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**INTEGRATED EMISSIONS CONTROL SYSTEM
FOR RESIDENTIAL CWS FURNACE**

Annual Status Report Number 1

Report Period: September 20, 1989 to September 30, 1990

**By
J.C. Balsavich and R.W. Breault**

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October 1990

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**Work Performed Under Contract No. DE-AC22-89PC89804
September 20, 1989 to March 20, 1992**

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1. INTRODUCTION

One of the major obstacles to the successful development and commercialization of a coal-fired residential furnace is the need for a reliable, cost-effective emission control system. Ash, sulfur, and fuel-bound nitrogen make the control of NO_x , SO_x , and particulates much more difficult with coal-based fuels than with either natural gas or oil. While techniques for controlling these emissions in large utility power plants are well advanced, they generally would be too complex and costly to be applied directly to residential applications.

To meet the emission goals set by the Pittsburgh Energy Technology Center (PETC), Tecogen Inc. is developing a novel, integrated emission control system to control NO_x , SO_2 , and particulate emissions. At the heart of this system is a unique emissions control reactor for the control of SO_2 . This reactor provides high sorbent particle residence time within the reactor while doing so in a very compact geometry. In addition to controlling SO_2 emissions, the reactor provides a means of extracting a substantial amount of the particulates present in the combustion gases. Final cleanup of any fine particulates exiting the reactor, including respirable-sized particulates, is completed with the use of high efficiency bag filters.

With SO_2 and particulate emissions being dealt with by an emissions control reactor and bag filters, the control of NO_x emissions needs to be addressed. Under a previous contract with PETC (contract No. DE-AC22-87PC79650), Tecogen developed a residential-scale Coal Water Slurry (CWS) combustor. This combustor makes use of centrifugal forces, set up by a predominantly tangential flow field, to separate and confine larger unburned coal particles in the furnace upper chamber. Various partitions are used to retard the axial, downward flow of these particles, and thus maximize their residence time in the hottest section of the combustor. By operating this combustor under staged conditions, the local stoichiometry in the primary zone can be controlled in such a manner as to minimize NO_x emissions.

The development program for this project is divided into three facets, each having specific objectives with clear goals that would be met prior to proceeding to the next step. First, all system and component analyses would be completed, and the initial prototype component hardware would be tested and evaluated. Preliminary manufacturing and operating cost estimates would also be made. Second, final prototype hardware would be built and tested, and cost estimates updated. Finally, the entire furnace system would be tested to demonstrate that the emissions goals were met, and the high-volume production cost estimates would be finalized.

The entire program covers a period of 30 months. The first step will require 12 months, and the next two, 9 months each. This report summarizes work conducted during the first year of the program.

2. PROGRAM OBJECTIVE

The objective of this program is to develop a combined particulate, SO₂, and NO_x integrated control system for flue gas cleanup of residential furnaces fueled by coal water fuel mixtures. Specific objectives for this program are:

- To reduce flue gas emissions from the furnace to the following levels:

SO₂: 0.4 lb/MMBtu

NO_x: 0.2 lb/MMBtu

Particulates: 0.02 lb/MMBtu
 (99.9% capture of particles 0.5 to 10 microns)
- To achieve a high reliability and a service life of 20 years or more by utilizing a simple design concept with no critical moving parts.
- To keep scheduled maintenance to twice a year.
- To achieve efficient sorbent utilization in reducing SO₂ so that the volume of ash and spent sorbent collected before removal is acceptable.
- To use a simple design approach to keep manufacturing costs as low as possible.

In order to achieve these objectives, this program has been divided up into 8 individual tasks. These tasks, along with their various subtasks, provide the framework for this project and establish the various goals and milestones. The 8 main tasks for this program are:

- Task 1: Project Work Plan
- Task 2: System Definition
- Task 3: Prototype Component Analysis and Design
- Task 4: Prototype Component Fabrication and Assembly
- Task 5: Testing and Development
- Task 6: Integrated System Operation
- Task 7: Economic Evaluation
- Task 8: Reporting and Management

3. WORK PERFORMED DURING FIRST YEAR

During the first year of the program, work was conducted on Tasks 1 through 5 and Task 7. This work encompassed a wide range of the program's scope and included a literature search, developing an analytical model of the SO₂ reactor, fabricating, assembling the initial prototype components, testing the prototype component, and estimating the operating and manufacturing costs. A discussion of these activities follows.

3.1 TASK 2.1 - LITERATURE REVIEW

A literature review has been conducted to determine the level of understanding of the factors affecting emissions from small-scale coal-fired combustion systems and to form a basis for the development of an analytic model. Literature on coal combustion, slurry handling, NO_x reduction, and sulfur dioxide removal is summarized below.

3.1.1 Coal Combustion

A review of the existing literature on the various aspects of coal and coal-water mixture combustion has been conducted and is provided below. The main topics reviewed are coal make-up, devolatilization, char oxidation, volatile oxidation, soot oxidation, and coal-water mixture oxidation.

Coal is a complex, solid, heterogeneous material of carbon base, capable of supplying energy for heat and processing. The chemical and physical make-up of coal has been studied extensively and continues to be studied. Coal studies are usually divided into two areas - coal chemistry (chemical and physical make-up) and coal utilization (combustion, gasification, and liquefaction).

Coal Chemistry

Coal is classified by rank and grade.¹ Coal rank is a method of expressing the progressive metamorphism of coal from lignite (low) to metaanthracite (high). There are four ranks of coal: (1) lignite, (2) subbituminous, (3) bituminous, and (4) anthracite. Each rank has also been subdivided, based on ash-free heating values for low rank coals and moisture-ash-free fixed carbon content for high rank coals. The results of the subdivisions - lowest to highest rank - are: lignite B, lignite A, subbituminous C, subbituminous B, subbituminous A, high volatile bituminous C, high volatile bituminous B, high volatile bituminous A, medium volatile bituminous, low volatile bituminous, semianthracite, anthracite, and metaanthracite. The heating value increases from 13,900 kJ/kg for lignite B to 34,900 kJ/kg for low volatile bituminous A and then decreases to 30,100 kJ/kg for

metaanthracite. The fixed carbon content increases from 25 percent for lignite B to 90 percent for metaanthracite.

Coal is also classified by grade. The three factors that cause coal to have a low grade are: high ash content, low ash fusion temperature, and high sulfur content. Sulfur is the primary constituent that lowers the grade and thus has been studied extensively. Sulfur in coal lowers the quality of iron and steel, causes corrosion and deposits, and promotes air pollution. Sulfur ranges between 0.2 to 7.0 percent by weight, with the average being between 1 and 2 percent. Sulfur occurs as inorganic pyrite and marcasite (40 to 80 percent) with the balance contained in the organic structure. The highest sulfur coals are the bituminous coals of the Pennsylvanian age in the Appalachian, Illinois, and Western Interior coal basins. The lowest sulfur coals are the subbituminous coals and lignites in the Rocky Mountain and Northern Great Plains Regions. These coals contain less than 1 percent sulfur. The molecular structure of coal is not completely known. Investigators (Solomon, Wisner, and Heredy and Wender)² have gathered information from infrared measurements, nuclear magnetic resonances, ultimate and proximate analyses, and pyrolysis data to obtain models for the chemical structure of the organic backbone of coal. This organic backbone of coal is constructed of aromatic and hydro-aromatic units. Some of these units have various functional groups that cross-link the units together. The planar nature of the aromatics gives the coal a layered consistency. The layers may be twisted in such a way that a perfect laminate is not obtained. The imperfection in the laminate creates pores that may house ash or other impurities. Low rank coals have about 90 percent of the carbon associated with 5-unit layers, while high rank coals have about 90 percent of the carbon associated in 30-unit layers.^{1,2,3,4}

Devolatilization

Coal devolatilization has been studied widely, and many models have been developed.¹ The models reviewed are limited to coal particles less than or equal to 100 μm . These models are categorized as: (1) single reaction, (2) multiple parallel reactions, (3) multiple competing reactions, (4) complex schemes, and (5) schemes involving secondary char formation. These models vary from the very simple to the very complex. The details of these models are discussed below.

