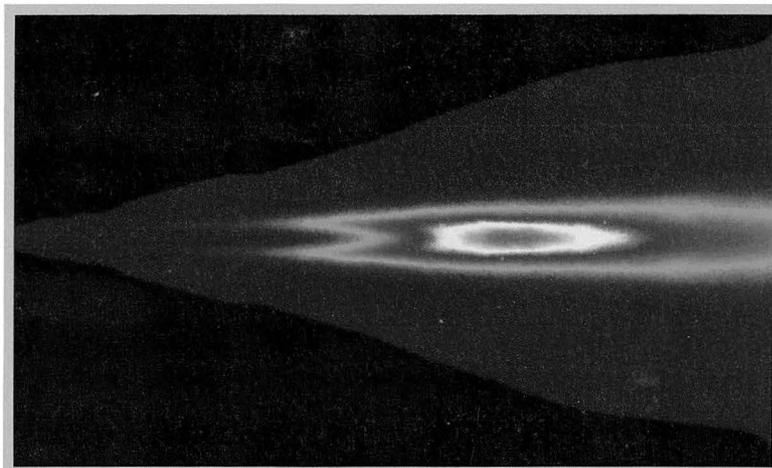


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Environmental Research Program 1992 Annual Report



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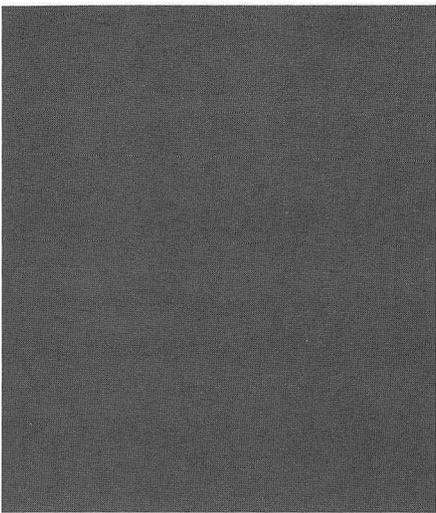
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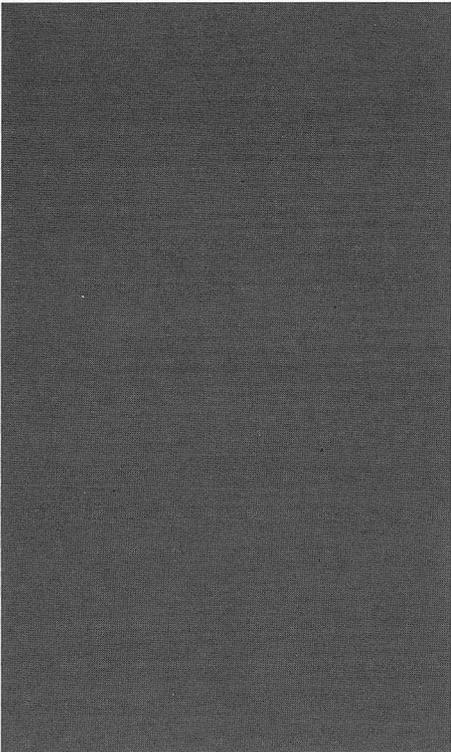
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Environmental Research Program 1992 Annual Report

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Introduction

The objective of the Environmental Research Program is to contribute to the understanding of the formation, mitigation, transport, transformation, and ecological effects of energy-related pollutants on the environment. The program is multidisciplinary and includes fundamental and applied research in chemistry, physics, biology, engineering, and ecology. The program undertakes research and development in efficient and environmentally benign combustion, pollution abatement and destruction, and novel methods of detection and analysis of criteria and non-criteria pollutants. This diverse group investigates combustion, atmospheric processes, flue-gas chemistry, and ecological systems.

Research in combustion science focuses on acquiring a fundamental understanding of the chemical and physical processes that occur during combustion for the purpose of optimizing the tradeoff between reducing emissions and increasing efficiency. Areas of application are engines, power generation, pollution abatement, thermal destruction of wastes, and fire research. Mod-

els have been developed to explore methods of reducing oxides of nitrogen in natural gas combustion processes, and to describe pollution formation and destruction in turbulent combustion systems. Parametric and functional sensitivity analysis studies of potential energy surfaces have been undertaken to extract fully the physical content from dynamics-to-kinetics modelling efforts. Novel diagnostics have been developed to aid in the investigation of the interaction between turbulence and combustion. A weak-swirl burner has been developed to aid in the investigation of the interaction between turbulence and combustion. The burner is an ideal configuration for studying turbulent flame speed and flame quenching, and also may be a prime candidate for technology transfer as it supports combustion under very lean fuel conditions. While continuing to develop laser photofragmentation/laser-induced fluorescence techniques and *in situ* FTIR techniques for examining chlorinated species, substantial progress has been made in understanding the chemistry that occurs in combustion of chlorinated hydrocarbons.

Research in flue-gas chemistry is devoted to developing new processes for simultaneous SO₂ and NO_x removal. Research in this area begins by studying the fundamental reaction kinetics and integrating these results to devise a process at the laboratory scale which is further tested at the bench scale. Subsequent vital steps in the hierarchy leading to commercial development are pilot plant testing and demonstration-scale evaluation. The LBL PhoSN₂OX process for the combined removal of both SO₂ and NO_x from flue gas has been successfully tested in conjunction with a consortium of industries. A method for preventing formation of nitrogen-sulfur compounds in scrubbing liquors was discovered and involves the addition of sulfamic acid. Ferrous thiocholate complexes have been found to be superior to the more commonly used techniques of using Fe(II)[EDTA] complexes for removal of NO from flue gas. Because large amounts of sulfur dioxide are produced from power plants, disposal of the products associated with its removal are often a problem. In response to this, several catalysts have been developed

(cont.)

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Introduction (cont.)

that are highly effective in converting sulfur dioxide to elemental sulfur, a valuable feed stock. Destruction of toxic waste is also an important research focus. Yellow phosphorus in the presence of moist air has been demonstrated to initiate chemistry that is effective in destroying various toxic organic compounds. The process is being optimized for both destruction efficiency and effectiveness of yellow phosphorus utilization.

The atmospheric process portion of the program is concerned with the investigation of the chemistry and physics of the atmosphere in the laboratory and field, and in the development of novel measurement techniques to characterize individual particles. Aerosol and cloud chemistry are a major area, and the influence of atmospheric aerosols on global and regional climate is being determined. Recent calculations suggest that anthropogenic sulfate aerosols may mask the effects of increasing concentrations of greenhouse gases. Central to this hypothesis is the assumption that there is a one-to-one relationship between cloud condensation nuclei and sulfate mass concentration. Research conducted at El Yunque Peak

in Puerto Rico has demonstrated that the relationship between sulfate mass and cloud condensation nuclei is far more complex than one-to-one, and that sulfate concentration is not the only factor that determines cloud droplet concentration. Empirically derived sensitivities are found to be much lower than those implied by the one-to-one relationship.

Research in ecological systems is concerned with developing new tools for risk assessment and site restoration. Bioassays and biophysical indices are used to elucidate environmental stress at the whole animal and cellular levels. An investigation of the efficacy of wetlands created to treat toxic storm water indicated that the wetlands could treat storm water only under certain conditions. Engineering improvements were implemented that were based on the study recommendations. In another effort, comparison of toxicity assays demonstrated that for certain chemicals, an anaphase aberration assay, which quantifies chromosomal breakage and other chromosomal effects, is a more sensitive assay technique than others currently used in ecological risk assessment. This technique is now being

used as a sensitive indicator of UV-B effects.

Bioremediation techniques are being developed for the decontamination of polluted environments. Biosorbents, derived from algal biomass, are being developed for pump-and-treat or soil washing methods; metabolically active bacterial systems are being developed for in situ bioremediation. Novel electron spin resonance (ESR) assays play an important role in understanding the metabolic processes involved.

Research is continuing on free radical damage mechanisms and biological oxidants. Several promising new damage markers of chronic environmental stress have been identified, including alterations of hemoglobin and myoglobin structure, which are detectable by ESR.

The potentially significant issues associated with geothermal energy generation on the Kilauea East Rift Zone and subsequent transmission of power to Oahu via submarine cable were identified. Of particular concern is the potential impact of cable-associated EMF on threatened and endangered species—notably the humpback whale—and on marine species which use EMF for navigation.

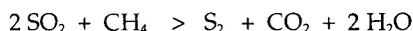
Flue-Gas Chemistry

Catalytic Reduction of Sulfur Dioxide to Elemental Sulfur

Sulfur dioxide in the atmosphere can cause acid rain. Processes have been developed to remove sulfur dioxide from flue gas of power plants. Most of these processes capture sulfur dioxide and then convert it into waste material, including calcium sulfite and calcium sulfate. These waste materials require disposal. Because of the large amount of sulfur dioxide that can be produced from power plants, the disposal of these solid wastes represents an environmental problem. There are several sulfur dioxide regenerable processes; some of them have been commercialized, while others are emerging. In these regenerable processes, sulfur dioxide from flue gas is first absorbed in an alkaline solution or on a solid substrate, and is subsequently desorbed to produce a stream of high-concentration sulfur dioxide. It is desirable to convert sulfur dioxide to elemental sulfur for storage, transporta-

tion, or conversion to valuable chemicals.

Sulfur dioxide can be reduced with either methane or CO/H₂ to produce elemental sulfur at elevated temperatures according to the reactions



In addition to the elemental sulfur, these reactions may produce several undesirable byproducts. These include hydrogen sulfide, carbonyl sulfide, carbon monoxide, and elemental carbon. These reaction can be facilitated with catalysts. Numerous research efforts have been carried out to develop a catalyst for this reaction such that it can proceed with high sulfur dioxide conversion efficiency and high selectivity to elemental sulfur at low temperatures.

We have developed several catalysts which were found to be highly effective in the reduction of sulfur dioxide to elemental sulfur. Results showed that a better than 95% sulfur dioxide conversion efficiency with a >95% selectivity to elemental sulfur can be achieved with a stoichiometric ratio of sulfur dioxide to the reducing gases as given in the reactions. Parametric studies on the conversion efficiency and product selectivity will be conducted. Parameters that will be investigated include temperatures, space velocity, and inlet molar feed ratio of sulfur dioxide to methane or CO/H₂. The lifetime of these catalysts will be determined.

Investigators

Q.Q. Yu
Y. Jin
S.G. Chang

Metal Chelate Processes for Removal of Nitric Oxide from Flue Gas

A number of metal chelates can bind nitric oxide to form metal nitrosyl complexes; the bound nitric oxide can later be converted to environmentally acceptable species. The metal chelates can then be recycled. This approach is very attractive because of its simplicity for integration into a wet sulfur dioxide scrubber. There may be no need for excessive new equipments and chemicals if an appropriate metal chelate is identified.

The most well studied metal chelate has been Fe²⁺(EDTA); the chemistry of a wet scrubber system involving Fe²⁺(EDTA) has been investigated extensively, and several processes have been derived and tested at the pilot plant stages. However, shortcomings have

been encountered. These include 1) the rapid oxidation of ferrous ions by O₂ to inactive ferric ions and the slow regeneration rate of ferrous ion in the EDTA system result in a low NO removal efficiency at a steady state, and 2) the production of undesirable byproducts, which require additional steps of processing for disposal.

We have developed a number of ferrous thiochelate complexes for the removal of nitric oxide from flue gas. These thio-complexes possess several advantages over Fe²⁺(EDTA): 1) larger nitric oxide absorption capacity resulting in better removal efficiency; 2) less unwanted byproducts resulting in lower waste treatment costs; 3) more re-

sistance to oxidation resulting in lower regeneration costs; and 4) applicability for nitric oxide removal from flue gas without sulfur dioxide. We have been studying several schemes for regenerating spent scrubbing solutions; these include thermodesorption, chemical and electroreduction methods. We will perform a bench-scale (7 KW) test of an integrated scrubber system using the newly developed ferrous thiochelate complexes.

Investigators

E. Pham
H. Li
S.G. Chang

LBL PhoSNOX Process for Combined Removal of Sulfur Dioxide and Nitrogen Oxides from Flue Gas

We have recently developed a novel process for combined removal of SO₂ and NO_x from flue gas. This method involves the use of chemical reactions of yellow phosphorus with oxygen to produce ozone, which then selectively oxidize insoluble NO to more soluble NO₂. Subsequently NO₂ and SO₂ are removed from flue gas through the dissolution into scrubbing liquors. This new technology has been tested jointly by the Lawrence Berkeley Laboratory and Bechtel Corporation with a 7 KW (20 cfm) bench-scale scrubbing absorber. The test results indicated that greater than 95% nitric oxide removal efficiency could be achieved with an L/G > 60 gal/1000 cu ft for nitric oxide concentrations ranging from 60 to 600 ppm. A stoichiometric ratio, defined as the molar ratio of yellow phosphorus consumed to nitric oxide removed, of as low as 0.6 has been achieved.

