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CHARACTERIZATION OF OPEN-CYCLE COAL-FIRED MHD
GENERATORS

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14th/15th Quarterly Technical Progress Report for the Period
February 1—July 31, 1980

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September 1980

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U. S. DEPARTMENT OF ENERGY

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14TH/15TH QUARTERLY TECHNICAL
PROGRESS REPORT

ON

CHARACTERIZATION OF OPEN-CYCLE
COAL-FIRED MHD GENERATORS

by

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ABSTRACT

The successful design of full-scale, open-cycle, coal-fired MHD generators for baseload electrical production requires a detailed understanding of the plasma chemical and plasma dynamic characteristics of anticipated combustor and channel fluids.

This report documents progress in efforts to model the efficiency of an open-cycle, coal-fired MHD channel based on the characterization of the channel flow as well as laboratory experiments to validate the modeling effort. In addition, studies related to understanding arcing phenomena in the vicinity of an anode are reported.

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1. INTRODUCTION

The contract modification to Aerodyne Research, Inc. for further study on the Characterization of Open-Cycle, Coal-Fired MHD Generators has three general goals. The first two goals are extensions of the work performed during the initial phase of the contract; they involve modeling plasma chemical effects on the core flow conductivity and efficiency of seed recovery and verifying the results of the computer model by first measuring coal plasma compositions in a laboratory burner, and then designing a full-scale, mass spectrometric probe to characterize the plasma flow from demonstration scale MHD combustors and generators. In order to fully characterize the laboratory burner, a CO line absorption temperature measurement device has been designed, constructed, and utilized to measure the radial temperature profile of the burner. In addition, a conductivity probe has been designed to measure the conductivity in the coal burner. The third goal of this work is to obtain a detailed understanding of the plasma and electro-chemical effects responsible for MHD electrode degradations. This understanding is to be quantified by computer modeling of the events at the electrode surface and in the electrode/plasma boundary layer under both diffuse and arcing discharge conditions.

In Section 3 of this report, parametric calculations using the PACKAGE code are presented. The changes in predicted performance caused by uncertainties in coal composition, negative ion thermochemistry, gas phase and condensed phase thermochemical properties, and electron momentum transfer cross sections are presented and discussed using PACKAGE calculations for a baseline generator design. In addition to the above parameters, studies of MHD generator performance with oxygen-enriched coal combustion are considered.

In Section 4, model validation measurements are presented. Modifications to the mass spectrometer vacuum system, which have resulted in an increased sensitivity, are discussed. Preliminary measurements of the concentration of the neutral potassium species KOH, KPO_2 and KPO_3 are reported.

In Section 5, the one-dimensional arc model designed by ARI was used to study the structure of the discharge at the vicinity of the anode and to estimate the electron-induced corrosion rate. This work is currently being extended to model an unsteady, two-dimensional arc discharge.

As part of model validation, a CO line absorption measurement technique was developed to accurately measure the temperature in Aerodyne's laboratory coal burner. In Section 6, the results of temperature profile measurements using CO line absorption at different vibrational levels are reported. In addition to accurate temperature measurements, PACKAGE code calculations indicate that plasma conductivity measurements in the burner are needed to assess the importance of phosphorus species on channel efficiency. Section 7 describes a conductivity probe design suited for use in ARI's coal burner.

2. TECHNICAL PROGRESS SUMMARY

A summary of progress achieved during the period February 1980 to August 1980 is presented in this section.

Task I - Modeling of Core Flow Plasma Chemical Effects on Conductivity and Seed Recovery

As part of the contract modification to Aerodyne Research, Inc., the PACKAGE code has been modified to include an ideal solution model, and a radiative heat loss model. A diffusion-controlled heterogeneous condensation model appropriate for inclusion into the PACKAGE code was also formulated. The PACKAGE code has been successfully used to perform parametric calculations to predict the effect of parameters such as coal composition, negative ion thermochemistry, gas phase and condensed phase thermochemical parameters, electron momentum transfer cross sections, and oxygen enrichment on generator efficiency. These studies resulted in papers presented at the 7th International Conference on MHD Electrical Power Generation and the AIAA 13th Fluid and Plasma Dynamics Conference. Reprints of these papers are included in this report. Other than documenting the diffusion-controlled heterogeneous condensation model, the work outlined in Task I has been completed.

Task II - Model Validation Measurements and Design of a Field Scale Mass Spectrometric Diagnostic

The mass spectrometer sampling device has been constructed and modified as described by designs in previous quarterly reports. These modifications have resulted in a better vacuum and improved sensitivity. Along with the sampling probe described in the 12th Quarterly Report, design of these individual components constitute the overall design of the Field Scale Mass Spectrometric Diagnostic. The in-house prototype mass spectrometer has been

successfully used on the ARI coal burner to identify the PO_2^- and PO_3^- negative ions. Studies during this reporting period have also identified the KOH, KPO_2 and KPO_3 neutrals. These studies constitute the completion of Task II under the current modification.

Task III - Electrode Boundary Layer Arc Modeling

The one-dimensional arc model has been successfully used to study the structure of the discharge in the vicinity of the anode and to estimate the electron-induced corrosion rate. The results of this study were presented at the 7th International Conference on MHD Electrical Power Generation and a reprint of this paper is presented in this report. Continued work on an unsteady, two-dimensional arc model is reported in this quarterly. It was originally thought that a 3-D arc funnel model would have to supplement a one-dimensional near electrode model in order to account for measured corrosion rates of anodes. From recent evaluations, however, it seems advisable to limit the simulation to a two-dimensional arc. The main effect lost by this simplification is the additional mixing, drag and cooling occurring through the third dimension of the funnel. These effects are discussed in this report. The development of an adequate arc model continues.

Task IV - Conductivity Probe Design

A design for a conductivity probe capable of making plasma conductivity measurements in the Aerodyne laboratory burner is presented in this report. This constitutes completion of Task IV under the current contract.

Task V - Temperature Measurements Using the CO Absorption Technique

Under the current contract, ARI has designed, constructed, calibrated and utilized the CO absorption temperature measurement device to measure the radial temperature profile in ARI's laboratory methane/coal burner. This work was presented at the AIAA Fluid and Plasma Dynamics Conference. A reprint of this paper is included in this report. The successful measurement of the burner temperature profiles completes the work on Task V.

3. COAL MODEL IMPROVEMENTS AND UTILIZATION

One of the main objectives of ARI's modeling effort during the course of this investigation has been the development of a computational technique to model the efficiency of open-cycle, coal-fired MHD channels based on the characterization of the channel core flow. To a large extent, the efficiency of MHD generators depends on plasma conductivity levels which can be affected by a variety of fluid parameters. In this analysis, the thermochemistry of the conducting multiphase fluid is modeled in detail so that the dependence of the predicted conductivity levels on parameters such as negative ions can be evaluated. This type of analysis can be used to both predict the channel efficiency in terms of variables like staged combustors, coal type, O/F ratio, and oxygen enrichment, and predict the sensitivity of the calculated efficiency with respect to uncertainties in such parameters as species thermodynamic data and electron-collision cross sections.

The formulation and analysis of the thermochemical model developed has been reported in detail in our previous quarterly reports. Essentials of the model include an ideal liquid solution, partial equilibrium/partial rate-controlled chemistry, and diffusion-controlled heterogeneous condensation model. The core flow is considered one-dimensional and steady with either the fluid velocity, pressure, or channel area specified along the channel axis. A radiative channel heat loss model is also included. Single or two-stage combustors are also considered with any fraction of the reactants added in the first or second stage and any fraction of the condensed species rejected from the first stage.

The PACKAGE (Plasma Analysis, Chemical Kinetics, And Generator Efficiency) code⁽¹⁾ has been developed to predict the generator performance under the options listed above. The current version of the PACKAGE code does not include the diffusion-controlled heterogeneous condensation and radiative heat loss models. These models have been programmed but have not been validated.

The code users manual which includes the detailed analysis and programming information has been submitted to the Technical Information Center for publication and distribution.

The PACKAGE code has been used here to study the MHD channel performance. The results were presented at the 7th International Conference on MHD Electrical Power Generation and the AIAA 13th Fluid and Plasma Dynamics Conference. Reprints of these papers follow.

A REVIEW OF PLASMA CHEMICAL CONSIDERATIONS IN MHD GENERATOR DESIGN

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Summary

Design calculations for MHD generators make assumptions about a number of properties of the seeded coal plasma. Among these input parameters are properties of the coal, such as heating value, moisture content, ash fraction, and ash chemical composition. In addition, other areas which must be considered include negative ion thermochemistry, gas-phase and condensed phase oxide and hydroxide thermochemical properties as they affect both negative ion populations and partitioning between potassium atoms and other potassium species, and electron momentum transfer cross sections used in calculating plasma conductivity. All these inputs used in a generator model have uncertainties, some of them having quite significant effects on the predicted plasma conductivity and therefore on the generator performance. The Aerodyne PACKAGE (Plasma Analysis, Chemical Kinetics, And Generator Efficiency) computer code is a method of including all the above effects in a calculation of channel length required to attain a desired enthalpy extraction. The changes in predicted performance caused by the uncertainties in the above input parameters are presented and discussed, using PACKAGE calculations for a baseline generator design. Changes in sensitivity to input uncertainties due to scaling, (changing combustor pressure or heat loss, for example) or to other design changes such as different degrees of oxygen enrichment or subsonic versus supersonic operation, are also discussed.

Introduction

Design activities for large scale test facility and prototype commercial open cycle, coal fired MHD generators are now underway. Proper scaling from laboratory and small demonstration facilities requires a detailed understanding of the processes affecting combustion plasma conductivity and enthalpy extraction efficiency under a variety of potential operating conditions.

The efficiency of open cycle MHD generator systems depends directly on the core flow plasma conductivity in the generator channel. This core flow conductivity is primarily determined by the temperature, pressure, and alkali (potassium) seed level output by the combustor, with generator inlet temperature being the single most important parameter governing the level of alkali seed ionization and therefore, free electron production. However, other parameters, such as the molecular composition of the plasma and the combustor/generator pressure profile can also play a significant role in setting core plasma conductivity levels and concomitant limits on generator efficiency.

Description of Calculations

Currently, MHD combustor and generator plasma properties and their influence on generator efficiency can be modeled by utilizing computer codes which calculate plasma constituents, the resulting plasma electrical conductivity, and the theoretical limit on MHD enthalpy

extraction in a comprehensive series of algorithms based on fundamental thermochemical, electron scattering and plasma dynamic properties. The calculations presented in this paper were performed with Aerodyne's PACKAGE (Plasma Analysis, Chemical Kinetics, And Generator Efficiency) code which has been developed with particular attention to the influence that nonfuel coal components, such as inorganic oxides arising from ash oxidation and vaporization, may have on coal combustion plasma composition and conductivity. The PACKAGE code employs a one-dimensional steady channel flow model, with a specified constant velocity condition used in these calculations. A prespecified channel area profile or pressure profile can be used in place of the specified velocity criterion if desired. The code also models the full MHD interaction with a variable Hall parameter. The plasma composition and conductivity are recalculated at each channel grid point. The chemical model used in this work is a full equilibrium model including an ideal solution model for liquid slag components. The code can also perform plasma composition calculations using partial equilibrium-partial finite rate or fully finite rate chemical models as required. The combustor in these calculations is modeled as a two-stage system, with both stages at the same equivalence ratio. The coal and oxidizer are allowed to reach the adiabatic flame temperature in the first stage and the resulting combustion gases are conveyed into the second stage after rejection of 85% of the condensed slag species. The K_2CO_3 seed is then added to the second combustor stage and the equilibrium combustion products are recalculated assuming a 3% combustor heat loss. The PACKAGE code includes not only combustor heat losses, but also arbitrary force and heat loss or addition terms in the channel flow energy and momentum equations. A combustor and channel radiant heat loss model is currently being added to the code. An extensive description of the PACKAGE code's capabilities and operation can be found in Reference 1.

Calculations of coal combustion plasma properties require an enormous range of basic input data including coal composition and heating value, thermochemical (and possibly kinetic) parameters of both charged and neutral coal/alkali seed combustion products, and electron-molecule scattering cross sections for major plasma components. Imprecisions or inaccuracies in currently available input data can lead to significant uncertainties in design performance. The purpose of this paper is to review the major plasma chemical effects on coal/seed combustion plasma conductivity, and to quantify the uncertainty in theoretical generator efficiency arising from the current levels of uncertainties in basic coal and combustion product properties.

Representative calculations have been performed for a Montana Rosebud fueled, potassium carbonate seeded, combustor/generator system over a range of operational parameters, including the degree of oxygen enrichment in the oxidizer flow, initial combustor pressure, and channel Mach number. Table 1 lists the nominal combustor and generator properties which define

TABLE 1

Baseline Combustor/Generator Properties

Coal:	Montana Rosebud Subbituminous
Oxidizer:	Air with 20% by volume O ₂ enrichment, (N ₂ 0.618 mass fraction, O ₂ 0.371 mass fraction), preheated to 866°K
Seed:	Dry K ₂ CO ₃ , 1% by weight of total flow
Combustor Stoichiometric Ratio (O/F)	0.92
Combustor Pressure:	4.5 atm.
First Stage Combustor Temperature:	2838°K
Slag Rejection Fraction (at first stage)	0.85
Second Stage Combustor Temperature (after seed addition)	2807°K
Channel Inlet Pressure	3.15 atm.
Channel Inlet Temperature	2715°K
Channel Inlet Mach Number	0.80
Magnetic Field Strength	6 Tesla initially, limited by 2100 V/m axial field
Load Factor	0.80
Channel Length	10m

the baseline system for the results and comparisons presented below. The 10m channel length is set by the requirement that the generator exit pressure exceed 0.7 atm.

Input data uncertainties were investigated for a variety of both coal and combustion product molecular properties. The properties considered are listed in Table 2 along with the range of uncertainties supported by data currently available.

TABLE 2

Input Parameters and Ranges of Variation

Description of Parameter Variation	Parameter Variation Code
<u>Coal Model Parameters</u>	
Coal heating value down by 6.5 kcal/mole	DH1
Coal heating value up by 6.5 kcal/mole	DH2
Coal heating value down by 25 kcal/mole	DH3
Coal heating value up by 25 kcal/mole	DH4
Coal water content from 5 to 2%	WA1
Coal water content from 5 to 10%	WA2
Ash fraction from 13.3 to 15.7%	AF1
Ash fraction from 13.3 to 10.9%	AF2
P ₂ O ₅ fraction of ash from 0.35 to 0.47%	POH
P ₂ O ₅ fraction of ash from 0.35 to 0.23%	POL
Fe ₂ O ₃ fraction of ash from 8.1 to 10.3%	FOH
Fe ₂ O ₃ fraction of ash from 8.1 to 5.9%	FOL
<u>Negative Ion Thermochemistry</u>	
PO ₂ ⁻ ΔH _f from -146 to -153 kcal/mole	P2P
PO ₂ ⁻ ΔH _f from -146 to -139 kcal/mole	P2M
PO ₃ ⁻ ΔH _f from -175 to -186.5 kcal/mole	P3P
PO ₃ ⁻ ΔH _f from -175 to -163.5 kcal/mole	P3M

Description of Parameter Variation	Parameter Variation Code
<u>Negative Ion Thermochemistry (Cont.)</u>	
FeO ₂ ⁻ ΔH _f from -50 to -62.5 kcal/mole	F2P
FeO ₂ ⁻ ΔH _f from -50 to -58.1 kcal/mole	F2M
AlO ₂ ⁻ ΔH _f from -140.9 to -147.9 kcal/mole	A2H
<u>Gas Phase Neutral Thermochemistry</u>	
KOH ΔH _f from 55.6 to 52.6 kcal/mole	KHP
KOH ΔH _f from 55.6 to 58.6 kcal/mole	KHM
PO ₂ ΔH _f from -62.44 to -67.24 kcal/mole	POP
PO ₂ ΔH _f from -62.44 to -57.64 kcal/mole	POM
FeOH ΔH _f from 16.5 to 11.7 kcal/mole	FHP
FeOH ΔH _f from 16.5 to 21.3 kcal/mole	FHM
FeO ΔH _f from -60 to -65 kcal/mole	FOP
FeO ΔH _f from -60 to -55 kcal/mole	FOM
<u>Electron Scattering Cross Sections</u>	
H ₂ O σ _e increased by 25%	SHP
H ₂ O σ _e decreased by 25%	SHM
KOH σ _e increased by 25%	SKP
KOH σ _e decreased by 25%	SKM
N ₂ σ _e increased by 10%	SNP
N ₂ σ _e decreased by 10%	SNM
CO ₂ σ _e increased by 10%	SCP
CO ₂ σ _e decreased by 10%	SCM
<u>Condensed Phase Modeling</u>	
Only Pure JANAF Condensed Phases	JAN
From Pure JANAF Case with AlO ₂ ⁻ ΔH _f from -140.9 to -147.9 kcal/mole	A2P
From Pure JANAF Case with AlO ₂ ⁻ ΔH _f from -140.0 to -133.9 kcal/mole	A2M

TABLE 2 (Cont.)

