

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 11/15/85

Project No. E-16-658

School XXX AE

Includes Subproject No.(s) Co-Project with E-16-661/~~E-16-603~~/~~E-16-675~~

Project Director(s) W. Strahle

GTRC / XXX

Sponsor AFOSR - Bolling AFB, DC 20332-6448

Title Combustion Dynamics in Rockets

Effective Completion Date: 9/30/85 (Performance) 9/85 (Reports)

Grant/Contract Closeout Actions Remaining:

- None
- Final Invoice or Final Fiscal Report
- Closing Documents
- Final Report of Inventions
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- Classified Material Certificate
- Other \_\_\_\_\_

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ORIGINAL  REVISION NO. \_\_\_\_\_

Project No. E-16-661 (Co-project is E-16-658) GTRI/~~GLX~~ DATE 10/ 13/ 83

Project Director: Edward Price School/~~DLX~~ Aerospace Engineering

Sponsor: Air Force Office of Scientific Research

Bolling AFB, D.C. 20332

Type Agreement: Grant No. AFOSR-83-0356

Award Period: From 9/30/83 To 9/29/84 (Performance) \_\_\_\_\_ (Reports) \_\_\_\_\_

Sponsor Amount: This Change 9-30-85 Total to Date

Estimated: \$ \_\_\_\_\_ \$ 102,219

Funded: \$ \_\_\_\_\_ \$ 102,219

Cost Sharing Amount: \$ 10,225 Cost Sharing No: E-16-337

Title: "Combustion Dynamics in Rockets"

ADMINISTRATIVE DATA

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Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

See Attached AFOSR Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval - Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT. For details, refer to section entitled "Title Permanent Equipment", page 9 of AFOSR Administration Brochure (Aug. '82)

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E-16661

ANNUAL REPORT

## COMBUSTION DYNAMICS IN ROCKETS

Prepared by

J. I. Jagoda, E. W. Price, R. K. Sigman,  
W. C. Strahle and R. E. Walterick

Submitted to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
BOLLING AIR FORCE BASE  
WASHINGTON, DC 20332

September 30, 1984

**GEORGIA INSTITUTE OF TECHNOLOGY**

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

SCHOOL OF AEROSPACE ENGINEERING

ATLANTA, GEORGIA 30332

1984



REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR-84	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Combustion Dynamics in Rockets		5. TYPE OF REPORT & PERIOD COVERED Research Summary & Forecast 1 Oct. 83 - 30 Sept. 84
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. I. Jagoda, E. W. Price, R. K. Sigman, W. C. Strahle, R. E. Walterick		8. CONTRACT OR GRANT NUMBER(s) AFOSR-83-0356
9. PERFORMING ORGANIZATION NAME AND ADDRESS Georgia Institute of Technology School of Aerospace Engineering Atlanta, Ga 30332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NA Bldg. 410 Bolling AFB, D. C. 20332		12. REPORT DATE Sept. 1984
		13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Approved for public release; distribution unlimited		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Solid propellant combustion; Aluminum; Turbulence; Ramjets		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Progress is reported on two distinct projects which are administered as a group. A summary for each task follows: <u>Task I:</u> Laser velocimetry has mapped two velocity component data for the backward facing step facility with and without blowing of air and CO <sub>2</sub> from the bottom wall of the facility. Comparison of experiment with theory, using a k-ε turbulence		



model, has shown good agreement between the two. Diagnostic development has continued with the Rayleigh scattering system now operational and the Raman spectroscopy system still under development. Software development for simultaneous Rayleigh concentration and laser velocimeter measurements has been completed. Dominant results are the general predictability of the length scales of the flow field and the appearance of a second recirculation zone under the action of sidewall blowing.

#### Task II:

Studies continued on the behavior of aluminum and other nonvolatile ingredients in the propellant combustion zone. A method for observation of particle behavior and interaction during controlled heat-up was developed using an improvised hot stage in the scanning electron microscope. Notable difference was observed in this experiment in behavior of aluminum from different sources.

Studies were made of the effect of  $\text{Fe}_2\text{O}_3$  on aluminum agglomeration in an AP-Al-PBAN propellant. The results showed enhanced agglomeration, and indicate that  $\text{Fe}_2\text{O}_3$  affects agglomeration through two competing mechanisms.

Combustion of zirconium carbide was observed in several experiments. Results indicate that particles do not concentrate on the propellant burning surface; ignite near the surface; burn rapidly, but less brightly than aluminum; and burn in a unique manner involving fissuring of the particles, formation of a hollow shell of as yet undetermined product material (oxycarbide?), with solid ZrC inside the shell. The burnout phase of particles has yet to be studied.

Studies of surface concentration of various nonvolatile additives were conducted using AP-PBAN sandwiches with 10% additive in the binder laminae (equivalent to roughly 1% level in a propellant). Of the nine common nonvolatile additives tested, only two concentrated on the surface ( $\text{Fe}_2\text{O}_3$  and  $\text{CuCr}_2\text{O}_4$ ). Only these two "concentrators" showed significant enhancement of burning rate.  $\text{Fe}_2\text{O}_3$  was chosen for further study of its surface concentration mechanism. Similar behavior was verified in propellant burning.

As a preliminary to studies of dynamic response of the combustion zone to flow perturbations, a review of perturbation models was started. This review revealed a deficiency in the conventional application of the acoustic admittance concept to stability analyses, and a modified theory based on modern acoustic analysis for duct flows was carried out.

## TASK I

### HETEROGENEOUS DIFFUSION FLAME STABILIZATION

J. I. JAGODA

WARREN C. STRAHLE

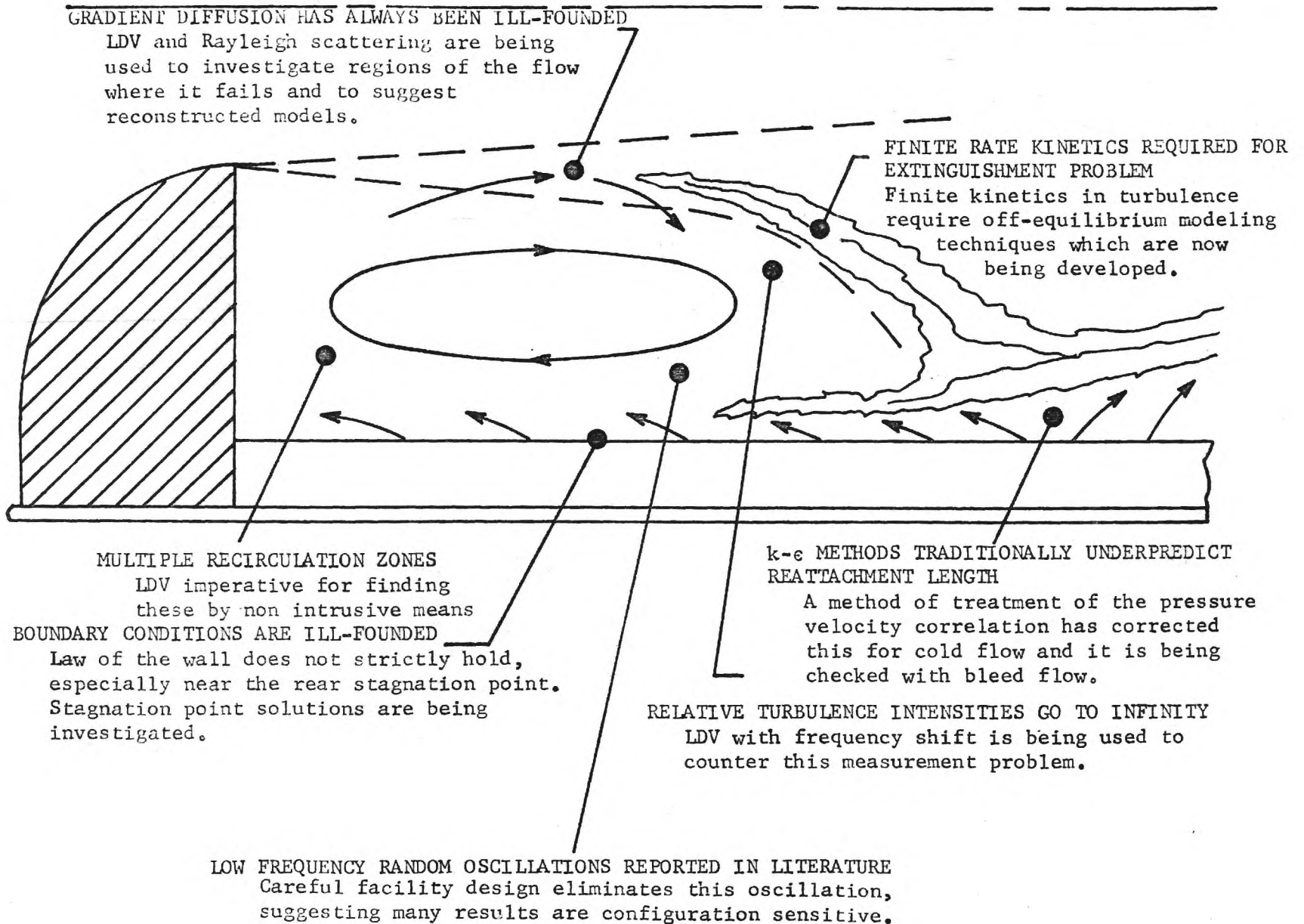
#### A. Research Objectives

The overall objective of the program is to understand and be able to predict recirculatory turbulent reactive flows, flame stabilization limits and fuel regression rates in a flame stabilization region as occurs in a solid fueled ramjet. The specific goals for the past year were to a) complete the laser velocimeter measurements in cold flow with and without foreign gas injection, b) to complete the cold flow calculations with and without foreign gas injection, c) to complete development of the Rayleigh scattering apparatus, d) continue development of the RAMAN spectroscopy system and e) begin foreign gas injection concentration measurements.

