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**CROSS-FLOW,
FILTER-SORBENT
CATALYST FOR
PARTICULATE,
SO₂ AND
NO_x CONTROL**

**Technical Progress
Report**

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1.0 INTRODUCTION

1.1 Background

Emission control systems for small-scale combustors must be designed to provide highly effective removal of three criteria pollutants (particulate matter, SO_2 and NO_x) under a set of operational constraints that are unique to the small-scale application. In residential homes, commercial buildings, and light industrial facilities, the availability of space is limited and there may be no trained, on-site technicians. In this environment, any piece of installed equipment must be safe, reliable, quiet, small, easy to access and maintain, and should produce no waste by-products that cannot be handled by local waste handling systems.

In addition to satisfying these operational requirements, the emission control systems must clean the flue gas down to emission levels that are comparable to those produced by existing (fuel-oil) combustors. Reduction or elimination of respirable particulates, odors, and acid mists will be critical because the stacks of these combustors will be low and located in densely populated areas. The deposition of acid-coated particulates will be particularly noticeable in residential areas because these acid smuts eat away the paint on cars and houses.

For high reliability, safety, compactness and cost effectiveness, the emission control system should have few moving parts, involve a minimum of extra flows or treatment process, have high area to volume ratios and produce no additional waste products. It would be desirable to have particulate matter, SO_2 and NO_x controlled by one device that could be easily serviced on a monthly, quarterly or seasonal basis.

These requirements make dry, regenerative clean-up processes particularly attractive. This synopsis describes a new concept for integrated pollutant control: a cross-flow filter comprised of layered, gas permeable membranes that act as a particulate filter, an SO_2 sorbent, and a NO_x reduction catalyst.

1.2 Description of Single-Unit, Three Pollutant Control Device

The device described in this section will simultaneously remove particulates, SO_2 and NO_x from the combustion gases of coal combustors. The device is configured as a cross-flow filter, as shown in Figure 1.¹ The gas flows from the inlet passages to orthogonally oriented discharge channels via thin, multilayered porous walls. As shown in Figure 1, flue gas enters from both the front and back of the device. With the left wall of the filter sealed, gas discharges from the right side of the device. The key to combined physical (fly ash) and chemical (SO_2/NO_x) cleaning is to utilize chemically active sorbent-catalysts (e.g., metal oxides) in the layered walls of the filter. A cross-flow filter wall with layered construction is shown in Figure 2. This arrangement avoids use of pellet beds that plug in the presence of soot and fly ash and require larger reactor volumes because of low surface/volume ratios. (This concept is currently under evaluation at MIT; a patent application has been filed.)² The top (tight-pore) layer serves as a barrier filter blocking passage of fly ash particles. As the gas flows through the porous

Figure 1. Schematic of a Ceramic Cross-Flow Filter-Sorbent Catalyst

Figure 2. Close-Up of Filter-Sorbent-Catalyst Wall and Gas Flow Scheme

walls, particulate impurities are trapped on the walls of the inlet passage. The second layer of the porous walls carry at least one active sorbent-catalyst material to absorb SO_2 into the porous wall. Once the metal oxide is bound with sulfur-oxides (e.g., CuSO_4), it becomes a catalyst for NO_x reduction. Thus, with the addition of NH_3 into the flue gas stream, the sorbent layer could also serve as a NO_x reduction catalyst. However, in order to effect NO_x reduction throughout the absorption time, a second metal oxide serving as a selective NO_x reduction catalyst, e.g., $\text{CeO}^{2(5,4)}$, will be added in the (second) sorbent layer. If it becomes necessary, a third layer, containing (and protecting) the deNO_x catalyst phase can be provided.

This configuration offers a compact filter (10 times higher surface-to-volume ratio than a typical baghouse), a low-attrition sorbent-catalyst (no moving or fluidized solid bed), low pressure drop (through a few mm-thick macroporous membrane), and a very simple flow scheme.

We estimate that better than 90% removal efficiency of SO_2 and NO_x is achievable with the use of mixed metal oxides (CuO , CeO_2 , or Fe_2O_3) in the device. Also, high sulfur capacity is possible by increasing the metal oxide content of the active SO_2 sorbent phase. Aluminum oxide, Al_2O_3 , is planned to be used as a dispersant and/or catalyst support in the active sorbent-catalyst layer(s). The composite is expected to keep its bifunctional characteristics throughout its operation and not deactivate or lose its structural integrity in the presence of fly ash and trace metals.

Flyash particles trapped by the cross flow structure can be periodically removed by a back-flushing procedure. Pulse-jet backflushing is a well established technique for high pressure applications of the cross-flow filter.¹ This technique may have to be modified for small-scale applications. Modifications may include frequency of back-flush, duration and pressure of each pulse and pressure source for the pulsation. The modifications may be necessary to make the system as simple as possible for small-scale use. The active composition for SO_2 absorption can be renewed by a regeneration procedure that produces either elemental sulfur or concentrated gaseous sulfur species which can be converted to elemental sulfur by well established processes.

The single unit, particle filter, SO_2 sorbent, NO_x reduction catalyst is an ideal device for small-scale applications. It is modular in configuration, compact, without any moving parts, quiet, producing no toxic materials or new solid wastes to be disposed of and requiring little auxiliary power.

