received at the sampling plant via truck or rail car. The drums are unloaded using fork trucks at either of three unloading docks. One of the docks is equipped with a conveyor system to transfer drums to the storage pad area where they may be stored prior to sampling. As ore is received into the plant, accountability personnel input lot information into a computer system. This information consists of a lot control number, number of drums, and gross weight of each drum.

Figure 3-7. Auger Sampling System
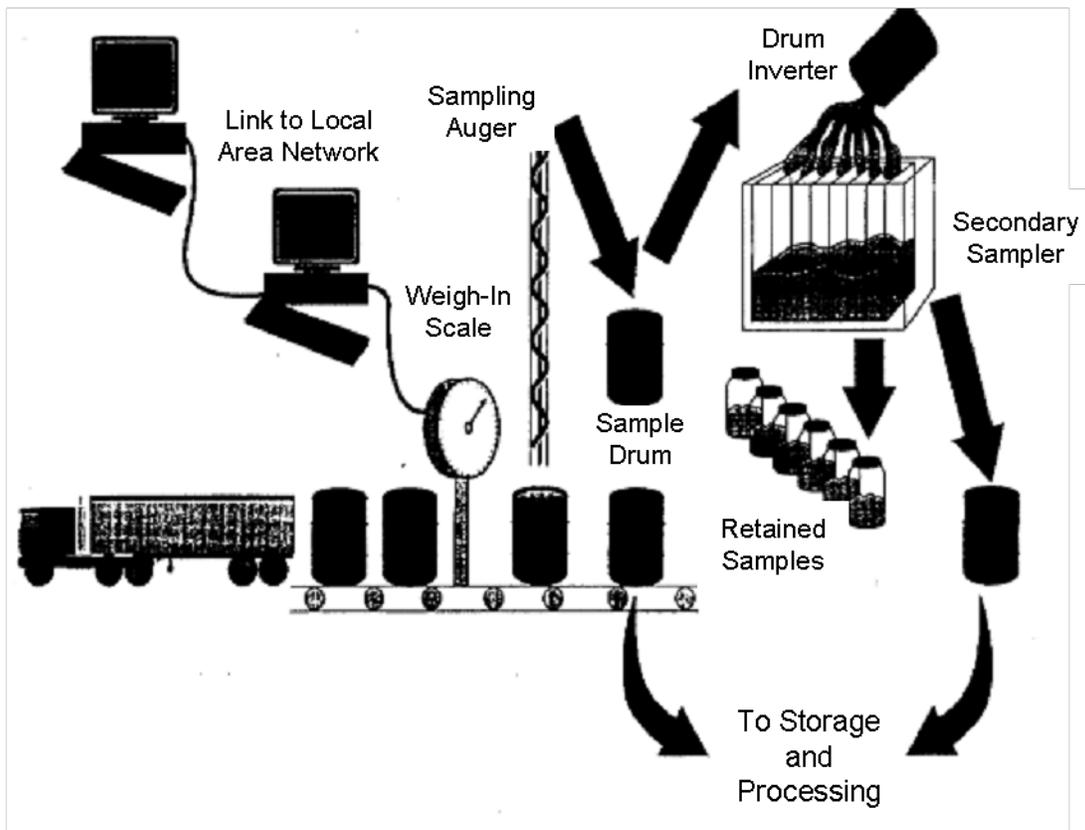
At the Sampling Plant

Individual lots of material are transferred from the storage area to the sampling plant using fork trucks. The drums are placed onto the conveyor system to initiate the sampling process. The powered conveyor system is designed to accept drums until the line is full. Electric photocells are used to operate the conveyor and properly stage the drums.

Drums are conveyed up to the scale, where the gross weight of each drum is determined. A unique dual scale is used to achieve two independent weights at this point, and agreement between the two scales must be within 0.5 pound. The movement of drums onto the dual scale is controlled by the operator from the system control console. After weights are entered, the drums are conveyed to the lid removal station.

The lid removal station will accommodate two drums at a time. Bolts, rings, and lids are removed in this hooded area and set aside for reuse after the drums have been sampled. When the auger area is clear, the operator activates the conveyor to send the drums to the proper positions underneath the stationary augers. Switching is provided so that both augers may be operated simultaneously (normal operations) or that either of the two augers may be operated independently. A bypass feature is also provided in case the operator determines that a drum should not be sampled.

In the Auger Room

The auger room is operated under a negative pressure to prevent airborne contamination of the operator work area. The drums stop in positions that are centered under the augers. The lift tables are then positioned by a hydraulic system to provide sampling from a specific location in the drum, namely center, halfway between the center and the side of the drum, or near the side of the drum. Only one sample is collected from each drum, and a random position chart is used to program the Programmable Logic Controller (PLC) for this positioning. The lift tables are then raised to engage the augers, which start turning after the drums are properly positioned. The lifts continue to raise the drums until the augers are approximately one inch from the bottom of the drum.

At the lidding station, lids, rings, and bolts are attached in order to secure the drum contents. Upon completion of this task, the operator then activates the conveyor to move the drums along the conveyor system.

STEP 1 – PRETREATMENT

Product in: could be a mixture of:

◉ Ore concentrate

◉ Triuranium octoxide (U_3O_8)

◉ Yellowcake

Product out: the same as product in with less impurities.

The uranium concentrate is pretreated to remove sodium by a four stage countercurrent treatment with ammonium sulfate [$(NH_4)_2 SO_4$] solution according to the following reaction:

$$Na_2U_2O_7 + (NH_4)_2SO_4 \rightarrow (NH_4)_2U_2O_7 + Na_2 SO_4$$
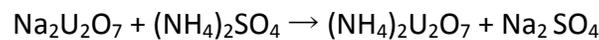
Sodium removal is essential because sodium forms a compound that causes caking and sintering in the fluid bed fluorinators. The countercurrent treatment also removes impurities like Radium-226 (Ra-226), Thorium-230 (Th-230), selenium, and molybdenum. See Figure 3-8, Sodium Removal.

Figure 3-8. Sodium Removal
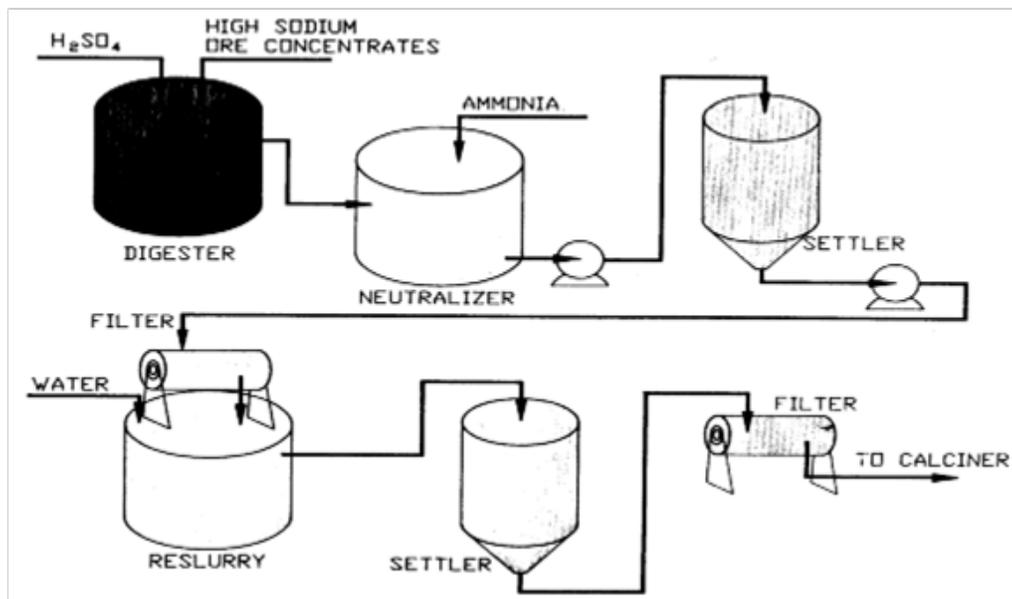
Potential Hazards

The following potential hazards could occur in pretreatment areas:

- ◙ Acid burns to employees working in process area.

- ◙ Corrosion of equipment causing leaks, resulting in area surface contamination and potential airborne contamination.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in pretreatment areas:

- ◙ Ore concentrates are mixed into a slurry to prevent dusting.

- ◙ Level, pressure, pH, and flow control systems are used to assist the operator in maintaining process control.

- ◙ Rubber-lined vessels and equipment are provided in the leach and precipitation steps to eliminate corrosion.

- ◙ Process equipment is constructed of stainless steel to reduce corrosion.

- ◙ Workroom air is routinely monitored for airborne exposure control.

- ◙ Surface contamination is routinely monitored and decontamination initiated when appropriate.

STEP 2 - PREPARED FEED AND CALCINATION

Product in: same as product out from Step 1

Product out: Black oxide (a form of U_3O_8)

The $(NH_4)_2U_2O_7$ (ADU) is removed from the last pretreatment stage and sent to the main feed preparation section for calcination to U_3O_8 according to the following reaction:

$$3(NH_4)_2U_2O_7 \rightarrow 6NH_3 + 2U_3O_8 + 3H_2O + O_2$$
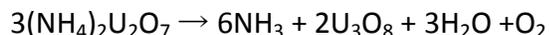
See Figure 3-9, Prepared Feed. Calciners are mechanical devices utilized for heating materials to elevated temperatures in order to change the material by driving off vapors and gases to leave a powdery solid.

The calciner off-gas, containing ammonia, water vapor, sulfur dioxide (SO_2), and U_3O_8 particulates, and passes through two baghouses in series before venting through the stack.

The calcined material (U_3O_8) is then blended, agglomerated with water or sulfuric acid depending on the concentrate characteristics, dried (rotary dryer at 371-482°Celsius [C] or 700°F-900°Fahrenheit [F]), crushed, and sized for conversion to uranium dioxide (UO_2).

The final step ensures that the concentrates have the optimum particle size and density necessary for fluid bed operations. Uniform sizing of the concentrate is essential in order to optimize reactions in the subsequent steps of the conversion process.

Note: The uranium-ore concentrates are to be free-flowing and of a particle size not to exceed 6 mm (0.25 in.) or as agreed upon with the conversion plant and the supplier. Ore concentrates are analyzed to ensure that the average moisture content does not exceed 5.0% of the weight of the uranium-ore concentrates.

Dusts and fumes from this process are controlled by use of dust collectors. The dust collectors have primary and secondary (backup) units arranged in series. Secondary dust collector exits have an investigation limit of 5,000 disintegrations per minute (dpm), except the ash dust collector, which has an investigation limit of 10,000 dpm because it is exposed to 2% to 3% uranium. Primary dust collector exits have an investigation limit of 15,000 dpm. When the investigation limit is exceeded on three successive samples, an informal investigation is conducted and actions taken to decrease emissions. If the action does not remedy the situation, additional actions are taken, including shutdown of the unit. The results of the effluent monitoring analyses are submitted to the NRC in semi-annual monitoring reports.

Ventilation air from the feed preparation building is filtered before release to the atmosphere, solid waste filter bags are produced in this operation, and a contaminated liquid stream produced in drum washing is routed to settling ponds.

Figure 3-9. Prepared Feed
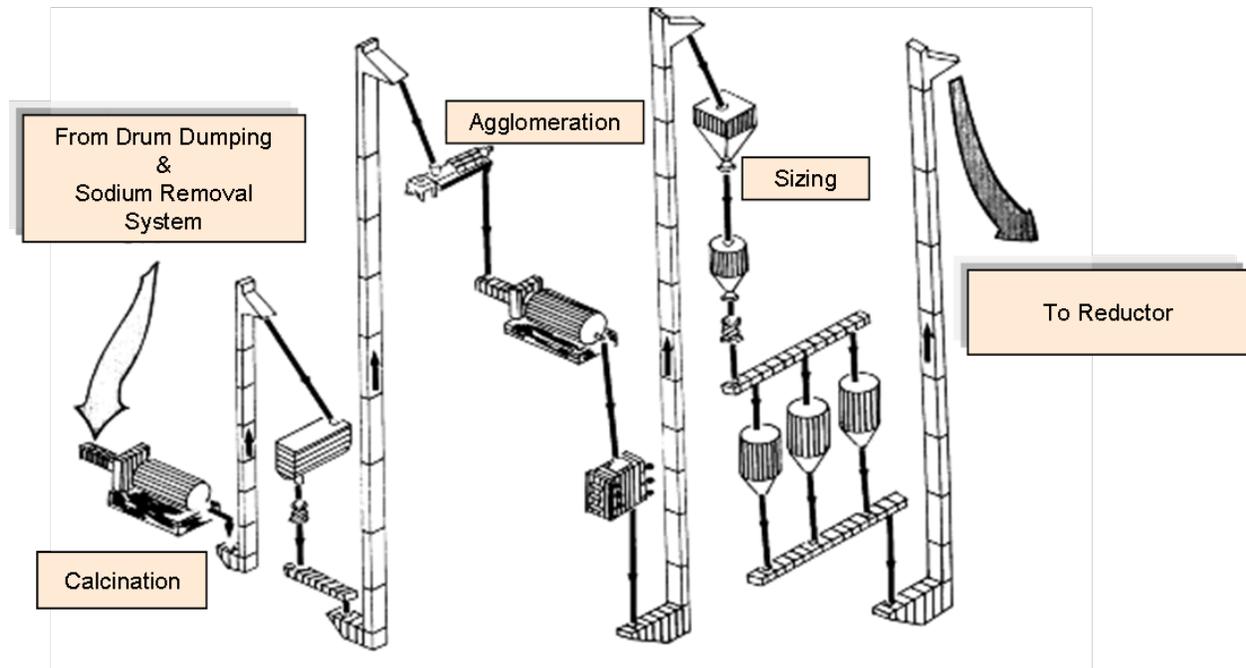
Potential Hazards

The following potential hazards could occur in prepared feed areas:

◎ Internal radiation exposure from leaks or spills of the dry uranium compounds processed.

