Investigation of Mechanisms of Ash Deposit Formation From Low-Rank Coal Combustion

Final Report

F.T. Greene
J.E. O'Donnell

August 1987

Work Performed Under Contract No.: DE-AC21-81FC10287

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Grand Forks Projects Office
Grand Forks, North Dakota

By
Midwest Research Institute
Chemical and Biological Sciences Department
Kansas City, Missouri

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PREFACE

This final report is for the program entitled "Investigation of Mechanisms of Ash Deposit Formation from Low-Rank Coal Combustion," which was carried out by Midwest Research Institute for DOE under Contract No. 18-81FC10287, issued by the Grand Forks Energy Technology Center. Dr. Mike Jones was the project manager. The contract was subsequently transferred to the Grand Forks Project Office. Dr. Fred Bauer then became the project manager.

The principal investigator on this program is Dr. Frank T. Greene. Other MRI staff contributing to this program include Mr. J. Eugene O'Donnell, Dr. John Y. Huang and Dr. Fred L. Brill. Dr. Larry J. Shannon, Dr. K. P. Ananth, Dr. James L. Spigarelli, Dr. John Going, and Mr. Gil Radolovich have had administrative responsibility for this project at various times.

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MIDWEST RESEARCH INSTITUTE

John E. Going, Director
Chemical Sciences Department

August 21, 1987

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ABSTRACT

This project was undertaken to determine the chemical behavior of alkali metal and other species implicated in the ash fouling which can occur during the combustion of low rank coals. The coal combustion was studied in unaugmented premixed pulverized coal flames. Vapor species were measured by molecular beam mass spectrometry. Temperatures were also measured, and time-resolved coal/ash particulate samples were collected and analyzed.

A major part of the research on this project was devoted to (1) the development and refinement of techniques for the MBMS analysis of trace quantities of unstable and reactive high temperature vapor species from the pulverized coal flames and (2) the time-resolved sampling and collection of particulates. The equipment is now operating very satisfactorily. Inorganic species, some of which were present at parts-per-million levels, were quantitatively sampled and measured in the pulverized coal flames. Time-resolved particulate samples which were free of vapor deposited contaminants were collected without the use of an interfering substrate. Profiles of the alkali metal species in Beulah lignite and Decker sub-bituminous coal flames were obtained. It was found in both flames that sodium is volatilized as the atomic species early (milliseconds) in the combustion process. The gaseous Na reacts, also in milliseconds, to form an unknown species which is probably an oxide fume, but which is not NaOH or Na₂SO₄. This is probably the mechanism for the formation of the alkali "fumes" observed in other systems. Measurements were also made of a number of other gaseous species, and time-resolved coal/ash samples were obtained and analyzed.

I. INTRODUCTION

This project was undertaken to determine the chemical form and behavior during coal combustion of the several elements implicated in ash fouling and slagging problems. The research was a collaboration between MRI and Grand Forks Energy Technology Center (now the University of North Dakota Energy Research Center). Techniques for burning premixed, laminar, pulverized coal-air flames, which had previously been developed at MRI, were used to study the relevant combustion processes. The gas phase was analyzed by molecular beam mass spectrometry, and gas temperatures were measured by the use of thermocouple techniques. Ash samples, which were coordinated with the vapor phase measurements, were obtained by MRI and analyzed by GFETC/UNDERC by SEM and ESCA techniques.

A major part of the research on this project was devoted to the development and refinement of techniques for the MBMS analysis of trace quantities of unstable and reactive high temperature vapor species from the pulverized coal flames and the time-resolved sampling and collection of particulates. The equipment is now operating very satisfactorily. Inorganic species, some of which were present at parts-per-million levels, were quantitatively sampled and measured in the pulverized coal flames. Time-resolved particulate samples which were free of deposited contaminants were collected without the use of an interfering substrate. Profiles of the alkali metal species in Beulah lignite and Decker subbituminous coal flames were obtained. It was found in both flames that sodium is volatilized as the atomic species in milliseconds early in the combustion process. The gaseous Na reacts, also in milliseconds, to form an unknown species which is probably an oxide fume, but which is not NaOH or Na₂SO₄. This is probably the mechanism for the formation of the alkali "fumes" observed in other systems. Measurements were also made of a number of other gaseous species, and time-resolved coal/ash samples were obtained and analyzed.

II. OBJECTIVES AND EXPERIMENTAL APPROACH

The principal objective of this research is the determination of the behavior of several elements, including sulfur, silicon, the alkali metals, and the alkaline earth metals, during the combustion of low rank coals. This includes the identification and measurement of the partial pressures of the high temperature gaseous species as a function of time during the combustion process. Coordinated analyses of the ash composition are also made, so it is possible to track the location and molecular form of the suspect elements through the combustion process.

The combustion processes were studied in premixed, laminar pulverized coal-air flames. These flames provided a well-defined, experimentally accessible system. The composition measurements of the vapor phase were made using molecular beam mass spectrometry (MBMS). This technique provides a number of capabilities needed for this study, including high sensitivity, good spatial resolution, and the ability to analyze unstable, condensable,

and highly reactive species such as high temperature oxides and hydroxides. Coal/ash particles were sampled using both isokinetic and free-jet sampling techniques. The resulting samples were analyzed by SEM and ESCA techniques by the Grand Forks Energy Technology Center/University of North Dakota Energy Research Center. Temperatures were measured using a modified thermocouple technique.

III. APPARATUS AND TECHNIQUES

As discussed in the previous section these combustion studies were carried out in laminar premixed coal dust-air flames. These flames, and the techniques used for making the separate measurements, including gas composition, particulate/ash sampling, and temperature, are discussed below.

A. Coal Dust-Air Flames

Techniques for burning unaugmented laminar premixed flames were developed at MRI.¹ To maintain these flames, which may consist only of pulverized coal and air with no added heat, methane, or flame holders, it is necessary to uniformly feed, deagglomerate, and disperse the pulverized coal and to maintain a uniform flow field. In most of the experiments carried out to date with these flames, air classified coal has been used because this provides better defined and more stable flames. In some cases the air has been enriched with oxygen in order to permit a wider range of equivalence ratios to be investigated.

