



Hydrogen Selenide

H₂Se is manufactured by the reduction of molten selenium in a batch reactor.

I have manufactured H₂Se from 1979-2009 as well as supported its use, during this time I investigated 2 major H₂Se releases as well as 3 minor releases. In all cases the major symptom was respiratory distress and severe irritation of the body caused by moisture reaction to form selenious acid. This typically affected the wet parts of the body such as eyes, nose, armpits.

Dr. Neil Mann a medical doctor from Massachusetts has treated patients exposed to metal hydride gases states:

“Garlic” breath is one of the classic symptoms of exposure to selenium. A disorder known as “rose cold” characterized by sore throat, bronchitis, cough and coriza (inflammation of nasal passages) as well as severe eye irritation and dermatitis.

As noted in my article Tox and Hound – Fellow Friday – Metal Hydrides I <https://emcrit.org/toxhound/ff-metal-hydrides/>

Hydrogen selenide smells of decayed horseradish and is primarily used to grow zinc selenide lenses for infrared detectors. The gas is quite irritating upon inhalation and quickly forms selenious acid when encountering moisture in or upon us, producing a garlic odor. Hydrogen selenide mixed in vitro with guinea pig blood also produced deformed red cells, but did not produce hemoglobinuria. There exist **no reports of H₂Se producing hemolysis in animals or humans. Inhalation toxicity appears mainly to be irritation.**

From the standpoint of acute inhalation, **then, it is difficult to imagine a likely cause of massive hemolysis and renal failure** other than arsine. A list of ingested or injected substances capable of causing severe oxidant hemolysis with some methemoglobinemia is long and can't be discussed here. Some were mentioned in a previous post on methylene blue infusions for methemoglobinemia. We'll simply note naphthalene, chlorates, chromates, dapsone, aniline and nitrobenzene as examples. We also don't have space here to address workers who may have severe glucose-6-phosphate dehydrogenase deficiency and implications for exposure to industrial chemicals.

Hydrogen selenide reacts with the moisture in the air or system to form red selenious acid



Fig. 1: Red selenium

These tend to plug systems such as MFC and regulators.

Proper system cleaning and conditioning is critical. Water absorbed on CGA 660 PTFE Gasket will react with H_2Se . Impregnated PTFE (Calcium Fluoride) had less moisture.



Figs 2 and 3: PTFE Gasket and Impregnated Gasket

Release is colorless and can immediately envelop the victim. Immediate Reaction with moisture to form selenious acid which coats any wet area red. Strong irritant to skin and immediate choking and tearing. Uncontrollable Coughing. The victims body smells like garlic, decontamination, 1% bleach.

Dr. Neil Mann a medical doctor who has treated patients exposed to metal hydride gases stated: "Garlic" breath is one of the classic symptoms of exposure to Selenium. A disorder known as "rose cold" characterized by sore throat, bronchitis, cough and coriza (inflammation of nasal passages) as well as severe eye irritation and dermatitis.

As noted in my article Tox and Hound – Fellow Friday – Metal Hydrides I <https://emcrit.org/toxhound/ff-metal-hydrides/>

Hydrogen selenide smells of decayed horseradish and is primarily used to grow zinc selenide lenses for infrared detectors. The gas is quite irritating upon inhalation and quickly forms selenious acid when encountering moisture in or upon us, producing a garlic odor. Hydrogen selenide mixed in vitro with guinea pig blood also produced deformed red cells, but did not produce hemoglobinuria. There exist no reports of H_2Se producing hemolysis in animals or humans. Inhalation toxicity appears mainly to be irritation.

From the standpoint of acute inhalation, then, it is difficult to imagine a likely cause of massive hemolysis and renal failure other than arsine. A list of ingested or injected substances capable of causing severe oxidant hemolysis with some



methemoglobinemia is long and can't be discussed here. Some were mentioned in a previous post on methylene blue infusions for methemoglobinemia. We'll simply note naphthalene, chlorates, chromates, dapsone, aniline and nitrobenzene as examples. We also don't have space here to address workers who may have severe glucose-6-phosphate dehydrogenase deficiency and implications for exposure to industrial chemicals.

