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Arthur D Little

Advanced Byproduct Recovery:

Direct Catalytic Reduction of Sulfur Dioxide to Elemental Sulfur

Third Quarterly
Technical Progress Report

DOE/PC/95252--T2

Report to
Department of Energy
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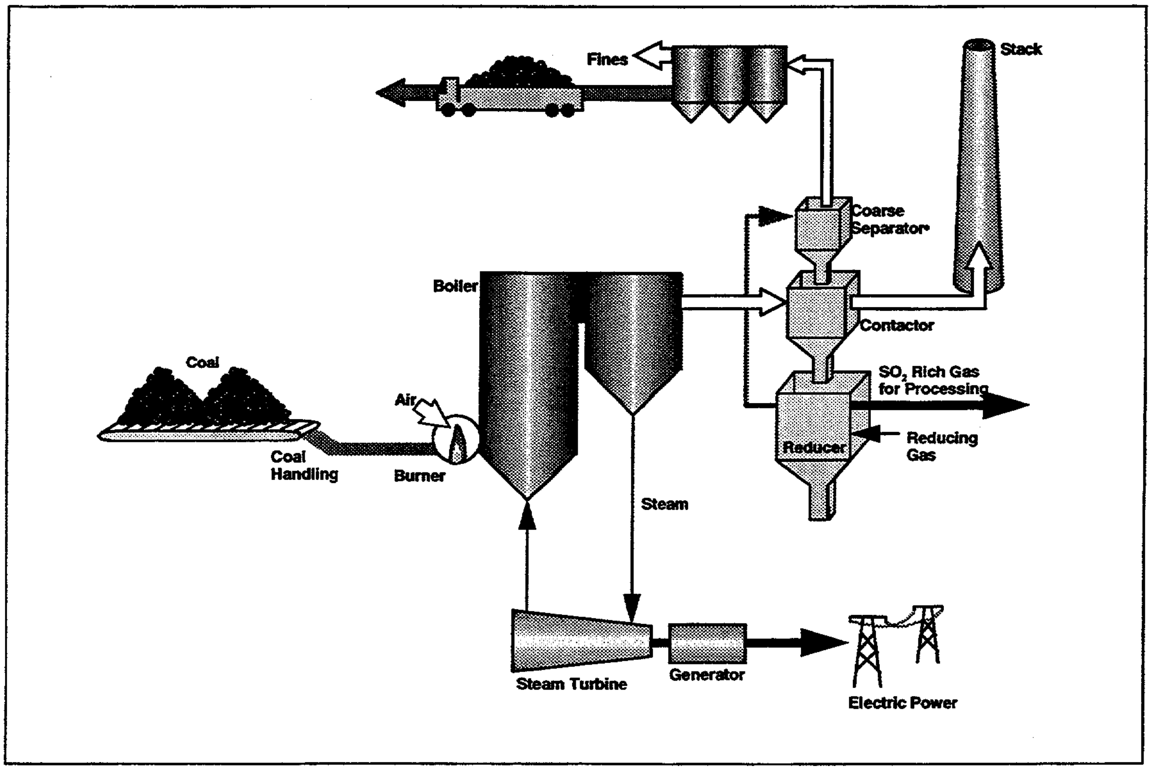
1. Introduction

1.1 Background

More than 170 wet scrubber systems applied, to 72,000 MW of U.S., coal-fired, utility boilers are in operation or under construction[1]. In these systems, the sulfur dioxide removed from the boiler flue gas is permanently bound to a sorbent material, such as lime or limestone. The sulfated sorbent must be disposed of as a waste product or, in some cases, sold as a byproduct (e.g. gypsum). Due to the abundance and low cost of naturally occurring gypsum, and the costs associated with producing an industrial quality product, less than 7% of these scrubbers are configured to produce useable gypsum[2] (and only 1% of all units actually sell the byproduct). The disposal of solid waste from each of these scrubbers requires a landfill area of approximately 200 to 400 acres. In the U.S., a total of 19 million tons of disposable FGD byproduct are produced, transported and disposed of in landfills annually[3].

The use of regenerable sorbent technologies has the potential to reduce or eliminate solid waste production, transportation and disposal. In a regenerable sorbent system, the sulfur dioxide in the boiler flue gas is removed by the sorbent in an adsorber. The SO_2 is subsequently released, in higher concentration, in a regenerator. All regenerable systems produce an off-gas stream from the regenerator that must be processed further in order to obtain a saleable byproduct, such as elemental sulfur, sulfuric acid or liquid SO_2. A schematic of a regenerable sorbent system is shown in Figure 1-1.

Figure 1-1: Regenerable Sorbent System



In addition to reducing solid waste, many regenerable systems have other benefits compared to non-regenerable scrubbing technologies, including higher sulfur removal efficiencies, and the capability of combined SO_2/NO_x removal.

1.2 Description of Byproduct Recovery System

The team of Arthur D. Little, Tufts University and Engelhard Corporation are conducting Phase I of a four and a half year, two-phase effort to develop and scale-up an advanced byproduct recovery technology that is a direct, single-stage, catalytic process for converting sulfur dioxide to elemental sulfur. This catalytic process reduces SO_2 over a fluorite-type oxide (such as ceria and zirconia). The catalytic activity can be significantly promoted by active transition metals, such as copper. More than 95% elemental sulfur yield, corresponding to almost complete sulfur dioxide conversion, was obtained over a Cu-Ce-O oxide catalyst as part of an on-going DOE-sponsored, University Coal Research Program (at MIT with Dr. Flytzani-Stephanopoulos). This type of mixed metal oxide catalyst has stable activity, high selectivity for sulfur production, and is resistant to water and carbon dioxide poisoning. Tests with CO and CH_4 reducing gases indicate that the catalyst has the potential for flexibility with regard to the composition of the reducing gas, making it attractive for utility use. The performance of the catalyst is consistently good over a range of SO_2 inlet concentration (0.1 to 10%) indicating its flexibility in treating SO_2 tail gases as well as high concentration streams.

1.3 Research and Development Activity

Arthur D. Little, Inc., together with its industry and commercialization advisor, Engelhard Corporation, and its university partner, Tufts, plans to develop and scale-up an advanced, byproduct recovery technology that is a direct, catalytic process for reducing sulfur dioxide to elemental sulfur. The principal objective of our Phase I program is to identify and evaluate the performance of a catalyst which is robust and flexible with regard to choice of reducing gas.

In order to achieve this goal, we have planned a structured program including:

- Market/process/cost/evaluation;
- Lab-scale catalyst preparation/optimization studies;
- Lab-scale, bulk/supported catalyst kinetic studies;
- Bench-scale catalyst/process studies; and
- Utility Review

The flow of and interaction among the planned work elements are illustrated in Figure 1-2 for Phase I. A description of the methods of investigation to be used for these program elements is described below.

Market, Process and Cost Evaluation. Interviews will be conducted with electric utilities and regenerable sorbent system developers to define key market issues, such as: preferred reducing gas; variability of off-gas stream composition; system contaminants; emissions limitations; cost constraints; and reliability/durability issues. From the interview responses, key performance criteria for the system will be defined. The performance and cost of the proposed catalytic process will be evaluated and compared to these criteria. In addition, these performance criteria will be used to define milestones and to focus catalyst and process development.

