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Progress Report

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Hydrogen Safety and Environmental Control Assessment

November 1, 1976—September 30, 1979

Final Report

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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OFFICE MEMORANDUM

TO : Holders of LA-8225-PR

DATE: May 20, 1980

FROM : F. J. Edeskuty

SUBJECT : ERRATA

SYMBOL : ISD-6

MAIL STOP: 418

Please correct the stated equations in Appendix C of LA-8225-PR
as follows:

Page 76, last equation should be:

$$\frac{d}{dt} (\rho y \Delta x Z \frac{dZ}{dt}) = \int_0^Z 2y g \Delta \rho \Delta x d\xi = 2y g \Delta \rho \Delta x Z$$

Page 77, 2nd and 3rd equations should be:

$$u \frac{d}{dx} \left\{ u \rho y Z \frac{dZ}{dx} \right\} = 2y g \Delta \rho Z ,$$

$$u^2 \rho y Z \frac{dZ}{dx} = \int_0^x 2y g \Delta \rho Z d\zeta .$$

Page 84, 1st equation should be:

$$\begin{aligned} \Delta \bar{T} = \Delta Z \left\{ \frac{dT_a}{dZ} \left[x \frac{R_a}{R_H} + (1-x) \right] - 1/2 \frac{dT}{dZ} - x/Z \right\} \left[\frac{R_a}{R_H} - 1 \right] [T_a + Z \frac{dT_a}{dZ}] \\ - [Z/2 \frac{d}{dx} (\frac{dT}{dZ})] \left\{ \right\} + \Delta \bar{T} (x/T) \left\{ \left[\frac{R_a}{R_H} - 1 \right] [T_a + Z \frac{dT_a}{dZ}] \right. \\ \left. - \frac{Z}{2} \frac{d}{dx} (\frac{dT}{dZ}) \right\} - \Delta y x/y \left\{ \left[\frac{R_a}{R_H} - 1 \right] [T_a + Z \frac{dT_a}{dZ}] - \frac{Z}{2} \frac{d}{dx} (\frac{dT}{dZ}) \right\} . \end{aligned}$$

Page 84, 2nd equation should be:

$$\begin{aligned} \Delta Z = & \left\{ \Delta T \left[1 - \frac{x}{T} \left(\frac{R_a}{R_H} - 1 \right) \left(T_a + Z \frac{dT_a}{dZ} - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right) \right] \right. \\ & + \Delta y \left(\frac{x}{y} \right) \left\{ \left[\left(\frac{R_a}{R_H} - 1 \right) \left(T_a + Z \frac{dT_a}{dZ} \right) - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right] \right\} \div \\ & \left\{ \frac{dT_a}{dZ} \left[x \frac{R_a}{R_H} + (1-x) \right] - \frac{1}{2} \frac{dT}{dZ} - x/Z \left\{ \left[\left(\frac{R_a}{R_H} - 1 \right) \right. \right. \right. \\ & \left. \left. \left(T_a + Z \frac{dT_a}{dZ} \right) - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right] \right\} \right\} . \end{aligned}$$

Page 85, 1st equation should be:

$$\frac{d}{dX} \left(\frac{dT}{dZ} \right) = \frac{C_{pH} \cdot C_{pa} \left(\frac{dT_{Ho}}{dZ} - \frac{dT_{ao}}{dZ} \right)}{[x C_{pH} + (1-x) C_{pa}]^2} .$$

Hydrogen Safety and Environmental Control Assessment

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Final Report

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HYDROGEN SAFETY AND ENVIRONMENTAL CONTROL ASSESSMENT

by

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ABSTRACT

A proposed program has been developed to provide an ongoing assessment of hydrogen safety and environmental control. As hydrogen use and its public interactions continue to expand, new concerns are identified and old ones loom larger. These are here identified, together with a coordinated program for resolving them. The program contains elements of assessment and analysis in the following areas: hydrogen production methods, especially thermochemical and coal gasification processes; storage methods, including liquid, hydrides, high pressure gas, and gas in underground chambers; transport and transmission; end uses, including vehicular and space heating; and understanding the dispersion, ignition, and effects of large scale releases of gaseous or liquid hydrogen. Support for various recommendations are given in the appendixes.

1. EXECUTIVE SUMMARY

At the request of the Environmental Control Technology Division of the US Department of Energy (DOE) the Los Alamos Scientific Laboratory (LASL) has conducted a 2-1/2 year assessment program (ending September 1979) on concerns in hydrogen safety and environmental control. This assessment produced a

current status base for the areas covered by this report, including: transmission of gaseous hydrogen by pipeline, transport of liquid hydrogen, hydrogen embrittlement of metals, safety regulations, and environmental aspects of hydrogen production and use. Details of previous work are published in previous annual reports.^{1,2} Further, the assessment conducted by LASL found that hydrogen will be used ever increasingly in closer proximity to the general public, even if hydrogen has little impact on new energy markets. Because of this, and because the assessment conducted by LASL identified needs which could not be met as a result of time and funding limits, the need continues for an ongoing assessment program in hydrogen safety and environmental control. The cost of the proposed program is estimated to be one million dollars for a four year effort (an average of \$250,000 per year). This document outlines such a coordinated program and includes in appendices a report on some of the details of the assessment program conducted by LASL.

Regarding hydrogen production, the assessment points out that the areas of new thermochemical processes and coal gasification are ones needing further work on potential emissions and their effects on the environment, their control and disposition. (See Appendix A.)

Hydrogen storage systems include cryogenic liquid, metallic or chemical hydrides, and compressed gas in cylinders at high pressure, or in underground chambers at low pressure. Safety and environmental features of these must be assessed for generic and specific locations.

Safety in the transport of increasing amounts of hydrogen as compressed gas, metal hydride, or cryogenic liquid requires continued assessment and analysis. Especially needed are relative assessments comparing hydrogen with natural gas and liquefied natural gas. As specific proposals are made for the introduction of hydrogen into natural gas pipeline systems, further detailed questions arise concerning compressors, pipes, leaks and associated hazards.

The program outlined for assessing end uses of hydrogen includes the following: pollutant emissions and novel methods of control for internal combustion engines; environmental effects of emissions of water in combination with other pollutants from high-flying, hydrogen-fueled aircraft; safety of hydrogen-fueled vehicles; and pollutant emissions and effects from hydrogen consuming equipment in homes and industry.

The final major, and most expensive, element of needed assessment is of effects of large scale spills of liquid or gas. This includes work to understand better the dispersion and ignition of combustible hydrogen mixtures.

2. INTRODUCTION

2.1. Purpose

The purpose of this document is to identify the safety and environmental problems in the production, delivery, storage and end use of hydrogen in energy systems; also, to identify additional assessment or research and development needs. This report is compiled from the large amount of information available on hydrogen energy systems and is a result of a program conducted at LASL to assess safety and environmental problems with hydrogen energy systems.^{1,2} The program conducted by LASL was funded by the Environmental Control Technology Division of the USDOE and is described in more detail in paragraph 4.6 and the Appendices of this report. The program described in this document is not intended either to advocate or discourage development of hydrogen energy systems, but, rather to identify problem areas and research which may resolve those problems.

The program suggested herein might profitably be considered part of an overall assessment program involving many different fuels or mixtures of fuels.

2.2. Hydrogen As An Energy Carrier

Hydrogen is a very attractive energy carrier. Hydrogen or hydrogen-rich gases can be used as a replacement for or a supplement to dwindling supplies of portable fossil fuels. Hydrogen can be stored as a gas, liquid (NBP 20 K) or hydride (metal or chemical). It can be transported as a high pressure gas or as a cryogenic liquid and it can be directly used in either the gaseous or liquid form as a fuel with little pollution and it can be produced from water. The annual production of hydrogen in the US is substantial, $7.4 \times 10^{10} \text{ m}^3$ ($2.6 \times 10^{12} \text{ SCF}$) or 0.6 quad. However, it is produced primarily from fossil fuels. Herein lies the main disadvantage of hydrogen. It is an energy carrier, not an energy source, and therefore energy must be expended to produce hydrogen. Current production is primarily by natural gas reformation. Near term future sources of hydrogen are from nonrenewable resources, for example, coal gasification or thermochemical water splitting using a nuclear fission heat source. Further in the future, hydrogen may be produced

from the inexhaustible resource, water, using primary energy sources such as solar energy or a nuclear fusion reactor as the heat source for the water splitting.

2.3. Present Hydrogen Usage and Demands

The primary use of hydrogen today is as a chemical intermediate in the chemical and petroleum industries. The users of hydrogen and the approximate percent of the total United States market is given in Table I. The total hydrogen demand in 1974 was approximately $7.4 \times 10^{10} \text{ m}^3$ ($2.6 \times 10^{12} \text{ SCF}$). Details of the production processes and the demand for hydrogen can be found in References 3-5.

Most of the hydrogen is produced and consumed on site and is called "captive" hydrogen. "Merchant" hydrogen is gas produced by independent suppliers and shipped to users. Only about 7 percent of the total United States hydrogen demand is filled by merchant hydrogen.

Hydrogen is generally used as a relatively pure gas, however, in many processes mixtures of hydrogen with impurities (CO, etc.) are used. The environmental conditions under which the hydrogen is used vary. Pressures up to 12 000 psi and temperatures to 300°C are not uncommon. Hydrogen use as a fuel is presently limited. The U.S. space program uses hydrogen as a rocket fuel. Liquid hydrogen along with liquid oxygen provides the highest performance of any of the practical propellants considered to date. A few demonstration projects exist to test the use of hydrogen in transportation, i.e., auto and bus. These projects use hydrogen stored either as a metal hydride or as a cryogenic liquid.

TABLE 1
HYDROGEN USE IN THE UNITED STATES

Use	Approximate Percentage
Ammonia synthesis	41
Oil refining	41
Methanol synthesis	10
Miscellaneous chemical process	5
Electronic industry	2
Production of metal ores	1
Rocket propellant	1
Hydrogenation of fuels and oils	0.5
Electric generator cooling	-

Historically, hydrogen has been used as a fuel for lighting or heating. Impure hydrogen gas known as fuel gas, producer gas, town gas, or water gas was common in the United States before the large scale introduction of natural gas, and is still used in other parts of the world.

It is important to note that hydrogen in the past has been handled safely relative to other fuels. Except for the Hindenburg accident, which killed 37, no major incident involving hydrogen has occurred. A study by Zalosh,⁶ comparing the hazards of hydrogen to those of natural gas by investigating accident insurance claim records, has shown no significant difference in the hazards of hydrogen and natural gas.

2.4. Anticipated Future Hydrogen Demand

Several possible scenarios can be used to predict the increase in demand for hydrogen. These are described in References 3 and 5 and include either new uses for hydrogen as a fuel (described later in this section) or merely the expected increase in demand from present day users. By the year 2000, the latter scenario predicts an increase in hydrogen use of approximately 4 or 5 times that of today and the former an increase of 23 times over that used today. It is clear from this statement that with just the expected increase in demand from today's uses a program assessing the environmental and safety problems associated with hydrogen is justified.

The following gives a brief overview of possible future uses of hydrogen as a fuel. More comprehensive descriptions of these applications are given in Reference 1 and other references cited in the text.

Utility Applications

- a. Energy storage for electrical peaking power generation. Hydrogen can supply the energy storage media for load leveling for the electric utilities. Hydrogen can be stored as either a gas, metal hydride or liquid for this application.
- b. Energy transmission. Hydrogen can be used as a replacement for natural gas as an easily transportable gaseous fuel. Gregory⁷ has done an in-depth study on hydrogen as an energy carrier from both economic and technical bases. These studies indicate hydrogen is an attractive alternate to natural gas. Hydrogen can also be used to supplement existing natural gas supplies.⁸
- c. Fuel cells. Hydrogen-oxygen fuel cells are a practical method of electrical generation from hydrogen.

- d. Hydrogen-fueled gas turbines.
- e. Hydrogen-oxygen MHD Generation.
- f. Hydrogen/oxygen-water turbine system.

The last three systems are described in detail in Reference 3.

Gaseous or Liquid Fuel

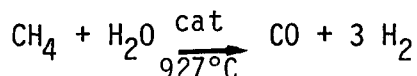
- a. Process Heat. A large portion of the energy consumption in the United States is for production of industrial process heat. This could be supplied by low BTU, impure hydrogen fuel gas.
- b. Residential and commercial. Technologically, hydrogen can be implemented for residential heat use in any capacity. Hydrogen can be used in conventional heat pumps and suggestions have been made to use hydrogen in hydride systems as the working fluid in a heat pump.
- c. Vehicular transportation. Many studies of hydrogen fueled vehicles have been performed and several demonstration projects have shown that both cryogenic and metal hydride hydrogen fueled vehicles are technologically feasible. Reference 9 gives discussions of hydrogen fueled autos, Ref. 10 gives a discussion of hydrogen fueled trucks, Ref. 11 gives a discussion of a hydrogen fueled train and Refs. 12 and 13 give proposals for liquid hydrogen fueled aircraft.

2.5. Hydrogen Production

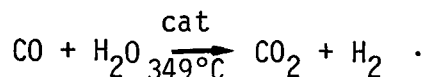
The most critical issue to be addressed for the implementation of future larger scale hydrogen usage is that of the source of hydrogen. Without an economical hydrogen source (with respect to other energy options), hydrogen cannot be considered as practical. In this section we give a brief review of past, current and future hydrogen production methods. We do not intend to evaluate the relative merit of the production options. The details of the various processes are given in References 3 and 14.

All current and past hydrogen production is either directly or indirectly based on fossil fuels. The most common historical method was by the water gas reaction in which steam was passed over hot carbon to form hydrogen and carbon monoxide. This gas was then used as natural gas is used today. Many of these plants existed in the United States; however, now all are decommissioned. Some foreign countries still use hydrogen produced in this manner.

The most common method for current hydrogen production is by the catalytic steam reforming of natural gas. The reactions are



and



This process is endothermic so energy must be supplied by burning of additional fuel, not necessarily natural gas.

In refineries, most hydrogen is produced by the catalytic reforming of naphtha or some other light hydrocarbon derived from oil. This method is usually used only when low-cost natural gas is not available.

Hydrogen can also be produced by the partial oxidation of heavy oils. Residual oil is subjected to partial combustion in the presence of steam. The energy needed to drive this process is about 40% greater than that necessary for the light hydrocarbon feedstock.

One method which is promising for future hydrogen production and is currently being used in Europe and South Africa is that of partial oxidation of coal or coal gasification. Coal, steam and oxygen react in the basic gasifier processes to produce hydrogen. The energy requirements for this process are substantially higher than for the partial oxidation of residual oil and reflect, in part, the low heating value of coal relative to petroleum feedstocks. Researchers in the United States are currently working on new processes with higher efficiencies than those currently available. Two modifications of this process which have also been suggested are nuclear-assisted coal gasification and in situ coal gasification. In the first method a nuclear reactor is used as the heat source for the gasifier. It appears that this may be a very expensive method because of the high cost of the nuclear reactor.

An important question regarding coal gasification has to do with the economics of production of hydrogen relative to methane. The USDOE is currently funding work to determine, if possible, which method is more economical. Another possible problem has to do with the environmental effects of the production of hydrogen versus those of methane. Also, many technical questions regarding the individual process need to be evaluated.

A small percentage of hydrogen is currently produced by electrolysis of water. Most electrolyzers are used to produce hydrogen for laboratories, food processors, semiconductor manufacturers and similar users for whom the cost of

hydrogen has a minor impact on the cost of the product. The USDOE is currently funding research into advanced electrolyzer systems. These could be tied to a fission or fusion reactor, to a solar system producing electricity or to a hydroelectric plant to make hydrogen.

Thermochemical dissociation of water produces hydrogen by breaking up the water molecule through a series of chemical reactions between water and other chemicals, such as bismuth sulfate or bromine. This method promises an increased efficiency over that of first generating electricity and then running an electrolyzer to produce hydrogen. The temperatures required to obtain the desired chemical reactions are moderate enough to make solar energy an attractive primary power source. Chemicals such as bismuth sulfate and bromine are recovered and reused so that the process requires only a constant supply of water and heat.

Other methods suggested for production of hydrogen are described in Ref. 3 and include: photovoltaic-electrolysis, heterogeneous photo-assisted oxidation-reduction reactions, homogeneous photo-assisted oxidation-reduction reactions, photosynthesis of hydrogen, and anaerobic fermentations.

2.6. Hydrogen Transmission and Distribution

Most hydrogen is produced very close to its point of consumption and not shipped great distances (captive hydrogen). Merchant hydrogen which is produced and consumed at different sites accounts for only 7% of the hydrogen market in the United States. Because these systems have an excellent safety record, no major problems would appear to inhibit the scaling up of the present distribution system and adding new components such as high pressure hydrogen gas lines.

2.7. Hydrogen Transportation Methods¹⁵

Numerous scenarios have been written for the transportation and distribution of hydrogen in an expanded hydrogen technology system. Each of these plans has its own ground rules, some of them quite restricted in application. For example, the Institute of Gas Technology (IGT) has published the results of several studies primarily concerned with the replacement of natural gas with hydrogen as a fuel.^{7,16} Another study by the National Bureau of Standards proposes eight scenarios that are restricted to the transportation of LH_2 for use as an energy source.¹⁷ The costs are compared to those of transmitting equivalent amounts of electrical energy.

As pointed out in a previous section, the bulk of merchant hydrogen consumption is in the form of an intermediary in the chemicals industry. The growth patterns of these processes indicate that this use will continue to dominate the hydrogen market over the next decade or two. In any set of comprehensive hydrogen delivery scenarios, particular attention should be paid to both the state in which hydrogen is shipped and that in which the user desires it. The possible applications of each of these techniques will be discussed, and an assessment of their relative importance made to assign priorities for equipment and regulation safety studies. The different shipping methods will be discussed in the order of increasing importance.

Shipment as Hydrides. The transportation and storage of hydrogen in metallic hydrides, particularly for storage with controlled release, has many advocates. With some hydride systems one can obtain hydrogen packing densities greater than those of LH_2 . However, as a means for transporting large quantities of hydrogen, hydride systems must be regarded as being in an early stage of development, although much hydride research is in progress at several laboratories. At best, these hydride systems can contain only a few percent by weight of hydrogen; thus, the payload/total weight ratio is unattractive for commercial shipping. In addition, those systems that potentially have the best ratios require the expenditure of considerable energy to effect the hydrogen release. One of the few presently demonstrable chemical systems, iron-titanium hydride, provides only about 1.25% by weight of useful hydrogen. This percentage is further lessened by the weight of containers, heat exchanger, etc.

Shipment as Gas in High-Pressure Tube-Trailers and Cylinders. This method is already well developed, but is applicable only to a small fraction of the total hydrogen market, namely the small-lot user. It suffers from the same low payload deficiency as metal hydride systems and is bulky. Its major application is the delivery of GH_2 from centralized distributors to small volume users.

Transportation of Liquid Hydrogen by Pipeline. For the movement of large quantities of hydrogen over intermediate distances (about 100 km), transportation of LH_2 by pipeline is feasible but the initial large capital investment required is the main deterrent to use of this method in the immediate future. A major cost item would be the vacuum-jacketed pipeline needed

to maintain liquid conditions. However, localized energy demands, availability of nonfossil source hydrogen, and environmental restrictions on above-ground power corridors may well make this method competitive in the future if the end-use requirement is for liquid product.

A modification of this method, which might prove attractive in specific situations, is to transport both hydrogen and electrical power. The electrical energy would be transmitted by an enclosed liquid hydrogen-cooled cryo-resistive or superconductive electrical transmission line. In this case the hydrogen refrigerant would not be returned to the original liquefier but used at the consumer's end. One application would be to generate additional electricity by means of conventional steam plants, gas turbines, or by fuel cells. Such supplementary electricity could be generated as high-value peaking power since the hydrogen could be readily stored in the liquid form.

Transportation by High-Pressure Gas Line. The US has a vast network of natural gas transmission and distribution lines, portions of which might be converted to use for hydrogen transportation. Because of the difference in physical properties of methane and hydrogen, significant modifications in parameters, such as line compressor station spacings, compressor and driver sizes, compression ratios, and the source of driver energy, would be necessary to use these lines for hydrogen gas.

The most common objections to such conversions are fears that materials in existing lines may not be adequate for hydrogen service, or that the known leakage of existing lines might be unacceptable for such use. Existing gas transmission lines differ considerably in these characteristics because of their varying materials, construction methods, and length of service. Thus each proposed conversion would have to be studied as an individual case. Note that although hydrogen can leak through a given-sized orifice at three times the volume rate of methane, the energy content of hydrogen per unit volume is only about one-third that of methane. Consequently, the energy lost from leakage would be about equal in the two cases for a given piping system and operating pressure. From a safety standpoint, the lost hydrogen would diffuse away from the leak area about three times as rapidly as would methane. This would appear to be a safety advantage except in enclosed areas. Experimental investigations should be performed to confirm and quantify this supposition.

Considerable experience exists for hydrogen transportation in conventionally built pipelines. As late as 1945, approximately 115 000 km (72 000

miles) of pipeline in the US were dedicated to the transportation of producer or town gas containing up to 50% hydrogen. During the past three decades, these lines have been converted to natural gas transportation, and now only a few hundred kilometers of pipeline are in use for hydrogen-bearing fuel gases. Additional information can be obtained on recent producer gas experience from European and Japanese fuel systems.

From a marketing standpoint, transporting hydrogen by high-pressure pipeline is by far the least expensive of all the methods studied. It is currently the method of choice for moving essentially all captive hydrogen over short distances. However, for longer hydrogen pipelines, transmission costs are estimated to be two to three times the cost (dollars/10⁶Btu·mile) of similarly transported natural gas. This is primarily because of the lower energy per unit volume for hydrogen and the higher fuel cost for compressor stations.

In both the US and Germany, hydrogen pipelines providing merchant hydrogen to users are in operation. Air Products and Chemicals, Inc., operates such a line in the Houston area that services about a dozen customers with hydrogen at two purity levels. Chemische Werke Huls has operated a hydrogen pipeline in the Ruhr Valley since the early 1940's.

Transportation of Liquid Hydrogen by Various Carriers. Hydrogen can be shipped as a bulk liquid in vacuum-insulated containers installed on trucks, trains, barges, or sea-going tankers (in order of their decreasing costs per unit volume of payload). Although the latter two methods are most cost effective, their use is limited by the scarcity of useful origin-destination combinations. Liquid hydrogen barges have been used in the space program, but no hydrogen tankers have been constructed. Truck and rail shipment of hydrogen are well-developed technologies and at present constitute the primary methods for transporting merchant liquid hydrogen. Because of their present widespread use, highway and rail delivery techniques will probably expand to meet increased hydrogen use in the next decades.

Note that all methods involving the transportation of LH₂ exact an economic penalty when the user has no need for hydrogen in the liquid form except as a storage convenience. Ideally, the costs of cooling and liquefaction are equivalent to approximately 10% of the available combustion energy of the hydrogen. However, because of practical thermodynamic limitations and

mechanical inefficiencies, in practice the actual liquefaction energy is about 25-30% of the hydrogen heating value.

When appropriately situated, many hydrogen users could recover a sizable fraction of this energy through a system of pumps and heat exchangers. The available cooling potential could be used for such purposes as the quick freezing of foods, the desalination of brackish water or sea water, and the air conditioning of nearby industrial park units.

Delivery system safety studies of an expanding merchant hydrogen market through the end of the century should emphasize methods involving LH_2 highway tractor-trailers and rail tank cars, and high-pressure GH_2 pipelines. Other transportation methods such as LH_2 barges will be used, but these will likely be dedicated to specific producer-user combinations and constitute only a small portion of the total market.

The most probable hydrogen transmission methods have been examined in detail.² Distribution systems for hydrogen have been investigated at the IGT.¹⁶ There appear to be no major technological problems for the implementation of a hydrogen distribution system with current technology.

2.8. Hydrogen Storage

Storage of hydrogen will be an important consideration in hydrogen energy systems. Storage will be necessary in distribution systems to provide an inventory to buffer variations in supply and demand and may also be useful in peakshaving systems. Hydrogen can be stored in the gaseous, liquid, or hydride form. Each of these storage methods has its own advantages and disadvantages and no system satisfies all requirements.

Gaseous hydrogen can be stored at high pressures in tanks, however because of the weight of the tanks it appears this will be impractical for mobile applications for all except the smallest uses. Studies are underway to investigate the feasibility of storage at 15 000 to 20 000 psi. Gaseous hydrogen can be stored underground in either natural or manmade caverns, depleted natural gas fields, or in suitable aquifers. The USDOE is currently funding programs to study these storage methods.

Hydrogen can be liquefied at 20.4 K and stored as a cryogenic liquid. This reduces the volume necessary for storage but energy is required to effect the liquefaction. Also more expensive storage containers are required to keep the hydrogen in its liquid state for extended periods of time. Storage of

hydrogen in either metal or chemical compounds with hydrogen density greater than that of hydrogen in the liquid state is also possible. Hydride systems look promising from a safety and convenience standpoint; however, drawbacks exist because of the extremely heavy weights (less than 5% of the weight is hydrogen), long recharging times, heat transfer requirements, and contamination from impurities in hydrogen.

2.9. Anticipated Safety and Environmental Control Problem Areas

A number of unresolved safety and environmental control problems have been identified in the course of conducting a review and assessment of environmental and safety problems in hydrogen energy systems.² These have been categorized in the following areas:

- Production
- Storage
- Transport
- Transmission
- End Use
 - Vehicle Applications
 - Space Heating
 - Chemical Feedstock
- Hydrogen Embrittlement
- Regulations and Standards
- Safety
- Miscellaneous

Many of these areas have been adequately treated in the assessment program conducted by LASL. However, a small but finite continuing effort is necessary on a periodic basis to follow new developments. In some cases the necessity for additional assessments are recommended, either as a continuation of present programs or as new programs. The problems in each of these categories are summarized in Sec. 3.3 and described in detail in Sec. 5.0.

3. PROGRAM OVERVIEW

This section contains a general description of a suggested Hydrogen Safety and Environmental Control Assessment Program, its structure, its elements and tasks, and its expected output. The program presented herein was prepared as a result of current and anticipated future needs for information

about safety, environmental aspects, and design considerations of hydrogen energy systems.

3.1. Objective

The objective of this program is to gather, analyze, and disseminate technical information on hydrogen safety and environmental control in a timely manner. With this information, safety and environmental control decisions relating to hydrogen operations can be made on a firm technical foundation by industry, regulatory agencies and the general public.

This program will not provide all of the technical answers in regard to hydrogen systems; however, the information developed will be useful in making decisions regarding future hydrogen facilities, for devising control techniques for hazards arising in new uses of hydrogen, and for upgrading existing facilities as necessary. Thus, the program will provide data for present as well as future hydrogen systems and usage.

3.2. Importance of the Program

An understanding of the fundamental processes that can lead to a mishap or an unwanted occurrence is necessary in the pursuit of any technology, especially if this is to be accomplished on a very large scale in a safe manner.

Under the supervision of specialists, significant quantities of hydrogen have been produced, transported, handled, and used with an excellent safety record. The continuation of this excellent safety record, and protection of the earth's environment, depends upon a sustained effort to understand and to improve such understanding by research into still unsolved problems, to develop methods appropriate for broad public use in formulating and answering questions, and to resolve doubts that may impede timely exploitation of a new energy system. This will become increasingly important to hydrogen as its usage and exposure to the general public increases.

The projected future demand for hydrogen strongly supports the need for an integrated hydrogen safety and environmental control program of the type presented here. A coordinated approach will achieve the maximum meaningful results with the limited available resources of funds, facilities, and qualified personnel.

Although the hydrogen safety record is good, the need for this program arises from the projected change in industry size and characteristics coupled

with incomplete data for extrapolating to these operations. These are indirectly related to public confidence and the potential high cost of mistakes.

The comprehensive, integrated hydrogen safety and environmental control assessment program presently envisaged and described herein includes:

(1) a continued in-depth assessment of the safety and environmental control aspects of hydrogen operations (e.g. production facilities, distribution facilities, end uses) to identify areas where current understanding is inadequate; and

(2) performing specific technical assessments to provide the necessary understanding and to identify promising improved control techniques.

3.3. Approach

The objective of the program will be achieved through the assessments described in nine major Program Elements:

- Production (Section 5.1)
- Storage (Section 5.2)
- Transport (Section 5.3)
- Transmission (Section 5.4)
- End Use (Section 5.5)
 - Vehicle Applications (Section 5.5.1)
 - Space Heating (Section 5.5.2)
- Hydrogen Embrittlement (Section 5.6)
- Regulations & Standards (Section 5.7)
- Safety (Section 5.8)
- Miscellaneous (Section 5.9)

These Program Elements, or categories, are selected as a result of the assessment described in Ref. 2.

The assessments identified in these nine Program Elements should be subjected to a continuing evaluation and correlation effort to insure that individual efforts are integrated to achieve the program objectives. The program direction can be altered if necessary based on technical and fiscal considerations as well as a periodic evaluation of the program status and the needs of the program. This periodic program evaluation should involve input from industry, academia, regulatory agencies, public interest groups, and interested, concerned individuals as well as internal reviews.

A brief summary of each of these nine Program Elements follows.

3.3.1. Production. The safety and environmental impacts of future hydrogen production methods (especially thermochemical and coal gasification) must be determined. Assessments of emissions from promising thermochemical cycles for hydrogen production by water splitting were begun in FY 1979 but will need to be continued as these cycles evolve and new cycles are proposed.

The purpose of this element is to provide an assessment of potential safety problems and an early evaluation of the quantities, concentrations, and effects of potential pollutants in effluent streams and the possible disposition of any pollutants that must be removed from these streams.

Some industrial processes yield by-product hydrogen that in the past has not been economically recoverable. Estimates have placed quantities as equivalent to thousands of megawatts of power now being wasted. The safety and environmental aspects of this wasteful venting should be assessed. Under present conditions the economic value of collecting and using this hydrogen as an energy source should not continue to be ignored and an assessment is needed.

A brief report on environmental control considerations in the production of hydrogen is included in Appendix A.

3.3.2. Storage. The safety and environmental control aspects of possible hydrogen storage systems (including metal and chemical hydrides, underground chambers, compressed gas, and cryogenic liquid) will need further assessment. This topic has been partially treated in the assessment program conducted by LASL. As more knowledge and experience are gained, or as new systems are proposed, these will need consideration. A brief assessment of liquid, gaseous and hydride storage of hydrogen is given in Appendix B.

3.3.3. Transport. The safety and environmental aspects of the transportation of hydrogen have already been assessed.² As new developments occur, or as more accident data become available, this assessment can be updated. Liquid hydrogen spill tests and the dispersion of hydrogen into the atmosphere are also discussed in Appendix C.

3.3.4. Transmission. Hydrogen may be transmitted as a compressed gas or as a liquid via pipelines. The transmission of LH_2 by pipeline has not been attempted except for distances less than about a thousand meters on private or government controlled property and no further assessment of this topic is seen necessary at this time. The safety of the transmission of hydrogen gas is being assessed.² However, as proposals such as the addition of hydrogen to natural gas are implemented, an update of the assessment will be

necessary as experience is gained. Discussion concerning transmission of gaseous hydrogen/natural gas mixtures is included in Appendix D.

3.3.5. End Use.

3.3.5.1. Vehicle Applications. Contrary to popular belief, engines (including aircraft jet engines and conventional internal combustion engines) operating on hydrogen fuel are not pollution-free. Nitrogen oxides (NO_x) are generated and about twice as much water, not ordinarily considered a pollutant, is formed per mile than is the case for hydrocarbon fueled engines (for an equivalent energy expenditure).

The assessment program conducted by LASL included a small study of nitrogen oxide emission control by means of catalytic reduction methods. A brief report on this study is included in Appendix E.1. However, more study is needed. Also, as hydrogen fueled vehicle projects are continued (such as those at LASL, the University of Miami, Billings Energy Associates, and Riverside, CA) a safety assessment should be made.

Hydrogen fueled aircraft will generate about twice as much water vapor emissions as do conventionally fueled aircraft. If these emissions occur in the upper atmosphere they will persist for relatively long times. The extent and effects of water vapor, and water vapor in conjunction with NO_x , deposited in the upper atmosphere by high-flying aircraft have been considered,¹⁸ and some work is reported in Appendix E.2. However work on this subject is continuing and future results will also need to be assessed.

