Informasjon til Sikkerhetsforum.

Mulige senskader (følgeskader) etter kortvarig høy eksponering for «knock down gassen» hydrogensulfid (H_2S).

Møte i Sikkerhetsforum 16. februar 2017

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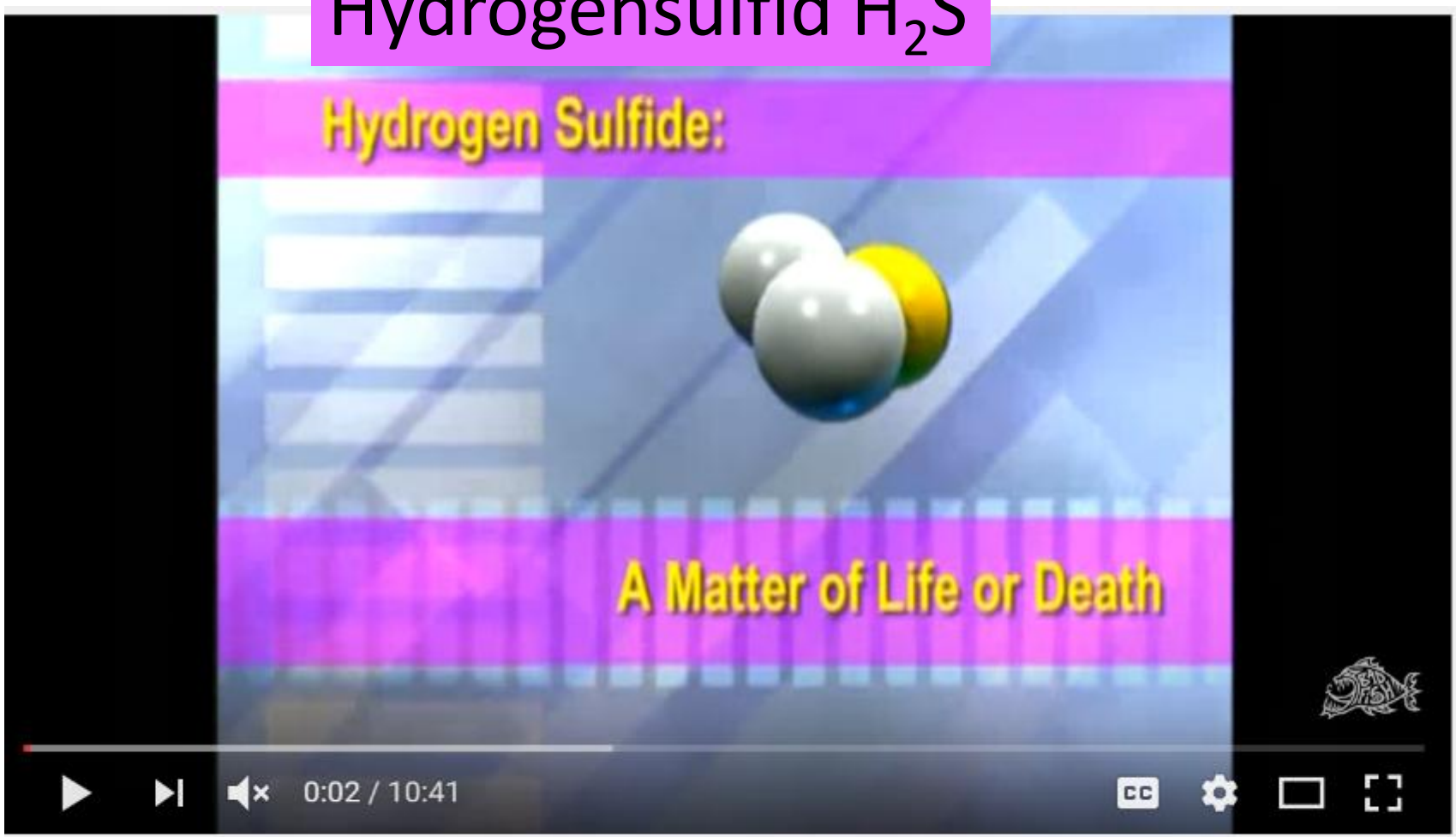
Hydrogensulfid H_2S