◎ Physical stress and pinch points in handling drums at the drum dumper.

◎ Compressed gases, extreme temperatures, and molten metal contained within the calciner.

◎ Potential impact from process stack emissions.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in prepared feed areas:

◎ A dust collector system to maintain slight negative pressure on equipment.

◎ Electrical interlocks for proper start-up and shutdown of process equipment.

STEP 3 - REDUCTION

Product in: Black oxide

Product out: Brown oxide (Uranium dioxide) (UO_2 powder)

The calcined material (U_3O_8) is reacted with hydrogen in a fluidized medium to form uranium dioxide (UO_2). The dissociated NH_3 (a mixture of H_2 and N_2) removes impurities and yields a minimum of 99% reduction to the intermediate UO_2.

The sized U_3O_8 enters a single-stage fluidized-bed reduction reactor for reduction to UO_2 according to the following reaction:

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O$$
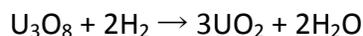
Figure 3-10 shows the Reduction process. Dissociated NH_3 (in the presence of a nickel catalyst) is used to supply a mixture of hydrogen and nitrogen as the fluidizing gas. The off-gas from the fluid bed reducer principally contains a mixture of H_2, N_2, water vapor, sulfur vapor, hydrogen sulfide (H_2S), and arsine (AsH_3). The reducer off-gas is filtered through a sintered metal filter to remove particulate uranium; the residual off-gas is incinerated to convert the H_2S to sulfur dioxide (SO_2). The powdered UO_2 is withdrawn continuously from the bottom of the bed and then sent to the hydrofluorinator for conversion to uranium tetrafluoride (UF_4 - green salt).

The UO_2 obtained in the dry process, when of exact chemical stoichiometry (99% reduction to the intermediate UO_2), is a cinnamon-colored powder that may be used directly in the manufacture of pellets for fuel fabrication.

The reductor reactor is fitted with relief valves, alarmed H_2 analyzers, a rupture disk, and pressure sensors to prevent and mitigate the effects of potential explosion conditions.

The uranium solids filtered from the reactor off-gas are recycled to the ore preparation system. No liquid effluent stream is produced by the reduction process.

Figure 3-10. Reduction
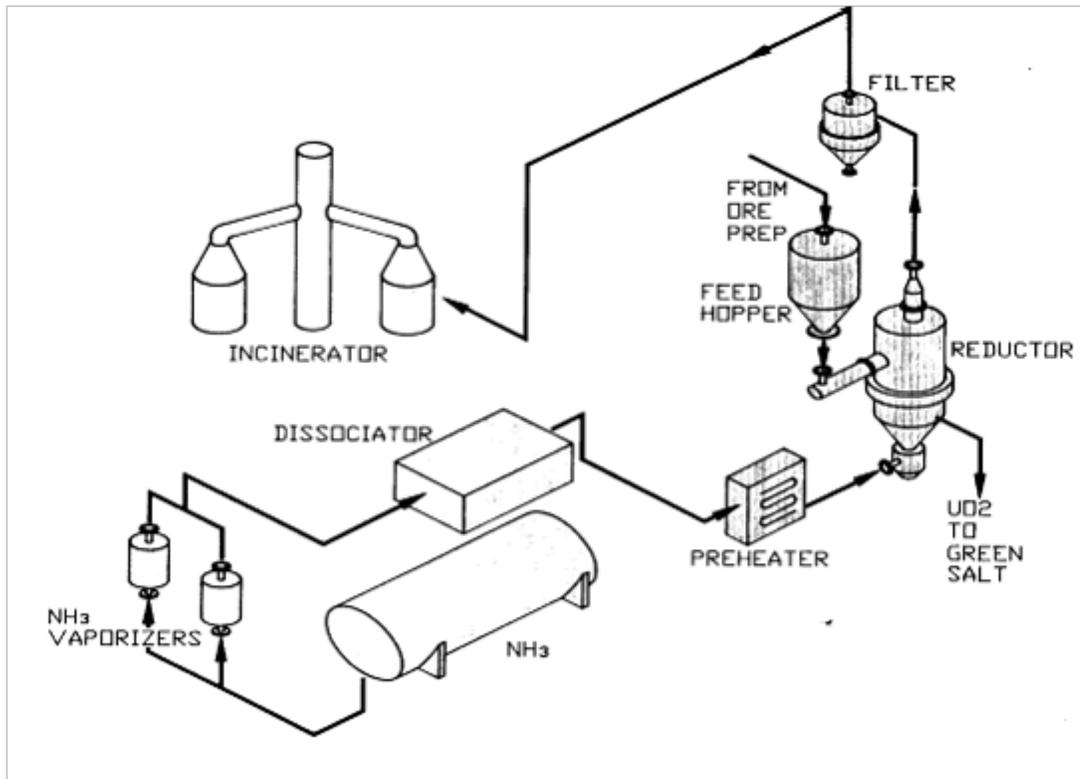
Potential Hazards

The following potential hazards could occur in reduction areas:

- ◙ The process consumes hydrogen, which is flammable.

- ◙ Uranium decay products present in the UO_3 tend to concentrate in unreacted waste.

- ◙ Collection and removal of UO_2 present some potential for airborne contamination.

- ◙ System maintenance presents significant potential for creating airborne contamination.

- ◙ Internal exposure to insoluble UO_2 (Class "Y") material.

- ◙ Extreme process temperatures (600°C) are associated with reduction.

- ◙ Process stack emissions may have an impact.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in reduction areas:

◉ The reductor system has a continuous on-line analyzer system to detect the presence of hydrogen.

◉ Process gases from the reductor are filtered to remove particulate uranium and incinerated to eliminate hydrogen and hydrogen sulfide.

◉ Process equipment, excluding fluidized-bed reactors, is enclosed and ventilated to dust collector baghouses to prevent personnel exposure to uranium.

◉ Reductors are constructed of special alloys to reduce corrosion during the reaction process.

STEP 4 - HYDROFLUORINATION (GREEN SALT)

Product in: Brown oxide

Product out: Green salt (Uranium tetrafluoride) (UF$_4$)

UO$_2$ is hydrofluorinated to uranium tetrafluoride (UF$_4$-green salt) according to the following reaction:

UO$_2$ + 4HF $\rightarrow$ UF$_4$ + 2H$_2$O, $\triangle$H° = -78.1 KJ/mole
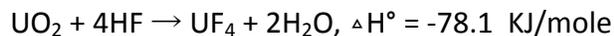
UF$_4$ has monoclinic green crystals that melt at 2012°F. When heated in air, UF$_4$ will change to U$_3$O$_8$. UF$_4$ is a corrosive compound that is insoluble in water. It is soluble in concentrated acids and alkalines but decomposes readily.

Anhydrous hydrogen fluoride (HF) gas is used to carry out the hydrofluorination reaction. The reaction temperature is around 750°F to 930°F, and is highly exothermic.

See Figure 3-11, Hydrofluorination. The UO$_2$ from the reduction reactor is fed into two monel fluid bed hydrofluorinators operated in series with counter-current gas and solid flow. Anhydrous HF vapor in nitrogen (N$_2$) diluent is used as a fluidizing medium to permit contact between the UO$_2$ and HF to form UF$_4$. The reactor off-gas, containing excess HF (required for good conversion) and volatile fluorides like SiF$_4$, BF$_3$, molybdenum, vanadium fluorides, and H$_2$S, is treated (burned). The solid drawn off at the bottom of the primary reactor is transferred into the secondary reactor through a feed screw.

The hot (455°C; 851°F) reactor off-gas is filtered and scrubbed with potassium hydroxide (KOH) solution before release to the atmosphere. The spent scrubber liquid is processed through the environmental protection facility (EPF) for neutralization and recovery of fluorine as calcium fluoride (CaF$_2$). The UF$_4$ solids filtered from the off-gas are combined with the UF$_4$ product stream for transfer to fluorination reactors.

Hydrofluorination of UO$_2$ must be carried out with extreme caution because HF:

- ◉ Is a very reactive chemical that reacts with water or steam to produce toxic and corrosive fumes.

- ◉ Reacts with metals and can result in formation of hydrogen in containers and piping to create an explosion hazard.

- ◉ Is a poisonous gas that may be fatal if inhaled or absorbed through skin.

- ◉ Contact may cause burns to skin and eyes.

- ◉ Is a highly corrosive gas that corrodes most substances except lead (Pb), wax, polyethylene, teflon (PTFE), and platinum (Pt).

◙   Is incompatible with concrete and ceramics.

◙   Liquid (aqueous) or anhydrous HF also attacks some forms of plastics, rubbers, and coatings. It attacks glass and stoneware, dissolving the silica.

Figure 3-11. Hydrofluorination
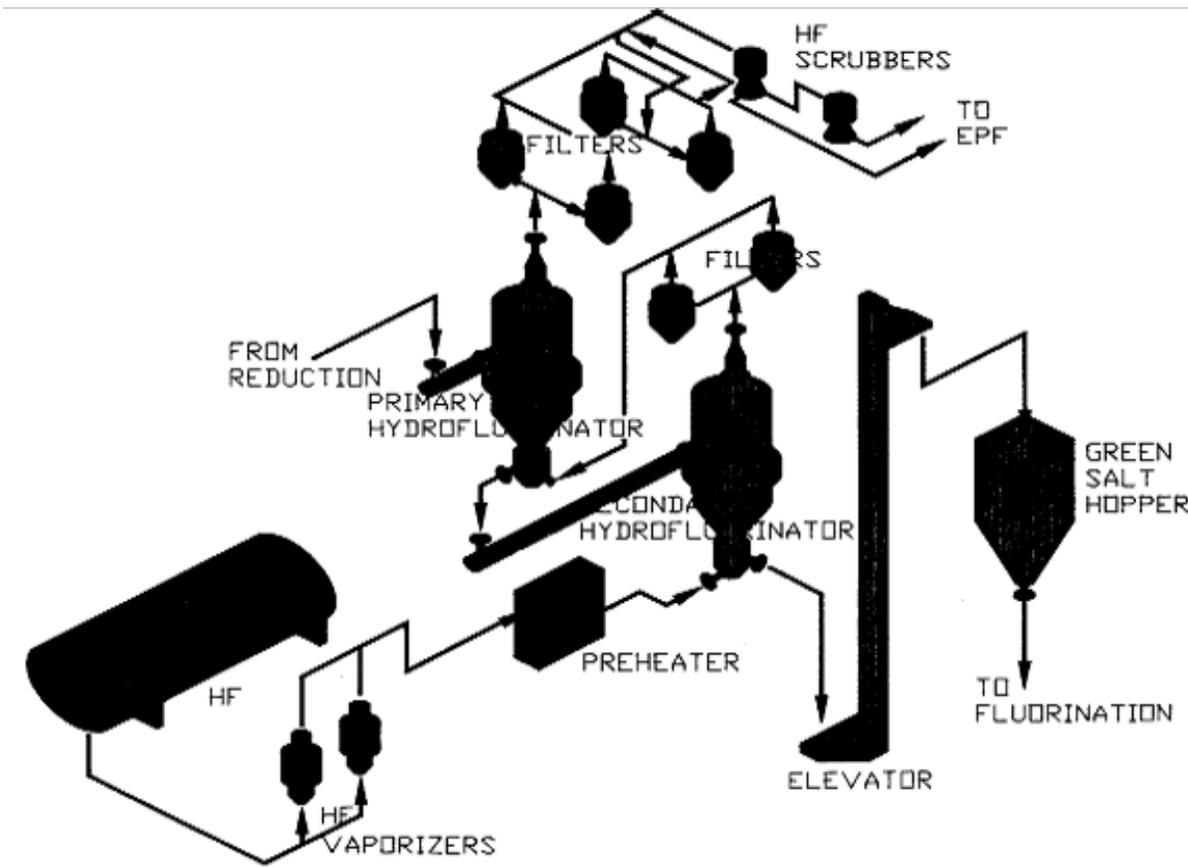
Potential Hazards

The following potential hazards could occur in hydrofluorination areas:

◙   The process consumes HF, which is corrosive to equipment and may cause serious burns from skin contact or inhalation.

◙   Internal radiation exposure to mixed-solubility uranium compounds ("D," "W," and "Y") may occur.

◙   Uranium decay products will tend to concentrate in unreacted waste and may produce significant exposure rates.

◙   System maintenance could involve significant beta dose rates from internal surfaces.

◙   The process temperature is extreme at 475°C.

◙   Stack emissions may have an impact.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in hydrofluorination areas:

◙   Process equipment, excluding the fluidized-bed reactors, is enclosed and ventilated to dust collector baghouses to prevent personnel exposure to uranium.

◙   Fluidized-bed reactors and vessels used in the vaporization of HF utilize relief valves and rupture discs to prevent overpressurization of vessels.

◙   Relief valves are vented to scrubbers, dust collectors, or sumps to reduce impact on the environment and exposure to operating personnel.

◙   Process gases from the fluidized-bed reactors are filtered to remove particulate uranium.

◙   Stack emissions of uranium are routinely monitored.

STEP 5 - FLUORINATION

Product in: Green salt

Product out: Crude UF_6 (Uranium hexafluoride)

Green salt (UF_4), is fluorinated by direct fluorination with elemental fluorine (in fluid bed fluorinators) according to the following reaction:

$UF_4 + F_2 \rightarrow UF_6$, $\triangle H° = -110.4$ KJ/mole

The fluorination reaction is highly exothermic.

