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Army Plasma/Propellant Interaction Workshop - U.S. Army Research Office, 17–18 November 1998

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Abstract

This workshop was organized by the U.S. Army Research Office (ARO) as part of an ongoing U.S. Army Research Laboratory (ARL)-ARO effort to develop a coordinated research program to address the needs of advanced gun propulsion, in particular, in the application of plasmas as ignition and energy augmentation sources for solid propellant guns, known as electrothermal-chemical (ETC) propulsion systems. We sought to bring leading scientists and engineers from outside the Army with expertise in plasma properties and behavior (especially energy transfer) and in chemical reactions by mechanisms likely to be caused by interactions of plasmas with solids.

Presentations were made by ARL to give a background on ETC and the observed effects of plasmas on ballistics. Succeeding talks discussed experiments and modeling related to the physics and chemistry of plasma propellant interaction being carried out at ARL and other institutions. In addition to technical details on current research, the presenters also discussed "wish lists" on data, projects, etc., that ARL believed to be important in the solution of the problem. After the presentations, focus groups were formed from the attendees to discuss the problem and possible solutions. Subsequently, very specific issues, questions, and research suggestions were collectively discussed and are reported here. Finally, collaborations between investigators were initiated and conclusions and recommendations were drawn up for future research.

Table of Contents

Page

1. **Introduction** 1

2. **Workshop Rationale** 2

3. **Overviews** 3

3.1 Overview and Ignition Experiments 4
3.2 Overview of ARL Basic Research Program in Plasma-Propellant Interaction ... 7
3.3 Modeling of Plasma Igniters, Plasma Jets, and Plasma-Propellant Interactions. 8
3.4 Plasma Modeling for the Capillary 11
3.5 Kinetic Modeling of Energetic Materials Combustion and Plasma-Propellant Interaction 16

4. **Specific Issues, Questions, and Research Suggestions** 21

5. **Collaborations** 26

6. **Conclusions and Recommendations** 27

6.1 The Plasma Source 28
6.1.1 *Convective Heating* 28
6.1.2 *Other Remarks on the Plasma* 29
6.2 Plasma/Propellant Chemistry 29
6.2.1 *Ions* 29
6.2.2 *Radicals* 30

7. **References** 31

Appendix A: Agenda 33

Appendix B: Focus Groups and Attendees List 37

Distribution List 43

Report Documentation Page 49

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1. Introduction

This workshop was organized by the U.S. Army Research Office (ARO) as part of an ongoing U.S. Army Research Laboratory (ARL)-ARO effort to develop a coordinated research program to address the needs of advanced gun propulsion, in particular in the application of plasmas as ignition and energy augmentation sources for solid propellant guns, known as electrothermal-chemical (ETC) propulsion systems. We brought leading scientists and engineers from outside the U.S. Army with expertise in plasma properties and behavior (especially energy transfer) and in chemical reactions by mechanisms likely to be caused by interactions of plasmas with solids.

Presentations were made by ARL personnel after which focus groups were formed from the attendees to discuss the problem and possible solutions. From the standpoint of ARO, the purpose of the workshop was to become familiar with the research programs in ETC currently being carried out within ARL and related organizations. ARL had an additional goal, namely, to generate ideas through the discussion groups for projects that would assist in the understanding of the plasma-propellant interaction and could be performed at the participants' facilities. These projects could, if desired, be submitted to ARO for consideration. Presentations were made by ARL to give a background on ETC and the observed effects of plasmas on ballistics. Succeeding talks given by ARL personnel, K. White, W. Anderson, J. Powell, and M. Nusca, discussed experiments and modeling related to the physics and chemistry of plasma-propellant interaction being carried out at ARL and other institutions. In addition to technical details on current research, the presenters also discussed "wish lists" on data, projects, etc., that ARL believed to be important in the solution of the problem. Some of the needs discussed came directly from the Joint Army-Navy-NASA-Air Force (JANNAF) workshop report presented at the 34th Combustion Subcommittee Meeting in October 1997 (Oberle, White, and Powell 1997).

This report consists of:

- **Workshop Rationale** provided to participants before the workshop.

- **Overviews** of the presentations made by ARL scientists during the workshop; these were provided to participants before the workshop.

- A listing of **Specific Issues, Questions, and Research Suggestions** that came up during the meeting.

- **Collaborations** developed during the workshop.

- A summary of **Conclusions and Recommendations** developed after the conclusion of the workshop.

Appendix A contains the meeting Agenda. Appendix B lists the members of the focus groups and the address, phone numbers, and e-mail addresses of the attendees.

2. Workshop Rationale

Propulsion benefits resulting from optimized plasma/propellant interaction include short and reproducible ignition delays with maximum performance over required temperature regimes: efficient ignition, combustion and flamespreading in low vulnerability, low-molecular-weight hypervelocity propellants under high-loading density configurations, and minimal electrical power supply requirements from efficient plasma-propellant energy coupling.

A research program addressing plasma/propellant interactions will determine the convective, ionic, radiative, and gas dynamic components of plasmas to gain a greater understanding of the mechanisms of propellant ignition and combustion under the influence of a plasma source. Identification of the underpinning mechanisms associated with plasma/propellant interactions will serve as a basis to enable the development of future advanced solid propellant formulations and plasma igniter compositions (with optimized radiation/conduction profiles) that are tailored to exploit the benefits of plasma ignition.

The goals of the research program will be:

- Determination of the effects of radiative, conductive, and chemical components of plasmas on the chemistry and mechanical properties of gun propellants, using, for example, characterization of propellants recovered from "interrupted burn" experiments.

- Development of a theoretical model of plasma/propellant interactions based on (1) constitutive model of the plasma; (2) computational fluid dynamics (CFD) simulation of simplified plasma jet impingement on a solid surface; and (3) review of possible reactions between plasma components and propellants.

- Development of refined theoretical model of plasma/propellant interactions, which will include new information from efforts of continuing experimental and analytical programs.