The apparatus required to burn these mixtures consists of a coal dust feeder, disperser, and burner together with appropriate gas flow and pressure measurement equipment. The coal dust feeder is shown in Figure 1. This feeder consists of a stirred, fluidized bed from which the coal dust is extracted and immediately mixed with a diluent gas. Nitrogen is generally used for both the fluidizing and diluent gases in order to avoid possible oxidation of the finely divided coal. The burner and disperser are shown in Figures 2 and 3. This disperser produces highly turbulent flow in which large shear forces deagglomerate the coal. The burner contains "flow-straightening" screens and a honeycomb section at the face to produce laminar flow. A sheath flame or an inert gas sheath can be used with this burner; however, neither of these were used in the experiments reported here. A typical flame is shown in Figure 4.

B. Molecular Beam Mass Spectrometry

1. Background: MBMS has been described in detail in the literature,²⁻²⁰ and so only a brief summary of this technique will be given here. In the molecular beam sampling technique, the gas to be sampled is drawn through a small orifice in the sampling probe and expanded to collisionless flow in a free-jet. This free-jet is then collimated into a molecular beam which is introduced into the ion source of the mass spectrometer.

Figure 1 - Fluidized Bed Coal Dust Feeder

Figure 2 - Sheathed Burner and Disperser Used to Burn Laminar Coal Dust-Air Flames

Figure 3 - Photograph of the Sheathed Burner and Disperser
Used to Burn Coal Dust-Air Flames

Figure 4 - Photograph of Typical Coal Dust-Air Flame Burning on
an Uncooled, 6.3-cm Diameter Burner

Because the free-jet expansion produces an extremely rapid drop in temperature and pressure, thereby quenching the sampled species, and because the sampled gas does not contact any surfaces during sampling and mass spectrometric analysis, MBMS can be used to study unstable species ranging from free radicals to high temperature oxides. Also, this technique is capable of high analytical precision since the beam formation process is highly reproducible.

The MBMS system, which had been used in earlier studies of coal dust-air flames and which was planned for use on this system, had the quadrupole mass spectrometer in the crossed beam mode as shown in Figure 5. In this configuration the coal/ash particles (and the molecular beam) passed through the ion source and were lost in the vacuum system. However, diagnostic studies carried out in part on this program showed that with the quadrupole mass spectrometer in the crossed beam mode there was serious mass discrimination which varied with gas temperature (beam velocity) as shown in Figure 6 and that there was significant loss of sensitivity when high temperature gases were sampled. These effects, which were not detected in the earlier work because measurements were made only over a relatively narrow temperature range, appeared to be the result of poor ion extraction perpendicular to the beam. The quadrupole was therefore placed in the axial mode. This resulted both in improved sensitivity and in greatly reduced mass discrimination as shown in Figure 6. The relatively small variation in $28+/40+$ is probably the result of effects other than ion extraction, and would be a second order correction. However, in the axial mode the coal/ash particles can strike the quadrupole structure and produce ions, which result in "particulate noise" at a level which sometimes swamped all but the strongest signals. It was therefore necessary to modify the molecular beam sampling system to permit complete trapping of ash and other particulates. This modification included the addition of two additional collimating apertures, physical and electrical modifications of the quadrupole mass spectrometer housing and electron multiplier, the addition of a beam swallowing ion pump, and the design and construction of a precision lateral and angular adjustment mechanism. The modified system, except for the adjustment mechanisms, is shown schematically in Figure 7. This apparatus performed satisfactorily in tests with coal dust flames, with the particulate noise reduced to below the normal limit of detection.

The axial arrangement of the quadrupole is clearly the preferred configuration for the detection of molecular beams, particularly those having high velocities. Consequently the axial MBMS system shown in Figure 7 was used for the initial measurements of species in pulverized coal flames made on this project. The alignment of the quadrupole assembly to achieve complete "swallowing" of the particulate beam was extremely critical. It was never possible, using a reasonably sized beam, to completely swallow the gas beam. Consequently, after extended operating time surfaces near the multiplier apparently accumulated traces of alkali metals, and the alignment required for acceptable signal-to-noise became increasingly more sensitive and almost impossible to achieve and maintain. The extensive redesign of the then government-owned sampling system was beyond the scope of this project.

Figure 5 - Molecular Beam Mass Spectrometric System Used for Previous Coal Dust-Air Flame Studies

Figure 6 - Combined CO and N₂ Intensities Relative to Argon Obtained Along the Axis of a Premixed Methane-Air Flame Using a Quadrupole Mass Spectrometer in the Axial and Crossed Beam Modes

Figure 7 - Molecular Beam Mass Spectrometric Sampling System Modified to Eliminate Particulate Noise from Coal Dust-Air Flames

Consequently, the quadrupole was returned to the crossed beam mode and mounted in a high conductivity, completely bakeable chamber pumped by a new MRI-supplied 170 L/sec turbomolecular pump. This configuration is shown in Figure 8. The reduced levels of background gases resulted in sufficiently improved signal-to-noise when using the chopped beam that, in spite of the reduced quadrupole sensitivity, concentrations of species of parts-per-million levels could be measured. Calibration of the system for each resolution, focusing condition and beam velocity was then required to make the larger corrections for mass discrimination. This MBMS system was used to obtain most of the measurements of the species in pulverized coal flames reported here.

C. Particulate Sampling

Two techniques for the quantitative sampling of coal/ash particulates from coal dust-air flames were developed in previous work at MRI. One utilizes isokinetic sampling; the other is an adaptation of free-jet sampling. Both techniques were evaluated for use on this project.

1. Sampling probes: The isokinetic probe is shown in Figure 9. When using this probe the gas velocity at the probe tip is matched to that of the flow in order to minimize flame disturbance. Additional inert gas is mixed with the sampled gas just behind the probe tip. This serves to provide both a much higher quenching rate and sufficient total gas flow to efficiently operate the Brink impactor. The Brink impactor can be used to classify the particles into several fractions according to their aerodynamic size. It was found that the use of a minimum of two stages was required to avoid the loss of particles, apparently as the result of "bounce" which occurred even when the collection surfaces were heavily coated with an adhesive substrate. It was therefore impossible to collect a complete sample on a single stub for analysis.

The free-jet sampling probe is shown in Figure 10. In this probe the heterogeneous fluid is expanded as a free-jet, with the pulverized coal and ash forming a high velocity particle beam with a relatively small solid angle. These particles are collected on a SEM stub coated with a suitable substrate. The pressure in the sampling chamber, when a typical 0.5-mm sampling orifice was used, was maintained at about 20 Torr with a mechanical pump.