For the single reaction, coal $\rightarrow$ solid + volatile, the reaction rate models are simple and quite limited. Both an Arrhenius expression:

$$\frac{dV}{dt} = k (V_{\infty} - V)^n \quad (3.1)$$

and a non-Arrhenius expression

$$\frac{dV}{dt} = BV_{\infty}/t \quad (3.2)$$

have been developed. The order n in the Arrhenius expression has been estimated to be between 1 and 8, depending on the investigator. The non-Arrhenius expression neglects the observed temperature dependence on devolatilization.

The second category consists of multiple parallel reactions that are first-order Arrhenius expressions. This category has been subdivided by Ubhayakar¹ into two sections, namely, two first-order Arrhenius models and multiple first-order reactions with a statistical distribution of the activation energy. The devolatilization process is modeled by the first of these techniques by the following set of equations:

where:

$$\frac{d C_{1,2}}{dt} = -k_{1,2} C_{1,2} \quad (3.4)$$

The second technique is described by the equations below:

where:

$$\frac{dV_i}{dt} = k_i (V_{i,\infty} - V_i) \quad (3.6)$$

$$k_i = A \exp (-E_i/RT) \quad (3.7)$$

$$\int_0^{\infty} f(E) dE = 1 \quad (3.8)$$

Equation (3.8) gives a complete statistical distribution of activation energy.

Multiple competing reaction models, the third category, are also used to express the devolatilization process. In this category, the devolatilization reaction is expressed:

with two rate equations

$$\frac{d(\text{coal})}{dt} = - \left(\sum_{i=1}^n k_i \right) \text{Coal} \quad (3.10)$$

and

$$\frac{dV}{dt} = \left(\sum_{i=1}^n Y_i V_i \right) \text{Coal} \quad (3.11)$$

Kobayashi^{1,2} used this model with $n = 2$. Smith and Smoot² applied this model in their pulverized coal combustion and gasification models with good success.

The fourth category, complex schemes, includes the multiple consecutive parallel first-order reaction:

and the parallel competing first order reaction:

These two mechanisms are complicated, producing several intermediate and final products. A coal combustion model needs a simple, straightforward model of the devolatilization process. These two models do not provide these criteria.

The final category, schemes involving secondary char-forming reactions, contains two models: (1) consecutive competing char-forming reactions and (2) parallel competing char-forming reactions. These models are too complex to be included in a combustor model. The first has seven reactions, producing seven product types, while the second has $n + 2$ reactions and a statical distribution of activation energies.

The models presented above indicate that the fraction of volatile matter evolved is a function of both the temperature and the length of time for which devolatilization occurs. For bituminous coals, Kobayashi et al.² report that at a temperature of 1260°K and for a time of 200 milliseconds, 30 percent of the coal is volatilized.

Char Oxidation

The devolatilization process produces a solid residue, char. The char consists of the fixed carbon and ash. In actuality, the char is a composite material containing carbon, hydrogen, sulfur, oxygen, nitrogen, and ash. An ultimate analysis of the char shows that the fractions of each of these elements in general are in approximately the same ratios as in the parent coal. Char oxidation is a heterogeneous chemical reaction. These reactions have been studied extensively,⁵ and the reaction mechanism developed in those studies is discussed below.

Heterogeneous Char Reactions

Char consists of three major elements: carbon, hydrogen, and sulfur, which are oxidized. The general heterogeneous chemical reaction is expressed as:

Written in this manner, the reactions for carbon, hydrogen, and sulfur become:

This group of reactions is a simplification of possible reactions that have been researched and shown to exist in minor amounts.¹

Smith has reviewed the question as to which product is favored – CO or CO₂ – and suggests that CO is the most likely.²

Kinetics of Heterogeneous Char Oxidation

Heterogeneous chemical reactions have also been studied extensively. Levenspiel⁵ has proposed a mechanism for gas-solid reactions that has withstood numerous investigations and applications. Heterogeneous reactions are envisioned to proceed by the following steps:

- (1) Diffusion of reactant gas from the bulk fluid through the gas film surrounding the particle to the solid surface.
- (2) Penetration and diffusion of reactant gas through a blanket of ash (solid product) to the unreacted core.
- (3) Chemical reaction of reactant gas with solid at the reaction surface.
- (4) Diffusion of the product gas through the gas to the exterior surface of the particle.
- (5) Diffusion of the product gas through the gas film surrounding the particle to the bulk fluid.

One or all of these steps may be involved in the chemical reaction sequence. The steps that offer the greatest resistance to the propagation of the reaction are called the rate controlling steps. For reactions such as char oxidation in which a stationary ash layer is not formed, Steps 2 and 4 have negligible resistances and can be neglected. The driving force for the product gas between the surface and the bulk fluid is in general quite large since the bulk contains little or no product gas. Thus, Step 5 offers negligible resistance and is neglected.

The rate of chemical reaction for the general reaction with Steps 1 and 3 controlling is given by:

$$R = \frac{dm_B}{dt} = \frac{A \, b \, M_B \, C_A}{\frac{1}{k_c} + \frac{1}{k_d}} \quad (3.19)$$

The two terms, $1/k_c$ and $1/k_d$, are the chemical reaction resistance and the mass transfer resistance, respectively. The chemical reaction rate constant, k_c , has been studied extensively for the carbon-oxygen reaction.^{1,2} However, reaction rate constants for the hydrogen-oxygen and sulfur-oxygen reactions are not available in published literature. The mass transfer coefficient, k_d , has been studied extensively for a single particle in a fluid.⁵

The reaction rate coefficient, k_c , for the carbon-oxygen reaction has been well studied by investigators² using the conventional Arrhenius expression $k = A \exp(-E/RT)$ to model the effect of reaction temperature. Table 3.1 summarizes the values for the frequency factor A , and activation energy E , along with the type of coal char and particle size used in the experiment. As can be seen in Table 3.1, the type of coal char greatly influences the values of the frequency factor and activation energy.

The mass transfer coefficient is expressed:

$$k_d = \frac{Sh D}{d_p} \quad (3.20)$$

The Sherwood Number, Sh , is modeled by:

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (3.21)$$

The Sherwood Number or the mass transfer coefficient modeled by these equations shows good agreement with the experimental data and is an accepted approach to modeling the mass transfer resistance.

Volatile Matter Oxidation

Experimental information on the volatile oxidation rate has not been found in the literature. Experimental research in this area is needed to verify the theoretical predictions.^{1,2} Volatile product combustion times are estimated by considering only mass transfer resistances and chemical reaction rate resistances.³ The burning time, assuming the volatiles have a molecular weight of 100 and the coal has a volatile fraction of 0.5, is 7 milliseconds for a 50- μ m coal particle at 1273°K. If the mass transfer resistance is negligible, such that only the chemical reaction is considered and assuming the reaction rate to be that for CO going to CO₂ (the slowest step), the combustion time can be estimated. These assumptions provide only an order of magnitude value. The burning time for a 50- μ m particle at 1273°K is 3.2 milliseconds. These two burning time values are approximately the same, such that the volatile oxidation process is neither only diffusion controlled nor reaction rate controlled.

TABLE 3.1
CARBON-OXYGEN REACTION RATE CONSTANTS, k_p

$$\text{where } k_p = \frac{k_c M_{O_2}}{T_g R} = A \exp(-E/RT)$$

Type of Coal Char	Particle Size	Frequency Factor	Activation Energy
(μm)	$\left(\frac{g}{cm^2 s atm O_2} \right)$		$\left(\frac{k_{cal}}{kgmol} \right)$
Bituminous	28	92	21,900
38			
82			
105			
Non-Swelling	27	45.7	17,263
Bituminous	38	80.3	21,787
Swelling	31	94.3	23,463
Bituminous	72	1000	35,194
Anthracites	23	20.4	19,000
and			
Semi-Anthracites	78		
Flash Pyrolysis Char	85	16.3	17,597
Petroleum Coke	--	15	19,000

Soot Oxidation

The oxidation time for soot has been estimated.³ For a soot particle with a 500A° diameter the combustion time is 0.173s at a temperature of 1600°K.³ Lee, Thring, and Beer³ obtained the following expression for the soot combustion rate:

$$r = 1.085 \times 10^4 P_{O_2} T^{1/2} \exp (-39300/RT) [=] \frac{g}{Cm^2 s} \quad (3.22)$$

for 400A° soot particles.

