COMPARATIVE ANALYSIS OF HYDROGEN
FIRE AND EXPLOSION INCIDENTS

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FOREWORD

This report describes work performed under Department of Energy, Contract No. EE-77-C-02-4442 during the three-month period, September 1, 1977 to November 30, 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 are described, as well as statistics on hydrogen and natural gas production and use. Future reports will present, tabulate, and analyze the data in order to satisfy the cited objectives of the study.

ABSTRACT

A hydrogen accident data base covering industrial and other forms of hydrogen use is being developed. Ten different sources of hydrogen accident reports have contributed 168 reports for the period 1971-1976 and 402 reports for the years prior to 1971. Additional data are being sought through a survey of major hydrogen consuming industries. National gas consumption and accident data have also been collected to serve as a basis for comparison with the hydrogen accident data. During the next quarter, a computer data entry and retrieval program will be written to sort and tabulate the hydrogen accident data.

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I

INTRODUCTION

The nature and quantity of hydrogen production and use are expected to change dramatically over the next several decades. In 1973, 2,575 billion standard cubic feet of hydrogen were produced in the United States⁽¹⁾. By the year 2000, U.S. demand for hydrogen is forecast to range from 8,800 to 28,000 billion standard cubic feet⁽¹⁾. This huge increase in demand is primarily due to 1) the anticipated use of hydrogen in synthetic fuel processing, and 2) substantial growth of the existing hydrogen market for ammonia fertilizer to meet the worldwide need for food and other agricultural products. Beyond the year 2000, additional major markets for hydrogen as an energy storage and transmission medium will probably evolve (reference 2, Chapter VI).

In order to meet the forecast increase in hydrogen demand, new hydrogen production techniques need to be implemented. The primary source of hydrogen today is steam reforming of natural gas. As the supply of natural gas dwindles, more readily available feedstocks and energy sources will be utilized. The most likely near term candidate is the partial oxidation of coal, i.e., reacting coal with steam and oxygen to form hydrogen, carbon monoxide, and carbon dioxide. Over the long term, thermochemical and electrolytic water splitting reactions, using nuclear or solar energy, offer the greatest potential (reference 2, Chapter VII).

A potential problem associated with this scenario for expanded hydrogen production and use is that the highly flammable nature of hydrogen may introduce some hazards for which we are unprepared. In this study, a hydrogen safety data base is being developed to help identify any significant new hazards. The safety data base is being compiled by collecting hydrogen accident reports from a variety of sources. These sources represent the spectrum of current hydrogen users. The emphasis is on industrial users who account for the overwhelming majority of total hydrogen consumption. Thus, the data base will be more comprehensive and relevant to future hydrogen use than previous published hydrogen accident data compilations which were restricted to NASA and AEC operations.^(3,4)

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Since many of the anticipated new hydrogen uses and production methods involve the replacement of natural gas, the natural gas safety record will provide a benchmark for evaluating hydrogen accident report compilations. The comparative evaluation should help us predict what new safety problems will arise when current natural gas users become large hydrogen users.

Activity on this project so far has centered around the collection of accident data and use statistics for both hydrogen and natural gas. The remainder of the report describes the data collected to date and the type of compilations planned during the next few months.

II

CURRENT HYDROGEN PRODUCTION, USE AND BYPRODUCT GENERATION

A brief overview of present industrial applications of hydrogen is presented in this Section in order to provide perspective for interpreting the hydrogen accident reports. More comprehensive descriptions of current hydrogen applications are available in references 1, 2, 5 and 6.

2.1 PRODUCTION

Most of the hydrogen produced in the United States is made by the catalytic reforming of natural gas with steam in a two- or three-stage process. The first step is the reforming reaction:

and the second step, called the water/gas shift conversion, or CO shift conversion, is

The combined reaction is:

The steam reforming step (1) is usually conducted in catalyst-coated tubes lining the inner wall of a furnace which provides the reaction heat. The water/gas shift reaction (2) is exothermic and heat exchangers are usually employed to heat the incoming gases and/or generate some of the process steam. The final stage in the production process is to pass the gases through a CO₂ absorber, such as ethanalamine.

In petroleum refineries, most of the required hydrogen is produced by catalytic reforming of naphtha (CH_{2.2}) or some other light hydrocarbon derived from oil. The process is similar to that for methane reforming, but the naphtha must first be desulfurized.

A third hydrogen production technique sometimes employed in refineries is the partial oxidation of heavy residual oils. In this process, the oil is partially burned in an oxygen and steam environment. Since pure oxygen is required, the partial oxidation process is used far less than the catalytic steam reforming processes in domestic refineries.

Hydrogen production in the United States (2,575 billion scf in 1973) is approximately equal to domestic demand, so there are virtually no imports or exports. Foreign production of hydrogen in 1973 amounted to about 4,800 billion scf (about 2,900 billion scf in Europe). The total worldwide production level in 1973 was 7,400 billion scf⁽¹⁾.

2.2 CURRENT HYDROGEN USES

The primary industrial use of hydrogen is as a chemical intermediate in the chemical and petroleum industries; the three largest users are ammonia plants, petroleum refineries and methanol plants. Table I shows the distribution of hydrogen demand by these and other industrial users in 1974. The combined consumption by ammonia plants, petroleum refineries, and methanol plants accounted for 92 percent of the hydrogen used in the United States in 1974.

Almost all of the hydrogen used in the petrochemical industry is produced and consumed on site, and is called "captive" hydrogen. Only the relatively small users in Table I employ "merchant" hydrogen, i.e., hydrogen produced off site and sold as industrial gas. Less than one percent of the total domestic hydrogen demand is met by merchant hydrogen, which is shipped either as a cryogenic liquid in tank trucks or rail cars, or in compressed gas cylinders. There are only a few interplant hydrogen pipelines operating in the United States and the longest one is only 15 miles long. The largest foreign operating hydrogen pipeline network is in Germany. It has a total length of about 130 miles and an annual throughput of about 10 billion scf (reference 2, p. 103).