3. Overviews

Overview handouts were prepared and given to all attendees prior to the meeting. This facilitated the discussions, as many of the investigators were not involved in ETC research. These summaries acted as background material for the meeting. Moreover, the authors of the overviews started the meeting with presentations that expanded the discussions presented in the following sections. The first review by K. White was essentially an outline of the presentation to be made at the meeting and covered the ETC concept, some of the historical development, ballistic results and observations, diagnostic testing of plasma-propellant interaction, modeling of radiation and convective heating, and related research in universities. The second review by W. Anderson covered chemical analysis and chemical reaction modeling programs related to plasma-propellant in interactions. The third review by M. Nusca covered the modeling of the plasma-propellant interaction within a propellant bed and modeling of the freely expanding plasma jet and its interaction with propellants. The fourth review by J. Powell outlined the modeling efforts for the ablation-supported capillary plasma generator and recent modeling of the plasma generator where solid conductors are placed periodically along the plasma path. Future directions in this work were also discussed. Finally, in the fifth review, W. Anderson reviewed what has been done in modeling of ignition and combustion of energetic materials (propellant components) involving complex mechanisms (species with their thermodynamics and elementary reactions) and also the development of a complex kinetic mechanism for an ETC plasma interacting with a propellant

3.1 Overview and Ignition Experiments (Kevin White, ARL).

- Purpose of the meeting and ARL's goals.

- ETC propulsion concept—past and present.

- Methods of introducing plasma energy into a propellant bed.

- Proposed mechanisms of interaction.

- Ballistic results with plasma ignition.

  - Reduced ignition delay.

  - Reduced propelling charge temperature sensitivity.

  - Closed chamber experiments and results; altered mass generation rates.

- Plasma radiation and possible relationship to the observed ballistic results; propellant heating by radiation.

- Optical (absorption) properties of propellants; integrating sphere experiments.

- Ballistic experiments with polyethylene centercore.
- Plasma/propellant interaction observations.
  - Chemical analysis.
  - Mechanical analysis.
  - Plasma spectra and time sequence of radiation output.
- Analysis of plasma convective and radiative heating; results indicate that heating is substantially greater than with conventional chemical ignition and flame spreading.
- Gun conditions with plasma ignition: What will the propellant see? How will it react?
- Techniques developed to measure plasma pressure and convective and radiative heat flux.
- Problems encountered in a plasma environment.
- Ballistic simulator; experimental results, Soreq Nuclear Research Center, Science Applications International Corporation (SAIC).
- Modeling of radiation distribution in a propellant bed; LightTools, Monte Carlo model.
- Modeling of plasma convective heating in a propellant bed (Nusca).
- ARL program in plasma/propellant interaction.
  - Experimental.

    - Propellants subjected to plasma; open air, interrupted burner tests.

    - Chemical and physical analysis of recovered propellants (open air and interrupted burner).

  - Modeling.

    - Energy propagation within a propellant bed and plasma jet expansion in open air (Nusca).

    - Radiation model (McQuaid).

    - Chemical modeling (Anderson).

- Related programs.

  - University of Texas (Varghese et al.).

    - Experimental analysis of plasmas; photography, spectra, T, electron density.

    - Experimental analysis of plasma/propellant interaction; photography, spectra.

    - Modeling (analytical) of plasma and plasma/propellant interactions.

  - North Carolina State University (Bourham et al.).

    - Experimental studies of varying plasma properties on plasma/propellant interactions.

    - Modeling of boundary layers in plasma propellant interactions.

  - Pennsylvania State University (Tynell et al.).

· Experimental analysis of chemical products from plasma/propellant interaction.

3.2 Overview of ARL Basic Research Program in Plasma Propellant Interaction (William Anderson and Rose Pesce-Rodriguez, ARL). The objectives of the work unit are (1) to identify the main features of the underpinning physics and chemistry of ETC plasma as it interacts with solid gun propellant, and (2) to understand and quantify, allowing optimization of plasma-propellant coupling, via influencing gun design and/or advanced propellant formulations.

A brief description of other work units in the Ballistics and Weapons Concepts Division follows:

- Projected payoff of success, qualitative and quantitative.

- Two major thrusts of work unit:

  - Experimental characterization of propellants exposed to plasma with and without "shields" (samples from K. White).

    · Propellants selected for study:

      (1) Start with JA-2 and M30, nitrate ester types.

      (2) Later in year, study M43, an RDX nitramine type with energetic plasticizer.

  - Analytical methods:

    · Surface physical changes by scanning electron microscopy (SEM).

    · Mechanical properties by servo-hydraulic tester.

- Nanoscale morphology by small angle x-ray and neutron scattering.

- Chemical makeup by infrared (IR) photoacoustic and microreflectance Fourier transform infrared (FTIR) spectroscopy, gas chromatography-mass spectroscopy (GC-MS), liquid chromatography-mass spectroscopy (LC-MS), and thermal analysis (differential scanning calorimetry and thermal gravimetric analysis).

- Modeling: Initially plasma/air, later plasma/air impinging on propellant (probably the latter cannot be done this year): Use results of existing model of plasma formation in capillary (which assumes chemical equilibrium) for properties of emerging plasma mixture for all of following:

  - Overall Computational Fluid Dynamics (CFD) model of plasma constituents emerging from capillary interacting with air.

  - To consider spectral and radiation properties, chemistry, energy content, temperature, density, velocity, mixing. This depends on the following two submodels:

    (1) Submodel for spectral and radiative properties.

    (2) Submodel of chemical kinetics of gas phase mixture.

3.3 Modeling of Plasma Igniters, Plasma Jets, and Plasma-Propellant Interactions (Michael J. Nusca, ARL). ARL has developed the Next-Generation (NGEN) interior ballistics model (Gough 1993, 1995; Nusca and Gough 1998) for use in the investigation of a full spectrum of gun propulsion systems, including the ETC system. The NGEN interior ballistics code is based on a solution of the conservation equations for a multiphase reacting flow. Two phases are considered: a continuous phase (multicomponent mixture of gases and liquids in local mechanical equilibrium), and a discrete phase (aggregate of particles made up of solid/liquid propellant reactants and combustion products as well as pieces of the propellant containers). The continuous phase is characterized by single local values for the dependent variables and is assumed to be comprised of continuous species (e.g., air, plasma, solid propellant gaseous products, and liquid propellant products) with local values of the mass fraction. The discrete phase consists of components (e.g., unburnt or burning solid propellant, liquid droplets) characterized by individual values for the dependent variables as well as number density, volume, and surface area. The continuous phase is represented by the balance equations for a multicomponent mixture (i.e., conservation of mass [global and for each species], momentum, and energy) and solved using a Eulerian approach in a part of the code termed the Central Flow Solver (CFS). The primary solution algorithm for the CFS is the Flux-Corrected Transport (FCT) algorithm (Boris et al. 1992). The presence of a dispersed phase requires that a macroscopic representation of the governing equations is adopted based on properties of the flow over length scales whose size is large compared to the length scale of the individual particles. For the solid phase, an overall porosity is defined and equations for the conservation of mass and momentum are prescribed. A Lagrangian approach is adopted for these equations, which are solved in a part of the code, termed the Large Particle Integrator (LPI).