See Figure 3-12, Fluorination. The UF_4 feed is introduced into the bottom of two parallel monel fluid bed fluorinators that contain calcium fluoride (CaF_2) as inert bed material. Under less than a full capacity process, the UF_4 is introduced into one fluorinator. Elemental fluorine (F_2), prepared by on-site electrolysis of hydrogen fluoride (HF) in a fused bath of potassium fluoride, is used as the fluidizing gas or fluidizing medium that reacts with UF_4 to produce UF_6 vapor. The bed temperature is maintained above 482°C (900°F). The UF_6 vapor exits the reactor along with excess F_2, unreacted UF_4 particulates, and volatilized impurities. UF_6 is first cooled and then passed through a series of sintered nickel filters for particulate removal. The exit gas then passes through a series of three cold traps for UF_6 collection. Residual uranium and nonvolatile uranium progeny products remain in the bed material, which is recycled and reused until the buildup of contaminant levels prohibits its further use. The bed material is then retired for radioactive decay and recovery of the uranium content.

The bulk of the UF_6 exiting the reactor is condensed in a primary cold trap operated at -20°F. The secondary and the tertiary traps operate at lower temperatures and remove the residual UF_6. Following liquefaction, crude UF_6 is removed intermittently from the cold traps by heating. It is then transferred to the distillation still bed tanks to await purification by fractional distillation. Uncondensed gases from the traps are scrubbed with KOH solution, (which also neutralizes traces of fluorine), before release to the atmosphere.

A potassium fluoride mud is removed from the scrubber solution, washed, and recycled to the uranium recovery system. The spent scrubber solution is transferred to the EPF for neutralization, recovery of KOH, and recovery of fluorine as CaF_2. Filtered and scrubbed offgases are released to the atmosphere.

Potential Hazards

The following potential hazards could occur in fluorination areas:

- ◉ The process consumes fluorine (F_2), an extremely strong oxidizing agent that is corrosive to equipment and causes skin burns upon contact.

◙ Contact of oil with F_2 or UF_6 may initiate an uncontrolled reaction resulting in fire and explosion.

◙ Uranium progeny products accumulate in the fluorinator bed material (CaF_2). This produces external radiation levels that are higher than those of other process areas.

◙ Fluorine leaks from process equipment may produce a significant safety hazard.

◙ Possible internal exposure to highly soluble UF_6 could produce HF burns and chemical toxicity.

◙ Process temperatures are extreme, ranging from 427°C to 537°C.

◙ Stack emissions may have an impact.

The following potential hazards could occur in cold traps:

◙ Heating of cold traps containing excessive amounts of UF_6 could produce overpressurization.

◙ Hydrocarbon or glycol contamination of UF_6 can cause vigorous reactions.

◙ Fluorine leaks may create a significant safety hazard.

◙ Internal exposure to highly soluble UF_6 could cause skin burns and chemical toxicity.

◙ Overpressurization and potential line rupture associated with thermal expansion of liquid UF_6 in transfer lines.
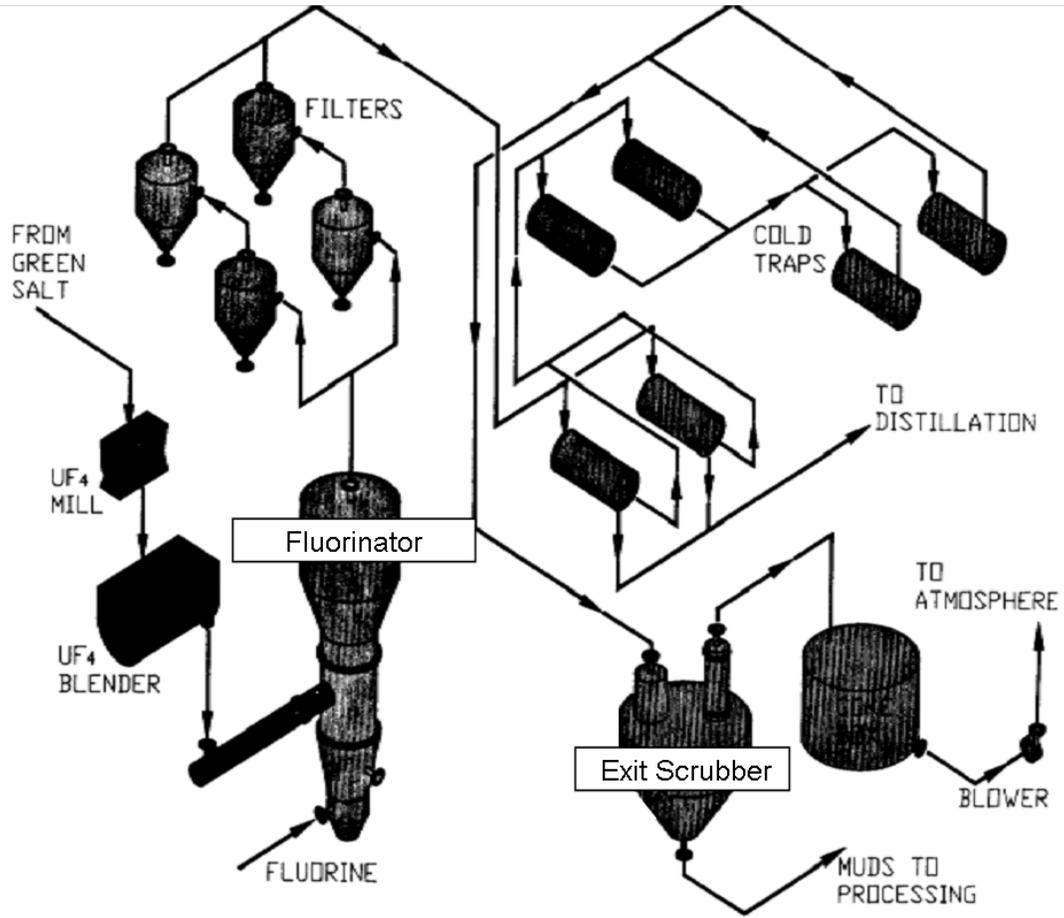
Figure 3-12. Fluorination

FILTERS

FROM
GREEN
SALT

COLD
TRAPS

UF₄
MILL

TO
DISTILLATION

Fluorinator

TO
ATMOSPHERE

UF₄
BLENDER

Exit Scrubber

BLOWER

FLUORINE

MUDS TO
PROCESSING

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in fluorination areas:

◙ Automated movement of spar in and out of reactor and dust collection equipment reduces risk of inhalation to operating personnel.

◙ All vessels used in fluorine and UF_6 service are degreased before being put into service.

◙ The fluorination process operates at below atmospheric pressure.

◙ Fluidized-bed reactors are constructed of special alloys to reduce corrosion during the reaction process.

◙ Specific procedures are provided to control external radiation exposures to uranium progenys.

◙ Specialized equipment and procedures are provided to control employees' exposure to F_2, HF, and UF_6.

◙ Workroom air and stack emissions of uranium are continuously monitored.

The following administrative and engineering controls should be considered for preventive measures in cold trap areas:

◙ Administrative controls are in place to prevent traps from being overfilled.

◙ Vessels used in fluorine and UF_6 service are degreased prior to being used.

◙ The system is designed to operate at below atmospheric pressure to prevent fluorine leaks.

◙ Specialized equipment and procedures are provided to control employee exposure to F_2, HF, and UF_6.

STEP 6 - DISTILLATION

Product in: Crude UF_6

Product out: Purified UF_6

The crude UF_6 produced in the fluorination reactor contains fluorides of vanadium, molybdenum, silicon, carbon, sulfur, thorium, and protactinium that have to be separated from the UF_6 before it can be used for enrichment. The UF_6 is purified from these fluorides by fractional distillation at a pressure greater than the triple point of 1,134 mm of Hg.

See Figure 3-13, Distillation. Crude UF_6 is melted in the still feed tanks and feeds into a low-temperature boiler bubble-cap distillation column. In this column, the low boiling fluorides of vanadium, molybdenum, silica, carbon, and sulfur and an oxyfluoride (UOF_3) are volatilized and exit from the top of the column. The UOF_3 impurity is condensed in the UOF_3 condenser, cleaned, and stored. Impurities not removed in the condenser are fed back to the system just before the cold traps.

The bottom of the low boiling distillation column contains liquid UF_6 and high-boiling non-volatile fluorides like thorium and protactinium fluorides. This liquid is fed to the high boiler bubble-cap distillation column for purifying the UF_6 from the high boiler fluorides. In this column, the UF_6 vapor exits at the top and is condensed in two cold traps that operate in series. The bottom product of the column contains the high boiling/non-volatile fluorides, which are disposed of as wastes.

The high boiler distillation column bottom contains nonvolatile thorium and protactinium fluorides, which are gamma emitters. The distillation process yields a UF_6 product of high purity (99.99%). See Figure 3-14, NUF_6 Filling Station.

Figure 3-13. Distillation
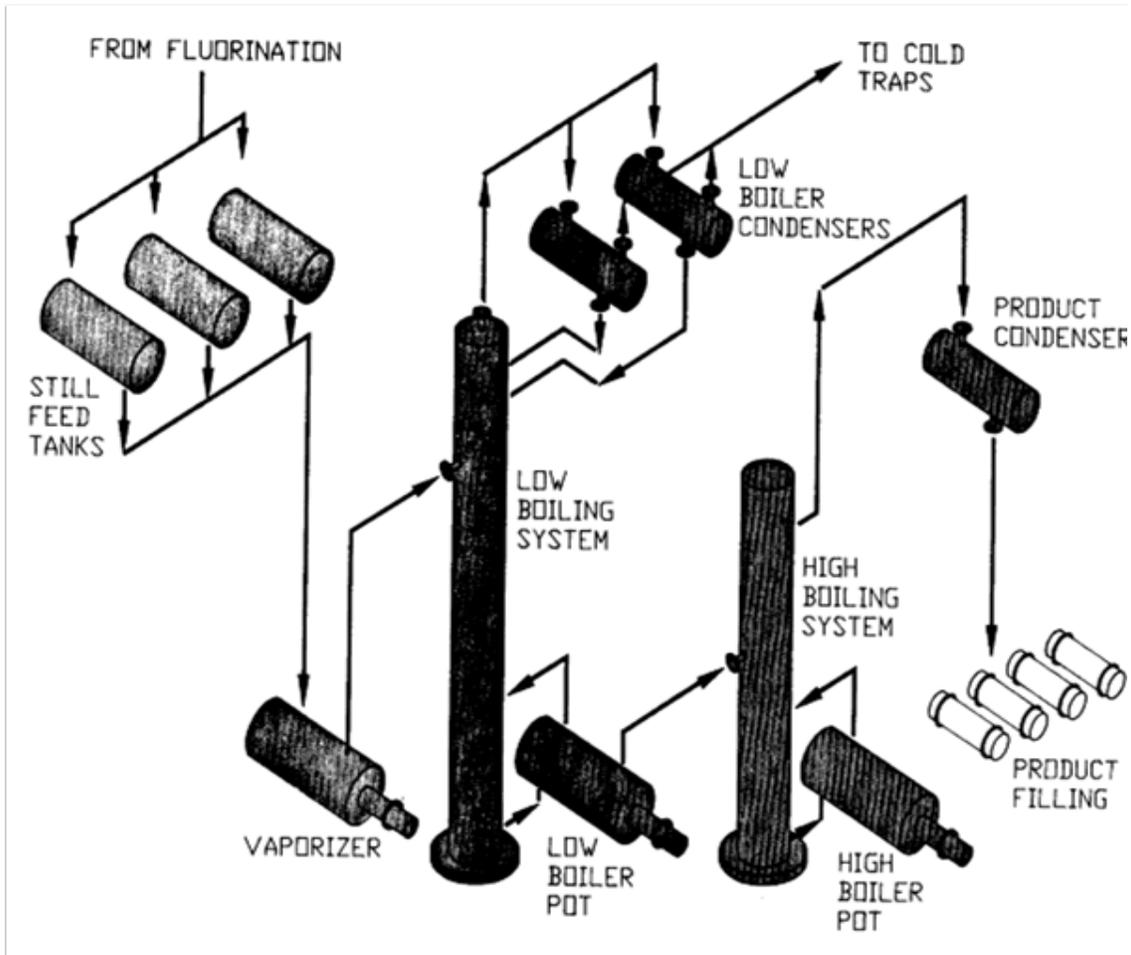
Figure 3-14. NUF$_6$ Filling Station

Potential Hazards

The following potential hazards could occur in distillation areas:

- ◉ Heating of vessels and cylinders containing excessive amounts of UF$_6$ could cause overpressurization.

- ◉ The potential for UF$_6$ release is increased because the UF$_6$ is processed as a liquid and a gas under pressure.

- ◉ Exposure to operating personnel could occur from a release of UF$_6$ from process equipment.

- ◉ UF$_6$ releases can occur at pigtail connectors, manifolds, and cylinder valves, and as a result of dropping cylinders filled with liquid UF$_6$.

- ◉ Hydrocarbon contamination of UF$_6$ can cause vigorous reactions.

- ◉ Possible internal exposure to highly soluble UF$_6$ could cause skin burns and chemical toxicity.

- ◉ Potential failure of cylinder crane, e.g., cables, lifting eyes, clevises, or strong backs, could crush workers and result in UF$_6$ release from a damaged cylinder.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in distillation areas:

◙   Relief valves are installed on each vessel to prevent overpressurization.

◙   All UF_6 product cylinders and valves are manufactured and inspected in accordance with NRC "Quality Assurance Program Approval for Radioactive Material Packages."

◙   Automatic steam shutoff valves are located on all vessels in the distillation process that vaporize UF_6.

◙   Portable CO_2 fire extinguishers are located on each floor of the Feed Materials Building.

◙   Each UF_6 product cylinder and pigtail is tested prior to filling.

◙   Safety features are installed in the distillation filling process to reduce the potential for overfilling a cylinder.

STEP 7 - PRODUCT LOADING AND SHIPPING

The purified UF_6 from the distillation column cold traps is packaged into 2.5-ton, 10-ton or 14-ton cylinders where it is allowed to cool for five days for solidification. After being analyzed, the final product is shipped to a gaseous diffusion plant. Typical shipping cylinders for UF_6 are shown in Figures 3-15 and 3-16. The UF_6 condensed in the cold traps is transferred to the shipping cylinders by liquefying it and allowing the material to drain into the cylinders. Table 3-1 shows the maximum cylinder heel weights for shipping.