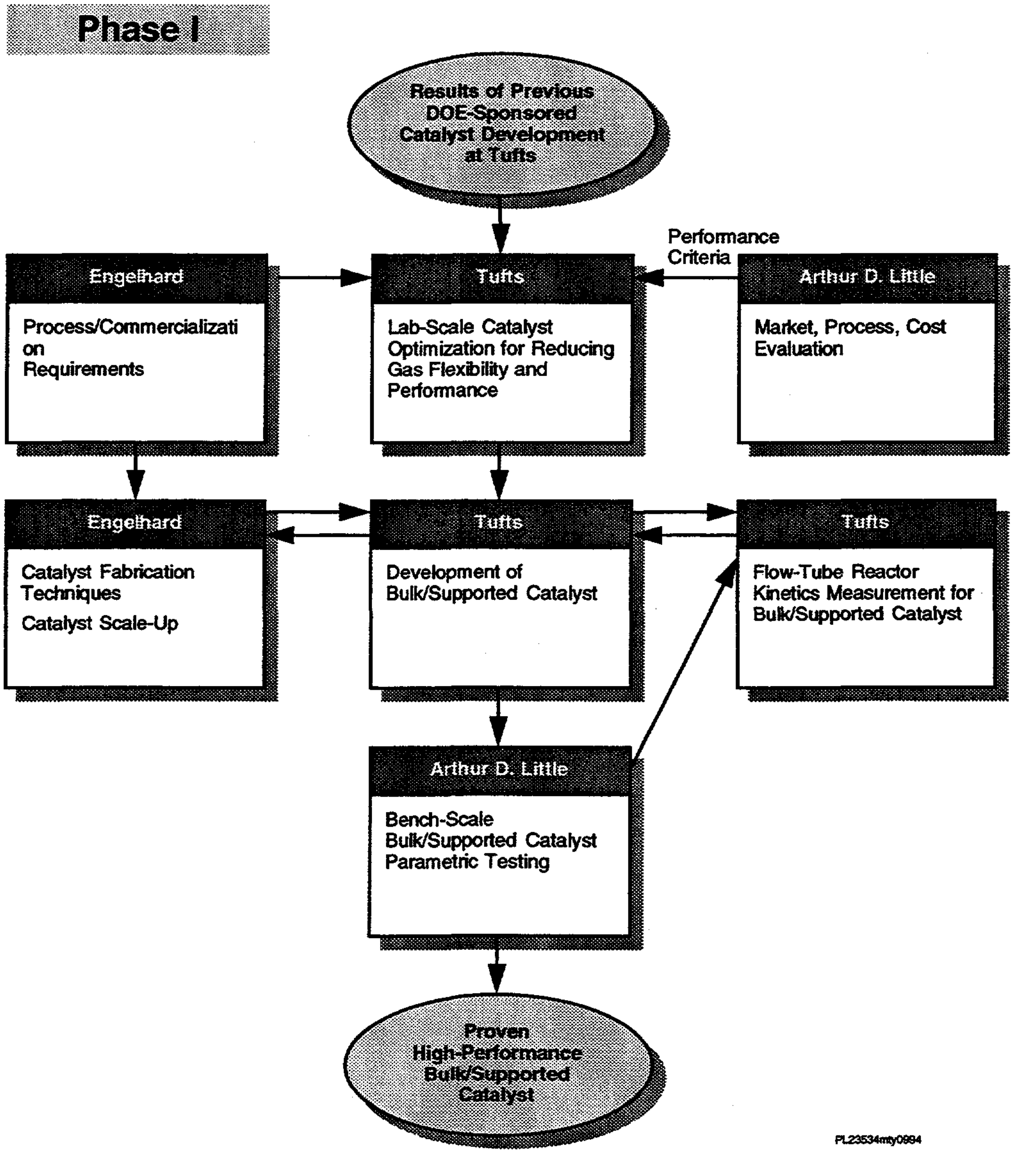
Lab-scale Catalyst Preparation/Optimization Studies. Catalyst will be prepared using a variety of methods (such as co-precipitation, sol-gel technique) from two candidate fluorite oxides (CeO_2, ZrO_2) and four candidate transition metals (Cu, Co, Ni, Mo). These catalyst materials will be tested at Tufts in the same apparatus as was used in the previous work discussed above with a variety of reducing gases (CO, $CO+H_2$, CH_4). Data will be gained in order to determine the key underlying reaction mechanisms. Parametric tests will determine the relative effects of temperature, concentration, space velocity, catalyst preparation method, and reducing gas. To reduce the amount of screening work, statistical experiment design methods will be used and catalyst characterization will be used to discriminate between active compositions. Some catalyst characterization work (x-ray diffraction, microscopy) will be conducted by Tufts staff at MIT laboratories.

Lab-scale, Bulk/Supported Catalyst Kinetic Studies. The best-performing catalysts will then be either appropriately supported (pellet, tablets, honeycomb, etc.) or formulated in bulk form. The bulk/supported catalyst will be tested in a laboratory-scale flow-tube reactor at Tufts to determine kinetic data.

Bench-scale Catalyst/Process Studies. Larger quantities of the bulk/supported catalyst will be tested in a bench-scale flow tube reactor at Arthur D. Little. Parametric tests will be conducted to assess the influence of temperature, inlet SO_2 concentration, space velocity, and choice of reducing gas on performance. Some cyclic and duration testing will also be conducted at this scale.

Utility Review. A utility review team will be assembled, consisting of one or more utilities that have experience with regenerable desulfurization technologies or are considering their application in the near future. We will work closely with the utilities to inform them of the developments and solicit their perspective on utility needs and development issues.

Figure 1-2: Work Elements



2. Work Breakdown Structure

2.1 Phase I Task 1: Market, Process and Cost Evaluation

Lead Contractor: Arthur D. Little

Objectives:

- To identify the critical market forces, technical requirements and cost constraints in order to focus the catalyst/byproduct recovery process research effort;
- To evaluate the costs and benefits of the advanced byproduct recovery process, and to compare these attributes to those of state-of-the-art technologies;
- To determine the extent to which application of the advanced byproduct recovery process improves the competitiveness of regenerable sorbent systems.

Approach:

This task is being conducted by Arthur D. Little. We are interviewing utilities, leading architect/engineering companies, regenerable sorbent system developers, industry consultants and EPRI to define key market issues, including: preferred reducing gas; variability of SO_2-rich off-gas stream composition; compatibility/flexibility in coupling with the adsorption/regeneration step; system contaminants; emissions limitations; cost constraints; and reliability/durability issues. Based on these interviews, we will define the key performance criteria for the system. We will estimate the potential market for advanced, catalytic reduction of SO_2 to elemental sulfur in utility and industrial applications.

We are preparing a Process Evaluation, in which we will prepare or specify process energy balances, temperature requirements, reactor volumes, and recycle rates, for one or more reducing gas production methods. These analyses will be tied to the requirements of utilities and the various regenerable sorbent technologies under development. We are also preparing a Cost Evaluation of the byproduct recovery system in the context of its use with one or more regenerable SO_2 removal systems and compare the costs of the proposed technology to that of state-of-the-art technology.

Deliverables:

Market, process and cost analyses of the proposed byproduct recovery system; definition of key areas to focus research efforts; assessment of the potential market for the process.

2.2 Phase I Task 2: Lab-Scale Catalyst Testing/Optimization

Lead Contractor: Tufts

Objectives:

To optimize catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including syn-gas and natural gas.

Approach:

This task is being carried out by Tufts University, a subcontractor to Arthur D. Little. Under four subtasks, Tufts will prepare and characterize the catalysts, conduct adsorption/desorption studies, measure catalytic activity in a packed-bed microreactor, and conduct parametric tests and kinetic measurements. Specifically, Tufts will optimize the catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including synthesis gas and natural gas.

The transition metal-promoted fluorite-type oxides previously identified as very active and selective catalysts for the reduction of SO_2 to elemental sulfur with carbon monoxide will be tested with other reductants, namely synthesis gas (H_2 and CO mixed with H_2O and CO_2) and natural gas. Various transition metals (including Cu, Co, Ni, and Mo) will be examined as promoters to obtain a catalyst composition active in various reducing gases. The fluorite oxides to be used in this work are ceria (CeO_2) and zirconia (ZrO_2).

Arthur D. Little, with assistance from Tufts, will develop a detailed Test Plan for the laboratory-scale catalyst testing and optimization activities. The Test Plan will be submitted as an amendment to the Management Plan. No testing will begin until the Test Plan has been approved by the DOE Project Manager.

Catalyst Preparation and Characterization Tufts will prepare the catalysts by the co-precipitation method to produce a surface area in the range of 20 - 60 m^2/g. To achieve high surface area, high elemental dispersion, and uniform pore-size distribution, other preparation techniques (such as gelation and impregnation of high surface area supports) will also be examined.

Catalysts will routinely be characterized by X-ray powder diffraction for crystal phase identification and by nitrogen adsorption/desorption for BET surface area and pore size distribution measurements. The elemental composition of the catalyst will be analyzed Inductively Coupled Plasma Atomic Emission Spectrometry. Selected active catalysts will be further characterized by X-ray Photoelectron Spectroscopy (XPS) and Scanning Transmission Electron Microscopy (STEM).

Adsorption/Desorption Studies In parallel with the preparation of the new catalyst composition, the Cu-Ce-O catalyst will be evaluated in adsorption/desorption studies with CO, COS, and SO_2 to determine the reaction mechanism. These experiments will lead to an understanding of the low selectivity of this catalyst to the undesirable byproduct COS and facilitate catalyst optimization. A thermo-gravimetric analyzer, coupled with a residual gas analyzer, will be used for these tests.

