PREDICTIVE MODEL FOR PLUME OPACITY

by

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(ABSTRACT)

In recent years, as control systems for boiler emissions have been upgraded, some utility sources have experienced increased plume opacity. Cases of plume opacity exceeding in-stack opacity are due to 1) the aerosol formed by condensation of primary sulfuric acid and water vapor onto polydisperse plume particles and 2) the presence of fine particles which grow into the visual size range by heterogeneous condensation and coagulation processes as the plume is cooled and diluted by mixing with the ambient air.

In order to better understand the factors leading up to acid plume formation, a computer simulation model has been developed. This plume opacity model has been utilized to simulate sulfuric acid aerosol formation and growth. These processes result from homogeneous nucleation, condensation and coagulation which substantially increase the concentration of submicrometer sized aerosols. These phenomena bring about significant increases in plume opacity.

Theoretical relationships have been derived and transformed into a computer model to predict plume opacity at
various downwind distances resulting from pulverized coal combustion operations. This model consists of relatively independent components -- such as an optics module, a bimodal particle size distribution module, a polydisperse coagulation module, a vapor condensation and nucleation module and a plume dispersion module -- which are linked together to relate specific flue gas emissions and meteorological conditions to plume opacity.

This unique, near-stack, plume-opacity-model approach provides an excellent tool for understanding and dealing with such complex issues as:

- increasing plume opacity observed for emissions containing sulfuric acid aerosols,

- explaining the correlation between primary particle size distribution and light-scattering effects,

- predicting the opacity level resulting from combustion of various coal types,

- predicting control equipment effects on plume opacity.
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I. INTRODUCTION

BACKGROUND

Many stationary sources discharge visible emissions into the atmosphere. A visible plume can be a problem either from the viewpoint of particulate emission standards or of aesthetics and public concern. Visible plumes from utility and industrial sources are caused by solid particles and/or condensing materials. Coal and oil burners have traditionally generated visible smoke plumes which are caused by unburned carbon particles. The plume will appear dark if unburned carbon particles are present usually due to a faulty burner or lack of adequate combustion air.

With modern steam generation systems, markedly incomplete combustion is the exception. Combustible air contaminants are seldom present in sufficient concentrations to obscure visibility. Nevertheless, visible plumes of greater than 40% opacity occur at large power plants burning high-sulfur coal where there are only minimum quantities of unburned materials in exhaust gases. These opaque emissions are mainly due to fine sulfate particles or condensed sulfuric acid aerosols rather than to unburned carbon particles.

In recent years, with the installation of high efficiency particulate emission control devices on utility boilers, de-
tached plumes have become more of a problem because formerly
the emissions of primary particulate matter obscured and/or
served as a condensing surface for the condensable material.
The problem common to some of these installations is the vi-
olation of opacity standards due to the presence of a de-
tached, high-opacity, persistent plume that emits from the
stack. The composition of these plumes may have considerable
impact on the overall air quality of the respective areas.
This kind of plume not only presents a plume opacity problem
but also represents a previously disregarded source of pri-
mary sulfate emissions that may contribute significantly
to the acid rain and atmospheric visibility problems.

In some cases when the in-stack opacity level is below the
compliance level and grain loading is below the emission
standard, a detached plume is observed which has a higher
 opacity level than exists in the stack. The bluish-white
 coloration of the plume denotes the presence of a fine,
sulfuric acid aerosol and negates the possibility that the
plume is due to soot from combustion. The persistent nature
of the plume and its color eliminates the possibility that the
plume originates from condensation of water vapor. The
increase in opacity as the flue gas moves from the stack to
the atmosphere is due to formation of additional optically

1 Metal sulfates and sulfuric acid vapor or aerosol emitted
directly from stationary sources are called primary
sulfate.
effective material within the plume. It has been proposed that the condensation of sulfuric acid vapor is a major con-
tribution to detached plume opacity.

RESEARCH SIGNIFICANCE

Particulate emissions from coal-fired and oil-fired boilers are currently regulated by two types of standards. One standard specifies an allowable emission rate on a mass per unit combustion energy basis (lb/10^6 Btu). The second type specifies the allowable light obscuring properties of the flue gas as "read" by visual observations and reported in terms of percent plume opacity.

Most new sources are subject to particulate emission regulations measured by both opacity and particulate mass loading. A source must comply with both the mass emission and visual opacity standards to meet the current regulations. It has been observed that compliance with the mass emission standard does not assure compliance with visual opacity standard. This typically is the case when electrostatic precipitators have been used for collecting the particulates in the flue gases from power plants. In some cases increased plume opacity due to acid aerosol formation makes it diffi-
cult for power plant operators to meet opacity regulations even with high efficiency electrostatic precipitators. At
present, some plants use scrubbers with electrostatic precipitators but still have opacity problems. This generally occurs in modern plants with strictly controlled emissions, apparently because the current particulate control systems collect almost all of the particles greater than 1 μm in size but allow a significant number of the submicron sized particles to escape collection.

Opacity control is one of the most challenging tasks in recent developments of advanced coal-fired power plants. The major stumbling block now is the fact that control equipment suppliers customarily design and guarantee control equipment on the basis of mass emissions. Because regulations to control stack emissions from stationary sources are in the form of both mass emission and visual opacity standards, the air pollution engineers responsible for designing emission control system must develop criteria relating directly to both regulations to make rational control equipment decisions.

A key environmental problem facing the utility industry is the continued emphasis by regulatory agencies on the application of high efficiency particulate control devices to utility boilers. This increased emphasis is manifested by the 0.03 lb/10^6 Btu New Source Performance Standard (NSPS) for particulate emissions. In addition, attention continues to be focused on control of fine particulates and plume opacity.

A literature review and personal contacts with field personnel indicated that detached plumes emanate from several
types of sources due to a combination of physical and chemical factors. Two types of sources which experience detached plumes most often are found to be coal-fired boilers and Portland Cement plants. A significant number of diverse source categories have been reported to be in apparent violation of the opacity standard. However, even with reduced opacity levels, there will still be special problems for operating and enforcement personnel, inasmuch as the Environmental Protection Agency (EPA) requirements are being met, but the public will still object to the appearance of smoke plumes.

RESEARCH OBJECTIVES

Visual opacity standards have become an important regulatory issue, and compliance is difficult for some types of stationary sources. The ability to predict resulting plume opacity with the application of different types of control equipment is needed to predict compliance status with respect to existing and future air pollution regulations.

The fact that the opacity of flue gas at the stack exit is lower than the downwind opacity indicates that the particulates in the flue gas in the stack have a lower optical obscuration than the downwind plume. Thus, downwind plume opacity cannot be related to the particulate mass con-
centration and size distribution at the stack exit in a simple manner.

In order to better understand the phenomenon of detached plumes, a model has been formulated to describe in mathematical terms the relationship between the particle suspension leaving the stack and the particulate composition of the plume as it evolves downwind of the stack. This model provides a means of relating parameters that govern plume opacity which is not feasible from a monitoring standpoint. Input parameters can be put into the model to investigate the effects on resulting plume opacity levels.

The purpose of this study was to develop a systematic method for predicting plume opacity. Emphasis on control of particulate emissions without corresponding control of acid gases has not produced the needed improvement in plume opacity. Relationships among the variables generating detached plume problems are quantified in such a way as to relate to the operation of control equipment to meet EPA's opacity standards.

The plume opacity model; which is based on the Beer-Lambert law, Mie light scattering theory, aerosol physics, plume dynamics and physical chemistry; allows the theoretical prediction of plume opacity. The pertinent equations are programmed in FORTRAN for machine computations.

To relate the impact of the size distribution of submicron aerosols and primary sulfuric acid vapor concentration to
plume opacity, it is required to quantify these interference effects and to develop a sound theoretical basis for this quantification. Particle size distribution curves in conjunction with plume entrainment and spreading are used to predict the particulate fraction of the plume opacity. In addition, the plume opacity due to condensed sulfuric acid aerosols is evaluated by formation of plume mass, momentum and energy balances over elapsed time from stack exit to account for acid vapor condensation and aerosol coagulation as these processes relate to plume opacity.

This study did not consider the role of long-range atmospheric transformation and transport in the ambient air. The focus of this study is on the impact of the primary emissions within one hundred meters of the stack exit.
II. PLUME CHARACTERISTICS

PHYSICAL PROPERTIES OF AEROSOL PLUMES

The interaction of light and aerosol particles is of two different types. The radiant energy received may be reradiated by receiving particles at the same wavelength in various directions but with different intensities in different directions. This process is called scattering. Alternatively, the radiant energy can be absorbed and transformed into other forms of energy, such as heat, activation energy or it may be reradiated at a different wavelength [1].

The interactions occur at all wavelengths in the electromagnetic spectrum and involve all atmospheric optical materials -- molecules of the various gases, small particles having a wide range of sizes and an astonishing diversity of sources and compositions, water droplets, etc. Air pollutant particles will scatter and absorb radiation; the relative but concurrent effects depend on particle size, shape, refractive index and the wavelength of the incident light. For very small particles, much smaller than the wavelength of the visible light, little scattering occurs and attenuation is in the form of absorption. For particles of the same or larger magnitude than the wavelength, scattering of light is the predominant form of attenuation [2].
The optical phenomena are all a direct result of the scattering and absorption of light by aerosol particles abounding near the earth's surface. For example, black smoke looks dark because the particles absorb all color fractions of visible light. Dense rain clouds look black even though the droplets absorb negligible radiation because the scattering by droplets is so complete that the light energy is essentially dissipated by the clouds. White clouds appear that color because of the extensive scattering of the incident light over all visible wavelengths [3].

All combustion processes are prolific sources of air pollutant particles. After being emitted from a stack the larger particles settle from the stack plumes within minutes. Those smaller than about 1 μm move with the plume and mingle with the hygroscopic particles for prolonged periods of time over long distances.

For example, the burning of coal produces fine mineral residues, known as fly ash, and unburned bits of carbon and tar, known as soot, as well as carbon monoxide, carbon dioxide, and sulfur dioxide [4]. All these materials except fly ash are also produced by the burning of petroleum derivatives, whether in furnaces or in internal combustion engines [5]. The latter device is also a source of several nitrogen oxides formed by recombinations of atomic nitrogen and oxygen produced by molecular dissociation at high combustion temperatures. Several of the gases noted above undergo
photochemical reactions, yielding additional types of gases and small hygroscopic particles [6]. The result is a polluted atmosphere with a noticeable haze. The air above and around industrial and metropolitan regions is marked by a pall of this dark haze.

Another common criterion of vision obscuration is the reduction in meteorological visual range [1]. In addition, the number concentration, size distribution and optical properties of particles in the plume are of great importance in the air pollution field because the degree of air pollution is typically judged by the visual appearance of stack plumes. An important part of air pollution control involves achieving compliance with opacity standards designed to control the appearance of these plumes.

The particle number concentration and size distribution in the plume play an important role in establishing plume opacity [3]. Those particles in the visual size range between 0.4 and 0.7 μm primarily govern plume visibility. The total plume opacity due to aerosols and suspended particulates results from a wider range of sizes covering from a practical standpoint of the submicrometer size range of 0.1 to 1.0 μm. Even though aerosol particles in this range are present at low mass concentration their number concentration and visual impact are significant. A change in suspended particle number concentration outside this range has little effect on light
extinction or visibility and has not therefore been of signi-
ificance in air pollution interest.

OPACITY OF PLUMES

THEORETICAL CALCULATIONS

The amount of light attenuated by a smoke plume depends on the number, size and optical properties of particulate matter in the plume. Thus, the opacity of a plume is an intrinsic physical property of the aerosol particles being emitted. A general relationship is developed in this section.

When a beam of light is passed through a suspension of particles, the intensity of the beam is attenuated as a result of the scattering and absorption. The law of extinction of the beam has been derived from simple considerations. Let the intensity of the beam be $I_0$ at a position $x_0$. After traversing a distance $dx$, the intensity will be reduced by $dI$ such that:

$$dI = \sigma I_0 \, dx \quad (2.1)$$

where $\sigma$ is the total extinction coefficient. Integrating Equation (2.1) gives:

$$I = I_0 \exp(-\sigma x) \quad (2.2)$$

which is known as the Beer-Lambert law [7]. The extinction coefficient is primarily a function of aerosol particle num-
ber concentration and size distribution. This formula may be used as the basis for an optical method for relating either of these latter quantities to opacity.

Much effort has been expanded to relate the mass concentration of particulate emissions to the optical characteristics of various plumes in the atmosphere [8-10]. The transmittance of a gas dispersoid containing suspended particles is defined as the ratio of the transmitted radiation intensity to the incident radiation intensity. The transmittance, \( \frac{I}{I_0} \), then can be expressed as:

\[
\frac{I}{I_0} = \exp(-\sigma L) \quad (2.3)
\]

where \( L \) is the path length or diameter in the case of a stack or plume. The opacity, \( \sigma \), is the degree to which the visible light intensity is attenuated when passing through the plume and is given by:

\[
\sigma = 1 - \frac{I}{I_0} \quad (2.4)
\]

Emissions which transmit all incident light are invisible, have a transmittance of 100%, and an opacity of zero. Emissions which attenuate all incident light are totally opaque, having an opacity of 100% and a transmittance of zero.

The total extinction coefficient, \( \sigma \), is given by [8]:

\[
\sigma = \frac{W}{K' \rho} \quad (2.5)
\]

where \( W \) is the concentration of the particulate mass
in suspension(g/m³),
\( \rho \) is particle material density(g/cm³),
\( K' \) is specific particle volume/light extinction
coefficient ratio(cm³/m²).

\( K' \) is primarily a function of the particle size distribution,
refractive index, and the wavelength of light. It has been
used to relate the opacity to the particle properties.

The opacity as a function of total suspended mass concen-
tration, particle material density, extinction path length,
and parameter \( K' \) can be related by Equations (2.3), (2.4) and
(2.5) and is given by:

\[
O = 1 - \exp(-\sigma L) \quad (2.6)
\]

\[
= 1 - \exp(-WL/K'\rho) \quad (2.7)
\]

The ability to relate opacity to other properties of aer-
osol particles has been an important factor for many years
in achieving an insight into the variables governing opacity
levels.
MEASUREMENT

The opacity of plumes has long been used to regulate the emissions from stationary sources. To comply with the opacity standards, a plume must not exceed the applicable opacity standard before it leaves or after it exits the stack.

In the case of a transmissometer a light source is used to transmit a collimated beam of light perpendicular to the flue gas in the stack. The opacity measured is a function of both particle number concentration and optical path length. In the case of in-stack opacity determination the opacity measured by the transmissometer must be adjusted to account for the difference in stack or duct diameter at the transmissometer location [11].

If there is no condensed aerosol formation in the plume after it leaves the stack, the in-stack opacity and plume opacity will be identical after adjustments for plume size have been made and no atmospheric air entrainment is taken into account. When condensable materials are present, plume opacity may be much greater than the in-stack opacity because more light is scattered by increased aerosol concentration.

Opacity may be measured instrumentally by optical devices such as Lidar (laser radar) and polarized light meters or may be assessed by trained opacity observers. These techniques and corresponding instrumentation are discussed below.
Certified Opacity Observer: Owing to greater general applicability to all types of stationary sources, the EPA has developed Reference Method 9 for determining opacity by trained observers [12]. Method 9 includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity.

It has been shown that a person can learn to visually determine the plume opacity readings through training and practice with a standard smoke generator and certification runs at the "Smoke School" of an air pollution control district. Method 9 is retained as the primary and accepted means for determining compliance in order to have a consistent regulatory enforcement approach for all stationary sources.

Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. When the condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible.

When water vapor in the plume condenses and becomes visible at a distinct distance from the emission discharge location, the opacity of emissions should be evaluated prior to the condensation of water vapor which forms what is called a steam plume.
The observer is trained not to look continuously at the plume, but instead to observe the plume momentarily at 15-second intervals. A minimum of 24 observations are to be recorded. Opacity is calculated as an average of 24 consecutive observations recorded at 15-second intervals [12].

LIDAR: Lidar, an acronym for Light Detection and Ranging, has been developed as a measurement technique for plume opacity, and has been approved as an alternate to Reference Method 9 [13]. This alternate method provides the objective and quantitative determination of the opacity of an emission plume remotely by a mobile Lidar unit. It has been used successfully at night as well as during the day because a pulsed light source is a self-contained component of the instrument.

The optical receiver within the Lidar measures the difference in backscattered (reflected) light from the atmosphere and aerosols in the beam passing through the plume and passing beside the plume. The receiver's detector converts the backscatter optical signal into an electronic signal. A plume's transmittance is calculated from the backscattered signal difference for the two beam positions. In practice the Lidar beam scans across the plume.

Lidar measurements should be made in the region of greatest opacity within the residual plume where the condensed water vapor is no longer visible. When the water vapor in a hydrated plume condenses and becomes visible at a finite
distance from the stack, the opacity of the emissions shall be measured in the region of the plume between the emissions outlet and the water vapor condensation region.

During daylight hours the Lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night-vision scope, or low-light-level TV, etc., can be used as an aid to locate the residual plume. Therefore, a laser may become a standard technique for measuring the transmittance of plumes.

Transmissometer: Performance specifications and test procedures for transmissometer systems which are used to continuously monitor opacity of in-stack emissions have been promulgated [14]. The principle of transmissometer is that light having specific spectral characteristics is projected from a lamp through the effluent in the stack, and the intensity of the projected light is measured by a sensor. The projected light is attenuated because of absorption and scatter by the particulate matter in the effluent. The percentage of visible light attenuated is defined as the opacity of the flue gas in the stack.

When differences occur between a certified visual observer's reported opacity and that determined by a transmissometer, Method 9 results takes precedence as specified by EPA. Data collected with an in-stack transmissometer are not accepted as a means for demonstrating compliance with
opacity standards. However, in-stack transmissometer data may be submitted as probative (but not conclusive) evidence of the actual opacity of emissions [15].

REGULATIONS

Controlling plume opacity due to emissions from utility and industrial sources is an important part of the program to improve air quality. To mitigate the effects of air pollution on human and animal health, plants, materials and the general quality of the environment, the EPA has established a standard for the maximum allowable plume opacity. State and local control agencies may adopt stricter standards if they feel they are warranted in light of the pollution problems in their particular region. The EPA and state and local agencies are empowered by law to enforce these standards.

Plume opacity, while not a pollutant, is indicative of the concentration and size distribution of the particulate matter emitted from boiler and process stacks. Regulations limiting stack emissions to a certain degree of opacity are based on the percentage of light absorbed by the stack plume as the light passes through it. They are used by regulatory agencies to regulate stack discharges. The plume observation method is simple and inexpensive for the regulatory inspector to use. The method provides an easy way for an air pollution
control authority to respond to pollution compliants from the public.

Current EPA New Source Performance Standards (NSPS) include an opacity limit of 20% [16]. It is possible that a more stringent limitation will be placed on the plume opacity in the near future. If the limitation is to ensure an invisible plume, then it will correspond to the 5% opacity which is at the lower limit discernable to the human eye [17]. Future particulate emission standards would need to be in the range of 0.01 to 0.03 lb/10^6 Btu to be consistent with this clear plume limitation [18].

DETACHED PLUMES

CAUSES OF DETACHED PLUMES

A detached plume is the persistent, visible plume which is not continuous at the point of emission. Usually, it exhibits an increase in downwind plume opacity as the hot plume is mixed with the cooler surrounding atmosphere. This increase in plume opacity is due to formation of additional optical effective material within the plume. The following processes may produce a higher plume opacity.

Gas-to-Particle Conversion: As the plume is carried downwind, pollutants such as sulfur dioxide and oxides of nitro-
gen will undergo chemical reactions to form aerosols in the form of sulfates and nitrates. Sulfur dioxide and its oxidation products have been found to cause little or no effect on the optical properties of plumes at distances up to 100 km [19]. The formation of secondary aerosols in the plume was detected in the 0.01 to 0.1 μm particle size range at such low particle concentrations that they caused no significant light scattering. New aerosols larger than 0.1 μm in the presence of the variations in the background aerosol concentration were essentially nondetectable and therefore were found to make a negligible contribution to light scattering in the near stack plume. Generally, detached plume opacity increases very quickly, within a few seconds, after the plume is released from the stack. This indicates that the condensing flue gas vapors are present in the stack gas instead of being formed by the gas to particle conversion in the plume. The formation of secondary aerosol from gas-to-particle conversion, therefore, is not discussed in this study since the focus is on the near stack plume. In the case of long range plume transport, however, secondary aerosol is thought to be the most significant source of visibility reduction [1].

Condensation of H₂SO₄ Vapor: From the stack exit, the plume is cooled by expansion and mixing with ambient air. The temperature of the plume approaches ambient levels rather quickly. As the plume expands and cools condensation of H₂SO₄
may occur at short distances from the stack. This condensation process forms a highly refractive aerosol of submicron droplets and is reported to be the most important factor in increasing plume opacity level as the plume moves away from the stack [20].

Agglomeration of Fine Particles: In modern power plants with strictly controlled emissions, the control equipment removes the larger particles with high efficiency (99.5%+), while submicron particulates are removed at efficiencies in the 30 to 70% range [21]. Particles may grow from cluster size into the 0.4 to 0.7 μm size range owing to their hygroscopic properties under some conditions when the plume surface contacts the air. Fine particles scatter light due to their reflective and refractive properties, thereby creating opacity problems.

The primary particulate emissions have a significant effect on the appearance of the plume and are generally the major cause of plume opacity when the plume is viewed near the source. Therefore, the number concentration and size distribution of the primary particles in the plume must be accounted for in detailed analytical investigations.

Condensation of Water Vapor: Water vapor contained in the flue gas emitted to the atmosphere may produce a visual impact if conditions are such that condensation occurs. When
a plume is cooled by mixing with ambient air, it may become supersaturated. Water vapor will then condense and form small droplets. These water particles scatter light and produce a white steam plume.

Generally, the condensed water plume will disappear as the plume is transported downwind. The distance taken for revaporation to occur depends on the specifics of the case of interest: plume temperature and moisture, atmospheric pressure, temperature and relative humidity, and the degree of mixing between the hot effluent gases and the ambient air [22].

For sources with wet scrubber control systems, methodology and instrumentation are needed to measure the condensed water content (not a pollutant) from the particulate concentration and size distribution. Regulations specify that opacity observations are to be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. Some air pollution regulations allow the contribution of uncombined water (water not chemically bound to the aerosol particles) to be subtracted from the observed plume opacity.

SO₃/H₂SO₄ FORMATION

During combustion, the sulfur which is present in the fuel oxidizes to sulfur dioxide. A portion of this sulfur dioxide
is further converted to sulfur trioxide, which reacts with water vapor to form sulfuric acid. At temperatures above the acid dewpoint, sulfuric acid is present as a vapor which condenses to aerosol form at the acid dewpoint.

The degree to which formation of $SO_2$ to $SO_3$ occurs depends on many factors, such as the level of excess oxygen, combustion temperature, residence time of the combustion gas and the catalytic activity of both the interior boiler surfaces and the slag deposits originating from impurities in the fuel.

Two major mechanisms for $SO_3$ formation are known. The first is $SO_2$ oxidation which takes place by a homogeneous reaction with an oxidizing flame species, thought to be oxygen atoms:

$$SO_2 + O \rightarrow SO_3$$

This conversion is due to the thermodynamic instability of the reaction at the elevated flame temperatures and tends to occur only in the range of 1500 to 3000 °F [23]. The second is the oxidation of $SO_2$ by reaction with molecular oxygen on catalytic boiler surfaces:

$$SO_2 + 1/2 O_2 + M \rightarrow SO_3 + M$$

M depicts the catalyst, usually an oxide of iron, vanadium or nickel. Equilibrium reactions favor almost complete conversion of $SO_2$ to $SO_3$; however, reaction rates are slow so that equilibrium is never reached during the short residence time involved. As a consequence, it is generally accepted
that about 1 to 5% of the SO2 is converted to SO3 in coal-fired boilers [24].