1.3 Research and Development Activity

In October 1989, the team of Arthur D. Little, Massachusetts Institute of Technology, and GTE began a three-year, USDOE/PETC (Pittsburgh Energy Technology Center) funded program to research and develop the filter-sorbent-catalyst. The research priorities of this effort are listed below:

- Sorbent-catalyst material development

- Which metal oxide materials provide best combined performance for SO₂ removal, NO_x reduction and sorbent regeneration?
- Under what regeneration conditions is the production of elemental sulfur maximized?
- Active Filter selection
 - What ceramic filter design (thickness, porosity, size, active-phase layering) leads to acceptable pressure drop, particulate matter capture, and structural integrity at expected operating conditions?
 - What backflushing scheme is required?
- System design
 - How will these systems be incorporated into furnaces?
 - What will be the device size, seals, cost, and operating constraints?

2.0 TASK DESCRIPTIONS

A complete description of the program plan is included in this section for current and future reference.

The objective of this program is to successfully carry out the experiment and design tasks described herein that will lead to the development a single-unit, cross flow filter-sorbent-catalyst. We plan to carryout this research and design work in two stages.

The first stage of the work will be fundamental in nature: we will investigate the SO₂ removal and NO_x reduction characteristics of different sorbent-catalyst compositions (in granular form), and we will conduct exploratory tests of cross-flow filters under conditions similar to those found in the combustion gases of small-scale combustors. After a year of these fundamental studies, we will conduct a preliminary evaluation of the component performance and will design two or three prototype configurations.

In the subsequent stage of the program, we will investigate the pollutant control characteristics of prototype filter-sorbent-catalyst devices. The SO₂ removal and NO_x reduction efficiency of a 'unit-element' prototype will be investigated. This 'unit element' will be a slot reactor comprised of two flat porous walls, or 'slabs' of filter-sorbent-catalyst material separated by a 0.5 centimeter gap. The particulate collection efficiency and back-flushing requirements of a multi-element version of this device will be tested.

Concurrent with these efforts will be the investigation of a sorbent regeneration scheme that has the potential to produce elemental sulfur in a one step process. Final evaluation

of component performance and the design of these emissions control devices for residential, commercial, and small industrial applications will be conducted at the conclusion of the project.

Table 1 summarizes the tasks to be performed in this program. These tasks are described in more detail in the following section. A milestone chart is shown in Table 2.

Task 1.0: Test Plan

The first task is to prepare a detailed test plan for this program (Test Plan I). We will hold a kick-off meeting at ADL with MIT and GTE to review program objectives and coordinate our approaches. MIT and ADL will prepare test plans individually and then meet again to coordinate schedules and filter material requirements. Filter materials needed from GTE (individual layers, single channels, multiple channels) will be selected and ordered according to these plans. The test plan will include test matrices, schedule, and research decision trees. The output of this task will be a flow chart of tasks that will be undertaken over the two and one half year program. The test plan will be revised annually (Test Plan II), or as required.

Task 2.1: Component Development - Preparation for SO₂/NO_x Studies

Preparation for SO₂/NO_x control work involves (a) laboratory upgrading and (2) the synthesis and characterization of sorbent/catalyst compositions to be tested in Task 2.2.

Laboratory Preparation Activities Include:

- Order gases, regulators, tubing, fittings
- Shakedown reactor and gas chromatograph equipment
- Calibrate and refurbish chemiluminescence/IR detectors for NO_x, NH₃ analysis

Sorbent-Catalyst Synthesis

Eight to ten different sorbent compositions will be prepared in granular form (-20 +35 mesh) from pyrolysis-calcination of citrate complexes of the metal salts (e.g., nitrates) in desired proportions.

In this work, the single oxides CuO and CeO₂, binary oxides Cu-Al-O and Ce-Al-O, and ternary oxides, Cu-Ce-Al-O, will be prepared with relatively high surface area (10-50 m²/g) and large pore volume (0.7 - 1.5 cm³/g). The single oxides will be used as "control" composition in comparative experiments. The physical parameters of the proposed sorbent-catalysts are chosen such that pore diffusion limitations and pore plugging are suppressed or completely eliminated. Thus, rapid reaction rates and high sorbent utilization are possible. The most suitable combination of chemical composition and physical properties of the mixed oxide materials will be determined after screening tests (first of sulfation and subsequently NO_x reduction).