Catalytic Activity Measurements in a Packed-Bed Microreactor Tufts will conduct catalyst activity tests under steady conditions in an existing packed- bed microreactor. Screening tests will be conducted with a reducing gas consisting of 1% SO_2 and 0.5% CH_4. Additional tests of the most promising catalysts will be conducted with two additional synthesis reducing gases. However, final selection of reducing gases will be made based on input from regenerable sorbent system developers and utilities (the Task 1 findings). We currently envision the two additional synthesis test gases to be:

(i) wet feed gas mixture containing 1% SO_2 and stoichiometric amount of synthesis gas with $H_2/CO = 0.3$, 2% H_2O and 2% CO_2; and

(ii) wet feed gas mixture containing 1% SO_2, stoichiometric amount of synthesis gas with $H_2/CO = 3$, 2% H_2O, and 2% CO_2.

The existing data on performance with pure CO and the new data to be developed using methane and wet synthesis gases will cover the range of possible regeneration gases available. It is not necessary to test dry synthesis gases since the tests with CO and methane provides information on ideal performance without water. For each reacting gas mixture, the reactor temperature will be increased and then reduced to establish light-off and fall-off behavior of each catalyst. Elemental sulfur yield, catalyst activity and catalyst selectivity will be used to identify the most promising catalysts.

Parametric Studies and Kinetic Measurements After identifying promising catalysts, an extensive parametric study and kinetic measurements will be carried out to provide reactor design information. The parametric studies will address:

(i) the effects of water vapor and/or carbon dioxide on catalyst activity and elemental sulfur yield; and

(ii) effect of reducing gas composition (H_2/CO ratios/CH_4) on catalyst activity and sulfur yield.

Long-term and hydrothermal catalyst stability will be evaluated for the preferred catalyst composition in Task 4, Bench-Scale Testing.

The parametric studies will be conducted at space velocities in the range 1,000 to 100,000 h^{-1}, SO_2 concentrations from 0.1% to 10%, H_2O contents from 0 to 10%, H_2/CO ratios from 0 to 3, and CH_4 concentrations from 0.1% to 10%. The temperature will be in the range 50 to 700°C. A kinetic model will be developed from the data obtained at short contact time (< 0.1g s/cc) in a small diameter catalytic reactor. This will include the effects of H_2O and CO_2 on the specific activity.

Deliverables:

An optimized catalyst composition/preparation method for bench-scale catalyst tests. Kinetic data for use in reactor design.

2.3 Phase I Task 3: Catalyst Preparation and Costing

Lead Contractor: Engelhard

Objectives:

- Provide guidance regarding the establishment of activity and simulated aging tests to quickly and efficiently determine performance characteristics of catalyst formulations;
- To prepare supported or bulk (extruded) catalysts in the form of pellets or honeycombs for bench-scale testing;
- To provide catalyst manufacturing and cost analysis for inclusion in the analysis of process economics.

Approach:

Engelhard will work closely with Tufts and Arthur D. Little to specify the appropriate catalyst structures to meet the engineering requirements for the targeted sulfur recovery systems. Included in this activity will be the training of scientists and engineers on the Tufts team by Engelhard staff members in the formulation of commercially viable catalyst structures. Engelhard staff will observe and participate in laboratory-scale and bench-scale testing at Tufts and Arthur D. Little to interpret/analyze results. The resulting analysis will be used to redesign catalysts which resist deactivation.

Engelhard will apply their expertise in process and cost evaluation of catalytic systems to the sulfur byproduct recovery system. Engelhard will provide catalyst manufacturing cost details to allow the process economics to be established.

Deliverables:

Catalysts for bench-scale testing; manufacturing/cost analysis of catalysts for inclusion in system evaluation task.

2.4 Phase I Task 4: Bench-scale Testing

Lead Contractor: Arthur D. Little

Objectives:

To conduct bench-scale, parametric tests to evaluate the performance of three to five supported/extruded catalyst preparations.

Approach:

Arthur D. Little will develop a Test Plan for the bench-scale parametric tests and will incorporate this plan into an amendment to the Management Plan. No work will begin on the bench-scale tests until the Test Plan has been approved by the DOE Project Manager. Arthur D. Little is designing, and will fabricate and commission a bench-scale SO_2 reduction reactor facility. The facility will consist of gas supply controls (for the simulated regenerator off-gas stream and the reducer gas stream); gas heaters; a catalytic reduction reactor (approximately 1-2 l in size); a heat exchanger for sulfur knock-out; gas analysis instrumentation (SO_2, H_2S on-line analyzers, gas chromatograph) and an afterburner for clean-up of off-gases. The system will be fabricated and shaken-down in the first 6 months of the program following approval of the Management Plan.

We will initiate bench-scale tests using the catalyst materials that have been proven as highly active and selective for sulfur production from the previous/ongoing catalyst development programs: a copper promoted ceria catalyst, Ce-Cu-O. Tests on supported materials will reveal the performance changes associated with the use of supported or bulk extruded materials compared to powders. We will investigate the effects of space velocity, temperature, and reducer gas and regenerator gas composition on catalyst performance.

Subsequent parametric tests will be performed on catalyst formulations selected from the lab-scale catalyst optimization work. The operating variables are expected to be as follows: space velocity: 10,000, 25,000, 50,000 hr^{-1}; temperature: 450, 500, 600°C; inlet stream composition: SO_2 concentration: 0.1 to 10%; H_2O concentration 2 to 30%; CO_2 concentration 2 to 30%; reducing gas composition: CO/H_2 ratio: 0.5 to 3.0; CO/CO_2 ratio: 0.5 to 3.0. Information developed from this task will provide insights for the process evaluation task, the catalyst optimization work, and the Phase II efforts in reactor scale-up.

Deliverables:

Performance map for 3 to 5 catalyst preparations; selection of catalyst preparation for dynamic response and pilot-scale testing.

2.5 Phase I Task 5: Utility Review

Lead Contractor: Arthur D. Little

Objectives:

- To provide electric utility perspective and review of development program
- To focus development effort on issues of key importance to utilities

Approach:

We will identify a utility review team, consisting of one or more utilities that have experience with regenerable desulfurization technologies or are considering their application in the near future. We will work closely with the utilities to inform them of the developments and solicit their perspective on utility needs and development issues. We plan to communicate through monthly meetings and will share data as it becomes available. Possible Utility Review Team members are Niagara Mohawk, Public Service of New Mexico, and Ohio Edison. All these utilities are participants in either regenerable sorbent programs or Clean Coal Development programs and would therefore have a valuable perspective to provide to our program, and would have a stake in the development of an improved byproduct recovery system.

Deliverables:

Utility review of the bench-scale developments; input to developments concerning issues of key importance to utilities.

2.6 Phase I Task 6: Management and Reports

Lead Contractor: Arthur D. Little

This task will be conducted by Arthur D. Little and will involve coordinating the catalyst/process development effort, coordinating the activities of the prime contractor and two subcontractors, and preparing the monthly, quarterly, topical, and final reports for DOE.

3. Objectives for Third Quarter Activity

The objectives for the third quarter were to:

- Continue work on catalyst screening using the laboratory-scale packed bed reactor at Tufts. Effects of dopant type, dopant level, reducing gas type, stoichiometry, and temperature on selectivity and activity of a range of fluorite-type catalysts will be assessed.

- Continue work on the market/process/cost evaluation, developing more detailed information regarding the range of conditions of the byproduct SO_2 streams, focusing on those in the Primary category. This will include variability in concentrations of principal constituents, rates of concentration and/or temperature fluctuations and the concentration ranges of trace contaminants.

- Continue the development of the bench-scale testing system by commencing detailed design and procurement of the hardware for the bench-scale experiment. The range of process conditions to be simulated will be based on the interim results of the Market, Process and Cost Evaluation.

The focus of this report is on the results of the catalyst screening experiments at Tufts and the details of the bench-scale experiment design at Arthur D. Little.

4. Third Quarter Technical Progress

4.1 Catalyst Screening Experiments

In previous DOE-supported work[4], the activity and selectivity of fluorite-type oxides, such as ceria and zirconia, for reduction of SO_2 were investigated. A wide range of transition metal-impregnated ceria and zirconia catalyst formulations were evaluated in a packed bed reactor, under both dry gas and wet gas (2% H_2O) conditions. Under dry gas conditions, more than 95% yield of elemental sulfur and essentially complete SO_2 conversion were obtained for a variety of catalysts. Under wet gas conditions, Cu/CeO_2 catalyst showed the lowest light-off temperature, the greatest resistance to water, and gave over 90% SO_2 conversion and more than 70% elemental sulfur yield.