#### B. Status of Research

In solid fueled ramjet flame stabilization the fundamental flow configuration is as shown in Fig. 1. Illustrated there are some of the fundamental technical issues involved, which are being addressed in this program. The tasks for the current year include continued facility development, instrumentation and analysis development and data generation. Progress in these areas is summarized in the following paragraphs.

Figure 1. Typical technical issues.





## 1. Facility

By way of review, the facility is depicted in Fig. 2. It is a backward facing step, open return flow system. The freestream velocity is nominally 245 ft/sec, set by an orifice downstream of the centrifugal blower. The facility is operated with the inlet, test section diffuser and plenum on the upstream suction side of the blower. The test section is fitted with anti-reflection coated windows for optical access.

During the past year the facility has been fitted with a porous plate floor for the injection of several gases, including combustibles. It has been noted that this facility is quite stable, as opposed to other facilities with backward facing step configurations. Careful acoustic and hot wire checks have shown no "flapping" of the dividing streamline as has been reported in the literature. A striking feature is the measurement of a 1.5% freestream "turbulence" level. This cannot, however, be turbulence because, operating in the suction mode from quiescent laboratory air, there is no vorticity source in the freestream. What it is is sound- an intense broadband sound field. This has important implications in the interpretation of modelling efforts - both ours and others'. Normal turbulence equations are not equipped to deal with an acoustic motion of the gases. If it turns out that results are sensitive to freestream turbulence levels then modelling is suspect. Fortunately, our calculations show that the results are not sensitive to this quantity. This acoustic observation is still more than an academic curiosity, however, since it may be linked to system acoustic stability.

## 2. Diagnostics

During the past reporting period the optical system for Rayleigh scattering, which had previously been tested using laminar flows of air/CO<sub>2</sub> mixtures, was incorporated into the velocimeter set-up. This assures that the vector and scalar

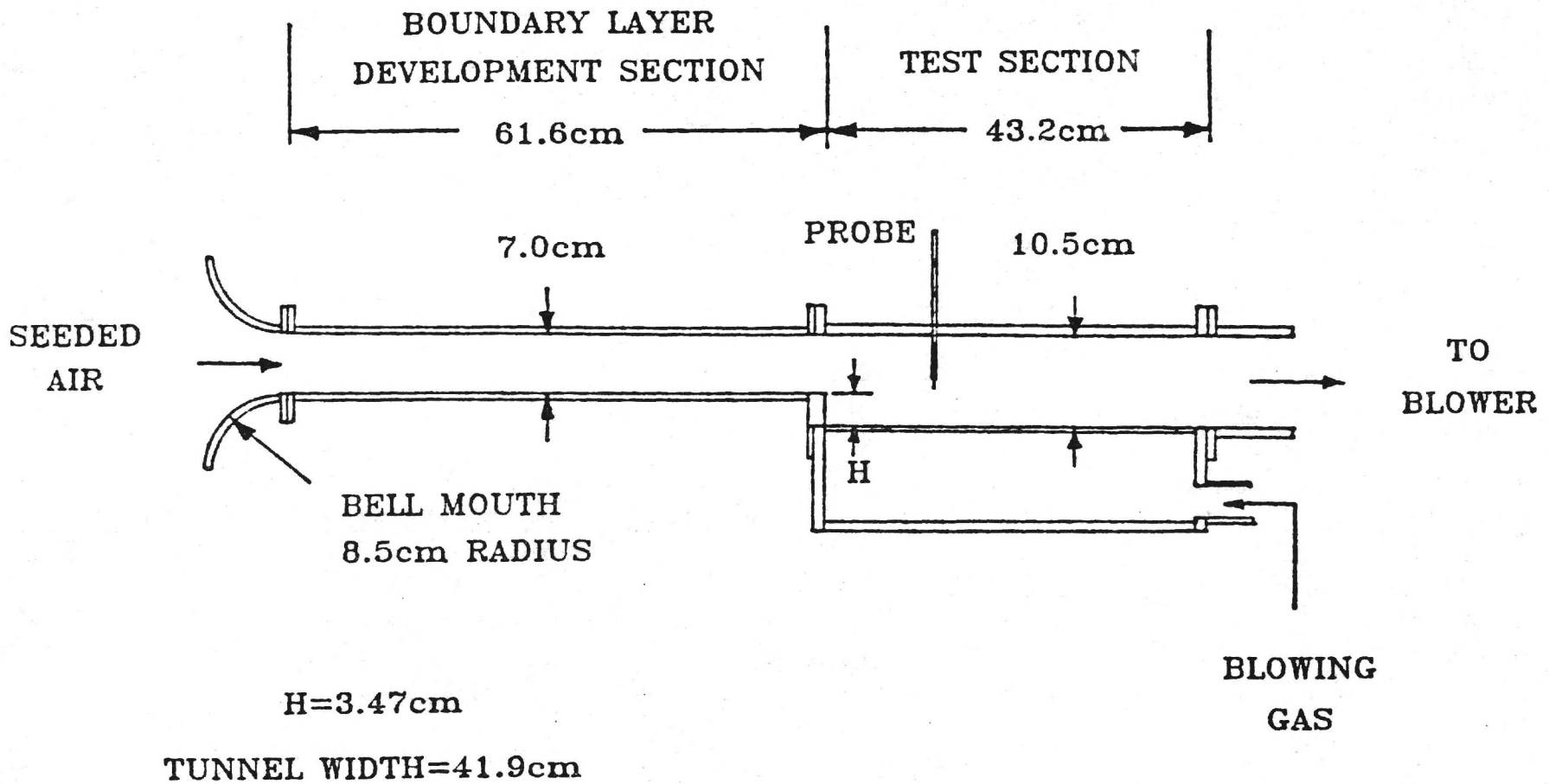


Figure 2. Wind tunnel schematic.

measurements are easily carried out at the same location. To test the technique under more realistic conditions, temperature fluctuations were measured in a turbulent premixed flame jet and compared with fine wire thermocouple measurements. Comparison of the results obtained by the two methods showed excellent agreement.

In order to be able to correlate the species measurements (Rayleigh) with the velocity determinations (LDV) both sets of data must be digital. To this end a software package has been developed which continuously passes the digitized Rayleigh data through a series of memory buffers. Since Rayleigh measurements cannot be carried out when a velocimeter particle is in the test volume, a number of measurements within 100  $\mu$  sec prior to and after each velocimeter burst will be stored along with the instantaneous velocity values in the two directions. The special difficulty in designing this program arose from the fact that the Rayleigh data before as well as after each velocimeter point are to be recorded, which has not been done by previous investigators who combined Rayleigh and velocimeter measurements.

The Rayleigh technique has been tested in the tunnel to determine the effect of glare from the windows and the tunnel floor on the signal. By the careful use of apertures and screens the Rayleigh noise was essentially zero for clean windows. To avoid the problems from the deposit of such particles on the tunnel windows, the possibility of using a fine spray of distilled water for seeding the cold flow has received a successful test. For this purpose, an in-house designed atomizing nozzle is being used. The combined Rayleigh-velocimeter set-up is now operational and awaits the CO<sub>2</sub> bleed experiments to be completed before the end of the first grant year.



A three channel pulsed laser Raman system for ultimate use in hot flow has been designed and set-up. This system is capable of measuring three Raman lines (e.g. Stokes and anti-Stokes of  $N_2$  and Stokes of one further constituent) with a time resolution of  $1 \mu$  sec and a repetition rate of 3-5 Hz. A number of dyes were tested and R600 was selected because of its high power (1.3 watt/shot), long half-life and relatively low cost. This dye has become a viable choice in spite of its high radiation wavelength (590 nm), since new photomultiplier cathode materials have recently become available which perform well to 700 nm. The overall system has been tested using a propane-air flame and fine tuning is currently being carried out.

Since the combined Raman-velocimeter system is too heavy for the actuator system currently in use for the velocimeter, a separate moveable optical table has been designed to carry the Raman equipment. It will be located on the side of the tunnel opposite to the velocimeter. A tracker system based on a small He-Ne laser and a photodiode will be used to keep the velocimeter and Raman beams aligned. The Raman table is currently under construction. A computer program is currently under design for simultaneous measurements of the velocimeter and Raman systems.

In addition to the water droplet seeder, necessary for better signal to noise ratio for the Rayleigh system, a change in the seed material for ordinary velocimeter measurements was made during the past year. Scanning electron microscope photos of the  $Al_2O_3$  seed, which was originally used, revealed a large number of large particles (larger than our fringe spacing which is small due to our large focal length). This was causing a low signal to noise ratio for the velocimeter. This has since been corrected by changing to  $TiO_2$  particles.

### 3. Analysis and Experiment

The following analyses were completed this year using a modified k- $\epsilon$  turbulence model:

- a) Full cold flow - no injection.
- b) Cold flow-air injection through the wall.
- c) Cold flow-CO<sub>2</sub> and He injection.

The no-injection case was thoroughly compared with experiment. It was tested against our laser results, our past intrusive probe results and others' experiments in a similar facility. Quantities compared were both mean and fluctuating velocities in two dissections and the shear stress. A typical comparison for mean axial velocity is shown in Fig. 3. The axial station here is fairly close to the step where the analysis is known to have the most difficulty. The comparison is generally favorable except deep into the recirculation zone. However, in the unfavorable region it may not be necessary to be particularly accurate since combustion would not occur there (see Fig. 1) in the hot flow case.

Shown in Fig. 4 are the experimental data on the full development of the axial mean velocity along with a calculation of the zero mean velocity line. This shows that the general length scales of the problem are adequately predicted by the analysis method. As a consequence, the k- $\epsilon$  approach will be retained in following work.

In the blowing case the most interesting structural change in the flow, that has been analytically predicted, is the appearance of a second recirculatory region. This has now been experimentally confirmed.

The following experiments have either been completed or will be complete by the end of the current grant year.

