OECD

Analysis of H_2S – incidents

in geothermal and other industries

Preliminary analysis of data

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September 4th 2009

OECD WGCA Steering Group of Analysis of H_2S Incidents

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Summary

A preliminary search for available data on incidents involving Hydrogen Sulphide (H_2S) incidents in industry generally and in particular the geothermal industry was carried out. The search was directed at publicly accessible information sources and specialised databases. In particular databases which document chemical accidents were considered, concentrating on the accidental release of H_2S.

General data on occupational exposure to H_2S (accidental or long-term low level) were not collected and analysed to any large extent, these data are kept in national accident or medical databanks by OSH and health care agencies. Therefore, a comprehensive search into occupational incidents, neither geothermal nor other, could be performed at his stage.

From the incidents considered the following general observations can be made.

- In those incidents in which toxic effects due to H_2S were experienced there appears to have been a lack of adequate knowledge of the hazards. That is a lack of knowledge that a H_2S release could occur and the potential consequences of H_2S exposure.
- Due to the lack of awareness relating to the occurrence of H_2S, there was, in many cases, a lack of adequate preparedness to deal with the release of toxic gas.
- The lack of suitable gas alarms and personal protective equipment led, in a number of cases, to fatal H_2S exposure.
- H_2S is a life threatening hazard in the geothermal industry and a number of other industrial activities as indicated by the data shown here.
- Some industries (chemical processing, petroleum refining and petrochemical), whilst having H_2S-incidents, do not appear to suffer fatal consequences to the same degree as perhaps the geothermal and waste treatment industries. Here is an opportunity to learn lessons relating to good practice across industry sectors.

- In particular an apparently disproportionate involvement of contractor employees in H_2S incidents, carrying out repair, maintenance and cleaning activities is of particular concern.
- Data on geothermal incidents which are readily available were few, however there are indications that more detailed information may be obtainable within the major geothermal nations
- Many occupational exposures to H_2S either go unrecorded or escape a systematic documentation and data collection. Generally it can be said that occupational accidents with fatalities are systematically recorded, however access to this data is limited.

1 Introduction

Within the Chemical Accidents 2009 – 2012 Work Programme Iceland proposed the project on the analysis of H_2S-incidents and offered to take the lead. H_2S is very toxic, quickly reactive, and causes serious accidents. Geothermal wells are a source of H_2S that pose specific problems. It is proposed to collect data and analyse incidents and accidents caused by hydrogen sulphide in industry with a focus on geothermal facilities.

The proposed project originates from discussions on geothermal stations work environment at AOSH in Iceland. Such a project will be relevant to many member countries, where geothermal energy is used. However, there are many other situations in which H_2S is an issue.

The objective of the proposed project is to collect data and undertake an analysis to better understand H_2S accidents in the geothermal industry as well as other industries involving H_2S.

The data collected will be used to determine counter-measures to H_2S hazards. Those will be applicable to geothermal power plants and to some other industrial facilities. The accessibility of data could limit the analysis of accidents' causes. Geothermal areas are of varying types when comes to H_2S.

Problems with the data and the accessing of data are discussed. Conclusions that can be drawn from this preliminary study are given in a general manner at the end of the report and outlines of possible further study are also discussed.

At the 18th Working Group on Chemical Accidents Meeting a steering group was formed and it was agreed to collect and review accident data / statistics from the geothermal industry as well as from other relevant (industrial) sectors such as the petro-chemical industry.

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.

Prolonged exposure (for several hours or days) to concentrations as low as 50-100 ppm can lead to rhinal inflammation, cough, hoarseness, and shortness of breath. Prolonged exposure to higher concentrations can produce bronchitis, pneumonia and a potentially fatal build-up of fluid in the lungs (pulmonary oedema).

The interim AEGL-values are:

Hydrogen sulphide 7783-06-4 (Interim)

ppm 9/10/02					
	10 min	30 min	60 min	4 hr	8 hr
AEGL 1	0.75	0.60	0.51	0.36	0.33
AEGL 2	41	32	27	20	17
AEGL 3	76	59	50	37	31

3 H_2S environments in industry

Hydrogen sulphide is encountered in many workplaces. These include:

- chemical and related industries where the gas itself is used,
- industries handling sulphides or other sulphuric substances, or where it occurs as an intermediate or as a waste product.
- the oil & gas industry and other types of raw-material extraction and handling where it is part of the original raw material. This includes geothermal fluid extraction and processing.
- workplaces where fermentation and other anaerobic decomposition of organic material, organic or inorganic sulphur containing material occur, such as in biomass processing, farm work and waste handling and processing. This is caused by groups of so called sulphate-reducing bacteria that reduce sulphur compounds, including sulphite, thiosulphate or elemental sulphur, to sulphide

Following are examples of industries where H_2S hazard occurs:

- -Oil and gas:

Crude oil refineries (primarily sour crude oil), crude oil processing/handling plants and transmissions/pipelines, sour natural gas processing/handling plants/stations storages and transmissions/pipelines

- Animal fat and oil processing
- Asphalt storage
- Blast furnaces
- Breweries and fermentation processes
- Chemicals and related production processes, various:
  Carbon disulphide, dyes, thiophene, sulphur, bromide-bromine, soap, phosphate purification, hydrochloric acid purification, cellophane, rubber, plastics, soap, silk, rayon, photoengraving, synthetic fibers, polysulphide caulking, artificial flavour, refrigerants, glues, textile printing, etc
- Clean-up activities of organic/sulphur containing slurry/sludge, various
- Coal gasification plants
- Coke ovens
- Copper ore sulphidising and metallurgy, gold ore, lead ore, lead removal, barium carbonate and barium salt production, pyrite burning etc.
- Farms and livestock operations
- Fertilizer production
- Fishing vessel holds, fat fish processing

- Geothermal plants and utilities
- Landfills of municipal/farm/organic waste
- Metal processing, various:
- Pulp and paper production
- Sewage treatment plants
- Slaughterhouses and rendering plants
- Sugar production
- Sulphur and hydrogen sulphide production
- Tanneries
- Waste treatment operations

There are numerous case reports of deaths, especially in the oil and gas extraction industry [25], sewage maintenance, and on farms. Most fatalities have occurred in relatively confined spaces (e.g. sewers, sludge tanks, cesspools, or H_2S collecting in depressions on open land or in buildings) [7]. In many cases, multiple deaths have occurred at a single site. Rescuers, attempting to save an unconscious co-worker, have entered a confined area without respiratory protection or safety lines. They, in turn, have been overcome by H_2S. Workers who survive a serious short-term H_2S exposure may recover completely or may experience long-term effects. [4, 1, 2, 3, 7, 32].

4 Geothermal industry and H_2S

4.1 Widespread and growing geothermal utilisation

Many countries have utilised geothermal energy for decades and some for centuries. These are mainly in the tectonic rift zones where the continental plates either collide or diverge. There the heat from the Earth's interior is closest to the surface and cracks and porous rock allows water to seep down into the hot crust and steam and hot water to seep upwards. Geothermal heat can also be found in other locations where the temperature increase with depth may be slower and porosity for water less than in the rift zones but in some instances the heat is worthwhile drilling for. Even hot deep rock is being used to heat water and return to surface [17]. The following table lists countries that utilise geothermal energy (see also IGA lists [29] of both total geothermal energy and geothermal electric energy production).

Table of geothermal utilisation by country, GWh/year (year 2000) [28].

Rank	Countries	Amount
1	China	8,724
2	United States	5,640
3	Iceland	5,603
4	Turkey	4,377
5	New Zealand	1,967
6	Georgia	1,752
7	Russia	1,703
8	Japan	1,621
9	France	1,360
10	Sweden	1,147
11	Mexico	1,089
12	Italy	1,048
13	Romania	797
14	Hungary	785
15	India	699
16	Switzerland	663
17	Serbia and Montenegro	660
18	Slovakia	588
19	Israel	476
20	Bulgaria	455
21	Austria	447
22	Algeria	441
23	Germany	436
24	Jordan	428
25	Canada	284

26	Slovenia	196
27	Lithuania	166
28	Croatia	154
29	Macedonia, The Former Yugoslav Republic of	142
30	Finland	134
31	Argentina	125
32	Greece	107
33	Australia	82
34	Poland	76
35	Colombia	74
36	Tunisia	48
37	Czech Republic	36
= 38	Belgium	30
= 38	Guatemala	30
40	Denmark	21
41	Netherlands	16
42	Peru	14
43	Indonesia	12
44	Portugal	10
45	Norway	9
46	Philippines	7
= 47	United Kingdom	6
= 47	Nepal	6
49	Honduras	5
= 50	Thailand	4
= 50	Venezuela	4
52	Kenya	3
53	Chile	2
	Total	44,709

Part of the geothermal calories that are tapped as steam from the high temperature areas is used for electricity generation, in particularly USA, Philippines, Mexico, Indonesia, Italy, Japan, New Zeeland and Iceland. There are 24 countries who have installed geothermal electric capacity. The total world-wide geothermal electricity production capacity was 9.7 GW in 2007 and is projected to grow to nearly 11 GW in 2010 [30].

