

# OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR CALCIUM CYANAMIDE

## INTRODUCTION

This guideline summarizes pertinent information about calcium cyanamide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

## SUBSTANCE IDENTIFICATION

### • Formula



### • Structure



### • Synonyms

Aero-cyanamid; cyanamide, calcium salt; aero cyanamid granular; calcium carbimide; aero cyanamid special grade; Alzodef; lime-nitrogen; nitrogen lime; nitrolim, nitrolime

### • Identifiers

1. CAS No.: 156-62-7
2. RTECS No.: GS6000000

3. DOT UN: 1403 40 (not hydrated, containing more than 0.1% calcium carbide)
4. DOT label: None (not hydrated, containing more than 0.1% calcium carbide)

### • Appearance and odor

Calcium cyanamide is a noncombustible, colorless, gray, or black crystalline solid or powder. No information is available on the odor of this substance. The commercial grade may contain a small amount of calcium carbide, which may produce acetylene in closed containers and vessels.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 80.11
2. Boiling point (760 mm Hg): Sublimes at 1,150° to 1,200°C (2,102° to 2,192°F)
3. Specific gravity (water = 1): 2.29 at 20°C (68°F)
4. Vapor density: Data not available
5. Melting point: 1,340°C (2,444°F)
6. Vapor pressure: Not volatile
7. Solubility: Decomposes in water to liberate acetylene gas and ammonia
8. Evaporation rate: Data not available

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

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

## Reactivity

1. Conditions contributing to instability: Moisture
2. Incompatibilities: Contact with any form of moisture (ice, steam, moist air, water) causes calcium cyanamide to decompose, liberating acetylene and ammonia. Contact with all solvents tested also causes calcium cyanamide to decompose.
3. Hazardous decomposition products: Toxic gases (such as oxides of nitrogen) may be released in a fire involving calcium cyanamide.
4. Special precautions: None

## Flammability

The National Fire Protection Association has not assigned a flammability rating to calcium cyanamide. In pure form, this substance is not combustible; however, the commercial product may contain calcium carbide, which may liberate very flammable gases and vapors on contact with moisture.

1. Flash point: Not applicable
2. Autoignition temperature: Not applicable
3. Flammable limits in air: Not applicable
4. Extinguishant: Use dry chemical, soda ash, sand, or lime to fight fires involving calcium cyanamide. Do not use foam or water. Water may be ineffective, but it may be used to cool fire-exposed containers.

Fires involving calcium cyanamide should be fought upwind from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of calcium cyanamide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving calcium cyanamide. Structural firefighters' protective clothing may not provide protection against permeation by calcium cyanamide.

## EXPOSURE LIMITS

### • OSHA PEL

The Occupational Safety and Health Administration (OSHA) has not promulgated a permissible exposure limit (PEL) for calcium cyanamide [29 CFR 1910.1000, Table Z-1].

### • NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.5 mg/m<sup>3</sup> as a TWA for up to a 10-hr workday and a 40-hr workweek [NIOSH 1992].

### • ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned calcium cyanamide a threshold limit value (TLV) of 0.5 mg/m<sup>3</sup> as a TWA for a normal 8-hr workday and a 40-hr workweek [ACGIH 1993].

### • Rationale for limits

The ACGIH limit is based on the risk of irritation and vasomotor effects associated with exposure to calcium cyanamide [ACGIH 1991].

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Exposure to calcium cyanamide can occur through inhalation, eye or skin contact, dermal absorption, or ingestion.

### • Summary of toxicology

1. *Effects on Animals:* Calcium cyanamide can be a severe irritant of the eyes and skin in animals. In pure water or alkaline solutions, it may polymerize to dicyandiamide, a less toxic product. When instilled into rabbits' eyes, the dust of this material was quite irritating [ACGIH 1991]. When applied as a paste to the clipped skin of rabbits under occlusion for 24 hr, a 10-g/kg dose of calcium cyanamide killed two of five rabbits; all animals survived when the dosage was reduced to 5 g/kg [ACGIH 1991]. All surviving animals developed severe skin irritation several days

after application [ACGIH 1991]. In marked contrast to the previous data concerning rabbit dermal lethality, other investigators reported the dermal LD<sub>50</sub> in rabbits to be 590 mg/kg [NIOSH 1991]. The lowest lethal concentration in rats is 86 mg/m<sup>3</sup> for 4 hr [ACGIH 1991]. The oral LD<sub>50</sub> in rats is 158 mg/kg [NIOSH 1991]. Calcium cyanamide is mutagenic in bacterial test systems [NIOSH 1991; NLM 1992]. Rats and mice fed a diet containing 63 or 126 ppm (male rats), 63 or 252 ppm (female rats), or 315 or 1,260 ppm (male and female mice) of calcium cyanamide for 2 years failed to develop tumors that were treatment related at statistically significant levels; however, some of the mice did develop hemangiosarcomas of the circulatory system, lymphomas, and leukemia [ACGIH 1991].