The SO3 vapor combines with water vapor to form H2SO4 vapor in a reversible reaction for which the equilibrium state is highly temperature dependent:

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$

During the time that the flue gas is being transported from the boilers and cooled by heat exchange at the air heaters all of the SO3 has been converted to H2SO4 [25]. At this point, the H2SO4 in the flue gas stream may be present in one or more of the following states:

- As a free vapor in the gas stream,
- As a vapor adsorbed on a fly ash particle,
- As a liquid aerosol (at temperatures below the acid dewpoint).

As the temperature of the flue gas decreases further below the acid dewpoint, the vapor continues to condense as an acid droplet. The amount of H2SO4 aerosol in power plant flue gases is considered the principal cause of the visible plume. Those plants firing high-sulfur fuels may have serious opacity compliance problems. At stack temperatures above 300 °F, H2SO4 vapor is normally above its dewpoint and will not
affect in-stack opacity. When the H$_2$SO$_4$ vapor leaves the stack and is cooled below its dewpoint, H$_2$SO$_4$ aerosol droplets form which cause the rapid increase in the plume opacity. Droplet condensation may be enhanced by the presence of particulates, which serve as condensation nuclei. High opacity levels may result. When the visible plume is detached from the stack, the gas stream immediately above the stack outlet is invisible but becomes somewhat opaque further downstream.

The opacity levels of detached plumes may be significantly affected by the level of sulfuric acid vapors in stack gas emissions. The sulfuric acid vapor concentration is governed by the sulfur content in the fuel, the concentrations of catalytic elements in the gas stream, and the excess air in the gas stream during combustion.

The sulfur content, percent ash, and metals concentration of the fuel affect SO$_3$ formation in different ways. Because most all of the sulfur present in oil and coal is converted to SO$_2$, which in turn may be oxidized to SO$_3$, the sulfur content of the fuel is directly proportional to the amount of SO$_3$ that may be produced (assuming all other parameters to be constant).

The ash content and composition affects the amount of particulate sulfate which forms, thereby reducing the concentration of free SO$_3$. This is directly related to the
metal content of the fuel because metal oxides frequently react with SO₃ to yield particulate sulfate.

Vanadium, iron, and nickel when oxidized, are effective catalysts in converting SO₂ to SO₃. These metal oxides are deposited in the boiler, preheater, economizer, and ductwork which then become catalytic surfaces.

The effect of excess oxygen is to control the completeness of oxidation of the combustion products. When excess oxygen is high more complete combustion is achieved, thus reducing unburned carbon but increasing acid and sulfate salt formation. At low excess oxygen levels the converse is true. Low excess oxygen (0.2 - 0.3%) operation requires precise control over the air-fuel ratio in all parts of the combustion system but has been shown to reduce plume opacity in oil-fired boilers due to the reduced acid content of the flue gas [26].

SUBMICROMETER PARTICLES IN FLUE GAS

Particulate measurements at the outlets of coal-fired utility boilers produced a typical bimodal size distribution with one peak at a particle diameter near 0.1 μm and the other peak at about 2.0 μm, depending on the ash content of the coal [27-29]. This submicrometer mode appears to be a general feature of coal combustion that results from a vaporization-condensation mechanism in utility boilers. The formation of submicron sized particles probably occurs by
homogeneous nucleation of volatilized ash, soot and sulfates as well as by the breakup of burning coal particles [30]. The submicrometer mode is characterized by a sharp distribution and contains less than 2% of the total fly ash mass generated in the boilers [31]. Although the contribution of the submicrometer mode to the total fly ash mass is small, its impact on plume opacity can be significant because particles in the submicrometer size range are more difficult to collect with conventional particulate control devices than larger particles.

The particulate collection mechanism changes with particle diameter [29]. Above 1.0 μm, the collection efficiency increases with increasing size because of interception and impaction. In the submicron range, the small particles are efficiently removed by Brownian diffusion. The smaller the particles, the more intense their Brownian motion and the easier their removal in the diffusion range. The most difficult particles to collect are those in the size range between diffusional and inertial deposition. This results in a dip in the collection efficiency curve for particles in the 0.1 to 1.0 μm range. Thus, the submicrometer mode can contain a disproportionately large fraction of the total outlet mass emissions. This mode contained about 20% of the particulate mass in utility plant stack emissions [31].

It is generally recognized that the opacity is due to the presence in the plume of a tremendous number of fine parti-
cles in the size range of 0.1 to 1.0 μm, which have a highly
effective absorbing or scattering effect but contribute lit-
tle to the mass of emission. The mass of the emission is
contributed by the larger particles, which may have little
light-scattering or light-absorbing effect [3].

In practice, coal-fired sources are equipped with either
ESP, baghouse, or FGD units for particulate or sulfur oxide
removal. By comparison, most oil-fired sources are uncon-
trolled with respect to fine particles and sulfur oxide
emissions. Submicron-particle-size distributions in
coal-fired and oil-fired emission have been measured using
low-pressure cascade impactors, diffusion batteries and
electrostatic aerosol mobility analyzers. Knapp et al. [32]
have noted the bimodality of stack gas particulate emissions
from oil-combustion sources with up to 50% of the mass occur-
rning in the 0.1 to 0.5 μm diameter particle size range.
Sulfur was identified as a major component of the submicron
aerosol. In addition, particle size measurements at
oil-fired utility boilers by Piper et al. [33] showed a
submicrometer mode at a particle diameter about 0.1 μm, which
suggested that the phenomenon may not be limited to coal
combustion.
VAPOUR CONDENSATION AND AEROSOL COAGULATION

The formation and growth of aerosol particles by vapor condensation is the principal method of aerosol production in nature [34]. This process usually requires a supersaturated vapor and is initiated by the presence of nuclei that serve as sites for particle formation. Homomolecular nucleation is a nucleation process to form new particles with one substance. The nucleation of pure water or pure sulfate droplets cannot occur under normal atmospheric conditions. The homomolecular nucleation of water droplets requires relative humidities well in excess of 100% and, similarly, the homomolecular nucleation of pure sulfuric acid droplets requires acid vapor supersaturations much larger than values to be found in the free atmosphere [35]. On the other hand, heteromolecular nucleation is a nucleation process to form new particles with more than one substance. Particles in the atmosphere are usually formed through the heteromolecular process [34]. The case with which a heteromolecular nucleation process takes place is based on the fact that the free energy barrier for the formation of solution droplets is lower than the free energy barrier for droplets of pure substances [36].

The aerosol formation process with SO₃ in the stack gases consists of three stages:
• combination of $\text{SO}_3$ and water molecule to produce $\text{H}_2\text{SO}_4$ vapor,

• nucleation of $\text{H}_2\text{SO}_4$ vapor to the critical-sized cluster (groups of molecules of condensable vapor formed by fluctuation in the gas) through the combination of several numbers of molecules of water and $\text{H}_2\text{SO}_4$,

• growth of nucleated cluster to a larger aerosol particle through the condensation of $\text{H}_2\text{SO}_4$ and water molecules, and through the coagulation with other particles.

There are two generally held mechanisms by which new aerosols can be formed in stack gases by way of sulfuric acid vapor condensation [37]. One is homogeneous heteromolecular nucleation of gaseous water and sulfuric acid molecules to form small dilute sulfuric acid droplets. The second is heterogeneous heteromolecular condensation of gaseous water and sulfuric acid molecules onto preexisting solid nuclei particles to form droplets of dilute sulfuric acid coating the nuclei particles.

Homogeneous Nucleation: When either a pure vapor or one of the constituents of a gas-vapor mixture which is free from all of foreign nuclei equals or exceeds its saturation pressure at the existing temperature, vapor condenses to form a
cluster. This homogeneous nucleation or self-nucleation is dependent upon the vapor pressure of the condensable species which is temperature dependent. For saturation ratios (a ratio of the actual pressure of the gas to its equilibrium vapor pressure) greater than 1, the vapors begin to self-nucleate and produce a large number of fine droplets of a certain critical size. The total amount of vapor condensed by this mechanism is usually small compared with that condensing on the foreign particles, but it provides a large surface area on which the condensation can proceed by heterogeneous condensation.

Heterogeneous Condensation: When large concentrations of particles are present and the vapor pressure of a vapor is low compared to saturation, condensation may take place on the existing particles without formation of new nuclei. This process is called heterogeneous condensation. In stack gases, upon reaching the dewpoint, acid vapors may begin to condense heterogeneously on the available surface area of existing nuclei. Liquid sulfuric acid continues to form on nuclei as long as the layer of sulfuric acid is at a concentration below the acid vapor equilibrium point.

Heterogeneous condensation occurs at much lower values of supersaturation than homogeneous nucleation. Thus, when particles already exist in sufficient quantities, heterogeneous condensation of acid vapor onto existing particles is
the dominant process occurring to relieve the supersaturated condition of the vapor phase material during cooling and dilution of the plume [38].

Because sulfuric acid vapor is strongly hygroscopic, it is necessary to consider binary condensation of sulfuric acid and water vapor. Under typical power station operating conditions, stack gas may have 5-15% by volume water vapor and 1-30 ppm $\text{H}_2\text{SO}_4$ [38]. The concentration of the $\text{H}_2\text{SO}_4$ vapor is much lower than the concentration of water vapor. Thus, the partial pressure of water vapor greatly exceeds that of $\text{H}_2\text{SO}_4$ vapor. For heteromolecular nucleation and condensation to occur, the growth of the particle is controlled by the diffusion rate of the rarer $\text{H}_2\text{SO}_4$ vapor, the more abundant $\text{H}_2\text{O}$ vapor being virtually always available to maintain the equilibrium concentration of both $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ vapor in the condensate.

Growth and formation of new aerosol particles by vapor condensation change the particle number concentration and size distribution in the plume. In addition, for aerosol particles of submicron diameter, aerosol coagulation also changes the particle size spectrum. Coagulation of aerosols is a process by which discrete particles collide with each other due to a relative motion between them and adhere to form larger particles. The net result is a continuous decrease in number concentration and an increase in particle size.
It is anticipated that vapor condensation and coagulation will lead to growth of molecular size particles into the 0.4 to 0.7 μm size range which is most readily visible to human eyes. Hence the light scattered due to the coagulation of small particles increases with time. Therefore, the plume opacity will increase due to formation of additional optically effective material within the plume.
III. REVIEW OF LITERATURE DEALING WITH PLUME OPACITY

OPACITY COMPLIANCE PROBLEMS

Cases of plume opacity exceeding in-stack opacity are due to 1) the aerosols formed by condensation of primary sulfuric acid and water vapor onto polydisperse plume particles and 2) the presence in the plume of particles smaller than the visual size range which grow into the visual size range by heterogeneous condensation as the plume is cooled and diluted by mixing with the ambient air.

Nader and Conner [26] compared in-stack and plume opacity at oil-fired and coal-fired boilers. They found that the plume opacity from oil-fired boilers increased with increasing sulfuric acid concentration, whereas the in-stack opacity was not affected. The observed plume opacities from a high-sulfur coal-fired boiler with an sulfur dioxide scrubber were very high (70 to 90%). They concluded that the higher plume opacity was probably caused by sulfuric acid droplet formation as the hot flue gas was cooled to below the acid dewpoint.

Conner [39] compared the in-stack and plume opacities of three oil-fired power plants of different sizes, operating at various loads and excess oxygen levels and burning fuels with different sulfur content at a high-sulfur oil-fired
power plant. Plume opacities of over 50% were reported by both opacity observer and plume Lidar. This was believed to be due to sulfuric acid aerosol formation resulting from condensation which is not monitored by transmissometer.

Dellinger et al. [40] reported a detached, high-opacity, persistent plume that emanated from an oil-fired cement kiln stack at a plant in Glens Falls, NY. The plume opacity readings ranged as high as 85% for this source while the in-stack opacity was only about 10%. The source was found to have emissions of gaseous ammonia, sulfur dioxide and water vapor. Under high relative humidity and/or low temperature, where water droplets would form before the plume dispersed, absorption of sulfur dioxide and ammonia occurred. They concluded that this plume was due to ammonium salts of sulfur oxides and sulfuric acid that formed in condensed water droplets in the plume by the pseudocatalytic action of ammonia.

Cheney et al. [41] conducted a coordinated study of process, source emission, and plume sampling at a coal-fired cement production plant. During normal production, compliance with in-stack opacity and mass loading was met but the plume opacity levels were reported to be more than 40% when measured with Lidar. Comparison of the results from the plume and source measurements indicated the formation of the plume was the result of the reaction of ammonia and hydrochloric acid. The analysis indicated that the particle size of the ammonium
chloride crystals was predominantly between 0.2 to 0.6 µm, which is a very effective size to scatter light. Consequently, plumes containing these particles are quite visible.

Armstrong et al. [42] used a remote-controlled tethered balloon sampling system to collect aerosols from the Glens Falls Portland cement plant while a very dense, bluish-white, persistent plume was being emitted. An electrostatic precipitator was used to control particulate emissions from the exhaust gases of the cement kiln. Under normal plant operations the in-stack opacity levels were less than 10% measured continuously by transmissometer. But the production of the persistent plume with an opacity often as high as 85% occurred outside the stack. They found that this plume was dominated by submicrometer, sulfur-rich liquid particles. These particles reacted with ammonia gas to form stable crystals which were similar to ammonium sulfate, ammonium bisulfate, and other ammonium salts of sulfur oxide. Subsequent condensation of droplets resulted in a persistent visible plume.

Albanese [43] observed a heavy bluish-white plume emanating from a midwestern high-sulfur coal-fired power plant equipped with an electrostatic precipitator. Flue gas sampling showed a very low particulate emission level, and in-stack opacity was consistently below 15%. Plume opacity, however, reached as high as 60-80%. This plume was "detached"
from the the stack -- a good indication that sulfuric acid condensation was occurring as the plume expanded and cooled.

Gray [44] reported a power plant using Kentucky-mined high-sulfur coal. A new high-efficiency electrostatic precipitator was installed to meet the EPA emission standards. Following the startup of the new ESP, a dense bluish-white plume developed, which maintained a consistent range of approximately 30 to 40% and could not be eliminated by any operational changes to the steam generator. The tests indicated that the plume was a condensation of sulfuric acid vapor in the flue gas which was present in two distinct forms -- free sulfuric acid aerosol and submicron fly ash particles that had absorbed sulfuric acid.

Sparks [45] investigated a utility plant burning low sulfur coal and using an electrostatic precipitator/scrubber system to meet the particulate standard at Southwest Public Service, Harrington Station. Measured emissions were 0.45 lb/10^6 Btu and 38% opacity. It was concluded that the high opacity was primarily due to the fine aerosol produced by the precipitator/scrubber system.

An interesting case involved a northern utility [46] that was burning an eastern high-sulfur coal at one plant equipped with a normal cold-side electrostatic precipitator. This plant was meeting the opacity standard but not the emission standard. After changing to a western low-sulfur coal, the plant was able to meet the mass emission standard but could
no longer meet the opacity requirement. They also reported that a power plant in Wyoming using a cold-side electrostatic precipitator was operating near the particulate emission standard but was not meeting the opacity standard. Three other western power plants had the same problem. They concluded that this can be attributed in large part to the generally fine particle size distribution of ash obtained from burning western low-sulfur coal. This tendency to produce a fine outlet particle size distribution should cause higher opacities for a given mass emission.

A high sulfur (4% S) coal-fired power plant [47] with two 240 MW units followed by an ESP and a FGD unit of the limestone spray tower type typically had residual plume opacity levels in the 30-50% range. Pilot and full scale studies were conducted in order to make recommendations for solving the opacity problem among others. It was found that a venturi scrubber operating at a pressure drop in excess of 30" W.G. would be required to reduce the opacity to the required 20% level. The energy consumption to operate the venturi unit would be enormous.

A venturi scrubber at Pennsylvania Power & Light's Holtwood Station [48] is installed in parallel with a baghouse and during the performance test the scrubber was handling 59% of the flow. An efficiency of 99.4% corresponding to a mass emission rate of 0.13 lb/10⁶ Btu was obtained. The opacity of emissions ranges from 35 to 40% and , there-
fore, is allegedly out of compliance with the EPA's 20% opacity limit.

CONTROL TECHNIQUES ASSESSMENT

The Power Plant and Industrial Fuel Use Act of 1978 was designed to minimize the use of petroleum and natural gas and to emphasize the use of coal [49]. Implementation of this act will increase the contaminant load to local environments from the combustion products of coal. However, an environmental problem facing the utility industry is the increased need for use of high efficiency (99.5%+) particulate control devices with pulverized coal-fired boilers. This is related to EPA's NSPS of 0.03 lb/10⁶ Btu and the increasing attention to control of fine particles and plume opacity. In response to these constraints, three flue gas particulate clean-up systems are considered feasible for meeting the stricter regulations of future. These systems include:

- Electrostatic precipitator (ESP) unit -- located upstream or downstream of the air heater,
- Fabric filter (Baghouse) facility -- located downstream of the air heater,
Wet scrubber system -- combination of wet particulate scrubber and flue gas desulfurization (FGD) system

Electrostatic precipitation is the dominant particulate control technique for the electric utility industry, but baghouses have received increasing attention for use on power plants and for sulfuric acid removal. Scrubbers for particulate control have not found much application in the past, but some interest has been shown in use of a moderately efficient ESP followed by a wet scrubber for both particulate and \( \text{SO}_2 \) control.

UTILITY EQUIPPED WITH ESP

Prior to the 1970s, electric utilities used ESPs for particulate emission control. There have been more than 1400 ESPs installed at coal-fired power plants since 1923. The average design collection efficiency has increased from 93.5% in 1950 to 99.0% in 1970, and by 1980 this had increased to levels in excess of 99.5% [50].

Recent regulations require much greater particulate control efficiency than did previous regulations. There is little doubt that ESPs can be constructed to meet the new stringent requirements. Technologies may also be developed and implemented that will significantly improve the perform-
ance of existing ESPs to meet both mass emission and visual opacity requirements in a continuous manner.

Electrostatic precipitators have been the dominant means of controlling particulate emissions at coal-fired power plants. With stringent SO₂ emission standards, many utility industries began shifting from high-sulfur to low-sulfur coals. However, with low-sulfur coal burning when SO₃ concentration in the flue gas is below optimum, the natural acid conditioning effect is smaller. This results in high electric resistivity of fly ash. The initial effect in this case is increased sparking, requiring a reduction of the operating voltage in order to hold a designated spark rate. Lower corona current and power input cause a decrease in collection efficiency for a given collection area [51]. Therefore, an increase in particulate emissions and an inability to meet compliance regulations for plume opacity will occur.

But with very high-sulfur coal applications where SO₃ concentration is also high, fly ash is more conductive. When low resistivity particles reach the collecting plate, they become discharged quickly and may even take an induced charge opposite to that derived from the corona system. The holding forces on the collected dust layer are small and reentrainment may occur. Thus, upon rapping, the dust tends to fly off the plate in a "puff" that is easily drawn back into the gas stream. Therefore, it is difficult to collect low resistivity dusts in ESPs. For these reasons high sulfur
coal combustion generates emissions that do not meet compliance levels for both mass emission and visual opacity.

UTILITY EQUIPPED WITH BAGHOUSE

In recent years, the electric utilities have made significant progress in designing and operating baghouses for the collection of fine particulate matter produced in the coal combustion process. In contrast to ESPs, baghouses are less sensitive to the sulfur content in the coal, boiler operating conditions, and ash compositions. Also, the success of baghouses in removing fine particles from flue gas streams encouraged use of combined dry-scrubbing/baghouse systems for the dual purpose of removing both particulates and SO₂ simultaneously. Dry scrubbing systems may offer viable alternatives to wet scrubbing and ESPs for SO₂ and particulate control.

A comprehensive analysis shows that ESP and baghouse technology are equivalent economically on fly ash from high- and medium-sulfur eastern coals which, because of their moderate electric resistivity ash, are relatively easy to precipitate. For precipitating high resistivity fly ash from low-sulfur western coals, however, baghouses are the economic choice [52]. If the future emission standards below the NSPS of 0.03 lb/10⁶ Btu are required, the advantage is to shift to the baghouse in all cases.
Currently, over 110 baghouse installations associated with more than 20,000 MW of generating capacity are either in operation, design, or under construction [53]. Most of these are being installed on plants fueled by low-sulfur coal, but interest is growing in high-sulfur coal application as well.

Utility experiences indicate that no opacity problem is found in power plants burning low-sulfur coal equipped with baghouses. In 1982, EPRI began operating a pilot plant to determine the applicability of baghouses on utility boilers burning high-sulfur coal [54]. This unit, located at Gulf Power's Scholz station, filters up to 35,000 acfm of flue gas from a 40 MW pulverized coal-fired boiler burning 2.6 to 3.2% sulfur coal. The result shows overall particulate mass collection efficiency is over 99.9% with outlet concentrations of about 0.0004 lb/10^6 Btu, well below any current particulate emission standard. The result also indicates the in-stack opacity levels are very low.

The lack of persistent plumes from these facilities could well be the result of adsorption of reactants on the filter cake, or perhaps, some sort of chemical reaction of the plume constituents with the filter cake.

**UTILITY EQUIPPED WITH FGD**

In the early 1970s, electric utility operators were faced with the requirement of reducing SO₂ emissions. As a result,
utilities selected FGD systems to meet these requirements. The most recent set of NSPS promulgated by EPA will require \( \text{SO}_2 \) removal devices on all 350 new power plants expected to be built in the United States between now and 1995. New plants are currently required to demonstrate a 70 to 90% reduction in \( \text{SO}_2 \) emissions depending on the sulfur content and heating values of the coal. It is generally believed that if more stringent regulations are imposed, wet scrubbers will provide the best available technology to meet these requirements, especially for high-sulfur coals [55].

As of September 1983, there were 111 operational FGD systems installed on electric utility boilers [56]. FGD systems are currently in operation on boilers burning coals with sulfur content ranging from 0.3 to 7.0% and \( \text{SO}_2 \) removal efficiency ranging from 50 to 92% depending on the sulfur content of coal and the type of FGD system in use.

All future coal-fired power plants will be equipped with some form of FGD [57]. Therefore, there is a trend for utilities to use the cheaper, high-sulfur coals in combination with FGD systems to meet emission standards. For example, a power plant which presently burns 1 to 2% sulfur coal to meet emission standards could switch to 5 to 6% sulfur coal and meet a more stringent standard through the use of an FGD system. But conventional FGD systems are not effective for removal of sulfate emissions and sulfuric acid from flue gas. This means that use of high-sulfur coal with FGD control will
keep SO₂ emission within bounds but may result in a significant increase in primary sulfate emissions. Thus, in controlling SO₂ emissions and reducing their contribution to secondary sulfate formation, the result will be to increase primary sulfate emissions.

Some of these units were found to emit plumes with high opacity levels. The opacity problems encountered with high sulfur coal fired boiler emissions treated with combined ESP and FGD units are mainly due to primary sulfate emissions. Concentrations of sulfate in combustion gases at scrubber outlets have been reported to exceed scrubber inlet sulfate values. It was found that on the average a wet limestone scrubber with venturi-absorber will remove sulfuric acid and metal sulfate at the 29% efficiency level while scrubbing SO₂ at the 78% level [58].