4.2 Hazards from H_2S and other geothermal gasses

In Icelandic "hveralykt" means the smell of geysers, the rotten-egg smell of hydrogen sulphide usually associated with hot springs. Geologists distinguish between high-temperature and low-temperature fields. The high-temperature fluid, steam with boiling water droplets torn up in varying amounts brings up more gases but their concentration varies from one place to the other and even in time. The low temperature areas give geothermal water which contains dissolved gasses such as N_2, and smaller amounts of CO_2 and H_2S. The geothermal steam from the high-temperature areas, of which 0.5-1 w% can be gas, contains a different blend of gasses such as CO_2, H_2S, H_2 and CH_4 in varying concentrations. The CO_2 is usually in the largest concentration followed by H_2S and hydrogen (when molar concentration is considered). As an example, one 200 MW electric geothermal plant in Iceland uses geothermal steam of which around 0.5 w % is gas, of that about 80-85 w% is CO_2 and about 15 w % is H_2S. This plant produces nearly 10,000 tons annually of H_2S. The gasses are left as the steam condenses. Any container, closed or semi-closed space in a geothermal plant where pressure drops or cooling of the geothermal steam occurs can contain or even accumulate H_2S gas. It is heavier than air and settles in low lying areas. H_2S is a good scavenger of oxygen in aqueous solution and consumes oxygen dissolved in the geothermal water. Consumption of oxygen by H_2S in the gas phase, when it mixes with atmospheric oxygen, is less well known but given the right environment and sufficient time, H_2S will react with oxygen and deplete it in stagnant air bodies. If the oxygen content goes (from 21%) below 10% in the working environment, inhaling a breath can cause nearly immediate unconsciousness, a similar effect to what happens when the H_2S content reaches a few hundred ppm. This means that plant equipment to handle geothermal fluids as well as the plant working environment can be hazardous to workers as experience from Iceland and other countries show. Sudden and even unpredictable presence of H_2S, as well as the other asphyxiating non-poisonous geothermal gasses, causes incidents and the oxygen scavenging effect of H_2S plus the oxygen thinning effect of the other gasses can make spaces dangerously low in oxygen. This complicates analysis of the chemical cause of incidents.

To sum up the special properties of geothermal steam that makes it hazardous:

- Geothermal gasses remain in the steam processing and turbine system, after the steam has condensed, until vented out
- Seemingly harmless leaks of steam from piping or equipment inside buildings, into confined or semi-confined spaces, can generate large volumes of gas
- Accumulation of gas in low lying, poorly ventilated spaces

- Knock-down effect of H_2S: Inducing unconsciousness in seconds without warning
- H_2S is an oxygen scavenger and, given the right conditions, consumes oxygen in stagnant air.

Icelandic firms and institutions working internationally in the geothermal business have encountered stories of many H_2S incidents and near-misses. There is a lack of written and organised data on these incidents many of whom have occurred at the stage of development or start-up, some in rather remote areas, some in developing countries. An example can be the following verbal account from a senior researcher in the Icelandic Energy Authority:

> In a geothermal plant in Kenya a photographer went into a manhole to photograph the inside of a flash tank to record corrosion on its walls. He was knocked down whereupon a person went into the tank to save him and was also knocked unconscious whereupon the third person tried to save the two and was also knocked down. All died and it appears H_2S was the main cause of death.

5 Data search

A preliminary search for information on H_2S incidents was carried out using readily accessible databases and other information sources without special inquiries or requests. Following are some excerpts and abstracts of pertinent data encountered in the search.

5.1 International medical abstracts on H_2S -poisoning.

From Ovid Medliner database:

- Hydrogen sulphide poisoning: Clarification of some controversial issues.

Hydrogen sulphide is a toxic gas about which much has been written. We discuss here several issues we believe would benefit from further clarification. Conclusions: We conclude that: 1) Certain neurotoxic effects of exposure are probably due to a direct toxic effect on the brain, while others are almost certainly a result of hypoxia secondary to H_2S -induced respiratory insufficiency; 2) pulmonary oedema is a common consequence of poisoning and there is suggestive evidence of hyperactive airway responses in some individuals following brief H_2S -induced unconsciousness (knockdown); 3) criteria for acceptable community levels are very different than those governing occupational standards; 4) urinary thiosulphate determinations can be useful for monitoring occupational exposure; and 5) determination of sulphide ion concentrations in blood or major organs can be useful in corroborating a diagnosis of fatal H_2S toxicity, but there are many pitfalls in collecting, storing, and analyzing tissue and fluid samples [10].

- A review of 152 cases of acute poisoning of hydrogen sulphide.

Clinical data of 152 cases of acute poisoning of hydrogen sulphide were analysed. Of these cases 5 were diagnosed as irritant reaction, 10 mild poisoning, 56 moderate, and 81 severe. Eight of the 152 cases died, with a fatality rate of 5.3%. 137 cases (90%) lost consciousness temporarily. The degree of disturbance of consciousness provided important basis for determining diagnostic grade. Recommendations for treatment were mainly comprehensive, supportive measures as well as first aid. Certain neuropsychic sequelae were found in some of the 95 cases followed up for 1 to 10 years[13].

5.2 France, ARIA database.

The search term “hydrogène sulfuré” generates a report of 108 incidents from the ARIA database, which covers incidents from France and also other countries. The database is maintained by BARPI [27]. A selection of some of the more recent incidents is summarised in English in Annex 1.

The ARIA database contains a range of incidents from smaller (sub-Seveso) to larger industrial events which are also reported in the EU MARS database. ARIA also contains a number of incidents from outside France. All reports are in French, a few “special cases” are also provided in English.

The fatal accidents are commonly in various waste handling and processing (including waste water and sewage treatment) followed by petroleum extraction and processing. A number of incidents occurred within inhabited areas, leading to effects within the local population

5.3 Germany. ZEMA-database and other sources

In Annex 2 there is a table of incidents recorded in Germany from 1969-2007

Eleven incidents are registered by the ZEMA [21] database which is the German federal database for recording reportable major accidents under the Major Accident Ordinance (Störfall-Verordnung). The most serious incident, i.e. those involving loss of life, injuries to persons, large scale contamination of the environment or substantial damage to property are then reported to the EU MARS database.

Five of the incidents listed have been reported in the media and were either amaller scale incidents or outside the scope of the Major Accident Ordinance

Five incidents are documented in the UBA publication Handbuch Störfälle (out of print) which records a large number of incidents of various types, details are often lacking and the original sources for the entries were very often press reports and not official investigations [22].

Of the 21 incidents above, over ½ are in chemical industry and somewhat less than ½ is in waste treatment or recycling activities. The more recently notified accidents are mostly in the chemical and oil & gas industry but waste treatment and recycling suffer more fatal accidents. As previously noted, temporary personnel in particularly maintenance, clean-up and loading/unloading are those who are most often seriously affected by H_2S-incidents. Production shut-down and start-ups are the most hazardous phases of plant operation as demonstrated in the list, half of the accidents are during construction, start-ups/shut down or maintenance and only about a third during normal process runs. In normal operation corrosion often plays a major part in the release of H_2S. In the recent fatal accidents, the known pattern of double/multiple fatality is demonstrated when helping hands to the first victim become victims as well

5.4 UK. Incidents of exposure in industry, 1990-2003.

HSE compiled a list of 35 on-shore H_2S -incidents between 1990 and 2003. Of those, nearly a half were apparently caused by some form of biological decomposition in a variety of environments where organic matter was present; from various waste, sludge, slurries, sumps and manure. Also acidification of sulphide containing residues in clean-up operations caused H_2S-releases. About a half of the listed incidents involve confined and semi-confined spaces. The other half of the incidents in the list were mostly in the handling of chemicals, from leaking H_2S equipment in chemical and related industries and in chemicals production. A few were in metallurgy and in labs. This half of the incidents did not as a rule involve confined spaces. Oil & gas industry incidents off-shore are not in the list. Six of the incidents (17%) are said to have been fatal and, alarmingly, two of them (33%) double, both by biologically generated H_2S; in a distillery effluent tank and in a slurry storage at a farm. Many of the incidents were serious and lead to unconsciousness. The brief accounts of these incidents show again how often it is difficult to make a distinction between asphyxiation and poisoning, let alone quantify a combined effect of both H_2S-poisoning and oxygen deficiency. The list states in some instances that asphyxia was the cause of illness. See Appendix 2 [19].