Hydrogen Sulfide (H2S): A Matter of Life or Death

https://www.youtube.com/watch?v=ZSI9Rh19c5Q

Det typiske ved H_2S ulykker og skader etter hendelser er følgende generelle observasjoner:

- Det hvor det har vært forgiftning på grunn av H_2S synes det å ha vært mangel på tilstrekkelig kunnskap om farene.
- Det har vært mangel på kunnskap om at H_2S utslipp kan forekomme og de potensielle konsekvensene et slikt utslipp kan ha.
- På grunn av manglende oppmerksomhet om forekomsten av H_2S, var det i mange tilfeller mangel på tilstrekkelig beredskap til å håndtere utslipp av slik giftig gass.
- Mangelen på tilpassede gassalarmer og personlig verneutstyr gav i en rekke tilfeller dødelig utgang på H_2S eksponeringen.

- Norsk oversettelse av sammendrag til rapporten Analysis of H2S – incidents in geothermal and other industries Preliminary analysis of data September 2009 OECD WGCA

http://www.vinnueftirlit.is/media/greinar-og-skyrslur/2009_oecd_analysis_of_h2s-incidents.pdf

Opplag av borerigger og skip øker risikoen for H2S dannelse

Stillestående forhold gir store muligheter for at H2S utvikles i tanker, slanger, rør, mannhull, utstyr osv……

Opplag og nedstenging av plattformer og produksjon krever ekstra kontroll, forsiktighet og opplæring

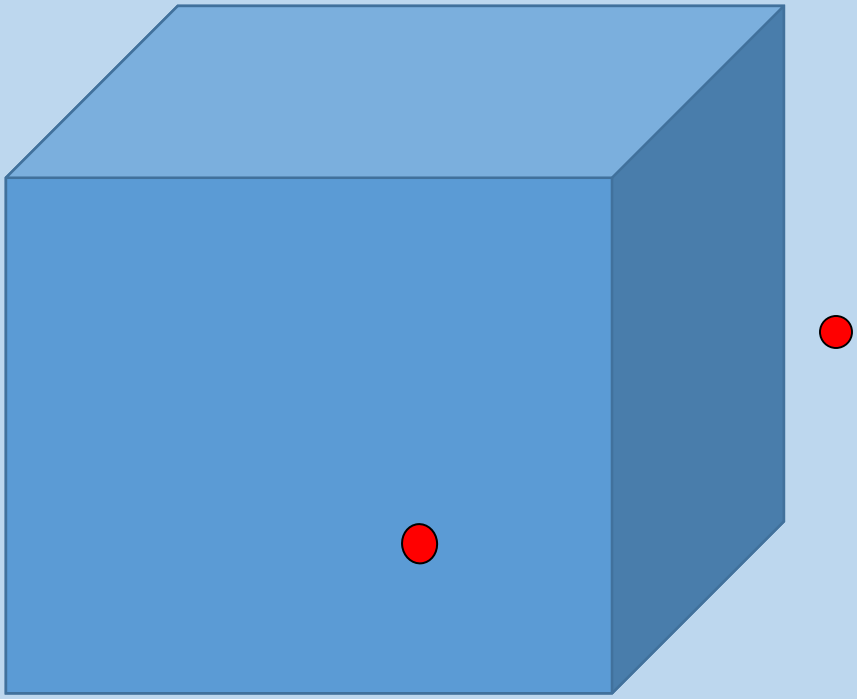
Det er forskjell på å måle om det er brannfarlig miljø eller om det er helsefarlig miljø.

Brann- og eksplosjonsfare måles i volumprosent (hundredeler) %.
Helserisiko måles i milliondeler ppm

1Volum% = 10000 ppm

Konsentrasjonsangivelser av kjemisk eksponering

1 kubikkmeter (m^3)
= 1000 liter



Grenseverdier oppgis i parts pr million (ppm) eller milligram pr. kubikkmeter (mg/m^3)

1 ppm er en gassboble på 1 cm^3 (1 milliliter) tynnet ut i $1m^3$.