2. Substrates for particle collection: The particulate samples obtained using either of the techniques discussed above are collected on SEM stubs coated with an adhesive substrate. In previous work it was found that the substrate sometimes impeded analysis by SEM/EDX. A study was therefore carried out, at the request of GFETC, directed toward the development of improved adhesive films for the collection of ash particles for analysis by SEM/EDX and ESCA.

Figure 8 - High Sensitivity Molecular Beam Mass Spectrometric System
with the Quadrupole in the Crossed Beam Mode

Figure 9 - Isokinetic Probe and Impactor Arrangement Used to Sample Coal Cust-Air Flames

Figure 10 - Free-Jet Impactor Used to Sample Coal Dust-Air Flames

Methods of producing films of variable thickness were not developed in the previous work at MRI, and so a limited literature search was carried out and several possible techniques evaluated. The technique selected was that of "spin casting."¹ For this application a solution of the adhesive material is poured on a spinning stub, the excess solution allowed to "spin" off and the remaining solvent removed with mild heat applied to the still spinning stub. The thickness of the film of solution on the spinning disk is a unique function of the viscosity of the solution and the angular velocity. As a result, predictable and reproducible films can be produced.

Films of General Electric Co. SE-33 polydimethyl silicone as well as the Apiezon L low vapor pressure vacuum grease used for the earlier test samples were produced. These films ranged in thickness from approximately 100 Å to 10 μm , and were found to be reproducible to within $\pm 30\%$. Test films of both materials having thicknesses ranging from 0.2 μm to about 5 μm were produced, and samples were collected from the reaction zone and burned gas region of a 10-20 μm Decker air flame. These test samples were evaluated by GFETC, and the 0.2 μm film of Apiezon L was selected.

The 0.2 μm thick film of Apiezon L was used for the collection of the coal/ash samples during the first part of the project, and for the evaluation of particulate sampling techniques. However, it was later found that the film interfered with some SEM and ESCA analysis. Subsequent investigation showed that the particulates could be satisfactorily collected on clean graphite surfaces using the free-jet sampling technique discussed below.

3. Evaluation of particulate sampling techniques: Test samples were obtained to evaluate the two particulate sampling techniques, isokinetic and free-jet, discussed above. For this evaluation, samples were obtained from two positions in each of two flames: 10-20 μm Beulah Lignite-Air and 0-10 μm Beulah Lignite-Air. All samples were collected on graphite SEM stubs coated with a thin film of Apiezon L.

The isokinetic sampling apparatus was similar to that used in previous work.²² In this device, the isokinetic samples were extracted through a 0.125 in. diameter orifice and quenched by dilution with room temperature N_2 immediately after extraction. For each flame and sampling position, a trial sample was taken with five stages of the cascade impactor arranged in order of decreasing cutoff size in order to determine which stage collected the smallest particles present. All other stages were then removed. It was found that, with this single stage, a significant fraction of the sample was not collected. This can probably be attributed to the bouncing of larger particles which would have been removed by the preceding stages. A second stage having a larger cutoff size was therefore placed downstream from the first. Adequate collection efficiency was obtained with the two combined stages.

The free-jet particulate sampling system, which was also used in the previous work cited above, utilized a 0.015 in. diameter sonic orifice. It was found that much less sample was collected than by the isokinetic technique even after correction for the difference in the volumes of flame

gas extracted. It is postulated that a large fraction of the particulates may bounce at the higher velocities produced in this technique. However, this does not necessarily imply greater mass discrimination.

The particulate samples were shipped to GFETC for SEM analysis. This analysis led to the selection of the free-jet sampling technique, which was more convenient while showing no detectable mass discrimination.

D. Temperature Measurements

Temperatures were measured along the axis of the coal dust air flames. The technique used, which has been applied previously in this laboratory,²² involves the use of 0.002 in. diameter Pt/Pt-Rh thermocouples coated with SiO₂. These thermocouples are inserted quickly into the flame and the EMF measured in a short time (i.e., 10 to 20 msec) before the thermocouple can be coated or eroded by the coal/ash particles. Although the temperatures shown have not been corrected for radiation, previous work in this laboratory has shown that the corrections are small for these thermocouples in these flames, and are negligible compared to the flame fluctuations and other uncertainties.

IV. ALKALI SPECIES MEASUREMENTS IN BEULAH LIGNITE AND DECKER SUBBITUMINOUS COAL FLAMES

Measurements were made of the behavior of the alkali metal and other relevant species in both the vapor and condensed (coal/ash) phases of premixed coal dust-air flames. The premixed flames and the techniques used are discussed in Section III.

A. The Coals Studied

The coals selected for study were Beulah lignite and Decker subbituminous coal. Both of these coals were supplied by the Grand Forks Energy Technology Center who ground the coals and arranged for air classification by the Donaldson Company.²³ Two size fractions were provided: 0-10 μm and 10-20 μm ; the third 20-30 μm fraction originally planned for study was not available. The 0-10 μm fractions were used only for preliminary measurements in accordance with following technical direction from GFPO.

The analysis of the two coals is given in Table I. The analysis of the ash from the two coals is given in Tables II and III. All of these analyses were performed by GFETC on the coal as supplied.

TABLE I
ULTIMATE ANALYSIS OF THE COALS USED IN THIS STUDY

Sample Description	Analysis Results, Wt%, As Received						VM	Btu
	C	H	N	S	Ash	H ₂ O		
Beulah Hi Na	44.01	6.36	0.55	0.76	5.5	33.3	28.3	7,424
Decker Coal	53.75	6.28	0.82	0.36	3.8	25.7	30.5	9,109

TABLE II
ANALYSIS OF THE ASH FROM THE BEULAH LIGNITE USED IN THIS STUDY
OBTAINED BY THE ENERGY DISPERSIVE X-RAY TECHNIQUE

	Weight %	Std. Dev.		Oxide %	Std. Dev.
O	43.87				
Na	10.79	0.19	Na ₂ O	14.55	0.25
Mg	4.012	0.057	MgO	6.652	0.095
Al	6.69	0.04	Al ₂ O ₃	12.65	0.08
Si	6.00	0.03	SiO ₂	12.83	0.06
P	0.344	0.005	P ₂ O ₅	0.787	0.011
S	10.38	0.02	SO ₃	25.91	0.06
Ca	14.77	0.05	CaO	20.67	0.07
Ti	0.332	0.006	TiO ₂	0.554	0.010
Fe	6.028	0.002	Fe ₂ O ₃	8.618	0.003
Total	103.21				