3.3.5.2. Space Heating. The combustion of fuels in unvented home appliances and industrial equipment, such as stoves, water heaters, and furnaces, can produce undesirable concentrations of nitrogen oxides, especially in today's homes which are made tighter for energy conservation. The emissions from open flames and catalytic heaters in home appliances and industrial equipment running on hydrogen fuel will be assessed in this element. Likewise, methods for reducing, neutralizing, or eliminating undesirable emissions will be determined.

Safety problems and corresponding solutions for the use of hydrogen as a fuel for home appliances and industrial equipment must also be determined.

3.3.6. Hydrogen Embrittlement. A primary concern is whether materials used in hydrogen systems will be subject to embrittlement by hydrogen. This

problem has been assessed and has been found to be actively studied. The subject is extremely complicated because of the multiplicity of mechanisms proposed. However the work in progress (mostly DOE funded) is leading to the understanding of this problem and as results are obtained the assessment will need to be updated. The assessment as of the end of FY 1978 is included in the last annual report of the program.²

3.3.7. Regulations and Standards. Regulations and existing codes have been assessed.² However, since completion of this assessment, a new federal regulation has been proposed which would much more completely cover the transportation of LH_2 .¹⁹ This new proposal is discussed in Appendix F but, because modifications and final acceptance will take more time, an updated assessment must be made at a later date.

3.3.8. Safety. The assessment conducted by LASL considered safety in existing hydrogen transport^{1,2}. However safety requires a continuing effort, especially where new uses are being proposed or public exposure is increasing. The assessment conducted by LASL detected areas where additional safety data is required. These experimental data must be obtained and when it is available an updating of the assessment will be necessary.

3.3.9. Miscellaneous. Several areas of concern that are not covered in the preceding elements will be assessed in this element. Some of these problems already exist while others are related to the larger quantity of hydrogen that will be produced in the future. These concerns include problems arising from the use of hydrogen under unusual conditions, instrumentation, and the possible uses of oxygen and deuterium by-products.

4. PROGRAM IMPLEMENTATION AND MANAGEMENT

The Hydrogen Safety and Environmental Control Assessment Program described herein will involve numerous individuals and organizations representing many disciplines and interests such as model developers, experimenters, government agencies, DOE contractors, government laboratories, universities, private R&D organizations, and companies within the hydrogen industry. Consequently, it is essential that these various sources be integrated and coordinated properly in the implementation and management of this program.

Program management activities, along with a summary of funding are described in this section.

4.1. Planning

The initial planning for this program has resulted in this report being prepared. After obtaining comments, suggestions, and recommendations from all interested parties, a more detailed program plan should be developed.

4.2. Implementation

The USDOE, Environmental Control Technology Division will be responsible for development and implementation of the plan.

4.3. Control

Program management and control will be under the direction of the USDOE, Environmental Control Technology Division. The program management will involve a continuous review of all work to ensure that it is of a high technical quality, that it remains relevant to the program goal, and that it is consistent with other program activities.

A continuous coordination and evaluation effort will enable the program to be redirected as required to achieve effectively and efficiently the program objectives by using information that is generated in the various projects to update the work statement of each project and to redirect the technical efforts as required. This effort to coordinate and evaluate continuously the projects individually, and the program as a whole, will be accomplished by the DOE with inputs from other regulatory agencies, R&D organizations, universities, the hydrogen industry, and the public.

4.4. Crucial Items

Several items are crucial, because of high cost or long lead times, and require early, continuous attention. The assessment of safety of some proposed uses of hydrogen requires theoretical analysis backed up by large scale tests. This is especially true in considering the atmospheric dispersion of large leaks or spills. The minimum time to complete the program may be limited by the time required to locate and select a test site, prepare the site, and conduct these large leak and spill tests. It is expected that the large-scale tests will be the most expensive item in the program.

4.5. Funding

As presently envisaged this program is estimated to cost one million dollars for a four year effort (an average of \$250,000 annually). Many of the

elements can be proportionally continued as long as new developments are recurring. This cost estimate should be revised as the program direction and costs are reevaluated periodically. The cost breakdown by element is summarized in Table 2.

Several major considerations will be involved in the development of the program schedule:

- (1) The leak and spill tests that are an important aspect of the program are time-limited in that there is a minimum time involved in each of the many steps involved, and there is a sequencing between steps to permit preparation for, and conduct of, the tests. Funding for these tests (not included in this program) must be such that they will be limited only by the time required to accomplish the tests (including planning and preparation).
- (2) Instrumentation, especially that for the large-scale tests could become a limitation. Consequently, early attention to the required instrumentation in each of these elements is essential.

TABLE 2
Estimated Program Cost by Program Element

<u>Element</u>	<u>Annual Cost (thousands)*</u>
Production	\$ 20
Storage	20
Transport	25
Transmission	10
End Use	25
Vehicle Applications	
Space Heating	
Chemical Feedstock	
Hydrogen Embrittlement	15
Regulations and Standards	15
Safety	100
Miscellaneous	20
Total	<u>\$250</u>

* 1979 dollars

- (3) Information from many of the program elements (especially information on hydrogen dispersion, deflagration and detonation) will be required early in the program as input to large leak and spill tests. The remaining information to be developed from these elements may be deferred until the latter part of the program thus reducing the peak funding and manpower requirements.

The development of a schedule for the program will require consideration of the resource limitations relevant to the program such as funding, qualified personnel, and information limitations. Some trade-offs are usually possible with these limitations. The program schedule must have a balance between the resources and limitations, yet bring the program to a close as efficiently and effectively as possible. The program can be accomplished now in a timely and orderly manner. If it were delayed for too long the necessity for crash programs would probably cause loss of public confidence, inefficiencies, make-shift fixes, and incomplete investigations.

4.6. Program Status

This document has been prepared as a result of a just completed program, "Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy Systems" funded by the USDOE, Environmental Control Technology Division, and conducted by the Los Alamos Scientific Laboratory of the University of California.^{1,2} This program, originated in mid FY77, was intended to assess the safety of the shipment of hydrogen, but subsequently it was expanded into an assessment of the safety and environmental control aspects of the production, storage, shipment, and end-use of hydrogen. Program elements of the proposed program are areas that have been identified as needing additional study in the "Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy Systems."²

The following tasks have just been completed in the "Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy Systems" and reports on these tasks are included in the appendices.

- (1) studying the nitrogen oxides emissions from internal combustion engines and the process of removal of these oxides by catalytic reduction.
- (2) performing an environmental analysis of the five leading candidate thermochemical cycles for hydrogen production.

- (3) analysis and computer modeling of the dispersion of a hydrogen cloud after a gas leak or a large liquid spill.
- (4) participating with NASA in planning of liquid hydrogen spill tests to be performed to obtain dispersion data.
- (5) reviewing and assessing gaseous hydrogen shipment by pipeline, including a review of accidents in the transmission of natural gas for comparison with hydrogen service.
- (6) studying the effect on explosive characteristics of the addition of hydrogen to methane.
- (7) assessing the existing work on the environmental impact of emissions of water and NO_x from high-flying, hydrogen-fueled aircraft.

The assessment program conducted by LASL has already assessed hydrogen embrittlement, the bulk transport of liquid hydrogen and the existing rules and regulations controlling this form of hydrogen shipment.²

In addition to the just completed "Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy Systems" there are numerous studies in progress in hydrogen embrittlement, atmospheric dispersion of spills, safety, etc. that are directly related to the Hydrogen Safety and Environmental Control Assessment Program described above. The initial task in each element of this program is to update the evaluation of the applicable work that has been done or that is in progress for each element to avoid repeating or duplicating effort.

4.7. Feedback and Updating

The information generated in this program will be made available or disseminated periodically through a variety of methods such as progress reports and technical publications to permit evaluation and utilization as early and as widely as possible.

Based on technical and fiscal considerations the technical plan will be periodically reviewed, evaluated, updated, and revised as necessary to guide the work and to achieve the most benefit from the program. Objectives may be changed and new elements or new tasks added as the program progresses. Many of the program elements are interrelated, making correlation and communication between those involved in the various parts critical.

5. ASSESSMENT PROGRAM

The actual quantity of hydrogen being used is increasing. It has been predicted that its usage will increase by a factor of four by the year 2000 without any new applications. However, new uses for hydrogen are constantly being proposed and, although none of these are implemented to a great degree at the present, an advisable course is to continue experimentation and demonstrations so that rapid implementation could be achieved if necessary. Under these conditions a continuous assessment (which might not require a large effort) is desirable. The assessment conducted by LASL identified specific areas worthy of continued assessment that are described in this section.

5.1. Production

5.1.1. Objective. The objective of the Production Element is to assess the safety and environmental impacts of hydrogen production methods, especially coal gasification and thermochemical methods using solar or nuclear heat sources.

5.1.2. Background. The claims made for the environmental acceptability of the use of hydrogen seldom consider more than the end-use of the hydrogen, ignoring the pollution potential of the extra prime energy necessary for the hydrogen production. Of the many methods for future production of hydrogen, the thermochemical and coal gasification methods appear to be the most likely to be used. An assessment of the environmental impact of promising thermochemical water splitting cycles for producing hydrogen was begun in FY79 (see Appendix A). The assessment of emissions from hydrogen production by coal gasification make it appear that these emissions are similar to those produced by the production of methane from coal. However, this cursory conclusion should be evaluated in more depth for specific processes and specific coals. In addition, both thermochemical and coal gasification methods for producing hydrogen need to be examined for potential safety problems.

During assessment conducted by LASL, it was found that by-product hydrogen is produced, vented, and flared in numerous locations. An assessment should be made of the quantity and distribution of this vented hydrogen with the economic value in mind as well as the safety and environmental effects of this venting.

5.1.3. Tasks. The objective of the Production element will be achieved through the following tasks.

- (1) Continue to evaluate promising thermochemical hydrogen production cycles for potential pollutants and safety problems.
- (2) Begin to evaluate possible pollutants and safety problems for specific processes and specific coals for hydrogen production by coal gasification. This should be coordinated with work on methane production by coal gasification.
- (3) Assess potential methods for reducing or eliminating possible pollutants or for removal of pollutants from effluent streams.
- (4) Assess possible disposition of any pollutants that are removed from effluent streams.
- (5) Examine other hydrogen production methods (such as electrolysis) based on solar or nuclear energy sources as in the above tasks to determine if they have potential environmental impacts or safety problems.
- (6) Assess the environmental, safety, and economic impact of venting of by-product hydrogen.

5.1.4. Cost. The cost for completion of the Production element is estimated to be \$20k per year.

5.2. Storage

5.2.1. Objective. The objective of the Storage element is to assess the safety and environmental control aspects of hydrogen storage systems.

5.2.2. Background. Hydrogen may be stored in several forms: (1) Compressed Gas, (2) Cryogenic Liquid, (3) Metallic Hydride, and (4) Chemical Compound. In addition, hydrogen may be stored in various containers; for example, compressed gaseous hydrogen may be stored at high pressure in metal cylinders or it could be stored at a lower pressure in underground chambers (depleted salt cavity or aquifer), or at an intermediate pressure in a metallic hydride. Further discussion may be found in Appendix B.

5.2.3. Tasks. The objective of the Storage element will be accomplished through the following tasks.

- (1) Compile applicable information and data on existing and proposed hydrogen storage methods and storage containers.
- (2) Compile applicable information and data on existing and probable locations where these storage methods and containers will be used.
- (3) Assess the possible or probable safety and environmental impacts of these storage methods and containers in the identified locations.

- (4) Determine methods to reduce or eliminate the identified safety and environmental impacts.

5.2.4. Cost. The cost for completion of the Storage element is estimated to be \$20k per year.

5.3. Transport

5.3.1. Objective. The objective of the Transport element is to assess likely safety problems associated with the various modes of bulk quantities of hydrogen transport from one location to another.

5.3.2. Background. Hydrogen transport from one location to another will be in the form of compressed gas, metallic hydride, and cryogenic liquid; however, a variety of means such as portable high pressure cylinders and mobile dewars will be involved. Thus a variety of potential safety problems exist.

At the present time the only methods of hydrogen transport in common use are those of compressed gas for small quantities (up to 135,000 SCF per load) and cryogenic liquid (up to 28,000 gal, equivalent to 3,000,000 SCF). The transport of compressed gas has not been assessed.

The safety of liquid hydrogen transport has been assessed.² This technology is well developed and has an excellent safety record. However as quantities increase and exposure to the public reaches higher level greater care may be necessary. A preliminary risk analysis has been made¹ and indicates that the risk associated with this method of transport is very low. However, the data base is too small for accurate prediction. A continued assessment would allow the data base to be expanded. Also there is insufficient knowledge of the consequences of spills and leaks; an experimental program to obtain this data is discussed in Sec. 6. NASA is doing some work in this area and a continued assessment of NASA results plus future accident experience in shipping liquid hydrogen is desirable.

5.3.3. Tasks. The objective of the Transport element will be accomplished through the following tasks.

- (1) Continue to identify and assess potential safety problems that arise as a result of the increased transport of hydrogen (see Appendix C).

- (2) Continue to compare hydrogen transport with transport of natural gas and LNG. Determine if, under the same circumstances, conceivable accidents involving natural gas or LNG would be more or less hazardous than those involving gaseous or liquid hydrogen instead.
- (3) Investigate hydrogen transport systems for failure, using failure modes and effects analysis or a fault tree analysis.
- (4) Assess future and ongoing experimental studies to confirm or validate the assessments and analyses made in these tasks.

5.3.4. Cost. The cost for completion of the Transport element is estimated to be \$25k per year.

5.4. Transmission

5.4.1. Objective. The objective of the Transmission element is to assess likely safety problems associated with the transmission of hydrogen from one location to another via pipelines.

5.4.2. Background. It appears that it is more economical to transmit gaseous hydrogen from a production source than to produce and transmit electricity. Hydrogen can be transmitted in existing natural gas transmission lines or in new lines optimized for hydrogen. The economics of these two modes have been studied and it appears that only in specific instances will existing natural gas lines be useful. This is because of the location of the existing lines and the fact that the existing lines will have to be derated for hydrogen service from the pressures allowed for natural gas. The derating of the maximum allowable pressure for hydrogen service is necessary because of the problems associated with hydrogen embrittlement. This is an extra restriction, because in most natural gas systems the maximum pressures are less than 1000 psi, whereas, systems optimized for hydrogen and delivering equivalent energy would operate at around 2000 psi.

Therefore, for hydrogen gas transmission, compressor pumping stations will be required, and we can expect local pressure and temperature transients and local vibrations and stress that can magnify the hydrogen embrittlement problem. Economical and readily available, high-strength, embrittlement resistant materials will need to be developed for compressor applications.

There appears to be no reason why hydrogen cannot be safely transported in existing or new transmission networks. Different safety systems for hydrogen will need to be installed. For example, better leak detection techniques

may be necessary at all pipeline joints. One method of protection of transmission pipelines could be by installing an electrical wire in the ground adjacent to the pipe. Thus, when the wire is broken, a signal would indicate potential break in the pipeline due to a "dig in" or other disturbance. Also, both theoretical and experimental studies on the dispersion of hydrogen after pipeline ruptures will need to be performed.

5.4.3. Tasks. The objective of the Transmission element will be accomplished through the following tasks.

- (1) Continue to review suggestions for hydrogen transmission systems and determine which are likely to be used in an expanded hydrogen system.
- (2) Identify potential safety problems that could occur as a result of the transmission of hydrogen as identified in Task (1). Compressor stations should be included as a part of a pipeline for this analysis.
- (3) Assess the potential hazards associated with the safety problems identified in Task (2). Preliminary work was begun in two areas (see Appendix D).
- (4) Investigate hydrogen transmission systems for failure, using failure modes and effects analysis or a fault tree analysis.
- (5) Assess the results of future experimental studies to confirm or validate the assessments and analyses made in these tasks.

5.4.4. Cost. The cost for completion of the Transmission element is estimated to be \$10k per year.

5.5. End Use of Hydrogen in Energy Systems

There have been numerous suggestions for the use of hydrogen in energy systems. Those most frequently suggested are included here. If other end uses become more common, they should also be included in future assessments.

5.5.1. Vehicle Applications. The safety and environmental assessment of the use of hydrogen in vehicular applications is divided into three parts: Internal Combustion Engine Emissions, High Altitude Aircraft Emissions, and Vehicular Fuel Safety Assessment.

5.5.1.1. Internal Combustion Engine Emissions.

5.5.1.1.1. Objective. The objectives of this portion of the element are (1) to assess catalytic processes for reducing or eliminating NO_x in

exhaust gases without producing ammonia; (2) to determine if there are operating conditions under which significant quantities of other pollutants such as ammonia and hydrogen peroxide are produced; and, (3) to assess methods for reducing or eliminating these pollutants.

5.5.1.1.2. Background. Emissions from hydrogen fueled internal combustion engines (both spark and compression ignition types) will include NO_x and possibly ammonia or hydrogen peroxide. Numerous studies and experiments, both past and present, have investigated these pollutants and means for reducing or eliminating the pollutants. Most studies concentrate on NO_x , with other possible pollutants receiving very little attention. Most of the past and current work involves engine design or adjustment of engine operating conditions to keep combustion temperatures low, thus preventing NO_x formation. Catalytic processes, using either naturally occurring or supplemental hydrogen as a reductant in the exhaust system, may also be used, but these processes have not been given much consideration as yet. An initial look at this possibility is being made by Prof. Robert Adt at the University of Miami under contract for the assessment program conducted by LASL.² (See Appendix E.1.)

5.5.1.1.3. Tasks. The objective of this portion of the element will be accomplished through the major task areas of Catalytic Processes and Other Pollutants.

However, the assessment will not be complete without the research work described in Section 6.4.

5.5.1.1.3.1. Catalytic Processes. Tasks related to this topic include:

- (1) Survey possible catalytic processes for reducing or eliminating NO_x in exhaust gases in the exhaust system without producing ammonia.
- (2) Compare and evaluate these processes.
- (3) Obtain needed data to determine which process is best and to determine the extent of the capability to reduce NO_x emissions using this method.

5.5.1.1.3.2. Other Pollutants. Tasks related to this topic include:

- (1) Characterize operating conditions for production of other possible pollutants such as ammonia and hydrogen peroxide.
- (2) Determine the concentration and quantity of these pollutants.

- (3) Determine the effects these pollutants would have on the environment.
- (4) Develop methods for elimination of these pollutants as necessary.

5.5.1.2. Emissions of Water at High Altitude.

5.5.1.2.1. Objective. The objective of this portion of the element is to determine the extent and effects of water vapor deposited in conjunction with NO_x in the upper atmosphere by high-flying hydrogen fueled aircraft.

5.5.1.2.2. Background. Hydrogen fueled aircraft will generate substantially more water emissions than do conventionally fueled aircraft (approximately double). These water emissions will persist relatively long times (up to 5 years) if they are deposited in the upper atmosphere by aircraft flying at high altitudes. The assessment program conducted by LASL followed work in progress at the Lawrence Livermore Laboratory as reported in Appendix E.2.

Past and current studies have led to a decrease in the concern for aircraft NO_x emissions being a threat to the ozone layer; however, these same studies have led to increased concern over the possible effects of aircraft water vapor emissions.¹⁸

The effects of water vapor emissions depend upon various feedback mechanisms, among which are possible induced alterations of stratospheric water content because of changes in tropopause temperatures. Evaluation of ozone changes and climate changes because of water emissions involves new modeling and data requirements in that sources, transports, sinks, and feedback effects of water vapor at all altitudes are not well understood; the feedback effects involve difficult multidimensional aspects normally associated with climate modeling. In an effort to address the uncertainties existing in modeling atmospheric transport, the FAA is undertaking a feasibility study of a global experiment in which an inert tracer will be injected into the atmosphere near the tropopause and its distribution observed over a sufficiently long interval.¹⁸

Effects of aircraft effluents are particularly dependent on the dynamics and chemistry of the atmosphere near the tropopause. Because tropopause height is strongly variable with latitude and season, and aircraft traffic is concentrated in midlatitudes, aircraft effects computations are best handled by models which include both latitudinal and longitudinal dimensions. This is

not presently the case, although the FAA has initiated efforts in this direction.¹⁸

A later study which included hydrogen fueled aircraft concluded, "The effect of stratospheric oxides of hydrogen (HO_x) emissions by a hypothetical fleet of 200 liquid hydrogen-fueled aircraft cruising at 20.6 km was found to be minimal with regard to both temperature and ozone (less than 0.25 percent increase in ozone and a maximum temperature perturbation of 0.7 K)."¹⁹ This study too, however, found an inability to draw conclusions and need for further study regarding effects of HO_x emissions near the tropopause.

Because hydrogen is a likely fuel for future aircraft, high altitude water emissions in conjunction with other emissions should be a part of current studies and be the subject of special studies to assess environmental effects as early as possible. Initial results in this area are encouraging and are discussed in detail in Appendix E.2.

5.5.1.2.3. Tasks. The objective of this portion of the element will be achieved through an assessment of the data and mathematical models required for this portion of the element.

5.5.1.3. Vehicular Fuel Safety Assessment.

5.5.1.3.1. Objective. The objective of this portion of the element is to assess the safety aspects of using hydrogen as a fuel in ground (including below ground), water, and air transportation systems.

5.5.1.3.2. Background. Hydrogen is an excellent fuel and it is compatible with nearly every type of engine or power conversion device. Consequently its use is likely to be widespread in diverse applications. The hydrogen storage methods that will be used will have an effect on safety as well as the location and manner in which hydrogen will be used as a fuel. The quantity of hydrogen that will be involved will vary from small amounts for small prime movers to large quantities for such applications as aircraft or ships. An assessment of the safety problems involved in these complicated possibilities would be prudent to minimize difficulties and avoid hazardous situations as much as possible.

5.5.1.3.3. Tasks. The objective of this portion of the element will be achieved through the following tasks.

- (1) Determine scope or extent of potential hydrogen usage as a fuel.

- (2) Assess the safety problems for these applications including effect of storage method and quantity of hydrogen that will be involved.
- (3) Assess the extent of the hazards involving accidents such as collision, airplane crash, ship sinking, vehicle overturning in a mine, etc.

5.5.2. Space Heating

5.5.2.1. Objective. The objective of this element will be to determine the emissions from open flames and catalytic heaters in unvented home and industrial equipment operating on hydrogen and to assess methods for reducing or eliminating these emissions.

5.5.2.2. Background. The combustion of hydrogen in unvented home appliances, such as stoves and water heaters, and industrial furnances, could produce undesirable concentrations of nitrogen oxides, especially in today's homes and buildings which are made tighter for energy conservation. A method may be needed for reducing such emissions without using a low-temperature catalytic oxidation to replace a high-temperature flame. Or if catalytic heaters are used, the emissions from these must be determined.

5.5.2.3. Tasks. The objective of this element will be achieved through the following tasks; however, the assessment will not be complete without the research work described in Section 6.3.

- (1) Determine emissions (especially NO_x) from open hydrogen flames in home appliances and industrial equipment.
- (2) Determine emissions from catalytic burners using hydrogen.
- (3) Determine effect of these emissions (from (1) and (2)) within an unvented space.
- (4) Determine data and mathematical models required for this element.

5.5.3. Cost. The cost for completion of the end-use element is estimated to be \$25k per year.

5.6. Hydrogen Embrittlement

5.6.1. Objective. The objective of this element is to maintain an assessment of research and development efforts in hydrogen embrittlement to permit economical, nonstrategic materials to be used safely in hydrogen systems.

5.6.2. Background. Substantial efforts have been expended in the search for an understanding of the hydrogen embrittlement phenomenon. Several

theories and models have been developed to describe some phase of the embrittlement process; however, none of these is widely accepted as completely and accurately describing the entire hydrogen embrittlement process by most of the experts in this field. An assessment of both completed work and projects in progress has been made recently;² however, this is an active field involving numerous projects and considerable effort. Consequently, a continuation of the assessment of this topic is advisable.

5.6.3. Tasks. The objective of this element will be achieved by periodic updates of the recently completed hydrogen embrittlement assessment including findings on new materials, experimental results, mathematical models, theories, welding techniques, codes and regulations, and effectiveness of coatings or liners to control or eliminate embrittlement.

5.6.4. Cost. The cost for continuation of this element is estimated to be \$10k annually.

5.7. Regulations and Standards

5.7.1. Objective. The objective of this element is to maintain an assessment of new regulations and standards that are put into effect and the development of the need for new regulations and standards.

5.7.2. Background. Existing regulations, standards, and codes have been assessed;² however, these are subject to change and new ones are being implemented. As a result, this assessment should be updated periodically to remain useful. For example, even as this document is being prepared, a proposed new regulation dealing with the transport of liquid hydrogen is being evaluated.²⁰ (Appendix F)

5.7.3. Tasks. The objective of this element will be achieved by periodic updates of the recently completed LASL assessment of regulations, standards, and codes dealing with hydrogen.

5.7.4. Cost. The cost for continuation of this element is estimated to be \$10k annually.

5.8. Safety

The objective of this element is to assess the safety aspects of the following events:

- a deliberate hydrogen release
- an unwanted or accidental hydrogen release from a leak or spill
- the dispersion of a hydrogen cloud
- the deflagration of a hydrogen cloud

- the possibility of the detonation of a hydrogen cloud
- the thermal radiation flux from hydrogen fireballs and flames.
- the flameless (nonchemical) reaction of spilled liquid hydrogen upon contact with water

The prevention of a hydrogen release (venting, leak, or spill) and the prevention or accomplishment of the ignition of a combustible mixture of hydrogen are two primary factors in hydrogen safety. However, hydrogen releases do occur and frequently ignite; therefore, an assessment of the safety aspects of these occurrences is needed. This has been accomplished partially in the assessment program conducted by LASL,² as well as others.

The Factory Mutual Research Corporation has made a comparative analysis of industrial hydrogen fire and explosion incidents from data collected mostly from insurance records.⁶ The preliminary results of this study indicate that for similar energy content the explosive damage resulting from hydrogen accidents is no larger than from natural gas accidents; however the frequency of accidents in hydrogen systems was found to be higher. Also, capital cost losses were found to be higher for hydrogen accidents, probably because of the more expensive equipment used in today's hydrogen systems.

A matter of concern is evaluation of the fire hazards or damage potential from hydrogen fires compared with those from natural gas fires. The percentage of thermal energy radiated from flame to surroundings for hydrogen and methane is similar. However, because the hydrogen radiates outside the visible (in the infrared) portion of the spectrum, the thermal energy hazard from the hydrogen fire will be less than from the equivalent natural gas fire because of absorption in the air by water vapor. The lack of a visible fire, however, can increase the hazard.

Another concern is that of shock ignition of hydrogen. Under certain geometrical conditions, a shock wave can form when hydrogen is vented. The temperature in the wave can exceed the auto-ignition temperature of hydrogen, causing it to ignite. Theoretical and experimental investigations should be carried out to determine the parameters of this reaction.

Potential structural damage from ignition of leakage into confined areas is more probable with hydrogen than with natural gas. It can be a serious problem in distribution systems where gas is used in buildings such as homes or factories. For a given leak size and gas pressure leakage into confined

spaces reaches the lower flammable limit four times faster for hydrogen than for natural gas, even though the lower flammable limits are approximately equal for these two gases.

The possibility of detonation in confined spaces is perhaps the greatest problem for hydrogen systems. Basically, the transition from a deflagration to detonation is more likely to occur in a hydrogen-air mixture than a natural gas-air mixture. The wider limits of detonability of hydrogen increase the probability of higher-order explosions with attendant high overpressures. The pressure ratios in such a situation can be as high as 120:1. Research is needed to determine the physical condition under which detonation occurs and to find ways to decrease the potential for damage (by use of blowout panels or damping mechanisms, for example).

The rapid burning velocity in hydrogen also makes hydrogen ignition more hazardous. The instantaneous pressure rise due to the ignition of a fuel-air mixture contained in a spherical vessel is proportional to the cube of the burning velocity. Experiments should also be performed to study the effects of hydrogen deflagration in confined spaces.

The topics listed in Section 5.8.1 of this element were identified as requiring further assessment. These topics will be addressed individually as a part of this element.

5.8.1. Hydrogen Release and Dispersion.

5.8.1.1. Objective. The objectives of this element component are (1) to assess the safety of hydrogen release systems, and (2) to assess the dispersion of hydrogen after release.

5.8.1.2. Background. A hydrogen release can occur as a result of intentional hydrogen venting or as the result of an accident causing a gaseous hydrogen leak or a liquid hydrogen spill. Ideally hydrogen should be recovered, not vented; however, the existence of facility recovery systems depends upon such factors as recovery system cost, hydrogen cost, and safety aspects of releasing hydrogen. Situations that could involve unwanted hydrogen releases to a vent or recovery system include (1) relief valve failure, and (2) unintentional overfilling of liquid storage tanks or overpressurization of gaseous storage systems. Routine operations such as liquid hydrogen transfer for storage tank refilling require hydrogen venting or recovery.

Hydrogen from a release will mix with air and if indoors will accumulate in the enclosure, or if outdoors will be dispersed as a result of its buoyancy, wind, or air turbulence.

Liquid hydrogen when spilled on land or water will spread until limited by complete vaporization or by some surface feature such as a dike. Rapid boiling and a high rate of vaporization will occur when liquid hydrogen contacts a surface. An important task in this element is the determination of liquid hydrogen vaporization rates as this is an important factor in determining vapor dispersion following vaporization.

Gaseous hydrogen, either from a leak or generated by liquid vaporization, gradually mixes with air forming a hydrogen cloud that can be carried away by the wind. The hydrogen cloud extending downwind from the leak or spill has a decreasing concentration of hydrogen in the air; and this hydrogen cloud constitutes a hazard. One simplified dispersion calculation indicated that flammable mixtures of hydrogen may extend for many miles downwind from a large liquid hydrogen spill. This estimate was questioned because of oversimplified assumptions. An independent calculation is given in Appendix C.5.

The major factors affecting hydrogen concentration and vapor cloud size are:

- (1) The quantity, rate, and mode of release
- (2) The type of surface on which liquid hydrogen is spilled
- (3) Meteorology (atmospheric stability).

Other factors that may have a significant effect on the dispersion of a hydrogen cloud include changes in elevation or terrain and the effects of structures such as storage tanks and dikes in generating turbulence. Also, liquid hydrogen vapors are initially very dense and tend to remain near the surface until warmed sufficiently. Until pure hydrogen has warmed approximately 2°C, it will exhibit a negative buoyancy, but dilution with air will prolong the period of negative buoyancy.

The hazard from the dispersion of a vapor cloud can be limited in several ways such as (1) by limiting the vapor generation rate, (2) storing the vapor initially produced until the generation rate is lower, (3) increasing the mixing and dispersion by the wind, (4) increasing the buoyancy of the hydrogen cloud and (5) igniting the cloud. Methods that may be used to accomplish this include (1) high dikes, (2) sloping dike floor and walls, (3) water

sprays, and (4) low density foams. In addition, the size and rate of an accidental release of hydrogen could be controlled by using release detection and interruption systems such as a fast-acting valve that activates automatically in the event of a line break.

Some liquid hydrogen spill tests were made in the 1950's;^{21,22} however, these depended on visual monitoring of the hydrogen cloud to determine dispersion and actual hydrogen concentration was measured at only a very few points.

Present and expected increases in the use of hydrogen make it appropriate to conduct additional, larger, and better instrumented tests to gain an understanding of the mechanism of dispersion.

5.8.1.3. Tasks. The objectives of this element component will be accomplished through the following tasks; however, the assessment will not be complete without the research work described in Section 6.1.

- (1) Assess consequences of venting hydrogen to determine the conditions under which hydrogen releases should be flared (ignited).
- (2) Assess the methods for describing and predicting hydrogen cloud dispersion.
- (3) Assess the methods for describing and predicting vapor generation from liquid hydrogen spills on land or water.
- (4) Assess the requirements for separation of hydrogen storage containers (gaseous and liquid) from one another and from inhabited buildings as a function of storage capacity.

