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COMPARATIVE ANALYSIS OF HYDROGEN FIRE AND EXPLOSION INCIDENTS

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DISCLAIMER

ABSTRACT

Additional hydrogen incident reports compiled during this quarter have increased the size of the computerized data base to a current total of 280 incidents. Listings of 165 incidents that have occurred in industrial and transportation operations since 1968 are presented here. Sample case histories in six different cause categories are provided together with a discussion of common safety problems contributing to these incidents. Some of these problems are inadequate detection measures for hydrogen leaks and fires and ineffective purging with inert gas.

A preliminary comparison of losses due to natural gas fires/explosions and hydrogen incidents indicates that hydrogen explosions have been, on the average, four-to-six times as damaging as natural gas explosion. Some tentative explanations for this result are presented but await confirmation from a more sophisticated statistical analysis.

FOREWORD

This report describes work performed under Department of Energy, Contract No. EE-77-C-02-4442 during the three-month period, December 1, 1977 to February 28, 1977. The overall objectives of the study are: 1) to conduct a comparative evaluation of the safety records of hydrogen and natural gas; 2) to identify hydrogen safety aspects requiring further research or standard/code modification; and 3) to quantitatively assess the relative hazards of alternative modes of hydrogen storage, transport, utilization, and disposal.

In the first quarterly report, available sources of hydrogen and natural gas accident data were described, as well as statistics on hydrogen and natural gas production and use.

In this second quarterly report, a tabulation of hydrogen incidents is discussed in terms of generic types of accidents. A brief comparison of property damage from hydrogen and natural gas incidents is slso presented. Future reports will provide a more detailed comparison and analysis of the hydrogen losses.

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I
INCIDENT REPORT COMPILATION STATUS

Additional hydrogen accident reports have been collected and report forms completed during the period covered by this Progress Report. Currently, there are 280 report forms completed and entered in the computer data bank. A listing of the sources for these loss reports and the periods covered is given in Table I. Approximately half of the reports have been obtained from the Factory Mutual Loss Files for the period 1966-77.

Besides the sources listed in Table I, many other organizations have reports of hydrogen fires and explosions. Our efforts to obtain additional loss reports from these other organizations have so far been unsuccessful. The reasons are: 1) it is difficult to identify and extract hydrogen reports in a large data bank of losses; and 2) many companies regard their accident/loss reports as confidential information. We have attempted to deal with the confidentiality problem by requesting anonymous reports not containing any proprietary information. Nevertheless, the response has been discouraging.

As an example of the response to our inquiries, consider the results of our survey of industrial hydrogen users. Forty four requests for hydrogen accident data were sent to ammonia and methanol manufacturers, edible oil hydrogenation plants, iron ore reduction plants, and tungsten and molybdenum processors. Only nine replies (20-percent response) have been received so far containing a total of four incident reports.

One problem with the set of reports we have obtained so far (Table I) is that it is difficult to estimate what fraction they represent of the total industrial hydrogen use population. Most of the reports were submitted either voluntarily (API and MCA reports) or for an insurance claim exceeding the deductible value of the policy (FM and OIA reports). It is clear they are only a small, unknown fraction of all the industrial hydrogen incidents. Unless we can somehow estimate the relative size of our sample, it will be impossible to estimate an absolute occurrence frequency for hydrogen incidents. In order to make a meaningful comparison with natural gas incidents, only reports from the same sample population subset can be used. This approach is discussed in Section III of this report.

TABLE I

HYDROGEN LOSS REPORTS COMPILED AND ENTERED IN COMPUTER DATA BANK

Source		Number of Reports	Period Covered
Factory Mutual Loss Files		147	1966 - 77
AEC - Nuclear Regulatory Commission		40	1962-66, 70-76
American Petroleum Institute		31	1973 - 76
Department of Transportation - OHM		25	1971 - 75
British Fire Protection Association		12	1965 - 74
Oil Insurance Association		10	no dates
Miscellaneous*		15	scattered
	Total	280	

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*Miscellaneous sources include case histories of major petrochemical plant fires and explosions published by the National Fire Protection Association, Manufacturing Chemists Association, the American Institute of Chemical Engineers, and insurance companies. In addition, four reports were received in response to our mail survey.

The 280 reports indicated in Table I do provide enough information to perform an engineering analysis of the causes and effects of hydrogen fires and explosions. A preliminary analysis based on 173 incidents in the period 1968-1977 is presented in Section II. The analysis will be updated in future reports as computerized tabulations of our completed data bank become available.

II

GENERIC TYPES OF INDUSTRIAL HYDROGEN ACCIDENTS

Table II[*]contains a chronological listing of 145 hydrogen fires and explosions that have occurred in industrial occupancies since 1968. The listing for each incident includes the type of accident, i.e., fire or explosion, and oxidant involved, the type of plant, the ignition source, the extent of damage, and a comment on the cause of the incident. Although the listing is not complete, Table II is a representative sampling of hydrogen accident experience in industrial operations.

The accident data in Table II provide an indication of the relative fire and explosion hazards of hydrogen. Of the 145 incidents in Table II, 84 (58%) were explosions, 53 (37%) were fires, and the remaining 8 (5%) were either combined fire-explosions or unignited releases due to vessel rupture. Similarly, of the 11 incidents in which the damage exceeded $1 million, 6 (55%) were explosions, 4 (36%) were fires, and one (9%) was a combined fire-explosion. The relative severity of the hydrogen explosion hazard is even more pronounced in terms of injuries. All eight of the multiple injury incidents in Table II were explosions.

The causes of the accidents listed in Table II have been categorized in terms of the reason for the hydrogen release and/or the formation of a flammable mixture. The following seven generic cause categories have been defined:

Category	No. of Incidents
Undetected Leaks	32
Hydrogen-Oxygen Off-Gas Explosions	25
Piping and Pressure Vessel Ruptures	21
Inadequate Inert Gas Purging	12
Vent and Exhaust System Incidents	10
Hydrogen-Chlorine Incidents	10
Other Incidents	35
Total	145

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[*] See Appendix A

The categories: Undetected Leaks, Inadequate Purging, and Hydrogen-Chlorine Incidents have in common the undetected presence of hydrogen (or an oxidant) at a concentration in the flammable regime. The same is true for several of the Vent/Exhaust Incidents and for many "Other Incidents" caused by inadequate ventilation or by an improperly closed or open valve allowing a combustible mixture to form. Altogether, these incidents involving the undetected presence of hydrogen account for more than half of the total number of fires and explosions. Thus, there is a need to develop and/or implement improved hydrogen detection techniques. Further examples of the lack of adequate hydrogen detection are given in the discussion of individual categories.

2.1 UNDETECTED LEAK INCIDENTS

Hydrogen leaks typically originate from valves, flanges, diaphragms, gaskets, and various types of seals and fittings. Usually, the leaks are undetected because of the absence of a continuous hydrogen monitor in the area. When the escaping hydrogen mixes with air or some other oxidant, ignition of the combustible mixture will cause a fire or explosion, depending on the degree of confinement. As an example of hydrogen's propensity to leak without being detected, consider the following synopsis of an explosion at a vegetable oil hydrogenation plant.