The following is a brief description of hydrogen use in specific industries.

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TABLE I
HYDROGEN USE IN THE UNITED STATES IN 1974*

<u>Use</u>	<u>1974 Demand (10⁹ scf)</u>	<u>Percentage</u>
Ammonia Synthesis	1,060	41.2
Oil Refining	1,065	41.4
Methanol Synthesis	247	9.6
Miscellaneous Chemical Processes	118	4.6
Hydrogenation of Fats and Oils	10	0.4
Production of Metal Ores	18	0.7
Rocket Propellant	14	0.6
Electric Generator Cooling		
Electronics Industry	38	1.5
Other		
Total	2,570	100

*The figures in Table I are from Bureau of Mines Bulletin 667⁽¹⁾ which is the most recent published compilation. Other authors have presented somewhat different estimates, with the main difference due to refinery operation. For example, Kelley and Laumann⁽²⁾ have estimated that 1,434 billion scf of hydrogen was used in refinery operations in 1973, and that the total amount of hydrogen consumed in the United States was 3,057 billion scf. Darrow et al⁽⁵⁾ have estimated refinery demand to be 780 billion scf and total domestic hydrogen consumption to be 2,200 billion scf in 1974.

2.2.1 Ammonia Synthesis

Synthesis gas for ammonia (NH_3) production consists of hydrogen and nitrogen in the ratio 3 to 1. The hydrogen/ammonia input/output ratio is about 72,500 scf of hydrogen per ton of ammonia⁽⁵⁾. In 1976 there were about 100 operating ammonia synthesis plants in the United States with a total capacity of 18.9 million short tons⁽⁷⁾. In the new high-capacity (1,000 tons per day) plants, the synthesis reaction takes place in a catalytic converter at a pressure of 2,000-3,000 psi, while in the older plants the reactor operates at a pressure of 9,000 to 12,000 psi⁽⁸⁾. Until the winter of 1976-77, almost all of the ammonia plants produced their hydrogen from natural gas feedstocks. Gas curtailments in the winter of 1976-77 forced the temporary closing of many plants, and it is not clear what new hydrogen sources will be used if these curtailments continue.

2.2.2 Petroleum Refineries

According to Darrow et al⁽⁵⁾, the three main uses for hydrogen in refineries are hydrotreating, hydrocracking, and fuel burning of excess byproduct. Hydrotreating is the reduction of sulfur content in distillate feeds. Up to 50 scf of hydrogen per barrel of distillate can be consumed in hydrotreating. Hydrocracking is the combined cracking, i.e., pyrolysis, and desulfurization of heavy sour crude and residue oil to produce refined products such as high-octane gasoline. From 1,800-2,500 scf of hydrogen is consumed per barrel of crude oil during hydrocracking. Domestic refineries generate the hydrogen they need, either by catalytic reforming of naphtha or the steam reforming of methane, but foreign locations often use partial oxidation of heavy oils.

2.2.3 Methanol Synthesis

The synthesis gas for methanol (CH_3OH) contains hydrogen and carbon monoxide in the ratio 2 to 1. The synthesis reaction is endothermic and is usually conducted at a pressure of 3,500-4,500 psi and a temperature of about 300°C in the traditional Lurgi process. In the newer ICI process, the reactor operates at 750 psi and 360°C, and uses a different catalyst (reference 2, p. D-2). Hydrogen consumption during methanol production is 52,000 to 75,000 scf per ton of methanol, and is usually obtained from steam reforming of natural gas feedstock.

2.2.4 Hydrogenation of Fats and Oils

The hydrogenation process in the food processing industry consists of adding hydrogen to unsaturated animal and vegetable fats and oils to produce saturated oils. Edible oils in foods such as soybeans, corn, and peanuts are often hydrogenated in order to reduce their reactivity and, thus, retard oxidation and the resulting rancidity. The oil hydrogenation process normally occurs at 50-250 psi and 120-150°C in the presence of a catalyst. As in the other hydrogen addition reactions, a severe explosion hazard can exist during startup and shutdown operations, unless the reactor is thoroughly purged with an inert gas.

2.2.5 Reduction and Heat-Treating of Ferrous Metals

Hydrogen gas is sometimes used in the steel industry to reduce iron oxide to sponge iron and to prevent metal oxidation during heat treating. A hydrogen-nitrogen atmosphere (hydrogen concentration varies from 3 percent to 30 percent) is often used during heat treating operations (reference 2, p. D-4). Heat treating can increase metal ductility, improve machinability, and alter electrical and magnetic properties.

2.2.6 Reduction and Metalworking of Nonferrous Metals

The oxides of tungsten, molybdenum, and magnesium are all reduced by hydrogen. A hydrogen-nitrogen reducing atmosphere is also used for annealing nonferrous metals in order to prevent oxidation and improve surface brightness. Hydrogen is also used in the production of sintered metal parts and, occasionally, for plasma arc welding.

2.2.7 Rocket Propellant - Nuclear Research

Most of the liquid hydrogen produced is used as rocket propellant in launch vehicles such as the Centaur and Saturn (second and third stages). Some liquid hydrogen is also used in bubble chambers for experiments on subatomic particles.

2.2.8 Miscellaneous Chemical Processes

Hydrogen is used in the production of a variety of chemicals, including hydrogen peroxide, hydrogen chloride, ethylene, styrene, aldehyde, and ketones. It is also used to make benzene which, in turn, is used to produce cyclohexane, phenol, aniline, and other chemicals^(1,2). Almost all of these processes utilize on-site hydrogen generators.

