SITE LOCATION

- 50 miles east of Knoxville
- 75 miles northwest of Asheville
- 3 miles east of Newport, Tennessee
SITE CHARACTERISTICS

- Laboratory complex consisting of 14 individual laboratories and supporting facilities
- 15,000 sq.ft. of laboratory space
- 30 acre wooded mountaintop
- Less than 1 mile from French Broad River
- Locally karst topography
SITE HISTORY
COMMERCIAL USES

• Chemetron Laboratory (1959-1973)
  – Chemical Research & Development Lab
  – Chemical Producer

• Arapahoe / Syntex Chemical Laboratory (1974-1982)
  – analytical laboratory
  – small batch producer

• Facility idle (1983-1987)

• Flura Chemical established in 1988
  – PhD Fluorine chemist
    • Former owner and operator of Armageddon Chemical in Raleigh, NC
  – made custom halogenated gases for industrial and military use
  – Conducted research with halogenated organic gases
April 26, 1999

EPA responded to spill from 20,000 gallon AST of 1,2 dichloroethane and recognized problems at the facility

In May, 1999, EPA performed a RCRA compliance inspection
  - Initial RCRA inspection found hundreds of poorly kept cylinders and solid and liquid chemicals containers
  - Most cylinders in non-DOT condition
  - EPA issued order to bring the facility into compliance
UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION 4

IN THE MATTER OF:

Flura Corporation
610 Rock Hill Road
Newport, Cocke County
Tennessee 37821
TND 977 76276

DOCKET NO. RCRA-04-2000-003

Proceeding under Section 7003(a)
of the Resource Conservation and
Recovery Act, 42 U.S.C. § 6973(a)

RESPONDENT.

ADMINISTRATIVE ORDER

I. PRELIMINARY STATEMENTS

1. This is an administrative action instituted pursuant to Section 7003(a) of the Resource Conservation and Recovery Act (RCRA), 42 U.S.C. § 6973(a).

2. Respondent is Flura Corporation, a company doing business in the State of Tennessee (Respondent) at 610 Rock Hill Road in Newport, Cocke County, Tennessee (the Facility).

3. Complainant is the Director of the Waste Management Division, United States Environmental Protection Agency (EPA), Region 4. Complainant, acting pursuant to the authority vested in the Administrator by Section 7003(a) of RCRA, 42 U.S.C. § 6973(a), duly delegated, and having been presented with evidence that Respondent's contribution to the past or present handling, storage, treatment, transportation or disposal of any solid waste or hazardous waste, as defined by Sections 1004(5) and 1004(27) of RCRA, 42 U.S.C. §§ 6903(5) and 6903(27), at the Facility may present an imminent and substantial endangerment to health or the environment, hereby issues this Administrative Order (Order).

4. Pursuant to Section 7003(a) of RCRA, 42 U.S.C. § 6973(a), EPA has notified the Tennessee Department of Environment and Conservation (TDEC) of this action.

5. This Order is based upon the administrative record compiled by EPA and incorporated herein by reference. The record is available for review by Respondent and the public at EPA's regional office at 61 Forsyth St., Atlanta Federal Center, Atlanta, Georgia 30303.

II. PARTIES BOUND

6. The provisions of this Order shall apply to and be binding upon Respondent and its officers, employees, agents, successors and assigns, and shall apply whether or not Respondent's
REMOVAL ACTION

• EPA began a removal action in April, 2000
• After assessing the situation, a work plan was developed
• Stabilize the site by securing containers in poor condition and develop an inventory
• Sample the contents
• Derive treatment and disposal options using a cost-benefit analysis
• Decommission cylinders and dispose of solid and liquid wastes
TEAM FLURA

EMERGENCY RESPONSE AND REMOVAL BRANCH
- Lead agency on site

ENVIRONMENTAL RESPONSE TEAM
- Technical support through its contractors:
  - REAC
    - Air monitoring
    - Laboratory
  - SignalCorp
    - Compatibility testing