Input Parameters and Ranges of Variation

Description of Parameter Variation	Parameter Variation Code
<u>Condensed Phase Modeling (Cont.)</u>	
From Pure JANAF Case with $\text{Al}(\text{OH})_2 \Delta H_f$ from -22.7 to -15.5 kcal/mole	ARM
From Pure JANAF Case with Alumina Fraction in Ash from 0.22 to 0.24	AOH
From Pure JANAF Case with Alumina Fraction in Ash from 0.22 to 0.20	AOL
<u>Plasma Chemical Conductivity Effects</u>	

Three generic types of plasma chemical conductivity effects were addressed in this study. These are: 1) parameters which reduce the adiabatic combustion temperature of the coal/oxidizer/seed mixture; thus reducing the level of thermal ionization and electron production; 2) molecular parameters for combustion species which reduce the level of free electrons at a given plasma temperature; and 3) molecular parameters which influence the collision frequency of free electrons in the combustion plasma.

Type 1 - Thermal Effects on Conductivity

Coal properties which result in thermal penalties leading to conductivity reductions of the first type include: coal heating value, coal moisture content, and coal ash fraction. Uncertainties in coal and ash analyses arise from both inconsistencies in analytical techniques and from the inherent variability in coal samples. A compilation was made of published coal and ash analyses for Montana Rosebud Coal. The baseline model for this study was that developed by MHD office personnel and recommended for CDIF and ETF design studies.⁴

The most dramatic type one effect on combustion plasma conductivity are due to uncertainties in the heating value. There are two general types of uncertainty present. The first is due to reported variations in calorimetric oxidation measurements of Montana Rosebud heating value. We calculate the root mean square deviation of the compiled literature values to be ± 450 BTU/lb or ± 25 kcal/mole. A second level of uncertainty arises in the interpretation of bomb calorimeter results, due to a lack of knowledge of thermal reaction products. This uncertainty has been analyzed by Spencer and co-workers using a linear programming technique.² They calculated an uncertainty of ± 6.5 kcal/mole for Illinois No. 6, a value we have adopted as representative for other coals.

Table 3 illustrates the results of PACKAGE calculations of plasma properties at the channel entrance for the nominal case represented by conditions listed in Table 1 and the coal model from Reference 4. Table 3 also shows the fractional change in channel entrance plasma parameters and the enthalpy extraction for the first 10 meters of channel for each coal property variation. As shown in Table 3, the ± 6.5 kcal/mole uncertainty inherent in the bomb calorimetric technique for measuring coal heating value leads to a $\pm 0.4\%$ (11°K) uncertainty in temperature and a $\pm 6\%$ (0.45 mho/m) uncertainty in conductivity at the channel entrance. Its effect on enthalpy extraction for a 10m channel is a $\pm 5\%$ variation of the 20.9% calculated for the baseline case. The ± 25 kcal/mole

uncertainty calculated as the rms variation of heating values obtained in various literature analyses leads to a more dramatic $\pm 25\%$ or $\pm 22\%$ variation in initial conductivity and a $\pm 18\%$ or $\pm 19\%$ variation in enthalpy extraction for a 10m channel. By comparison, changing assumed combustion heat loss from 3% to 5% gives rise to an 11% decrease in enthalpy extraction at 10m. The fractional enthalpy extractions as a function of channel length for the smaller heating value variations are plotted in Fig. 1.

A second major type one effect is variation in the moisture content of the coal. The nominal case assumes a moisture content of 5%, which is the level recommended for calculation with the CDIF Rosebud model. Table 3 also shows the effect of coal drying to a 2% level, which results in a 0.5% increase in inlet temperature (14°K) with an 11% (0.8 mho/m) increase in conductivity. The increase in conductivity is due to both an increase in temperature resulting in a 10% increase in thermal electrons, and a decrease in the H_2O content on the plasma which is reflected in the 2% decrease in the plasma frequency also noted in Table 3. The net result is a 6% fractional increase in enthalpy extraction for a 10m channel. Table 3 also shows the result of doubling the moisture content to 10%. This results in an 0.8% drop in inlet temperature, a 14% loss in free electrons and a 17% decrease in conductivity at the channel entrance. For an 10m channel, there is a 10% drop (from 20.9% to 18.8%) in enthalpy extraction. The fractional enthalpy extractions as a function of generator length for these losses are also shown in Fig. 1.

A third uncertainty in coal properties which directly effect the thermal properties of the plasma is the ash fraction. The nominal case uses the CDIF recommended value of 13.3%. The compiled data suggest a rms variation of 2.4%. As shown in Table 3, variation of the ash fraction up to 15.7% and down to 10.9% results in a -0.2 and $+0.3\%$ variation in inlet temperature and a $\pm 11\%$ variation in inlet conductivity. This leads to a -7% or $+6\%$ variation in fractional enthalpy extraction. Fractional enthalpy extractions versus channel length for these cases are also plotted in Fig. 1. The changes in conductivity reflect both type one and type two effects-both the direct temperature influence on conductivity and enthalpy extraction and the increased role of ash derived negative ions at the higher ash loadings.

Type 2 - Free Electron Reductions Due to Combustion Product Properties

The products of the coal/oxidizer/seed combustion can influence the level of free electrons of a given plasma temperature by two distinct mechanisms. The first mechanism involves the level of plasma species which can attack electrons to form stable negative ions. The existence of such ions increases the total ionization level of the plasma, but not by a sufficient amount to prevent a loss of free electrons. Since free electrons are much more mobile than negative ions, there is a net decrease in plasma conductivity. Furthermore, the resulting increase in both positive and negative ions leads to a higher plasma scattering frequency, due to coulombic ion/electron interactions. This results in a further degradation in conductivity. Mass spectrometric measurements on Montana Rosebud combustion plasmas performed in our laboratory³ along with literature reviews performed by Aerodyne personnel and other MHD modelers⁴ have identified PO_2^- , PO_3^- , AlO_2^- , FeO_2^- , and OH^- as the major negative ion species which may significantly degrade coal combustion plasma conductivities. Of these ions, all but OH^- arise from inorganic ash components. The importance of a given ion is dependent on both the fraction of its elemental components in the

TABLE 3
Effect of Uncertainty in Coal Model Parameters

	ΔH at 10m	T, °K	P, atm	σ , mho/m	f, sec ⁻¹	[K ⁺]	[PO ₂]	[FeO ₂ ⁻]	[e]
Baseline Case	0,298	2715	3.15	7.56	7.81(11)	4.93(-5)	1.33(-5)	4.08(-6)	2.45(-5)
Code	Fractional Change from Baseline Case								
DH1	-0.05	-0.004	-	-0.06	+0.003	-0.03	-	-	-0.06
DH2	+0.05	+0.004	-	+0.06	-0.004	+0.03	-0.01	-	+0.06
DH3	-0.19	-0.015	-	-0.22	+0.02	-0.12	+0.02	-0.06	-0.22
DH4	+0.18	+0.095	-	+0.25	-0.01	+0.12	-0.03	+0.01	+0.26
WA1	+0.06	+0.005	-	+0.11	-0.02	+0.05	+0.01	+0.02	+0.10
WA2	-0.10	-0.008	-	-0.17	+0.04	-0.08	-0.02	-0.07	-0.14
AF1	-0.07	-0.003	-	-0.11	-	+0.02	+0.14	+0.19	-0.11
AF2	+0.06	+0.002	-	+0.11	-	-0.02	-0.16	-0.25	+0.11
POH	-0.07	-	-	-0.07	+0.01	+0.07	+0.40	-0.07	-0.06
POL	+0.08	-	-	+0.08	-0.01	-0.07	-0.32	+0.05	+0.08
FOH	-0.004	-	-	-0.01	+0.001	+0.01	-	+0.21	-0.01
FOL	+0.005	-	-	+0.01	-0.001	-0.01	-	-0.24	+0.01

Fig. 1. Baseline Enthalpy Extraction and RMS Bounds (solid lines) for Variations in Coal Model Parameters, with the Space Between Dashed Lines Indicating Contributions from Individual Parameter Variations. Parameter Variation Codes Are Given in Table 2

mixture and the thermochemical molecular parameters of of the species in question (the heat of formation, which includes the molecular electron affinity of the neutral precursor and the heat of vaporization of refractory oxides in the case of AlO_2^- and FeO_2^-). For easily vaporized species such as phosphorus oxides the phosphorus content of the ash can be the limiting factor, while for refractory ions such as FeO_2^- or AlO_2^- , the vapor pressure of neutral gaseous precursors at combustor and channel pressures is often the controlling parameter.

The molecular parameters for the "clean fuel ion", OH^- , are quite well known. Unfortunately, the molecular parameters for the ash derived ions are currently quite uncertain. The uncertainties are most serious for PO_2^- , PO_3^- , and FeO_2^- . The literature choice heats of formation for these ash derived negative ions currently used in the nominal PACKAGE model are: -146, -178, and

-50 kcal/mole, for PO_2^- , PO_3^- , and FeO_2^- , respectively.

The value for PO_2^- is derived from the flame equilibrium studies of Miller⁵ while the PO_3^- value is derived from Miller's value for PO_2^- and measurements of PO_3^-/PO_2^- ratios at ARI reported in Reference 3. The stated uncertainties in these measured heats of formation are +7 kcal/mole and +11.5 kcal/mole, respectively. However, further work on these systems is needed, particularly given the reported minimal impact of phosphorus seeding on the conductivity of ethanol combustion plasmas as reported by Annen and co-workers at this conference, (a calculation using phosphorus negative ion parameters consistent with their results gave an increase in enthalpy extraction at 10m of 27%).

Knowledge of the heat of formation of FeO_2^- is limited by the fact that only a lower limit to its electron affinity is available.⁶ We estimate that the current uncertainty in the heat of formation is -11.5 or +8.1 kcal/mole.

Fractional enthalpy changes due to uncertainties in the level of PO_2^- , PO_3^- , and FeO_2^- precursors in coal ash (P_2O_5 and Fe_2O_3) are shown in Table 3 and the phosphorus case is also plotted in Fig. 1. A roughly +33% change in initial ash P_2O_5 content is suggested by the standard deviation of P_2O_5 literature analyses leads to a -7% (+33% P_2O_5) and +8% (-33% P_2O_5) variation in fractional enthalpy extraction and a -7% and +8% change in inlet conductivity, respectively, using the nominal ion heats of formation noted above. Table 3 also shows the effect of varying the value of Fe_2O_3 of 8.1% of the ash by +2.1% to 10.3% and 5.9%, respectively. This variation leads to less than +1% change in the initial conductivity and about +0.5% in fractional enthalpy extraction. The difference between the P_2O_5 and Fe_2O_3 cases is caused by the fact that phosphorus oxide compounds are all vaporized at combustor and generator temperatures, so all the ash P_2O_5 contributes directly to gas phase equilibria producing PO_2^- and PO_3^- . The gas phase population of iron oxide compounds is vapor pressure limited and addition or deletion of iron to the condensed phase reservoir has only a small impact on the gas phase equilibrium producing FeO_2^- .

The effect of individually varying the heats of formation for PO_2^- , PO_3^- , and FeO_2^- within the assessed

uncertainties is shown in Table 4 and the resulting changes in calculated fractional enthalpy extraction versus channel lengths are plotted in Fig. 2.

Variations of ± 7 kcal/mole (0.3 eV) in the PO_2^- heat of formation (positive increments indicate a less stable ion) change the inlet conductivity by +9% and -11%, the inlet PO_2^- concentration by -61% and +85% and the fractional enthalpy extraction at 10m by +8% and -10%, respectively. Similarly, variations in the PO_3^- heat of formation by ± 11.5 kcal/mole (0.5 eV) lead to a +3% change in enthalpy extraction for the less stable ion model (making PO_3^- fairly unimportant as an ionic species) and a -11% change in fractional enthalpy extraction which results from the 330% increase in PO_3^- inlet concentration and the -11% change in inlet conductivity resulting from the more stable ion model. The results upon variation of FeO_2^- heat of formation are similar to the PO_3^- case, resulting in a 2% enthalpy extraction increase for the less stable ion model, but a -11% change for the more stable ion model.

The calculated impact of negative ion species such as PO_2^- , PO_3^- , and FeO_2^- may also be influenced by the thermochemical models used for major gas phase phosphorus and iron containing neutral species in equilibrium with the ions. The PACKAGE code predicts that under generator conditions the major phosphorus gas phase neutral species is PO_2 while major neutral iron gas phase species include FeO and FeOH. The thermochemical model for PO_2 is based on work by Drowart and co-workers,⁷ the model for FeO is taken from the JANAF Tables,⁸ and the FeOH model is based on work by Jensen and Jones.⁹ The nominal values and assessed uncertainties in the heats of formation for PO_2 , FeO, and FeOH are -62.44 ± 4.8 , -60 ± 5 , and 16.5 ± 4.8 kcal/mole, respectively.

The variation in inlet plasma properties and enthalpy extraction at 10m for variations in the assessed uncertainty limits for the three neutral precursor compounds are shown in Table 5 while the results for fractional enthalpy extraction versus channel length for the PO_2 cases are shown in Fig. 3. As shown in Table 5, the variation in the PO_2 thermochemical model of ± 4.8 kcal/mole leads respectively to a moderately significant +8% or -6% change in enthalpy extraction as a more stable PO_2 reduces the population of PO_2^- (and PO_3^-) while a less stable PO_2 allows increased PO_2^- (and PO_3^-) formation thus reducing conductivity. More stable models for both FeO and FeOH also deplete FeO_2^- by 31 and

Fig. 2. Baseline Enthalpy Extraction and RMS Bounds (solid lines) for Variations in Negative Ion Parameters with Dashed Lines Indicating Contributions from Individual Parameter Variations

23%, respectively, thus leading to small increases in inlet conductivity and fractional enthalpy extraction. The ion system is still dominated by the equilibria between condensed and gas phase species, and small shifts among the gas phase species do not lead to a dramatic impact on plasma electrical properties.

A second way in which thermochemical models can influence the calculated conductivity is by affecting the level of free potassium available to the thermal ionization process. One concern is the correct distribution of total K between free potassium and KOH, which are the predominant forms of potassium under generator conditions.

The thermochemical model for KOH used in the PACKAGE code is taken from the JANAF Tables⁸ and its heat of formation is stated to be 55.6 ± 3 kcal/mole. As shown in Table 5 and plotted in Fig. 3, the ± 3 kcal/mole uncertainty leads to a calculated range of enthalpy extraction decreasing by 12% and increasing by 9%, respectively. There has been some recent experimental evidence from visible chemiluminescence experiments indicating that the heat of formation of KOH may actually be as much as 8 kcal/mole lower than the JANAF value.¹⁰ If substantiated, the impact of changes in

TABLE 4
Effect of Uncertainty in Negative Ion Parameters

	ΔH at 10m	T	P	σ	f	$[\text{K}^+]$	$[\text{PO}_2^-]$	$[\text{PO}_3^-]$	$[\text{FeO}_2^-]$	$[e^-]$
Base Case	0.209	2715	3.15	7.56	7.81(11)	4.93(-5)	1.33(-5)	0.46(-5)	4.08(-6)	2.45(-5)
Code	Fractional Change From Baseline Case									
P2P	-0.10	-	-	-0.11	+0.01	+0.11	+0.83	-0.50	-0.10	-0.10
P2M	+0.08	-	-	+0.09	-0.01	-0.08	-0.61	+0.43	+0.07	+0.08
P3P	-0.11	-	-	-0.11	+0.01	+0.11	-0.50	+3.30	-0.10	-0.10
P3M	+0.03	-	-	+0.03	-0.002	-0.03	+0.14	-0.87	+0.02	+0.03
F2P	-0.19	-	-	-0.24	+0.01	+0.28	-0.14	-0.13	+5.40	-0.22
F2M	+0.02	-	-	+0.04	-0.004	-0.04	+0.02	+0.02	-0.76	+0.04

TABLE 5
Effect of Uncertainty in Gas-Phase Neutral Molecule Parameters

	ΔH at 10m	T	P	σ	f	$[K^+]$	$[K]$	$[KOH]$	$[PO_2^-]$	$[FeO_2^-]$	$[e]$
Base Case	0.209	2715	3.15	7.56	7.81(11)	4.93(-5)	3.47(-3)	3.53(-3)	1.33(-5)	4.08(-6)	2.45(-5)
Code	Fractional Change From Baseline Case										
KHP	-0.12	-	-	-0.14	-0.01	-0.13	-0.26	+0.28	-0.09	-0.15	-0.14
KHM	+0.09	-	-	+0.12	+0.01	+0.11	+0.27	-0.27	+0.06	+0.14	+0.13
POP	+0.08	-	-	+0.08	-0.01	-0.07	-	-	-0.33	+0.08	+0.08
POM	-0.06	-	-	+0.06	+0.01	+0.06	-	-	+0.26	+0.05	-0.06
FHP	+0.01	-	-	+0.01	-0.001	-0.01	-	-	-	-0.23	+0.01
FHM	-0.004	-	-	-0.007	+0.001	+0.005	-	-	-0.01	+0.14	-0.005
FOP	+0.02	-	-	+0.02	-0.001	-0.02	-	-	+0.005	-0.31	+0.02
FOM	-0.01	-	-	-0.01	+0.001	+0.01	-	-	-0.01	+0.22	-0.01

Fig. 3. Baseline Enthalpy Extraction and RMS Bounds (solid lines) for Variations in Gas Phase Neutral Molecule Parameters. Dashed Lines Indicate Contributions from Individual Parameter Variations. Contributions from Iron Species Would be Barely Visible on the Above Scale

the KOH heat of formation on calculated generator performance would be quite serious.