The major oxidation product of yellow phosphorus is phosphoric acid mists which can be recovered as a valuable commercial product. We have per-

formed experiments to determine the size distribution of mists in order to determine an appropriate collector for use in scale-up tests. The size of the mists was measured by means of a cascade impactor and an optical particle counter. Results showed that the geometric mean size of the mists was 0.7, 0.9, and 1.1 μ with a residence time of 3, 6.5, and 11 seconds, respectively. In addition, we have built a mist collector using the impactor and capillary action principles. The mists were collected by the collector and the concentration of phosphoric acid in the mists was determined to be about 10% by weight.

Furthermore, we have invented a method to prevent the formation of nitrogen-sulfur compounds in scrubbing liquors. This was accomplished by the use of sulfamic acids to convert nitrite ions to N₂. Nitrogen-sulfur compounds are produced from the reaction of nitrite with bisulfite ions. Sulfamic acids compete effectively with bisulfite ions for reaction with nitrite ions. Consequently, the formation of nitrogen-sul-

fur compounds can largely be prevented. The up-dated economic projections for the PhoSNOX process have been made by Bechtel Corporation. The estimated costs compare favorably with the SCR method for high removal and are competitive with urea injection processes for low levels of nitric oxide removal.

A safety study has been conducted by FMC Corporation and indicated that the potential safety hazards of yellow phosphorus can be avoided if proper precautions are taken. Currently, there are more than eighty chemical plants which convert yellow phosphorus to phosphoric acid. These plants are spread around the country. Some of these plants are located nearby residential areas. The operation of these plants has not caused any major accidents for many decades.

Investigators

S.M. Wang
H. Li
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Use of Yellow Phosphorus to Destroy Toxic Organic Compounds

The remediation of hazardous pollutants in waste water is necessary to avoid damage to the biological world. Many toxic pollutants possess refractory structures and are difficult to detoxify by conventional waste water treatment processes. The refractory organics include the derivatives of chemicals such as aromatic amines, biphenyls, dioxines, polycyclic arenes, nitroarenes, and heterocyclic nitrogen containing compounds. Several methods such as ozonation assisted by uv irradiation and plasma-enforced degradation have been developed to destroy these refractory organic compounds; however, they are complicated and expensive to use.

A novel method to generate active species for destroying various types of toxic organic compounds has been developed. This method involves the use of the reaction of yellow phosphorus with oxygen molecules in moist air to produce oxygen atoms and ozone. In addition to oxygen atoms and ozone, several reactive phosphorus oxide inter-

mediates such as PO and PO₂ are generated during the course of the reaction. Ozone is one of the most powerful oxidizing agents widely used for destroying toxic organic compounds. The phosphorus oxide intermediates possess reductive chemical properties and are expected to undergo electrophilic reactions with organics. Furthermore, uv and near uv/visible radiations are observed during the course of the reaction. The uv radiations could also contribute to the decomposition of toxic organic compounds. Therefore, the reaction of yellow phosphorus with moist air provides three concurrent components: oxidative species, reductive species, and uv radiations, which are capable of destroying toxic organic compounds.

This method has been demonstrated to be very efficient for destroying various types of organic wastes. The compounds that have been destroyed include benzene, naphthalene, dimethylaniline, phenol, benzoic acid, nitrobenzene, isophorone, pyridine,

chlorobenzene, Aroclor 1221 and 1242, trichloroethylene, tetrachloroethylene, 1,1-dichloro-ethane, chloroform, carbon tetrachloride, Eriochrome black T azo-dye, and dimethoate pesticide. The destruction products identified were small molecular weight organic acids, including formic acid, citric acid, and malonic acids; nitrate, chloride, sulfate, and phosphate ions were also detected for organics containing nitrogen, chlorine, sulfur, and phosphorus respectively. We have been investigating parameters which affects the destruction efficiency and the effectiveness of yellow phosphorus utilization. Parameters studied include the relative concentration of toxic organics to yellow phosphorus used, the concentration of oxygen, and the gas-liquid contact efficiency.

Investigators

K. Y. Hu
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Oxidative Destruction of Nitrogen Sulfonates

Nitrogen sulfonate compounds are formed and can build up in aqueous solutions used for the removal of sulfur dioxide (SO₂) and nitrogen oxides from power plant exhaust gases. Hydroxyimidodisulfate (commonly referred to as HADS) is the compound initially formed by the reaction of hydrogen sulfite ion (HSO₃⁻) with nitrous acid (HNO₂). HADS can undergo a number of reactions to form a number of other nitrogen sulfonate compounds. While these compounds are not considered toxic, increasingly stringent waste disposal requirements can make disposal of solutions or solids containing nitrogen sulfonates costly. An effective method of eliminating these compounds from solutions is needed.

We have previously studied the solubilities and reactions of these compounds to develop processes for removing them from solution. In general, the common salts of these compounds are fairly soluble, making precipitation of these materials difficult. We have investigated oxidation of these compounds to determine if this can be an effective technique for their destruction. The oxidants that have been used in this study include nitrogen dioxide (NO₂), hydrogen peroxide (H₂O₂), ozone (O₃), and phosphorus (P₄). The LBL PhoSNOX flue-gas treatment process, developed in this laboratory, utilizes the reaction of phosphorus with oxygen to convert nitric oxide to nitrogen dioxide. Nitric oxide (NO) is the most abundant nitrogen oxide in flue gas and is much less soluble than nitrogen dioxide. Ozone is generated by the reaction of phosphorus with oxygen, in addition to a number of phosphorus oxide species that are ultimately converted to phosphoric acid. If the oxidants involved with the PhoSNOX process are capable of reacting with the nitrogen sulfonates formed in the scrubbing solution, it will simplify the design and operation of the flue gas scrubbing system.

Solutions of the nitrogen sulfonates were prepared and contacted with the oxidants used in this study. Raman spectra of the solutions were recorded periodically. The spectra were analyzed to determine the changes in solution. The rates of destruction of the compounds were compared to determine the most effective oxidation method. Phosphorus was not particularly effective in the arrangement used because of poor gas-solid contacts. Studies on the other oxidants showed that ozone was most effective, followed by nitrogen dioxide, then hydrogen peroxide. In general, the nitrogen sulfonates with N-OH moieties were more easily oxidized than the others. The nitrogen sulfonate ATS resisted oxidation by all of the oxidants used. However, it readily hydrolyzes to ADS, which can be oxidized or hydrolyzed.

The products of the oxidation of the nitrogen sulfonates were also investigated. Some oxidant products are more desirable than others. The sulfur in the nitrogen sulfonate compounds is converted to sulfate. The nitrogen in the compounds was not always completely converted to nitrate ion. In some cases, nitrite and other compounds were formed. Oxidation of these species to nitrate occurred fairly slowly under some conditions. If the concept of oxidative destruction proves to be successful in this application, it may be possible to apply it to other undesirable materials in aqueous solutions.

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Investigators

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Combustion

Combustion Chemistry

Combustion modeling is a broad endeavor that can begin with calculation of potential energy surface and involve intermediate stages (e.g., calculation of state-to-state cross sections) that are averaged to yield thermal rate coefficients. The thermal rate coefficients are then used in a combustion model which includes both a chemical and fluid mechanical description to predict bulk quantities of interest to combustion—e.g., concentrations, temperature, pressure, and heat release. Our research is concerned with the development and use of sensitivity analysis tools to probe the response of dependent variables to model input variables. Sensitivity analysis is important at all levels of combustion modeling.

During the past five years there have been several dramatic advances

in both experimental and theoretical capabilities to describe chemical reactions at the fundamental level of quantum mechanical reactive scattering. Our research in this area continues to be focused on elucidating the interrelationship between features in the underlying potential energy surface (obtained from ab initio quantum chemistry calculations) and their responses in the quantum dynamics, e.g., reactive transition probabilities, cross sections, and thermal rate coefficients. The goals of this research are: 1) to provide feedback information to quantum chemists in their potential surface refinement efforts, and 2) to gain a better understanding of how various regions in the potential influence the dynamics. These investigations are carried out with the methodology of quantum functional sensitivity

analysis (QFSA).

This past year, we have concluded the development of the QFSA techniques using the log-derivative Kohn variational method¹ for scattering, and applied it to the collinear H + H₂ exchange reaction.^{2,4} One paper³ was concerned with the development of a general description for calculating sensitivity coefficients independent of the scattering formalism employed in the calculations. Another⁴ described a methodology for predicting observables on a new or perturbed potential energy surface (PES) without calculating dynamics on the new potential energy surface. The third² examined the sensitivity of the thermal rate coefficient to structure in the potential energy surface.

Recently, we began to investigate the same reaction in three dimensions.

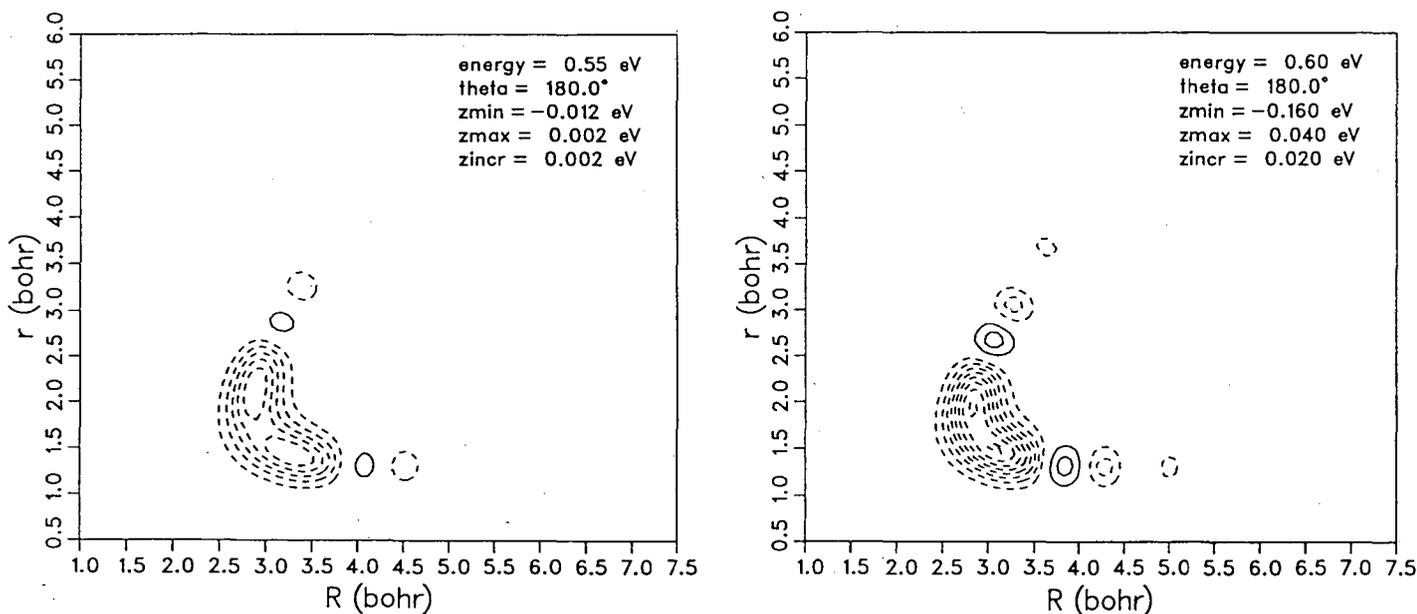
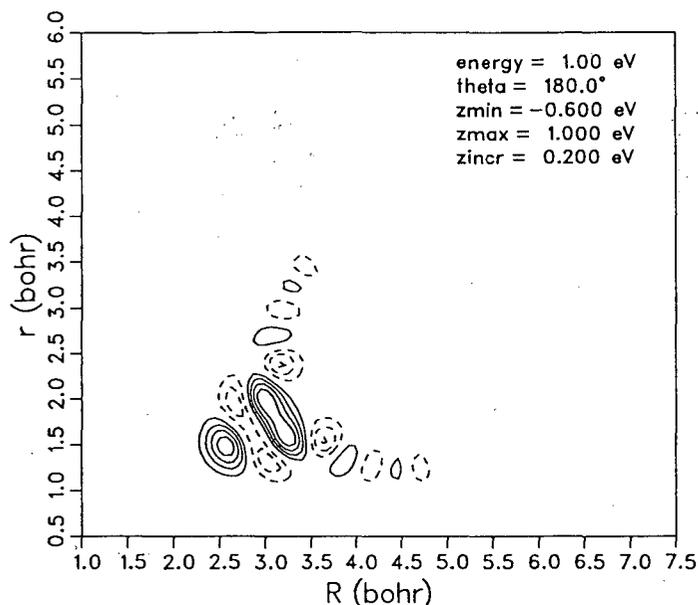


Figure 1.