3.1.2 Slurry Handling

The in-house handling of CWF will typically consist of pumping CWF to the atomizer, piping, and cleaning systems.

Pumping

The pumping of the CWF is of critical concern since the CWF fuels are abrasive and exhibit complex rheological behavior. Depending on the shear rates, the CWF can have pseudoplastic, dilatant, or Newtonian shear stress/shear rate behavior. The low solids CWF (50 to 60 percent) generally exhibit Newtonian behavior for shear rates magnitudes comparable to handling systems and do not require the same concern for fuel handling.^{1,2} In general, pumping system design has to avoid high shear rates and must match the pumping velocities to the type of fuel used.

The rheology of CWF depends strongly on coal type, extent and method of beneficiation, solids content, particle size distribution, and additives used in the formulation, as well as time. Initially, the CWF's show a reduction in viscosity,⁷ the magnitude of which is based on the additive levels and particle size distribution.

After the initial reduction, and especially for heavily loaded slurries, the viscosity remains constant at a particular shear rate until the accumulated amount of shear increases to the design point. Once this level of shear is reached, the viscosity of the fuel gradually increases and a yield point forms. This viscosity continues to increase with accumulated shear until the fluid is no longer pumpable. If a sample of this CWF were tested, it would exhibit a completely different shear stress/shear rate behavior from its original rheogram. There are many causes for this behavior: comminution, deagglomeration, additive evaporation, or changes in the zeta potential.⁷

Three types of pumps have been used for CWF: progressing cavity pump, diaphragm pump, and centrifugal pump. Most of the CWF industry has centered on the use of progressing cavity pumps since they develop low shear rate, have minimal or no wear problems, and have a wide selection of flow rate and discharge pressures. Materials compatible with CWF's include modular iron, carbon steel, stainless steel, Buna N, and various polymer compounds.

In general, progressing cavity pumps are highly suitable for handling CWF.⁸ They have predictable performance and pulsationless discharge. Erosion is kept to a minimum by the use of elastomers for the outer stationary gear. Also, the compression fit between the elastomeric stator and rotor makes the pump capable of pumping high viscosity and abrasive CWF's. Progressing cavity pumps have been used extensively and successfully in government research facilities, industrial trial combustion tests, and in commercial slurry producers' plants, both in the United States and abroad. Most of the pumping of the highly loaded CWF, however, has not been continuous so far.

Centrifugal pumps have high internal shear rates and, thus, accelerate the alteration of CWF properties.⁸ CWF behavior is affected more dramatically in cases of highly loaded CWF, as compared to pumping moderately loaded CWF. Thus, the CWF formulation (with respect to the combination of particle size distribution, interaction of chemical dispersant, and stabilizers) greatly affects the performance of the centrifugal pumps. In view of these limitations, centrifugal pumps are not suitable for residential furnace applications.

Another type of pump that has been used for pumping CWF in residential furnace applications is the peristaltic pump.⁹ Because of the manner in which it operates, the peristaltic pump offers several advantages over the progressing cavity and centrifugal pumps. First, none of the mechanical parts of the pump come in contact with the CWF. This eliminates any wear problems associated with the pump as a result of the abrasive nature of CWF. Second, because of the positive displacement nature of the pump, it can be calibrated and used as a metering pump to measure the flow rate of the CWF being burned. These pumps are much less expensive than progressing cavity pumps, and the only maintenance they require is the replacement of pump head tubing after about 1,000 to 1,500 hours of operation. Finally, the peristaltic pumps are available in very small capacities as required for residential applications; therefore, there is no need for recirculation of the excess CWF back to the storage tank.⁷

Should the CWF characteristics require recirculation for keeping the coal in suspension, a peristaltic pump with multiple heads can be installed on the same drive shaft, as shown in Figure 3.1. In this arrangement, the pumps can be sized for slurry recirculation and the amount of CWF needed for atomization.

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Figure 3.1 Peristaltic Pump with Dual Pump Heads

Piping

By designing the piping for laminar flow, the shear rate in the piping is kept low. At higher velocities, the differential pressures are too great and may also lead to erosion problems. The design of valve pressure drops should also be kept low to minimize erosion. For pipe sizing, Newtonian assumptions are used with standard design equations.

To minimize settling problems, all of the piping is pitched, piping dead-legs are avoided, and rod-out ports are used at branch points. The piping system is provided with a water flushing or cleaning system for removal of residual fuel in the lines. Although the inherent stability of the CWF will allow the slurry to be pumped to the atomizer without the need for flushing during routine operation, during extended outages the water flushing system is operated to avoid buildup of CWF in the piping system.

3.1.3 NO_x Reduction

Slurry-fueled systems have a number of advantages over dry pulverized coal systems in controlling NO_x emissions (NO and NO₂). Lower operating temperatures significantly reduce the amount of NO_x produced by oxidation of the nitrogen in the combustion air (often referred to as "thermal NO_x").

However, in coal-fired systems as much as three-quarters of the NO_x results from the oxidation of fuel-bound nitrogen (or "fuel-NO_x"). Fuel-NO_x formation appears to depend on the local availability of oxygen during combustion, the complex evolution of intermediate nitrogenous radical species, and coal properties such as volatility. Meeting future stringent NO_x emissions limits without relying on post-combustion controls will require effective control on chemistry of fuel-bound nitrogen.

Figure 3.2 simplistically demonstrates the pathway in which fuel nitrogen converts to NO and NO₂. Pyrolysis produces volatile nitrogen species, primarily in the amine and cyanide groups. These in turn undergo oxidation and thermal degradation, producing NO and NH_i (i = 1,2,3) species. The char nitrogen is oxidized to NO. The NO is reduced to N₂ by reaction with CO, CaSO₃, C, or NH₃. These reactions are given in Table 3.2.^{9,10,11}

The first four reactions shown in Table 3.2 are the nitrogen oxide generating reactions. Oxidation of the fuel nitrogen is an essential step in the mechanism transforming fuel-bound nitrogen to N₂ molecule. Careful control of the stoichiometry in this initial region where pyrolysis occurs and NO production begins will provide an abundance of chemical species able to reduce the NO to N₂ by consuming oxygen.

Figure 3.2 Nitrogen Pathway

TABLE 3.2
CHEMICAL REACTIONS INVOLVING FUEL NO_x
FORMATION AND DESTRUCTION

Reaction Number	Reaction
1	Coal + heat $\rightarrow$ volatile N + char N
2	Volatile N + O ₂ $\rightarrow$ NO + NH ₃
3	Char N + O ₂ $\rightarrow$ NO
4	NH ₃ + 5/4 O ₂ $\rightarrow$ NO + 3/2 H ₂ O
5	NO + C $\rightarrow$ CO + 1/2 N ₂
6	NO + CO $\rightarrow$ CO ₂ + 1/2 N ₂
7	NO + 2NH ₃ + O ₂ $\rightarrow$ 3H ₂ O + 3/2 N ₂
8	NO + CaSO ₃ $\rightarrow$ CaSO ₄ + 1/2 N ₂
9	NO + 1/2 O ₂ $\rightarrow$ NO ₂

Staged combustion provides a chemical environment favorable to NO reduction by supplying a relatively high concentration of unoxidized carbon in the char, carbon monoxide, ammonia, and calcium sulfite (where calcium oxide is used to control SO₂ emissions). It should be pointed out for clarity, however, that NO is produced throughout the combustor from oxidation of the nitrogen in the char.

Researchers have shown that the reduction of NO by oxidizing the other reactant in reactions 5 through 8 progresses at rates approximately 2/3 as fast as oxidation with O₂.^{9,10} Reaction 9 shows the conversion of NO to NO₂, producing a mixture of NO and NO₂ referred to as NO_x. This mechanism has been used to predict NO_x formation from an industrial steam generator¹² with good results.

3.1.4 Sulfur Dioxide Removal

Desulfurization

The introduction of the Clean Air Act has nurtured the development of sulfur dioxide removal processes. Both wet and dry techniques have been developed to date, with wet processes dominating the market. These processes are expensive to manufacture and operate. Dry processes such as limestone injection systems and fluidized bed coal combustion in a limestone bed are both being researched.

Dry sulfur dioxide removal processes utilize the following chemical overall reaction.