5.5 EU. The MARS database

The MARS-database of the EU is maintained by the Major Accident Hazards Bureau at the JRC and contains now about 600 accidents and near misses in establishments that come under the Seveso Directives, i.e. those that handle large amounts of dangerous substances. It is for the EU similar to what ZEMA is for Germany and would include accidents counted for there also. Accounts date back to 1982.

As an example of an on-line search in the database, it gives 39 major accidents where hydrogen sulphide releases led to human injuries between the years 1985 and 2008. Of the 39, 7 (18%) were fatal. The accidents were mainly in larger process plants of chemicals, oil, metallurgy and waste processing [31]. MARS is also the reporting database for the OECD Chemical Accidents programme. In this case the reports by non-EU countries is on a voluntary basis.

5.6 USA. Institutions. Workplace deaths by H_2S

CSB (The Chemical Safety Board) investigates chemical incidents in the US [8]. OSHA keeps also records of chemical incidents in industries. For a period of one decade (´84-´94) there were an average of 8 fatalities per year from H_2S-poisoning whereof nearly a quarter were co-workers rushing to help the first victim, a familiar pattern of H_2S fatal accidents generally.

-Occupationally related hydrogen sulphide deaths in the United States from 1984 to 1994

Alice Hamilton described fatal work injuries from acute hydrogen sulphide poisonings in 1925 in her book *Industrial Poisons in the United States*. There is no unique code for H_2S poisoning in the *International Classification of Diseases, 9th Revision*; therefore, these deaths cannot be identified easily from vital records. We reviewed US Occupational Safety and Health Administration (OSHA) investigation records for the period 1984 to 1994 for mention of hazardous substance 1480 (hydrogen sulphide). There were 80 fatalities from hydrogen sulphide in 57 incidents, with 19 fatalities and 36 injuries among coworkers attempting to rescue fallen workers. Only 17% of the deaths were at workplaces covered by collective bargaining agreements. OSHA issued citations for violation of respiratory protection and confined space standards in 60% of the fatalities. The use of hydrogen sulphide detection equipment, air-supplied respirators, and confined space safety training would have prevented most of the fatalities [23].

5.7 Canada. Oil & gas workers. Environmental releases.

-Oil and gas workers exposed to H_2S in Alberta

In their 1997 study, Hessel et al. submitted a questionnaire about health effects from hydrogen sulphide exposure to 175 oil and gas workers in Alberta, Canada, a known region for sour gas wells associated with the oil and gas industries. Of the 175 workers, on third reported having been exposed to H_2S, and 14 workers (8%) experienced knockdown, a term for the loss of consciousness due to inhaling high concentrations of hydrogen sulphide. The workers who had experienced knockdown exhibited the respiratory symptoms of shortness of breath, wheezing while hurrying or walking up hill, and random wheezing attacks. The investigators found no "measurable pulmonary health effects as a result of exposure to H_2S that were intense enough to cause symptoms but not intense enough to cause unconsciousness [24, 25].

- Environmental release occurrences in Canada 2000-2009

Records that cover nearly a decade, from 2000 to 23.6 2009, show 117 release incidents. Most of them are in petroleum or gas, waste water treatment plants and pulp and paper industries. In the oil and gas sectors, gas well blowouts are the most common cause. The Lodgepole incident in Alberta 1982 is perhaps the most significant and well documented in the literature. Since then, Alberta Energy Conservation Board has done risk research on modelling sour gas releases. Of the listed causes of releases equipment failure, likely often because of lack of maintenance, seems to be the most frequent single cause in cases where the cause is known. No quantifications of damages or fatalities are included in the list but most of them could apparently have been hazardous and caused H_2S poisoning [18].

5.8 *Japan. The RISCAD-database.*

The RISCAD database registers chemical incident in Japan. The number of serious accidents in the chemical industry decreased although accidents still happen with e.g. H_2S during non-operating condition in process plants [33].

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-Trends in chemical hazards in Japan

In the past, the chemical industry in Japan has been the cause of a number of major industrial accidents. Subsequent to each accident, specific lessons have been learned. These lessons learned have been implemented in terms of safety education of the employees and/or safety measures of the equipment and facilities resulting in a rapid decrease of corresponding accident frequencies. In this paper, we summarized both recent and past major accidents caused by chemical substances in fixed installations in Japan. Case studies show that runaway reactions are among the main causes of major accident occurrences in the chemical process industry in Japan. A recent fatal poisoning accident caused by H_2S gas generated during maintenance work again highlights the necessity of adequate safety management in a chemical factory. Therefore, even if hazard evaluation of chemical substances and chemical processes is necessary to prevent runaway reactions, human error is also an important factor contributing to reaction hazards [26] (se also: Wakakura, M. (1997) Human factor in chemical accidents, J. Safety Eng. High Press. Gas. Safety Inst. Japan, 34, 846).

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5.9 Iceland. Data of incidents in geothermal industry.

-General discussion of H_2S-hazards in geothermal plants

Records of accidents with gas poisoning in the geothermal industry are remarkably scarce in Iceland. One of the problems of finding H_2S poisoning incidents in older accounts in Icelandic records is that they are often unrecognisable from confined space accidents.

People in the geothermal industry have nevertheless many stories to tell of incidents with H_2S where luckily no lasting effects were observed. The geothermal springs have been utilised for heating for a long time although distant heating by piping started in 1906. Drill holes have so called hole-cellars built around them where workers often encountered H_2S that accumulated there, originating in the steam that leaked from the piping. Today, the drill hole cellars are shallower and have a ventilation system that ensures constant draft up from the cellar floor. The geothermal steam condenses and disappears or becomes a small drying pool on the floor but H_2S stays and accumulates in the cellars or building with deficient ventilation as it is heavier than air. Experience has taught people in the industry to be aware of this property of H_2S. Caution, including gas masks and alarm sensors, is exerted in buildings and confined spaces as well as outdoor areas in the geo-electric power plants nowadays. The short term exposure limit is 15 ppm but the alarms are often set on 10 ppm, the 8-hour limit.

Most fearsome is the special property of the gas to induce immediate loss of consciousness at one breath at concentration of several hundred ppm. Those exposed have in most instances regained consciousness within minutes with seemingly no lasting health effects. Some accounts indicate that sheer luck has prevented a fatality. Often contractor personnel have been most prone to accidents, as familiar in the chemical industry.

In the last decades, new geothermal plants that primarily produce electricity in steam turbines has increased the H_2S problem as these plants are fed high-temperature geothermal steam with relatively high H_2S-contents compared to the regional heating systems in the low-temperature (hot water) areas. When the steam condenses, the H_2S-laden gas is left in the steam system where it is usually vented off to special stacks together with the other gasses and exhaust steam that is released to the atmosphere. There are plants, at least in the US, that clean the H_2S from the exhaust gas by oxidation processes in a similar fashion to what the gas and oil refineries do by e.g. the Claus process. The loss into buildings of this H_2S-laden gas from the turbine piping system, before venting, can cause poisoning incidents, e.g. when starting up or closing down turbines, switching well feeds or on maintenance holds. Most unrecorded incidents are of short time exposures where people have been able to leave the exposure area without external help.

-Recent recorded H_2S-incidents in geothermal plants in Iceland

-In September, 2007, turbines in a new electric power plant were being started and restarted during a plant start-up program. Pressure built up after start in the condensate collectors and relive valves opened and the H_2S-laden gas (which was left in the condensers when the steam condensed after turn-off) escaped into the machine hall where operators and contractor personnel was working. The turbine hall had to be closed on occasions and smoke divers with SCBA brought in to close the valves. On an occasion, three workers were seriously affected. One of them narrowly escaped to a walkway from the hall, there he lost consciousness but regained it quickly. The others had milder poisoning symptoms. Medical examination indicated no lasting health effect and the men returned to work the day after. After these incidents, the faulty valves were replaced, escape routes were redesigned and air fed respirators installed in critical places [16].

-In December 2008, a worker standing outside the plant building was exposed to H_2S from an up-wind gas venting chimney. He was taken ill with reddened eyes and face and by midday developed nausea and subsequently vomited blood on the way to the hospital. He recovered fully in a short time. The cause was judged by doctors to be H_2S. It was possibly in rather low concentration [16].

-Recent H_2S -related fatal accident in a geothermal plant in Iceland

-In august, 2008, two workers died in a new geothermal electric plant in Iceland. They entered a steam evaporator tank immediately after they had cut a manhole on its side. Doctors' report said the case was of lack of oxygen but implicated other gasses, among them H_2S, as a contributing cause. A chemical engineering evaluation of the gas that entered the tank originally, and the formation of the deadly atmosphere inside the tank, indicated that H_2S had probably consumed a substantial part of the atmospheric oxygen from the air that was vented into the evaporator after turn-off several weeks before the accident. This was a case of confined or semi-confined space with stagnant air and H_2S together with other geothermal gasses in equipment that had been put on hold for modification. Entry through the manhole had been banned. The deaths occurred very suddenly just inside the manhole [16].