Flow totalizers are used to measure the amount of UF_6 transferred to the cylinder and the UF_6 entering the cylinder is continuously sampled. On occasion, filled cylinders are placed and heated in a steam chest for vaporization or sampling.

Figure 3-15. 30B Cylinder (2.5-ton Shipping Container)

Figure 3-16. 48Y Cylinder (14-ton Shipping Container)

Table 3-1. Maximum Cylinder Heel Weights for Shipping

Cylinder Model No.	Heel		Maxium Uranium-235 %
	Lb UF$_6$	Kg UF$_6$	
5B*	0.1	0.045	100.00
5B**	0.5	0.227	100.00
8A*	0.5	0.227	12.50
12A or 12B*	1.0	0.454	5.00
30B*	25.0	11.34	5.00
48X, 48G, 48G, 48H, 48HX or 48OM*	50.0	22.68	4.50

*49 CFR 173.417(a)(7) authorizes shipment of these cylinders without a protective overpack if heels are at or below the limits in the above table.

**In protective overpacks.

Note: Heels weighing in excess of values in this table may require removal by cylinder cleaning. Systems should be configured and inspected to assure that contaminants or impurities are not injected into the cylinders during evacuations.

Self-Check Questions 3-2

INSTRUCTIONS: Complete the following questions. Answers are located
in the answer key section of the Trainee Guide.

---

1.   What is the purpose of the auger sampling system?

2.   How are drums of uranium ore concentrate received at the sampling plant?

3.   As ore is received at the Honeywell plant, what information does accountability personnel input into a computer system?

4.   What kind of scale is used to determine gross weight of each drum at the Honeywell facility?

5.   Why is the Honeywell auger room operated under a negative pressure?

6.   While in the Honeywell auger room, what three specific locations within the drum could be sampled?

7.   Match the steps of the dry volatility conversion process in column A with its description in column B.

Column A Steps

A.   Pretreatment

B.   Prepared Feed and Calcination

C.   Reduction

D.   Hydrofluorination

E.   Fluorination

F.   Distillation

G.   Product Loading and Shipping

Column B Description

1. _____   The UF_4 feed is introduced into the bottom of two parallel monel fluid bed fluorinators that contain calcium fluoride as inert bed material.

2. _____   Anhydrous hydrogen fluoride vapor in nitrogen diluent is used as a fluidizing medium to permit contact between the UO_2 and HF to form UF_4.

3. _____   Crude UF_6 is melted in the still feed tanks and feeds into a low-temperature boiler bubble-cap column.

4. _____   The calcined material is blended, agglomerated, dried, crushed, and sized for conversion to UO_2.

5. _____   Removes sodium by a four stage countercurrent treatment with ammonium sulfate solution.

6. _____   The calcined material is reacted with hydrogen in a fluidized medium to form UO_2.

7. _____   Purified UF_6 is packaged into 2.5-ton or 14-ton cylinders.

8.   In the dry conversion process, what other impurities besides sodium are removed from the pretreatment step?

9.   In the dry conversion process pretreatment step, what preventive measure is used to prevent dusting from ore concentrates?

10.   Calciners are used in the prepared feed and calcination step of the dry fluoride volatility conversion process. What are calciners?

11.   In the dry conversion process prepared feed and calcination step, what happens to calcined material prior to conversion to uranium dioxide?

12.   In the dry conversion process prepared feed and calcination step, why is uniform sizing of the concentrate essential?

13.   Name two potential hazards associated with the prepared feed and calcination step of the dry conversion process.

14.   In the dry conversion prepared feed and calcination step, what preventive measures are used for proper start-up and shutdown of process equipment?

15.   In the dry conversion process reduction step, what is calcined material reacted with in a fluidized medium to form UO_2?

16.   In the dry conversion process reduction step, what happens to uranium solids filtered from the reactor off-gas?

17.   From potential hazards associated with the reduction step, fill in the missing word(s) in each statement. Choose from the following words:

airborne	decay	flammable	insoluble
maintenance	stack	temperatures (600°C)	

◎   The process consumes hydrogen, which is＿＿＿＿＿＿＿＿＿＿ .

◎   Uranium＿＿＿＿＿＿＿＿＿＿＿products present in the UO_3 tend to concentrate in unreacted waste.

◎   Collection and removal of UO_2 present some potential for ＿＿＿＿＿＿＿＿＿contamination.

◎   System＿＿＿＿＿＿＿＿＿＿presents significant potential for creating airborne contamination.

◎   Internal exposure to ＿＿＿＿＿＿＿＿＿ UO_2 (Class "Y") material.

◎   Extreme process ＿＿＿＿＿＿＿＿＿are associated with reduction.

◎   Process＿＿＿＿＿＿＿＿＿emissions may have an impact.

18.   In the dry conversion process reduction step, what preventive measure prevents personnel from exposure to uranium?

19.   What is a common name for UF_4?

20.   In the dry conversion process, what gas is used to carry out the hydrofluorination process?

21.   In the dry conversion process, hydrofluorination reactor off-gas is filtered and scrubbed with what before release to the atmosphere?

22.   Give two reasons why hydrofluorination of UO_2 must be carried out with extreme caution.

23.   In the dry conversion process hydrofluorination step, what three potential radiological hazards are present?

24.   In the dry conversion process hydrofluorination step, what are relief valves vented to for preventive measures?

25.   In the dry conversion process fluorination step, what is used as the fluidizing gas or fluidizing medium to react with UF_4 to produce UF_6 vapor?

26.   In the dry conversion process fluorination step, exit gas passes through what for UF_6 collection?

27.   In the dry conversion process fluorination step, what could happen if oil comes into contact with F_2 or UF_6?

28.   In the dry conversion process fluorination step, where does external radiation levels occur?

29.   In the dry conversion process fluorination step, why is overpressurization and potential line rupture a potential hazard in cold traps?

30.   In the dry conversion process fluorination step, the fluorination process operates at (above or below) atmospheric pressure for preventive measure?

31.   In the dry conversion process distillation step, what happens to crude UF_6?

32.   In the dry conversion process distillation step, where can UF_6 releases occur?

33.   In the dry conversion process distillation step, what are installed on each vessel to prevent overpressurization?

34.   In the dry conversion process product loading and shipping step, what size cylinders are used for shipping?

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

URANIUM RECOVERY

Fluorinator filter fines and bed material, solids from settling ponds, and process liquids may be processed for uranium recovery. The uranium recovery system is a series of mixing, settling, and separation tanks in which uranium is precipitated as a sodium uranyl carbonate salt through contact with sodium carbonate and sodium hydroxide. The settled or filtered uranium solids are dried and recycled to the feed pretreatment system. The spent liquid is transferred to the EPF for neutralization and fluoride recovery.

Potential Hazards

The following potential hazards could occur in uranium recovery areas:

◉ Limited potential for internal exposure to airborne radioactivity, since the system processes liquors.

◉ Possible surface contamination from leaks and spills of uranium-bearing liquors.

◉ Possible employee exposure to corrosive alkaline chemicals used in the process.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in uranium recovery areas:

◉ Workroom air concentrations of radioactivity are continuously monitored.

◉ Expanded metal walking surfaces are provided to minimize personnel contamination, and the area is routinely monitored for surface contamination.

◉ Specific procedures and equipment are provided when employees may be exposed to alkaline solutions.

Self-Check Questions 3-3

INSTRUCTIONS: Complete the following questions. Answers are located
in the answer key section of the Trainee Guide.

1.   What is the uranium recovery system at Honeywell?

2.   What materials may be processed for uranium recovery at Honeywell?

3.   What are three potential hazards in uranium recovery?

4.   For preventive measure, how often should workroom air concentrations of radioactivity be monitored in uranium recovery areas?

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

CYLINDER WASH FACILITY

Before loading of the purified UF_6 to the shipping containers, the product cylinders must be washed if the heel exceeds the limit, and pressure-tested every five years per American National Standards Institute (ANSI) 14.1 to assure design integrity and to meet certification requirements. Note: The Department of Transportation (DOT) and Department of Energy (DOE) require that the vapor pressure has to be negative (a vacuum) before a cylinder can be shipped. The cylinders are washed with sodium carbonate solution to leach the uranium from the residual solids. The leach liquors are then filtered to remove the unleached solids and transferred to the uranium recovery facility. The remaining solids containing progeny products of uranium, principally Th-234 and Pa-234m, are stored on-site in drums and eventually disposed of at a low-level waste disposal facility.

Potential Hazards

The following potential hazards could occur for cylinder wash areas:

- ◉ Possible external radiation exposure from concentrated uranium progeny products.

- ◉ Possible surface contamination from spills or leaks of leach liquors.

Engineering Controls/Preventive Measures

The following engineering controls should be considered for preventive measures in cylinder wash areas:

- ◉ Filters used to remove particulate material containing the uranium progeny products are enclosed in lead shielding.

- ◉ Used filters are stored in an isolated, barricaded area to allow radioactive decay before disposal.

- ◉ Dikes and sumps are provided to contain any leaks of liquid solutions.

- ◉ Surface contamination monitoring is routinely performed.

Self-Check Questions 3-4

INSTRUCTIONS: Complete the following questions. Answers are located in the answer key section of the Trainee Guide.

---

1. Before loading of purified UF_6 to shipping containers, what should happen to product cylinders if their heel exceeds the limit?

2. What do DOT and DOE require before a cylinder can be shipped?

3. What happens to leach liquors from cylinder washing?

4. What are two potential hazards that could occur in cylinder wash areas?

You have completed this section.
Please check off your progress on the tracking form.
**Go to the next section.**

CHEMICAL HAZARDS

Uranium is handled in many different chemical forms in UF_6 conversion plants, but UF_6 is the only chemical form of uranium that can be readily dispersed off-site. UF_6 will react with water to form HF and UO_2F_2. Since airborne moisture is a generally available source, the reaction can be expected to occur if UF_6 is released to the atmosphere. The reaction is exothermic (heat-producing) for UF_6 existing in the gaseous state; therefore, heated UF_6 represents the only significant release hazard. Both the HF and the UO_2F_2 produced are hazardous chemicals. The HF is produced as a corrosive acid vapor that can severely harm the lungs and exposed portions of the body. The UO_2F_2, formed as particulate material, produces radioactive and chemical effects when taken into the body; the chemical effect is the most important because much of the uranium is present in soluble form. According to NUREG-1140, a release of natural UF_6 gas would not result in radiation doses exceeding one rem TEDE but would be lethal due to the chemical toxicity of uranium.

As previously mentioned, the Honeywell facility produces UF_6 by fluorination of UF_4. The UF_6, which is produced in a gaseous state, is collected in cold traps, where it is solidified by refrigerant cooling. Subsequent heating of the cold traps liquefies the UF_6 for transfer to cylinders, where the UF_6 cools to ambient temperature and again solidifies.

The cold traps and the cylinders contained within the Feed Materials Building (Honeywell) represent the largest accumulations of heated UF_6 and therefore pose the greatest risks of a significant release of UF_6. The filled cylinders represent the greater risk because of their temporary use in the process, the large numbers of individual cylinders utilized, their typically larger inventories of UF_6, and their routine movement within the facilities before solidification. Although the filled cylinders are considered to be the greater risk, these risks are also applicable to filled cold traps.

Because UF_6 is volatile above room temperature, the quantity of UF_6 released could be significant. The UF_6 released will react with water in the air as follows:

$$UF_6 + 2H_2O \text{---}> UO_2F_2 + 4HF + 52.2 \text{ kcal/mole}$$
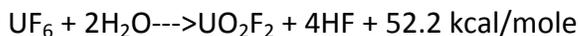
The release of 1 kilogram (kg) of UF_6 combining with 0.1 kg water results in a release of 0.88 kg of UO_2F_2 (which contains 0.68 kg of uranium) and 0.23 kg of HF.

The following chemicals have been identified through Honeywell's chemical hazard assessment:

- ◉ Uranium hexafluoride
- ◉ Anhydrous ammonia
- ◉ Anhydrous hydrofluoric acid
- ◉ Liquid fluorine

◙   Liquid Propane Gas (LPG)

◙   Hydrogen (produced in process, but not stored anywhere on site)

Self-Check Questions 3-5

INSTRUCTIONS: Complete the following questions. Answers are located in the answer key section of the Trainee Guide.

---

1.   When UF_6 reacts with water, what chemical hazards result?

2.   Where are the largest accumulations of heated UF_6 at Honeywell and what risk does this pose?

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

ENVIRONMENTAL MONITORING PROGRAM

The environmental monitoring program at Honeywell involves sampling of air, soil, vegetation, surface water, and sediment. It also measures ambient radiation at locations on or near the facility.

An investigation level for gaseous uranium emissions is used based on the average of four continuous air samples collected at the restricted area fence line. The samples are collected and analyzed for trends on a weekly basis. The investigation level is based on a quarterly uranium concentration, which would produce an annualized dose of 10 mrem. In addition, uranium in the air is monitored at sampling location adjacent to the home of the nearest residence north-northeast of the plant. If the average concentration of total alpha radioactivity (the sum of natural uranium, Ra-226, and Th-230) measured from samples collected from this location exceeds 3.0×10^{-14} µCi/ml over any calendar quarter, then within 30 days Honeywell must submit a written report to NRC identifying the cause for exceeding the dose constraint under Title 10 CFR Part 20 and the corrective actions to reduce the radioactivity release rates. This concentration would produce an annualized dose of 10 mrem committed effective dose equivalent (CEDE) if someone were continuously present at the fence line.

HONEYWELL HAZARD SCENARIOS

Accident scenarios that are possible at Honeywell include a spill of U_3O_8 powder, inadvertent venting of a pigtail during connection and disconnection of lines used for UF_6 transfer, a UF_6 (solid) cylinder leak, a UF_6 (liquid) cylinder rupture, or an ammonia storage line failure. The following scenarios are extracted from a Honeywell safety analysis report.