Table 1
Summary of Tasks

Task #	Description	Lead Contractor	Schedules
1	Test Plan	ADL	Oct. 1989 - Dec. 1989
2	Component Development		
2.1	Preparation for SO ₂ /NO _x Studies	MIT	Oct. 1989 - Oct. 1990
2.2	SO ₂ /NO _x Screening Tests	MIT	Oct. 1989 - Sept. 1990
2.3	Particulate Tests	ADL	Jan. 1990 - June 1990
2.4	Regeneration Studies	MIT	Aug. 1990 - Aug. 1991
3	Prototype Tests		
3.1	Filter Fabrication	GTE	Jan. 1991 - Mar. 1991
3.2	SO ₂ /NO _x Tests	MIT	Apr. 1990 - Mar. 1991
3.3	Particulate Tests	ADL	Sept. 1991 - April 1992
4	Evaluation and Design	ADL	Aug. 1990 - Nov. 1990 and Nov. 1991 - March 1992
5	Management and Reports	ADL	Oct. 1989 - Oct. 1992

Table 2

Program Schedule and Milestone Plan

Milestones

- △ Test Plan Complete
- △ Topical Report Particulate/SO₂/NO_x Control
- △ Revised Test Plan for Prototype Development
- △ Topical Report: Regeneration Studies
- △ Program Review/Tech. Feasibility/Preliminary Design Guidelines/Measures of Success
- △ Technical Feasibility Evaluation Complete
- △ Design Complete
- ① Draft Report
- △ Final Report

Sorbent-Catalyst Characterization

Detailed sorbent-catalyst characterization will be performed on fresh, sulfated and regenerated samples using the following techniques:

- (i) BET, N_2 desorption porosimetry, and mercury porosimetry for surface area, pore volume and pore size distribution determination. This analysis will be conducted for all compositions prepared.
- (ii) X-ray Diffraction (XRD) for crystalline phase and low-angle XRD for crystallite size identification. This analysis will be conducted on selected (3-10) fresh binary and ternary oxides, and as necessary for reacted sorbent samples.
- (iii) Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Analysis (EDS) for surface morphology and spatial variations of elemental composition examinations. This analysis will be conducted on selected fresh and reacted sorbents as necessary.
- (iv) Atomic Absorption (AA) analysis or X-ray fluorescence spectroscopy for elemental composition determinations. This analysis will be conducted for selected sorbent composition as necessary.

Task 2.2: Component Development - SO_2 Absorption and NO_x Reduction Screening Tests

The sorbent-catalysts prepared in Task 2.1 will be screened for their ability to absorb SO_2 and selectively reduce NO_x to N_2 selectively with ammonia. Screening tests will be performed in a lab scale fixed bed reactor. These tests involve characterizing the following performance of the sorbent catalyst materials:

- a. SO_2 removal efficiency, pollutant breakthrough profiles, regeneration products (specifically elemental sulfur) and cyclic performance of sorbents.
- b. Catalytic activity and selectivity of selected mixed oxide sorbents for NO_x reduction by NH_3 and the effects of SO_2 and cycling on the catalyst properties.

The latter screening tests will take place after a period of approximately six months. Screening will be first for SO_2 removal and subsequently for NO_x reduction. So, if SO_2 removal efficiency of a particular sorbent is poor, the sorbent material will not be tested for NO_x reduction effectiveness.

More detailed laboratory-scale evaluation of the activity and regenerability of 3 to 5 Cu-Ce-Al-O selected sorbent-catalyst compositions will be performed in a series of 3-5 consecutive cycles of SO_2/NO_x removal-sorbent regeneration in a packed-bed microreactor. The reactor will consist of a quartz tube of 1.5 cm I.D. vertically mounted inside an electric furnace equipped with a temperature controller. The sorbent-catalyst granules will be supported on a fritted quartz disc in the middle in the reactor tube. A K-type thermocouple moving inside a quartz thermowell (0.3 cm I.D.) concentric to the reactor

will be used to monitor the axial bed temperature. The reactor pressure will be slightly above atmospheric. Premixed gas streams of typical flue gas compositions will flow through the reactor in the upward (sulfation- NO_x reduction) or downward (regeneration) direction. Water vapor will be introduced into the feed stream by nitrogen bubbling through a water vaporizer held at constant temperature. The reactor system is shown schematically in Figure 3.

To facilitate comparison of reactivity and utilization of the various sorbent-catalyst compositions, the screening experiments will be performed under the same selected sets of the operation parameters, as follows:

SO_2/NO_x Removal: $T = 300^\circ\text{C}$ and 400°C , Gas Composition (molar): O_2 (3%),

SO_2 (0.15%), NO (0.06%), NH_3 (0.06%), H_2O (3%), balance N_2 .

Comparison tests with gases containing CO_2 will be conducted to evaluate the effect (if any) that CO_2 has on sorbent sulfation.

A volumetric hourly space velocity in the range of $2000\text{--}5000\text{ h}^{-1}$ (STP) will be used in these experiments. Sorbent regeneration will be conducted with $\text{CO-CO}_2\text{-N}_2$ mixtures at 400 or 500°C .

Product gases will be analyzed for SO_2 (during sulfation) and SO_2 and other sulfur compounds, e.g., COS , CS_2 (during regeneration) by a Hewlett-Packard 5880A gas chromatograph equipped with flame photometric and thermal conductivity detectors. NH_3 and NO will be analyzed by continuous non-dispersive infrared (NDIR) and chemiluminescence analyzers. Any elemental sulfur produced in regeneration will be condensed in an ice-cooled trap installed downstream of the reactor. The amount of elemental sulfur collected in the trap will be determined iodometrically by a standard technique.

Task 2.3: Component Development - Particulate Matter Collection

The purpose of this task is to investigate the performance of a cross-flow filter under the conditions expected in small scale combustors. These conditions are approximately 400°C and atmospheric pressure. In residential systems, the particulate loading is expected to be about 2600 ppm. This is assuming a coal with 2% ash and a burnout of 98%. In larger systems, it is expected that the burnout of the coal will be greater (approx. 99%), and the particulate loading will be 2000 ppm.