5.8.2. Combustion.

5.8.2.1. Objective. The objective of the Combustion element component is to assess the state of understanding of the factors that influence the combustion of hydrogen to undergo a transition from deflagration to detonation.

5.8.2.2. Background. The cause of ignition of hydrogen leaks is largely unknown. Joule-Thomson heating upon expansion is, in general, not sufficient to cause ignition. However, shock waves in rapid expansion might be able to result in ignition and this possibility should be investigated.

One study of ignition sources⁶ listed the most frequent ignition sources responsible for reported hydrogen fires and explosions as (1) high temperature spontaneous ignition, (2) electrical sparks, and (3) electrostatic discharges. High temperature spontaneous ignition occurred in situations in which hydrogen at an elevated temperature and pressure was released to the

atmosphere or inadvertently mixed with an oxidant. If these high temperature spontaneous ignitions were accurately labeled, the released hydrogen would still be above the autoignition temperature after it had mixed with enough air/oxygen to be in the flammable range. The electrostatic discharge ignitions were associated with high velocity emergency releases of hydrogen, but the actual discharge ignition mechanisms were not understood.

What happens when a hydrogen cloud ignites? The answer to this question depends upon numerous parameters about which there is inadequate data and many unknowns. The effects of quantity, impurities, degree of confinement, geometry, and strength and distribution of ignition source or sources must be investigated. Flame front velocities as a function of these parameters must be determined so that tendencies toward detonation can be detected.

Another concern is whether a "fireball" can develop in a hydrogen cloud and if so under what conditions. A fireball is described as the nearly simultaneous combustion (deflagration) in all parts of a premixed hydrogen/air cloud having a potential for emitting thermal radiation at a high rate. This thermal radiation coupled with a large view factor could produce damaging heat fluxes at large distances. We have made a theoretical study of fireball radiation and the next step is to check it against experimental data.²

Under certain conditions, the burning of extensive amounts of unconfined, flammable gases results in flame velocities that increase until the deflagration becomes a detonation (explosion). The conditions for, and characteristics of, hydrogen/air or hydrogen-natural gas/air detonations and the transition from a deflagration to a detonation must be investigated to obtain an understanding of the phenomena involved.

Furthermore, the detonation of a flammable gas mixture in a confined space can, in some cases, produce rapidly oscillating pressures that can limit the rate of pressure release through relief devices such as blowout panels. The occurrence of these oscillations is a poorly understood function of gas properties. Further studies are needed to understand and make proper provisions for this possibility.

Heat will be transmitted from a hydrogen fire to neighboring objects by thermal radiation and convection. Both empirical and theoretical methods are used to predict the thermal radiation intensity on an object near a fire. These methods require a knowledge of:

- (1) The absorption of thermal radiation in the atmosphere between the flame and the object.
- (2) The temperature throughout the flame.
- (3) The amount of soot in the flame. (Soot will not be produced by burning hydrogen, but by burning of nearby materials.)
- (4) The gas composition, (in addition to a hydrogen/air mixture, a hydrogen and natural gas/air mixture is also of interest).

5.8.2.3. Tasks. The objectives of this element component will be achieved through the following tasks; however, the assessment will not be complete without the research work described in Section 6.2.

- (1) Assess ignition conditions such as ignition strength and geometry and methods for describing and predicting hydrogen cloud ignition.
- (2) Assess and evaluate conditions for which deliberate ignition of hydrogen releases is advisable.
- (3) Assess methods for describing and predicting hydrogen cloud ignition deflagration, fireballs, transition from deflagration to detonation, and fire and thermal radiation hazards.

5.8.3. Flameless Reactions.

5.8.3.1. Objective. The objective of this element component is to assess the safety aspects of flameless (nonchemical) reaction of spilled liquid hydrogen upon contact with water.

5.8.3.2. Background. Flameless (nonchemical) reaction of LNG on contact with water was first reported in 1970. The basic mechanisms involved in this process appear to be adequately understood. Tests have indicated that overpressures in the air and water near LNG/water reaction are low, sufficient to cause only minor damage such as breaking glass panes.

Although presently little, if any, liquid hydrogen is shipped by water, an accident could result in liquid hydrogen being spilled onto water. Also, scenarios of future energy systems include some that would involve the transport of liquid hydrogen by ship. Consequently, an assessment of the extent of liquid hydrogen/water reaction would be appropriate.

5.8.3.3. Tasks. The objective of this element component will be accomplished by an assessment of liquid hydrogen/water reaction to determine the extent of this possible hazard.

5.8.4. Cost. The cost for completion of this element is estimated to be \$100k annually.

5.9. Miscellaneous

Several areas of concern not covered elsewhere in this program are considered here. Some of these are related to the large quantity of hydrogen that might be produced in the future.

5.9.1. Instrumentation.

5.9.1.1. Objective. The objectives of the Instrumentation element is to assess the need for hydrogen detectors, flame detectors, and other instrumentation required for the elements of this program, and to assess the instrumentation needs for an expanded hydrogen usage.

5.9.1.2. Background. Many of the other elements in this program will have special instrumentation requirements. Those needs must be identified early in the program to permit their development as a part of this element.

The widespread use of hydrogen will require hydrogen detectors and hydrogen flame detectors that are inexpensive, rugged, simple, and reliable. These detectors must be such that operation, calibration, and maintenance can be done by a person with little training, yet without compromising the capability to detect hydrogen or a fire. Hydrogen detectors that can scan large areas and measure hydrogen concentrations at a distance are required (Sonic detectors have been suggested for this purpose). These instruments must be suitable for operation in a variety of locations such as vehicle parking areas and airport refueling terminals, and in a variety of environments (hot, cold, humid, dry, dirty etc.) that vary from day to day.

A pure hydrogen/air flame is invisible to the naked eye; consequently, a hydrogen flame detector is needed.

5.9.1.3. Tasks. The objective of the Instrumentation element will be accomplished through the following tasks.

- (1) Compile applicable information and data on existing hydrogen detectors, hydrogen flame detectors, and other instruments that might be needed for this program or in an expanded hydrogen system.
- (2) Assess what instruments will be required for this program and in an expanded hydrogen system.
- (3) Establish the capabilities, requirements, and specifications for the required instruments.

- (4) Evaluate the capabilities of existing instruments to meet the instrument needs established in Task (2) and whether they have the capabilities and requirements established in Task (3).
- (5) Assess the need for the required instruments to meet the needs of the suggested research program.

5.9.2. Oxygen By-Product.

5.9.2.1. Objective. The objective of this element is to assess the disposition of the oxygen co-produced when hydrogen is produced from water.

5.9.2.2. Background. Eight tons of oxygen are produced for each ton of hydrogen produced from water. The safety and environmental effects from the disposition of this oxygen is a concern. A beneficial use, without adverse environmental effects, appears possible and should be sought for this oxygen.

The oxygen by-product could probably be dispersed to the atmosphere without harm but this supposition should be verified. However, rather than waste this by-product, numerous possibilities for environmental benefits are easily recognized. Several large classes of environmental problems are caused or aggravated by an oxygen deficiency in water or nitrogen diluent in combustion air.

Among the fundamental aspects of water pollution are three parameters related to the oxygen balance: Biological Oxygen Demand, Chemical Oxygen Demand, and Dissolved Oxygen. Reduction or exhaustion of dissolved oxygen is one of the most harmful effects of many water pollutants - including many industrial chemicals, municipal sewage, agricultural runoff (fertilizers), and feedlot wastes. Oxygenation of these waters, either before or after they enter tributaries could be an effective, economical anti-pollution treatment.

As a result of using air in nearly all combustion processes, NO_x is the fifth largest air pollutant and fastest increasing in the US, now amounting to more than 20 million tons annually. The use of enriched oxygen in combustion processes rather than air would reduce this problem.

In addition, the large volume of nitrogen in the air causes an energy waste as it passes through the combustion process unnecessarily. This nitrogen also causes a significant increase in the expense of removing sulfur dioxide and other pollutants from the flue gases. Again, the use of oxygen in the combustion process would be beneficial both from the standpoints of reduced energy waste and of pollution control.

5.9.2.3. Tasks. The objective of this element will be achieved through an assessment of the benefits accrued from a beneficial use of by-product oxygen and the effect on the cost of the hydrogen produced.

5.9.3. Deuterium By-Product.

5.9.3.1. Objective. The objective of this element is to assess the safety and environmental control aspects of separating the naturally-occurring isotope deuterium from hydrogen produced from water if such a process is adopted.

5.9.3.2. Background. The production of large quantities of hydrogen from water could lead to cheaper separation of a substantial quantity of deuterium, a useful material in both nuclear fission and nuclear fusion power plants. The safety and environmental effects of the production and disposition of this hydrogen isotope must be assessed.

5.9.3.3. Tasks. The required tasks will be developed when appropriate.

5.9.4. Hydrogen Properties.

5.9.4.1. Objective. The objective of this element is to assess the necessity for extending hydrogen property knowledge. New uses being suggested include the extending of both temperature and pressure ranges which may include areas for which physical properties have not previously been determined.

5.9.4.2. Background. Hydrogen may become involved in situations that were not expected nor covered in the other elements of this program. For example, during the recent Three-Mile Island nuclear reactor incident, hydrogen was creating a problem in an unusual atmosphere for which data on hydrogen's behavior was unknown which, in turn, complicated the decisions that were required. In this case, more data were needed on hydrogen solubility under existing temperature and pressure and the combustion-suppression effectiveness of water vapor diluent.

5.9.4.3. Tasks. The objectives of this element will be accomplished through the following tasks.

(1) Assess proposed conditions for new hydrogen uses.

(2) Assess the availability of data needed for these conditions.

5.9.5. Cost. The cost for completion of this element is estimated to be \$20k annually.

6. RESEARCH WORK

During the assessment program conducted by LASL, several topics were revealed that require additional assessment and several were identified that require additional data to make the assessment complete. Those additional assessments that were considered desirable were described in Section 5. of this report, and the research needed to provide the additional data necessary for their completion (more than just an assessment) are discussed in this section.

The assessment conducted by LASL made it obvious that additional experimental work was needed to resolve unanswered safety and environmental problems and concerns. It was also recognized that much of this work would not be the sole responsibility of the Environmental Control Technology Division of the USDOE but also of other organizations within DOE as well as other organizations such as the US National Aeronautics and Space Administration (NASA). Although the Environmental Control Technology Division funded the assessment conducted by LASL, we feel that it is important to include a section in this report to describe the additional work that has been identified as important. In many cases, the assessments described in Section 5. cannot be completed without having the data obtained from the research work discussed here in Section 6. It should be noted that all of these topics involve safety or the environment.

6.1. Hydrogen Releases

A crucial factor in hydrogen safety is the dispersion of hydrogen following a release such as a gaseous hydrogen leak or a liquid hydrogen spill. Dispersion data needed for a comprehensive safety assessment can be obtained by releasing various quantities of hydrogen under varying conditions and monitoring the resulting hydrogen dispersion. NASA is beginning such tests.

Liquid hydrogen storage tanks exist today with capacities of up to 850,000 gallons, and storage capacities of up to several million gallons are mentioned as a possibility at airports for liquid hydrogen fueled aircraft. Obviously, a release of this quantity of hydrogen in a test is impractical (if not impossible). Consequently, an analytical solution (a mathematical model) is needed to predict the results of a release of large quantities of hydrogen. The assumptions necessary for an analytical model are numerous and each has a significant effect on the results. Confidence in the computational

model must be established by release tests in varying quantities and under varying conditions. Release tests with spills up to 1500 gallons are currently being considered by NASA. These tests will probably require extension to larger sizes involving expensive facilities and a large number of instrumentation points. The required tests must provide data to show the effects of the size and rate of release, the surface on which the spill is made, surrounding topography, and weather (atmospheric) conditions.

An analytical model validated by experimental results, is required to complete the assessments described in Tasks (1), (2), (3), and (4) of Section 5.8.1.3.

6.2. Deflagration-to-Detonation Transition

Some of the needed results on ignition and the transition from a deflagration to a detonation may be obtained from the tests and models described in Section 6.1 if some of the releases are ignited. The ignition of a release can provide some of the required data, but not all. Additional tests are necessary to determine the effects of strength and distribution of the ignition source and the degree of confinement. For a complete experimental program the required number of tests would be impractical; thus an analytical model is needed to determine the effects and importance of the many variables involved in this problem.

An analytical model, validated by experimental results, is required to complete the assessments described in Task (3) of Section 5.8.2.3. for a comprehensive safety assessment.

6.3. Open Flame NO_x Emissions

Experimental tests and studies are desirable to determine the extent of the production of NO_x from open hydrogen flames to complete the assessment described in Section 5.5.2.

6.4. Internal Combustion Engine NO_x Emissions

The assessment of a catalytic process for converting NO_x in the exhaust gases of an internal combustion engine to nitrogen and water (Section 5.5.1.1.) is an initial look at this possibility. From the results of this initial effort, a continuation of the assessment may be beneficial.

Regardless of the results of the catalytic conversion assessment, the internal combustion engine design and operating conditions should be investigated to determine if it is possible to reduce or eliminate NO_x emissions by these means rather than by a catalytic conversion process. Initial results

indicate some reduction of NO_x emissions is possible, but only over a severely limited range of fuel to air ratios. Further details are given in Appendix E.1.

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APPENDIX A

ENVIRONMENTAL CONSIDERATIONS IN THE PRODUCTION OF HYDROGEN

A.1 Environmental Impact of Primary Energy Requirements

A chief conclusion of this assessment is that potential environmental problems in hydrogen energy systems lie far more with the primary sources of energy used than in the transmission and end uses of hydrogen itself. The severity of these problems obviously depends on the sources of energy used (coal, nuclear, or solar); the types of environmental controls employed; and on the quantity of primary energy required for hydrogen production and, perhaps, liquefaction.

The early studies of additional energy requirements were summarized¹ as follows:

"The first question to be answered is how much must the primary energy supply be augmented to support a full-scale hydrogen economy? This question was addressed by the Synthetic Fuels Panel convened in 1972 by the Federal Council on Science and Technology and the US Atomic Energy Commission. The panel concluded that just to meet one-half of the projected transportation fuel needs for year 2000 with electrolytically produced hydrogen would require an additional electrical generating capacity of nearly 1,000,000 MW or about 2-1/2 times the currently expected nuclear generating capacity at that time. To put 1,000,000 MW into another perspective, the present total installed generating capacity of the US is about 500,000 MW.

"Gregory and co-workers at the Institute of Gas Technology have addressed the question of augmented electrical capacity for hydrogen production from a slightly different tack. They examined the electrical requirements (based on three different H₂ production methods) for supplying enough hydrogen to: 1) replace the actual 1968 natural gas consumption, or 2) replace the projected natural gas consumption of the year 2000, or 3) replace all fossil fuels, other than those used for electricity generation, by the year 2000. Their results are shown in Fig. 2*. Again we see 1-5 million MW added capacity will be needed--or 2-10 times the present total US capacity must be added for hydrogen production beyond the capacity needed to cover other increases in electrical demand.

"This energy is required just for the production of hydrogen. If it is found advantageous to ship or store hydrogen for transportation use in the form of liquid, considerable additional energy would be needed to cool and liquefy hydrogen gas."

These early studies perhaps did not utilize all the best practicable efficiencies of energy conversion. Overall systems studies are needed using conversion techniques and efficiencies consistent with recent or potential technological advances.

A.2 Environmental Impact of Hydrogen Production

After the primary energy source, a second area of major concern for environmental impacts relates to the hydrogen production step. Under this program, assessments were made of emissions from promising thermochemical cycles for hydrogen production by water splitting.

A.2.1 Introduction. Hydrogen production by thermochemical water splitting is a new technology introduced in the early 1970's and is still in its research phase. Presently, three thermochemical cycles for hydrogen production are being investigated in a continuous mode on a rather small scale of operation (2 liters H₂/min). It therefore may be premature to discuss the "environmental impact" of conceptual plants designed to manufacture hydrogen on a large scale by use of this technology, nevertheless a preliminary assessment of likely problems based on plant designs can be attempted and may prove helpful in guiding the further development of thermochemical cycle research. Prior to this, it may be useful to provide some background material regarding thermochemical cycles and their relation to the more conventional approach, water electrolysis, to hydrogen production.

*See Fig. A-1, p.48

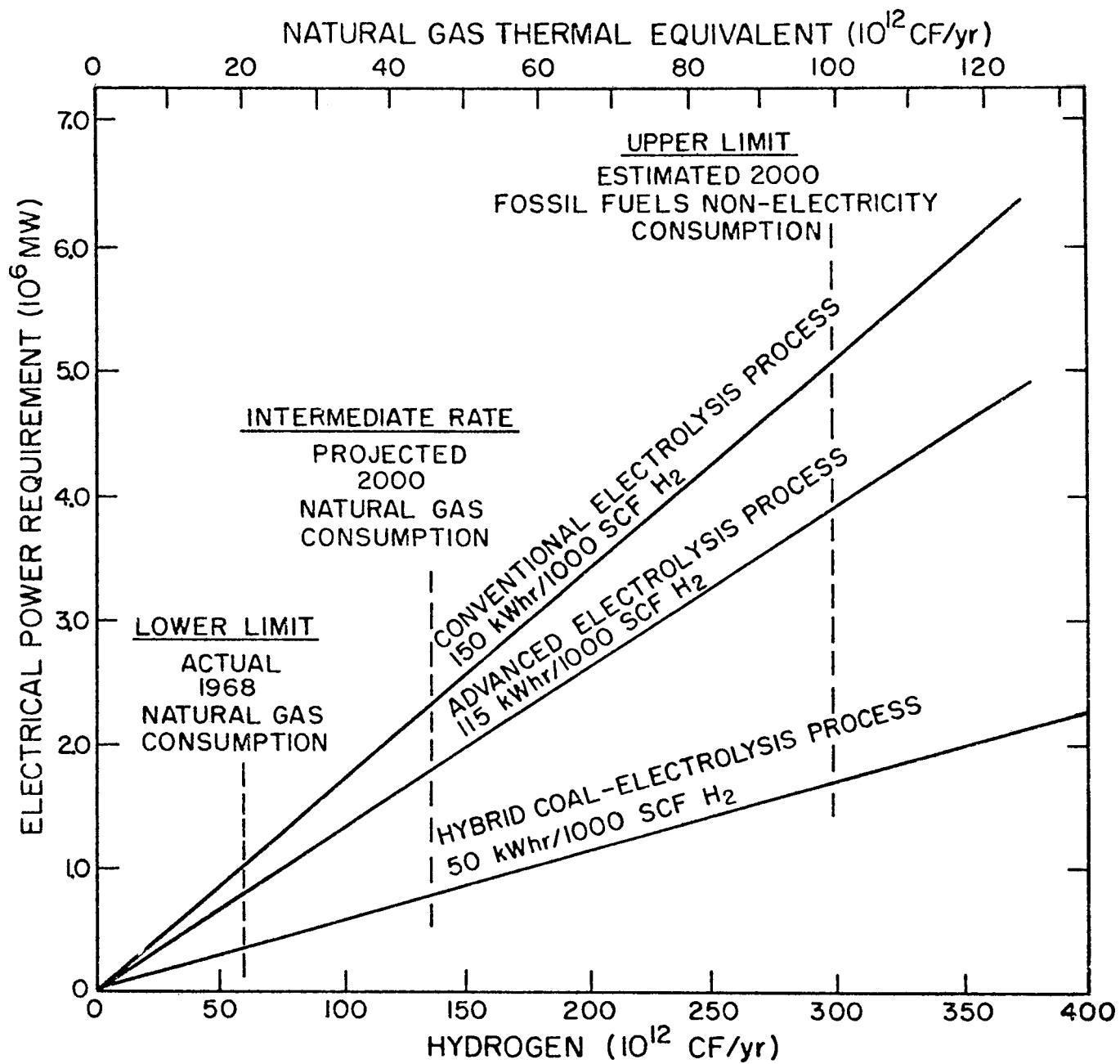


Fig. A-1.

Electrical power requirements needed to produce projected hydrogen demands (identified as Fig. 2 in Ref. 1).

Figure A-2 illustrates both these approaches to hydrogen production from water. We note that a primary energy source such as fusion, fission (high-temperature reactor) or solar energy must be provided and coupled to either the electrolysis process or the thermochemical cycle. In the latter case, the thermal energy must be made available at temperatures greater than about 1100 K. In this work we will neglect the environmental impact of the primary energy source used to drive the hydrogen production process.

A key parameter governing the choice of hydrogen production process employed is the thermal efficiency of that process. The thermal efficiency of hydrogen production is defined as the ratio of the higher heating value of hydrogen (286 kJ/mol) to the total thermal energy (including the heat equivalent of any work) entering the process. For the conventional electrolysis process, the thermal efficiency of the overall system, primary energy source

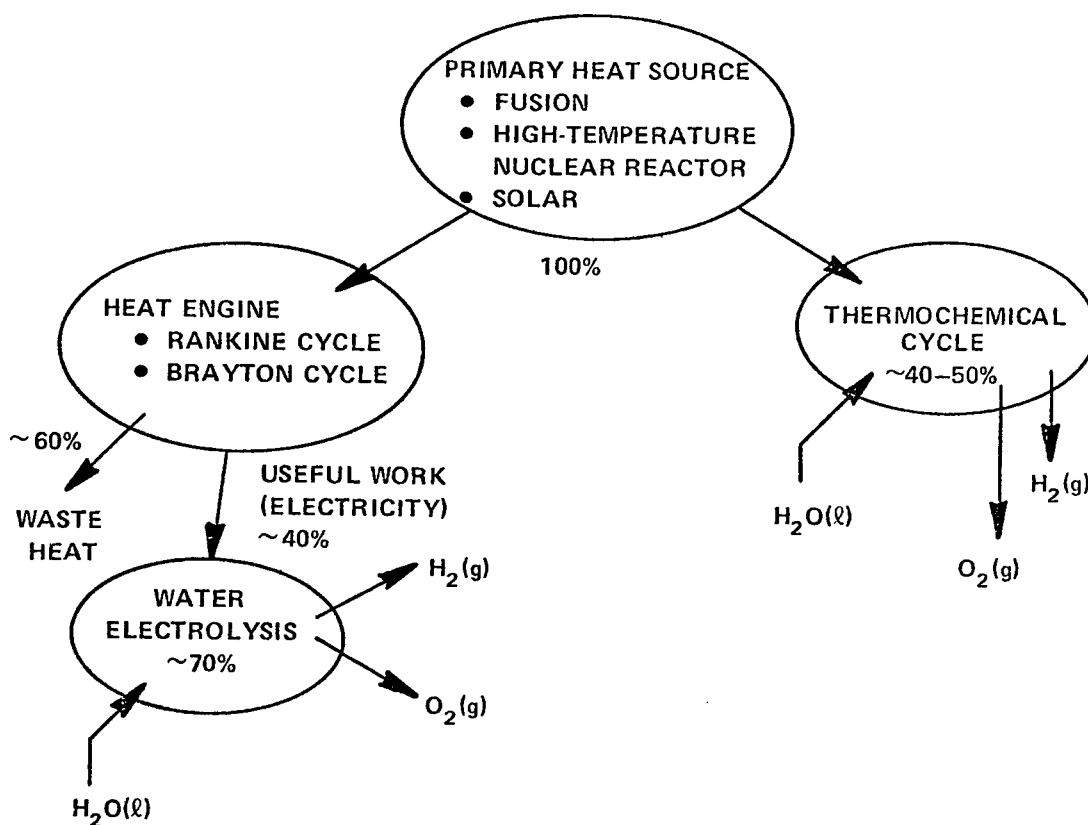


Fig. A-2.
Hydrogen from a thermal energy source.

to electrolyzer output, can be seen (Fig. A-2) as 28%. Increases in both the efficiencies of the power generation step and in the electrolyzer from advanced technology may raise the overall thermal efficiency to 40%.

The justification for the development of thermochemical cycles is the potential of achieving higher thermal efficiencies by elimination of the electricity generation step and the electrolyzer by use of a chemical scheme to decompose water. There are obvious thermodynamic irreversibilities in thermochemical cycles arising from incomplete reactions and from separation steps. While it is possible to derive theoretical limits for the efficiency from thermodynamic considerations, the actual thermal efficiency of a thermochemical cycle and the resulting cost of hydrogen can thus far only be determined by engineering flowsheet evaluation.

Practical considerations that have to be understood before thermochemical cycles prove workable include the following:

- Availability of accurate thermodynamic data.
- Kinetic data.
- Effect of unwanted side reactions and by-products.
- Losses of reactants/products.
- Separation methods.
- Minimization of heat exchange surface.
- Materials, resistance to high-temperature and corrosion.

From the environmental viewpoint, thermochemical cycles should prove benign. All chemical reactants and products are ideally 100 percent recycled, in an ideal cycle there are no waste streams. The only inputs to a cycle are water and thermal energy and the only outputs are hydrogen, oxygen, and some reject heat. Indeed, the point has been made that a 99.9% or better degree of recovery of all chemical intermediates must be made, otherwise thermochemical cycles for hydrogen production may be rendered uneconomic just on the basis of replacement costs alone, not to mention the environmental costs of disposal or cleanup². However, even 99.9% recovery leaves some emissions for air and water courses. Whether actual thermochemical hydrogen plants can meet these high recovery levels depends largely on pilot plant and demonstration unit tests which have not yet taken place. An obvious result of the recovery criterion has been the development of cycles that use relatively inexpensive reactants; indeed proposed thermochemical cycles that are based on expensive chemical reactants are almost automatically excluded from further consideration.

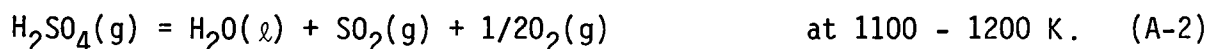
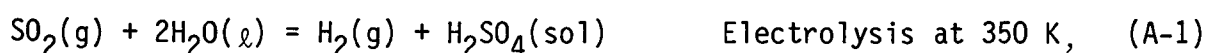
A.2.2 Thermochemical Cycles Under Active Research and Development.

Research programs in the United States and abroad (Europe, Japan) have already identified large numbers of prospective thermochemical cycles since 1972. Few cycles have survived screening through laboratory tests and preliminary engineering/economic analysis for further developmental effort. A preliminary estimate of the thermal efficiency for a proposed cycle should be in the 40-50% range to warrant further testing. Among the cycles chosen for study are:

- The Hybrid Sulfuric Acid Cycle (Westinghouse)³
- The Sulfuric Acid - Iodine Cycle (General Atomic (GA))⁴
- The Hybrid Sulfuric Acid - Bromine Cycle (Euratom Mark 13)⁵
- The LASL Hybrid Bismuth Sulfate Cycle⁶
- The Livermore Zinc Selenide Cycle⁷

Details of the cycles and their present state of development are provided in the references. For those unfamiliar with cycle chemistry, a brief summary of each cycle is included.

A.2.2.1. Hybrid Sulfuric Acid Cycle.³ Hybrid cycles are those in which some of the reactions are thermally driven and others are effected by electrolysis at a lower voltage than that employed in the electrolysis of water (1.6 - 2.0 V). The electrochemical reaction in this cycle was studied at an early stage in the LASL Thermochemical Hydrogen program⁸. The two step cycle is written as:



In the United States, active development of this cycle has been done by the Westinghouse Electric Corp. A schematic of the cycle is shown on Fig. A-3. Westinghouse has constructed a continuous bench-scale unit to produce hydrogen at a 2 liter/min rate. Cycle problems include the electrolyzer design and its operating voltage, drying of sulfuric acid solutions and decomposition of sulfuric acid, as well as materials. Some testing of this cycle is being done at Euratom, Ispra, Italy where the cycle is termed "Mark 11".

A.2.2.2. The Sulfuric Acid - Iodine Cycle.⁴ This cycle is a "pure" thermochemical cycle - no electrolytic steps are included. In the USA,

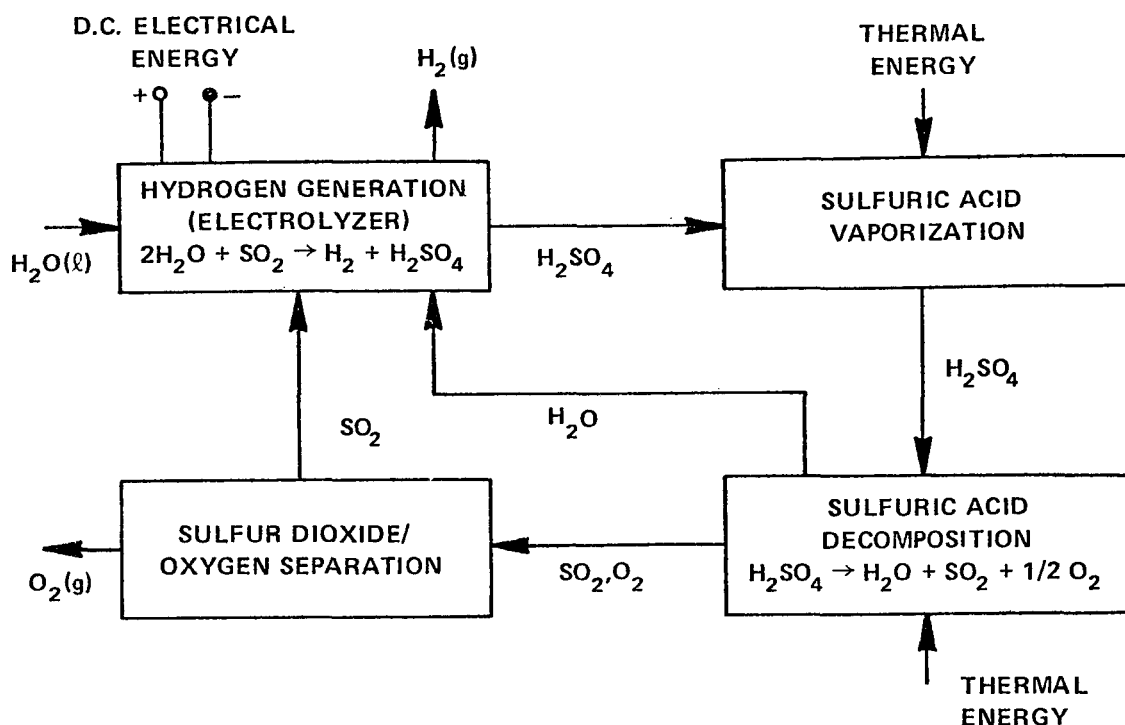
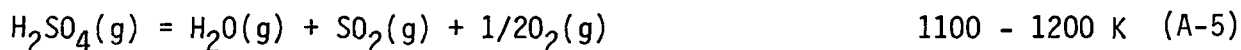
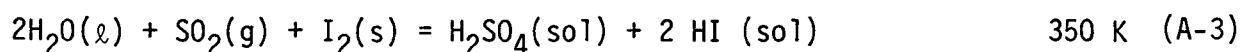


Fig. A-3.
Hybrid sulfuric acid cycle, schematic diagram.

bench-scale testing at a 2 liter per minute hydrogen rate is being done at General Atomic (GA). Three basic steps constitute this cycle.