The reaction proceeds forward at temperatures up to 1500°K for sulfur dioxide concentrations of approximately 3000 ppm.¹³ The calcium oxide is generated by the calcination of limestone (CaCO₃) and dolomite (CaCO₃/MgCO₃). The calcium oxide and magnesium oxide obtained by calcination are both capable of sulfinating. Formulation of magnesium sulfate occurs at temperatures below 1110°K. However, experimental evidence shows the reaction to occur only slightly in the 700 to 970°K temperature range.¹³

The sulfination reaction rate has been found to decay with time. This phenomenon is explained by the observation that pores are created in the stone structure by the calcination process. The actual decay in rate is attributed to the substitution of the much larger sulfur trioxide molecule for the carbon dioxide molecule. Researchers have taken two approaches in modeling this phenomenon. Some have used a simple exponential decay models^{13,14,15} while others have used

complicated grain models.^{16,17} The grain models are more theoretical in nature and probably describe the actual decay phenomenon as it truly is. However, the grain models' complexities limit their use in a combustion process model.

Borgwardt¹³ has conducted extensive experimental studies on stone sulfination. He modeled the reaction rate time delay phenomenon by modifying the conventional Arrhenius frequency factor. Borgwardt presented the following model:

$$R = \frac{\eta}{\rho_s} A_0 e^{-\beta\eta/w} e^{-E/RT} C_{SO_2}^m \quad (3.24)$$

He presents a method to obtain β , the exponential decay coefficient.

Lee^{14,15} has developed a simple model, based on two experimental parameters, which predicts the time decay quite well. This model is discussed below. The rate of reaction is expressed by the product of the initial rate and an exponential decay term.

$$R = R_0 e^{-t/\tau_p} \quad (3.25)$$

The exponential decay term contains the pore plugging time constant, τ_p , which is taken as one third the pore plugging time.

$$\tau_p = \frac{t_p}{3} \quad (3.26)$$

The pore plugging time has been shown to be inversely proportional to the sulfur dioxide concentration, thus τ_p can be expressed by:

$$\tau_p = \frac{P^*}{C_{SO_2}} \quad (3.27)$$

where P^* is the pure plugging constant. The initial rate, R_0 is expressed by:

$$R_0 = \frac{\pi d_p^3}{6} \rho_s k S \eta C_{SO_2} \quad (3.28)$$

The group $\rho_s k_S \eta$ is combined into one constant, τ_{SF} , which has been provided for a number of limestone and dolomite stones. Upon substituting, Lee obtained the following equation:

$$R = \frac{\pi d_p^3}{6} \frac{C_{SO_2}}{\tau_{SF}} e^{(-tC_{SO_2}/P^*)} \quad (3.29)$$

The only parameters needed from experimental data are P^* and τ_{SF} . Lee provided these data¹⁴ and conducted all experimental work using 1000 μm particles.

The performance predicted by these models, particularly Borgwardt's model, agrees nicely with experimental data.^{18,19} Only a 3.5-percent deviation was obtained between predicted and experimental results for an industrial scale steam generation unit. This shows that the Borgwardt reaction model is usable in an engineering model of a desulfurization reactor.

3.2 TASK 3.1 - ANALYTICAL MODELING

In developing an analytical model of the SO_2 reactor, several complexities are encountered due to the coupling of the flow field in the main body of the reactor to that of the axial recirculation loop. These two highly coupled flow fields result in the need to solve a three-dimensional, highly nonisotropic turbulent flow field with a dispersed second phase of particles that undergo chemical reactions.

One possible approach to modeling the reactor is to use available computational fluid dynamics (CFD) computer codes. Several codes are commercially available; however, each has limitations when applied to modeling the SO_2 reactor. The turbulent flow field within the reactor is nonisotropic and as such, the standard two-equation $k - \epsilon$ model used in most codes is not the best representation of the turbulence within the reactor. In order to more accurately model the flow within the reactor, an algebraic stress model (ASM) should be used. A survey of codes that are commercially available shows that codes that have ASM turbulence models are not capable of accurately modeling the reactor geometry due to the recirculation line. The codes that are available that can handle the reactor geometry are typically limited to using the two-equation $k - \epsilon$ model, which is not the best choice for this problem.

In addition to the problems of geometry and turbulence models, the use of CFD codes to model the process inside the reactor can require a considerable computational effort. For example, it was estimated by a software vendor that in order to resolve the flow within a residential-sized SO_2 reduction reactor,

approximately 72,000 nodes would be required. In order to obtain a solution, the code must solve as a function of position within the reactor the three velocity components, pressure, a minimum of two turbulence parameters, particle trajectories, and chemical reactions with the gas and the particles. This can result in the need to solve more than 500,000 simultaneous, nonlinear equations, which is typically beyond the capabilities of engineering work stations for reasonable turnaround times.

As an alternative to the use of CFD codes, a simplified model of the reactor was developed. The purpose of this model was to determine the dominant parameters that govern the reduction of SO_2 within the reactor, as well as to provide performance estimates under various operating conditions.

In developing the analytical model, one of the prime areas of concern is for given gas-flow conditions, the ability of the reactor to detain particles of a given size. Though the flow within the reactor is quite complex, if the recirculation line effect is neglected, then the reactor is quite similar to a cyclone separator. The ability of cyclones to collect particles of a given size has been well documented, for example, by Zenz.⁽²⁰⁾ For a given geometry and gas flow conditions the theoretically smallest-size particle size that a cyclone can collect, typically called the cut point diameter, can be found by:

$$Dp_{th} = \left[\frac{9 \mu_g L_w}{\pi N_s V_{in} (\rho_p - \rho_g)} \right]^{\frac{1}{2}} \quad (3.30)$$

where:

μ_g is the gas viscosity

V_{in} is the inlet velocity

ρ_p, ρ_g are the particle and gas density, respectively

N_s is the number of spiral turns, which is found from experiment

L_w is the cyclone inlet width

For application of this equation to the axial recirculation reactor, L_w is defined as the radial distance between the reactor wall and the outside radius of the recirculation tube.

Once the cut point diameter is determined, the separation efficiency of any other size particle can be determined from normalized separation efficiency data, as shown by Zenz.⁽²⁰⁾ With a knowledge of the separation efficiency of a given-size particle, its residence time in the reactor relative to the gas can be determined.

Under steady-state conditions and assuming that the reactor is capable of fluidizing all the particles within it, as one particle is added to the reactor, one particle must leave. However, the particle that is added to the system will be recirculated N times before it leaves. The number of times a particle of a specific diameter within the reactor circulates, N , is dependent on the separation efficiency for this size particle. This relationship can be expressed as:

$$N = 1 + \eta + \eta^2 + \eta^3 + \dots \quad (3.31)$$

where η is the separation efficiency. This relation can be expressed in closed form as:

$$N = \frac{1}{1 - \eta} \quad (3.32)$$

Once N is determined, the amount of solid material in the reactor that can participate in the reduction of SO_2 can be found since it is equal to N times the inlet solids flow rate.

With a knowledge of the amount of solids present in the reactor, one-dimensional species-continuity equations for the concentration of SO_2 in the gas phase and CaO in the solid phase can be written as:

$$\frac{d [\text{SO}_2]}{dz} = \frac{-6 (1 - \epsilon) [\text{SO}_2]}{\epsilon D_p V_g \left(\frac{1}{k_c} + \frac{1}{k_d} \right)} \quad (3.33)$$

$$\frac{d [\text{CaO}]}{dz} = \frac{-6 [\text{SO}_2]}{D_p V_s \left(\frac{1}{k_c} + \frac{1}{k_d} \right)} \quad (3.34)$$

where

$[\text{SO}_2]$ is the concentration of SO_2 in the gas phase

$[\text{CaO}]$ is the concentration of CaO in the solid phase

V_g, V_s are the gas and solid phase velocities, respectively

ϵ is the void fraction (adjusted to account for particle recirculation)

k_c, k_d are the chemical kinetics and diffusion resistances, respectively

D_p is the particle diameter

The diffusion resistance, k_d , can be found from the relationship:

$$Sh = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad (3.35)$$

where:

Sh is the Sherwood number defined by:

$$Sh = k_d \frac{D_p}{D} \quad (3.36)$$

D is the diffusivity

Re is the Reynolds number based on the slip velocity

Sc is the Schmidt number

The chemical kinetics resistance is determined by using Borgwardt's model, which takes into account the decrease in the rate of reaction due to pore plugging:

$$K_c = A_o \exp \left(- \beta \frac{n'}{w} \right) \exp \left(- \frac{E}{RT} \right) \quad (3.37)$$

where:

A_o is the frequency factor

n' is the sulfate in the stone

W is the weight of the solid sample

R is the universal gas constant

T is the absolute temperature

E is the activation energy

β is a stone-dependent constant determined by experiment

This set of coupled equations is solved numerically as a function of length in order to determine reactor performance.