1volum% = 10000 ppm

ppm
1 – 5 ppm

20 – 50

100 – 200

250 – 500

500

500 - 1000

2 H_2S -occupational hazards

Hydrogen sulphide (H_2S) is a very toxic gas at normal temperatures. It poses a very serious inhalation hazard. Effects at various exposure levels are believed to be as follows [4].

0.001-0.13 ppm	odour threshold (highly variable)
1-5 ppm	moderately offensive odour, possibly with nausea, or headaches with prolonged exposure;
20-50 ppm	nose, throat and lung irritation, digestive upset and loss of appetite, sense of smell starts to become "fatigued", odour cannot be relied upon as a warning of exposure;
100 -200 ppm	severe nose, throat and lung irritation, ability to smell odour completely disappears;
250-500 ppm	potentially fatal build-up of fluid in the lungs (pulmonary oedema) in the absence of central nervous system effects (headache, nausea, dizziness), especially if exposure is prolonged;
500 ppm	severe lung irritation, excitement, headache, dizziness, staggering, sudden collapse ("knockdown"), unconsciousness and death within 4-8 hours, loss of memory for period of exposure;
500-1000 ppm	respiratory paralysis, irregular heart beat, collapse, and death. It is important to note that the symptoms of pulmonary oedema, such as chest pain and shortness of breath, can be delayed for up to 48 hours after exposure.

Analysis of H2S – incidents in geothermal and other industries
OECD WGCA Preliminary data analysis Geothermal H2S-incidents, Sept. 2009
http://www.vinnueftirlit.is/media/greinar-og-skyrslur/2009_oecd_analysis_of_h2s-incidents.pdf

SAFETY AND HEALTH TOPICS

Hydrogen Sulfide

Hazards | Hydrogen Sulfide in Workplaces | Evaluating/Controlling Exposure

Hazards

Health Hazards

Hydrogen sulfide gas causes a wide range of health effects. Workers are primarily exposed to I breathe and for how long. Exposure to very high concentrations can quickly lead to death.

Short-term (also called acute) symptoms and effects are shown below:

Concentration (ppm)
0.00011-0.00033
0.01-1.5
2-5
20
50-100
100
100-150
200-300
500-700
700-1000
1000-2000

Worker Exposure Limits
NIOSH REL (10-min. ceiling): 10 ppm
OSHA PELs: General Industry Ceiling Limit: 20 ppm General Industry Peak Limit: 50 ppm (up to 10 minutes if no other exposure during shift) Construction 8-hour Limit: 10 ppm Shipyard 8-hour limit: 10 ppm
NIOSH IDLH: 100 ppm
IDLH: immediately dangerous to life and health (level that interferes with the ability to escape) (NIOSH)
PEL: permissible exposure limit (enforceable) (OSHA)
ppm: parts per million
REL: recommended exposure limit (NIOSH)

Concentration (ppm)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

https://www.osha.gov/SLTC/hydrogensulfide/hazards.html

Mengde H_2S gass for å gi 1000 ppm

- 1 liter gass i

1 kubikkmeter (m^3)

- 10 liter gass i 10 m^3

Gassmåling – nok oksygen, men hva med forurensningen?

Måler du 20,0% O_2 har du 0,9% (9000 ppm) av noe annet.

Kan vi være sikre på at dette annet ikke er helsefarlig?

Artikkel som viser varige skader hos pasienter som har vært bevisstløse etter H_2S forgiftning.

American Journal of Industrial Medicine 20:91–101 (1991)

Brain Damage Caused by Hydrogen Sulfide: A Follow-Up Study of Six Patients

Bjørn Tvedt, MA, Knut Skyberg, MD, Olaf Aaserud, MD, Ånund Hobbesland, MD, and Tove Mathiesen, MA

Hydrogen sulfide (H_2S) poisoning involves a risk of hypoxic brain damage. Six patients who lost consciousness due to H_2S poisoning are described. The symptoms varied from anosmia in the patient with the shortest but highest exposure to delayed neurological deterioration in the patient with the longest exposure. The two patients with the most serious symptoms developed pulmonary edema, which may have prolonged the hypoxia. The patients were reexaminated 5 years or more after the poisoning. The five patients who had been unconscious in H_2S atmosphere for from 5 to 15–20 min showed persisting impairment at neurological and neuropsychological re-examination. Memory and motor function were most affected. One patient was seriously demented. Recent reports of large groups of H_2S-poisoned workers probably underestimate the risk of sequelae, due to the inclusion of cases with exposure of short duration and lack of follow-up.