Hydrogen was stored at the plant in a 42 1/2-ft (13 m) diameter sphere made of 3/16-in. (4.8 mm) steel. The sphere was partitioned into two hemispheres by a neoprene diaphragm attached around the equator. Hydrogen was stored under the diaphragm while the upper hemisphere contained air. An explosion-proof fan was situated on top of the sphere in order to provide a slight positive pressure on top of the diaphragm.

When the plant was shut down for the Thanksgiving Holiday on November 27, 1974, the fan on top of the hydrogen sphere was also stopped. During plant startup on November 29, a violent explosion occurred in the sphere. The sphere shell was torn into many sections by the explosion and some of the sections were propelled as far as 1,200 ft (366 m). Some of these sections struck flammable liquid storage tanks and cracked the roofs of adjacent buildings. Most of the windows in the surrounding buildings were broken by the blast wave. Fortunately, there were no serious injuries.

A loss investigation indicated that hydrogen had leaked past the diaphragm when the fan was shut down. (The diaphragm had been installed about a year before the explosion as a replacement for another leaky diaphragm.) Ignition of the resulting hydrogen-air mixture was attributed to an electrostatic discharge caused by the motion of the diaphragm when a compressor was started downstream of the sphere. However, another possible ignition source was the "explosion-proof" fan at the top of the sphere. In any event, the explosion could have been avoided either by using an inert gas instead of air across the diaphragm, or by monitoring the hydrogen concentration in the upper hemisphere.

Since a pure hydrogen-air flame is virtually invisible, undetected hydrogen leaks can sometimes lead to undetected or underestimated hydrogen fires. An example of this situation has been reported as Case History No. 7 in the Oil Insurance Association brochure on loss prevention guidelines for Hydrorefining Process Units(1).

The incident occurred at an oil refinery hydrotreater used to desulferize naphtha. A small leak developed in one of the finned tubes of the heater for the naphtha-hydrogen mixture. The leak resulted in a 2-ft long torch flame which was eventually noticed by an employee. Upon discovering the fire, the hydrotreater was shut down by cutting off the flow of naphtha and the flow of fuel to the burners in the heater. The hydrogen flow was maintained in order to cool and sweep the reactor during the shutdown operation.

The torch flame appeared to diminish significantly while only the hydrogen was flowing. However, molten metal dripping from the heater indicated that a much more severe fire was still in progress. The fire was eventually controlled by reducing the hydrogen flow and injecting steam into the heater. Inspection of the damaged heater revealed that the fire had completely melted 12-ft long sections of 32 finned tubes.

The hydrotreater incident illustrates how a hydrogen fire which appears to be "quite small" can actually be only the visible portion of a much larger fire. Observation alone is not a reliable technique for detecting pure hydrogen fires and/or assessing their severity. Potential odorant additives for hydrogen leak detection and illuminants for flame visualization have been suggested(2) but the necessary experimental and feasibility studies have not yet been performed.

2.2 HYDROGEN-OXYGEN OFF-GAS EXPLOSIONS

The 25 off-gas explosions listed in Table II refer to incidents involving hydrogen-oxygen mixtures formed in the cooling loop of boiling-water-reactor (BWR) nuclear power plants. The hydrogen and oxygen are generated by the radiolytic decomposition of some of the steam flowing through the reactor. When the steam is condensed, the off-gas is ejected into an off-gas treatment system. Contemporary off-gas treatment usually consists of 1) diluting the stoichiometric hydrogen-oxygen mixture with either steam or air, 2) catalytically recombining the hydrogen and oxygen and removing the resultant moisture, 3) passing the gas through a charcoal bed and/or a delay pipe to reduce the radioactivity level of the noble gases, 4) flowing the gas through a high-efficiency particulate filter to remove radioactive decay products, and 5) venting the gas to the atmosphere through an elevated stack. At some of the older BWR power plants, there are no dilution, recombination, and charcoal adsorber bed components in the off-gas system(3).

Explosions have occurred in various components of BWR off-gas systems from the condenser air ejector downstream to the vent stack. Ignition sources have included 1) mechanical sparks from rapidly closing valves, 2) electrostatic discharges in ungrounded particulate filters, 3) sparks from electrical equipment, 4) negligent welding and cutting operations, 5) catalyst particles encountering undiluted mixtures, and 6) lightning strikes near the vent stack. Equipment damage has been minimal in most of the off-gas explosions, probably because the Nuclear Regulatory Commission requires the system upstream of the recombiner to be designed to withstand hydrogen-oxygen explosions.*

Most of the reported injuries in these explosions are due to workers being exposed to radioactive gases released during or before the explosion. Since the gases are usually short-lived radionuclides, contaminated workers have recovered rapidly, i.e., within a day or two. The following narrative is an example of an off-gas explosion involving worker contamination.

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*For stoichiometric H_2-O_2 mixtures saturated with water vapor at 100°C, the peak reflected detonation pressure can exceed 30 times the initial pressure(4).

An explosion in a stack filter house on January 19, 1976(5) was preceded by anomalously high radiation level readings from a monitor in the vent stack. When two plant employees entered the filter house to check the trouble, they were exposed to a radiation level of 6 mR/hr. Another employee, outfitted with proper protective clothing entered the area a few hours later and observed water on the floor and a mist overhead. He refilled the off-gas loop seals with water and left the filter house. The explosion occurred four hours later.

The off-gas loop seals had been blown because of a back pressure generated by a partially blocked filter in the vent stack. The filter was clogged by water that had bypassed an improperly installed demister. Hydrogen escaping from the blown loop seal accumulated in the filter house and was ignited when a relay activated to isolate the loop seals.

Incidents similar to the filter house explosion have also occurred in other types of industrial plants handling hydrogen. However, the large number of hydrogen explosions in the safety-conscious nuclear power industry is evidence of the need for increased diligence in future industrial uses of hydrogen. Special precautions will be needed in water-splitting hydrogen production and fuel cell plants where stoichiometric proportions of hydrogen and oxygen are situated in close proximity to each other.

2.3 PIPING AND VESSEL RUPTURE INCIDENTS

The 21 piping and vessel rupture incidents listed in Table II were caused by a variety of materials problems including hydrogen embrittlement, stress corrosion, and weld failures. Most of the damage was incurred by ignition of the hydrogen following the rupture. In several cases ignition was due to a furnace flame or some other obvious high temperature source. However, in many other cases, spontaneous autoignitions were reported. An example of at least one spontaneous autoignition is described in the following synopsis of two related pipe rupture incidents at an ammonia plant.

The rupture occurred in a 24-in. (61-cm) synthesis gas line connecting the primary and secondary reformers. The pipe contained hydrogen and carbon monoxide at a pressure of about 400 psi and a temperature of about 930°C. The ruptured section of pipe had a high-temperature alloy steel outer wall, a refractory liner, and a stainless steel interliner. The refractory lining had been repaired several times before (the latest time was October 1973) because of localized deterioration and hot spots. The repair procedure consisted of cutting a section of pipe, repouring the refractory liner, and patch welding the outer wall.

On January 30, 1974, the 42-in. long welded section of the pipe suddenly blew out. Plant employees heard a rumble and observed a flame above the ruptured pipe. A shower of catalyst pellets from the secondary reformer was also emitted at the rupture site. The hot catalyst ignited several secondary fires in oil deposits in the area.