2.2.9 Electric Generator Cooling

Electric utilities employ hydrogen as a coolant for large generators because of its high thermal conductivity compared to other industrial gases. The hydrogen is circulated through heat exchangers in the shell of the rotor and through the stator windings. About 1 scf of hydrogen per day per megawatt of electrical capacity is usually needed to make up for normal losses in the cooling loop⁽²⁾.

2.2.10 Electronics Industry

Hydrogen is often used to provide a reducing atmosphere during the brazing of metals and silicon compounds used by electronic equipment manufacturers. The brazing, or bonding process, must be conducted at temperatures above 400°C in order for brazing filler material to melt and flow. Hydrogen is also used for silicon crystal growing and related semiconductor manufacturing processes.

2.2.11 Other Industrial Uses

The category "other uses" in Table I includes oxygen-hydrogen glass cutting, pharmaceutical manufacturing, nuclear fuel processing, artificial stone production and fuel cell operations^(1,2). Of course, many new hydrogen applications as a fuel are being considered; however, their implementation must await a more reliable and economical hydrogen source.

2.3 BYPRODUCT GENERATION

A significant, but difficult to quantify, amount of hydrogen is generated as an unused byproduct in several different industries. The electrolytic chlorine manufacturing industry is a primary example. About 90 percent of the chlorine produced in the United States is by the electrolysis of an alkaline chlorine brine. When the brine is subjected to high electric current, hydrogen and sodium hydroxide are evolved, in addition to the chlorine gas. In many cases, the hydrogen is vented to the atmosphere. The hydrogen byproduct of these electrolytic chlorine plants represents a special explosion hazard because hydrogen-chlorine mixtures, as well as hydrogen-air mixtures, have wide explosion limits.

Battery charging operations in a wide variety of industries also represent a source of byproduct hydrogen that goes unused. Since the charging operation can produce hydrogen and oxygen in stoichiometric proportions, a severe explosion hazard can exist if the evolved gases are not vented effectively.

Another example of byproduct hydrogen is the off-gas generated in the cooling loop of boiling water nuclear reactors. Hydrogen and oxygen are formed by radiolytic decomposition of the steam flow through the reactor and must be removed by the off-gas handling system downstream of the condenser. The off-gas system dilutes the explosive mixture with either steam or air and then recombines the hydrogen and oxygen through the use of a catalyst.

A fourth example of byproduct hydrogen is the epitaxial chamber for depositing silicon films or chips for semiconductor manufacturing. Here, silane (SiH_4) or some other silicon-bearing gas is decomposed at high temperature into elemental silicon and hydrogen. The byproduct hydrogen is usually vented even though merchant hydrogen is needed for the other electronic equipment fabrication operations described in Section 2.2.10.

These, and other industrial sources of byproduct hydrogen, often present more of a safety problem than the hydrogen consuming operations because economic considerations may allow the hydrogen to be handled carelessly. It will be interesting to see if the loss statistics reflect the difference in attitude toward hydrogen safety.

III

SOURCES OF HYDROGEN ACCIDENT REPORTS

During the past three months, accident/loss reports involving hydrogen fires or explosions have been collected from various organizations. A list of the number and type of reports obtained from these organizations is shown in Table II. Examples of these loss reports are presented in Appendix A on the standardized hydrogen incident forms prepared for this project.

The organizations and report data shown in Table II represent different types of hydrogen handling activities in industry, transportation, and government/scientific operations. However, there are reasons to believe that the list and totals in Table II cover only a fraction of the total number of hydrogen incidents that have occurred. The following is a brief description of the information obtained by each of the sources in Table II. Other sources that have been unable to provide information or that haven't yet received or responded to our request are listed at the end of this Section. The latter includes a survey of selected industrial plants that handle hydrogen in large quantities.

3.1 FACTORY MUTUAL LOSS RECORDS

The Loss Analysis Department at Factory Mutual (FM) maintains a computer data bank of losses and claims at FM-insured occupancies. The data bank includes 82 losses involving hydrogen during the period 1971-1976 and 210 incidents prior to 1971. Although these losses originated in almost all of the hydrogen handling industries discussed in Section II, there are relatively few reports from petroleum and chemical plants, because 1) FM does not insure many petrochemical plants and refineries, and 2) minor incidents of these plants often result in losses under the deductible value (which is often greater than \$100,000 at the larger plants).

The descriptions and analysis provided in the FM loss reports are usually accurate and complete because the reports are prepared by experienced FM engineering loss investigators and adjustors. As with the other sources, the identity of the company involved is omitted in transcribing the loss data onto the forms shown in Appendix A.

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TABLE II
SOURCES SUPPLYING HYDROGEN LOSS REPORTS

<u>Source</u>	<u>Number of Reports</u> <u>pre 1971 1971-1976</u>		<u>Type of</u> <u>Occupancy and Incident</u>	<u>Report</u> <u>Detail</u>
FM	210	82	Industrial	Good
API	-	30 ⁽¹⁾	Refineries & Petro- chemical Plants	No Location or Exact PD
DOT-OHM	-	24	Truck Transport*	Fair
Man. Che. Assoc.	14	3	Chemical Industry*	No PD, Date, or Location
OSHA	-	3	Industrial, 5+ Injuries	Fair
NFPA	-	2	General	Fair
Journals/Miscellaneous		10	General	Varies
NASA	96 ⁽²⁾		NASA Centers & Contractors*	No PD, Date, or Location
NRC		14	BWR Off-Gas Explosions	Good
AEC	82		Nuclear Laboratories	Good
Total	402	168		

*These incidents include all significant accidental releases of hydrogen, whether or not an ignition occurred.