Key words: amnesic syndrome, delayed encephalopathy, anoxia, neuropsychological tests, neurotoxin, hydrogen sulfide exposures, ammonia, animal waste products

6 pasienter som hadde vært bevisstløse etter H_2S forgiftning ble fulgt opp etter 5 år eller mer etter ulykkene.

For 5 pasienter som hadde vært bevisstløse i H_2S atmosfære i 5 til 15-20 minutter ble det vist varig nedsettelse av nevrologisk og neuropsykologisk funksjon. Hukommelse og motoriske funksjoner var mest påvirket. En pasient var alvorlig dement.

http://www.csun.edu/~dorsogna/byron/H2Snew.pdf

TABLE I. Medical Findings in the Patients at Follow-Up, and Duration of Unconsciousness in the H_2S Atmosphere

Patient number	Age[a]	Years[b]	Main affected functions	EEG	CT PEG	Test[c]	H_2S exposed unconscious (min)
1	46	5	(Smell, vision, memory)[d]	–[e]	–	–	<1
2	31	8	Dementia, motor function, vision	–			5–10
3	59	7	Memory, motor function (vision)	+[f]	+	+	~15
4	53	6	Motor function (memory, vision)	(+)		+	~10
5	30	10	Visual abilities, memory	+	–	+	<15
6	31	6	Motor function, vision, memory	+	+	+	15–20

[a]Age at the time of the poisoning.
[b]Number of years between the poisoning and the last examination.
[c]Neuropsychological examination.
[d]Temporary and uncertain findings are given in parenthesis.
[e]Normal.
[f]Pathological finding.

Ann. N.Y. Acad. Sci. ISSN 0077-8923

ANNALS OF THE NEW YORK ACADEMY OF SCIENCES
Issue: *Countermeasures Against Chemical Threats*

Acute hydrogen sulfide–induced neuropathology and neurological sequelae: challenges for translational neuroprotective research

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Hydrogen sulfide (H_2S), the gas with the odor of rotten eggs, was formally discovered in 1777, over 239 years ago. For many years, it was considered an environmental pollutant and a health concern only in occupational settings. Recently, however, it was discovered that H_2S is produced endogenously and plays critical physiological roles as a gasotransmitter. Although at low physiological concentrations it is physiologically beneficial, exposure to high concentrations of H_2S is known to cause brain damage, leading to neurodegeneration and long-term neurological sequelae or death. Neurological sequelae include motor, behavioral, and cognitive deficits, which are incapacitating. Currently, there are concerns about accidental or malicious acute mass civilian exposure to H_2S. There is a major unmet need for an ideal neuroprotective treatment, for use in the field, in the event of mass civilian exposure to high H_2S concentrations. This review focuses on the neuropathology of high acute H_2S exposure, knowledge gaps, and the challenges associated with development of effective neuroprotective therapy to counteract H_2S-induced neurodegeneration.

Keywords: brain; hydrogen sulfide; neuropathology; neurodegeneration; neuroprotection