TABLE III
ANALYSIS OF ASH FROM THE DECKER SUBBITUMINOUS COAL USED IN THIS STUDY
OBTAINED BY THE ENERGY DISPERSIVE X-RAY TECHNIQUE

	Weight %	Std. Dev.		Oxide %	Std. Dev.
O	44.05				
Na	6.624	0.150	Na ₂ O	8.930	0.202
Mg	2.372	0.042	MgO	3.933	0.070
Al	8.98	0.05	Al ₂ O ₃	16.97	0.10
Si	10.32	0.04	SiO ₂	22.08	0.08
P	0.910	0.008	P ₂ O ₅	2.085	0.018
S	8.02	0.02	SO ₃	20.02	0.05
Ca	11.45	0.05	CaO	16.02	0.07
K	0.293	0.012	K ₂ O	0.352	0.014
Ti	1.112	1.011	TiO ₂	1.855	0.018
Fe	4.391	0.006	Fe ₂ O ₃	6.279	0.008
Total	98.52				

B. Vapor Phase Measurements

Measurements were made of the profiles of the alkali metal species in the premixed coal dust-air flames using the MBMS techniques discussed in Section III. The general experimental considerations and constraints, the profiles of alkali metal species, and the measurements of species in the burned gas region of the flame are discussed in the following subsections. The extensive calibration measurements required are also discussed below.

1. Experimental considerations and constraints: There are two major constraints on the measurements using coal dust-air flames and the available MBMS techniques. Both of these constraints become important only when dealing with part-per-million levels of inorganic gaseous species found to be present in the coal dust-air flames.

The coal dust-air flames can be burned with stoichiometries which vary from very fuel rich to a moderately lean conditions in which there is up to 10% excess oxygen (using oxygen enriched air). The fundamental problem is that of obtaining a speed for the upward flowing, downward burning flame such that the coal dust can be entrained without the flame either lifting from the burner or burning back through the burner grid. This requirement results in a rather narrow envelope of conditions for which a stable lean flame can be maintained and does not permit a wide range of equivalence ratios for lean flames. Consequently, a single standard lean flame was selected and used for most of the MBMS studies.

Stoichiometric and rich flames have higher flame speeds and do not have the same limitations. However, the MBMS system with sufficient pumping capability to permit the use of the large sampling orifices essential for these heterogeneous flame studies has only a low resolution (quadrupole) mass spectrometer. Consequently, it was not possible to distinguish between organic species, which were prominent in stoichiometric and rich flames, and low level inorganic species. Therefore, the MBMS measurements of inorganic species, except for sodium, were limited to lean flames. This same constraint also applied to measurements in the reaction zones in even lean flames, where information on the formation of the inorganic species should be obtainable. Future MBMS research on coal dust-air flames should include high resolution capability. Such capability in conjunction with a suitable sampling system is now becoming available at MRI.

2. Species profiles: Measurements were made of the concentrations of the combustion reactants and products and the alkali metal species as a function of distance along the axis of the "standard" Beulah and Decker flames. All measurements were made using the equipment and techniques discussed above and in Section III.

Profiles of combustion products and reactants are shown in Figures 11 and 12. The primary purpose for obtaining these profiles was to locate the "reaction zone" of the flame, which is the region characterized by rapid rise in CO_2 and H_2O and rapid decrease in O_2 concentrations. Therefore, the points plotted represent only the raw signal intensities of the particular species at a given position in the flame and have not been corrected

Figure 11 - Stable Product Profiles Observed in a Lean 10-20 μm Subbituminous Coal Flame

Figure 12 - Stable Product Profiles Observed In A Lean 10-20 μm Beulah Lignite Air Flame.

for relative beam strength, fragmentation in the ion source, ionization cross sections, mass-dependent quadrupole transmission, or mass separation in the free jet. The apparent minor peak in H_2O in Figure 11 is an artifact resulting from the simultaneous increase in H_2O concentration with the decrease in beam strength due to the higher gas temperature. The increase in the O_2 concentration at large distances is the result of entrainment of the ambient air.

A search was made for a number of possible alkali metal species in the Beulah and Decker flames including Na, NaOH, Na_2SO_4 , NaO, NaO_2 , Na_2O , K, and KOH. Peaks corresponding to possible alkali metal species were observed at $m/e = 23, 39, 40, 56$, and 142. There are no reasonable combinations of C, H, O, and N which could yield a singly charged ion with $m/e = 23$. Measurements in which the electron energy was reduced, and in which no major species was found at $m/e = 46$, effectively eliminated a doubly charged ion. This peak was therefore assigned to gaseous Na. The peak at 40, which appears in the reaction zone and which persists at almost constant concentrations through the burned gas region, was assigned to NaOH. The only other reasonable assignment under analyzing conditions in the absence of hydrocarbons or Ar would be to Ca^+ . However, any calcium should be present as the hydroxide or sulfate, neither of which were found to be present in sufficiently large concentrations to account for the 40 peak. The peak observed at $m/e = 142$ was assigned to Na_2SO_4 . This assignment was confirmed by adding SO_2 to the flame as discussed below. In addition to the sodium species, peaks at $m/e = 39$ and 56 were observed. These peaks were assigned to K and KOH, and are both almost certainly produced from KOH(g) . It was not possible to follow the production of K in the reaction zone because of the presence of large concentrations of C_3H_3^+ and other hydrocarbon ions.

Profiles of the Na^+ and NaOH^+ mass spectrometer peaks through the lean Beulah and Decker flames are shown in Figures 13 and 14. The concentrations shown were calculated from the intensities measured relative to N_2^+ , assuming that Na and NaOH were the neutral precursors of Na^+ and NaOH^+ , with corrections for fragmentation, ionization cross sections, mass-dependent quadrupole transmission, multiplier efficiencies, and mass separation in the free jet. High purity N_2 and O_2 were used to synthesize the combustion air for these measurements so that Ar, which appears at mass 40 and would not be distinguishable from NaOH, could be eliminated. The apparent rise in NaOH at long distances in Figure 13 is due to entrainment of Ar from the ambient air.