The third way in which thermochemical models can impact gas phase free potassium levels is through the absorption of potassium into the condensed phase slag components in the combustor or generator. For instance, many MHD modelers calculate plasma composition with codes that model the condensed phase by including only pure, binary condensed phase species such as Al_2O_3 , SiO_2 , and MgO . Such models will not predict any condensed phase potassium content under combustor or generated conditions. Other condensed phase options, which are available in the PACKAGE code, are the inclusion of complex condensed phase species such as liquid or solid $KAlO_2(SiO_2)_n$ or the absorption of potassia (K_2O) into an ideal solution of liquid species. The choice of condensed phase model influences not only the partitioning of potassium between the gas and liquid phases, thus affecting electron production, but also the partitioning of neutral precursors of refractory oxide negative ions such as AlO_2^- and FeO_2^- , thus affecting electron scavenging. The nominal PACKAGE condensed phase model which was used in the baseline calculation consists of an ideal solution which typically incorporates Al_2O_3 , SiO_2 , Fe_2O_3 , Fe_3O_4 , $MgSiO_3$, K_2CO_3 , K_2SO_4 , $K_2Si_2O_5$, and $KAlO_2(SiO_2)_n$ with n being 0 to 3. A second extreme model is the inclusion of only JANAF tabulated condensed species with no solution model. As shown by the first entry in table 6, the difference in computed fractional enthalpy extraction at 10m between

TABLE 6
Effect of Condensed Phase Model on Performance and Sensitivity

	ΔH at 10m	T	P	σ	f	$[K^+]$	$[Al_2O_3(l)]$	$[KAlO_2(l)]$	$[Al(OH)_2]$	$[AlO_2^-]$	$[FeO_2^-]$	$[e]$
Baseline Case	0.209	2715	3.15	7.56	7.81(11)	4.93(-5)	1.35(-8)	5.08(-4)	2.19(-7)	2.32(-8)	4.08(-6)	2.45(-5)
Code	Conditions, and Change from Nominal Values, for Only Pure JANAF Condensed Phases											
JAN	0.199	2701	3.15	6.57	7.97(11)	5.42(-5)	2.48(-4)	-	7.36(-5)	7.98(-6)	4.13(-6)	2.16(-5)
	-0.05	-0.005	-	-0.13	+0.02	+0.10	-	-	+335.	+340.	+0.005	-0.11
Fractional Change From Pure JANAF Condensed Phase Case												
A2P	-0.09	-	-	-0.14	+0.02	+0.15	-0.02	-	-	+1.65	-0.13	-0.13
A2M	+0.03	-	-	+0.06	-0.01	-0.06	-0.01	-	-	-0.65	+0.06	+0.0
AHM	-	-	-	-	-	-	-0.04	-	-0.73	-	-	-
AOH	+0.01	-	-	+0.01	-	+0.005	+0.08	-	+0.01	+0.02	-0.03	+0.0
AOL	-0.01	-	-	-0.01	-	-0.005	-0.08	-	-0.01	-0.02	+0.03	-0.0
A2H	-	-	-	-	-	-	-	-	-	to 7.7(-8)	-	-

these two models is only -5% (0.209 for the baseline versus 0.199 for the JANAF pure species model.) One method of increasing this difference is to additionally vary the AlO_2^- heat of formation from its JANAF value of -140.9 to the -147.9 kcal/mole uncertainty limit. As shown in Table 6, this results in an additional decrease of 9% in enthalpy extraction at 10m, resulting from the 68% increase in AlO_2^- and the additional 13% decrease in conductivity. As shown by the other entries in Table 6, changes in the thermochemical models for gas phase aluminum species other than AlO_2^- have a relatively small effect, even on calculations using the pure JANAF species condensed phase model. Calculations using the ideal solution model effectively immobilize aluminum in the condensed phases so that AlO_2^- has no significant effect on plasma conductivity, even when modeled at the limit of its JANAF estimated stability. Figure 4 shows fractional enthalpy extraction as a function of temperature for significant differences in condensed phase and aluminum thermochemical models.

Type 3 - Parameters Affecting Conductivity Through Electron Scattering

The last set of molecular parameters which influence plasma conductivity and generator efficiency are electron/molecule scattering cross sections which determine the plasma scattering frequency. As noted above, due to the long range of Coulombic scattering, variations in plasma ionization levels due to negative ion effects are calculated to have a non-negligible effect on the scattering frequency. However, the bulk of the electron collisions are with the major combustion species N_2 , CO_2 , H_2O , and KOH . The latter two species are particularly effective because of their large permanent dipole moments. The available data for electron scattering cross sections for MHD combustion plasma species has been assembled and evaluated by Spencer and Phelps.¹¹ The major new work reported since this evaluation is a calculation of the KOH cross section recently published by Collins and Norcross.¹²

A review of the source data in Spencer and Phelps leads us to estimate the uncertainty in N_2 and CO_2 scattering cross sections as $\pm 10\%$ and the uncertainty in H_2O cross sections as $\pm 25\%$. Spencer and Phelps had no theoretical or experimental data on KOH scattering, but offered a cross section based on calculations for similar polar molecules such as LiF . We have adopted the calculated values of Collins et al. for KOH with their estimated uncertainty of $\pm 25\%$.

Table 7 compares the results from the nominal scattering cross sections of Spencer and Phelps for N_2 , CO_2 , and H_2O and the value of Collins et al. for KOH with the variations caused by their estimated uncertainties. Note that only the $\pm 25\%$ change in the water value shows a 10m fractional enthalpy extraction which varies by more than 1% of the 0.209 baseline value. In general, uncertainties in electron scattering cross sections for MHD combustion plasma species do not lead to significant uncertainties in plasma properties or generator performance.

Effect of Design Parameter Changes

The comparisons of input data uncertainties on plasma properties and generator efficiency detailed above were all made for a system utilizing a combustor pressure of 4.5 atm and a oxidizer consisting of 20% O_2 enriched air with modest preheat.

Fig. 4. Enthalpy Extraction Calculations for Baseline Case and for Case Using Only Pure Phases of JANAF Condensed Species. Above This Latter Condensed Phase Model, Variation of the AlO_2^- Electron Affinity, Cases A2P and A2M (see Table 2), Can Lead to a Substantial Effect on Performance

The larger scale generator systems now being designed may employ significantly higher pressure combustors and a different trade-off between air preheat and oxygen enrichment.

In order to assess how the influence of uncertainties in input parameters on generator performance scales with changes in design parameters such as O_2 enrichment or combustor pressure, calculations leading to significant changes in the baseline case were repeated for reasonable variations in these design parameters.

In the case of variable O_2 enrichment, comparable cases were run for 0, 20, and 40% O_2 enrichment. Our criterion for comparable cases was equivalent combustor conductivities at the same equivalence ratio, which were achieved by varying the oxidizer preheat. However, it is important to note that equal conductivity plasmas are not equivalent in other regards. Replacing N_2 with O_2 in the oxidizer flow also requires an increase in the fuel fraction in order to maintain the same equivalence ratio. The resulting plasma is certainly more expensive in terms of O_2 and coal input costs. It also has a significantly different molecular composition. In general, the higher the O_2 enrichment, the greater the fractional concentration of effective electron scatters such as H_2O , KOH , and CO_2 , and inorganic oxide negative ions such as PO_2^- , PO_3^- , FeO_2^- , and OH^- . Thus, an oxygen enriched plasma must be heated to a higher temperature to attain the same conductivity. Both the higher temperature and greater concentration of triatomic species such as CO_2 and H_2O lead to a higher heat content per unit mass. The ratio of heat capacity per unit mass of an equal conductivity 0% enriched plasma to the baseline 20% enriched case is about 0.8, while the same ratio of the baseline case heat capacity to that of a 40% enriched, equal conductivity plasma is 0.85.

TABLE 7
Effect of Uncertainty in Electron Scattering Cross Sections

	ΔH at 10m	At Channel Entrance σ	f	At 10 Meters σ	f	$[e]$	T	P
Baseline Case	0.209	7.56	7.81(11)	3.45	2.06(11)	1.14(-4)	2404	0.72
Code	Fractional Change From Baseline Case							
SHP	-0.03	-0.08	+0.09	-0.06	+0.15	+0.035	+0.004	+0.05
SHM	+0.03	+0.10	-0.09	+0.08	-0.13	-0.035	-0.004	-0.04
SKP	-0.003	-0.008	+0.008	-0.006	+0.014	-	-	-
SKM	+0.003	+0.009	+0.009	+0.005	-0.011	-	-	-
SNP	-0.01	-0.025	+0.025	-0.014	+0.036	+0.009	+0.001	+0.01
SNM	+0.01	+0.026	-0.025	+0.014	-0.032	-0.009	-0.001	-0.01
SCP	-0.004	-0.011	+0.011	-0.01	+0.02	-	-	-
SCM	+0.004	+0.011	-0.011	+0.008	-0.016	-	-	-

Table 8 shows the functional enthalpy extractions for three nominal 0, 20, and 40% O_2 enrichment cases compared to the enthalpy extraction for the same cases with significant variations in input parameters. Note that input variations which decrease inlet conductivity all result in a slightly larger percentage loss of fractional enthalpy extraction with increasing enrichment while variations which increase conductivity result in a similarly increasing gain in fractional enthalpy extraction with increasing enrichment.

Combustor efficiency can be increased by increasing combustor pressures. However, plasma conductivity suffers at higher combustion and front end channel pressures. Not only does the collision frequency go up as the molecular density is increased, but LeChatelier's principle works to recombine K^+ with electrons, K and OH to form KOH, and electrons with inorganic species to

form negative ions such as PO_2^- . The resulting decrease in conductivity results in longer channel requirements to achieve equivalent fractional enthalpy extractions.

Table 9 compares fractional enthalpy extractions for 4.5 and 8.3 atm combustors. The higher combustor pressure case is seen to be uniformly more sensitive to uncertainties in input data affecting initial conductivity, with input variations acting to increase conductivity leading to higher percentage gains in the higher pressure case and factors which lower conductivity resulting in greater percentage losses.

In the third study of changes in parameter sensitivity with changes in design, several variations were performed on a generator model similar to the baseline but having a Mach number of 1.5. Here, no significant differences in sensitivity were found.

TABLE 8
Effect of Oxygen Enrichment on Parameter Sensitivities

Code	Enthalpy Extraction Fractions for Nominal Cases		
	0 moles/100 0.162	20 moles/100 0.209	40 moles/100 0.227
	Enthalpy Extractions, and Fractional Changes, for Parameter Perturbation		
F2P	0.135, -0.17	0.169, -0.19	0.179, -0.21
P2P	0.149, -0.08	0.188, -0.10	0.200, -0.12
KHP	0.144, -0.11	0.184, -0.12	0.198, -0.13
POP	0.173, +0.07	0.226, +0.08	0.247, +0.09
DH3	0.136, -0.16	0.169, -0.19	0.176, -0.23
DH4	0.189, +0.17	0.246, +0.18	0.277, +0.22
JAN	0.157, -0.03	0.199, -0.05	0.209, -0.08
SHP	0.162, -	0.202, -0.03	0.218, -0.04

TABLE 9
Enthalpy Extraction Fractions and Relative Changes in Performance With Parameter Perturbations for Chamber Pressures of 4.5 and 8.3 atm

Code	4.5 atm, Nominal Extraction at 10m 0.209	8.3 atm, Nominal Extraction at 10m 0.086	8.3 atm, Nominal Extraction at 20m 0.195
	Relative Changes		
F2P	-0.10	-0.13	-0.17
F2P	-0.19	-0.26	-0.31
KHP	-0.12	-0.16	-0.19
POM	-0.06	-0.08	-0.10
DH3	-0.19	-0.26	-0.30
DH4	+0.18	+0.35	+0.31
JAN	-0.05	-0.09	-0.07
SHM	+0.02	+0.12	+0.09

Conclusions

A number of input data uncertainties are seen to have significant impact on the calculated performance of large scale MHD combustor/generator systems. The range of inherent uncertainties in coal parameters such as heating value, moisture content, ash fraction, and the level of key ash impurities such as P_2O_5 stand as warning signs for both demonstration facility and power plant operators. The plant's theoretical output is clearly sensitive to the characteristics of the input fuel, and some of these input characteristics will have to be monitored and the plant's operation adjusted to their variations. The sensitivity to these input parameters will increase with increasing combustor pressure and O_2 enrichment.

The sensitivity of generator performance to uncertainties in molecular parameters such as ionic and neutral heats of formation and the details of condensed phase equilibria seems to justify continued laboratory and theoretical research programs designed to reduce the current uncertainty levels. As these uncertainty levels fall, careful comparison of well designed plasma property measurements with model predictions become meaningful, and will serve to validate and confirm model predictions and allow confident use of detailed models for system design tasks.

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Abstract

This paper presents calculations made using the Aerodyne PACKAGE (Plasma Analysis, Chemical Kinetics, and Generator Efficiency) computer code which bear on two questions which arise in connection with choices between oxygen enrichment and air preheating to attain the high combustion temperatures needed for open-cycle, coal-fired MHD power generation. The first question is which method produces the highest enthalpy extraction per unit channel length. The second is, in test facilities intended to study tradeoffs between oxygen enrichment and preheated air, can good generator performance be obtained from the same physical channel for different combustor compositions. The answer to the first question is found to depend on what combustor conditions are taken to be comparable. As for the second question, it is found that operation with channel input from off-design combustor conditions can cause serious problems, which can be partially alleviated by changing the channel load factors.

1. Introduction

Background and Outline

Experimental open-cycle, coal-fired MHD generators in planning or under construction will utilize oxygen enrichment to achieve the high combustor temperatures necessary to provide desired plasma conductivity levels at the channel entrance. The use of oxygen enriched combustion should allow the testing of larger scale, higher interaction channels without waiting for the development of large scale, high temperature (1700-1900°K) air preheat systems. However, reliance on oxygen enrichment will produce a plasma with significantly different chemical and physical properties than that resulting from preheated air combustion. The effects of these changes in plasma properties must be predicted in order to properly design experimental generator systems and well understood in order to interpret the relevance of data obtained in such systems to the design of commercial scale generators which may rely on air preheat rather than oxygen enriched combustion.

The focus of this paper is to predict the chemical and physical effects oxygen enriched combustion has on generator plasma properties and identify and, where possible, quantify, the effects of altered plasma properties on generator performance. No discussion of the economic or engineering reliability aspects of the oxygen enrichment/air preheat question will be presented.

The obvious and overriding beneficial effect of oxygen enrichment is that it leads to higher combustor temperatures for a given preheat temperature, resulting in higher K atom and electron concentrations. Higher electron concentrations, in general,

mean higher plasma conductivity and higher fractional enthalpy extraction for comparable generator design.

A more subtle effect is due to higher concentrations of CO₂ and H₂O found in oxygen enriched cases. Higher fractional concentrations of these triatomic molecules lead to higher heat capacity per gram of plasma. This difference in plasma enthalpy content per unit mass will generally cause a different temperature and pressure history for channels with the usual constant velocity condition. In particular, for similar temperature drops, the enthalpy extraction from the higher heat capacity, oxygen-enriched mixture, will be larger with a corresponding larger pressure drop.

However, several differences in the chemistry of oxygen-enriched plasmas, detailed in Section 2, lead to substantial reductions in channel plasma conductivity when compared to air preheat plasmas at the same temperature. The combination of increased enthalpy per unit plasma mass and lower than anticipated plasma conductivity, when compared with isothermally produced plasmas produced by nonenriched combustion, makes comparison of oxygen enriched and air preheat generator systems a complex process. The examples in Section 3 will show that the first effect dominates when initial conductivity is held constant in the comparison, while the second prevails when comparison is made between combustor/generator systems with identical starting temperatures. The different mixture specific heats also make it impossible to maintain the constant velocity condition when changing oxygen enrichment while retaining the same channel area profile. Examples of the consequences will be given in Section 4.

PACKAGE Code

The quantitative comparisons of plasma properties and generator efficiency for oxygen enrichment and air preheat cases which are presented below were calculated with Aerodyne's PACKAGE computer code. A full description is available in the program manual.⁽¹⁾ Here we simply note that it employs a one-dimensional steady flow model, intended to represent the core plasma. A pre-specified channel area profile or pressure profile can be used in place of the specified velocity criterion if desired. The plasma composition and conductivity are recalculated at each channel grid point. In addition to the usual conservation equations for mass and chemical elements, and equations of state contained in the chemical equilibrium calculation, the equations used to describe MHD channel flow are those for momentum,

$$\rho u \frac{du}{dx} = - \frac{dp}{dx} + \rho u B^2 (K - 1) \quad (1)$$

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energy,

$$\rho u \frac{dh}{dx} + \rho u^2 \frac{du}{dx} = \sigma u^2 B^2 K (K - 1) \quad (2)$$

and Ohm's law for transverse current density, J_y ,

$$J_y = \frac{\sigma}{1 + \beta^2} (E_y - uB + \beta E_x) \quad (3)$$

In these equations, x is axial position in the channel, u is axial velocity, ρ is mixture density, p the pressure, h the enthalpy, σ is the plasma conductivity, B the magnetic field, E_x and E_y the axial and transverse electric fields, K is the load factor defined by E_y/uB , and β is the Hall parameter, which is the ratio eB/mv_e , with e and m being electron charge and mass and v_e the electron collision frequency.

The axial current density, J_x , is assumed to be zero. The Ohm's law for J_x then becomes the relation

$$E_x = \beta u B (K - 1) \quad (4)$$

Since a large axial electric field, E_x , can lead to destructive arcing between the electrodes, Eq. (4) can be used to limit the magnitude of E_x below a specified value. Here, the magnetic field is reduced so that E_x does not exceed 2.1 kV/m, a limit typically reached in the first few meters of channel. In addition to the above conditions on axial current density and magnetic field, the axial profiles of pressure, velocity, or area, and of load factor, must be specified.