The critical issues to resolve are:

How fully can the filter be loaded before the pressure drop increases beyond acceptable levels?

How does filter configuration or orientation affect acceptable loadings?

Figure 3. Schematic of Packed-Bed Microreactor System

How does build-up of particles in the filter affect pressure drop and capture efficiency?

How frequently must the filter be backflushed or serviced?

Subtask 2.3.1--Characterize Exhaust Particulate of DOE Small Scale Combustors

The first task is to determine the flue gas characteristics of the small-scale coal combustors which are currently being developed by the Department of Energy and private industry. The particulate matter loadings and size distributions may vary widely from combustor to combustor depending on the combustion efficiency, the form of coal used (dry or CWS) and the atomization characteristics of the injection system. The particulate matter loading (determined by the combustor efficiency and the coal ash content) and the fraction of particles less than 1 micron are particularly important to ascertain. Though the target fuels and combustion efficiency of these combustors were set forward in the DOE PRDA, their actual performance may be significantly different.

We will contact the principal investigators of the PETC small-scale combustor development program to obtain as much information as possible from the combustor developers themselves. The information we will request will include particulate loadings and particulate size distributions. If they have not conducted this type of analysis, we will request samples of their exhaust particulate (e.g. from Baghouses attached to their laboratory set-up). We will analyze the particulate in an SEM to determine overall particulate size and morphology. For a more detailed determination of the particle size distribution, we will suspend the particulate matter in water and determine the PSD from a Malvern laser diffraction size analyzer or a Coulter counter.

If there is no information about the furnace or boiler flyash, and if the characteristics of the particulate matter have been significantly altered by the laboratory collection device (e.g. a wet scrubber), we will estimate the properties of the fly ash particles from known parameters (size distribution of the raw coal, combustor efficiency, nozzle type, etc.)

Subtask 2.3.2--Obtain, Fabricate Ash for Cross Flow Filter Tests

Ideally, we would utilize the flyash from the combustors being developed to test the particulate control system. As part of the survey of ongoing work described above, we will attempt to obtain exhaust particulate material from the companies who are developing small scale combustors. If large enough quantities of the particulate are available, we will certainly utilize this resource for the cross-flow filter tests. If such samples are not available, we will have to 'fabricate' ash of the correct characteristics.

We will 'fabricate' ash by one of the following means:

Obtain coal ash from other sources (MIT combustion research facility, DOE "fly-ash bank", UND, etc.) and sieve or grind ash to the appropriate size distribution.

Use sand, or glass beads of the appropriate size distribution.

Subtask 2.3.3--Design, Fabricate Cross-Flow Filter for Particulate Tests

A cross-flow filter will be designed and fabricated by GTE for particulate collection tests. The filter geometry will be designed to be compatible with (1) the conditions in a future small-scale coal-fired furnace; (2) the test rig set-up at ADL; and (3) existing manufacturing methods at GTE. This filter may be a single or a few channels of a filter that would ultimately contain hundreds of channels. We will fabricate filters with a single porosity and filters with a thin low porosity layer on each side of a high porosity layer that acts as a barrier to prevent ultra fine particulates from becoming imbedded in the filter itself.

Subtask 2.3.4--Test Cross-Flow Filter

The particulate matter control tests conducted in the first year will be exploratory in nature and will involve the testing of ceramic cross-flow filters of varying configurations. These filters will be tested in the flow bench shown in Figure 4. Solids will be introduced into the gas stream via a fluidized bed feeder, or a "Wright" particle feed system. The gases down stream of the filter will be refiltered through a glass fiber filter. Pressure drop across the filter will be monitored continuously. A particle capture efficiency will be calculated. The particulate material collected will be examined in a PSD analyzer (Malvern, Coulter Counter) or a scanning electron microscope to determine the size of the particulates captured. After a large number of filtering and cleaning cycles, the cross-flow filter will be sectioned to determine the migration of small particles into the porous membranes. The sectioning will not be done on a regular basis since it will destroy the filter.

The test matrix will include as parameters cross-flow filter porosity and thickness, filter face velocity and backflow frequency. Particle loadings will depend on those found in actual small scale coal combustors, but will be roughly 2000 - 3000 ppm.

Task 2.4: Component Development - Sorbent Regeneration Studies

Two types of tests will be performed to evaluate the regenerability of the most promising sorbent-compositions prepared in Task 2.1 and screened in Task 2.2. The regeneration experiments will be conducted on 2-3 sorbent compositions and will include: (1) parametric studies in a packed bed microreactor and (2) kinetic and product selectivity studies in a thermo gravimetric analyzer (TGA). The sulfated sorbents will be regenerated with a reducing gas mixture such as CO-N₂ (including small amounts of CO₂ to prevent CO disproportionation). The TGA studies will be carried out in an existing Cahn 113-X apparatus in our laboratory equipped with a Micricon temperature controller and a Bascom-Turner data acquisition system. Two to three compositions will be tested two to three times each.