5.10 International medical abstracts on geothermal H_2S - poisoning.

From Ovid Medliner:

-A fatal case of hydrogen sulphide poisoning in a geothermal power plant.

An adult man entered an oil separator room to remove waste oil from a vacuum pump in a geothermal power plant. He suddenly collapsed and died soon after. Since hydrogen sulphide gas was detected in the atmosphere at the scene of the accident, poisoning by this gas was suspected and toxicological analysis of sulphide and thiosulphate in blood, brain, lung, femoral muscle was made using the extractive alkylation technique combined with gas chromatography/mass spectrometry (GC/MS). The concentrations of sulphide in these tissues were similar to those previously reported for fatal cases of hydrogen sulphide gas. The concentration of thiosulphate in the blood was at least 48 times higher than the level in control samples. Based on these results, the cause of death was attributed to hydrogen sulphide gas poisoning [9].

-Health hazards from volcanic gases: A systematic literature review.

Millions of people are potentially exposed to volcanic gases worldwide, and exposures may differ from those in anthropogenic air pollution. A systematic literature review found few primary studies relating to health hazards of volcanic gases. SO_2 and acid aerosols from eruptions and degassing events were associated with respiratory morbidity and mortality but not childhood asthma prevalence or lung function decrements. Accumulations of H_2S and CO_2 from volcanic and geothermal sources have caused fatalities from asphyxiation. Chronic exposure to H_2S in geothermal areas was associated with increases in nervous system and respiratory diseases. Some impacts were on a large scale, affecting several countries (e.g., Laki fissure eruption in Iceland in 1783-4). No studies on health effects of volcanic releases of halogen gases or metal vapors were located. More high quality collaborative studies involving volcanologists and epidemiologists are recommended. [11]

-Investigation of health effects of hydrogen sulphide from a geothermal source.

Little is known about health effects from chronic exposure to hydrogen sulphide (H_2S). The city of Rotorua, New Zealand, is exposed to H_2S by virtue of its location over a geothermal field. In this study, the authors classified areas within Rotorua as high-, medium, or low-H_2S exposure areas. Using 1993-1996 morbidity data, standardized incidence ratios were calculated for neurological, respiratory, and cardiovascular effects. Poisson regression analysis was used to confirm results. Results showed exposure-response trends, particularly for nervous system diseases, but also for respiratory and cardiovascular diseases. Data on confounders were limited to age, ethnicity, and gender. The H_2S exposure assessment had limitations. Assumptions were that recent exposure represented long-term exposure and that an individual's entire exposure was received at home. The results of this study strengthen the suggestion that there are chronic health effects from H_2S exposure. Further investigation is warranted [12].

-Hydrogen sulphide poisonings in hot-spring reservoir cleaning: Two case reports.

The potential hazards to maintenance personnel cleaning hot-spring reservoirs are reported following two severe and unusual episodes of acute hydrogen sulphide poisoning involving seven workers. In the first episode, five victims lost consciousness immediately after climbing down a manhole to the bottom of a reservoir disregarding a strong odour of rotten eggs. One of them died immediately. Of the four who lived, three developed hemorrhagic keratoconjunctivitis and aspiration pneumonia, but no sequelae were observed 2 years later. In the second episode, two workers had been cleaning the reservoir for about 2 hours when one collapsed and his companion went to seek help. Both died of acute respiratory distress syndrome due to pulmonary oedema within 12 hours. Since hot-spring bathing is a popular recreation in Taiwan, other accidents of hydrogen sulphide poisoning may have occurred but have not been reported. Such clinical information is helpful to enable regulators to initiate proper precautions to safeguard those workers involved [14].

-The health hazards of volcanoes and geothermal areas

Volcanoes and their eruptions can result in a wide range of health impacts, arguably more varied than in any other kind of natural disaster. At least 500 million people worldwide live within potential exposure range of a volcano that has been active within recorded history. Many volcanic and geothermal regions are densely populated and several are close to major cities, threatening local populations. Volcanic activity can also affect areas hundreds or thousands of kilometres away, as a result of airborne dispersion of gases and ash, or even on a hemispheric to global scale due to impacts on climate. Healthcare workers and physicians responding to the needs of volcanic risk management might therefore find themselves involved in scenarios as varied as disaster planning, epidemiological surveillance, treating the injured, or advising on the health hazards associated with long range transport of volcanic emissions [15].

6 Data sources

The search for data described in this report is intended for preliminary analysis of H_2S-poisoning incidents with focus on the geothermal industry. Information was sought from specialised databases, especially those who register accidents at larger establishments with dangerous substances, a medical database as well as publicly accessible information sources and a few national data. The data collection was not intended as a complete assembly of records on H_2S-poisoning incidents. Request for information on incidents from authorities or agencies in OECD-member countries was deemed to be premature and too time consuming given the limited scope and time frame of this preliminary analysis. Therefore, analysis of data from national OSH-bodies is not included.

Following are our comments to the search, information sources and obtained data:

1. Besides information sources that are accessible to the general public, we have identified the following specialised pertinent data sources on H_2S-incidents in industry: MARS in the EU, records at the CSB and OSHA in the USA, ZEMA in Germany, ARIA in France, RISCAD in Japan, HSE records in the UK. Also Ovid medical database where research papers on medical aspects of H_2S poisoning in industry are registered.

2. Accidents in the main chemical, oil & gas as well as many other advanced or larger industries are well documented in developed countries in databases such as those mentioned above and some of the data are relatively accessible there. Information on off-shore oil & gas incidents were as a rule not included in the scanned data.

3. Systematic scanning of databases on occupational injuries of H_2S was not performed although some information from a few countries is included. These databases were inaccessible and evidently also deficient in some instances. It is probably still more difficult to gain exact information on smaller workplaces as well as from less industrially developed countries.

4. Literature references of H_2S-incidents in the geothermal industry are scarce and inaccessible and authors of this report found rather few publicly accessible sources that specifically mention geothermal source of the H_2S in cases of H_2S-poisoning in occupational environments. Exemptions were a few pertinent references in medical science journals. Information, such as national accident accounts or statistics from the main geothermal countries turned out to be rather unavailable. There are also apparently cases where accounts are non-existent and/or incidents not registered in accessible databases. Specific enquiries to OSH institutions in the geothermal countries would possibly reveal if there are data on the geothermal industry which could provide patterns and statistics about poisoning incidents in this industry.

7 Preliminary analysis of obtained data

1. From the incidents considered general conclusions may be drawn.

- In those incidents in which toxic effects due to H_2S were experienced there appears to have been a lack of adequate knowledge of the hazards. That is a lack of knowledge that a H_2S release could occur and the potential consequences of H_2S exposure.
- Due to the lack of awareness relating to the occurrence of H_2S, there was, in many cases, a lack of adequate preparedness to deal with the release of toxic gas. There could be a lack in awareness in some industries that there is no warning by the odour of hydrogen sulphide, as the ability to smell hydrogen sulphide disappears if a hazardous concentration is reached. The lack of suitable gas alarms and personal protective equipment led, in a number of cases, to fatal H_2S exposure. Filter gas masks are potentially perilous in many of these circumstances of high H_2S-concerntration as they can become saturated quickly and provide false security. Air-fed respirators are necessary in the geothermal industry and works need instruction in their use. A personal gas sensor with alarm is also a necessary piece of personal protection equipment (PPE).
- H_2S is a life threatening hazard in the geothermal industry and a number of other industrial activities as indicated by the data shown here.
- Some industries (chemical processing, petroleum refining and petrochemical), whilst having H_2S-incidents, do not appear to suffer fatal consequences to the same degree as perhaps the geothermal and waste treatment industries. Here is an opportunity to learn lessons relating to good practice across industry sectors.

2. H_2S remains a serious occupational hazard in many workplaces as demonstrated recently by 80 workplace fatalities reported during one decade in the US alone, as well as other data.
3. Accidents involving fatalities or serious injuries seem mostly to occur at non-standard operating, intermittent conditions such as start-ups, production halts

for modifications, repair and maintenance and clean-ups or at loading and unloading.