Spill of U_3O_8 Powder

Uranium is present in several solid forms at the Honeywell facility. Past experience has demonstrated that the procedures used in handling containerized or entrained solids can result in spills of the material. Spills in powder form can create an airborne situation where uranium intake could occur.

Inadvertent Venting of a Pigtail

Connection and disconnection of lines used for UF_6 transfer are normal in the loading of a cylinder following product purification. Normally, such lines are evacuated or de-gassed before disconnection. However, procedures may be misunderstood or improperly executed with a resulting release into the process area and subsequent release to the environment through the ventilation system.

Leak from a UF_6 Cylinder (Solid)

Mechanical equipment is used to transport cylinders to and from the filled-cylinder storage area. Because of an initially damaged valve or because of impact in the storage area, solid UF_6 within a cylinder may be exposed to the atmosphere. After the valve is damaged, air enters the

cylinder and UF_6 begins to react with atmospheric moisture and the reaction produces HF and UO_2F_2, which could flow out of the cylinder.

Rupture of a UF_6 Cylinder (Liquid)

At the Honeywell facility, UF_6 in the liquid state is in purification system surge tanks and distillation columns and in product cylinders. When uranium hexafluoride temperature is above 60°C (148°F), it is in a liquid state and potentially hazardous. The hazard is from the potentially large quantity of particulate uranium and gaseous HF that could be released on loss of confinement of the liquid UF_6. If a release were to occur indoors, plate-out and deposition would reduce the amount of material released to the environment. However, because the ventilation system changeover rates in areas where liquid UF_6 is handled are high and the vents are not elevated, release rate could be high. While the potential consequences of occurrence of the event are severe, the likelihood of occurrence is low because of design and procedural controls.

Overpressurization is controlled by periodic washing and testing of cylinders, by limiting the temperature of steam used to liquefy the UF_6, and by use of independent load cells and flow totalizers during filling of cylinders. Controls against a cylinder drop include preventive maintenance for the cylinder crane that includes weekly service and independent monitoring of cylinder movements by two operators.

Release of Gaseous Ammonia

Large quantities of industrial chemicals are stored at the Honeywell facility. Anhydrous HF is stored in a tank, which is vented to a backup tank fitted with a scrubber. Thus, protection is provided for mitigation of failure of the primary storage system. Large quantities of sulfuric acid are also stored at the facility. Sulfuric acid is not as volatile as other chemicals stored at the site and is therefore less hazardous. Ammonia, a strong base that can be lethal at high concentrations, is representative of the hazards associated with stored chemicals at the facility.

Ammonia is stored under pressure as a liquid in the tank farm area. Development of a leak in the tank or associated piping could result in an uncontrolled release of this substance.

Releases of ammonia would be expected to produce noticeable effects onsite and offsite. Large releases could result in life-threatening conditions either onsite or offsite.

Release of Anhydrous HF

The UF_6 conversion process consumes relatively large quantities of corrosive raw materials; in particular, anhydrous HF. Plant accidents that release substantial amounts of HF could produce short-term offsite environmental effects.

For the analysis of atmospheric release of HF, it was assumed that the release persists for one hour, that it occurs at ground level, and that it occurs in the open so that there is no attenuation by filtration or scrubbing.

MODULE 3.0:   URANIUM CONVERSION

Experimental data and occupational experience indicate that man is susceptible to irritation from gaseous HF. At 10 mg/m^3, the mucosa are irritated; at 26 milligrams (mg)/m^3 for 3 minutes, the worker is uncomfortable and able to taste the gas; at 50 mg/m^3, the severity of the irritation increases; at 100 mg/m^3, a stinging sensation of the skin is added, and other irritations are so severe as to make exposure for more than a minute intolerable. For this reason, it is unlikely that persons able to escape would remain in the toxic cloud for any length of time. Figure 3-17 shows Protective Action Recommendations.

There have been two significant releases of HF in the 31-year operating history of the Honeywell plant. The first involved the leakage of 95 lb of UF$_6$, which, fully hydrolyzed, is equivalent to about 22 lb of HF. The leak occurred in the UF$_6$ building as a result of a valve failure in the distillation section. Elevated fluoride concentrations were not detected offsite because of the effectiveness of emergency control procedures.

In the second incident, a leak was detected in an HF tank car awaiting delivery to the plant. It is estimated that a total of about 250 lb of HF was lost over a period of more than one hour; emergency procedures were instituted to prevent the spread of the material, and no off-site impact was observed.

Releases of HF would be expected to produce noticeable effects onsite and offsite. Large releases could result in life-threatening conditions either onsite or offsite. Honeywell has added a spray nozzle deluge system to mitigate the potential effects of small chemical releases in the tank farm area. See Figure 3-18.

Figure 3-17. PAR – Protective Action Recommendations
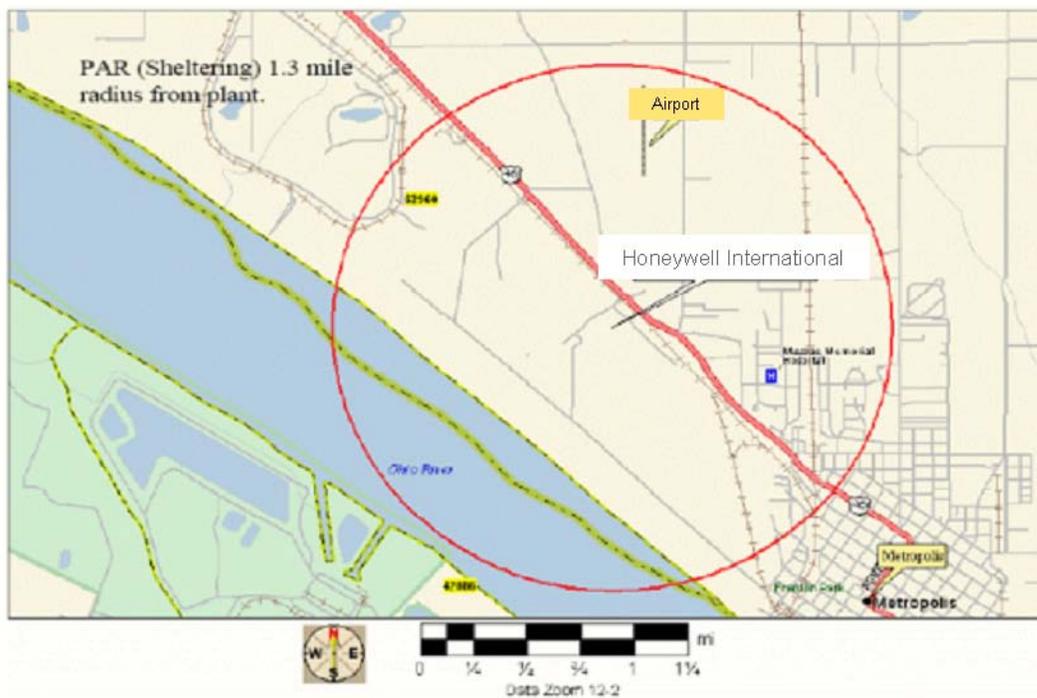
Figure 3-18. Tank Farm Area and Deluge Nozzles (on columns)

Self-Check Questions 3-6

INSTRUCTIONS: Fill in the missing words in each statement. Answers are located in the answer key section of the Trainee Guide. Choose from the following words.

---

atmosphere	evacuated	intake	reduce	UO_2F_2
crane	HF	load cells	steam	Valve
de-gassed	Improperly	procedures	surge	washing
distillation	Independent	product	tank car	

1. Spills in powder form can create an airborne situation where uranium _____ could occur.

2. Connection and disconnection of lines used for UF_6 transfer are normal in the loading of a cylinder following product purification. Normally, such lines are _____or _____ before disconnection.

3. Inadvertent venting of a pigtail could occur if _____ are not followed or the pigtails are _____ handled.

4. Solid UF_6 may be exposed to the _____ due to a damaged valve or ruptured cylinder.

5. UF_6 reacts with atmospheric moisture and the reaction produces _____ and _____, which could flow out of a cylinder.

6. At the Honeywell facility, UF_6 in the liquid state is in purification system tanks and _____ columns and in _____ cylinders.

7. If a uranium hexafluoride release were to occur indoors, plate-out and deposition would _____ the amount of material released to the environment.

8. Overpressurization is controlled by periodic _____ and testing of cylinders, by limiting the temperature of _____ used to liquefy UF_6, and by use of independent _____ and flow totalizers during filling of cylinders.

9. Controls against a cylinder drop include preventive maintenance for the cylinder _____ that includes weekly service and _____ monitoring of cylinder movements by two operators.

---

10.   Large quantities of industrial chemicals such as anhydrous HF, sulfuric acid, and
_____ are stored at the Honeywell facility.

11.   Two significant releases have occurred at Honeywell: the first one occurred in the UF_6
building as a result of a _____ failure in the distillation section, and the
second one occurred when a leak was detected in an HF _____ awaiting
delivery to the plant.

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

RADIOLOGICAL AND NON-RADIOLOGICAL HAZARDS

Chemical conversion processes tend to concentrate uranium decay products in the waste streams. Alpha particles resulting from the primary disintegration of uranium present no external radiation problem, because they do not penetrate the skin. However, the decay products of uranium include isotopes that emit mildly penetrating beta rays and highly penetrating gamma rays. Beta radiation levels as high as 200 mrad/hr may be found at the surface of UF_6. When UF_6 is vaporized from a cylinder, the decay products usually remain behind. Thus, the internal surfaces of an empty cylinder may have beta radiation levels up to several rad/hr. Similarly, the gamma radiation from an empty cylinder will be much higher than from a filled cylinder and may range up to 200 mrad/hr.

The chemical characteristics of these contaminants will cause significant exposure levels of beta and gamma radiation from the uranium decay product activity in certain sections of the process. The risk of radiation exposure increases during maintenance of process equipment, transfer of product, and handling of UF_6 cylinders.

From a chemical toxicity standpoint, the Class D transportable (soluble) compounds of uranium (e.g., UF_6, UO_2F_2, $UO_2(NO_3)_2$) present the greatest concern. However, with insoluble uranium compounds (uranium metal, uranium oxides, etc.), the dominant hazard is normally the radiotoxicity.

The Honeywell facility releases radioactive material to the atmosphere through 52 monitored release points and reports measurements of the activity released to the NRC on a semi-annual basis. The uranium emissions by isotope and by solubility class from the feed materials building, the uranium recovery facility, and the ore sampling plant are summarized in Table 3-2.

Table 3-2. Summary of Atmospheric Releases from the Metropolis Facility (1990 through 1993)

	Release by Solubility Class (Ci/yr)		
Building	**D**	**W**	**Y**
Feed Materials Building			
U-234	0.024	0.0044	0.013
U-238	0.024	0.0044	0.013
U-235	0.001	0.002	0.00058
Uranium Recovery Facility			
U-234	4.6×10^{-6}	8.4×10^{-7}	2.4×10^{-6}
U-238	4.6×10^{-6}	8.4×10^{-7}	2.4×10^{-6}
U-235	2.1×10^{-7}	3.8×10^{-8}	1.1×10^{-7}
Ore Sampling Plant[a]			
U-234	4.0×10^{-4}	7.3×10^{-5}	2.1×10^{-4}
U-238	4.0×10^{-4}	7.3×10^{-5}	2.1×10^{-4}
U-235	1.8×10^{-6}	3.3×10^{-6}	9.7×10^{-6}

[a]2.3 x 10-4 Ci/yr of Th-230 and 1.9 x 10-5 Ci/yr of Ra-226 are also released from the Metropolis facility, but are not attributed to a specific emission point or building. These emissions were allocated to the ore sampling plant because emissions from this building had the largest atmospheric dispersion factor.

Radiological Accident Analysis

A large UF_6 release is the only radiological event that has the potential to cause health hazards to the nearby population. Although a major chemical spill might have an impact on the nearby population, a condition has not been hypothesized in which a major chemical spill would result in the release of UF_6. During such an event, the UF_6 production operation could quickly be shut down and employees evacuated from the affected production areas.

The currently installed engineered safeguards in the UF_6 cylinder filling and handling area are adequate to preclude a large, uncontrolled release of UF_6, which might produce significant off-site consequences.

Computerized dispersion modeling has also been used to determine the potential impact of this maximum credible accident. Using the conservative assumption that one-third of the indoor release escapes the building vents, the calculated concentration at the nearest fence line would be 2.4 mg/m^3 of UO_2F_2 in air. This concentration is visible and would be declared a Site Area Emergency. If a member of the public were present at the fence for the entire duration of the 30-minute release modeled, the intake of soluble uranium would be 1.1 mg. This intake is below the 8-mg threshold that might produce some transient changes in urine, indicating some effect; it is significantly below the 40-mg intake level, which might be the beginning of permanent kidney damage.

Although a release of this magnitude might be visible at the nearest plant boundary, it would not be expected to produce measurable changes in the off-site environment.

Liquid Waste Management

Liquid waste streams generated at the Metropolis facility are categorized as low-level radioactive and nonradioactive waste streams. Each of the waste streams are recycled or treated separately. All liquid effluent from the plant is discharged from outfall locations and drain to the Ohio River in a natural drainage.

Low-level radioactive liquid wastes produced at the Metropolis facility consist of wash water from the ore sampling building, ammonium sulfate process solutions from the pretreatment facility, HF scrubber liquors from the hydrofluorinators, KOH scrubbing solutions from air pollution abatement equipment, sodium carbonate leach liquors from uranium recovery and UF_6 cylinder washing, and uranium contaminated stormwater from the feed material building area. The uranium recovery leach liquors are recycled in the uranium recovery process until the fluoride concentrations exceed the operating specifications. The KOH scrubbing solutions are regenerated and recycled on-site and solids removed from the scrubber solutions are processed for calcium fluoride recovery.