http://onlinelibrary.wiley.com/doi/10.1111/nyas.13148/full

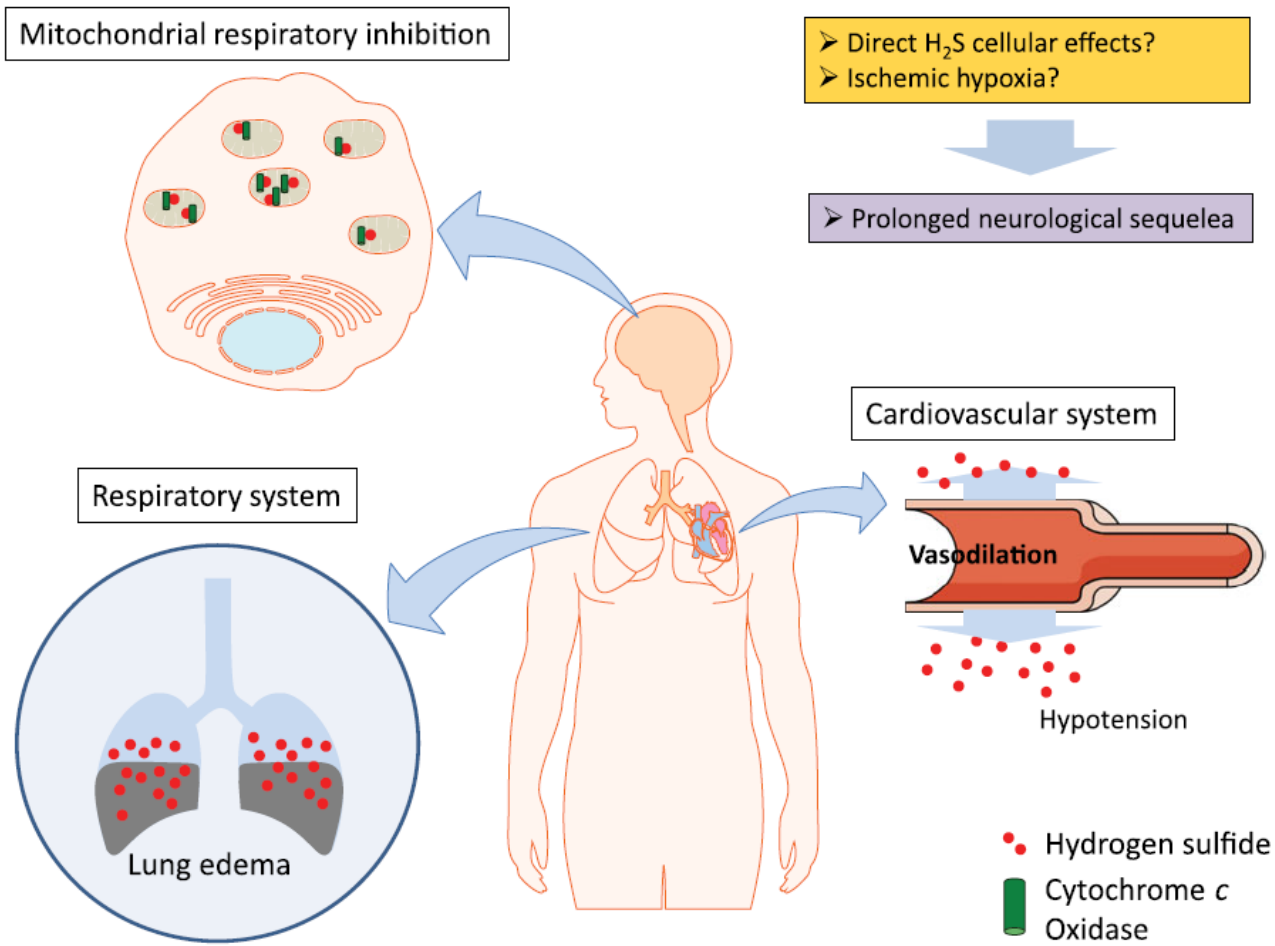

Figure 4. Proposed pathophysiology of H_2S-induced neurotoxicity. Acute exposure to high levels of H_2S induces lung edema, leading to reduced oxygen absorption in the lungs. H_2S also affects the cardiovascular system, inducing vasodilation leading to hypotension. Together, both lead to development of ischemic hypoxia in the brain. The function of cytochrome *c* oxidase in the mitochondrial electron transport chain is also inhibited by H_2S, leading to reduced ATP production. Collectively, these pathophysiologic effects, coupled with direct cellular effects, account for the acute neurotoxic effects and the subsequent development of prolonged neurological sequelae.