Sensitivity contours for two energy slices of the $v = j = 0 \rightarrow v' = j' = 0$ (reactive) transition probability in the threshold region at $E = 0.55$ and $E = 0.60$ eV at a scattering angle of 180° . Smallest, largest, and incremental contour values are given by z_{\min} , z_{\max} , and z_{incr} , respectively.

Figure 2.

Sensitivity contours for $v=j=0 \text{ \AA} v'=j'=0$ (reactive) transition probability at 1.00 eV and at a scattering angle of 180° .



The goal of this study is to use QFSA to study the $\text{H} + \text{H}_2$ reaction and its isotopic analogs to determine the level of chemical accuracy required in the PES to duplicate experimental results. This is important because the H_3 system plays a fundamental role in developing theories of chemical reactivity. Our initial effort is concerned with collisions with the total angular momentum restricted to zero. This is a substantial increase in complexity as the theoretical description of the 3-D quantum dynamics includes rotational motion, increases in basis size (with concomitant increases in matrix dimensions and equations that need to be solved), and complexities in molecular symmetry. The calculation of quantum sensitivities involves issues not normally encountered in typical reactive scattering calculations, e.g., the phase of individual scattering matrix elements.

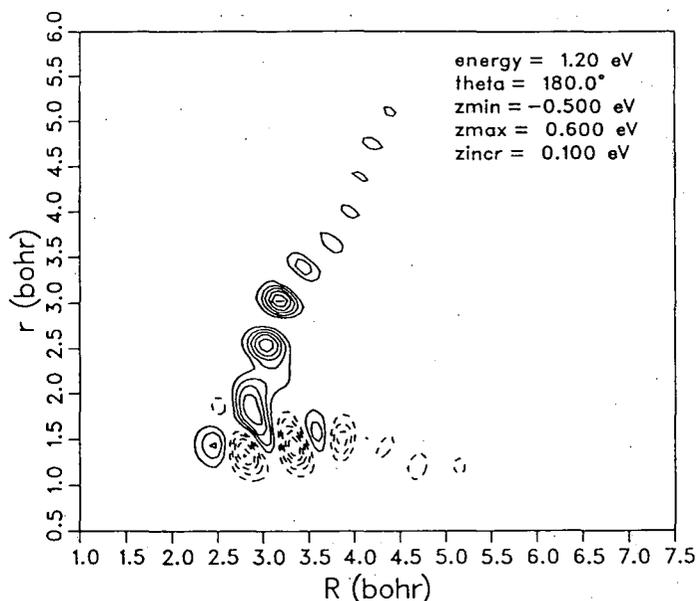
Figure 1 shows two energy slices of the $v=0, j=0 \text{ \AA} v'=0, j'=0$ (reactive) transition probability sensitivities in the threshold region at $E=0.55$ and $E=0.60$ eV for the Liu-Siegbahn-Truhlar-Horowitz⁵ potential energy surface. The slices are taken at a scattering angle of 180° . The dashed contours represent regions of negative sensitivity, i.e., regions of the potential surface where an increase in potential values will decrease the reactive transition probability. Similarly, the solid contours are regions of positive sensitivity where an increase in the potential will increase the proba-

bility for this particular transition. The largest (negative) sensitivities are on the two sides of the reaction barrier slightly removed from the barrier top. These are the regions where quantum mechanical tunneling is important. This particular feature has also been seen before for the collinear reaction.³ The main difference between the two energy slices is that at the lower energy, tunneling plays a dominant part in the reactive transitions, and an increase in the shoulders

of the barrier (which roughly corresponds to the classical turning points along the vibrationally adiabatic reaction path) adversely affects the tunneling probability. At the higher energy, the classical turning points are beginning to coalesce, with the largest sensitivities near the top of the barrier.

Figure 2 shows the $v=j=0 \text{ \AA} v'=j'=0$ transition probability sensitivities taken at a higher total energy of $E=1.00$ eV at a scattering angle of 180° . At this energy there are areas of large positive sensitivities in the inner and outer corners of the saddle point region. At even higher energies, the sensitivities become much more speckled in nature. The increase in structure of the sensitivities is due to the higher oscillatory nature of the scattering wave functions at the higher collision energies.

Figure 3 shows the $v=j=0 \text{ \AA} v'=0, j'=2$ transition probability sensitivities at $E=1.20$ eV and 180° . These sensitivities are formed from the product of two wave functions with different rotational quantum numbers. One wave function is determined by an incoming wave in the $v=0, j=0$ state of the reactant arrangement; the other wave function is determined by an incoming wave in the $v'=0, j'=2$ state of the product arrangement. Thus, the


Figure 3.

Sensitivity contours for $v=j=0 \text{ \AA} v'=0, j'=2$ (reactive) transition probability at 1.20 eV and at a scattering angle of 180° .

sensitivities are asymmetric about the symmetric stretch line.

The potential barrier for the $H + H_2$ reaction is much higher in non-collinear geometries. Hence, both the wave functions and the sensitivities are much smaller at scattering angles that are quite different from those associated with the collinear geometry. In order to facilitate a thorough investigation of the sensitivities at different scattering angles and at different collision energies, it will be necessary to use advanced visualization tools to sweep over several slices in a continuous fashion. We are currently beginning to apply these visu-

alization technologies which will also be useful for studying other 3-D reactions in the future.

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Investigators

N.J. Brown
J. Chang

Combustion Fluid Mechanics

Turbulent combustion is the dominant process in heat and power-generating systems. Its most significant aspect is that turbulent mixing enhances the burning rate and volumetric power density. Turbulent mixing, however, also influences chemical rates and has a direct effect on formation of pollutants, flame ignition and extinction. Therefore, research and development of modern combustion systems for power generation, waste incineration and material synthesis must rely on a fundamental understanding of the physical effect of turbulence on combustion to develop theoretical models which can be used as design tools.

The overall objective of our program is to investigate (primarily experimentally) the interaction and coupling between turbulence and combustion. These processes are highly complex and are characterized by scalar and velocity fluctuations with time and length scales spanning several orders of magnitude. They are also influenced by the difference in flow and burner geometries. Our approach is to gain a fundamental understanding by investigating idealized laboratory flames. Laboratory flames are amenable to detailed interrogation by laser diagnostics and their flow geometries are chosen to simplify numerical modeling and simulations and to facilitate comparison between experiments and theory.

Our current goal is to obtain a physi-

cal understanding of the effects of combustion heat release on turbulence characteristics, and to quantify the relation between turbulence intensity and the burning rate. The experiments are concentrated on flames with moderate turbulence intensity where chemical reaction rates are not significantly affected by turbulence mixing. The turbulent burning rate can be determined from the flame front topology (i.e., the flamelet geometry*) which can be compared to the turbulence characteristics. The flamelet geometry and turbulence statistics are analyzed to elucidate the flame propagation processes and to validate numerical turbulent combustion models.

The next goal is to investigate flames with high turbulence intensity to provide a closer simulation of the combustion processes in practical systems. The effect of turbulence on chemical reaction rates can be significant and may lead to the reduction of burning rate and intermittent flame quenching and re-ignition. This study requires in situ measurement of the local burning rate of the flamelets. The steep scalar gradients across the flamelets coupled with rapid flamelet motion makes the task quite challenging even with the applica-

*The turbulent flame zone consists of wrinkled thin flamelets (< 1 mm) which can be characterized by the local flamelet curvature and by the wrinkle size.

tion of advanced laser diagnostics. Our current study of flames with moderate turbulence forms the necessary scientific and theoretical background for this work.

Recognizing that both the flowfield and local turbulence affect turbulent flame characteristics, our experimental program has emphasized investigating flame propagation under a variety of flow geometries. We have thus far developed five laboratory flame configurations. The experimental results are compared to those of statistical one-dimensional (1-D) models, deterministic two-dimensional (2-D) models, and three-dimensional (3-D) direct numerical simulations. Our first two laboratory flames are simulations of flame configurations used in many practical systems. They are an unconfined rod-stabilized v-flame propagating in turbulent flow, and a large axis-symmetric Bunsen-type conical turbulent flame stabilized by a pilot flame. These flames are oblique to the approach flow and their flowfield can be treated as 2-D. The next two are developed because the flowfield and flame orientation lend themselves easily to theoretical modeling. They consist of planar premixed turbulent flame stabilized in stagnation flows produced by a plate or by two opposed streams. The flames are locally normal to the approach flow and do not rely on flow recirculation for flame stabilization. The latest configuration is

a new discovery which has commercial potential in addition to its significance to fundamental research. This freely propagating flame stabilized by weak swirl provides a close approximation to the flow field of a 1-D flame. Typical turbulence intensities studies in these flame configurations are from 5 to 10% of mean flow velocity. The turbulence Reynolds number, Re_t , is in the range of about 100. These turbulent flames are characterized as wrinkled laminar flamelets because the chemical time scales seem small when compared with those of turbulence.

Several well-established laser diagnostic techniques with high spatial and temporal resolutions are used to measure statistical moments and correlations of velocity and scalars (i.e., gas density, reaction progress variable). These techniques include laser Doppler anemometry (LDA) for simultaneous measurement of two velocity components and Rayleigh scattering from a focused laser beam for density measurements. We pioneered development of linear-array Rayleigh scattering, the applications of LDA to measure conditional velocity statistics and flowline tracing by auto feed-back control.

Other scalar diagnostics include laser-induced Mie scattering from silicone-oil aerosol (MSOD) for measuring the reaction progress variable and flame crossing frequencies. Mie scattering is also used for laser sheet imaging of the flame geometry by high-speed tomography. Further diagnostic developments include Particle Image Velocimetry (PIV) combined with MSOD. This technique will be used to investigate the interaction between vortical turbulence structures and flamelet curvature.

At high Damköhler number—typical of our experimental conditions—the flame brush can be treated as a region of reactants and products separated by strained laminar flamelets. This concept has been successfully employed in a variety of models including the statistical 1-D model by Bray, Moss and Libby (BML), and the 2-D deterministic vortex dynamics model by Chorin. Under these conditions the global turbulent burning rate may be determined in terms of the flame surface geometry and the local burning rate. In the most recent description by Bray, the mean burning rate at a point in the flame zone is characterized by a parameter I_0 ,

which describes the effects of the strain field and flamelet curvature on the local burning velocity through the local flame stretch, k . If it is assumed that positive and negative curvatures cancel, and the flame response to curvature is linear and anti-symmetric, I_0 can be modeled from a knowledge of the distribution of the strain rates and a "library" of strained laminar flame calculations. Another significant parameter in Bray's model is the flamelet surface area-to-volume ratio, S . Various transport equations for it have been developed. A simple expression for S is based on the spatial distribution of flame crossings along a contour of constant progress variable, c ($c = 0$ in the reactants and $c = 1$ in the products), and it includes a mean direction cosine of the flame normal which is also open to direct experimental investigation.

Our experimental work for 1992 has been focused on using a weak-swirl burner to investigate premixed turbulent flame propagation. This novel weak-swirl burner was discovered in 1991 and has shown to provide a flame that is a close approximation to the 1-D

planar flames described in the model of Bray, Moss and Libby. As reported last year, the flames are not in contact with any physical surfaces or objects and they can be considered as adiabatic. Another attribute is that the flame zone gives free access to laser diagnostics for detailed measurements. We have also found, however, that the original design of the swirl air injectors produces slightly asymmetric flames.

To produce a more uniform flame brush, we have redesigned and constructed a new swirl section for the burner. Shown in Figure 1 is the correlation of flame speed, S_t , with turbulence kinetic energy, q' . The experimental conditions have been extended to cover a wider range to infer the linear dependency of S_t on q' . As can be seen, the results are linear and compare well with those obtained previously using the stagnation plate stabilized flames. Because the weak-swirl burner has the potential of stabilizing highly turbulent flames, it is an ideal configuration for investigating turbulent flame speed and flame quenching.