The evolution of gaseous Na during pulverized coal combustion has not been previously observed. This phenomena is extremely rapid, appearing and disappearing in 2-3 mm, which is about the resolution of the relatively large molecular beam sampling orifice. Since the gas flow is of the order of 50-60 cm/sec, this corresponds to ~ 5 msec. This very rapid evolution of gaseous Na, which may be the result of decarboxylation or reduction of Na species by the hot char, may not be too surprising. However, the reactions which are responsible for the equally rapid decay and the ultimate fate of the evolved Na are not clear. The sodium is not converted to NaOH since no peak in the NaOH concentrations was observed and since the vapor

Figure 13 - Profiles of Na and NaOH Observed in Lean 10-20 μm Decker Subbituminous Coal-Air Flow

Figure 14 - Profiles of Na and NaOH Vapor Observed in a Lean 10-20 μm Beulah Lignite-Air Flame

pressure of NaOH at this temperature is above 1 atm based on existing thermochemical data. A search for large concentrations of the other sodium species in the spatial region of the peak was unsuccessful.

Measurements were made in which SO_2 was injected into the burned gas region of the lean Beulah flame using a simple 1/8 in. diameter stainless steel capillary. It was found that the concentration of the neutral precursor of the species producing the peak at $m/e = 142$ increased by a factor of up to 5 and was roughly in proportion to the concentration of SO_2 added. The quantity of SO_2 added could not be precisely controlled. However, when SO_2 was added to the burned gas region at varying distances below the sampling probe, it was found that the increase in $m/e = 142$ peak was obtained even when the injector was just below the probe (2-3 mm) and that approximately the same increase was achieved regardless of the position of the injector in the flame. These observations confirm that the neutral precursor of the peak at $m/e = 142$ is indeed Na_2SO_4 , indicate that the reactions of SO_2 with the sodium species for Na_2SO_4 is fast, and further support the assumption that Na_2SO_4 , SO_2 , O_2 , and the sodium species are in equilibrium in the burned gas region of the coal dust-air flame.

The useful measurements which can be made in rich flames are limited because of the presence of hydrocarbons which cannot be distinguished from low level gaseous inorganic species. However, it is possible to follow the peak at $m/e = 23$ for the reasons given above and to follow the major combustion products and reactants which are present at high levels and are relatively unambiguous. Profiles of Na^+ (from Na and NaOH), CO_2 , and O_2 were obtained for a rich and a nearly stoichiometric Decker flame. The results, which are shown in Tables IV and V, were obtained prior to the discovery of the Na "spike," and were made only downstream of the reaction zone and do not show the rapid evolution of gaseous Na. However, they do show a reduction in the rate of decay of gaseous Na when the partial pressure of O_2 is reduced, and suggest that the gaseous Na evolved early in the coal combustion process may react with oxygen, possibly to form an oxide fume.

3. Composition of the burned gas region: Measurements of the concentrations of SiO_2 and several calcium species were attempted in the burned gas region of the Beulah and Decker flames. These measurements, together with the measurements of the alkali metal species discussed above, provide a reasonably complete composition for the burned gas region of these flames. These results are summarized in Tables VI and VII. The CaSO_4 measurement was hampered by very poor signal-to-noise at that peak, and so a trace of CaSO_4 may be present in addition to the Ca(OH)_2 . These species, in addition to the alkali metal hydroxides and sulfates, are the only metal species detected. Other species found in the ash are presumably transported as a condensed phase.

TABLE IV

SPECIES OBSERVED IN THE VAPOR PHASE OF A RICH 10-20 μm DECKER AIR FLAME

Distance (mm)	Concentrations			T ($^{\circ}\text{C}$)
	Na (ppm)	O ₂ (ppm)	CO ₂ (%)	
3.2	251	8×10^4	5.1	1,490
6.4	110	*574	14.0	1,568
9.5	83	262	12.8	1,361
15.9	75	100	12.5	1,464
25.4	72	68	11.8	1,516
38.1	45	24	12.6	1,206
63.5	134	220	12.3	1,283
101.6	49	4.9×10^3	11.7	1,154

TABLE V

SPECIES OBSERVED IN THE VAPOR PHASE OF A LEAN 10-20 μm DECKER AIR FLAME

Distance (mm)	Concentrations		
	Na (ppm)	O ₂ %	CO ₂ (%)
3.2	150	3.90	11.8
6.4	57	1.73	15.4
9.5	37	1.60	15.5
15.9	32	1.17	18.2
25.4	36	0.95	17.4
50.8	25	1.89	14.2

TABLE VI

INORGANIC SPECIES OBSERVED IN 10-20 μ m BEULAH LIGNITE-AIR FLAMES

<u>Species</u>	<u>Concentration (ppm)</u>
SO ₂	1,022
Na ₂ SO ₄	trace
NaOH	88
NaCl	1.2
HCl	ND*
Ca(OH) ₂	trace
CaSO ₄	ND
SiO ₂	ND

* Not detectable.

TABLE VII

INORGANIC SPECIES OBSERVED IN 10-20 μ m DECKER SUBBITUMINOUS COAL-AIR FLAMES

<u>Species</u>	<u>Concentration (ppm)</u>
SO ₂	235
Na ₂ SO ₄	trace
NaOH	27
NaCl	trace
HCl	ND*
Ca(OH) ₂	trace
CaSO ₄	ND
SiO ₂	ND

* Not detectable.

C. Condensed Phase Measurements

Particulates were collected as a function of distance along the axes of lean 10-20 μm Beulah lignite- $\text{N}_2\text{-O}_2$ and 10-20 μm Decker subbituminous coal- $\text{N}_2\text{-O}_2$ flames using the sampling techniques discussed in Section III. The initial samples were collected on graphite SEM stubs coated with 100 Å films of Apiezon. Subsequent investigation indicated that adequate collection efficiency was obtained using bare stubs, and so the analyses were performed on samples collected without the presence of the potentially interfering adhesive.