NATIONAL STRIKE FORCE
- Federal oversight
- Health and Safety Coordination

CMC, Inc.
- Cylinder operations

EARTH TECH, Inc.
- Solid and liquid chemicals
SITE STABILIZATION

• Phase 1
  – Designed to ensure worker safety and prevent further leakage of waste
  – Perform “elevated” Level B site walk through
  – Gauge integrity of each cylinder and chemical container
SITE STABILIZATION

- Phase 1
  - Eight perimeter air monitoring stations were set up
  - Analyte specific
  - Computer controlled
  - Weather info fed into computer
  - Closed-circuit cameras monitoring site
  - Decon stations set up
SITE STABILIZATION

• Phase 1 (cont.)
  – Overpack any leaking or deteriorated containers
  – Immediately treat or dispose of unsafe containers
SITE STABILIZATION

Waste treated in
Unstable Oxalyl Chloride
recovery unit
SITE STABILIZATION

Overpacking and inerting air reactive compounds

Overpacking deteriorated cylinders of chemical warfare agent
SITE STABILIZATION
PFIB

- PERFLUOROISOBUTYLENE
- 13 cylinders initially found in unsecured storage shed
- 10 additional cylinders found in wooden box in small laboratory
  - hidden in box beneath debris
  - shed secured with wooden dowel through hasp
PERFLUOROISOBUTYLENE
$\text{C}_4\text{F}_8$

- Properties
  - gas formed as a by-product during the production of some perfluorinated polymers, e.g. Teflon. It has no commercial application.
  - The toxic effects are hemorrhagic, causing victims’ lungs and other internal organs to bleed internally after exposure in the low ppb range.
  - Limited medical treatment options are available.
  - TLV: 0.01 ppm; 0.082 mg/m$^3$ (ceiling values) (ACGIH 1993-1994).
  - Schedule 2 WMD under the UN’s CONVENTION ON THE PROHIBITION OF THE DEVELOPMENT, PRODUCTION, STOCKPILING AND USE OF CHEMICAL WEAPONS AND ON THEIR DESTRUCTION, signed by 174 nations.
PUBLIC NOTIFICATION

- Local community advised of PFIB existence through public meetings
- Site gained national media attention as a result
- EPA - PFIB Task Force formed

- Emergency preparedness plan developed for Team FLURA and local residences
SITE STABILIZATION

• Phase 2 - Inventory
  – Each cylinder and container numbered
  – Documentation recorded
  • Labels, color, dimensions, condition, markings, and symbols
  • Cylinder ICC/SPEC#, rated pressure, serial number, collar information, test dates, stamps, valve information
SITE STABILIZATION

• Phase 3 - Sampling
  • After all containers and cylinders were inventoried, the cylinder operations and the solid and liquid chemical operations separated
  • Occurred concurrently
SITE STABILIZATION

• **Cylinders**
  – Measurements taken and additional info gathered
  – Compared with CGA standards
  – Sampling groups formed based on suspected contents
  – Sampled
  – Placed into treatment groups
  – Treated
  – Decommissioned
• **Chemicals**
  – Segregated into suspected sampling groups
  – HazCat tests performed
  – Bulking/treatment groups devised
  – Treated on-site or bulked
  – Disposal
Sampling occurred over a 4 month period
- 15-30 minutes per cylinder
- 8-20 cylinders per day
- dependant on suspected gas types and condition of cylinder

Cylinder sampling complicated by
- physical condition of cylinders
- unknown constituents
- reactivity of suspected contents

Level A PPE
- fully encapsulating Trellborg suits
- supplied air (line)
BORON TRIFLUORIDE
BF₃

A colorless, nonflammable gas which breaks down in moist air to hydrofluoric acid, fluoroboric acid, and boric acid. Penetrating odor. Very toxic. Attacks eyes and mucous membranes. Causes lung damage.