In addition to its scientific significance,

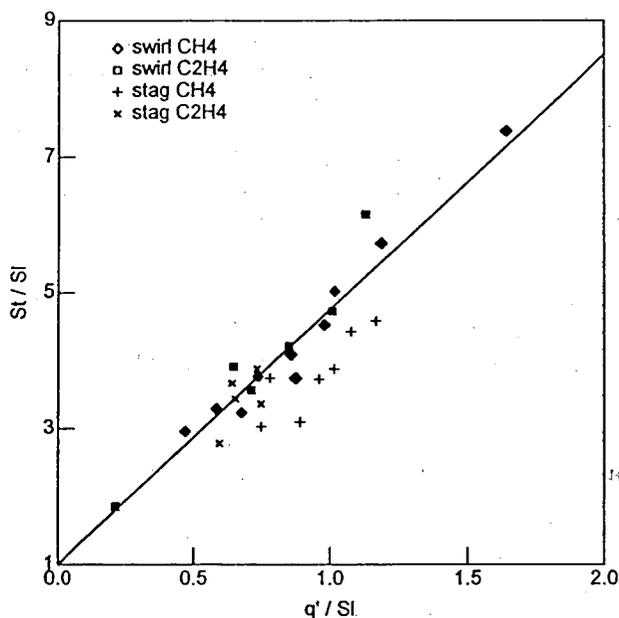


Figure 1. Turbulent flame speed, S_t , obtained using weak-swirl burner are compared with speeds of flames stabilized by stagnation flow. Methods previously used to measure flame speed have led to large discrepancies; the two configurations represented here provide the most unambiguous results to date. q' = turbulence kinetic energy.

the weak swirl burner is a prime candidate for technology transfer. The burner operates under a much broader range of mixture conditions than any of our laboratory burners. In particular, it supports stable combustion in very fuel-lean conditions. This feature can be exploited in designing a low NO_x emission furnace. Development of reliable lean-burn systems to replace current models will contribute to the improvement of regional and indoor air quality. Our laboratory burner has about the same power rating as residential air and water heaters. Therefore application of the weak swirl burner to these furnaces seems appropriate. Several approaches to implement this new technique can be sought. One is to retrofit existing furnaces with the swirl burner. Another is to design new furnaces to take full advantage of the unique flame shape produced by this burner. In either case, the operating principle is understood. Scaling the design to different power ratings would be relatively straightforward using the kind of flame speed data shown (Fig. 1). A patent is being sought for the weak-swirl burner and potential licensees and co-developers are being pursued through the Technology Transfer Department at LBL.

In 1992, we initiated an experimental program to investigate low-Reynolds-number premixed turbulent flames in microgravity to gain a fundamental understanding of the gravitational effects

on flame-turbulence interaction processes. This aspect of turbulent flame propagation is not well understood and has yet to be considered in current turbulent combustion theories. Our experimental results are expected to provide guidance and validation for the development of turbulent combustion models to include the effects of gravity. The work is focused on developing the methodology, experimental apparatus and laser diagnostics for application in the NASA Lewis Research Center 2.2 drop tower. Flow visualization techniques coupled with computer controlled image processing are used to characterize the behavior of the aerodynamic flowfield and mean flame properties under microgravity. To provide the necessary scientific background for the microgravity experiments, a parallel study of laminar and turbulent flames subjected to +g (upward-pointing flame) and -g (downward-pointing flame) forces is also conducted. These +g and -g laboratory flames are investigated with the use of more sophisticated laser diagnostics such as laser Doppler anemometry to obtain statistical data.

The behavior of laminar and turbulent Bunsen type premixed flames under microgravity has been observed by the use of laser schlieren. This is the first successful application of the schlieren technique to drop tower experiments. The schlieren images are re-

corded on video tape and are analyzed by computer controlled image processing. Figure 2 shows the comparison of the +g, -g and mg (microgravity, i.e., $g \ll 1$) flames. The most distinct feature of the normal gravity results is the interface between the products and the ambient air. The video shows that the +g flames flicker due to the buoyancy driven instability of the interface. This is the process through which gravity affects flame propagation. On the other hand, the -g flames do not flicker, because the interface is stable and encloses the flame zone. Under mg, the buoyancy driven instability is absent and is not dominant in inducing flame motion. However, the laminar flame still exhibit some flame instability which is small compared to the normal gravity flame flickering. In the turbulent flames due to the random nature of the wrinkled flame fronts, the difference between normal and mg flames are more difficult to identify and quantify. The differences will be investigated using the appropriate image analysis and display software for characterizing the flame wrinkle scales and their evolution. This work is in progress and the results will be forthcoming.

Our theoretical study of premixed turbulent flames involves the development of deterministic models of turbulent combustion employing Chorin's vortex dynamics method. In contrast to the statistical modeling approach where

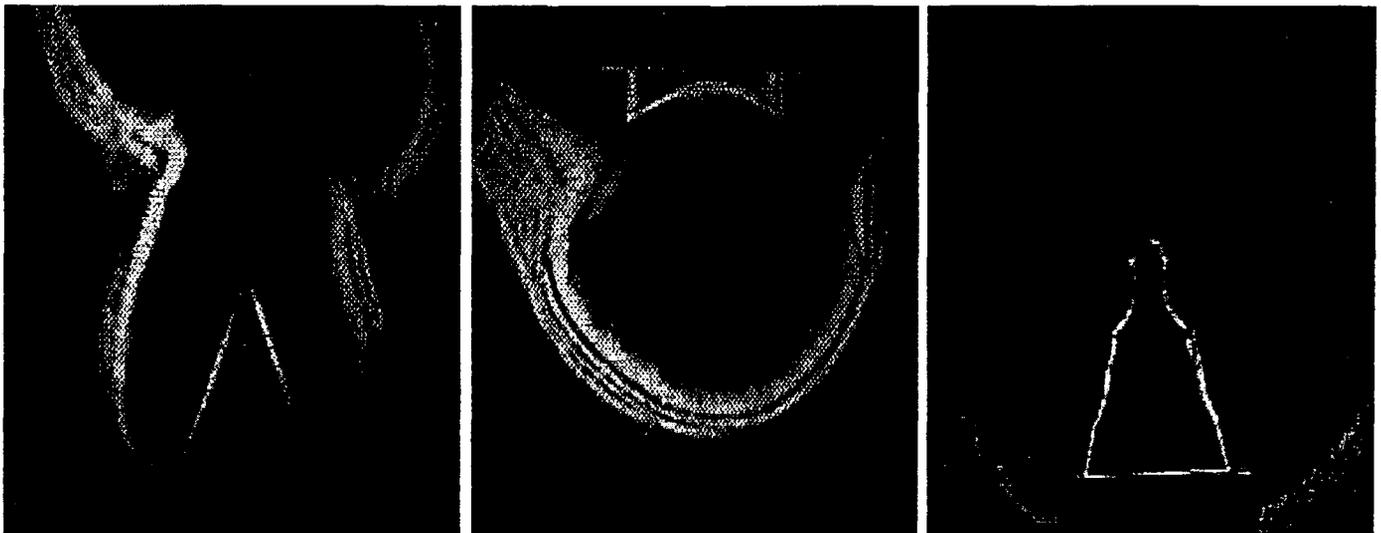


Figure 2. Laser schlieren images of a laminar Bunsen flame, obtained under normal gravity (left), negative gravity (center), and microgravity (right). Under normal gravity, the conically shaped flame is surrounded by an unstable, pulsating interface formed between the hot products and the room air. The flame and surrounding interface undergo significant changes when inverted (i.e., when subjected to negative gravity). In microgravity, the interface does not pulsate and the flame is not influenced by its surround.

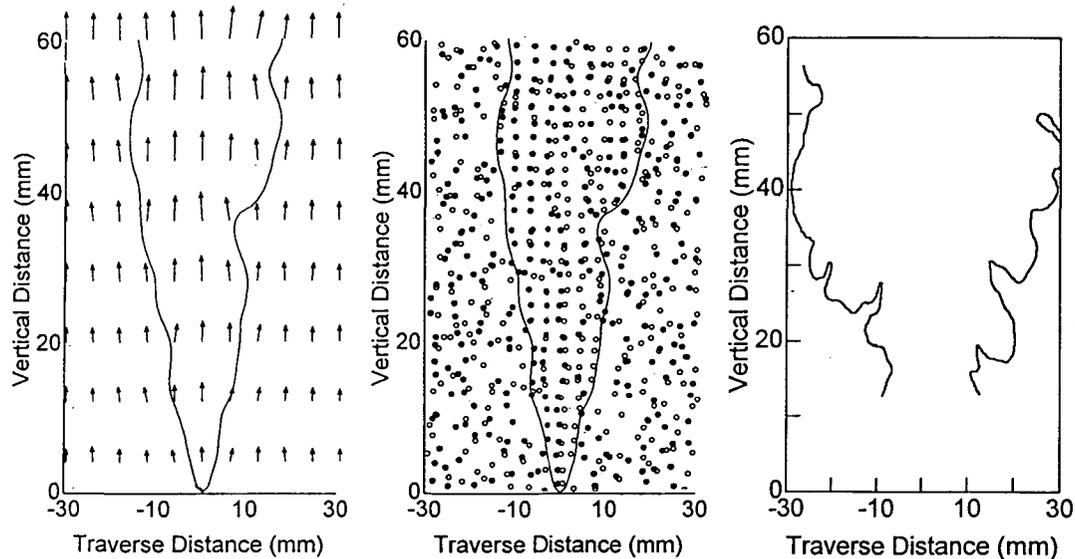


Figure 3.

Comparison of 1) flame edge deduced from experimental tomographic record (left) and 2) results of vortex-dynamics simulations of a rod-stabilized turbulent v flame (center, right). Numeric simulation provides insight into changes in the flame's internal vortices (center) and velocity vectors (right).

the changes in flame turbulence are modeled and used as input parameters, the vortex dynamics model is capable of predicting these changes and other flame phenomena, the flamelet geometry in particular. In simulating the flamelets, one needs to follow the evolution of the flamelets whose speed depends on the local curvature. The algorithms approximate the equations of motion of propagating fronts with curvature-dependent speed, which are called PSC schemes, for Propagation of Surfaces under Curvature. These algorithms are coupled to a vortex dynamics approach to describe both the turbulence in the oncoming stream and turbulence production by the flame itself, and a volume production model to represent combustion heat release. Various statistical data, including conditioned and unconditioned mean and RMS values of the two velocity components and the Reynolds stress can be deduced from the numerical results and compared with experimental data.

We have developed a two-dimensional premixed turbulent flame model which focuses on the structure of v -shaped free-burning anchored flames, including the effects of advection, volume expansion, flame generated vorticity, and curvature effects on the laminar flamelet propagation speed. Except for the restriction to two-dimensionality, this model is a fairly complete numerical

representation of our previous experimental work, under the assumptions inherent in the wrinkled laminar flamelet model, where the flame can be treated as a vanishingly thin interface separating reactants and products.

Our starting point in the analysis is a set of numerical algorithms developed by Sethian which captures faithfully the motion of a surface propagating with curvature-dependent normal velocity. Our task at the outset was to adjoin to the basic algorithms three additional processes: 1) the production of local straining and curvature variations at the flame interface due to turbulence; 2) the incorporation of volume expansion; and 3) the local flame-generated vorticity caused by baroclinicity. All these processes are interactive with each other, in determining the subsequent global flame motion. The calculation is a time dependent one; an initial flame configuration is assumed, and the calculation proceeds in time steps until a statistically stationary limit is achieved.

The results obtained thus far are extremely interesting, and as shown (Fig. 3), they bear a striking resemblance to the tomographic data we have obtained previously on turbulent v -flame structure. The numerical results obtained for each time-step have been transferred to a video disk and can be viewed at slow speed to infer the development of the flame wrinkles and their dynamic inter-

action with the turbulent flow in the reactants ahead and in the products behind. One of the numerical predictions is that the included angle of the v flame is determined more by volumetric expansion than by enhancement of the burning velocity due to turbulence. This is a feature we observed in our experiments.

Our numerical results also show that vorticity production by baroclinicity at the flame front alters the mean angle of the flame. The thickness of the flame brush due to oscillations produced by the incoming turbulence appears to be consistent with what we observe experimentally. In addition, the numerical results can be analyzed to obtain detailed velocity statistics for direct comparison with our LDA data. These quantities include the vorticity, integral scale and Reynolds stresses in the burnt gas. We have experimental data on the integral scale and Reynolds stresses, with which our numerical results can be compared, and we are in the process of doing this.

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Controlled Combustion

According to current technological standards, combustion chambers for prime movers are treated solely as sources of power without much attention given to their performance as chemical reactors. Consequently their tendency to produce air pollutants is relatively unconstrained. In the automotive industry, for example, the strategy adopted throughout the world to deal with the problem of pollutant emissions is to reduce their concentration by chemical processing of combustion products in the exhaust system.

The basic purpose of our studies is to provide a scientific basis for controlling the combustion process so that pollutant formation is reduced. The means of doing this are beneficial also to fuel economy (a prominent factor in reducing CO₂ pollution) and engine tolerance to a wide variety of fuels—a significant effect in simplifying the task of fuel supply and, hence, rendering it less energy-demanding.