Plasma injection has been facilitated in the NGEN code by making the ARL plasma code (Powell and Zielinski 1992) a module. At each time step in the computation, this module is employed to provide boundary conditions (i.e., plasma temperature, energy, momentum) to the NGEN code at the point(s) of plasma injection (e.g., the breech end or along the chamber centerline). The NGEN code provides the pressure imposed at the injection point(s). The plasma is then treated as a continuous species in the computation. Radiation transport is treated using a black body formulation. The plasma module requires a time history of the electrical current as well as the properties of the capillary that are used to form the plasma. Computations have been achieved for a typical tank-gun chamber filled with granular propellant and ignited using plasma injection at the breech end and through a piccolo-type igniter tube positioned along the chamber centerline (Nusca and White 1997; Nusca et al. 1998). Several plasma jets can be observed acting normal to the propellant bed and causing a two-dimensional (2-D) flame to spread through the bed. It has been found that the plasma is more efficient than standard igniter gas at achieving full flamespread through the propellant bed.

In a separate effort aimed at understanding the physics of a single plasma jet, ARL in cooperation with the Naval Research Laboratory (NRL) has begun a computational study of open-air plasma discharge experiments conducted at ARL. This computational study is based on the NRL gas-phase CFD code FAST3D, which employs the same computational algorithm FCT that embodies the CFS (i.e., solver for the gas-phase) of the ARL-NGEN code. This cooperation has been fostered by the Department of Defense (DOD) Common HPC Software Support Initiative (CHSSI) program for high-performance computing (HPC) in the computational technology area (CTA) for CFD.

ARL is conducting experimental tests of an open-air plasma firing, described by K. White at this workshop. In this series of tests, the plasma jet resulting from energizing an ETC cartridge is expelled through a nozzle and into the ambient air. The cartridge consisted of a polyethylene liner and an exploding wire attaching the anode to the cathode of the cartridge. The anode and cathode are also attached to a pulse-forming network (PFN). Recent extensions to this effort at ARL include a set of probes that are held near the igniter. These probes include pressure taps, heat flux gauges, and samples of solid propellant directly exposed to the plasma igniter efflux.

The current approach to modeling the open-air plasma jet uses a solution of the unsteady, three-dimensional (3-D), gas dynamic Euler equations. These equations are a set of partial differential equations in conservation form that can be discretized and solved using FCT algorithm in the FAST3D code. The FCT algorithm was originally designed to solve generalized continuity equations for space and time-varying coordinates by Boris and Book. The most recent version of the algorithm by Boris is fourth-order accurate in space and second-order accurate in time (Boris et al. 1992). The FCT algorithm is well-tested monotone (positive-preserving), conservative, and relatively high order. FCT uses timestep-split and direction-split techniques to resolve the coupled, 3-D continuity equations into a very efficient sequence of one-dimensional (1-D) integrations. The FAST3D code has been implemented in parallel on the SGI Origin 2000 supercomputer. The ARL plasma code (Powell and Zielinski 1992) is used to determine the ETC cartridge-exit/nozzle-throat conditions based on a specified power-time history supplied to a given plasma cartridge (i.e., polyethylene capillary liner). These conditions are then used by FAST3D to simulate the unsteady jet that results. As an initial effort (Nusca et al. 1997), the plasma jet is assumed to be either calorically perfect or thermally perfect and consists of a single specie—the electrons and ions are not currently modeled nor are the chemical kinetics during plasma expansion. The numerical simulations show a plasma jet of very low density relative to the open air (factor of 0.1) traveling at a very high velocity (initially 5,000 m/s) with a strong precursor shock wave. Within the jet were observed strong variations in density as the plasma jet crosses shock waves and then experiences expansion. The existence of the precursor shock, as well as the detailed internal structure of the jet, has important implications for mechanical/structural effects during plasma/propellant interactions. This work was extended to include a pressure probe placed at various distances in front of the nozzle exit (White, Williams, and Nusca 1998; Nusca et al. 1998, 1999). Data from the probes are compared to computed results in an attempt to glean further information on the internal structure of the plasma jet and predict the effects on solid propellant chemistry and ignition.

Extensions to the physical model are ongoing as further information on ablation plasmas is revealed. For example, extensions to real-gas effects, electron and ion diffusion and chemistry, and a model of the particulates in the plasma are all planned or underway (Nusca and McQuaid 1999).

3.4 Plasma Modeling for the Capillary (John Powell, ARL). Intermittently during the last decade, ARL has been involved in the development of various models to describe plasma injection in ETC launchers. The intent of these efforts has been to explain the operation and efficacy of different injector designs, as well as to provide an integral link in the description of the entire ETC process. Many of the models that have been developed have now been coupled to interior-ballistic and power calculations for ETC by investigators both at ARL and elsewhere. The purpose of this presentation is to describe the past, present, and future modeling efforts at ARL; describe some related work that has been undertaken at other places; indicate results of some specific calculations;

and indicate some areas where additional work is desired. Much of the additional work is particularly important to support Army interest in investigating the plasma-propellant interaction problem from a fundamental point of view.

The earliest and most commonly studied type of capillary is the breech injector. This injector consists of an insulating tube of material, connected across two electrodes, and located at the breech end of an ETC gun. Current is conducted through the tube by a plasma arc that is generated initially by, for example, an exploding wire. The plasma is heated ohmically to typically a temperature of a few electron volts and is free to expand into the combustion chamber of the gun where it can interact with the propellant. The plasma that is lost from the capillary in this manner is then replenished by ablation of additional material from the tube walls. The plasma so generated can be employed to ignite the propellant, to help control the combustion process, and, in some cases, to augment the acceleration of the projectile.

The most general model developed at ARL for investigating the breech injector is transient and 1-D in the axial direction (Powell and Zielinski 1992, 1993). The governing equations, which are solved numerically, consist of the relevant conservation equations, equations of state, and equations that determine the electrical conductivity, ionization state, and ablation rates. Mass addition and outflow are accounted for, and energy transport to the capillary walls is assumed to occur by blackbody radiation. The plasma is assumed to consist of a homogeneous mixture of ions and neutrals that are ablated from the insulating material. A simplified version of the model, partially analytic and suitable for many approximate calculations, can be obtained if the additional assumptions are made that the process is quasi-stationary and that the plasma temperature is constant along the axial direction. Both the general and simplified models account for certain nonideal properties that are present in plasmas at the low temperatures and high densities that tend to characterize these injection problems. The principal effects of the nonideal properties are to produce a reduction in the electrical conductivity at a given temperature and pressure relative to that of an ideal gas, and to produce a reduction in the effective ionization potential relative to that of an isolated ion.