3.2.1 Parametric Investigation

With the model established, a parametric investigation was conducted to determine which factors have a significant effect on the performance of the reactor. For this investigation, the conditions shown in Table 3.3 were considered.

TABLE 3.3
SO₂ MODEL PARAMETERS

Operating Temperature	1,650°F
Excess Air	20%
Firing Rate	100,000 to 400,000 Btu/hr (Nominal: 100,000 Btu/hr)
Inlet SO₂ Concentration	330 to 4,000 ppm (typical of 0.5 to 6% sulfur coal, Nominal: 3,000 ppm)
Calcium to Sulfur Ratio	0.5:1 – 5:1 (Nominal: 3:1)
Reactor Diameter	4, 6, 8 inches
Reactor Height	0 to 100 inches (Nominal: 50 inches)
Limestone Properties	
Activation Energy	10,000 cal./g-mole
Frequency Factor	335,000 l/s
Beta	333.33 g/g-mole
Density	150 lbm/ft³
Particle Diameter	10 to 1,000 microns

a. Effect of Particle Diameter

The effect of particle diameter on reactor performance is shown in Figure 3.3 for reactor diameters of 4, 6, and 8 in. For this case, the reactor height was chosen to be 50 in., the unit was operated at a gas flow rate equivalent to an input rate of 100,000 Btu/hr, the concentration of SO_2 was 3,000 ppm, and the Ca/S ratio was 3:1. Figure 3.3 shows that for each different diameter reactor there is an optimum sorbent particle diameter that maximizes SO_2 capture. For the conditions considered in this analysis, this corresponds to particle diameters of 30, 75, and 130 microns for reactor diameters of 4, 6, and 8 inches, respectively.

The fact that the model predicts an optimal particle diameter for a particular set of operating conditions can be attributed to the way in which the reactor operates. At particle diameters smaller than the optimal, a tremendous amount of sorbent surface area is available to participate in SO_2 capture; however, since these particles are small and cannot be separated and detained effectively within the reactor, their ability to capture SO_2 is not realized. At particle diameters above the optimal, performance again decreases, though not as rapidly for particles smaller than the optimal. The reason for the decrease is that these larger sized particles are easily separated and detained within the reactor. As the particle diameter is increased, however, its surface area relative to its volume is decreased. As a result, there is less surface area in the reactor relative to optimal conditions, and performance decreases.

In addition to each reactor diameter having an optimal particle diameter for SO_2 capture, this particle diameter increases with increasing reactor diameter. This is due to the fact that smaller diameter reactors have higher separation efficiencies for smaller sized particles. Even though the smaller diameter reactors are capable of separating smaller diameter particles and as such for a given Ca/S ratio would have more available surface area within the reactor, their ability to capture SO_2 is not as great as the larger diameter reactors. The reason for this is that for a fixed reactor height, the smaller diameter reactor would have a higher axial velocity and a shorter residence time within the reactor compared to larger diameter units for similar operating conditions.

b. Effect of SO_2 Concentration

The effect of inlet SO_2 concentration on reactor performance is shown in Figure 3.4. For this case, the reactor height was chosen to be 50 in., the unit was operated at a gas flow rate equivalent to an input rate of 100,000 Btu/hr, and the Ca/S ratio was 3:1. The concentration of SO_2 was varied between 330 and 4,000 ppm, which is equivalent to coal with between 0.5 and 6 percent sulfur. Figure 3.4 shows that as the concentration is increased, the percent reduction in SO_2 also increases.

Predicted SO₂ Reduction Reactor Performance
 Input: 100,000 Btu/hr at 20 Percent Excess Air
 Inlet Conc.: 3,000 ppm (Ca/S = 3:1)

TF22-790

Figure 3.3 Effect of Particle Diameter on Reactor Performance

Predicted SO₂ Reduction Reactor Performance
Input: 100,000 Btu/hr at 20 Percent Excess Air
Reactor Height: 50 in. Ca/S = 3:1

TF23-790

Figure 3.4 Effect of SO₂ Concentration on Reactor Performance

The reason for the increase in performance can be explained by referring to equation (3.33). For a fixed Ca/S ratio, as the concentration is increased the term on the right hand side of the equation becomes a larger negative number since both concentration and effective solids loading are increasing. Thus there is a stronger gradient in SO₂ concentration as a function of reactor length.

As illustrated in Figure 3.4, for a given SO₂ concentration, as the reactor diameter increased reactor performance also increased. This is due to the increased residence time associated with the larger diameter reactors when they are operated with their optimum particle diameter (found in Figure 3.3).

c. Effect of Calcium-to-Sulfur Ratio

The effect of calcium-to-sulfur ratio (Ca/S) on reactor performance is shown in Figure 3.5. For this case, the reactor height was chosen to be 50 in., the unit was operated at a gas flow rate equivalent to an input rate of 100,000 Btu/hr, and the concentration of SO₂ was 3,000 ppm. For this case, each reactor diameter considered was operated at its optimum particle diameter (found in Figure 3.3).

As the Ca/S ratio is increased, reactor performance also increases with the larger diameter reactors capable of removing more SO₂ due to their longer gas residence times. For the 6- and 8-in. diameter reactors, as Ca/S is increased, the gain in performance starts to level off at a much quicker rate than for the 4-in. diameter reactor. For example, consider increasing Ca/S mole ratio from 3 to 4. For the 8-in. diameter reactor, the percent reduction in SO₂ increases from 88.9 to 94.7; however, for the 4-in. diameter reactor, this increase is from 61.6 to 72.2 percent.

d. Effect of Reactor Height

The effect of reactor height (directly proportional to gas residence time) on reactor performance is shown in Figure 3.6. For this case, the unit was operated at a gas flow rate equivalent to an input rate of 100,000 Btu/hr, the concentration of SO₂ was 3,000 ppm, and the Ca/S ratio was 3:1. For this case, each reactor diameter considered was operated at its optimum particle diameter, as found in Figure 3.3.

As reactor height is increased, performance increases due to the longer gas residence time within the reactor. Increasing reactor height for a given diameter reactor tends to increase performance to the point where it approaches an exponential limit. With the 8-in. diameter reactor, this limit is approached in a much shorter reactor than with the 4-in. unit.

Predicted SO₂ Reduction Reactor Performance

TF24-790

Input: 100,000 Btu/hr at 20 Percent Excess Air

Inlet Conc: 3,000 ppm (Reactor Height: 50 in)

Figure 3.5 Effect of Calcium-to-Sulfur Ratio on Reactor Performance

Predicted SO₂ Reduction Reactor Performance
Input: 100,000 Btu/hr at 20 Percent Excess Air
Inlet Concentration: 3,000 ppm, Ca/S = 3:1

TF25-790

Figure 3.6 Effect of Reactor Height on Reactor Performance

e. Effect of Input Rate

The effect of increasing the flow rate through the reactor at equivalent input rates ranging from 100,000 to 400,000 Btu/hr on reactor performance is shown in Figure 3.7. For this case, the reactor height was chosen to be 50 in., the Ca/S ratio was 3:1, and only a reactor diameter of 8 in. was considered. The reason for considering only the 8-in. diameter reactor was that as the flow rate increased for the 4- and 6-in. reactors, pressure drop became considerable.

As input rate is increased, reactor performance decreases in a linear fashion from 88.9 percent at 100,000 Btu/hr to 58.5 percent for an input rate of 400,000 Btu/hr. The linear decrease in performance (as opposed to an inverse decrease in performance with increasing flow rate) is due to the ability of the reactor to separate smaller particles at higher tangential velocities. As the input rate increases, the gas residence time decreases as the inverse of the input rate. Therefore, since the higher inlet velocities allow the reactor to be operated with a smaller size optimal particle diameter at the higher input rates, there is essentially more relative surface area within the reactor to participate in SO₂ capture. For this reason there is not as much of a dramatic decrease in performance as flow rate is increased. The effect of input rate on optimal particle diameter for an 8-in. diameter reactor is shown in Figure 3.8.