(1) API reports are for 1973, 75 and 76.

(2) The dates of the NASA incidents are not yet available, but most occurred prior to 1971.

3.2 AMERICAN PETROLEUM INSTITUTE (API)

Member companies of the American Petroleum Institute participate in a voluntary survey of fire losses. Based on this survey, the API Committee on Safety and Fire Protection distributes an annual computer listing and summary of fires for various oil industry occupancy categories. We have received the listings for refineries and for petrochemical chemical plants for the years 1973, 75, and 76. Out of a total of approximately 400 incidents, there were 30 hydrogen fires or explosions. Many of the hydrogen incidents occurred in the naphtha catalytic reforming process.

The API fire listings are geared toward statistical compilations and do not contain detailed descriptions of the accident circumstances and the response measures. The property damage is given in terms of a wide range rather than an exact figure. Nevertheless, the API fire loss data provide useful information that is not available elsewhere. A few transcribed API reports are presented in Appendix A.

3.3 DEPARTMENT OF TRANSPORTATION (DOT) - OFFICE OF HAZARDOUS MATERIALS

The DOT Office of Hazardous Materials has provided us with 24 completed Hazardous Material Incident Reports (DOT Form F 5800.1) involving the accidental release of hydrogen. In many of these incidents the hydrogen was vented either manually or automatically to relieve excessive pressures within cryogenic liquid tanker trucks. The property damage was usually less than \$1,000 and there were few injuries, since the hydrogen was not ignited in most cases. Sample transcribed hydrogen incident reports based on DOT reports are included in Appendix A.

3.4 MANUFACTURING CHEMISTS ASSOCIATION (MCA)

MCA, the trade association for the chemical industry, publishes volumes of Accident Case Histories⁽⁹⁾ based on reports submitted voluntarily by member companies. The case history accounts are designed to be instructional by illustrating hazardous practices and equipment designs. Apparently, only a small fraction of the member companies regularly submit accident reports, so MCA cannot be considered as an exhaustive source of hydrogen loss data from ammonia and methanol plants.

3.5 OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION (OSHA)

OSHA requires that reports be submitted for all industrial accidents involving at least five injuries to workers. Computer files containing abstracted information from these reports are maintained at OSHA Headquarters in Washington, D.C. At our request, the computer files were scanned for hydrogen accidents and only three were identified. We have requested completed copies of these reports.

3.6 NATIONAL FIRE PROTECTION ASSOCIATION (NFPA)

NFPA has recently instituted a computer data bank for the fire and explosion loss reports received from a variety of private and public organizations. Unfortunately, the computer retrieval program cannot distinguish hydrogen incidents from those involving other "specialty" flammable gases. An informal hand search through this category of reports yielded only two hydrogen incidents, both of which were already obtained from other sources.

3.7 JOURNALS AND NEWSPAPERS

The FMRC Library maintains a file of newspaper and journal accounts of major industrial fires and explosions involving multiple injuries or widespread property damage. This file, plus a search through Fire Journal, Chemical and Engineering News, Fire Prevention, the Oil and Gas Journal, the New York Times, and a Marsh and McLennan publication⁽¹⁰⁾ yielded 10 hydrogen incident reports that were not available from other sources.

3.8 NATIONAL AERONAUTICAL AND SPACE ADMINISTRATION (NASA)

The 96 NASA hydrogen incidents listed in Table II refer to Ordin's compilation in 1974⁽³⁾. These incidents occurred either at NASA centers or contractor facilities in connection with liquid hydrogen rocket propulsion projects. A short description of each mishap and its cause is provided, but there are no dates, locations, or property damage estimates. It will be helpful to have the missing information in order to avoid duplications of incidents obtained from other sources. NASA is presently considering a means for providing this information without jeopardizing the anonymity of the center or company involved in each incident.

3.9 NUCLEAR REGULATORY COMMISSION (NRC)

The NRC hydrogen incidents refer to off-gas explosions in boiling water nuclear reactor power plants. Reports on these incidents are available from the recent Factory Mutual compilation of fire and explosion incidents at nuclear power plants⁽¹¹⁾, and from the history of operational accidents in Nuclear Safety. Newspaper accounts of the most recent off-gas explosion are also available⁽¹²⁾.

3.10 ATOMIC ENERGY COMMISSION (AEC) - ERDA

Most of the 82 hydrogen incidents at AEC-ERDA facilities were reported by Weintraub in his 1965 review of liquid hydrogen hazards⁽⁴⁾. Since then, there have been a few hydrogen incidents reported in WASH 1192, the periodic update of accidents in ERDA-D.O.E. facilities⁽¹³⁾.

3.11 MISCELLANEOUS SOURCES

Many organizations collect large numbers of accident reports but do not categorize them in a manner that allows hydrogen incidents to be identified. In addition to the National Fire Protection Association (Section 3.6), these organizations include the National Fire Prevention and Control Administration and the National Petroleum Refiners Association. Inquiries to these organizations have not produced any identifiable hydrogen accident data.

Requests for hydrogen accident data are also being sent to various organizations in the insurance industry, both domestic and foreign. In addition to individual insurance companies, inquiries are being sent to the American Insurance Association and the German Property Insurance Association.

Other foreign organizations that may be probed are the British Fire Protection Association, and the Berufsgenossenschaft der Chemischen Industrie.

We would appreciate receiving information from any other accident source.