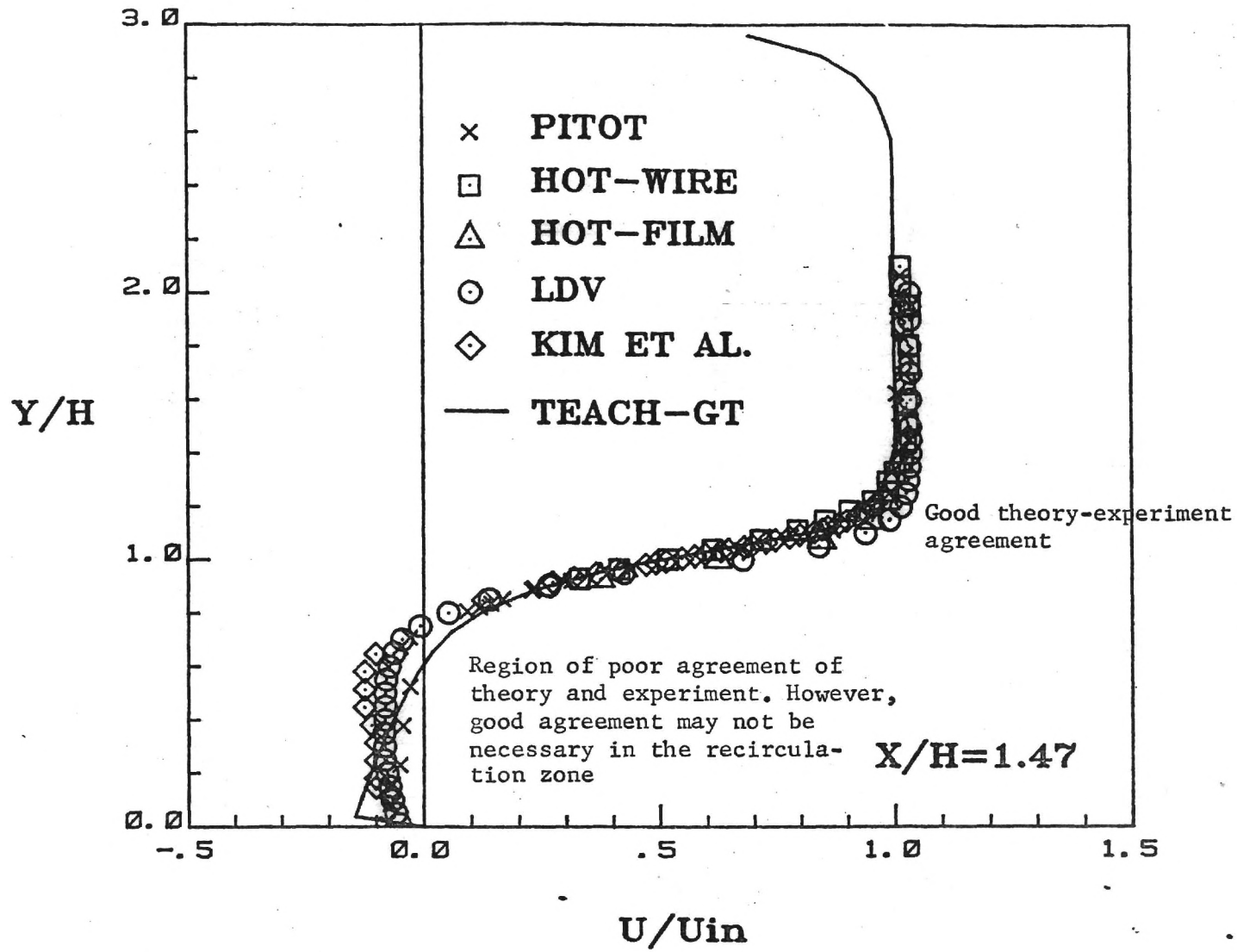
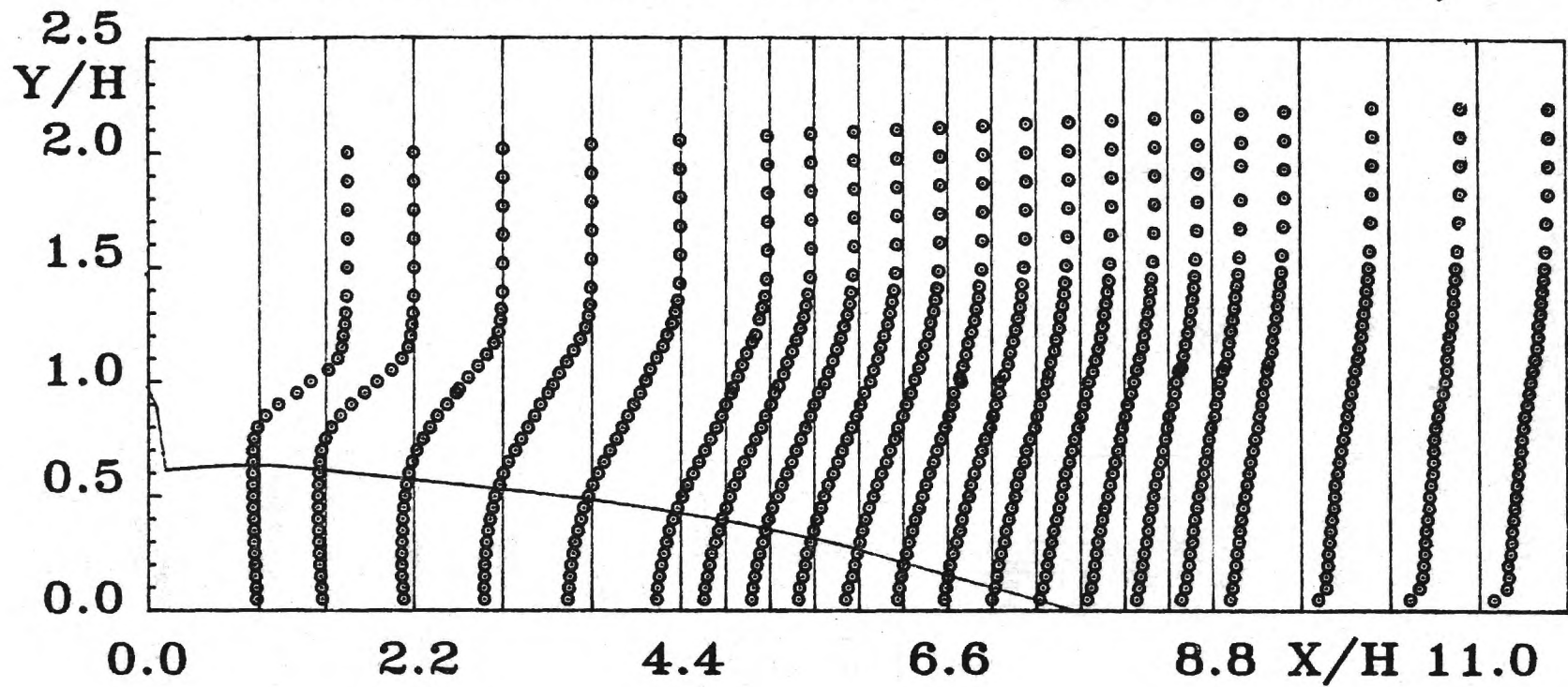


Figure 3. Mean streamwise velocity close to the step. Theory and experiment.



• LDV MEASUREMENTS     $\text{---} = U_{\text{LOC}}/U_{\text{INLET}} = 1.0$   
 - CALCULATED ZERO CROSSING (K- $\epsilon$  METHOD)



### AXIAL VELOCITY PROFILES :NON BLEEDING CASE

Figure 4. Mean streamwise velocity measurements and calculation of zero axial velocity line.

- a) Shear stress, two component mean velocities, and turbulent intensities at 21 axial stations in cold flow with no blowing.
- b) The same information for two injection velocities with air as the injectant.
- c) The same information for one injection velocity with CO<sub>2</sub> as the injectant.
- d) In the CO<sub>2</sub> case the first Rayleigh measurements will be made for mean CO<sub>2</sub> concentration, mean square fluctuation and correlations with velocity fluctuations.

#### C. Publications

1. Richardson, J. "Analysis of a Sudden Expansion Flow in a Two-Dimensional Duct with and without Sidewall Injection Using the k- $\epsilon$  Turbulence Model," Ph.D. Dissertation, Georgia Institute of Technology, 1984.
2. Chandran, S. B. S., Komerath, N. M., Grissom, W. M., Jagoda, J. I. and Strahle, W. C. "Time Resolved Thermometry by Simultaneous Thermocouple and Rayleigh Scattering Measurements in a Turbulent Flame" submitted to Combustion Science and Technology.

#### D. Personnel

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Graduate Research Assistants - Wilhelmus de Groot

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E. Professional Activities

J. I. Jagoda - Member AIAA Propellants and Combustion Technical Committee

W. C. Strahle - Chairman, Georgia Tech/AFOSR Conferences on Turbulent Reacting Flows

Walterick, Richardson, de Groot, Strahle, Hubbartt and Jagoda, "Heterogeneous Diffusion Flame Stabilization: Constant Density Results," 20th JANNAF Combustion Meeting, 1983.

Walterick, Jagoda, Richardson, de Groot, Strahle and Hubbartt, "Experiments and Computation on Two-Dimensional Flow over a Backward Facing Step" AIAA Paper No. 84-0013.



## TASK II

### BEHAVIOR OF ALUMINUM AND NONVOLATILE PARTICLE INGREDIENTS IN SOLID PROPELLANT COMBUSTION

E. W. PRICE

R. K. SIGMAN

#### A. Research Objectives

The overall objective of this program is to understand, predict, and control the unique combustion behavior of relatively nonvolatile ingredients (NVIs) in composite rocket propellants. Such ingredients include metal powders used as fuel ingredients (e.g., aluminum); certain metal compounds used as burning rate modifiers (e.g.,  $\text{Fe}_2\text{O}_3$ ); and other metal compounds used as instability suppressants (e.g.,  $\text{Al}_2\text{O}_3$  and  $\text{ZrC}$ ). They share the common features that they do not vaporize readily in the combustion zone, often concentrate on the burning surface of the propellant, and exist in consolidated condensed form in the combustor cavity. Previous effort on this program focused primarily on aluminum fuel powder. The specific goals of the past year were: 1) to develop a hot-stage scanning electron microscope experiment to observe the behavior of individual and interacting particles during heating to combustion zone temperatures; 2) to study the behavior of several ballistic modifiers on the burning surface, with particular emphasis on  $\text{Fe}_2\text{O}_3$ ; 3) to study the combustion of  $\text{ZrC}$  (an instability suppressant); 4) to modify the acoustic admittance theory to accommodate for more realistic representation of the interaction of flow and combustion oscillations; and 5) to extend the understanding of aluminum agglomeration to a wider range of propellants.