The particulate samples obtained at several distances in the two flames were analyzed by UNDERC using the ESCA technique in conjunction with an ion sputtering gun which permitted the determination of the elemental composition of the particulates as a function of depth in a given particle, although only to about 100 Å because of the low rate of removal. The average concentrations of several elements in ash sample which were collected at several positions along the axis of lean Beulah lignite flames were measured as a function of depth. The results are shown in Figures 15 through 19. The surface of the particle contained a significantly larger concentration of silicon than the subsurface layer. At slightly greater depths the condensed phase consisted of approximately 40% each of sodium and oxygen, approximately 7% sulfur, and smaller quantities of other elements, as summarized in Table VIII. This stoichiometry is inconsistent with sodium sulfate as the condensed phase. Furthermore, the sodium peak did not appear at the binding energy corresponding to Na_2SO_4 . However, it was not possible to identify the condensed phase from the binding energy. Similar measurements were also made for ash samples collected from the lean Decker subbituminous coal flames, and generally comparable results were obtained.

In previous research in this laboratory, ash samples were collected from comparable lean Beulah lignite and Decker subbituminous coal flames.²⁶ Analyses of these flames by EDAX showed that there are significant differences between the compositions of surface layers and the interior of the particles, with the surface being substantially enriched in alkali metals.²⁷ This result strongly indicates that the ash particles were coated with alkali metal vapor species or particulates either in the flame or during sample collection. In this work the relatively high concentration of silicon on the surfaces of the ash particles may be the result of the deposition of SiO_2 fume, which could be formed by the vaporization and subsequent oxidation of SiO in the "reaction zone" of the flame, on the sample. However, since the silicon rich layer is less than 15 Å thick, it could be the result of contamination or loss of sodium from the surface. The subsurface layer consists principally of equal mole fractions of sodium and oxygen, with smaller amounts of sulfur and other elements. In this layer the sodium is probably present as sodium hydroxide produced by the reaction of an unknown sodium phase on the particle surface with atmospheric water during the extended interval between sample collection and analysis. Although it is not clear whether the subsurface sodium layer was deposited in the flame or during sampling, Na was observed on the SEM stub between the ash particles.

Figure 15 - Concentration of O and Na as a Function of Sputtering Time in Ash Particles Sampled at 3 mm from the Burner Surface in Lean Beulah Lignite- N_2 - O_2 Flames. The total depth profiled was approximately 100 Å.

Figure 16 - Concentration of S, Ca, and Fe as a Function of Sputtering Time in Ash Particles Sampled at 3 mm from the Burner Surface in Lean Beulah Lignite- N_2 - O_2 Flames. The total depth profiled was approximately 100 Å.

Figure 17 - Concentration of S, Si, Al, and Cl as a Function of Sputtering Time in Ash Particles Sampled at 3 mm from the Burner Surface in Lean Beulah Lignite-N₂-O₂ Flames. The total depth profiled was approximately 100 Å.

Figure 18 - Concentration of O and Na as a Function of Sputtering Time in Ash Particles Sampled at 100 mm from the Burner Surface in Lean Beulah Lignite-N₂-O₂ Flames. The total depth profiled was approximately 100 Å.

Figure 19 - Concentration of S, Fe, Ca, P, and Cl as a Function of Sputtering Time in Ash Particles Sampled at 100 mm from the Burner Surface in Lean Beulah Lignite-N₂-O₂ Flames. The total depth profiled was approximately 100 Å.

TABLE VIII

SUBSURFACE CONCENTRATION OF SEVERAL ELEMENTS IN ASH SAMPLES OBTAINED
AT SMALL AND LARGE DISTANCES ABOVE THE GRID OF A
LEAN BEULAH LIGNITE-N₂-O₂ FLAME

<u>Species</u>	<u>Atomic Percent</u> <u>3 mm Above Burner</u>	<u>Atomic Percent</u> <u>100 mm Above Burner</u>
O	40	40
Na	40	40
Al	2	-
Si	1	-
P	1	1-5
S	8	7
Cl	1	1
Ca	5	2
Fe	2	3

Also, more Na was observed on the front than on the back surface of the sampled particles.²⁶ Since the particle sampling conditions were selected to avoid vapor deposition on the SEM stub, these two observations suggest that a fume containing Na was formed in the flame. Additional research is needed to identify the condensed phases produced in the flame and to determine the mechanisms by which they are formed.

D. Temperature Measurements

Temperature profiles were obtained for the several flames studied using the thermocouple techniques discussed in Section III. The temperature profiles obtained for the "standard" lean Decker and Beulah flames are given in Figures 20 and 21. The "error" bars represent fluctuations in the flame resulting from wafting of the flame at large distances, not experimental error. Consequently, the actual flame temperature is very close to the highest temperature shown. Temperature profiles were also obtained for the rich and nearly stoichiometric Decker flames discussed above. These data are given in Tables IV and V. Note that all these flames show relatively little difference in their temperature profiles, and so the results of change in gas compositions of these flames can be directly compared.

E. Calibration Measurements

Calibration measurements were required both to correct for mass discrimination in the quadrupole and to obtain fragmentation patterns for the high temperature species under the conditions studied. The calibration procedure and the supplementary flame studies undertaken to obtain fragmentation patterns are discussed below.

1. Calibration procedures: Calibration of the quadrupole mass spectrometer was required both for the differences in the extraction of ions having different momenta imparted by the molecular beam from the ion source into the analyzer as well as the inherent discrimination of the quadrupole analyzer. Consequently, the calibration gas must be contained in a molecular beam having a velocity comparable to that produced by the system being studied. This was accomplished by the use of a CH₄-air flame which was burned using air synthesized from N₂ containing 1.0% He, Ne, Ar, Kr, and Xe. The apparent concentration of these species in the flame was measured and a calibration curve for the specific focusing condition and resolution used was calculated using known cross sections and with a correction for mass separation in the molecular beam. The calibration curve obtained for approximately unit resolution is shown in Figure 22. Clearly, very large corrections are required when quadrupole mass spectrometers in the crossed beam mode are used to detect high velocity molecular beams. The calibration curves obtained, which include an inherent correction for mass dependent electron multiplier efficiency and differential scattering of species in the molecular beam, were used to calculate concentration of the species in the coal dust air flames.