Acute exposures

College student (Female 21) was exposed once per week for 1 year in the lab. Conc was high enough to cause choking. Complained of chronic diarrhea and abdominal pain for 6 months. Bitter metallic taste and garlicky breath. Good health except for conjunctivitis and nasal congestion. Problem went away after she left her position.¹

A 24 year-old male who accidentally inhaled hydrogen selenide immediately developed cough and wheeze and was admitted to hospital 18 hours later with progressive dyspnoea. Examination and investigations revealed pneumomediastinum (but no other chest X-ray abnormalities), hypoxia (pO₂ 9.2 kPa) and a severe obstructive ventilatory defect. Substantial improvement ensued during the next five days with conventional therapy (Schechter et al, 1980).²

Incidents

These are the most significant incidents.

Gas User, US, 1982

A cylinder was accidentally vented in a R&D hood. No details

Gas User, US, 1986

In an R&D hood 4 hydrogen cylinders were tied to a manifold with stainless braided pigtails. A 38 liter trichlorosilane container and a 90 lb hydrogen selenide cylinder were also stored in the hood. A pigtail ruptured as a hydrogen cylinder valve is opened, operator quickly exited the R&D lab. A Lab furnace ignites the hydrogen and the explosion blows out the exit door which hits him in the back of the head. Roof blows upward and resettles back onto the concrete block walls. Falling debris injures another operator.

The fire melts the valve outlet cap gasket (CGA660) and the valve seat (Kel F) of the hydrogen selenide cylinder, releasing its contents. Trichlorosilane ball valve PTFE packing melted releasing the TCS.

Fire was extinguished by the room sprinkler system. Heavy smoke when fire dept made entry.

A number of people are acutely exposed.

- 15 firefighters (3 held overnight)
- 3 police officers
- 2 company employees
- 1 visitor
- 16 employees from surrounding companies
- 1 cablenews person

Medical treatment primarily for upper respiratory irritation. Rotten egg odor could be detected 1 mile away.

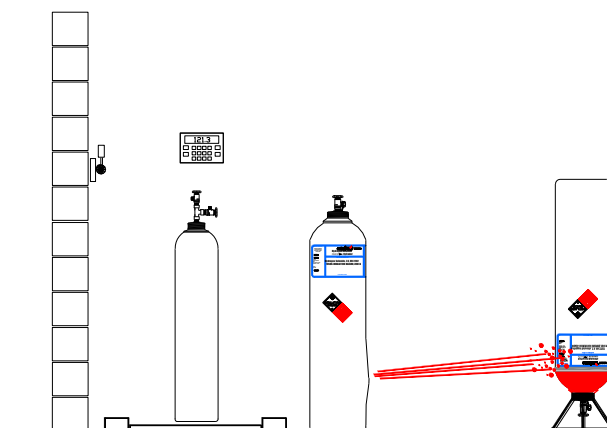


Gas Manufacturer, US, 1986

Vent for manufacturing system was partially blocked by slide damper in duct. High pressure mixture was being vented and the gas came out of the hood exposing 4 operators.

Gas Manufacturer, US, 2001

Overfilled cylinder ruptured releasing 160 lbs in less than a minute.



Eight workers or subcontractors were acutely exposed, four had to be rescued. All suffer from severe respiratory distress and irritation of the body. Immediate uncontrolled coughing and tearing of the eyes. Bodies reeked of garlic. EMS refused to transport victims until they were decontaminated using a dilute bleach solution. Five others went to hospital for observation. No permanent injuries although most suffer easily from respiratory ailments.



Eugene Ngai

Chemically Speaking LLC

References:

1. Alderman, L.C., Bergin, J. J. "Hydrogen Selenide Poisoning: An Illustrative Case with Review of Literature", Archives of Environmental Health, Nov/Dec 1986 Vol 41 No. 6, pp 354-358
2. Schecter A, Shanske W, Stenzler A, Quintilian H, Steinberg H. Acute hydrogen selenide inhalation. Chest 1980; 77: 554-5
3. EXPLOSION RIPS WOBURN FIRM CHEMICAL FUMES SEND 38 FOR TREATMENT, The Boston Globe, April 24, 1986
4. Overfilled tank caused explosion, REBECCA MB. PEARSON, Courier Times, Jan 30, 2001