3.12 SURVEY OF INDUSTRIAL HYDROGEN USERS

The data sources listed in Table II may not reflect the heavy use of hydrogen by ammonia and methanol manufacturers and some of the other industrial users described in Section II. Therefore, a survey of these plants is being

conducted by asking individual companies to complete and return copies of the hydrogen incident form shown in Appendix A. Major domestic ammonia and methanol plants, edible oil hydrogenation plants, and companies employing hydrogen for the direct reduction of ferrous and nonferrous metal ores, are listed in the Institute of Gas Technology (DGT) report by Biederman et al⁽⁶⁾, and will be the recipients of our questionnaire. So far, report forms have been sent to the eight largest ammonia manufacturers. It is too early to estimate the expected percentage of responses.

IV

NATURAL GAS USE AND ACCIDENT DATA

Natural gas consumption and accident data are discussed here to provide a yardstick for interpreting hydrogen accident data. In particular, we will confine our attention to industrial use of natural gas to provide a fair basis for comparison with industrial use of hydrogen. Thus, of the 17.7×10^{15} Btu of natural gas produced in 1974, approximately 46 percent was consumed by industrial customers. The distribution of natural gas disposition in 1974 and 1975 is shown in Table III based on American Gas Association Statistics⁽¹⁴⁾.

It is significant to note from Table III that industrial consumption of natural gas decreased in 1975, even though residential and commercial consumption increased slightly. This reflects the gas industry's policy to curtail or cut back industrial customers when supplies are short. Ammonia manufacturers, among others, are worried about this policy and many are considering alternative fuel sources and feedstocks for hydrogen production⁽⁶⁾.

Natural gas accident statistics are much more difficult to acquire than data on gas consumption. Sources of accident reports that have been acquired so far are listed in Table IV. Most of the accident reports indicated in Table IV are computer listings with much less detail than is available for the hydrogen loss reports. Since we are merely using the natural gas statistics for background information instead of detailed analysis, the abbreviated computer testings should suffice for our purposes.

The National Fire Prevention and Control Administration (NFPCA) data noted in Table IV are based on reports submitted via the National Fire Incident Reporting System (NFIRS). Five states now participate regularly in NFIRS by sending the NFPCA reports of every public fire department response for assistance. The 2,751 natural gas incidents were reported in Ohio in 1975 and in California in 1976⁽¹⁵⁾. Over 2,000 of the incidents occurred in residential occupancies. Only 146 occurred in basic industrial or manufacturing occupancies. In order to extrapolate this sample to obtain an estimate of nationwide industrial natural gas incidents, it will be necessary to acquire some information on the geographical distribution of industrial consumers or natural gas.

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TABLE III
NATURAL GAS DISPOSITION 1974 AND 1975
(10^{15} Btu or 10^{12} scf)

	<u>1974</u>	<u>1975</u>
Industrial Consumption	8.15	6.84
Residential Consumption	4.86	4.99
Commercial Consumption	2.29	2.39
Gas Producer Consumption	1.38	1.20
Other	1.03	1.39
<hr/>		
Total	17.71	16.81

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TABLE IV
NATURAL GAS LOSS REPORTS ACQUIRED TO DATE

<u>Source</u>	<u>Number of Reports</u>	<u>Years</u>	<u>Type of Occupancy/Incident</u>	<u>Form of Report</u>
NFPCA	2,751**	1975-76	Ohio and California Public Fire Dept. Involved	Computer Listing
D.O.T.-Off Pipe Safety	5,600	1972-75	Pipeline Failure*	Computer Listing
NFPA	318	1969-73	General	Statistical Summary and Selected Abstracts
N.Y. Times	90	1971-76	General - often in Metropolitan NYC	Newspaper Articles
Other Newspapers/Journals	50-150	1971-76	General - Local Fires and Explosions	Newspaper Articles
FM	482**	1971-76	Industrial	Loss Reports

*Most of the OPS reports involved unignited leaks or pipeline malfunctions.

**These incidents involve either natural gas or LP gas.

The Department of Transportation Office of Pipeline Safety (OPS) incidents noted in Table IV are based on a mandatory reporting system involving all natural gas transmission and distribution companies. In 1975, there were 980,000 miles of natural gas pipelines in the United States⁽¹⁴⁾. The incidents reported to OPS involve pipeline faults resulting in inadvertent release of gas. It is not yet clear how many incidents involved fires or explosions. We are trying to obtain a breakdown of incidents from OPS.

The count of natural gas incidents reported in selected major newspapers is based on a scan through annual newspaper indices that are available for the New York Times, the Washington Post, Los Angeles Times, New Orleans Times-Picayune, and a few other urban dailies. Most of these incidents refer to leaks, fires, and explosions in residential or commercial occupancies. The newspaper articles do not have a parallel for hydrogen incidents and will probably not be used in our analysis.

Almost all of the data indicated in Table IV refer to natural gas consumers. Data on incidents that have occurred during natural gas production are also available from such sources as the American Petroleum Institute, the Geological Survey, and OSHA. This data will be collected during the next few months.

V

DATA COMPILATION AND ANALYSIS PLANS

It is difficult to anticipate all of the potential uses of the hydrogen accident data bank being compiled in this study. Some safety-related hydrogen issues are evident now, but more will become apparent as hydrogen energy use begins to evolve. Therefore, the scope of the hydrogen accident reports compiled will be kept as general as possible, and will incorporate as many of the reports indicated in Table II as possible without introducing duplications.

The type of data retained for each incident corresponds to the hydrogen incident forms shown in Appendix A. Approximately 120 incident forms have been completed so far. We are tabulating the type of incident (i.e., fire, explosion, or unignited release), type of occupancy, equipment and process involved, ignition source, protection/response measures, property damage, and casualties. The tabulations will be performed via a data entry and retrieval computer program currently being developed. The computer program and data files will be made available to the Department of Energy or any other designated organization.