4. Contractors in installation, maintenance and clean-up operations seem to be in most danger by H_2S-hazards. It is most likely that contractors are more often affected whilst carrying out these activities because cleaning and maintenance operations are regularly contracted out to specialised companies.
5. Many of the fatal incidents seem to be associated with confined or semi-confined spaces.
6. Part of the data (e.g. US study) indicates that personnel of smaller companies are more prone to the H_2S-hazards although the place of incident may be a large workplace.
7. Biologicaly generated H_2S from organic material, including many types of waste, seems to be the cause of disproportionately many H_2S fatalities as compared to the chemical and related process industries.
8. The larger chemical industry, petroleum refining and other developed industries, have apparently a relatively good control of the H_2S occupational hazards although serious incidents do occur, as shown by the major accidents databases (e.g. MARS and ZEMA). The hazard can also affect their neighbourhood due to large quantities besides the contractors or temporary engaged personnel on site.
9. The borderline between asphyxia and H_2S-poisoning seems sometimes to be blurred in the accounts of incidents. Medical examinations as well as on-site investigations do not always reveal what the real causes of injury/death were only that H_2S was found to be present at the scene. Asphyxiating non-poisonous gasses with small amounts of H_2S can work together to impair consciousness
10. Many incidents probably go unrecorded. This could particularly be a problem where the gas appears as an unexpected product of waste or other organic material decomposition and in incidents involving unplanned reactions outside chemical plants, such as acidification of sulphides in waste and residues.
11. Analysis of data on the geothermal industry.

From the small number of accounts it is clear that H_2S is a very serious and life-threatening hazard to people in the geothermal industry and quite many fatalities have occurred considering the modest size of that industry worldwide. The data acquired reveal the same quality of the gas as evident in other industries; workers taken by surprise and the knock-down effect leaves them helpless and too often their first helpers also. The data also indicate that more education and personal gas alarm sensors would have averted the incidents. Data also reveal that not only the high-temperature geothermal steam, which contains H_2S in larger quantities, is hazardous but also the lower temperature geothermal liquid (hot water) used for heating and baths, which usually contains less amount of H_2S. Further analysis of data would have to be made on incident data from the national occupational safety and health authorities in the countries that use geothermal energy in order to give an industry specific pattern of causes and statistics.

8 General Conclusions for Chemical Accident Prevention, Preparedness and Response as they relate to Hydrogen Sulphide

From this analysis of data on incidents involving H_2S releases it is clear that key Guiding Principles [35] as highlighted in the “Golden Rules” need to be applied to the industries concerned. It is absolutely vital that the industry identifies and understands the hazards and their associated risks as they apply to the activities being carried out. This means, with particular consideration of H_2S that:

- The industries concerned must be aware of where H_2S may be found (generated), how it may be released (also unintentionally) and what the impact of such releases may be.
- The industries need to consider specific characteristics associated with the very toxic gas Hydrogen Sulphide. This means not only the toxic, and dispersive aspects, but also the corrosive attack which may be associated with moist H_2S atmospheres and the related potential for loss of containment.

- The industries need to develop their safety culture, striving for a “zero” or at least minimal release tolerance. Incidents should be reported and investigated and appropriate measures to prevent their repetition adopted and shared within the industrial communities.
- Appropriate planning and training to deal with emergencies needs to be carried out. This includes thorough training relating to the rescue of collapsed employees, who may have been exposed to a toxic atmosphere.
- The Authorities which oversee, regulate and inspect the industries concerned need to be aware of the risks within these industries which are due to the potential release of Hydrogen Sulphide. They need to ensure that the industries address these risks and that appropriate communication and co-operation amongst stakeholders takes place
- Emergency responders should be aware of those industries in their locality for which a release of Hydrogen Sulphide is a potential risk. Appropriate response plans, training and measures to communicate with the local community should be put in place. In particular because of the obnoxious odour at very low concentrations, which may lead to widespread concern in the community.
- Regulations and recommendations on occupational safety for entering confined spaces have to be communicated to and respected by all industries.

9 Outline of further study

A- This preliminary study did not establish the real extent of H_2S-incidents in the geothermal industry or some of the other industries of interest. In order to quantify the injurious impact H_2S has had, a more detailed data search would be needed. Lessons from such a search could improve understanding of the specific causes of incidents in certain industries but to what extent is difficult to say at this stage, considering the fact that for example the geothermal industry is relatively small and new.

B- The incidents seem often to stem from lack of experience and knowledge, both by the workplace management and also by the competent authorities that oversee the activities. In order to improve the situation, collected experiences and lessons learned from incidents in these specific industries could be a base for developing guidelines, recommendations or information booklets to be targeted at the operators of these workplaces and possibly the overseeing agencies also.

C- This study indicates that well established methods of prevention and preparedness (Chapter 8), such as education, training and protective equipment, would have averted the majority of the injurious incidents we found accounts of. Definition of potential future work or redefinition of the project should take this into account.

D- In case further studies are undertaken, the main issue seems to be why relatively many accidents happen in certain industries and if there are unique conditions in these industries, as for example the geothermal industry, which further studies could shed light on.

E- To better map the present condition in the geothermal industry, it would be necessary to gain cooperation with institutions in the countries that utilise geothermal energy.

In case further analysis is undertaken, it would have to involve a more detailed review of, besides the data sources scanned in this report, data assembled by means of inquiries or otherwise, particularly data on occupational injuries generally, from many countries, of what human toll H_2S takes in industry. These data collections should already be in place in many countries although they are not easily accessible but could be gained access to by further search and direct approach to pertinent institutions, particularly national ones who could have information on incidents hidden away in their own institutional files or buried in statistics. This seems valid for not least the information on incidents in the geothermal industries. A way would be to send inquiries to national authorities, for example in the main geothermal countries´ OSH administrations. There are 53 nations that use geothermal energy but only 24 that use the more H_2S-laden steam from high temperature fields. Information on the other exposed branches, such as biological decomposition and certain contractor activities, could also be gained access to by direct inquiries to government agencies. There are also associations and other non-government bodies that could have information worth looking at. Science journals abstracts should also be explored better.

In case a further study is done, a preliminarily outline could be as follows:

a- Definition and selection of specific exposed industries, in particularly new, emerging or expanding sectors, such as:

1- Geothermal industry
2- Waste processing/recycling industry
3- Selected sectors of bio-technology industry
4- Selected industries outside the main chemical and oil & gas sectors
5- Contractors in process industry installation, repair, maintenance and industrial clean-up and a few other services

b- A questionnaire could be sent to appropriate branches of government and particularly OSH and health institutions, to furnish national data or provide a country report on H_2S-related accidents.

c- Processing of data to deduct conclusions and patterns as to causes, common features, statistics and general lessons from the accidents in order to evaluate actions of prevention and preparedness to the hazards of H_2S.

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Annex 1: Selection of incidents involving the release of hydrogen sulphide in the ARIA database

www.aria.ecologie.gouv.fr

The search term “hydrogène sulfuré” generates a report of 108 incidents from the ARIA database, which covers incidents from France and also other countries. The database is maintained by BARPI.

A selection of these incidents is provided in the following table

ARIA-No.	Date	Industry	Description
35905	02/09/2008	Petroleum Refining	BELGIUM - ANTWERP The plant at which the incident occurred is a refinery in Antwerp. It produces fuels like propane, butane. LPG, benzene, kerosene and gas oil, and chemical products like hexane, heptane, benzene, toluene and others. The capacity of the refinery is 13.5 million tons a year. The plant is situated at the eastern riverbank of the river Schelde to the north of Antwerp about 6 kilometres south of the border between Belgium and The Netherlands. Electrical power is supplied tot the refinery by two 36 kV power lines. The morning of September the second, maintenance work was planned by the company that supplies the electrical power to the refinery. The two power lines had proved to be fragile and it was planned to replace the connections in both power lines. To that order one of the power lines was shut of at 11.56 am. A plan to do this had been communicated beforehand, and it was tested that the remaining power supply would have enough capacity to transmit the necessary electrical power. At 11.57, whilst maintenance work was being carried out at one of the two the electrical power supply lines, the remaining second supply line failed, thus rendering the refinery

ARIA-No.	Date	Industry	Description
			without electrical power supply. At 11.57, start of the execution of the emergency plan, implying emergency shut down of the refinery, evacuating all not necessary personnel and retaining only the emergency staff and starting of the emergency power supply to restart the central operating desk. At 12.00, product stream is led to torch, leading to large flame and release of soot (carbon black) to the atmosphere. At the same time opening of several safety valves emitting several kinds of hydrocarbons to the atmosphere among which Benzene. Also H_2S (hydrogen sulphide) is emitted. At 12.14, the Antwerp environmental services are by fax informed of the incident with an emergency shut down. No assistance was deemed necessary by the operator or the environmental services. At 12.30, assistance of emergency services is requested by neighbouring companies because of large soot deposits on their sites and respiratory problem of some of their personnel. At 12.41, arrival of the emergency services at the site. They are informed of the incident. At 13.00, the crisis staff of the ministry of the interior of the state of Belgium is informed about the incident. At 17.15, the supply of electrical power is restarted, and preparations are started to restart the refinery. In the first minutes of the incident a safety valve opened and released 70 kilograms of hydrogen sulphide (approximately 40 m3 of pure H_2S gas). The safety valve is situated at a height of about 40 meters. After the release a cloud of H_2S formed, which migrated, with a speed of 45 kilometres/hour in north-north-eastern direction. Later analysis revealed that at ground level the concentration of H_2S reached about 0.6 ppm whilst in the centre of the cloud the concentration was in excess of 10 ppm. After ca. 5 minutes the cloud reached inhabited areas to the north of the refinery, causing acute illness, nausea, respiratory problems and a general feeling of unwell being. In the course of the next 70 minutes the cloud travelled about 50 kilometres over Belgium