The injector must, of course, be coupled to the combustion chamber as well as to the power supply in order to close the set of equations that describe its operation. This coupling can be effected by supplying the current and the pressure at exit from experimentally measured values or by iterating between calculations until self-consistency is achieved. If the pressure in the chamber is lower than some critical value, such as during the early stages of the firing, flow from the capillary will choke at the exit point and the operation of the capillary becomes independent of the chamber conditions. At later stages, however, the flow becomes unchoked and the exit speed depends upon the chamber pressure.

Results of a recent calculation undertaken with the model will be presented. The purpose of the calculation was to analyze some experimental work carried out at the Institute of Saint-Louis (Daree, Hensel, and Zimmermann 1997) and to compare results with those predicted by investigators there as well as at other institutions. The input data required for the calculation were taken directly from the experiment in question. In particular, time-dependent profiles of the pulsed current and exit pressure were used to provide the coupling just discussed. The maximum pulsed current was about 60 kA, and the maximum pressure measured at the capillary exit was about 140 MPa. These parameters are reasonably typical for ETC firings. The calculation yielded time and spatially dependent values of all thermodynamic and electrical properties of the plasma. Specific results indicated a maximum temperature in the arc of about 2.5 ev, an exit velocity at maximum current of about 5 km/s, and an arc resistance as a function of time that was a few 10s of mΩ. A comparison of the experimentally measured and theoretically predicted resistance yielded reasonably good agreement.

For practical applications, breech-type injectors have generally been supplanted by other designs. Among the more popular concepts are various types of "piccolo" injectors, the most common of which are located completely inside the combustion chamber. Current is still conducted through the injector along the axial direction by a plasma that is produced by ablation from the tube walls. However, the plasma generated flows into the chamber through a series of small holes located along the surface of the piccolo tube rather than through a single hole at the end. The plasma can then interact with the propellant located in the chamber. Models for this type of injector, which to some extent resembles a breech capillary turned on its side, are based on the same basic principles and assumptions as the breech device. The popularity of the piccolo designs arises because they are believed to be a more efficient type of injector than the breech type.

The simplest model for the piccolo injector is zero dimensional and quasi-static (Powell 1996). Results of one calculation undertaken with the model will be presented. The calculation corresponds to an actual ETC firing undertaken for ARL by one of its contractors. Again, measured values of current and combustion-chamber pressure as a function of time are used as input in the calculations. It is found that the flow is choked at the exit holes at early times but eventually becomes limited by the pressure developed in the chamber. All of the thermodynamic and electrical properties of the plasma are predicted by the calculations; the maximum temperature is about 4.5 ev, and the maximum pressure is about 400 MPa. The voltage across the device was also calculated from the plasma properties and found to exceed the measured value by a substantial amount. It has been hypothesized that the lack of good agreement results from some part of the current being conducted outside the piccolo tube, an effect that is not accounted for in the model. It is interesting that the properties of the plasma produced by the breech and piccolo devices are not greatly different for a given geometry and operating current.

Still more recent designs are somewhat similar to those just discussed, except that solid conductors are placed periodically along the plasma path (Powell and Thornhill 1999). Depending upon the specific design, the solid conductors may serve as a source of plasma through partial evaporation, may provide a means of controlling the total impedance of the device, and may provide a way in which the current can be stabilized. A significant part of the analysis of these types of devices is to determine the preferred conduction pathways through the plasma-solid array, and we have developed a 2-D model for performing these types of calculations. It is found that the details of the geometry can affect those pathways in a significant and rather counterintuitive way. The plasmas produced can also have properties that are somewhat different from those in either the breech or piccolo. For example, the plasma generally consists of both metal ions from the solid fuses as well as hydrocarbon material that arises from the insulating walls. Furthermore, the geometry is sufficiently different from the other types of injectors that, for a given current, the thermodynamic and electrical properties of the plasma may vary considerably from those studied before. These types of injectors are now under active investigation both experimentally and theoretically at ARL and elsewhere. Some model calculations that have been carried out on generic types of these igniters will be described. Most of the calculations are concerned with determining the appropriate conduction and impedance characteristics of the devices.

Most of the recent research in plasma injection for ETC has been concerned with analyzing specific injector designs rather than addressing fundamental issues. Consequently, there are several areas in which reasonably basic research is required for improving models that characterize the plasma source and for providing information necessary for the plasma-propellant interaction studies. Many of these problems worthy of future study were recently outlined at a JANNAF workshop on the plasma-propellant interaction problem (Oberle, White, and Powell 1997). Some of the conclusions relevant to modeling the plasma source are summarized here.

First, it would advisable to extend the capillary models to treat 2-D, axisymmetric, or even 3-D effects. It would be particularly worthwhile to develop a fully self-consistent plasma-interior ballistic model in which the capillary and combustion chamber are both, say, 2-D and completely coupled. The resulting model should account not only for momentum and energy transfer between the source and the propellant gases but also allow for mixing of the various species. Second, more detailed models for radiation transport are desirable. In particular, it may be necessary to understand the spectral content of the radiation in future efforts to describe plasma-propellant interactions, and the assumption that the radiation is blackbody may not be adequate. Transmission of radiation near the boundaries as well as the significance of the vapor shield need to be investigated. Third, for plasma devices that involve high flow velocities, such as the breech-fed capillary, Reynolds numbers typically predict flow that is far into the turbulent regime. Account of turbulent effects in existing models, if taken at all, is ad hoc and empirical. More detailed studies of turbulence and convective heat transfer need to be undertaken in future work if the properties of the plasma are to be understood in detail. Finally, there needs to be more study of plasma properties under the low-temperature, high-pressure conditions that prevail in most plasma-source devices, and appropriate modifications made to the various equations of state. Especially, the electrical conductivity, which, at a given temperature and pressure, can differ markedly from one model to another, needs to be studied and recommendations made concerning a reasonable model to use. Unfortunately, comparison of voltage profiles for different experiments is of little help, since frequently the nonlinear coupling of the governing equations is such that fairly similar results for voltage are obtained regardless of the particular conductivity model. Consequently, although voltage measurements are clearly important for determining the energy dissipated in the plasma and subsequently transmitted to the propellant, they constitute a rather ineffective diagnostic for investigating the dynamics or flow characteristics of the arc or assessing the value of any particular model.