Based on these results, and the fact that a 25 hour test indicated that the Cu/CeO_2 catalyst was stable at the reacting conditions, the Cu-Ce-O system was selected for detailed studies of the SO_2 reaction with CO. The effects of copper content, temperature, presence of water, and presence of CO_2 on the selectivity and activity of this catalyst system were evaluated. This work led to the selection of bulk $Cu_{0.15}Ce_{0.85}(La)O_x$ for further study. More than 95% elemental sulfur yield, corresponding to almost complete sulfur dioxide conversion, was obtained over a Cu-Ce-O oxide catalyst with a feed gas of stoichiometric composition ($[CO] / [SO_2] = 2$) at temperatures above 450°C. This catalyst showed no apparent deactivation during a 35-hour run in the presence of 2% water at 470°C. In addition, the performance of this catalyst with other reducing gases was briefly investigated. Elemental sulfur yields of 50 - 66% were obtained using H_2 at 600°C and an elemental sulfur yield of 72% was obtained using CH_4 at 800°C. It is noteworthy that all tests mentioned above were conducted at high space velocities, on the order of 40-50,000 h^{-1} (STP).

Thus previous work has shown that the catalytic activity of fluorite-type oxides, such as ceria and zirconia, for the reduction of sulfur dioxide by carbon monoxide to elemental sulfur can be significantly promoted by active transition metals, such as copper. This type of mixed metal oxide catalyst has stable activity and is resistant to water and carbon dioxide poisoning. The performance of the catalyst was consistently good over a range of SO_2 inlet concentration (0.1 to 10%) indicating its flexibility in treating SO_2 tail gases as well as high concentration streams.

The overall objective of the current two-phase program is build on the results described above to advance the SO_2-reduction technology from the laboratory to commercial scale. The principal objective of our Phase I program is to identify and evaluate the performance of a catalyst which is robust and flexible with regard to choice of reducing gas (methane, carbon monoxide, or syn-gas).

Work to date at Tufts University has focused on screening tests of a variety of catalyst formulations. The catalyst preparation technique used consists of mixing a solution of nitrate salts and urea and heating the solution to 100°C under strong stirring. Co-precipitation occurs as the solution is heated for 8 hr. The precipitate is then filtered, washed twice with hot deionized water, dried overnight, and then calcined in air at 650°C for 3 hr.

Catalysts with nominal metal content 15 at%, namely 15%Cu-Ce(La)-O, 15%Co-Ce(La)-O, 15%Ni-Ce(La)-O, and Ce(La)O_2 ,were chosen for initial activity tests using methane reductant. Subsequent elemental analysis identified 15 at% Cu, 6 at% Co, and 2 at% Ni on the corresponding bulk oxide catalysts. The apparatus used in these experiments is the same packed-bed micro-reactor used in the prior work described above. The reactor consists of a 0.6 cm I.D. ´ 50 cm long quartz tube with a porous quartz frit placed at the middle for supporting the catalyst. The reactor tube is heated by a Lindberg furnace and temperature-controlled. The reacting gases and helium are mixed prior to the reactor inlet and the resulting gas mixture flows downward through the packed bed. Water vapor is introduced by bubbling the helium through a heated water bath. The pressure drop of gas flowing through the assembly is small, thus the experiments are carried out essentially at atmospheric pressure. A cold trap installed at the outlet of the reactor is used to condense out the elemental sulfur from the product gas stream. The product gas, free of sulfur and particulate matter, is analyzed by a gas chromatograph with a Thermal Conductivity Detector (TCD).

Initial activity tests were performed under the following conditions: stoichiometric amount of reacting gases, which consist of 1% SO_2 and 0.5% CH_4 (balance He) at a total flow rate of 100 cm^3/min. The contact time was 0.09 gs/cm^3, which corresponds to a space velocity of approximately 80,000 h^{-1}. The fresh catalysts are typically activated by heating for one hour in 9.9% CO/He at 600°C. After activation the reacting gases were introduced at 600°C and the reaction temperature was raised to about 780°C in steps of 50°C. Both light-off and fall-off behavior were examined to check for possible hysteresis effects and deactivation.

Ni, Co, Cu, Mn, Cr, and Fe containing Ce(La)O_2 and Zr(Y)O_2 catalysts, as well as pure CeO_2 and Ce(La)O_2 were tested using reacting gases at stoichiometric ratio. All tests were performed at a gas flow rate of 100 cm^3/min, at contact times of 0.09gs/cm^3 and 0.18 gs/cm^3, and in the temperature range 500°C to 750°C. Results of these screening experiments are shown in Figure 4-1. The results are shown in terms of sulfur dioxide conversion, X-SO_2, and elemental sulfur yield, Y-[S], defined as follows:

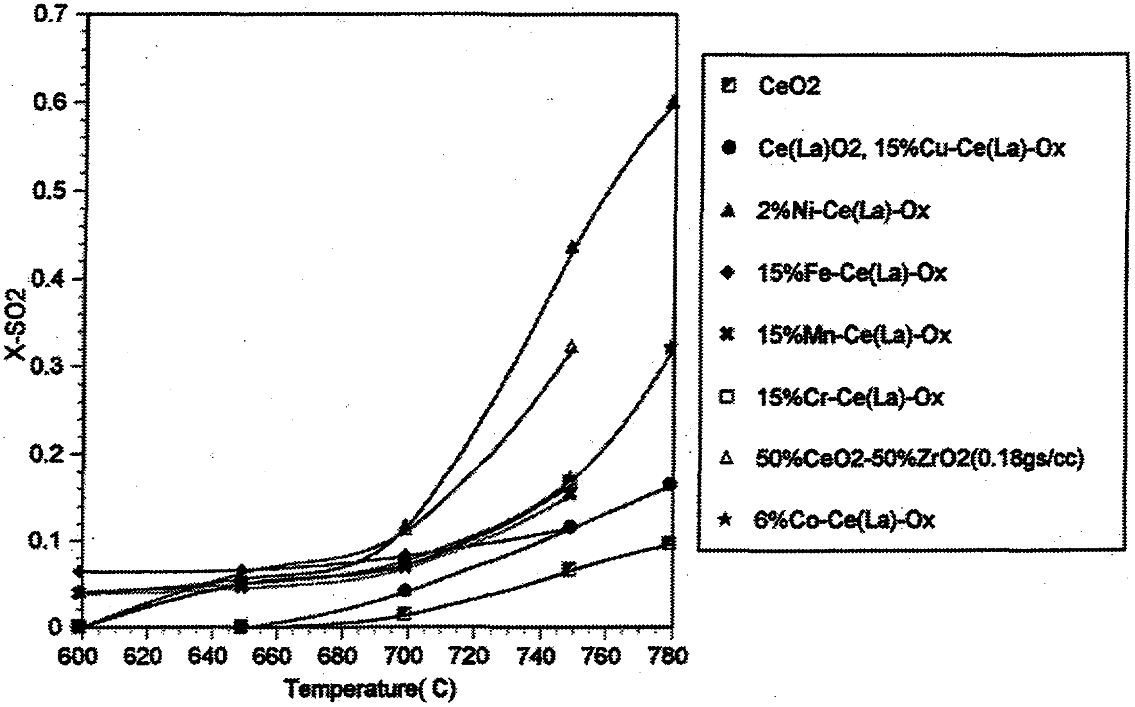


Figure 4-1 Results of screening experiments in 1% SO_2 / 0.5% CH_4 (balance He), contact time = 0.09 gs/cc (approximately 80,000 h^{-1}), pre-reduced in 9.9% CO/He at 600°C for 1 hr.

$$X-SO_2=\frac{([SO_2]_0-[SO_2])}{[SO_2]_0} \qquad Y-[S]=\frac{[S]}{[SO_2]_0}$$

where $[SO_2]_0$ and $[SO_2]$ are the inlet and outlet sulfur dioxide concentrations, respectively, while [S] is the outlet elemental sulfur concentration. [S] is calculated from the difference:

$$[S] = [SO_2]_0 - [H_2S] - [COS] - [SO_2]$$

Ni-Ce(La)-O catalyst showed the highest activity, even at relatively low Ni concentrations (2%). Figure 4-2 shows the effects of molar ratio R of CH_4 to SO_2 on the activity and selectivity of $Ni_{0.02}[Ce(La)]_{0.98}O_x$. R=0.5 indicates a stoichiometric mixture. Although the SO_2 conversion ($X-SO_2$) increases to essentially unity as an excess of CH_4 is supplied (R=1 or 1.5), the sulfur yield levels off at about 50-60%, leading to significant amounts of H_2S and, to a lesser extent, COS in the reactor outlet stream. Figure 4-3