This disparity in efficiency levels is explained by the fact that SO₂ absorption is effective with the typical low energy (pressure drop) scrubber operation whereas highly efficient removal of the submicron sulfate aerosol requires high energy scrubber operation. After passing through the scrubber the submicron sulfate aerosol is essentially unabated in its pass through the mist eliminator and forms an aerosol plume with its characteristic bluish white hue. The submicron size range of the aerosol is such that plume opacity may be well above the 20% opacity standard even when
mass emissions are at or below the 0.03 lb/10^6 Btu standard or lower.

ENFORCEMENT AGAINST OPACITY VIOLATION

Detached plumes have presented a problem in efforts to regulate air pollution sources. Transmissometers installed in the stack may indicate an acceptable opacity level while the plume opacity may be quite high and unacceptable. More than forty class Al 2 power plants regulated by existing NSPS and State regulations operate with plume opacity in excess of opacity standards as measured by EPA Reference Method 9. Enforcement action against these plants consists of Federal Court Orders, Federal Consent Decrees, Administrative Consent Orders and State Stipulation Agreements [59].

Table 1 indicates overwhelmingly that ESP controlled plants generate the majority of the opacity compliance problems. EPA policy has been "... not to pursue visible emission violations where we believe it is probable that the source is in compliance with the mass standard" [60]. Due to this EPA policy, limited visible emission enforcement action has been instigated against coal-fired power plants

---

2 Emissions of more than 100 tons per year of criteria pollutant from plant with operating air pollution control equipment.
with FGD equipment because of the difficulty of measuring opacity in emissions with large quantities of water vapor.

Consultation with certified opacity observers in several states and Lidar operators indicated that a number of FGD type coal-fired power plants do have plume opacity levels above the standards. Therefore, the four FGD plants indicated in Table 1 depict only a fraction of the FGD type plants with non-compliance status with reference to plume opacity standards. The number of these units experiencing problems in complying with plume opacity standards should be determined. Some plumes are subject to a no visible plume standard (5% opacity) and some a 10 or 20% standard for 3 minutes maximum depending on the state having jurisdiction and any applicable Prevention of Significant Deterioration (PSD) or State Implement Plan (SIP) designations.

The factors affecting plume opacity in reactive plumes were not well understood in 1971 when EPA promulgated NSPS for power plants. As a result the enforcement of regulations was such that the power plant plume opacity required by the standard could be overlooked after it had been demonstrated that mass emission limits were being met and that steps were taken to operate the source so as to minimize opacity emissions [61].
### Table 1 Electric Utility Data

<table>
<thead>
<tr>
<th>Power Plants Operating</th>
<th>Pollution Control Equipment</th>
<th>Collection Efficiency (%)</th>
<th>Opacity Violations Reported</th>
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<tr>
<td>178</td>
<td>ESP</td>
<td>95-99.5</td>
<td>41</td>
</tr>
<tr>
<td>59</td>
<td>FGD</td>
<td>45-99</td>
<td>4</td>
</tr>
<tr>
<td>31</td>
<td>Baghouse</td>
<td>99-99.9</td>
<td>0</td>
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</tbody>
</table>
IV. MODEL FORMULATION

RECENT RESEARCH RELATED TO OPACITY MODEL

Very little research has been done so far to model and predict the opacity of detached plumes caused by sulfuric acid aerosols. Most related information on this problem either is unpublished or has not been developed in a systematic manner. A brief description of several relevant studies is given below.

Pilat and Wilder [38] considered the formation mechanisms of primary sulfuric acid droplets in cooled industrial emissions. The plume opacity was calculated by Equation (2.6). Calculation assumptions include heterogeneous condensation of sulfuric acid and water onto monodisperse nuclei of 0.05 μm diameter, three aerosol particle number concentrations of $10^6$, $10^7$ and $10^8$ per cm$^3$ and plume diameter of 6 m. The calculated results showed that at stack gas temperatures in excess of 125°C, initial sulfuric acid stack gas concentrations of 10 ppm or less would result in plume opacities of 20%. The equations and calculation procedures presented are of significance in explaining the plume opacities observed for emissions containing sulfuric acid.

Ensor et al. [62] presented a calculation procedure for theoretically predicting the magnitude of light transmittance.
across a smoke plume downwind of an emission source. This procedure is based on a combination of the Mie light scattering theory and the Gaussian plume diffusion equations. Emission source information needed to estimate the downwind opacity includes the meteorological conditions, stack height, stack gas temperature and exit velocity, aerosol emission mass flow rate, size distribution and particle refractive index.

Wilder and Pilat [63] mathematically investigated the influence of primary condensed sulfuric acid on the composition, size distribution, and opacity of particles in industrial and power plant emissions. The plume opacity of the polydisperse condensed aerosol was calculated using Equation (2.6). They assumed the gas cooling mechanism was by adiabatic dilution with cool ambient air and the condensed droplets were pure light scatters. Condensational droplet growth of an initial nuclei distribution was only calculated in a simplified approach for various dilution ratios. The calculated results showed that maximum condensed plume opacity should increase significantly for higher acid vapor concentrations in the flue gas, and should depend very strongly on the number concentration of condensation nuclei in the flue gas.

Damle et al. [64] described the condensation processes occurring in detached plumes and the resulting increase in plume opacity. This model is for condensation of vapors in a
plume based on fundamental aerosol physics and plume dynamics and its effect on plume opacity. The plume opacity depends on the obscuration properties of the particulate phase expressed as specific extinction coefficient and on the light path length which is the plume radius. They considered the continuous and gradual dilution of the plume and determined plume properties as a function of time. Suspended particle size distribution and light scattering information were input manually for 25 selected particle size ranges. Vapor condensation and the presence of submicron particles in the plume gases were related to plume opacity.

Dietz and Wieser [65] conducted a study of sulfate formation in oil-fired power plant plumes and produced the following empirical equation which the authors called a "somewhat speculative correlation".

\[
TPO = 1.67[\text{MSO}_4] + 3([\text{H}_2\text{SO}_4] - 6) \tag{4.1}
\]

where TPO is the total plume opacity in %,

\([\text{MSO}_4]\) is the concentration of the metal sulfate in the flue gas(ppm),

\([\text{H}_2\text{SO}_4]\) is the concentration of the sulfuric acid in the flue gas(ppm).

The value of \([\text{MSO}_4]\) was predicted by

\([\text{MSO}_4] = (0.175/7.07+0.32[O_2])(1-\text{ESP}^{0.8}/100)\)
\[
\times\{[\text{Na}]+0.38([\text{V}]+[\text{Mg}])+10[\text{H}_2\text{SO}_4]\} \tag{4.2}
\]

where \([\text{O}_2]\) is the furnace oxygen in Vol. %,

ESP is the ESP efficiency in %,

\([\text{Na}], [\text{V}], [\text{Mg}]\) are the ppm on a weight basis of sodium, vanadium and magnesium in the fuel oil.

The sulfuric acid concentration in the flue gas was given by

\[
[\text{H}_2\text{SO}_4] = 1300 \times \frac{L \times [\text{O}_2][\text{S}]}{(7.07+0.32[\text{O}_2])^2} \times ([\text{V}]/[\text{V}]+[\text{Mg}]+[\text{Na}]+[\text{M}]+1/2[\text{C}]) \tag{4.3}
\]

where \([\text{H}_2\text{SO}_4]\) is the sulfuric acid concentration in the flue gas (ppm),

\(L\) is the fraction of full plant power output capacity,

\([\text{S}]\) is the sulfur content of the fuel oil in wt. %,

\([\text{M}]\) is the wt. % of metal other than \([\text{V}], [\text{Mg}],\)

and \([\text{V}]\) in the fuel,

\([\text{C}]\) is the unburned carbon in the fly ash as a fraction of carbon in the fuel oil, wt. ppm.

Since this opacity correlation is based on sparse data from various sources with incomplete data sets, additional studies must be carried out to validate its range of applicability.
DESCRIPTION OF THE MODEL

Many complex factors control the opacity of smoke plumes. Modeling power plant plume opacity involves various aspects of the physics and chemistry of air pollutants. A near-stack aerosol plume opacity model has been developed in this research to deal with light interactions, plume dynamics and aerosol physics. The objective of this model is to obtain sufficient understanding of the major factors to formulate a theoretical analysis of the plume opacity.

A schematic flow diagram of the model is shown in Figure 1. It shows that four streams of input information enter the preprocessing module. The preprocessing module takes this information and renders it useful for the main computational part of the opacity model. It transmits to the main program the various channels of input data shown on the diagram. Then plume opacity as a function of time constitutes the output of the model. A more detailed description of the various model components is given in the following sections.

THE OPTICS MODULE

Light extinction refers to the interaction of the sunlight with aerosols and gases and is caused by scattering and absorption. The light scattering and absorption of aerosols depend on their sizes and compositions. Light scattering is
Source emissions \rightarrow \text{Control equipment} \rightarrow \text{Preprocessing module} \rightarrow \text{Optical parameters} \rightarrow \text{Meterological conditions}

\begin{itemize}
  \item Background and initial conditions
  \item Initial conditions
  \item Plume cooling and spreading
  \item Vapor condensation and nucleation
  \item Particle coagulation
  \item Numerical integration
  \item Light scattering and absorption
\end{itemize}

\begin{itemize}
  \item Plume opacity
  \item Particle concentration and size distribution
  \item Rate of change of $\text{H}_2\text{SO}_4$ concentration due to vapor condensation
  \item Rate of change of size distribution due to coagulation, condensation and nucleation
  \item Total light extinction coefficient
\end{itemize}

Figure 1. Schematic Logic Flow Diagram of Opacity Model
partially responsible for the optical effects caused by aerosol particles and plays an important role in plume opacity. Light scattering equations vary according to the relationship between the wavelength of the radiation being scattered and the size of the particles causing scattering. The scattering of light by very small and very large particles can be treated from a relatively simple point of view. Unfortunately, most light scattering problems in air pollution fall into the difficult intermediate size range and the scattering of light by these particles is a complicated phenomenon.

The wavelengths of light in the visible range fall in the 0.4 to 0.7 μm range. For particles much smaller than the visible wavelength range, the scattering is called Rayleigh scattering or molecular scattering. The scattered intensity is proportional to the sixth power of the particle diameter and inversely proportional to the fourth power of the wavelength of the light used [6]. Rayleigh's law of scattering is valid for small particles of size up to about 0.1 the wavelength of light. The principal Rayleigh scatterers in the atmosphere are the molecules of atmospheric gases. In polluted atmospheres molecular scattering is usually small compared with aerosol scattering.

In the case of very large spheres, geometric optics may be used to estimate the scattering field, that is, one may trace rays of light by the classical laws of refraction and reflection at the interface [1]. The quantity of extinction
efficiency converging to a value of 2 for large particles implies that a large particle removes from the beam twice the amount of light intercepted by its geometric cross-sectional area.

As the particle size increases beyond the region described by the Rayleigh approximation, the scattering relationship becomes very complex and Mie theory applies. As the particle size increases further, the intensity of scattering becomes more pronounced in the forward direction. In this size range, expressions for the scattering are obtained by solving Maxwell's wave equations for the regions inside and outside the sphere with proper boundary conditions [3].

The scattering of light by aerosol particles whose size is of the same order as the wavelength of light in the visual range is a complicated phenomenon. However, atmospheric visibility and plume appearance are governed by particles which have the size range from 0.1 to 1.0 μm in diameter. For this case Mie's solution is applicable since it includes formulation for light scattering and absorption over the particle size range of interest in this research.

THE EXTINCTION COEFFICIENT

It is now generally recognized that light scattering in the aerosol plume is primarily due to particles with diameters in the size range 0.1 to 1.0 μm. Aerosol particles can
also interact with light through absorption, although the effect of absorption is usually smaller than that of scattering. Therefore, the total extinction coefficient includes the effects of absorption and scattering:

\[ \sigma = \sigma_1 + \sigma_2 \]  

where \( \sigma_1 \) is the scattering coefficient (m\(^{-1}\)),  
\( \sigma_2 \) is the absorption coefficient (m\(^{-1}\)).

The quantity of \( \sigma \) represents the fraction of the incident light scattered and absorbed by the aerosol particle per unit length of path. The advantage of dealing with the total extinction coefficient is that it is closely related to one of the most common measures of visual air standard, the plume opacity.

From the definition of the extinction coefficient, a monodisperse aerosol having \( n \) particles per unit volume (cm\(^3\)) of air the extinction coefficient per unit length (m) is given by:

\[ \sigma = 10^{-6} \left( \pi d^2/4 \right) \Omega n \]  

where \( d \) is the particle diameter (\( \mu m \)),  
\( \Omega \) is the extinction efficiency factor.

The extinction efficiency of a particle is the sum of its scattering efficiency (\( \Omega_1 \)) and its absorption efficiency (\( \Omega_2 \)).
\[ Q = Q_1 + Q_2 \] \hspace{1cm} (4.6)

If there is no light absorption, the \( Q \) is identical to the \( Q_1 \) and \( \sigma \) is identical to the \( \sigma_1 \).

For a polydisperse distribution of particles, the total extinction coefficient is a function of the particle size distribution, particle composition and the incident light wavelength. The value of \( \sigma \) is calculated from the particle number concentration and the light extinction cross-sectional area for each particle size class:

\[ \sigma = 10^{-6} \int_0 \left( \pi d^2/4 \right) Q(d,m,\lambda)n(d)d(d) \] \hspace{1cm} (4.7)

where \( n(d) \) is a continuous function defined within the diameter interval from \( d \) to \( d+d(d) \) representing the number of particles per unit volume (cm\(^3\)) of each size range. The value of \( Q(d,m,\lambda) \) is evaluated for each particle size \( d \) and are a function of the refractive index of the particle material as well as wavelength of the incident light.

The extinction coefficient plays a central role in the optical behavior of particulate systems. If the aerosol is composed of a mixture of particles from separate sources with different refractive indices, the composite value of \( \sigma \) must be evaluated by summing over different aerosols and their respective size distributions.
MIE THEORY

Scattering of electromagnetic radiation is the result of an interaction between the incident wave and electrons contained in the scattering material. Secondary waves are emitted at the wavelength of the incident radiation. The scattered field has been derived theoretically by finding solutions to Maxwell's equations for the associated electric and magnetic field strengths from a single particle (Mie, 1908). This original paper was written in German, but a complete discussion of applications of the Mie solution may be found in Deirmendjian [66], Kerker [67], or van de Hulst [68].

The Mie scattering theory treats the scattering of light by a homogeneous spherical particle of arbitrary size and refractive index. The resulting general solution to the problem of light scattering and absorption by spheres is valid for absorbing and nonabsorbing spheres from molecular dimensions to particles of several \( \mu m \) in diameter. An important application of the Mie theory is the study of plume opacity, the most striking feature of fine particle pollution.

For computation purposes, \( Q_1 \) and \( Q \) according to the Mie model are given by [66]:

\[ \text{[Equation]} \]
\[ Q_1 = \sum_{n=1}^{\infty} \frac{(2/n) \left( (2n+1) \right) \left[ |a_n|^2 + |b_n|^2 \right]} {n} \tag{4.8} \]

\[ Q = \sum_{n=1}^{\infty} \frac{(2/n) \left( (2n+1) \right) \text{Re}[a_n + b_n]} {n} \tag{4.9} \]

where \( \text{Re} \) signifies the real part of the complex variable expression. The expression \( x = \pi d/\lambda \) is a dimensionless size parameter relating particle diameter, \( d \), to the wavelength, \( \lambda \), of the incident electromagnetic wave. The complex amplitude functions \( a_n \) and \( b_n \) represent the \( n \)th electric and magnetic partial waves contributing to scattering. They depend on size parameter \( x \) and the complex index of refraction of an aerosol particle \( m \) but are independent of the scattering angle and the state of polarization of the incident light.

To solve the amplitude functions \( a_n \) and \( b_n \), we start with the Mie formulae given by van de Hulst [68] which are:

\[ a_n = \frac{x\psi_n'(y)\psi_n(x) - y\psi_n'(x)\psi_n(y)} {x\psi_n'(y)\xi_n(x) - y\xi_n'(x)\psi_n(y)} \tag{4.10} \]

\[ b_n = \frac{y\psi_n'(y)\psi_n(x) - x\psi_n'(x)\psi_n(y)} {y\psi_n'(y)\xi_n(x) - x\xi_n'(x)\psi_n(y)} \tag{4.11} \]

where \( y = mx \), \( m \) is the refractive index in complex number form, and the primes represent first derivatives with respect to
the functions $\psi_n(z)$ and $\xi_n(z)$ which are the Riccati-Bessel functions. They can be written in terms of Bessel functions of the first kind of order $(n+\frac{1}{2})$ by using the definitions of spherical Bessel functions as follows:

$$\psi_n(z) = (\pi z/2)^{\frac{1}{2}}J_{n+\frac{1}{2}}(z)$$  \hspace{1cm} (4.12)$$

$$\xi_n(z) = (\pi z/2)^{\frac{1}{2}}[J_{n+\frac{1}{2}}(z) + (-1)^n J_{-n-\frac{1}{2}}(z)]$$ \hspace{1cm} (4.13)$$

The third Riccati-Bessel function is:

$$\chi_n(z) = (-1)^n(\pi z/2)^{\frac{1}{2}}J_{-n-\frac{1}{2}}(z)$$ \hspace{1cm} (4.14)$$

and

$$\xi_n(z) = \psi_n(z) + i\chi_n(z)$$ \hspace{1cm} (4.15)$$

The basic computational problem involved in the Mie theory is that of evaluating $a_n$ and $b_n$ for given values of $m$ and $x$. Define:

$$A_n(y) = \frac{\psi'_n(y)}{\psi_n(y)}$$ \hspace{1cm} (4.16)$$

and use the recursion formulae for Bessel functions of arbitrary order and argument. The Bessel function derivatives can be shown to be:
\[
\psi_n(x) = (\pi x/2)^{\frac{1}{2}} [J_{n-\frac{1}{2}}(x) - (n/x) J_{n+\frac{1}{2}}(x)] 
\]  
(4.17)

and

\[
\xi_n'(x) = (\pi x/2)^{\frac{1}{2}} [J_{n-\frac{1}{2}}(x) - (n/x) J_{n+\frac{1}{2}}(x)] + (-1)^{n+1} [J_{-n+\frac{1}{2}}(x) + (n/x) J_{-n-\frac{1}{2}}(x)] 
\]  
(4.18)

Substituting these expressions into Equations (4.10) and (4.11) and simplifying by cancellation and rearrangement of terms give the expression:

\[
a_n = \frac{(A_n(y)/m + n/x) Re(\xi_n(x)) - Re(\xi_{n-1}(x))}{(A_n(y)/m + n/x) \xi_n(x) - \xi_{n-1}(x)} 
\]  
(4.19)

\[
b_n = \frac{(mA_n(y) + n/x) Re(\xi_n(x)) - Re(\xi_{n-1}(x))}{(mA_n(y) + n/x) \xi_n(x) - \xi_{n-1}(x)} 
\]  
(4.20)

To generate \(\xi_n(x)\) the recurrence relations:

\[
\xi_n(x) = (2n-1/x) \xi_{n-1}(x) - \xi_{n-2}(x) 
\]  
(4.21)

\[
\xi_0(x) = \sin x + i \cos x 
\]  
(4.22)

\[
\xi_{-1}(x) = \cos x - i \sin x 
\]  
(4.23)
were used. $A_n(y)$ is given by:

$$A_n(y)=-(n/y)+[(n/y)-A_{n-1}(y)]^{-1} \quad (4.24)$$

$$A_0(y) = \cos y / \sin y \quad (4.25)$$

Since $y=mx=p'-iq'$, where $p'$ and $q'$ are the real and imaginary part of the index of refraction, $A_0(y)$ may be expressed in terms of circular and hyperbolic functions of real argument. In rationalized form:

$$A_0(y)=(\sin p \cos p + i \sinh q \cosh q) / (\sin^2 p + \sinh^2 q) \quad (4.26)$$

This is the generating function used in the model in combination with Equation (4.24) to compute $A_n(y)$. Equations (4.19-4.26) are in a form suitable for machine computation of $a_n$ and $b_n$ for given $m$ and distribution of $x$. The efficiency factors given by Equations (4.8) and (4.9) are calculated by summing up the terms in the series. In practice the series is said to converge when the addition of one additional term alters the sum by less than a preassigned value such as 0.1 of 1%. Convergence was found to be fairly rapid for small values of $x$ and less rapidly converging when $x$ was increased over the particle size range of the flue gas.
GOVERNING EQUATIONS FOR PLUME DYNAMICS

The opacity levels of plumes discharged from coal-fired and oil-fired boilers depend strongly on the plume parameters such as plume spread, particle number concentration and size distribution and condensed acid vapor concentration. A few stack diameters downwind from stack exit, the spread of the plume resulting from entrained air causes the cross-sectional area of the plume to increase, and the concentration of inert particles in the plume to decrease. The plume temperature approaches the acid dewpoint level as the ambient air entrainment continues. Condensation processes cause existing particles to grow in size. The model component to account for these processes is discussed in the following section.

When a hot gas plume is emitted into a cooler environment, a major factor in determining plume behavior is the rate at which it entrains ambient air. Entrainment formulation of an empirical nature has been developed to predict plume entrainment of ambient air into the plume which results from two mechanisms. The first is due to shear. The second is due to transport. Hoult et al. [69] assumed that two mechanisms are additive and that (Figure 2):

\[ E = a_1 2\pi r (U - V_0 \cos \theta) + b_2 2\pi r V_0 \sin \theta \]  

(4.27)

where \( E \) is the entrainment rate \((m^2/sec)\),

\( V_0 \) is wind speed \((m/sec)\),
Figure 2. Coordinate system for near-stack plume
U is the mean plume speed (m/sec),
θ is the plume orientation angle related
to the horizontal plane,
ν is the plume radius (m),
α and β are the dimensionless parallel and
perpendicular entrainment coefficients,
α=0.11 and β=0.55 [70].

The entrainment velocity, \( V \), is related to the plume centerline velocity by:

\[
V = \alpha(U - \nu \cos \theta) + \beta \nu \sin \theta \tag{4.28}
\]

Observation of the behavior of the plumes escaping from stacks into the atmosphere reveals great variations in plume rise and spread. Relating plume trajectory and spread of a plume was carried out from fundamental considerations of conservation of mass, energy and momentum as applied to a plume element [64,69-71].

Model development was based on the following assumptions:

- Hot emissions are cooled by adiabatic dilution with ambient air under near-stack plume conditions.
• The effects of atmospheric turbulence on plume behavior are less than entrainment effects for short distances from the stack exit.

• The wind direction changes with plume rise are negligible.

• The plume is essentially axisymmetric.

• All condensable \( H_2SO_4(g) \) and \( H_2O(g) \) are primary gases.

• The initial fly ash is considered to be inert with respect to condensed sulfuric acid vapor. Every particle is assumed to be a condensation nuclei.

The mass entrainment rate in the direction of plume motion is equal to the rate of change of mass flow in the diverging plume such that:

\[
d(\rho r^2U)/ds = 2\rho_0 V \tag{4.29}
\]

where \( \rho \) is plume gas density \((g/cm^3)\),
\( \rho_0 \) is air density \((g/cm^3)\),
\( s \) is the plume displacement \((m)\).