The cycle schematic is shown in Fig. A-4. At Euratom, the cycle is called "Mark 16". The cycle was made possible by the discovery (GA) that excess iodine present in step 3 caused two immiscible liquid phases which are separable. The light phase is predominantly sulfuric acid solution and the heavy phase is the HI solution. Problems of this cycle include the

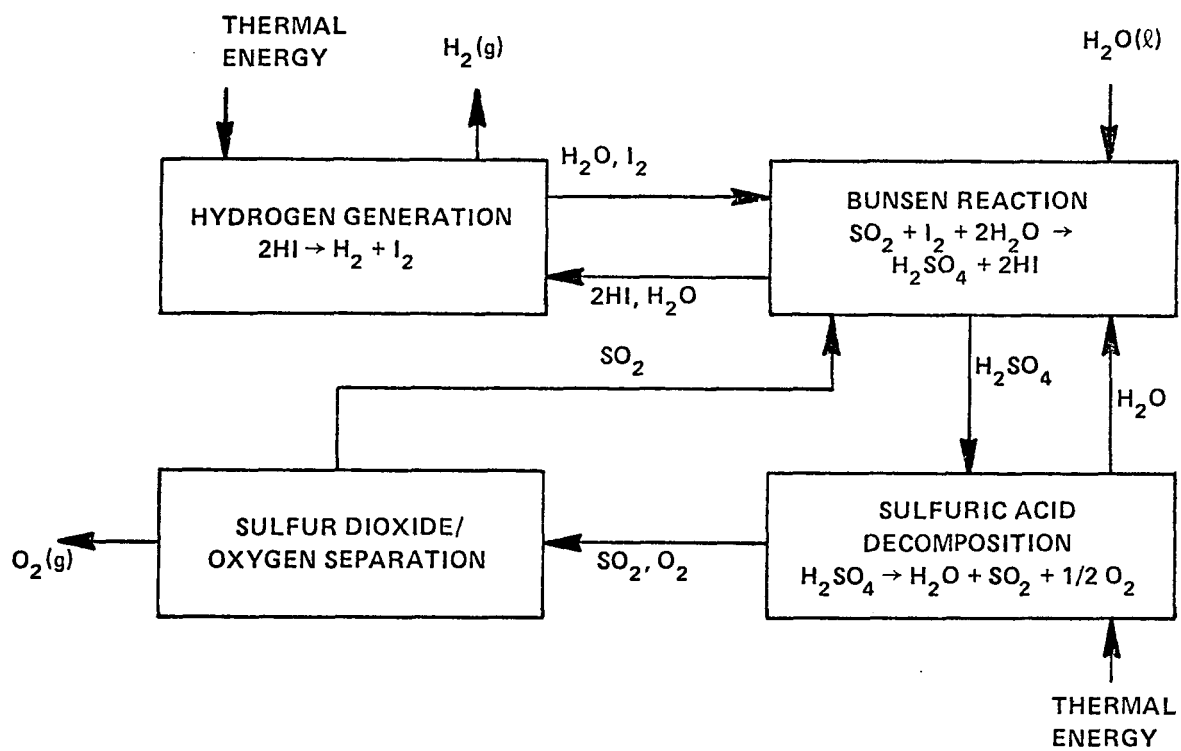
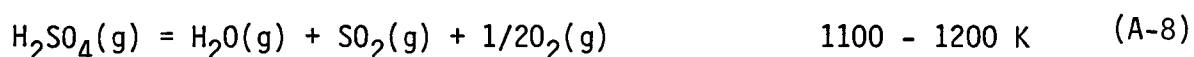
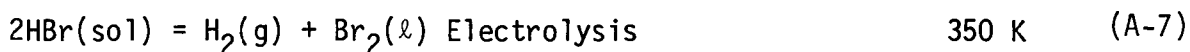
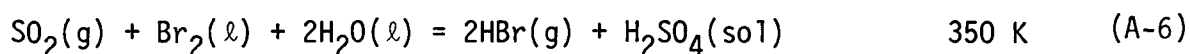


Fig. A-4.
Sulfuric acid-iodine cycle, schematic diagram.

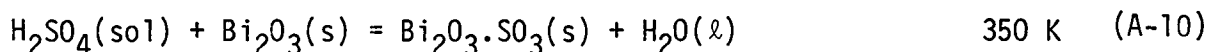
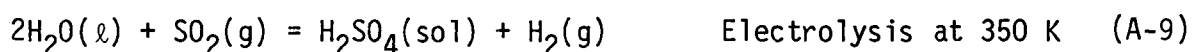
elimination of water from various solutions as well as hydrogen iodide and acid decomposition, steps 4 and 5.

A.2.2.3. The Hybrid Sulfuric Acid - Bromine Cycle.⁵ This cycle developed at Euratom is termed "Mark 13" and has the following steps.



Electrolytic means are used to decompose hydrogen bromide because chemical means have not been successful. Figure A-5 is a schematic of the cycle. Bench-scale investigation is continuing at the Ispra laboratory. Problems include the electrolyzer and its operation as well as containment of the bromine species present. This cycle also possesses the already mentioned sulfuric acid problems.

A.2.2.4. The LASL Hybrid Bismuth Sulfate Cycle.⁶ This cycle is being developed at LASL in order to bypass some of the major problems that occur in the above three sulfuric acid based cycles. Sulfuric acid drying poses serious materials and heat recovery problems. Latent heat recovery may be effected by multiple effect evaporation, however, this will add to the capital cost of the plant. In the bismuth sulfate cycle, below:



an anhydrous precipitate of bismuth oxysulfate is formed from sulfuric acid solution. This sulfate is then dried and decomposed thermally. A schematic of this cycle is shown in Fig. A-6. Problem areas may occur in the handling

and decomposition of solid material as well as in latent heat recuperation when the solid precipitate is dried.

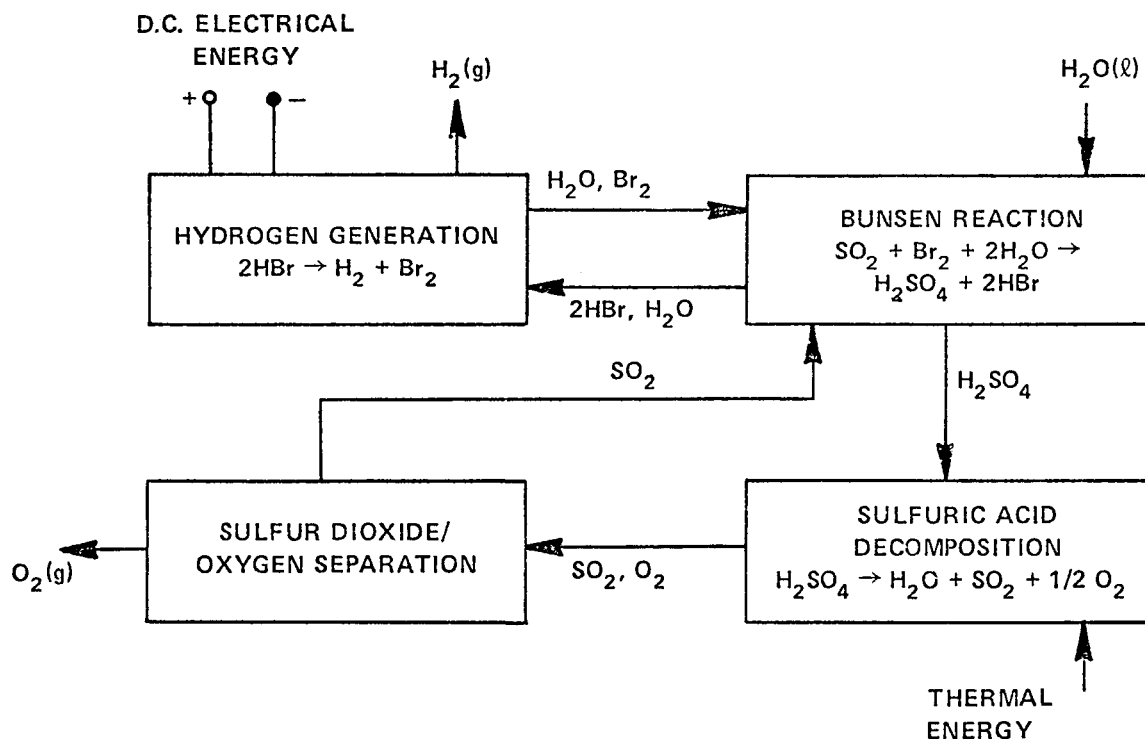
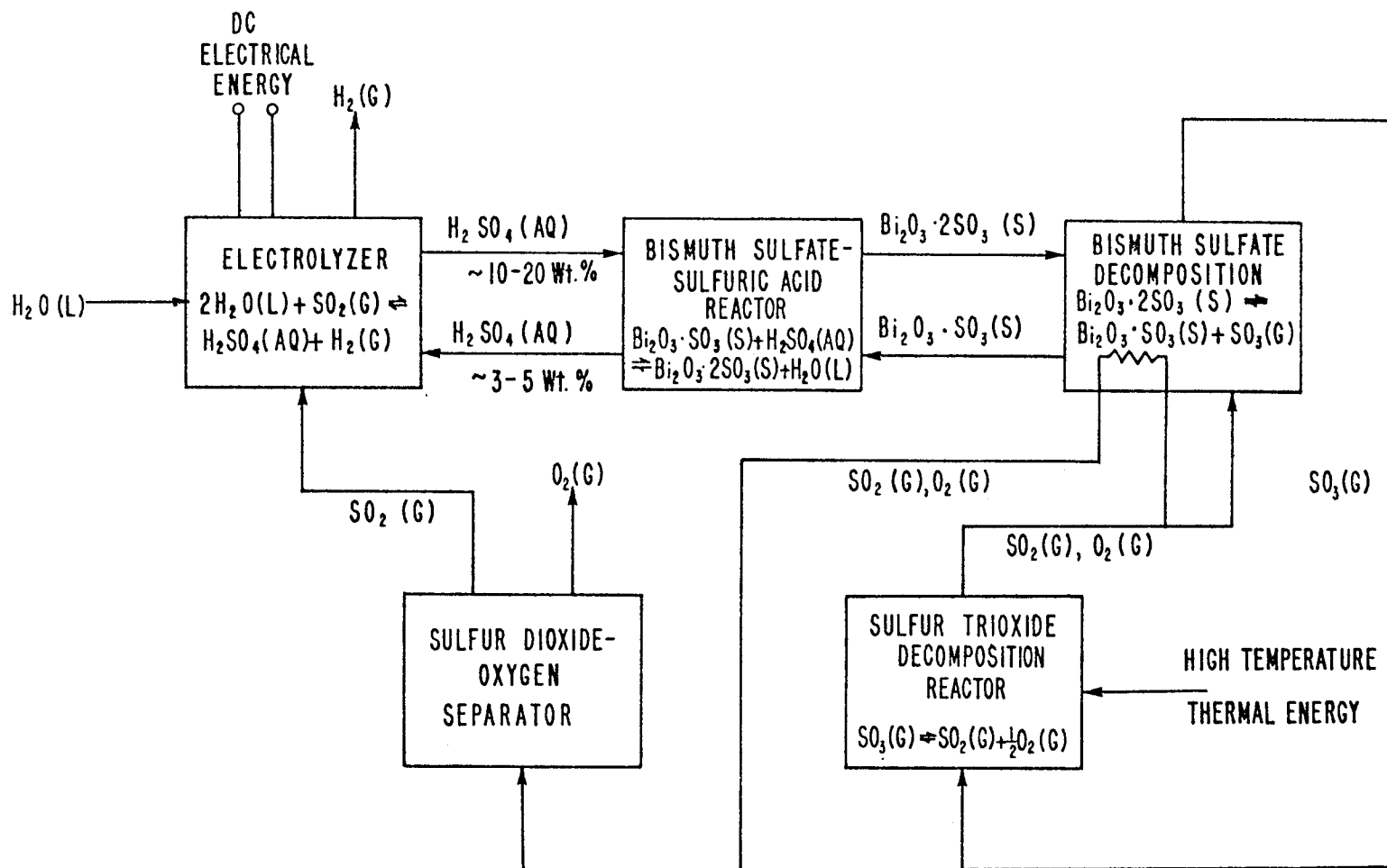
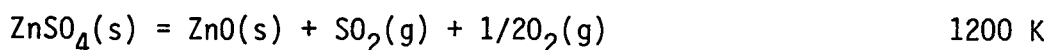
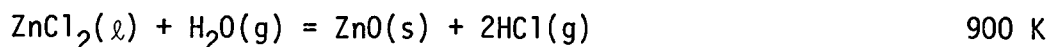
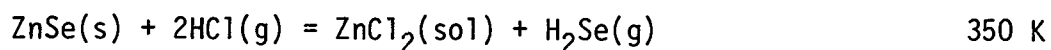
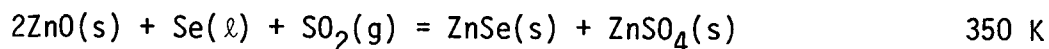


Fig. A-5.
Hybrid sulfuric acid-bromine cycle, schematic diagram.

Fig. A-6.
LASL hybrid bismuth sulfate cycle schematic diagram.



A.2.2.5. The Livermore Zinc Selenide Cycle.⁷ The major reaction steps of the ZnSe cycle are listed below.



The cycle schematic is shown in Fig. A-7. This cycle is a "pure" thermochemical cycle and avoids the use of sulfuric acid by the decomposing solid ZnSO_4 to recover SO_2 . Problems occur in the drying of soluble species, and in areas of separation. Also solids must be handled.

A.2.3. Environmental Impacts. The environmental impact of thermochemical cycles will be examined in general with specific mention being made of unique impacts that pertain to one or more of the individual cycles listed earlier. Factors not addressed are the specific energy source, plant location, and plant design.

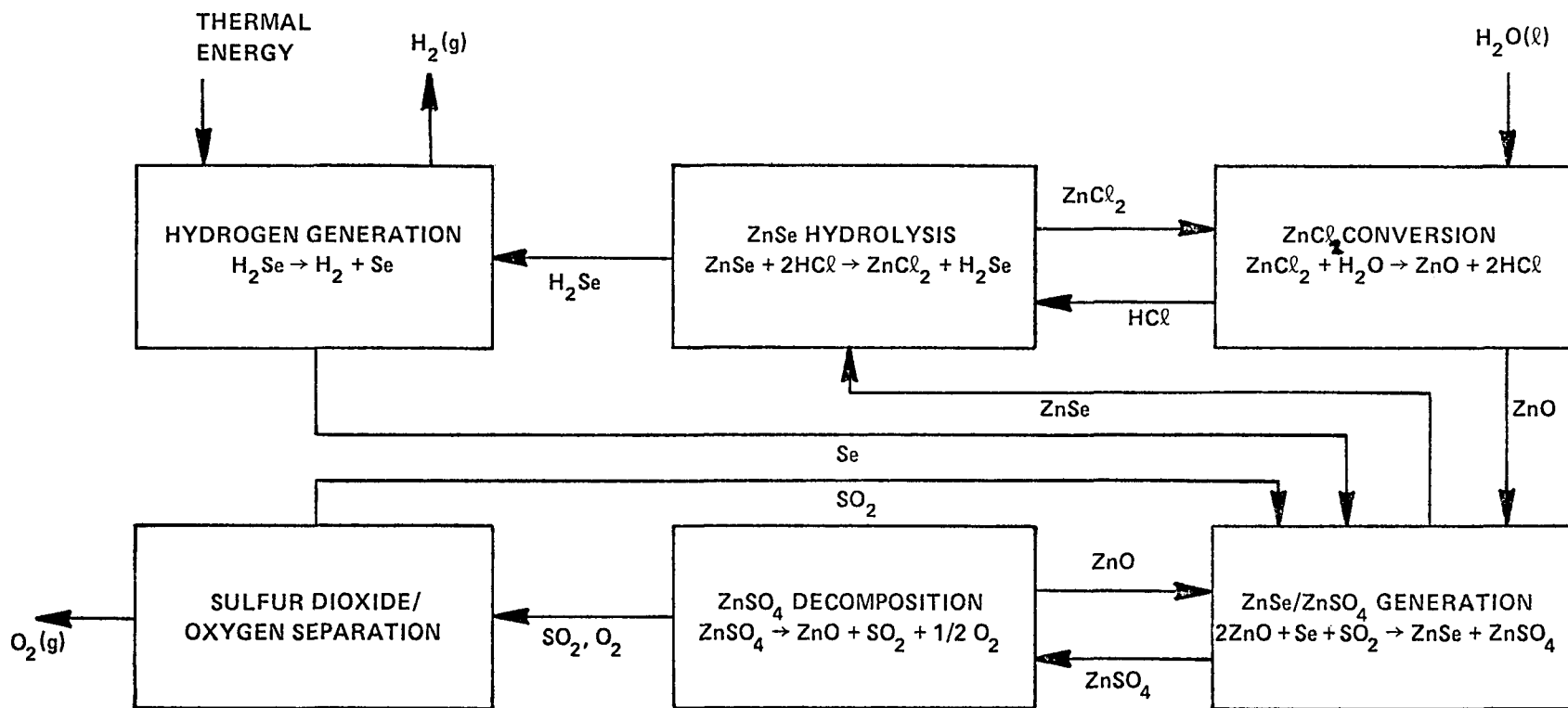
1. Resource Consumption.

The major resources required by a 3000 MW_{th} thermochemical hydrogen plant are land, water (to be discussed below), energy, and chemicals. In many ways the thermochemical plant should be similar to a 3000 MW_{th} (or 1140 MW_{e}) electrical generating plant; thus the amount of land in use, the water consumed for cooling purposes and the energy input should be equivalent. The plant should be sited on an adequate piece of land close to a large supply of cooling water (a river, say). Chemicals that form the plant's inventory and materials of construction are expected to be met by available supplies. In the event of exotic materials of construction, some difficulty may result if imported materials have to be used.

2. Air Impact

Two major waste discharge streams are emitted to the atmosphere by a thermochemical hydrogen plant in "normal" operation. These streams are the

Fig. A-7.
Schematic of the ZnSe cycle.



oxygen vent stream and the air vent stream from the plant's cooling towers. For the conceptual plant of 3000 MW_{th} operating at 50% efficiency as regards hydrogen generation, the oxygen stream would total 304 t/h. This amount of oxygen is not expected to have any adverse impact because rapid dispersion is expected. Sulfur dioxide loss from the process as a result of incomplete separation from oxygen may become a problem unless strict standards governing its recovery are adopted. Plant designs generally specify the SO₂ content in the oxygen stream at 1 ppm; on this basis we estimate the amount of SO₂ emitted to be negligible (7 kg/d).

The water vapor in the air effluent from the cooling water towers could produce a visible plume of condensed water and cause localized ground fog on some days dependent on local atmospheric conditions (temperature, relative humidity, etc.). This problem is not unique to thermochemical hydrogen plants but is common to the electric power generation industry. Cooling towers and their impact are more fully discussed in the next section.

A.2.4. Water Impact. The amount of water consumed as reactant in a 3000 MW_{th} plant is estimated at 340 t/h (8160 t/d). Water will also be used in the cooling tower if it is of the evaporative cooling design. Blowdown from the cooling tower will contain intake water chemicals at a far higher concentration together with specific chemicals (fungicides, anti-corrosion agents, etc.) that are added to the water to preserve the tower's materials of construction. This blowdown will also have a small thermal component which would be about 9°C over ambient in a conventional design. Environmental impacts of large cooling towers have been reviewed elsewhere.⁹ The amount of water lost by evaporation can be quickly computed by a simple heat balance assuming all the heat is dissipated as latent heat of vaporization. For the 1500 MW_{th} energy loss, the water evaporated (in metric tons, t) is

$$\frac{1500 \times 10^3 \times 3600 \text{ kJ/h}}{2300 \text{ kJ/kg} \times 1000 \text{ kg/t}} = 2350 \text{ t/h} .$$

The total water consumption then is: 340 + 2350 = 2690 t/h. We stress again that this quantity is about equal to that used in a large conventional electrical power plant of the same energy input as the thermochemical hydrogen plant.

A.2.5. Solid Wastes. Two types of solid wastes from a thermochemical hydrogen plant can be expected. These include any replaced chemicals or catalyst, and the solid sludge from the water treatment plant. The feed water to the thermochemical cycle should be of high purity (resembling distilled water). We estimate for water containing 500 ppm dissolved and suspended solids that the sludge alone would amount to 4080 kg/d. In a parallel study,¹⁰ Westinghouse estimates a sludge amounting to 18000 kg/d with a 50% water content. The additional amount of solids is probably a result of different assumed feed water and chemicals used to flocculate suspended solids and to control the pH of the water. The sludge would not be expected to contain any unique or particularly toxic chemicals and thus would be disposed of either at the site or at an off-site landfill.

A.2.6. Accidental Spills or Leaks, and Non-Idealities. The concept of water dissociation to produce hydrogen is based on the regeneration of all the reagents involved. For environmental purposes we have made estimates of losses based on arbitrary recovery rates, as it is known that chemical processes do not conform ideally to their reaction stoichiometry and that deviation from 100% yield may be a result of such causes as:

- Accidental spills or leaks
- Incomplete separation of recovered products
- Side reactions
- Blowdown during maintenance, etc.

Joly² pioneered the approach in making estimates of allowable losses from thermochemical plants in developing economic criteria for their evaluation, i.e., he was interested in the costs of replacing lost reactants. In addition, he stated: "Unless nearly absolute quantitative recovery of all reagents involved can be achieved, thermochemical plants will be highly potential polluters." Estimated losses from thermochemicals plants are presented in Table A-I on the basis of a 3000 MW_{th} input plant operating at 50% efficiency producing 304 800 t of hydrogen per year. Two levels of recovery were considered: 99.9% and 99.99% corresponding to loss levels of 0.1% and 0.01% respectively. For expensive chemicals, recoveries of 99.99% or better must result.² Table A-I shows that losses are directly proportional to molecular weights as thermochemical cycles operate in a stoichiometric manner. Thus cycles operating with heavier compounds, such as bismuth derivatives, will

TABLE A-I
ESTIMATED LOSSES FROM THERMOCHEMICAL CYCLES
AS A FUNCTION OF PERCENT RECOVERY

Basis: 3000 MW_{th} plant, 50% efficiency; Hydrogen Production: 38.1×10^3 kg/h, or 304 800 t/y. (8000 h/y = 90% availability)

Cycle*	Recovery (%):		99.9		99.99	Remarks
	Compound	Mol. Wt.	t/d	t/y	t/y	
1,2,3,4,5	H ₂	2.016		305	30.5	Gas phase (product)
5	HCl	36.5	16.8	5590	559	Gas, poss. aq. sol.
1,2,3,4,5	SO ₂	64	30	9800	980	Gas
3	HBr	80.9	37.2	12400	1240	Aq. sol., gas
3	Br ₂	159.8	73.5	24460	2446	Gas
5	H ₂ Se	81	37.2	12400	1240	Gas
2	I ₂	253.8	117	38850	3885	Solid, poss. vap.
4	Bi ₂ O ₃ ·SO ₃	626	288	95820	9582	Solid, poss. as dust.

*Cycles

1. Hybrid Sulfuric Acid; 2. Sulfuric Acid - Iodine; 3. Hybrid Sulfuric Acid - Bromine; 4. Hybrid Bismuth Sulfate; and 5. Zinc Selenide

show greater losses than those with lighter compounds at the same percentage recovery. To place these quantities in perspective, we note that copper smelters typically dispose of 700 - 1000 t/d of SO₂ into the atmosphere, coal-fired electrical generating plants: 350 t/d (1000 MW_e) without scrubbers; with scrubbers the value of SO₂ emissions drops to about 35 t/d, 1/10th of the previous value. For a thermochemical hydrogen plant based on a cycle containing SO₂ as a reactant, we see that 30 t/d are emitted if the recovery rate is 99.9% which is an amount roughly comparable to that emitted by a low sulfur coal-fired power generating station equipped with scrubbers.

It is important to stress here that the actual amount of pollutants emitted by a thermochemical plant is unquantifiable at this time. Estimates such as those presented in Table A-I can act as important guidelines in the design of such plants to ensure that high recovery rates are achieved for the sake of environmental protection as well as of economics.

It may be of interest to compare the SO₂ emission rates from Table A-I with allowable SO₂ emission as set by air pollution regulations for stationary coal-fired electrical power generating plants. These standards are given

as "lbs $\text{SO}_2/10^6$ BTU (input)." For the San Juan (NM) plant, the allowable emissions are: 0.34 lb $\text{SO}_2/10^6$ BTU; maximum national emissions: 1.2 lb $\text{SO}_2/10^6$ BTU. For the 3000 MW_{th} thermochemical hydrogen plant, the allowable emissions based on the maximum standard would be 130 t/d of SO_2 . Table A-I shows a 30 t/d SO_2 emission at a recovery rate of 99.9% which corresponds to 0.28 lb $\text{SO}_2/10^6$ BTU. A thermochemical hydrogen plant at the 99.9% recovery rate is equivalent to current technology for a low sulfur coal-fired electrical generating plant equipped with scrubbers and as such would meet today's air quality standards for SO_2 emission.

From another point of view, several of the reactants/products listed in the thermochemical cycles presented have toxic properties and are potentially hazardous. Table A-II lists the "threshold limit value" (TLV) of some of the potentially hazardous chemicals employed in the cycles. The "toxic hazard rating" (THR) is given where TLV's are not available. The data are taken from Sax.¹¹

From Table A-II, it appears that the zinc selenide cycle has the most dangerous potential due to its use of hydrogen selenide and selenium compounds. The next most toxic cycle is the hybrid sulfuric acid - bromine cycle. The least toxic cycle is the one using bismuth compounds.

Clearly the engineering development of all cycles must guard against the release of any toxic substance by rigorous specification of plant items such as piping, welds, valves, gaskets, etc. Plant safety should be kept to standards by frequent inspection and periodic maintenance. All of the compounds listed in Table A-II can be properly handled if adequate precautions are observed.

A.2.7. Summary and Conclusions. Plants for the thermochemical production of hydrogen should prove to be environmentally benign in normal operation. This is a result of water and thermal energy being the only plant input and, ideally, hydrogen and oxygen the only output together with some reject heat. Analysis of the air, water and solid waste impacts of these plants shows environmental impacts little different from that for an electrical power generating plant of the same thermal energy input. The major environmental impact from thermochemical hydrogen plants may be due to accidental spills or leaks releasing certain of the chemical reactants/products used in the thermochemical cycle. This amount of release is impossible to quantify at this time, however, estimates have been made of amounts lost to the process on the

TABLE A-II
TLV's AND THR's FOR CHEMICALS USED IN THERMOCHEMICAL HYDROGEN CYCLES

<u>Threshold Limit Value</u>				
<u>Substance</u>	<u>ppm</u>	<u>mg/m³</u>	<u>Cycle*</u>	
Bromine	0.1	0.7	3	
Hydrogen Bromide	3	10	3	
Hydrogen Chloride	5	7	5	
Hydrogen Selenide	0.05	0.2	5	
Selenium Compounds (Se, ZnSe)	--	0.2		
Sulfur Dioxide	5	13	1,2,3,4,5	
Sulfuric Acid	--	1	1,2,3,4	
Zinc Chloride (fume)	--	1	5	
Zinc Oxide	--	5	5	

<u>Toxic Hazard Rating</u>				
<u>Substance</u>	<u>Acute Local Irritant</u>	<u>Acute Systemic Ingestion</u>	<u>Inhalation</u>	<u>Cycle*</u>
Hydrogen		(asphyxiant)		1,2,3,4,5
Hydroiodic Acid	3	3	3	2
Iodine	3	3	3	2
Sulfur Trioxide	3	3	3	1,2,3,4,5
Bismuth Compounds (Bi ₂ O ₃ .SO ₃ , Bi ₂ O ₃ .2SO ₃)	1	1	2	4
Zinc Selenide		(Recognized Carcinogen)		5
Zinc Sulfate		(Low Toxicity)		5
(Toxic Hazard Rating: 1 = Slight, 2 = Moderate, 3 = High)				

*Cycles

1. Hybrid Sulfuric Acid
2. Sulfuric Acid - Iodine
3. Hybrid Sulfuric Acid - Bromine
4. Hybrid Bismuth Sulfate
5. Zinc Selenide

basis of a specified recovery rate. For a compound such as SO_2 , a 99.9% recovery rate shows a 30 t/d loss based on a hypothetical 3000 MW_{th} plant operating at 50% efficiency. This loss is well within air pollution standards set for coal-fired electrical generating plants. For other chemicals in the cycle, the acceptable recovery rate may have to be set by the expense of chemical replacement or by the toxicity of the compound. Precautions should therefore be taken to minimize the possibility of accidental spillage or release on both environmental as well as on economic grounds.

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APPENDIX B

STORAGE OF HYDROGEN

Hydrogen can be stored in three forms, either as a gas, as a cryogenic liquid, or as a hydride in either chemical or metal form. All of these methods have potential application in hydrogen energy systems. No one method is superior to the others in all respects.

B.1 Gaseous Hydrogen Storage

As a gas, hydrogen can be stored either at low pressures (around one atmosphere) in natural or man made underground reservoirs or at high pressures (2000 psi to 20 000 psi).¹ The former has only specific locations and specific uses for which it is applicable. DOE is currently funding research into the practicality of various methods of storage. This will include the environmental and safety aspects.

Compressing hydrogen increases the energy density; however, several problems are created. From a safety standpoint, the energy of the compressed gas irrespective of the combustion energy of hydrogen becomes significant. The energy stored in the compressed gas system is given by

$$E = RT \ln \frac{P_f}{P_i} ,$$

where T is the temperature in kelvin, R is the gas constant and P_i and P_f are the initial and final pressures. For a standard "K" cylinder ($\sim 1.5 \text{ ft}^3$ at 2000 psi) this energy is 3.3×10^6 joules or 3060 BTU. Higher pressure storage, 10 000 to 20 000 psi is also being considered. These systems will have to be carefully examined for safety implication.

The primary disadvantage of compressed gas storage is the ratio of the weight of hydrogen stored to the weight of the storage container. In the past this ratio has been in the range of 1%. New advances are being made in container design which may increase this ratio as much as ten-fold thus making the compressed gas storage more economical.

B.2 Liquid Hydrogen Storage

Storage of hydrogen as a liquid at cryogenic temperatures is common. Liquid hydrogen is routinely delivered in barges, railcars, and highway trailers. Detailed discussion of the transmission of liquid hydrogen and the

safety implications for increased transport of liquid hydrogen in hydrogen energy systems are given in Ref. 2 and 3.

The largest LH_2 storage vessels in existence today are the two 850 000-gallon spherical containers located at the Kennedy Space Center (KSC). As described by Bain,⁴ the inner shell is stainless steel and is 18.8 m (61 ft 9 in.) in diameter. The outer shell is carbon steel and is 21.3 m (70 ft 0 in.) in diameter. The annulus between the inner and outer shells is filled with perlite insulation and evacuated. The container's working pressure is 620 kPa (90 psi), and the measured daily boil-off rate with hydrogen is 0.03% or about 225 gallons/day. Means of pressure-building by an external heat exchanger is provided along with remote and manual valves and controls.

Several means of disposing of hydrogen gas vented from the tank are provided:

- (1) Free-venting to the atmosphere of quiescent boil-off,
- (2) "Burn pond" or underwater distributor and provision for ignition and combustion in a 100-ft square containment area filled with about 2 ft of water, for safe disposal of large quantities, and
- (3) Gaseous hydrogen recovery of vented gas (considered, but not yet implemented; increasing cost of hydrogen and amount of hydrogen being handled may provide the incentive).

Also at KSC are several other LH_2 containers of 15 000-gallon (spherical) and 28 000-gallon (horizontal cylinder) capacities. Other large LH_2 containers are located at the Nevada Test Site at Jackass Flats where reactor testing was conducted for the nuclear rocket program.

The above descriptions of large LH_2 storage containers serve to illustrate the state-of-the-art and to characterize the construction and operation of such storage facility items. In Hallett's earlier assessment,⁵ both aboveground and underground LH_2 storage was considered. The aboveground tanks were categorized as single- or double-wall designs. The single-wall designs were either externally or internally insulated, while the double-wall designs used either purged-powder or vacuum-insulated configurations.

More recently, the Boeing Co. assisted by Air Products and Chemicals,⁶ Inc. and the Lockheed Aircraft Co.,⁷ assisted by the Linde Division of Union Carbide Corp., reexamined future large-quantity LH_2 storage at large

commercial airports. Both studies concluded that several spherical containers of essentially identical construction as the two large KSC spheres (vacuum-jacketed with perlite powder insulation) would be the appropriate system.

The Boeing study describes the installation as follows:

"The storage tanks are located aboveground. An aggregate of stones enclosed in a concrete retaining wall is placed underneath the storage tanks to serve as a heat sink in the event of tank rupture. This accelerates the vaporization of LH_2 . The storage tank is of double-wall construction with a 23.2-m (76 ft) diam stainless steel inner sphere.

The annular space is evacuated and filled with perlite powder insulation."

Both Boeing and Lockheed concluded that, for an entire airport LH_2 fueling system, the recovery and reliquefaction of vented hydrogen gas was cost-effective and would be incorporated in the design of the facilities.