ARIA-No.	Date	Industry	Description
			and parts of The Netherlands, affecting several hundreds of people. Fifty-seven people needed medical care, but nobody was seriously injured.
35850	06/02/2009	Petroleum Refining	FRANCE - 76 - GONFREVILLE-L'ORCHER A release of carbon monoxide (CO) and hydrogen sulphide (H_2S) wass produced in a refinery during maintenance operations on a tank. 3 employees were injured and transported to hospital. Concentrations of 80 ppm CO and 20 ppm H_2S in the vessel and 0 ppm CO and 4 ppm of H_2S on the platform outside the tank were measured.
35703	05/01/2009	Petroleum Refining	FRANCE - 13 - CHATEAUNEUF-LES-MARTIGUES An employee was found unconscious at about 11:15 in the visbreaking unit of a refinery. He was transported to the hospital, but died in the night. The suspected cause is poisoning by inhalation of hydrogen sulphide (H_2S) as beforehand the victim carried out an activity on equipment that may contain H_2S. An autopsy has been performed and a judicial inquiry is to be conducted.
35293	16/10/2008	Manufacture of basic organic chemicals	FRANCE - 64 - LACQ Leakage of hydrogen sulphide (H_2S) from a transport pipe (DN 50, pressure 5 bar) was detected at around 4 pm by an employee at a bridge in a chemical plant. Upon receipt of the alert, the operator decompress the pipe actuates the automatic sectioning valves and alerted the emergency services. Fire fighters used fire hoses to disperse the hydrogen sulphide fumes, and established a security perimeter and subsequently carried out concentration measurements. The concentrations measured were 300 ppm to the right of the leak, and 50 ppm at 20m. No casualties or environmental impact occurred. External corrosion by changing atmospheres following the stagnation of rain water is the cause of the event. The corrosion area is about 20 cm after the pipeline exits the soil, and was not protected by a coal tar coating.
34786	24/06/2008		FRANCE - 92 - Villeneuve-la-Garenne

ARIA-No.	Date	Industry	Description
			In the afternoon, hydrogen sulphide (H_2S) leaked from the sewage pipes into a building of 66 Apartments, severe intoxication girl 13 years (coma), who was hospitalized for several hours. The 200 inhabitants of the building were evacuated for the night. Evacuees can return home the next day at 18 h. The police carry out an investigation and samples were taken The accident could be an accident or malicious. It was finally concluded by the investigators that it was probably the result of a spill of incompatible chemicals into the sewers.
34316	15/11/2007	Extraction of crude petroleum	FRANCE - 64 - Burosse-Mendousse Two employees were injured by a product of hydrogen sulphide (H_2S) during operations on a pigging station of a 10” pipeline. After checking for the absence of a toxic atmosphere, the operators proceeded to isolate, purge and then open the station. After closing the latter, one of the employees suddenly collapsed and lost consciousness. Having brought him to safety and ensured his resuscitation, the decided to continue the work to close the station. He also collapsed and lost consciousness. The first person who had remained on site, to helped him in turn. They then left the scene, raise the alarm and then proceeded to the medical centre near by. Investigations were conducted to determine the origin of the toxic gases.
34177	01/11/2007	Treatment and disposal of hazardous waste	UNITED STATES - SUPERIOR In a landfill, 4 employees died of asphyxiation by hydrogen sulphide gas, when they were repairing a pump in a sewer.
32802	05/09/2006	Petroleum Refining	FRANCE - 76 - GONFREVILLE-L'ORCHER Around 9:30 am, an emission of carbon monoxide (CO) and hydrogen sulphide (H_2S) occurred which required the evacuation of 980 people on site of a unit being built at one of the entrances to the refinery. Fire fighters from the refinery carried out measurements and detected H_2S levels up to 7 ppm. Eight people contacted the hospital, 7 of them were hospitalized and kept for 24 h observation. Traces of CO were detected in their blood but the symptoms were due to H_2S. No installation of this new unit was likely to emit H_2S, the operator identified the unit CR4/FCC

ARIA-No.	Date	Industry	Description
			(catalytic cracking unit) as leading to the emission of H_2S. During the initial phase of the FCC, CO is generated during the 30 min during which the load through the catalyst at a temperature below 700 ° C. Similarly, the H_2S from the smoke from the furnace receiving waters of the stripping unit, is discharged directly to the atmosphere. The amount of H_2S released is estimated at 225 kg. Restart following 5 days of stoppage generated CO and H_2S discharged directly to stack during exceptional weather conditions (low wind). No anomaly in the start-up process was identified and the consequences of this event are allocated to the combination of weather conditions and continued massive human presence near the stack. To reduce the likelihood of renewal of this event, the weather will be taken into account before any restart of the FCC to ensure good conditions for dispersion of smoke.
32429	07/08/2006	Extraction of crude petroleum	FRANCE - 64 - LACQ The emergency plan is triggered at 22:15 following the warning gas detectors following the loss of containment of a network line entry of bleed desulphurization units. The network is isolated and unpacked. The failure of the line comes from an external corrosion under insulation at the level of support. The fluid released (approximately 500 l) corresponds to condensate of hydrocarbons containing hydrogen sulphide, the substance of which was collected.
32205	06/06/2006	Extraction of crude petroleum	UNITED STATES - ALLENTOWN In an extraction of crude oil, 2 employees of subcontractors were poisoned, 1 fatally, by hydrogen sulphide, during standard maintenance on the valve of a tank. The extraction wells had previously been stopped for intervention. An investigation is conducted to determine the exact causes of the accident. On the site, hydrogen sulphide, a byproduct from extraction of crude oil, is fed back to a depth of 4 500 m underground.
31863	12/06/2006	Other cleaning activities	FRANCE - 78 - POISSY During the flushing of a settling tank of sewage works to Poissy, 3 sewer workers, aged 22 to 44 years, dies, another is seriously injured as a result of a release of hydrogen sulphide (H_2S).

ARIA-No.	Date	Industry	Description
			Twice a year, 4 employees of sanitation firm clean the settling tank for the neighbourhood "La Collegiate." The operation was to pump the contents of the settling tank of 30 m and 5 m deep in to trucks to remove sludge and other wastes. Preventive work started at 9:30 am to guarantee a good flow of wastewater into the sewers. Around 10 am, 3 workers were overcome by toxic fumes, probably as they reached a pocket of H_2S, occurring as the result of the decomposition of organic matter. The fourth worker, who was a little further back, was seriously affected and transported to hospital. Once the alarm was given by a passer-by, almost fifty fire fighters with twenty vehicles attended the scene, joined by 4 ambulance teams. Two investigations were conducted; one judicial and the other by the labour inspectorate to check whether all protocols to be implemented for this type of activity have been complied with.
29906	27/05/2005	Collection and Wastewater Treatment	FRANCE - 78 - HOUDAN Eleven children of a group of 53, ages 8 to 11 years are affected by stomach pains and nausea, following the visit of a sewage treatment plant in the morning. They were taken to hospital for examination. Measures of toxicity at the site of the WWTP are positive for hydrogen sulphide (H_2S).

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Annex 2: Selection of incidents involving the release of hydrogen sulphide in Germany from the ZEMA Database and other sources

Source	Date	Industry	Description
ZEMA 2007-11-21 Fire in an oil gasification plant of a refinery	21/11/2007	Distillation, refining and processing of mineral oil and products	GERMANY - NORDRHEIN WESTFALEN In an oil gasification plant sulphur containing cracker residues are converted to synthesis gas (H_2 + CO) in the presence of steam and oxygen at a temperature of 1,300 °C and pressure of 30 bars. The gasification takes place in three reactors which are connected to a common flare stack for start-up and shut-down operations. - On 21st November 2007 two of the three reactors were out of operation due to repair work on the exhaust gas line. In preparation for the start-up operations they were heated up, but still separated from the flare system. - Due to a leakage of "false air" a sulphur-iron fire occurred in the flare stack. Natural gas, which is to support the ignition flame, ignited on the flare stack (probably due to the sulphur-iron fire) and an explosion occurred. A short while later a second, but weaker explosion occurred with flames emanating from the manhole of the flare. The flare stack has a dished end for the collection of condensates; this has a drain pipe with a valve connected on the outside of the stack. - Following the explosion of the flare the dished end was blown into the base of the flare construction and the drainage pipe was found next to the base. The flare was now open towards the base and the sulphur-iron fire was further supported. The causes were given as two possibilities: 1. a leak on an imperfect weld of the dished end (poor weld quality and corrosion) led to the ingress of air into the flare system. 2. During the start-up and the operation of the vacuum system a valve which was either open or not gas-tight allowed air to be sucked into the flare system.