## B. Status of Research

In combustion of solid propellants, those propellant ingredients that do not vaporize easily tend to concentrate on the surface of the propellant during burning. This often leads to sintering and agglomeration on the surface, and enhanced chemical activity there. Upon detachment from the surface, these ingredients exhibit protracted droplet burning (metals), and two-phase flow effects important for damping oscillatory behavior. Figure 1 illustrates the kinds of behavior involved, their importance to motor performance, and the relation of the objectives 1 - 5 (noted above) to such combustion behavior. Progress toward these objectives is summarized in the following.

1. Hot Stage Scanning Electron Microscopy of Particle Behavior. The primary difficulty in understanding behavior of particles and groups of particles is the small size of the particles (typically 1 - 40  $\mu\text{m}$ ). Much of their behavior is determined by surface effects that operate on a submicron scale. As a result, our knowledge of behavior is based primarily on inference from more macroscopic effects, and remains speculative in nature. In an effort to provide direct microscopic observation of particle behavior, the feasibility of real-time observation of particles during heating was explored. Earlier studies in the hot stage of an optical microscope had provided some insight into particle behavior, but did not provide a suitable combination of magnification and depth of focus to reveal the detailed particle behavior.

Recent effort has been directed to adaptation and use of the scanning electron microscope, which does not have the above limitations, and offers the possibility of video-recording of sample behavior during heating. Heating has been accomplished by depositing samples on electrically heated platinum and palladium wires. Tests to date have been on aluminum particles, and heating has been to temperatures of roughly 750<sup>o</sup> C, the temperature range being determined to exceed that required to produce behavior associated with melting of the metal. Recalling that the typical aluminum

Admittance Surface

Objective #4 Dynamic Response

---

Ignited  
Particle

Objective #3 Combustion of ZrC

Agglomerating  
Igniting Concentrate

Objective #2 Behavior of

Ballistic Modifiers

Objective #5 Extend Range of

Propellant Ingredients

Sintering  
Concentrates

Objective #1 HSM Study of

Sintering

Objective #2 Behavior of

Ballistic Modifiers

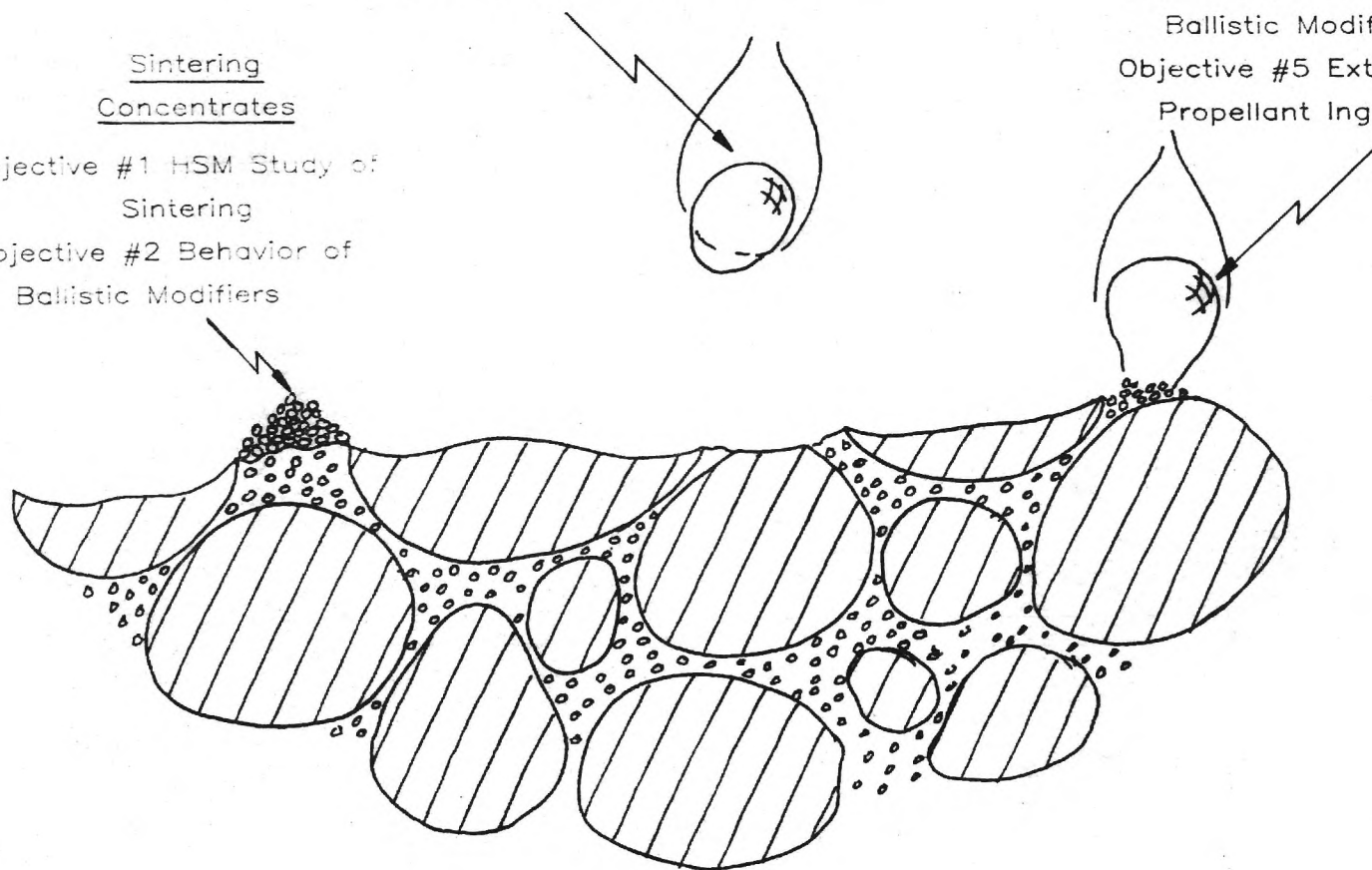


Figure 1. Relation of present studies to processes in propellant combustion and rocket motors. The indicated processes affect burning rate, combustor stability, combustion efficiency, slag formation, and component erosion.

particle is a "potato-shaped" object with a refractory oxide "skin", the heating tests show the following behavior (mostly at the melting point of the metal where it expands in volume by 6%).

- a) Expansion accompanied by some degree of spheroidization (inflation of the oxide skin).
- b) In many cases, abrupt reversal of the expansion, with evidence that molten aluminum has escaped through ruptures of the oxide skin. Surface features suggestive of cracks in the oxide become visible, but are not clearly resolved as cracks.
- c) Agglomeration of contacting particles has thus far been observed only sporadically, possibly in part because of choice of test and sample conditions. When observed, it is an abrupt event, occurring under conditions as in (b) above, conditions typical of oxide skin rupture and identified by occurrences of abrupt reversal of expansion.
- d) Under the conditions in (b) above, rupture of the oxide skin is often followed by drainage of the molten metal onto the heater wire, leaving an empty oxide shell or collapsed "balloon". This drainage process is much slower than agglomeration events; the details are dependent on the choice of metal for the heater wire.
- e) All of the processes described above are highly dependent on the source of aluminum powder and condition of the oxide skin.

The behavior of the aluminum in the propellant combustion zone varies in a similar way, and our understanding of controlling processes involves these same microscopic particle and interparticle responses to heating. The present studies are being used to further clarify the microscopic processes and to determine why they differ for different aluminum sources. The experimental methods hold promise for clarification of behavior of all particle ingredients (not just aluminum).



2. Behavior of Ballistic Modifiers. A variety of NVIs are used in solid propellants at the 0.2 to 5% concentration level to control burning rate and combustor stability. The mechanisms by which such additives produce their beneficial effect are not generally known, but there is evidence that concentration on the burning surface is important. To explore this issue, combustion photography and interrupted burning tests were run with a number of additives (see Fig. 2) to determine extent of surface concentration and effect on burning rate. The tests were run on edge-burning oxidizer-binder laminates (sandwiches) to simplify the interpretation of results, which are summarized in Fig. 2. Weight % of additive in the binder was 10%, corresponding to a 1% loading in a propellant. The results indicate that surface concentration was minimal with all the additives but  $\text{Fe}_2\text{O}_3$  and  $\text{CuCr}_2\text{O}_4$ , which formed sintered layers on the binder surface (Fig. 3). The results suggest two tentative general conclusions:

- a) Most NVI additives at this loading leave the burning surface with minimal coagulation, and
- b) Modification of burning rate depends on concentration of the additive on the binder surface.

Results on a companion project (Ref. 1) suggest that catalysis involves percolation and breakdown of heavy fuel molecules in the catalyst concentrate, resulting in closer proximity of the AP-binder flame to the burning surface, and correspondingly higher burning rate.  $\text{Fe}_2\text{O}_3$  and  $\text{CuCr}_2\text{O}_4$  are recognized decomposition catalysts for large hydrocarbon molecules, so this interpretation seems plausible, and is being studied further on the companion project.