3.5 Kinetic Modeling of Energetic Materials Combustion and Plasma-Propellant Interaction (William Anderson, ARL). This discussion will be divided into two sections, roughly half the time being spent on each. The first will be a review of what has been done in modeling of ignition and combustion of energetic materials (propellant components) involving complex mechanisms (species with their thermodynamics, and elementary reactions). The second will be a presentation of the development of a complex kinetic mechanism for an ETC plasma interacting with a propellant, work that has just recently started. The author's plans along these lines and views as to needs that outside researchers might fulfill will be presented.

Efforts to develop 1-D models for the combustion of propellants by solving a system of simultaneous mass and energy conservation equations date back to the Second World War. Until the mid 1980s, the models were chemically nonspecific, assuming only a single gasification reaction to some intermediate at the surface of the condensed phase and a single overall reaction of this intermediate to final products in the gas phase, evolution of heat in the gas phase driving the reactions. By their simple nature, the pre-1980s models could provide little guidance for chemical formulation or the effects of additives. (A few models with very simple kinetics appeared prior to this time, but no one solved the simultaneous condensed and gas phase conservation equations previously, likely due to limitations in computer capabilities and/or the understanding of how and why to proceed.) Hatch (1986) presented the first such combustion model in which a complex combustion mechanism was utilized and the conservation equations were solved numerically to obtain a chemical structure and burning rate (rate of steady combustion wave traveling through solid). The mechanism consisted of 19 species and 60 chemical reactions. This was a major step forward in terms of showing what could be done, which has gone largely uncredited. Criticisms are that the code used was not readily adaptable to other propellants, nor easily used by other researchers, and that the chemistry utilized was limited.

Premixed laminar flame modeling in general took a large step forward in the mid-1980s when the user-friendly code PREMIX, developed at Sandia National Laboratories, was written and distributed (Kee et al. 1991). In the late 1980s, Melius focused much attention on the possibilities for energetic materials combustion modeling by using an adapted form of this code to model the combustion of RDX (cyclotrimethylene-trinitramine), one of the most commonly used nitramine (R2-NNO2 compound) propellant ingredients. A series of ARO and Office of Naval Research (ONR) workshops then led to a concerted effort directed at understanding the physics and chemistry of RDX as a prototypical system, resulting in many refinements. Three groups have published results, including excellent agreement of computed burning rate vs. pressure curves as compared to experiment. The gas phase chemical mechanisms employed typically considered about 50 species and 200 reactions. Physics of the condensed phase near-surface region has varied considerably between the models. Chemistry assumed in the condensed phases is much simpler than in the gas phase. It is important to note there were large variations in the intermediate gas phase species evolving from the condensed phase surfaces, in spite of their agreement regarding burn rate and other features. Experimental examination of the chemical and physical structure of the near-surface region, including composition, foam layer formation, and even such simple features as exact location of the surface, has long been the major problem in this research area. The region is very thin (10's or, at most, 100's of μ) at typical pressures of interest and is also never quite flat, making probing quite difficult if not impossible.

Miller (1996) has recently modeled the combustion of solid ozone (O_3) with a three-phase model. This compound was chosen as a prototype to test physics of the model because the gas phase chemistry is very simple and well understood and some experimental burn rate data were available. Following the development of this physically sophisticated model, he developed a two-phase model for comparison. He has applied both models to O_3 and RDX (the latter as yet unpublished). Computed burn rates and even gas phase species profiles compare favorably. The latter model, it is felt, does have limitations, but simplifies computations so drastically that further pursuit is felt worthwhile.

More recently at ARL, Miller and Anderson (to be published) have begun modeling the combustion of nitrocellulose (NC) and reinvestigated nitroglycerine (NG) using Miller's two-phase model (Miller 1996). NC and NG are two nitrate esters (R-ONO_2 compounds) commonly used in single and double base propellants. Best comparisons with burn rate data have thus far been obtained for NG. A variety of assumptions regarding intermediate species evolving from the surface can lead to the correct slope of burn rate vs. pressure curves. The absolute magnitudes for these predicted curves vary greatly, indicating that if the chemical pathways can somehow be controlled, there are great possibilities for burn rate control. Another idea we have begun to pursue is the first, simple steps toward modeling the effects of additives, the first attempt we are aware of at propellant formulation science. Trace amounts of fuel type additives were used such that the mixtures had the same fuel/oxidizer ratios. Modeling of NG with a trace of added NH_3 indicates the NH_3 can have a strong effect, increasing the burn rate. Similar traces of CH_2O or H_2 had much smaller effects. A very exciting result (thus far only modeled with PREMIX by comparing effects on gas phase temperature profile, not with the full burn rate model) is that a trace of HNCO has an effect about half the magnitude of NH_3, but in the opposite direction. Thus, we have additives that can either increase or decrease the burning rate. While NH_3 and HNCO are impractical as solid propellant additives, there are a number of possible precursor compounds of these that are practical. Obviously, these have become of interest to us for future modeling and experiment. Some of these have already been used as propellant ingredients.

Efforts to model detailed chemistry of the plasma propellant interaction will clearly be influenced heavily by the prior propellant combustion work. It will have to begin, however, with an understanding of the constituents and conditions in the plasma. Modeling of the plasma (Powell and Zielinski 1992) in the typical polyethylene-lined capillary indicates conditions of very high pressure and temperature (typically about 2,000 atm and 50,000 K). At these conditions, the plasma consists primarily of C^+ and H^+ ions and electrons. Prior to contacting the propellant, the plasma expands and pushes through and/or mixes with air. Calculations with a nonreactive plasma (Nusca) indicate the temperature rapidly drops below 10,000 K. Note that convection of the plasma through air-filled spaces in the propellant bed occurs. Thus, prior to considering reactions of the C^+ and H^+ ions with the propellant, it would be wise to consider the chemical evolution of the plasma/air mixture. For example, if the mixing and chemistry are fast enough, the ionic species mentioned may not interact with the propellant at all. In addition, the spectral properties of radiation from the mixture, and thus predictions thereof, depend heavily on its chemical and physical composition. It is thought the plasma radiation may be strongly affecting the propellant. For these reasons, a literature search has, within the last few weeks, begun in earnest with the purpose of developing a complex mechanism for a plasma of C^+ and H^+ ions and electrons mixing with air. Selection of reactions for the initial focus has been guided by some simple thermodynamic considerations. The principal investigator notes the consideration of ion and electron chemistry is outside his past experience, but he is nonetheless undeterred. One thing noted immediately is that many of the reactions involved have extremely large rate coefficients compared to neutral species reactions. A second point is that we are well aware that the very high temperatures and pressures involved make this a very difficult problem. Doubtless, a number of simplifying assumptions and extrapolations will have to be made. There are several points in which the outside community might help in this effort. These are discussed in the following paragraphs.