Storage of LH_2 is typically required in each of the three basic parts of a hydrogen energy system: production, delivery, and use. This is illustrated in the industrial gas business today. For example, LH_2 is stored at a tonnage production plant to allow continuous production while also allowing for periodic loading of rail tank cars or tractor-trailer delivery units (themselves "rolling storage containers"). Then, at distribution centers such as Linde's McCook facility (near Chicago), storage is provided as a means of matching supply of liquid product arriving from the production facility and demand for that departing for the customers' using facilities. Finally, at the using site typically a LH_2 container is located to match local demand and supply by the industrial gas deliveries.

Liquid hydrogen presents all the hazards normally attendant to the handling of hydrogen as well as those of a cryogenic fluid - namely, high volatility and low temperature. Except for liquid helium, LH_2 is the most volatile of all liquids. The volatility, along with the unavoidable heat leak into the cryogen containers, provides a mechanism for unwanted pressure build-up within containers that are not properly vented. In the case of spills of LH_2 , rapid vaporization can be expected with a consequent rapid spread of a combustible mixture of hydrogen and air (see Appendix C.5). While for completeness we should mention the possibility of the exclusion of enough air to cause an asphyxiating atmosphere in confined spaces, the ease of ignition and wide range of combustibility limits of hydrogen could usually be expected to make this problem of a secondary nature in the case of spills.

Hydrogen boils at a temperature (20.4 K at one atm) lower than any other liquid except liquid helium. This temperature is sufficiently low to condense air. If the air enters the hydrogen space, it can be condensed to a solid. If the air is cooled by an externally exposed surface and can then drip off, pools of liquid air can be formed. The air that condenses from normal air is enriched in oxygen to approximately 50%. This condensate can result in explosive mixtures when falling on combustible materials. Even if falling on noncombustibles, damage or hazard can be caused by cold embrittlement or dimension changes in materials not intended to withstand cooling to temperatures approaching 90 K. The low temperature can also cause tissue damage. However, the possibility of immersion in LH_2 or even of encountering a stream of the fluid for more than a few seconds is remote, and such tissue damage would be more likely to result from inadvertent contact with the external surface of an internally cooled pipe.

In spite of these hazards, the production, storage, transport, and use of LH_2 has an excellent safety record. This record reflects the safety research done either prior to, or concurrent with, the expanding of LH_2 technology. As a consequence, we can say that for the present level of use and also for well-controlled demonstration projects, the existing controls and equipment are adequate.

One additional concern is that of hydrogen embrittlement. Many believe that none of the mechanisms for hydrogen embrittlement is active at LH_2 temperatures. However, this has not been demonstrated. Also, LH_2 equipment will usually experience hydrogen at ambient temperature at some time during its use, either in testing or because of temperature gradients existing within the equipment.

However, "safety is a moving target." It is becoming obvious that additional safety research must be done. While an attempt has been made to assess the hazard associated with the present shipment of LH_2 , the results cannot be considered satisfactory. There is neither sufficient data on which to base the probability or severity of an accident, nor is there adequate information on the spread of combustible vapors after a catastrophic spill. We also need to understand better the effects on hydrogen combustion of variables such as size of spill, modes of spill, partial confinement, impurities, rates of spill, and rates of vaporization.

NASA has recognized a need for some of this data and has initiated a small research program to study the effects of LH_2 spills. This work and its continuation is important to the assessment of safety and environmental control aspects of hydrogen safety.

B.3 Hydride Storage of Hydrogen

Metal hydride storage of hydrogen is very attractive in many respects. The density of recoverable hydrogen in some systems is higher than the density of hydrogen in the liquid state. Some of the hydride systems are inherently safe. Rupture of a vessel containing FeTi with a full charge of hydrogen may result in a small fire as the hydrogen slowly escapes; however, it does not result in the same hazard as if the equivalent amount of hydrogen was stored as liquid or compressed gas and ruptured.

The disadvantages to hydrides in some cases may prohibit their use. The ratio of the weight of hydrogen stored to hydride and container weight is small. Five percent is the best to date in laboratory situations and much less in practical application. This is a drawback for vehicular applications. Some hydrides are toxic and some, when exposed to air, are pyrophoric. Hydrides are poisoned to some degree by impurities.

In this program we have not made an indepth study of the safety and environmental problems of large scale usage of metal hydride. Above we have mentioned a few of the problems which will have to be examined for each hydride which is considered.

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APPENDIX C

TRANSPORT OF HYDROGEN

C.1 Introduction

With present technology large quantities of hydrogen can be transported as a liquid. Although there are some concerns about hydrogen embrittlement in the pipeline transport of hydrogen gas, such transport is also being done safely. It can be expected that both of these methods will be used in any future expansion in the use of hydrogen. Both methods are already in use and are capable of undergoing considerable expansion.

The assessment program has identified several areas where additional efforts are either desirable or necessary. One such area is the assessment of the consequences of a large release of hydrogen gas or a large spill of LH_2 . The proposed use of hydrogen as an aircraft fuel implies aircraft tanks of up to 1 000 000 L (250,000 gal) and airport storage tanks up to 12 000 000 L (3 000 000 gal). Even if the hydrogen fueled aircraft should never materialize, it must be remembered that in the US LH_2 is already stored in Dewars up to over 3 000 000 L (850 000 gal) in size, and transported in highway trailers up to 50 000 L (13 000 gal) over a great deal of the US. Rail tank cars with a capacity of 100 000 L (28 000 gal) leave almost daily for shipment of LH_2 from Los Angeles to Chicago. Except in a very few instances, mishaps to date have mainly been those of vehicular origin rather than due to the nature of the cargo.

We feel there is a need for a study of the probability and consequences of a release of hydrogen comparable in size to the above mentioned quantities. In particular, this study should use both analytical and experimental methods and it will need to add to present knowledge of the combustion of large quantities of hydrogen and of the factors affecting the dispersion of hydrogen after a release has occurred. Preliminary attempts to assess the size of a hydrogen release and its consequences have not been successful. Obviously a mathematical analysis and modeling of various spill scenarios is desirable; however, the necessary assumptions are numerous and the extrapolations from known cases are enormous. Consequently this problem must be attacked with both an experimental and an analytical approach. In Sec. C.4 we discuss LH_2 spill tests and in Sec. C.5, an analytical solution.

C.2 Combustion

The physical properties of hydrogen are well known. Although it has a high ignition temperature, the ignition energy is very low. Thus even though the ignition source is not always known, it is not surprising that hydrogen releases frequently lead to fires. Once ignition has occurred the destructive power of the combustion is much greater if the deflagration can transit to a detonation.

It is known that the degree of confinement imposed upon burning hydrogen has a great effect upon the transition to detonation. Frequently combustion takes place in a partially confined area. Under these circumstances there is little knowledge about the possibility of a detonation. Another factor that needs investigation is the effect of size of combustible cloud resulting from a hydrogen release. As releases become larger, an attempt should be made to look for increasing flame front velocities indicating approaching detonation. The rate of release is also an important consideration to be included.

Two other factors needing further investigation are the strength and distribution of the ignition source. Ordinarily one could expect that only low energy ignition sources are present for the ignition of a hydrogen release, because high energy sources mean high explosives. However, on at least one occasion, hydrogen being released to the atmosphere has found a confined area where transition to detonation then provided an ignition source sufficiently energetic to propagate a larger scale detonation. There is also the possibility that increasing size of a release alone could lead to the detonation by allowing longer distances for acceleration of the combustion wave.

C.3 Dispersion

The dispersion of hydrogen after a large LH_2 leak or gaseous release is also in need of further study. Some LH_2 spill tests were performed by the Arthur D. Little Co. and by the US Bureau of Mines in the 1950s. Except for one test involving 19 000 L (5 000 gal) the spills were of a few liters and very little instrumentation was used. The location of the hydrogen cloud was traced by observing the visible vapor cloud (water vapor). This method is not reliable for LH_2 spills and would be useless for following a gaseous hydrogen release.

Previous attempts to model the dispersion of hydrogen analytically after a release have not produced believable results. In such a calculation, factors which must be considered are heat transfer to the surrounding atmosphere,

atmospheric mixing, the quantity of release, the rate of release, the condition of the hydrogen upon release, and the topography of the release area.

C.4 Liquid Hydrogen Spill Tests

The NASA is undertaking a program to investigate the consequences of a spill of LH_2 . This work is now scheduled to take place at the NASA test facility at White Sands, New Mexico during the winter and spring of 1980. In these tests, approximately 100 instrumentation points will be used to detect the presence of, and monitor the concentration of hydrogen after an intentional spill of up to 6 000 L (1 500 gal). Tests both with and without ignition are planned. These tests will be combined with the results of calculations such as discussed in Sec. 4. After a comparison of analytical and experimental results, the decision will be made as to what size and how many larger scale tests will be performed.

C.5 Atmospheric Dispersion Modeling

Calculations have been made by an expert in air dispersion modeling (Dr. Michael Williams) for the dispersion of vapor from a large spill of cryogenic hydrogen. The final report from this contract follows.

Introduction

An item of concern in a liquid hydrogen fuel program is the consequences of a major spill of liquid hydrogen. Estimates made by other investigators suggest that a large scale liquid hydrogen spill might produce a combustible cloud that can travel many kilometers downwind. The worst case circumstance was identified as stable flow case where vertical atmospheric dispersion is greatly suppressed.

In order to make the estimates, the investigators used a number of simplifying assumptions, one of the most important of which was the assumption that the hydrogen would be warmed by the underlying soil until it reached neutral buoyancy with respect to the ambient air, after which no further heating would occur and the plume would drift for large distances with little mixing.

These assumptions are not likely to be realized in practice. A liquid hydrogen spill produces a very unusual plume in that at neutral buoyancy the plume is very much colder than the ambient air. For a plume near the ground this implies that the ground below and the air above the plume are much warmer than the plume. Heat transfer from the ground to the plume will be greatly enhanced because of the sharp temperature gradient near the ground. Heating of the plume by the ground would increase the temperature of the plume and make it buoyant. The buoyancy will cause the plume to lift and ambient air will be mixed into the plume from below. The result of this process would be to increase the dispersion. The object of this effort is to model the dispersion in the presence of plume heating by the ground and to determine whether soil heating significantly enhances the rate of dispersion. If an improved approach, treating soil heating, also gives plumes combustible to large distances, more confidence can be attached to this result.

Theoretical Treatment

In the atmosphere, material diffuses primarily through the interchange of parcels of air across boundaries. Generally this interchange is much more effective than is molecular diffusion even for very light atoms such as hydrogen. The vertical eddy diffusion can be either enhanced or inhibited by the thermal regime extant in the atmosphere. If the lapse rate is steeper, that is temperature decreases faster with height, than the adiabatic lapse rate, eddy diffusion is very effective and mixing is quite rapid. For example, a plume from a ground level source with an initial depth of 30 meters may double in depth in only 80 meters travel during unstable conditions. On the other hand, during stable conditions the same change will require 2400 meters. Furthermore, these differences become even larger at larger downwind distances. In the case of unstable conditions both mass and heat are transferred rapidly while the opposite is true during stable conditions.

In the case of a hydrogen spill, the gas will generally be much colder than the ground with the result that heat transfer from the ground will be quite effective. On the other hand, the air above the plume will be much warmer and, during stable conditions, less dense with the result that there will be little heat and mass transfer between the plume and the air above. However, effective heating of the hydrogen by heat transfer from the ground will increase the temperature of the plume causing it to rise, and as it does so, the air below it will be rapidly mixed into the plume producing a dilution of the plume. This analysis suggests that the vertical profile of hydrogen and temperature will appear similar to that shown in Fig. C.5-1.

With this background, the following approach is suggested. The actual vertical distribution of hydrogen and the temperature may be approximated as a step function at each downwind distance. Then equations for conservation of mass, vertical momentum, and energy can be used to describe the average hydrogen concentration, vertical extent of the plume, and the average temperature as a function of downwind distance. We first consider a small element of plume which is idealized as a slab with crosswind dimension $2y$, height Z , and alongwind dimension x . As the slab expands in height the center of gravity rises. The vertical velocity corresponding to a given streamline at an initial position z_0 is

$$w(z_0) = \frac{z_0}{Z_0} \frac{dZ}{dt}$$

where the height of the slab at $x = x_0$ is Z_0 and t = time. The vertical momentum of the slab is then

$$\int_0^Z \rho \, 2y \, \xi \, \frac{dZ}{dt} \, \Delta x \, d\xi = \rho \, y \, \Delta x \, Z \, \frac{dZ}{dt}$$

conservation of momentum then gives:

$$\frac{d}{dt} (\rho \, y \, \Delta x \, Z \, \frac{dZ}{dt}) = \int_0^Z 2y \, g \, \Delta \rho \, d\xi = 2y \, g \, \Delta \rho \, Z$$

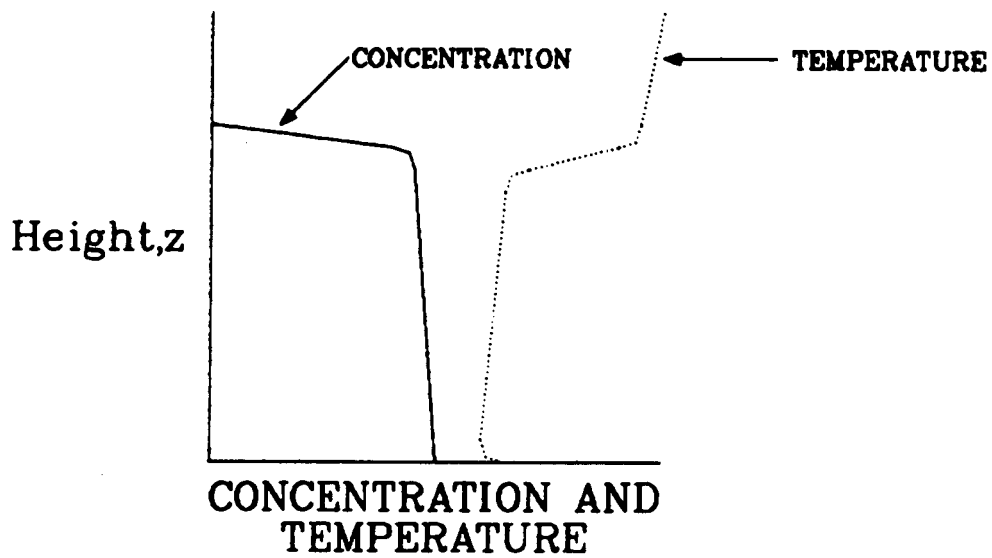


Figure C.5-1.
Expected profiles of temperature and concentration.

for a system following the slab we have

$$\frac{d}{dt} = \frac{d}{dx} \frac{dx}{dt} = u \frac{d}{dx} \quad ,$$

so that

$$\frac{d}{dx} \left\{ u \rho y Z \frac{dZ}{dx} \right\} = 2y g \Delta \rho Z \quad ,$$

$$u \rho y Z \frac{dZ}{dx} = \int_0^x 2y g \Delta \rho Z d\zeta \quad .$$

For conservation of energy we have:

$$2y \Delta x Z \rho C_p \Delta T = 2y h \Delta x (T_G - T) \Delta t + \Delta(2y Z \Delta x) \rho_a \int_T^{T_a} C_{pa} d\gamma$$

For conservation of mass we have:

$$x \rho_H 2y Z \Delta x u = C_H$$

the total mass flow of hydrogen is constant. With these equations together with the equation of state, relationships governing heat capacities and descriptions for y as a function of x , the change in hydrogen concentration as a function of downwind distance can be described.

A key item in this treatment is the heat flow from the ground to the hydrogen cloud. Near the ground it was assumed that turbulent heat transfer would occur. In this case the heat transfer coefficient, h , is given by¹

$$h = \frac{k}{x} (.0289) Pr^{1/3} \left(\frac{ux}{\nu}\right)^{0.8} ,$$

where

x is the downwind distance

k is the thermal conductivity

Pr is the Prandtl Number

u is the wind velocity

ν is the kinematic viscosity.

For this work, the thermal conductivity was calculated by the approximation.²

$$k = \left(\tilde{C}_p + 1.25 \times \frac{1.987}{M}\right) \mu .$$

For the viscosity μ_a of air, the following relation was used.³

$$\mu_a = 6.895 \times 10^{-5} (T/100)^{0.893} \text{ gm cm}^{-1} \text{ sec}^{-1}$$

and for hydrogen,⁴

$$\mu_H = 3.893 \times 10^{-5} (T/90)^{0.693} \text{ gm cm}^{-1} \text{ sec}^{-1} .$$

For mixtures of two gases the viscosity μ_m , is given by⁵

$$\mu_m = \frac{\chi \mu_H}{\sum_i \phi_{iH} \chi_i} + \frac{(1-\chi) \mu_a}{\sum_i \phi_{ia} \chi_i}$$

where

$$\phi_{aa} = 1 = \phi_{HH}$$

$$\phi_{aH} = \frac{\left[1 + \sqrt{\mu_H/\mu_a} (M_a/M_H)^{1/4} \right]^2}{2\sqrt{2} \sqrt{1 + M_H/M_a}}$$

$$\phi_{Ha} = \frac{\left[1 + \sqrt{\mu_a/\mu_H} (M_H/M_a)^{1/4} \right]^2}{2\sqrt{2} \sqrt{1 + M_a/M_H}} .$$

Similarly for the thermal conductivity of the mixture we have,⁶

$$k_m = \frac{\chi k_H}{\sum_i \phi_{iH} \chi_i} + \frac{(1-\chi) k_a}{\sum_i \phi_{ia} \chi_i} .$$

Relations for the heat capacity of hydrogen are based on linear fits at 30°K intervals for para-hydrogen.² The heat capacity and enthalpies for air are based on relations for a perfect diatomic gas.⁷

Another question deals with the transient heat flow from the ground to the hydrogen cloud. A full solution to the problem with a finite cloud would be a significant undertaking. However, a reasonable approximation can be developed much more simply. In order to develop this approximation we consider a semi-infinite slab with one side insulated and the other side exposed at $t = 0$ to a fluid with a lower temperature. Initially the slab is assumed to be at a uniform temperature. The excess temperature of the ground θ is given by:⁸

$$\theta = \sum_{n=1}^{\infty} A_n e^{-\lambda_n^2 \alpha t} \cos \lambda_n L ,$$

where L is the vertical height above the bottom of the ground which has been cooled, and

where the eigenvalues λ_n satisfy:

$$\cot \lambda_n \ell = \frac{\lambda_n k}{h}$$

where

k is the thermal conductivity of the slab

h is the heat transfer coefficient of the gas

α is the thermal diffusivity of the slab

ℓ is the width of the slab

t is the time.

The A_n are given by:

$$A_n = \frac{2\theta_0 \sin \lambda_n \ell}{\lambda_n \ell + \sin \lambda_n \ell \cos \lambda_n \ell} .$$

Strictly speaking this treatment would apply only to an infinite fluid with fixed temperature. However, in our case the fluid temperature varies with downwind distance and also with time. These difficulties are ignored in this treatment and the excess temperature is used as its local value. In addition, the time is lagged by the amount x/u so that the first parcel will be exposed to the surface temperature T_G throughout its travel. The parcel leaving at time t will be exposed to

$$T_G(x) - T_{Go}(x) = \sum_{n=1}^{\infty} A_n e^{-\lambda_n^2 \alpha t} \cos \lambda_n \ell .$$

In this way transient effects associated with the cooling of the soil can be addressed.

Results

With the simple model used here, the data suggest that during stable conditions heating by the soil will not be sufficient to produce marked increases in the rate of dispersion for large spills over brief periods of time. For smaller spills spread over large areas soil heating becomes much more important. Also with large spills over longer periods of time the buoyancy effect can account for significant dilution. Unfortunately, even the enhanced dilution produced by soil heating is not sufficient to keep the plume from a large spill from extending beyond 50 kilometers.

The transient analysis suggests that the soils used here, coarse gravelly earth, would be able to sustain significant heat releases over the period of major spills. Figure C.5-2 depicts the dilution of a hydrogen spill with initial cloud dimensions 12.5 meters height and 400 meters crosswind width. These dimensions are based on equal mole fractions of air and hydrogen with an equilibrium temperature of approximately 155 K. These conditions approximate a 3 million gallon spill with a duration of 1400 seconds. Although the duration of the spill is only 1400 seconds, the hydrogen may drift downwind for a longer time. When the hydrogen cloud drifts past some point downwind it may be combustible. Of course, at any given point the duration of a combustible cloud in the immediate vicinity is rather short. If there had been no heating this model would have provided only horizontal dilution with a mole fraction concentration at 50 kilometers of 0.158.

One reason the dilution is not more rapid relates to the slight differences between the heat capacity of hydrogen and that of air. In the range of interest, hydrogen has a slightly higher heat capacity so that the equilibrium temperature reached after mixing ambient air and cold hydrogen is such as to produce negative buoyancy. Thus much of the soil heating merely compensates for the difference in heat capacities. In the real world there are two effects which would affect the buoyancy of the plume. The first is the role of water vapor. The heat of condensation would tend to produce a buoyant plume upon mixing which would accelerate mixing and dilution. On the other side of the coin, the conversion from para-hydrogen to ortho-hydrogen would diminish buoyancy.

There is another question which is worthy of study. In this model the entire plume must be buoyant in order for vertical mixing to occur. In the atmosphere when a cold air mass passes over heated land, mixing occurs for the

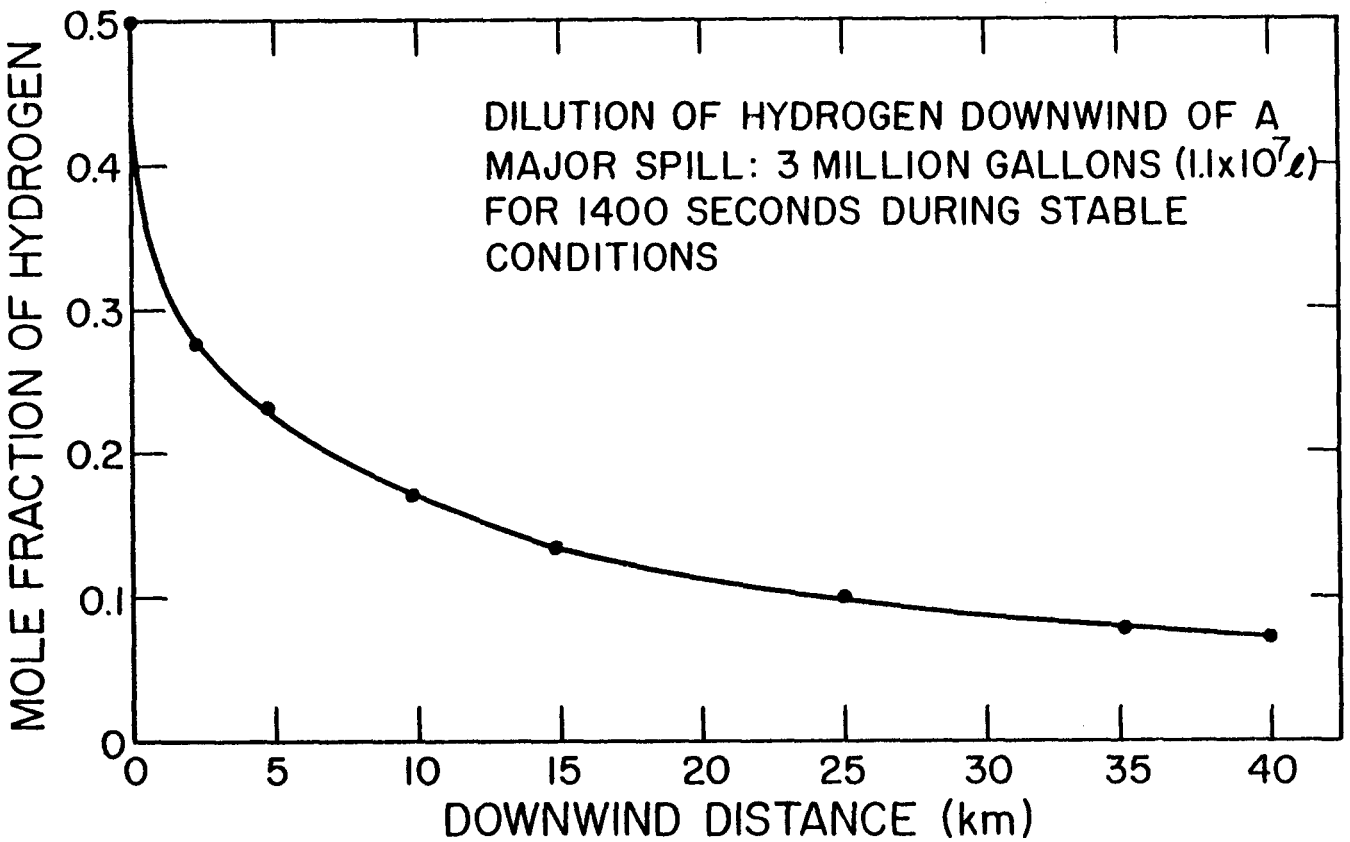


Fig. C.5-2.

Atmospheric dispersion of a three million gallon LH_2 spill of 1400 second duration. The time required for the cloud to travel to the indicated downwind distance is not shown.

portion of the air with neutral buoyancy rather than only positive buoyancy. On this basis the dilution would be expected to be enhanced over that calculated with the model described above. In this context the fact that hydrogen has a much lower lapse rate - 0.068 K/100 m as opposed to air 0.98 K/100 m - is significant. This means that air parcels containing hydrogen in a neutral atmosphere will act as though the atmosphere were significantly unstable.

Neutral Buoyancy Approach

Another way to address the dispersion of a hydrogen cloud over a warm soil is to use an approach similar to that used to describe mixing which occurs as cold air from a large body of water moves over heated land. In this case the top of the mixed layer has the same density as the stable air at the same point. Below the top of the layer the temperature distribution is approximately adiabatic. The height of the mixed layer grows as the air next to the ground is warmed. With the temperature of the top of the layer defined and the temperature distribution defined within the layer; the energy equation can be used to determine the rate of growth of the layer as a function of energy added to the layer.

In the case of hydrogen, the density of the top of the plane is set equal to the ambient density of the air at the same height. This leads to the following relation for the mean temperature $\bar{T}$ of the mixed layer:

$$\bar{T} = \left[T_a + \frac{dT_a}{dZ} Z \right] \left[x \frac{R_a}{R_H} + (1-x) \right] - \frac{Z}{2} \frac{dT}{dZ} ,$$

where Z is the height of the top of the layer and $\frac{dT}{dZ}$ is the temperature gradient within the layers, which is given by

$$\frac{dT}{dZ} = \frac{x C_{pH} \frac{dT_{Ho}}{dZ} + (1-x) C_{pa} \frac{dT_{ao}}{dZ}}{x C_{pH} + (1-x) C_{pa}} .$$

In this description C_{pH} and C_{pa} refer to the specific heats at constant pressure of hydrogen and air on a gram mole basis. The adiabatic lapse rates for pure hydrogen and pure air are denoted $\frac{dT_{Ho}}{dZ}$ and $\frac{dT_{ao}}{dZ}$ respectively.

The change in mean temperature after travel time t is merely:

$$\begin{aligned} \Delta \bar{T} = \Delta Z \left\{ \frac{dT_a}{dZ} \left[x \frac{R_a}{R_H} + (1-x) \right] - \frac{1}{2} \frac{dT}{dZ} - \frac{x}{Z} \left\{ \left[\frac{R_a}{R_H} - 1 \right] \left[T_a + Z \frac{dT_a}{dZ} \right] \right. \right. \\ \left. \left. \left[- Z \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right] \right\} \right\} + \Delta \bar{T} (x/T) \left\{ \left[\frac{R_a}{R_H} - 1 \right] \left[T_a + Z \frac{dT_a}{dZ} \right] \right. \\ \left. - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right\} - \Delta y \frac{x}{y} \left\{ \left[\frac{R_a}{R_H} - 1 \right] \left[T_a + Z \frac{dT_a}{dZ} \right] - \frac{Z}{2X} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right\}. \end{aligned}$$

Since $\Delta \bar{T}$ can be determined from the energy equation, the above equation may be solved for ΔZ

$$\begin{aligned} \Delta Z = \left\{ \Delta T \left[1 - \frac{x}{T} \left(\frac{R_a}{R_H} - 1 \right) \left(T_a + Z \frac{dT_a}{dZ} - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right) \right] \right. \\ \left. + \Delta y \left(\frac{x}{y} \right) \left\{ \left[\left(\frac{R_a}{R_H} - 1 \right) \left(T_a + Z \frac{dT_a}{dZ} \right) - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right] \right\} \right\} \div \\ \left\{ \frac{dT_a}{dZ} \left[x \frac{R_a}{R_H} + (1-x) \right] - \frac{1}{2} \frac{dT}{dZ} - \left\{ \frac{x}{Z} \left[\left(\frac{R_a}{R_H} - 1 \right) \right. \right. \right. \\ \left. \left. \left(T_a + Z \frac{dT_a}{dZ} \right) - \frac{Z}{2} \frac{d}{dX} \left(\frac{dT}{dZ} \right) \right] \right\} \right\}. \end{aligned}$$

where

$$\frac{d}{dx} \left(\frac{dT}{dz} \right) = \frac{C_{pH} - C_{pa} \left(\frac{dT_{Ho}}{dz} - \frac{dT_{ao}}{dz} \right)}{[xC_{pH} + (1-x)C_{pa}]^2} .$$

Equations for ΔZ and ΔT can then be solved numerically.

The effect of water vapor can be easily incorporated into the approach. First, the partial pressure of water vapor in the ambient atmosphere is calculated as

$$PP_{H2O} = .02039 (RH/100) \text{ Exp } \left\{ 18.198 \left[1 - 293/T_a + \frac{ZdT_a}{dz} \right] \right\} .$$

The mass of water in unit volume is then

$$m_{H2O} = 804 \left(\frac{273}{T_a + \frac{ZdT_a}{dz}} \right) PP_{H2O} \quad (\text{gm/m}^3) .$$

The energy released for condensation and freezing is

$$HV = 620 \times 804 \left(\frac{273}{T_a + \frac{ZdT_a}{dz}} \right) .$$

Results of the Neutral Buoyancy Approach

With the modified approach, virtually identical results were obtained. Furthermore the addition of water vapor makes relatively little difference during cold dry conditions (273⁰K and 35% relative humidity).

For smaller spills, dilution is fairly rapid but much of this is horizontal dilution unrelated to heating by soil. Figure C.5-3 depicts dilution from a 1500 gallon spill with a 60 s duration. In this context neither soil type, gravelly soil or clay, makes significant difference in the dilution. Furthermore, the dilution at the end of the spill is not much less than that at the beginning of the spill which indicates that the soil is capable of supplying similar amounts of heat over the entire duration of the spill.