Figure 20 - Temperature Profile Observed For a Lean 10-20 μm Decker Subbituminous Coal-Air Flame

Figure 21 - Temperature Profile Observed for a Lean 10-20 μm Beulah Lignite-Air Flame

Figure 22 - Calibration Curve for Mass Discrimination of Quadrupole in Crossed Beam Mode

2. Supplementary flame studies: Measurements of gaseous alkali and alkaline earth species in the coal dust-air flames are of particular importance since these elements have been generally implicated in ash fouling problems. Existing thermochemical data indicate that the hydroxides of the Group I and II elements are likely to be the major vapor phase species under typical coal combustion conditions. Although these species are extremely intractable at high temperatures, there is no problem making MBMS measurements of their concentrations. However, the mass spectrometric data needed to interpret these measurements, including fragmentation patterns and, to a very much lesser extent, relative ionization cross sections, is very limited. A limited literature search produced little information on the fragmentation of the alkali metal hydroxides and nothing on the alkaline earth hydroxides. Furthermore, in previous work, we found an apparently serious discrepancy between the observed and reported extent of fragmentation of KOH.²³ A limited series of survey experiments was, therefore, carried out in which Na and Ca species were identified and measured in well-defined premixed CH₄-air flames.

a. Apparatus: For these experiments the inorganic constituents were introduced to the premixed CH₄-air flames as aqueous aerosols. The apparatus used is shown in Figure 23. The burner consists of a 1-in. ID, water-cooled copper tube containing several smoothing screens and having a fine stainless steel flame grid. The CH₄ is introduced through a jet in the center of the burner. All of the combustion air was passed through the nebulizer and into the burner via a high conductance line so that the nebulizer could be operated at very close to atmospheric pressure. The solution of the inorganic material was dispersed into the combustion air by means of a Hospal ultrasonic nebulizer. The quantity of solution added to the flame was monitored continuously by measuring the flow of solution into the nebulizer required to maintain a constant level. The density of the aerosol, and hence the concentration of additive in the flame, could be varied simply by changing the nebulizer power.

The MBMS equipment used was the same as that used for the pulverized coal-air flame studies. This equipment is discussed in Section III. Matheson ultrahigh-purity N₂ and O₂ was used in order to reduce the interference due to Ar at mass 40. The measured amount of Ar in the ultrahigh-purity N₂ and O₂ and technical grade CH₄ was 10, 15, and 80 ppm, respectively. In order to determine the amount of interference at mass 40 due to the entrainment of atmospheric Ar near the flame, the ion intensity of mass 40 relative to that of mass 28 in a CH₄/Ar-free air flame was measured at several burner-to-probe distances. We found that the interference level was about 20 ppm at distances shorter than 1 in. Thereafter, all of our experiments were done at burner-to-probe distances shorter than 1 in. In measuring the concentration of metal-containing species in flames, the baseline intensity of the ions that were of interest were first measured without the aerosol. Usually each ion intensity was measured five times to provide a basis for statistical error assessment. Then the aerosol generator was turned on and intensity measurements were started when nebulization had reached steady state.

Figure 23 - Schematic of the Burner System Used to Study Inorganic Materials in Premixed Gas Flames

b. Measurements: Measurements were made of the species in selected premixed CH₄-air flames to which CaCl₂ and NaCl were added as an aqueous aerosol.

(1) Ca species: The ion intensities at m/e = 28, 40, 57 and 74 were measured at a burner-to-probe distance of 1 in. above the burner in a stoichiometric flame. These results are given below.

<u>Observed Ion</u>	<u>Mole Fraction without Aerosol</u>	<u>Mole Fraction with Aerosol</u>	<u>Net Mole Fraction in Flame</u>
Ca(OH) ⁺ ₂	0.5 ± 0.7 ppm	14 ppm	14 ppm
CaOH ⁺	1 ± 3 ppm	50 ppm	50 ppm
Ca ⁺	40 ± 10 ppm	53 ppm	13 ppm

(2) Na species: The ion intensities at m/e = 23, 28 and 40 were measured at a burner-to-probe distance of 1 in. in a nearly stoichiometric CH₄-air flame. The results are given below.

<u>Observed Ion</u>	<u>Fraction Without Aerosol</u>	<u>Mole Fraction with Aerosol</u>	<u>Net Mole Fraction</u>
NaOH ⁺	30 ± 10 ppm	115 ppm	85 ppm
Na ⁺	4 ± 1 ppm	275 ppm	270 ppm

3. Comparison with thermochemical data: Comparison of the observed concentrations of metal species with those calculated from thermochemical data provides a direct means of evaluating fragmentation effects. This does, of course, require that the thermochemical data be reasonably correct. More extensive measurements would be required to test the existing thermochemical data.

For the purpose of these approximate calculations the CH₄-air flames were assumed to be at their adiabatic flame temperatures and to have the equilibrium compositions in the burned gas region. Previous work supports the validity of the assumption.³ Since a significant quantity of liquid water was added to the flame in the aerosol, the adiabatic flame temperature for the CH₄-air-H₂O flame was calculated to be 2131°K, which is about 100°K below that for the CH₄-air flame. Changes in the flame composition due to the addition of the water were found to be insignificant for these calculations and were neglected. All thermochemical data were taken from the JANAF tables.

The concentration of Ca added to the flame was approximately 250 ppm. At this concentration a CaO condensed phase will be formed, and will account for over 80% of the total Ca. The calculated concentrations of Ca species in the vapor phase are:

<u>Vapor Species</u>	<u>X (Mole Fraction)</u>	<u>Relative Concentrations</u>
Ca(OH) ₂	8.7 x 10 ⁻⁵	1.18 x 10 ⁴
CaOH	1.1 x 10 ⁻⁶	143
CaO	1.0 x 10 ⁻⁸	1.3
Ca	7.7 x 10 ⁻⁹	1

The thermochemical calculations show that NaCl, NaOH, and Na are the only important species at T = 2131°K and P = 1 atm. Their calculated concentrations are:

<u>Vapor Species</u>	<u>X (Mole Fraction)</u>	<u>Relative Concentrations</u>
NaCl	9.8 x 10 ⁻⁴	3.6
NaOH	5.4 x 10 ⁻⁴	2
Na	2.7 x 10 ⁻⁴	1

For the Ca system, the calculations show that about 90 ppm of Ca introduced into flame exists in the vapor phase. We observed a total of about 77 ppm of Ca species. This is surprisingly good agreement. However, the calculated mole fraction ratios are

$$X_{\text{Ca(OH)}_2} : X_{\text{CaOH}} : X_{\text{Ca}} = 1.16 \times 10^4 : 145 : 1$$

while the experimental data shows ratios of

$$X_{\text{Ca(OH)}_2} : X_{\text{CaOH}} : X_{\text{Ca}} = 1 : 5 : 1$$

Since the MS data were taken at 70 ev ionizing energy, one would suspect that fragmentation contributes, at least partly, to the discrepancy in the mole fraction ratios. If the JANAF data are accurate, then the observed CaOH⁺ and Ca⁺ were entirely fragment ions of Ca(OH)₂, and the observed ratios constitute the fragmentation pattern for Ca(OH)₂. However, it should be noted that the validity of JANAF data for alkaline-earth species has been questioned by some data compilers.