The regeneration temperature will be varied in the range of 300-600°C. Two levels of CO concentration will be tested. A total of 30-50 tests will be conducted in both the micro-reactor and the TGA.

Figure 4. Schematic of Bench-Scale Filter Test System

Product gases from the microreactor, after condensation (to remove any elemental sulfur formed), will be analyzed by the gas chromatograph. Effluent gases from the TGA will be analyzed directly by gas chromatography. In this case, due to the small sample size only minute amounts of elemental sulfur will be produced and captured in a glass wool plug in the exhaust gas line. A 10-port gas sampling valve will be used to store gas samples from the initial few minutes of regeneration when gas composition changes rapidly. These samples will be injected into the gas chromatograph after completion of the reaction.

The microreactor and TGA tests will provide an overview of the regenerability of 2-3 sorbent materials. The one or two most promising of these compositions will be studied in greater detail in both reactor systems. The operating conditions (temperature, gas composition) of regeneration that maximize the selectivity to elemental sulfur will be determined. This information will be used to propose practical regeneration schemes (potentially including a recycle) that will eliminate the current need for downstream processing of the regeneration off-gas.

Task 3.1: Unit Element Prototype Tests - Preparation and Cyclic Testing of Active Layers for SO₂ Absorption-Regeneration and NO_x Reduction

In this task, porous ceramic membranes carrying the selected sorbent-catalyst phases from Tasks 2.1 and 2.2 will be prepared and tested for combined SO₂/NO_x removal and regenerability at the operating conditions specified in Tasks 2.1 and 2.2. One to three compositions will be tested, depending upon the results of Task 2.1 and 2.2.

Single layers of an alumina cross-flow monolith, such as the one shown in Figure 1, will be provided by GTE. Each layer will be a flat slab, approximately 6" x 4". The thickness of the slabs will be in the range of 1-4 mm. A slot reactor will be constructed for 2 slabs parallel to each other at a distance of 0.4 - 0.5 cm. Thus, the volume of this single element will be approximately 6" x 4" x 0.5".

The approach we plan to follow for coating the porous membranes with the active sorbent-catalyst is twofold. Firstly, we can use incipient wetness impregnation to load a desired solution of the sorbent-catalyst material into the pores of the alumina or Cordierite membranes, followed by drying and calcining in air at a temperature of 500-700°C. This process can be repeated a few times up to a metal oxide loading of about 30 wt%. Secondly, and more importantly, we plan to coat the membranes with the viscous, partially dehydrated citrate complex of the metal salts. Complete drying, and pyrolysis-calcination will then produce a thick macroporous layer of the active mixed-oxide onto the alumina membrane. This approach can lead to much higher loadings (75-80 wt%), thus, to higher sorbent capacity.

After preparation and characterization, the slabs will be tested in a cross-flow slot reactor arrangement with gas inlet and discharge suitably manifolded so that the gas will enter through one side of the slot and exit from the flat membrane sides, and then taken

for on-line analysis of SO_2 , NO_x and NH_3 by the gas chromatograph and chemiluminescence analyzers. This cross-flow prototype will be extensively tested in cyclic operation (15-20 cycles) at fixed operating conditions (temperature and gas composition).

Task 3.2: Unit Element Prototype Tests - Particulate Collection Performance

A cross-flow filter, coated with sorbent-catalyst material, will be tested in the same test set-up described in Task 2.3.4. GTE will provide MIT with a 6"x 4" alumina or Cordierite layers to be coated with active phases (configured as determined in Task 3.1). GTE will work with MIT and ADL to fabricate these active layers into a multi-element cross-flow filter.

ADL will investigate the pressure drop across the device, the required backflushing frequency, any elutriation of the particles that occurs, the migration of particles into the porous sorbent layer and the mechanical integrity of the layered surfaces. The test conditions and set-up for this task will have been established in Task 2.3.4. The importance of this task, and the difference between it and Task 2.3.4 is that we will be testing a complete cross-flow filter-sorbent-catalyst system instead of a cross-flow filter alone.

ADL will also conduct one test of the active filter with SO_2 , NO_x , NH_3 and particulate matter in a simulated flue gas. The test will not include regeneration.

Task 4: Evaluate System Performance Design Conceptual Systems for Small-Scale Combustors

This task will be performed in two stages. Preliminary performance evaluation will be conducted at the end of the first year of research. At this point, we will review the results of the research work and evaluate how the new information affects the design of the filter-sorbent catalyst device (size, configuration, operating conditions, pressure drop, etc.). At this time, we will also update our knowledge of the small-scale furnace designs and the constraints that these designs put on emissions control designs. We will assess the technical feasibility of the concept and develop preliminary design guidelines for the device. These design guidelines will lead to the specifications for the unit element prototypes prepared for Task 3 testing.

The evaluation and design task will be put on hold until November 1991, after some unit element prototype tests have been conducted. The second phase of evaluation and design will begin at this point. The questions which need to be answered with respect to system design are:

What is the optimal flow velocity through the filter, balancing pressure drop, sulfur capture, NO_x control and space constraints?

What is the most suitable combination of chemical composition and physical properties of the sorbent-catalyst material which will provide an acceptable balance between capture effectiveness, regenerability and high structural stability in extended cyclic operation?