From momentum consideration for the case when net buoyancy and gravity forces acting on the plume are large compared to the vertical shear forces.
\[
\frac{d(\rho r^2 U^2 \sin \theta)}{ds} = r^2 g(\rho_0 - \rho) \quad (4.30)
\]

where \( g \) is gravitational acceleration (m/sec^2).

The horizontal component of the momentum equation is given by

\[
\frac{d(\rho r^2 U^2 \cos \theta)}{ds} = 2\rho_0 V_0 V \quad (4.31)
\]

From conservation of energy consideration it may be stated that the change in plume energy content as it develops is equal to the rate of energy transport into the plume which may be written as:

\[
\frac{d(\rho \pi r^2 U C_1 T)}{ds} = \rho_0 (2\pi r ds) V C_2 T_0 \quad (4.32)
\]

where the specific heats of the plume gas \((C_1)\) and surrounding ambient air \((C_2)\) are treated as equal. Equation (4.32) may thus be written as:

\[
\frac{d(\rho r^2 U T)}{ds} = 2\rho_0 r V T_0 \quad (4.33)
\]

where \( T \) is the plume temperature (°K),

\( T_0 \) is the ambient air temperature (°K).

Also note that (Figure 2):

\[
\frac{dX}{dt} = U \cos \theta \quad (4.34)
\]
\[
\frac{dZ}{dt} = U \sin \theta \quad (4.35)
\]

Equations (4.29-3.31 and 4.33) can be rearranged and written as:

\[
\frac{dr}{dt} = V(2 - V_0 \cos \theta / U)(\rho_0 / \rho) - (r \gamma \sin \theta / 2U)(\rho_0 / \rho - 1) \quad (4.36)
\]

\[
\frac{dU}{dt} = (2V/r)(V_0 \cos \theta - U)(\rho_0 / \rho) + \gamma \sin \theta (\rho_0 / \rho - 1) \quad (4.37)
\]

\[
\frac{d\theta}{dt} = (\gamma \sin \theta / U)(\rho_0 / \rho - 1) - (2VV_0 \sin \theta / rU)(\rho_0 / \rho) \quad (4.38)
\]

\[
\frac{dT}{dt} = (2V/r)(T_0 - T)(\rho_0 / \rho) \quad (4.39)
\]

Finally, in order to examine the effect of condensing species and fine particle concentrations on plume opacity, it is necessary to incorporate acid vapor condensation, nucleation and coagulation processes. Applying the mass conservation principle to each condensing species, C, gives:

\[
\frac{d(r^2 UC)}{ds} = 2rVC' \quad (4.40)
\]

where C is the molar concentration of the condensing species in the plume (g-mole/cm³),

C' is the molar concentration of the condensing
species in ambient air (g-mole/cm³).

Equation (4.40) can be combined with Equations (4.29-4.33) and written with time as the independent variable as:

\[
\frac{dC}{dt} = \left(\frac{2V}{r}\right)\left(C' - \frac{C_p}{\rho}\right)
\]

(4.41)

The derivation of Equations (4.36-4.39) and (4.41) is given in Appendix B.

Water vapor and sulfur trioxide, which are generated in the combustion process, react to form H₂SO₄ in the flue gases. As the flue gases are progressively cooled below the acid dewpoint in the plume a sulfuric acid condensate forms. The prediction of acid dewpoint from flue gas composition and temperature using aqueous sulfuric acid vapor-liquid equilibrium information is critical.

An empirical correlation of the acid dewpoint temperature as a function of the concentrations of H₂SO₄ and H₂O vapors for the prediction of dewpoints in flue gases was given by [72]:

\[
T_1 = [0.002276 - 0.00002943 \ln P_2 - 0.0000858 \ln P_1 \\
+ 0.0000062 (\ln P_1)(\ln P_2)]^{-1}
\]

(4.42)

where \(T_1\) is the acid dewpoint temperature (°K),

\(P_1\) is the partial pressure of H₂SO₄ vapor (mm Hg),

\(P_2\) is the partial pressure of water vapor (mm Hg).
The acid dewpoint temperatures predicted by this formula have been compared with independent experimental data. The calculated dewpoint temperatures corresponded closely to the experimental values, the deviation was within ±3 or 4°C over the range of dewpoints between 100 and 230°C, which is almost within experimental error. The H₂SO₄–H₂O system dewpoint depends on the gaseous H₂SO₄ and H₂O concentrations. The acid dewpoint temperature increases with higher H₂SO₄ and H₂O vapor concentration.

In general, the equilibrium partial pressures of sulfuric acid and water vapor are estimated from an equation of the following form [73]:

\[
\log P' = f(w, T)
\]

(4.43)

where \( P' \) represents the equilibrium partial pressure of either sulfuric acid or water vapor (mm Hg),

\( w \) is the weight fraction H₂SO₄ in the aqueous H₂SO₄ mixture,

\( T \) is the flue gas temperature (°C).

For model calculations, Equation (4.44) was developed based on data plotted in Figure 3 as given by Gmitro and Vermeulen [74]. The equation is:

\[
\log P' = a_1 + a_2 w + a_3 T + a_4 w T + a_5 w^2 + a_6 T^2 \\
+ a_7 w^2 + a_8 w T^2 + a_9 w^2 T^2
\]

(4.44)

where the coefficients \( a_1 \) – \( a_9 \) are listed in Table 2. The data produced by Gmitro and Vermeulen relating the equilib-
rium pressures of water and \( \text{H}_2\text{SO}_4 \) above sulfuric acid solutions as a function of the weight fraction \( \text{H}_2\text{SO}_4 \) and at various temperatures are shown in Figure 3 [75].

In the case of plumes containing acid gases, acid vapor condenses onto fly ash particles to create droplets. When high concentrations of particles are present and supersaturation is low, condensation takes place on the existing particles without formation of new nuclei. This process is known as heterogeneous condensation. The molecular condensation rate due to diffusion of \( \text{H}_2\text{SO}_4 \) vapor molecules to a particle of size \( d \) is given by [3]:

\[
N = 2\pi D d \left[ \frac{P - P'}{kT} \right] \left[ \frac{1 + Kn}{(1 + 1.71Kn + 1.333Kn^2)} \right] \tag{4.45}
\]

where \( N \) is the molecular condensation rate

- on a single aerosol particle (molecules/sec)
- \( D \) is the diffusivity of acid molecules in the plume (cm\(^2\)/sec),
- \( d \) is the particle size (\( \mu \)m),
- \( P' \) is the equilibrium vapor pressure at the droplet surface (mm Hg),
- \( P \) is the partial pressure of the condensing vapor (mm Hg),
- \( k \) is the Boltzmann's constant (dyne-cm/\(^\circ\)K)
- \( T \) is the plume temperature (\(^\circ\)K)
- \( Kn \) is the Knudsen number (= 2l/d),
- \( l \) is the mean free path of the gas (\( \mu \)m).
Table 2  Equation coefficients

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{SO}_4$ vapor</th>
<th>$\text{H}_2\text{O}$ vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>-33.76300</td>
<td>-1.96200</td>
</tr>
<tr>
<td>$a_2$</td>
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<td>14.24500</td>
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<tr>
<td>$a_3$</td>
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<td>0.02246</td>
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<tr>
<td>$a_7$</td>
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<td>0.08250</td>
</tr>
<tr>
<td>$a_8$</td>
<td>0.00289</td>
<td>0.00020</td>
</tr>
<tr>
<td>$a_9$</td>
<td>-0.00191</td>
<td>-0.00026</td>
</tr>
</tbody>
</table>
Figure 3. Aqueous Sulfuric Acid Properties
The mean free path can be calculated from the kinetic theory of gases. As a good approximation for a gas composed of molecules that act like rigid elastic spheres:

\[ \ell = v (\pi m / 2kT)^{\frac{1}{2}} \]  \hspace{1cm} (4.46)

where \( v \) is the kinematic viscosity of the gas (cm²/sec),

\( m \) is the molecular mass (g/molecule).

For normal temperatures and pressures, the mean free path in the air is about 0.065 μm.

Therefore, these foreign particles may consume most of the \( \text{H}_2\text{SO}_4 \) concentration by condensation. The expression for a net loss of condensing vapors in g-mole per second per unit volume of plume due to condensation onto polydisperse aerosol particles in the plume is given by:

\[ H = \sum_{i=1}^{h} N_i n_i / N_0 \]  \hspace{1cm} (4.47)

where \( H \) is the net loss of condensing vapors from the plume (g-mole/cm³·sec),

\( n_i \) is the number concentration in \( i^{th} \) channel (cm⁻³μm⁻¹),

\( h \) is the number of size channels,

\( N_0 \) is Avogadro's number.

Modifying Equation (4.41) to account for the condensation gives:
\[ \frac{dC}{dt} = (-2VC_p/\rho r) - H \quad (4.48) \]

where ambient $H_2SO_4$ concentration is assumed to be zero.

In typical industrial emission conditions the $H_2SO_4$ vapor concentration is very small compared to water vapor concentration. Since the heterogeneous condensation process will not consume significant amounts of water vapor, the concentration of water vapor will not be changed significantly. The rate of growth by vapor condensation is controlled by the impinging rate of $H_2SO_4$ vapor onto the preexisting particles.

As a hot stack plume spreads and cools, the particle size distribution will depend on the extent of the self nucleation and condensation of water and sulfuric acid molecules on aerosol particles. The interparticle collision of fine particles will also be a factor in governing the final size distribution.

By conservation consideration of particulate components in the plume, the dynamic equation for the particle concentration for each size channel to account for plume spread, condensation and coagulation is given by:

\[
\frac{dn_i}{dt} = [dn_i/dt]_{\text{spread}} + [dn_i/dt]_{\text{coagulation}} + [dn_i/dt]_{\text{growth}} \quad (4.49)
\]
where \( \frac{dn_i}{dt} \text{spread} \) is given by \(-\frac{2V}{r}(\rho_0/\rho)n_i\) and ambient particle number density is negligible when compared to plume values.

The time rate of change of the number of particles in a given channel due to acid vapor molecules condensing on existing fly ash particles per unit volume of plume is given by:

\[
\frac{dn_i}{dt} \text{growth} = I_{i-1} - I_i \tag{4.50}
\]

where \( I_i \) is given by \((N_i v/V_i)n_i\),

\( v \) is the molecular volume(\( \mu m^3 \)),

\( V_i \) is the volume of particle with size \( d_i (\mu m^3) \).

Molecules of a condensable specie may self-nucleate. At high supersaturations, heteromolecular nucleation will occur, leading to the formation of high concentrations of small particles. The Kelvin effect sets a lower limit on the particle size of a polydisperse aerosol that can serve as condensation nuclei [1].

\[
d_c = \frac{4\gamma v}{kT \ln S} \tag{4.51}
\]

where \( d_c \) is critical droplet diameter(\( \mu m \)),

\( \gamma \) is the surface tension of sulfuric acid solution droplet(\( \text{dyne/cm} \)),

\( S \) is the saturation ratio(=\( P/P' \)).
In making these calculations, it is assumed that the surface tension is constant and therefore independent of droplet size.

The time rate of change of the number of molecular clusters formed by the homogeneous nucleation process is given by [1]:

\[ I_1 = \frac{(2P_n v/kT)(\gamma/2\pi m)^{3/2}}{v} \exp\left[ -5.33 \frac{\gamma' v^2}{(kT)^3 (\ln S)^2} \right] \]  

(4.52)

New particles formed by nucleation are very small -- on the order of molecular size (0.005 \( \mu \)m) -- and therefore will only affect the number concentration of particles in the first size channel (0.01 \( \mu \)m) in this model.

Smoluchowski [76] applied the theory of Brownian diffusion to the statistical problem of the collision in a coagulating system containing particles of very different sizes. Let \( F_{jk} \) be the number of collisions occurring per unit time per unit volume between the two sizes of particles of size \( d_j \) and \( d_k \). All particles are assumed to be spherical. When two particles collide, they coalesce to form a third whose volume is equal to the sum of the original two. The collision frequency \( F_{jk} \) can be written as follows:

\[ F_{jk} = B(j,k)n_j n_k \]  

(4.53)

where \( B(j,k) \) is the coagulation coefficient which
is non-negative and symmetric, i.e. \( B(j,k) = B(k,j) \).

\( n_j \) and \( n_k \) are the number of particles per unit volume with size \( d_j \) and \( d_k \).

For the coagulation coefficient, \( B(j,k) \), we assume that particle collisions are two body and that Brownian diffusion is the dominant collision mechanism. The equation is given by:

\[
B(j,k) = \pi (d_j + d_k) (D_j + D_k) \tag{4.54}
\]

where \( D_j \) and \( D_k \) are the coefficients of diffusion (cm\(^2\)/sec).

The coefficient of diffusion is one of the important transport properties in an aerosol. An expression for \( D \) can be derived as a function of the size of the particle and the properties of the gas [1].

\[
D = kT C_3 / 3 \pi \mu d \tag{4.55}
\]

where \( \mu \) is the viscosity (dyne-sec/cm\(^2\)).

The slip correction factor \( C_3 \) is given by [1]:

\[
C_3 = 1 + (2 \ell / d) [1.257 + 0.4 \exp(-0.55d/\ell)] \tag{4.56}
\]

In the case of a discrete size spectrum, the number of size \( d_i \) particles increase by collisions of size \( d_j \) and \( d_k \) particles such that \( j + k = i \) and decrease by collisions with any
size $d_i$ particles. Thus the net rate of generation of size $d_i$ particles is given by [1]:

$$\left[ \frac{dn_i}{dt} \right]_{\text{coagulation}} = \frac{1}{2} \sum_{j=1}^{i-1} B(j,k) n_j n_k - n_i \sum_{k=1}^{\infty} B(i,k) n_k$$

(4.57)

where the factor $\frac{1}{2}$ corrects for the fact that collision is counted twice in the summation.

This analysis mathematically describes an aerosol cloud under the influence of continuous and spontaneous coagulation where only binary collision occur. The actual rate of coagulation depends on the number concentrations of coagulating particles and the coefficient of coagulation. The coagulation coefficient is much higher for coagulation between very large and very small particles. As the difference between the sizes of coagulating particles decreases, the coefficient also decreases.

COMPUTATIONAL TECHNIQUE

Based on the theoretical analysis, the plume opacity variation with downwind distance can be determined from a restatement of Equation (2.6):

$$O = 1 - \exp(-2r\sigma)$$

(4.58)

where $O$ is the fraction of plume opacity,

$\sigma$ is the total extinction coefficient($m^{-1}$),

$r$ is the plume radius(m).
This is done basically by following the plume dynamically with time, considering continuous and gradual spreading and vapor condensation in the plume.

The optics component of the model first calculates the light scattering and absorption properties of the plume particles. The following data are needed to calculate the extinction efficiency factor ($Q$) and extinction coefficient ($\sigma$):

- fly ash number concentration and size distribution
- the refractive index of the particle
- light wavelength

To acquire $Q$ from the Mie theory for arbitrary refractive indices and for arbitrary size is a large computational task. Complicated infinite series expressions were computed using recursion relationships. Those equations were carefully programmed and carried out in double precision on an IBM PC and IBM/370. The results of the series calculations were verified by comparing with existing tables in the literature [77-79].

The calculation of extinction coefficients from the light scattering and absorption properties of aerosols and gases was carried out by using Equation (4.7). To compute the total extinction coefficient due to a polydisperse distribution of
particles, particle number concentration is required as input. It is necessary to use small size intervals in order to permit computation of the actual extinction coefficients for measured size distributions of polydisperse particles in which a small size interval dominates. Therefore, we must have a continuous and integrable particle size/number distribution function \( n(d) \) that takes into account all sizes within any range of interest.

Fly ash produced during pulverized coal combustion has been found to have a bimodal distribution [29-31]. A number of researchers have broken down the bimodal distributions into two log-normal distributions [80-83]. They used a function created by the sum of two log-normal functions to create bimodal forms to describe the data. However, this has not been satisfactory in general. There are distributions for which this cannot be carried out without introducing errors of considerable magnitude.

To improve on past results and produce a much better fit of measured bimodal distributions, a general expression has been developed and is given by

\[
n(d) = \exp\left[-(A_6 d^6 + A_5 d^5 + A_4 d^4 + A_3 d^3 + A_2 d^2 + A_1 d + A_0)\right] \quad (4.59)
\]

where \( d \) represents particle size in \( \mu m \),

\( n(d) \) represents the concentration of particles per unit size interval (\( cm^{-3} \mu m^{-1} \)),

\( A_6 - A_0 \) are coefficients that have been evaluated
to fit this function to aerosol data.

This calculation is based on the selection of seven reference particle sizes and the corresponding values of \( n(d) \) and solving seven simultaneous equations. By careful selecting of values of \( d \) corresponding to peaks and dips an accurate analytic expression was found. The modes and minimum point of the curve coincide with the experimental data. The FORTRAN listing used to process this expression is given in Appendix C.

In order to predict plume behavior and plume parameters including opacity, Equations (4.34-4.39), (4.48) and (4.49) were first converted to nondimensional form as follows:

\[
\begin{align*}
\frac{dr^*}{dt^*} &= M^*V^*T^*(2 - \cos \theta/U^*) - (Ar^*\sin \theta/2U^*)(M^*T^* - 1) \\
\frac{dU^*}{dt^*} &= (2M^*V^*T^*/r^*)(\cos \theta - U^*) + A\sin \theta(M^*T^* - 1) \\
\frac{d\theta}{dt^*} &= (A\cos \theta/U^*)(M^*T^* - 1) - (2M^*V^*T^*\sin \theta/r^*U^*) \\
\frac{dT^*}{dt^*} &= (2M^*V^*T^*/r^*)(1 - T^*) \\
\frac{dZ^*}{dt^*} &= U^*\sin \theta \\
\frac{dX^*}{dt^*} &= U^*\cos \theta \\
\frac{dC^*}{dt^*} &= (-2M^*V^*T^*C^*/r^*) - H^* \\
\frac{dn^*}{dt^*} &= (-2M^*V^*T^*n^*/r^*) + K^* + G^*
\end{align*}
\]

where dimensionless parameters were defined as:
\[ t^* = t V_0 / r_0 \]
\[ r^* = r / r_0 \]
\[ U^* = U / V_0 \]
\[ V^* = V / V_0 \]
\[ T^* = T / T_0 \]
\[ Z^* = Z / r_0 \]
\[ X^* = X / r_0 \]
\[ C^* = C / C_0 \]
\[ n^* = n / n_0 \]
\[ H^* = H_r / C_0 V_0 \]
\[ K^* = K_r / n_0 V_0 \]
\[ G^* = G_r / n_0 V_0 \]
\[ M^* = M_0 / M \]
\[ A = r_0 g / V_0^2 \]

where \( r_0 \) is the stack radius (m),
\( C_0 \) is the molar concentration of condensing species at stack exit (g-mole/cm³-scec),
\( n_0 \) is particle number concentration at stack exit for each size channel (cm⁻³·µm⁻¹),
\( K \) represents \([dn_i/dt]_{coagulation} \)
\( (cm^{-3}·µm^{-1}·sec^{-1}) \),
\( G \) represents \([dn_i/dt]_{growth} \)
\( (cm^{-3}·µm^{-1}·sec^{-1}) \),
\( M_0 \) is the molecular weight of air (g/mole),

\( M \) is the molecular weight of plume gas (g/mole).

Equation (4.67) is applicable to each size channel in the model simulation. This system of first order ordinary differential equations was solved simultaneously using a Runge Kutta-Verner Fifth and Sixth Order Method incorporating a variable time step length with initial conditions as formulated in the subroutine DVERK which is one of the subroutines included in the International Mathematics Subroutine Library (IMSL).

The particle number concentration and size distribution of primary stack emissions are modified by the condensation and coagulation processes occurring in the plume. By determining the changes in particle size distribution and plume width for each time step, plume opacity levels were computed as a function of time.

COMPUTER IMPLEMENTATION

This computer program is designed to predict plume opacity as a function of downwind distance or time. It is made up of a main program and several subroutines. Figure 4 provides a flow chart overview of the main program. A listing of the program code for the main program and subroutines is given in Appendix C.
Read data

Calc. particle size channels

Call LEQIF, Calc. No. of particles in each size channel

Calc. extinction efficiency for any particle size

Initialize plume variables at t=0

Sum extinction coefficients of all particles

Calc. plume opacity

Call CGC, Calc. dynamics of particle distribution

Calc. entrainment velocity

Call EQUA, Update plume variables

Print results

Figure 4. Flow chart for opacity model
To obtain the number concentration \( n_i \) for 41 size channels in the bimodal distribution model, an appropriate IMSL subroutine LEQIF is called to solve the matrix equations. Next, the extinction efficiency factor \( Q \) for any size particle is calculated in Mie scattering model. Then the control initializes the plume variables for the time \( t=0 \) and calculates the total extinction coefficient \( \sigma \) and plume opacity at the stack exit.

The subroutine CGC is responsible for the particle coagulation, vapor condensation and nucleation. The detailed calculation procedures for subroutine CGC are shown in Figure 5. The entrainment velocity is computed at each time step with updated values of the variables. After the above elements have been evaluated, the control is passed to subroutine EQUA where the IMSL subroutine DVERK is applied to solve 49 differential equations simultaneously. The output from this subroutine is used to re-initialize the plume variables for the next time step. The plume opacity at each time increment after release from the stack exit is accomplished by looping through these subroutines, once for each time step.
Figure 5. Flow chart for aerosol dynamics
V. MODEL SIMULATION AND DISCUSSION

PARAMETERS AFFECTING THE SCATTERING PROPERTIES

The efficiency factors for extinction, scattering and absorption are dependent on:

PARTICLE SIZE

The particle sizes of interest in aerosol behavior range from molecular clusters of 0.001 μm to dust particles as large as 100 μm. The optically active portion of the size distribution is in the range of particle diameter from 0.1 to 1.0 μm. The ratio of particle size to wavelength of light (x=πd/λ) is one of the important parameters determining the light scattering characteristics.

Most of the theory on light scattering is limited to homogeneous spherical particles. Unfortunately, very few types of small particles of practical interest are really spherical. However, particles of similar size, despite different shapes, generally exhibit similar scattering characteristics [3].
PARTICLE REFRACTIVE INDEX

Light propagation in matter depends on the refractive index of the material. The refractive index is a complex number, \( m = p' - iq' \). The real part, \( p' \), describes the light scattering properties and the imaginary part, \( q' \), describes the light absorption of the particle material. The value of \( q' \) is zero for nonabsorbing particles. For a given wavelength the index of refraction depends only on the material, but it varies slightly with the wavelength of the light used. Listed in Table 3 are the real and imaginary components of \( m \) for ten different substances [9,84].

LIGHT WAVELENGTH

For very small particle, less than 0.05 \( \mu m \) in diameter, the extinction is proportional to \( \lambda^{-4} \). After the value of \( Q \) passed through the first resonance peak, the wavelength dependence becomes reversed and is known as anomalous extinction. For light in the visible range, \( \lambda \) is on the order of 0.5 \( \mu m \), and for particles whose size is of the same order as the wavelength of light, from 0.1 to 1 \( \mu m \) in diameter, it is necessary to make use of Mie theory.