Watersheds from the ore sampling building and ammonium sulfate solutions from the pretreatment facility area are routed to uranium settling ponds where the pH is maintained slightly basic to minimize dissolved uranium loss. Effluent flow from ponds averages about 94 liters per minute (25 gallons per minute) and is mixed with other plant effluents before discharge at an outfall location. Sludge from ponds is periodically removed to maintain at least 0.6 meters (2 feet) of freeboard. It is pumped to the pond's mud calciner to be dried and packaged into drums. The dried solids are processed through the uranium recovery system for uranium recovery.

Wastewaters with significant quantities of fluoride (i.e., HF scrubbing liquors and uranium recovery leach liquors) are routed to the EPF for lime treatment and recovery of the fluoride as CaF_2 in settling ponds. The effluent from the EPF and settling basins has a pH of approximately 13, which is adjusted with sulfuric acid to a pH range of 6 to 9. This stream is combined with other plant effluents before discharge at an outfall location. Calcium fluoride that precipates in the EPF settling basins is recovered for recycle by commercial industry to use as a substitute for natural fluorspar.

There are no mixed waste streams generated as part of the UF_6 manufacturing process. Liquid mixed waste currently in on-site storage was generated from either maintenance or laboratory activities. Typical mixed wastes include items such as radiologically contaminated xylene paint thinner, used lubricating oils, and waste naphtha from maintenance or cleaning activities; and waste acetone, tributylphosphate, TEHP, and CFC-113 from various laboratory activities.

Nonradiological aqueous waste streams include sulfuric acid waste, sanitary waste water, and

storm water runoff from non-process areas. An Imhoff tank is used for primary treatment of sanitary waste water before discharge to an outfall location. Storm water runoff from non-process areas and process waters from the power house (used in boilers and for cooling purposes) are discharged without treatment. Hazardous liquid wastes are drummed, analyzed, and disposed of using outside contractors.

All of the facility's liquid effluent (i.e., process wastewater, treated sanitary sewage, storm water runoff) is discharged from the outfall location into the Ohio River via natural drainage in accordance with a NPDES permit. The 1989-93 average effluent discharge rate was 3.4 million gallons per day (mgd) or about 5.3 ft^3/s. Effluent at the outfall location is continuously sampled and monitored.

Solid Waste Management

Solid wastes generated at the Metropolis facility include low-level radioactive, nonradioactive and hazardous wastes. As described in the following text, a combination of recycling, compaction, incineration, and offsite disposal are used in management of these wastes.

Dry active waste, which consists primarily of contaminated filters, papers, floor sweeping compounds, cleaning rags, and gloves, is generated at a rate of about 10 metric tons/year (yr) (220,000 lb/yr) with an average uranium content of 440 pCi/g. This waste is collected in marked containers, segregated by radioactivity, drummed and either compacted onsite or shipped to a licensed supercompactor before final disposal at a licensed site. The estimated annual compacted volume is about 56.6 to 142 m^3/yr (2,000 to 5,000 ft^3/yr).

About 680 metric tons (1,500,000 lb) of fluorination reactor ash with an annual average uranium concentration of 10,000 pCi/g is produced each year. The reactor ash is processed through the on-site uranium recovery system along with other miscellaneous waste streams including recovered dust and scrap materials. Waste materials from the uranium recovery process (principally inorganic fluorides) are packaged for recycling or storage pending disposal at a licensed low-level radioactive waste disposal facility.

About 3,220 metric tons (7,100,000 lb per year) of synthetic calcium fluoride (CaF$_2$) containing about 105 pCi/g of uranium are shipped to commercial plants that can use this synthetic CaF$_2$ in industrial processes.

Contaminated pieces of process equipment and other scrap metal being discarded are decontaminated where feasible. Contaminated scrap metal waste is also compacted for volume reduction before disposal. An estimated 28 m^3/yr (1,000 ft^3/yr) of contaminated metal (primarily crushed drums) will be generated by continued operation of the Metropolis facility. This will be sent to a licensed low-level waste disposal facility whenever practical.

Nonradioactive Solid Waste and Treatment

Nonradioactive solid waste generated at the Metropolis facility includes miscellaneous trash, paper, scrap metal, and wood. Non-contaminated scrap metal and wood are sold to scrap dealers or are released for reuse after thorough radiation monitoring is performed to assure that the residual radioactivity level is below the NRC release criteria. It is estimated that about 212 to 255 cubic meters (7,500 to 9,000 cubic feet) of non-contaminated solid waste is annually produced at the plant. The plant also has an operating permit for incineration of miscellaneous combustible trash.

NUCLEAR CRITICALITY SAFETY

The Committee on the Safety of Nuclear Installations (CSNI) Specialist Meeting on the safety problems associated with the handling and storage of UF_6, held in 1978, concluded the following: (1) the existing processes for uranium refining and conversion to UF_6 give rise to no significant radiological hazards, and (2) the safety problems associated with these operations are essentially those of a conventional industry dealing with toxic chemicals. However, adequate precautions should be implemented to protect workers from exposures to high-radiation fields associated with the flame reactor and ash handling operations, and from the hazards of inhaling uranium dust.

It should be noted that uranium conversion facilities receive yellowcake from milling operations that contain 0.711% uranium-235. As a result, there are no nuclear criticality concerns at uranium conversion facilities. The only material having an uranium-235 enrichment greater than 1% are classified as potential nuclear criticality hazards.

FIRES AND EXPLOSIONS

The principal fire hazards in a uranium conversion facility are related to storage, transfer, and use of flammable and combustible liquids, such as LPG, anhydrous ammonia, and hydrocarbon solvents; flammable gases, such as natural gas and hydrogen; and chemicals, such as nitric acid and fluorine, which may combine with organic materials to cause fire.

A number of chemical substances are used as bulk reactants or as source material for production of such reactants in the UF_6 production process. The most prominent presenters of fire hazards and the nature of those hazards follow.

◉ **Nitric acid:** In the solvent extraction process, yellowcake is digested with nitric acid in large tanks. Nitric acid itself is nonflammable, but under certain conditions, it nitrates organic materials, making them easily ignitable. Nitric acid spills thus constitute a fire hazard. In addition, nitric acid poses a corrosion and toxicity hazard.

◉ **Flammable and combustible liquids:** The solvent extraction process uses a mixture of organic solvents, some components of which may have flash points (temperatures, determined by standard tests under atmospheric pressure, at which vapor issuing from the solvent will ignite upon receiving an ignition stimulus) in the range of 90°F to 165°F.

The digested feed, uranyl nitrate, is introduced in the solvent extraction circuit, where the solvent mixture absorbs by stages more and more of the uranium nitrate. Spills from the large solvent extraction vessels are fire hazards to be protected against.

◉ **Sulfuric acid:** Sulfuric acid is the reagent used for digesting yellowcake with high sodium content before reduction in the hydrofluoric "dry" process. In addition to its corrosion and toxicity hazards, this chemical can absorb water from organic materials, accompanied by an exothermic reaction, which may ignite them.

◉ **Anhydrous ammonia:** This chemical is used as source material for production of hydrogen for use in reduction processes, such as the hydrofluoric process of UF_6 production. Anhydrous ammonia is a flammable gas, which is stored and pumped in the liquefied state and undergoes high temperature dissociation at about 1650^oF, into hydrogen and nitrogen. Both gases thereafter flow through heaters and reductors. Anhydrous ammonia presents fire and explosion hazards, the latter if ignited in a confined space. It also presents a toxicity hazard.

◉ **Hydrogen:** Hydrogen is well known as having the highest burning velocity of all gases, as well as a wide range of flammability in mixtures with air. There would obviously be fire and explosion hazards in the event of a leak from any equipment handling or using hydrogen. Further explosion hazards are presented by vessels such as reductors, heaters and filters, where explosive mixtures of hydrogen and oxidizers may form inadvertently.

◉ **Fluorine:** Elemental gaseous fluorine is used in the final reaction to produce UF_6. Fluorine is produced in a battery of electrolytic cells in which hydrofluoric acid is decomposed into hydrogen and fluorine. Fluorine is compressed by centrifugal compressors and delivered to the fluorination reaction vessels. The hydrogen component is either burned off or released to the atmosphere. Fluorine is one of the most reactive elements known. In addition to being highly corrosive and toxic, it reacts violently with hydrogen and many organic materials, causing fires, even though it is itself nonflammable. Fluorine may also cause explosions in contact with metallic powders and water vapor.

Other process-related fire hazards are connected with the high temperatures used in calciners, which may be heated electrically or by natural gas flames, and in ammonia dissociators.

Fire Accident Analysis

A major fire cannot be hypothesized in a radioactive materials usage area due to nonflammable materials of construction. However, a fire could occur in office or storage areas, which are generally some distance from chemical usage areas. These areas are provided with sprinkler systems, fire extinguishers, and fire hoses. The plant emergency response team would be activated to control any major fire that might occur.

NATURAL PHENOMENA

Tornadoes/Extreme Winds

Tornadoes and extreme winds do occur in the Midwest and present a potential hazard to the Honeywell facility. Extreme winds have a locally devastating effect and require special construction design. High winds, coupled with steep pressure changes, may damage the integrity of ventilation systems and may result in loss of containment at conversion facilities. This probability increases in the event of damage to process equipment from missiles.   These conversion facilities are not designed to withstand tornados, and damage to a chemical tank or liquid UF_6 area could result in significant releases and onsite and offsite effects. The effects could be lethal.

Earthquakes

Conversion facilities are not seismically qualified. A significant earthquake could result in significant damage and large releases, with onsite and offsite effects. The effects could be lethal. The New Madrid fault is located near Honeywell; a seismic event from this fault could have catastrophic effects upon the Honeywell facility and produce large releases with life-threatening effects.

Emergency Shut Down

The decision to shut down processes or the entire plant during a major emergency is the responsibility of the shift supervisor. This individual has the necessary information and authority to determine which processes should be shut down, as well as appropriate response actions.

The entire plant can be shut down immediately, as the result of a major power outage, with no release of hazardous materials. Systematic securing of all operating units and dispensing of standby power normally require approximately three hours. All raw materials flow can be stopped immediately; therefore, the major emphasis during an emergency shutdown is placed on providing steam to vessels and lines containing UF_6. This prevents UF_6 blockage of lines and eliminates the potential of a UF_6 release when the production process resumes.

1.   Chemical conversion processes tend to concentrate uranium decay products in waste streams. Why is this a problem?

2.   What radiological hazards occur when UF_6 is vaporized from a cylinder?

3.   Risks of radiation exposure increases during what types of activities?

4.   From a chemical toxicity standpoint, the class D transportable (soluble) compounds of uranium present the greatest concern. What are three examples of class D compounds?

5.   With insoluble uranium compounds (uranium metal, uranium oxides, etc.), the dominant hazard is normally what?

6. Match the area within the Honeywell facility in column A with the low-level radioactive liquid wastes listed in column B.

	Column A Area		Column B Low-level Liquid Wastes
A.	Air pollution abatement equipment	1.	Sodium carbonate leach liquors
B.	Feed material building	2.	KOH scrubbing solutions
C.	Hydrofluorinators	3.	Uranium contaminated storm water
D.	Ore sampling building	4.	Ammonium sulfate process solutions
E.	Pretreatment facility	5.	HF scrubber liquors
F.	UF$_6$ cylinder washing and Uranium recovery	6.	Wash water

7. What happens to uranium recovery leach liquors?

8. What happens to KOH scrubbing solutions?

9. What happens periodically to sludge from ponds?

10.   What happens to wastewaters with significant quantities of fluoride?

11.   What happens to hazardous liquid waste?

12.   How often is effluent at the outfall location sampled and monitored?

13.   What happens to dry active waste (contaminated filters, papers, floor sweeping compounds, cleaning rags, and gloves)?

14.   What should occur prior to non-contaminated scrap metal and wood being sold to scrap dealers?

15. Are there nuclear criticality hazards at a conversion facility? Briefly explain your conclusion.

16. What are six chemicals that present a fire or explosion hazard at Honeywell?

17. In what process area could nitric acid spills be prevalent?

18. What is the reagent used for digesting yellowcake with high sodium content before reduction in the hydrofluoric dry process and what hazards could it pose?

19. What is well known as having the highest burning velocity of all gases?

20. Explosion hazards are presented by vessels such as reductors, heaters, and _____ where explosive mixtures of hydrogen and oxidizers may form inadvertently.

21. Why is fluorine considered a possible fire and explosion hazard?

22. At a conversion facility, what problems could occur with high winds coupled with steep pressure changes?

23. At the Honeywell facility, all raw materials flow can be stopped immediately; therefore the major emphasis during an emergency shutdown is placed on providing steam to vessels and lines containing UF_6. Why?

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

Activity 1 – Sequoyah Fuels Accident

PURPOSE: The purpose of this activity is to review the Sequoyah Fuels Accident and then based on the information provided, list the probable causes of the accident, recommendations to prevent reoccurrence of the accident, and identify lessons learned from the accident.

INSTRUCTIONS: Read the following accident information and answer the questions at the end of the activity. Answers are located in the answer key section of the Trainee Guide. Additional information can be found in the following references:

"Release of UF$_6$ from a Ruptured Model 48Y Cylinder at Sequoyah Fuels Corporation Facility: Lessons-Learned Report," U.S. Nuclear Regulatory Commission, NUREG-1198, June 1986.

"Assessment of the Public Health Impact from the Accidental Release of UF$_6$ at the Sequoyah Fuels Corporation Facility at Gore, Oklahoma," U.S. Nuclear Regulatory Commission, NUREG-1189, Vol. 1, March 1986.

Introduction

A serious accident involving a UF$_6$ release occurred in January 1986 when a Model 48Y cylinder filled with UF$_6$ beyond its 14-ton capacity ruptured while it was being heated in a steam chest at the Sequoyah Fuels Conversion (SFC) Facility, Oklahoma. Figure 3-16 shows the specifications for the Model 48Y cylinder.