The tabulations will be analyzed in terms of existing safety codes and standards and in terms of hydrogen flammability properties. The analyses will be geared toward identifying any inadequacies in the existing codes and potentially fruitful areas of hydrogen safety research. As an example of this analysis, consider some preliminary observations of reported hydrogen ignition sources. In the NASA and DOT-OHM incidents, several hydrogen vented releases were ignited by unknown sources. In the API incidents, there were many reports of "spontaneous ignition" of hydrogen from leaking, ruptured, or vented equipment. If the compilations indicate a large number of mysterious ignitions of this type, it may be necessary to reevaluate standards for maximum hydrogen venting rates and velocities. Perhaps a study of electrostatic discharges during venting would be in order. Similarly, the identification of a particular type of equipment, e.g., reformer furnace tubes, prone to hydrogen accidents may become apparent from the tabulations.

In addition to the statistical tabulations, several major hydrogen accidents will be described and analyzed in detail. The analysis will include a discussion of damage-producing mechanisms (e.g., flame radiation for fires and overpressure for explosions) and alternative response measures (e.g., leak detectors, water curtains, explosion vents, etc.)

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As for comparing hydrogen accident data with natural gas data, the comparisons will be normalized both in terms of billions of scf consumed in industrial operations, and in terms of energy content consumed. The numbers of fires, explosions, property damage and injuries will be compared, including estimates of damage and injuries per incident. The comparisons will indicate whether accident statistics conform to existing hypotheses about hydrogen being more explosive than natural gas, but a less severe fire hazard with respect to flame radiation damage.

Our plans are to enter most of the hydrogen accident data into computer files during the next quarter. Over 100 hydrogen incident forms have been prepared to date and keypunching will begin in January. The tabulations and analyses will be conducted during the third and fourth quarters of the project.

REFERENCES

1. Adkins, D.C. and Jaske, R.J., "Hydrogen," A Chapter from Mineral Facts and Problems, 1975 Edition, Bureau of Mines Bulletin 667, 1975.
2. Kelley, J.H. and Laumann, E.A., "Hydrogen Tomorrow, Demand and Technology Requirements," Report of the NASA Hydrogen Energy Systems Technology Study Jet Propulsion Laboratory, December 1975.
3. Ordin, P.M., "Review of Hydrogen Accidents and Incidents in NASA Operations," NASA TMX-715G5, 1974.
4. Weintraub, A.A., "Control of Liquid Hydrogen Hazards at Experimental Facilities - A Review," AEC Report HASL-160, 1965.
5. Darrow, K., Biederman, N., and Kopopka, A., "Commodity Hydrogen from Off-Peak Electricity," International Journal of Hydrogen Energy, Vol 2, No 2, pp 175-188, 1977.
6. Biederman, N.P. and Darrow, K.G., "Utilization of Off-Peak Power to Produce Commodity Hydrogen," EPRI RP320-1, 1975.
7. Harre, E.A., Goadson, M.N., and Bridges, J.D., "Fertilizer Trends 1976," Bulletin Y-111, National Fertilizer Development Center, TVA, Muscle Shoals, Alabama, 1977.
8. Factory Mutual Loss Prevention Data Sheet 12-22, "Ammonia Synthesis Units," Factory Mutual Engineering Corporation, 1968.
9. Manufacturing Chemists Association, Case Histories and Accidents in the Chemical Industry, Vol 1-1962, Vol 2-1966, Vol 3-1970, Vol 4-1975.
10. Marsh and McLennan Protection Consultants, "A Review in the Oil, Gas, Chemical and Petrochemical Industries," M & M Inc., New York, 1977.
11. Buckley, J.L., Krasner, L.M. and Wiener, S.A., "Evaluation of Fire Hazards in Nuclear Power Generating Stations," Final Report to Nuclear Regulatory Commission, Factory Mutual Research Corporation Report RC76-7-35, 1976.
12. "One Hurt in Blasts in a Nuclear Utility," New York Times, Wednesday, December 14, 1977.
13. "Operational Accidents and Radiation Exposure Experience Within the USAEC 1943-1975," WASH 1192, 1975.

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14. Gas Data Book (excerpted from Gas Facts) 1975 Data, published by American Gas Association, Arlington, Virginia, 1976.
15. Klem, T., National Fire Prevention and Control Administration, private communication, 1977.
16. Office of Pipeline Safety Annual Reports for 1973, 1974, 1975.

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APPENDIX A

SAMPLE HYDROGEN INCIDENT REPORTS

HYDROGEN INCIDENT REPORT

DATA SOURCE

FM Loss # EX-230

DATE OF INCIDENT

11/29/74

LOCATION (STATE)

U.S.A (La.)

TYPE OF INCIDENT

☐ FIRE☒ EXPLOSION☐ PRESSURE RUPTURE☐ UNIGNITED RELEASE☐ OTHER (Specify)

BRIEF NARRATIVE

The Hydrogen Plant ~~Operator~~ OPERATOR BEGAN START-UP AFTER A NORMAL SHUT-DOWN FOR A HOLIDAY. AT START-UP THE OPERATOR TURNED ON A SMALL COMPRESSOR ~~USED TO~~ LOCATED IN THE CONTROL ROOM, USED TO CIRCULATE HYDROGEN THRU THE HYDROGEN UNIT. A LOUD, SHARP EXPLOSION WAS THEN HEARD AT THE SPHERICAL HYDROGEN STORAGE TANK.

TYPE OF OCCUPANCY

☒ INDUSTRIAL PLANT☐ TRANSIT☐ RESEARCH LAB☐ ROCKET PROPULSION☐ OTHER (Specify)

MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.)