Source	Date	Industry	Description
			The investigation came to the conclusion that within the flare system sulphur-iron compounds had accumulated which can auto-ignite in contact with air. No injuries were reported and amounts of H_2S released are not given.
ZEMA 2007-06-18 Release of Hydrogen Sulphide from the Conversion Unit of a Refinery	18/06/2007	Distillation, refining and processing of mineral oil and products	GERMANY - NORDRHEIN WESTFALEN Hydrogen sulphide is removed from the refinery gas in an absorptions column by using ADIP (Di-isopropanolamine). The cleaned gas is passed onto the heating gas system of the refinery and the loaded ADIP is regenerated. The Hydrogen sulphide which is won in the regeneration process is converted to sulphur in the Claus unit. - At the time of the incident the level-low trip of the column was activated. Normally following this a regulator valve would be closed and the level in the column would rise. However, the regulator value was blocked in the "open" position by metal pieces (internal to the column). Thus the column level fell to null, the loaded ADIP was completely directed to the regenerator and a Hydrogen Sulphide break through via the ADIP-Generation to the Claus unit occurred. Not only the Claus unit, but also the catalytic thermal combustion unit were overloaded and the H_2S gas was released with almost no conversion to Sulphur dioxide through the 175m chimney of the conversion unit. In total 1,275 kg H_2S were released. No injuries were recorded, however a strong odorous nuisance for more than an hour occurred.
ZEMA 0525 (2005-12-29) Release of Hydrogen Sulphide at an hazardous waste treatment installation BARPI, ARIA Report No.: 32574	29/12/2005	Waste - chemical-physical treatment and handling plant	GERMANY – BADEN-WÜRTEMBERG On 29th December 2005 an accident took place in a hazardous waste treatment facility in which an employee was killed and six others (two employees, two members of the emergency services, and two employees of contact companies) suffered injuries and required hospital treatment. The cause, based on current knowledge, was the release of hydrogen sulphide (H_2S) from the tank vent of the vacuum truck whilst liquid wastes were being pumped from steel drums into the vacuum-truck. A fork-lift truck driver who happened to be in the immediate vicinity was found dead near by; the cause of death being the toxic effects of hydrogen sulphide. Five of those

Source	Date	Industry	Description
			treated in hospital were also suffering from the health effects of hydrogen sulphide The fire-brigade could not identify any hazardous gas concentration on arrival at the scene. The fire-brigade then left the site. To secure the scene for the police investigation, the police ordered that the contents of the suction hose should be drawn into the vacuum-truck. The vacuum pump was restarted and once again hazardous sub-stances were released from the tank vent. This process led to the collapse of the vacuum-truck driver. As a result the police ordered that the operation should cease and the fire-brigade and an emergency doctor were called to the scene. The immediate cause of the production of toxic gas was the combining of liquid wastes which on mixing react together releasing H_2S. An organo-sulphur (thio) compound was mixed with an organic, acidic compound leading to an unexpected liberation of hydrogen sulphide The indications are that the organisational measures which had been taken were not adequate to prevent this event. The operator was not able to demonstrate that adequate measures for the identification, assessment and documentation of the hazards of the individual containers of hazardous waste received. The hazardous wastes which were received in drums and brought together in a vacuum-truck were to be transported from the waste treatment facility to another location because they could not be treated on site. The operator was not able to demonstrate that adequate measures were in place to regulate how the drums should be pumped into the vacuum-truck (order, ruling out of any hazardous chemical reactions). There were no adequate measures for the safe discharge of gases vented from the vacuum-truck.
ZEMA 0430 (2004-12-14) Release of Hydrogen Sulphide	14/12/2004	Chemicals Production, Mineral oil	GERMANY – SACHSEN-ANHALT The failure of the pump on an exhaust gas scrubber led to the release of Hydrogen Sulphide. The plant went automatically into a safe mode. The

Source	Date	Industry	Description
from an evaporation plant.		refining and processing of mineral oil products	cause of the failure was a short circuit in the motor of the pump. Two employees suffered effects from the release. As a precautionary measure for the future the personnel is to be provided with gas detection and warning equipment.
ZEMA 0414 (2004-05-18) Release of Hydrogen sulphide and Sulphur dioxide from a Carbon Disulphide Plant	18/05/2004	Chemicals Production, Mineral oil refining and processing of mineral oil products	GERMANY - NORDRHEIN WESTFALEN Following a shut down of several weeks duration the Carbon Disulphide plant was restarted. In doing so the reactor furnace, the Claus unit and the exhaust gas combustion unit were started up one after the other. The exhaust gas combustion unit showed an irregular operation caused by an excess natural gas feed into the reaction furnace due to a defective Methane measurement. As a result the Natural gas could not be completely reacted in the reaction furnace and the excess gas reached the exhaust gas system and the combustion unit. - Until the exhaust gas combustion could be stabilized unreacted amounts of H_2S and SO_2 were emitted via the 150m high stack. The process upset lasted for about 50 minutes. Estimates give the emitted amount of H_2S as between 40 kg (best case) and 120 kg (worst case). - Near to a school there were complaints of health effects (nausea, headaches and vomiting) 47 persons received medical treatment. 19 persons were taken to hospital for observation as a precautionary measure. Two of these were kept in overnight.
ZEMA 9925 (1999-07-17) Release by a crude oil tank	17/07/1999	Storage of mineral oil or liquid mineral oil products or methanol (capacity 50000 tonnes or more)	GERMANY – BADEN-WÜRTTEMBERG A tank was filled with crude oil. During a control an employee smelled the oil and discovered that the floating roof was covered with crude. The filling of the tank was stopped and the fire fighters covered the crude on the roof with foam.
ZEMA 9901 (1999-01-25) Release of Hydrogen Sulphide from a multi-purpose chemical	25/01/1999	Installation for the industrial production of	GERMANY – BADEN-WÜRTTEMBERG Wash water from a reactor was transferred to a multi-purpose collection tank

Source	Date	Industry	Description
production		substances by chemical reactions	by nitrogen pressure. The automatic pumping of the waste water to the waste water treatment could not take place as the tank was full and the valve closed. This led to an overfilling of the multi-purpose collection tank and the escape of waste water into the exhaust gas system leading to the exhaust gas treatment. Another container into which ca. 4,000 kg Phosphorous Pentasuphide had been charged was also connected to the same exhaust gas system. Water was thus able to enter this container so that the Phosphorous Pentasulphide and water were able to react, generating Hydrogen Sulphide. Due to the sudden increase in pressure a seal partially failed releasing Hydrogen Sulphide into the room in which the plant was housed. The H_2S-alarm was triggered automatically. Through the mechanical ventilation system and through doors and windows, the Hydrogen Sulphide was able to escape into the neighbourhood were it was rapidly dispersed. However the smell was clearly noticeable in the nearby residential area. There were no injuries or fatalities recorded.
ZEMA 9403 (1994-02-13 Explosion of Hydrogen and Gasoil causing a fire	13/02/1994	Distillation, refining and processing of mineral oil and products	GERMANY – BRANDENBURG During the heating up process in a heat exchanger for gas products a leak occurred which ignited ca. 1,200 kg of flammable gases, 100 kg Hydrogen and 10 kg H_2S were released. No injuries were recorded, however approximately 0.5 Mill. EUR damage to the installation was reported. The cause of the accident was suggested as material failure
ZEMA 9310 (1993-03-24) Fire of highly flammable and flammable liquids	24/03/1993	Distillation, refining and processing of mineral oil and products	GERMANY – NORDRHEIN WESTFALEN Hydrocarbons were release by the burst of a pipe and were ignited due to a temperature of 350 - 370 °C. An emergency shut off was made and the system depressurised to the flare. The burst was caused by corrosion by hydrogen sulphide containing water.
ZEMA 9302 (1993-02-02) Release of H_2S-containing	02/02/1993	Distillation, refining and	GERMANY – NORDRHEIN WESTFALEN