The chemical model used in this work is a full equilibrium model including an ideal solution model for liquid slag components. It has been developed with particular attention to the influence that nonfuel coal components, such as inorganic oxides arising from ash oxidation and vaporization, may have on coal combustion plasma composition and conductivity. The code can also perform plasma composition calculations using partial equilibrium-partial finite rate or fully finite rate chemical models as required. Additional options not used in the present study include channel heat loss due to radiation and convection (only combustor heat loss is assumed) and nonequilibrium slag condensation models.

II. Model Generators

Combustor and Channel Parameters

The combustor in these calculations is modeled as a two-stage system, with both stages at the same equivalence ratio. The coal and oxidizer are allowed to reach the adiabatic flame temperature in the first stage and the resulting combustion gases are conveyed into the second stage after rejection of 85% of the condensed slag species. The K_2CO_3 seed is then added to the second combustor stage and the equilibrium combustion products are recalculated assuming a 3% combustor heat loss.

Table 1 presents specifications, first for all model generators sharing the same oxygen enrichment percentage, then for two sets of model combustors, one with identical temperatures, and one with identical channel inlet conductivities. The

20% oxygen case is patterned after Reference Plant 3 of the recently completed PSPEC study,⁽²⁾ with two significant exceptions. First, the Montana Rosebud coal model is that developed by MHD office personnel as a baseline for CDIF design studies.⁽³⁾ Second, combustor pressure is reduced from 8.3 atm to 4.5 atm, more appropriate to a CDIF scale device.

It will be seen that the differences in conductivity between the three 2800°K combustors are quite substantial. However, Table 1 shows that less than 100°K difference in combustor temperature is required to redress these differences. The last line in Table 1 demonstrates the large difference in adiabatic flame temperature with oxygen content for identically preheated air.

Plasma Properties

This investigation was initially motivated by the observation that at a given temperature, the conductivity of an oxygen enriched plasma is substantially lower than that of a preheated air plasma. However, considering plasmas at the same temperature is, in general, not an appropriate comparison, unless materials and heat loss problems impose an upper limit. Conductivity is such a strong function of temperature that only a relatively small increase is needed to overcome the oxygen-related changes - an increase much smaller than that produced if oxygen is added while maintaining the same air pre-heat. The comparison between performance of plasmas with identical initial conductivities is only one of many which might be thought of as fairer than that between identical initial temperatures.

However, it is useful to begin by comparing plasma properties at the same temperature, since in this way the relative importance of several sources of changing conductivity can be discerned. These changes are:

1. Higher CO_2 and H_2O concentrations leading to higher electron collision frequencies,
2. Larger concentrations of ash-derived negative ions, all derived from oxides, leading to decreased electron population and increased collision frequency,
3. Greater concentrations of condensed phase slag oxide species, which may lead to lower gas phase atomic K and electron concentrations, and
4. A decrease in the gas phase K/KOH ratio again leading to lower than anticipated electron concentrations.

Table 2 displays a number of combustor plasma parameters for all three degrees of oxygen enrichment. It also includes similar parameters for combustors using methane as a fuel in which effects due to coal ash are absent.

In the coal cases, the K to KOH ratio indeed decreases from 5 to 4 with no enrichment to 4 to 5 with 40% oxygen, and the condensed potassium species fraction rises from 0.06 to 0.10. However, these trends are countered by the increasing concentrations of negative ions, which acts to increase potassium ionization levels. Therefore, K^+ mole fractions actually increase as a fraction of total

Table 1 Combustor/Generator Properties

<u>Common Properties</u>			
Coal	Montana Rosebud subbituminous, 5% Moisture		
O ₂ Enrichment of Air, by volume	<u>0%</u>	<u>20%</u>	<u>40%</u>
N ₂ Mass Fraction	0.754	0.618	0.523
O ₂ Mass Fraction	0.232	0.371	0.467
Combustor Stoichiometric Ratio (O/F)		0.92	
Combustor Pressure		4.5 atm	
Slag Rejection Fraction (at first stage)		0.85	
Channel Inlet Pressure		3.15 atm	
Channel Inlet Mach Number		0.80	
Magnetic Field Strength	6 Tesla initially, limited by 2.1 kV/m axial field		
Load Factor		0.80	
<u>Equal Channel Entrance Conductivities (8.0 mho/m)</u>			
Air Preheat Temperature (°K)	1700	920	330
Combustor Temperature (°K)	2769	2818	2845
Channel Inlet Temperature (°K)	2665	2725	2757
<u>Equal Combustor Temperatures (2800°K)</u>			
Air Preheat Temperature (°K)	1800	840	300*
Combustor Temperature (°K)	2800	2800	2800
Channel Inlet Temperature (°K)	2695	2709	2717
Conductivity (mho/m)	12.26	8.92	7.46
Combustor Temperature for 840°K Preheated Air (°K)	2460	2800	2928

*Combustor heat loss 8%. All other combustor heat losses are 3%.

potassium with increasing oxygen. (It must be noted that since potassium weight fraction is kept constant, and mixture molecular weight increases with increasing oxygen, absolute K species mole fractions increase even more than the ratio of K⁺ to total potassium)

For the coal plasmas, over half the total effect on conductivity is due to reduction in electron concentrations. This reduction is even larger than the loss of gaseous K, and is, in fact, due primarily to increased negative ion concentrations. The most important negative ions in these calculations are those formed from elements in the ash, in particular PO₂, PO₃, FeO₂, and AlO₂. The additional negative ions also contribute to the increased collision frequency.

In comparison, the conductivity in the methane cases is affected primarily by changing collision frequencies, and to a much lesser extent by electron concentration reduction by negative ions. Negative ions, primarily OH⁻ and O⁻, are now a small fraction of the electron concentration. Therefore, they also contribute little to increasing

potassium ionization. Note the K/KOH ratio is shifted towards KOH, and shifts even further with increasing oxygen. The major contribution to changing collision frequency is from large changes in water concentration. Water has a very large electron scattering cross section, and water plays a larger role in methane plasmas because the C/H is 0.25 rather than the coal value of approximately 1. The larger hydrogen concentration also accounts for the increased importance of KOH.

III. Enthalpy Extraction Comparisons

Table 3 presents the results of performance calculations, for both coal and methane fueled generators. Given first are results for identical channel inlet conductivities (meaning somewhat higher temperatures for oxygen-enriched cases), followed by results for identical combustion temperatures (as if limited by materials).

Identical Channel Inlet Conductivities

It can be seen simply by consulting the entries in Table 3 giving fractional enthalpy extraction at

Table 2 Combustor Plasma Chemical Properties (2800°K, 4.5 atm)

Oxygen Enrichment	0%	20%	40%
<u>Coal-Fired Combustor</u>			
<u>Mole Fractions</u>			
$K^+(g)$	5.28×10^{-5}	5.46×10^{-5}	5.59×10^{-5}
$K(g)$	3.87×10^{-3}	3.38×10^{-3}	3.11×10^{-3}
$KOH(g)$	3.03×10^{-3}	3.55×10^{-3}	3.74×10^{-3}
Condensed K Species	4.51×10^{-4}	6.26×10^{-4}	8.04×10^{-4}
Electrons	3.42×10^{-5}	2.88×10^{-5}	2.62×10^{-5}
Negative Ions	1.86×10^{-5}	2.58×10^{-5}	2.97×10^{-5}
$H_2O(g)$	0.069	0.104	0.135
Collision Frequency (sec^{-1})	0.93×10^{12}	1.08×10^{12}	1.17×10^{12}
Conductivity (mho/m)	12.26	8.92	7.46
Average Molecular Weight	29.3	30.0	30.5
<u>Methane-Fired Combustor</u>			
<u>Mole Fractions</u>			
$K^+(g)$	4.07×10^{-5}	3.86×10^{-5}	3.76×10^{-5}
$K(g)$	3.19×10^{-3}	2.78×10^{-3}	2.53×10^{-3}
$KOH(g)$	3.46×10^{-3}	4.00×10^{-3}	4.10×10^{-3}
Electrons	3.62×10^{-5}	3.32×10^{-5}	3.18×10^{-5}
Negative Ions	4.54×10^{-6}	5.42×10^{-6}	5.86×10^{-6}
$H_2O(g)$	0.166	0.256	0.312
Collision Frequency (sec^{-1})	1.18×10^{12}	1.47×10^{12}	1.64×10^{12}
Conductivity (mho/m)	10.15	7.52	6.42

10m point, that in this comparison, increasing oxygen enrichment clearly improves performance.

As mentioned before, this is due to the differing mixture specific heats, indicated by the variation in specific heat ratio. This comes about because conductivity controls enthalpy extraction, and conductivity is in turn determined by mixture temperature. Therefore, mixtures with higher heat capacities can support larger enthalpy losses for the same loss in temperature and conductivity, or alternatively can maintain higher rates of enthalpy extraction further into their extraction history.

It is not immediately clear, of course, that comparing enthalpy extractions at a given length is the appropriate measure of performance, since fixing combustor pressure and channel length will determine channel exit pressure. This pressure must at least be in the range such that a diffuser of appropriate design can expand it to ambient pressure. In fact, the 40% enriched, coal case exit pressure could not be expanded to a full 1 atm even by ideal diffuser (isentropic expansion), although the stagnation pressure of 0.82 atm would be appropriate for higher elevations than sea level (mean atmospheric

pressure in Butte, Montana is 0.8 atm). On the other side of the question, the 10m exit pressure for the 40% enrichment case indicates that further expansion (and enthalpy extraction) is desired.

If a generator is being designed to a specific length and enthalpy extraction, then an appropriate parameter to vary to obtain the desired exit pressure is the combustor pressure. Here, in order to reduce the amount of computation required, we have chosen to keep the combustor pressure constant, and to evaluate channel length and enthalpy extraction at 0.8 atm, the pressure which can be expanded to 1.0 atm by a diffuser with efficiency 0.5.

If enthalpy extractions at this point were equal, then the appropriate figure of merit would be generator length required to reach the same extraction. The lengths at 0.8 atm in Table 3 for both coal and methane cases do indeed follow the same order of preference as did extraction for fixed length, with the shortest generators being those with the highest degree of oxygen enrichment. Further, for the coal cases the associated enthalpy extractions are close enough to each other to make it clear that even if combustor pressure were varied

Table 3 Fractional Enthalpy Extractions With Oxygen Enrichment

<u>Equal Channel Entrance Conductivities (8.0 mho/m)</u>				
<u>O₂ Enrichment of Air, by Volume</u>	<u>0%</u>	<u>20%</u>	<u>40%</u>	
Fractional ΔH at 10m, Coal/Methane	0.177/0.156	0.219/0.179	0.235/0.191	
Static Pressure at 10m (atm), Coal/Methane	0.90/0.71	0.66/0.48	0.55/0.37	
Fractional ΔH at 0.8 atm, Coal/Methane	0.191/0.144	0.193/0.134	0.187/0.126	
Length at 0.8 atm (m) Coal/Methane	11.42/8.89	8.50/6.98	7.62/6.33	
Channel Entrance Specific Heat Ratio, Coal/Methane	1.146/1.157	1.130/1.138	1.123/1.130	
<u>Equal Combustor Temperatures (2800°K)</u>				
<u>O₂ Enrichment of Air, by Volume</u>	<u>0%</u>	<u>20%</u>	<u>40%</u>	
Fractional ΔH at 10m, Coal/Methane	0.212/0.157	0.202/0.140	0.190/0.128	
Fractional ΔH at 0.8 atm, Coal/Methane	0.200/0.148	0.195/0.134	0.192/0.128	
Length at 0.8 atm (m), Coal/Methane	9.10/9.12	9.36/9.50	10.11/10.00	
Channel Entrance Conductivity (mho/m) Coal/Methane	9.48/7.05	7.21/6.14	6.25/5.38	

to obtain identical extractions, channel length would still show a clear trend.

However, this is not immediately obvious in the methane cases, where the enthalpy extraction order has been reversed. The channel length ordering would be maintained if identical extractions were obtained by raising or lowering the combustor pressure while keeping the conductivity constant (which would require changing air preheat, since increasing pressure suppresses ionization by promoting recombination). This is because, given identical initial conductivities, the pressure profile versus length is simply multiplied by the factor used to change combustor pressures, while the enthalpy extraction with length remains essentially unchanged. Therefore, lowering the pressure in the methane/pure air combustor, and raising that of the 40% oxygen enriched case results in channels which reach identical enthalpy extraction fractions and exit pressures in essentially the same lengths listed in Table 3. The conclusion to be drawn is that extraction per unit length gives an immediate figure of merit which correctly predicts ordering by length required to achieve a desired fractional enthalpy extraction.

An additional point to be made is that since oxygen enriched generators work better when compared at identical conductivities, comparison at identical air preheat temperatures, meaning much higher combustor temperatures and conductivities, will be even more favorable to oxygen enrichment. Also, with a combustor temperature intermediate between the two given in Table 1, an oxygen-enriched generator could be designed which had the same fractional enthalpy extraction in a given length as the 2800°K combustor, pure air generator. However, because of the different expansion properties of the two mixtures, the generator area

profiles will be substantially different, a point which will be discussed below.

Identical Combustor Temperatures

Turning now to the second half of Table 3, we see that comparison at equal combustor temperatures produces the same ordering in enthalpy extraction as in initial conductivity. However, the differences in conductivity are larger than those in enthalpy extraction, because of the counterbalancing heat capacity effect discussed above. For the equal temperature cases, not only is the ordering in length at 0.8 atm the same as that for extraction at 10m, but the enthalpy extractions retain the same ordering, though the strength of the trend is reduced.

To give a better idea of the differences in operation of these model generators, Figs. 1 through 4 give the channel length profiles of four key parameters, the pressure, temperature, magnetic field, and conductivity, starting at each of the three equal temperature combustors. Compared with the equal conductivity exit pressures in Table 3, the pressure histories in Fig. 1 reach 10m closer together, in the opposite order, and well within a useful range of 0.80 atm. The 10m temperatures, on the other hand, are somewhat farther apart, though in the same order, than those of equal conductivities.

In Fig. 3, the decline in magnetic field begins when the axial field limitation is reached. The set of such points for constant conductivity cases lies inside the ones shown in Fig. 3 for constant temperature. It is particularly interesting to note that if no limit were imposed on axial electric field, and a constant magnetic field were maintained, the ordering by extraction at given length is maintained for both sets of coal cases. For identical

Fig. 1 Static pressure versus channel length for generators with equal (2800°K) combustor temperatures.

Fig. 2 Core flow temperature versus channel length for generators with equal combustor temperatures.

Fig. 3 Magnetic field versus channel length for generators with equal combustor temperatures.

channel inlet conductivities, where magnetic field reduction comes at similar channel points, keeping a constant magnetic field results in an increase of fractional extraction at 10m from 0.18 to 0.22 for pure air, but from 0.24 to 0.35 for 40% enrichment. However, axial electric field at 10m was over 12 kV/m in the 40% case, but only 6 kV/m in the pure air case. For identical combustor temperatures, reduction in magnetic field begins much earlier for the pure air case than for 40% enrichment. Therefore, for pure air enthalpy extraction at 10m increases from 0.21 to 0.29, with a final axial field of over 9 kV/m, while for 40% enrichment extraction is increased only from 0.19 to 0.22, but with an electric field at 10m of only 4.6 kV/m.

Finally, Fig. 4 shows conductivity as a function of channel length. Because the channel with the highest initial conductivity has the highest initial enthalpy extraction, it is cooled more rapidly, to the point where its conductivity can drop below that of channels with initially lower conductivities. When beginning at identical conductivities, there is no crossing, with final conductivities for 0, 20, and 40% oxygen enrichment being 3.0, 3.6, and 4.0 mho/m, respectively.

IV. Off-Design Operation

The discussion of channel area profile effects will be based around three slightly different combustors than those of Table 1. The 20% oxygen enriched case has precisely the air preheat temperature of the PSPEC generator,⁽²⁾ while the 0 and 40% air preheats are adjusted to give the same combustor conductivity (around 9.3 mho/m). The behavior of these combustors when attached to channels which ensure constant flow velocity is similar to that of the constant inlet conductivity combustors discussed above, as can be seen by the ordering of the first entries in Table 4.

One additional entry appearing in Table 4 which now must be defined is the isentropic efficiency. Here it is calculated as the ratio of enthalpy extracted at 0.8 atm to the ideal work. Ideal work is computed as the difference between stagnation

enthalpy at the inlet, and the enthalpy corresponding to the inlet entropy and the stagnation pressure corresponding to the static pressure of 0.8 atm. For generators operating under the constant velocity condition, these efficiencies are typically equal to or slightly higher than the load factor. This is not only seen to be true in the first section of Table 4, but was true for all generators in Table 3.

Figure 5 presents several of the properties of these three model generators in a format which clearly illustrates the explanation given above of the differences in performance. When conductivity is plotted as a function of enthalpy extraction, the curves remain in order of performance, rather than crossing as they did in the plots versus channel length in Fig. 4. From Fig. 5, it is clear that the higher heat capacity of the oxygen-enriched mixtures allow them to maintain higher conductivities and higher extraction rates, leading to higher extraction for a given channel length.