3.3 TASK 3.2 - PROTOTYPE COMPONENT DESIGN

In an effort to simplify NO_x and SO₂ emissions reduction work, two separate initial prototype component test facilities were designed. The purpose of having two separate test facilities was to have as high a degree of flexibility as possible for testing the individual components. For example, while one component in a particular test facility is being modified, testing can continue in the other test facility with no loss of continuity.

3.3.1 NO_x Reduction Test Facility

The first test facility was designed for NO_x reduction work. A schematic diagram of this test facility is shown in Figure 3.9. This test facility consists of the CWS combustor, transition box, heat exchanger, baghouse, and various support equipment and instrumentation. At the heart of the NO_x reduction test facility is the CWS combustor, where NO_x emissions are controlled by operating the unit under staged conditions.

The CWS combustor used in this work is a derivative of the one that was developed by Tecogen Inc. under contract No. DE-AC22-87PC79650. A cutaway

Predicted SO₂ Reduction Reactor Performance
Inlet Concentration: 3,000 ppm (Ca/S = 3:1)
Reactor Height: 50 in Reactor Diameter: 8 in.

TF26-790r

Figure 3.7 Effect of Input Rate on Reactor Performance

Optimal Particle Diameter as a Function of Input

TF27-790

Reactor Height: 50 in.

Inlet Conc.: 3,000 ppm (Ca/S = 3:1)

20 percent excess air

Figure 3.8 Effect of Input Rate on Optimal Particle Diameter

drawing of the combustor is shown in Figure 3.10. The combustor makes use of centrifugal forces, set up by a predominantly tangential flow field, to separate and confine larger unburned particles in the upper chamber. Various partitions are used to retard the downward, axial flow of these particles and thus maximize the residence time of these particles in the hottest section of the furnace.

As the particles burn and their size decreases, radial drag forces overcome the centrifugal forces, and the particles are able to exit the primary chamber. Combustion of these smaller particles is completed in a secondary chamber. Control of NO_x emissions in this combustor is accomplished by staging the combustion air between upper and lower sections of the primary combustion chamber, such that the unit operates in a substoichiometric manner in the upper section of the primary combustion chamber. The combustor was designed such that different inserts could be used to change the height of the upper primary chamber, and thereby change the residence time of the products of combustion in this fuel-rich zone.

The atomizer used in this work is similar in design to the supersonic CWS combustor previously developed at Tecogen Inc. This atomizer was annular in design, with CWS flowing in the central tube while atomizing air flowed in the annular passageway around the CWS tube. The airstream shears the CWS to an unstable ligament sheet which breaks up into droplets external to the atomizer. To aid in the atomization process, the airstream was accelerated to supersonic velocities by means of a converging/diverging section. A photograph of the atomizer operating with oil is shown in Figure 3.11. In order to accurately determine the primary/stoichiometric ratio in the upper primary chamber of the combustor, the atomizing airflow rate and the combustion inlet airflow rate were measured accurately.

3.3.2 SO_2 Reduction Test Facility

A schematic diagram of the SO_2 reduction test facility is shown in Figure 3.12. In order to have more control over the operation of the SO_2 reactor, it was decided to operate the facility with flue gases produced from an oil burner and inject SO_2 as required in order to obtain desired inlet concentrations. Also, since oil burners can operate over a very wide range of input rates, typically from 68,500 to over 400,000 Btu/hr for residential scale burners, they provide a great deal of flexibility in reactor operation.

The SO_2 reduction reactor was designed on the principle of axial recirculation. In a vortical flow field, the pressure at the periphery is greater than that at the centerline. This is shown in Figure 3.13 where normalized curves of pressure difference as a function of radial position are presented. By connecting

Figure 3.10 Cutaway Drawing of CWS-Fired Residential Combustor

TF54-290

Figure 3.11 Atomizer Operating with Oil

Figure 3.12 SO₂ Removal Test Facility

Figure 3.13 Normalized Static Pressure Distributions Inside Axial Recirculation Emissions Control Reactor

one end of a tube tangentially from the periphery at one axial location, and the other end at the centerline, an external axial recirculation flow path is established that operates only on the natural pressure difference present in the vortical flow field without the need of external assistance.

When the principle of axial recirculation is used in a gas/solids system, the residence time of the solids within the reactor can be significantly increased relative to that of the gas. A schematic diagram of both the internal and external particle recirculation paths is shown in Figure 3.14, while a photograph of the external particle recirculation is shown in Figure 3.15.

For the initial prototype reactor components, it was decided to fabricate the reactor from standard stainless-steel pipe in order to facilitate modifications. Two separate reactors were designed, one 6 inches in diameter, the other 8 inches in diameter. Both reactors were designed to be modular so that various length spool pieces could either be added or removed in order to vary the gas residence time.

3.4 TASK 4.1 - INITIAL PROTOTYPE COMPONENT FABRICATION AND ASSEMBLY

During the first year of this program, component fabrication and assembly of both the NO_x and SO_2 test facilities were completed. A photograph of the NO_x test facility is shown in Figure 3.16, and a photograph of the SO_2 reduction test facility is shown in Figure 3.17. In order to construct both test facilities in a cost-effective manner, it was decided to allow both facilities to share certain components. These included the baghouse and the cooling water/dump radiator loop.

3.5 TASK 5 - INITIAL PROTOTYPE COMPONENT TESTING

During the first year of this program, testing began on both the NO_x and SO_2 reduction test facilities.

3.5.1 NO_x Reduction Testing

The CWS combustor was tested under both unstaged and staged conditions. Under both operating conditions, the combustor geometry, specifically the upper primary chamber, was modified to determine the effect of residence time on NO_x emissions. The CWS used during this testing contained 65.16-percent coal by weight, with the parent coal having a mean particle diameter of 14.0 microns. All the properties of the CWS are summarized in Table 3.4.

Figure 3.14 External and Internal Circulation in the Emissions Control Reactor

1227-N

Figure 3.16 Photograph of NO_x Test Facility

Figure 3.17 SO₂ Test Facility

TABLE 3.4
FUEL PROPERTIES

Identification	Upper Elkhorn Number 3 Seam
Heating Value	15,251 Btu/lbm
Ash	1.32 percent (by weight)
Sulfur	0.66 percent (by weight)
Ash Fusion Temperatures Initial Softening Fluid T-250	2150°F 2300°F 2400°F 2509°F
Ultimate Analysis Carbon Hydrogen Nitrogen	85.40 percent 5.40 percent 1.59 percent
Solids Content	65.16%
Mean Particle Size	14 μm
Viscosity at 100 s₋₁	419 cps

a. Unstaged Operation

As part of unstaged testing, NO_x emissions were recorded under various input rates ranging from 113,400 to 181,700 Btu/hr, and for two different primary combustion chamber heights of 3 and 7.69 inches (see Figure 3.10). For these tests, the combustor tangential air inlet height equalled the entire length of the primary chamber. These results are shown in Figure 3.18 as a function of stoichiometric ratio. Preliminary results for unstaged operation have shown NO_x emissions to be fairly insensitive to input rate and primary chamber residence time. Peak NO_x emissions are on the order of 0.78 pound of NO_x per million Btu fired and occurred at just under 40-percent excess air. Operation of the combustor at stoichiometric conditions produced NO_x emissions on the order of 0.285 pound per million Btu fired.

Though primary chamber residence time has little effect on the total amount of NO_x produced during unstaged operation, it was found to have an effect on the amount of NO_x produced in the form of NO_2 . This is shown in Figure 3.19 where the percent of NO_x in the form of NO_2 on a weight basis is plotted as a function of stoichiometric ratio. At lower stoichiometric ratios, the amount of NO_2 produced is low for both chamber heights that were tested; however, as the stoichiometric ratio is increased, the longer chamber (which provides a longer gas residence time) has a higher percentage of total NO_x in the form of NO_2 .