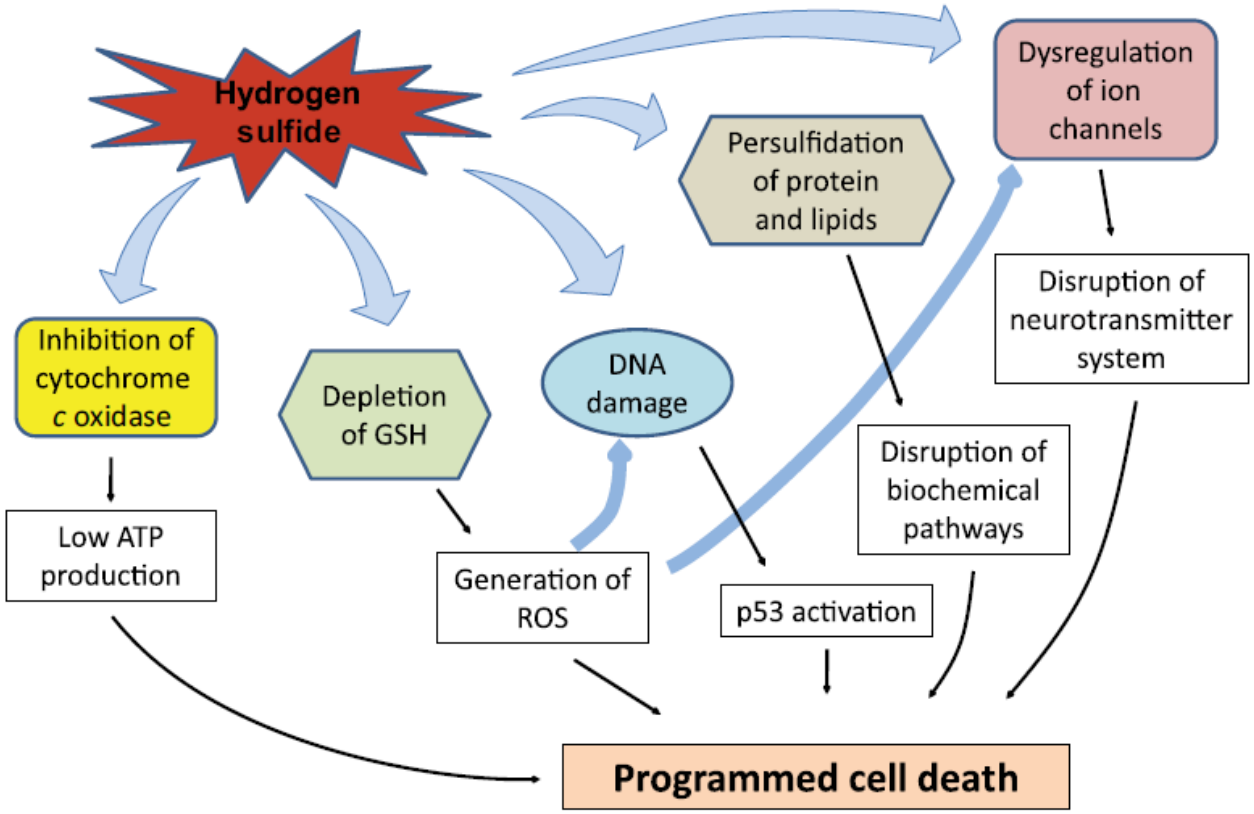

Figure 5. Potential mechanisms of H_2S-induced cytotoxicity. Hydrogen sulfide inhibits cytochrome *c* oxidase in mitochondria, leading to low ATP production. H_2S also disrupts calcium homeostasis, leading to high intracellular calcium. Depletion of reduced glutathione leads to generation of reactive oxygen species (ROS). H_2S induces DNA damage, persulfidation of protein and lipids, and dysregulation of ion channels, which are further aggravated by excessive intracellular levels of ROS. Collectively, these H_2S-induced effects may lead to programmed cell death in neurons and glia.