In Fig. 6, the channel area profiles for these three generators are plotted as a function of channel length. Although the differences are not tremendous, they are clearly systematic, with the curve for 20% oxygen being intermediate between the others. The differences are also quite significant, if one attempts to run the 0 and 40% combustors into the unchanged 20% channel. For 0%, fractional enthalpy extraction at 10m drops from 0.172 to 0.090. Worse yet, the 40% combustor flow becomes supersonic at 2m, an occurrence which introduces complications in generator design as well as in the present calculation. Therefore, the object of the investigation reported in this section was to modify channel parameters other than the area profile in order to increase enthalpy extraction per unit length and keep channel flow velocity within reasonable bounds.

The results of a first such effort are shown in Figs. 7 and 8, in which the upper curve represents channel flow Mach number as a function of channel length, and the lower curve is the difference between enthalpy extraction obtained in the 20% channel and that obtained in the appropriate constant velocity channel. The apparent cusp in each Mach number

Fig. 4 Conductivities versus channel length for generators with equal combustor temperatures

Table 4 Effect of Off-Design Channel Area Profiles

Baseline, Constant Velocity Channel, Load Factor 0.8

<u>O₂ Enrichment of Air, by Volume</u>	<u>0%</u>	<u>20%</u>	<u>40%</u>
Fractional ΔH at 10m	0.172	0.206	0.223
Static Pressure at 10m (atm)	1.03	0.73	0.55
Fractional ΔH at 0.8 atm	0.207	0.194	0.187
Length at 0.8 atm (m)	13.6	9.3	7.7
Isentropic Efficiency	0.800	0.805	0.808

Using Channel Area Profile for 20%, Constant Adjusted Load Factor

Load Factor	0.60	0.816
Fractional ΔH at 10m	0.149	0.145
Static Pressure at 10m (atm)	0.83	1.07
Length at 0.8 atm (m)	10.3	38.1
Isentropic Efficiency	0.588	0.787

Using Channel Area Profile for 20%, Tailored Load Factor

Fractional ΔH at 10m	0.150	0.150
Static Pressure at 10m (atm)	1.04	0.75
Fractional ΔH at 0.8 atm	0.142	0.182
Length at 0.8 atm (m)	9.5	18.2
Isentropic Efficiency	0.551	0.789

Fig. 5 Plasma conductivity as a function of enthalpy extraction for generators with differing degrees of oxygen enrichment and identical combustor conductivities. The dots denote 1 meter points along the channel.

Fig. 6 Channel area with channel length for the three baseline channels of Table 4.

curve is actually a slightly rounded maximum and can be explained by consulting Eq. (1). There, it can be seen that the rate of change of velocity is given by the sum of two terms. Since the pressure is monotonically decreasing, due to expansion and cooling, the first term is always positive, while since the load factor K is less than one, the second term is always negative. Further, since the pressure versus length profile is concave upward, the pressure derivative in Eq. (1) is decreasing in magnitude with length. The second term also decreases, due to the dependence on conductivity and eventually on magnetic field, but if its decrease is slower than that of the pressure term, the sign of the rate of change of velocity will reverse, causing a maximum. Neither maximum actually reaches Mach 1, although the one for pure air comes perilously close. The relative fractional enthalpy extraction curves closely parallel the Mach number curves. This can be understood by examining Eq. (2) for rate of enthalpy change, in which for small deviations from constant velocity and similar conductivity profiles, the difference in enthalpy extraction rates is simply proportional to the difference in flow velocities.

Fig. 7 Channel parameters for 0% oxygen combustor exhausting into channel designed for 20% enrichment, for constant load factor of 0.6.

Fig. 8 Channel parameters for 40% oxygen combustor exhausting into channel designed for 20% enrichment, for constant load factor of 0.616.

The second set of entries in Table 4 shows that enthalpy extraction behavior for both cases is now in an acceptable range, although still much poorer than that obtained in channels obeying the constant velocity condition. The isentropic efficiency in both cases is now below the minimum expected value for constant velocity channels of the load factor. There are other problems, such as in the 40% case where a low extraction rate at the back end of the channel results in an unacceptably long distance to reach 0.8 atm exit pressure. (It must be noted that the channel profile specified beyond 10m is not that which would cause the 20% enriched mixture to maintain a constant velocity, but rather a linear extrapolation of the slope at 10m. In fact, the curves in Fig. 6 are slightly concave upward even at 10m, closer to a linearly increasing channel width than a linearly increasing area, but the question of how to best accommodate an arbitrarily imposed area profile is still an interesting one.)

Finally, we wish to answer by example the question of whether one can do still better, for instance in enthalpy extracted in a given length, by varying the load factor along the channel. The criterion of extraction in a given length is an appropriate one here, since we are imagining the situation of an existing channel with given dimensions. The last section of Table 4 together with Figs. 9 and 10 show that by tailoring the load factor to bring the generators closer to constant velocity operation, the enthalpy extraction at 10m, as well as the length required to reach 0.8 atm, have both been improved. Additionally, both channel velocities do not approach Mach 1 as closely as those in Figs. 7 and 8. However, in the case of 0%

enrichment, the efficiency is lower. This is because, to a degree which is invisible on the scale of Figs. 7 and 9, the tailored channel does worse than the constant load factor channel until almost 10m, when it finally reaches a higher enthalpy extraction rate. Therefore, the constant load factor channel does more work at higher temperatures and is more efficient. The opposite situation obtains in comparing Figs. 8 and 10, where the tailored load factor case extracts considerably more between 5 and 7m, and then loses most of its advantage between 7 and 9m. Again, doing work at higher temperatures and pressures results in more efficient operation.

V. Conclusions

This paper set out to address two questions. The first was, given the freedom to design the most efficient MHD channel, whether use of air preheat or oxygen enrichment offer any advantage in terms of enthalpy extraction. The calculations presented here support the conclusion that equal extraction can be easily obtained with any degree of enrichment, and that choices between preheated air and oxygen enrichment will be based on economic considerations which are outside the scope of the present paper.

The second question is, given an existing channel intended as a test bed, whether substantial differences in performance will be encountered upon changing the degree of oxygen enrichment. Here the answer is clearly yes, even though by the first conclusion these differences could be removed by redesigning the channel. Therefore, the lesson is

Fig. 9 Channel parameters for 0% oxygen combustor exhausting into channel designed for 20% enrichment, with tailored load factor.

Fig. 10 Channel parameters for 40% oxygen combustor exhausting into channel designed for 20% enrichment, for load factor constant at 0.815 to 8m, then increasing linearly to 0.82 at 10m.

that test data obtained by varying the degree of oxygen enrichment must be compared to theoretical analyses of the expected performance in each case, and not to each other.

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4. MODEL VALIDATION MEASUREMENTS

4.1 Mass Spectrometer Upgrade

During this quarter, construction of the redesigned vacuum system was completed and checkout of the mass spectrometer was begun. Improvements which were expected to improve sensitivity included a shorter beam path, larger skimmer orifice, interchanging of pumps, and inserting a cold plate to improve the vacuum in the mass spectrometer chamber. Additional modifications resulted in a vacuum system which is easier to align and service. In addition, the mass spectrometer has been reconfigured for a maximum mass of 250 amu, resulting in larger signals for the same resolution. Detailed descriptions of changes can be found in earlier quarterly reports.

Preliminary checkouts indicate that additional sensitivity has indeed been obtained. Typical pressures in the three vacuum chambers when sampling from room-temperature air are now 1×10^{-3} , 8×10^{-5} , and 3×10^{-7} torr (with a lower limit in the mass spectrometer chamber of 1×10^{-7} with the cold plate in use), as compared to 1×10^{-3} , 1.4×10^{-4} , and 5×10^{-7} with the original system. Thus, pumping in both the inner two chambers has been improved. In the intermediate chamber, which now has a smaller pump, this has been achieved by larger ducts. In the mass spectrometer chamber now equipped with the larger pump, vacuum around the ionizer should be improved more than indicated by the gauge pressure, due to a shorter distance to the pump.

Mass scans showing sensitivity to neutral species in a room-temperature air beam and in combustion gases are shown in Figures 4.1 and 4.2. Ratioing the peaks at mass 36 and 38 to the argon peak at 40 gives the appropriate isotopic ratios of 3.4×10^{-3} and 6.3×10^{-4} . Since argon is 1% of air and the signal-to-noise ratio is about 10, this clearly indicates sensitivity to less than one part per million even in combustion gas, a sensitivity superior to that attained with the previous vacuum system.

Figure 4.1. Mass Spectrometer Scans of Room Temperature Air Beams, With Increasing Sensitivity.

Figure 4.2. Mass Spectrometer Scans of Combustion Gas Beam, With Increasing Sensitivity. Burner conditions are methane and air only, equivalence ratio 1.0, temperature 1850°K.

The mass peak at 37 in the room temperature scan is $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$. This cluster is clearly unstable in the higher temperature beam of combustion gas, and is not observed in Figure 4.2. However, in room-temperature air, successive cluster ions are observed up to the high mass limit. These clusters provide a convenient (every 18 mass units) calibration of mass tuning.

In addition to checkout of the rebuilt mass spectrometer, combustion gas sampling experiments directed at certain gas-phase neutral molecules, KPO_2 and KPO_3 , which may be of substantial importance in MHD systems were initiated. To understand their importance, we note that experiments have shown the existence of very stable phosphorus negative ions, PO_2^- at AeroChem⁽⁴⁻¹⁾ and PO_3^- at Aerodyne.⁽⁴⁻²⁾ Furthermore, when these ions and phosphorus oxide neutrals are included in MHD generator performance modeling calculations,⁽⁴⁻³⁾ they have a large negative effect on plasma conductivity and on enthalpy extraction efficiency. Phosphorus negative ions have the greatest effect on generator efficiency, even though other ions are formed from more abundant components of coal ash. In contrast to model predictions, a recent experiment in a laboratory MHD channel at Stanford⁽⁴⁻⁴⁾ has shown that, under MHD conditions (high potassium loading, for instance), the addition of phosphorus, even in amounts much greater than those found in coal, has a much smaller effect on electron concentration and conductivity than would be predicted by the above modeling.

Recently, the discovery of very stable lithium and sodium phosphate gas-phase molecules⁽⁴⁻⁵⁾ prompted the suggestion that similarly stable potassium molecules could dominate phosphorus gas phase chemistry under high potassium loading conditions like those in Ref. (4-4), while still allowing observation of abundant phosphorus negative ion production when potassium and phosphorus concentrations are roughly equivalent (as in Ref. 4-1). Modeling of both the AeroChem and Stanford experiments, using a KPO_2 model based on the known properties of KBO_2 indicated that such a molecule not only would be important, but could indeed provide a resolution of the seeming discrepancy in the effect of phosphorus addition on plasma electron concentrations.

With this background, experiments were performed measuring the height of mass peaks appropriate to KOH , KPO_2 , and KPO_3 upon addition of powdered H_2KPO_4 to the combustion gas. In these very preliminary experiments, all three peaks were seen at roughly the same intensity (less than 10 ppm), with apparently more KPO_3 than KPO_2 . More experiments using different seed materials and burner conditions are planned to confirm these observations.

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5. AN UNSTEADY, TWO-DIMENSIONAL STUDY OF MHD ARCS

5.1 Introduction

There are two basic components in an arc discharge, namely, the spot and the column. In the case of an MHD electrode operating in an arcing mode, the column is replaced by the main body of the plasma, but the "funnel" which collects current from an arc of the core and feeds it through the boundary layer to the spot, is still present. Any attempt to understand arcing phenomena and their effects, necessarily has to pay attention to both the spot and the funnel, since both play dominant roles in one or another aspect of the discharge.

The spot phenomena are related to the microscopic physics of the last few mean free paths above the electrode surface, as well as the physics of the surface itself. Charge carrier generation and sheath formation are the two main effects controlling the spot behavior. We have dealt with some of the aspects of these phenomena in our earlier work,^(1,2) particularly regarding anodic near-wall effects. The case of the anode is simplified by the fact that the wall can be (and usually is) a passive element, the ion flux being entirely generated in the gas phase (but very near the wall). By contrast, the cathode spot is an active region, emitting the electrons needed for the discharge; thus, cathode spot models⁽³⁾ are complex, numerous, and not yet well developed.

The funnel behavior has received comparatively little attention in the literature. Most models of MHD arcs⁽⁴⁾ calculate the funnel impedance by approximating it as a conical (or other geometrically simple shape) region connecting arc to spot. Yet, an accurate estimation of the funnel impedance is important on at least two accounts:

(a) Most of the macroscopic voltage drops actually measured in MHD electrodes can be ascribed directly to the funnel resistance. Thus, the funnel controls one of the most basic loss mechanisms of MHD generators.

(b) The size of individual arcs (or the number of arcs per electrode) is controlled by the funnel ballasting action. Basically, arc coalescence is expected if the combined spot-funnel voltage-current characteristic has a negative slope; as more current is collected per spot, the funnel contribution to the arc voltage drop increases, and coalescence is inhibited when enough ballasting is present to make $dV/dI \approx 0$ for each arc.

In addition to these effects, a still unresolved issue is whether MHD arcs are steady (or quasi-steady) phenomena or, on the contrary, they must of necessity fluctuate at high frequency. The experimental evidence is that large amplitude fluctuations at frequencies from tens of kilohertz to near-megahertz are indeed associated with arcing regimes,⁽⁵⁾ but the mechanism or mechanisms for these oscillations have not been identified. This is a serious situation, since practically all attempts at arc modelling in the past have assumed steady conditions.

5.2 Model Assumptions and Formulation

We have initiated work on the construction of a numerical model for the funnel of an MHD arc that will attempt to address these questions. First, the time variability is allowed in the model, at least to the extent that the fluid-dynamic equations retain their unsteady terms. Thus, the most obvious cause for unsteadiness, i.e., intermittent arc flowing by the high speed plasma flow, will be studied. Unsteady effects related to the electrical part of the phenomena are not included at this time; however, once some basic solutions are available, phenomena such as ionization-recombination kinetics can be addressed. Obviously, the "spot" itself can contribute its share to unsteadiness (sheath oscillations for example), but these are outside the scope of our model.

The three-dimensionality of an arc funnel attached to a small spot and being flown downstream by a gas flow with the characteristic boundary layer shear is apparent. We have examined the feasibility of a fully three-dimensional time-varying simulation of the arc region, and concluded that, although possible in principle, such a model would be at present very expensive in terms of machine time. It seems therefore advisable to limit the simulation to a fictitious two-dimensional arc; the main effect lost by this simplification is the additional mixing, drag and cooling occurring through the third dimension of the funnel. We hope to recover at least some of these effects by suitable alterations in the viscous and mixing terms of the transport equations. One additional potential problem due to the two-dimensionality of the model relates to spurious inter-arc effects. In order to ensure a finite current collection per spot, we impose periodic boundary conditions in the flow direction, the period being dictated by the core current density and the current per arc. This approximates the real situation in an electrode wall where many arcs coexist at a given time, except that the wake of any one arc is unlikely to affect arcs downstream of itself. In the numerical simulation, such wake impingement is to be expected, however, and we are seeking methods to minimize its distorting effects.

The first version of our model will assume zero magnetic field. This considerably simplifies the fluid-dynamic problem, while still retaining many fundamental aspects of the problem; also, experiments on MHD arcs have actually been performed most often in test rigs without a magnet, so that comparison to a body of data is possible. One obvious aspect of the problem that is missed is the questions of whether a force balance is established between drag and Lorentz force on the arc. Such a balance has been postulated in some past models, but its physical basis appears tenuous. In particular, arcing in zero magnetic field is totally ignored by these models.

The funnel is assumed to occur inside a turbulent boundary layer, whose equations of motion are solved as part of the model. For this purpose, a simple mixing-length turbulence model is used, including a laminar sublayer. Since the presence of the slanted wedge of hot arc gas is expected to deflect the flowing plasma transversally to the wall, the pressure is allowed to vary across the boundary layer in response to inertial forces; lateral viscous force is still ignored, though.

The plasma is modeled as an equilibrium ionized gas. The assumptions of Saha equilibrium and electron temperature equilibrium are adopted for simplicity only, and their validity must be monitored in light of the results; preliminary estimates do seem to validate them in the funnel region. The existence of an arc spot on the surface can be modeled in at least two ways:

- (a) By imposing insulating conditions over most of the electrode surface, but conducting conditions on a small area (spot).
- (b) By imposing a moderate temperature over most of the surface of the electrode, but a very high temperature on the spot area.

Both of these models are obvious idealizations, but it would seem that model (a) is more representative of cathode spots (which are essentially sources of electrons surrounded by non-emitting areas), while model (b) tends to represent anodic spots (which are basically electrothermally constricted plasma regions). Both models will be studied in our work.