The fact that NO_2 is present in the products of combustion of CWS is quite unexpected when thermochemical equilibrium is considered. As an indication of the amount of NO_x thermochemical equilibrium predicts for the combustion of CWS, Figure 3.20 shows the effect of both temperature and stoichiometric ratio on NO_x production, primarily in the form of NO. Equilibrium analysis predicts that NO_2 is present only in insignificant quantities, i.e., mole fractions of less than 10^{-5} . The fact that NO_2 is present in the products of combustion when equilibrium does not favor its formation is an interesting phenomenon.

One possible explanation for this occurrence is the presence of HO_2 radicals in the flame region. It has been suggested that in the flame region NO molecules are scavenged by HO_2 radicals to form NO_2 and OH. Due to the water present in the CWS, it is expected that there is a higher probability of HO_2 radicals being present, which would contribute to the formation of NO_2 .

Another reason for the presence of NO_2 in the products of combustion can be attributed to the presence of sodium. Sodium has been shown to aid in the formation of NO_2 , and since it is quite possible to have sodium present in the water used in the preparation of the CWS, it may help account for the presence of NO_2 .

Input: 143,700 Btu/hr
L/D (primary) = 0.353

Input: 113,400 Btu/hr
L/D (primary) = 0.353

Input: 134,500 Btu/hr
L/D (primary) = 0.904

Input: 181,700 Btu/hr
L/D (primary) = 0.904

Figure 3.18 NO_x as a Function of Stoichiometric Ratio for Unstaged Operation

Figure 3.19 Weight Percent of Total NO_x in the Form of NO₂ as a Function of Stoichiometric Ratio

Figure 3.20 Thermochemical Equilibrium NO_x Concentration as a Function of Temperature and Stoichiometric Ratio for the Combustion of Coal Water Slurry

b. Staged Operation

Under staged operating conditions, the CWS combustor was tested under two different configurations, shown schematically in Figure 3.21. The geometry of the first configuration, denoted Configuration 1, was the following. The combustor had a diameter of 8.5 in., and the height of the upper primary chamber was 7.69 in. The air inlet to this chamber extended the entire length of the upper primary chamber, and this air, along with that from the CWS atomizer, established the primary/stoichiometric ratio under which the combustor operated. The upper primary chamber was separated from the lower primary chamber by a partition that had an 5.75-in. diameter opening. The secondary air inlet was situated in the lower primary chamber, which was 3.5 in. high. Below the lower primary chamber was the secondary chamber, which was 15 in. high and was separated from the lower primary chamber by a 4-in.-diameter partition.

Combustor Configuration 1 was limited to a minimum primary/stoichiometric air ratio of about 0.6, since at lower airflow rates the tangential velocity in the upper primary chamber was not sufficient to prevent particle agglomeration on the wall. In order to reduce staging even further, the combustor was reconfigured in the following manner, which was denoted Configuration 2. The upper primary chamber was modified such that the upper partition was now 2.5 in. below the combustor head, with the primary air inlet extending the entire 2.5 in. length. Below the upper partition was a spacer section that was 9 in. high. This spacer section separated the upper primary section from the lower primary section and provided additional residence time for the products of combustion in the fuel-rich primary zone as compared to Configuration 1. The height of the lower primary chamber was reduced from 3.5 in. in Configuration 1 to 3 in. in Configuration 2. Beyond these changes, all other geometric relations were kept the same.

Testing of the CWS combustor in Configuration 2 yielded lower NO_x levels than were obtained in Configuration 1. A comparison of the two configurations as a function of primary/stoichiometric ratio is shown in Figure 3.22. In comparing data from Configurations 1 and 2 over the range of primary/stoichiometric ratios tested, Configuration 2 had consistently lower NO_x levels even for identical primary/stoichiometric air ratios. Also, since Configuration 2 was capable of operating at higher primary chamber tangential velocities, it could be operated at lower primary/stoichiometric ratios without agglomerations problems and achieve NO_x levels as low as 0.285 pound of NO_x per million Btu fired.

In comparing combustor Configurations 1 and 2, the main difference is the length of the upper primary chamber, which provides Configuration 2 with a longer

Figure 3.21 Combustor Configurations

Figure 3.22 Comparison Between Combustor Configurations
Configurations 1 and 2

residence time in the fuel-rich zone of the combustor. When NO_x data for Configurations 1 and 2 are plotted as a function of residence time in the primary chamber, it can be seen that the difference between the two configurations diminishes, and residence time becomes the key parameter affecting NO_x emissions over the data range tested to date. These results are shown in Figure 3.23.

As in the case of unstaged operation, NO_2 was found in the products of combustion even though thermochemical equilibrium predicts NO_2 should be present only in insignificant quantities. Figure 3.24 shows NO_2 emissions as a function of primary/stoichiometric ratio for combustor Configurations 1 and 2. Referring to Figure 3.24, NO_2 emissions appear to be a fairly linear function of primary/stoichiometric ratio, increasing as more air is available in the primary zone.

3.5.2 SO_2 Reduction Testing

SO_2 reduction testing began in the last quarter of the first year of this program, and to date has been of a preliminary nature. These tests have been conducted on the 6-in.-nominal diameter which has the following geometry:

Inside Diameter:	6.065 in.
Recirculation Line Diameter:	1.049 in.
Active Reactor Height:	45 in.

The sorbent used in this testing was a standard dolomite variety of lime used for residential lawn applications. This sorbent was approximately 60-percent calcium carbonate, CaCO_3 , and for identification purposes it was denoted Limestone 1. The particle size distribution of this limestone was determined by a sieve analysis, which yielded a mass mean particle diameter of 194 microns. Results of the particle size analysis are shown in Figures 3.25 and 3.26.

The test procedure for the SO_2 reduction reactor was as follows. First, the reactor was allowed to reach thermal steady state. At that point, a metered amount of SO_2 was injected well upstream of the reactor. Upon reaching steady state, a metered amount of limestone was injected at the reactor inlet. Limestone feed would continue until after the reactor had reached steady-state conditions, after which the limestone feed was discontinued, and SO_2 emissions were monitored until after the reactor had again reached steady state conditions. The percent reduction in SO_2 was then determined by using the average value of SO_2 from before the limestone was injected, and well after injection had stopped. During testing, important data were recorded via a microcomputer-based data acquisition system.

Figure 3.23 Comparison Between Combustor Configurations
Configurations 1 and 2

Figure 3.24 Effect of Primary/Stoichiometric Ratio on NO₂ Emissions for Staged Combustion

Figure 3.25 Particle Size Distribution for Limestone 1
(Weight Fraction of Particles Smaller
Than a Given Diameter)

Figure 3.26 Particle Size Distribution for Limestone 1
(Weight Fraction of Particles in a Given Size Range)

Results of a typical test are shown in Figure 3.27, in which SO_2 emissions are plotted as a function of time for an inlet concentration of 2,075 ppm of SO_2 . For this case, the reactor operated with an inlet mass flow rate of around 250 lbm/hr. This is equivalent to a coal combustor operating with 25-percent excess air, at a firing rate of over 200,000 Btu/hr. From Figure 3.27, each reduction in SO_2 refers to a specific Ca/S ratio, which was varied from 1.7 to 5.3:1. For these operating conditions, the percent reduction in SO_2 varied from 42 to 72.5 percent.

A plot of the percent reduction in SO_2 as a function of the Ca/S ratio is shown in Figure 3.28, where the data appears to exhibit an asymptotic behavior. The 72.5-percent reduction is quite good when the large diameter of the limestone is considered. In fact, while operating under these conditions, the reactor performed much better than what the model predicts. This is also shown in Figure 3.28, where the actual reduction in SO_2 achieved is more than twice what the model predicts (solid line). For the model predictions, it was assumed that the limestone had an activation energy of 10,000 cal/gmole and a frequency factor of 335,000 1/sec. These values were representative of data presented for a dolomite in Borgwardt's paper. However, it should be noted that the kinetic constants for several stones tested by Borgwardt differed greatly and that the kinetic constants for our dolomite most likely differ considerably from Borgwardt's data.

Another possible explanation for the large difference in actual performance when compared with the model is due to the effect of the sorbent particle diameter. The model predictions shown in Figure 3.28 are based on the 194-micron particle diameter determined by sieve analysis (solid line). Within the reactor, high tangential velocities can lead to particle erosion, and thus the mean particle diameter within the reactor can be less than what is injected at the reactor inlet. If for example, within the reactor, the mean particle diameter is 40 microns, the model predicts the reactor would achieve a 67-percent reduction in SO_2 , which is fairly close to the actual reduction of 72.5 percent (dashed line).