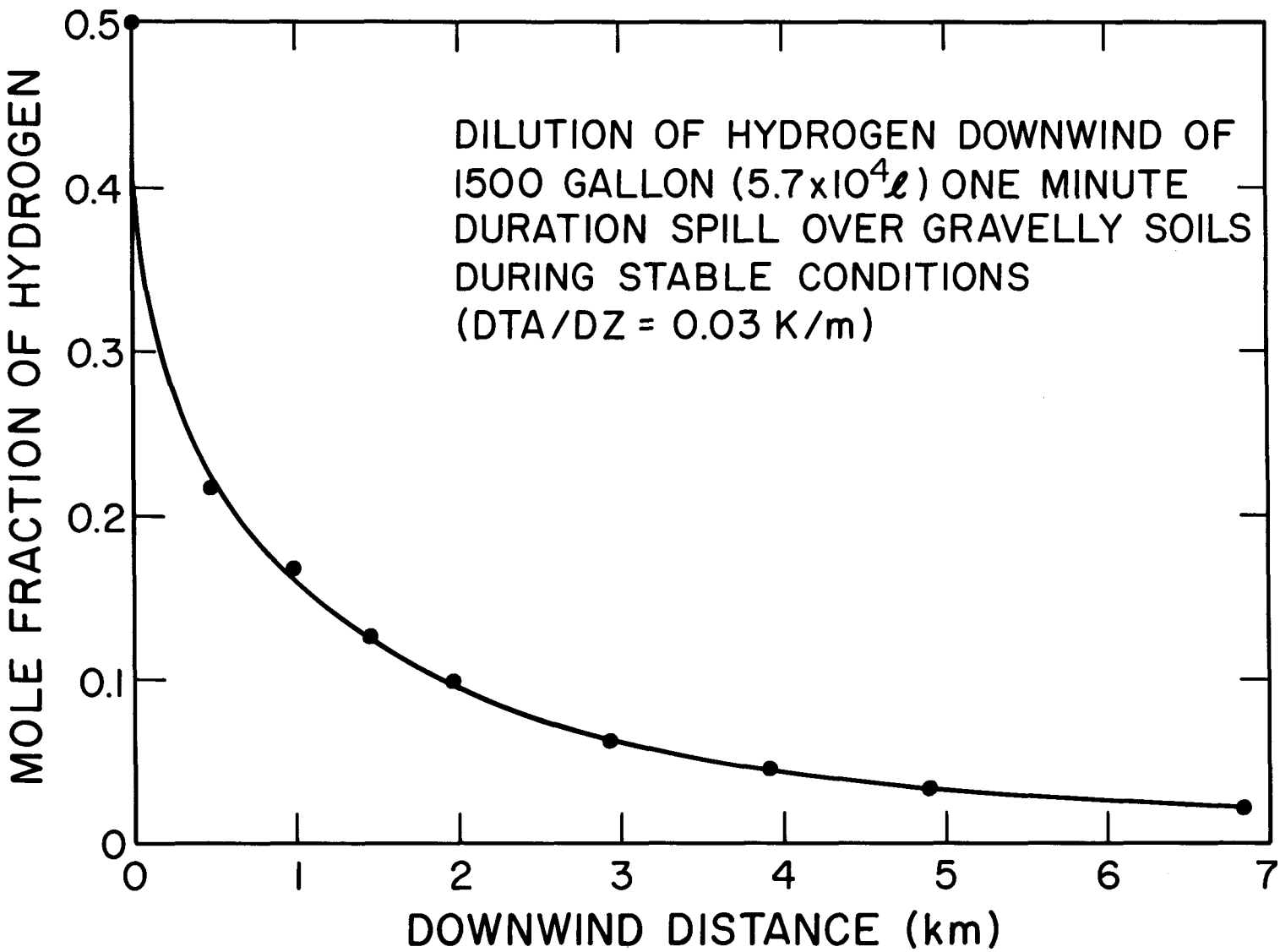


Fig. C.5-3.
Atmospheric dispersion of a 1500 gallon LH_2 spill.

The fact that the mixed layer does not expand in depth more rapidly probably relates to the major changes in density of the hydrogen-air mixture which occur with small changes in the hydrogen-air ratio. Heating of the layer causes it to increase in depth until the additional dilution produces a gas density equivalent to the ambient air. Since the density changes rapidly with mixing, the layer expands at a slow rate.

Conclusions

Soil warming of the hydrogen air mixture can influence the dilution; however, the rates of increased dilution are still quite low so that combustible plumes would be expected for large distances if major spills occur during stable nighttime conditions. In the Southwest, such conditions occur about 25% of the time. Another 7-15% of the time conditions might be nearly as bad.

For smaller spills dilution is more rapid and the combustible plume would extend to distances of less than 5 kilometers under conditions unfavorable for dilution.

Notation

A_n	= the nth coefficient of the eigenfunction
C_H	= total mass flow of hydrogen
C_{pH}	= specific heat of hydrogen per mol
C_p	= specific heat at constant pressure per gram
C_{pa}	= specific heat of air per mol
$\frac{dT}{dZ}$	= temperature gradient within the mixed layer
$\frac{dT_a}{dZ}$	= ambient temperature gradient before the release
$\frac{dT_{ao}}{dZ}$	= adiabatic lapse rate for air
$\frac{dT_{Ho}}{dZ}$	= adiabatic lapse rate for hydrogen
g	= acceleration due to gravity
HV	= energy released by condensation and freezing of moisture in the air
h	= heat transfer coefficient
k	= thermal conductivity
L	= vertical height above the bottom the the ground which has been cooled
ℓ	= depth of the ground affected
M	= molecular weight
m_{H_2O}	= mass of water per unit volume of air
M_H	= molecular weight of hydrogen
PP_{H_2O}	= partial pressure of water vapor
Pr	= Prandtl number
R_a	= gas constant for air
R_H	= gas constant for hydrogen
RH	= relative humidity
T	= temperature of the fluid
T_a	= ambient temperature at ground level
T_G	= ground temperature
t	= time
u	= wind velocity
$w(z_0)$	= vertical velocity of the given streamline of the mixed layer described by initial height z_0

x = downwind distance
 y = crosswind half width of the plume
 Z = the height of the mixed layer
 z = initial height of a given streamline of the mixed layer
 α = thermal diffusivity of the ground
 γ = dummy integration variable which corresponds to temperature
 Δx = alongwind distance element of the plume
 $\Delta \rho$ = difference between ambient density and plume density
 ΔT = change in temperature of the fluid
 ΔZ = change in the height during the time Δt
 $\Delta \bar{T}$ = change in the temperature of the mixed layer during the time Δt
 θ = excess temperature
 λ_n = the nth eigenvalue for the solution of the ground heat transfer problem
 μ = viscosity
 ν = kinematic viscosity
 ξ = dummy integration variable corresponding to Z
 ρ = density of the mixed layer
 ϕ_{iH} = coefficient used for computing viscosity of mixture between other species and hydrogen
 ϕ_{aa} = coefficient used for computing viscosity of mixture between air and air
 ϕ_{HH} = coefficient used for computing viscosity of mixture between hydrogen and hydrogen
 ϕ_{Ha} = coefficient used for computing viscosity of mixtures between hydrogen and air
 ϕ_{aH} = coefficient used for computing viscosity of mixtures between air and hydrogen
 X = mole fraction of hydrogen
 ζ = dummy integration variable corresponding to x
 subscripts
 a = air
 H = hydrogen
 i refers to the i th component
 m = mixture
 o refers to initial condition

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APPENDIX D

TRANSMISSION OF HYDROGEN

D.1 Hydrogen-Natural Gas Blends

One of the first large scale applications of hydrogen in the commercial and residential markets will most likely be the blending of hydrogen with natural gas to supplement natural gas supplies. Several studies have indicated that mixing of hydrogen and natural gas is technically possible and economic in many applications.^{1,2} To date this work is concerned primarily with the introduction of hydrogen into distribution systems rather than transmission systems. This results partly from the fact that the studies have been concerned mainly with using existing excess hydrogen sources which lend themselves to introduction into the distribution system. Hydrogen also may be blended into the transmission system. Sources of hydrogen located near transmission systems could be gradually introduced into the system, with the necessary modifications due to the combustion and pumping properties of hydrogen blends being made as the percent of hydrogen increases.

It is not within the scope of this program to assess the use of hydrogen blends in distribution systems. However we will report on this work because of its relevance to the introduction of hydrogen blends into transmission systems. Public Service Electric and Gas Company (PSE&G) of Newark, New Jersey was funded by DOE to study hydrogen-natural gas blends in their gas distribution system.¹ They investigated the following areas:

- (a) Flow of gas blends in distribution systems, mixing points for the hydrogen in distribution systems, and regulatory standards.
- (b) Combustion tests of hydrogen-natural gas blends in burners and appliances.
- (c) Leakage tests of selected distribution system components.

The studies resulted in the following principal findings:

1. Most existing natural gas distribution systems could adequately transport 20% blends of hydrogen by volume with little or no modification.
2. The best point of admission of the hydrogen into a natural gas distribution system would be at the metering and regulating stations supplying a particular distribution system.

3. The impact of hydrogen-natural gas blends on state regulatory standards appears to be minimal for PSE&G but requires further study for various National Codes and for other states.
4. Gas blends containing more than 6 - 11% hydrogen are the limiting mixtures for target type pilot burners.
5. Gas blends containing more than 20 - 22% hydrogen are the limiting mixtures for main burners operating in the open.
6. Gas blends containing more than 22 - 25% hydrogen are the limiting mixtures for main burners tested in appliances.
7. Modification of the orifice in target pilots or increasing the supply pressure to a minimum of 7 inches water column will permit the use of gas blends with 20% hydrogen.
8. Cast-iron joints and steel joints which did not leak with natural gas did not leak with blends of up to 40% hydrogen in natural gas.
9. Cast-iron joints and steel joints which had small leaks with natural gas did not leak at a higher rate with blends of up to 40% hydrogen in natural gas.
10. Cast-iron joints which had large leaks with natural gas showed a detectable increase in leakage as the hydrogen level in the gas blend increased.
11. Efforts to determine if the permeability of polyethylene tubing increases with increasing concentrations of hydrogen in natural gas, and with aging of the plastic, were inconclusive.
12. There was no preferential leakage of hydrogen in any of the joints tested using blends with up to 40% hydrogen in natural gas.

After considering the results of this study, PSE&G is currently distributing hydrogen-natural gas blends with no serious problems to date. They purchase oil refinery off gases and blend this with natural gas. Details of this work will be available in the near future.

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1. "Blending of Hydrogen in Natural Gas Distribution Systems Volumes 1, 2, and 3," US Department of Energy report CONS-2925-1, -2, and -3 (May 1978).
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D.2 Statistical Analysis of Natural Gas Transmission System

D.2.1. Introduction. In most cases, the most economical method for the transmission of large quantities of hydrogen is via high pressure gas transmission lines. One aspect of the LASL assessment program was to investigate any increased risk due to hydrogen gas transmission. Since a large transmission network is in existence for natural gas, we have made a study of the incidents in the natural gas system to determine if trends exist which should be considered in the design and operation of hydrogen or hydrogen-natural gas blend transmission systems. We have analyzed the data using statistical techniques which are briefly discussed. These results indicate several significant trends in the accident data for natural gas systems which are pertinent to hydrogen systems.

D.2.2. Data Base. Parameters of the natural gas transmission system which were statistically analyzed were the following:

- a. Leakage (expressed as leaks per thousand miles of pipeline/year)
- b. Age of pipelines
- c. Nominal diameter of pipelines
- d. Causes of leaks (corrosion, external effects, etc.)
- e. Fatalities from accidents from gas leakage
- f. Amount of gas lost during an accident
- g. Pipeline construction material.

The accuracy of any statistical analysis depends almost entirely on the completeness of the data base. The data, on the above mentioned parameters for natural gas systems, used in this report are not complete. It would be virtually impossible to obtain a complete data base for two reasons. First, some of the information on leakage and causes is not known. Secondly, the natural gas transmission companies which were contacted would not release data. Most companies stated it was against company policy to release accident data. The data which we used in the following analysis were obtained primarily from the following sources:

- 1) National Transportation Safety Board reports.
- 2) Annual reports on the administration of The Natural Gas Pipeline Safety Act of 1968, DOT.¹

- 3) "Energy Material Transport, Now through 2000 System Characteristics and Potential Problems: Task 4 Report Natural Gas Transportation."²

In addition some data on age of pipelines and pressures were obtained through private conversations.

D.2.3. Statistical Techniques. It is beyond the scope of our report to give details of the statistical and computer techniques used to analyze the data. Because of the limited data base available, high confidence cannot be placed on the detailed results. However, the general trends indicated may be significant and are of interest.

The data were statistically analyzed using a multiple regression analysis to a function of the form

$$Y = A_0 + A_1X_1 + A_2X_2 + \dots$$

where Y is the dependent variable (fatalities or leakage) and $X_1, X_2 \dots$ are the independent variables such as age of pipeline or material of pipe. Various combinations of the dependent variables were examined to determine which ones were statistically significant. We examined the following dependent variables:

- a) Leakage per 1000 miles of pipe
- b) Corrosion leakage
- c) Fatalities from accidental releases of natural gas

These were studied as a function of various combinations of the following independent variables.

- a. Age of pipe
- b. Year of pipeline installation
- c. Nominal pipeline diameter
- d. Pipeline protection methods used
- e. Welds in pipeline
- f. Volume of gas leaked
- g. Pipeline material
- h. Pipeline thickness
- i. Pipeline pressure

Because of the limited data, in many cases degree of correlation could not be determined.

In Tables I through VI we give the raw data on which the results given in the text are based.

TABLE D-I

Leakage by Age of Pipeline
(Leaks per 1000 miles per year)

Obs.	Year	Age in Years	Leakage
1	1970	45	9.92
2	1970	35	2.14
3	1970	25	1.14
4	1970	15	0.83
5	1970	5	0.54
6	1971	46	8.91
7	1971	36	3.08
8	1971	26	1.65
9	1971	16	0.95
10	1971	6	0.82
11	1972	47	9.41
12	1972	37	3.24
13	1972	27	1.81
14	1972	17	0.94
15	1972	7	0.71
16	1973	48	11.38
17	1973	38	3.18
18	1973	28	1.45
19	1973	18	1.36
20	1973	8	0.93

TABLE D-II

Leakage of Pipe by Nominal Diameter
(Leaks per 1000 miles per year)

Obs.	Year	Normal Diam. in Inches	Leakage
1	1970	1	2.74
2	1970	3	1.19
3	1970	5	1.68
4	1970	9	1.28
5	1970	5	1.18
6	1970	1	1.11
7	1970	17	0.62
8	1970	21	0.72
9	1970	25	0.34
10	1971	1	3.38
11	1971	3	1.76
12	1971	5	1.73
13	1971	9	1.43
14	1971	13	1.18
15	1971	17	1.15
16	1971	21	1.47
17	1971	25	0.20
18	1971	29	0.24

TABLE D-III
Corrosion Leakage by Age of Pipeline
(Leaks per 1000 miles per year)

Obs.	Year	Age	Leakage
1	1970	45	1.34
2	1970	35	0.17
3	1970	25	0.32
4	1970	15	0.06
5	1970	5	0.04
6	1971	46	0.93
7	1971	36	0.58
8	1971	26	0.41
9	1971	16	0.10
10	1971	6	0.09
11	1972	47	1.18
12	1972	37	0.81
13	1972	27	0.41
14	1972	17	0.17
15	1972	7	0.14
16	1973	48	1.55
17	1973	38	0.88
18	1973	28	0.10
19	1973	18	0.22
20	1973	8	0.05

TABLE D-IV

Leakage Through Body of Pipe by Age
(Leaks per 1000 miles per year)

Obs.	Year	Age in Years	Leakage
1	1970	45	511.7
2	1970	35	139.0
3	1970	25	39.4
4	1970	15	10.3
5	1970	5	15.0
6	1971	46	364.0
7	1971	36	126.7
8	1971	26	54.6
9	1971	16	15.2
10	1971	6	10.4
11	1972	47	477.4
12	1972	37	117.8
13	1972	27	68.2
14	1972	17	11.2
15	1972	7	5.7
16	1973	48	478.6
17	1973	38	127.7
18	1973	28	45.9
19	1973	18	14.6
20	1973	8	5.9

TABLE D-V

Leakage of Welds by Age
(Leaks per 1000 miles per year)

Obs.	Year	Age in Years	Leakage
1	1970	45	4.2
2	1970	35	8.1
3	1970	25	4.9
4	1970	15	1.9
5	1970	5	2.6
6	1971	46	2.6
7	1971	36	7.2
8	1971	26	3.3
9	1971	16	1.5
10	1971	6	1.9
11	1972	47	6.1
12	1972	37	3.3
13	1972	27	3.5
14	1972	17	1.9
15	1972	7	1.7
16	1973	48	4.1
17	1973	38	5.3
18	1973	28	2.4
19	1973	18	1.4
20	1973	8	1.1

TABLE D-VI

Fatalities as a Function of Age of Pipe
and Amount of Gas Lost During Accident

Fatalities	Age of Pipe	Total gas leak during rupture, SCF
17	21	1.03×10^{11}
0	18	5.3×10^7
0	28	2.35×10^{10}
6	27	6.65×10^8
0	17	6.20×10^9
3	44	7.92×10^{10}

D.2.4. Results. This study was concerned only with data from natural gas transmission systems. Results for distribution systems may differ significantly. In fact, some data on distributions systems were analyzed by similar techniques and the trends opposite from those we report here were found in several cases. Some of the trends reported here seem obvious however it is important to demonstrate that they are substantiated by the data and the statistical technique.

Dependence of transmission pipeline leakage on various parameters.

The leakage is defined as the measured number of leaks per year per 1000 miles of transmission pipelines. These are only the leaks reported. We do not know the number of unreported leaks located by the transmission line companies or the number of undetected leaks. The factors on which we found the leakage to be dependent were: year of installation of the pipeline, age of the pipeline, welds in the pipeline, nominal diameter of the pipe, and corrosion protection method used on the pipeline. Variables for which the data did not exist, or were insufficient to draw any conclusions, were: pipeline material, operating pressure, and pipeline wall thickness.

The dependence of number of leaks on the age of the pipeline is as expected, as the pipe ages the leakage increases. However, the analysis shows that the leakage in 1966 for a 30-year-old pipe (installed in 1936) would be higher than the leakage in 1977 for a 30-year-old pipe (installed in 1947). This implies an improved technology for either the manufacture, installation, or corrosion protection of the newer pipeline. The older pipeline systems (installed in 1920s or 1930s) also exhibit a significantly higher leakage.

The dependence found for the leakage on nominal pipeline diameter was surprising. The analysis indicates that for the smaller diameter pipelines a higher leakage exists than for systems having larger diameters. This could reflect the higher quality control in welds and pipeline construction which may be characteristic of the large diameter transmission lines or also larger lines may be more recent.

Corrosion is the most important cause of leaks in transmission pipelines, accounting for approximately 75% of the reported leaks. The next most important cause of leaks is material failure (excluding corrosion induced leaks), which accounts for approximately 10%. Significantly, outside forces and construction defects account for only 2-3% each. As expected, corrosion induced failures increase monotonically with age of the pipeline. Protection of the pipeline, either by cathodic protection or coating, drastically reduces the number of leaks as shown in Table VII.

The analysis of data on the relationship between the number of fatalities and the amount of gas leaked was performed. However the data were so limited that the results are inconclusive. The analysis did reveal the interesting point that the amount of gas leaked in each of the six accidents analyzed was approximately the same, about 10^{10} scf.

TABLE D-VII

Effect of Coating and Cathodic
Protection on Corrosion Leakage
(Leaks per 1000 miles per year)

<u>Year</u>	<u>Coating</u>		<u>Cathodic Protection</u>	
	<u>Coated</u>	<u>Bare</u>	<u>Yes</u>	<u>No</u>
1970	0.11	0.64	0.11	0.74
1971	0.11	0.53	0.09	0.71
1972	0.18	0.77	0.17	0.79
1973	0.16	0.65	0.19	0.63

D.2.5. Implications for Hydrogen Gas Transmission Systems. One clear conclusion from this work is that a more complete data base for systems transmitting hydrogen needs to be tabulated and made available. This is necessary to understand the problems which may occur due to hydrogen gas transmission. As shown from the paucity of the data on natural gas systems it is difficult, to obtain statistically the most meaningful results on the problems in natural gas systems.

These results also show that if existing natural gas transmission lines are to be used for hydrogen gas transmission each line has to be examined on an individual basis. Because the leakage depends on so many variables no general statements can be made concerning use of hydrogen in these lines.

D.3 Flame Propagation Studies

Hydrogen is now being used as a supplement to natural gas in a few natural gas distribution systems (see Appendix D.1). Amounts up to 10% by volume can be added without requiring modifications in the distribution or use equipment. We have made an initial effort to study the change in combustion properties of 10% hydrogen-natural gas mixtures with air to determine if the additional hydrogen significantly affects the burning characteristics, because studies of the increase in the detonability of the gas in confined geometry have indicated that relatively small additional amounts of impurities such as propane in methane gas significantly change the burning characteristics and may increase its detonability.

We subcontracted this work to the Terminal Effects, Research and Analysis (TERA) group at New Mexico Institute of Mining and Technology. Figure D.1-1 shows the experimental arrangement used. The basic plan was to contain a stoichiometric mixture of fuel and air in an 18-m long by 0.5-m diameter cardboard tube lined with 0.075-mm thick plastic tubing. Viewing holes were cut in the side of the tubing every 0.45 m for photographing of the flame front. Sample bottles were connected to the ends of the tube to take samples which could be analyzed later to determine the composition of the gas. A bare wire surrounded by fine metal wire was used to ignite the mixture.

Several experiments were planned starting with pure natural gas-air, and then hydrogen-natural gas-air mixtures. Due to technical problems encountered in the first two experiments, significant conclusions could not be drawn. Although we believe that these problems could be solved, time limitation

caused by the termination of the assessment program prevented the continuation of this work.

ACKNOWLEDGMENTS

The calculations and data collection for this section were done by Dr. Asok Ray at the Texas Tech University.

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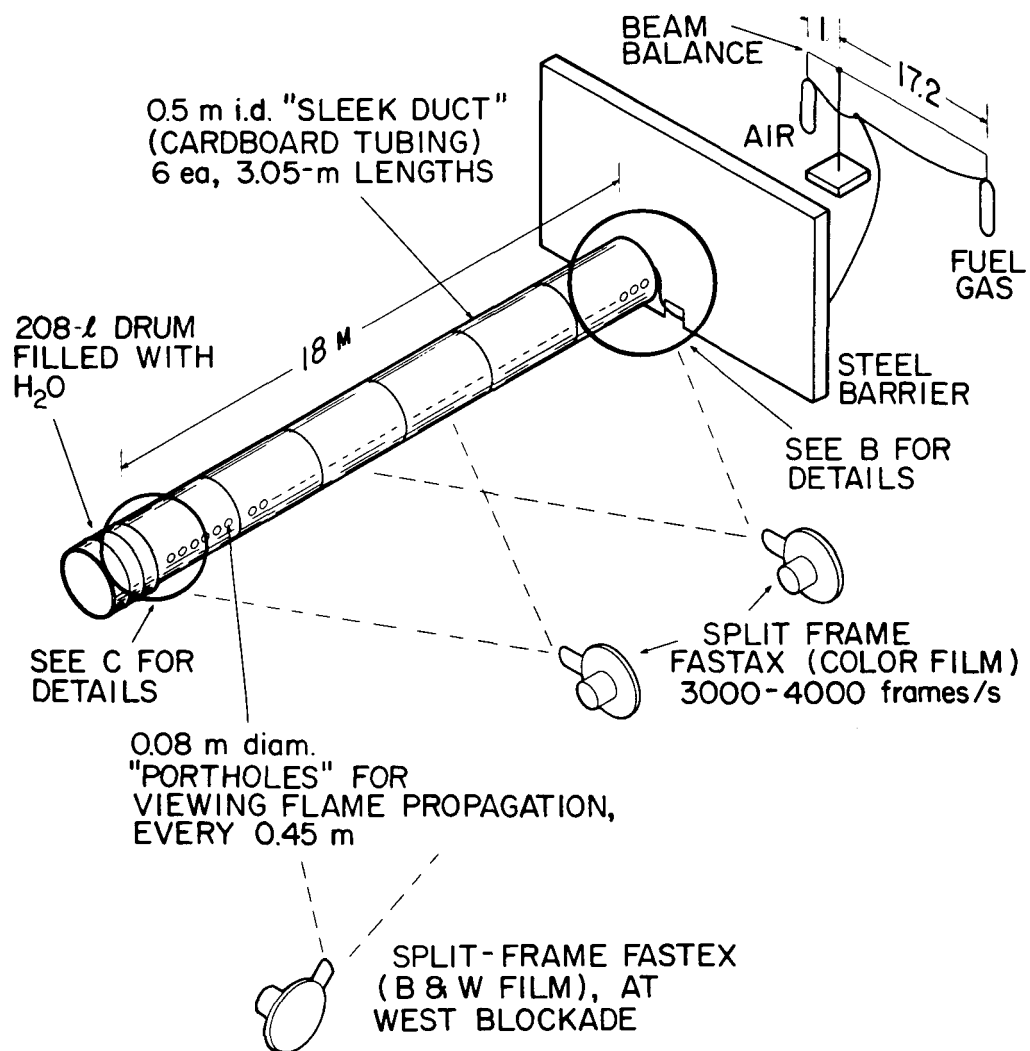


Fig. D.3-1a.
Schematic of overall experimental arrangement.

B) INLET-END DETAILS

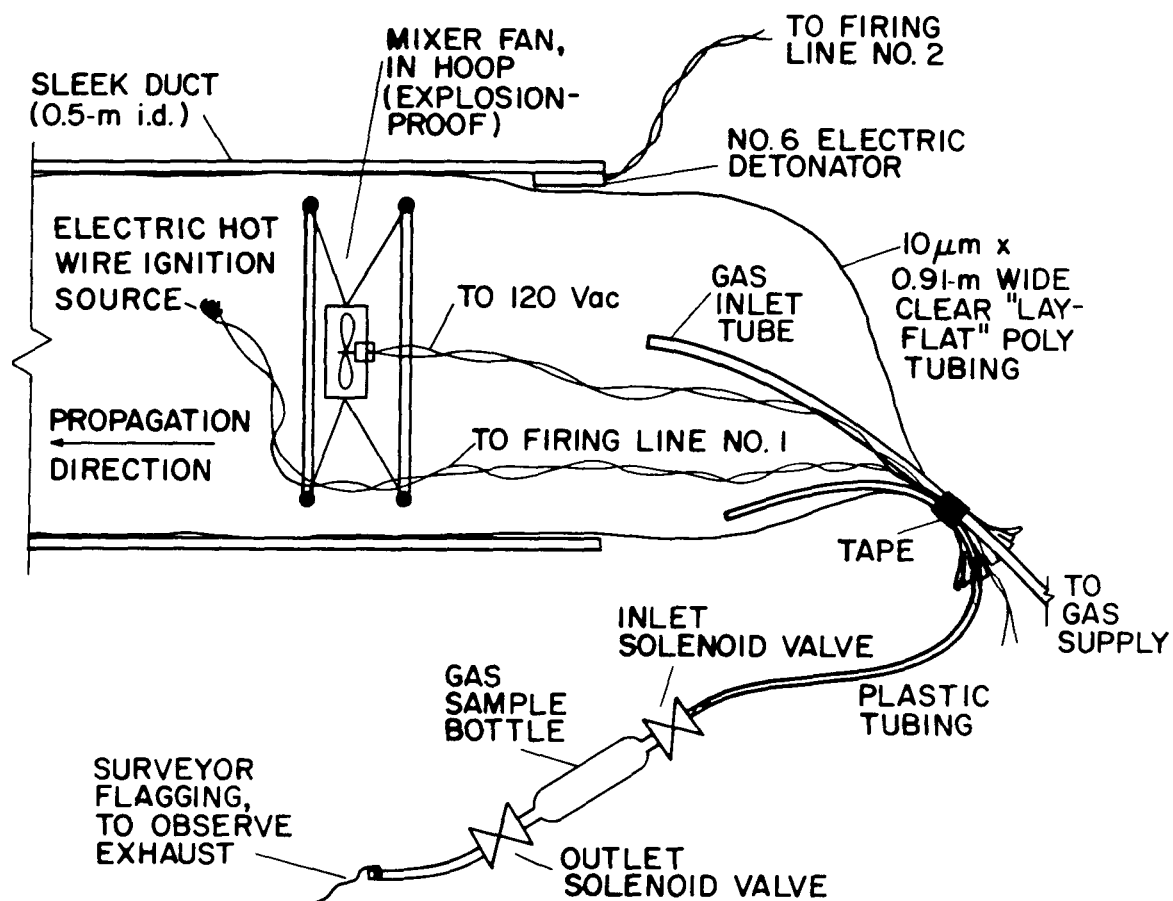


Fig. D.3-1b.

Inlet-end details of experimental arrangement.

C) TERMINAL-END DETAILS

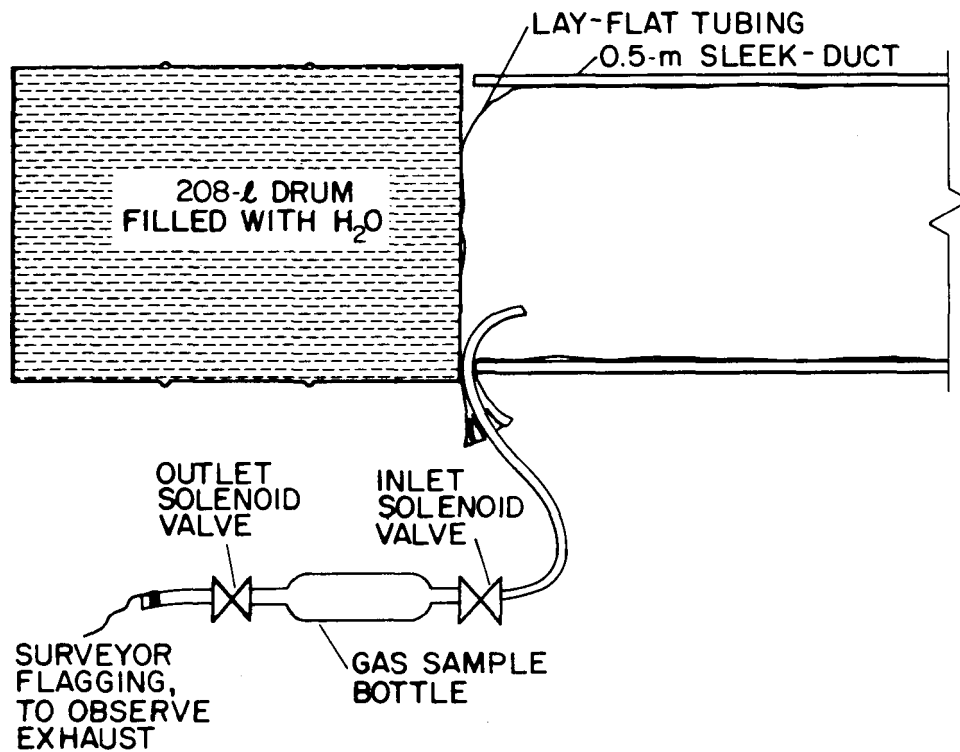


Fig. D.3-1c.

Terminal-end details of experimental arrangement.

APPENDIX E

END USES OF HYDROGEN

E.1 Control of Nitrogen Oxide Emissions from Internal Combustion Engines

Experiments done, by contract, under the direction of Professor Robert Adt at the University of Miami were aimed toward the selection and testing of a catalyst to utilize naturally occurring or supplemental hydrogen in the exhaust pipe of hydrogen-fueled vehicles to reduce NO to N₂ and H₂O. The results of this work showed that the most promising catalyst (Davex 178 catalyst containing rhodium, palladium, and platinum) produced relatively high concentrations (hundreds of ppm) of NH₃ in the exhaust when operating at an equivalence ratio (fuel to air ratio) above stoichiometric ($\phi > 1.0$). At $\phi < 0.92$, the catalyst was no longer effective in reducing NO. In the very limited operating range between ($0.92 < \phi < 1.0$), significant NO reduction without NH₃ production was possible. The complete report is reproduced here.

FINAL REPORT

CATALYTIC REDUCTION OF NO_x
IN HYDROGEN-FUELED AUTOMOBILE EXHAUST

ORDER NO. NP8-6684H

October 31, 1979

PROJECT DESCRIPTION

Nitrogen oxide pollutants present in exhaust gases from hydrogen-fueled internal combustion engines potentially can be decreased or eliminated by catalytically reducing the oxides, using naturally occurring or supplemental free hydrogen in the exhaust. Work was desired toward the development and testing of appropriate catalysts and systems to achieve this.

Toward this end, following an analysis of the available literature, a catalyst most likely to satisfy the following criteria was selected for testing:

- must function with no CO in the exhaust
- must function with an increased oxygen content in the exhaust
- must be stable in the oxygen and temperature environment of the exhaust
- must not produce high NH_3 levels in the exhaust

The selected catalyst was fabricated as a bed which was installed on a test engine. Measurements were made of NO_x , NH_3 and O_2 concentrations in the exhaust gas as a function of fuel/air equivalence ratios, while recording appropriate system parameters.

