United States
Environmental Protection
Agency

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S8-87/034a Sept. 1987

EPA

# Project Summary

# Prevention Reference Manual: Chemical Specific, Volume I: Control of Accidental Releases of Hydrogen Fluoride (SCAQMD)

D. S. Davis, G. B. DeWolf, and J. D. Quass

**The South Coast Air Quality Management District (SCAQMD) of southern California has developed a strategy for reducing the risk of a major accidental air release of toxic chemicals. This strategy involves monitoring and guiding communities and industry in the storage, handling, and use of certain chemicals, including hydrogen fluoride. The SCAQMD contracted for the preparation of a manual that would aid in identifying and controlling release hazards specific to the SCAQMD associated with hydrogen fluoride.**

**Anhydrous hydrogen fluoride is a corrosive liquid that boils at room temperature and rapidly absorbs moisture to form a highly corrosive hydrofluoric acid. Hydrogen fluoride gas has an IDLH (Immediately Dangerous to Life and Health) concentration of 20 ppm, making it an acute toxic hazard.**

**To reduce the risks associated with an accidental release of hydrogen fluoride, the potential causes of such a release from processes using hydrogen fluoride in the SCAQMD must be identified. Examples of potential causes and specific measures that may be taken to reduce the risk of an accidental release are identified. Such measures include: certain plant designs; prevention, protection, and mitigation technologies; and operation and maintenance practices. Prevention, protection, and mitigation costs are also estimated for some example systems.**

***This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

In 1985, the South Coast Air Quality Management District (SCAQMD) conducted a study to determine the presence, quantities, and uses of hazardous chemicals in the SCAQMD, which comprises Los Angeles, Orange, San Bernadino, and Riverside Counties. The resulting report, "South Coast Air Basin Accidental Toxic Air Emissions Study," outlined an overall strategy for decreasing the potential for a major toxic chemical release incident.

The hydrogen fluoride volume, one of a Prevention Reference Manual series, discusses storage and handling practice and process operations that relate to the prevention of accidental releases of hydrogen fluoride as it is used in the SCAQMD.

Hydrogen fluoride has a number of industrial uses throughout the country. In the SCAQMD specifically, hydrogen fluoride is used primarily to manufacture chlorofluorocarbons, as a catalyst in petroleum products alkylation process, and in repackaging. Hydrogen fluoride is a highly toxic, highly corrosive irritant to the skin, eyes, and respiratory system.

## Potential Causes of Releases

Both anhydrous hydrogen fluoride and hydrofluoric acid can be used safely in the appropriate processing and storage equipment; however, when exposed to

the atmosphere, hydrogen fluoride vaporizes readily and combines with moisture in air to form hydrofluoric acid.

Liquid hydrogen fluoride spills can occur when anhydrous hydrogen fluoride is released at or below its boiling point of 19.5°C (67°F) or when a sudden release of hydrogen fluoride above this temperature results in vapor flashing, which cools the remainder of the chemical to 19.5°C (67°F). Direct releases of gaseous hydrogen fluoride can also occur.

Hydrogen fluoride releases can originate from many sources, including leaks or ruptures in vessels, piping, valves, instrumentation connections, and process machinery such as pumps and compressors. The sources of accidental releases may be broadly classified as failures in or problems with: 1) the process or system of chemical production, 2) the equipment, and 3) operation or maintenance procedures, including human error.

Possible process causes of hydrogen fluoride releases include:

- Excess olefin feed to an alkylation reactor leading to an exothermic reaction, combined with failure of the cooling system;
- Backflow of alkylation process reactants to a hydrogen fluoride feed tank;
- Inadequate water and sulfur removal from hydrocarbon feeds to the alkylation process leading to progressive corrosion in downstream processing equipment;
- Excess feeds in any part of a system handling hydrogen fluoride leading to overfilling or overpressure equipment;
- Loss of condenser cooling in distillation units; and
- Overpressure in hydrogen fluoride storage vessels due to overheating or overfilling. This may be caused by fire exposure, unrelieved overfilling, or exothermic reactions from contamination.