In Figure 6, the calculated extinction efficiency factor (\( Q \)) was shown as a function of particle diameter for
### Table 3 Refractive index of air pollutants

<table>
<thead>
<tr>
<th>Substance</th>
<th>( m = p' - iq' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>2.0</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>1.77</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>1.544</td>
</tr>
<tr>
<td>( (\text{NH}_4)_2\text{SO}_4 )</td>
<td>1.53</td>
</tr>
<tr>
<td>( \text{NH}_4\text{NO}_3 )</td>
<td>1.53</td>
</tr>
<tr>
<td>Wood smoke</td>
<td>1.53</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>1.501</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_4 )</td>
<td>1.47</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>1.437</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>1.333</td>
</tr>
</tbody>
</table>
polydisperse spherical particles of refractive indices of 1.33, 1.5 and 1.8 for a light wavelength of 550 nm. The efficiency factors for transparent spherical particles show maxima and minima due to positive and negative interference between light transmitted through the particle and light diffracted around particle.

For nonabsorbing particles, the efficiency factors can vary from near 0 for very small particles, to about 4 when the particle diameter is near the wavelength of light, and approaches a theoretical limit of 2 for large particles. The maximum efficiency factor value occurs near $x=0.75\pi/m-1$ [85].

For absorbing spheres, the curve for $Q$ is usually of simpler form, increasing rapidly to reach a maximum at small values of $x$ and then decreasing slowly to approach two at large values. The effects of the magnitude of the absorbing index ($q'$) on extinction efficiency factor are shown in Figure 7.

Figure 8 illustrates the efficiency factors for the case of carbon particles. For small values of $x$, the extinction is due primarily to absorption, but for larger $x$, scattering and absorption are of almost equal importance.
Figure 6. Extinction Efficiency Factor for Nonabsorbing Particles
Figure 7. Extinction Efficiency Factor for Absorbing Particles
Figure 8. Efficiency Factor for Carbon Particle
RANGE OF IMPORTANT PARAMETERS USED IN MODEL SIMULATION

PARTICLE SIZE DISTRIBUTION OF EMISSION SOURCES

Plume particles usually have a variety of sizes. The particle size distribution in the emission from a given source depends on a number of factors (i.e. coal composition, boiler size and operating conditions, type and efficiency of control equipment and electric generating capacity) so that data found in literature is very scattered. The bimodal particle number/size distribution model can be used to describe a wide variety of polydispersed systems such as utility boilers.

For example, in a typical coal-fired boiler outlet, the combustion of pulverized coal produces a bimodal distribution with one mode at about 0.1 \( \mu \text{m} \) and the other mode at about 2 \( \mu \text{m} \) [29]. Based on this assumed initial particulate phase in the flue gas shown in Figure 9, the total particle size range between 0.01 and 10 \( \mu \text{m} \) was divided into 41 size ranges. The plume opacity levels varied for a test case showed that they are not significantly affected by changing particle size range steps from 35 to 55. Therefore, 41 particle size channels were used in the model calculation.

Because particle size extended over 4 orders of magnitude the values of size increment varied from 0.01 to 1.0 \( \mu \text{m} \). The size ranges chosen were close enough together so that coag-
Figure 9. Typical Boiler Outlet Distribution
ulation of particles of two adjacent size ranges would generate a particle size of the next larger size range.

THE REFRACTIVE INDEX OF FLY ASH

In a recent study by Cowen et al. [86], the fly ash refractive indices were measured for different pulverized coal-fired power plants. Table 4 shows that the real part of the fly ash refractive index ranged from 1.5 to 1.61, and the imaginary part ranged from 0.0004 to 0.0055. These refractive indices were selected to represent the extremes of the particulate pollutant emissions from utility sources.

Based on the simulation of test conditions for complex refractive indices shown in Figure 7, the opacity levels change from 8.5% to 9.0%. Therefore, the effect of imaginary refractive index on plume opacity is not significant.

LIGHT WAVELENGTH

The wavelength of incident light for the visible range of the electromagnetic spectrum varies between 400 and 700 nm. The opacity level varies for a test case from 8.28% for \( \lambda = 400 \) nm to 8.51% for \( \lambda = 550 \) nm to 8.71% for \( \lambda = 700 \) nm, therefore, \( \lambda = 550 \) nm is used in the model calculation as the wavelength of light that produced the average opacity. It is approxi-
### Table 4 Coal and Combustion for Fly Ash

<table>
<thead>
<tr>
<th>Coal</th>
<th>Heating values (Btu/lb)</th>
<th>Ash content (%)</th>
<th>Load (MW)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Sub-bituminous</td>
<td>10,500</td>
<td>5</td>
<td>40</td>
<td>1.57-0.0055i</td>
</tr>
<tr>
<td>Western Sub-bituminous</td>
<td>10,500</td>
<td>19</td>
<td>314</td>
<td>1.57-0.0019i</td>
</tr>
<tr>
<td>Eastern Bituminous</td>
<td>12,000</td>
<td>20</td>
<td>540</td>
<td>1.50-0.0043i</td>
</tr>
<tr>
<td>Western Bituminous</td>
<td>12,000</td>
<td>10</td>
<td>320</td>
<td>1.61-0.0004i</td>
</tr>
</tbody>
</table>
mately the wavelength of maximum sensitivity for the human eye.

As shown in Figure 10, the maximum scattering efficiency corresponds to the particle size of the same order as the wavelength to the incident light. Processes leading to the accumulation of particles in that size range produce the most severe plume opacity problem. Such processes depend on the chemical composition of the particles.

SOURCE EMISSION CHARACTERISTICS

Typical flue gas emissions from coal fired boilers are:

- fly ash loading -- 0.001-0.05 grains/acf (0.0023-0.1144 g/m³)

- H₂SO₄ -- 1-30 ppm

- water vapor content -- 5-15%

- particle number concentration -- 10⁶-10⁸/cm³

- stack gas temperature -- 80-200°C
Figure 10. Extinction Efficiency Factor as a Function of Particle Size

Extinction Efficiency Factor $Q$

Particle Size (μm)

$m=1.5$
TIME STEP IN THE MODEL CALCULATION

The computation time period for the studies presented here is chosen such that by the end of each calculation step both the particle number concentration and sulfuric acid vapor concentration are not changed significantly. For all of the atmospheric and flue gas conditions and initial concentrations considered, a time step from 0.01 to 0.05 second is found to be sufficiently small to achieve good accuracy.

The input parameters used in model simulation are summarized in Table 5.

SIMULATION RESULTS AND DISCUSSIONS

From the test calculation, the most important parameters affecting the peak plume opacity are the source emission conditions. Therefore, the parametric sensitivity study of the plume opacity was conducted by varying the key inputs such as initial particle number/size distribution, $\text{H}_2\text{SO}_4$ concentration, $\text{H}_2\text{O}$ content, stack temperature, etc. In addition, environmental parameters affecting the plume spread also show some influence on the plume opacity.

The objective of simulation is to quantitatively determine the effects of changes in a single parameter on opacity, while all other factors are held constant. Several arbitrary-
Table 5 Input parameters used in model simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ambient air</td>
<td></td>
</tr>
<tr>
<td>Wind speed (m/sec)</td>
<td>5-10</td>
</tr>
<tr>
<td>Ambient temperature (°C)</td>
<td>10.0</td>
</tr>
<tr>
<td>Ambient pressure (atm)</td>
<td>1.0</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>50.0</td>
</tr>
<tr>
<td>Background $\text{H}_2\text{SO}_4$ conc. (ppm)</td>
<td>0.0</td>
</tr>
<tr>
<td>Molecular weight of air (g/mole)</td>
<td>29.0</td>
</tr>
<tr>
<td>Stability class</td>
<td>B</td>
</tr>
<tr>
<td>Entrainment coeff., $\alpha$</td>
<td>0.11</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.55</td>
</tr>
<tr>
<td>2. Source emission</td>
<td></td>
</tr>
<tr>
<td>Flue gas temperature (°C)</td>
<td>100-200</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ vapor conc. (ppm)</td>
<td>0-20</td>
</tr>
<tr>
<td>Water vapor content (%)</td>
<td>1-10</td>
</tr>
<tr>
<td>Stack exit velocity (m/sec)</td>
<td>15-20</td>
</tr>
<tr>
<td>Stack height (m)</td>
<td>200.0</td>
</tr>
<tr>
<td>Stack diameter (m)</td>
<td>4.0</td>
</tr>
<tr>
<td>Fly ash density (g/cm$^3$)</td>
<td>2.5</td>
</tr>
<tr>
<td>Molecular wt. of plume gas (g/mole)</td>
<td>29.0</td>
</tr>
<tr>
<td>Plume inclination at stack exit (°)</td>
<td>90.0</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Bimodal (Fig. 11)</td>
</tr>
<tr>
<td>Control equipment</td>
<td>ESP</td>
</tr>
<tr>
<td>3. Optics</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.5-0.005i</td>
</tr>
<tr>
<td>Light wavelength (nm)</td>
<td>550.0</td>
</tr>
</tbody>
</table>
Figure 11. Typical ESP Outlet Distribution
ily selected conditions were used as a basis for conducting this parametric study.

CASE STUDY 1 -- DEWPOINT RELATIONSHIPS

A hot flue gas containing $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ vapor when cooled by ambient air will lose $\text{H}_2\text{SO}_4$ from the vapor phase if the temperature is below the acid dewpoint temperature. The $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ system dewpoint depends upon the initial $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ vapor concentrations. Equation (4.42) has been developed to estimate the effect of $\text{H}_2\text{SO}_4$ vapor concentration and moisture content of a flue gas on the acid dewpoint. The acid dewpoint temperature increases with higher $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ vapor concentration. The acid dewpoint temperature as a function of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ vapor concentration is shown in Figure 12.

Acid condensation should not occur until the plume temperature has been cooled to below the acid dewpoint. After the acid dewpoint is reached and condensation begins, the acid condensate concentration should increase rapidly. This process will result a rapid rise in the plume opacity. The acid condensate concentration is the highest at temperature just below the acid dewpoint. Additional dilution beyond that point results in little additional acid condensation.
Figure 12. Acid Dewpoint Relationship
Therefore, plume spread reduced condensed aerosol concentration and lowered the condensed plume opacity gradually. The acid condensate concentration should be proportional to the initial $\text{H}_2\text{SO}_4$ concentration in the flue gas.

CASE STUDY 2 -- EFFECT OF $\text{H}_2\text{SO}_4$ VAPOR CONCENTRATION

It was found in the simulation that the initial $\text{H}_2\text{SO}_4$ vapor concentration is the most significant contributor to the higher opacity of near-stack plume. At the acid dewpoint the plume opacity increases greatly for the higher $\text{H}_2\text{SO}_4$ vapor concentration and gradually for the lower $\text{H}_2\text{SO}_4$ vapor concentration. The severe impact of $\text{H}_2\text{SO}_4$ vapor concentration on the plume opacity at a stack temperature of 200°C is shown in Figure 13.

For higher $\text{H}_2\text{SO}_4$ vapor concentration, when supersaturation level is high enough, homogeneous nucleation contribution becomes dominant. This process will generate a large number of very small nuclei. These nuclei formed by homogeneous nucleation in the supersaturated region then mix with fresh saturated and supersaturated gas and may serve as foreign nuclei in other areas of the mixing zone. These molecular clusters provide a large surface area for rapid heterogeneous condensational growth. Therefore, the plume opacity increases sharply to a high level. But for $\text{H}_2\text{SO}_4$ vapor con-
Figure 13. Acid Vapor Effect on Opacity
centration less than about 10 ppm, the effect of homogeneous nucleation is less dramatic.

In Figure 13, the 8.5% in-stack opacity was entirely due to the carbon and fly ash particles, the increase in the plume opacity from 8.5% to 22% or 42% outstack appears to be due to condensed sulfuric acid aerosols. This supports the observation that substantially decreasing the H₂SO₄ vapor concentration issuing from the stack decreases the tendency for acid aerosol to form upon expansion of the plume.

From an air pollution control standpoint, it should be noted that it is not necessary to reduce SO₃/H₂SO₄ concentration in the flue gas to zero to avoid detached plume problems. Experiences [87] have shown that an acid plume's opacity does not appear to change proportionally with SO₃/H₂SO₄ concentration until a breakpoint is reached. The SO₃/H₂SO₄ concentration has to be lowered below approximately 5 ppm before a change is noticed. Once the SO₃/H₂SO₄ concentration drops below the 5 ppm breakpoint, the reduction in the plume opacity caused by acid vapor is dramatic.

CASE STUDY 3 — EFFECT OF WATER VAPOR CONTENT

The condensed plume opacity is also influenced by the initial water vapor concentration in the plume, but the dependence on water vapor is not so strong as that for H₂SO₄.
vapor. The increase of H$_2$O vapor content in the flue gas will increase the mass condensation rate on existing hygroscopic aerosols. Figure 14 shows the plume opacity as a function of water vapor content for a specified initial H$_2$SO$_4$ vapor concentration (15 ppm).

The cause of the increase in opacity is the result of increase in size of particles smaller than the visual range due to hygroscopic uptake. From the regulatory standpoint, the "pollutant opacity" means the effective opacity of the fly ash coated with aqueous H$_2$SO$_4$, without considering the influence of uncombined water. Thus, the plume opacity is somewhat dependent on the initial water vapor content in the plume.

CASE STUDY 4 -- EFFECT OF STACK GAS TEMPERATURE

The stack effluents for many industries are typically quite warm relative to the atmosphere. The buoyancy resulting from the reduced density of the effluent induces the plume to rise above the stack top. As it rises it cools primarily by entrainment of the cooler air until eventually the temperature differential is dissipated and the buoyant rise ceases.

Due to a rapid drop in plume temperature near the stack exit, the acid vapor condensation tends to lag somewhat;
Figure 14. Water Vapor Effect on Opacity
therefore, the H$_2$SO$_4$ vapor becomes supersaturated to a high enough level so that homogeneous nucleation occurs. For a specified flue gas composition, the nucleation rate may increase by many orders of magnitude as the stack gas temperature decreases from 200°C to 100°C. The plume opacity as a function of the gas temperature at the stack outlet is shown in Figure 15.

It should be noted that stack gas reheat dilutes the H$_2$SO$_4$ vapor concentration and correspondingly reduces the plume opacity. For example, in the case of wet scrubbers, there is a substantial cooling of the effluent, which reduces the plume rise. Stack gases exiting a wet scrubber may be reheated to raise the temperature above the acid dewpoint. Because of economic considerations, however, the gases are not reheated to the original flue gas temperature; the net effect of a wet scrubber installation is to reduce the plume rise and to increase plume opacity.

From another point of view, one convenient measure for mass emissions of particulate matter, which is reported in the literature and frequently used for comparisons between different coal-fired power plants, is grain loading (gr/scf). If such a measure is used, then variations in the temperature of the stack gas will influence the relationship between standard cubic feet and actual cubic feet of the stack gas. The higher the stack gas temperature, the higher the ratio
Figure 15. Stack Temperature Effect on Opacity
of actual to standard cubic feet, and the lower the particle concentration per cubic feet, thus decreasing the opacity.

CASE STUDY 5 -- EFFECT OF THE ATMOSPHERIC STABILITY

It is recognized that the rates of formation of aerosols and the visual appearance of plumes both depend on the dilution of the effluent gas. The turbulence induced by the plume's movement through the atmosphere and wind speed are considered in the atmospheric stability which plays a key role in making plume visible [88].

If the plume is caught in the turbulent wake of the stack, the effluent will be mixed rapidly downwind toward the ground (aerodynamic downwash). The beneficial effect of a significant vertical exit velocity of the plume is primarily to prevent the downwash of the stack effluent. It has been found that the exit velocity of the stack gas should be greater than 1.5 times the wind speed to prevent downwash in the wake of the stack [89].

Figure 16 illustrates the effect of atmospheric stability (or the effect of plume dilution rate) on plume opacity as a function of time. The peak plume opacity would increase with increasing stability (decreasing plume dilution). This can be explained by the fact that plume dilution is more rapid in the well-mixed unstable condition than in the stable con-
dition. As the ambient wind speed increases, the effluent from a continuous source is introduced into a greater volume of air per unit time interval. This exhibits a strong influence on plume spread rates and decrease the peak plume opacity.

CASE STUDY 6 -- EFFECT OF PARTICLE SIZE DISTRIBUTION

The size distribution of particles in the smoke plume is another variable that has a pronounced effect on the opacity. At a given grain loading, the smaller the mean particle size, the greater the number of particles in a given volume of gas and the greater the degree of light scattering and resultant opacity.

The presence of fine particles leads to higher plume opacity not only because of their light scattering properties but also because of their role in heterogeneous condensation. The effectiveness of the small condensed aerosols alone in increasing plume opacity is shown in Figure 17. The total mass loading of 0.021 g/m³ was the same in each case but the total particle number concentrations were 7.5×10⁷, 1.3×10⁷, 1.3×10⁵, and 2.2×10³ particles/cm³, respectively, for 0.06 μm, 0.11 μm, 0.5 μm and 1.93 μm.

The H₂SO₄ vapor concentration and the concentration of primary fine particles are of greatest importance in deter-
Figure 16. Atmospheric Stability Effect on Opacity
Figure 17. Particle Size Distribution Effect on Opacity
mining the peak plume opacity. Acid condensation has large effect on fine particle size, even for \( \text{H}_2\text{SO}_4 \) vapor concentration in the 5 to 10 ppm range. Through acid condensation and particle coagulation, the fine aerosol particles will grow into the fringe of the optically active particle size range. Therefore, these efficient light scattering condensed acid aerosols cause increased plume opacity.

Comparing upper and lower curves in Figure 18, it is seen that the plume opacity is increased by a factor of three by increasing 0.06 \( \mu \text{m} \) particle number concentration by 50% while maintaining the \( \text{H}_2\text{SO}_4 \) vapor concentration at 10 ppm. The lower two curves depict an approximate doubling of plume opacity resulting from maintaining 0.06 \( \mu \text{m} \) size number concentration constant while increasing the acid vapor concentration by 50%.

**CASE STUDY 7 -- EFFECT OF CONTROL EQUIPMENT**

The plume opacity is affected by mechanisms in the control equipment that change the particle size distribution in the flue gases. The influence of the control equipment in modifying particle size distribution can be great, depending on both the collection and entrainment processes.

The penetration curves [29] shown in Figure 19 for the high efficiency ESP(H.ESP), baghouse and moderately efficient
Figure 18. Concentration Effect on Opacity
ESP(M.ESP) can be used to estimate the outlet particle size distributions from the same boiler. The particle size distribution (such as those in Figure 11) exiting the control equipment was used as the input parameter for the opacity model to predict the plume opacity of the emission.

The calculated results from the simulation are shown in Figure 20. The predicted baghouse plume opacity would be below the visual range and satisfy the zero visual opacity standard. The high-efficiency ESP plume would satisfy the 20% opacity standard. Plume opacity violations would result from operations of moderately efficient ESP. Opacity relating to multiple cyclone operation predominated in high range.

Electrostatic precipitators, in some cases, are not as efficient as baghouses in removal of fine particles. Some precipitator installations have encountered high resistivity fly ash problems. It seems likely that the high opacity is related to a particle size distribution effect. Fine particle from combustion processes has an insignificant effect on opacity associated with high efficiency ESPs unless high H₂SO₄ vapor concentration is present.

Because of the interrelationship between particle size distribution and plume opacity, it is possible to meet mass emission standards and still have an opacity problem. In fact, control equipment causing a reduction in the total emission has produced an increase in near-stack plume opacity [39]. This is because control equipment generally removes
Figure 19. Collector Performance as a Function of Particle Size
Figure 20. Control Equipment Effect on Opacity
large size particles much more effectively than the submicron size particles.

At low $\text{H}_2\text{SO}_4$ vapor concentration, efficient ESPs and baghouses control plume opacity to compliance level. With high acid vapor concentration emissions, when the control equipment is installed at a point where the flue gas temperature is above the acid dewpoint, the equipment reduces the mass loading and number concentration of fly ash particles, but does not reduce the acid vapor concentration. The primary submicrometer sized particles emitted from the control equipment serve as sites for heterogeneous condensation of acid vapor. This causes significant increases in the peak plume opacity.

Utility sources burning high-sulfur coal experience a plume opacity problem caused by $\text{H}_2\text{SO}_4$ vapor concentration. On the other hand, fine fly ash particle size distributions are generally obtained from low-sulfur coal combustion which also generates an opacity problem. Therefore, the basic idea for solving the opacity problem is to enhance the submicron particle collection efficiency and to reduce $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration in the flue gas.

Recent work documented utility industry's use of flue gas additives to reduce plume opacity [90,91]. Researchers concluded that use of flue gas additives is a viable strategy for solving coal and oil combustion-related plume opacity problems. Alkaline additives that neutralize $\text{H}_2\text{SO}_4$ vapor in
the flue gas can prevent light-colored plumes of acid mist. Also, the number of particles having a size range of 0.1 to 1 μm must be reduced greatly to eliminate plume opacity.

CASE STUDY 8 -- EFFECT OF OPACITY REGULATION

A utility or industrial plant with particulate emissions that meet the mass concentration standard but exceed the plume opacity standard will emit more fine particles and have a greater impact on atmospheric visibility than will a plant with emissions that meet both standards.

With the present interest in a potential fine-particle regulation, it seems that opacity standards should be used to put a penalty on the very small particles in the plume without the onerous requirement of running particle size determinations for every compliance test.

If the opacity standards are to perform this purpose, they should not be written as a single value such as 20% equivalent opacity for all plumes from a given type industry, as is now done.

From Mie theory, it is seen that the extinction coefficient is a function of particle size. Small particles are much more effective for light extinction than are the larger particles.
Another important variable is the diameter of the stack, which fixes the path length that light traverses during penetration of a smoke plume. The larger the diameter, the greater the path length over which light is scattered by smoke particles, and the greater the apparent plume opacity. Table 6 shows the in-stack opacity levels calculated from the same emission source but different stack diameters.

To an approximation two 4.24 m diameter stacks would handle the same flue gas flow as one 6 m diameter stack with a 50% reduction in plume opacity. As seen in Figure 21, this translates a plume opacity violation to compliance status.

Therefore, the opacity standards should be written such that the allowable opacity of the plume varies with the stack diameter and an extinction coefficient for each industry.
Table 6  Opacity for Different Size Stack

<table>
<thead>
<tr>
<th>Stack diameter (m)</th>
<th>Extinction coefficient (m$^{-1}$)</th>
<th>Stack-exit opacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.04</td>
<td>14.8</td>
</tr>
<tr>
<td>8.0</td>
<td>0.04</td>
<td>27.4</td>
</tr>
<tr>
<td>10.0</td>
<td>0.04</td>
<td>33.0</td>
</tr>
</tbody>
</table>
Figure 21. Stack Size Effect on Opacity
VI. MODEL VALIDATION AND APPLICATION

MODEL VALIDATION

Opacity model presented above consists of relatively independent components such as an optics module, a bimodal particle size distribution module, a polydisperse coagulation module, a vapor condensation and nucleation module and a plume dispersion module, which are linked together to relate specific flue gas emissions and meteorological conditions to a visual effects of a plume. To adequately assess a complete model, each component must be evaluated individually.

In this model, the scattering and absorption properties of particles in the plume are computed by assuming a bimodal size distribution for primary particulates. The formulation and growth of sulfuric acid aerosol in typical industrial emission conditions have been theoretically modeled. In addition, the prediction is based on a combination of the Mie scattering theory and plume dynamics, both of which have had considerable experimental verification [66-71].

The physical principles used in the model are well established and the pertinent equations are properly formulated. These predictions have not been compared to field measurements for calibrating the model. This is because there were
no complete data sets taken under the conditions of detached plume formation to provide a test of the complete model.

However, with the limited LIDAR data available model validation can be carried out to some degree. The model prediction also agrees qualitatively with the limited existing data in the literature. Therefore, additional field studies to collect complete data are needed to allow the calibration of this model and to increase the confidence in estimating the detached plume opacity.