Our ultimate goal is to advance the technology of internal combustion engines. For this purpose the acquisition of knowledge on systems and processes in current use and the concomitant progress of science, albeit necessary prerequisites, are by themselves not sufficient. To be actually effective, this has to be supplemented by concepts and their assessment. After more than a decade of studies on the fundamentals of ignition and combustion of particular relevance to internal combustion engines, we are now entering the phase of the development and study of new concepts.^{1,2,3}

For this purpose it became incumbent upon us to re-examine the methodology of executing the exothermic process of combustion in an enclosure modeling typical engine conditions. In this connection we developed a novel approach to the thermodynamic analysis of combustion under the confinement of a container, such as a constant volume vessel or a cylinder-piston enclosure.⁴ Energy loss due to heat transfer to the walls was, on this basis, comprehensively studied, yielding information on the characteris-

tic relationship it bears with the mass fraction of products at thermodynamic equilibrium.⁵ This approach was confirmed experimentally by laser probe Rayleigh scattering density measurements.⁶

A variety of techniques based on the use of a Pulsed Jet Combustion (PJC) mode for the execution of the exothermic process of combustion were investigated leading to the development of a novel jet plume injection and combustion system, whereby the process is carried out in two steps: 1) injection of a jet to form a turbulent plume, and 2) ignition of the residual charge in the cavity of the jet generator to initiate combustion in the plume.⁷ Concomitantly a systematic study has been carried out to compare the effectiveness of a PJC system with plasma jet ignition.^{8,9}

In continuing this program of research, we are in developing a rational approach to evaluating the thermochemical processes associated with the initiation and execution of the exothermic process of combustion in engines. The study is supported by the Gas Research Institute.

The purpose of the study is threefold:

- provision of a rational background for estimating the consequences of a variety of modes in which the process of combustion can be executed. This concerns primarily Flame Traversing the Charge, or FTC, following spark ignition as is typical of current technology, in contrast to PJC. We expect to pave thereby the way for the development of controlled, clean combustion engines of the future;
- comprehensive rendition of the thermochemical processes of combustion in terms of integral curves (trajectories) in the phase (state) space, to serve as conditions of constraint for the Computational Fluid Mechanics (CFM) solution whereby the latter acquires the character of an eigenfunction problem in non-linear mechanics;
- formulation of the thermochemical nature of engine combustion as the object of an electronically governed control system.

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Investigators

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Combustion Modeling

Combustion modeling research is being performed to develop robust models of pollutant formation and destruction to use as design tools for future-generation combustors. The models will help identify combustion characteristics that are important in optimizing the tradeoff between reduced emissions and high energy efficiency. Our current modeling efforts have been concentrated in three areas:

- examining the suitability of using isocyanic acid (HNCO) to reduce NO in the exhaust of engines burning natural gas^{1,3};
- modeling nitrogen chemistry in combustion involving premixed laminar flames burning natural gas that are in contact with a reactive heat transfer surface; and
- adding chemistry to models of turbulent reacting flow.⁴

In these studies, model validation occurs by comparing calculated results with experiments.

A chemical mechanism, the Brown-Garay mechanism for the reduction of NO_x by HNCO was constructed to model NO_x reduction in exhausts typical of natural gas combustion with the addition of radical boosters (fuel). Variables considered were the initial concentrations of NO, NO₂, CO, O₂, CH₂, H₂, and HNCO as well as initial temperatures.

The NO reduction chemistry must be preceded by thermal ignition chemistry which generates radicals. The lowest temperature for which ignition occurs is the optimum temperature for reduction and defines the beginning of the temperature window. Reduction was not achieved for the "natural gas exhaust" for a reasonable residence time. Additional H₂ added to the exhaust mixture enhanced reduction, but the addition of CO and CH₄ did not.

Under some conditions the computed sensitivity coefficient for nitrogen species and temperature exhibited self similarity as shown (Figure). Self similarity occurs in dynamical systems where one or at most a few dependent variables dominate the physical behav-

ior of the system. Four reaction paths were identified which controlled the fate of the NO: the conversion of NO to NO₂ via HO₂, the conversion of NO₂ to NO via reaction with H or O, the reduction of NO via NCO, and the reduction of NO from reactions with NH_i species. The relative importance of the four was determined by the initial conditions.

Studies of premixed laminar flames have been undertaken to develop an understanding of processes that control the formation and fate of oxides of ni-

trogen and carbon monoxide in combustion occurring in residential, small industrial and commercial appliances. The properties of premixed CH₄/Air flames were determined for a range of equivalence ratios between 0.85 and 1.30. A two-point boundary value code that includes detailed chemistry was employed to describe the combustion. Sensitivity analysis was used to determine mechanistic details and to develop reduced chemical mechanisms for this system.

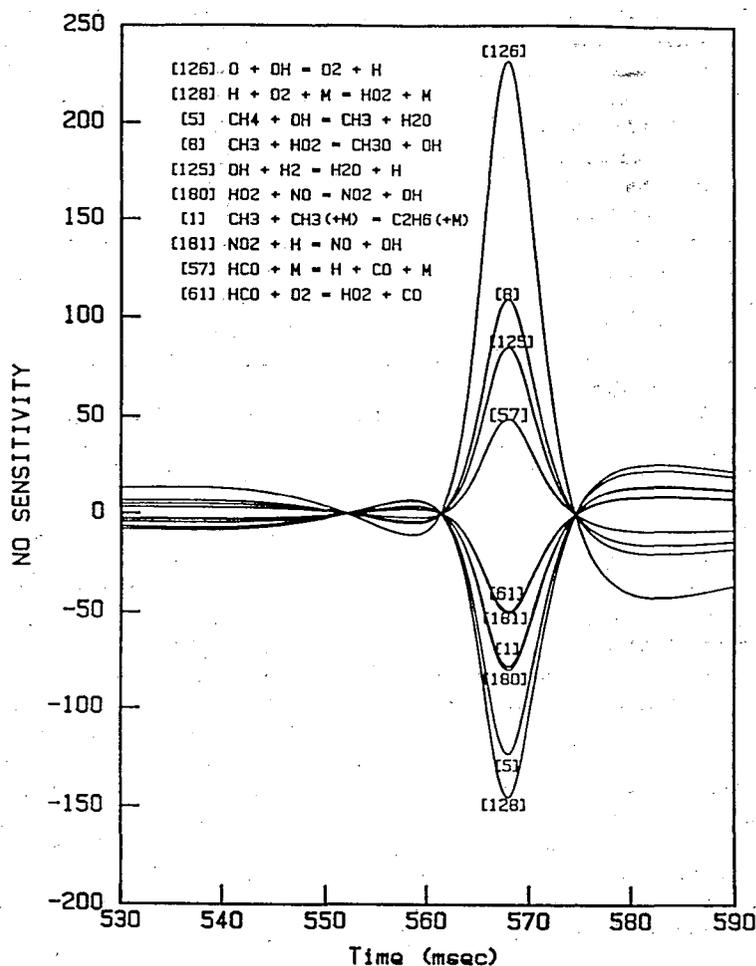


Figure.

Sensitivity coefficients of NO as a function of residence time for the ten most important reactions of the Brown-Garay mechanism for an exhaust at 1050 K for adiabatic, constant pressure combustion.

Final concentrations of NO and CO were determined for three chemical mechanisms and compared. The modeling calculations have confirmed the importance of prompt NO chemistry in lean flames, and that it is the dominant NO chemistry in rich flames. The final concentrations of CO in all flames were quite large and increased with equivalence ratio.

Model refinements were undertaken and these yielded a less complex (reduced) mechanism which mimics all attributes of the full mechanism with respect to species and temperature profiles. Flame calculations performed with the reduced mechanisms yield NO and CO concentrations that agree excellently with those determined from the full mechanism. Reduced mechanisms will be used in calculations with more complex fluid mechanics. We have compared the results of premixed laminar flame calculations with approximations that are often used to predict NO concentrations. Approximations like decoupling the NO chemistry from the hydrocarbon chemistry, or assuming that the NO is equilibrated, are extremely poor.

Many practical combustion systems have turbulent flow fields. In order to predict pollutant formation and destruction in these systems, the coupling between reactive and diffusive processes must be described properly. While fluid-mechanical turbulence models and detailed chemistry flame models are solvable on standard vector super computers, the combination of turbulent flow and detailed chemistry in the same model requires the next generation of super computer: the massively parallel machine. With colleagues at Sandia National Laboratory, we have begun to use parallel computing to model pollutant formation in a turbulent reacting jet. We have used a probability distribution function (PDF) model that primarily involves Monte Carlo calculations and is thus highly amena-

ble to efficient parallel implementation. The model was implemented on a distributed network of 25 IBM RS6000 workstations. With our computer science colleagues at LBL and SNL, we have designed a new Parallel Object Oriented Environment and Toolkit (POET) whose purpose is to provide the user with a transparent link to the power of parallel distributed computing. POET is a high-level, object-oriented framework that isolates the

description of the physical model from the code that implements the parallel algorithm and flow. The physics specific to a user's particular application problem is handled as a user add-on. Calculations describing a H₂/Air turbulent diffusion flame including detailed chemistry can now be performed on a dozen of RS6000 machines. We are continuing to develop the toolkit and increase the level of detail in the chemical description of the flame.

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Investigators

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Dilute Engine Combustion

Dilute engine combustion holds the promise of improved efficiency, extended fuel tolerance, and reduced emissions in gasoline engines. Excess air induction, exhaust gas recirculation, residual gas retention, or a combination provide dilution. The U.S. automobile industry is likely to use this approach to improve the fuel economy of current stoichiometric, three-way-catalyst-equipped vehicles.

Understanding the fundamental processes that limit dilute combustion under engine conditions is essential to the development and improvement of dilute combustion engines. We are studying three aspects of the combustion:

- inlet and in-cylinder flows and fuel-air mixing;
- flame propagation, including the effects of in-cylinder mixing; and
- wall heat transfer.

Experimental facilities include a unique spare piston engine simulator, which provides full optical access to the flow and combustion processes; a valve-flow simulator; and a constant-volume cell.

Experimental studies include visualization and quantification of intake flows, in-cylinder mixing of fuel and air, and combustion processes and measurement of time- and space-dependent heat transfer rates. Planar Mie scattering identifies the flamefront. Particle imaging velocimetry (PIV) provides mapping for velocity fields. Planar fluorescent imaging is planned to observe hydrocarbon formation processes. Theoretical models aid in the interpretation of experimental observations and contribute to comprehensive engine models.

During FY92 we obtained Mie scattering images of the combustion process (Figure), and we continued development of particle imaging velocimetry (PIV) with the introduction of a masking technique to identify particles (i.e., a technique which improves signal-to-noise ratios). A heated, rapid-response, platinum resistance thermometer measured the effect of wall temperature on

heat transfer, extending the range of wall temperatures observed.

During FY93 we will complete refinement of our PIV approach and apply it to flows in the square-piston engine simulator. We will obtain a new heat-

flux gauge with higher temperature capacity and apply it to wall heat flux measurements at higher wall temperatures. If requested funding is obtained, studies of hydrocarbon formation will be initiated.



Figure.

A planar Mie scattering image of combustion in the square piston engine simulator locates the flame front. Image processing accents the difference in scattering intensity which is high in the low temperature reactants and low in the high-temperature products.

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Thermal Destruction of Toxic Compounds

Incineration currently provides the highest available destruction efficiency for organic compounds. However, emerging regulations and growing public concerns require even higher destruction and control of all toxic emissions, and spur the development of new diagnostic and monitoring techniques. The goals of our research are to gain a fundamental understanding of the chemical processes that occur when chlorinated hydrocarbons are destroyed thermally, study new ways to enhance the destruction of these compounds, and to develop new diagnostic methods for the measurement of these species and their byproducts.

We are studying the thermal destruction of chlorinated hydrocarbons in a laboratory scale turbulent flow reactor, with products monitored by Fourier transform infrared (FTIR)/long-path absorption spectroscopy. We are injecting numerous gas and liquid phase C₁ and C₂ chlorinated hydrocarbons into the post flame gases of lean propane/air and methane/air flames. Pure compounds and mixtures of chlorinated hydrocarbons with fuels are used. We are also constructing a new vertical flow reactor that allows full optical access and is computer-controlled.

We have determined that the key reaction for the formation of phosgene from 1,1,1-trichloroethane is the gas phase oxidation of the dichlorovinyl radical by oxygen molecules. The radical is produced by the reaction of 1,1-dichloroethylene with chlorine or hydroxyl radicals. Photolysis and wall reactions are not significant in our system.