☐ STORAGE☒ PROCESSING (Type) Feed - Veg. Oil Prod. - Hydrogen Generation +☐ DISPOSAL (How?)☐ TRANSPORT (Mode)☐ H₂ GENERATION

FORM OF HYDROGEN

☒ GAS☐ LIQUID☐ HYDRIDE

ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN

☐ YES (Describe)☒ NO

EQUIPMENT INITIALLY INVOLVED

Storage TANK (SPHERICAL, STORAGE)

COMPONENT

DIAPHRAGM

FAILED MATERIAL

RELEASE

☐ INDOORS☒ OUTDOORS☐ BOTH

IGNITION SOURCE

STATIC ELECTRICAL DISCHARGE

PROTECTION/RESPONSE MEASURES

1. —

☐ SUCCESSFUL☐ UNSUCCESSFUL

2. —

☐ SUCCESSFUL☐ UNSUCCESSFULPROPERTY DAMAGE (10³ \$)

500

NUMBER OF INJURIES

0

NUMBER OF FATALITIES

0

HYDROGEN INCIDENT REPORT

DATA SOURCE <u>FM</u> <u>Loss # EX-142</u>		DATE OF INCIDENT <u>8/27/76</u>
LOCATION (STATE) <u>U.S.A. (Ohio)</u>		
TYPE OF INCIDENT		
☐ FIRE	☒ EXPLOSION	☐ PRESSURE RUPTURE
☐ OTHER (Specify) _____		☐ UNIGNITED RELEASE
BRIEF NARRATIVE		
<p><u>An Explosion occurred & OCCURRING IN A</u> <u>HYDROGEN - CHLORINE REACTOR USED IN THE PRODUCTION</u> <u>OF HYDROCHLORIC ACID SEVERELY DAMAGED THE REACTOR.</u> <u>IT IS BELIEVED THAT THE EXPLOSION WAS THE RESULT OF AN</u> <u>AUTOIGNITION OF AN ACCUMULATION OF UNBURNED HYDROGEN AND</u> <u>CHLORINE GAS. HOW THIS ACCUMULATION DEVELOPED IS</u> <u>UNKNOWN.</u></p>		
TYPE OF OCCUPANCY		
☒ INDUSTRIAL PLANT	☐ TRANSIT	☐ RESEARCH LAB
☐ OTHER (Specify) _____		☐ ROCKET PROPULSION
MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.)		
☐ STORAGE		
☒ PROCESSING (Type) <u>Chemical - Hydrogen - Chlorine reactor producing HCl Acid.</u>		
☐ DISPOSAL (How?) _____		
☐ TRANSPORT (Mode) _____		
☐ H ₂ GENERATION _____		
FORM OF HYDROGEN		ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN
☒ GAS	☐ LIQUID	☐ HYDRIDE
☐ YES (Describe) <u>Chlorine, HCl</u>		☐ NO
EQUIPMENT INITIALLY INVOLVED		
<u>Reactor</u>		
COMPONENT		
<u>TANK</u>		
FAILED MATERIAL		
RELEASE		
☐ INDOORS	☒ OUTDOORS	☐ BOTH
IGNITION SOURCE		
<u>Spontaneous - Autoignition</u>		
PROTECTION/RESPONSE MEASURES		
1. <u>Purging</u>	☐ SUCCESSFUL	☒ UNSUCCESSFUL
2. <u>-</u>	☐ SUCCESSFUL	☐ UNSUCCESSFUL
PROPERTY DAMAGE (10 ³ \$)	NUMBER OF INJURIES	NUMBER OF FATALITIES
<u>100</u>	<u>-</u>	<u>-</u>

HYDROGEN INCIDENT REPORT

#1

DATA SOURCE <u>A. P. I.</u>		DATE OF INCIDENT <u>11/75</u>
LOCATION (STATE) <u>Foreign (outside USA)</u>		
TYPE OF INCIDENT		
☒ FIRE	☐ EXPLOSION	☐ PRESSURE RUPTURE
☐ OTHER (Specify) _____		☐ UNIGNITED RELEASE
BRIEF NARRATIVE		
<u>Reformer Unit . Furnace feed pipe</u> <u>failed completely, releasing released material, formed</u> <u>vapor cloud which ignited. Inspection after incidents</u> <u>indicated that wrong material had been used in parts of line</u> <u>and one part failed due to corrosion.</u>		
TYPE OF OCCUPANCY		
☒ INDUSTRIAL PLANT	☐ TRANSIT	☐ RESEARCH LAB
☐ OTHER (Specify) _____		☐ ROCKET PROPULSION
MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.)		
☐ STORAGE		
☒ PROCESSING (Type) <u>Refinery</u>		
☐ DISPOSAL (How?) _____		
☐ TRANSPORT (Mode) _____		
☐ H ₂ GENERATION _____		
FORM OF HYDROGEN		ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN
☒ GAS	☐ LIQUID	☒ YES (Describe) <u>NAPHTHA</u>
☐ HYDRIDE	☐ NO	
EQUIPMENT INITIALLY INVOLVED		
<u>Furnace</u>		
COMPONENT		
<u>Piping.</u>		
FAILED MATERIAL		
RELEASE		IGNITION SOURCE
☒ INDOORS	☐ OUTDOORS	☐ BOTH
☐ OUTDOORS		<u>Fixed Flame - incl furnaces</u>
PROTECTION/RESPONSE MEASURES		
1. _____	☐ SUCCESSFUL	☐ UNSUCCESSFUL
2. _____	☐ SUCCESSFUL	☐ UNSUCCESSFUL
PROPERTY DAMAGE (10 ³ \$)	NUMBER OF INJURIES	NUMBER OF FATALITIES
<u>500 - 1000</u>	<u>4</u>	<u>0</u>