FUTURE APPLICATION

Visual opacity standard serves most importantly as a rapid indication of source operation status and as a control on submicron particles that may pose the most serious health hazard. The general public is probably more aware and concerned with visible emissions than with any other aspect of the air pollution problem, and the application of an opacity standard is a very effective means of demonstrating that measures are being taken to ameliorate the problem.

It has been noted recently that in some cases installation of particulate control devices on utility boiler emissions with high acid vapor concentrations actually cause a detached plume problem. For example, it is possible that the dry particulate mass concentrations and in-stack opacity are well within the allowable limits but the downwind plume opacity
may be in violation of opacity regulations. This may pose a problem from a regulatory point of view.

EPA stated [92], "Any source which is meeting the applicable concentration or mass standards will also be meeting the applicable opacity standard. If the source is exceeding the opacity standard, it is due to failure of that source to properly maintain its air pollution control equipment, and if tested, the source would have emissions in excess of the applicable concentration or mass standard." Thus the EPA position is that opacity can be used to enforce mass emission regulations. This is also the case with several other state and local regulatory agencies. All enforcement officers need do is to observe an emission of an opacity beyond that allowed by the regulations for a minimum time interval in order to cite a violator for excessive emissions.

A modern plant may comply with applicable particulate emission standards, yet it may be forced to reduce emissions even further to meet opacity requirements. From the standpoint of the plant operator, emission standards based on weight measurements are difficult to meet on a continuous basis because of the time lag involved in taking and analyzing samples by manual methods. The plant operator cannot correct a malfunction or process upset if it takes three or four days to make a measurement to determine whether or not emission have exceeded the acceptable limit. Therefore, opacity level is a good supplementary measurement because it
yields continuous, real-time emission data which can be related to the plant operation conditions.

For example, when a precipitator is operating properly, typical collection efficiency better than 99.5% can be expected. However, if the fuel's sulfur content is too low or too high the primary particulate emissions and the plume opacity will increase, often above the legal allowable level. Evaluation of precipitator performance in years past was generally a job of physical test for efficiency and outlet grain loading. Stack sampling calls for several men and considerable time. To avoid the tedious and time-consuming manual sampling and resulting time delay, the plant operator should use the opacity measurement as a means of process control to avoid or correct excessive emissions to the maximum extent possible.

EPA establishes opacity standards to ensure that control systems required by mass concentration standards are properly operated and maintained at all times. As a practical matter, the plume opacity standard is always more difficult to comply with than is the mass emission limit. This suggests the possibility that plume opacity standard alone would provide the most practical and inexpensive means of ensuring that control equipment is adequate maintained and operated, and that regulations based on weight measurements could be eliminated. Therefore, the only monitoring required by federal and state
regulations for particulate matter is to measure the plume opacity from the stack discharge.

Areas with existing plume opacity violation can be identified by instrumented monitoring or assessed by trained observers. However, as with other air quality issue involving future scenarios, the prediction of plume opacity level requires the application of mathematical modeling techniques.

The assessment of an air pollution problem (current or future) by a modeling system has great appeal. Various operational plans can be simulated quickly and easily. Furthermore, there is no necessity to wait for nature's cooperation in producing various combinations of wind and weather. Model results are valuable for use in selecting control equipment to meet plume opacity as well as mass emission standards.

For air pollution control equipment applications, it is desirable to obtain particle size distribution data from particle size measurements and calculations using fractional collection efficiency curves. Careful consideration of the effect of acid condensation processes is necessary because the extent of light scattering by plume particles depends strongly on their size. The opacity model presented here should enable designers to estimate the plume opacity to be expected from a projected plant, so as to avoid the emission of plumes of objectionable appearance or illegal opacity.
levels. Inlet and outlet particle size distributions and ESP operating parameters will provide the necessary information to predict the ESP efficiency requirements to achieve a given level of plume opacity.

In addition, the results of this model should provide background information for modelers, designers and regulatory personnel concerned with predicting, measuring, regulating and controlling plume opacity and fine particles from industrial emissions.

This model program may be used on either mainframe or personal computers as a practical tool for application of aerosol technology to opacity problems.
VII. CONCLUSION

A computer model for use in opacity characterization of combustion emissions was developed in this study. This dynamic, plume-opacity model required a multi-faceted approach. Technology from the diverse fields of particle physics, electromagnetic radiation, physical chemistry, fluid mechanics, statistics and computer science provided the ingredients for this model, which is applicable to a current air pollution problem.

A thorough understanding of the number concentration, size distribution, the formation mechanisms, aqueous acid composition and optical properties of condensed acid aerosols is essential for developing strategies for the characterization, monitoring, control and regulation of condensable emissions. The equations, calculation procedures and results presented in this study are a first step toward this understanding.

The model is applied in a parametric study to explore the effect of emissions and environmental conditions on plume opacity. The results of this study are applicable to:

- explaining the plume opacity observed for emissions containing sulfuric acid aerosols,
- determining the impact of the source on the environment,
• explaining the results of attempts to correlate particle size/number distribution and light scattering effects,

• predicting the opacity resulting from coal combustion in a wide range of steam generator types,

• designing or modifying control equipment to meet opacity standards,

• developing regulations to control emissions of submicron particulate air pollutants.

The following conclusions have been made based on an application of this model to typical cases:

• The light scattering contribution to plume opacity is moderately influenced by the refractive index of the suspended particulate material in stack plumes but is strongly under the influence of the number concentration of particles in the range of visible light wavelengths.

• The accuracy of the empirical acid-dewpoint equation being used is about ±3 or 4°C, which limits the models capability for predicting the exact origination point of acid condensation.
• The plume opacity actually decreases in the early stages because plume spread offsets coagulation processes when plume temperature is above the acid dewpoint near the stack.

• The acid condensation and associated uptake of hygroscopic water vapor occur simultaneously with ambient air entrainment into the plume and bring about dramatic changes in the particle number concentration and size distribution.

• The peak plume opacity increases significantly at higher acid vapor concentration and particle concentrations in the flue gas and increases slightly for higher moisture content.

• The peak plume opacity decreases with higher stack gas temperature and wind speed.

• High efficiency ESPs and baghouses reduce the effects of $\text{H}_2\text{SO}_4$ vapor on plume opacity at low sulfuric acid vapor concentration by controlling primary submicron particles.

• The larger the stack diameter, the greater the apparent plume opacity. Therefore, the opacity standards should
take into account the stack diameter and the extinction coefficient which is governed by the refractive index of the suspended particulate material.

Tests of this mathematical model against field measurement are needed to identify directions for refinement. Further work could be carried out to evaluate the performance of this model under different meteorological conditions and for other source emissions so that the predictive abilities can be improved.
REFERENCES


45. Sparks. L.E., "In-Stack Plume Opacity from ESP/Scrubber System at Harrington Unit 1." EPA-600/7-79-118, May 1979.


61. Memo: "Enforcement Against Opacity Violations from Power Plants." Director, Division of Stationary Source Enforcement to Enforcement Division Directors, Regions I-X, June, 1981.


# APPENDIX A. NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>dimensionless constant (gr_0/V_0^2)</td>
</tr>
<tr>
<td>A_0 ... A_6</td>
<td>equation coefficients [Eq. (3.59)]</td>
</tr>
<tr>
<td>a_1 ... a_9</td>
<td>equation coefficients [Eq. (3.44)]</td>
</tr>
<tr>
<td>a_n</td>
<td>complex amplitude function</td>
</tr>
<tr>
<td>B</td>
<td>coagulation coefficient ((cm^3/sec))</td>
</tr>
<tr>
<td>b_n</td>
<td>complex amplitude function</td>
</tr>
<tr>
<td>C</td>
<td>molar concentration of the condensing species in the plume ((g-mole/cm^3))</td>
</tr>
<tr>
<td>C'</td>
<td>molar concentration of the condensing species in the air ((g-mole/cm^3))</td>
</tr>
<tr>
<td>C_0</td>
<td>molar concentration of condensing species at the stack exit ((g-mole/cm^3))</td>
</tr>
<tr>
<td>C*</td>
<td>dimensionless molar concentration ((C/C_0))</td>
</tr>
<tr>
<td>C_1</td>
<td>specific heat of the plume gas</td>
</tr>
<tr>
<td>C_2</td>
<td>specific heat of the ambient air</td>
</tr>
<tr>
<td>C_3</td>
<td>slip correction factor</td>
</tr>
<tr>
<td>D</td>
<td>the coefficient of diffusion ((cm^2/sec))</td>
</tr>
<tr>
<td>d_C</td>
<td>critical droplet diameter ((\mu m))</td>
</tr>
<tr>
<td>E</td>
<td>entrainment rate ((m^2/sec))</td>
</tr>
<tr>
<td>F</td>
<td>collision frequency ((1/cm^3 - sec))</td>
</tr>
<tr>
<td>G</td>
<td>the rate of growth for each size channel due to condensation process ((l/cm^3 - sec))</td>
</tr>
<tr>
<td>G*</td>
<td>dimensionless growth rate ((Gr_0/n_0 V_0))</td>
</tr>
<tr>
<td>g</td>
<td>gravitational acceleration ((m/sec^2))</td>
</tr>
<tr>
<td>H</td>
<td>the net loss of condensing vapors from the plume ((g-mole/cm^3 - sec))</td>
</tr>
<tr>
<td>H*</td>
<td>dimensionless vapor loss ((Hr_0/C_0 V_0))</td>
</tr>
<tr>
<td>I</td>
<td>intensity of transmitted light</td>
</tr>
<tr>
<td>I_0</td>
<td>intensity of incident light</td>
</tr>
<tr>
<td>I_i</td>
<td>the particle current flowing from (i)th to ((i+1))th size channel ((l/cm^3 - sec))</td>
</tr>
<tr>
<td>J</td>
<td>Bessel function of the first kind</td>
</tr>
<tr>
<td>K</td>
<td>the net rate of change in particle number for each size channel resulting from coagulation process ((l/cm^3 - sec))</td>
</tr>
<tr>
<td>K*</td>
<td>dimensionless coagulation rate ((Kr_0/n_0 V_0))</td>
</tr>
<tr>
<td>K'</td>
<td>specific particulate volume/extinction coefficient ratio ((cm^3/m^2))</td>
</tr>
<tr>
<td>Kn</td>
<td>the Knudsen number</td>
</tr>
</tbody>
</table>
k  the Boltzman's constant (dyne-cm/°K)
L  stack diameter (m)
λ  the mean free path of the gas (μm)
M  the molecular weight of plume gas
M₀  the molecular weight of the air
M*  dimensionless molecular weight (M₀/M)
m  the refractive index
N  the molecular condensation rate (1/sec)
n  particle number density frequency distribution function (1/cm³μm)
no  particle number density frequency distribution at stack exit (1/cm³μm)
O  plume opacity (%)
P'  the equilibrium vapor pressure at the droplet surface (mm Hg)
P  the partial pressure of the condensing vapor (mm Hg)
P₁  the partial pressure of sulfuric acid vapor (mm Hg)
P₂  the partial pressure of water vapor (mm Hg)
P₁'  the equilibrium vapor pressure of sulfuric acid (mm Hg)
P₂'  the equilibrium H₂O vapor pressure (mm Hg)
p'  real part of the refractive index
p'x  extinction efficiency factor
Q  scattering efficiency factor
Q₁  absorption efficiency factor
q'  imaginary part of the refractive index
q'x  plume radius (m)
r  stack radius (m)
r*  dimensionless radius (r/r₀)
S  saturation ratio (P/P')
s  plume displacement (m)
T  plume temperature (°K)
T₀  ambient air temperature (°K)
T₁  acid dewpoint temperature (°K)
t  time (sec)
t*  dimensionless time (tV₀/r₀)
U  plume speed (m/sec)
U*  dimensionless plume speed (U/V₀)
V  entrainment velocity (m/sec)
V₀  wind speed (m/sec)
V*  dimensionless speed (V/V₀)
V  molecular volume (μm³)
W  particle mass concentration (g/m³)
w  weight fraction of H₂SO₄
x  dimensionless size parameter (πd/λ)
X  Cartesian coordinate (m)
\( X^* \)  
- dimensionless coordinate \( (X/r_s) \)

\( y \)  
- Cartesian coordinate \( (m) \)

\( Z^* \)  
- dimensionless coordinate \( (Z/r_s) \)

\( \alpha \)  
- entrainment coefficient

\( \beta \)  
- entrainment coefficient

\( \gamma \)  
- the surface tension \( (\text{dyne/cm}) \)

\( \theta \)  
- the plume orientation angle related to the horizontal plane

\( \lambda \)  
- light wavelength \( (\mu m) \)

\( \mu \)  
- the viscosity \( (\text{dyne-sec/cm}^2) \)

\( \nu \)  
- the kinematic viscosity \( (\text{cm}^2/\text{sec}) \)

\( \xi \)  
- Riccati-Bessel function

\( \pi \)  
- 3.14159

\( \rho \)  
- plume gas density \( (g/cm^3) \)

\( \rho_0 \)  
- air density \( (g/cm^3) \)

\( \sigma \)  
- total extinction coefficient \( (m^{-1}) \)

\( \sigma_1 \)  
- scattering coefficient \( (m^{-1}) \)

\( \sigma_2 \)  
- absorption coefficient \( (m^{-1}) \)

\( \chi \)  
- Riccati-Bessel function

\( \psi \)  
- Riccati-Bessel function
APPENDIX B. SOLUTION OF EQUATIONS FOR PLUME DYNAMICS

From the conservation of mass, energy and momentum:

\[
\begin{align*}
\frac{d(\rho r^2 U)}{ds} &= 2\rho_0 r V \\
\frac{d(\rho r^2 U^2 \sin \theta)}{ds} &= r^2 g(\rho_0 - \rho) \\
\frac{d(\rho r^2 U^2 \cos \theta)}{ds} &= 2r \rho_0 V V' \\
\frac{d(\rho r^2 UT)}{ds} &= 2\rho_0 r V T' \\
\frac{d(r^2 UC)}{ds} &= 2r V C'
\end{align*}
\]

Because \( ds/dt = U \), the above set of differential equations can be converted to:

\[
\begin{align*}
2\rho \frac{dr}{dt} + \rho r \frac{dU}{dt} &= 2\rho V \quad (B.1) \\
\rho r U \cos \theta \frac{d\theta}{dt} + 2\rho r \sin \theta \frac{dU}{dt} + 2\rho U \sin \theta \frac{dr}{dt} &= rg(\rho_0 - \rho) \quad (B.2) \\
2\rho \cos \theta \frac{dU}{dt} + 2\rho U \cos \theta \frac{dr}{dt} - \rho \sin \theta \frac{d\theta}{dt} &= 2\rho_0 V V' \quad (B.3) \\
\rho r \frac{dT}{dt} + \rho r T \frac{dU}{dt} + 2\rho T \frac{dr}{dt} &= 2\rho_0 T_0 V \quad (B.4) \\
\rho r \frac{dC}{dt} + rC \frac{dU}{dt} + 2C \frac{dr}{dt} &= 2VC' \quad (B.5)
\end{align*}
\]

Eq. (B.3) \( \times \cos \theta \) + Eq. (B.2) \( \times \sin \theta \):

\[
2\rho \frac{dU}{dt} + 2\rho U \frac{dr}{dt} = 2\rho_0 V V' \cos \theta + rg(\rho_0 - \rho) \sin \theta \quad (B.6)
\]

From Eq. (B.1)
\[
d\frac{U}{dt} = \frac{2U}{r} \left( \frac{V_0}{\rho} - \frac{dr}{dt} \right) \quad (B.7)
\]

Substitute Eq. (B.7) into Eq. (B.6) and rearrange, then,
\[
d\frac{dr}{dt} = \frac{V_0}{\rho} \left( 2 - V_0 \cos \theta / U \right)
- \left( \frac{rg \sin \theta}{2U} \right) \left( \frac{\rho_0}{\rho} - 1 \right) \quad (B.8)
\]

Substitute Eq. (B.8) into Eq. (B.7),
\[
d\frac{dU}{dt} = \left( \frac{2V}{r} \right) \left( \frac{\rho_0}{\rho} \right) \left( V_0 \cos \theta - U \right)
+ \frac{g \sin \theta (\rho_0 / \rho - 1)}{} \quad (B.9)
\]

Substitute Eq. (B.8) and (B.9) into Eq. (B.3),
\[
d\frac{d\theta}{dt} = \left( \frac{g \cos \theta}{U} \right) \left( \frac{\rho_0}{\rho} - 1 \right)
- \frac{2\rho_0}{\rho} \left( V_0 \cos \theta / rU \right) \quad (B.10)
\]

Substitute Eq. (B.8) and (B.9) into Eq. (B.5),
\[
d\frac{dT}{dt} = \left( \frac{2V}{r} \right) \left( \frac{\rho_0}{\rho} \right) \left( T_0 - T \right) \quad (B.11)
\]

Substitute Eq. (B.8) and (B.9) into Eq. (B.5),
\[
d\frac{dC}{dt} = \frac{2V}{r} \left( C' - C_{\rho_0 / \rho} \right) \quad (B.12)
\]
APPENDIX C. FORTRAN CODE FOR OPACITY MODEL

C PROGRAMMED BY KAI-TIEN LEE
C DEPARTMENT OF CIVIL ENGINEERING
C VIRGINIA TECH
C BLACKSBURG, VA 24061
C
C THIS PROGRAM IS DESIGNED SPECIFICIALLY TO PREDICT
C THE OPACITY OF A CONDENSABLE PLUME AS A FUNCTION
C OF DOWNWIND DISTANCE OR TIME.

C
C MAIN PROGRAM

C$JOB
REAL*8 D(50), ARG, TERM1, TERM2, AVO, AX, HL, AVCR(50)
REAL*8 CORR(50), DIFF(50), BB(50, 50), XKN(50)
REAL*8 COND, VMS, COAG(41), GROW(41), IH1, INUMB, DE
REAL*8 X, XOL, XEND, YPRIME(49), Y(49), C(24), W(49, 9)
REAL*8 PI, XLAM, RM, IM, XP, P, Q, RWOX, IWOX, RW1X, IWM1X
REAL*8 RW(70), IW(70), RA0Y, IAOY, RA0(70), IAO(70), RH1
REAL*8 RH2, IH2, RH3, IH3, RH5, IH5, Z, RN1, IN1, RNUM, INUM
REAL*8 RDEN, IDEN, RAN(70), IAN(70), RN2, IN2, RNUMB
REAL*8 RDENB, IDENB, IBN(70), RBN(70), SUM, QE(41), XJ
REAL*8 TOX, DOWN, UP, WP, CP, COW, SCALE, DD(50)
REAL*8 SUM2, IN2, KN(50)
REAL*8 T, PA, PW, WC1, WC2, WC3, AC1, AC2, AC3, W0, EWP
REAL*8 DP, RP, WH, ESAP, DPT, WC4, AC4, VX, XMOL, VTOL, VMW
REAL*8 XSR, RLE, XH, DEN, XAA, XCC, XHN, VHV, XDD, XEE, XBB
REAL*8 BIMO(50), ENTV, XCOAG(41), XCOND, XGROW(41), XFF
REAL*8 TOTAL, AAZ, RO, RSK, VO, USK, TO, TSK, CHAIR, CHO
REAL*8 CWAIR, CW0, HUM, CRH, XSUM
COMMON GROW, COAG, COND, VX, AAZ, CRH
C
C BIMODAL DISTRIBUTION MODEL
C CALCULATE PARTICLE SIZE DISTRIBUTION AND NUMBER
C CONCENTRATION FOR 41 SIZE CHANNELS
C IMSL LEQIF IS CALLED TO SOLVE THE MATRIX EQUATIONS

INTEGER N, MA, IA, IB, M, IJOB, IER
REAL*8 A(7, 7), B(7, 1), WK(21)

151
DO 10 I=1,7
DO 10 J=1,7
10 READ(5,50)A(I,J)
50 FORMAT(F24.16)
DO 20 K=1,7
20 READ(5,60)B(K,1)
60 FORMAT(F24.16)
N=7
MA=2
IB=7
IA=7
IJOB=0
M=1
CALL LEQIF(A,IA,N,MA,B,IB,M,IJOB,WK,IER)
WRITE(6,30)(B(K,1),K=1,7)
90 FORMAT(1X,7F8.4)
C
D(1)=0.01
D(2)=0.02
DO 40 I=1,41
D(I+2)=(D(I+1)**3+D(I)**3)**(1./3.)
D(I)=DLOG10(D(I))
ARG=B(1,1)*D(I)**6+B(2,1)*D(I)**5+B(3,1)*D(I)**4
1+B(4,1)*D(I)**3+B(5,1)*D(I)**2+B(6,1)*D(I)+B(7,1)
BIMO(I)=DEXP(-ARG)
D(I)=10.0**D(I)
BIMO(I)=10.0**BIMO(I)
DD(I)=DLOG10(D(I+1)/D(I))
WRITE(6,99)D(I),BIMO(I)
99 FORMAT(2X,F9.3,E12.4)
40 CONTINUE
C
C MIE SCATTERING MODEL
C CALCULATE EXTINCTION EFFICIENCY FACTORS FOR
C SPHERICAL PARTICLES OF ARBITRARY SIZE
C AND REFRACTIVE INDX
C
PI=3.141592653589
XLAM=0.55
SCALE=10.0**(-60)
RM=1.5
IM=0.005
DO 600 I=7,41
XP=PI*D(I)/XLAM
RWOX=DSIN(XP)
IWOX=DCOS(XP)
RWM1X=IWOX
IWM1X=-RWOX
RW(1)=RWM1X*SCALE
RW(2)=RWOX*SCALE
IW(1)=IWM1X*SCALE

152
IW(2)=IWOX*SCALE
P=RM*XP
Q=IM*XP
DE=DSIN(P)**2+DSINH(Q)**2
RAOY=DSIN(P)*DCOS(P)/DE
IAOY=DSINH(Q)*DCOSH(Q)/DE
RAO(1)=RAOY
IAO(1)=IAOY
DO 100 J=1,55
XJ=DFLOAT(J)
RH1=(XJ*P)/(P**2+Q**2)
IH1=(XJ*Q)/(P**2+Q**2)
RH2=RH1-RAO(J)
IH2=IH1-IAO(J)
RH3=RH2/(RH2**2+IH2**2)
IH3=-IH2/(RH2**2+IH2**2)
RH5=RH3-RH1
IH5=IH3-IH1
RAO(J+1)=RH5
IAO(J+1)=IH5
100 CONTINUE
DO 200 J=1,55
XJ=DFLOAT(J)
Z=(2.0*XJ-1.0)/XP
RW(J+2)=Z*RW(J+1)-RW(J)
IW(J+2)=Z*IW(J+1)-IW(J)
200 CONTINUE
DO 300 K=1,55
RN1=((RAO(K+1)*RM-IAO(K+1)*IM)/(RM**2+IM**2))+(K/XP)
IN1=(RAO(K+1)*IM+IAO(K+1)*RM)/(RM**2+IM**2)
RNUM=RN1*RW(K+2)-RW(K+1)
INUM=IN1*RW(K+2)
RDEN=RN1*RW(K+2)-(IN1*IW(K+2))--RW(K+1)
IDEN=(RN1*IW(K+2)+IN1*RW(K+2))--IW(K+1)
TOP=(RNUM/IDEN)+(INUM/RDEN)
DOWN=(RDEN/IDEN)+(IDEN/RDEN)
RAN(K)=TOP/DOWN
UP=(INUM/IDEN)-(RNUM/RDEN)
IAN(K)=UP/DOWN
300 CONTINUE
DO 400 K=1,55
RN2=(RAO(K+1)*RM+IAO(K+1)*IM)+(K/XP)
IN2=RM*IAO(K+1)-RAO(K+1)*IM
RNUMB=RN2*RW(K+2)-RW(K+1)
INUMB=IN2*RW(K+2)
RDENB=(RN2*RW(K+2)-IN2*IW(K+2))-RW(K+1)
IDENB=(RN2*IW(K+2)+IN2*RW(K+2))--IW(K+1)
WP=(RNUMB/IDENB)+(INUMB/RDENB)
COW=(RDENB/IDENB)+(IDENB/RDENB)
RBN(K)=WP/COW
VP=(INUMB/IDENB)-(RNUMB/RDENB)
IBN(K)=VP/COW