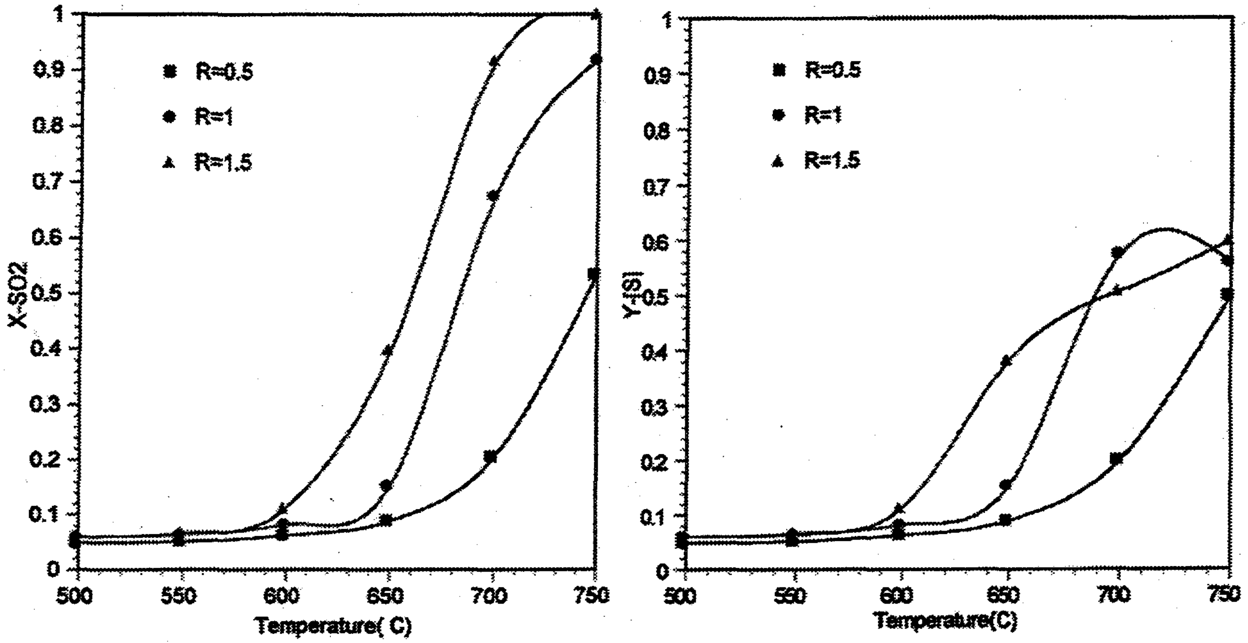


Figure 4-2 The effect of molar ratio R (CH_4 / SO_2) on the activity of $Ni_{0.02}[Ce(La)]_{0.98}O_x$. 1% SO_2, contact time = 0.18 gs/cc (approximately 40,000 h^{-1}), pre-reduced in 9.9% CO/He at 600°C for 1 hr

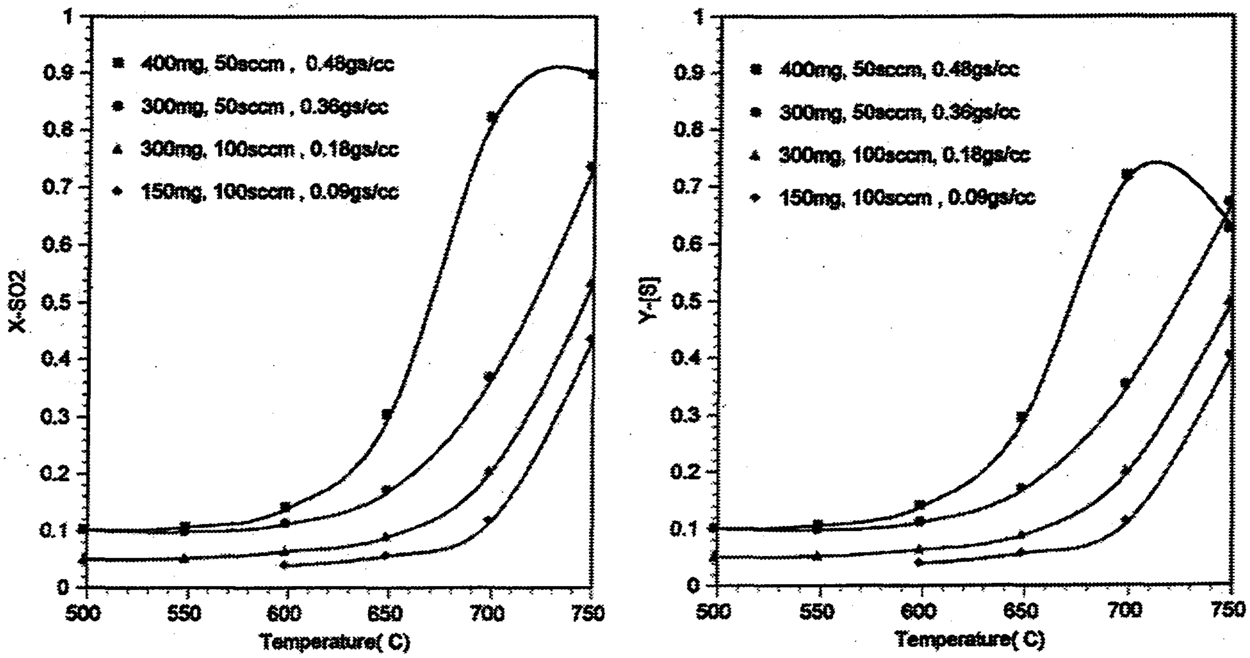


Figure 4-3 The effect of contact time on the activity of $Ni_{0.02}[Ce(La)]_{0.98}O_x$. 1% SO_2 / 0.5% CH_4 (balance He), pre-reduced in 9.9% CO/He at 600°C for 1 hr.

shows the effects of temperature and contact time (space velocity) on the activity and selectivity of $Ni_{0.02}[Ce(La)]_{0.98}O_x$. At long contact times and above 650°C, the selectivity to elemental sulfur drops (see difference between X-SO_2 and Y-[S]). At these conditions H_2S (and to a lesser extent COS) are also formed. However, at all other conditions, selectivity to sulfur exceeds 95%, and is typically 99%.

Further experiments have shown that the La_2O_3 dopant plays a more important role in the reduction of SO_2 by CH_4 than in the reduction of SO_2 by CO. Increasing the La_2O_3 content from 4.5% to 30% increase both the conversion of SO_2 and the sulfur yield, see Figure 4-4. No such changes were observed in the reduction of SO_2 by CO.