In the present project, the focus is on the question of why certain NVI materials concentrate on the surface, under what conditions concentration occurs, and what interactive processes occur between the particles and with the binder surface. Figures 4 and 5 show the effect of  $\text{Fe}_2\text{O}_3$  on burning rates of sandwiches and of an AP-PBAN propellant over a range of test conditions. Interrupted burning tests are being made to determine the nature of the  $\text{Fe}_2\text{O}_3$  concentration over this range of

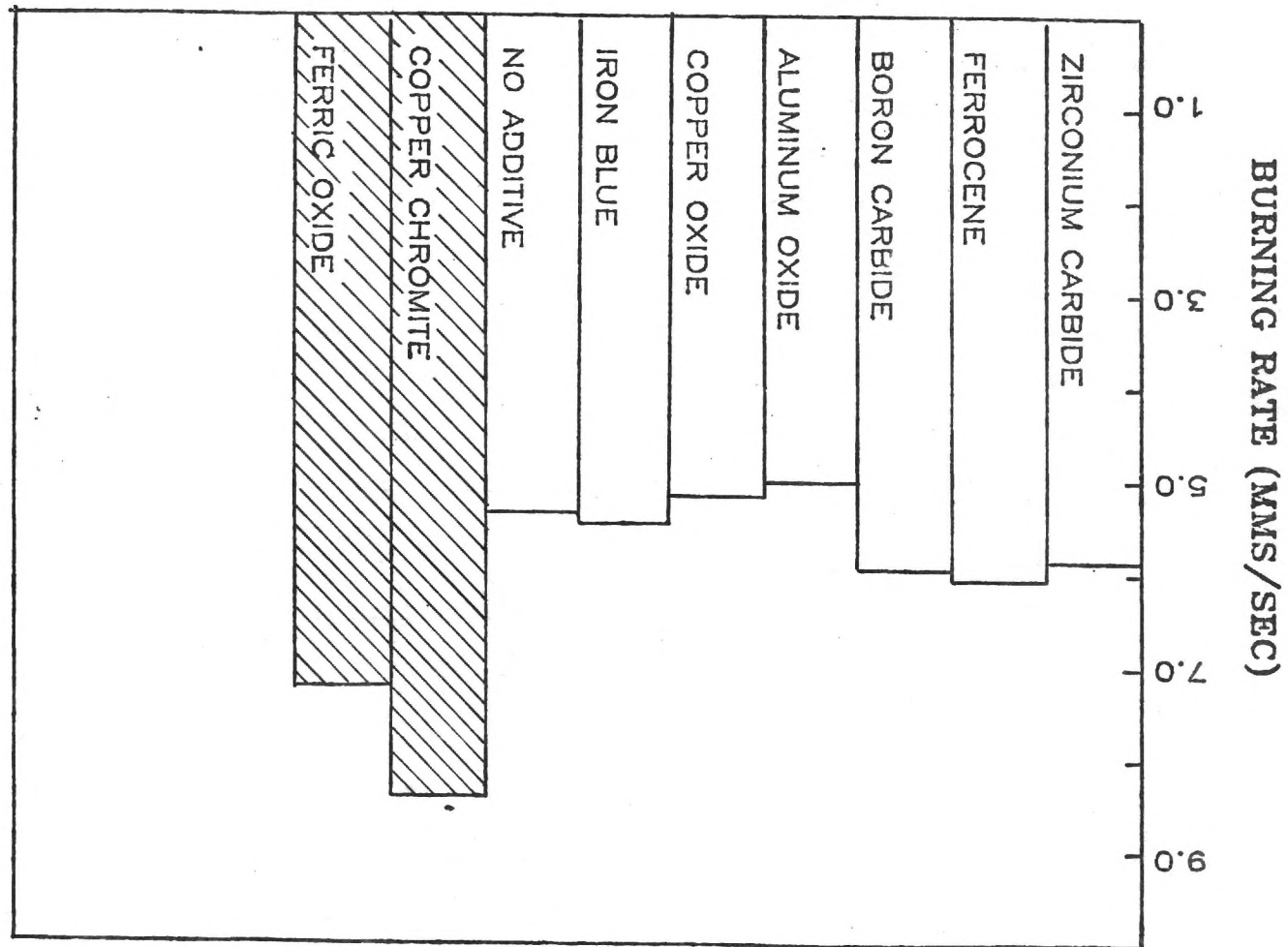


Figure 2. Behavior of various NVIs in sandwich burning. AP-PBAN sandwiches; binder lamina thickness 75  $\mu\text{m}$ ; additive mass fraction in binder 10%; additive particles in 10-20  $\mu$  size range. Height of columns indicates burning rate at 3.45 MPA. Shaded columns correspond to additives that concentrate on the binder surface.

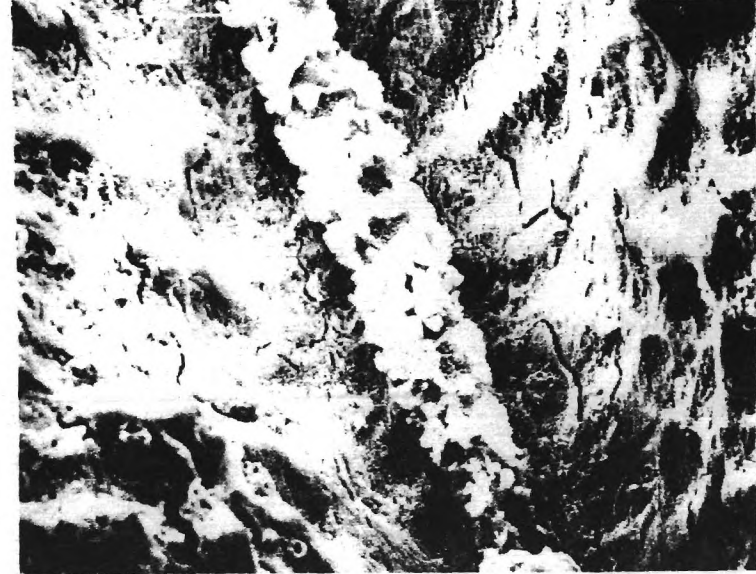


Figure 3. Comparison of quenched sandwich surfaces with nonconcentrating NVI additive and concentrating additive.

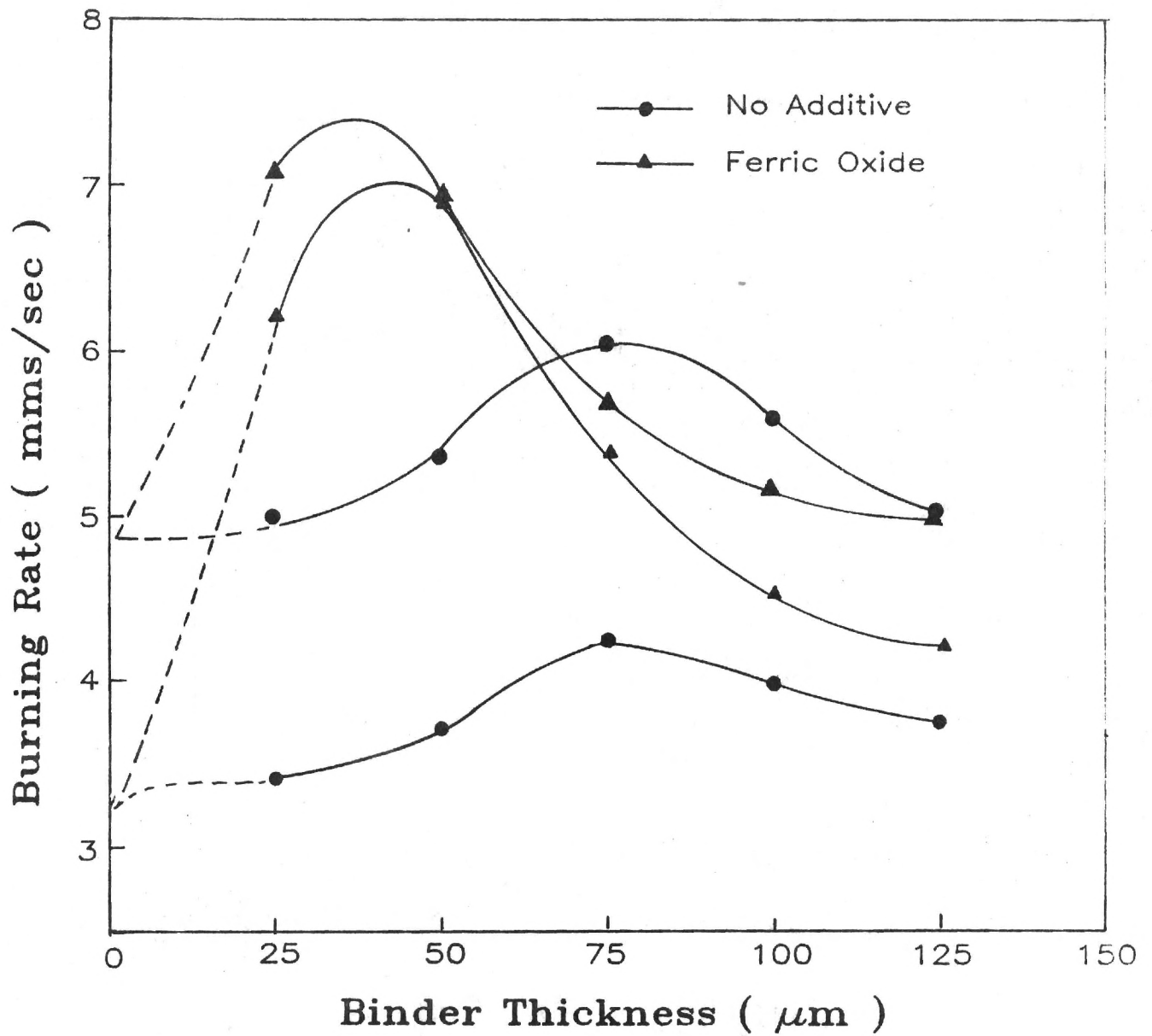


Figure 4. Effect of a concentrating NVI additive ( $\text{Fe}_2\text{O}_3$ ) on the burning rates of AP-PBAN sandwiches (10% additive in the binder lamina).