H_2S eksponerte trenger langvarig og systematisk oppfølging

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tih.sagepub.com
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Low-level hydrogen sulfide and central nervous system dysfunction

Kaye H Kilburn[1], Jack D Thrasher[2] and Michael R Gray[3]

Abstract

Forty-nine adults living in Lovington, Tatum, and Artesia, the sour gas/oil sector of Southeastern New Mexico, were tested for neurobehavioral impairment. Contributing hydrogen sulfide were (1) an anaerobic sewage plant; (2) two oil refineries; (3) natural gas/oil wells and (4) a cheese-manufacturing plant and its waste lagoons. Comparisons were to unexposed Wickenburg, Arizona, adults. Neurobehavioral functions were measured in 26 Lovington adults including 23 people from Tatum and Artesia, New Mexico, and 42 unexposed Arizona people. Participants completed questionnaires including chemical exposures, symptom frequencies and the Profile of Mood States. Measurements included balance, reaction time, color discrimination, blink reflex, visual fields, grip strength, hearing, vibration, problem solving, verbal recall, long-term memory, peg placement, trail making and fingertip number writing errors (FTNWE). Average numbers of abnormalities and test scores were adjusted for age, gender, educational level, height and weight, expressed as percent predicted (% pred) and compared by analysis of variance (ANOVA). Ages and educational attainment of the three groups were not statistically significantly different (ssd). Mean values of Lovington residents were ssd from the unexposed Arizona people for simple and choice reaction times, balance with eyes open and closed, visual field score, hearing and grip strength. Culture Fair, digit symbol substitution, vocabulary, verbal recall, peg placement, trail making A and B, FTNWE, information, picture completion and similarities were also ssd. The Lovington adults who averaged 11.8 abnormalities were ssd from, Tatum–Artesia adults who had 3.6 and from unexposed subjects with 2.0. Multiple source community hydrogen sulfide exposures impaired neurobehavioral functions.

Keywords

neurobehavioral, encephalopathy, reduce sulfur gases, sewage

http://journals.sagepub.com/doi/pdf/10.1177/0748233710369126

Krav til opplæring i håndtering av H2S i USA og UK. Norge har ingen spesifikke krav!

Recommended Practice for Drilling and Well Servicing Operations Involving Hydrogen Sulfide