We have been unable, as of yet, to locate any good reviews or other works on the chemical mechanisms of a plasma in air, such as electric discharges through air for trace pollutant removal. We would appreciate knowing of such published work. For the few models we have encountered, which considered complex chemical mechanisms, an assumption was made that only neutral species chemistry, e.g., radicals, needed to be considered. This apparently worked well for the conditions of interest in those studies but is unlikely to work well for the conditions of high ion and electron density of concern for ETC modeling.

Measurements of rate constants for key elementary reactions will almost assuredly need to be made. It is not possible to provide a very comprehensive list until the literature survey gets well underway. Additionally, some computational runs can help focus attention on highly sensitive reactions. However, some guesses at important steps can be made based on thermodynamics now. It is desirable that the measurements be performed over a broad range of temperature and pressure.

Experiments designed to test the plasma/air kinetics mechanisms developed are highly desirable. Currently, spectral studies of the plasma emerging from the capillary and mixing with air are being performed (K. White). It is planned that the data will be modeled (M. McQuaid, ARL) to, among other things, determine conditions and composition insofar as possible. It would be very useful, though perhaps quite challenging, to use a mass spectrometer probe, with both positive and negative ion detection capabilities as well as neutral species, in a similar experiment. Another possibility is to use mass spectrometer detection in a flow reactor system with a source of C^+ and/or H^+ ions and electrons. If clean sources of the charged species are available, this could provide a stringent test of the chemical mechanisms developed without worry about mixing properties. Obviously, we would like temperature and pressure as high as possible for these studies but will take what we can get.

A few simple calculations have been performed (Powell and Anderson 1998) to test common assumptions that are currently made about how fast reactions are under ETC gun conditions. At one extreme is the assumption that no reactions occur. At the other is the notion that reactions are so fast that chemical equilibrium applies within each computational grid element. These ideas have been tested using available neutral species mechanisms by assuming the electrons, C^+, and H^+ ions instantaneously recombine upon exiting the ETC capillary. Also, a simplifying homogeneous mixture assumption was used. Indications are that for the resulting mixture of C, H, O_2, and N_2, neither of the simplifying chemical assumptions is appropriate on the time scale of an ETC gun firing. Now, it is clear that some other reactions may occur prior to ion-electron recombination. Nevertheless, these results seem indicative that kinetics of the plasma-air mixture must be considered at some point.

4. Specific Issues, Questions, and Research Suggestions

- Use different liner materials for capillary. Purpose: Does chemistry matter? Teflon, carbon (only), metal, etc. (Experiments with different capillary liners are to be carried out by DelGuercio, ARL.)

- Suggested upgrades to the ARL gas-dynamic modeling effort, FAST3D code, included viscosity (dependence on temperature and constituents) and perhaps turbulence (Krier, Gundesen, Keefer), multitemperature thermodynamics (Gundersen, Nusca), mixing/diffusion of plasma-air (Nusca), and electrical conductivity of the plasma (Gundersen). Nusca responded that all of these are possible once appropriate relations describing each are obtained for the plasma. The group suggested that reasonable and currently available estimates be made and the code be tested for sensitivity using experimental data (e.g., ballistic simulator at ARL and Soreq) as a check. Keefer suggested that the MACH2 code, developed at Phillips Lab, could provide guidance in that relevant submodules may be extracted (this code has plasma and magnetohydrodynamics (MHD) capabilities and some degree of electromagnetic [EM] modeling used principally for 1D modeling of solid material comparison due to blast waves and EM pulses).

- Plasma interacting with a burning (steady-state combustion already established) propellant. Purpose: Can the effect on combustion of a plasma interacting directly with a propellant be observed? Strand burner with acoustic determination of instantaneous burn rate suggested by H. Krier. It must be determined that there is adequate time resolution on instantaneous burn rate measurement with the acoustic technique. Tsang suggested that the flame/vapor layer that will form on the propellant surface may shield it from plasma-air interactions. Others in the group expressed the necessity of quantifying the degree of plasma-air mixing and the mixture temperature.

- Closed chamber work replacing air with N_2 or Argon. Purpose: Does the air-plasma interaction affect the burn rate in any way? Anderson suggested air may be very important and, thus, announced his intent to review related chemical literature. However, there was considerable debate as to the importance and role of air in the plasma-propellant interaction. In particular, the extent to which the plasma mixes and interacts with the air in the chamber, as well as the relevance of undertaking calculations that attempt to account for these interactions, was questioned. The importance may be geometry dependent; for grains in the immediate vicinity of the plasma, the air may be unimportant. For propellant farther removed in the propellant bed, it may be more important. (Del Guercio, Birk could study air vs. N_2 vs. Ar in closed chamber experiments.)

- There should be a large body of data on plasma-air reactions that were done in the study of re-entry problems. Purpose: This could be helpful in determining important chemical mechanisms, viscosity, and thermodynamic parameters (suggested by Krier and Gundersen).

- Plasmas can be made to be more efficient in producing large amounts of ions if they are pulsed for a short time (10's of μs). To increase the total number, a high rep rate short pulse can be used (suggested by Gundersen). Purpose: To produce a plasma rich in ions to determine importance of ions on altering burn rates. (Does not Powell's in-capillary modeling indicate the plasma is all atoms or atomic ions and already well over 50% ionized under most conditions anyway?)

- Effect of ultraviolet radiation on combustion. The United Technology Research Center could use a frequency-doubled laser to interact with a burning propellant. Additionally, combustion of propellants could also be studied in a closed chamber after propellants have been subjected to radiation (Leone, Cool).

- Fiber optic measurement of emission directly within the plasma generator. Purpose: Determine plasma conditions. There was considerable debate on the potential difference between a piccolo-type plasma generator and an end injector cartridge because of the possible influence of the boundary layer on the plasma output for the piccolo cartridge (suggested by D. Keefer). Note, feasibility of virtually all experimental diagnostics for in-capillary measurements without serious systematic error is an important issue (optical depth may preclude spectral methods; probe perturbation may preclude physical probe methods).

- Can the small amount of plasma cartridge material chemically influence so much propellant in a gun firing? For closed chamber results that demonstrate a "burn rate" increase that persists after the plasma is turned off, how can chemical effects from a plasma persist long after the plasma has disappeared (note, not all propellants show burn rate increase after plasma is turned off)? Other comments on the fracture of propellant grains from exposure to the plasma igniter included: perhaps tests could be done using grains of various sizes or those that do not fracture as easily (Krier); if the process involves grain fracture, we would not expect to see repeatability among the ETC tests (Melnik); indeed, grain fracture could represent a ballistics event "out-of-control" (Varghese); reference was made to the "compact-charge" tests done at ARL (White) that showed poor repeatability.