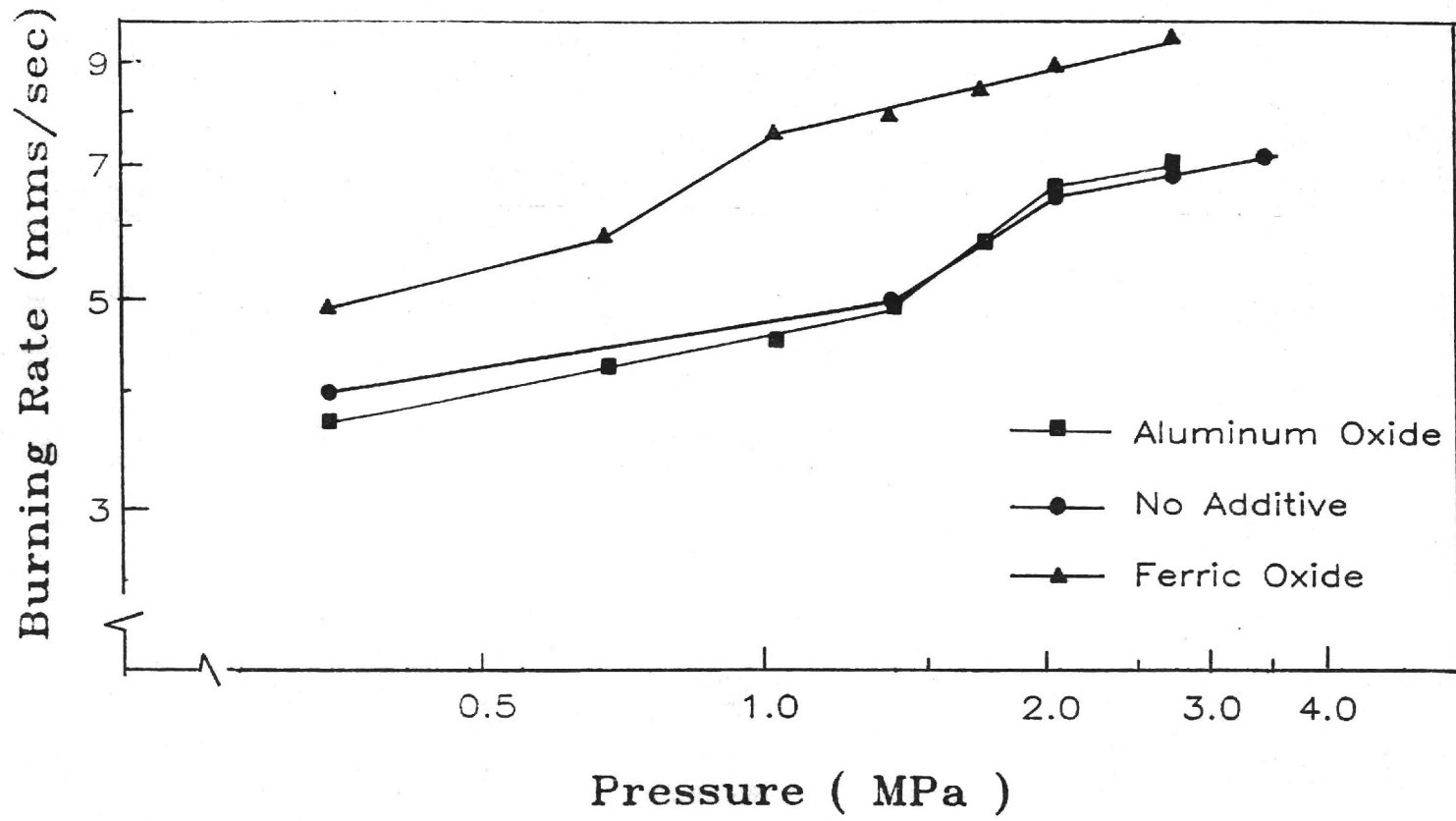


Figure 5. Effects of a concentrating NVI additive ( $Fe_2O_3$ ) on burning rate of an AP/PBAN propellant (p) with 1% additive, 87.5/12.5 ratio of AP to PBAN, and bimodal AP.

conditions. Tests are also being made on binder-catalyst samples in a hot stage microscope and differential scanning calorimeter to clarify the particle sintering process. Screening tests with other binders and other catalysts are planned to determine the validity of present results to other systems.

A further concern is with the surface behavior of aluminized propellants when ballistic modifiers are present. Since the aluminum is normally present with a weight fraction of 5-15 times the ballistic modifier content, it concentrates relatively easily on the surface, but, in this case, the accumulated material is "laced" with ballistic modifier. In the propellant trade it is generally believed that ballistic modifiers such as  $\text{Fe}_2\text{O}_3$  reduce aluminum agglomerate size. However, the modifiers seem to have two competing effects. The modifiers tend to bring the oxidizer-binder flamelets closer to the surface, which would hasten aluminum ignition and reduce concentration (Ref. 2). However, the modifiers are also known to oxidize aluminum (the "thermite" reaction), which enhances the sintering of concentrating aluminum and can cause larger areas of concentrate to coalesce during agglomeration. To test the effect of  $\text{Fe}_2\text{O}_3$  on aluminum behavior, plume quench tests were run on a propellant formulation studied last year (Ref. 3,4), but with  $\text{Fe}_2\text{O}_3$  added. This propellant is tailored to yield singular behavior indicative of transitions in the AP-binder flamelets that control aluminum ignition. The tests yield a measure of mass average agglomerate size, which is shown in Fig. 6 as a function of test pressure. The ordinate in the figure is the ratio of agglomerate size to the size obtained at 1 atm, and the figure compares the results for formulations with and without  $\text{Fe}_2\text{O}_3$ . The agglomerates with  $\text{Fe}_2\text{O}_3$  present were almost three times larger in mass than without  $\text{Fe}_2\text{O}_3$  at 1 atm, and appreciably larger also at other pressures. The singular trend with pressure is still present with  $\text{Fe}_2\text{O}_3$ , an indication of the continued importance of oxidizer-binder flamelets in igniting the aluminum. However, the larger agglomerate size with  $\text{Fe}_2\text{O}_3$  suggests that the concentrates are more extensively sintered at the time of ignition, probably due to the Al- $\text{Fe}_2\text{O}_3$  reaction.

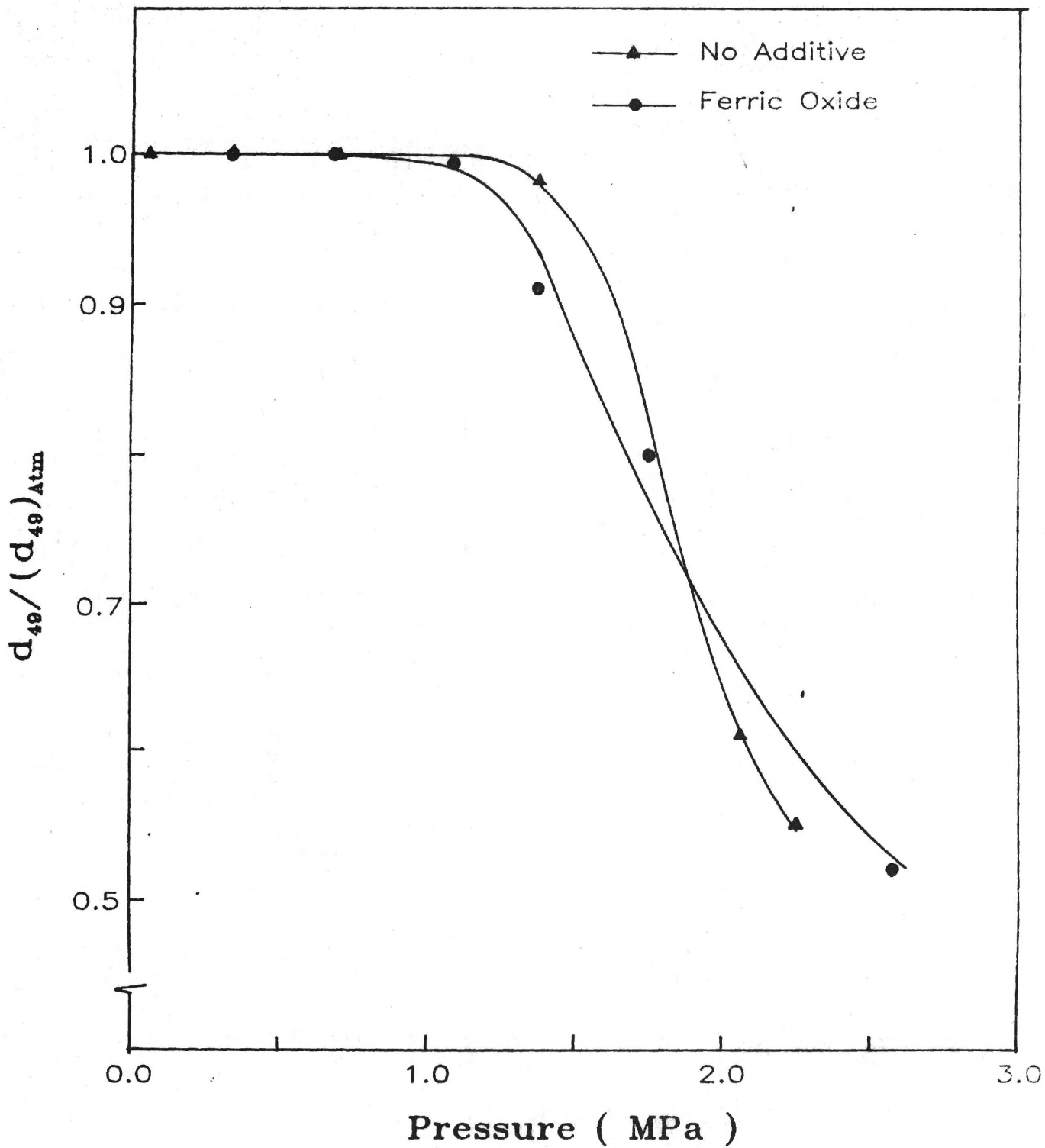


Figure 6. Comparison of agglomerate size distribution for an AP-Al-PBAN propellant with, and without 1%  $Fe_2O_3$ . The ordinate is the mass average size of agglomerates recovered 1.5 cm from the burning surface, divided by the mass average from the test at 1 atm. The average size at this pressure was 180  $\mu m$  for the propellant without  $Fe_2O_3$ , 252  $\mu m$  for the propellant with  $Fe_2O_3$ .