What is the optimal sorbent membrane thickness and porosity for these applications?

What are the requirements of the backflush system (frequency, duration, and pressure)?

How does cross-flow filter configuration affect backflush requirements?

We will answer these questions by thoroughly investigating the design constraints of small-scale coal fired furnaces, and by analyzing the results of Task 3 with respect to these constraints. We will review the state of small scale furnace development by contacting the PETC contractors who are working on these furnaces, and the PETC program managers overseeing these projects. The information we will attempt to obtain includes the following:

- An update of uncontrolled emissions from these combustors
- Allowable pressure drop through the furnace (blower power)
- Actual flow rates and cycle patterns of the furnace (furnace efficiency, excess air, heat-up, cool-down time)
- Furnace configuration and combustion gas temperature profile throughout the furnace.

With information about the furnaces and about the performance of the filter-sorbent-catalyst, we can develop design specifications for the emissions control device.

Once we have developed design specifications, we can design the device for residential, commercial and light industrial applications. The critical issue to be examined in this task is the integration of the emission control system into furnace design. The control system will probably be located before the final heat-exchanger pass in the furnace. Ease of access, removal and installation of the devices is critical for acceptable operation of the system. The design issues to be investigated and/or resolved are listed below:

Size

The size of the filter-sorbent-catalyst device will depend on the tradeoff between regeneration cycle time and pollutant capacity. The longer the period between regeneration cycles, the more capacity it has to have. Long periods between regeneration cycles are desirable from both a convenience and an economic standpoint, but the device cannot be so large as to become difficult to service or fit in the furnace.

Seals

There are a number of seals that will be important for the incorporation of the device in a residential or commercial furnace. The device will have to be sealed where it attaches to the furnace, where the gases exit the device and where the device is flanged. We will take advantage of the advances that GTE has made in flange and seal design for these cross-flow filters, by working with them on this design aspect.

Backflushing

We will explore backflushing options, including utilizing the furnace blower, using an auxiliary air or nitrogen source, or sizing the device such that collected particulate matter flush occurs on the same cycle as regeneration. Again, we will utilize the expertise of GTE who has done considerable work in the area of backflushing of their filters in high temperature, high pressure applications.

Regeneration Cycle

Design of on-site regeneration for industrial sized furnaces will require consideration of heat exchange for the regeneration gases, the most economic source of these gases, flow scheme, valving, down stream processing requirements (if necessary) and cost.

Integration with the Furnace

This is the most challenging design task; we will integrate the design of the filter-sorbent-catalyst package into the designs of small-scale coal-fired furnaces. We will attempt to design the system in such a way that the impact on the furnace design is kept to a minimum. We will work with the furnace developers, if necessary, to determine the best placement of these units in the furnaces.

Costs

We will make preliminary estimates of cross-flow filter-sorbent-catalyst capital and operating costs.

Task 5: Management and Reports

In this task we will set-up and implement the reporting, meeting and management systems to ensure a well coordinated, documented and successful program.

Bi-weekly meetings will be held between MIT and ADL project managers. MIT will submit summary technical progress reports to ADL on a monthly basis and will prepare topical reports, as required, covering each completed task. Formal project reviews at PETC between the contractors, ADL and MIT, and PETC will be held at the critical Milestone Schedule decision and information points, at the start of the project and at the end of the project. We will also attend contractor review meetings to share our results with contractors investigating similar issues. A.D. Little will submit to PETC the reports listed in the reports requirements checklist. Weekly test reports will be submitted during testing periods.

3.0 OBJECTIVES FOR FIRST QUARTER ACTIVITY

The objectives of the October-December 1989 period were to:

1. Prepare the MIT laboratory for sorbent preparation, characterization and screening tests.

2. Initiate work on sorbent preparation, characterization and screening.

4.0 APPROACH

4.1 Selection of Active-Phase Composition for Combined SO₂/NO_x Removal

Dry, regenerative flue gas cleanup processes, such as the Shell/UOP,^{7,8} Fluidized-Bed Cooper (DOE/PETC),^{9,13} and the Moving-Bed Copper Oxide (Rockwell International,¹⁴ use alumina-supported copper oxide, CuO, as a regenerable SO₂ sorbent. The choice of CuO is based on earlier screening studies of metal oxides¹⁵⁻¹⁸ for flue gas desulfurization at temperatures below 600°C. Additionally, CuO and, more so, its sulfate, CuSO₄, catalyze the reduction of nitrogen oxides by ammonia.

Another reactive SO₂ sorbent is cerium dioxide, CeO₂.¹⁶ In early work by Longo,¹⁹ both supported and bulk (unsupported) cerium dioxide was studied. Good regenerability was reported. More recent work at DOE/PETC^{20,21} has focused on alumina-supported CeO₂, which was found to convert fully to the sulfate.

Selective catalytic reduction (SCR) of NO_x using supported metal oxide catalysts has been commercialized by several U.S. and overseas companies.²²

Among those, V₂O₅ supported on titanium dioxide has prevalence. Cerium dioxide has also been tested as an SCR catalyst. In 1980, Mitsubishi patented a catalyst consisting of ≤ 5% CeO₂ on a support of Al₂O₃ and SnO₂.³ The support was soaked in Ce(NO₃)₃ and calcined at 800°C for 100 hours. A removal of 96% of NO_x was obtained at 570°C. This indicates that CeO₂ is an effective NO_x reduction catalyst.