Heating an overfilled cylinder was prohibited by company procedures and the NRC license. It was widely recognized in the industry as a dangerous and unacceptable practice. The cylinder ruptured because of hydrostatic pressure. The pressure was caused by the expansion of UF$_6$, which expands significantly when solid UF$_6$ melts and becomes a liquid. There was not enough room for expansion in the overfilled cylinder.

The rupture was about 4 ft long, and the release lasted for a period of about 40 minutes. Most of the contents--approximately 14,000 kg--escaped in less than a minute. See Figure 3-19, Cylinder Rupture Closeup.

One worker was killed because of pulmonary edema caused by HF. Several others experienced skin burns, irritation to the eyes and mucous membrane, and respiratory tract irritation. No symptoms were found among people exposed offsite, about one mile from the release point.

Facility Operation

The SFC facility produced high-purity UF_6 from uranium concentrates (yellowcake). The manufacturing process being used included wet chemical purification to convert yellowcake to pure uranium trioxide followed by dry chemical reduction, hydrofluorination, and fluorination techniques to produce UF_6. At the end of the UF_6 production process, the UF_6 is condensed into cold traps. When any cold trap is full, the UF_6 is melted and drained by gravity through porous Monel filters into evacuated 10-ton or 14-ton shipping cylinders, where it slowly solidifies at ambient temperatures. The amount of material introduced into a cylinder is measured by observing the weight gain of the cylinder while it is on a set of scales during the filling process.

After filling, the cylinders are weighed and transferred to the cylinder storage area in the yard. The cylinders are cooled for a minimum of five days before shipment.

Description of Accident

A cylinder containing about 29,500 lb of UF_6 ruptured at the SFC site, releasing its contents into the atmosphere. Plant employees had inadvertently overfilled a 14-ton cylinder (maximum limit is 27,560 lb) and were in the process of heating the cylinder to facilitate removing the excess UF_6 when the rupture occurred.

As a result of overpressurization, the wall of the 12-ft cylinder split over a length of about 52 in. parallel to the axis of the cylinder, forming an opening about 8 in. wide at the midpoint of the split. As a result of the high pressure in the cylinder, the large size of the opening, and the fact that the cylinder rotated so that the split was on the lower side of the cylinder, much of the UF_6 came out of the cylinder rapidly.

Figure 3-20 is a diagram of a UF_6 Model 48Y, showing normally filled content weight. Released UF_6 and its reaction products, UO_2F_2 and HF, made a dense white cloud, which, pushed by the wind, quickly engulfed the process building and formed a plume expanding to the south-southeast.

At the time of the incident, there were 42 workers at the plant site. Thirty-two were SFC employees, and ten were employees of various contractors. Of these latter ten, seven were reportedly located in a trailer well away from (and upwind of) the release point. One SFC employee was in a scrubbing tower adjacent to the release point; his location was promptly enveloped in the initial plume from the release, and he died of respiratory injuries within a few hours. The majority of the remaining SFC employees and three contractor employees were in the main process building. The on-site personnel who were in the process building or the

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attached administration building promptly evacuated this structure and moved to a rendezvous point well to the north (upwind) of the release point. To reach this site, some individuals had to pass through the plume. The contractor employees in the trailer also moved to the evacuation point, but did not pass through the plume and presumably had minimal opportunity for exposure.

Following the arrival of the evacuees at the evacuation point, eight workers returned to the area of the ruptured cylinder to attempt to control the release. These workers approached from the upwind direction and began spraying the area with water, using fogging nozzles in an attempt to minimize spread of the released material. During the initial stages of this procedure, they reportedly had no personal protective equipment, not even respiratory protection. Later they acquired cartridge respirators.

Figure 3-19. Cylinder Rupture Closeup

Figure 3-20. UF$_6$ Cylinder Model 48Y Normally Filled Contents Weight: 27,560 Pounds
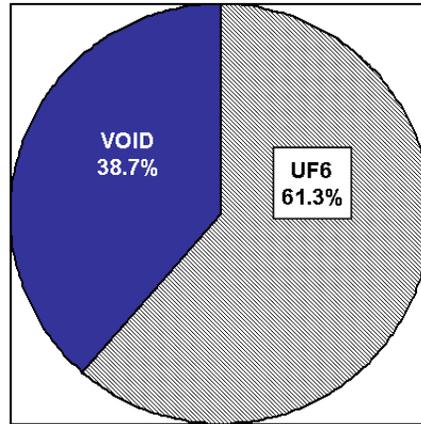
SOLID 100 F
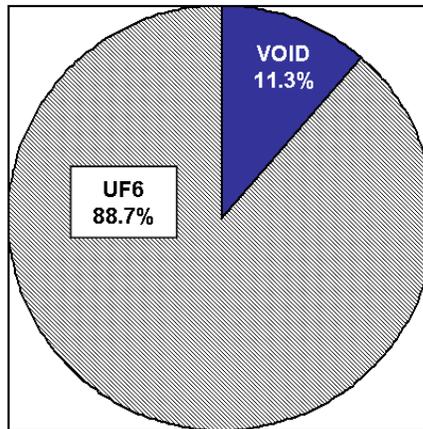
LIQUID 200 F
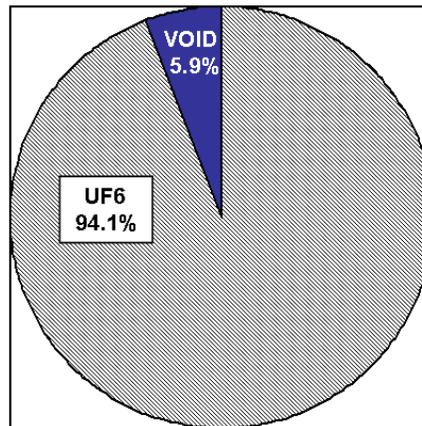
LIQUID 250 F

At the same time as the area was being sprayed, workers took steps to quench the flow of fumes and vapors that continued to escape from the damaged cylinder. A large number of towels and rags were soaked in water and stuffed into the rupture opening. These activities continued for 30 to 40 minutes after the initial release, until evolution of fumes and vapors stopped.

After the Accident

Approximately 37 people, mostly company employees, were hospitalized as a result of the incident. One worker died because he inhaled hydrogen fluoride fumes, a reaction product of UF_6 and airborne moisture. Several other workers were injured by the fumes, but none seriously. Much of the facility complex and some off-site areas were contaminated with hydrogen fluoride and a second reaction product, uranyl fluoride. The results of the off-site impact analysis indicated that no lasting health or ecological harm was done.

Bioassay results for 36 workers showed an average uranium intake of about 6.5 mg and a maximum intake of about 28 mg. Nine of the workers were exposed to uranium in excess of the NRC regulatory limit at that time (9.6 mg/week), but no symptoms of kidney injury were observed.

Released Quantities

As described previously, the cylinder was to have been filled with 27,500 lb of UF_6, but was actually filled with more than 29,500 lb. It has been estimated that at 212°F the cylinder volume had a volume equivalent of 31,400 lb.

When the UF_6 left the ruptured cylinder, it reacted with the available water to form UO_2F_2 and HF. Not all the UF_6 reacted immediately; pieces of solid UF_6 were scattered around the steam chest. Any UF_6 remaining when the area was sprayed down reacted with the water. Both UO_2F_2 and HF are highly soluble and thus were likely to have been captured in the water spray.

The SFC staff has estimated that the washdown of the ruptured cylinder and surrounding plant area has resulted in about 15,000 lb or about 8 tons of the released uranium being washed into the emergency pond. Therefore, the task force has estimated that the noxious white cloud that blew to the south-southeast was formed from the other half of the contents of the cylinder; i.e., it was formed from approximately 14,750 lb (6,700 kg) of UF_6. When totally reacted with water, 14,750 lb of UF_6 forms approximately 12,900 lb (5,900 kg) of UO_2F_2 and approximately 3,350 lb (1,500 kg) of HF.

Chronology

Date	Time	Event
9/20/85		Cylinder No. E-2047 received at Sequoyah facility.
9/27/85		Cylinder passes 20-point quality inspection conducted by site engineer.
1/3/86	10:00 a.m.	Cylinder passes second 20-point quality inspection conducted by day shift operator. Cylinder is moved to south filling bay within the plant process building and has begun to be filled with the UF_6 product. The operator adjusts the counterweight of the scales on which the cylinder is positioned so that the scale dial is indicating no weight. That is, the counterweight is positioned to counter-balance the tare weight of the empty cylinder so that the scales will directly measure the net weight of the product.
	3:30 p.m.	At the end of his shift, the day shift operator records that the cylinder has been loaded with 11,230 lb of product and is still being filled.
	11:30 p.m.	At the end of his shift, the evening shift operator records that the cylinder has been loaded with an additional 12,200 lb of product. The total weight of product in the cylinder is correctly noted as being 23,430 lb.
1/4/86	2:15 a.m.	The midnight shift operator continues filling the cylinder. Although the targeted net weight of the cylinder is 27,500 lb of product, the operator is unable to fill it beyond 26,400 lb. Upon closer investigation, the operator observes that one wheel of the cart holding the cylinder is not fully on the scales, which are set to indicate the net weight of the product in the cylinder. After the cart is restored to a position fully on the scales, the scale indicator pegs out at 29,500 lb.
		The operator informs the shift supervisor that the cylinder has been overfilled. The supervisor orders the operator to begin removing product from the cylinder using a vapor evacuation technique.

Date	Time	Event
1/4/86	6:00 a.m.	The operator moves the counterweight of the scales so that the scale dial indicator will be freed from its pegged position and will indicate the rate at which product is removed from the cylinder.
	6:15 a.m.	Evacuation of product from the cylinder begins. The scale indicates that 150 lb of product are removed in the succeeding 10 minutes. The operator can hear the flow of material through the cylinder valve.
	7:45 a.m.	At the end of the midnight shift, evacuation of UF_6 from the cylinder is still in progress.

The operator informs the oncoming day shift operator of the problem. |
| | 8:45 a.m. | The day shift operator is unable to draw off any more product from the cylinder, presumably because the UF_6 has begun to solidify. The operator confers with the day shift supervisor, who instructs the operator to transfer the cylinder to the northwest steam chest outside and north of the process building. The UF_6 will again be liquefied in the steam chest before the cylinder is returned to the filling bay for further product extraction. The supervisor instructs the worker to leave the cylinder in the chest for six hours. (Heating an overfilled cylinder is prohibited by company procedures.)

Before the cylinder is transferred from the scales, the counterweight is moved to its original position, which was demarked on the slide bar with a pen by the operator on the previous shift. The scale now again indicates 29,500 lb. |
| | 9:15 a.m. | The operator uses a forklift truck to transfer the cylinder to the steam chest. Steam heating of the cylinder begins. |
| | 11:30 a.m. | The cylinder ruptures while in the steam chest. The UF_6 quickly vaporizes, forming UO_2F_2 and hydrofluoric acid. The operator in a scrubber building 50 feet from the steam chest sustains lethal injuries caused by the acid fumes. Workers further away sustain less serious injuries. The plant is evacuated of approximately 40 workers. |

Contributing Factors

The following factors were identified as the primary contributors to the accident. They are arranged in the order in which they occurred.

1. The cylinder was overfilled because it was not placed fully on the scales. The fill bay and associated equipment were not designed to prevent improper positioning of cylinders in the bay. See Figure 3-21, Cart Not Fully on Scale.

    The 14-ton cylinder being filled was longer than the 10-ton cylinder for which the equipment was originally designed.

2. The time required for filling the cylinder was long enough to allow partial solidification of the UF_6, which inhibited product removal from the cylinder.

Figure 3-21. Cart Not Fully on Scale
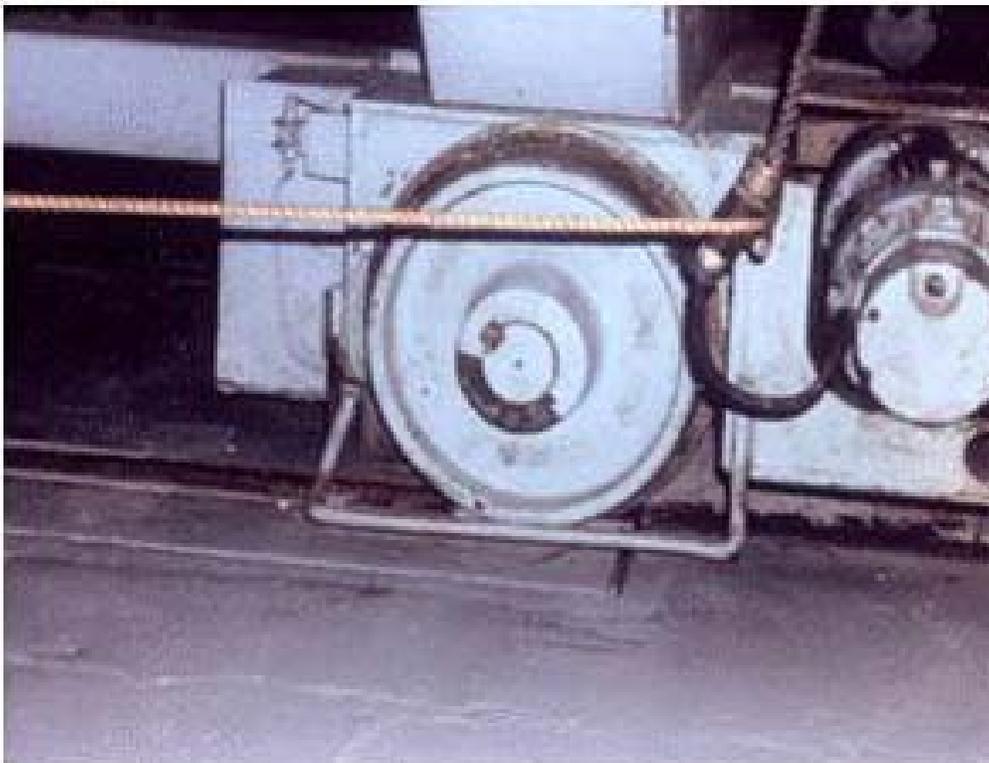
3. The precise weight of the cylinder was not readily determinable after it was overfilled.