Before the torch fire at the rupture site could be extinguished, it eroded the refractory lining in the secondary reformer and most of the remaining pipe. Instrumentation in the secondary reformer was damaged as was piping and vessel insulation in the vicinity of the rupture. The expansion loop between the primary and secondary reformers dropped about 1 in. (2.5 cm) and cracks were found in two ells on the loop.

Repairs were completed and the ammonia plant was brought up to production temperature and pressure on February 18. Employees taking readings after startup noticed flame coming from the same synthesis gas line that had just been repaired. When the reformers were shut down and the flame extinguished, a 10-in. (25-cm) crack was discovered in the inside radius of an ell in the expansion loop. The ell had apparently cracked on startup and allowed synthesis gas to escape and autoignite.

The January 30 pipe rupture was caused by weld failure. The February 18 fracture was apparently caused by excess stress on the ell as a result of the 1-in. displacement of the expansion loop during the first incident. One ironic result of these incidents was plant management's retrospective decision to eliminate the fractured synthesis gas expansion loop because it wasn't necessary in the first place.

An important lesson to be derived from the ammonia plant rupture incidents is the need to carefully engineer and test all repairs and modifications to high pressure process equipment. This lesson was reinforced by the devastating cyclohexane vapor cloud explosion at Flixborough, England in 1974. The Flixborough explosion was caused by the rupture of an improperly designed and installed temporary bypass pipe needed while a reactor was being repaired.(6)

2.4 INADEQUATE INERT GAS PURGE INCIDENTS

It is common practice to purge pipes and vessels with an inert gas before and after using hydrogen in the equipment. However, if the purging rate or duration or extent of mixing is too low, residual pockets of hydrogen or air will remain in the enclosure. This is particularly dangerous when plant operators are lulled into a false sense of security and are unaware that there is a combustible hydrogen-air mixture in the enclosure. Twelve of the hydrogen fire/ explosion incidents in Table II resulted from situations of this nature.

A typical hydrogen-air explosion caused by incomplete purging occurred at a coal-fired power plant in 1976. A 500-megawatt, hydrogen-cooled generator is driven by steam turbines at the power station. During maintenance shutdowns, the hydrogen cooling loop in the generator is purged with carbon dioxide. After CO_2 concentrations are measured with a densitometer to verify the complete removal of hydrogen, the generator is purged with air, and the maintenance is performed.

This purging procedure was used prior to the explosion. The CO_2 reading was reported to be 100-percent CO_2 at the top of the generator. The cooling system was then purged with air and a 1/2-in. (1.3-cm) pipe in the cooling loop was cut to install some new instrumentation. When the pipe was cut, pressurized gas was emitted at the opening. Workers assumed the gas was either carbon dioxide or air and proceeded with the new instrument installation. Unfortunately, there was still at least some hydrogen in the pipe and the rest of the cooling loop. When the welder struck an arc, a flame developed at the pipe opening and flashed back into the generator. This caused a low level explosion within the generator shroud. The explosion damaged ventilation baffle plates and auxiliary equipment in the generator so that it was out of service for 26 days.

This incident illustrates how difficult it is to completely purge hydrogen out of a large, complex piece of equipment. Uniform mixing and dilution is unlikely in all of the partially enclosed spaces, crevices, etc. If a hazardous operation such as welding must be performed with an air atmosphere (instead of inert gas) in the equipment, reliable gas concentration measurements should be obtained at several different locations. In the case of the generator, a direct measurement of hydrogen concentration may well have been more reliable than the 100-percent CO_2 reading on the densitometer. Furthermore, the gas composition should have been determined at the welding site as well as the top of the generator.

Another dangerous purging practice that has led to explosion is the isolation of a portion of a closed hydrogen loop in order to reduce the purge time and volume. Complete isolation usually cannot be assured because of hydrogen's propensity to leak.

2.5 VENT AND EXHAUST SYSTEM INCIDENTS

The 10 vent and exhaust system incidents listed in Table II can be divided into two subcategories. In the first subcategory, the vent/exhaust is designed to operate with diluted hydrogen but an inadequate ventilation rate causes the hydrogen concentration to increase above the lower flammable limit. In the second subcategory, air is inadvertently admitted into a pure hydrogen vent and a combustible mixture is formed.

A typical incident in the inadequate ventilation subcategory might be caused by exhaust fan failure or a clogged or frozen exhaust filter. One clogged/frozen exhaust filter incident in a BWR off-gas stack was described previously. Incidents of this nature can be avoided by monitoring the ventilation rate and the hydrogen concentration in the exhaust.

Incidents in the second subcategory arise when 1) there is a backflow or diffusion of air into the vent, or 2) there is some type of seal failure at the vent entrance, or 3) the hydrogen is not adequately dispersed above the vent outlet. Backflow or diffusion of air can be prevented by using check valves, "flapper"-type discs (ref. 7, p. 371) or molecular seals(8). Inadequate hydrogen dispersal into the atmosphere is a more difficult problem that has occurred with rupture disc activation as well as with vent stacks. There are several incidents of this type listed in Table III* - Transportation Incidents, and several more were previously identified by Ordin in his review of hydrogen incidents in NASA operations(9). Ignitions are usually attributed to lightning or local electrostatic discharge.

2.6 HYDROGEN-CHLORINE INCIDENTS

Ten of the hydrogen incidents listed in Table II were associated with the electrolytic manufacture of chlorine. The chlorine is generated by the electrolysis of heated brine, i.e., a sodium chloride water solution. Passage of a low-voltage, high electrical current through the electrolysis cell produces chlorine gas at the anode and sodium at the cathode. In a diaphragm type cell,

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* See Appendix A

the sodium immediately reacts with water to yield sodium hydroxide and hydrogen at the cathode, which is coated with a porous asbestos diaphragm. In a mercury amalgam type cell, most of the sodium reacts with mercury at the cathode to form amalgam, which is then decomposed under the influence of water to form sodium hydroxide, mercury, and hydrogen(10).

The chlorine outlet of each cell is connected to a chlorine header pipe which leads to coolers and driers or to further chemical process streams. The hydrogen output from the electrolysis cells goes to a hydrogen header which may lead to a compressor, a drier, or a vent depending upon the end use of the hydrogen. Most of the hydrogen-chlorine fires/explosions are due to hydrogen inadvertently entering the chlorine header for a variety of reasons including a local or momentary reversal of cell polarity. As the chlorine is gradually cooled and liquefied, the concentration of hydrogen increases in the vapor mixture. (The lower flammable limit of hydrogen in chlorine is reported to be 4.1 percent(11), i.e., approximately the same as it is in air or oxygen.) Thus, most of the ignitions have occurred in the chlorine processing equipment downstream of the electrolysis cells.

Consider the following example of an explosion caused by an increased hydrogen concentration in the chlorine gas stream. Hydrogen and chlorine concentrations at this plant are measured once each shift. On the morning of the explosion, the hydrogen concentration in the chlorine header leaving the cell bank was 0.47 percent. After passing through the chlorine coolers and liquid/gas separators, the hydrogen concentration of the gas streams increased to 2.5-3.2 percent H_2, i.e., 61-78 percent of the lower flammable limit.