- Gun simulator studies. Purpose: Analyze residue on inert propellants after firing to get some idea of distribution of products within the propellant bed. Distribute different types of propellants within the bed of inert grains: foil-coated grains eliminate chemical and radiative effects on ignition; grains that have different optical properties (with and without carbon) to see the effect of radiation (encapsulated in an optically transparent shield); the difficulty is finding proper material - maybe the ARL Materials people could help). Propellants with different heat transfer properties such as spherical grains vs. grains with sharp edges to contrast convective heating effects on ignition. Heat flux mapping within a propellant bed (suggested by Krier).

- An important task is to experimentally obtain plasma composition, to check plasma models, which is technically challenging: molecular beam sampling, to freeze chemistry; output from a plasma cartridge using time-of-flight (TOF) mass spectrometer. Purpose: Need to know chemical makeup of plasma; neutrals, ions, radicals; with air present, could see if plasma/air reaction products form (suggested by Anderson). T. Cool thinks this should be possible. S. Leone will consider doing it. R. M. Jordan (California) builds custom systems; Shaw asked, "Is the system of R. Sausa at ARL suitable?" (Anderson tasked to speak to Sausa and has—Sausa is considering.)

- Compare molecular flux and pressure of a plasma with a conventional igniter. Could be done in open air and also in a simulator. Purpose: What is the difference between the two igniters, quantitatively?

- Compare output of piccolo and end injector. Purpose: As discussed earlier, the boundary layer influence for the piccolo may be considerably different.

- There was skepticism on the importance of ions because of rapid neutralization (Leone and Anderson). There has been considerable work in ion-polymer reactions related to lithography and pulse radiolysis (W. Tsang). This work should be looked at.

- AF labs (Viggiano) are able and willing to measure ion-propellant reaction rate constants (first lab in the world to be able to do T > 1,200 K, thermal rate coefficients for ion reactions), but they would need to know what reactions to study. Some preliminary modeling with large reaction set, screening needed.

- Using an IR camera, look at propellants that have been subjected to a plasma radiation. Have different depth holes drilled in rear of propellant, camera looking in, to follow history of temperature rise. This may have to be done after the plasma has gone out, as the plasma radiation might interfere with the measurement. Purpose: Get in-depth heating effects from plasma (suggested by White).

- What is the propelling charge temperature sensitivity with different plasma cartridge configurations?

- Determine particle makeup of plasma output. Purpose: Plasma output.

- Elipsometry applied to a burning propellant; interrogate the surface during a burn and application of a plasma pulse. Purpose: Surface effects during burning.

- Photographic examination of propellant surface during plasma interaction. Purpose: Look for mechanical effects during plasma interaction.

- 2-D modeling of the plasma source. Purpose: How important is the boundary layer in the capillary, not explicitly accounted for in our 1-D models, and how accurately do existing models predict species concentrations and thermodynamic properties? Are electromagnetic forces important? Keefer proposed to exercise an existing 2-D code to undertake relevant axisymmetric calculation for breech-type injector.

- Plasma source output: How do plasma properties change in "newer" injector designs as opposed to those in breech and piccolo injectors? Are we addressing the right problems? Research participants need to be appraised of restricted or proprietary designs.

- Important: Measure absolute spectral intensity of plasma. Some information already available, and agreement between relative spectra obtained in several labs (including ARL) is striking.

But it's clear further work vs. parameters (time evolution, observation angle, air interaction/pressure—possibly even gas composition, electric pulse characteristics) is highly desirable. Photolysis of propellant components (R-NO_2 bonds in visible, C-C and C-H in UV), radiative heat transport at all wavelengths, even photolysis of air molecules to produce radicals just ahead of plasma by vacuum UV are all possible. Need absolute intensities to evaluate importance.

- Closed chamber results should be re-examined to see if an average 'action distance' can be extracted, assuming propellant grains are affected to some depth by plasma—a simple numerical integration of present data required. (Anderson: Idea has been communicated to Del Guercio.)

- CFD calculations could be expanded using a few generic A,B,C,D, ..., type species to examine limiting cases for possible importance of various effects, such as ion neutralization at walls/propellant surfaces, mixing of plasma/air, generic reaction with propellant, turbulence. (Suggested by Anderson; Nusca will do.)

- Possibly a good idea to have someone like Tsang do large-scale review of relevant ion/molecule kinetics, similar to what he has done in the past for propellant combustion chemistry. Anderson will look over status of current database and will consider the amount of reactions needing review.

5. Collaborations

During the course of the workshop, several collaborative efforts were developed and are listed below.

- Dr. Viggiano will send information to ARL on ion/molecule reactions.

- Dr. Keefer will do a 2-D simulation of the plasma capillary source using the code MACH and compare his results with Dr. Powell.

- Dr. Keefer will assist Dr. Nusca in exploring the use by ARL of the MACH2 (Phillips Lab) code modules.

- Dr. Nusca and Dr. Perelmutter will continue to discuss the 105 gun cartridge experiments by Soreq.

- Dr. Nusca and Prof. Bourham will couple the NCSU 2-D capillary model with the ARL CFD code.

- Dr. White and Dr. Melnik will discuss use of the Soreq experimental simulator to explore some of this workshop's recommendations.

6. Conclusions and Recommendations

We believe from the response of the attendees that the presentations were successful in giving an adequate background on the work in progress, which stimulated considerable discussion for the following 1 1/2 days on possible work areas to address the problem.

Some of these points, given in the **Specific Issues, Questions, and Research Suggestions** section, may be usefully incorporated into ongoing work. We hope other more extensive suggestions will possibly lead to proposals from the participants. Before proceeding, we mention briefly that many of the points center around physical or chemical characterization of the plasma, with or without interaction with air. This issue, of which we were aware prior to the workshop, kept recurring in many forms during the discussions. It is very difficult, perhaps impossible, sensibly to investigate proposed ways in which the plasma interacts with the propellant without better characterization than currently available. Modeling can help (and that such as done by Powell is likely the only way to get at in-capillary conditions) but is likely to be regarded as inconclusive because of the complexity—further experiments are essential. A second point—a review of what is currently known about how different propellants respond to plasma with focus on chemical composition and physical properties would be very helpful. The participants did not bring this up directly, but during the discussion, it became obvious it would be useful to have comprehensive information to see whether suggested cause/effect relations correlate with present data.