HYDROGEN INCIDENT REPORT

#8

DATA SOURCE <u>A.P.I.</u>		DATE OF INCIDENT <u>3/76</u>	
LOCATION (STATE) <u>U.S.A.</u>			
TYPE OF INCIDENT ☒ FIRE ☐ EXPLOSION ☐ PRESSURE RUPTURE ☐ UNIGNITED RELEASE ☐ OTHER (Specify) _____			
BRIEF NARRATIVE <u>Packing bolt on reactor inlet valve, on heavy oils hydrofinishing unit, broke releasing hot (700 D-F) hydrogen and oil at high pressure (2000 psi). Fire was autoignited.</u>			
TYPE OF OCCUPANCY ☒ INDUSTRIAL PLANT ☐ TRANSIT ☐ RESEARCH LAB ☐ ROCKET PROPULSION ☐ OTHER (Specify) _____			
MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.) ☐ STORAGE ☒ PROCESSING (Type) <u>Refinery - Hydrofinishing Process</u> ☐ DISPOSAL (How?) _____ ☐ TRANSPORT (Mode) _____ ☐ H ₂ GENERATION _____			
FORM OF HYDROGEN ☒ GAS ☐ LIQUID ☐ HYDRIDE		ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN ☒ YES (Describe) <u>Heavy Oil</u> ☐ NO	
EQUIPMENT INITIALLY INVOLVED <u>Vessel</u>			
COMPONENT <u>Packing Bolt on Reactor inlet valve</u>			
FAILED MATERIAL			
RELEASE ☒ INDOORS ☐ OUTDOORS ☐ BOTH		IGNITION SOURCE <u>SPONTANEOUS - Autoignition</u>	
PROTECTION/RESPONSE MEASURES 1. _____ 2. _____		☐ SUCCESSFUL ☐ UNSUCCESSFUL ☐ SUCCESSFUL ☐ UNSUCCESSFUL	
PROPERTY DAMAGE (10 ³ \$) <u>10 - 100</u>		NUMBER OF INJURIES <u>0</u>	NUMBER OF FATALITIES <u>0</u>

HYDROGEN INCIDENT REPORT

☐ TRANSMISSION CODE - (In field) (Change to delete) Grey blocks

DATA SOURCE Dept of Trans HMIR # 4080014 1. 2. 3. DATE OF INCIDENT 6/23/74 Y Y M M D D

LOCATION (STATE) Milpitas Calif STATE COUNTRY INCID. NO.

TYPE OF INCIDENT ☐ FIRE ☐ EXPLOSION ☐ PRESSURE RUPTURE ☒ UNIGNITED RELEASE

☐ OTHER (Specify) 20 39

BRIEF NARRATIVE

Driver failed to lower pressure to acceptable level before leaving plant. As a result he was required to stop and manually vent trailer to a safe level. Loss of product was about 4000 scf

TYPE OF OCCUPANCY

☐ INDUSTRIAL PLANT ☒ TRANSIT ☐ RESEARCH LAB ☐ ROCKET PROPULSION ☐ OTHER (Specify) 40

MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.)

☐ STORAGE ☐ PROCESSING (Type) ☐ DISPOSAL (How?) ☒ TRANSPORT (Mode) Truck Tank Trailer ☐ H₂ GENERATION

FORM OF HYDROGEN ☐ GAS ☒ LIQUID ☐ HYDRIDE ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN ☒ YES (Describe) NO

EQUIPMENT INITIALLY INVOLVED

COMPONENT

FAILED MATERIAL

RELEASE ☐ INDOORS ☒ OUTDOORS ☐ BOTH IGNITION SOURCE none

PROTECTION/RESPONSE MEASURES

1. Plant Procedures ☐ SUCCESSFUL ☒ UNSUCCESSFUL
2. Manual release ☒ SUCCESSFUL ☐ UNSUCCESSFUL

PROPERTY DAMAGE (10³ \$) 0 NUMBER OF INJURIES 0 NUMBER OF FATALITIES 0

HYDROGEN INCIDENT REPORT

☐ EXPLANATION
CODE - (in middle column delete)

Grey blocks

DATA SOURCE

Dept of Trans. HMIR #4010179

LOCATION (STATE)

Allen town Pa

DATE OF INCIDENT

STATE COUNTRY INC. NO.

TYPE OF INCIDENT

☐ FIRE ☐ EXPLOSION ☐ PRESSURE RUPTURE ☒ UNIGNITED RELEASE

☐ OTHER (Specify)

BRIEF NARRATIVE

Hazardous road conditions resulting in excessive delay required that driver manually vent tank to reduce pressure build up. Quantity released 2750 cu ft

TYPE OF OCCUPANCY

☐ INDUSTRIAL PLANT ☒ TRANSIT ☐ RESEARCH LAB ☐ ROCKET PROPULSION

☐ OTHER (Specify)

MODE OF OPERATION (Please identify type of process e.g. ammonia production, disposal method e.g. venting or flaring, or mode of transport if applicable.)

☐ STORAGE

☐ PROCESSING (Type)

☐ DISPOSAL (How?)

☒ TRANSPORT (Mode) Truck Tank Trailer

☐ H₂ GENERATION

FORM OF HYDROGEN

☐ GAS ☒ LIQUID ☐ HYDRIDE

ANY OTHER FLAMMABLE GAS MIXED WITH HYDROGEN

☐ YES (Describe)

☒ NO

EQUIPMENT INITIALLY INVOLVED

Tank trailer

COMPONENT

FAILED MATERIAL

none

RELEASE

☐ INDOORS ☒ OUTDOORS ☐ BOTH

IGNITION SOURCE

none

PROTECTION/RESPONSE MEASURES

1. manual venting

☒ SUCCESSFUL

☐ UNSUCCESSFUL

2.

☐ SUCCESSFUL

☐ UNSUCCESSFUL

PROPERTY DAMAGE (10³ \$)

0

NUMBER OF INJURIES

0

NUMBER OF FATALITIES

0