

# Occupational Health Guideline for Selenium and Its Inorganic Compounds (as Selenium)\*

## 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 selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

### Sodium selenite

- Formula:  $\text{Na}_2\text{SeO}_3$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Sodium selenate

- Formula:  $\text{Na}_2\text{SeO}_4$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Selenium dioxide

- Formula:  $\text{SeO}_2$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Selenium oxychloride

- Formula:  $\text{SeOCl}_2$
- Synonyms: None
- Appearance: Colorless to yellow liquid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium and its inorganic compounds is 0.2 milligram of selenium and its inorganic compounds (as selenium) per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

### • Effects of overexposure

*1. Short-term Exposure:* Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

*2. Long-term Exposure:* Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

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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.

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National Institute for Occupational Safety and Health

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

3. **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 selenium and its inorganic compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic compounds at potentially hazardous levels:

1. **Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m<sup>3</sup> for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In

control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m<sup>3</sup>, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

## CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Selenium**

1. Molecular weight: 78.96
2. Boiling point (760 mm Hg): 685 C (1265 F)
3. Specific gravity (water = 1): 4.45 to 4.8
4. Vapor density (air = 1 at boiling point of selenium): Not applicable
5. Melting point: 150 C (302 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenite**

1. Molecular weight: 173
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
5. Melting point: 710 C (1310 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 85
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenate**

1. Molecular weight: 188.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable

5. Melting point: Decomposes

6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg

7. Solubility in water, g/200 g water at 20 C (68 F): 83

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

• **Physical data—Selenium dioxide**

1. Molecular weight: 110.9

2. Boiling point (760 mm Hg): 315 C (599 F) (sublimes)

3. Specific gravity (water = 1): 3.95

4. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable

5. Melting point: 340 C (644 F)

6. Vapor pressure at 20 C (68 F): 0.001 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 257

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

• **Physical data—Selenium oxychloride**

1. Molecular weight: 165.9

2. Boiling point (760 mm Hg): 176 C (349 F)

3. Specific gravity (water = 1): 2.42

4. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7

5. Melting point: 10.8 C (51 F)

6. Vapor pressure at 20 C (68 F): 0.35 mm approximately

7. Solubility in water, g/100 g water at 20 C (68 F): Decomposes

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

• **Reactivity**

1. Conditions contributing to instability: None hazardous

2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable

3. Flammable limits in air, % by volume: Not applicable

4. Extinguishant: For selenium, water

• **Warning properties**

The *Documentation of TLV's* notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to

high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The *Hygienic Information Guide* for selenium states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation is not available.

## 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**

Sampling and analyses may be performed by collection of selenium and its inorganic compounds on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for selenium and its inorganic compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## 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 selenium oxychloride or liquids containing selenium oxychloride.
- 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 repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- 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 selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, 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 selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide 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 selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride 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 selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Workers subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

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

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photography and photocopy devices; manufacture of dyes, pigments, and colored glazes for metal etching and for printing on glass	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of lubricating oils and extreme pressure lubricants as antioxidants and detergency improvers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry for manufacture and use as vulcanization accelerators and antioxidants; use in manufacture of pharmaceuticals, fungicides, and dermatitis control	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst for hardening fats for soaps, waxes, edible fats, and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, parasiticides, bactericides, and herbicides for agricultural and citrus crops	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of flame-proofing agents on textiles and electric cables	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as solvents in paint and varnish removers; rubber, resin, and glue solvent; use for organic synthesis in oxidation, hydrogenation, and dehydrogenation	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in refining of copper, silver, gold, or nickel ores or during recycling of scrap metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in miscellaneous operations in manufacture of insect repellants, activators, hardeners, special ceramic materials, plasticizers, and mercury vapor detectors	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use for preparation of feed additives for poultry and swine	Local exhaust ventilation; general dilution ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If selenium or its inorganic compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of selenium, sodium selenite, sodium selenate, or selenium dioxide, 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 selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide 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 selenium or its inorganic compounds 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 selenium and its inorganic compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• **Waste disposal method:**

Selenium and its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Compounds (as Se)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1959.

• Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.

• Cerwenka, E. A., Jr., and Cooper, W. C.: "Toxicology of Selenium and Tellurium and Their Compounds," *Archives of Environmental Health*, 3:189-200, 1961.

• Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

• Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

• Glover, J. R.: "Selenium and Its Industrial Toxicology," *Industrial Medicine*, 39(1):50-54, January 1970.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• Halverson, A. W., et al.: "Development of Hemolytic Anemia in Rats Fed Selenium," *Toxicology and Applied Pharmacology*, 17:151-159, 1970.

• Hamilton, A., and Hardy, H.: *Industrial Toxicology* (3rd ed.), Publishing Sciences Group, Acton, Massachusetts, 1974.

• Hunter, D.: *Diseases of Occupations* (4th ed.), Little, Brown, Boston, 1969.

• *Hygienic Information Guide No. 59 - Selenium Compounds (as Se)*, Commonwealth of Pennsylvania, Department of Environmental Resources, Bureau of Occupational Health, 1971.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1974.

• Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.

• Nelson, A. A., et al.: "Liver Tumors Following Cirrhosis Caused by Selenium in Rats," *Cancer Research*, 3:230-236, 1943.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Robertson, D. S. F.: "Selenium - A Possible Teratogen?," *Lancet*, 1:518-519, 1970.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

• Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.

## \* SPECIAL NOTE

Selenium and its inorganic compounds (as selenium) appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

# RESPIRATORY PROTECTION FOR SELENIUM AND ITS INORGANIC COMPOUNDS (AS SELENIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m <sup>3</sup>
Particulate Concentration 10 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m <sup>3</sup> or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.
Greater than 100 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. 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 with a full facepiece. Any escape self-contained breathing apparatus with a full facepiece.

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