Following the above discussion, the sets of equations we used are:

Fluid

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial y} (\rho v) = 0 \quad (1)$$

$$\frac{\partial}{\partial t} (\rho u) + \frac{\partial}{\partial x} (\rho uu) + \frac{\partial}{\partial y} (\rho uv) + \frac{\partial p}{\partial x} = \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \quad (2)$$

$$\frac{\partial}{\partial t} (\rho v) + \frac{\partial}{\partial x} (\rho uv) + \frac{\partial}{\partial y} (\rho vv) + \frac{\partial p}{\partial y} = 0 \quad (3)$$

$$\begin{aligned} \frac{\partial}{\partial t} (\rho h_o) + \frac{\partial}{\partial x} (\rho u h_o) + \frac{\partial}{\partial y} (\rho v h_o) &= \frac{\partial}{\partial x} \left(k \frac{\partial T_o}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T_o}{\partial y} \right) \\ &+ \underline{E} \cdot \underline{J} \end{aligned} \quad (4)$$

where h_o and T_o are the total enthalpy and temperature, assuming $P_r \simeq 1$.

$$h_o = h + (u^2 + v^2)/2 \quad (5)$$

The equations of state are

$$p/\rho = R_g T \quad (6)$$

where R_g is assumed to be approximately constant, and

$$h = h(p, T) \quad (7)$$

from thermodynamic equilibrium data fitting. Depending on the distance from the wall, the viscosity μ can take its laminar value or a turbulent one. We use a simple mixing length model

$$\mu = \begin{cases} \mu_{\text{laminar}}(T) & \text{for } y < y_L \\ \rho \ell^2 \left| \frac{\partial u}{\partial y} \right| & \text{for } y_L < y < \delta \end{cases} \quad (8)$$

Here the laminar sublayer y_L is at $y^+ = 10$ where y^+ is the usual reduced variable $y^+ = \rho_w u^* y / \mu_w$. The mixing length ℓ is modelled by

$$\ell = \begin{cases} 0.4y & y_L < y < 0.225\delta \\ 0.09 & 0.225\delta < y < \delta \\ 0 & \delta < y \end{cases} \quad (9)$$

The thermal conductivity k is given by Reynolds analogy

$$k = \frac{\mu c_p}{P_r}, \quad P_r \sim 0.9 \quad (10)$$

Electrodynamics

$$\underline{J} = \sigma \underline{E} \quad (11)$$

$$\nabla \cdot \underline{J} = 0 \quad (12)$$

$$\underline{E} = -\nabla\phi \quad (13)$$

where the conductivity, σ , is assumed to be a given function of pressure and temperature.

$$\sigma = \sigma(p, T) \quad (14)$$

The boundary conditions far away from the wall are $u = u_\infty$, $v = 0$, $T = T_\infty$, $P = P_\infty(x)$, $\frac{\partial\phi}{\partial y} = -E_{y_\infty}$, $\frac{\partial\phi}{\partial x} = 0$. The last two conditions are due to the assumption of no magnetic field. At the electrode the spot is governed by

the heat transfer and current transport inside the electrode, i.e., one has to solve for both the temperature and the current distribution on the electrode from its resistivity and thermal conductivity distribution, together with the external ballasting and heat removal constraints. To simplify the computation while maintaining the physical features of the discharge, we do not solve for the temperature and current distribution on the electrode, but examine instead two choices of boundary conditions. (a) We can assume that conductivity is concentrated in a spot, i.e., $J_y = 0$ outside the spot, and $\phi = 0$ on the spot. The temperature of the electrode is kept uniform. This case is representative of cathode spots where thermal emission of electrons dominates the sheath conduction process. (b) Alternatively, we can assume that the spot is on an electrode at equal potential, ($\phi = 0$) everywhere on the surface, and initiate the spot by imposing a nonuniform temperature distribution. Since the conductivity, σ , is a very sensitive function of temperature, and current tends to flow along the path of least resistance, the current is automatically anchored on the hot spot. This case is representative of an anode discharge where the conduction electrons are provided by the thermally ionized plasma.

The upstream/downstream boundary conditions are the periodicity in all the variables except for p , with $\frac{\partial p}{\partial x}$ periodic instead. The length scale L for periodicity is determined by

$$I = \sigma_{\infty} E_{y_{\infty}} L \quad (15)$$

where I is the current per "strip" of electrode.

Equations (1) through (13) are solved numerically by finite difference schemes. Since the fluid mechanics part of the problem only influences the electrodynamics through the electrical conductivity σ , it is convenient to split the solution into two steps, separating the electrodynamics and the fluid mechanics.

In the electrodynamics calculation, we assume that the electric conductivity $\sigma = \sigma(p(x, y), T(x, y))$ is known from the solution to the fluid equations (Eqs. 1-10) in the previous computation step. Then the electrodynamic equations (Eqs. 11-13) may be simplified to a modified Poisson equation.

$$\sigma \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) + \frac{\partial \sigma}{\partial x} \frac{\partial \phi}{\partial x} + \frac{\partial \sigma}{\partial y} \frac{\partial \phi}{\partial y} = 0 \quad (15)$$

This equation is linear in ϕ since σ is known. A line relaxation scheme is used for solving Eq. (15),

$$\begin{aligned} \phi^{n+1} = & \phi^n + \sigma(\Delta_x^2 \phi^{n+1} + \Delta_y^2 \phi^n) \\ & + \left(\Delta_x^0 \sigma \right) \left(\Delta_x^0 \phi^{n+1} \right) + \left(\Delta_y^0 \sigma \right) \left(\Delta_y^0 \phi^n \right) \end{aligned} \quad (16)$$

The Δ_x^2 , Δ_y^2 , Δ_x^0 , Δ_y^0 are the usual second order accurate centered difference operators. The boundary condition at the outer edge of the domain and at the wall are put in explicitly. The periodic boundary condition in x can be incorporated into the implicit Eq. (16) and the resultant tridiagonal block matrix equation may be solved in a manner described in reference (6) (see especially the appendix for detail). This method will not be described here.

The temporal variation of the system is contained in the fluid equations (Eqs. 1 - 10). This set of equations is identical to the usual fluid equations for compressible flow except for the Ohmic heating term in the energy equation.⁽⁷⁾ Since both $\underline{J}$ and $\underline{E}$ are assumed to be known in this step, the $\underline{J} \cdot \underline{E}$ term does not present any computational difficulty.

The set of equations is cast into the following conservative form:

$$\partial_{\underline{t}} \underline{U} + \partial_{\underline{x}} \underline{F} + \partial_{\underline{y}} \underline{G} = \partial_{\underline{x}} \underline{V} + \partial_{\underline{y}} \underline{W} + \underline{\Omega} \quad (16)$$

where

$$\underline{F} = \begin{bmatrix} \rho u \\ \rho u^2 + p \\ \rho uv \\ (e+p)u \end{bmatrix} = \begin{bmatrix} \dot{m} \\ (\dot{m}^2/\rho) + p \\ \dot{m}\dot{n}/\rho \\ (e+p)\dot{m}/\rho \end{bmatrix} \quad \underline{G} = \begin{bmatrix} \rho v \\ \rho uv \\ \rho v^2 + p \\ (e+p)v \end{bmatrix} = \begin{bmatrix} \dot{n} \\ \dot{m}\dot{n}/\rho \\ (\dot{n}^2/\rho) + p \\ (e+p)\dot{n}/\rho \end{bmatrix}$$

$$\underline{U} = \begin{bmatrix} \rho \\ \rho u \\ \rho v \\ e \end{bmatrix} = \begin{bmatrix} \rho \\ \dot{m} \\ \dot{n} \\ e \end{bmatrix}$$

$$\underline{V} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ kT_{0x} \end{bmatrix}$$

$$\underline{W} = \begin{bmatrix} 0 \\ \mu u_y \\ 0 \\ kT_{0y} \end{bmatrix}$$

$$\underline{\Omega} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \underline{J} \cdot \underline{E} \end{bmatrix}$$

The equations are solved by an implicit approximate factorization scheme. The readers are referred to Reference (8) for the detail implementation.

5.3 Status of Two-Dimensional Arc Modeling

Currently, we have implemented and tested the electrodynamics calculation. We have stayed with Cartesian grids for simplicity so as to gain some experience on the computational scheme. Refined non-Cartesian grids may be used in the future to improve resolution and efficiency. The fluid mechanics code is under development and we expect to have a running version in the next quarter.

5.4 References

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5.5 Parametric Calculations Using a One-Dimensional Model

The structure of the discharge in the vicinity of the anode has been studied and the results used to estimate the electron-induced corrosion rate. The results of this study were presented at the 7th International Conference on MHD Electrical Power Generation. A reprint of this paper follows.

ELECTRON-INDUCED REACTION RATES IN THE
IMMEDIATE VICINITY OF ANODES

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Summary

We have studied the structure of the discharge at the vicinity of anodes and have estimated the electron induced corrosion rate. It was found that, as the current density is increased beyond the value that would saturate the anode in the absence of electron heating, a new active ionization region develops at the high field region immediately next to the wall. This is connected with the electron energy increase in response to the increasing field as the wall is approached, and, because of the steep dependence of ionization rate on electron energy, it leads to a value of the near-wall field which is essentially independent of current density, and is proportional to pressure and to the square root of the electron inelastic loss factor. Typical values for combustion gas are of the order of 10^5 V/m for 1 atm pressure ($E/n_{\text{gas}} \approx 3 \times 10^{-16}$ volt cm^2).

These values have been used in conjunction with published electron energy distributions in N_2 and N_2 -containing mixtures, and with literature values of the cross-sections for electron impact dissociation of H_2O , CO_2 , CO , O_2 , NO , and NO_2 to calculate an upper limit

for the rate at which potentially corrosive product species arrive at the anode surface. The most significant corrosive species production are the dissociative attachment of CO_2 , O_2 , and H_2O . On the basis of these results, it appears that the highest surface corrosion rate attributable to these gaseous species does not exceed 1 $\mu\text{g}/\text{coul}$ and cannot therefore explain measured corrosion rates in hot metallic electrodes (up to several hundred $\mu\text{g}/\text{coul}$). This supports the hypothesis of the presence of an electrolytic liquid or solid layer covering the electrode and being the seat of greatly accelerated corrosion processes.

Introduction

One of the lifetime-limiting factors for combustion-driven MHD generators with metallic electrodes is the high corrosion rates of anodes under current. Measured rates¹ range from 0.1 to several hundred $\mu\text{g}/\text{coul}$, depending on material and surface temperature. A possible contributor to this corrosion is the production of chemically reactive species at the high field region in the plasma immediately adjacent to the electrode surface. To adequately analyze this corrosion process, detailed modelling of the discharge boundary layer down to the last few mean free paths together with electron impact dissociation rate calculation is necessary. We have formulated a one dimensional electron ion transport model which includes the nonneutral sheath region, the ambipolar diffusion region, and the allowance for electron temperature nonequilibrium elevation. The resulting E/p values from this model are used together with electron impact dissociation cross section data to provide estimates of corrosion rate.

The 1-D Transport Model

In order to get an indication of the essential processes in the thin layer ($<100 \mu\text{m}$) over an anode, the one-dimensional formulation of the electron and ion

transport assumes the following: Constant electron and ion mobility, laminar conditions, no magnetic field, no convection, inert wall, electron-impact ionization, and electron as third body for recombination. In addition, in order to obtain reasonably simple solutions, the gas temperature was taken to be constant in the layer considered, although the electron temperature was allowed to respond to the electric field. Since the significant phenomena are seen to occur very near the wall (in the last few mean free paths) where the field dominates over thermal effects and the electron energy is decoupled from the gas energy, the errors introduced are not thought to be essential. Similar calculation by

Okazaki et al.² with a laminar thermal boundary layer arrives at values of the wall electric field of the order of 10^5 V/m, in close agreement with our result.

In nondimensional form, the equations of electron and ion transport, Poisson's equation, ion conservation, and electron energy are easily found to be as follows:

$$\theta \frac{dv_e}{d\xi} = 1 + \epsilon(1 - \gamma_1) - n v_e \quad (1)$$

$$\frac{dv_i}{d\xi} = -\gamma_1 + n v_i \quad (2)$$

$$\frac{dn}{d\xi} = p_4(v_i - v_e) \quad (3)$$

$$\frac{d\gamma_1}{d\xi} = p_5 \left(\frac{\alpha}{\alpha_\infty} \right) v_e \left(v_e^{*2} - v_e v_i \right) \quad (4)$$

$$n = p_6 v_e (\theta - 1) / [1 + \epsilon(1 - \gamma_1)] \quad (5)$$

$$\frac{\alpha}{\alpha_\infty} = \left(\frac{\theta_\infty}{\theta} \right)^{9/2}; \quad \theta_\infty = 1 + \frac{1}{p_6} \quad (6)$$

$$v_e^{*2} = \left(\frac{\theta}{\theta_\infty} \right)^{3/2} e^{-Y[(1/\theta) - (1/\theta_\infty)]};$$

$$Y = \frac{e v_i}{kT} \quad (7)$$

where the nondimensional variables are: $\theta = T_e/T_{e_\infty}$,

$v_e = n_e/n_\infty$, $v_i = n_i/n_\infty$, $\xi = e E_\infty x / dT$, $n = E/E_\infty$, $\gamma_1 = j_1/(j_1)_\infty$, and $\epsilon = \mu_i/\mu_e$. The subscript ∞ refers to conditions far away from the electrode. The parameters p_4 , p_5 , and p_6 are

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$$p_4 = \frac{n_\infty kT}{\epsilon_0 E_\infty^2}, \quad p_5 = \frac{kT \alpha n_\infty^2}{e \mu_1 E_\infty^2}, \quad p_6 = \frac{3}{2} \frac{\delta v_{e, \text{coll}} kT}{e \mu_e E_\infty^2}.$$

Here, μ_e and μ_1 are the electron and ion mobilities, so that $\epsilon \sim 0.004$, n_∞ is the electron and ion densities in the equilibrium bulk, $\alpha = 1.09 \times 10^{20}/T_e^{9/2}$ is the Hinov-Hirschberg ionization rate constant, and δ is the electron inelastic loss factor (equal to $2 m_e/m_g$ for purely elastic collisions).

The normalization is chosen such that $v_e(\infty) = v_1(\infty) = \gamma_1(\infty) = \gamma(\infty) = 1$. Since the point at infinity is a singularity of the system of differential Eqs. (1) through (4), the above conditions are met asymptotically, and are seen to be equivalent to only two boundary conditions, leaving two others to be satisfied at the wall. These are the continuity of electron and ion currents with the retarded wall random flux values. Since the collisionless sheath is thin (one m.f.p.), we assume the corresponding sheath voltage drop is simply the product of the wall field and the m.f.p. Thus, depending on whether the wall repels electrons or ions, we have at the wall

$$\left. \begin{aligned} \gamma_1 &= -\frac{v_1}{4M} \\ \gamma_e &= 1 + \epsilon(1 - \gamma_1) = \frac{v_e}{4M} e^{\tilde{\lambda}\eta} \end{aligned} \right\} \text{when } \eta_w < 0 \quad (8)$$

$$\left. \begin{aligned} \gamma_e &= 1 + \epsilon(1 - \gamma_1) = \frac{v_e}{4M} \\ \gamma_1 &= -\frac{v_1}{4M} e^{-\tilde{\lambda}\eta} \end{aligned} \right\} \text{when } \eta_w > 0 \quad (9)$$

where M is a sort of electron Mach number,

$$M = \frac{v_e E_\infty}{c_e}, \quad \tilde{c}_e = \sqrt{\frac{8}{\pi} \frac{kT}{m_e}}$$

and

$$\tilde{\lambda} = \frac{eE_\infty \lambda}{kT}, \quad \text{with } \lambda = \text{electron m.f.p.}$$

Structure of the Anode Layer

Far away from the wall $v_e = v_1$ and $\theta \approx 1$, so the system reduces to

$$2 \frac{dv}{d\xi} = (1 + \epsilon)(1 - \gamma_1)$$

$$\frac{d\gamma_1}{d\xi} = p_5 v(v^{*2} - v^2) \quad (10)$$

with the solution given by

$$v = \tanh(R(\xi - \xi_1)) \quad (11)$$

where $R = \sqrt{(1 + \epsilon)p_5/4}$. The characteristic nondimensional length scale, reflecting a balance of diffusion and ionization rates is seen to be $\Delta\xi = 1/R$, which is proportional to E_∞/n_∞ . The corresponding physical length is then proportional to $1/n_\infty$.

At high enough currents near the wall, when field drive dominates over diffusion and (for anodes) $v_1 \ll v_e$, if θ is still assumed to be near unity (namely T_e near $T_g = T$, which is a progressively worse approximation as the wall is approached), then we have simply

$$\eta \approx 1/v_e; \quad \frac{d\eta}{d\xi} = -p_4 v_e \quad (12)$$

which has the solution

$$\eta^2 = \eta_w^2 - 2p_4 \xi \quad (13)$$

Here, the characteristic dimensionless length is $\Delta\xi = \eta_w^2/2p_4$, and it represents the shielding distance for the wall field $\eta_w E_\infty$, or the collisional sheath thickness. Separating these regions, there is a thin transition layer where v_1 falls from v_e to much lower values.

The near-wall end of the collisional sheath is marked by the field reaching values high enough to trigger ionization despite the low electron density prevailing there. Thus, at high current densities, there are two regions of ionization. The first of them, towards the bulk side of the diffusion layer, supplies the ions needed to accompany the electrons in their ambipolar diffusion towards the wall. If the electron temperature is assumed to remain equal to T_g , the current to the anode would saturate at a value dictated by the maximum production rate of ions in this first ionization layer. From an analysis of Eq. (10), it is found that this current saturation happens when the parameter R decreases to the limiting value of

$$R = R_{\text{sat}} = 1/2 [1 - 16M^2(1 + \epsilon)^2] \approx 1/2 \quad (14)$$

which implies a current level of

$$j = j_{\text{sat}} = \sqrt{\frac{e \mu_e^2 (1 + \epsilon)^3}{\mu_1}} kT \alpha n_\infty^2 [1 - 16M^2(1 + \epsilon)^2] \quad (15)$$

Because of Saha's equation, this saturation current is very sensitive to T , and becomes low at even moderate near-wall temperatures (0.03 A/cm^2 at 2000°K for instance, but 3 A/cm^2 at 2500°K).