CONTINUE
SUM=0.0
DO 500 J=1,55
XJ=DFLOAT(J)
SUM=SUM+(2.0*XJ+1.0)*(RAN(J)+RBN(J))

CONTINUE
QE(I)=2.0*SUM/(XP*XP)
WRITE(6,102)D(I),XP,QE(I)
FORMAT(2F10.3,F12.5)
CONTINUE

C
C INITIALIZE PLUME VARIABLES AT t=0
C
RSK=2.0
R0=2.0
USK=15.0
V0=7.5
TSK=273.0+200.0
TO=273.0+10.0
CHAIR=2.6*(10.0**(-10))
CHO=2.6*(10.0**(-10))
CWAIR=1.3*(10.0**(-6))
CWO=1.3*(10.0**(-6))
AZZ=(R0*9.81)/(V0*V0)
HUM=4.8*(10.0**(-7))
CRH=HUM/CWO

DO 70 I=1,41
Y(I)=1.0
Y(42)=RSK/R0
Y(43)=USK/V0
Y(44)=1.57
Y(45)=TSK/TO
Y(46)=0.0
Y(47)=0.0
Y(48)=CHAIR/CHO
Y(49)=CWAIR/CWO

C
C UPDATE PLUME VARIABLES
C CALCULATE PLUME OPACITY AT TIME t+dt
C PRINT RESULTS
C
NX=0
DO 73 J=1,61
SUM2=0.0
DO 48 I=7,41
BE=(PI/4.0)*(D(I)**2)*QE(I)*Y(I)*0.000001*DD(I)
1*BIMO(I)
SUM2=SUM2+BE
 CONTINUE
XSUM = SUM2 * 2.0 * Y(42) * R0
OPAC = 1.0 - DEXP(-XSUM)
TOTAL = 0.0
DO 98 I = 1, 41
98 TOTAL = TOTAL + Y(I) * BIMO(I)
CALL CGC(D, COAG, COND, GROW, Y, TP, DPT, BIMO, TO, RO, VO)
CHAIR, CWAIR, W0)
ENTV = VO * ((0.11 * (Y(43) - DCOS(Y(44)))) + 0.55 * DSIN(Y(44)))
VX = ENTV / VO
CALL EQUA(N, X, Y)
NX = NX + 1
IF (NX.EQ.11) NX = 1
IF (NX.EQ.1) GO TO 72
GO TO 73
72 WRITE (6, 75) J, SUM2, OPAC, TOTAL
75 FORMAT (I5, 2F15.5, E15.5)
WRITE (6, 78) TP, DPT, COND, W0
78 FORMAT (2F15.2, E15.4, F10.2)
DO 103 I = 1, 41
WRITE (6, 77) COAG(I), GROW(I), AVCR(I)
77 FORMAT (3E15.4)
WRITE (6, 79) W0, EWP, WH, ESAP
79 FORMAT (F10.3, 2X, E10.3, 2X, F10.3, 2X, E10.3)
DO 44 I = 1, 49, 7
IF (Y(I).LT.0.0) Y(I) = 0.0
44 WRITE (6, 74) Y(I), Y(I+1), Y(I+2), Y(I+3), Y(I+4), Y(I+5), Y(I+6)
74 FORMAT (7E11.3)
73 CONTINUE
STOP
END

C C SUBPROGRAM
C
C USE RUNGE-KUTTA-VERNON FIFTH AND SIXTH ORDER TO
C SOLVE 49 FIRST ORDER ORDINARY DIFFERENTIAL
C EQUATIONS SIMULTANEOUSLY
C IMSL DVERK IS CALLED TO SOLVE THIS SYSTEM OF
C DIFFERENTIAL EQUATIONS
C
SUBROUTINE EQUA(N, X, Y)
INTEGER N, IND, NW, IER, K
REAL*8 Y(49), C(24), W(49, 9), X, TOL, XEND
EXTERNAL FCN1
NW = 49
N = 49
X = 0.0
TOL = 0.0001
IND = 1
XEND = 0.125
CALL DVERK(N, FCN1, X, Y, XEND, TOL, IND, C, NW, W, IER)
SUBROUTINE FCN1(N, X, Y, YPRIME)
INTEGER N
REAL*8 Y(49), YPRIME(49), X, SGRO(41), SCOA(41)
REAL*8 VS, YKK, HHR
COMMON SGRO, SCOA, SCND, VS, YKK, HHR
DO 46 I=1, 41
YPRIME(I) = (-2.0*VS*Y(45)*Y(I)/Y(42)) + SGRO(I) + SCOA(I)
46 CONTINUE
YPRIME(42) = (VS*Y(45)*(2.0-DCOS(Y(44))/Y(43)))*
((YKK/2.0)*Y(42)*DSIN(Y(44))/Y(43))*(Y(45)-1.0) +
1(YKK*DSIN(Y(44))*(Y(45)-1.0)/Y(43)) -
1((2.0*VS*Y(45)*DSIN(Y(44)))/(Y(42)*Y(43)))
YPRIME(43) = Y(43)*DSIN(Y(44))
YPRIME(44) = Y(43)*DCOS(Y(44))
YPRIME(45) = (-2.0*VS*Y(45)*Y(48)/Y(42)) - SCND
YPRIME(46) = (2.0*VS/Y(42))*(HHR-Y(49)*Y(45))
RETURN
END

C PARTICLE DYNAMICS MODEL
C CALCULATE AEROSOL DYNAMICS AND ACID VAPOR CONDENSATION
C
SUBROUTINE CGC(D, COAG, COND, GROW, Y, TP, DPT, BIMO, TO,
1 RO, VO, CHAIR, CWAIR, WO)
REAL*8 D(50), BB(50, 50), WO, EWP, DP, RP
REAL*8 BOLT, TP, VIS, MFP, KN(50), CORR(50), DIFF(50)
REAL*8 TERM1, TERM2, COAG(41), AVO, HL, DEP, XKN(50)
REAL*8 COND, AVCR(50), VMS, GROW(41), Y(49)
REAL*8 T, PA, PW, WC1, WC2, WC3, AC1, AC2, AC3
REAL*8 WH, ESAP, DPT, WC4, AC4, XMOL, VTOL, VMW
REAL*8 XSR, RLN, DEN, VHv, XAA, XCC, XHN, SUF, XDD, XEE, XBB
REAL*8 BIMO(50), XCOAG(41), XCOND, XGROW(41)
REAL*8 TO, RO, VO, CHAIR, CWAIR, XFF

C POLYDISPERSE PARTICLE COAGULATION MODEL
C
BOLT=1.38*(10.0**(-16))
TP=Y(45)*T0
VIS=0.00001458*(TP**1.5)/(TP+110.4)
MFP=0.0002206*TP
DO 21 I=1, 41
KN(I) = 2.0*MFP/D(I)
CORR(I) = 1.0 + (1.257 + 0.4*DEXP(-0.55*2.0/KN(I)))*KN(I)
DIFF(I) = CORR(I)*BOLT*TP/(3.0*3.1416*VIS*D(I)*0.0001)

CONTINUE
DO 22 I = 1, 41
DO 23 J = 1, I
BB(I, J) = 3.1416*(D(I)+D(J))*(DIFF(I)+DIFF(J))*0.0001
23 BB(J, I) = BB(I, J)
22 CONTINUE

DO 34 K = 1, 41
TERM1 = 0.0
IF(K.EQ.1) GO TO 29
KK = K - 1
DO 28 I = 1, KK
J = K - I
28 TERM1 = TERM1 + BB(I, J)*Y(I)*Y(J)*BIMO(I)*BIMO(J)
TERM1 = 0.5*TERM1
29 TERM2 = 0.0
IF(K.EQ.35) GO TO 27
DO 36 I = K, 41
36 TERM2 = TERM2 + BB(I, K)*Y(I)*BIMO(I)
TERM2 = TERM2*Y(K)*BIMO(K)
27 CONTINUE
IF(K.EQ.1) GO TO 25
XCOAG(K) = TERM1 - TERM2
25 XCOAG(K) = -TERM2
26 COAG(K) = RO*XCOAG(K)/(BIMO(K)*VO)
34 CONTINUE

C ACID VAPOR CONDENSATION RATE AND
C ACID VAPOR LOSS

PA = Y(48)*CHAIR*62400.0*TP
IF(PA.LE.0.0) GO TO 24
PW = Y(49)*CWAIR*62400.0*TP
DPT = 1.0/(0.002276-0.00002943*DLOG(PW) - 0.0000858*
1DLOG(PA) + 0.0000062*DLOG(PW)*DLOG(PA))
IF(TP.GE.DPT) GO TO 24
T = TP - 273.0
WC1 = -17.15+(0.0825*TP)-(0.00026*T**2)
WC2 = 14.245-(0.05525*TP)+(0.00002*T**2)
WC3 = -1.962+(0.02246*TP)-(0.00003*T**2)
AC1 = -27.5375+(0.44225*TP)-(0.00191*T**2)
AC2 = 56.445-(0.70725*TP)+(0.00289*T**2)
AC3 = -33.763+(0.32878*TP)-(0.00116*T**2)
DO 82 I = 1, 61
IF(I.GT.60) GO TO 61
WO = 0.91*0.99**I
WC4 = WC1*WO**2+WC2*WO+WC3
EWP = 10.0**WC4
DP=PW-EWP
RP=DABS(DP/PW)
IF(RP.LT.0.01)GO TO 81
CONTINUE

WO=0.5
EWP=10.0**((WC1*WO*WO+WC2*WO+WC3)
WH=0.5
GO TO 69

WH=W0
AC4=AC1*WH**2+AC2*WH+AC3
ESAP=10.0**AC4
IF(TP.LT.338.0)ESAP=0.0
DEP=PA-ESAP
IF(DEP.LE.0.0)GO TO 24
AVO=6.02*(10.0**23)

WL=0.0
DO 31 I=1,41
XKN(I)=(1.0+KN(I))/(1.0+1.71*KN(I)+1.333*(KN(I)**2))
AVCR(I)=0.083776*D(I)*XKN(I)*DEP/(BOLT*TP)
HL=HL+AVCR(I)*Y(I)*BIMO(I)
COND=HL/AVO
C
C PARTICLE GROW RATE DUE TO ACID CONDENSATION
C
VMS=1.6*(10.0**(-10))
VMW=3.0*(10.0**(-11))
XMOL=(18.0*WH)/(98.0-80.0*WH)
VTOL=VMS+((1.0-XMOL)*VMW/XMOL)
XDROW(1)=-AVCR(1)*Y(1)*BIMO(1)*VTOL/(0.5236*D(1)**3)
XDROW(41)=AVCR(40)*Y(40)*BIMO(40)*VTOL/(0.5236*
1D(40)**3)
DO 62 I=2,40
XDROW(I)=AVCR(I-1)*Y(I-1)*BIMO(I-1)*VTOL/(0.5236*
1D(I-1)**3)
XDROW(I)=XDROW(I)-(AVCR(I)*Y(I)*BIMO(I)*VTOL/(0.5236*
1D(I)**3)
CONTINUE
IF(ESAP.LE.0.0)GO TO 18
XSR=PA/ESAP
IF(XSR.LE.5.0)GO TO 18
RLN=DLOG(XSR)
SU=65.0
DEN=1.4
VHV=1.16*(10.0**(-22))
XAA=(0.63662*VHV*SU/DEN)**0.5
XCC=-16.755*(SU**3)*(VHV**2)/(BOLT**3)
XFF=XCC/((TP**3)*(RLN**2))
IF(XFF.LT.-70.0)GO TO 18
XBB=DEXP(XFF)
XHN=XAA*(AVO**2)*XBB*((Y(48)*CHAIR)**2)
XDD = 1.20/(TP*RLN)
XEE = XDD/D(1)
XGROW(1) = XGROW(1) + (XHN*(XEE**3))
18   DO 64 I = 1, 41
64   GROW(I) = R0*XGROW(I)/(BIMO(I)*VO)
       GO TO 65
24   DO 33 I = 1, 41
33   AVCR(I) = 0.0
33   GROW(I) = 0.0
       COND = 0.0
       W0 = 0.0
       WH = 0.0
       EWP = 0.0
       ESAP = 0.0
65   RETURN
END
C$ENTRY
**IMSL ROUTINE NAME — LEQIF**

```fortran
SUBROUTINE LEQIF (A,IA,N,MA,B,IB,M,IJOB,WK,IER)
    INTEGER IA,IB,N,MA,M,IJOB,IER
    DOUBLE PRECISION A(IA,N),B(IB,M),WK(N,3)

    INTEGER I,IBIG,IIK,IP1,IZ,J,JJ,JJJ,JZ,KB,KBP1,
    * KKB,LB,LIMK,LIMK0,LIMK1,LIMK2,LIML,LIMLO,
    * LIML1,LIML2,NBLOCK
    DOUBLE PRECISION ABIG,AM,REPS,TEMP
    DATA REPS/Z34100000000000000000/

    FIRST EXECUTABLE STATEMENT
    IER = 0
    DO 5 I=1,N
      WK(I,1) = I
      NBLOCK = (N—l)/MA+l
    5 CONTINUE

    BEGIN GAUSSIAN ELIMINATION
    DO 80 KB=1,NBLOCK
      LIMKO = (KB—1)*MA
      LIMK1 = LIMKO+1
      LIMK2 = MINO(LIMK0+MA,N)
      IF (KB.GT.1 .OR. IJOB.EQ.1) GO TO 20
      DO 15 J=LIMK1,LIMK2
        TEMP = 0.0D0
        DO 10 I=1,N
          JZ = WK(J,1)
          IF (DABS(A(JZ,I)).LE.ABIG) GO TO 25
          ABIG = DABS(A(JZ,I))
          IBIG = J
          10 CONTINUE
        TEMP = DMAX1(TEMP,DABS(A(I,J)))
        15 CONTINUE
      20 CONTINUE
    80 CONTINUE

    FACTOR FIRST BUFFER
    DO 40 I=LIMK1,LIMK2
      ABIG = 0.0D0
      DO 25 J=I,N
        JZ = WK(J,1)
        IF (DABS(A(JZ,I)).LE.ABIG) GO TO 25
        ABIG = DABS(A(JZ,I))
        IBIG = J
      25 CONTINUE
    40 CONTINUE
    IF (ABIG.EQ.0.0D0) GO TO 9000
    IF (IJOB.EQ.1) GO TO 30
    IF (ABIG.LE.10.0D0*REPS*WK(I,2)) GO TO 9000
    30 CONTINUE
    TEMP = WK(IBIG,1)
```

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WK(IBIG,1) = WK(I,1)
WK(I,1) = TEMP
IF (I.GE.N) GO TO 40
IZ = WK(I,1)
IP1 = I+1
DO 35 J=IP1,N
   JZ = WK(J,1)
   AM = A(JZ,I)/A(IZ,I)
   IF (AM.EQ.0.0D0) GO TO 35
   CALL DAXPY(M,-AM,B(IZ,1),IA,B(JZ,1),IA)
   IF (IJOB.EQ.1) GO TO 35
   IF (I.GE.LIMK2) GO TO 35
CALL DAXPY(LIMK2-I,-AM,A(IZ,I+1),IA,A(JZ,I+1),IA)
35 CONTINUE
40 CONTINUE
IF (IJOB.EQ.1) GO TO 80
IF (KB.GE.NBLOCK) GO TO 75
KBP1 = KB+1
DO 70 LB=KBP1,NBLOCK
   LIML0 = (LB-1)*MA
   LIML1 = LIML0+1
   LIML2 = MIN0(LIML0+MA,N)
   LIML = LIML2-LIML0
   IF (KB.GT.1) GO TO 55
   DO 50 J=LIML1,LIML2
      TEMP = 0.0D0
      DO 45 I=1,N
         TEMP = DMAX1(TEMP,DABS(A(I,J)))
45 CONTINUE
   WK(J,2) = TEMP
50 CONTINUE
55 CONTINUE
C DO ELIMINATION ON SECOND BLOCK
C USING FACTORS SAVED IN FIRST
DO 65 I=LIMK1,LIMK2
   IF (I.GE.N) GO TO 65
   IZ = WK(I,1)
   IP1 = I+1
   DO 60 J=IP1,N
      JZ = WK(J,1)
      AM = A(JZ,I)/A(IZ,I)
      IF (AM.EQ.0.0D0) GO TO 60
      CALL DAXPY(LIML,-AM,A(IZ,LIML1),IA,A(JZ,LIML1),IA)
60 CONTINUE
65 CONTINUE
70 CONTINUE
75 CONTINUE
80 CONTINUE
C BACK SUBSTITUTION
DO 105 KKB=1,NBLOCK
   KB = NBLOCK+1-KKB
   LIMKO = (KB-1)*MA
LIMK2 = MINO(LIMK0+MA,N)
LIMK = LIMK2-LIMK0
DO 100 IIK=1,LIMK
   I = LIMK2+1-IIK
   IZ = WK(I,1)
   TEMP = A(IZ,I)
   DO 85 JJJ=1,M
      B(IZ,JJJ) = B(IZ,JJJ)/TEMP
   85 CONTINUE
   IF (I.EQ.1) GO TO 100
   DO 95 JJ=2,I
      J = I+1-JJ
      JZ = WK(J,1)
      TEMP = A(JZ,I)
      DO 90 JJJ=1,M
         B(JZ,JJJ) = B(JZ,JJJ)·TEMP*B(IZ,JJJ)
   90 CONTINUE
95 CONTINUE
100 CONTINUE
105 CONTINUE
C SORT SOLUTION VECTOR
   DO 120 JJJ=1,M
      DO 110 I=1,N
         IZ = WK(I,1)
         WK(I,3) = B(IZ,JJJ)
   110 CONTINUE
   DO 115 I=1,N
      B(I,JJJ) = WK(I,3)
   115 CONTINUE
120 CONTINUE
   GO TO 9005
9000 IER = 129
   CALL UERTST(IER,6HLEQIF )
9005 RETURN
END
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IMSL ROUTINE NAME — DVERK

SUBROUTINE DVERK (N, FCN, X, Y, XEND, TOL, IND, C, NW, W, IER)
INTEGER N, IND, NW, IER
DOUBLE PRECISION X, Y(N), XEND, TOL, C(1), W(NW, 9)
INTEGER K
REAL*8 ZERO, ONE, TWO, THREE, FOUR, FIVE, SEVEN, TEN, HALF, P9
REAL*8 C4D15, C2D3, C5D6, C1D6, C1D15, C2D96, TEMP
REAL*8 RK(39), REPS, RTOL
DATA ZERO/0.0D0/, ONE/1.0D0/, TWO/2.0D0/, THREE/3.0D0/
DATA FOUR/4.0D0/, FIVE/5.0D0/, SEVEN/7.0D0/
DATA TEN/10.0D0/, HALF/0.5D0/, P9/0.9D0/
DATA C4D15/.2666666666666667D+00/
DATA C2D3/.6666666666666667D+00/
DATA C5D6/.8333333333333333D+00/
DATA C1D6/.1666666666666667D+00/
DATA C1D15/.6666666666666667D-1/
DATA C2D96/120.4272910821709D0/
DATA REPS/Z3410000000000000/
DATA RTOL/20D10000000000000/
DATA RK( 1)/.1666666666666667D+00/
DATA RK( 2)/.5333333333333333D-01/
DATA RK( 3)/.2133333333333333D+00/
DATA RK( 4)/.8333333333333333D+00/
DATA RK( 5)/.2666666666666667D+01/
DATA RK( 6)/.2500000000000000D+01/
DATA RK( 7)/.2578125000000000D+01/
DATA RK( 8)/.916666666666667D+01/
DATA RK( 9)/.6640625000000000D+01/
DATA RK(10)/.885416666666667D+01/
DATA RK(11)/.2400000000000000D+01/
DATA RK(12)/.8000000000000000D+01/
DATA RK(13)/.656045751639869D+01/
DATA RK(14)/.3055555555555556D+00/
DATA RK(15)/.3450980392156863D+00/
DATA RK(16)/.5508666666666667D+00/
DATA RK(17)/.1653333333333333D+01/
DATA RK(18)/.9455882352941176D+00/
DATA RK(19)/.3240000000000000D+00/
DATA RK(20)/.2337882352941176D+00/
DATA RK(21)/.203546511627907D+01/
DATA RK(22)/.6976744186046512D+01/

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DATA   RK(23)/  .5648179814561484D+01/
DATA   RK(24)/  .1373815676141258D+00/
DATA   RK(25)/  .2863022661036103D+00/
DATA   RK(26)/  .1441785567164738D+00/
DATA   RK(27)/  .7500000000000000D-01/
DATA   RK(28)/  .3899286987522282D+00/
DATA   RK(29)/  .3194444444444444D+00/
DATA   RK(30)/  .1350383631713555D+00/
DATA   RK(31)/  .1078329882677709D-01/
DATA   RK(32)/  .6980519480519481D-01/
DATA   RK(33)/  .6250000000000000D-02/
DATA   RK(34)/  .6963012477718360D-02/
DATA   RK(35)/  .6944444444444444D-02/
DATA   RK(36)/  .6138107416879795D-02/
DATA   RK(37)/  .6818181818181818D-01/
DATA   RK(38)/  .1078329882677709D-01/
DATA   RK(39)/  .6980519480519481D-01/

C FIRST EXECUTABLE STATEMENT
IER = 0
C BEGIN INITIALIZATION, PARAMETER
C CHECKING, INTERRUPT RE-ENTRIES
C ABORT IF IND OUT OF RANGE 1 TO 6
IF (IND.LT.1.OR.IND.GT.6) GO TO 290
C CASES - INITIAL ENTRY, NORMAL
C RE-ENTRY, INTERRUPT RE-ENTRIES
GO TO (5,5,40,145,265,265), IND
C CASE 1 - INITIAL ENTRY (IND .EQ. 1
C OR 2) ABORT IF N.GT.NW OR TOL.LE.0
5 IF (N.GT.NW.OR.TOL.LE.ZERO) GO TO 295
IF (IND.EQ.2) GO TO 15
C INITIAL ENTRY WITHOUT OPTIONS (IND
C .EQ. 1) SET C(1) TO C(9) EQUAL TO 0
DO 10 K=1,9
C(K) = ZERO
10 CONTINUE
GO TO 30
C SUMMARY OF THE COMPONENTS OF THE
C COMMUNICATIONS VECTOR
C PRESCRIBED AT THE OPTION OF THE USER
C C(1) ERROR CONTROL INDICATOR
C C(2) FLOOR VALUE
C C(3) HMIN SPECIFICATION
C C(4) HSTART SPECIFICATION
C C(5) SCALE SPECIFICATION
C C(6) HMAX SPECIFICATION
C C(7) MAX NO OF FCN EVALS
C C(8) INTERRUPT NO 1
C C(9) INTERRUPT NO 2
C C(10) RREB(REL ROUNDOFF ERROR BND)
C C(11) DWARF (VERY SMALL MACH NO)
C C(12) WEIGHTED NORM Y

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C C(13) HMIN
C C(14) HMAG
C C(15) SCALE
C C(16) HMAX
C C(17) XTRIAL
C C(18) HTRIAL
C C(19) EST
C C(20) PREVIOUS XEND
C C(21) FLAG FOR XEND
C C(22) NO OF SUCCESSFUL STEPS
C C(23) NO OF SUCCESSIVE FAILURES
C C(24) NO OF FCN EVALS
C C C(1) = 4 OR 5, C(31), C(32), ...
C C(N+30) ARE FLOOR VALUES

15 CONTINUE

C INITIAL ENTRY WITH OPTIONS (IND .EQ. 2) MAKE C(1) TO C(9) NON-NEGATIVE

DO 20 K = 1, 9
   C(K) = DABS(C(K))
20 CONTINUE

C MAKE FLOOR VALUES NON-NEGATIVE IF THEY ARE TO BE USED

IF (C(1).NE.FOUR.AND.C(1).NE.FIVE) GO TO 30
DO 25 K = 1, N
   C(K+30) = DABS(C(K+30))
25 CONTINUE

30 CONTINUE

C INITIALIZE RRREB, DWARF, PREV XEND, FLAG, COUNTS
C
C(10) = REPS
C(11) = RTOL

C SET PREVIOUS XEND INITIALLY TO INITIAL VALUE OF X
C
C(20) = X
DO 35 K = 21, 24
   C(K) = ZERO
35 CONTINUE

GO TO 45

C CASE 2 - NORMAL RE-ENTRY (IND .EQ. 3) ABORT IF XEND REACHED, AND EITHER X CHANGED OR XEND NOT

40 IF (C(21).NE.ZERO.AND.(X.NE.C(20).OR.XEND.EQ.C(20)))
1 GO TO 285

C RE-INITIALIZE FLAG
C
C(21) = ZERO
C
C CASE 3 - RE-ENTRY FOLLOWING AN INTERRUPT (IND .EQ. 4 TO 6) TRANSFER CONTROL TO THE APPROPRIATE RE-ENTRY POINT. THIS HAS ALREADY BEEN HANDLED BY THE COMPUTED GO TO.
CONTINUE

LOOP THROUGH THE FOLLOWING 4 STAGES, ONCE FOR EACH TRIAL STEP UNTIL THE OCCURRENCE OF ONE OF THE FOLLOWING
A) THE NORMAL RETURN (WITH IND .EQ. 3) ON REACHING XEND IN STAGE 4
B) AN ERROR RETURN (WITH IND .LT. 0) IN STAGE 1 OR STAGE 4
C) AN INTERRUPT RETURN (WITH IND .EQ. 4, 5 OR 6), IF REQUESTED, IN STAGE 1 OR STAGE 4

CONTINUE

STAGE 1 - PREPARE - DO CALCULATIONS OF HMIN, HMAX, ETC., AND SOME PARAMETER CHECKING, AND END UP WITH SUITABLE VALUES OF HMAG, XTRIAL AND HTRIAL IN PREPARATION FOR TAKING AN INTEGRATION STEP.