We are also studying the use of adding small amounts of fuel to post-flame combustion products to destroy trace amounts of chlorinated hydrocarbons that persist in normal incinerator exhausts. Methane, ethane, or carbon monoxide is injected at temperatures in the 900-1300 K range, where they react without producing a flame to provide radical species which then attack the more stable chlorinated hydrocarbons. We

have found that by changing the type of fuel added we can change the distribution of products. The radical levels in the reacting mixture are altered, which affects the reaction pathways.

Substantial progress continues to be made in developing new *in situ* diagnostic methods for detecting chlorinated hydrocarbons. A high-temperature, long-path infrared cell coupled to a small flow reactor can measure chlorinated hydrocarbons and reactive intermediates in combustion flows without introducing sampling artifacts and with minimal flow disturbance. Chlorinated hydrocarbons can be measured in this apparatus at 1000 K and at concentrations in the ppm range.

We have continued to develop non-intrusive optical diagnostics using photofragmentation/laser-induced fluorescence. A 193-nm ArF excimer laser is used to fragment the chlorine-containing species into smaller pieces, with the resulting fragments detected by their characteristic fluorescence, either from excited states formed in the photolysis process or by pumping ground states with a tunable dye laser. We have focussed on the CCl fragment formed when ethyl chloride is fragmented. We have determined that the CCl fragment is formed by a fast unimolecular process involving two or three photons, and it is produced in an excited state. Relaxation/reaction rates have been measured, and detection at sub-ppm levels in 1 sec has been accomplished.

Higher destruction efficiencies are needed for extremely toxic substances, such as nerve gas, and for compounds that are difficult to incinerate. We have developed a plasma flame apparatus to raise the normal flame temperatures by adding electrical energy through an inductively coupled radio frequency (RF) source. Small amounts of a potassium salt are used to facilitate and control the coupling of the radiation with the combustion products. Stable plasma flames have been obtained with pure ethyl chloride as the fuel.

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Atmospheric Aerosols

Atmospheric Aerosols Research

Recent calculations suggest that anthropogenic sulfate aerosols may mask the effects of increasing concentrations of "greenhouse" gases through their reflection of solar radiation and through their effect on cloud albedos. Central to this hypothesis is the assumption that there is a one-to-one relationship between sulfate mass concentration and cloud condensation nuclei (CCN) and, therefore, cloud droplet number concentration. To test this hypothesis, we have measured CCN, droplet number concentrations, and aerosol sulfate mass concentrations *in situ* in warm marine cumulus and stratocumulus clouds on El Yunque peak in Puerto Rico.

Our results show:

- sulfate mass concentration is not the only factor that determines droplet concentrations;
- the sensitivity of droplet concentrations to the changes in sulfate mass concentration depends on mixing processes characteristic of different clouds; and
- empirically derived sensitivities are much lower than implied by the one-to-one relationship used in assessments of the indirect forcings of anthropogenic sulfate aerosols.

The nss SO_4^{2-} concentrations for different 6-hr sampling periods can be compared to the CCN concentrations and the average droplet concentrations detected on the same days during approximately similar counting periods (5-6 hr). The data show that the clear sky CCN and nss SO_4^{2-} concentrations are correlated ($r = 0.82$). Correlations among CCN concentrations, methane sulfonate, and dimethyl sulfide concentrations have recently been observed

from *in-situ* measurements in the same air mass. We believe that our data represent the first reported *in situ* determination of the CCN-sulfate relationship.

Having demonstrated the proportionality between CCN number and nss SO_4^{2-} mass concentrations, we have examined the relationships between CCN, nss SO_4^{2-} , and droplet concentrations. As expected, the decrease in CCN concentration, ΔCCN , from pre-cloud to in-cloud conditions closely matches the increase in cloud droplet concentration, ΔNd , demonstrating that a fraction of these CCN is involved in droplet formation. However, the CCN scavenging ratios, $\Delta\text{CCN}/\text{CCN}$ (pre-cloud), can vary from 0.24 to 0.7 independently of pre-cloud CCN concentrations, suggesting that a variable fraction of the aerosols forms cloud droplets. Because of the correspondence between CCN and nss SO_4^{2-} mass concentration, we can expect that a similarly variable nss SO_4^{2-} aerosol mass fraction is incorporated into droplets, suggesting that a direct correspondence between Nd in clouds at our site and SO_4^{2-} may not always exist.

Unlike the CCN, the cloud drop number concentrations do not show a simple relationship with aerosol sulfate concentration. The data fall into two groups: those with low Nd concentrations ($\sim 160\text{-}220 \text{ cm}^{-3}$) and those with average liquid water content (LWC) concentrations ($\sim 350\text{-}420 \text{ cm}^{-3}$) and LWC ($\sim 0.15 \text{ g/m}^3$). Visual observations of low Nd and LWC clouds indicate that these were principally fair weather cumulus clouds. The high Nd and LWC clouds were visually identified as stratocumulus clouds. For the first group, increasing the nss SO_4^{2-} mass concentration from ~ 270 to $\sim 1400 \text{ ng/m}^3$ did not result in a discernible increase in droplet concentration. The droplet concen-

trations for the second data group, however, could be construed as showing a slight increase when the nss SO_4^{2-} concentration increases from $\sim 300\text{-}1100 \text{ ng/m}^3$.

Both cumulus and (to a lesser degree) stratocumulus clouds are affected by entrainment and mixing processes that can influence the response of droplet concentrations to the changes in CCN and nss SO_4^{2-} concentrations. The mixing processes can be distinguished by comparing the LWC and droplet number concentrations. For all cumulus cloud events, the mixing process was found to be highly inhomogeneous. In contrast the mixing in stratocumulus clouds has a significant homogeneous component.

Based on this evidence, we conclude that mixing processes have a definite influence on the relationship between nss SO_4^{2-} and droplet concentration. Extreme inhomogeneous mixing characteristic of cumulus clouds may effectively obscure the Nd vs. nss SO_4^{2-} relationship established in the first stages of droplet formation. Conversely, in stratocumulus clouds characterized by decreased inhomogeneous (or increased homogeneous) mixing, the Nd dependence on nss SO_4^{2-} becomes more apparent. We note that the differences in CCN scavenging ratios may also be caused by the mixing processes.

From the measured relationship between droplet and sulfate concentrations, the sensitivity of the relative droplet concentration change to the relative change in SO_4^{2-} mass concentration $S = (\Delta\text{Nd}/\text{Nd})/(\Delta\text{SO}_4^{2-}/\text{SO}_4^{2-})$ can be defined. The value of S is ~ 0.1 for the subset of clouds that we have classified as stratocumulus clouds. For fair weather cumulus clouds, $S = 0$ because no apparent dependence of Nd on sulfate is observed.

We can compare our results only with those obtained for continental clouds because similar measurements for marine clouds in other regions have not been reported. For continental cumuliform and stratiform clouds, reported sensitivities are ~ 0.19 and ~ 0.26 . The sensitivity of continental cumuliform clouds (which most likely include stratocumulus clouds) is about a factor of two higher than our value for marine stratocumulus clouds.

In view of the similarity between the sensitivities of marine stratocumulus clouds ($S \approx 0.1$) and continental cumuliform clouds ($S \approx 0.2$), we may speculate that marine stratus clouds could be characterized by $S \approx 0.3$, as indicated by the results obtained for continental stra-

tus clouds ($S \approx 0.26$). The value of $S \sim 0.3$ could be taken as a reasonable upper limit for average marine (stratocumulus and stratus) clouds considered in estimating the indirect aerosol effects. This value for S would reduce the estimate of indirect sulfate aerosol forcing from -1 W/m^2 (with assumed $S = 1$) to -0.3 W/m^2 .

This lowered indirect forcing would reduce the estimate of total anthropogenic sulfate aerosol forcing (direct and indirect) from $\sim 2 \text{ W/m}^2$ to close to $\sim 1.3 \text{ W/m}^2$. The direct and indirect forcings from aerosols produced by biomass burning were estimated to be -0.8 W/m^2 each. If we correct the indirect biomass aerosol forcing by using $S \approx 0.3$, we obtain a total biomass forcing of $\sim -1.0 \text{ W/m}^2$ or total anthropogenic (sulfate

plus biomass) forcing of $\sim -2.4 \text{ W/m}^2$. Previous estimates for total anthropogenic forcing are -3.8 W/m^2 . The lower estimate is closer to the estimated greenhouse forcing, $\approx 2.5 \text{ W/m}^2$, and possibly more consistent with observed temperature increases.

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Ecological Systems

Heavy-Metal Toxicology and Bioremediation

Heavy metals may exert their toxic action on animals and plants by promoting free radical reactions, either directly as electron transfer catalysts or indirectly by binding to enzymes that protect against free radical processes. Prevention and amelioration of heavy metal accumulation in the biosphere poses one of the great challenges of this and future generations. Biological heavy-metal control and remediation, in conjunction with physical and chemical removal processes, may be the most economical and effective approach for restoring and maintaining acceptable heavy-metal levels in the environment.

Free radicals (i.e., reactive molecules containing unpaired electrons) are implicated in the effects of many other environmental risks factors, e.g., cigarette smoke. Improvements in detecting "fingerprints" of free-radical damage could lead to more meaningful and efficient analyses of pollutant risks. Free radicals are also produced as an unavoidable consequence of aerobic metabolism in both animals and plants. The "free radical theory of aging" pos-

ulates that endogenously produced free radicals are responsible for the eventual deterioration of all higher organisms. Heavy-metal-catalyzed reactions may be a major source of chronic free radical damage and an improved understanding of such reactions may offer benefits not only for the abatement of pollutant exposure risk, but may lead to an understanding of "normal" deteriorative processes in biological systems and possible interventions in such processes.

Our purpose is to understand free-radical damage, particularly as it involves heavy metals and metalloproteins and possible interventions, including environmental management, to minimize free-radical-mediated risks in the biosphere. One component of our research program is to develop improved assays (biomarkers) of free-radical damage. Of particular interest is the role of free radicals in the adverse effects of cigarette smoke exposure. We are testing the hypothesis that iron released from oxidized heme proteins is subsequently complexed (chelated) by ciga-

rette tar components and is thereby converted to highly destructive free-radical catalysts.

Another component of our research program seeks to develop biological processes to remove heavy metals from contaminated environments. We are investigating microalgae and bacteria—as well as biomass derived from microalgae—with the objective of developing ion accumulation and binding systems that can remove heavy metals from water and soil.

Our principal experimental approach is electron spin resonance (ESR), which detects magnetic moments of free radicals. For our free-radical studies, the sensitivity of the ESR method is increased by working with "free radical traps" which accumulate ESR-detectable products. The ESR assays are being tested in the human red blood cell (erythrocyte). Many air pollutants readily pass across the lining of the lung and can react with blood components. Studies of human blood avoid many of the problems associated with animal studies.

We are also developing new ESR methods for detecting and quantifying paramagnetic heavy metals. We have introduced a new chromate assay that specifically detects the Cr(VI) species and allows us to detect chromate reduction products in metabolically active bacterial cell suspensions. A novel ESR copper assay distinguishes between free copper and complexed species and has proven especially useful for detecting copper-complexing agents released from cells and biomass.

We are also developing processes to modify, stabilize, and immobilize algal biopolymers for the selective removal of heavy metals from contaminated waste waters, and for the stripping of the bound heavy metals to generate a recyclable biofilter suitable for remediation of environmental toxins.

Studies of Heme Proteins and Transition Metal Ions

To help us understand the reactions of oxidants in cigarette smoke and other combustion gases with blood, we have characterized the interaction of hydroperoxides with hemoglobin and the related heme protein, myoglobin.

An analysis of the oxidation of a reduced nitroxide (2,2,6,6-tetramethyl-1,4-dihydropiperidine, TOLH) by ESR was used to resolve and quantify oxidants arising from the reaction of heme proteins with hydroperoxides.¹ Among these oxidants is chelatable iron, which is released upon oxidative cleavage of the heme ring. In conjunction with ascorbic acid (vitamin C), loosely chelated iron can produce the highly destructive hydroxyl radical. Iron released from myoglobin was distinguished from protein radicals and high iron oxidation states (ferryl heme) by analyzing TOLH oxidation in the presence of different chelating agents.

Treatment of metmyoglobin (metMb) with one mole of H₂O₂ per mole of heme produced protein-bound species that oxidized about two molecules of TOLH per heme. Some of the oxidizing species responsible for TOLH oxidation were highly persistent (t_{1/2} for their decay was 3 hrs at 25°C). Iron release, metMb bleaching and the catalysis of free-radical chemistry were analyzed in metMb solutions treated with tert butyl hydroperoxide (tBH). We found that iron release required about five-fold higher hydroperoxide concentrations than did metMb bleaching. Moreover,

alkoxyl and methyl radical production was catalyzed by iron released from metMb but not by protein-bound iron in oxidized metMb solutions treated with tBH and ascorbic acid. We have concluded from these studies that hydroxyl and alkoxyl radical production by hydroperoxide-treated metMb is due to released iron and not by protein-bound non-heme iron.