Equipment causes result from hardware failures, including:

- Excessive stress caused by improper construction or installation;
- Failure of vessels at normal operating conditions caused by excessive stress, external loadings, corrosion, or overheating;
- Mechanical fatigue and shock resulting from age, vibration, stress cycling, or collisions with moving equipment such as cranes;
- Thermal fatigue or shock in alkylation reactors, heat exchangers, and distillation columns;
- Brittle fracture, especially in carbon steel equipment subjected to extensive corrosion;
- Creep failure in equipment subject to extreme operational upsets, especially excess temperatures; and
- All forms of corrosion.

Incorrect operating and maintenance procedures include:

- Overfilled storage vessels;
- Improper process system operation;
- Errors in loading and unloading procedures;
- Inadequate maintenance, especially on water-removal unit operations and pressure relief systems; and
- Lack of inspection and nondestructive testing of vessels and piping to detect corrosion weakening.

## Hazard Prevention and Control

Prevention of accidental releases requires careful consideration of the design, construction, operation, and protective systems of facilities where hydrogen fluoride is stored and used.

Deviations from expected process design or operation can initiate a series of events that result in an accidental release. Process variables such as flow, pressure, temperature, composition, and quantity must be monitored and controlled. Most importantly, the overheating and overpressuring of systems containing hydrogen fluoride must be prevented. Equipment failure can occur in the absence of overpressure if corrosion has weakened process equipment. Also, temperature monitoring is important because hydrogen fluoride's corrosiveness increases with temperature.

The proper selection of construction materials for hydrogen fluoride service is dictated by conditions that directly and indirectly affect corrosion (temperature, pressure, moisture content, flow velocity, aeration, and the presence of impurities such as sulfur). Vessels, piping, valves, process machinery, and instrumentation must resist corrosion. For example, for anhydrous hydrogen fluoride or concentrated hydrofluoric acid solutions, carbon steel pipe is commonly used. However, carbon steel is not appropriate for wet hydrogen fluoride or dilute hydrofluoric acid solutions.

The location of systems and equipment must also be considered with reference to the proximity of population centers, prevailing winds, local terrain, and potential natural occurrences such as flooding or earthquakes. Anhydrous hydrogen fluoride and aqueous hydrofluoric acid storage and handling equipment should be located away from other potentially hazardous storage and handling facilities.

Two types of protective systems for hydrogen fluoride facilities are enclosures and scrubbers. Enclosures are structures which would capture and contain any hydrogen fluoride spilled or vented from storage or process equipment, thus preventing immediate discharge of the chemical to the environment.

Scrubbers absorb toxic gases from process streams. These devices can be used to control hydrogen fluoride releases from vents and pressure relief discharges, from process equipment, or from secondary containment structures. Types of scrubbers include spray towers, packed bed scrubbers, and venturis.

Mitigation measures for minimizing the effects of a large release of hydrogen fluoride should be part of a facility's emergency preparedness. Mitigation measures include physical barriers, water sprays, fogs, and foams. Secondary containment systems for hydrogen fluoride storage facilities commonly consist of an adequate drainage system that leads to a lime-containing neutralization basin, or a diked area. Water sprays may not always be suitable for hydrogen fluoride spills, but soda ash or a strong soda ash solution can be used to neutralize the chemical and prevent the release of toxic vapors. Although foams have been used successfully in vapor hazard control for many volatile chemicals, no foam systems appear to be currently available for hydrogen fluoride.

*D. S. Davis, G. B. DeWolf, and J. D. Quass are with Radian Corporation, Austin, TX 78766.*
***T. Kelly Janes** is the EPA Project Officer (see below).*
*The complete report, entitled "Prevention Reference Manual: Chemical Specific—Volume 1: Control of Accidental Releases of Hydrogen Fluoride (SCAQMD)," (Order No. PB 87-227 047/AS; Cost: $18.95, subject to change) will be available only from:*

*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*

*The EPA Officer can be contacted at:*

*Air and Energy Engineering Research Laboratory*
*U.S. Environmental Protection Agency*
*Research Triangle Park, NC 27711*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268



EPA/600/S8-87/034a