About 5 hr after those measurements were made, the d.c. power to the electrolysis cell bank was shut down because of intermittent power supply problems. At that time a low order explosion was heard from the chlorine drier area of the plant. Thirty seconds later, chlorine gas began escaping from the chlorine header pumps, and another explosion occurred in the electrolysis cell room. The first explosion blew off the steel plate cover on the drier by shearing off the 3/8-in. (0.95-cm) bolts on the cover. The second explosion blew off the heads of two electrolysis cells and broke 108 glass connections between the chlorine header and the cell bank. There was considerable damage to other chlorine processing equipment.

A loss investigation indicated that the hydrogen concentration in the chlorine header probably increased when d.c. power to the cells was cut off without completely shutting off the chlorine vacuum pumps. Thus, the vacuum pumps probably drew additional hydrogen into the chlorine header, and increased the hydrogen concentration further downstream where ignition occurred.

Although most of the incidents seem to occur on the chlorine side of the cell bank, at least one analogous incident occurred on the hydrogen side of the cells, at a plant where poorly designed safety interlocks allowed the hydrogen compressor to operate after d.c. power to the cells was automatically shut down. This created a sufficient vacuum in the hydrogen header to draw residual chlorine in from the cell bank. It also broke the water seal on the hydrogen compressor feed, thus allowing air to enter. The hydrogen-chlorine-air mixture exploded in the hydrogen header causing considerable damage to the header and the cell connections.

The electrolytic chlorine manufacturing process is similar in many respects to water electrolysis hydrogen production processes. Perhaps, water electrolysis plant designers will benefit from these experiences and provide more fail-safe plant shutdown procedures.

2.7 TRANSPORTATION INCIDENTS

A separate listing (Table III) of hydrogen incidents during transportation has been prepared because many of those incidents occurred outside of industrial plants. One noticeable difference between the transportation incident compilation and the industrial plant incidents (Table II) is that most of the transportation incidents involve liquid hydrogen, probably because most "merchant hydrogen" is transported in liquid form in cryogenic tank trucks.

Finally, an encouraging aspect of the transportation incident compilation is that 71 percent of the hydrogen releases did <u>not</u> lead to an ignition. Ordin has observed a similar trend in accidental outdoor hydrogen releases during NASA operations(9). The relatively few ignitions may be due to either a lack of ignition sources or to the rapid dispersal of hydrogen into the atmosphere. In any event, the accident data provide further incentive to transport, transfer and store hydrogen outdoors away from occupied areas.

III

PRELIMINARY COMPARISON OF HYDROGEN AND NATURAL GAS INCIDENTS

Natural gas accident data are being collected to provide a benchmark for interpreting the hydrogen accident data. The comparison is being conducted so as to identify any new safety problems that may arise when hydrogen begins to supplement the dwindling natural gas supply. Since the first supplements/substitutions are anticipated in industrial uses of natural gas, the comparison will emphasize the relative damage reported for incidents in industrial operations.

If the comparison is to be fair and meaningful, the accident data should be restricted to reports from the same sources. The only common source available for both hydrogen and natural gas incidents is the Factory Mutual Loss Files. Therefore, the preliminary comparison presented in Table IV is based on loss reports at FM insured plants during the period 1971-76.

The monetary loss figures in Table IV are original estimates of property damage plus business interruption. In most cases, the property damage was much larger than the business interruption loss. The losses also refer only to the portions of the plant underwritten by Factory Mutual, and in some cases there was additional damage incurred by other underwriters.

The average and median losses listed in Table IV provide an interesting measure of the relative damage produced in hydrogen and natural gas fires and explosions. The average and median losses for hydrogen fires are only slightly higher (14 percent and 22 percent respectively) than the corresponding values for natural gas fires. However, the average and median losses for hydrogen explosions are 5.9 times and 4.0 times, respectively, the corresponding values for natural gas explosions. Thus, hydrogen explosions can be expected, on the average, to produce much more damage than natural gas explosions.

There are at least two possible explanations for the more damaging effects of hydrogen explosions. One explanation is that the overpressures and resulting brisance produced in most hydrogen explosions in industrial operations are greater than those produced in equivalent natural gas explosions. Hord(12) has reached this conclusion for explosions in a confined environment by comparing the relevant flammability/explosivity properties (burning velocity and

TABLE IV

HYDROGEN AND NATURAL GAS LOSSES FOR THE PERIOD 1971-1976

Gas	Fire/Exp	Number of Losses	Median Loss ($ Thousand)	Average Loss ($ Thousand)
Hydrogen	Fire	22	30	124
Hydrogen	Explosions	29*	80	297
Natural Gas†	Fire	26**	24.5	109
Natural Gas†	Explosion	100	20	50

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* Includes three large losses for a total of $6.67 million

**Includes one large loss for $1.185 million

† The natural gas losses refer only to industrial occupancies and do not include losses at commercial, institutional, and residential properties.

detonable limits) of hydrogen and methane*. This is also the conclusion one would reach by comparing the explosion venting requirements for the two gases in order to avoid structural damage(13,14).

Another possible explanation for the larger losses incurred by hydrogen explosions is that there may be more valuable equipment, property, etc., at risk in industrial occupancies where hydrogen is used than in the occupancies handling natural gas. The basis for this suspicion is that many hydrogen explosions have occurred in large chemical plants which usually have a larger insured value than most other types of industrial plants. If the insured value of the equipment is high, then an explosion with a small or moderate brisance can produce high property damage and business interruption.

The authors' preliminary evaluation is that the damage differences are due more to the explosive nature of hydrogen than to differences in insured value between chemical plants and other industrial plants. Equipment at chemical plants is usually designed to withstand a more severe environment than in other plants and, consequently, should suffer <u>less</u> physical damage for an explosion of given severity.

Similar explanations can be hypothesized for the other results presented in Table IV. However, before presenting these debatable explanations, it would be helpful to have a more sophisticated statistical comparison of the hydrogen and natural gas losses. This analysis will be conducted in the coming months in the form of a multiple regression analysis of loss severity as a function of fuel type, occupancy category, insured value, and any other pertinent parameter likely to have a significant effect on the reported losses.

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*Hord also compared the explosive potential of hydrogen and methane on the basis of theoretical TNT equivalent, which is a measure of the energy potential of an ideal blast wave. On the basis of theoretical TNT equivalent per unit volume or per unit of energy stored, he observes that methane has the greater explosive potential.(12)