The agglomerate size with the catalyzed propellant also starts to drop off at lower pressure than is the case without  $\text{Fe}_2\text{O}_3$ , probably indicative of the catalytic effect described in the context of the burning rate transition with the unaluminized propellant (Fig. 5). The break to smaller agglomerate size with increasing pressure occurred at a slightly lower pressure, suggesting the effect of the catalyst in bringing high temperature flamelets closer to the surface. This effect was less conspicuous than the corresponding effect of the catalyst on burning rate in the unaluminized version of the propellant (Fig. 5).

In summary, the screening study of behavior of nonvolatile additives at a concentration comparable to 1% in a propellant indicates the following:

- a) Most additives showed minimal concentration on the binder laminae of "sandwiches", while the known burning rate catalysts  $\text{Fe}_2\text{O}_3$  and  $\text{CuCr}_2\text{O}_4$  formed sintered filigrees on the binder surfaces.
- b) Burning rate was catalyzed only by the two additives that concentrated, and available information indicates that such concentration leads to catalytic decomposition of large fuel molecules, greater proximity of O-F flamelets to the surface, with corresponding enhancement of burning rate and suppression of agglomeration.
- c)  $\text{Fe}_2\text{O}_3$  appears to have a second effect on aluminum involving enhanced sintering of accumulating aluminum and enhancement of agglomerate size. For the particular propellant used here, this latter effect of  $\text{Fe}_2\text{O}_3$  on agglomerate size was dominant, a result that is contrary to general results in the propellant trade, but probably due to the bimodal size distribution of the AP used.

The study of effect of  $\text{Fe}_2\text{O}_3$  on aluminum agglomeration indicates that:

- a) The catalyst enhances the opportunity for flamelets to ignite concentrating aluminum.
- b) The catalyst enhances the pre-ignition sintering of concentrating aluminum, leading to coalescence of larger areas when agglomeration occurs.



3. Behavior of ZrC in Solid Propellant Combustion. Zirconium carbide, used as an ingredient in solid propellants, is believed to increase the stability of the rocket motor (Ref. 5), but very little is known about the combustion of ZrC and the mechanism of suppression of combustion instability. Because of its potential, an exploratory study of the combustion of ZrC was performed.

To study the behavior of ZrC at high temperatures, a variety of tests was run using both controlled heating and combustion experiments. These included heating of ZrC particles in a gas burner flame, hot stage microscopy, and propellant combustion experiments. Observations were made during tests (visual observation by combustion photography), and on samples remaining after tests (microscopic and chemical analyses). The different particles tested are reported in Table I.

Heating particles to  $1000^{\circ}\text{C}$  in an inert gas environment such as argon and  $\text{CO}_2$  in a hot stage microscope showed no visible change. In an oxidizing environment, the particles exhibited swelling and deformation in the temperature range of  $680^{\circ} - 800^{\circ}\text{C}$ , accompanied by a change to a white color. The exact temperature at which the deformation occurred depended on whether the particles were heaped up or dispersed. When the particles were heaped, around  $600^{\circ}\text{C}$  the field of view turned dark (due to evolution of gases) and at about  $680^{\circ}\text{C}$  the sample reacted with a flash; the particles spontaneously deformed and turned white. When the particles were dispersed as a thin layer, the deformation and color change occurred gradually around  $780^{\circ}\text{C}$ . There was no flash. The flashing that occurred with densely packed particles may be due to reaction of accumulated CO gas with the  $\text{O}_2$  environment. When studied under the scanning electron microscope, it was found that the heated particles in all cases had changed surface appearance. The particles exhibited a fissured appearance (Fig. 7). This may be due to intercrystal fracture of ZrC particles due to preferential carbon oxidation (Ref. 6).

Combustion photography tests were run on propellants with 3% ZrC, 10% HTPB and 87% 90-125  $\mu\text{m}$  AP in a conventional window bomb at 4.14 MPa in a  $\text{N}_2$

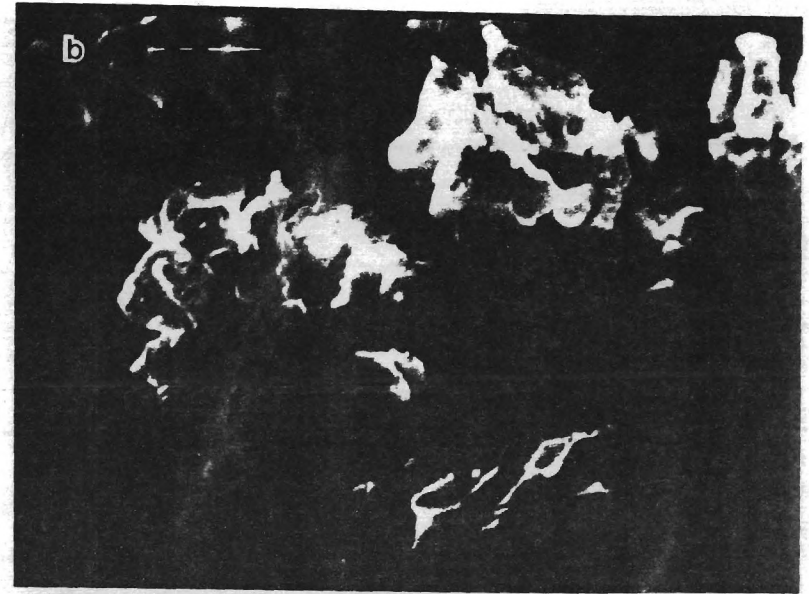
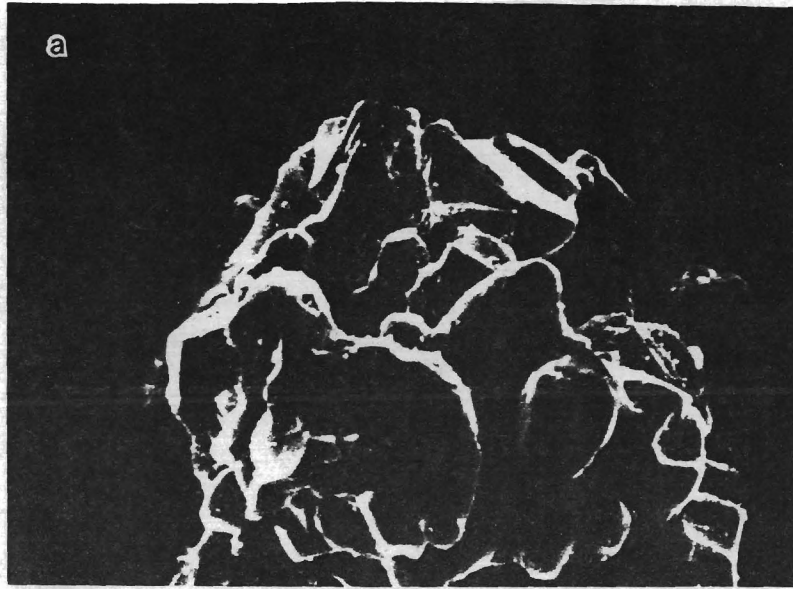


Figure 7. Fissured appearance of ZrC particles that have been heated in an oxygen atmosphere to a transition temperature in the 680-800°C range. a) Typical before heating; b) Post heating.

Table 1  
ZrC Powders Studied in This Investigation

	Source Designation	Particle Size	
		Celloscope	MSA
1	ABL-14	9.4	15.8
2	Hercules 608-C (Wahchang)	21.0	29.0

Table 2  
Conditions for Plume Quench Tests in Propellants with ZrC

Distance (cm)	Pressure		
	Atm.	1.4 MPa	2.8 MPa
1.5	Wahchang	Wahchang Starck	Wahchang
3.0		Wahchang	

environment. 9.4  $\mu\text{m}$  ZrC was tested in these experiments. The region above the propellant surface showed a uniform luminosity with brighter streaks made by reacting ZrC particles. No accumulation or agglomeration of ZrC particles on the burning surface was observed. The particles seemed to ignite close to the burning surface. No fragmentation was observed. Control tests run with aluminum particles did not show the diffuse luminosity (which remains unexplained). The burning aluminum particles were brighter than the ZrC particles.