Identification of Heme Protein-Specific Antioxidants:

We discovered that nitroxide free radicals interact with hemoglobin (Hb)/metHb, Mb/metMb and with peroxidases/phenols to induce a catalase-like conversion of H₂O₂ to O₂ (catalytic activity), without being substantially consumed in the process.² Thus nitroxides substantially prevent the formation and persistence of free radical catalysts that are produced when these proteins react with hydroperoxides. The mechanism of the nitroxide-induced catalytic activity was postulated to involve a one-electron oxidation of the nitroxide to the immonium oxene, which then reacts further to release oxygen and the nitroxide. An involvement of the immonium oxene in the reaction mechanism is consistent with the observation that the ferryl heme was reduced by nitroxides and the detection of reduced nitroxides when the reaction mixture was supplemented with the two-electron reductant sodium borohydride. The nitroxide-induced catalytic activity was completely inhibited when the reaction mixture was supplemented with glutathione. Nitroxides also suppressed free radical formation by hydroperoxide-activated heme proteins, as evidenced by their inhibition of the spin-trapping of glutathionyl radicals. We concluded that H₂O₂ decomposition and a suppression of reactive free-radical formation by heme proteins is an antioxidant activity of nitroxides that is distinct from their previously reported superoxide dismutating activity. We also suggested that this antioxidant activity could be a factor in their protective action in models of cardiac reperfusion injury.

New Assays for Free-Radical Production by Peroxidase Enzymes

We developed an electron spin resonance (ESR) assay for free radical prod-

ucts of peroxidases treated with either H₂O₂ or organic hydroperoxides.³ The assay detects the formation of the persistent nitroxide free radical Tempol from its hydroxylamine derivative (TOLH). TOLH is oxidized to Tempol by short-lived radicals produced when peroxidase cycle intermediates Compounds I and II react with a variety of phenols. Surprisingly, we found that low concentrations of Tempol altered the rate of TOLH oxidation (and therefore, probably, peroxidase activity) as a function of the concentrations of Tempol, phenol and H₂O₂. Calibration curves were derived to correct for this effect. Important information relating to free radical production by peroxidases could also be obtained with this assay, including the detection of peroxidase-oxidizable molecules, e.g., in tissue homogenates or in tissue culture media, and quantification of hydroperoxide formation in biological systems, including in opaque tissue preparations that would be unsuitable for optical assays. The high membrane permeability of TOLH also afforded the opportunity of estimating peroxidase activity in membrane-enclosed compartments when TOLH oxidation rates could be stimulated with exogenous peroxidase reductants, e.g., phenol.

Studies of Thyroid Peroxidase - Derived Free Radicals *In Vitro*

Peroxidase enzymes (e.g., from the thyroid gland) were found to generate powerful oxidants when activated by hydrogen peroxide or organic hydroperoxides.⁴ Thyroid peroxidase may be a significant source of free radicals when the thyroid gland is exposed to high hydrogen peroxide levels and phenolic compounds (e.g., cigarette smoke and other combustion components). We found that CHO cultured cells, including cells transfected with a truncated thyroid peroxidase gene (generously provided by Dr. B. Rapoport, UCSF), produced cytotoxic agents when they were exposed to otherwise non-toxic fluxes of H₂O₂ from glucose oxidase in the presence of peroxidases (horseradish or thyroid enzymes). Tissue culture medium was shown to contain free radical precursors, capable of oxidizing glutathione to glutathionyl radicals. TOLH conferred significant protection, consistent with functioning as an antioxidant, and supporting the concept of a free radical damage mechanism in the observed peroxidase toxicity.

Chromate Reduction by *Bacillus Subtilis*

Bacillus subtilis reduced carcinogenic hexavalent chromate to the less hazardous trivalent chromic state under either aerobic or anaerobic conditions.⁶ Disappearance of chromate and a concurrent appearance of Cr(III) in the extracellular phase of cell suspensions were demonstrated by electron spin resonance (ESR) and spectrophotometric assays. A more than five-fold stimulation of chromate reduction occurred when cells were lysed by freeze-thawing, indicating that intracellular reductases or non-enzymic reductants cause higher rates of chromate reduction than do intact cells. Concentrated cells (10% pellet volume after centrifugation) reduced approximately 40 mM chromate/min when exposed to a chromate concentration of 100 mM and when assayed within three hours of harvesting. Probably because of cell lysis, chromate reduction increased with time after cell harvesting. About six hours after harvesting, packed cells (70% pellet volume) removed more than 99.8% of 2 mM (100 ppm) chromate in the growth medium within 15 min; most of this chromate reduction occurred under anaerobic conditions. This rate of anaerobic chromate reduction is of the same order of magnitude as the rate of respiration in air-saturated cell suspensions. A substantial fraction of the reduction product (at least 75%) was

extracellular Cr(III), which could readily be separated from the cells by centrifugation. At high chromate concentrations, some fraction of reduced Cr(VI) appeared to be taken up by cells, consistent with a chromate-dependent appearance of intracellular paramagnetic products. Under appropriate conditions, *B. subtilis* appears to be an organism of choice for detoxifying chromate-contaminated soil and water.

Hg Removal from Waste Waters

Algal biomass incorporated into polyurethane foam was subjected to a range of treatments designed to enhance heavy metal binding. Combinations of salinity, pH and controlled thermal denaturation yielded a material that was ideally suited for the toxic heavy metal removal. The processed biomass was characterized by excellent mechanical stability, long shelf life, high density of incorporated biopolymers and could be placed into simulated waste streams without clogging. Tests on synthetic waste waters demonstrated a high degree of binding for Cu, Cr and Hg, all of which could be stripped into small volumes by salt or acid washes. The results with Hg were particularly encouraging, test waters with up to 1ppm Hg could be decontaminated to a level of less than 1 ppb (the limit of AA detection), with 93 % of the Hg being recoverable from the filter.

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Predicting Chronic Toxicity in Aquatic and Terrestrial Ecosystems

Our broad objective is to elucidate the chronic and sublethal effects of exposure to toxic substances on aquatic ecosystems. Our projects span a range of applied and basic research topics that have an impact in both environmental research and environmental management. A primary focus is to evaluate the effects of exposure to genotoxic substances on aquatic ecosystems.

Wetland Management, Design and Restoration: A Case Study in Urban Runoff Management

Restoration of wetland ecosystems has become an important national goal. Nevertheless, little research has been conducted to determine whether wet-

lands designed and created to treat wastewater, or contaminated urban runoff, also create beneficial habitat for wildlife.

These wetlands are created to treat wastewater and to provide wetland enhancement, yet toxicologists are rarely consulted to determine whether the marshes act both as effective treatment facilities and as viable habitat. Our laboratory has recently studied an experimental marsh, the Demonstration Urban Stormwater Treatment (DUST) marsh in southern Alameda County. Carefully integrated with projects conducted by the Alameda County Flood Control District and the San Francisco Bay Regional Water Quality Control

Board, our efforts demonstrate the efficacy of combining toxicity assessment with engineering design.

Our research addressed four key questions:

- Does the DUST marsh contain toxic urban runoff, or does toxic water flow untreated into San Francisco Bay?
- Does the marsh dilute toxicity?
- Does the marsh treat toxicity?
- Which toxic substances cause toxicity?

Toxicity tests using the water flea *Ceriodaphnia dubia* were used to characterize toxic effects in the marsh waters, and differences between the electrical

conductivity of stormwater and that of marsh water were used to trace the distribution of stormwater in the marsh.

Overall, our findings indicated that the marsh can treat stormwater effectively only under selected conditions. For example, it was determined that large storms (e.g., two-inch rainfall) are not contained within the marsh, and the stormwater flushes rapidly through the marsh system and into San Francisco Bay. In contrast, water from smaller storms is retained within the marsh but is treated only if sufficient mixing occurs to eliminate strong vertical gradients of toxic stormwater. Chemical fractionation studies indicate that oxidizable nonpolar organic molecules are responsible for the toxicity observed.

We conclude that improved marsh design would result in improved treatment of toxic stormwater as well as improved habitat for aquatic life. To our knowledge, this is the first study to use toxicity tests as a tracer for the fate of stormwater in experimental marshes. Past studies have combined chemical analyses with classical hydrologic modelling to determine the distribution of

stormwater in experimental systems. However, the latter approach does not result in predictions of how much of the water body will be toxic and under what conditions. The toxicity testing approach is also far more efficient economically.

Validation of a Short-Term Genotoxicity Assay for Application in Marine Ecosystems

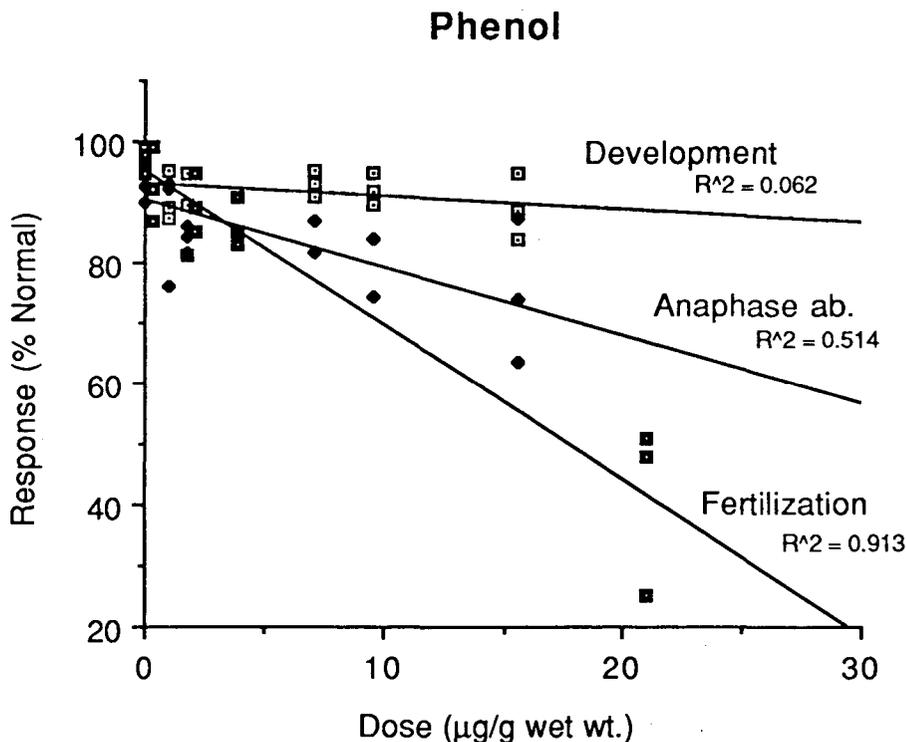
One of our primary goals is to develop and validate short-term assays to predict genotoxic effects in aquatic ecosystems. Although several short-term tests have been developed in various laboratories, almost nothing has been done to determine these assays' sensitivity and response characteristics to standard chemicals. In addition, little has been done to determine the sensitivity of such assays in comparison to the sensitivity of standard assays now used in health and environmental management. Ultimately, such characterizations must be made if the value of genetic toxicology in ecological risk assessment is to be firmly established.

We have recently compared the sensitivity of a sea urchin (*Strongylocentrotus purpuratus*) anaphase aberration assay to the sensitivity of assays—also using this species—in which development and fertilization responses are quantified. We have also characterized the sensitivity of this anaphase aberration assay in comparison to literature values for health and aquatic life. The chemicals used were phenol, pentachlorophenol, and benzidine. Radiotracer techniques were employed, and dose to the embryos as well as water concentrations were determined. Our collaborators were Dr. Jo Ellen Hose of Occidental College and Dr. John Knezovich of Lawrence Livermore National Laboratory.

We determined that the anaphase aberration assay provided the most sensitive responses to two of the three chemicals. These findings are exemplified by the data provided for phenol (Figure). For phenol, there was no significant response for developmental success. Although fertilization success was impaired in a dose-dependent manner, the lowest significant effects occurred at 21 ppm. In contrast, the

Figure.

Anaphase aberrations, development, and fertilization in *Strongylocentrotus purpuratus* embryos exposed to phenol. Symbols indicate replicate values for each response.



anaphase aberration assay detected significant effects at 1.8 ppm. Significantly, the fertilization assay is one of the most commonly used assays in environmental management. In addition, we determined that the sensitivity of the urchin anaphase aberration assay equalled or exceeded that of dozens of published results on health-based assays. These findings indicate that health-based assays should not be used to extrapolate effects on aquatic organisms.