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APPENDIX A

TABLES II AND III

TABLE II

INDUSTRIAL HYDROGEN INCIDENTS

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
1-11-68	GH_2 and air exploded during shutdown of sodium chloride electrolysis system	Electrolysis of sodium chloride	Grounding electrode	0	195	During shutdown feed lines backfilled with H_2 and air and ignited
1-15-68	Excess GH_2^* in system resulted in runaway reaction which resulted in vessel rupture and fire	Hydrogenation process-ethylene purification	Spontaneous autoignition	0	5	Reduction of flow of impure ethylene caused vessel rupture by extreme heat permitting air into vessel which spontaneously ignited
1-23-68	Venting Cl_2 and H_2 autoignited when H_2 conc. was allowed to exceed 5%; mixture ignited when mixed w/air	Electrolytic chlorine process chlorine and caustic mfg.	Spontaneous autoignition	0	6	H_2 monitors were out of calibration allowing H_2 to exceed 5%
1-30-68	An explosion occurred in scrubber tank due to an increase of H_2 in the entrainment separator	Electronic-silicon crystal growing reactor	Unknown	0	5	Scrubber shutdown w/out exhaust fan shutdown caused increase of H_2 in entrainment separator
2-7-68	Explosion in special atmosphere annealing furnace due to insufficient purging	Metal processing, annealing of wire	Spontaneous autoignition	0	3.6	Excess GH_2 resulted from insufficient purge with monogas (96% N_2 and 4% CO)
2-14-68	GH_2 fire	H_2 generation	Pressure switch	0	39	GH_2 escaped from leaking Bourdon valv
3-14-68	GH_2 explosion and fire	Chemical plant cryogenic separation of H_2 feed gas	Static electric discharge	0	1900	Cracks in aluminum welds allowed H_2 to collect in cold box
8-14-68	Explosion occurred in special atmosphere retorts used to heat treat jet engines	Heat treating of jet engines	Unknown	0	4	Retort was not purged with nitrogen before introducing H_2
9-13-68	Explosion occured in furnace used in ore reduction	Tungsten oxide ore refinery	Hot spot on ore	1	7	H_2 had not been vented completely
9-20-68	Arcing from high capacity generator through H_2 feed line caused melting of line and fire	Electric power, equipment mfg.	Electrical spark	0	159	Insulation failure in starter coil caused arcing
10-4-68	H_2 leaked from a valve resulting in a fire; fire melted solder connections which caused H_2 at 90 psi to release adding to fire	Electronics components mfg - electronic tubes	Unknown	0	5.5	Valves were reportedly closed
10-31-68	GH_2 leaked into an area containing electrical equipment which resulted in a fire	Zirconium metal mfg	Electrical equipment	0	8	Leakage of GH_2 was allowed when exhaust system failed (H_2 released in zirconium mfg)

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* GH_2 denotes hydrogen stored and processed in the gaseous state.

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
1-16-69	Explosion occurred when GH_2 did not vent properly	Chem plant-sodium chlorate prod	Unknown	0	4	GH_2 is vented from a vapor space when given off in process; high H_2 conc. exploded
1-31-69	GH_2 ignited when contacted air while venting	Chemical plant ammonia mfg	Spontaneous auto-ignited	0	6	GH_2 product of ammonia mfg
2-14-69	Fire occurred when GH_2 leaking from synthesis converter ignited	Chemical plant ammonia mfg	Arc from welder	0	175	Draped arc welding handle shifted causing arc which ignited gas
7-13-69	GH_2 released from leak in reformer tube ignited causing fire	Chemical plant ammonia mfg	Natural gas burners (used as indirect heaters)	0	80	Occurred during a plant shutdown
12-21-69	GH_2 entered duct and was ignited by scrubber flame resulting in fire	Epitaxial chamber semiconductor plant	Flame from scrubber	0	50	Exhaust fan shutdown caused H_2 accumulation
4-12-70	GH_2 entered chlorine header igniting spontaneously causing explosion	Chemical plant chlorine production using mercury amalgam	Spontaneous	0	25	Did not vent properly, H_2 analyzer provided not used
7-8-70	GH_2 ignited with explosion resulting	Chemical plant cadmium sulfate mfg	Unknown	0	5	GH_2 is released during dissolving process
9-22-70	GH_2 given off by batteries exploded	Battery mfg	Electrical arc	0	3	Filters of exhaust fan clogged resulting in GH_2 buildup
11-5-70	A quick H_2 purge seemed to stabilize hydrogenator but explosion occurred	Chemical plant H_2 generation	Catalytic reaction or static spark			High pressure situation in bottom of hydrogenator; rupture disc relief valve successfully vented explosion
12-27-70	Air mixed with GH_2 and exploded	Chemical plant H_2 generation	Metal spark	0	15	Incorrect water sealing procedures resulted in air entering H_2 holder and metal spark to develop
12-5-70	Excess GH_2 entered reactor resulting in a runaway reaction w/explosion	Refinery hydrocracker	Runaway reaction	3	27000	Resulting explosion caused widespread damage to refinery and nearby plants
2-10-71	GH_2 and super heated naphtha ignited resulting in fire	Refinery	Hot process line or static spark	0	12500	Although plant was shut down after ignition much of piping became superheated and ruptured
4-13-71	GH_2 leak developed in diaphragm with fire resulting	Refining oil to solid oil	Heat of reaction or heat produced by H_2 traveling through orifice	0	5.5	Vacuum transmitter diaphragm leak w/H_2 released at 300 psi
4-30-71	GH_2 leaked in off gas system w/fire resulting	Nuclear power plant	Unknown	0		GH_2 leak due to faulty gasket ignition occurred at leak; GH_2 produced in reactor
5-26-71	Excessive GH_2 in absorber resulted in fire	Chemical plant chlorine mfg	Unknown	0	25	

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
6-19-71	GH_2 leaked into furnace and exploded when furnace started	Chemical plant H_2 and Cl_2 produced then used to form HCl	Furnace	0	14	H_2 leaked as a result of loss of water seal or ruptured cell
8-10-71	GH_2 and nitrogen mixture collected in building and exploded	Heat treatment of metals	Furnace	0	41	Faulty purging procedure allowed furnace gas to be released in building
8-12-71	Radiolytic hydrogen and oxygen exploded	Nuclear power plant;BWR	Static charge	0		Improper grounding of filters on off-gas system resulted in charge
9-14-71	GH_2 line melted with fire resulting	Electronics; capacitor mfg	Arc from shorted power cables	0	7	Copper dust collected on insulators causing short which resulted in arcing
12-21-71	GH_2 & N_2 escaped from compressor shaft and caught fire	Chemical plant ammonia mfg	Spontaneous auto-ignition	1	625	Fire spread to involve lubricating and gas and oil lines feeding fire
1971	GH_2 exploded when line was cut	Nuclear power plant; BWR	Acetylene torch	0		H_2 off-gas line cut w/acetylene torch prior to purging; GH_2 produced in BWR
3-15-72	Radiolytic hydrogen and oxygen exploded	Nuclear power plant; BWR	Recombination of radiolytic hydrogen and oxygen	0		GH_2 produced in BWR, explosion blew rupture diaphragms
3-20-72	Methane mixed w/GH_2 and air and exploded	Chemical plant ammonia synthesis	Unknown	0	130	Methane valve was not completely closed allowing methane seepage during shutdown
7-13-72	GH_2 being vented backed up in system and exploded	Chemical plant production of chlorine water	Unknown	0	90	GH_2 is liberated in process, was not venting fast enough exceeded LEL
8-8-72	GH_2 and cracked distillate exploded	Oil refinery	Heater fire box	1	1875	Stainless steel tube ruptured releasing GH_2 and distillate into fire box exploding
8-27-72	GH_2 leaked resulting in explosion	Chemical plant	Burner flame in preheater	0	200	Tube in desulphurizing preheater leaked.Damage confined to preheater
8-29-72	GH_2 leaked with fire resulting	H_2 production	Dissociator heating elements	0	8	Weld in retort chamber ruptured allowing GH_2 to escape and cause fire
9-8-72	GH_2 and air mixture in degassifier exploded	Chemical plant sodium chlorate	Improper grounding or arcing in cell	0	15	Negative pressure drew air into degassifier through vent
10-23-72	Oxygen was allowed to mix w/GH_2 causing explosion	Chemical plant argon purification	Static discharge	0	140	Leak in the oxygen condenser allowed oxygen to enter argon column mixing w/GH_2
11-30-72	GH_2 and naphtha leaked into furnace and exploded	Oil refinery	Flames in furnace	0	500	Furnace coil fractured releasing naphtha and GH_2 into furnace; fire after explosion spread
1972	GH_2 explosion	Nuclear power plant; BWR	Electric preheater or catalytic action in recombiner	0		Erroneous steam flow indication resulted in reduction of steam flow allowing detonation