3.5.3 Particulate Control

In order to meet the particulate emissions objective, a baghouse was used as a final particulate filter. The bag filters used in this system were made of Teflon and glass fibers needled into a woven scrim, known under the trade name of Tefaire. In order to facilitate filter cleaning, a pulse jet system was used. For this system, the bag filters were mounted on cages that are attached to a venturi. A photograph of the venturis and cages are shown in Figure 3.29. A pulse of compressed air, supplied from a delivery tube situated above the venturis induces a flow into the bags, which establishes a traveling wave that removes particulates from the filters.

Figure 3.27 SO₂ Concentration as a Function of Time for Various Ca/S Ratios

Figure 3.28 Effect of Ca/S Ratio on Reactor Performance

Figure 3.29 Venturis and Cages

The baghouse was designed to have two separate chambers within the single baghouse. In this way, the same unit could be used for both the NO_x and SO_2 test facilities.

3.6 TASK 7.1 - PRELIMINARY MANUFACTURING COST ESTIMATE

When the high-volume manufacturing cost of the emissions control system hardware was estimated, the system was broken up into three major subassemblies. These were the sorbent feeder and storage hopper, the SO_2 reactor, and the particulate collector, or baghouse. The cost estimate was performed at two levels of detail. The first and most conservative was to simply cost out the components as discrete items patterned after the laboratory unit, but built in high volume. However, since such a design would go through a detailed value engineering analysis before going into production, a second level of cost refinement was done. In this second instance, it was assumed that except for purchased component assemblies (motors, controls, fittings) the major components would be fabricated and assembled in a high-volume production facility. As such, steel plate would arrive as rolled stock, ready to be cut and formed with in-house presses. Also, all purchased components would be purchased directly from the manufacturer and not through local distributors.

In the preliminary cost analysis, the manufacturing cost of the screw feeder assembly, SO_2 reactor assembly, and baghouse were \$322, \$336, and \$378, respectively. Since the original manufacturers would have already taken a substantial markup (often over 100 percent), it was anticipated that these costs should come down by a factor of two or more.

In the second level of cost refinement, shown in Table 3.5, significant cost reductions were indeed projected. The screw feeder assembly was reduced by 27 percent to \$236. However, the major component cost remains the auger screw and gear motor drive. As such, alternative feed systems such as pneumatic or vibratory may prove to be more cost-effective at this scale.

The SO_2 reactor assembly was reduced by almost 66 percent. Since almost all the components were assumed to be fabricated from sheet stock, this cost reduction was made possible. The baghouse assembly was reduced by almost 44 percent to \$213. Again, this was achieved by in-house fabrication of sheet metal components.

While these costs should still be considered preliminary until detailed component designs have been completed, there remains an additional and potentially significant level of cost reduction. In the previous analyses, the

TABLE 3.5

MANUFACTURING COST ESTIMATE

SO ₂ Emissions Control System	Quantity	Unit Cost	Steel	Purchased Parts	Material Handling	Labor	Overhead	Total
I. SCREW FEEDER ASSEMBLY								
Auger Screw	1	\$60		60.00	6.00			\$ 66.00
A.C. Gearmotor	1	\$55		55.00	5.50			60.50
Motor Controls	1	\$30		30.00	3.00			33.00
Storage Tank, C.S. 18 ga	31 lb	\$0.35/lb	10.85			2.00	4.00	16.85
Structural Support, CS	30 lb	\$0.35/lb	10.50			2.00	4.00	16.50
Miscellaneous Fittings	—			15.00	1.50			16.50
Components Assembly	—					9.00	18.00	27.00
SUBTOTAL								\$236.35
II. SO₂ REACTOR ASSEMBLY								
Main Body, S.S., 16 ga	19 lb	\$1.60/lb	30.40			2.00	4.00	\$ 36.40
Internal Partition, S.S., 16 ga	1 lb	\$1.60/lb	1.60			0.20	0.40	2.20
Top and Bottom Headers, S.S., 16 ga	2 lb	\$1.60/lb	3.20			0.40	0.80	4.40
Recirculation Line, S.S., 16 ga	5 lb	\$1.60/lb	8.00			1.00	2.00	11.00
Inlet Duct, S.S., 16 ga	2 lb	\$1.60/lb	3.20			0.20	0.40	3.80
Exhaust Duct, S.S., 16 ga	2 lb	\$1.60/lb	3.20			0.20	0.40	3.80
Insulation	20 ft ²	\$0.90/ft ²	18.00			1.00	2.00	21.00
Miscellaneous Fittings	—			15.00	1.50			16.50
Components Assembly	—					6.00	12.00	16.00
SUBTOTAL								\$115.10

Base Prices – CR Steel = \$0.35/lb
 304 S.S. = \$1.60/lb

Labor = \$12.00/hr
 Overhead = 200% of Direct Labor

Material Handling = 10% of Purchased Parts

TABLE 3.5 (Continued)
MANUFACTURING COST ESTIMATE

SO ₂ Emissions Control System	Quantity	Unit Cost	Steel	Purchased Parts	Material Handling	Labor	Overhead	Total
III. BAGHOUSE ASSEMBLY								
Bag Filter	4	\$3		12.00	1.20			\$ 13.20
Support Cage, S.S.	4	\$1		4.00	0.40			4.40
Venturi, Plastic	4	\$3		12.00	1.20			13.20
Enclosure, S.S. 22 ga	54 lb	\$1.60/lb	86.40			3.00	6.00	95.40
Insulation	35 ft ²	\$0.50/ft ²	17.50			1.00	2.00	20.50
Inlet Duct, S.S., 16 ga	2 lb	\$1.60/lb	3.20			0.20	0.40	3.80
Exhaust Duct, S.S., 16 ga	2 lb	\$1.60/lb	3.20			0.20	0.40	3.80
Air Manifold, C.S.	6 lb	\$0.35/lb	2.10			2.00	4.00	8.10
Solenoid Valve	1	\$10		10.00	1.00			11.00
Miscellaneous Fittings	—			15.00	1.50			15.50
Components Assembly	—					8.00	16.00	24.00
SUBTOTAL								\$212.90
TOTAL COST								
Screw Feeder								\$236.35
SO ₂ Reactor								98.60
Baghouse								<u>212.90</u>
								\$547.85

components were costed as discrete assemblies. However, in a real system, these assemblies would be engineered to function as an integrated unit, with components serving in dual roles. For example, the baghouse enclosure can also possibly serve as a heat transfer surface between the combustion gas and circulation airstreams. In this way, the original gas-to-air heat exchanger will be much smaller or not necessary at all. Thus, the total system should be more cost-effective. This final cost analysis will be done once the final design has been established and detailed drawings made.

4. SUMMARY STATUS ASSESSMENT AND FORECAST

During the first year of this program, several major project milestones were met. These include the construction of two test facilities for NO_x and SO_2 reduction testing, the development of a model to predict the performance of the SO_2 reduction reactor operating under various conditions, as well as obtaining NO_x and SO_2 reduction data. In addition, preliminary manufacturing cost estimates were obtained so that a system economic analysis can be performed. Test results from the NO_x and SO_2 test facilities have shown that:

- NO_x levels of 0.285 lbm/MMBtu under staged combustion conditions have been achieved. This represents a 65-percent reduction compared to uncontrolled emissions levels.
- Reduction levels in SO_2 have exceeded model predictions.

During the next year of the program, work will continue on lowering NO_x levels to the 0.2 lbm/MMBtu level that is required. This will include altering the combustor geometry further and lowering the temperature in the combustor primary zone. For the SO_2 reactor, extensive testing will be conducted in order to obtain data on the effect of SO_2 concentration, flow rate, particle size distribution, and reactor diameter in an effort to determine the optimum operating conditions for a residential-scale reactor. Upon obtaining the required NO_x and SO_2 levels, the components will be integrated together to form a fully operational CWS furnace system that will be tested extensively. At the point where the baghouse must handle both fly ash and spent sorbent simultaneously, detailed particulate capture testing will be performed.

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