

# Occupational Health Guideline for Hafnium and Compounds (as Hafnium)

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all hafnium and compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Hafnium

- Formula: Hf
- Synonyms: Hafnium, metallic; hafnium, elemental
- Appearance: Gray solid

### Hafnium tetrachloride

- Formula: HfCl<sub>4</sub>
- Synonyms: None
- Appearance and odor: White solid with an acrid odor in moist air.

### Hafnium oxychloride

- Formula: HfOCl<sub>2</sub> · 8H<sub>2</sub>O
- Synonyms: Hafnium oxychloride octahydrate
- Appearance and odor: White, odorless solid

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hafnium and compounds (as hafnium) is 0.5 milligram of hafnium and

compounds (as hafnium) per cubic meter of air (mg/m<sup>3</sup>) averaged over an eight-hour work shift.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Hafnium, hafnium tetrachloride, or hafnium oxychloride can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

### • Effects of overexposure

Exposure to hafnium salts has caused irritation of the eyes and skin in animals. Hafnium chloride has caused liver damage in animals on prolonged feeding.

### • Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hafnium and compounds (as hafnium).

### • Recommended medical surveillance

Routine medical examinations should be provided to each employee who is exposed to hafnium and compounds at potentially hazardous levels. The employer should screen employees for history of liver disease. Hafnium compounds have been reported to cause liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function. Only those giving a positive history of these conditions should be referred for further medical examinations.

### • Summary of toxicology

Hafnium and its compounds have been reported to cause liver damage in animals. The LD<sub>50</sub> of hafnium, chiefly as the oxychloride, was 76 mg Hf/kg for mice. A 90-day hafnium chloride feeding study in rats at 1.0% and 0.1% resulted in unspecified liver effects. Studies with radioactive Hf mandelate indicate slow elimination from the body. Some compounds may cause irritation of eyes, skin, and mucous membranes.

---

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data—Hafnium

1. Molecular weight: 178.5
2. Boiling point (760 mm Hg): 3100 C (5612 F) approximately
3. Specific gravity (water = 1): 13.3
4. Vapor density (air = 1 at boiling point of hafnium): Not applicable
5. Melting point: 2227 C (4040 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data —Hafnium tetrachloride

1. Molecular weight: 320.3
2. Boiling point (760 mm Hg): 317 C (603 F)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium tetrachloride): Not applicable
5. Melting point: 432 C (809 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F):

### Reacts

8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Hafnium oxychloride

1. Molecular weight: 409.5
2. Boiling point (760 mm Hg): Decomposes (data not available)
3. Specific gravity (water = 1): Data not available
4. Vapor density (air = 1 at boiling point of hafnium oxychloride): Not applicable
5. Melting point: Less than 50 C (less than 122 F)
6. Vapor pressure at 20 C (68 F): Very low
7. Solubility in water, g/100 g water at 20 C (68 F):

### Very soluble

8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of hafnium metal with chlorine and strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving hafnium, hafnium tetrachloride, or hafnium oxychloride.

4. Special precautions: None

### • Flammability

1. Flash point: Not applicable
2. Autoignition temperature: Hafnium: Data not applicable; hafnium tetrachloride and hafnium oxychloride: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Hafnium: Water; hafnium tetrachloride and hafnium oxychloride: Not applicable

### • Warning properties

Hafnium is not known to be an eye irritant; however, Haley reports that hafnium compounds may prove irritating to the mucosal surfaces.

## MONITORING AND MEASUREMENT PROCEDURES

### • General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Method

An analytical method for hafnium and compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

## RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with wet or dry hafnium powder. The clothing should be flame-resistant and should be treated or should be of a type so as to minimize the static electricity hazard of ignition.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent skin contact with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, where skin contact may occur.

- If employees' clothing has had any possibility of being contaminated with wet or dry hafnium powder, employees should change into uncontaminated clothing before leaving the work premises.
- If employees' clothing may have become contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with wet or dry hafnium powder should be placed in fireproof closed containers for storage until it can be discarded or until provision is made for the removal of hafnium from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hafnium, the person performing the operation should be informed of hafnium's hazardous properties.
- Clothing contaminated with hafnium tetrachloride or hafnium oxychloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to wet or dry hafnium powder, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Where exposure of an employee's body to hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Any clothing which becomes contaminated with wet or dry hafnium powder should be removed promptly but in a careful and cautious manner so as to reduce the probability of ignition by friction, static electricity, or other causes. Such clothing should not be reworn until the hafnium is removed from the clothing.
- Non-impervious clothing which becomes wet with hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to wet or dry hafnium powder, hafnium tetrachloride, hafnium oxychloride, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergen-

cy use.