As this limiting current is approached, however, high fields develop near the wall, and the second ionization region eventually appears when the electron temperature reaches a critical value, which is not very sensitive to current, since the ionization rate is exponential in θ . This new ionizing region supplements the ionization produced in the first layer until enough ions are produced to satisfy the wall conditions; in particular, γ_1 must, at the very least, become negative, since the wall cannot (by assumption) supply ions. The preceding

ideas can be given analytical form in order to obtain approximate formulae for the limiting values of the field and the electron temperature elevation (at the wall). One obtains

$$\eta_w = \sqrt{p_6(1-R)(\theta_w-1)} \quad (16)$$

where

$$\frac{\theta_w-1}{\theta_w} = \frac{1}{Y} \ln \left[\frac{4R(1-2R)}{1-R} \frac{p_4 \theta_w^3}{f \eta_w} \right] \quad (17)$$

and f is a somewhat arbitrary small factor (f is the nondimensional length over which the ion current γ_1 drops out), $f = 0.01$ seems adequate. Eqs. (16) and (17) are coupled expressions for η_w and θ_w , but because of the logarithmic factor in Eq. (17), and since $R \ll 1/2$ in this regime, the main dependence for the wall field is $\eta_w \sim \sqrt{p_6}$, or $E_w \sim E_m \sqrt{p_6}$.

From the definition of p_6 , we see that E_w is, to a first approximation, independent of E_m and of n_m .

Inserting well known kinetic theory expressions for v_e and $v_{e, \text{coll}}$, we obtain a simple approximate formula for E/p at the wall:

$$\frac{E_w}{p} = \sqrt{\frac{24}{\pi}} \delta \cdot \frac{Q_{eg}}{e} \sqrt{\frac{(1-R)}{2} (\theta_w-1)} \quad (18)$$

where Q_{eg} is the momentum-transfer cross section for electron-gas collisions. A good first guess is $\theta_w \approx 2$, $R \approx 0$. Thus, a quasi-universal E/p is seen to prevail near the anode for a given gas mixture. For products of combustion in air, N_2 is the species that dominates momentum transfer, and $Q_{eg} \approx 30A^2$, with only moderate variability. At the higher fields ($E/n_{\text{gas}} \geq 10^{16}/\text{cm}^2$), N_2 also dominates the inelastic electron losses, as can be seen by inspection of Nighan's results³, and δ reaches values of about 0.085 when $kT_e/e = 1$ eV (corresponding to $E/n_{\text{gas}} \approx 5 \times 10^{-16}$). Inserting these values in Eq. (18), we obtain $E_w/p = 1(\text{V/m})/(N/\text{m}^2)$, or $E_w = 10^5$ V/m at one atm pressure.

Another consequence of the near-wall ionization layer is that the near-wall voltage drop (sheath plus ambipolar plus resistive; but not including the drop due simply to the low near-wall temperatures, which is the one usually calculated with equilibrium assumptions), also tends to saturate at a limiting value

$$\left(\frac{e\Delta V}{kT} \right)_{\text{sat}} \approx \frac{1-R}{R} \ln \left(\frac{\eta_w}{1-R} \right) \quad (19)$$

which is approximately equal to the product of E_m and the thickness of the diffusion layer.

Numerical Solutions of the Model Equations

The Gear method is used to integrate Eqs. (1) - (4) backwards towards the wall. An analytically derived

asymptotic ratio of γ_1 to v_e is used to step the solution away from the asymptotes. The detailed process is described in Ref. (4). Because of the stiffness of the equations as represented by the ratio of the Debye length to the ionization diffusion length, charge neutrality is assumed for some distance until the implied field calculated from (the difference of) the ion and electron transport equations becomes significant. At that point, a sweep is made of the value of $v_e - v_1$, while the other variables (η , γ_1 , v_1) are initialized at the level given by the outer neutral solution. Integration of the full set to where either $\gamma_1 = -v_1/4M$ or $\gamma_e = 1 + e(1-\gamma_1) = v_e/4M$ is satisfied, is then carried out for each starting $v_1 - v_e$, and the field, η , at that point is compared to the value required for retarding the other species, i.e., either $\eta = \ln(4M \gamma_e/v_e)/\tilde{\lambda}$ or $\eta = \ln(-4M \gamma_1/v_1)/\tilde{\lambda}$, respectively. When these values of η coincide, a solution has been found.

Figure 1 shows typical electron temperature and ionization rate profiles. At low current density ($200A/m^2$), the ionization peak is located at the outer ionization-diffusion region while the electron temperature stays close to the gas temperature (2000°K) throughout the boundary layer. As current increases beyond "saturation", the electron temperature increases towards the wall and a second ionization region appears at the vicinity of the anode. This confirms the analytical description of the previous section. Typical special distributions of the field, electron, and ion densities are shown in Fig. 2.

Fig. 1. Electron Temperature and Ionization Rate Profiles at $T_{\text{gas}} = 2000^\circ\text{K}$. The "saturation" Current for This T is $280 A/m^2$.

Fig. 2. Field and Density Profiles at $T_{\text{gas}} = 2000^{\circ}\text{K}$, $J = 275 \text{ A/m}^2$.

For currents higher than "saturation", the argument in the last section indicates that a limiting field value E_w at the wall is expected. Figure 3 shows $T_g = 2000^{\circ}\text{K}$, the flattening of E_w versus J at about $0.8 \times 10^5 \text{ V/m}$. At a higher temperature, the current saturation level is much higher, but the same leveling off of the wall field is observed (Fig. 4). As anticipated, E_w is about the same for the two temperatures, despite the large difference between the saturation currents, charge densities, and non-equilibrium layer thicknesses.

In Figs. 3 and 4, we also plot ΔV versus current. This is the difference between the wall voltage and what it would be if the field E_w were maintained to the wall. Since the model is with constant gas temperature, this ΔV does not include the most obvious contribution to voltage drop in a boundary layer, namely, the lower conductivity in the colder regions of the layer, even those where ionization equilibrium prevails. The reported ΔV is a measure of ambipolar plus sheath effects mostly.

Fig. 3. Field at Wall and Potential Drop Versus Current Density at $T_{\text{gas}} = 2000^{\circ}\text{K}$

Fig. 4. Field at Wall and Potential Drop Versus Current Density at $T_{\text{gas}} = 2500^{\circ}\text{K}$.

The "Saturation" Current Density For These Conditions is About $3 \times 10^4 \text{ A/m}^2$

Corrosion Rate Calculation

The corrosion rate can be estimated from the rate of formation of the corrosion species in the high field region near the wall. By assuming all the corrosive species arrive at the wall and react with the wall material, an upper limit on corrosion rate can be obtained. Since the high field region is typically adjacent to the free fall sheath, there is little recombination and the above estimate should be fairly realistic.

It is convenient to normalize the active species production rate to the ionization rate in this high field region, since they result from similar electron impact processes. The latter can be related directly to the total current density J by the ratio of the electron and ion mobility. If $\dot{n}_s$ and $\dot{n}_i$ are the rates of production of the corrosive species and ions, the flux Γ_s of the corrosive species would be:

$$\begin{aligned} \Gamma_s &= \frac{\dot{n}_s}{\dot{n}_i} \Gamma_i \\ &= \frac{\dot{n}_s}{\dot{n}_i} \frac{J}{e(1 + \mu_e/\mu_i)} \end{aligned} \quad (20)$$

where Γ_i is the ion flux. This expression relates Γ_s directly to the current density J .

The production rates $\dot{n}_s$ and $\dot{n}_i$ are obtained from the electron impact dissociation and ionization cross sections

$$\dot{n}_s = n_M n_e \int v Q_{eM} f(u) \sqrt{u} du \quad (21)$$

$$\dot{n}_i = n_K n_e \int v Q_{eK} f(u) \sqrt{u} du \quad (22)$$

Here, n_M is the concentration of the parent molecule giving rise to n_s ; n_e is the total electron concentration, n_K is the concentration of the potassium seed; Q_{eM} and Q_{eK} are the dissociation and ionization cross

sections, $f(u)$ is the electron distribution in the energy space with normalization $\int f(u) \sqrt{u} du = 1$, and v is the relative impact velocity. Note that the electron densities cancel out when Γ_s is evaluated.

For combustion products in air, N_2 , by its abundance and large vibrational cross section at 3 eV, is the dominant species in the electron energy loss process. Nighan³ has numerically computed the electron distribution function f for various E/n values. These distributions are folded into the cross section data discussed in the following to obtain the corrosive species production rate and the ionization rate.

The major parent species considered for active species productions are CO , CO_2 , NO , NO_2 , O_2 , and H_2O . In addition, we need cross section data for K ionization. From Nighan's results³ the range of energy of interest is from 0 to 20 eV.

For potassium ionization ($K + e \rightarrow K^+ + 2e$), the cross section rises sharply at 4.3 eV and reaches a value of $8 \times 10^{-16} \text{ cm}^2$ level up to 40 eV. This behavior is very different from that of the other dissociative processes to be discussed, which, in general, have well defined peaks in the 0 to 20 eV range.

The cross sections for the various dissociation processes are shown in Fig. 5. These data are obtained from References 5-7. The processes are: dissociative attachments of CO ($CO + e \rightarrow C + O^-$), CO_2 ($CO_2 + e \rightarrow CO + O^-$), NO ($NO + e \rightarrow N^+ + O^-$), NO_2 ($NO_2 + e \rightarrow NO + O^-$), O_2 ($O_2 + e \rightarrow O^- + O$), and H_2O ($H_2O + e \rightarrow H + OH^-$). Note that the cross section for H_2O is significantly higher than the rest of the parent species. This, together with the high H_2O contents of the combustion gas, makes OH^- the major active species.

The active species production rate is obtained from Eq. (21) by numerical integration using the cross section data discussed. The electron distribution functions are taken from Nighan's result³ with E/n values at 5, 8, and $15 \times 10^{-16} \text{ V cm}^2$. These E/n values are consistent with the values calculated in the one dimensional modeling at the ionization region near the anode wall. The mole fractions of the parent species are representative of coal combustion gas at the wall temperature of 1000°K. The parent species mole fractions are: $H_2O = 5.5 \times 10^{-2}$, $O_2 = 4.2 \times 10^{-2}$, $NO_2 = 1.4 \times 10^{-6}$, $NO = 1.5 \times 10^{-5}$, $CO_2 = 1.36 \times 10^{-1}$, and $CO = 10^{-3}$. In addition, the ionization rate Eq. (22) is also integrated numerically using the corresponding $f(u)$ and a potassium mole fraction of 0.0075 so as to obtain $\dot{n}_s/\dot{n}_K^+$ and the flux Γ_s of the active species as discussed previously.

The most significant active species production rate is found to result from the dissociative attachment of H_2O , CO_2 , and O_2 . The result of the calculation is shown in Fig. 6. For H_2O dissociative attachment, $\dot{n}_s/\dot{n}_K^+$ starts at a level of 2×10^{-2} at $E/n = 0.5 \times 10^{-15} \text{ V cm}^2$, drops to 1.3×10^{-2} at $E/n = 10^{-15} \text{ V cm}^2$, and stays at that level with increasing E/n . For O_2 and CO_2 dissociations, the $\dot{n}_s/\dot{n}_K^+$ values are comparable. They follow the same trend as in H_2O ,

Fig. 5. Electron Impact Cross Sections for Various Dissociative Attachment Processes

with values ranging from 0.6×10^{-2} at $E/n = 0.5 \times 10^{-15} \text{ V cm}^2$ to 0.4×10^{-2} for $E/n > 10^{-15} \text{ V cm}^2$.

The decrease of $\dot{n}_s/\dot{n}_K^+$ with increasing E/n may be explained as follows. As E/n increases, the population of electrons in the high energy tail of the distribution also increases. Having a relatively constant ionization cross section from 5 to 40 eV, the K^+ production rate increases rapidly with the increasing number of energetic electrons at high E/n . However, the dissociative attachment cross sections are localized at 6 to 10 eV, therefore, $\dot{n}_s$ is less sensitive to the increase of E/n . Hence, the ratio $\dot{n}_s/\dot{n}_K^+$ decreases with the increase of E/n .

To estimate a typical corrosion rate, it is hypothesized that a steel electrode is attacked by the OH^- from the H_2O dissociation to form $Fe(OH)_2$ (M.W. 90), and it is also attacked by the O^- and O from the CO_2 and O_2 dissociation to form FeO (M.W. 72). The flux of active species is related to the current density by Eq. (20). When Eq. (20) is normalized with respect to the current density J , the following corrosion rate is obtained:

$$\text{corrosion rate} = \frac{\left\{ \frac{(-\dot{n}_{H_2O})}{\dot{n}_K^+} \times 90 + \frac{2(-\dot{n}_{O_2})}{\dot{n}_K^+} + \frac{(-\dot{n}_{CO_2})}{\dot{n}_K^+} \right\}}{Ae(1 + \mu_e/\mu_i)} \quad (21)$$

(gm/coulomb)

Here, A is Avogadro's number, e the electron charge and μ_e and μ_i are the electron and ion mobilities.

Fig. 6. Ratio of Active Species Production Rate and Ionization Rate for Various Dissociative Attachment Processes as a Function of E/n

The calculated corrosion rates as a function of E/n are shown in Fig. 7. These rates are upper bounds because it has been assumed that there is no recombination of the active species. The total corrosion rate, of the order of 10^{-1} $\mu\text{gm/coulomb}$, is quite a bit lower than the corrosion rate of up to 100 $\mu\text{gm/coulomb}$ quoted in the literature.¹ Based on these results, it appears that the highest surface corrosion rate attributable to these gaseous species cannot explain the measured corrosion rates in hot metallic electrodes.

Fig. 7. Corrosion Rate as Function of E/n with Parent Species Typical of Combustion Gas at 1000°K and K Seed Mole Fractions = 0.0075

Conclusion

We have modeled the diffusive discharge process in the anode region, taking into account the ambipolar diffusion, ionization, space charge, and electron-molecule energy transfer effects. This discharge "boundary layer" has the general feature that there is an ionization region close to the edge of the layer. This is due to the ionization nonequilibrium set-up by the field depletion of the ions. At the vicinity of the wall, because the plasma has a lower conductivity, a high electric field tends to develop. This field causes an elevated electron temperature. As a result, there is a second ionization region close to the wall. This second region is especially prominent in high current situations.

Active species such as OH^- , O , and O^- can form in this second ionization region by dissociating molecules such as H_2O and CO_2 with the energetic electrons.

These active species, when they arrive at the wall, can react with the metallic electrode and cause corrosion. We have studied the active species production rate using E/n values and parent species typically encountered in a combustor gas driven MHD generator environment. With the published data on electronic dissociation cross sections, the most important parent species are H_2O , CO_2 , and O_2 . A corrosion rate of 0.1 $\mu\text{gm/coulomb}$ has been estimated. However, these rates are too low compared with the rate of up to 100 $\mu\text{gm/coulomb}$ observed in various MHD test generators. Hence, the gaseous phase corrosion processes do not seem to be the dominant cause of corrosion. This supports the hypothesis of the presence of an electrolytic liquid or solid layer covering the electrode being the seat of greatly accelerated corrosion processes.

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6. TEMPERATURE MEASUREMENTS USING THE CO ABSORPTION TECHNIQUE

During the past quarter, construction of the CO absorption temperature-monitoring device was completed. Using this device, the temperature profile of ARI's laboratory methane/coal burner was measured. This work was reported at the AIAA 13th Fluid and Plasma Dynamics Conference. A reprint of this paper follows.

6.1

TEMPERATURE PROFILE MEASUREMENTS USING CO LINE ABSORPTION AT DIFFERENT VIBRATIONAL LEVELS*

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Abstract

The temperature profile of a laboratory methane/coal burner is measured by taking the ratio of absorptions for a pair of CO vibration rotation lines with a tunable diode laser system. Assuming an axisymmetric temperature profile, a scan of the cross section of the burner provides an absorption profile which can be inverted into a radial temperature profile by Abel transformation. By selecting the vibrational levels of the CO absorption lines, different optical depths can be achieved in probing the flame. The feasibility of temperature profile measurement is demonstrated by measuring the temperature of a methane/coal burner using a second derivative system on the $P_{0(32)}$ and the $P_{2(21)}$ CO absorption lines.

I. Introduction

The gas temperature and temperature profile are important parameters in determining the performance of a combustor. Measurements of these parameters using thermocouples have the problem of thermocouple survival in high temperature oxidizing flames. Point measurements using optical techniques such as coherent anti-Stokes Raman Spectroscopy⁽¹⁾ require large optical access not often available in such furnaces. We use a line-of-sight optical technique and Abel inversion to obtain the temperature profile in a laboratory methane/coal burner.

The standard technique for the determination of flame temperature is to use sodium or potassium line reversal.⁽²⁻⁴⁾ When the optical depth becomes large, however, measurements become difficult because of the self-absorption in cold boundary layers. Line-of-sight measurements of temperature using CO vibrational line absorption^(5,6) has the advantage over line reversal techniques in that nonoptically black absorption lines can be chosen by selecting different vibrational transitions of CO. An additional advantage in using the CO absorption of radiation from a tunable diode laser is that this system can be used through a limited optical access by collimating the laser radiation.

We have measured gas temperature using the CO absorption technique in the wing of the $v = 0$ vibrational band and near the maximum of the $v = 2$ vibrational band in the presence of a cool boundary layer in an axisymmetric methane/coal burner. By making an Abel transformation on line-of-sight measurements across the flame, the temperature profile is obtained. In the following sections, we discuss the temperature sensitivity to vibration levels and present measurements made in our laboratory methane/coal burner together with thermocouple measurements for comparison.