In order to further determine the surface behavior and possible effects of ZrC, plume quench tests on propellants containing ZrC were performed. The burning particles were quenched in an alcohol bath at a distance of 1.5 cm from the burning surface. Propellant samples were made by dry-pressing a mixture of 10% ZrC, 10% carnauba wax and 80% 90-125  $\mu\text{m}$  AP. Test conditions are reported in Table 2. Part of the collected particles were subjected to heating in concentrated HCl to dissolve the  $\text{ZrO}_2$ . The residues, as well as the unetched particles, were studied in a scanning electron microscope. At atmospheric pressure, all the particles collected had a fissured appearance. Acid treatment did not show significant change in appearance. At a higher pressure of 1.4 MPa, about one half of the particles collected were spherical, or in the process of spheroidizing. Some of the spherical particles were cracked open and the interior of the particles had the fissured appearance common to the surface of samples from the low pressure test. The spherical particles appeared to exhibit a large void space inside (Fig. 8), and the particle interior was not fully integrated with the outer shell. The shell thickness was about 1-2  $\mu\text{m}$ . The results suggest that liquid shells had formed around incompletely burned ZrC particles. The non-spherical particles that were collected had a fissured appearance similar to the low pressure samples. The percentage of spherical particles collected increased with pressure and distance of the quench from the burning surface. There was no significant change in the character of the spherical particles with change in pressure or quench distance. Acid treatment of particles under all test conditions produced no

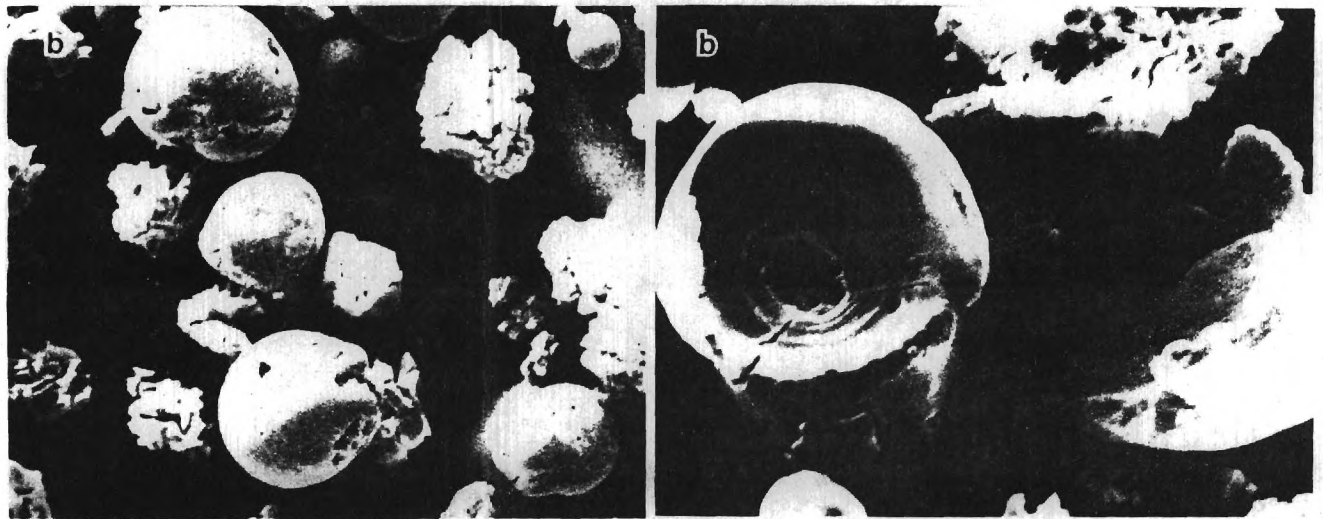


Figure 8. ZrC particles quenched 1.5 cm above the propellant burning surface. a) Fissure of particles, typical of low pressure tests; b) Partially spheroidized particles, typical of tests at 1.4 MPa.



significant changes. The absence of change during acid treatment suggests that the particles may be oxycarbides of Zr, coating or surrounding residual ZrC.

These results indicate that ZrC burns by a complex process involving surface oxidation and formation of fissures. As burning progresses, accumulating liquid product tends to enclose the ZrC, the liquid apparently being an oxycarbide. It is not yet clear what happens later in burning, or whether conversion to oxide is finally achieved. It is clear that particles ignite and leave the propellant surface individually and burn as they move out from the surface. It seems likely that larger particles may experience prolonged burning.

4. Dynamic Response of Combustion to Flow Disturbance. Combustion of low volatility ingredients poses a unique problem in nonsteady combustion, just as in steady burning. Ideally, one would like to be able to describe how the surface accumulation, ignition and agglomeration processes fluctuate in response to flow disturbances, and calculate the resulting fluctuations in the rest of the combustion zone (including fluctuations in combustion in the aluminum droplet cloud) (Ref. 7). However, the present methods for analytical description of combustion response are much too simplistic to accommodate such behavior. In considering this problem it became evident that the conventional representation of acoustic output of the combustion zone as an acoustic admittance is simply not suitable to describe the essential physics. The essence of the problem is (Ref. 8) to describe the collective acoustic output from a microscopically complex combustion region, which is perturbed by fluid dynamic oscillations of rather uncertain nature. The classical approach in theory is to assume a one-dimensional interaction with a thin one-dimensional combustion zone. For simplicity of analysis of combustor stability, the acoustic cavity is assumed to be bounded (in the region of the propellant) by a mathematical surface close to the burning surface, and the combustion is assumed to be confined to an acoustically thin region between the propellant and the

mathematical boundary of the acoustic cavity. In the stability analysis, the contribution of the combustion to gas oscillations is represented by an acoustic admittance at the mathematical surface between the acoustic cavity and the thin combustion region, and determination of the admittance is viewed as an independent problem, essentially as a property of the propellant. This view of the combustion response is sometimes reasonably realistic, if the flow oscillations are perpendicular to the combustion layer, there is no mean flow parallel to the admittance surface, the mass flow leaving the burning surface is not accelerating or decelerating, and the combustion zone is really thin. In a rocket motor, these conditions are rarely satisfied, and it seems important to examine the extent of the error involved. A variety of efforts has been made to explore this question and/or improve the relevance of analytical models, using more complete descriptions of the gas flow field and/or the wave propagation into the combustion layer. In reviewing this problem, it was noted that there is a basic inconsistency in retention of acoustic qualities in the usual application of the admittance concept to the acoustic cavity-combustion layer interface in the presence of an arbitrary local mean flow. This problem has been resolved by modelers of acoustic behavior in ducts. In the present work, this more realistic representation from duct acoustics was adapted to the problem of axial mode oscillations in rocket motors (Ref. 9). The results of the analysis show that while the propellant admittance is still considered a property of the propellant, the more rigorous mass flux matching procedure produces a boundary condition for the normal mass flux oscillations which is dependent on the local mean flow parallel to the admittance surface and the acceleration or deceleration of the mean flow as it turns toward the axis. Thus, the local response involves the propellant admittance and local mean flow properties. Since the boundary is assumed to transmit only normal stresses (generally viewed as p-v work by the boundary on the gas in the acoustic cavity) the combustion zone influence should be viewed as a pressure coupled response. However, this rigorous matching indicates that the local response depends

on the local acoustic pressure and acoustic pressure gradient. Since linear stability analyses view the acoustic pressure gradient and acoustic velocity as interchangeable, the rigorous matching procedure appears to introduce a velocity coupling term. This is not the case and data reduction schemes which attempt to extract pressure and velocity coupling response functions from experimental measurements are not obtaining the true response to local pressure fluctuations (normal boundary stresses) and to axial velocity oscillations (tangential boundary stresses).

5. Study of NVIs in a Wider Range of Propellants. Most of the studies on this project have been made with PBAN binder and AP as the primary reactants, with aluminum as the NVI. Because of its wide use in other propellant systems, it is known that aluminum behavior depends on the primary propellant ingredients (e.g., NC, NG, HMX, etc.). From the present studies it is evident why this is so, but a sound basis for prediction is not yet possible. It has been proposed that a screening study of behavior of aluminum in modern propellant systems be made, using combustion photography and quench tests. Efforts to obtain small amounts of such propellants have been unsuccessful, primarily because of restraints on shipping. While efforts are continuing, attention has changed to more achievable strategies. Small amounts of azido polymer and flouorocarbon binder ingredients have been obtained that are expected to exhibit singular behavior of aluminum. For safety and economy reasons, preliminary tests will be run on sandwiches with AP and aluminum-filled binders. Small propellant samples will be prepared and tested as needed to validate conclusions from sandwich burning tests. Efforts will be continued to obtain other aluminum propellants.

## References

1. Price, E. W., "Behavior of Aluminum in Solid Propellant Combustion," presented at AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, California, March 1984.
2. Price, E. W., J. K. Sambamurthi, R. K. Sigman and T. S. Sheshadri, "Conditions for Inflammation of Accumulated Aluminum in the Propellant Combustion Zone," CPIA Publication No. 383, Vol. I, October 1983.
3. Price, E. W., J. K. Sambamurthi, C. J. Park and R. K. Sigman, "Aluminum Agglomeration and Ignition in Propellants with Bimodal AP Size Distribution," CPIA Publication No. 366, Vol. I, October 1982.
4. Sambamurthi, J. K., E. W. Price and R. K. Sigman, "Aluminum Agglomeration in Solid Propellant Combustion," accepted for publication, AIAA Journal, in press.
5. Cohen, Joseph and Gilbert Zimmerman, "Smokeless Propellants with Stable Combustion," Chemical Abstracts, 12976, 1977.
6. Berkowitz-Mattuck, Joan B., "High Temperature Oxidation of ZrC and HfC," Journal of Electrochemical Society, Vol. 114, No. 10 (1967), pp. 1030-1032.
7. Price, E. W., "Relevance of Analytical Models for Perturbation Combustion of Solid Propellants," AIAA Journal, Vol. 7, No. 1 (January 1969), pp. 153-154.
8. Price, E. W., "Velocity Coupling in Oscillatory Combustion of Solid Propellants," AIAA Journal, Vol. 17, No. 7 (July 1979), pp. 799-800.
9. Sigman, R. K., "Boundary Condition for Rocket Motor Stability," submitted to AIAA Journal (April 1984).

C. Publications

1. Sambamurthi, J. K., E. W. Price and R. K. Sigman, "Aluminum Agglomeration in Solid Propellant Combustion," accepted for publication, AIAA Journal, in press.
2. Price, E. W., J. K. Sambamurthi, R. K. Sigman and T. S. Sheshadri, "Conditions for Inflammation of Accumulated Aluminum in the Propellant Combustion Zone," CPIA Publication No. 383, Vol. I, October 1983.
3. Price, E. W., "Combustion of Metalized Propellants," chapter in AIAA Progress Series Book "Combustion of Solid Propellants," to be published in August 1984.
4. Price, E. W., "Experimental Observations of Combustion Instability," chapter in AIAA Progress Series Book "Combustion of Solid Propellants," to be published in August 1984.
5. Sigman, R. K., "Boundary Condition for Rocket Motor Stability," submitted to AIAA Journal (April 1984).

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