## SANITATION

- Workers subject to skin contact with wet or dry hafnium powder should wash any areas of the body which may have contacted hafnium powder at the end of each work day.
- Skin that becomes wet with wet or dry hafnium powder should be promptly washed or showered with soap or mild detergent and water to remove any contaminant.
- Skin that becomes contaminated with hafnium tetrachloride, hafnium oxychloride, or liquids these compounds should be promptly washed or showered to remove any contaminant.
- Eating and smoking should not be permitted in areas where wet or dry hafnium powder, hafnium tetrachloride, or solid hafnium oxychloride or liquids containing these compounds are handled, processed, or stored.
- Employees who handle hafnium or its compounds or liquids containing hafnium or its compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hafnium and compounds may occur and control methods which may be effective in each case:

| Operation   | Controls   |
|---|--|
| Liberation from mining and purification of hafnium (separation from zirconium); manufacture and fabrication of special alloys   | Local exhaust ventilation; personal protective equipment |
| Use as control rods in water-cooled nuclear reactors; use in gas-filled tubes and incandescent lamps as scavenger for oxygen and nitrogen; use in the manufacture of photographic flash bulbs, light bulb filaments, and in electronic equipment as cathodes and capacitors | Local exhaust ventilation; personal protective equipment |

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid proce-

dures and send for first aid or medical assistance.

- **Eye Exposure**

If hafnium, hafnium tetrachloride, or hafnium oxychloride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If hafnium gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If hafnium tetrachloride or hafnium oxychloride get on the skin, promptly flush the contaminated skin with water. If hafnium or its compounds soak through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of hafnium, hafnium tetrachloride, or hafnium oxychloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When hafnium, hafnium tetrachloride, or hafnium oxychloride have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If hafnium, hafnium tetrachloride, or hafnium oxychloride are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill.

Liquid containing hafnium, hafnium tetrachloride, or hafnium oxychloride should be absorbed in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

Hafnium, hafnium tetrachloride, or hafnium oxychloride may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Hafnium," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

- Haley, T., et al.: "The Toxicologic and Pharmacologic Effects of Hafnium Salts," *Toxicology and Applied Pharmacology*, 4:238-246, 1962.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

- Manufacturing Chemists Association, Inc.: *Chemical Safety Data Sheet SD-92, Hafnium*, Washington, D.C., 1966.

- Stauden, A. (exec. ed.): *Kirk-Othmer Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1972.

## RESPIRATORY PROTECTION FOR HAFNIUM AND COMPOUNDS (AS HAFNIUM)

| <b>Condition</b>   | <b>Minimum Respiratory Protection*<br/>Required Above 0.5 mg/m<sup>3</sup></b>  |
|--|---|
| <b>Particulate Concentration</b>   |   |
| 2.5 mg/m <sup>3</sup> or less  | Any dust and mist respirator, except single-use.  |
| 5 mg/m <sup>3</sup> or less  | Any dust and mist respirator, except single-use respirator or quarter mask.<br>Any fume respirator or high efficiency particulate respirator.<br>Any supplied-air respirator.<br>Any self-contained breathing apparatus.  |
| 25 mg/m <sup>3</sup> or less   | A high efficiency particulate filter respirator with a full facepiece.<br>Any supplied-air respirator with a full facepiece, helmet, or hood.<br>Any self-contained breathing apparatus with a full facepiece.  |
| 250 mg/m <sup>3</sup> or less  | A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.<br>A powered air-purifying respirator with a high efficiency particulate filter.   |
| Greater than 250 mg/m <sup>3</sup> or entry and escape from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.<br><br>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode. |
| Fire Fighting  | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.   |
| Escape   | A high efficiency particulate filter respirator.<br>Any escape self-contained breathing apparatus.  |

\*Only NIOSH-approved or MSHA-approved equipment should be used.