II. Theory of Measurement

The technique of measuring temperature using the ratio of CO line absorption from two vibration rotation levels has been previously discussed.⁽⁶⁾ The two lines are typically chosen within 1 cm^{-1} from each other so that they can be scanned by the same mode of a tunable laser diode. For a homogeneous medium in thermal equilibrium, the ratio of the transmittance at the line center of the two neighboring lines, assuming that there is no line interference, is

$$\frac{\left[\ln(I/I_0)\right]_2}{\left[\ln(I/I_0)\right]_1} = \frac{S_2(T)}{S_1(T)} \quad (1)$$

where the ratio of the temperature dependent line strengths S_2/S_1 , is given by⁽⁷⁾

$$\frac{S_2}{S_1} = \frac{\{(v+1) G(J) N_{vJ}/[N(2J+1)]\}_2}{\{(v+1) G(J) N_{vJ}/[N(2J+1)]\}_1} \quad (2)$$

Here (v, J) are the lower state quantum numbers, $G(J) = J$ for a P branch transition and $J+1$ for an R branch transition, and N_{vJ}/N is the fractional Boltzmann distribution at temperature T . Therefore the temperature can be calculated from the ratio of the measured transmittance.

The temperature dependence of S_2/S_1 is contained in the Boltzmann factor N_{vJ}/N , for which the temperature sensitivity is given, to first order in v and J , by

$$\frac{d \ln(N_{vJ}/N)}{d \ln(T)} = -1 + J(J+1) \frac{hcB_v}{kT} + \frac{hc\omega_v}{kT} \left[v - \frac{\exp(-hc\omega_v/kT)}{1 - \exp(-hc\omega_v/kT)} \right] \quad (3)$$

This expression is a monotonically increasing function of both v and J , with a much larger dependence on v than on J . Contour plots of the temperature sensitivity (Eq. (3)) as a function of v and J values at 2000°K are shown in Fig. 1. High temperature sensitivity can be obtained by ratioing a high v, J line to a low v, J line. In practice, however, the absorption for the high v, J lines is very low, and trade offs must be made between high temperature sensitivity and measurement accuracy.

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Fig. 1 Temperature sensitivity ($d\ln(N_{v,J}/N)/d\ln T$) contours for various v , J CO lines at 2000°K.

Since the temperature sensitivity is much more sensitive to the vibrational level than to the J level of the CO lines, it is instructive to study the temperature dependence of the temperature sensitivity for various v by arbitrarily fixing $J = 2$. Such a dependence is shown in Fig. 2. The temperature sensitivity increases with increase in v and decreases with increase in temperature. Fortunately, as the temperature increases, more high v states are populated and the absorption, hence the signal-to-noise ratio of the absorption measurement for the high v lines, increases with increase in temperature. Therefore, optimal temperature sensitivity can be achieved by going to the highest v line with acceptable measurement accuracy.

Fig. 2 Temperature sensitivity at various temperatures for different v lines, $J = 2$.

We have developed a system using second derivative spectroscopy for our temperature measurement. Such a system, which suppresses the base line, can offer substantial improvement in accuracy over direct absorption measurements. It is straight forward

to show that the second derivative signal at the line center of a pressure broadened line is given by (8)

$$\left. \frac{d^2 I}{d\omega^2} \right|_{\omega_1} = \left(\frac{S_1 \chi p}{\pi} \frac{2}{b^3} \right) I I(\omega_1) \quad (4)$$

where S_1 is the line strength, χ the mole fraction of CO, p the pressure, b the line collisional half width and l the absorption path length. Hence,

$$\left(\frac{1}{I} \frac{d^2 I}{d\omega^2} \right)_{\omega_2} \left/ \left(\frac{1}{I} \frac{d^2 I}{d\omega^2} \right)_{\omega_1} \right. = S_2/S_1 \quad (5)$$

Similar to Eq. (1), Eq. (5) involves measurements of ratios and therefore, is self-calibrating if the measurements are made simultaneously. However, unlike Eq. (1), where the incident intensity $I_0(\omega)$ is required in the intensity ratio, Eq. (5) involves the transmitted intensity $I(\omega)$. The need for a reference beam measurement is thus eliminated. Line interference effects are minimized since the variation of the tail of the interfering line is usually small at the absorbing line. Similarly, effects of absorption and scattering due to presence of particulates is also minimized.⁽⁹⁾ The merits and signal-to-noise considerations of a second derivative system are discussed in Ref. (10). A lower limit of detectable absorption of 2×10^{-5} in a quiescent environment has been reported.⁽¹¹⁾ For absorption measurements in practical burner environments, the S/N is degraded by refractive index variations of the hot gas, turbulent temperature and CO concentration fluctuations of the flame, and the mechanical vibration of the optical components.

III. Temperature Profile Measurement

For a nonhomogeneous medium, Eq. (4) may be generalized as

$$\left. \frac{d^2 I}{d\omega^2} \right|_{\omega_1} = I(\omega_1) \int \frac{S_1 \chi p}{\pi} \frac{2}{b^3} dx \quad (6)$$

where the integration is evaluated along the line-of-sight. The measurement is, therefore, a convolution of the line strength and the line width profiles with the CO concentration profile.* A line-of-sight temperature may be calculated by direct application of Eq. (5), but the actual temperature can only be obtained by deconvoluting measurements at different line-of-sight positions.

A particularly simple, yet often encountered situation is an axisymmetric medium such as the hot gas in a cylindrical burner. In this case, (Fig. 3a), line-of-sight measurement at one position can be subtracted from a measurement at an adjacent position to yield information on the property of the medium at the differential optical path. This is formally expressed by the Abel transform which inverts the line-of-sight measurements $g(y)$ to the

* We assume that p is constant.

radial profile $f(r)$. Referring to Fig. 3b, the line-of-sight measurement is

$$g(y) = 2 \int_0^{\sqrt{1-y^2}} f[r(x,y)] dx \quad (7)$$

and the radial profile is then

$$f(r) = \frac{1}{\pi} \int_r^1 \frac{dg}{dy} \frac{dy}{\sqrt{y^2 - r^2}} \quad (8)$$

In the above equations, all lengths are normalized with respect to the radius of the burner. Applying Eq. (8) to Eq. (6), the values of Sx/b^2 for the two lines as a function of radius can be obtained. By ratioing the values obtained for each line, S_2/S_1 , and therefore the temperature can be obtained for each radial position. The details of the inversion process are presented in the Appendix.

Fig. 3(a) Illustration of the principle of Abel inversion; (b) geometry of Abel inversion.

IV. Selection of CO Absorption Lines

In applying the CO absorption line temperature measurement technique to large burners, the absorption for the low vibrational (v) rotational (J) lines at line-of-sight through the center of the burner are often black which renders accurate measurement difficult. This difficulty can be avoided either by using the absorption lines of the CO isotopes ($^{13}\text{C}^{16}\text{O}$ is 1.11% abundant and $^{12}\text{C}^{18}\text{O}$ is 0.2% abundant), or by using the higher v , J lines. Since the temperature measurement is most sensitive when the absorption from a high v , J line is ratioed to that of a low v , J line, the optimal line selection is therefore a high v , J absorption line of $^{12}\text{C}^{16}\text{O}$ combined with a low v , J absorption line of one of the isotopes.

Where the line-of-sight is close to the edge of the burner, however, there is little absorption for the high v , J lines because of the lower

temperature. Therefore, to measure temperature profiles accurately, it is necessary to use more than one pair of v , J lines. To illustrate this concept, consider a 5m radius burner (Fig. 4). Assume the line-of-sight temperature is 2000°K in position 1 and 1000°K in position 2. Also assume that there is 1% CO. If we use the line pair $P_4(9)$ of $^{12}\text{C}^{16}\text{O}$ (at 2003.17 cm^{-1}) and $P_0(23)$ of $^{13}\text{C}^{16}\text{O}$ (at 2003.52 cm^{-1}) the absorptions at position 1 are 42% and 47%. These are easily measurable numbers. However, the absorptions at position 2 become 0.08% and 20% respectively. Accurate measurement of the $P_4(9)$ line may be difficult. Alternatively, consider the line pair $P_0(16)$ of $^{13}\text{C}^{16}\text{O}$ (at 2033.42 cm^{-1}) and $P_1(2)$ of $^{12}\text{C}^{16}\text{O}$ (at 2034.15 cm^{-1}). The absorptions at position 2 are 5% and 83%, which are easily measurable. However, the absorptions at position 1 are 4% and 400%. The latter is optically black and not readily measurable. It is therefore necessary to use both line pairs for accurate temperature profile measurement.

Fig. 4 Line-of-sight positions

The additional constraint in selecting CO line pairs is that there are no interfering absorption lines from other molecules along the line-of-sight. Because of the very strong radiances from $\text{CO}_2(v_3)$ centered at 4.3 μm , and $\text{H}_2\text{O}(v_1, v_3)$ at 6.3 μm , the measurement is limited to a region just below 5 μm .

V. Experimental Configuration

Temperature profile measurements have been performed on the Aerodyne methane/coal burner.⁽¹²⁾ The burner has an inside diameter of 12.25 cm and is 75 cm long. The burner wall is made of zirconia which is a good insulator and can withstand temperatures up to 2300°K. The burner has two flame zones. An inner core where pulverized coal is burnt with premixed methane and oxygen enriched air and an outer guard flame of premixed methane and oxygen enriched air.

The optical setup is shown in Fig. 5. Optical access to the burner is provided by two 12.25 x 0.3 cm slits located 55 cm downstream of the burner. Radiation heat loss by the flame through the slit is minimal. The light source is provided by a cryogenically cooled laser diode from Laser Analytics, Inc. Wavelength tuning can be achieved by varying the temperature of the diode or the diode current. Referring to Fig. 5, the laser radiation is focused into a 2 mm diameter beam by a germanium lens and toroidal mirror. The beam is steered through the optical access of the burner into the monochromator/detector system by a pair of vertical translators so that the cross section of the burner can be scanned. The diode laser usually

Fig. 5 CO line absorption temperature measurement optical schematic.

lasers in several modes separated by 0.5 to 1 cm^{-1} in the region around 2000 cm^{-1} . This wavelength region was selected as it fell between the strong $\text{CO}_2(\nu_3)$ and water bands. The monochromator selects the single mode whose wavelength is current tunable through the absorption line. In addition, the monochromator rejects much of the blackbody radiation from the burner to improve signal-to-noise ratio.

The second derivative signal and the transmission signal are measured simultaneously using the same detector. The laser line is current tuned with a small wavelength modulation at 1 kHz while at the same time a slow current ramp is applied which tunes the wavelength over the absorption lines. In addition, a mechanical chopper is also used. Two locking amplifiers are used so that by locking one to the chopping frequency and locking the other to twice the modulation frequency, the transmission and the second derivative signals are obtained simultaneously from the respective amplifier outputs. By ratioing the second derivative signal to the transmission signal, the above arrangement has calibrated out the laser intensity variation, monochromator slit function, detector drift and optical misalignments.⁽¹⁰⁾ Then ratioing again the results of the pair of absorption lines, the gain transfer functions of the second derivative system and the transmission system is calibrated out, making the method self-calibrating.

VI. Experimental Results

We have measured the temperature profile of the burner operating at a fuel rich condition (stoichiometric ratio = 1.12). The overall gas flow rate is 100 gm/min and the pulverized coal flow rate is 2 gm/min . Luminous particles from incomplete combustion of coal are sometimes visible through the optical access slits but they do not seem to interfere with the temperature measurement.

The CO absorption lines used for the temperature profile measurements are the $P_0(32)$ and $P_2(21)$ lines

of $^{12}\text{C}^{16}\text{O}$. A typical transmission spectrum and second derivative spectrum is shown in Fig. 6. The disruptive signal between the two absorption lines in the second derivative spectrum is due to an anomaly of the diode laser. It is evident from the transmission spectrum that there is great uncertainty in assigning I_0 at the absorption peak, hence a measurement of transmission is difficult. However, measurement of I from the transmission spectrum and $d^2I/d\omega^2$ from the second derivative spectrum can be done easily. This comparison illustrates the advantage of the second derivative method over the direct transmission measurement.

In Fig. 7, the second derivative signal normalized by the transmitted signals for the two absorption lines are plotted as a function of the line-of-sight positions. A fourth degree polynomial, forced to be symmetric about the center line, is fit to the data. These line-of-sight profiles are then inverted by the Abel transform (see Appendix) to obtain the radial temperature profile. The scatter in the data was attributed to variations in CO concentration with time. This was borne out by the correlation between measurements of the two vibrational levels with each other when the two measurements were taken at the same time.

The inverted temperature profile is plotted in Fig. 8 together with the temperature profile obtained from traversing thermocouple measurements in two orthogonal directions for comparison. In addition, the line-of-sight temperature obtained from direct application of Eq. (5) without inversion is also plotted. In general, the line-of-sight temperature is different from the true temperature because it is a convoluted average of the temperature profile.

Fig. 6 (a) transmission spectrum of the $P_0(32)$ and $P_2(21)$ lines of CO. Horizontal axis is laser diode current. The structure between the two lines is due to diode laser anomaly; (b) corresponding second derivative spectrum.

It is difficult to assign exact error estimates to the inverted temperature profile because of the Abel transformation. A reasonable assumption is the temperature error is of the same order as the line-of-sight temperature error estimate. The inverted temperature profile and the thermocouple measured profile agree with each other to within experimental error.

The scatter of the data points in Figure 7 may be reduced if we assume the time variation of CO concentration does not change the radial concentration profile. Then by ratioing the signal from the two absorption lines measured at the same time, this concentration variation can be canceled. A temperature profile can then be fit to match the line-of-sight data.

Fig. 7 (a) normalized second derivative data, $P_0(32)$ CO absorption line. Line-of-sight position is normalized with respect to burner radius; (b) data for $P_2(21)$ CO absorption line. Solid line is polynomial fit to the data.

Fig. 8 Abel inversion temperature profile, thermocouple measured temperature profile, and line-of-sight temperature profile.

VII. Conclusions

We have studied the technique of measuring the flame temperature by ratioing the line strengths of a pair of vibrational lines of CO. By taking the ratios of the second derivative of the absorption with respect to the laser wavelength for two lines as well as the ratios of their transmittances, a self-calibrating temperature measurement technique has been devised. We have determined the temperature profile of an axisymmetric methane/coal burner by taking line-of-sight measurements into a radial profile using the Abel transformation. The temperature profile obtained from a fit to the data from $P_0(32)$ and $P_2(21)$ shows a large scatter which can be attributed to temporal variation of CO concentration.

In applying this method to large, power plant scale burner, it would be necessary to use more than one line pair for making an accurate temperature profile measurement. This is because of the difference in optical depths of the absorption lines comparing a line-of-sight through the hot burner core to a line-of-sight through the cooler boundary layer.

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Appendix

Abel Inversion

Equation (8) involves the derivative of the measurement g , which in general, may be noisy. Therefore, it is necessary to do some filtering on g before Eq. (8) is used. Furthermore, for each value of r , Eq. (8) involves an integral from r to 1. Error can be substantial for r close to 1 because not many data points are available for numerical integration. Therefore, it is best to solve Eq. (8) exactly. This is possible if we fit a least square polynomial to the profile $g(y)$.

$$g(y) = a_0 + \sum_{i=2}^N a_i y^i$$

a_1 is equal to zero because by symmetry dg/dy has to be zero at $y = 0$.

Then

$$f(r) = \frac{1}{\pi} \sum_{i=2}^N a_i h_i(r)$$

where

$$h_i(r) = \int_r^1 \frac{y^{i-1}}{\sqrt{y^2 - r^2}} dy$$

The analytic results for $l = 2$ to 6 are

$$h_2(r) = \sqrt{1-r^2}$$

$$h_3(r) = \frac{r^2}{2} \log r + \frac{1}{2} \sqrt{1-r^2} \\ + \frac{r^2}{2} \log \left(1 + \sqrt{1-r^2} \right)$$

$$h_4(r) = \left[\frac{(1-r^2)^{3/2}}{3} + r^2 \sqrt{1-r^2} \right]$$

$$h_5(r) = -\frac{3}{8} r^4 \log r + \left(\frac{1}{4} + \frac{3}{8} r^2 \right) \sqrt{1-r^2} \\ + \frac{3}{8} r^4 \log \left(1 + \sqrt{1-r^2} \right)$$

$$h_6(r) = \left[\frac{1}{5} (1-r^2)^{5/2} + \frac{2}{3} r^2 (1-r^2)^{3/2} \right. \\ \left. + r^4 (1-r^2)^{1/2} \right]$$

7. DESIGN OF CONDUCTIVITY PROBE

Analytical and experimental work at ARI has established the potential importance of some electronegative species previously neglected in calculation of plasma conductivity. As further verification of the importance of these species, it is proposed to make direct measurements of plasma conductivity for conditions where significant effects are expected. A relatively simple d.c. discharge probe (a preliminary design is shown in Figure 7.1) has been designed to measure the conductivity in ARI's coal burner facility. The relatively low thermal throughput of the ARI rig requires a relatively careful probe thermal design, however, this technique is straightforward and reliable. Measurement of the current and the probe voltage differences yields the conductivity averaged over the volume between the probes. Assumed or measured profiles could be used to obtain further detailed information, however, for the measurements anticipated, even relative conductivity levels would be sufficient. The first measurement would compare conductivity with and without phosphorus additive for two or three plasma temperatures.

Figure 7.1. Conductivity Probe Design.