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
1-16-73	GH_2 leak resulted in explosion	Rare metals refining	Unknown	0	70	GH_2 leaked from valve filling boiler room and exploding
2-9-73	Synthesis gas (hydrogen & nitrogen) leaked causing explosion	Chemical plant ammonia mfg	Lightning storm	0	30	Synthesis gas leaked from synthesis gas compressor to cooling tower when explosion occurred
6-8-73	GH_2 explosion	Chemical plant chlorine mfg	Boiler startup	0	10	Malfunctioning pressure relief valve allowed too much GH_2 to enter boiler
6-12-73	GH_2 off-gas explosion	Nuclear power plant; BWR	Lightning	0		A direct strike to off-gas ventilation resulted in explosion
8-1-73	GH_2 & Cl_2 mixture exploded	Chemical plant H_2, Cl_2 and caustic soda mfg	Short in cells	0	50	GH_2 concentration in GCl_2 piping was allowed to exceed 5%
9-3-73	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Cause unknown, but detonation occurred in off-gas system
9-5-73	GH_2 & CO leak resulted in explosion	Iron ore reforming	Hot pellets or fire in pan conveyor	0	27.5	Furnace gas (H_2&CO) leaking from bottom seal of furnace ignited
9-6-73	GH_2 leak resulted in fire	Chemical plant ammonia mfg	Spontaneous auto-ignited	0	250	GH_2 leaked from reformer
9-9-73	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Detonation in off-gas system fractured rupture disc
1973	GH_2 off-gas explosion	Nuclear power plant; BWR	Lightning	0		Lightning strike caused explosion in off-gas system
1973	GH_2 off-gas explosion	Nuclear power plant; BWR	Welding arc	2		GH_2 in filter of off-gas system when welding arc was struck 8' away during shutdown
1973	GH_2 off-gas explosion	Nuclear power plant; BWR	Lightning	0		A direct lightning strike was observed at the top of the plant ventilation stack
1973	GH_2 fire	H_2 generation reforming of naphtha	Reforming furnace	0		Weld on reforming furnace failed and GH_2 ignited on furnace
1973	GH_2 fire from leak	Refinery	Autoignited	0		Gasket leak in recycle gas line autoignited this caused adjacent line to rupture
1973	GH_2 fire when tube failed	Refinery	Unknown	0		Fin fan cooler tube pulled away from header releasing GH_2 at 3000 lb fire occurred when press. was 500 lb
1973	GH_2 fire when metal failed	Refinery; reforming of naphtha	Autoignited	0		Carbon steel corrosion resulted in release of 500°C GH_2 from hydrogen reformer
1973	GH_2 unignited release	Refinery	None	0		Failure in hydrogen compressor unit caused failure of suction and discharge lines

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
1973	GH_2 fire	Petro chemical plant	Unknown	0		Expansion joint ruptured during heatup of reactors
1973	GH_2 explosion due to reaction of water and $NaBH_4$	Chemical plant	Autoignited	0		$NaBH_4$ and H_2O reacted generating GH_2 and enough pressure and heat for explosion to occur
1973	GH_2 unignited release	Chemical plant	None	1		Attempt to bleed hydrogenator at 1000 lb resulted in chemist's arm inflated w/GH_2
1-18-74	GH_2 fire	Boron filiment mfg	Autoignited	0	175	Excessive pressure blew mercury seals allowing release of hot GH_2
1-22-74	GH_2 and GCl_2 explosion	Chemical plant chlorine mfg	Autoignited	0	85	High concentration of GH_2 in the chlorine cell gas process equipment resulted in an explosion
1-25-74	GH_2 fire	Electronics plant	Burners	0	35	GH_2 escaped from a loose fitting at a solenoid valve gas line resulting in fire
1-30-74	GH_2 explosion due to pipe rupture in synthesis gas line	Ammonia mfg; steam reforming of natural gas	Autoignited	0	2170	Two explosions occurred, the first due to weld failure, the second due to overstress in elbow
2-8-74	GH_2 explosion	Metal annealing	Furnace ignition	0	75	A faulty relay allowed gas to enter furnace prior to startup; mixture exploded at furnace ignition
4-23-74	GH_2, monomethylamine, cyclohexanone fire	Chemical plant cyclohexylamine	Reaction with catalyst	0	30	Reagents leaked around sight glass and ignited in the presence of the catalyst
5-20-74	GH_2 off-gas explosion	Nuclear power plant	Metal spark from closing valve	0		During startup of reactor w/a new off-gas system a spark from a closing valve initiated an explosion
5-29-74	GH_2 cylinder unignited release	Refractory mfg	None	0	350	No. 4 oil escaping from piping was ignited; the heat caused pressure buildup and rupture of cylinder
6-14-74	GH_2 and chlorine fire	Chemical plant chlorine mfg	Autoignited	0	55	GH_2 and GCl_2 mix autoignited in an experimental diaphragm cell
7-2-74	GH_2 fire	Food processing (edible oil and shortenings)	Lightning	0	5	GH_2 being vented from a relief valve was ignited by lightning
8-6-74	GH_2 fire	GH_2 generation by cracking of anhydrous ammonia	Autoignited	0	35	During storage of cylinders at plant one of cylinder's rupture discs ruptured prematurely
8-6-74	GH_2 fire	Purification of zinc	Unknown	0	10	Fire in the exhaust stack of an acid leaching tank
8-8-74	GH_2 explosion	Chlorine, caustic soda plant produced electrolytically	Unknown	0	156	A rapid increase in current in amalgam cells provided excess GH_2 which exploded

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
9-10-74	GH_2 and oil fire	Chemical plant ammonia mfg	Hot steam lines	0	710	Seal oil pump failed blowing GH_2 and oil out which ignited when it came in contact w/steam lines
9-24-74	GH_2 fire	Metal annealing	Hot air in furnace	0	20	GH_2 leaked through rubber seal into furnace
9-74	GH_2 explosion	Refinery	Electrical	0	10-100	Explosion occurred at startup because GH_2 had leaked into motor enclosure during shutdown
10-22-74	GH_2 explosion	Chemical plant silicone products	Silane fire	0	125	GH_2 in fume scrubber and acid tanks was ignited by a silane fire w/explosion resulting
12-2-74	GH_2 and GCl_2 mixture explosion	Chemical plant chlorine, sodium hydroxide	Unknown	0	395	Mixture in electrolytic chlorine production equipment exploded
2-20-74	GH_2 off-gas explosion	Nuclear power plant; BWR	Improper grounding	0		During startup explosion occurred in off-gas system
3-2-74	GH_2 off-gas explosion	Nuclear power plant; BWR	Improper grounding	0		While unit operating at level of 2232 MWT an explosion occurred in off-gas filter
1974	GH_2 off-gas explosion	Nuclear power plant; PWR	Sparks from pipe cutting	0		With construction underway in filter building workers accidentally cut GH_2 pipe
1-75	GH_2 fire	Refinery naphtha reforming	Fixed flame in driers	0	1-10	Exchanger shell for regeneration gas heater on H_2 drier ruptured, automatic shutdown failed
3-7-75	GH_2 explosion	Chemical plant	Unknown	0	1250	Flammable liquid and GH_2 escaped from a reactor when valve failed to close completely
3-11-75	GH_2 explosion	Copper production	Flame in monitoring equipment	0	70	GH_2 leak filled 8'x8'x8' monitoring building.Flame in sulfur dioxide monitor ignited it
3-20-75	GH_2 explosion	Glass mfg	Hot metal on furnace	0	60	O_2 valve was left open allowing explosive mix to form in idle furnace which exploded
3-75	GH_2 fire	Refinery; hydrocracking	Spontaneous auto-ignition	0	1-10	Flange opened up during H_2 sweep on hydrocracker
6-30-75	GH_2 fire	Electronics plant LED mfg	Hot material (phosphide)	0	25	A molten piece of phosphide ignited a H_2-air mixture
7-7-75	GH_2 explosion	Chemical plant HCl	Lance flame	0	10	GH_2-air mixture in hydrogen-chlorine reactor was ignited w/explosion resulting