Application of Toxicity Assays to Field Assessments of San Francisco Bay Sediment

We recently compared the sensitivity of a variety of toxicity assays along a gradient of contamination in San Francisco Bay. This large collaborative study was coordinated by the San Francisco Bay Regional Water Quality Control Board and involved a sampling team and toxicologists from the California Department of Fish and Game as well as chemists from the University of California at Santa Cruz. The study site was Castro Cove, located near Richmond, California, and adjacent to the Chevron oil refinery. The broad goal of this study was to determine whether the toxicity tests could be applied to assess the toxicity of pore water prepared from contaminated sediment. Pore water is prepared by squeezing sediment cores to collect the water that animals would actually be exposed to in the spaces between sediment grains. Some scientists consider this to be the primary route of exposure for animals dwelling in aquatic sediments. This is one of the first large-scale assessments of pore water chemistry and toxicity along a gradient of contamination in any estuarine system.

We assessed toxicity at five field sites (five field replicates per site) using two standard toxicity tests and three genotoxicity tests. Our goal was to determine whether the genotoxic responses were sensitive in comparison to development and fertilization responses. We determined that the only assay that was highly sensitive to the contaminants present in the pore water was the devel-

opment test performed using sea urchin embryos. In the development assay, highly significant toxicity was observed even in 50% dilutions at several sites. There was no significant effect using the fertilization assay. The anaphase aberration assay showed no significant effect in the 50% dilutions. However, significant cytologic damage was discovered in preliminary analyses of the samples obtained from the 50% dilution exposures.

Two additional genotoxicity tests were conducted. In the first, we found that pore waters collected from two sites and concentrated 40 times were mutagenic in an Ames Test microsuspension assay (conducted by our collaborator Dr. Normal Kado at the University of California at Davis). In the second, no significant effect was observed on either broodsize or mutagenesis in an assay using the nematode *Caenorhabditis elegans*.

These findings indicate that the predominant substances causing toxicity were not genotoxic substances. Although final data on organic chemicals present in the prewater are not yet available, the data on metal contaminants indicate that several metals are present in quantities that exceed criteria for aquatic life protection, for some of the metals, the exceedances are greater than an order of magnitude. The metals would not be expected to be highly genotoxic, and metals such as copper and silver are known to be extremely toxic to marine invertebrate embryos, with lethal concentrations to several species below 10 ppb. The high concentrations of metals in prewater were not expected, and they raise significant new questions regarding the bioavailability and toxicity of metals in sediment pore water throughout the Bay.

Our work in the coming year will include three additional projects. First, we will be initiating a new and larger effort on sediment toxicity, and we will be integrating our ongoing efforts to assess field applications of genotoxic responses into this effort. Secondly, we are developing and further validating two additional genotoxicity assays.

One is a micronucleus assay using the bullfrog tadpole *Rana catesbeiana* and the other is a mutagenicity assay which utilizes the aquarium fish *Oryzias latipes*. An additional effort in the laboratory has been the assessment of UV effects as a consequence of stratospheric ozone depletion. We anticipate completion of two pilot projects this year.

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Environmental Impact Statement of The Hawaiian Geothermal Project: The Scoping, Marine Impacts, and Marine Alternatives Sections



In 1989, the State of Hawaii proposed to construct a geothermal power generation facility on the Island of Hawaii that would provide 500 MW of power to Oahu via transmission lines and submarine cable. By the State's definition, the project, the Hawaiian Geothermal Project (HGP) consisted of four phases; two have been completed: (1) exploration and testing of the geothermal resource on the Kilauea East Rift Zone and (2) demonstration of the feasibility to deploy and retrieve a cable in the Alenuihaha Channel between Hawaii and Maui. The potential environmental impacts Phases 3 and 4 (*Resource Verification and Characterization and Facility Construction and Operation*) must be addressed in a federal Environmental Impact Statement (EIS) being conducted by the U.S. Department of Energy. LBL has provided analysis of the oral scoping comments and those written comments referring to the marine and alternatives sections of the EIS. LBL will be providing sections on the marine environment and an analysis of various energy alternatives to the proposed action including a discussion of their environmental and economic impacts to aid in preparation of the EIS.

Scoping

Because of the high public interest in the HGP, ten scoping meetings and numerous information exchange meetings were held in Hawaii. Formal scoping meetings were held in Pahoa and Kamuela/Waimea on Hawaii, Wailuku (Maui), Kaunakakai (Molokai), and in Honolulu. The issues raised were broad in scope covering political and cultural [primarily Native Hawaiian] concerns, economics, competing uses, and a plethora of environmental concerns including impacts of the facility on the rain forests on the East Kilauea Rift Zone, the dryland forests and archeological regions of southeast Maui, and the impacts on the sensitive marine species in the four-island region (Maui-Kahoolawe-Lanai-Molokai) notably the humpback whale. Health and safety concerns were expressed frequently, focusing on the impacts of developing a geothermal facility in a residential

area with its associated H₂S and other toxic releases, noise, and psychological impacts. The probability of facility failure associated with the problems of constructing and operating a geothermal facility on an actively erupting volcano was of concern, as was the probability of failure of the cable in the extreme sea states experienced in the Alenuihaha Channel.

Nearly fifty percent of the commenters stated that the EIS should identify and assess the relative merits and impacts of alternative energy supply options that are cost-effective, viable and safe, and could supply Hawaii's energy needs for the future, to make Hawaii more energy self-sufficient, and to reduce its dependency on imported fossil fuels. Alternatives include scenarios that focus primarily on conservation and renewable options, various geothermal options and "no action." The commenters stated that alternative scenarios should be considered within the framework of integrated resource planning and least-cost planning as this may provide a lower-cost energy supply than geothermal power in terms of both economic and environmental cost.

Marine Impacts

LBL will provide an assessment of the impacts of the project on the marine environment—that is, the impacts of installation, operation and maintenance of the undersea cable, from the deep sea through the surf zone. The submarine cable and its alternatives (including alternative routes, alternative cable technologies, and alternative power transmission schemes) will be described. The project will describe the physical, biological, and, to a limited extent, chemical oceanography of Hawaii from eastern Oahu to northern Hawaii. The potential impacts of the cable will be identified and assessed.

Water quality considerations encompass impacts to the quality of marine waters due to: construction, dredging, drilling, or maintenance; erosion due to HGP-related activities on land; leakage from the oil-filled cable or oil spill from associated shipping; and impacts to water quality (dissolved oxygen/or-

ganic carbon/nutrients, turbidity) due to such factors as marine or land-based construction operations. Impacts to marine species, including threatened, endangered or endemic species, and commercial/recreational fisheries could occur in the coastal zone, reefs, benthic communities, or at sea and may be due to construction (including dredging and drilling), operation, deployment, or maintenance of the cable, cable electromagnetic fields (emf), oil leaks/spills, and increased siltation and turbidity. Protected species in Hawaiian waters include the humpback whale, green and hawksbill sea turtles, and the Hawaiian monk seal.

Economic considerations abound, for example, costs of the cable project, including costs of fabrication, transportation and deployment (if necessary, ship and harbor construction), maintenance, operation, retrieval, and mitigation/rehabilitation; economic impacts of cable failure; impacts to commercial and recreational fisheries and mariculture; to recreational areas both at sea and in the coastal zone; impacts to precious corals; and impacts to fishponds used for mariculture. The cable may impact Native Hawaiian subsistence fishing and mariculture operations. In Hawaii, aesthetic impacts, such as visual effects or noise, can have important and widespread implications. Even the presence of the cable in the marine environment is an important consideration, because the cable may attract or repel certain species, which in turn affects commercial and recreational fisheries, as well as snorkeling and scuba diving.

Public health could be affected by effects of possible ciguatera (a fish poisoning associated with marine dredging or drilling operations in Hawaii). Because the Alenuihaha Channel is known for its extreme conditions, safety considerations, important to any marine operation, are critical, and include assessing the numerous hazards on land, in the coastal zone, and at sea with respect to fabrication, transportation, construction, deployment, maintenance, or retrieval operations. Competing uses include coastal zone uses for marine sanctuaries, recreation; archeological/

historical sites and regions (including fishponds); use of channels for communications cables; commercial and recreational fishing/shipping use of waterways and coastal zone; national defense use of waterways and coastal zone; and Native Hawaiian access to beaches and ocean for subsistence fishing or other uses.

Marine Alternatives

LBL will examine scenarios alternative to the proposed action: 1) "no action"; 2) renewable energy resources (biomass, wind, solar thermal, and photovoltaics) and demand-side management (DSM) strategies; and 3) geothermal alternatives, all within a framework of integrated resource planning (IRP) to meet the purpose and needs of the proposed action. The economic analyses of the IRP should be conducted as economic issues are important to many Hawaiians as was noted in most scoping meetings. The extent of this analysis will depend on the availability of credible data input from the Hawaiian utilities and from the individual alternative assessments.

No Action

An analysis of this option, required by the National Environmental Policy Act, will consider a business-as-usual energy resource plan based on current resource mixes (mostly oil-fired generation with some renewables), increased reliance on coal-fired plants, and resource planning trends in the State as described by utility plans. Coal-fired power generation is increasingly used in Hawaii and could replace 500 MW of existing oil generation with one moderately-sized unit on Oahu. LBL will assess the potential economic and environmental costs, benefits, and impacts associated with the use of coal as a power-generation fuel. This analysis will include description of the technical and economic feasibility of coal-based technology, including capital costs, energy costs, economic risks, and other factors; assessment of potential environmental impacts such as ash disposal and air quality; and preparation of analysis results for use in IRP assessment. Of particular interest is the concern that in order to stop the destruction of rain

forests in Hawaii to construct the geothermal facility, "no action" may cause destruction of rain forests in Indonesia due to the strip-mining of coal to meet the needs of new coal-fired facilities.

Conservation and Renewables

In considering renewable resources, LBL will: 1) take inventory of available resources; 2) examine existing new energy conversion technologies such as biomass gasification with steam-injected gas turbines; solar technologies, including central receiver, photovoltaic, and solar hot water heater technologies, and various wind-power configurations; 3) compare each alternative according to its costs, feasibility, environmental and socioeconomic impact, and ability to replace geothermal energy as a fuel for electricity production; and 4) prepare results from this assessment for use in the IRP analysis. The potentially significant environmental impacts will be identified and to the extent possible, using available literature, assessed. LBL will assess the potential for electricity savings in Hawaiian buildings. The study of Hawaii's DSM resources in buildings will involve 1) gathering available information on the stock of buildings, building characteristics (current level of insulation, square footage, etc.) and equipment, and weather data; 2) assessing the changes in energy use and costs from incorporating efficiency measures through simulation and other means; 3) calculating the cost-effectiveness of efficiency measures applied in new and retrofit situations; and 4) preparing the results for use in the IRP analysis.

Integrated Resource Planning Assessment

To assess the advantage of various alternative scenarios, power plants, DSM plans, and other alternatives must be compared with each other on a utility system basis, not simply on a project basis. Alternative resources of the same nominal capacity have very different impacts on the reliability of the utility system and on the cost of providing service, due to differences in forced and unforced outage rates, dispatchability, economics of scale, siting and transmission requirements, reserve requirements, ratios of fixed and variable costs,

costs during early and later years of the planning period, and dispatch-dependent emissions and externality costs. Due to the above factors, alternatives to the HGP will be evaluated through the simulation of alternative resource plans using production cost modeling. Production cost modeling is a minimum requirement for capturing the interaction in the utility system of exiting and marginal resources and of resources of different types under specific reliability criteria.

LBL will review and assess the data, methods, and resource assessments used in the ongoing IRP activities of Hawaii's utilities. In particular, LBL will examine the efforts made to acquire field and survey data on end-use consumption and on DSM measures and costs, the methods by which these data are translated into demand-side resource estimates, the end-use disaggregations and assumptions on market-implemented DSM underlying the electricity demand forecasts, and the resource potential and cost assumptions used in the utilities' analyses.

LBL will define inputs to the LBL IRP assessment in close coordination with the Hawaii utilities and State of Hawaii, including suitable time horizons, demand forecasts by the Hawaiian utilities, technical and achievement potentials, and cost assumptions for each energy-supply option (i.e., biomass, wind, geothermal, solar thermal, photovoltaic, fossil fuel, geothermal, and demand-side management potential for buildings).

LBL will 1) model a limited number of scenarios to explore those questions that are important to the HGP EIS regarding the economic and financial impacts of IRP options on the electricity system of Hawaii after scenario definition and model calibration, using a PC-based production cost model (U-Plan or Elfin); and 2) prepare scenario results in graphic and tabular form as part of a final summary document. LBL will examine aspects related to the alternatives as described above: the proposed action, "no action," conservation and renewables, and geothermal on the Big Island.

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