2. *Effects on Humans:* Calcium cyanamide is a primary irritant and sensitizer of the eyes, skin, and mucous membranes. The dust of calcium cyanamide is a primary irritant that can induce skin ulcers and be caustic to the eyes [Clayton and Clayton 1981; NLM 1992]. Skin contact with this substance also causes skin sensitization in approximately 0.5% to 1% of exposed workers [ACGIH 1991]. Inhalation of the dust can cause rhinitis, pharyngitis, laryngitis, and tracheobronchitis. Nasal septal perforation has also been reported in chronically exposed workers. Workers exposed to calcium cyanamide at unspecified concentrations may develop miosis, salivation, lacrimation, and twitching plus a transient vasomotor disturbance that can cause skin and mucous membrane flushing, nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, and low blood pressure; in severe cases, shock, coma, and death may follow [ACGIH 1991; Gosselin et al. 1984; NLM 1992]. Attacks are usually transient, lasting for 30 min to 2 hr, and the ingestion of alcohol may precipitate or intensify this syndrome [Gosselin et al. 1984]. Although an oral dose of 571 mg/kg has proved fatal in humans, the estimated total lethal dose ranges from 20 to 50 grams [NIOSH 1991; NLM 1992]. However, death occurred within 1 hr when a patient drank ethanol following ingestion of 100 mg calcium cyanamide [NLM 1992].

• **Signs and symptoms of exposure**

1. *Acute exposure:* Calcium cyanamide can cause eye irritation, runny nose, sore throat, and coughing. Itchy, reddened skin, especially on the exposed areas of the body, has been reported; continued skin contact

may cause skin burns. Inhalation exposure can produce respiratory tract irritation and may cause facial and upper-body flushing, accompanied by nausea, vomiting, headache, fatigue, vertigo, dyspnea, rapid breathing, a sense of oppression in the chest, and shivering. Low blood pressure, circulatory collapse, and coma may follow in more serious exposures. These symptoms may be triggered or intensified by alcohol ingestion, and a marked intolerance to alcoholic beverages can develop.

2. *Chronic exposure:* Calcium cyanamide may cause some individuals to develop skin sensitization, with raised, reddened, and itching areas of the skin (hives). Chronic rhinitis and nasal septal perforation have also been reported in workers exposed to the dust.

• **Emergency procedures**

<p style="text-align: center;"><b>WARNING!</b> <b>Transport victims immediately to emergency medical facility</b></p>
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Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. *Immediately* initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. *Eye exposure:* Tissue destruction and blindness may result! *Immediately but gently* flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.
2. *Skin exposure:* Severe burns, skin corrosion, and absorption of toxic amounts may result! *Immediately* remove all contaminated clothing! *Immediately*, continuously, and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.
3. *Inhalation exposure:* Move the victim to fresh air *immediately*. Have the victim blow his or her nose or use a soft tissue to remove particulates or residues from the nostrils.

If the victim is not breathing, clean any chemical contamination from the victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. *Ingestion exposure*: Take the following steps if calcium cyanamide or any material containing it is ingested:

—Do *not* induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and *no more*.

—Do *not* permit the victim to drink milk or carbonated beverages!

—Do *not* permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

**NOTE:** These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk may impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. *Rescue*: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA's hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.

## EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve calcium cyanamide and may result in worker exposures to this substance:

- Use in the nitridation and desulfurization of steel
- Use as a raw material in the manufacture of dicyandiamide and calcium cyanide
- Use as a fertilizer and in the manufacture of nitrogen products
- Use in human medicine to treat alcoholism
- Used formerly as a defoliant, herbicide, and pesticide

The following methods are effective in controlling worker exposures to calcium cyanamide, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:

1. ACGIH [1992]. *Industrial ventilation—a manual of recommended practice*. 21st ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
2. Burton DJ [1986]. *Industrial ventilation—a self study companion*. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
3. Alden JL, Kane JM [1982]. *Design of industrial ventilation systems*. New York, NY: Industrial Press, Inc.
4. Wadden RA, Scheff PA [1987]. *Engineering design for control of workplace hazards*. New York, NY: McGraw-Hill.
5. Plog BA [1988]. *Fundamentals of industrial hygiene*. Chicago, IL: National Safety Council.

## MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

### • Preplacement medical evaluation

Before a worker is placed in a job with a potential for

exposure to calcium cyanamide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the skin and on a history of allergies or alcohol intake. All potentially exposed workers should be warned of the adverse signs and symptoms associated with exposure to calcium cyanamide and the concomitant ingestion of alcohol.

A preplacement medical evaluation is recommended to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to calcium cyanamide at or below the prescribed exposure limit. The licensed health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history of alcohol intake or allergies and other findings consistent with skin diseases.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to calcium cyanamide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of calcium cyanamide on the skin (including allergic sensitization) and on any vasomotor episodes that have occurred. All workers should be reminded of the adverse effects associated with concomitant exposure to calcium cyanamide and the ingestion of alcohol. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitor-

ing test acceptable for routine use has yet been developed for calcium cyanamide.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

## **WORKPLACE MONITORING AND MEASUREMENT**

A worker's exposure to airborne calcium cyanamide is determined by using a mixed cellulose ester filter (MCEF) (0.8 micron). Samples are collected at a maximum flow rate of 2 liters/min until a maximum air volume of 960 liters is collected. Analysis is conducted by atomic absorption spectroscopy. This method is included in the OSHA Laboratory In-House Methods File [OSHA 1989].

## **PERSONAL HYGIENE**

If calcium cyanamide contacts the skin, workers should flush the affected areas immediately with plenty of water for 15 min, and then wash with soap and water.

Clothing contaminated with calcium cyanamide should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed of the hazardous properties of calcium cyanamide, particularly its potential to cause irritation of the eyes and skin.

A worker who handles calcium cyanamide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, or applying cosmetics.

Workers should not eat, drink, use tobacco products, or apply cosmetics in areas where calcium cyanamide or a solution containing calcium cyanamide is handled, processed, or stored.

## **STORAGE**

Calcium cyanamide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled

in accordance with OSHA's hazard communication standard [29 CFR 1910.1200]. Containers of calcium cyanamide should be protected from physical damage and should be stored separately from moisture, calcium carbide, heat, sparks, and open flame. Because containers that formerly contained calcium cyanamide may still hold product residues, they should be handled appropriately.

## SPILLS AND LEAKS

In the event of a spill or leak involving calcium cyanamide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Ventilate potentially explosive atmospheres.
5. Prevent any contact of calcium cyanamide with water.
6. Use nonsparking tools and equipment for cleanup.
7. For small dry spills, use a clean shovel and gently place the material into a clean, dry container creating as little dust as possible; cover and remove the container from the spill area.

## SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

### • Emergency planning requirements

Calcium cyanamide is not subject to EPA emergency

planning requirements under the Superfund Amendments and Reauthorization Act (SARA) [42 USC 11022].

### • Reportable quantity requirements for hazardous releases

Employers are not required by the emergency release notification provisions of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the National Response Center of an accidental release of calcium cyanamide; there is no reportable quantity for this substance.

### • Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of calcium cyanamide per calendar year are required by EPA to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of calcium cyanamide emitted or released from their facility annually.

### • Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Although calcium cyanamide is not specifically listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424-9346 or at (202) 382-3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

## RESPIRATORY PROTECTION

### • Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of calcium cyanamide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

### • Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information about the selection and use of respirators and about the medical screening of respirator users, consult the *NIOSH Respirator Decision Logic* [NIOSH 1987b] and the *NIOSH Guide to Industrial Respiratory Protection* [NIOSH 1987a].

## PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with calcium cyanamide. Chemically resistant gloves, boots, aprons, and gauntlets are recommended to prevent contact of the skin with this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers' recommendations, and evaluation of the clothing under actual conditions of use.

No reports have been published on the resistance of various protective clothing materials to permeation by calcium cyanamide. If permeability data are not readily available, protective clothing manufacturers should be requested to provide information on the best chemical protective clothing for workers to wear when they are exposed to calcium cyanamide.

Safety glasses, goggles, or face shields should be worn during operations in which calcium cyanamide might contact the eyes (e.g., through dust particles or splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with calcium cyanamide. Contact lenses should not be worn if the potential exists for calcium cyanamide exposure.

## REFERENCES CITED

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