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
7-13-75	GH_2 explosion	Iron ore reduction plant	Static spark	3	200	Plant was shutting down and purging was in progress when trapped GH_2 and methane exploded
7-75	GH_2 fire	Refinery	Failed connecting rod friction	0	10-100	Mechanical failure
8-17-75	GH_2, air and chlorine mixture explosion	Chemical plant sodium chlorate	Static charge	0	175	Insufficient air purge allowed explosive mixture to accumulate in head tank
8-75	GH_2 fire	Refinery	Fixed flame in heater	0	100-500	Due to tube rupture in H_2 heater
9-19-75	GH_2 fire	Chemical plant ammonia mfg	Unknown	0	50	GH_2 escaped from reactor due to faulty gasket
9-29-75	GH_2 explosion	Chemical plant ammonia mfg	Cutting torch	0	380	Synthesis line was cut prior to purging
9-75	GH_2 pressure rupture	Chemical plant ammonia mfg	None	0	1-10	Furnace tube leak caused excessive heat on H_2 tube causing rupture
9-75	GH_2 fire	Refinery-reforming of naphtha	Spontaneous auto-ignition	0	100-500	Flange leak on hydrogen reformer
10-75	GH_2 fire	Refinery	Fixed flame in fire box	0	1000	Furnace tube ruptured, unit depressured into fire box
10-75	GH_2 fire	Refinery-reforming of naphtha	Spontaneous auto-ignited	0	10-100	Overinsulation of hydroformer unit caused bolt failure at flange leaking GH_2
11-5-75	GH_2 explosion	Nuclear power plant; BWR	Unknown	2		Closed valve resulted in GH_2 buildup in sump which exploded
11-5-75	GH_2 explosion	Heat treating metal annealing	Unknown	0	75	No purging allowed explosive mixture to form in retort
11-25-75	GH_2 fire	H_2 generation by a recharging battery	Electric spark	0	7	GH_2 from a recharging battery collected in battery compartment; short in battery cable caused spark
12-14-75	GH_2 explosion	Filling of H_2 cylinders	Tramp metal spark	0	55	Cl_2 tank (railroad car) ruptured and debris broke H_2 tubing on cylinder bank
12-17-75	GH_2 fire	Foundry	Spark in converter	0	9	GH_2 hose leaked w/H_2 collecting in electrical converter
12-27-75	GH_2 explosion	Chemical plant sodium chlorate mfg	Static charge	0	350	Insufficient purge allowed mixture of air, GH_2 and chlorine to collect in cell liquor tanks
12-29-75	GH_2 explosion	Lead smelting	Chem reaction	0	290	Water leaked into a drum of Ca chemical reaction released GH_2 and energy for explosion

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
12-75	GH_2 fire	Refinery	Spontaneous auto-ignition	0	10-100	H_2 leaked from 2 flanges on reactor resulted in fire
1975	GH_2 explosion	Nuclear power plant	Welding spark	0		GH_2 collected in vapor space and was ignited by spark from welder
1975	GH_2 off-gas explosions	Nuclear power plant; BWR	Catalyst pellets	0		Pellets in the recombiner vessels caused 2 explosions before problem was discovered
1975	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Recombiner was being cut into off-gas train when explosion occurred in off-gas system
1-19-76	GH_2 offgas explosion	Nuclear power plant; BWR	Relay actuation	2		Improperly installed demister caused back pressure to actuate relay which caused explosion of sump
2-17-76	GH_2 fire	Precious metals recovery	Platinum catalyst	0	147.5	Scrap being acid treated released excessive amounts of GH_2 which was ignited
2-76	GH_2 pressure rupture, fire	Petrochemical chem plant	Fixed flame	0	10-100	Lead pipeline failed due to cold
4-7-76	GH_2-Cl_2 explosion	Micro-electric circuit fabrication	Unstable gaseous reaction	0	8.4	Lack of nitrogen purge allowed unstable gases to react and ignite GH_2
5-3-76	GH_2 fire	Chemical plant sodium chlorate	Spark from cell plates (electrostatic)	1	7	Lack of nitrogen purge in empty electrolytic chlorate cells allowed H_2 to accumulate
5-11-76	GH_2 explosion	Chlorine plant	Sparks from welding	3	200	GH_2 and air formed an explosive mix in electrolysis cells
6-9-76	GH_2 explosion	Chemical plant sodium chlorate	Electrostatic spark	7	127	Inadequate nitrogen purge allowed explosive mix (H_2 air) to form in cells
6-12-76	GH_2 fire	Power plant	Heat of friction	0	20,000	Mistakes in taking turbine generator off-line resulted in destruction of turbine and release of GH_2 coolant
7-8-76	GH_2 fire	Chemical plant chlorine plant	Short in cell	0	69	Power surge affected equipment resulting in an excess of H_2 in cells

TABLE II (Continued)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
7-27-76	GH_2 fire	Semiconductor mfg	Motor brush sparks	0	275	Drill bit punctured copper tubing releasing H_2
7-31-76	GH_2 explosion	Chemical plant chlorine	High temp. of mfg process	0	75	Excess acid was flowed into chlorine cells, this caused excessive H_2 liberation
7-76	GH_2 fire	Refinery	Autoignited; high temp	0	1000-10000	Valve leakage permitted hot vapors to enter vent system when mixed w/air autoignited
10-26-76	GH_2 explosion	Ammonia plant	Autoignited; high temp	0	3250	H_2 embrittlement caused weld fracture from which H_2 leaked
10-29-76	GH_2 explosion	H_2, O_2, N_2, and Argon prod.	Unknown	0	15	H_2 line in electrolytic building leaked
12-2-76	GH_2 explosion	Power plant	Welding sparks	0	150	Inadequate H_2 purge w/CO_2 resulted in explosive mixture when CO_2 was later purged with air
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		During steady-state operations explosion occurred in off-gas system
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Electrostatic spark	0		Explosion occurred in off-gas system; filters were by-passed and another explosion occurred when power was increased again
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Poor training resulted in high H_2 conc. in system
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		W/power at 85% explosion occurred in stack filter house
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Ice blockage of dilution fan caused high H_2 concentration; explosion demolished filter house
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	0		Recombiner was being cut into off-gas train when explosion occurred
1976	GH_2 off-gas explosion	Nuclear power plant; BWR	Unknown	3		Manhole to sump was being removed when H_2 ignited unauthorized wiring change of valve caused H_2 buildup
1976	GH_2 explosion	Chemical plant	Arc from switch	0		Piping leak allowed H_2 to collect in a control panel where LEL was reached