ERROR RETURN (WITH IND=-1) IF NO OF FCN EVALS TOO GREAT

IF (C(7).EQ.ZERO.OR.C(24).LT.C(7)) GO TO 55
IND = -1
GO TO 9005

CONTINUE

CALCULATE SLOPE (ADDING 1 TO NO OF FCN EVALS) IF IND .NE. 6
IF (IND.EQ.6) GO TO 60
CALL FCN (N,X,Y,W(1,1))
C(24) = C(24)+ONE

CONTINUE

CALCULATE HMIN - USE DEFAULT UNLESS VALUE PRESCRIBED
C(13) = C(3)
IF (C(3).NE.ZERO) GO TO 120
CALCULATE DEFAULT VALUE OF HMIN
FIRST CALCULATE WEIGHTED NORM Y -
C(12) - AS SPECIFIED BY THE ERROR CONTROL INDICATOR C(1)
TEMP = ZERO
IF (C(1).NE.ONE) GO TO 70
ABSOLUTE ERROR CONTROL - WEIGHTS ARE 1
DO 65 K=1,N
TEMP = DMAX1(TEMP,DABS(Y(K)))
65 CONTINUE
C(12) = TEMP
GO TO 115

CONTINUE

RELATIVE ERROR CONTROL - WEIGHTS ARE 1/DABS(Y(K)) SO WEIGHTED NORM Y IS 1
C(12) = ONE
GO TO 115
75 IF (C(1).NE.THREE) GO TO 85
C  WEIGHTS ARE 1/MAX(C(2),ABS(Y(K)))
   DO 80 K=1,N
      TEMP = DMAX1(TEMP,DABS(Y(K))/C(2))
80 CONTINUE
   C(12) = DMIN1(TEMP,ONE)
   GO TO 115
85 IF (C(1).NE.FOUR) GO TO 95
C  WEIGHTS ARE 1/MAX(C(K+30),ABS(Y(K)))
   DO 90 K=1,N
      TEMP = DMAX1(TEMP,DABS(Y(K))/C(K+30))
90 CONTINUE
   C(12) = DMIN1(TEMP,ONE)
   GO TO 115
95 IF (C(1).NE.FIVE) GO TO 105
C  WEIGHTS ARE 1/C(K+30)
   DO 100 K=1,N
      TEMP = DMAX1(TEMP,DABS(Y(K))/C(K+30))
100 CONTINUE
   C(12) = TEMP
   GO TO 115
105 CONTINUE
C  DEFAULT CASE - WEIGHTS ARE
C  1/MAX(1,ABS(Y(K)))
   DO 110 K=1,N
      TEMP = DMAX1(TEMP,DABS(Y(K)))
110 CONTINUE
   C(12) = DMIN1(TEMP,ONE)
115 CONTINUE
C(13) = TEN*DMAX1(C(11),C(10)*DMAX1(C(12)/TOL,
C  DABS(X)))
120 CONTINUE
C  CALCULATE SCALE - USE DEFAULT UNLESS
C  VALUE PRESCRIBED
C  C(15) = C(5)
C  IF (C(5).EQ.ZERO) C(15) = ONE
C  CALCULATE HMAX - CONSIDER 4 CASES
C  CASE 1 - BOTH HMAX AND SCALE PRESCRIBED
C  IF (C(6).NE.ZERO.AND.C(5).NE.ZERO)
C  CASE 2 - HMAX PRESCRIBED, BUT SCALE NOT
C  IF (C(6).NE.ZERO.AND.C(5).EQ.ZERO) C(16) = C(6)
C  CASE 3 - HMAX NOT PRESCRIBED, BUT SCALE IS
C  IF (C(6).EQ.ZERO.AND.C(5).NE.ZERO) C(16) = TWO/C(5)
C  CASE 4 - NEITHER HMAX NOR SCALE IS PROVIDED
C  IF (C(6).EQ.ZERO.AND.C(5).EQ.ZERO) C(16) = TWO
C  ERROR RETURN (WITH IND=-2) IF HMIN.GT.HMAX
IF (C(13).LE.C(16)) GO TO 125
IND = -2
GO TO 9005
CONTINUE

CALCULATE PRELIMINARY HMAG - CONSIDER 3 CASES

IF (IND.GT.2) GO TO 130

CASE 1 - INITIAL ENTRY - USE PRESCRIBED VALUE OF HSTART, IF ANY, ELSE DEFAULT

C(14) = C(4)
IF (C(4).EQ.ZERO) C(14) = C(16)*TOL**C1D6
GO TO 140

130 IF (C(23).GT.ONE) GO TO 135

CASE 2 - AFTER A SUCCESSFUL STEP, OR AT MOST ONE FAILURE, USE MIN(2,
.9*(TOL/EST)**(1/6))*HMAG, BUT AVOID POSSIBLE OVERFLOW. THEN AVOID REDUCTION BY MORE THAN HALF.

TEMP = TWO*C(14)
IF (TOL.LT.C2D96*C(19)) TEMP=P9*(TOL/C(19))**C1D6*C(14)

C(14) = DMAX1(TEMP,HALF*C(14))
GO TO 140

135 CONTINUE

CASE 3 - AFTER TWO OR MORE SUCCESSIVE FAILURES

C(14) = HALF*C(14)

140 CONTINUE

CHECK AGAINST HMAX

C(14) = DMIN1(C(14),C(16))

CHECK AGAINST HMIN

C(14) = DMAX1(C(14),C(13))

INTERRUPT NO 1 (WITH IND=4) IF REQUESTED IF (C(8).EQ.ZERO) GO TO 145
IND = 4
GO TO 9005

RESUME HERE ON RE-ENTRY WITH IND .EQ.4

145 CONTINUE

CALCULATE HMAG, XTRIAL - DEPENDING ON PRELIMINARY HMAG, XEND

IF (C(14).GE.DABS(XEND-X)) GO TO 150
C(14) = DMIN1(C(14),HALF*DABS(XEND-X))
C(17) = X+DSIGN(C(14),XEND-X)
GO TO 155

150 CONTINUE

HIT XEND EXACTLY

C(14) = DABS(XEND-X)
C(17) = XEND

155 CONTINUE

CALCULATE HTRIAL

C(18) = C(17)-X

STAGE 2 - CALCULATE YTRIAL (ADDING 7
DO 160 K=1,N
W(K,9) = Y(K)+C(18)*W(K,1)*RK(1)
160 CONTINUE
CALL FCN (N,X+C(18)*C1D6,W(1,9),W(1,2))
DO 165 K=1,N
W(K,9) = Y(K)+C(18)*(W(K,1)*RK(2)+W(K,2)*RK(3))
165 CONTINUE
CALL FCN (N,X+C(18)*C4D15,W(1,9),W(1,3))
DO 170 K=1,N
W(K,9) = Y(K)+C(18)*((W(K,1)*RK(4)-W(K,2)*RK(5))
1 + W(K,3)*RK(6))
170 CONTINUE
CALL FCN (N,X+C(18)*C2D3,W(1,9),W(1,4))
DO 175 K=1,N
W(K,9) = Y(K)+C(18)*(-W(K,1)*RK(7)+W(K,2)*
1RK(8)-W(K,3)*RK(9)+W(K,4)*RK(10))
175 CONTINUE
CALL FCN (N,X+C(18)*C5D6,W(1,9),W(1,5))
DO 180 K=1,N
W(K,9) = Y(K)+C(18)*((-W(K,1)*RK(11)-W(K,2)*RK(12)
1+W(K,3)*RK(13)-W(K,4)*RK(14)+W(K,5)*RK(15))
180 CONTINUE
CALL FCN (N,X+C(18),W(1,9),W(1,6))
DO 185 K=1,N
W(K,9) = Y(K)+C(18)*(-W(K,1)*RK(16)+W(K,2)*RK(17)
1-W(K,3)*RK(18)-W(K,4)*RK(19)+W(K,5)*RK(20))
185 CONTINUE
CALL FCN (N,X+C(18)*C1D15,W(1,9),W(1,7))
DO 190 K=1,N
W(K,9) = Y(K)+C(18)*((W(K,1)*RK(21)-W(K,2)*RK(22)
1+W(K,3)*RK(23)-W(K,4)*RK(24)+W(K,5)*RK(25)
2+W(K,7)*RK(26))
190 CONTINUE
CALL FCN (N,X+C(18),W(1,9),W(1,8))
C CALCULATE YTRIAL, THE EXTRAPOLATED
C APPROXIMATION AND STORE IN W(*,9)
DO 195 K=1,N
W(K,9) = Y(K)+C(18)*((W(K,1)*RK(27)+W(K,3)*RK(28)
1+W(K,4)*RK(29)+W(K,5)*RK(30)+W(K,7)*RK(31)
2+W(K,8)*RK(32))
195 CONTINUE
C ADD 7 TO THE NO OF FCN EVALS
C(24) = C(24)+SEVEN
C STAGE 3 - CALCULATE THE ERROR
C ESTIMATE EST. FIRST CALCULATE THE
C UNWEIGHTED ABSOLUTE ERROR ESTIMATE
VECTOR (PER UNIT STEP) FOR THE
UNEXTRAPOLATED APPROXIMATION AND
STORE IT IN W(*,2). THEN CALCULATE
THE WEIGHTED MAX NORM OF W(*,2) AS
SPECIFIED BY THE ERROR CONTROL
INDICATOR C(1). FINALLY, MODIFY
THIS RESULT TO PRODUCE EST, THE
ERROR ESTIMATE (PER UNIT STEP) FOR
THE EXTRAPOLATED APPROXIMATION YTRIAL.
CALCULATE THE UNWEIGHTED ABSOLUTE
ERROR ESTIMATE VECTOR.

DO 200 K=1,N
W(K,2) = W(K,1)*RK(33)+W(K,3)*RK(34)-W(K,4)*RK(35)
1 +W(K,5)*RK(36)+W(K,6)*RK(37)-W(K,7)*RK(38)-W(K,8)
2 *RK(39)
200 CONTINUE

CALCULATE THE WEIGHTED MAX NORM OF
W(*,2) AS SPECIFIED BY THE ERROR
CONTROL INDICATOR C(1)

TEMP = ZERO
IF (C(1).NE.ONE) GO TO 210
ABSOLUTE ERROR CONTROL
DO 205 K=1,N
TEMP = DMAX1(TEMP,DABS(W(K,2)))
205 CONTINUE
GO TO 260
210 IF (C(1).NE.TWO) GO TO 220
RELATIVE ERROR CONTROL
DO 215 K=1,N
IF (Y(K).EQ.ZERO) GO TO 280
TEMP = DMAX1(TEMP,DABS(W(K,2)/Y(K)))
215 CONTINUE
GO TO 260
220 IF (C(1).NE.THREE) GO TO 230
WEIGHTS ARE 1/MAX(C(2),ABS(Y(K)))
DO 225 K=1,N
TEMP=DMAX1(TEMP,DABS(W(K,2))/DMAX1(C(2),DABS(Y(K))))
225 CONTINUE
GO TO 260
230 IF (C(1).NE.FOUR) GO TO 240
WEIGHTS ARE 1/MAX(C(K+30),ABS(Y(K)))
DO 235 K=1,N
TEMP=DMAX1(TEMP,DABS(W(K,2))/DMAX1(C(K+30),
1DABS(Y(K))))
235 CONTINUE
GO TO 260
240 IF (C(1).NE.FIVE) GO TO 250
WEIGHTS ARE 1/C(K+30)
DO 245 K=1,N
TEMP = DMAX1(TEMP,DABS(W(K,2)/C(K+30)))
245 CONTINUE
GO TO 260

250 CONTINUE
C DEFAULT CASE - WEIGTHS ARE
C 1/\text{MAX}(1,\text{ABS}(Y(K)))
DO 255 K=1,N
TEMP=\text{DMAX1}(TEMP,\text{DABS}(W(K,2)))/\text{DMAX1}(\text{ONE},\text{DABS}(Y(K)))
255 CONTINUE
260 CONTINUE
C CALCULATE EST - (THE WEIGHTED MAX
C NORM OF W(*,2))*HMAG*SCALE - EST
C IS INTENDED TO BE A MEASURE OF THE
C ERROR PER UNIT STEP IN YTRIAL
C(19) = TEMP*C(14)*C(15)
C STAGE 4 - MAKE DECISIONS. SET IND=5
C IF STEP ACCEPTABLE, ELSE SET IND=6
IND = 5
IF (C(19).GT.TOL) IND = 6
C INTERRUPT NO 2 IF REQUESTED
IF (C(9).NE.ZERO) GO TO 9005
C RESUME HERE ON RE-ENTRY WITH IND .EQ. 5 OR 6
265 CONTINUE
IF (IND.EQ.6) GO TO 275
C STEP ACCEPTED (IND .EQ. 5), SO
C UPDATE X, Y FROM XTRIAL, YTRIAL,
C ADD 1 TO THE NO OF SUCCESSFUL
C STEPS, AND SET THE NO OF
C SUCCESSIVE FAILURES TO ZERO
X = C(17)
DO 270 K=1,N
Y(K) = W(K,9)
270 CONTINUE
C(22) = C(22)+\text{ONE}
C(23) = \text{ZERO}
C RETURN(WITH IND=3, XEND SAVED, FLAG
C SET) IF X .EQ. XEND
IF (X.NE.XEND) GO TO 50
IND = 3
C(20) = XEND
C(21) = \text{ONE}
GO TO 9005
275 CONTINUE
C STEP NOT ACCEPTED (IND .EQ. 6), SO
C ADD 1 TO THE NO OF SUCCESSIVE FAILURES
C(23) = C(23)+\text{ONE}
C ERROR RETURN (WITH IND=-3) IF HMAG .LE. HMIN
IF (C(14).GT.C(13)) GO TO 50
IND = -3
GO TO 9005
C END STAGE 4
C END LOOP
280 CONTINUE
C RELATIVE ERROR OPTION SELECTED AND Y(K) IS ZERO
      IER = 132
      GO TO 9000
285 CONTINUE
C X OR XEND WAS NOT CHANGED FROM PREVIOUS CALL
      IER = 131
      GO TO 9000
290 CONTINUE
C IND OUT OF RANGE
      IER = 130
      GO TO 9000
295 CONTINUE
C N.GT.NW OR TOL.LE.0
      IER = 129
C BEGIN ABORT ACTION
9000 CONTINUE
   CALL UERTST (IER,6HDVERK )
9005 CONTINUE
RETURN
END
APPENDIX D. PROGRAM PARAMETERS

<table>
<thead>
<tr>
<th>Program Symbol</th>
<th>Text Symbol</th>
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<td>C₈(H₂SO₄)</td>
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<tr>
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<td>Im{b_n}</td>
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<td>Im{(A_n(y)/m + n/x)×(\xi_n(x)-\xi_{n-1}(x))}</td>
</tr>
<tr>
<td>IDENB</td>
<td>Im{(mA_n(y)+n/x)×(\xi_n(x)-\xi_{n-1}(x))}</td>
</tr>
<tr>
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<tr>
<td>IN2</td>
<td>Im(mA_n(y)+n/x)</td>
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\[ \text{INUM} \quad \text{Im}((A_n(y)/m + n/x) \times \text{Re} \left[ \xi_n(x) \right] - \text{Re}[\xi_{n-1}(x)] \]

\[ \text{INUMB} \quad \text{Im}((mA_n(y) + n/x) \times \text{Re} \left[ \xi_n(x) \right] - \text{Re}[\xi_{n-1}(x)] \]

\[ \text{IW}(1) \quad \text{Im}(\xi_{-1}(x)) \]

\[ \text{IW}(2) \quad \text{Im}(\xi_0(x)) \]

\[ \text{IW}(J+2) \quad \text{Im}(\xi_{n}(x)) \]

\[ \text{IWM1X} \quad \text{Im}(\xi_{-1}(x)) \]

\[ \text{IWOX} \quad \text{Im}(\xi_{-1}(x)) \]

\[ \text{KN} \quad \text{Re}(a_n) \]

\[ \text{MFP} \quad \text{Re}(A_n(y)) \]

\[ \text{OPAC} \quad \text{Re}(A_n(y)) \]

\[ \text{PI} \quad \text{Re}(b_n) \]

\[ \text{PA} \quad \text{Re}(A_n(y) + n/x) \times \xi_n(x) - \xi_{n-1}(x) \]

\[ \text{PW} \quad \text{Re}(mA_n(y) + n/x) \times \xi_n(x) - \xi_{n-1}(x) \]

\[ \text{Q} \quad \text{Re}(n/y - A_{n-1}(y)) \]

\[ \text{QE} \quad \text{Re}(n/y - A_{n-1}(y))^{-1} \]

\[ \text{RAN} \quad \text{Re}(n/y - A_{n-1}(y))^{-1} - n/y \]

\[ \text{RBA} \quad \text{Re}(A_n(y) + n/x) \times \ln S \]

\[ \text{RBN} \quad \text{Re}(a_n) \]

\[ \text{RDEN} \quad \text{Re}(\xi_n(x) - \xi_{n-1}(x)) \]

\[ \text{RDENB} \quad \text{Re}(\xi_n(x) - \xi_{n-1}(x)) \]

\[ \text{RH1} \quad \text{Re}(n/y) \]

\[ \text{RH2} \quad \text{Re}(n/y - A_{n-1}(y)) \]

\[ \text{RH3} \quad \text{Re}(n/y - A_{n-1}(y))^{-1} \]

\[ \text{RH4} \quad \text{Re}(n/y - A_{n-1}(y))^{-1} - n/y \]

\[ \text{RN1} \quad \text{Re}(A_n(y)/m + n/x) \]

\[ \text{RN2} \quad \text{Re}(mA_n(y) + n/x) \]

\[ \text{RLN} \quad \ln S \]

\[ \text{RM} \quad \text{Re}(a_n) \]

\[ \text{RNUM} \quad \text{Re}(\xi_n(x) - \xi_{n-1}(x)) \]

\[ \text{RNUMB} \quad \text{Re}(\xi_n(x) - \xi_{n-1}(x)) \]
\begin{align*}
\text{RO} & \quad r_0 \\
\text{RSK} & \quad r \\
\text{RW}(1) & \quad \text{Re}\{\xi_{-1}(x)\} \\
\text{RW}(2) & \quad \text{Re}\{\xi_{0}(x)\} \\
\text{RW}(J+2) & \quad \text{Re}\{\xi_{n}(x)\} \\
\text{RWX} & \quad \text{Re}\{\xi_{-1}(x)\} \\
\text{SUF} & \quad \tau \\
\text{SUM} & \quad \sum (2n+1)\text{Re}(a_n + b_n) \\
\text{SUM2} & \quad \sum \sigma_i \\
\text{T} & \quad T \\
\text{TERM1} & \quad 1/2\sum B(j,k)n_j n_k \\
\text{TERM2} & \quad n_i \sum B(i,k)n_k \\
\text{TP} & \quad T \\
\text{TOT} & \quad \sum n_i \\
\text{TSK} & \quad T \\
\text{TO} & \quad T_0 \\
\text{USK} & \quad U \\
\text{VO} & \quad V_0 \\
\text{VIS} & \quad \mu \\
\text{VMW} & \quad \nu(H_2O) \\
\text{VMS} & \quad \nu(H_2SO_4) \\
\text{VX} & \quad V^* \\
\text{WH} & \quad w \\
\text{WO} & \quad w \\
\text{XCOAG} & \quad K \\
\text{XCOND} & \quad H \\
\text{XEND} & \quad dt^* \\
\text{XGROW} & \quad G \\
\text{XHN} & \quad I_1 \\
\text{XKN} & \quad 1+K_n/1+1.71Kn+1.333Kn^2 \\
\text{XLAM} & \quad \lambda \\
\text{XP} & \quad x \\
\text{XSR} & \quad S \\
\text{XSUM} & \quad 2r\sigma \\
\text{Y(1)}...\text{Y(41)} & \quad n_1 ... n_{41} \\
\text{Y(42)} & \quad r^* \\
\text{Y(43)} & \quad U^* \\
\text{Y(44)} & \quad \theta \\
\text{Y(45)} & \quad T^* \\
\text{Y(46)} & \quad z^* \\
\text{Y(47)} & \quad x^* \\
\text{Y(48)} & \quad C^*(H_2SO_4) \\
\text{Y(49)} & \quad C^*(H_2O) \\
\text{Z} & \quad 2n-1/x
\end{align*}
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