Principal issue: Does the plasma source simply act as thermal source or is the plasma chemistry important also?

6.1 The Plasma Source. The source emissions must be characterized. Species (atomic and molecular) and energy fluxes at the source exit must be determined. This is a first "primary need" to make sense of all the other questions and results. There is some concern that first principles modeling the plasma source may be too hard; we may have to treat it as a black box and measure the output.

6.1.1 Convective Heating. Related to the above, we must measure the density, velocity, temperature of the emission to determine the convective heating.

- To measure convective heating (suggestions for experiments with no details about how to make them work):
  - Fast laser probe of propellant bed using IR sensitive dyes (related to D Dlott's experiments using dyes to learn about propagation of shocks through condensed materials). This work is supported by ARO and the Air Force Office of Scientific Research (AFOSR) Chemistry.
  - Use laser-induced fluorescence to track excited molecular species (but this will be hard due to high background signal).

- We should know the heat capacity of the source emission to understand energy transfer from the plasma to the propellant (polyatomics will behave much differently from atoms).

- To understand the heat transport, we must unravel the roles of radiation vs. molecules and atoms.

- The favored experiment to determine the molecular species composition of the plasma is direct (ion and molecular beam) extraction into a mass spectrometer. Of the participants, Cool and Leone are experts in this technology and could design a system.

6.1.2 Other Remarks on the Plasma. Inside the source, the boundary layer is relatively cold and not in equilibrium, yet it is likely to be an important part of the source output.

We must learn about the time evolution of the source, the change in source emission with time, and what the propellant experiences as a function of time.

Tests have shown that the ballistics are very dependent on plasma device design, energy, etc. This suggests that workers should agree on a common design so that they can compare data. Now the question is: What design? Should we choose a source designed to study the properties of the plasma or one designed (based on experience) for propellant ignition?

6.2 Plasma/Propellant Chemistry. We had a consensus of support for studies of propellant grains subjected separately to fluxes of ion, radicals, radiation. These studies may distinguish chemical, erosive, and mechanical effects of the plasma.

6.2.1 Ions. Plasma ions will be kinetically slow; therefore their chemistry may not be important; they will just neutralize on their first collision with a surface (almost certainly a propellant grain).

Before doing any experiments to study chemistry of ions with condensed materials, one should look at related literature: pulsed radiolysis, polymer film lithography (in this case, the ions are at relatively high kinetic energy).

The Air Force is set up to measure ion molecule chemistry.

6.2.2 Radicals. One participant pointed out that, given the mass of the plasma, no more than approximately 1 g of radicals can be formed. This seems insufficient to affect the combustion of 10 kg of propellant. But another participant pointed out that radicals can initiate chains that grow into chemical avalanches.

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Appendix A:

Agenda

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Army Plasma/Propellant Interaction Workshop at the U.S. Army Research Office (ARO)

17–18 Nov 1998

Workshop Agenda

Tuesday, 17 Nov, Morning:

Status of the U.S. Army Research Laboratory (ARL) projects: presenters discuss experiments and calculations, assumptions used, conclusions, mysteries, and obstacles caused by lack of information. These presentations provide the specific issues for the Focus Groups.

0800–0830	Arrive and Register at ARO.
0835	Welcome B. Andrew Crowson, Director of Physical Sciences, ARO.
0845	Electrothermal-Chemical (ETC) Propellant Ignition, Gun Firings and Experiments (Kevin White).
0945	ARL Basic Research Program in Plasma Propellant Interaction (Bill Anderson).
1015	Break.
1030	Plasma Modeling for the Capillary (John Powell).
1100	Modeling of Plasma Jets/Propellant Interaction (Mike Nusca).
1130	Kinetic Modeling of Energetic Materials Combustion and PPI (Bill Anderson).
1200	Summary, What's Needed (Kevin White).
1230–1330	Lunch at ARO.

Tuesday, 17 Nov, Afternoon:

1330–1730

Discussion on major research issues - 1 hr.

Assignment of Focus Groups (FG) led by ARL.

Preliminary FG discussions - 3 hr.

Questions raised by FG discussions (all participants) - 2 hr.

1830 Dinner.

Tuesday, 17 Nov, Evening:

Focus Groups convene, discuss on their own.

Wednesday, 18 Nov, Morning:

Subgroups develop recommendations for experiments, computations.

0830 Discussions, etc., at ARO.

1200 Lunch at ARO.

1300 Focus Groups present recommendations* - 1 hr/FG.

1500 Finish.

* The FGs are not expected to write the workshop report, but they are encouraged to present their recommendations clearly and completely so that the writing can be straightforward.

Appendix B:

Focus Groups and Attendees List

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Focus Groups

Energy Transfer

Group Leaders: John Powell and Kevin White

Philip Vargese

Martin Gundersen

Lior Perelmutter

C. Randy Jones

Dennis Keefer

Marc Kushner

Dave Mann

Chemistry and Modeling

Group Leaders: Bill Anderson and Mike Nusca

Steve Leone

Wing Tsang

Al Viggiano

Lourdes Q. Maurice

Mohamed Bourham

Herman Krier

Terry Cool

Mike Berman

Bob Shaw

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13. ABSTRACT *(Maximum 200 words)*

This workshop was organized by the U.S. Army Research Office (ARO) as part of an ongoing U.S. Army Research Laboratory (ARL)-ARO effort to develop a coordinated research program to address the needs of advanced gun propulsion, in particular, in the application of plasmas as ignition and energy augmentation sources for solid propellant guns, known as electrothermal-chemical (ETC) propulsion systems. We sought to bring leading scientists and engineers from outside the Army with expertise in plasma properties and behavior (especially energy transfer) and in chemical reactions by mechanisms likely to be caused by interactions of plasmas with solids.

Presentations were made by ARL to give a background on ETC and the observed effects of plasmas on ballistics. Succeeding talks discussed experiments and modeling related to the physics and chemistry of plasma propellant interaction being carried out at ARL and other institutions. In addition to technical details on current research, the presenters also discussed "wish lists" on data, projects, etc., that ARL believed to be important in the solution of the problem. After the presentations, focus groups were formed from the attendees to discuss the problem and possible solutions. Subsequently, very specific issues, questions, and research suggestions were collectively discussed and are reported here. Finally, collaborations between investigators were initiated and conclusions and recommendations were drawn up for future research.

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electrothermal-chemical (ETC), propulsion, ballistics, ignition, combustion, plasma

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