EXPERIMENTAL APPARATUS

Ammonia concentration was measured with a Beckman Model 864 Non-Dispersive Infrared Ammonia Analyzer. This analyzer was chosen because of its high accuracy, relatively low cost, and availability of usable sensitivity ranges. The ranges 0-2000 and 0-10000 ppm were chosen because the literature survey revealed as much as 100% of the NO_x produced could be catalytically converted to ammonia. Thus, the highest NO_x reading recorded to date on the University of Miami Hydrogen Engine project was chosen as an upper limit. An optical filter was installed in the analyzer to eliminate interference due to water vapor.

The span gases chosen for testing and calibrating the analyzer were ordered from Linde Co. This supplier was chosen because other vendors were unable to provide the required accuracy of their gas mixtures. The four concentrations chosen were 9400 ppm, 6948 ppm, 1880 ppm and 500 ppm ammonia in nitrogen.

The catalyst was tested on a single cylinder version of the four-cylinder, 1600 cc Toyota 2TC engine. The engine was run at 1800 rpm and 51 bmepp*. A Beam carburetor was used to induct hydrogen into the engine, and a motor-generator dynamometer was used for load control. The catalyst was located approximately two feet downstream of the exhaust port. A chromel-alumel thermocouple was installed in the catalyst bed. Sample taps were located far enough upstream and downstream of the catalyst to insure that backflow would not affect the results.

The sampling system consisted of heated stainless steel and teflon sample line to transport the gas from the exhaust system to the analyzer console. Heated line is used to prevent the water and ammonia from condensing in the system. Also, condensation in the sample system would foul the analyzers and produce erroneous readings. In addition to the heated line, the system was operated under a vacuum to insure that condensation would not occur inside the NH_3 analyzer. A Thomas Co. sample pump along with a Thermoelectron heated filter is incorporated into the system to provide the filtered flow rate required by the analyzers. Sample flow rate is measured with a Brooks rotameter. A Linde Co. corrosion resistant, single-stage regulator is used to dispense the span gas. All materials used in the sampling system are either teflon or stainless steel. This was done because of the corrosive nature of the sample gas.

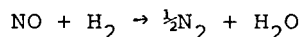
* The load which represents 51 bmepp in the four-cylinder version of this motor.

It should be noted that NO_x is catalytically active with stainless steel, but not at the^xrelatively low system temperatures used (approximately 200^oF).

The catalyst, obtained from W. R. Grace Co., is of the three-way type that will be used in 1980 on the California version of GM's turbocharged V-6. W. R. Grace Co. refers to this catalyst as Davex 178 Three-Way Catalyst. The active ingredients in the catalyst are rhodium, palladium and platinum with small amounts of base metals. The catalyst is supported on 5-7 mesh spherical alumina pellets. Space velocities range from 73,000 to 84,000 hr⁻¹.

SELECTION OF A NO REDUCTION CATALYST

The catalytic reduction of NO in internal combustion engine exhausts is affected by four major factors. They are: temperature, exhaust gas composition, catalyst composition and space velocity. The overall chemical reaction for NO reduction to nitrogen by hydrogen is as follows:



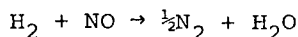
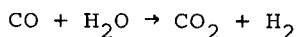
However, the actual mechanism can be much more complicated than this. The process probably occurs in two or more stages involving the reduced and oxidized states of the catalyst. Significant reactions for hydrogen-fueled IC engine exhausts are shown in Table 1. Several researchers have shown that the relative importance of the various reactions in Table 1 are dependent on the factors listed above. Thus, an examination of the effects of these variables is necessary before a suitable NO reduction catalyst can be selected.

TABLE 1 Possible Catalytic Reactions for Hydrogen Engine Exhausts

<u>Reaction</u>	<u>Desirable?</u>	<u>Reference</u>
1. $\text{NO} + \text{H}_2 \rightarrow \frac{1}{2}\text{N}_2 + \text{H}_2\text{O}$	Yes	1, 5, 9
2. $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$	Yes	1, 5, 9
3. $\text{MO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{M}$	Yes	5, 9
4. $\text{NO} + \text{M} \rightarrow \frac{1}{2}\text{N}_2 + \text{MO}$	Yes	5, 9
5. $\frac{1}{2}\text{O}_2 + \text{M} \rightarrow \text{MO}$	No	5, 9
6. $2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$	No	5, 9
7. $3\text{NO} + 2\text{NH}_3 \rightarrow 5/2\text{N}_2 + 3\text{H}_2\text{O}$	Yes	1, 9
8. $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$	Yes	9
9. $2\text{NH}_3 + 3/2\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$	Yes	1, 5
10. $2\text{NH}_3 + 5/2\text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$	No	5

EXHAUST GAS COMPOSITION

The catalytic reduction of NO to N₂, as its name implies, requires a reducing agent to perform the reduction. In the case of a hydrogen engine, where the products of combustion are H₂O, H₂, O₂, N₂ and NO, H₂ is the only reducing agent available. In contrast, a gasoline engine has CO and HC in addition to H₂ for reducing agents. In the beginning of this study, the question was raised concerning the need for CO to accomplish the reduction. The answer is that while CO is a powerful reducing agent for NO, reduction of NO by H₂ alone presents no problem. In fact, several researchers (7, 9, 11, 16) have shown that one of the basic mechanisms for NO reduction by CO occurs through the water gas shift in which CO combines with H₂O to form H₂ and CO₂. The hydrogen thus formed, in turn, reduces the NO to N₂ as shown.



Hence, it can be seen that even in the case where no H₂ was initially present, H₂ plays an important role in NO reduction. This effect was demonstrated by Shelef and Gandhi¹⁶. Several researchers (8, 9, 13, 17) also demonstrated that NO reduction by H₂, in the absence of CO, is practical with conversion efficiencies equalling those of CO.

In all cases, it was necessary to have a net reducing atmosphere in order to obtain complete conversion. Gandhi et al.⁸ defined a parameter called the "Redox Potential," which is a measure of the strength of the gas as a reducing agent. For gasoline engine exhausts, he defined the "Redox Potential" as

$$R = \frac{P_{\text{CO}} + P_{\text{H}_2} + 3nP_{\text{C}_n\text{H}_{2n}} + (3m + 1)P_{\text{C}_m\text{H}_{2m+2}}}{P_{\text{NO}} + 2P_{\text{O}_2}}$$

which reduces to

$$R = \frac{P_{\text{H}_2}}{P_{\text{NO}} + 2P_{\text{O}_2}}$$

for hydrogen engine exhausts. Thus, for $R > 1$, the exhaust is net reducing; $R = 1.00$ stoichiometric, and $R < 1$, net oxidizing. In nearly all of the studies reviewed, as R was reduced to 1.00, the effectiveness of the catalyst rapidly diminished and the temperature required for good conversion increased. Thus, for cata-

lytic reduction to occur to a significant degree at attainable temperatures (500-600°C), R must be greater than or equal to 1. However, Jones et al.⁸ and OHara¹³ both showed that significant NO reduction can occur even with $R < 1$ for NO, H₂ and O₂ mixtures. For our H₂ engine, the "Redox Potential," R , is a strong function of the equivalence ratio, ϕ . For example, when $\phi = 0.90$, $R = 0.3$; when $\phi = 1$, $R = 1$; and when $\phi = 1.1$, $R = 5.3$. Thus, small changes in ϕ result in large changes of R . The result of all this is that in terms of reducing NO, all that will be required is to operate at equivalence ratios slightly greater than 1.00.

Overall the "Redox Potential" establishes the trends for NO conversion efficiency. Shelef and Gandhi^{14, 15} noted that by increasing the inlet oxygen concentration while still maintaining a net reducing mixture (decreasing R), an upward shift in the temperatures for maximum conversion occurs. Also, the temperatures required for selective NO $\rightarrow$ N₂ conversion also increased for base metal catalysts. In contrast, they noted that the addition of O₂ had very little effect on Nobel metal catalysts.

Several researchers (8, 15) also noted the effects of reducing R by increasing NO concentration. They found that as NO concentration was increased, the percentage of NH₃ formed decreased. Shelef and Gandhi¹⁵ attributed this to the fact that for low NO concentrations, the probability of two N atoms pairing to form N₂ was approximately equal to that for N combining with H₂. However, at high NO concentrations, the probability of N atoms pairing is greater because more active catalyst sites are occupied by N atoms.

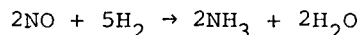
In most of the studies, it was demonstrated that as H₂ (or equivalently CO) concentration was increased, NO conversion efficiency increased. However, further increases in H₂ concentration above that value lead to rapid increases in NH₃ formation. This was accounted for by the increased number of catalyst sites containing H atoms in place of N atoms due to the concentration advantage. Thus, high R values should be avoided in order to preclude excessive NH₃ formation, not to mention improved fuel consumption.

The effect of water vapor addition appears to have very little influence on NO reduction. However, Klimisch and Barnes⁹ showed that water vapor had a large retarding effect on NH₃ decomposition. Thus, higher temperatures were required to produce similar NH₃ emissions. This retarding effect is due to the similar chemisorption behavior of NH₃ and water. Hence, the high water vapor content of our H₂ engine exhaust would severely inhibit the adsorption and subsequent decomposition of NH₃ on the catalyst surface.

TEMPERATURE

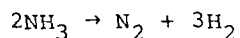
NO conversion efficiency and NO to N₂ selectivity are functions of temperature. NO reduction catalyst in general follow the behavior shown in Figure 1.* It can be seen that at low temperatures (< 100 °C), the catalyst is relatively inactive. As the temperature increases so does the conversion efficiency. Further increases in temperature have little effect on NO conversion efficiency until the temperature becomes high enough to thermally degrade the catalyst (1500 → 1800 °F). Thus, in terms of NO conversion, there is no point in operating at temperatures higher than the "light off" temperature.

Ammonia formation, on the other hand, increases initially with temperature, peaks out, and then decreases as the temperature is increased further. Thus, there are two temperature regimes in which low NH₃ formation occurs. The reason for this type of behavior is that in the low temperature regime, NH₃ is limited by temperature in much the same way as NO reduction. The primary formation reaction is thought by many researchers (1, 5, 9) to be through the reaction



This reaction is enhanced by high reducing agent, in our case H₂, concentrations: in other words, very rich mixtures.

At high temperatures, NH₃ undergoes elementary decomposition to N₂ and H₂ by the reaction



as was demonstrated by Klimish and Barnes⁹. Thus, as temperature increases, the rate of decomposition exceeds the rate of formation until zero net production of NH₃ results.

It is generally desirable to operate at temperatures well above the point where NH₃ production becomes negligible because exhaust gas temperatures can fluctuate between very wide limits, depending on load, speed and environmental conditions. It is also desirable to locate the catalyst close to the exhaust manifold to reduce thermal losses.

* Figure 1 is attached to this report.

CATALYST COMPOSITION

NO conversion efficiency and selectivity vary greatly with catalyst composition. Nearly all of the catalysts reviewed were able to attain at least 90% conversion; however, the temperatures required varied from one catalyst to another. In general, it was found that the base metals (NiO, CuO, FeO) required high temperatures ($>400^{\circ}\text{C}$) before good conversion resulted. Also, base metals produce moderate amounts of NH_3 until the temperature is raised to at least 600°C ¹⁴. On the other hand, noble metal catalysts have very high conversion efficiencies at low temperatures ($200^{\circ}\text{--}300^{\circ}\text{C}$); however, ammonia formation is very high until the temperature reaches about 500°C . Because of the high temperatures required for base metals, noble metal catalysts appear to be more suitable for engine exhaust reduction in terms of ammonia formation. Most notably are catalysts containing platinum, palladium, rhodium and ruthenium.

One of the earliest noble metal catalysts tried by investigators was platinum. Pt catalysts have good NO conversion activities at low temperatures. Shelef and Gandhi¹⁵ reported 90% conversion of NO at 280°C for very rich ($R = 14$) H_2 -NO mixture. The biggest problem with Pt catalyst³ is ammonia formation. This was demonstrated by Bauerle and Nobe. They found the Pt selectively converts NO to NH_3 for temperatures up to 500°C ($R = 5.7$ with only H_2 , NO and N_2). Shelef and Gandhi¹⁵ report similar results.

Palladium catalysts were found by many researchers (3, 8, 10, 15) to be very similar to Pt in terms of NO conversion and slightly inferior in terms of NH_3 formation. It must be stressed that these results were for very rich mixtures (high R values) and also, that the catalysts contained no other active ingredients. In general, it was found that mixtures of different active ingredients produced better results than single component catalysts. This is analogous to the alloying of steels to produce desired mechanical and chemical properties.

Several researchers (1, 3, 7) found rhodium catalysts to be highly active for NO conversion. Bauerle and Nobe³ report 90% at 150°C with $R = 5.7$. Investigators note that ammonia formation over Rh is very high when R is large (greater than approximately 2.0) and the temperature is low (less than 500°C). However, the advantage of Rh catalysts is that when operated close to stoichiometric ($R \approx 1.0 \rightarrow 1.6$) at temperatures around 550°C , they are highly selective for $\text{NO} \rightarrow \text{N}_2$ conversions with very high net conversion efficiencies. Another advantage of Rh is that if the engine undergoes a lean excursion, the increased oxygen will not affect the catalyst. Further, once the exhaust gas becomes re-

ducing again, steady state conditions are reached quickly without altering catalyst activity as demonstrated by Bauerle et al. (1972)⁴. The only problem with Rh catalysts is that they can be poisoned by phosphorus. Gandhi et al. (6, 7) demonstrated this by adding engine oil to gasoline that was subsequently burned in the engine. However, their oil consumption rate of one qt per 2500 miles would most likely cause other problems in the H₂-fueled engine, namely flashback. Additionally, low phosphorus oils may be used.

Recently, ruthenium catalysts have seen a lot of attention. Ru, like Rh, is very active for NO conversion in the presence of H₂. Ru yields 100% NO conversion at approximately 275°C with R = 5.7, according to Bauerle and Nobe (1974)³. Ammonia formation under these conditions is less than 11% and almost nil when the temperature is raised to 380°C. Thus, Ru performs ideally under these rich conditions.

Problems arise with Ru catalysts when the exhaust is leaned out to only slightly rich (R = 1.0-2.0). As R is decreased, NO to N₂ selectivity and NO conversion efficiency decrease. This presents a practical problem in H₂ engine use because NO production is high close to stoichiometric and decreases rapidly as ϕ (or equivalently R) increases. Thus, the Ru catalyst is most effective at an operating point where NO production is small and marginal, where NO is a problem. Further, rich operation results in high fuel consumption and, theoretically, lower power output.

Another problem with Ru catalysts is that they become oxidized during lean excursions, especially if the exhaust temperature rises. Under these conditions, Ru forms volatile oxides and results in permanent catalyst deactivation due to catalyst weight loss, as shown by Bartholomew² and Ashmead et al.¹ among others. Thus, toxic Ru oxide emissions and generally low near-stoichiometric activity preclude the use of Ru catalysts in H₂-fueled engines.

SPACE VELOCITY

The space velocity is defined as the volume flowrate of the exhaust divided by the volume of the catalyst or

$$S_v = \frac{\dot{V}_{\text{exhaust}}}{V_{\text{catalyst}}}$$

and is usually expressed in units of $\frac{L^3/hr}{L}$ or simply hr^{-1} . The space velocity is the reciprocal of the residence time and is a measure of the time available for reactions to occur.

In terms of NO conversion, the effect of space velocity is negligible until its value is increased to such a point where there is just not enough time for reaction to occur. This corresponds to values on the order of $10^5 hr^{-1}$ (10, 12). Klimish and Taylor (10) found that for S_v ranges where NO reduction is complete, ammonia output increases with increasing S_v (decreasing residence time). From this, they concluded that (using CO as the reducing agent) ammonia was an intermediate in the NO to N_2 reduction process. Thus, increases in S_v limit the time available for NH_3 decomposition.

Kuroda et al.¹² found that not only is S_v important but linear velocity through the catalyst is also a factor. By varying catalyst volume and exhaust flowrate, they found that low linear velocities led to low NH_3 output.

Another factor that must be considered is the pressure drop across the catalyst. Large pressure drops result in poor volumetric efficiency and reduced engine performance. In this regard, a large cross-sectional area catalyst with low linear and space velocities would be desirable. Additionally, this configuration should also produce good results in terms of selective NO to N_2 reduction.

Based on the literature survey, a rhodium catalyst should be used for NO reduction in the H_2 -fueled engine because of its good near-stoichiometric activity, resistance to oxygen degradation, high selectivity and thermal stability.

RESULTS

The results are depicted in Figures 2 and 3. Figure 2 shows the conversion efficiencies for the catalyst. Gross NO_x conversion efficiency is defined as

$$\frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\%$$

and is a direct measure of the activity of the catalyst. As can be seen in Figure 2, the catalyst does not reduce NO to an appreciable degree until the equivalence ratio approaches $\phi = 1.0$. This effect is due to the fact that the relative amount of reducing agent to oxidizer is very low, leading to a net oxidizing atmosphere. As ϕ increases, the exhaust switches from oxidizing to neutral to reducing. As this occurs, the activity of the catalyst increases to 100% conversion, as expected.

Ammonia conversion efficiency is defined as

$$\frac{\text{NH}_3_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\%$$

and is a measure of the selectivity of the catalyst for converting NO to N₂. It is readily apparent that significant ammonia formation does not occur until ϕ is increased above 1.0. This is a result of the competition between adsorbed NO and H₂ on the catalyst surface, with the hydrogen having an approximate ten-fold concentration advantage at $\phi = 1.07$. Thus, the richer the mixture, the less selective the catalyst becomes toward NO → N₂ conversion.

Net NO conversion is a measure of how well the catalyst performs its job. It is defined as

$$\frac{\text{NO}_{\text{in}} - (\text{NO}_{\text{out}} + \text{NH}_3_{\text{out}})}{\text{NO}_{\text{in}}} \times 100\%.$$

As shown in Figure 2, Net NO conversion efficiency is high for only a narrow range of ϕ centered on the rich side of stoichiometric. It is limited on the lean side by low catalyst activity and on the rich side by high NH₃ formation. Thus, if the catalyst is to achieve high net conversion efficiencies, the equivalence ratio must be restricted to a narrow range.

Figure 3 shows the effects of the catalyst on exhaust

emissions. One can see that NO production by the engine peaks for $\phi < 1.0$, remains high for ϕ slightly greater than 1.0 and decreases as ϕ is further increased. Available oxygen decreases rapidly as ϕ approaches 1.0 and asymptotically approaches zero as ϕ is further increased. If available hydrogen was plotted, one would find that it becomes large as ϕ increases above 1.0. From Figure 2, it was shown that the catalyst activity was high only for $\phi > 1.0$. Also, NH_3 formation is high for $\phi > 1.0$. Thus, the effects of the catalyst are: 1) to substantially reduce the NO for near and rich of stoichiometric, 2) to produce moderate levels of NH_3 rich of stoichiometric and 3) to produce no net reduction for lean equivalence ratios. The catalyst is most effectively used for equivalence ratios between 1.0 and 1.05, where both NO and NH_3 levels are approximately 10% of the inlet NO. Operation of the catalyst richer than $\phi = 1.05$ results in reduced net pollution emissions (i.e. NO plus NH_3) until all of the oxygen is consumed, at which point the NO is converted solely to NH_3 . Thus, the presence of oxygen helps reduce net production of NH_3 , most likely by way of increased NH_3 decomposition.

Catalyst bed temperatures ranged from 437°C to 452°C (819°F to 845°F). One would expect the net NO conversion efficiency to improve if higher bed temperatures were obtained. Additionally, one would expect lower NH_3 production rates if a lower space velocity had been chosen. The reasons for improved net conversion efficiency are primarily increased NH_3 decomposition rates and longer time constants for NH_3 decompositions.

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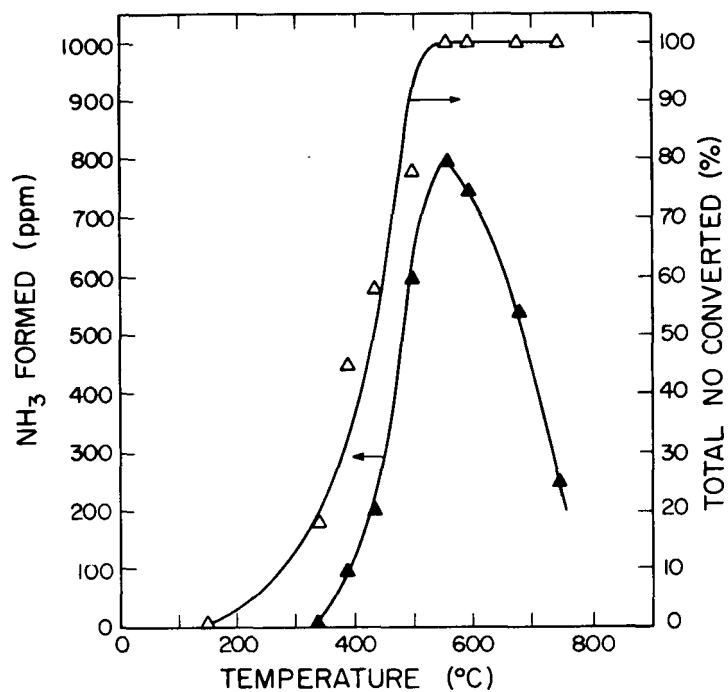


Figure 1 - Ammonia Formation and NO Conversion in NO-H₂ Reaction as a Function of Temperature Over Ironoxide Catalyst. Inlet Concentration: NO, 1000 ppm; H₂, 1.4%; balance N₂. Taken from Reference 14.

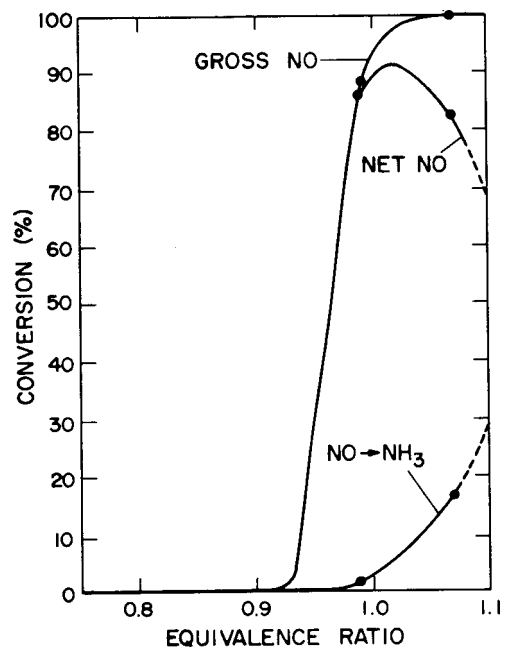


Figure 2 - Conversion Efficiencies versus Equivalence Ratio

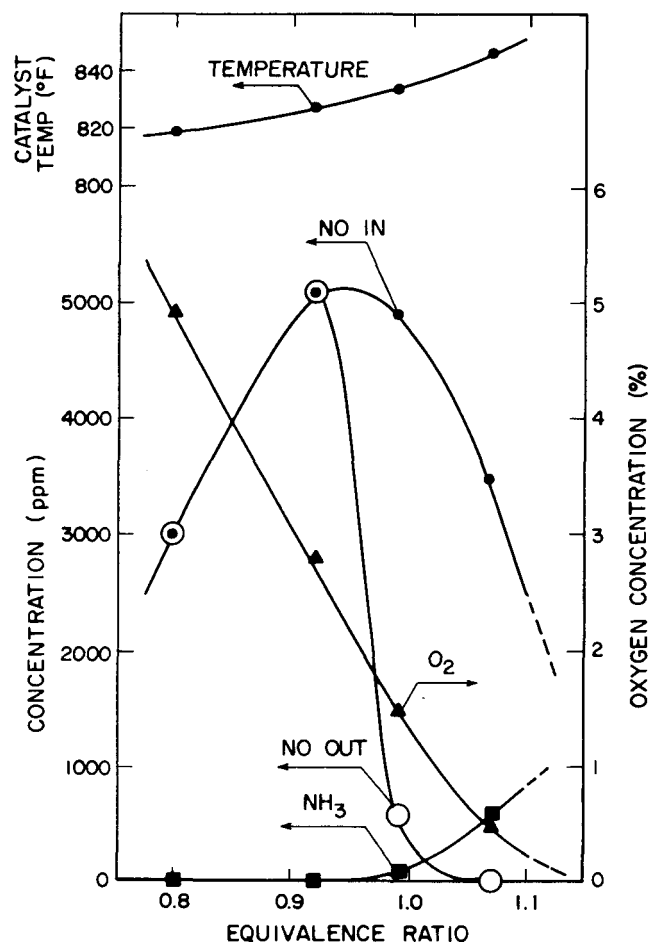


Figure 3 - Catalyst Temperature and Exhaust Gas Constituents versus Equivalence Ratio

E.2 Emissions from High Altitude Aircraft

Calculations are being made by atmospheric modeling experts at Lawrence Livermore Laboratory (LLL) on the environmental effects of emissions deposited in the tropopause and stratosphere by high-altitude aircraft. At our suggestion, the emissions of increased quantities of water vapor from hydrogen-fueled aircraft were added to the Livermore studies. The results of these calculations have been sent to us by Frederick M. Luther of LLL in a section of their forthcoming report. This section is reproduced here with their permission.

UCRL-

POTENTIAL ENVIRONMENTAL EFFECTS OF AIRCRAFT EMISSIONS

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ABSTRACT

An assessment is provided of the potential environmental effects of fleets of subsonic, supersonic, and hypersonic aircraft. A general discussion of photochemical and transport modeling techniques is included along with a description of the LLL one-dimensional transport-kinetics model that was used in the assessment. Model simulations of the natural and perturbed stratosphere are used to compare theory with observations as a means of verification of model processes. A review is provided of engine emission indexes and 1990 fleet projections. Assessments of the potential effects of subsonic and supersonic aircraft fleets indicate a small increase in total ozone. However, the change in total ozone is the net difference between regions of ozone increase (in the lower stratosphere and upper troposphere) and ozone decrease (in the upper stratosphere). The percent change in the local ozone concentration is much larger than the change in total ozone. The effect of a proposed hydrogen fueled hypersonic transport fleet is a small reduction in total ozone. A study is made of the effect on these results of uncertainties in chemical rate coefficients, speculative chemical reactions, temperature feedback, hydrostatic adjustment, and various model parameters. The potential effect on ozone of aircraft emissions is compared with potential changes due to other anthropogenic perturbations.

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ACKNOWLEDGMENTS

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CHAPTER 4. POTENTIAL CHANGES IN OZONE DUE TO AIRCRAFT EMISSIONS

EMISSION INDEXES AND FLEET PROJECTIONS

In this report we consider the potential effects on atmospheric ozone of several different aircraft emissions scenarios. These emission scenarios were developed for three basically different applications: (1) the projected 1990 fleet, (2) supersonic transport emissions, and (3) hypersonic transport emissions.

1990 Fleets

We developed emission profiles for both high and low projected 1990 aircraft fleet sizes. In the case of the projected 1990 high fleet, we adopted the emissions factors and fleet projections used by Oliver et al. (1977) in their Table 2-33. The projection used by Oliver et al. (1977) was based on A. D. Little, Inc. (1976) with corrections to the mean flight altitude of the projected SST fleet of 142 Concorde and TU 144's and an emissions factor ~ 4 times larger than used by A. D. Little, Inc. (1976) for CF6 engines (which Oliver et al. (1977) treated as having the same emissions indexes as JT9D engines). The NO_x emission index for SST's was assumed to be 20 g NO_2 /kg fuel.

In converting the projected emissions in Table 2.33 of Oliver et al. (1977) to a format compatible with the one-dimensional model, we treated the model as a Northern Hemisphere model, summed emissions over all latitudes between 0 and 90°N at a given altitude, converted kg/year to $\text{molecules cm}^{-3} \text{ s}^{-1}$ and then assigned those emissions to altitude intervals in the LLL model (our intervals are 1 km thick, centered at even kilometer altitudes for the altitude range 0.5 to 35.5 km). Table 2 gives the emission rates actually used in our calculation.

In order to examine the effects of the projected subsonic fleet without the SST contribution, we simply used the emissions in Table 2 for altitudes below 15 km but set the emissions to zero above 15 km.

TABLE 2. Projected 1990 aircraft emissions of NO_x (Oliver et al. (1977) high estimate). The low estimate of emission rates equals 0.633 times the high estimate.

Injection Altitude (km)	NO _x Injection Rate Total Fleet (molecules cm ⁻³ s ⁻¹)	NO _x Injection Rate Subsonic Only (molecules cm ⁻³ s ⁻¹)
6	90	90
7	179	179
8	265	265
9	665	665
10	1167	1167
11	1161	1161
12	520	520
13	75	75
14	18*	12
15	18	
16	33	
17	43	
18	29	
19	8	

*Emissions from the SST fleet are included at 14 km and above.

We generated a 1990 low estimate by multiplying the 1990 high estimate emissions by 0.633, the ratio of the 1990 low estimate fuel usage to 1990 high estimate fuel usage given in Table 2.25 of Oliver et al. (1977).

SST Fleets of Commercially Viable Size

In treating hypothetical SST fleets of commercially viable magnitude, we have considered a fleet emitting 1.0×10^8 molecules of NO_x cm⁻²s⁻¹ and 1.77×10^{10} molecules of H₂O cm⁻²s⁻¹ in the Northern Hemisphere, or 6.2×10^8 kg of NO_x (as NO₂) and 4.3×10^{10} kg of H₂O per year. These emission rates correspond to a fuel usage of 3.5×10^{10} kg yr⁻¹ by SST's assuming the emission indexes are 18 g NO₂/kg fuel and 1.25 kg H₂O/kg fuel. The NO_x

emissions index for currently realizable SST engines has been estimated to be as high as 22 g NO₂/kg fuel or as low as 15.6 g NO₂/kg fuel. Future technologies may be capable of reducing this by several fold. A three fold reduction in NO_x emissions index is projected for some existing design concepts (Popoff et al., 1978). We consider NO_x emission indexes of 18 g NO₂/kg fuel for current technology and 6 g NO₂/kg fuel for future technology.

The number of SST's corresponding to a fuel usage of 3.5×10^{10} kg yr⁻¹ is problematical. The number of SST's corresponding to a given fuel usage is inversely proportional to the expected hours/day of flight and the fuel usage per hour. Estimates of the hours per day of flight at cruise altitude have varied from 7.5 to 4.4 hrs. Estimates of fuel usage have ranged from 16,800 to 19,100 kg/hr for the Concorde, from 52,000 up to 60,000 kg/hr for the B2707, and as low as 44,000 kg/hr for a hypothetical advanced design similar to the B2707 (Popoff et al., 1978). Thus, more than a two-fold variation in engine emissions from a projected SST fleet is possible based on different estimates of aircraft operation and fuel consumption. A fuel usage of 3.5×10^{10} kg yr⁻¹, therefore, corresponds to about 750-1000 Concorde's, or 180-660 advanced SST's. Thus, our standard emissions rates are compatible with a large, nearly mature fleet of SST's.

Hypersonic Transport Emissions

In addition to the effects of subsonic and supersonic fleets, we made an attempt to project a range of emissions and environmental impacts of a possible hypersonic transport (HST) fleet. For this purpose, we adopted the emissions indexes given in CIAP Monograph 2, Chapter 6 for a fleet of research HST's of gross takeoff weight 2.27×10^5 kg operating at Mach 8 and cruise altitude of "36.68" km. According to data in CIAP Monograph 2, the hypothesized HST operations would consist of an initial acceleration to hypersonic speeds (and cruise altitude) using rocket engines, followed by about five minutes of SCRAMjet operation, followed by a cruise mode during which most emissions would consist of liquid hydrogen boil-off for cooling. The SCRAMjet would use 670 kg/flight of liquid H₂; the rocket engines would use 2450 kg/flight of liquid H₂ and 14,650 kg/flight of liquid oxygen (CIAP Monograph 2, p. 6-7) but only release a total of 1650 kg/flight of water vapor and 615 kg/flight of H₂ (CIAP Monograph 2, p. 6-8).

Thus, the fuel use and emissions estimates given in CIAP Monograph 2 for rocket operations are incompatible, with not enough mass being emitted. The resolution of this difficulty is almost certainly an error in the water vapor emissions of a factor of 10. Cooling at cruise altitude would consume an additional 309 kg of liquid hydrogen per flight.