API RECOMMENDED PRACTICE 49
THIRD EDITION, MAY 2001
REAFFIRMED, MARCH 2007

ftp://ftp.consrv.ca.gov/pub/oil/SB4EIR/docs/API_2001.pdf

OPITO APPROVED STANDARD

Basic H_2S Training

OPITO Standard Code: 9014

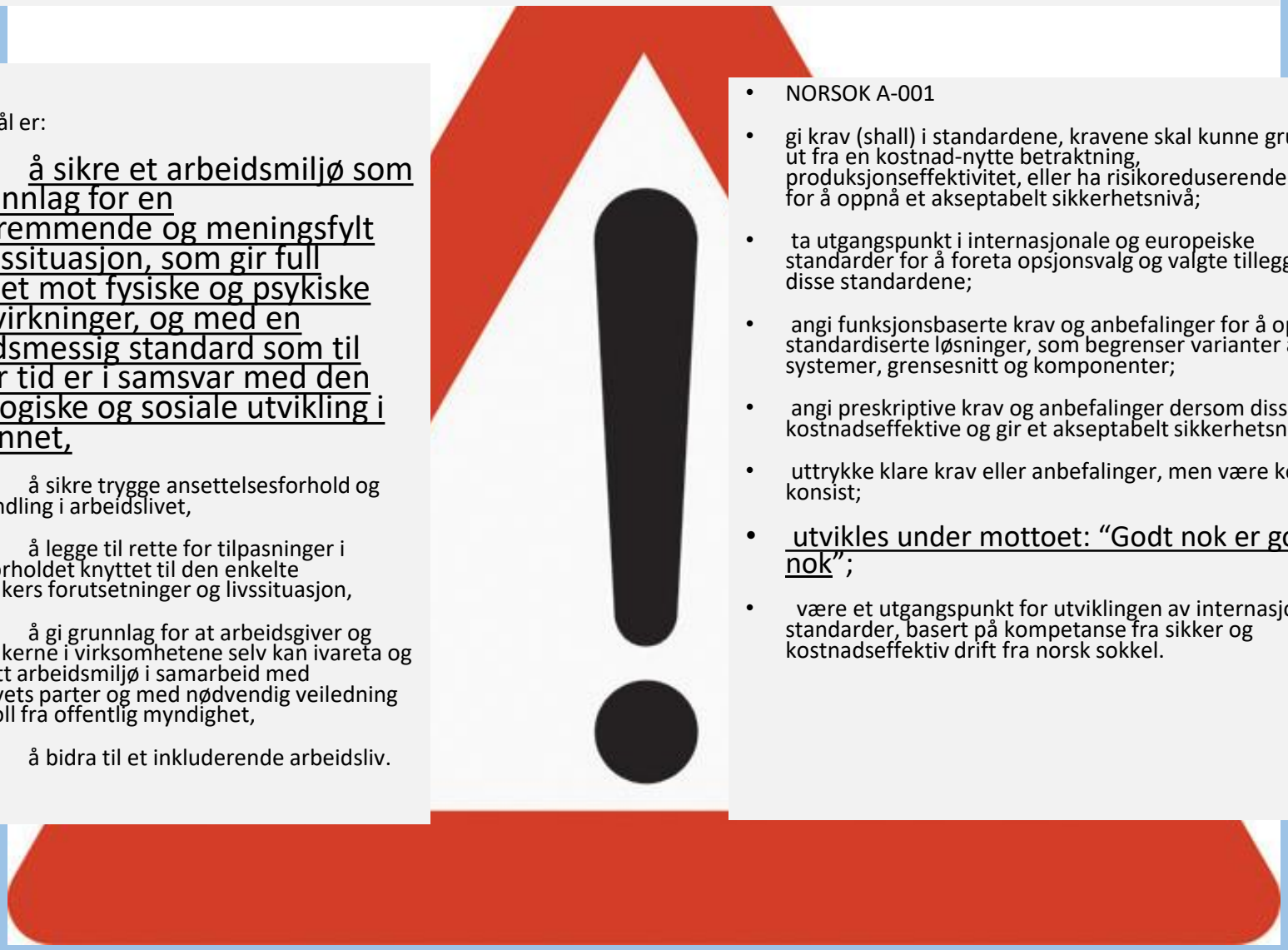
http://www.opito.com/media/downloads/basic-h2s-training.pdf

Arbeidsmiljøloven står over NORSOK!

Arbeidsmiljøloven § 1 vs. NORSOK A-001

Lovens formål er:

- a) å sikre et arbeidsmiljø som gir grunnlag for en helsefremmende og meningsfylt arbeidssituasjon, som gir full trygghet mot fysiske og psykiske skadevirkninger, og med en velferdsmessig standard som til enhver tid er i samsvar med den teknologiske og sosiale utvikling i samfunnet,
- b) å sikre trygge ansettelsesforhold og likebehandling i arbeidslivet,
- c) å legge til rette for tilpasninger i arbeidsforholdet knyttet til den enkelte arbeidstakers forutsetninger og livssituasjon,
- d) å gi grunnlag for at arbeidsgiver og arbeidstakerne i virksomhetene selv kan ivareta og utvikle sitt arbeidsmiljø i samarbeid med arbeidslivets parter og med nødvendig veiledning og kontroll fra offentlig myndighet,
- e) å bidra til et inkluderende arbeidsliv.



- NORSOK A-001
- gi krav (shall) i standardene, kravene skal kunne grunngis ut fra en kostnad-nytte betraktning, produksjonseffektivitet, eller ha risikoreduserende effekt for å oppnå et akseptabelt sikkerhetsnivå;
- ta utgangspunkt i internasjonale og europeiske standarder for å foreta opsjonsvalg og valgte tillegg til disse standardene;
- angi funksjonsbaserte krav og anbefalinger for å oppnå standardiserte løsninger, som begrenser varianter av systemer, grensesnitt og komponenter;
- angi preskriptive krav og anbefalinger dersom disse er kostnadseffektive og gir et akseptabelt sikkerhetsnivå;
- uttrykke klare krav eller anbefalinger, men være kort og konsist;
- utvikles under mottoet: "Godt nok er godt nok";
- være et utgangspunkt for utviklingen av internasjonale standarder, basert på kompetanse fra sikker og kostnadseffektiv drift fra norsk sokkel.