4. There was no secondary or alternate way to measure the quantity of material in a cylinder being filled.

5. Employees violated company procedures when they heated an overfilled cylinder.

   Workers, including line management personnel, had not been trained in regard to company procedures.

   Procedural controls such as checklists or approval points were not an integral part of plant operations.

6. Equipment for monitoring or automatically venting cylinders that are being treated was not provided for by the plant design.

7. The fill limits were exceeded on numerous occasions at SFC and were routinely exceeded prior to sampling.

8. Several incidents with safety significance similar to the Sequoyah event had previously occurred at facilities with NRC licenses, federal installations, and foreign facilities. At least one event involving an NRC licensee was not reported because the licensee concluded the event was not reportable under 10 CFR 20.

Investigative Team Findings

1. The incident occurred as a result of a cylinder containing UF_6 being grossly overfilled and then heated in a steam chest to facilitate removal of some UF_6.

2. The heating of the overfilled cylinder caused expansion of the UF_6, as it changed from the solid to the liquid state, and the further thermal expansion of the liquid as it was heated.

3. The review of the UF_6 production process and the design of the facility indicated that modifications to improve some design deficiencies could have prevented or mitigated the incident. The design modifications reviewed include monitoring to prevent overpressurization; better monitoring to avoid overfilling; redesign of filling, sampling, and heating stations to limit the need for movement of heated cylinders; and provisions for monitoring releases of hazardous materials.

4. The licensee's radiological contingency plan was developed, but not properly implemented or maintained.

5.   Training for contingencies appeared to be less than adequate. Off-site organizations that might be expected to support an emergency response were not trained.

6.   The communication system was inadequate to handle the emergency, and emergency equipment and kits became unavailable during the event.

QUESTIONS

1.   Based on the information provided, list the probable causes of this accident.

2.   What recommendations would you make to prevent the recurrence of an accident of this type?

3.   What are the lessons learned from this accident?

Activity 2 – Sequoyah Fuels Accident — Review of Slides

PURPOSE: The purpose of this activity is to review slides of the Sequoyah Fuels Accident that was previously discussed in Activity 1. The slides are on the CD located in the front pocket of the course manual.

INSTRUCTIONS: Read the following brief descriptions as you review each slide.

Note: Slides and description numbers correspond with each other.

Slide No.   **Description**

Slide No.	Description
1	Area view of Sequoyah Plant
2	Site view — shows process area where worker who died was standing
3	Area where floor is contaminated
4	Steam chest surrounding cylinder
5	General area — yellow area is where worker who died was standing (steam chest to the right)
6	Cold trap — holding tank; (48Y) cylinder
7	Another view of process area cold traps
8	After accident; monitoring
9	Pressure gauge in process area
10	Valves in process area
11	Weighing area; blue part shows cradle — how to move cylinders downstairs
12	Weighing area — see scale platform
	Very front end of scale — see reading dial; in back is cylinder
	Filling cylinder here; 2500 max allowed
13	Another view — side view — see front end of scale platform and dial in back
14	Front view
15	View of cradle
16	Phalanges of cylinder too much — destructive
17	Dial — other side
18	View of steam chest (outside in yard)
19	Another view of steam chest; jets of steam in bottom
20	View of damaged cylinders; lid supported
21	Same; rags plugging gap in cylinder
22	Different view
23	Yellow — deposits of uranyl fluoride
24	Yellow — deposits of uranyl fluoride

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25   Yellow deposits — side view
26   Yellow deposits — side view
27   Yard — residue (yellow) on floor of yard; will see response team soon
28   Another view of yard
29   Response team — wash area with misting jet of H_2O (solid jet would have violent reaction — misting allows cooling)
30   Another slide of response team with protective clothing
31   Response team; fan spray mist; oxygen respirators, chemical respirators
32   See team on right; steel chest elevated
33   Uranyl fluoride in cylinders — took rags off/out and see material already
34   Another view
35   Managers behind barrier watching response team; no protective clothing and masks
36   After mist — now using direct jet stream
37   Another view of same
38   Closer view; notice that they moved the cylinder (rotated)
39   Shows hole
40   Team looking at hole
41   Putting in something with two sticks
41 (a) Different view
41 (b) Side view
42   See yellow solution of uranyl fluoride and H_2O (acid)
43   See where pressure formation occurred
44   View of room where protective team dressed/undressed; see disorder
45   Surveying outside area to check for contamination
46   Surveyors with equipment — house in distance
47   Surveyors and cows
48   Close-up of surveyors and cows
49   DOE plane

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

Learning Objective

When you finish this section, you will be able to:

3.1.4   Identify British and French conversion processes.

BRITISH AND FRENCH PROCESSES

The British process calcines the ammonium diuranate crystals to UO_3 by driving off the moisture and the ammonia. In the French process, the uranium tetroxide (UO_4) is converted to UO_3 by calcining at 750°F. Following calcination, both the British and the French processes use reduction, hydrofluorination, and fluorination to produce UF_6. Both the British and the French use batch processes.

British Process

In the British process, calcination of ammonium diuranate crystals is carried out batchwise in an electrically heated furnace according to the following reaction:

$$(NH_4)_2U_2O_7 \rightarrow 2NH_3 + H_2O + 2UO_3$$

The charge is initially heated to drive off steam and ammonia and convert the uranium to the trioxide (UO_3) form. The same electrically heated furnace is used in the second stage to carry out the reduction. The diuranate filter cake is charged in horizontal trays and loaded into the furnace.

In the British process, the same electrically heated furnace used for the calcination is used again to reduce UO_3 to UO_2 in presence of hydrogen in batchwise operation.

In the British process, the UO_2 and the anhydrous HF are fed to the same electrically heated furnace, where calcination and reduction were performed in the first and second stages. Like calcination and reduction, hydrofluorination is also carried out in a batchwise manner.

French Process

In the French process, UO_4 is converted to UO_3 by batch operation. The UO_4 is heated to 750°F and calcined to UO_3 according to the following reaction:

$$2UO_4 \rightarrow 2UO_3 + O_2$$
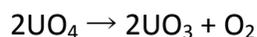
The UO_3 is pelletized and loaded into a vertical furnace for reduction to UO_2.

In the French process, UO_3 reduction to UO_2 is achieved in a current of NH_3 gas at 1380°F. NH_3 cracks and liberates, in situ, nascent hydrogen and nitrogen according to the following reaction:

$$2NH_3 \rightarrow 2N + 6H$$
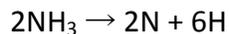
Nascent hydrogen speeds up the reduction effectively, and nitrogen acts as an inert diluent to control the temperature of the exothermic reduction reaction to preventing sintering of the UO_2. A vertical furnace is used in the French process, where pelletized UO_3 is loaded and reduced to UO_2 in batchwise conversion.

In the French process, UO_2 pellets are transferred to a vertical monel metal tube in an electric furnace and converted to UF_4 in a current of anhydrous HF vapor. Some nitrogen or hydrogen diluent is added along with the anhydrous HF vapor to control the exothermic reaction. At least 20% more HF is used than the stoichiometric requirement because of the reversible character of the reaction.

Self-Check Questions 3-8

INSTRUCTIONS: Complete the following questions. Answers are located
in the answer key section of the Trainee Guide.

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1.   What are the similarities between the British and French processes?

2.   In the British process, what happens in the calcination step?

3.   In the British process, what happens in the reduction step?

4.   In the French process, what happens in the calcination step?

5.   In the French process, what happens in the reduction step?

6.   In the French process, how is UO_2 converted to UF_4?

You have completed this section.
Please check off your progress on the tracking form.
Go to the next section.

It's time to schedule a progress meeting with your administrator.
Review the progress meeting form on the next page. In Part III, as a
Regulator, write your specific questions to discuss with the administrator.

PROGRESS REVIEW MEETING FORM

Date Scheduled: _____Location:_____

I.   The following suggested items should be discussed with the administrator as to how they pertain to your current position:

◉   NRC regulation of conversion facilities

◉   Dry fluoride volatility conversion

  □   Pretreatment

  □   Prepared feed and calcination

  □   Reduction

  □   Hydrofluorination

  □   Fluorination

  □   Distillation

  □   Product loading and shipping

◉   Sampling and measurement activities

◉   Hazards

◉   Wet acid digestion conversion

  □   Digestion

  □   Solvent extraction

  □   Concentration

  □   Denitration/acid recovery

  □   Reduction

  □   Hydrofluorination

□   Fluorination

□   Product loading and shipping

◉   Sequoyah fuels accident

◉   Comparisons of dry and wet conversion processes

◉   British process

◉   French process

II. Use the space below to take notes during your meeting.

III. As a Regulator:

◉   Tell me about uranium hexafluoride releases associated with uranium conversion facilities.

◉   What are the NRC and Department of Transportation (DOT) regulations associated with shipping product cylinders to enrichment facilities?

◉   Before I visit Honeywell, what documentation should I review?

Use the space below to write your specific questions.

IV. Further assignments? If yes, please note and complete. If no, initial completion of progress meeting on tracking form.

**Ensure that you and your administrator have dated and initialed
your progress on your tracking form for this module.
Go to the module summary.**

MODULE 3.0:   URANIUM CONVERSION

MODULE SUMMARY

Key Points:

◙ U.S. conversion facilities are licensed under the requirements of 10 CFR Part 40, Domestic Licensing of Source Material.

◙ Uranium source material is shipped under DOT requirements from uranium mills as "yellowcake" in plastic-lined drums. In addition to U_3O_8, the yellowcake contains contaminants, including radioactive decay daughter products and various rare earth and other metals.

◙ The yellowcake contains natural uranium, which has only 0.711% U-235. Hence, a criticality accident is not possible. The greatest radiation exposure rates come from processes that concentrate the radioactive decay daughter products in waste streams.

◙ Soluble forms of uranium present the greatest health risk from source material at conversion facilities. The health risk is due to the toxic nature of uranium, which is similar to other heavy metals. The radioactive risk is small.

◙ Honeywell chemically processes the uranium source material from U_3O_8 to UF_6 prior to shipping the product to the Paducah Gaseous Diffusion Plant for enrichment. The three main bulk chemicals used at Honeywell are ammonia (NH_3, the source of hydrogen), anhydrous hydrofluoric acid (HF), and fluorine (F_2). Each is a highly hazardous chemical. Release of bulk quantities of UF_6, NH_3, HF, or F_2 could have off-site consequences due to the hazardous nature of the chemicals.

◙ NH3, HF, and F_2 are regulated under the OSHA Process Safety Management rule, 29 CFR 1910.119. The NRC only regulates those chemicals when they come in contact with licensed material, evolve from licensed material, as in HF from the UF_6/water reaction, or adversely impact the safe handling of licensed material.

◙ The first major step in the Honeywell process is the "reduction" of U_3O_8 by hydrogen. The hydrogen is produced through a catalytic disassociation process to breakdown the ammonia into elemental hydrogen and nitrogen. The product is particulate (solid) UO_2. The excess hydrogen, all of the nitrogen and other volatile waste gases (hydrogen sulfide and arsine), are filtered to remove any particulate uranium and than incinerated. The powdered UO_2 is than sent to the hydrofluorinator for conversion to uranium tetrafluoride (UF_4), also known as "green salt."

◙ The second major step is the hydrofluorination of UO_2 by the addition of HF to produce UF_4. The solid UF_4 is sent to the fluorinator for the last step in the process. The waste gas stream containing excess HF and other volatile fluoride gases (SiF_4, BF_3, molybdenum, vanadium and H_2S) is filtered to remove particulate uranium and scrubbed with potassium hydroxide (KOH) to neutralize the fluorides.

◉   The third major step is the fluorination of particulate (solid) UF_4 through the addition of F_2 gas to produce UF_6, which is in a gaseous state for the existing process conditions. The fluorine comes from on-site electrolysis of HF. The UF_6 product is cooled, filtered to remove any particulate material, and passed through a series of three cold traps, where it is condensed into a solid form. Filled cold traps will be "heated" to liquify the UF_6 for transfer to distillation. The fluorination waste stream and other non- condensables are processed through a scrubber.

◉   The fourth major step in the process is purification through fractional distillation. There are two main steps. In the low boiling step, liquid UF_6 remains in the bottom of the column and the more volatile fluorides exit the top. The liquid UF_6 is sent to the high boiler column, where the UF_6 is volatilized and removed as a gas, leaving the less volatile contaminants behind. The UF_6 is then sent to a condenser. Liquid UF_6 is used to fill the Mark-48 cylinders.

◉   All liquid UF_6 filled cylinders must be allowed to cool for 5 days to reach ambient temperature. The UF_6 solidifies and volume drops from about 95% to about 60% full. The internal cylinder pressure is now about 3 psia. Only "solid" cylinders are allowed to be shipped off-site. UF_6 is in a solid form under ambient temperature and pressure conditions. Any cylinder breach will have a limited release, and then only due to the moisture in air and UF_6 chemical reaction which will release HF gas and UO_2F_2 particulate.

◉   The most likely causes of a release of licensed material at a conversion facility would come from: (1) a cylinder rupture caused by heating an overfilled cylinder, (2) a process line rupture caused by "cold spots" or other cooling mechanism that allows UF_6 to solidify or plug in the piping and the subsequent direct application of heat to the area containing the solid UF_6, and (3) pigtail leaks during cylinder connection/disconnection.

◉   Two other conversion processes still used in the world are the British process and French process. Both use reduction, hydrofluorination, and fluorination, and operate in the batch process mode. The British process calcines ammonium diuranate crystals to form UO_3, which is then processed further. The French process converts UO_4 to UO_3 by calcination.

Congratulations! You are ready to go to the next assigned module.

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