IDLH = 25 ppm  TLV/TWA = 1.0 ppm
Sampling and analytical labs constructed on-site
- Fully sealed
- Negative pressure
- Ventilated to treatment system
- Closed-circuit TV monitoring
- Fire suppression system

Laboratory instruments
- Fourier-Transformed Infra-Red spectrometer (FTIR)
- Gas Chromatograph / Mass Spectrometer (GC/MS)
The manifold was attached and purged with inert gas. The cylinder valve was opened slightly to allow a small amount to enter manifold.
CYLINDER OPS SAMPLING

• Two sample syringes extracted from each cylinder
  • One for in-lab HazCat
  • Second for on-site analytical
CYLINDER OPS SAMPLING

- Analytical results compared with library of thousands of gases

Unknown sample analysis

Library comparison

Perfluoroisobutylene
• 752 total compressed gas containers in 16 disposal groups
• Cost-benefit analysis showed on-site treatment preferable
• Three main disposal schemes developed
  – Recycling
  – On-site treatment
    • Pyrolysis & Hydrolysis
    • Acid Gas Neutralization
    • Thermal Destruction
  – Venting - gases like N₂ and O₂
Recycling was first option explored

Benefits the environment

Cost savings

Dependent on:
  – Condition of cylinder
  – Nature of contents
    • product or waste?
    • off-spec?

HF being recycled off site
Halogenated organics can be effectively treated through a two-step process. Achieve destruction of compound by **pyrolysis** and reformulation by **hydrolysis**.

- **Pyrolysis** (pI-'rä-le-ses), n. chemical change brought about by the action of heat in the absence of an atmosphere.
  - py·ro·lyt·ic /"pI-r&-'li-tik/ adjective
  - py·ro·lyt·i·cal·ly /-ti-k(&-)1E/ adverb

- **Hydrolysis** (hI-'drä-le-ses), n. a chemical process of decomposition involving the splitting of a bond and the addition of the hydrogen cation and the hydroxide anion of water.
  - hy·dro·lyt·ic /"hI-dr&-'li-tik/ adjective
  - hy·dro·lyt·i·cal·ly /-ti-k(&-)1E/ adverb

*SOURCE: Merriam Webster Collegiate Dictionary, 2001*
TREATMENT CHEMISTRY
Perfluoroisobutylene

5-STEP TREATMENT PROCESS

PYROLYSIS

• Removal of fluorine from carbon chain
  – $C_4 + 8F$

• Destruction of the carbon chain
  – C + C + C + C

HYDROLYSIS

• Introduction of water vapor
  – $+ H_2O$

• Formation of manageable products
  – CO$_2$ + HF

• Neutralization of HF with Ca(OH)$_2$
  – CaF + CO$_2$
Perfluoroisobutylene

\[ \text{C}_4\text{F}_8 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{CO}_2 \]

TREATMENT CHEMISTRY

INERT GAS

GAS BEING TREATED

H_2O

FLUORINE STRIPPED

913°F

NICKEL CATALYST
TREATMENT CHEMISTRY
Perfluoroisobutylene

Ca(OH)_2 Shower

Column filled with diffusers to increase residence time

Neutralization of HF

H^+ + F^- + Ca^+ + OH^- \rightarrow CaF + H_2O + CO_2

Carbon polishers to remove any remaining organics

CaF

H_2O BUFFER
Target gas

Inert gas

Introduction of water vapor

Furnaces
- Temp varied depending on gas
- Sample ports before, between, and after for QA/QC

TREATMENT
Elvira I (E1)
TREATMENT
Elvira I (E1)

Vented to atmosphere

Ring compressors provide negative pressure

Carbon polishers

Reaction vessels contained
Thu Apr 19 13:40:20 2001 Sample 3

Perfluoroisobutylene; 139 ppm-m

Carbon dioxide

Tetrafluoromethane; Carbon tetrafluoride; CFC-14

Wavenumbers (cm⁻¹)
TREATMENT
Elvira II (E2)