For the Na system, the calculated and experimental data show a significant discrepancy in the absolute concentrations of NaOH and Na in vapor phase. The calculated mole fraction of total Na is 1,800 ppm, while the total mole fraction observed is about 400 ppm. Although NaCl, which

the thermochemical calculations indicate will be the major gaseous sodium species, was not measured, it is known that it fragments extensively to Na^+ ²⁴ and was, therefore, included in the mass balance. The low total Na may be the result of incomplete vaporization of the NaCl. However, it may also indicate that there are additional gaseous sodium species or more likely, the formation of a fume or other condensed phase. This may be the same phenomenon which was encountered in the pulverized coal flames. If so, simple premixed flames may be preferred media for its study.

V. STUDIES OF THE COMBUSTION OF ION EXCHANGED COAL

A major activity, which was included in this project at the direction of GFPO, was the preparation and study of the combustion of ion exchanged Beulah lignite and Decker subbituminous coal. Both coals are known to have ion exchangeable alkali metals.

A. Coal Preparation

Samples of 10-20 μm Beulah lignite and Decker subbituminous coal were treated with 1 M solutions of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ to attempt to replace the sodium with Ca and H. The coal was allowed to remain in the solutions at room temperature for about 16 hr and then vacuum filtered under N_2 . The resulting coal cake was found to retain about 40% of the original ion exchange solution. This cake was then washed 9 times with distilled water and filtered under N_2 , thereby reducing the calculated concentration of the original solution retained in the cake to 10 ppm. The coal was then dried in vacuum while maintaining the temperature of the coal at or below ambient. In order to complete the drying of the coal, it was necessary to construct an apparatus in which a heat exchanger through which water was circulated was inserted into the coal cake. Drying was continued until the temperature of the cake approached ambient and the pressure in the vacuum chamber was approximately that of the original coal.

B. Combustion Measurements

The ion exchanged Beulah and Decker coals were burned using the techniques discussed previously. It was found that the ion exchanged coals did not fluidize well, resulting in erratic coal feeding and an unstable flame. The problem was corrected by blending the coal with 1% Aerosil fluidizing agent. The resulting coal produced an adequately stable flame.

Measurements were made of the concentrations of NaOH (at $m/e = 23$) in the burned gas region of the pulverized coal flames and the concentration of Na at its maximum in the reaction zone in the flame. The peak Na concentration in both the coals exchanged with $\text{CaC}_2\text{H}_3\text{O}_2$ were approximately 50 ppm compared to the 2000-3000 observed in the two raw coals. The NaOH concentrations in the burned gas region were less than 1 ppm for the Beulah and Decker coals. It is, therefore, clear that the sodium was effectively removed from the two coals.

An attempt was made to detect the evolution of gaseous Ca in both ion exchanged coals. The position in which peak evolution of the residual Na was located, the flame sampled at adjacent positions, and a Ca spike of $m/e = 40$ sought. No spike was detected. The absence of a Ca spike may be the result of failure to substitute Ca for Na or differences in the chemistry and volatility of Ca and its compounds. Analyses of the ion exchanged coals will be obtained, and will be included in the publications derived from this research.

VI. DISCUSSION AND CONCLUSIONS

In this research a major portion of the experimental activity was devoted to the development and modification of the equipment and techniques needed to measure the changes in gas and coal/ash composition as a function of combustion time in the premixed pulverized coal flames. Profiles of alkali metal species through Beulah lignite and Decker subbituminous coal flames were also obtained. Measurements were also made of alkaline earth metal and other relevant gaseous species, and coal/ash particulate profiles were obtained. Diagnostic experiments were also performed.

Profiles of Na and NaOH through lean Beulah and Decker flames showed that gaseous Na evolved and decayed in 5 msec, reaching peak concentrations, which were sometimes in excess of 3,000 ppm, early in the combustion processes. This rapid evolution of gaseous sodium, which has not been previously reported, may be associated with the decarboxylation of the coal or may be the result of the rapid reduction of sodium species by the hot char and hydrocarbons. Since the rates of evolution of sodium from much larger particles (1-4 mm) of Beulah lignite and a bituminous coal, for which the sodium was present as mineral inclusions, were found in other research to be comparable, the latter explanation seems more probable. A mechanism for the equally rapid disappearance of the gaseous Na is less obvious. The sodium does not react to form NaOH since the concentration of NaOH does not increase downstream of the sodium spike and since the vapor pressure of NaOH is about 1 atm at this temperature. The gaseous Na could also be converted to Na_2SO_4 . However, Na_2SO_4 is not present as a condensed phase since its concentration increases with the addition of SO_2 . Since the combined Na_2SO_4 and NaOH concentrations are not sufficiently high to account for the gaseous Na observed in the reaction zone, the Na must be converted either to an unobserved gaseous species or to a condensed phase. A reaction with oxygen seems likely, particularly since the reaction of gaseous Na with H_2O has been shown to be relatively slow even at high temperatures.²⁵ This postulate is supported by the apparent reduction in the sodium decay rate with decreasing O_2 concentration observed in the rich and nearly stoichiometric flame studies. The product is probably a condensed phase oxide, which can later react with H_2O or SO_2 to form NaOH or Na_2SO_4 fumes at lower temperatures.

In addition to the results discussed above the development of equipment and techniques for the sampling of coal/ash particulates and for the analysis of gaseous species in pulverized coal flames are also important results. It is now possible to collect particulate samples on graphite

SEM/ESCA stubs without contamination by vapor deposition and without the need for an interfering adhesive. The MBMS equipment now available permits the measurement of free radicals and high temperature species in pulverized coal flames at 10-100 ppb levels. Future work should, however, include the use of high resolution mass spectrometric capabilities which will eliminate ambiguities and permit studies of species in the reaction zone and in stoichiometric and rich pulverized coal flames.

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