The emissions consist of H_2O , H_2 , H , OH , NO , and O as given in Table 3. In analyzing the effects of HST emissions, only cooling and SCRAMjet emissions were treated, and these were based on the data presented on page 6-22 (CIAP Monograph 2). Rocket emissions were neglected since much of the rocket emissions would occur in the troposphere. In order to project to a commercially viable fleet, we increased the emissions given in Table 6-22 of CIAP Monograph 2 for 20 flights

TABLE 3. HST emissions on a per flight basis. Data are from CIAP Monograph 2, Ch. 6, assuming a cruising speed of MACH 8, a cruise altitude of 36.68 km, and $H_2:O_2$ ratio of 1.

	Emissions (kg/flight)	Altitude	Emissions in Moles
<u>SCRAMJet</u>			
H_2O	5705.	36.68	317,000
H_2	136.7	36.68	68,350
H	13.1	36.68	13,100
OH	132.3	36.68	7,800
NO	137.4	36.68	4,580
O	34.4	36.68	2,150
<u>Rocket (not included in calculation)</u>			
H_2O^*	16,500	0-36 mostly tropospheric	917,000
H_2	615	0-36	307,500
<u>Cooling in Flight</u>			
H_2	308.5	36	154,200

* H_2O emissions from rockets have been increased by a factor of ten to permit mass balance.

per year, to an anticipated 1000 flights/day. Because even these emissions are relatively small, and the CIAP Monograph 2 based emissions estimates may not apply to commercial scale fleet operations (they are based on research flights), we also examined the effects of a 10-fold larger emission, perhaps interpretable as longer flights or flights of heavier aircraft. The emissions of H_2O , H_2 , NO , and OH were treated simply as a source of the molecules in question. Emissions of H-atoms (the code calculates H-atoms as an equilibrium species) were treated as emissions of an equivalent number of HO_2 molecules, while the small emissions of O atoms were ignored.

We wish to emphasize that we performed no independent calculations of HST emissions indexes and that the fleet projections are no more than crude parametric estimates of the approximate level of activity that might be associated with a mature, commercially successful fleet of HST's. If specific aircraft designs were to be proposed, the emissions should be independently projected.

CURRENT ASSESSMENT RESULTS

The LLL one-dimensional transport-kinetics model has been used to assess the potential chemical effects of aircraft engine emissions in the troposphere and the stratosphere. Calculations were made using projected fleet sizes for subsonic and supersonic aircraft as well as for a range of emission rates at particular injection altitudes. In order to determine the effect of uncertainties in various input parameters on the assessment calculations, several sensitivity studies were also performed and are reported in the following section.

Two different chemistries were used in these calculations. Most of the calculations were performed prior to the NASA Workshop at Harpers Ferry, Pennsylvania, and utilized chemical rates based primarily on JPL (1979). After the NASA Workshop we repeated several of the perturbation calculations using chemical rates based on the recommendations of the chemistry panel at the NASA Workshop. These two chemistries are described in Appendix A as 1979a and 1979b chemistry.

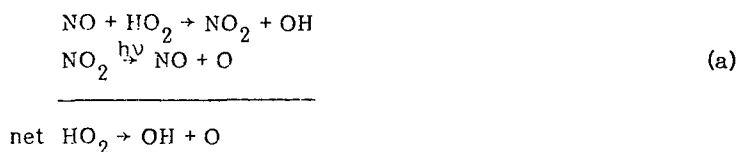
Subsonic and Supersonic Aircraft Fleets

The altitude of injection has a significant effect on the computed change in ozone because of the increase in residence time with altitude and because of the variation with altitude of the dominant chemical reactions and cycles. Table 4 shows the effect on total ozone at steady state of the same NO_x injection rate at different injection altitudes. An injection rate of $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ over a 1-km-thick layer was used for NO_x , and there was no injection of H_2O .

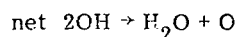
TABLE 4. The change in total ozone resulting from an NO_x injection of $1000 \text{ molecules cm}^{-3}\text{s}^{-1}$ distributed over a 1-km-thick layer centered at the injection altitude. The calculations were made using 1979a chemistry (Appendix A).

Injection Altitude (km)	Change in Total Ozone (%)	
	Fixed B. C.	Flux B. C.
7	0.25	0.32
9	0.40	0.49
11	0.64	0.72
13	0.84	0.91
17	1.34	1.38
20	1.31	1.34

Injections of NO_x over the altitude range of 7 to 20 km resulted in a net increase in total ozone in each case. The change in total ozone increased with increasing injection altitude for the troposphere and lower stratosphere. Throughout this region HO_x chemistry is the dominant chemical destruction process for ozone. When HO_x chemistry is more efficient than NO_x catalytic destruction of ozone, injections of NO_x lead to a net increase in odd oxygen production through the reactions:



and



The set of reactions (a) acts to shift HO_x more toward OH, thereby increasing the loss rate of HO_x by the reaction $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$. Reaction set (b) acts to reduce HO_x as OH and HO_2 are converted to H_2O and HNO_3 . Conversion to H_2O , and to a lesser extent HNO_3 , acts as a sink for HO_x since the chemical lifetimes of these reservoir species is long compared to the time for transport into the troposphere. Injections of NO_x act to increase the rates of the above reactions. The net effect of reactions (a) and (b) is a reduction of HO_x and an increase in odd oxygen production, both of which contribute to an increase in ozone.

Increases in NO_x concentration in the upper stratosphere lead to a reduction in ozone concentration in this region due to the greater importance of the NO_x catalyzed ozone destruction at these altitudes. The 20-km injection of NO_x resulted in a smaller net increase in total ozone than did the 17-km injection case since more NO_x reached the upper stratosphere causing a greater reduction in ozone concentration at high altitudes relative to the increase at lower altitudes. This effect was found to be sensitive to the shape of the K_z profile used, however.

The effect of different lower boundary conditions for the species N_2O , CH_4 , CH_3Cl , HCl , and CCl_4 is also shown in Table 4. Using fixed value boundary conditions results in slightly smaller changes in total ozone ($\sim 0.1\%$ in absolute change) when compared to the flux boundary condition case. Consequently, the choice of boundary condition has only a very small effect on the assessment results.

The model was tested for interference effects by comparing the effect of simultaneous injections at the various injection altitudes given in Table 4 with the sum of the changes in ozone for individual injection altitudes. Table 5 shows that there is a destructive interference. That is, the simultaneous injections resulted in less change in total ozone than the sum of the changes due to individual injections.

This implies that summing the results of separate calculations for subsonic and supersonic fleets will not give the same answer as considering the effect of the two fleets simultaneously.

The effect of NO_x emissions by subsonic and supersonic fleets projected for 1990 are given in Table 6. Using the high estimate of the fleet sizes, the effect of subsonic and supersonic aircraft combined is estimated to be an increase in total ozone of 2.01%. This number represents the steady state change in ozone due to constant NO_x emission rates at the rates estimated for 1990. The subsonic fleet alone (injection altitudes up to 14 km) is estimated to cause an increase in total ozone of 1.86%. The small effect of the supersonic fleet is due primarily to the small fleet size projected for 1990. Using the lower estimate for fleet emissions, the corresponding numbers for ΔO_3 are 1.39% for the combined fleets and 1.29% for the subsonic fleet alone.

It should be noted that the effects of the existing 1979 subsonic fleet are of the order of 0.5% increase in total ozone. This effect is not negligible when compared to the estimated present-day effects of CFMs. Thus, an accurate assessment of the effects of subsonic aircraft will be important in interpreting ozone data for trends due to other anthropogenic influences.

TABLE 5. Synergism test using fixed boundary conditions and 1979a chemistry.

Case	$\Delta\text{O}_3(\%)$
Simultaneous injections	3.68
Sum of individual injections	4.78

TABLE 6. The computed change in total ozone at steady state using NO_x emission estimates for 1990 subsonic and supersonic fleets (1979b chemistry).

Case	Change in Total Ozone (%)	
	Subsonic and Supersonic	Subsonic Only
Oliver et al. (1977) high 1990 fleet estimate	2.01	1.86
Low 1990 fleet estimate	1.39	1.29

The changes in ozone concentration for the high and low estimates of subsonic fleet emissions are shown in percent in Fig. 20 and in absolute concentration in Fig. 21. The largest absolute increase in ozone concentration occurs near 12 km, and the region of increasing ozone extends up to about 26 km. Between 26 and 39 km there is a small decrease in ozone concentration.

It should be recognized that the bulk of the ozone change calculated for the subsonic fleet occurs in the upper troposphere. As a result, it is sensitive to the treatment of such poorly understood phenomena as wet and dry removal processes and surface boundary conditions for rarely measured species. The tropospheric pressures differ from the pressure conditions used in most direct measurements of chemical rate coefficients (to a greater degree than stratosphere pressures). Heterogeneous reactions, which might have a significant effect on the calculations, are not included, and the one-dimensional treatment is not as good an approximation for the troposphere as it is for the stratosphere because of the strong latitudinal and longitudinal gradients in many trace species. Thus, the results for the 1990 fleet estimates are suggestive but are by no means definitive.

Assessments of potential changes in ozone due to future large fleets of supersonic transports have focused on injection altitudes of 17 and 20 km. In updating these assessments, we have assumed an emission index of 18 kg fuel for NO_x and 1250 kg fuel for H_2O . These emission indexes are based upon current engine technology. It may be possible through future advances in technology that the NO_x emission index could be reduced to 6 kg (one-third of present value). Calculations of ΔO_3 given a constant fuel consumption rate at cruise altitude (1.37×10^{11} kg/yr in a hemispheric shell) are shown in Table 7 for different emission indexes. The NO_x emission rate of $1000 \text{ molecules cm}^{-3} \text{ s}^{-1}$ was arbitrarily chosen as a reference case. The equivalent annual hemispheric injection rates of NO_x and H_2O are given in Table 8.

For each of the perturbations considered, there was an increase in total ozone. When the water vapor injection is included with the NO_x injection, there is less of an increase in total ozone because of the additional ozone destruction caused by HO_x which is produced from dissociation of H_2O . For the advanced technology case (reduced NO_x emission), the increase in total ozone due to the NO_x injection is still greater than the reduction due to the H_2O injection, the net effect being a very small increase in total ozone.

TABLE 7. The change in total ozone due to NO_x and H_2O emissions distributed over a 1-km-thick layer centered at the injection altitude.

Injection Altitude (km)	Injection Rate (molecules $\text{cm}^{-3}\text{s}^{-1}$)		Change in Total Ozone (%)	
	NO_x	H_2O	1979a Chemistry	1979b Chemistry
17	1000	0	1.34	1.25
17	1000	177,000	1.18	
17	333	177,000	0.32	
20	1000	0	1.31	1.14
20	1000	177,000	0.91	
20	333	177,000	0.07	

TABLE 8. Equivalent annual hemispheric injection rates for various NO_x and H_2O emissions.

Species	Injection Rate	
	(molecules $\text{cm}^{-3}\text{s}^{-1}$)	(kg/yr*)
NO_x	333	2.1×10^8
NO_x	1,000	6.2×10^8
H_2O	177,000	4.3×10^{10}

*Hemispheric injection assuming uniform injection over a 1-km-thick layer.

In comparing the results from different models, a method that proved useful in the past was to compare the ratio $\Delta\text{NO}_x(\%)/\Delta\text{O}_3(\%)$ rather than just comparing ΔO_3 (Chang and Johnston, 1974; Chang, 1974). Although models differed in their computed values for ΔO_3 , they gave quite similar values for the ratio $\Delta\text{NO}_x/\Delta\text{O}_3$. At that time the models were predicting reductions in total ozone, and a typical value for the ratio was -5 or -6. Values of this ratio for the current model results are shown in Table 9. The ratio has a value of approximately 10 for a 17 km injection altitude with some dependence on the NO_x injection rate. ΔNO_x varies linearly with NO_x injection rate, but ΔO_3 is nonlinear,

TABLE 9. Changes in O₃ and NO_x column densities for various NO_x emission rates.

Injection Altitude (km)	NO _x Injection Rate (molecules cm ⁻³ s ⁻¹)	ΔO ₃ (%)	ΔNO _x (%)	ΔNO _x /ΔO ₃
17	500	0.72	7.0	9.7
17	1000	1.34	14.0	10.4
17	2000	2.37	28.0	11.8
20	500	0.75	11.8	15.7
20	1000	1.31	23.6	18.0
20	2000	1.91	47.0	24.6

particularly for injection rates greater than 1000 molecules cm⁻³s⁻¹. This is even more apparent for the 20-km injection altitude results where the ratio is 15.7 for an NO_x injection rate of 500 and increases to 24.6 for an injection rate of 2000. Because of the nonlinear characteristic of ΔO₃ for large injection rates, the ratio ΔNO_x/ΔO₃ is only useful for comparing model results for small injection rates.

Hypersonic Transport Fleet

The hypothesized hypersonic transport fleet making 1000 flights per day was calculated to cause a -0.218% change in column ozone. Emissions from a fleet ten times larger were calculated to cause a -2.06% change in column ozone. The NO_x emissions from the latter fleet by themselves caused an ozone change of -2.13%.

Figure 22 shows the local percentage changes in ozone vs. altitude for the 10,000 flight per day HST emissions and the NO_x emissions alone from 10,000 flights per day of HST's. (Because O₃ is roughly linear in emissions rate over the range considered, large fleets were chosen to avoid comparing very small local changes that might contain significant numerical noise.) As is evident, the NO_x emissions dominate the ozone changes below ~ 40 km, while H₂O and H₂ emissions are responsible for most of the ozone change at higher altitudes. Because most of the ozone column is below 40 km, the integral column change is largely a

result of the NO_x emissions. It might be possible to control the NO_x emissions by using more than the stoichiometric amount of H_2 in the SCRAMjets.

SENSITIVITY STUDIES

Effect of Variations in K_z

Use of the vertical transport parameter K_z in the one-dimensional model enables atmospheric transport to be parameterized in a mathematically simple and convenient manner resembling diffusion. Various K_z profiles have been developed for use in 1-D models using N_2O and CH_4 measurement data. Because of variations in the data and because neither N_2O nor CH_4 are perfect tracers, there is no unambiguously correct K_z profile.

The K_z profile currently being used in the LLL 1-D model is shown in Fig. 23. The K_z values averaged over the stratosphere are considerably higher than was typical of K_z profiles used during the DOT's Climatic Impact Assessment Program (CIAP), which ended in 1975. Two profiles that were used for many of the assessments included in the CIAP Report of Findings (Grobecker et al., 1974) are also shown in Fig. 23. The Chang (1974) and Hunten (1975) K_z profiles result in slower transport between the middle stratosphere and the troposphere, so there is a larger build-up of emitted species in the stratosphere for constant injection rates.

Calculations of the change in total ozone due to an NO_x injection rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$ are shown in Table 10 using the LLL, Chang (1974), and Hunten (1975) K_z profiles. The Chang (1974) and Hunten (1975) profiles are used to provide continuity with the earlier CIAP assessments; They are not representative of K_z profiles currently in use by any modeling group.

TABLE 10. The effect of the choice of K_z profile on the change in total ozone computed for an NO_x emission rate of 1000 molecules $\text{cm}^{-3}\text{s}^{-1}$.

Injection Altitude (km)	Change in Total Ozone (%)		
	LLL K_z	Chang (1974) K_z	Hunten (1975) K_z
17	1.34	1.91	2.65
20	1.31	2.49	2.07

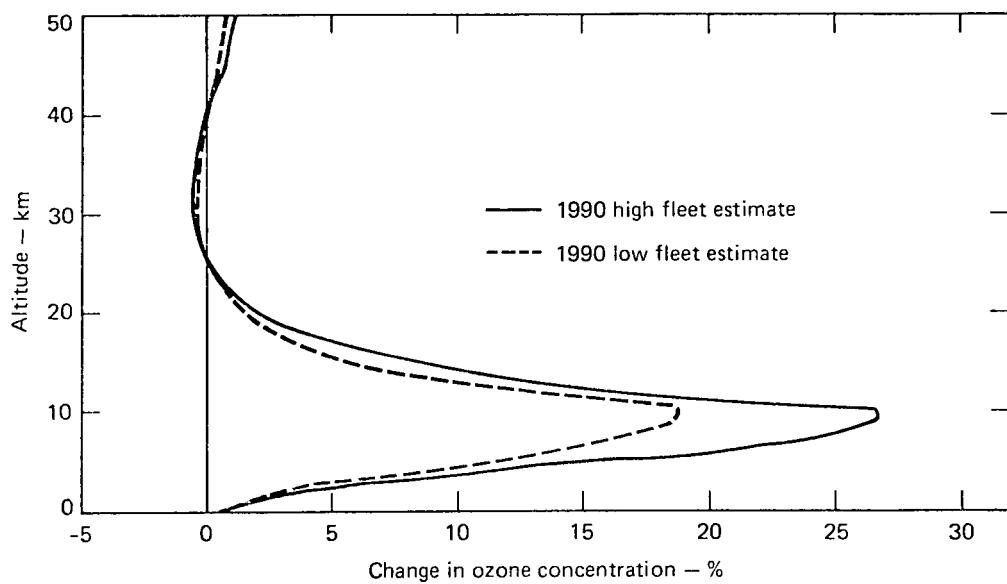


Figure 20. The change in ozone concentration due to subsonic aircraft computed for 1990 high and low fleet estimates.

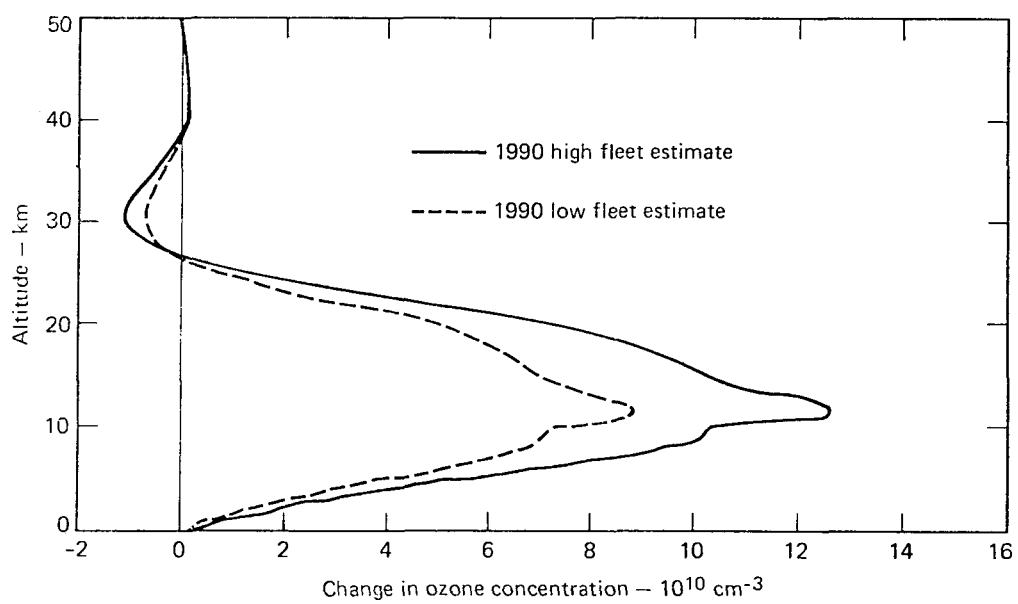


Figure 21. Same as Fig. 20 except the change in ozone concentration is expressed in molecules cm^{-3} .

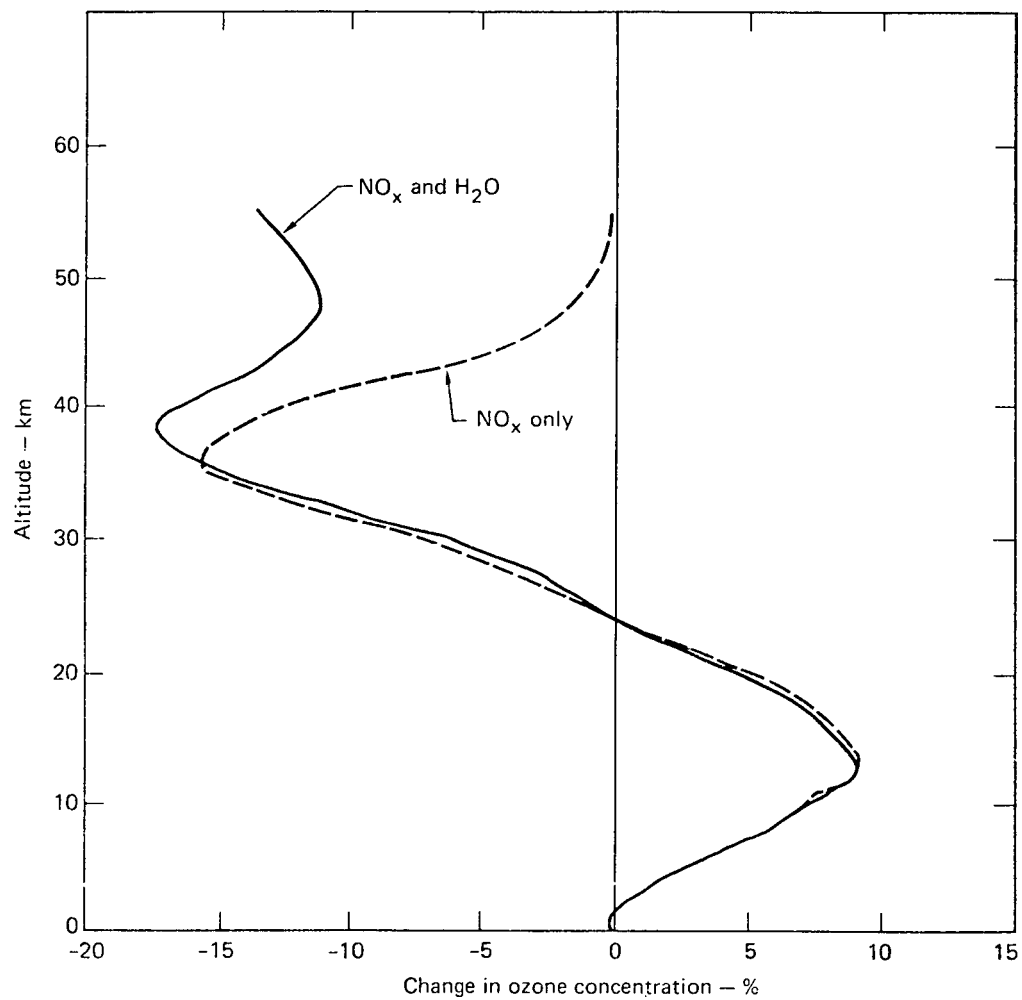


Figure 22. The change in ozone concentration for the 10,000 flight per day HST emissions.

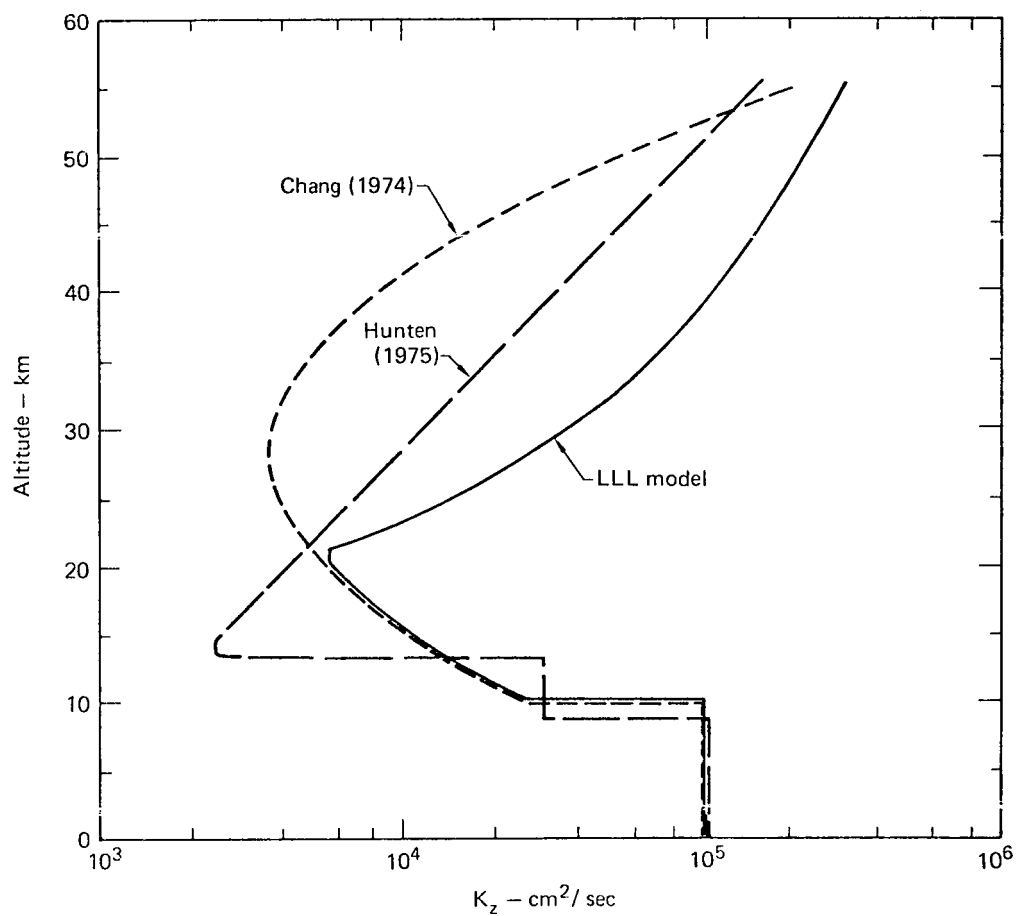


FIGURE 23. Vertical transport coefficient profiles used in the sensitivity study. The Chang (1974) and Hunten (1975) profiles are included for historical purposes.

APPENDIX F
REGULATIONS FOR HYDROGEN SHIPMENT

In the previous reports^{1,2} we presented a discussion of the codes, standards and regulations regarding hydrogen transportation. To those reports we add the following on a new, proposed regulation on transport of cryogenic liquids.

"Cryogenics Liquids"
(Notice of Proposed Rulemaking and Public Hearing)
Thursday, March 8, 1979

PART II

Department of Transportation
Materials Transportation Bureau

(Corrections and additions April 5, 1979)
49 CFR Parts 171, 172, 173, 174, 176, 177, 178, 179

This proposed set of rules for transportation of cryogenics aims specifically to eliminate the need for special permits and exemptions which have been used for many years. This has been particularly true for liquefied hydrogen although this material has been transported in the public domain for more than 25 years.

The principal spokesman for the industry will be the Compressed Gas Association although individual firms may contribute comments. Probably the National Fire Protection Association will involve itself in the subject as it is an important consensus body for combustible cryogenic liquids; this may also be true for the American Gas Association with respect to liquefied natural gas.

These proposed rules of 1979 are a revision and extension of work done in 1974 which sought to produce a body of rules for flammable or pressurized cryogenic liquids. Presently, non-flammable, non-pressurized cryogenic liquids, which make up the vast majority of container shipments are not regulated under

the Hazardous Materials Regulations for overland transportation. To quote from the opening paragraphs of subject document (page 12826, 1st paragraph under SUMMARY: "It is also proposed that nonflammable, non-pressurized cryogenic liquids, currently not generally subject to the Hazardous Materials Regulations, be made specifically subject to certain regulations due to the hazard presented by their extremely low temperature". This is a major enlargement of the regulations because it does not allude to size of shipment nor limit the scope of low temperature concern. Low temperatures can adversely affect materials and individuals. Although tissue damage can occur from contact with cryogenic liquids and gases evolving from cryogenics or surfaces cooled by the above, the personal risk from cold has not been significant compared to other problems of cryogenics (pressure, fire, toxicity, asphyxiation, material damage).

(On page 12827, first column, 2nd paragraph, stronger words are used, "the MTB is proposing that certain requirements apply due to the extreme hazard these low temperature materials pose to human tissue.")

Although the matter of Federal regulations for transportation of cryogenics has been considered for years, even before the 1974 revision, there is a current national concern in the general area of transportation of hazardous commodities. In the past two or three years many public comments have been made about mishaps involving bulk toxic and combustible chemicals in transport. Strong views have been expressed about railroad coupler design and tank car shields, as examples of need for increased government regulation.

Despite this real concern about shipment of hazardous commodities it is a reasonable assessment to state that the need for enhanced government regulations for cryogenics does not have the urgency that exists for the toxic and flammable* chemicals moved in non-insulated containers. The risk to the public from cryogenic fluids does not have the imminence of those fluids carried in unlagged containers. That is not to say there should not or will

*One well-known risk of flammable fluids transported at ambient temperatures in bare tanks is the boiling liquid expanding vapor explosion (BLEVE) phenomenon. In the BLEVE a torching fire might strike a point in a tank containing flammable fluid. The tank thus heated will relieve pressure build-up through its safety relief valves but the torched point may weaken to a point below its designed strength and burst with the release of its boiling liquid flammable product and produce horrendously large fire and explosions. This is much less likely to occur with insulated tanks.

not be an enlargement of the federal role in regulating cryogenics but it is to say that there are priorities demanding more immediate attention.

Training and Emergencies

The subject code specifies training requirements for drivers to the following extent:

- (1) The training must be in written form.
- (2) Training must be done at time of initial employment and every two years after that.
- (3) The training should include knowledge of the regulations, the properties, and potential hazards of the material being carried, the operation of type cargo tank including emergency features and loading limitations.
- (4) Emergency procedures for accidents or other emergencies must include unanticipated pressure increase or decrease.
- (5) Certificates of the above training must be kept in the drivers qualification file and a copy must be kept on his person while operating.

In motor vehicle transport of a cryogenic liquid in a package exceeding 125 gallons water capacity the vehicle must carry the following information:

- (1) General precautions
- (2) Manual venting instructions
- (3) Emergency procedures
- (4) Names and telephone numbers of persons to be contacted in case of an emergency or accident.

All over the US emergency response capabilities have been enhanced by chemical manufacturers and public emergency response groups, and many political jurisdictions have consolidated their emergency plans and organizations.

An assessment of this portion of the subject standard is that it seems to be non-controversial.

However, the training of drivers while required to be in written form (thus insuring literacy as a condition of employment) does not allude to the need for a test to ensure what the driver may have learned or failed to learn. The matter of testing is complex and sensitive and subject to much controversy. It may be that some carriers will go further than the regulations herein require.

Specific Examples of Regulatory Problems

1. Compliance of existing equipment with new requirements.

Comment: Without going into details there may be much existing hardware that could be exempted by "grandfather" clauses or scheduled for replacement at times varying with the determined degree of risk.

2. The new standard requires periodic retest at a pressure of 1.5 times the design pressure of the tank.

Comment: This raises objections from those who believe a retest at 1.25 times the design pressure is sufficiently safe and lessens the possibility of cyclic failure of inner tanks.

3. The standard prevents venting the atmospheric gases (N_2 , O_2 , Ar, He) if shipped as cryogenics pressurized over 25.3 psig.

Comment: There is not complete agreement that the venting of such gases represents much of a hazard.

Summary Assessment:

1 - After the cryogen has been established as a reasonably common commodity, shipment of cryogenics ought to be controlled by regulation rather than by exemption or special permits.

2 - Serious accidents in recent years in the transport of hazardous commodities have involved and disturbed the public sector because of multiple deaths and large property losses. Enhanced regulation and surveillance have been suggested to lessen this problem.

3 - Cryogenic fluids in insulated transport tanks have a significantly better safety record than fluids shipped at ambient temperatures in bare tanks.

4, - The acceptance of the significant additional requirements of these "Cryogenic liquid" rules will be difficult for industry, particularly for non-flammable gases.

5 - It is difficult to envisage the early enactment (within two years) of this body of rules.

REFERENCES

1. "Analysis and Management of a Pipeline Safety Information System" Department of Transportation Report DOT-TST-75-47.
2. "Energy Material Transport, Now Through 2000, System Characteristics and Potential Problems - Task 4 Progress Report, Natural Gas Transportation," Battelle Pacific Northwest Laboratory report PNL-2422, UC-71 (July 1978).

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