There are three patents that pertain to the use of CeO₂ in simultaneously removing SO_x and NO_x.⁴⁻⁶ Ginger (1981)⁴ contacted a gaseous mixture containing NO_x, SO_x, oxygen and ammonia with a solid containing copper and cerium on an alumina support. The ammonia was in a 0.5:1 to 2.5:1 mole ratio with the NO_x content of the gaseous mixture. The temperature of the reaction as well as the regeneration of the acceptor was 350°C to 450°C. Regeneration was carried out with a mixture of H₂ and 50-90% steam. The acceptor was formed by impregnating alumina with copper nitrate trihydrate and ceric ammonium nitrate then calcining at 535°C for 1 hour. A 94% NO_x removal was achieved and 85% of the SO_x was removed as averaged over 8 regeneration cycles.

Recent work in this laboratory²³ with CeO₂ has shown it to be a very efficient and regenerable SO₂ sorbent. Similarly active was a mixed oxide sorbent, CuO-CeO₂ on alumina.²³ Regeneration of sulfated CeO₂ with CO/N₂ produced mainly COS and, to a lesser extent, SO₂ in the off-gas. Mixtures of sulfated CuO-CeO₂ also showed high selectivity for COS production.

The mixed oxide CuO-CeO₂ system has not been adequately studied as either a sulfation sorbent or an SCR catalyst. It has been chosen for the combined SO₂/NO_x removal studies of this project based on the information of the patent literature⁴⁻⁶ and the promising results from the preliminary runs of sulfation/regeneration with supported CuO-CeO₂.

recently obtained at MIT.²³ In this project, the potential of using the sorbents in bulk form will also be considered. In addition, detailed studies of the selectivity of the regeneration reactions with CO/N₂ streams will be carried out with selected CuO-CeO₂ sorbents.

4.2 Sorbent Preparation/Screening Test Plan

The test matrix shown in Table 3 covers the first six months of sorbent screening activity. In these tests, SO₂ capture and NO_x reduction effectiveness will be measured independently. A total of 10 sorbent compositions will be prepared, analyzed and screened for removal efficiency, sulfur capacity, and regenerability (2-3 cycles). On the basis of these tests, 3-5 sorbent compositions will be selected for NO_x reduction tests.

Table 3. Sorbent Screening Test Matrix

Sorbent Composition	Preparation* Conditions	Characterization** Methods	Screening Tests	
(mol %)	Calcination (°C, h)		Sulfation* (°C)	Regeneration # (°C)
CuO (100)	500, 3	BET, Hg, XRD	400	500
CeO ₂ (100)	500, 800, 3	BET, Hg, XRD	400, 500	500
CuO-Al ₂ O ₃ (50-50; 80-20; 20-80)	500, 3	BET, Hg, XRD	400	500
CeO ₂ -Al ₂ O ₃ (50-50; 20-80)	500, 3	BET, Hg, XRD	400, 500	500
CuO-CeO ₂ (50-50; 80-20)	500, 3	BET, Hg, XRD, SEM	300, 400	500
CuO-CeO ₂ -Al ₂ O ₃ (33-33-34; 31-14-55; 62-13-25)	500, 3	BET, Hg, XRD, SEM	300, 400	500

* Bulk mixed oxide preparation by amorphous citrate complexation of nitrate salts 24,25; calcination is preceded by pyrolysis in air at 450°C for 1/2 hr.

** All sorbents in -20 to + 35 mesh granules.

+ Sulfation with O₂ (3 mol %) - SO₂ (0.15-0.3%) - N₂ (bal.)

Regeneration with 10% CO-N₂ mixture.

4.3 Procedures for Preparing Sorbents

The mixed metal oxide sorbents tested in this program will be prepared according to the well established amorphous-citrate technique.^{24,25} This involves rapid dehydration (under vacuum, at 70°C) of an aqueous solution containing the metal salts and citric acid in desired proportions, followed by pyrolysis and further calcination of the resulting amorphous solid foam at relatively low temperatures (500-650°C). Citric acid is added

in a 1 to 1 mole ratio to the metal salts included in the solution. In the MIT program, the nitrate form of metal salts will be used. Homogeneous, highly dispersed mixed oxides or oxide solid solutions are, thus, formed. These materials can be made with larger average pore size than is generally the case in coprecipitated mixed oxides. This is an important feature in gas-solid reactions where a higher molecular volume product (e.g., sulfate) can cause pore mouth blocking. Also, for the application intended here, large pores are needed to allow free gas flow (low pressure drop).

Eight to ten different sorbent compositions will be prepared in granular form (-20 +35 mesh) from pyrolysis-calcination of citrate complexes of the metal salts (e.g., nitrates) in desired proportions.