- Second treatment system built
- E2
  - treatment mechanisms identical
  - larger scale
  - able to treat 5 cylinders at once

Multiple furnaces leading to common acid neutralization
Neutralization columns
Carbon polishers
Ring compressors providing negative pressure
Ventilation to atmosphere
Thermal Destruction Unit
• Acid gas neutralization
• Process similar to 2nd half of E1 and E2
• Products are water and Ca salt.
• Reaction occurs in 5k gal stainless steel vessel.
TREATMENT
Heartburn

NaOH SCRUBBER

Ca(OH)$_2$ RESERVIOR

FROM RESERVIOR

DIRECTED FLOW
• Simple flammable gases (propane, acetylene) flared off
• TDU more advanced, combining thermal decomposition with scrubbing
• Used for certain off-spec gases and the small amount of still-bottoms and gas fractions that did not volatilize during E1 and E2 treatment
DECOMMISSIONING

- Compressed Gas Association Decommissioning Standards
  - Devalved
  - Decontaminated
  - All labels removed
  - All serial numbers removed
  - Cylinder physically cut in half
On-Site Treatment of Cylinders by Treatment Type and Number of Cylinders Treated

- Halogenated Organics: 270
- Inoperatable Valves: 12
- Neutralization Group: 29
- Soluable Group: 6
- HCl and HF biproducts: 72
- Fuel Gases: 11
- Vent and MT: 232
On-Site Treatment (Weight in Pounds)

- Halogenated Organics: 1181 pounds
- Inoperable Valves: 53 pounds
- Neutralization Group: 318 pounds
- Soluble Group: 10 pounds
- HCl and HF biproducts: 330 pounds
- Fuel Gases: 170 pounds

Legend:
- Blue: Halogenated Organics
- Purple: Inoperable Valves
- Yellow: Neutralization Group
- Cyan: Soluble Group
- Brown: HCl and HF biproducts
- Pink: Fuel Gases
Off-Site Treatment

T&D 43%

Return To Owner 57%

Return To Owner  
T&D
CHEMICAL OPS
OVERVIEW

• Chemical operations occurred simultaneously with cylinder operations
• Initial inventory found 5,927 total containers, 300 of which were completely unlabeled
• Work plan derived
  – HazCat containers
  – Bulk larger volumes and consolidate smaller containers in lab-packs
  – Treat where applicable
  – Dispose of wastes
HAZard CATegorization tests performed on over 5000 solid and liquid waste containers

- Radioactivity
- Air reactivity
- Water reactivity
- Hexane solubility
- Peroxide
- Specific gravity
- Flash point
- Oxidizer
- Halide
- Sulfide
- Cyanide
- PCB
CHEMICAL OPS

BULKING

- HazCat results used to develop bulking schemes
- Chemicals undergo bench scale testing for compatibility prior to bulking
CHEMICAL OPS TREATMENT

• 40 bulking and treatment groups developed
• When able, a variety of on-site treatment methods used.
  – neutralizations
  – stabilization
  – thermal destruction
  – incineration
  – oxidation and reduction
  – hydrolysis
Neutralization of ammonia with nitric acid. Created ammonium nitrate which was used to fertilize the onsite lawn.

Stabilization of solid material in concrete.
CHEMICAL OPS
BULKING

- Small containers lab-packed into 60 drums
- Many materials were lab packed and bulked into larger containers -
CHEMICAL OPS
DISPOSAL

- Approximately 300 drums of haz waste
- 4,020 yd$^3$ of solids
- 23,900 gallons of liquid
Total soil excavated in the five areas identified as burial areas, approximately 11,804 cubic yards.
EXCAVATION ACTIVITIES
Brockwell Farm RSE September 2001
CONCLUSIONS

• Safety
  – Cylinder operations inherently dangerous
  – OSC’s must make worker safety highest priority

• Recycling
  – Always best option but not always applicable

• Onsite vs. offsite treatment and disposal
  – Innovative on-site treatments may be very cost effective