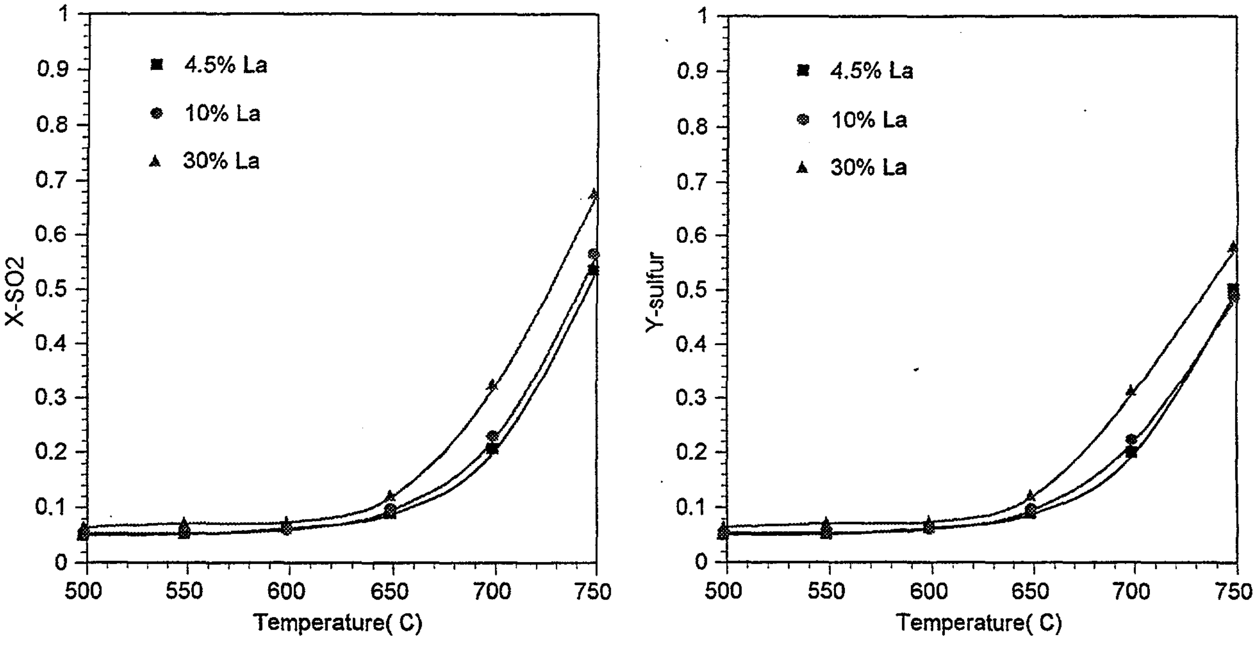
The Cu-Ce(La)-O_x material was tested again, this time at much lower copper contents (5 at%). As shown in Figure 4-5, this catalyst was comparable to the low nickel content (2 at%) catalyst. Apparently a low metal content is necessary to avoid agglomeration and sintering of the metal oxide (CuO, NiO) at high temperatures.

To assess flexibility with respect to choice of reducing gas, two catalysts were tested using synthesis gas ($H_2/CO = 2$) as a reductant. The two catalysts were $Ni_{0.02}[Ce(La)]_{0.98}O_x$ and $Cu_{0.05}[Ce(La)]_{0.95}O_x$ and the activity data are shown in Figures 4-6 and 4-7. The $Ni_{0.02}[Ce(La)]_{0.98}O_x$ catalyst was more active than the $Cu_{0.05}[Ce(La)]_{0.95}O_x$ catalyst, but the latter showed higher selectivity to elemental sulfur than the former. The light-off temperatures for these two catalysts were comparable to that of $Cu_{0.15}[Ce(La)]_{0.85}O_x$ for SO_2 reduction by CO, while the sulfur yield was much less at high temperatures. The major byproduct in the reaction was H_2S and a significant amount of this was observed above 450°C. The COS level was constant from 350°C to 750°C.

It should be noted that many coal gasifier outlet streams have a much higher CO to H_2 ratio than that used to date ($CO/H_2 = 1$-2, vs 0.5 for these experiments). The higher CO levels are expected to change the selectivity to elemental sulfur, and this will be xamined in future tests. A significant finding of the work with synthesis gas to date is that the light-off temperature can be shifted back to the values previously reported for pure CO.

4.2 Bench-Scale Experiment

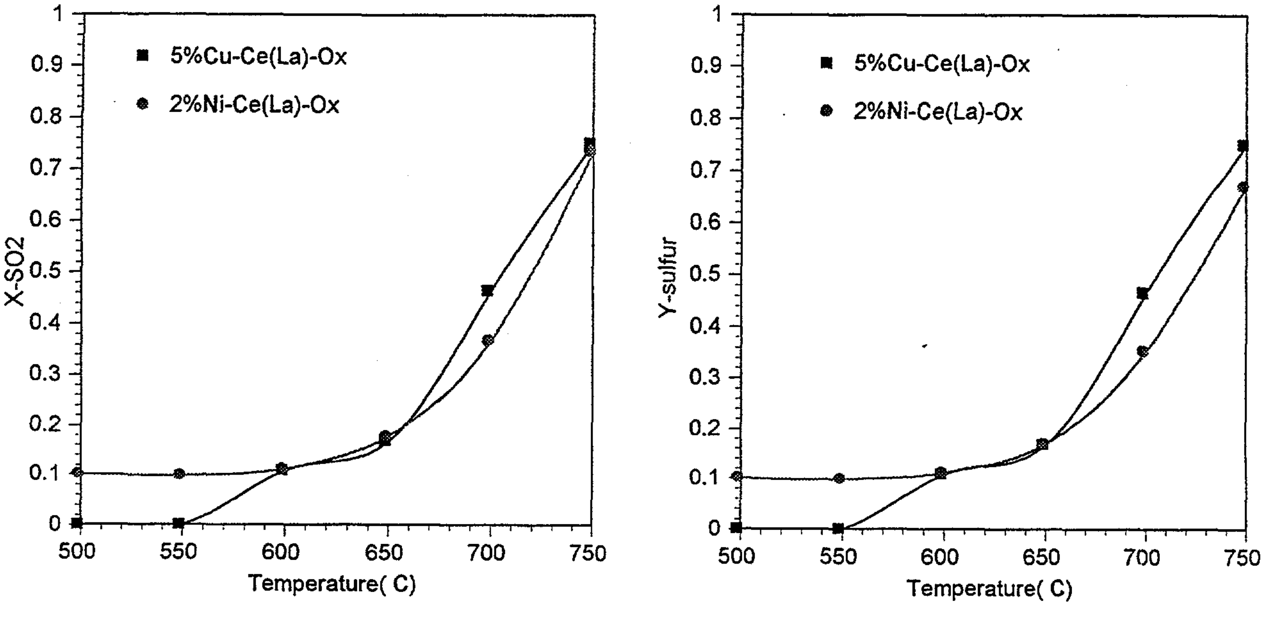
The bench-scale reactor has been sized for a nominal flow rate of 100 slpm. Depending on the regenerable FGD process being simulated, this will correspond to between 10 - 100 kW_e equivalent scale. Based on the market assessment work to date, two processes have been selected for simulation: zinc-based IGCC desulfurization systems and the copper oxide SO_2/NO_x flue gas treatment system. The widely different off-gas



(a) SO2 conversion

(b) Sulfur yield

Figure 4-4 Effect of La dopant on the activity of pre-reduced $Ni_{0.02}[Ce(La)]_{0.98}O_x$, 1% SO_2 / 0.5% CH_4, balance He, contact time 0.18 gs/cc (S.V. approx 40,000 h^{-1}).



(a) SO2 conversion

(b) sulfur yield

Figure 4-5 Activity curves of $Cu_{0.05}[Ce(La)]_{0.95}O_x$ compared with $Ni_{0.02}[Ce(La)]_{0.98}O_x$, 1% SO_2 / 0.5% CH_4, balance He, contact time 0.36 gs/cc (S.V. approx 20,000 h^{-1}).

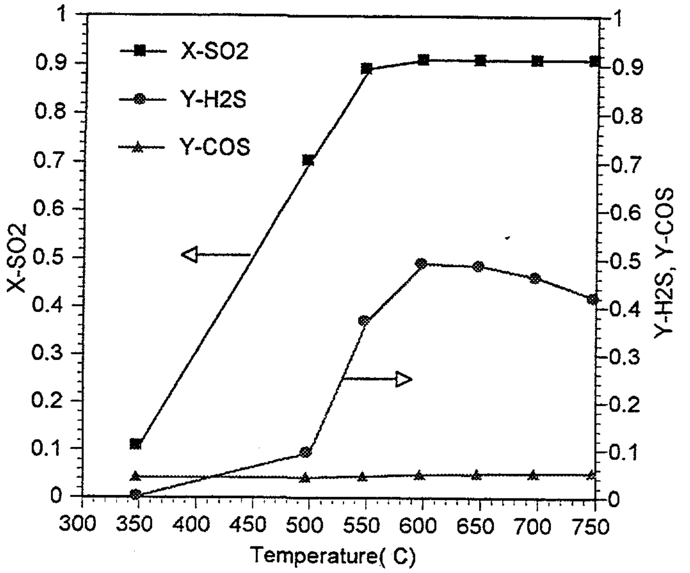


Figure 4-6 Activity of $Ni_{0.02}[Ce(La)]_{0.98}O_x$, 1% SO_2 / 2% H_2+CO, balance He, contact time 0.18 gs/cc (S.V. approx 40,000 h^{-1}).