In this work, the single oxides CuO and CeO₂, binary oxides Cu-Al-O, Ce-Al-O and Cu-Ce-O, and ternary oxides, Cu-Ce-Al-O, will be prepared with relatively high surface area (10-50 m²/g) and large pore volume (0.7 - 1.5 cm³/g). The single oxides will be used as "control" compositions in comparative experiments. The physical parameters of the proposed sorbent-catalysts are chosen such that pore diffusion limitations and pore plugging as well as product layer diffusion limitations are suppressed or completely eliminated. In other words, by providing the mixed oxide sorbents with both high dispersion (small grain size) and high macro-porosity, rapid overall reaction rates and high sorbent utilization are expected.

4.4 Procedures for Characterizing Sorbents

The surface and bulk solid analyses will be performed by the characterization techniques described in Section 2 under Task 2.1.

4.5 Procedures for Screening Sorbents

The sorbent screening procedures to be followed in the project were discussed in Section 2 under Task 2.2.

5.0 LABORATORY PREPARATION ACTIVITIES

Various activities were undertaken this quarter to prepare the MIT laboratory for the program.

- The packed-bed microreactor and associated gas manifold, flowmeters, etc. were overhauled and calibrated as appropriate.
- The gas chromatograph equipped with Flame Photometric Detector (FPD) and Thermal Conductivity Detector (TCD) for COS, CS₂ and SO₂ gas detection was completely recalibrated.
- Gas cylinders and regulators were ordered and received for SO₂ capture and sorbent regeneration tests.

6.0 TEST RESULTS AND DISCUSSION

The tables below summarize the sorbents prepared, characterized, and tested this quarter.

Table 4. Preparation and Characterization of SO₂ Sorbents*

Sorbent	Composition (mol)	Composition (wt %)	Surface Area (m ² /g)
CuO (B1)#	CuO	100% CuO	1.01
CeO ₂ (B1)	CeO ₂	100% CeO ₂	21.0
CeO ₂ (B2)	CeO ₂	100% CeO ₂	24.5

* Prepared by the amorphous citrate technique. Pyrolyzed in air at 450°C for 30 min; calcined in air at 500°C for 3 hr; granule size: 20-35 mesh.

B indicates batch number; see also Table 3.

Table 5. Sulfation Reactivities of Sorbents

Sorbent	T sulf (°C)	S. V. (h ⁻¹)	Breakthrough (t/t*)#		
			1st	2nd	3rd cycle
CuO (B1)	400	4,800	0.0 ^a		
CeO ₂ (B1)	400	1,700	0.03 ^b		
CeO ₂ (B2)	400	2,000	0.03 ^b		
			0.08 ^a		

Gas composition:

a. 10% O₂ - 0.15% SO₂ - N₂ balance.

b. 3% O₂ - 0.15% SO₂ - N₂ balance

Theoretical breakthrough time, t*, was calculated by assuming the final stoichiometries of sulfates as: CuSO₄ and Ce₂(SO₄)₃. Breakthrough time is for 90% SO₂ removal or 150 ppmv SO₂.

The single unsupported oxides of copper and cerium showed little sulfation reactivity. The SO₂ removal efficiency of 90%, corresponding to an exit SO₂ level of 150 ppmv, was attained by cerium oxide, but after a sorbent conversion (t/t*) of only 3-8%, while for CuO immediate breakthrough took place. As shown in Table 5, these results were for a sulfation temperature of 400°C, where CuO is known to sulfate readily, while CeO₂ reacts much less, but still appreciably.

The bulk CuO used here has a very low surface area (Table 4), which may explain the observed lack of reactivity. Visually, the sample appeared highly agglomerated, even though a relatively low calcination temperature (500°C) was used for its preparation. The results from the tests of bulk CeO₂ are more surprising, because both batches (B1 and B2) of the sorbent were prepared with a surface area of 21 and 24.5 m²/g, respectively (Table 4). Also, in preliminary testing the CeO₂ (B1) sorbent²³ had shown better reactivity, namely a 16-17% conversion at breakthrough of 300 ppm SO₂, when run at identical conditions as in Table 5, except with 3000 ppmv SO₂ in the reactant gas.

Further work with the bulk, uncombined sorbents is currently underway. Physical characterization and XRD analysis of the solids will be performed to aid the reaction studies. However, the main emphasis of the project is on binary and ternary metal oxide systems, which can be prepared in dispersed form, thus, enhancing reaction rates. The uncombined single oxide sorbents are of interest only as baseline systems of this work.

7.0 PLANS FOR NEXT QUARTER

7.1 Sorbent Work

During the next reporting period, the binary and ternary Cu-Ce-Al-O sorbent systems shown in Table 3 will be prepared fully characterized and tested at the conditions specified in Task 2.2. Several of the sulfated and regenerated materials will be examined by XRD and SEM/EDS to identify crystalline phases and grain size and morphology changes that will aid in evaluation of the most promising sorbent compositions. Three to five sorbents will be tested in cyclic operation for further performance evaluation. The most promising compositions will be selected for the next phase of testing as deNO_x catalysts.

7.2 Filter Work

Next quarter we will begin the filter development work with the following activities:

- Obtain and characterize particulate matter from small-scale combustor exhaust
- Prepare detailed test plan for filter studies
- Obtain filter samples from GTE
- Meet at GTE to discuss standard and active filter preparation techniques
- Design filter test apparatus
- Investigate particle feed methods

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