TABLE II (Concluded)

Date	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
1-5-77	GH_2 fire	Methanol plant	High temp spontaneous autoignition	0	700	Synthesis gas line rupture resulted in leak which caused fire
1-27-77	GH_2 explosion	Caustic chlorine production	Runaway chem reaction	0	1450	Air and chlorine entered H_2 header mixing with H_2 to form explosive mixture
3-7-77	GH_2 fire	Power plant	Arc from generator	0	625	Turbine vibration caused release of H_2 from generator resulting in fire
3-22-77	GH_2 fire and explosion	Chemical plant; sodium aluminum hydride	Unknown	0	150	H_2 leak at pump resulted in fire then explosion
4-7-77	GH_2 explosion	Chemical plant chlorine	Runaway chem reaction	0	375	H_2 entered Cl_2 header and reached proper ratio for reaction
4-16-77	GH_2 explosion	Metal heat treating	High temp spontaneous autoignition	0	50	H_2/air mixture remained in furnace due to poor purge
10-23-77	GH_2 explosion	Chemical plant ammonia	Unknown	0	225	H_2 line ruptured admitting H_2 into distribution pipe where explosion occurred
11-11-77	GH_2 fire	Electronics-semiconductor mfg	Unknown	0	1	H_2 exhaust gas from epitaxial reactor ignited in the exhaust duct
12-13-77	GH_2 off-gas explosions	Nuclear power plant; BWR	Welding arc	1	100	Arc struck H_2 instrumentation line causing initial explosion, second and more violent explosion occurred during shutdown cause unknown
1977	GH_2 unignited release	Chemical plant	None	0		H_2 under pressure was released when Bourdon tube on H_2 reservoir ruptured

TABLE III

INCIDENTS INVOLVING HYDROGEN TRANSPORT

Date	Location	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
9-3-66	Chelmsford G.B.	GH_2 fire	Transfer at electronics plant	Unknown	0		During transfer of H_2 from truck to cylinder banks leak and fire developed on delivery hose
1-68	U.S.A.	LH_2 unignited release	Transfer from tank trailer to storage tank	None	0		During transfer leak developed resulting in an unignited release
8-2-71	N.Y.,U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	.66	Vacuum on trailer deteriorated causing pressure buildup causing rupture disc to burst
10-4-71	S.C., U.S.A.	GH_2 fire	Tube trailer in transit	Sparks from metal on pavement	2	70	Trailer overturned w/one of ten tubes igniting. H_2 in remaining tubes released later
2-21-72	Texas,U.S.A.	GH_2 fire	Tube trailer in filling area	Tramp metal spark	0	100	Safety slug in vent tubing failed damaging tubing w/H_2 fire damaging several other trailers
6-18-72	Ariz.,U.S.A.	LH_2 fire	Tractor tank trailer in filling area	Unknown	0	22	H_2 leak from filling station ignited enveloping trailer and resulting in release of H_2 from trailer
9-26-72	Fla., U.S.A.	LH_2 fire	Tractor tank trailer in transit	Tramp metal spark	2	128	Car ran stop sign hitting truck; ruptured gasoline tank, piping, inner and outer H_2 tanks tractor trailer completely destroyed
6-11-73	Plymouth, G.B.	GH_2 fire	Lorry w/cylinders in transit	Unknown	0	0	Chain holding cylinders in place on lorry broke; cylinders ruptured with small fire resulting
6-15-73	Pa., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	2.5	Vacuum on trailer was lost resulting in H_2 release both manually and through bursting of ruptured disc
9-10-73	Calif., U.S.A.	GH_2 no release or fire	Tractor tank trailer in transit	None	1	15	No release occurred after trailer hit by car because of sturdy construction of trailer
1-6-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Faulty rupture disc failed prematurely releasing 750 cu ft of H_2
1-7-74	Pa., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Excessive delay in trip resulted in excessive pressure requiring manual venting releasing 2750 cu ft of H_2
6-23-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Driver failed to lower tank pressure before leaving plant so he had to stop en route and vent 4000 scf
9-25-74	Ariz., U.S.A.	LH_2 unignited release	Train tank car in transit	None	0	0	Inner tank leaked destroying vacuum in tank car; this caused LH_2 to revert to GH_2 resulting in pressure buildup and venting through relief valve

TABLE III (Continued)

Date	Location	Type of Accident	Mode of Operation	Ignition Source	No. of Injuries	Property Damage ($1000)	Comments
10-5-74	Ala., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Tank was slightly overloaded; this forced driver to vent tank manually releasing 5000 cu ft
10-13-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Unit was returning to plant empty when pressure buildup forced driver to vent manually
10-13-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	After LH_2 transfer from trailer driver failed to wait for pressure stabilization so he had to stop and vent manually on way to plant
12-2-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Vent valve on trailer vibrated open allowing a slight H_2 discharge
12-4-74	Pa., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	1.7	Unexplained loss of vacuum resulted in release of all H_2 by manual venting and relief valve
12-23-74	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Prior to loading the trailer had been purged w/nitrogen for maintenance work after loading driver failed to allow H_2 to stabilize in warm tank so he had to vent 6000 cu ft
1-6-75	Va., U.S.A.	LH_2 unignited release	Tractor tank truck	None	0	0	Pressure building valve vibrated open allowing pressure buildup; drivers vented tank's closed valve
1-7-75	Calif., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Pressure buildup resulted in driver venting 6000 cu ft of H_2 from trailer
1-10-75	Va., U.S.A.	LH_2 unignited release	Tractor tank trailer	None	0	0	Pressure buildup in tank was manually vented by driver releasing 1000 cu ft
9-21-75	Ala., U.S.A.	LH_2 unignited release	Tractor tank trailer in transit	None	0	0	Tank was manually vented prematurely on its empty return trip; 9,000 cu ft released
11-5-75	Ohio, U.S.A.	GH_2 fire	Tractor tube trailer	Static electrical discharge	0	0	Trailer was loaded and parked in the sun; the heat caused a pressure buildup; a frangible disc failed prematurely venting H_2 which ignited; 13,360 cu ft released
12-31-75	Calif., U.S.A.	GH_2 fire	Tractor tube trailer	Spontaneous	0	0	Tube trailer was filled and parked in yard when a rupture disc on one of the tubes failed w/escaping H_2 igniting 9583 cu ft released
3-24-75	Conn., U.S.A.	LH_2 unignited release	Tractor tank trailer	None	0	0	Tank trailer became detached from tractor due to equipment failure; during LH_2 transfer to another trailer release of 58,000 cu ft occurred
5-10-75	Alberta, Canada	GH_2 unignited release	Tractor tube trailer in transit	None	0	0	Tractor trailer went off road on return trip shearing off rear valves and manifolds releasing 2000 cu ft of GH_2