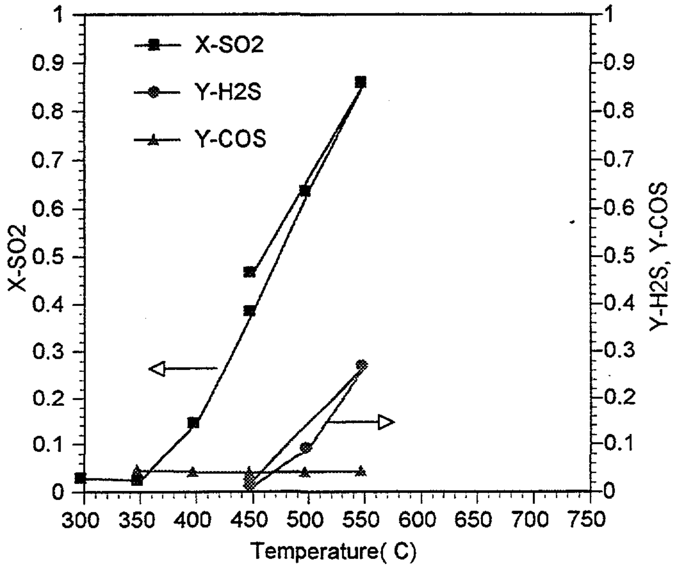


Figure 4-7 Activity of $Cu_{0.05}[Ce(La)]_{0.95}O_x$, 1% SO_2 / 2% H_2+CO, balance He, contact time 0.18 gs/cc (S.V. approx 40,000 h^{-1}).

compositions present a challenge in the design of the experiment, see below:

Characteristic	Zn Systems		CuO System		
Developer/Supplier	GE, METC/RTI, Amoco, Phillips		PETC/UOP		
Regeneration	Dilute oxygen		Hydrogen or methane		
Application Focus	IGCC		Boilers		
Off-gas Temperature	750 C		25 C		
Off-gas Composition				Regeneration with	
				H_2	CH_4
	SO_2	1.3%	SO_2	92%	63%
	H_2S	-	H_2S	Trace	Trace
	CO_2	Trace	CO_2	-	30%
	CO	Trace	CO	-	Trace
	H_2O	-	H_2O	8%	7%
	O_2	Trace	O_2	-	-
	SO_3	Trace	SO_3	-	-
	N_2	98.7%	N_2	-	-

The sulfur species analysis equipment and sampling protocol have been specified. The approach to be used is shown below in Figure 4-8. We will first of all condense and separate the elemental sulfur from the sample stream. The sample will then be filtered and diluted with clean dry air. Then the sample will be dried using a membrane drier. The clean, dry, sulfur-free sample will be analyzed using two continuous UV SO_2 analyzers, one of which will be equipped with a total sulfur oxidizer. In addition, we will obtain continuous analysis of CO and CO_2. Bag samples can be taken for periodic off-line analysis by gas chromatograph.

The overall experimental arrangement is shown in Figure 4-9. Bottled gases are metered via mass flow controllers and mixed with compressed natural gas (from the building 50 psi supply) and steam. The mixture of reactants is electrically heated before being introduced into the catalytic reactor. Pellet or honeycomb catalyst can be loaded into the reactor to any desired level. The products from the reactor flow through a sulfur condenser and trap and then to an afterburner, where any CO and remaining reduced sulfur species are oxidized. The reactor itself is shown in Figure 4-10. It is approximately 2 in internal diameter and 4 ft long. Depending on the quantity of catalyst loaded, space velocities in the range 10,000 to 100,000 h^{-1} can be achieved at a reactor flow rate of 100 slpm., see Figure 4-11.

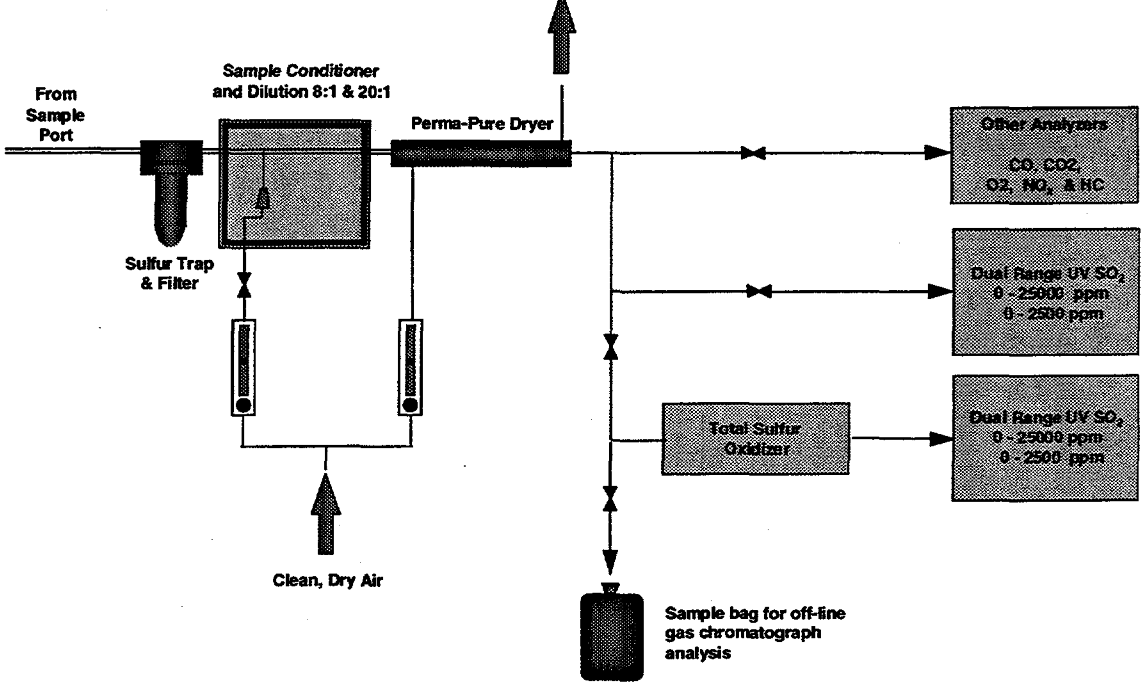


Figure 4-8 Gas Sampling and Conditioning System

The reactor is constructed of low-nickel stainless steel and coated internally with alumina. Radiant electric heaters and an external convective cooling passage allow for temperature control. Multiple sample probe locations are provided to allow product gas measurements to be obtained at several different space velocities. The vertical orientation of the reactor avoids bypassing of the catalyst bed.

Several safety features have been incorprated into the design of the experiment. An exhaust hood is located over the entire experiment and maintains a large positive airflow over the apparatus. Hazardous gas detectors will be located around the