Source	Date	Industry	Description
flammable gases		processing of mineral oil and products	During repair work in a hydrocracker, on a pipe under pressure, (hot tapping) the gas tight casing was damaged leading to the releasing of ca 14.5 t Hydrocarbons. The released hydrocarbons contained 1,380 kg H_2S. Three employees of a contractor were injured, one of which died. The cause of the damage to the gas tight casing was the incorrect feed indicator on the drilling machine which was used.
http://www.n24.de http://www.gsb-mbh.de	04/08/2008	Waste - chemical-physical treatment and handling plant	GERMANY – BAYERN Maintenance works in the pump building caused a release of H_2S at the chemical and physical hazardous waste treatment plant of the GSB at München-Fröttmaning. The release occurred when the plant manager drained a pipe to install a new valve. The plant manager, four employees and three police officers were injured. The plant, operating since 1990, is located next to a new constructed football stadium.
http://www.mz-web.de	20/03/2008	waste landfill	GERMANY – SACHSEN-ANHALT Authorities inspected the former clay pit of the Sporkenbach Ziegelei GmbH at Möckern and analysed the releases to air. They found H_2S and HCN in the releases and assume that these releases are caused by the illegal dumping of waste. The operator declared that there are no release of H_2S and HCN according to own analyses.
http://.www.abendblatt.de	27/11/2006	Distillation, refining and processing of mineral oil and products	GERMANY – HAMBURG A H_2S release at a lubricant oil refinery injured 46 employees. The CEO said, the release may be caused by the failure of a valve.
http://www.westline.de	04/10/2006	hazardous waste, landfill	GERMANY – NORDRHEIN WESTFALEN An employee of a cleaning company entered a leachate tank of a hazardous waste landfill wearing protective gear including a respirator mask. The connection from the air supply hose to the mask broke. The employee

Source	Date	Industry	Description
			collapsed in the tank. The company owner at the manhole regarded this and entered the tank without protective gear. Both died.
http://www.webserver-nrw.de	10/11/2005	Waste water treatment	GERMANY – NORDRHEIN WESTFALEN Two of the clarifiers of the waste water treatment plant at (51766) Bickenbach released H_2S. The operator introduced iron salts in the clarifiers to precipitate the sulphide.
http://www.sicherheitserziehung-nrw.de/uploads/media/Unfall_in_der_Biogasanlage2005.pdf http://www.landenergietechnik.de/PDF/Unfall%20Zeven.pdf BARPI, ARIA Report No. 31000	08/11/2005	Waste treatment, biogas4.4-1	On the 5th of November 2005, after collecting the Heparin by a pharmaceutical company in the Netherlands and adding bisulphite, the remaining material was transported by truck to a fermentation facility in Germany. The truck arrived too late and had to wait for unloading overnight in front of the facility. On site the normal unloading procedure was not followed due to the failure of the unloading equipment. The reception pit was open because the hoist used to close the heavy metal doors was defective. In this pit there were some acidic remains present from earlier loads. While unloading the material (pH 8,5, >60°C) a large quantity of hydrogen sulphide (H_2S) was emitted. Due to the H_2S emission an operator was poisoned. Another operator, the truck driver and some other people who were present also suffered the toxic effects of H_2S. The outcome was 4 fatalities and one seriously ill in hospital. Members of the rescue team which had been involved in the reanimation and who had not worn protective equipment suffered later from skin irritation, headache and nausea. It is assumed that this was caused by release of hydrogen sulphide from the clothing of the persons rescued. Therefore all clothing worn and material used inside the reception building was enclosed for decontamination.
Release of toxic gas (69003) Handbuch Störfälle (UBA, Germany)	25/04/1969	Distillation, refining and processing of mineral oil and	GERMANY – NORTHRHEIN WESTFALEN Release of H_2S from a flaring unit during maintenance.

Source	Date	Industry	Description
		products plant	
Release of toxic gas (76001) Handbuch Störfälle (UBA, Germany)	24/02/1976	Automotive industry – production of car parts	GERMANY – HESSEN Release of H_2S from a tank during maintenance work
Release of toxic gas (78019) Handbuch Störfälle (UBA, Germany)	07/09./1976	Waste water treatment, sewage pipe	GERMANY – BADEN-WÜRTTEMBERG Release of H_2S during construction work
Release of toxic gas (79002) Handbuch Störfälle (UBA, Germany)	06/01/1979	Installation for the industrial production of substances by chemical reactions	GERMANY – BAVARIA
Release of toxic substances (79015) Handbuch Störfälle (UBA, Germany)	08/06/1979	Coking plant	GERMANY – NORTHRHEIN WESTFALEN Release of H_2S from the waste water treatment

Annex 3: UK on-shore hydrogen sulphide incidents 1990 -2003

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Exposure

Date	Description
9006	Double fatality in a distillery biological effluent treatment plant. The fatalities occurred in an underground sump tank.
9007	Gassing incident involving slurry mixing. A young farmer was overcome and 17 cattle died.
9009	Two men overcome in fish storage silo.
9101	The pathologist's report on a tanker driver, who was found dead in a sitting position underneath a sludge tanker, was that he died of asphyxia.
9101	As part of the operation of clearing blocked drains, four men pumped nearly empty one deep chamber. One man then climbed down into it and collapsed. Three would-be rescuers successively climbed down and collapsed. The first three men died and the fourth recovered after a long illness. Analysis indicated that hydrochloric acid was put into two of the chambers. This and the disturbance of the sludges produced large quantities of hydrogen sulphide gas.
9108	Two construction workers collapsed underground
9209	Visit made to determine cause of failure of valve on a 1 cubic metre hydrogen sulphide drum. The gland locking nut had failed. The valve spindle had seized in the nylon packing. In my opinion the nut was on the point of failure and when an operator tried to open the valve during the drum filling process the nut fractured and he inadvertently unscrewed the gland nut which allowed the spindle to be blown out. The operator was wearing protective clothing and no persons were injured.
9308	Three sullage lighter workers were affected by hydrogen sulphide which was generated in-situ in the cargo wastes from Naval vessels, probably by sulphate-reducing bacteria. The hazard had not been recognised at Portsmouth though it has elsewhere. Aeration of the cargo produced hydrogen sulphide concentrations up to 450 ppm.
9411	Visit to investigate collapse of worker in confined space at Whittlesea STW.
9412	A pipe manifold situated on top of a high pressure gas storage vessel failed. Hydrogen sulphide gas was released. The failure occurred in a pipe branch T-piece.
9504	Two of three persons had been overcome on 13 April 1995 while working with in a port wing tank of a barge undergoing repair. The wing-tank was a confined space. On the day of the visit the air within the tank was fit to breathe. However a sample of sludge from the bottom of the tank emitted hydrogen sulphide gas when acidified.
9504	An operative in a metal processing factory was overcome by H_2S fumes when he removed the plastic lid from a drum containing freshly milled material. The actual exposure is not known but is likely to have been in excess of 200ppm.
9604	Opened manlid of 7 tonne vessel. Exposed to H_2S and mercaptan fumes.
9608	H_2S exposure in newly upgraded press house when lifted lids to inspect sludge cake.
9610	IP cleaning tanning drum. Overcome by H_2S fumes from reaction of sodium sulphide and cleaning agent.

Date	Description
9611	Leakage from H_2S 550kg cylinder.
07/01/97	Leak from 500 kg cylinder of hydrogen sulphide. Cylinder removed and connected to scrubber. Vented and purged with nitrogen. Smell persisted for 27 hours as leak could not be stopped during purging/venting process. 8 ppb at site boundary FOCUS
9707	Release of vapours, 5ppm H_2S from refinery header unit.
9708	Fitter fell down supernatant liquid well when overcome by H_2S fumes. Broke leg. Trying to clear blockage in a submersible pump and entered the tank without ppe.
9709	Maintenance technician testing pressure sensors. Did not follow procedures. Did not close valve when purging with nitrogen. H_2S in autoclave released.
9711	Failure of PTW. Attempting to clear product line from reactor. Opened wrong line. Fumes including H_2S released. RPE not suitable for H_2S.
98/02	IP cleaning out tanning effluent sump. Overcome by H_2S fumes from sludge.
9804	Accidental mixture of chemicals resulted in H_2S fumes. IPs affected during clean up operations.
9804	DP asphyxiated in tanning effluent sump at NCT Leather Ltd. DP entered to clear block age. High levels of H_2S
11/09/98	IP cleaning out reactor. Opened the manhole and was overcome by fumes. Smell suggested H_2S.
9904	Escaped from tunnel when detected 10ppm H_2S.
09/04/99	Sour gas (natural gas with 1000ppm H_2S) released from amine tank. Scrubber could not cope.
20/03/00	Man entered slurry tank at pig farm and was overcome by fumes including 500 ppm H_2S.
4/00	Repairing aluminum rudder to allow connection of anodes. Drilled holes when explosion occurred. Believed hydrogen sulphide had accumulated inside rudder.
06/07/00	IP in school laboratory knocked over bottle of ammonium sulphide. Ammonia and H_2S fumes.
26/07/00	10 workers complained of illness after working in pumped out water course. High levels of H_2S in sludge.
23/03/01	IP overcome by fumes when sampling from tank. Gas generated by mixing acid and sulphides
July 2001	Fatality DP overcome by hydrogen sulphide fumes leaking from a tank. Health and Safety at Work March 2003
06/03/02	Cylinder venting released H_2S at oil service company.
27/01/03	Farmer and worker trying to rescue young cow from slurry storage system. Overcome by H_2S fumes. 2 fatalities.

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