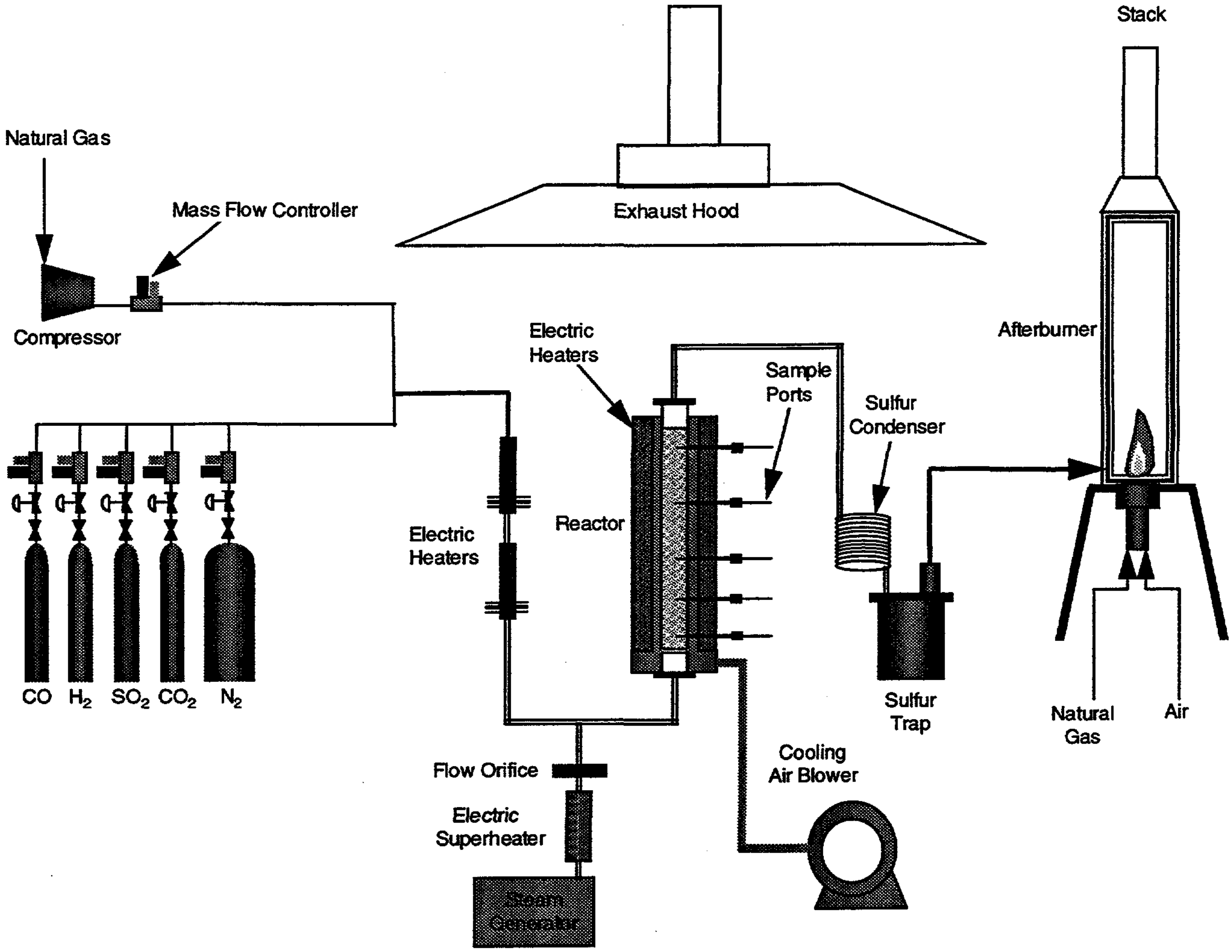


Figure 4-9 General Arrangement of Bench-Scale Experiment

experiment and connected to the main building gas detection system. An automatic safety system will shut off the gas flows in the event of:

- A power outage to the exhaust hood blower;
- Excessive pressure in the reactor;
- Excessive temperature in the reactor;
- Loss of flame in the afterburner; and
- Detection of hazardous gases.

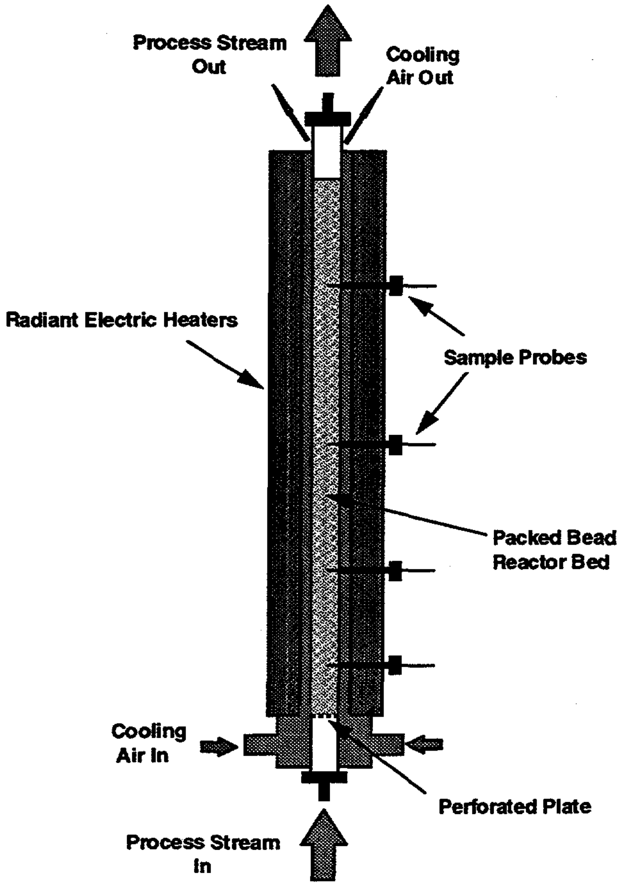


Figure 4-10 Schematic Diagram of Bench-Scale Catalytic Reactor

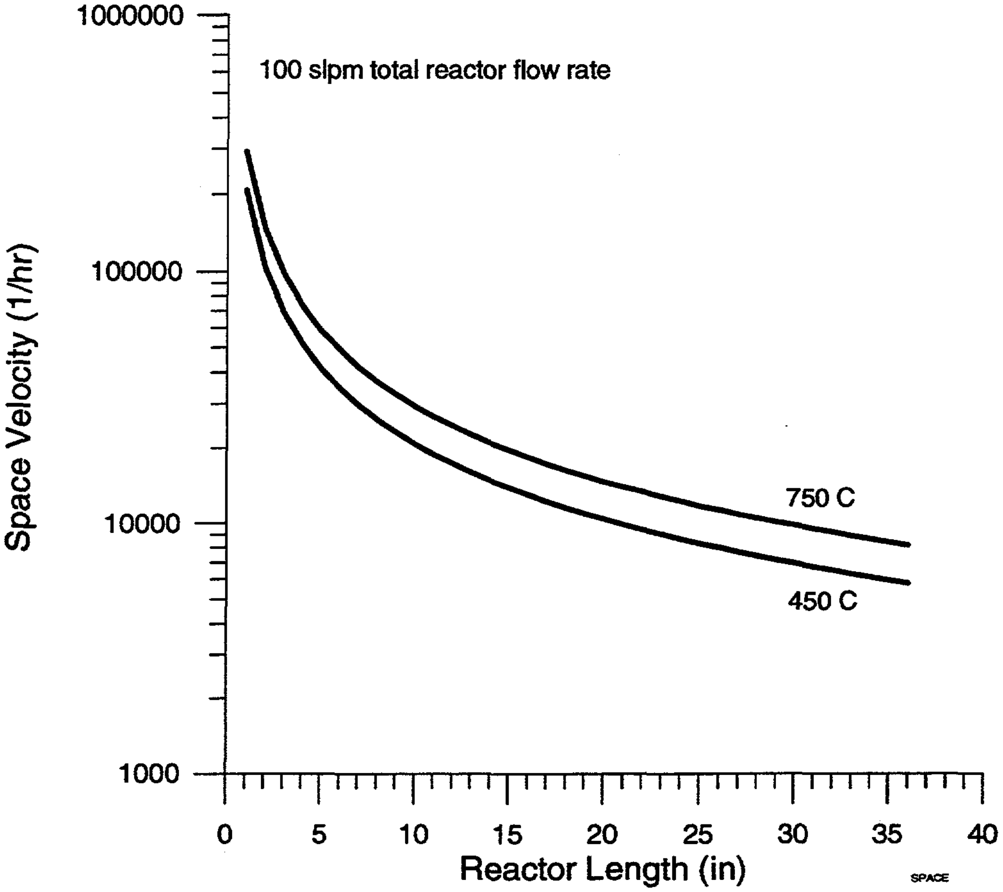


Figure 4-11 Range of Space Velocities Achievable in Bench-Scale Reactor

5. Plans for Next Quarter

Work plans for the next quarter include the following efforts:

- Work will continue on catalyst screening using the laboratory-scale packed bed reactor. Effects of dopant type, dopant level, reducing gas type, stoichiometry, and temperature on selectivity and activity of a range of fluorite-type catalysts will be assessed.

- Catalysts containing Cu, Co, Ni and Mo will continue to be examined. High surface area (150 m^2/g) ceria samples recently obtained from Engelhard will be impregnated with nitrate salts of the metals under consideration. The performance of the supported catalysts will be compared to that of the bulk mixed oxide catalysts.

- The effect of water vapor will be examined on the best catalyst of each type. Other reducing gases, such as synthesis gas, will be tested.

- Catalysts will routinely be characterized by X-ray powder diffraction for crystal identification and by nitrogen adsoption/desorption for BET surface area and pore size distribution measurements. The elemental composition of the catalyst will be analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry.

- We will complete the initial process, market and cost evaluation.

- We will complete fabrication of the bench-scale experiment, conduct shake-down tests and commence supported catalyst testing.

6. References

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4. "Reduction of Sulfur Dioxide by Carbon Monoxide to Elemental Sulfur Over Composite Oxide Catalysts," Liu, W., Sarofim, A. F., and Flytzani-Stephanopoulos, M. *Applied Catalysis B: Environmental* 4 (1994) 167-186.